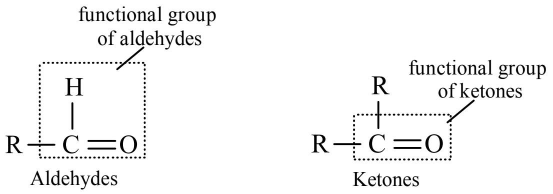
JEE ADVANCED

Class XII

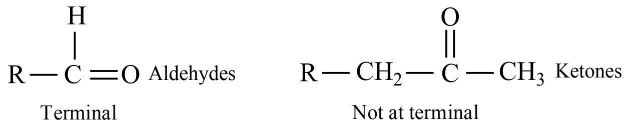
Chapter 1

Aldehydes and Ketones

- Aldehydes are compounds of the general formula RCHO and ketones are compounds of the general formula RCOR′. The groups R and R′ may be aliphatic or aromatic.
- Both aldehydes and ketones contain a carbon-oxygen double bond ($>C=O$). This unit is referred as carbonyl group ($>C=O$) and aldehydes and ketones are collectively called as carbonyl compounds.

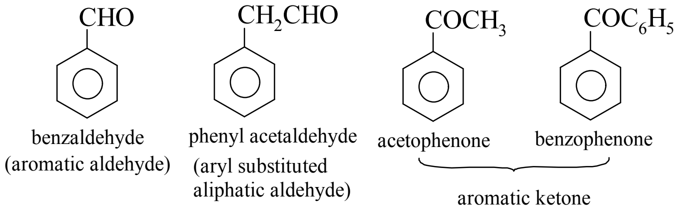


- The above structure indicates that in aldehyde, carbonyl group is attached to one hydrogen atom while in ketone, carbonyl group is linked to two alkyl or aryl groups. Aldehyde group is always present at the terminal carbon atom whereas ketone is never at terminal but atleast adjacent to terminal.



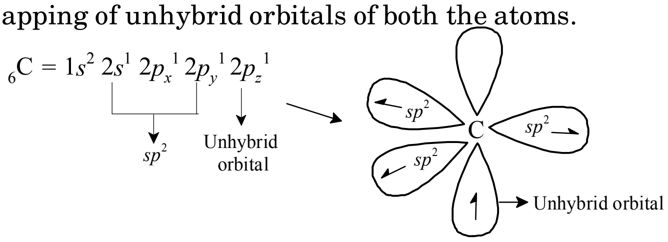
$$\underset{\text{Terminal}}{R-\overset{\overset{\displaystyle H}{|}}{C}=O}\ \text{Aldehydes} \qquad \underset{\text{Not at terminal}}{R-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3}\ \text{Ketones}$$

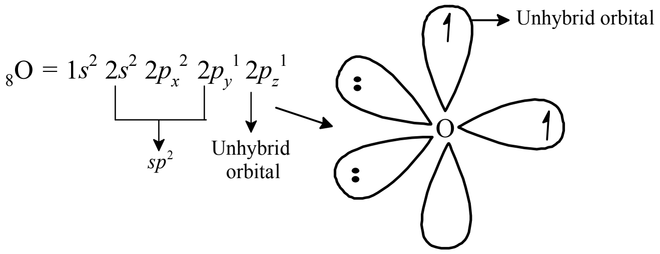
- Aromatic aldehydes are compounds in which – CHO group is attached directly to an aromatic ring.
- However, the compounds in which the – CHO group is not attached directly to the ring are considered as aryl substituted aliphatic aldehydes.
- Aromatic ketones are compounds in which a carbonyl group is attached to either two aryl groups or one aryl and one alkyl group.

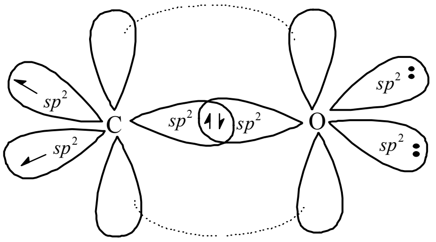


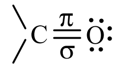
STRUCTURE OF CARBONYL GROUP

- Carbonyl group consists of one σ and one π bond like $>C=C<$. Here both carbon and oxygen are in sp^2 hybridized state. One of the sp^2 hybrid orbitals of C-atom forms σ bond by overlapping of one of like sp^2 hybrid orbital of O-atom and π bond is formed by sidewise overlapping of unhybrid orbitals of both the atoms.



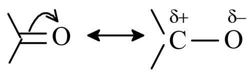






Carbonyl group

- Two of the hybridized orbitals of carbon form sigma bonds with two hydrogen atoms or one hydrogen atom and one alkyl group or two alkyl groups. Carbon atom is, thus, joined to three atoms by σ-bonds. Since, these bonds utilize sp^2-orbitals, they lie in the same plane and are 120° apart. Hence, carbonyl group is planar.
- Two unshared electron pairs of oxygen atom occupy the sp^2 hybrid orbitals of oxygen.
- The electrons in the π bond of the carbonyl group are not equally shared *i.e.* they are pulled towards the more electronegative oxygen atom. This results in polarization of bond as

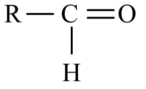


- Alternatively the polar nature of the carbonyl group can also be indicated by the following resonating structures:

$$\rangle C=O \longleftrightarrow \rangle \overset{+}{C}-\overset{-}{O}$$

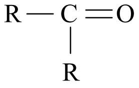
NOMENCLATURE

- According to IUPAC name 'e' of alkane is replaced by 'al' in case of aldehyde and 'e' of alkane is replaced by 'one' in case of ketone. Aldehyde is always at terminal hence position of aldehydic group is normally not indicated. In case of ketone we use position of carbonyl group whenever it is needed.



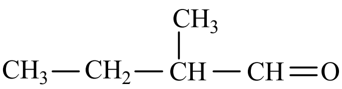
$$R-\underset{\displaystyle H}{\underset{|}{C}}=O$$

Alkanal



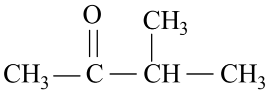
$$R-\underset{\displaystyle R}{\underset{|}{C}}=O$$

Alkanone



$$CH_3-CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}H}-CH=O$$

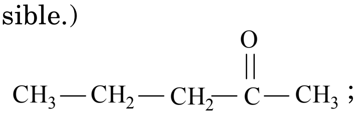
2-methylbutanal



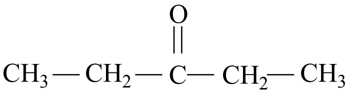
$$CH_3-\overset{\displaystyle O}{\overset{||}{C}}-\overset{\displaystyle CH_3}{\overset{|}{C}H}-CH_3$$

3-methylbutanone or 3-methylbutanone-2

(Here we may write position '2' or may not because other position is not possible.)



$$CH_3-CH_2-CH_2-\overset{\displaystyle O}{\overset{||}{C}}-CH_3$$



$$CH_3-CH_2-\overset{\displaystyle O}{\overset{||}{C}}-CH_2-CH_3$$

Pentanone-2 ; Pentanone-3

Some formulae, their common names and IUPAC names are given below

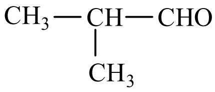
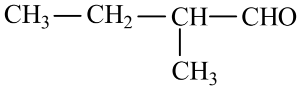
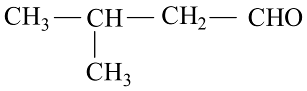
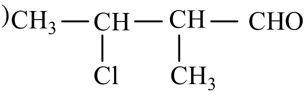
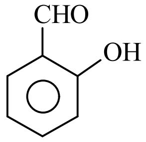
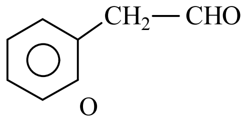
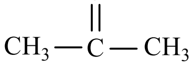
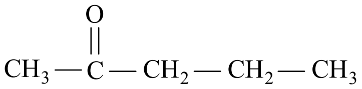
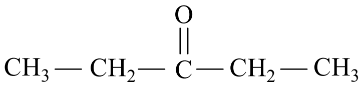
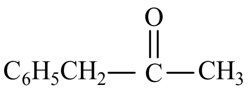
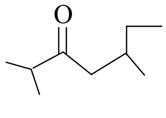
Formula	Common Name	IUPAC Name
(i) $HCHO$	Formaldehyde	Methanal
(ii) CH_3-CHO	Acetaldehyde	Ethanal
(iii) $CH_3-CH_2-CH=O$	Propionaldehyde	Propanal
(iv) $CH_3-CH_2-CH_2-CHO$	*n*-Butyraldehyde	Butanal
(v)  $CH_3-\underset{CH_3}{\underset{\mid}{CH}}-CHO$	*iso*-Butyraldehyde	2-Methylpropanal
(vi)  $CH_3-CH_2-\underset{CH_3}{\underset{\mid}{CH}}-CHO$	α-Methyl butyraldehyde	2-Methylbutanal
(vii)  $CH_3-\underset{CH_3}{\underset{\mid}{CH}}-CH_2-CHO$	β-Methyl butyraldehyde	3-Methylbutanal
(viii)  $CH_3-\underset{Cl}{\underset{\mid}{CH}}-\underset{CH_3}{\underset{\mid}{CH}}-CHO$	β-Chloro-α-methyl butyraldehyde	3-Chloro-2-methylbutanal
(ix) $CH_3-CH_2-CH_2-CH_2-CHO$	*n*-Valeraldehyde	Pentanal
(x) $CH_3-CH=CH-CH=O$	Isotonaldehyde	But-2-enal
(xi) $C_6H_5-CH=CH-CH=O$	Cinnamaldehyde	3-Phenylprop-2-enal
(xii) 	Salicylaldehyde	2-Hydroxybenzaldehyde
(xiii) 	α-Phenyl acetaldehyde	2-Phenylethanal
(xiv)  $CH_3-\overset{O}{\overset{\Vert}{C}}-CH_3$	Dimethyl ketone (Acetone)	Propanone
(xv)  $CH_3-\overset{O}{\overset{\Vert}{C}}-CH_2-CH_2-CH_3$	Methyl-*n*-propyl ketone	Pentanone-2
(xvi)  $CH_3-CH_2-\overset{O}{\overset{\Vert}{C}}-CH_2-CH_3$	Diethyl ketone	Pentanone-3
(xvii)  $C_6H_5CH_2-\overset{O}{\overset{\Vert}{C}}-CH_3$	Benzyl methyl ketone	1-Phenylpropanone

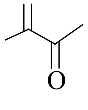
Illustration - 1 : Write the IUPAC name for the following given compounds:

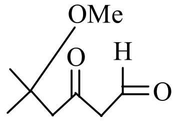
(a) Divinyl ketone (b) Methyl isopropyl ketone (c) α, α-Dichloroacetone
(d) β-Hydroxy valeraldehyde (e) Acrolein

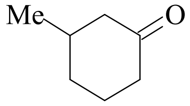
Ans.: (a) 1, 4-Pentadien-3-one (b) 3-Methylbutanone (c) 1, 1-Dichloropropanone
(d) 3-Hydroxypentanal (e) Prop-2-enal

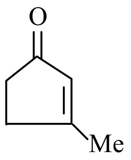
Illustration - 2 : Write the IUPAC name for the following structures:

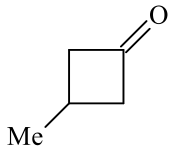
(a) 

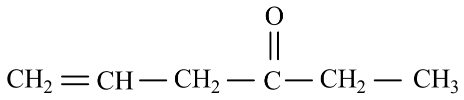
(b) 

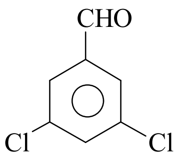
(c) 

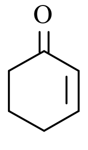
(d) 

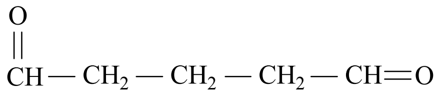
(e) 

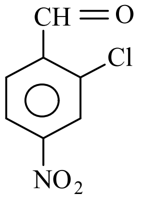
(f) 

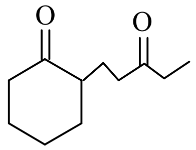
(g) 
$CH_2=CH-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_3$

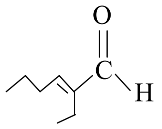
(h) 

(i) 

(j) 
$\overset{\overset{\displaystyle O}{\|}}{CH}-CH_2-CH_2-CH_2-CH=O$

(k) 

(l) 

(m) 

Ans.: (a) 2, 5-Dimethylheptan-3-one (b) butane-2, 3-dione
(c) 5-methoxy-5-methyl-3-oxohexanal
(d) 3-methylcyclohexanone (e) 3-methylcyclopent-2-en-one (f) 3-methylcyclobutanone
(g) hex-5-en-3-one (h) 3, 5-dichlorobenzaldehyde (i) cyclohex-2-en-one
(j) pentane-1, 5-dial (k) 2-chloro-4-nitrobenzaldehyde
(l) 2-(3-oxopentyl)-cyclohexanone (m) 2-ethylhex-2-enal

ISOMERISM

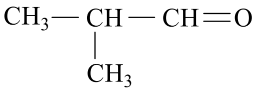
Aldehydes show chain, functional and tautomerism while ketones show chain, position, functional, metamerism and tautomerism.

Isomerism in aldehyde

- **Chain isomerism:** It starts from four carbon atoms.

$CH_3-CH_2-CH_2-CH=O$

Butanal

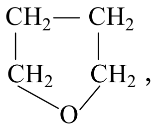

$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH=O$

2-Methylpropanal

- **Functional isomerism:** Aldehydes show functional isomerism with ketone, cyclic ether, unsaturated alcohol and epoxy alkane.

e.g. $CH_3-CH_2-CH_2-CH=O$, Butanal (a)

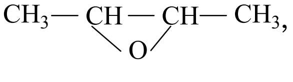
$CH_3-COCH_2-CH_3$, Butanone (b)



Tetrahydrofuran
(c)

$CH_3-CH=CH-CH_2-OH$

Crotyl alcohol
(d)



2,3-Epoxybutane
(e)

$CH_2=CH-O-CH_2-CH_3$

Ethylvinyl ether
(f)

All the above structures from (a) to (f) show functional isomerism with each other.

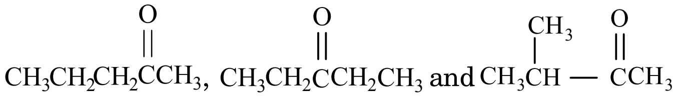
- **Tautomerism:** If a carbon atom having OH group is linked to double bond then it is enolic form of corresponding carbonyl compounds. *e.g.*,

$CH_3-CH=O \rightleftharpoons CH_2=CH-OH$;
Ethanal   Ethenol

$CH_3-CH_2-CH=O \rightleftharpoons CH_3-CH=CH-OH$
Propanal   Prop-1-en-1-ol

Isomerism in ketones

- **Chain isomerism:** Starts from five C-atoms.
  $CH_3-CH_2-CH_2-COCH_3$; $CH_3-CH(CH_3)COCH_3$
  Pentanone-2   3-Methylbutanone
- **Functional isomerism:** Ketones show functional group isomerism similar as in case of aldehydes.
- **Position isomerism:** Position isomers of ketones are metamers *i.e.* having same functional group but are attached to different alkyl radicals; *e.g.* are metamers of each other.



$CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3$, $CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_3$ and $CH_3\overset{CH_3}{\overset{|}{CH}}-\overset{O}{\overset{\|}{C}}CH_3$

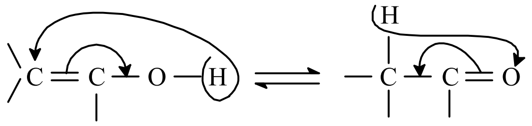
Pentanone-2   Pentanone-3   3-Methylbutanone

- **Tautomerism:** Ketones having α-hydrogen atom show tautomerism.

$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \rightleftharpoons CH_2=\overset{OH}{\overset{|}{C}}-CH_3$

Propanone   Prop-1-en-2-ol

Among the structural isomers, it is tautomer which exists in dynamic equilibrium. Basic need for tautomerism is C-atom having – OH group must be linked to double bond. There is proton transfer from Ist atom to IIIrd atom.



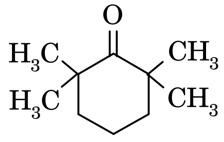
Enol   Keto

A carbonyl compound having α-hydrogen shows tautomerism.

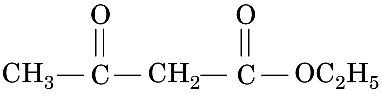
Illustration - 3 : What will be enolic form for the following structures?

(a) CH_3COCH_3 (b) C_6H_5CHO (c) $C_6H_5COC_6H_5$

(d)



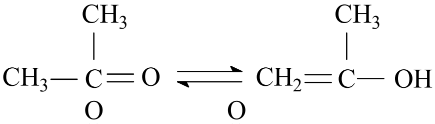
(e)



$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5$

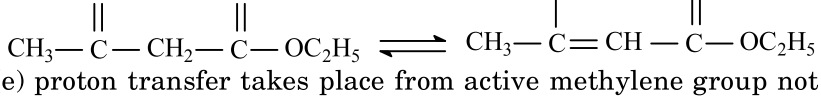
Soln.: On the basis of informations for the existence of enolic form of a given compound it is clear that structures (b), (c) & (d) do not have α-hydrogen atom hence do not exhibit tautomerism. Structures (a) & (e) show tautomerism as—

(a)



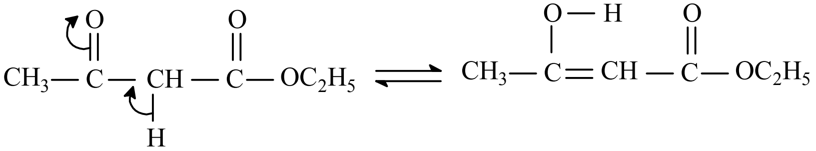
$CH_3-\overset{CH_3}{\overset{|}{C}}=O \rightleftharpoons CH_2=\overset{CH_3}{\overset{|}{C}}-OH$

(e)



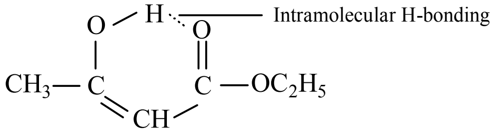
$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5 \rightleftharpoons CH_3-\overset{OH}{\overset{|}{C}}=CH-\overset{O}{\overset{\|}{C}}-OC_2H_5$

In (e) proton transfer takes place from active methylene group not from methyl group, as $-CH_2-$ (active methylene group) contains most acidic hydrogen atom.



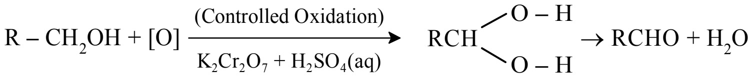
$CH_3-\overset{O}{\overset{\|}{C}}-\underset{H}{CH}-\overset{O}{\overset{\|}{C}}-OC_2H_5 \rightleftharpoons CH_3-\overset{O-H}{\overset{|}{C}}=CH-\overset{O}{\overset{\|}{C}}-OC_2H_5$

(This enolic form contains intramolecular H-bonding)



PREPARATION OF ALDEHYDES

- **Oxidation of primary alcohol**



$$R-CH_2OH + [O] \xrightarrow[K_2Cr_2O_7 + H_2SO_4(aq)]{\text{(Controlled Oxidation)}} RCH(O-H)(O-H) \rightarrow RCHO + H_2O$$

Controlled oxidation can be carried out by using Collin's reagent [CrO_3 + Pyridine] or Sarett-Colline's reagent and PCC (Pyridinium Chlorochromate, $CrO_3 \cdot C_5H_5N \cdot HCl$). Since in the absence of water, hydrated aldehyde cannot be formed, therefore, further oxidation does not take place. Solvent in these reactions is CH_2Cl_2.

- **Dehydrogenation of primary alcohol**

$$RCH_2OH \xrightarrow[575\text{ K}]{\text{Cu.}} RCHO + H_2$$

- **Reduction of acid chlorides (Rosenmund's reaction)**

$$RCOCl + H_2 \xrightarrow[\text{(quinoline, Boiling Xylene)}]{Pd/BaSO_4;\text{ S or}} RCHO + HCl$$

Lithium tri-*t*-butoxyhydride (LiAl [O-*t*-But]$_3$H) or SnH_2 also reduces RCOCl to RCHO

- **Hydration of Alkynes (Kuchrov's reaction)**

$$HC\equiv CH + H_2O \xrightarrow[60°C]{HgSO_4/\ H_2SO_{4(aq.)}} CH_3CHO$$

- **When calcium formate is heated alone formaldehyde is obtained**

$$(HCOO)_2Ca \xrightarrow{\Delta} HCHO + CaCO_3$$

- **Distillation of calcium salt of fatty acids with calcium formate**

$$(RCOO)_2Ca_{(s)} + (HCOO)_2Ca_{(s)} \xrightarrow{\text{Distill}} 2RCHO\uparrow + 2CaCO_{3(s)}$$

- **Ozonolysis of alkenes**

$$RCH = CHR \xrightarrow[\text{(ii) } H_2O/Zn]{\text{(i) } O_3/CCl_4} 2RCHO + H_2O$$

- **Oxo process**

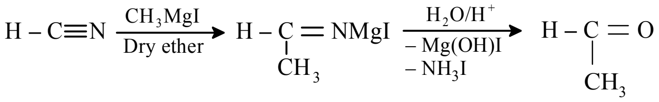
$$H_2C{=}CH_2 + CO + H_2 \xrightarrow[\Delta,\text{ high pressure}]{[Co(CO)_4]_2} H_3C-CH_2CHO$$

- **Wacker method**

$$H_2C = CH_2 + PdCl_2 + H_2O \xrightarrow[\text{Air or } O_2]{CuCl_2} CH_3CHO + Pd + 2HCl$$

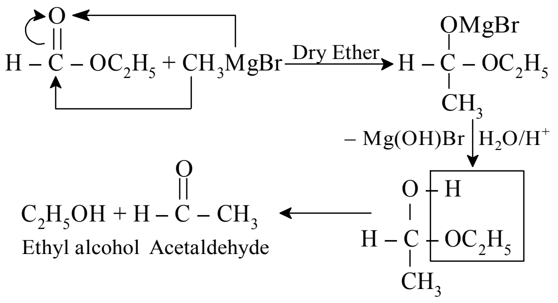
- **From Grignard's reagent**

(i) **From hydrogen cyanide**

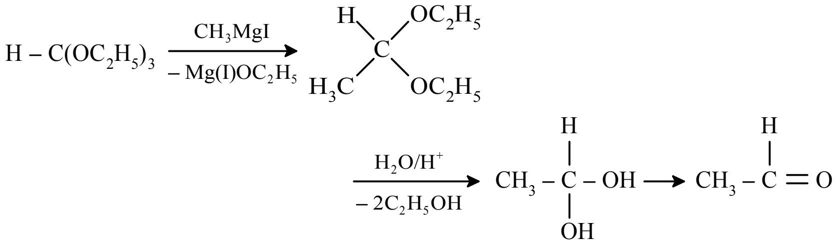


$$H-C\equiv N \xrightarrow[\text{Dry ether}]{CH_3MgI} H-\underset{CH_3}{\underset{|}{C}}=NMgI \xrightarrow[-Mg(OH)I,\ -NH_3I]{H_2O/H^+} H-\underset{CH_3}{\underset{|}{C}}=O$$

(ii) **From alkyl formate**



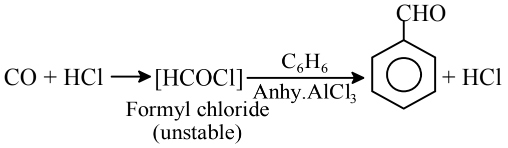
(iii) **From alkyl ortho formate :**



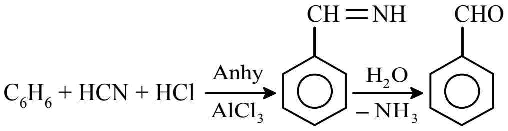
- **Hydroboration – Oxidation of terminal alkynes:**

$$CH_3C\equiv CH \xrightarrow[\text{(ii) } H_2O_2,\ OH^-]{\text{(i) } R_2BH} CH_3CH_2CHO$$

- **Gattermann Koch Synthesis**



- **Gattermann aldehyde synthesis**



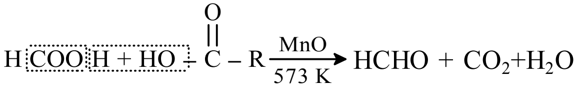
- **From cyanides (Stephen's reduction)**

$$CH_3-C\equiv N + 2[H] \xrightarrow[\text{ether}]{SnCl_2/HCl_{(g)}} CH_3-CH=NH\cdot HCl$$

Iminochloride

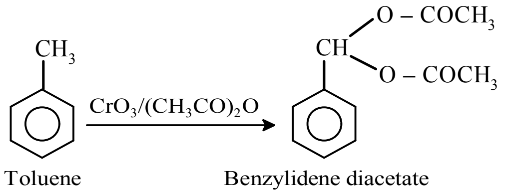
$$\xrightarrow[H^+]{H_2O} CH_3CHO + NH_4Cl$$

- **By passing vapours of formic acid and any one of its homologous acids over MnO**



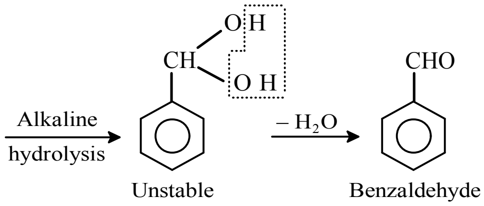
$$H\boxed{COO}\boxed{H + HO}-\overset{\overset{\large O}{||}}{C}-R \xrightarrow[573\ K]{MnO} HCHO + CO_2 + H_2O$$

- **By Oxidation of methyl benzene**

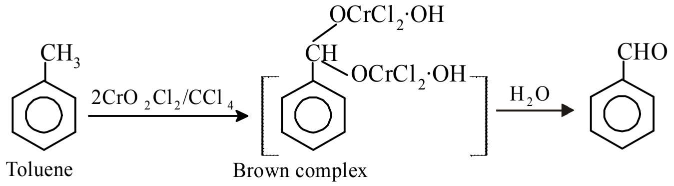


Toluene

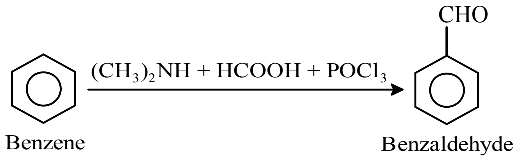
Benzylidene diacetate
(gem-diacetate)



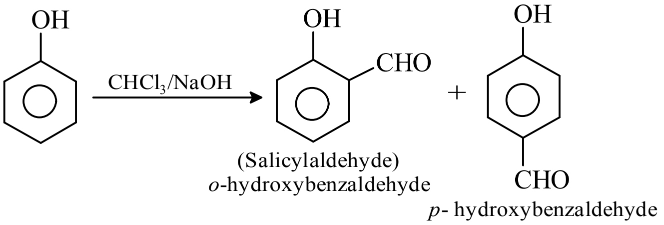
- **Etard's reaction**



- **Vilsmeyer reaction**

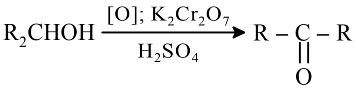


- **Riemer-Tiemann reaction**

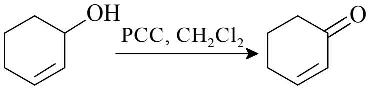


PREPARATION OF KETONES

- **Oxidation of secondary alcohols**



$$R_2CHOH \xrightarrow[H_2SO_4]{[O];\ K_2Cr_2O_7} R-\underset{\underset{O}{||}}{C}-R$$



- **Dehydrogenation of secondary alcohols**

$R_2CHOH \xrightarrow{Cu/575\ K} RCOR$

- **From acid chlorides**

$RCOCl + R_2'Cd \longrightarrow 2RCOR' + CdCl_2$

- **Hydration of higher alkynes**

$CH_3{\cdot}C \equiv CH + H_2O \xrightarrow{HgSO_4/H_2SO_4} CH_3COCH_3$

- **Distillation of calcium salt of fatty acids**

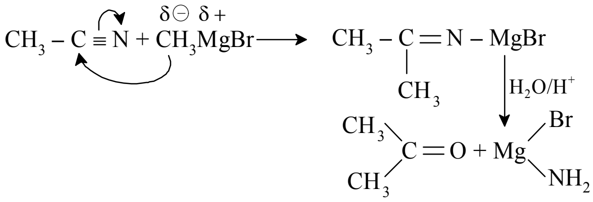
$(RCOO)_2Ca \xrightarrow{Distill} RCOR + CaCO_3$

- **By passing the vapours of any monocarboxylic acid other than formic acid over MnO at 573 K**

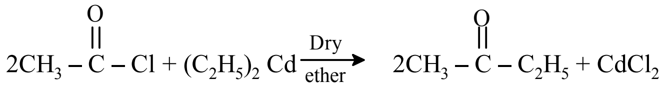
$2RCO_2H \xrightarrow[573\ K]{MnO} R_2CO + CO_2 + H_2O$

- **From organometallics**

i)

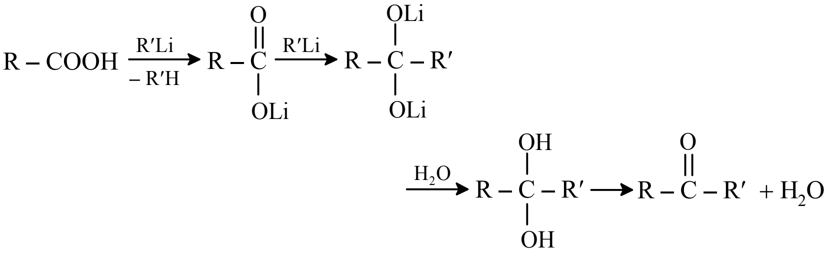


ii)



$$2CH_3-\overset{\overset{O}{\|}}{C}-Cl + (C_2H_5)_2Cd \xrightarrow[\text{ether}]{\text{Dry}} 2CH_3-\overset{\overset{O}{\|}}{C}-C_2H_5 + CdCl_2$$

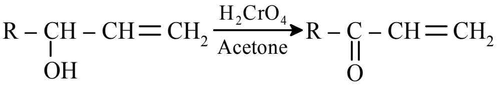
- **From carboxylic acids**



$$R-COOH \xrightarrow[-R'H]{R'Li} R-\underset{\underset{OLi}{|}}{\overset{\overset{O}{\|}}{C}} \xrightarrow{R'Li} R-\underset{\underset{OLi}{|}}{\overset{\overset{OLi}{|}}{C}}-R'$$

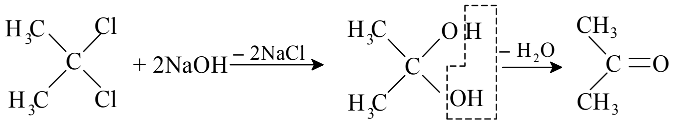
$$\xrightarrow{H_2O} R-\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{C}}-R' \longrightarrow R-\overset{\overset{O}{\|}}{C}-R' + H_2O$$

- **Oxidation of allylic alcohols to vinyl ketones**

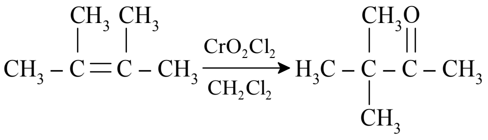


$$R-\underset{\underset{OH}{|}}{CH}-CH=CH_2 \xrightarrow[\text{Acetone}]{H_2CrO_4} R-\underset{\underset{O}{\|}}{C}-CH=CH_2$$

- **By hydrolysis of gem dihalides**



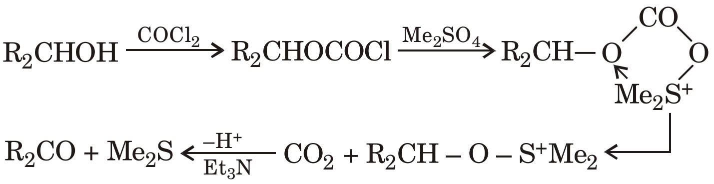
- **CrO_2Cl_2 in CH_2Cl_2 oxidises alkenes to aldehydes and ketones**



$$CH_3-\overset{\overset{CH_3}{|}}{C}=\overset{\overset{CH_3}{|}}{C}-CH_3 \xrightarrow[CH_2Cl_2]{CrO_2Cl_2} H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{\overset{O}{\|}}{C}-CH_3$$

Pinacolone

- **From Phosgene**



- Methylene group of alkyl radical attached with benzene ring is oxidised to keto group by CrO_3 in the presence of CH_3COOH.

$$C_6H_5CH_2CH_3 \xrightarrow{CrO_3, CH_3COOH} \underset{\text{Acetophenone}}{C_6H_5COCH_3}$$

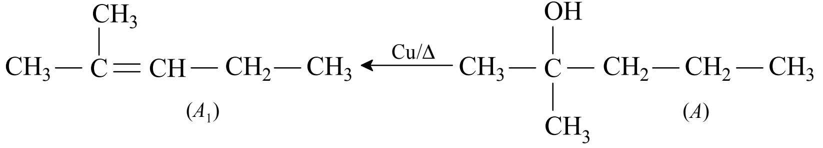
Illustration - 4 : An alcohol (A) when heated with copper gives a product (A_1) not having oxygen atom. (A) on ozonolysis gives two isomeric products (B) & (C). (B) on oxidation gives a monocarboxylic acid (D), silver salt of which contains 59.6% Ag. Write structure of (A).

Soln.: Molecular mass of silver salt of $D = \frac{108}{59.6} \times 100 = 181$

RCOOAg = 181

R = 181 – (108 + 12 + 32) = 181 – 152 = 29

Thus R = $-CH_2-CH_3$ and hence acid salt is $CH_3-CH_2-COOAg$. Corresponding to this salt acid is CH_3-CH_2-COOH which is obtained by oxidation of (*B*), an ozonolysis product. Thus *B* is $CH_3-CH_2-CH=O$. Since (*B*) and (*C*) are isomers, hence (*C*) is $CH_3-\overset{\overset{CH_3}{|}}{C}=O$. On the basis of (*B*) & (*C*) we can get product (A_1) and finally (*A*).

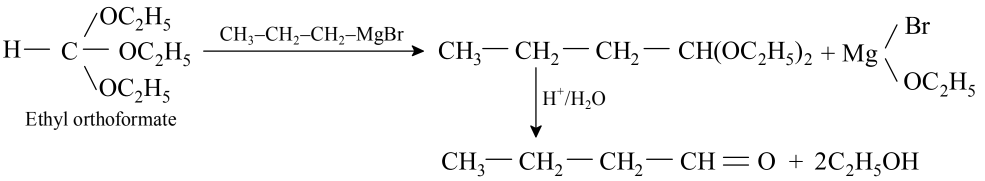


$$\underset{(A_1)}{CH_3-\overset{\overset{CH_3}{|}}{C}=CH-CH_2-CH_3} \xleftarrow{Cu/\Delta} \underset{(A)}{CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2-CH_2-CH_3}$$

Illustration - 5 : *n*-butyraldehyde can be synthesized from *n*-propyl magnesium bromide and

(a) ethyl orthoformate (b) acetyl chloride (c) *n*-butyl formate (d) formic acid

Soln.:

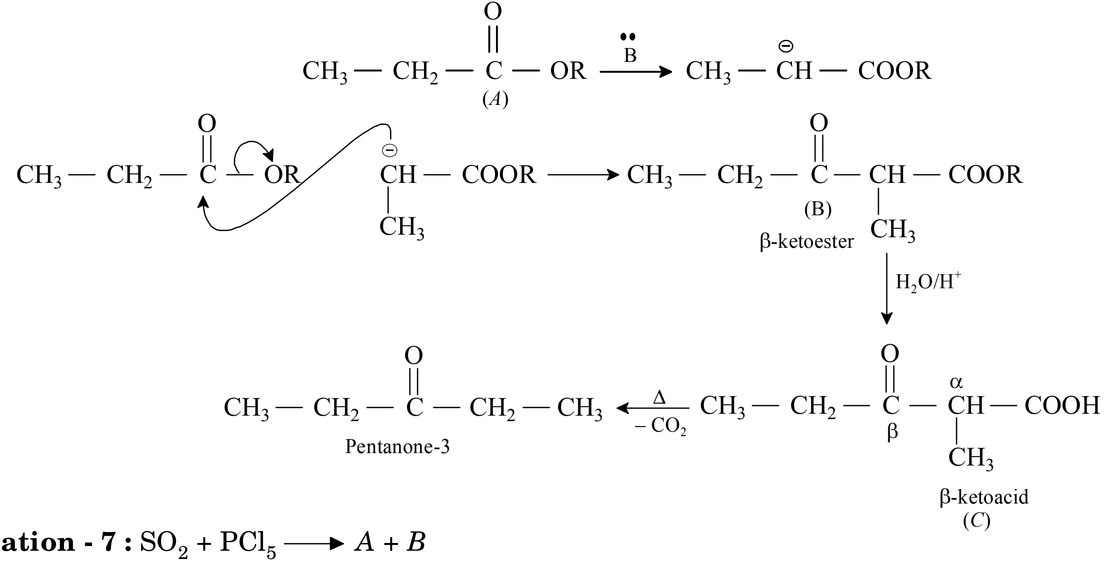


$$\underset{\text{Ethyl orthoformate}}{H-\overset{/OC_2H_5}{\underset{\backslash OC_2H_5}{C}}-OC_2H_5} \xrightarrow{CH_3-CH_2-CH_2-MgBr} CH_3-CH_2-CH_2-CH(OC_2H_5)_2 + Mg\begin{smallmatrix}/\,Br\\ \backslash\,OC_2H_5\end{smallmatrix}$$

$$\xrightarrow{H^+/H_2O} CH_3-CH_2-CH_2-CH=O + 2C_2H_5OH$$

Illustration - 6 : Two moles of an ester (*A*) when treated with base like sodium ethoxide we get a β-ketoester (*B*) which on acid hydrolysis gives a β-ketoacid (*C*). (*C*) on heating gives pentanone-3. Assign structures from (*A*) to (*C*) with proper reasoning.

Soln.: Since ketone is pentanone-3 hence β-ketoacid (*C*) corresponding to this ketone is $CH_3-CH_2-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-COOH$. As (*C*) is obtained on β-ketoester hydrolysis hence (*B*) is $CH_3-CH_2-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-COOR$. Thus corresponding anion will be $CH_3-\overset{\ominus}{C}H-COOR$ and hence ester will be CH_3-CH_2-COOR. The over all mechanism can be represented as



$$\underset{(A)}{CH_3-CH_2-\overset{\overset{O}{\|}}{C}-OR} \xrightarrow{\ddot{B}} CH_3-\overset{\ominus}{C}H-COOR$$

$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-OR \quad \underset{\underset{CH_3}{|}}{\overset{\ominus}{C}H}-COOR \longrightarrow \underset{\text{β-ketoester}}{\underset{(B)}{CH_3-CH_2-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-COOR}}$$

$$\xrightarrow{H_2O/H^+}$$

$$\underset{\text{Pentanone-3}}{CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-CH_3} \xleftarrow[-CO_2]{\Delta} \underset{\underset{(C)}{\text{β-ketoacid}}}{CH_3-CH_2-\underset{\beta}{\overset{\overset{O}{\|}}{C}}-\overset{\alpha}{\underset{\underset{CH_3}{|}}{C}H}-COOH}$$

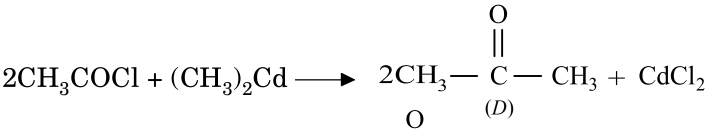
Illustration - 7 : $SO_2 + PCl_5 \longrightarrow A + B$

$CH_3COOH + A \longrightarrow C + SO_2 + HCl$

$2C + (CH_3)_2Cd \longrightarrow 2D + CdCl_2$

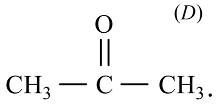
Soln.: $\underset{(A)}{SO_2 + PCl_5 \longrightarrow SOCl_2} + \underset{(B)}{POCl_3}$

$$CH_3COOH + SOCl_2 \longrightarrow \underset{(C)}{CH_3COCl} + SO_2 + HCl$$



$$2CH_3COCl + (CH_3)_2Cd \longrightarrow 2\underset{(D)}{CH_3-\overset{\overset{\large O}{||}}{C}-CH_3} + CdCl_2$$

Thus, $A = SOCl_2$, $B = POCl_3$, $C = CH_3—COCl$, $D =$



$$CH_3-\overset{\overset{O}{||}}{C}-CH_3.$$

PHYSICAL PROPERTIES

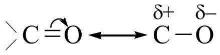
- **Physical state :** Formaldehyde is a gas at room temperature. The remaining members of both the families are either colourless liquids or solids depending upon the size of the alkyl/aryl groups.
- **Smell :** Lower members of aliphatic aldehydes have unpleasant odour. Benzaldehyde smells like bitter almonds. The lower members and ketones have mostly pleasant smell.
- **Solubility :** The lower members of the family containing upto four carbon atoms are water soluble due to the intermolecular hydrogen bonding. The solubility in water gradually decreases with the increase in the size of alkyl group since it tends to mask the polar $>C=O$ group involved in hydrogen bonding. Aromatic aldehydes and ketones are insoluble in water.
- **Boiling points :** (i) Aldehydes and ketones, both have higher boiling points because of dipolar attraction in the polar carbonyl groups, present in these compounds.

  (ii) Among the isomeric aldehydes and ketones, the latter have slightly higher boiling points because of the two electron releasing alkyl groups around carbonyl carbon, which makes them more polar.

CHEMICAL PROPERTIES

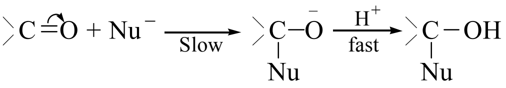
Nucleophilic Addition Reactions

- The carbonyl group is highly polar due to shifting of the π electrons towards the more electronegative oxygen atom.



$$>C=O \longleftrightarrow \overset{\delta+}{C}-\overset{\delta-}{O}$$

- The two charged centres can be attacked by nucleophile (at carbon) and electrophile (at oxygen). In addition reactions, nucleophilic attack is preferred because the anion produced is more stable than the cation.



$$>C=O + Nu^- \xrightarrow[\text{Slow}]{} >\underset{Nu}{\underset{|}{C}}-\overset{-}{O} \xrightarrow[\text{fast}]{H^+} >\underset{Nu}{\underset{|}{C}}-OH$$

- The order of reactivity for aldehydes and ketones towards nucleophilic addition is:

  $HCHO > CH_3CHO > C_2H_5CHO > C_3H_7CHO....$

  $HCHO > CH_3\,CHO > CH_3COCH_3 > CH_3COC_2H_5 > C_2H_5COC_2H_5...$
- As the size of alkyl group increases, its $+I$ effect decreases the positive charge on the carbonyl carbon and thus decreases its reactivity.

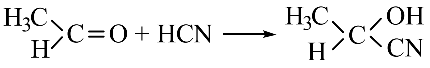
- Larger the alkyl groups, more is steric hinderance which affects the reactivity along with +I effect.
- Aromatic aldehydes and ketones are less reactive than the corresponding aliphatic analogues due to the additional +R effect of the benzene ring, *e.g.* the order:

  $C_6H_5CHO > C_6H_5COCH_3 > C_6H_5COC_6H_5$
- Presence of electron withdrawing group (–I effect) in carbonyl compounds increases the reactivity by increasing the positive charge on the carbonyl carbon, *e.g.*

  $NO_2\,CH_2CHO > ClCH_2CHO > CH_3CHO > CH_3COCH_3$

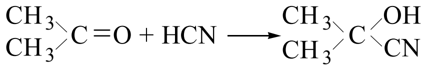
Addition of HCN

- Aldehydes and ketones react with HCN in presence of a base to form cyanohydrins which on hydrolysis yield α-hydroxy acids.



$$\begin{matrix}H_3C\\H\end{matrix}\!\!>C=O + HCN \longrightarrow \begin{matrix}H_3C\\H\end{matrix}\!\!>C\!<\!\begin{matrix}OH\\CN\end{matrix}$$

acetaldehyde　　acetaldehyde cyanohydrin



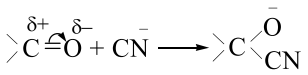
$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O + HCN \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C\!<\!\begin{matrix}OH\\CN\end{matrix}$$

acetone　　acetone cyanohydrin

- **Mechanism.** The reaction takes place in the following steps:

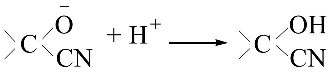
  Step-1: $HCN + OH^- \longrightarrow H_2O + \overset{-}{CN}$

  Step-2:



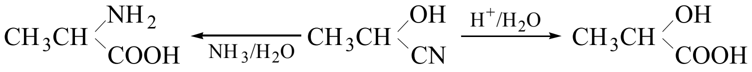
$$>\overset{\delta+}{C}=\overset{\delta-}{O} + \overset{-}{CN} \longrightarrow\ >C\!<\!\begin{matrix}\overset{-}{O}\\CN\end{matrix}$$

  Step-3: Addition of proton (usually from water as solvent)



$$>C\!<\!\begin{matrix}\overset{-}{O}\\CN\end{matrix} + H^+ \longrightarrow\ >C\!<\!\begin{matrix}OH\\CN\end{matrix}$$

- All aldehydes form cyanohydrins but only a few ketones show this reaction, *e.g.* acetone, butanone, pentan-3-one etc.
- Hydrolysis of cyanohydrin:

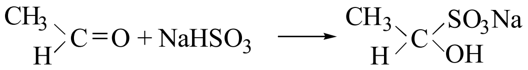


$$CH_3CH\!<\!\begin{matrix}NH_2\\COOH\end{matrix} \xleftarrow[NH_3/H_2O]{} CH_3CH\!<\!\begin{matrix}OH\\CN\end{matrix} \xrightarrow{H^+/H_2O} CH_3CH\!<\!\begin{matrix}OH\\COOH\end{matrix}$$

Alanine (α-amino propionic acid)　　Lactic acid (α-hydroxy acid

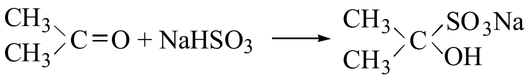
Addition of sodium bisulphite

- Most aldehydes and methyl ketones yield crystalline solids with aqueous solution of sodium bisulphite.



$$\begin{matrix}CH_3\\H\end{matrix}\!\!>C=O + NaHSO_3 \longrightarrow \begin{matrix}CH_3\\H\end{matrix}\!\!>C\!<\!\begin{matrix}SO_3Na\\OH\end{matrix}$$

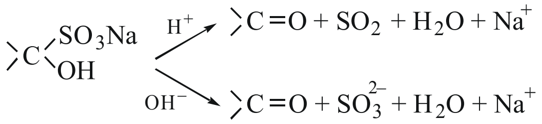
acetaldehyde bisulphite



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O + NaHSO_3 \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C\!<\!\begin{matrix}SO_3Na\\OH\end{matrix}$$

acetone bisulphite

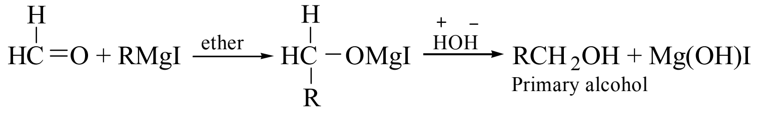
- The bisulphite derivatives are formed to separate out pure aldehydes and ketones from impure mixtures. The aldehyde or ketone is regenerated on treating the bisulphite with dil. HCl or an alkali, *e.g.*



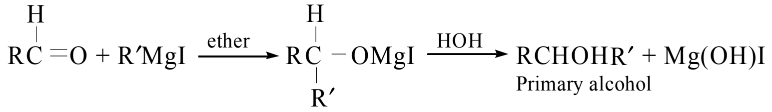
$$>C<^{SO_3Na}_{OH} \xrightarrow{H^+} >C=O + SO_2 + H_2O + Na^+$$
$$>C<^{SO_3Na}_{OH} \xrightarrow{OH^-} >C=O + SO_3^{2-} + H_2O + Na^+$$

Addition of Grignard reagent

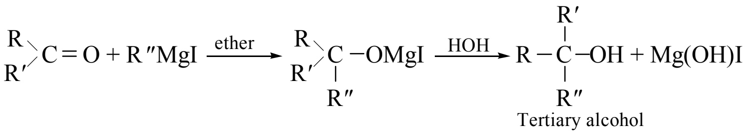
- Grignard reagents in ether add to the carbonyl compound and subsequent hydrolysis of the addition product yields alcohols.
- Formaldehyde forms a primary alcohol while all other aldehydes yield secondary alcohols. Ketones yield tertiary alcohols.



$$\overset{H}{\overset{|}{H C}}=O + RMgI \xrightarrow{ether} \overset{H}{\overset{|}{\underset{R}{\underset{|}{HC}}}}-OMgI \xrightarrow{\overset{+\ -}{HOH}} \underset{\text{Primary alcohol}}{RCH_2OH} + Mg(OH)I$$



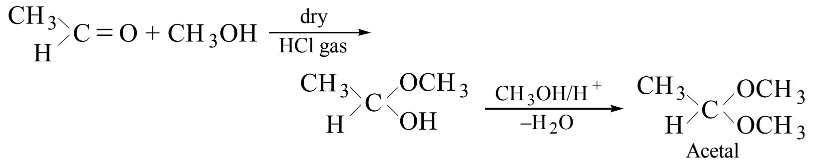
$$\overset{H}{\overset{|}{RC}}=O + R'MgI \xrightarrow{ether} \overset{H}{\overset{|}{\underset{R'}{\underset{|}{RC}}}}-OMgI \xrightarrow{HOH} \underset{\text{Primary alcohol}}{RCHOHR'} + Mg(OH)I$$



$$\genfrac{}{}{0pt}{}{R}{R'}>C=O + R''MgI \xrightarrow{ether} \genfrac{}{}{0pt}{}{R}{R'}>\underset{R''}{\underset{|}{C}}-OMgI \xrightarrow{HOH} \underset{\text{Tertiary alcohol}}{R-\overset{R'}{\overset{|}{\underset{R''}{\underset{|}{C}}}}-OH} + Mg(OH)I$$

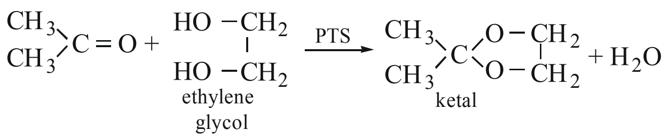
Addition of alcohols

- Aldehydes form addition products, called acetals, with monohydric alcohols in presence of dry HCl gas.



$$\genfrac{}{}{0pt}{}{CH_3}{H}>C=O + CH_3OH \xrightarrow[\text{HCl gas}]{\text{dry}} \genfrac{}{}{0pt}{}{CH_3}{H}>C<\genfrac{}{}{0pt}{}{OCH_3}{OH} \xrightarrow[-H_2O]{CH_3OH/H^+} \underset{\text{Acetal}}{\genfrac{}{}{0pt}{}{CH_3}{H}>C<\genfrac{}{}{0pt}{}{OCH_3}{OCH_3}}$$

- Ketones react with only dihydric alcohols in presence of *p*-toluene sulphonic acid (PTS) to form cyclic ketals, *e.g.*

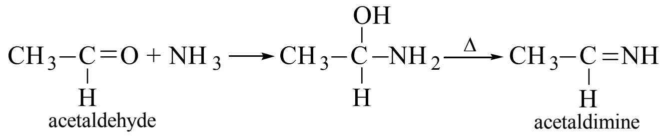


$$\genfrac{}{}{0pt}{}{CH_3}{CH_3}>C=O + \underset{\text{ethylene glycol}}{\genfrac{}{}{0pt}{}{HO-CH_2}{HO-CH_2}} \xrightarrow{PTS} \underset{\text{ketal}}{\genfrac{}{}{0pt}{}{CH_3}{CH_3}>C<\genfrac{}{}{0pt}{}{O-CH_2}{O-CH_2}} + H_2O$$

- Acetals and ketals are ethers, stable towards alkalies but on hydrolysis with dilute acids give back the original aldehyde and ketone.
- This reaction is useful for protecting these groups in organic synthesis.

Addition of ammonia

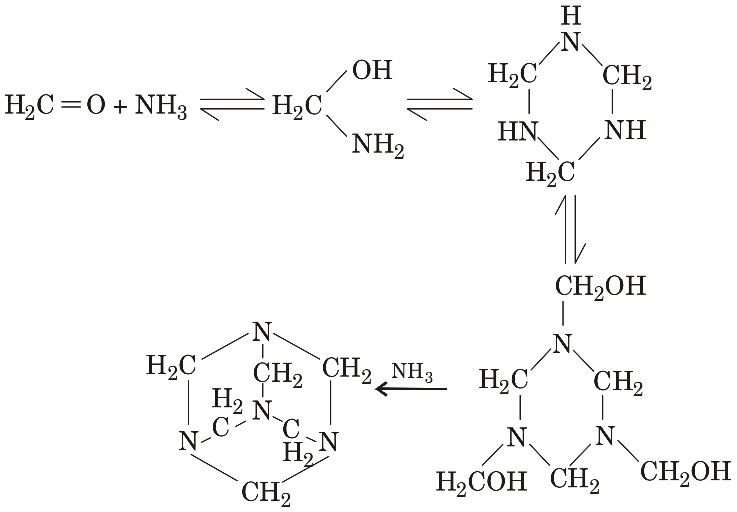
- Aldehydes, except formaldehyde, add ammonia to form aldehyde ammonia which on heating yield aldimines.



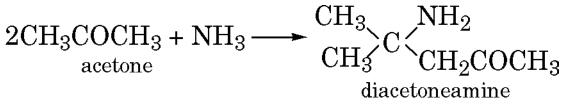
$$\underset{\text{acetaldehyde}}{CH_3-\underset{H}{\underset{|}{C}}=O} + NH_3 \longrightarrow CH_3-\overset{OH}{\overset{|}{\underset{H}{\underset{|}{C}}}}-NH_2 \xrightarrow{\Delta} \underset{\text{acetaldimine}}{CH_3-\underset{H}{\underset{|}{C}}=NH}$$

- Formaldehyde yields an important antiseptic *Urotropine*, which is hexamethylene tetraammine.

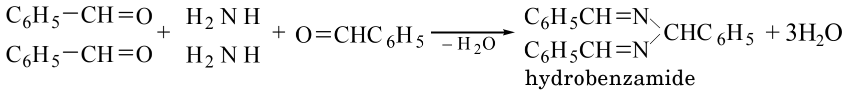
$$6HCHO + 4NH_3 \longrightarrow (CH_2)_6N_4 + 6H_2O$$



- Ketones and aromatic aldehydes yield complex condensation products.



$$2\underset{\text{acetone}}{CH_3COCH_3} + NH_3 \longrightarrow \underset{\text{diacetoneamine}}{\overset{CH_3\quad NH_2}{CH_3 - C - CH_2COCH_3}}$$



$$\begin{matrix}C_6H_5-CH=O\\ C_6H_5-CH=O\end{matrix} + \begin{matrix}H_2NH\\ H_2NH\end{matrix} + O=CHC_6H_5 \xrightarrow{-H_2O} \underset{\text{hydrobenzamide}}{\begin{matrix}C_6H_5CH=N\\ C_6H_5CH=N\end{matrix}}>CHC_6H_5 + 3H_2O$$

Oxidation

- Aldehydes undergo oxidation by even mild oxidising agents like *Tollen's reagent* (ammoniacal silver nitrate solution), *Fehling's solution* (alkaline $CuSO_4$ and sodium potassium tartarate) and *Benedict's solution* (alkaline copper sulphate, sodium citrate and sodium carbonate) to yield corresponding acids with same number of carbon atoms.

$$CH_3CHO + \underset{\text{Tollen's reagent}}{2Ag(NH_3)_2OH} \longrightarrow CH_3COOH + 2Ag + 4NH_3 + H_2O$$

$$CH_3CHO + \underset{\text{Benedict/Fehling's solution}}{2Cu^{2+} + 4OH^-} \longrightarrow CH_3COOH + Cu_2O + 2H_2O$$

- Aromatic aldehydes reduce Tollen's reagent but not Fehling's or Benedict's solution.
- Ketones are oxidised by strong oxidising agents like alkaline $KMnO_4$, acidified $K_2Cr_2O_7$ and hot concentrated HNO_3 etc. to yield acids with lesser number of carbon atoms.

$$CH_3COCH_3 \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3COOH + CO_2 + H_2O$$

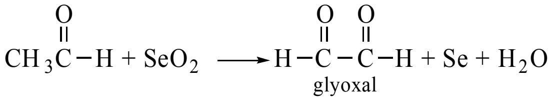
$$CH_3COC_3H_7 \xrightarrow{K_2Cr_2O_7/H_2SO_4} CH_3COOH + C_2H_5COOH$$

- According to Popoff's rule, during oxidation of mixed ketones the carbonyl group remains with the smaller alkyl group.
- Aldehydes, however yield an acid with same number of carbon atoms.

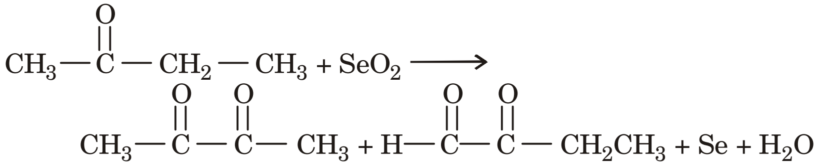
$$CH_3CHO \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3COOH$$

Oxidation with Selenium dioxide

- Aldehydes and ketones with a methyl or methylene group adjacent to the carbonyl group are oxidised by SeO_2 at room temperature to yield an α-dicarbonyl compound, *e.g.*



$$CH_3\overset{O}{\overset{\|}{C}}-H + SeO_2 \longrightarrow \underset{\text{glyoxal}}{H-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H} + Se + H_2O$$



$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3 + SeO_2 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3 + H-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_2CH_3 + Se + H_2O$$

Illustration - 8 : Compound *A*, $C_5H_{10}O$, forms a phenyl-hydrazone, gives negative Tollen's and iodoform test and is reduced to pentane. Identify *A*.

Soln.:

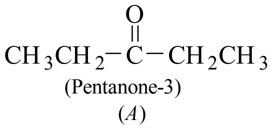
Conclusion:

(1) Compound (*A*) forms a hydrazone hence it has a *carbonyl group*.

(2) It does not reduce Tollen's reagent, therefore it should be a *ketone*.

(3) It does not give iodoform test hence ketone does not have a methyl group.

(4) The structure of *A* will be:

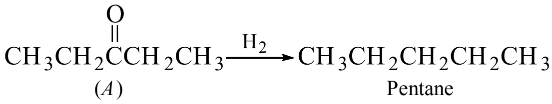


$$CH_3CH_2-\overset{O}{\overset{\|}{C}}-CH_2CH_3$$

(Pentanone-3)

(*A*)

(5) On reduction *A* gives pentane:



$$\underset{(A)}{CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_3} \xrightarrow{H_2} \underset{\text{Pentane}}{CH_3CH_2CH_2CH_2CH_3}$$

Reduction

- Aldehydes and ketones undergo reduction to yield different products, depending on the nature of the reducing agent.

Catalytic reduction

- On reduction with hydrogen in presence of nickel or platinum as catalyst or with complex metal hydrides ($LiAlH_4$ or $NaBH_4$) aldehydes yield primary alcohols while ketones yield secondary alcohols.

$$CH_3CHO \xrightarrow{H_2/\text{Ni or Pt}} CH_3CH_2OH$$

$$C_2H_5CHO \xrightarrow{LiAlH_4/NaBH_4} C_2H_5CH_2OH$$

Aldehydes Primary alcohols

$$CH_3COCH_3 \xrightarrow{H_2/\text{Ni or Pt}} CH_3CHOH\,CH_3$$

$$CH_3COC_2H_5 \xrightarrow{LiAlH_4/NaBH_4} CH_3CHOHC_2H_5$$

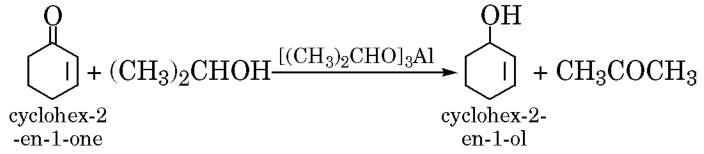
Ketones Secondary alcohols

Meerwein-Ponndorf Verley (MPV) reduction

- Aluminium isopropoxide in presence of excess of isopropyl alcohol reduces ketones to corresponding alcohols.
- Aluminium isopropoxide is a specific reducing agent for carbonyl group and is used for selective reduction of compounds in which other reducible functional groups are present, *e.g.*

  $-NO_2$, $-C=C-$ or $-C\equiv C-$, are not reduced by it.

$$CH_3COC_2H_5 \xrightarrow[(CH_3)_2CHOH]{[(CH_3)_2CHO]_3Al} CH_3CHOHC_2H_5 + CH_3COCH_3$$



Clemmensen's reduction

- Aldehydes and ketones yield the corresponding alkanes on reduction with zinc amalgam and concentrated hydrochloric acid, *e.g.*

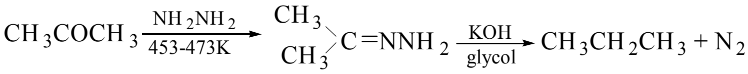
$$CH_3CHO + 4[H] \xrightarrow[\text{Conc. HCl}]{\text{Zn} - \text{Hg}} CH_3CH_3 + H_2O$$

$$CH_3COCH_3 + 4[H] \xrightarrow[\text{Conc. HCl}]{\text{Zn} - \text{Hg}} CH_3CH_2CH_3 + H_2O$$

Wolf-Kishner reduction

- Aldehydes and ketones on being treated with hydrazine followed by reaction with KOH in ethylene glycol yield alkanes.

$$CH_3CHO \xrightarrow[\text{453-473K}]{NH_2.NH_2} \underset{\text{Hydrozone}}{CH_3CH = NNH_2} \xrightarrow[\text{glycol}]{\text{KOH}} CH_3CH_3 + N_2$$



$$CH_3COCH_3 \xrightarrow[\text{453-473K}]{NH_2NH_2} \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C{=}NNH_2 \xrightarrow[\text{glycol}]{\text{KOH}} CH_3CH_2CH_3 + N_2$$

Reduction with HI and red phosphorus

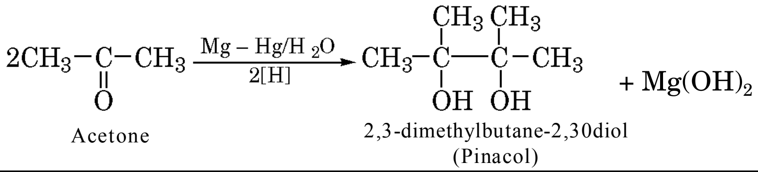
- Aldehydes and ketones on heating with red phosphorus and hydroiodic acid yield alkanes.

$$C_2H_5CHO + 4HI \xrightarrow[\text{423 K}]{\text{Red P}} C_2H_5CH_3 + H_2O + 2I_2$$

$$C_2H_5COC_2H_5 + 4HI \xrightarrow[\text{423 K}]{\text{Red P}} C_2H_5CH_2C_2H_5 + H_2O + 2I_2$$

Bimolecular reduction or Pinacol reduction

- Only ketones undergo reduction in neutral or alkaline medium to yield *pinacols* (symmetrical, 1, 2-diols).

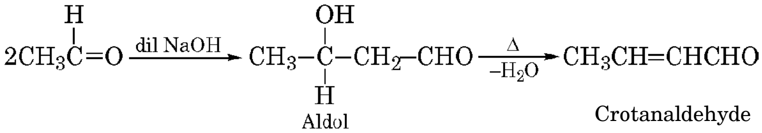


$$2CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow[2[H]]{\text{Mg} - \text{Hg}/H_2O} CH_3-\overset{CH_3}{\underset{OH}{C}}-\overset{CH_3}{\underset{OH}{C}}-CH_3 + Mg(OH)_2$$

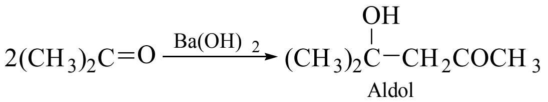
Condensation reactions

Aldol Condensation

- Two molecules of aldehydes or ketones (containing α-H atoms) add in presence of dilute alkali to yield β-hydroxy aldehydes or ketones, called aldols.
- The aldol undergoes dehydration on heating with dilute acids to yield α, β-unsaturated aldehydes or ketones, *e.g.*

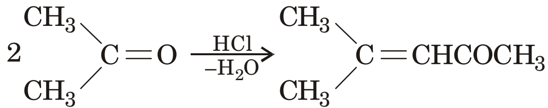


$$2CH_3\overset{H}{C}{=}O \xrightarrow{\text{dil NaOH}} \underset{\text{Aldol}}{CH_3-\overset{OH}{\underset{H}{C}}-CH_2-CHO} \xrightarrow[-H_2O]{\Delta} \underset{\text{Crotanaldehyde}}{CH_3CH{=}CHCHO}$$



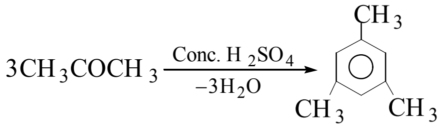
$$2(CH_3)_2C{=}O \xrightarrow{Ba(OH)_2} \underset{\text{Aldol}}{(CH_3)_2\overset{OH}{C}-CH_2COCH_3}$$

Aldol condensation can also take place in presence of acids, *e.g.*



$$2\,(CH_3)_2C{=}O \xrightarrow[-H_2O]{HCl} (CH_3)_2C{=}CHCOCH_3$$

4-methylpent-3-en-2-one
(Mesityl oxide)



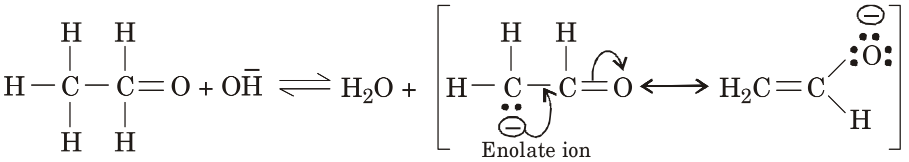
$$3CH_3COCH_3 \xrightarrow[-3H_2O]{\text{Conc. } H_2SO_4}$$

Mesitylene

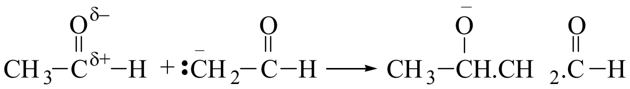
Mechanism

- Aldol condensation involves the following steps:

  Step-1: Formation of carbanion

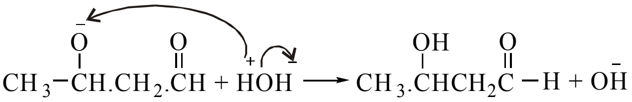


Step-2: The enolate ion acts as a nucleophile and attacks the second carbonyl carbon.



$$CH_3-\overset{O^{\delta-}}{\overset{\|}{C^{\delta+}}}-H + :\bar{C}H_2-\overset{O}{\overset{\|}{C}}-H \longrightarrow CH_3-\overset{\bar{O}}{\overset{|}{C}}H.CH_2.\overset{O}{\overset{\|}{C}}-H$$

Step-3: A proton is added (usually from water)



$$CH_3-\overset{\bar{O}}{\overset{|}{C}}H.CH_2.\overset{O}{\overset{\|}{C}}H + HOH \longrightarrow CH_3.\overset{OH}{\overset{|}{C}}HCH_2\overset{O}{\overset{\|}{C}}-H + \bar{O}H$$

Crossed Aldol Condensation

- This is the condensation between two different carbonyl compounds. The reaction is not very useful as the product is usually a mixture of all possible condensations and cannot be separated easily.
- Good yield of a single product can be obtained if one of the reactants does not contain any α-hydrogen, *e.g.* aromatic aldehydes or formaldehyde, *e.g.*

$$CH_3COCH_3 + HCHO \xrightarrow{\text{Dil NaOH}} CH_3COCH_2CH_2OH$$

Claisen-Schmidt Condensation

- It is a reaction between an aromatic aldehyde and aliphatic aldehyde or ketone.

$$C_6H_5CHO + CH_3CHO \xrightarrow{\bar{OH}} \underset{\text{aldol}}{C_6H_5CHOHCH_2CHO} \xrightarrow[-H_2O]{\text{Heat}} \underset{\text{Cinnamaldehyde}}{C_6H_5CH{=}CHCHO}$$

- Formaldehyde undergoes repeated aldol condensation to yield formose (a sugar).

$$6HCHO \xrightarrow[\substack{\text{or}\\ Ca(OH)_2}]{Ba(OH)_2/\Delta} \underset{\text{formose}}{C_6H_{12}O_6}$$

Crossed Claisen Condensation

- Only ketones undergo this condensation with an ester in presence of sodium ethoxide.

  $CH_3COOC_2H_5 + CH_3COCH_3 \xrightarrow{NaOC_2H_5} CH_3COCH_2COCH_3 + C_2H_5OH$

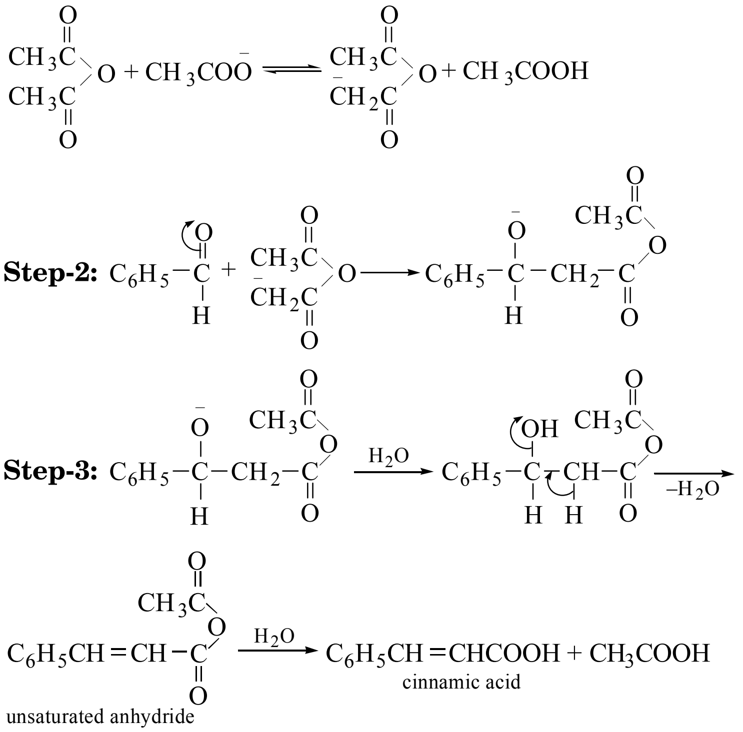
Perkin Condensation

- Aromatic aldehydes condense with an acid anhydride to yield cinnamic acid in presence of salt of the carboxylic acid related to the anhydride and subsequent hydrolysis.

$$C_6H_5CHO + (CH_3CO)_2O \xrightarrow[\text{(b) Hydrolysis}]{\text{(a) } CH_3COONa} \underset{\text{Cinnamic acid}}{C_6H_5CH = CH\,COOH} + CH_3COOH$$

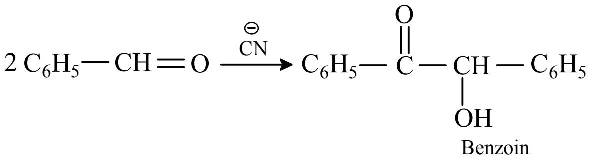
- Other bases like sodium carbonate, quinoline, pyridine, triethylamine etc. may also be used.
- **Mechanism.** The reaction is initiated by the formation of a carbanion by abstraction of α-H atom of the anhydride by the base.

Step-1: $CH_3COONa \longrightarrow CH_3COO^- + Na^+$



Benzoin condensation

- When an ethanolic solution of benzaldehyde is heated (refluxed) with strong alkali potassium cyanide or sodium cyanide, we get benzoin.



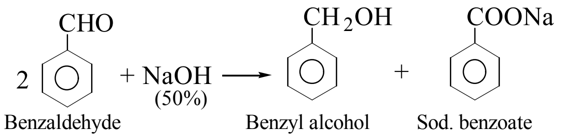
$$2\,C_6H_5-CH=O \xrightarrow{\overset{\ominus}{CN}} C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle OH}{|}}{CH}-C_6H_5$$

Benzoin

Cannizaro Reaction (Disproportionation)

Aldehydes having no α-hydrogen atoms undergo self-redox reaction in aqueous or alcoholic alkali.

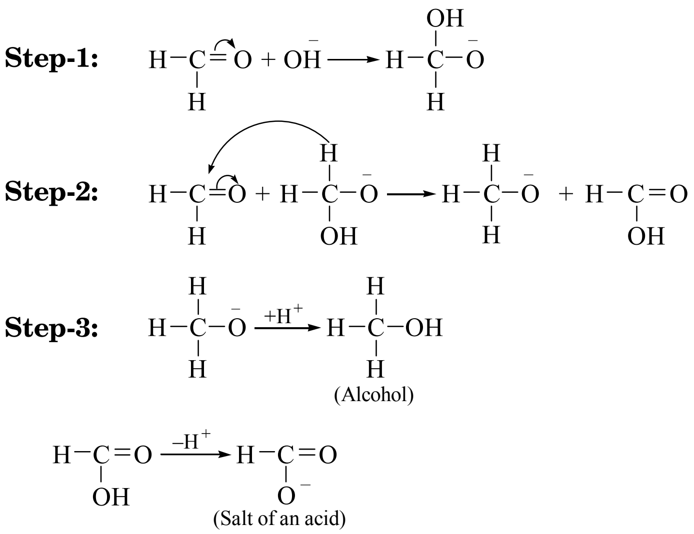
$$2HCHO + \underset{(50\%)}{NaOH} \longrightarrow \underset{\text{sodium formate}}{HCOONa} + \underset{\text{methanol}}{CH_3OH}$$



Benzaldehyde Benzyl alcohol Sod. benzoate

Mechanism

- The reaction mechanism involves a hydride ion transfer and the possible steps may be:



Step-1: $$H-\underset{H}{C}=O + \overset{-}{O}H \longrightarrow H-\underset{H}{\overset{OH}{C}}-\overset{-}{O}$$

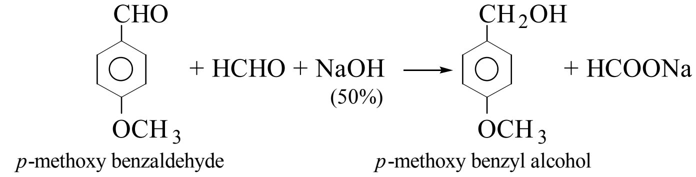
Step-2: $$H-\underset{H}{C}=O + H-\underset{OH}{\overset{H}{C}}-\overset{-}{O} \longrightarrow H-\underset{H}{\overset{H}{C}}-\overset{-}{O} + H-\underset{OH}{C}=O$$

Step-3: $$H-\underset{H}{\overset{H}{C}}-\overset{-}{O} \xrightarrow{+H^+} \underset{\text{(Alcohol)}}{H-\underset{H}{\overset{H}{C}}-OH}$$

$$H-\underset{OH}{C}=O \xrightarrow{-H^+} \underset{\text{(Salt of an acid)}}{H-\underset{O^-}{C}=O}$$

Crossed Cannizzaro reaction

- When reaction occurs between two different aldehydes (having no α-hydrogen atom) different products may be obtained.
- This reaction is very useful when one of the aldehydes is formaldehyde which always gets oxidised to sodium formate whereas the other aldehyde gets reduced to the corresponding alcohol, *e.g.*



p-methoxy benzaldehyde *p*-methoxy benzyl alcohol

Tischenko Reaction

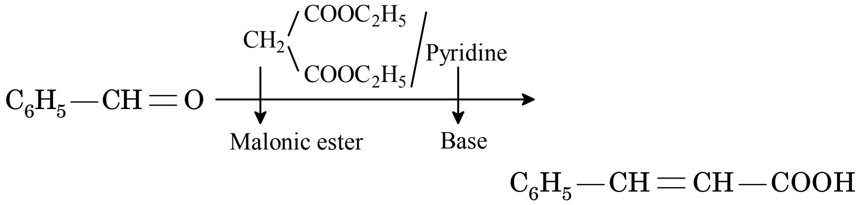
- This is a modified Cannizzaro reaction where all aldehydes, with or without α-hydrogen atoms undergo the redox reaction on treatment with aluminium ethoxide. The alcohol and the acid produced under these conditions combine to form esters, *e.g.*

$$2CH_3CHO \xrightarrow{Al(OC_2H_5)_3} CH_3COOH + CH_3CH_2OH \xrightarrow{-H_2O} CH_3COOCH_2CH_3$$

$$\underset{\text{Propionaldehyde}}{2CH_3CH_2CHO} \xrightarrow{Al(OC_2H_5)_3} CH_3CH_2COOH + CH_3CH_2CH_2OH \; \Big\downarrow {-H_2O} \; \underset{\text{Propyl propionate}}{CH_3CH_2COOCH_2CH_2CH_3}$$

Knoevenagel reaction

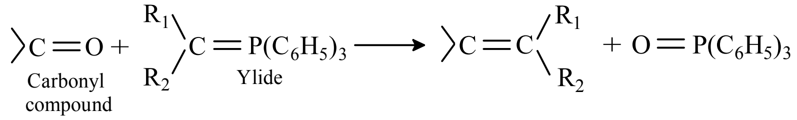
- It is condensation of aromatic aldehydes or any aldehyde or ketone with compound having α-hydrogen atom in the presence of pyridine base. Formation of cinnamic acid from benzaldehyde and malonic ester using pyridine base also comes under this reaction.



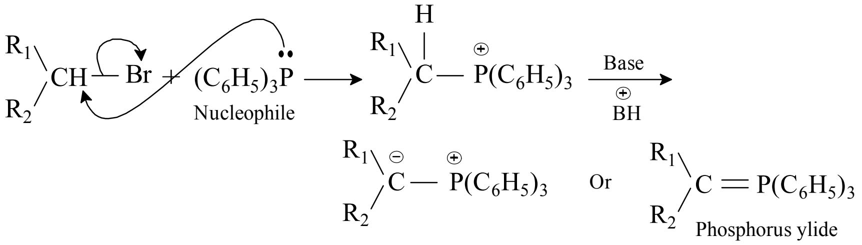
$$C_6H_5-CH=O \xrightarrow[\text{Malonic ester}]{CH_2(COOC_2H_5)_2} \xrightarrow[\text{Base}]{\text{Pyridine}} C_6H_5-CH=CH-COOH$$

Wittig reaction

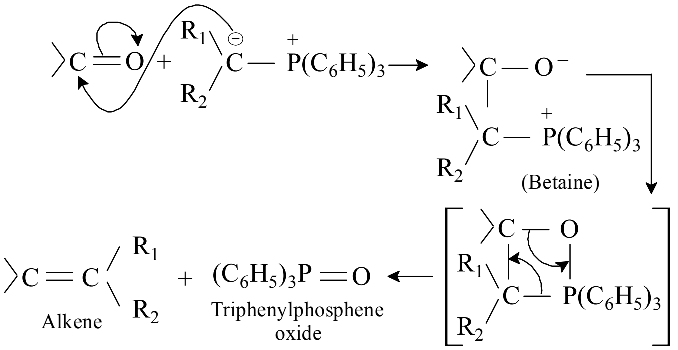
- It is used to get alkene from carbonyl compounds using phosphorus ylide.



- Phosphorus ylides are prepared from primary alkyl halide and triphenyl phosphine in the presence of base like sodium ethoxide as –

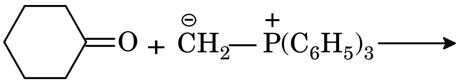


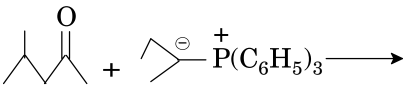
- Preparation of alkene proceeds via the formation of cyclic structure betaine. The mechanism of reaction proceeds as follows:

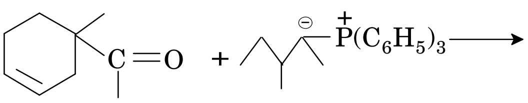


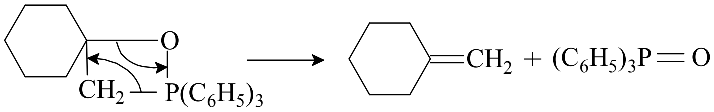
Elimination of triphenylphosphine oxide from betaine gives alkene as a product.

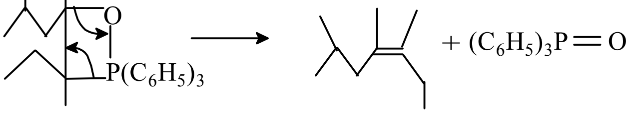
Illustration - 9 : Predict the product for the following:

(a)


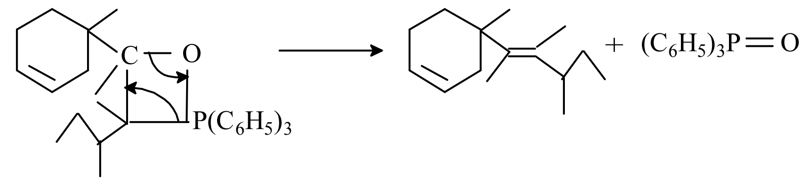
(b)


(c)


Soln.: (a)


(b)


(c)

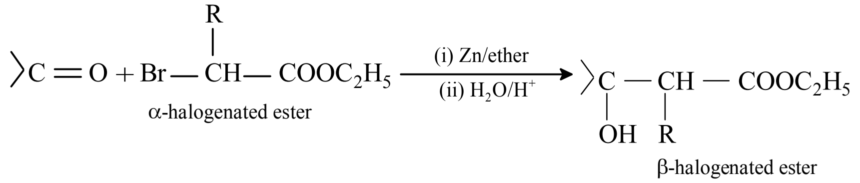


Haloform Reaction

- This reaction is given by acetaldehyde and all methyl ketones ($RCOCH_3$). The carbonyl compound is treated with an excess of halogen (Cl_2, Br_2 or I_2) in presence of alkali when haloform is produced.
  $CH_3CHO + 3Br_2 \xrightarrow{NaOH} CBr_3.CHO \xrightarrow{NaOH} CHBr_3 + HCOONa$
  $CH_3COCH_2CH_3 + 3I_2 \xrightarrow{NaOH} CI_3COCH_2CH_3$
  $\xrightarrow{NaOH} CHI_3 + CH_3CH_2COONa$
- This reaction is also used as a test for CH_3CO- group as iodoform gives yellow coloured crystals.
- The haloform reaction is based on the fact that the three hydrogen atoms of the same carbon are successively replaced by halogen.
- Electron withdrawal by the three halogens makes $-CX_3$ an excellent leaving group.

Reformatsky reaction

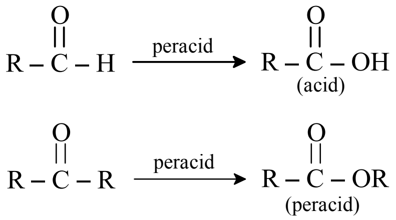
- In this reaction carbonyl compound is treated with α-halogenated ester in the presence of zinc and the product obtained on acid hydrolysis gives β-hydroxyester which may further on hydrolysis and heating gives α, β-unsaturated acid as a final product.



$$\rangle C{=}O + \underset{\alpha\text{-halogenated ester}}{Br{-}\overset{R}{\overset{|}{C}H}{-}COOC_2H_5} \xrightarrow[\text{(ii) } H_2O/H^+]{\text{(i) Zn/ether}} \underset{\beta\text{-halogenated ester}}{\rangle \underset{OH}{\underset{|}{C}}{-}\underset{R}{\underset{|}{C}H}{-}COOC_2H_5}$$

Baeyer-Villiger oxidation

- Oxidation of aldehydes and ketones by peracids is called Baeyer-Villiger oxidation. The net result is the insertion of an oxygen atom adjacent to the carbonyl group.



$$R-\overset{O}{\overset{||}{C}}-H \xrightarrow{\text{peracid}} \underset{\text{(acid)}}{R-\overset{O}{\overset{||}{C}}-OH}$$

$$R-\overset{O}{\overset{||}{C}}-R \xrightarrow{\text{peracid}} \underset{\text{(peracid)}}{R-\overset{O}{\overset{||}{C}}-OR}$$

- The reaction is particularly interesting in case of ketones. Peracids such as *m*-chloroperbenzoic acid (*m*-CPBA), peracetic acid, trifluoroperacetic acid are commonly used.

Illustration - 10 : A ketone (*A*) which undergoes haloform reaction gives compound (*B*) on reduction. (*B*) on heating with H_2SO_4 gives (*C*) which forms a mono-ozonide (*D*). (*D*) on hydrolysis in presence of zinc dust gives only acetaldehyde. Identify (*A*), (*B*) and (*C*) giving the reactions involved.

Soln.: (1) Compound (*A*) gives haloform reaction, hence it must have the group CH_3CO-.

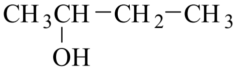
(2) Compound (*C*) forms a mono-ozonide (*D*) hence it must have a double bond.

(3) Since (*D*) gives only one product, CH_3CHO, on hydrolysis, (*C*) should be a symmetrical alkene of four carbon atoms. The possible structure may be:

$CH_3CH=CHCH_3$

(*C*) But-2-ene

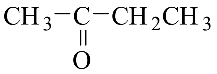
(4) Compound (*C*) is obtained by dehydration of *B*, thus *B* should be an alcohol with structure:



$CH_3\underset{\underset{OH}{\mid}}{CH}-CH_2-CH_3$

(*B*) (Butan-2-ol)

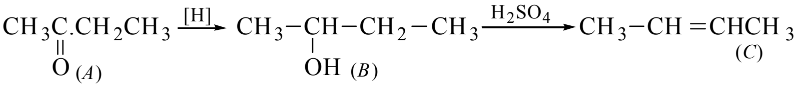
(5) (*B*) is obtained by reduction of *A*, hence structure of *A* should be:



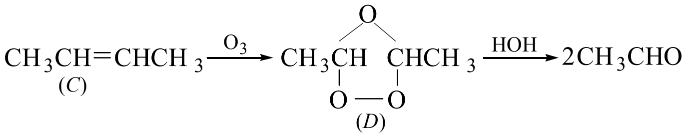
$CH_3-\underset{\underset{O}{\|}}{C}-CH_2CH_3$

(*A*) 2-Butanone

Reactions:



$$CH_3\underset{\underset{O\,(A)}{\|}}{C}.CH_2CH_3 \xrightarrow{[H]} CH_3-\underset{\underset{OH\,(B)}{\mid}}{CH}-CH_2-CH_3 \xrightarrow{H_2SO_4} \underset{(C)}{CH_3-CH=CHCH_3}$$



$$\underset{(C)}{CH_3CH=CHCH_3} \xrightarrow{O_3} (D) \xrightarrow{HOH} 2CH_3CHO$$

Reaction with ammonia derivatives

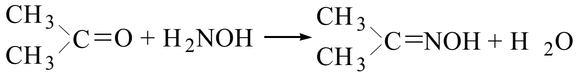
Reaction with Hydroxylamine (NH_2OH)

Aldehydes and ketones react with hydroxylamine to form oximes along with formation of water.

$$CH_3CHO + H_2NOH \longrightarrow CH_3CH=NOH + H_2O$$

Acetaldehyde oxime

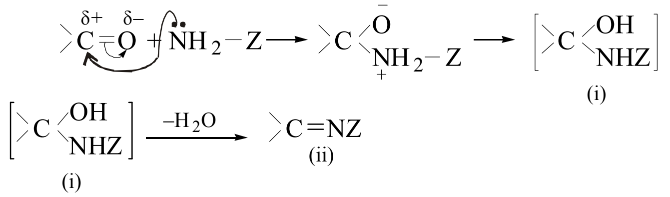
(Aldoxime)



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O + H_2NOH \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=NOH + H_2O$$

Acetone oxime
(keto-oxime)

- Oximes are solids with specific melting points and are therefore used for separation and identification of aldehydes and ketones.
- The reaction with ammonia derivatives involves removal of the carbonyl oxygen and formation of a carbon nitrogen double bond.

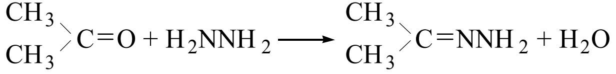


Reaction with Hydrazine (NH_2NH_2)

- Aldehydes and ketones react with hydrazine to form hydrazone and a molecule of water is eliminated.

$$CH_3CH_2CHO + H_2NNH_2 \longrightarrow CH_3CH_2CH=NNH_2 + H_2O$$

Propionaldehyde
hydrazone



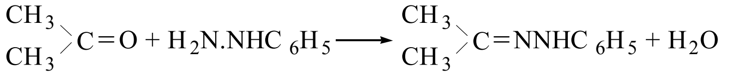
$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O + H_2NNH_2 \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=NNH_2 + H_2O$$

acetone hydrazone

- **Reaction with Phenyl Hydrazine ($C_6H_5NHNH_2$)**

$$CH_3CHO + H_2NNHC_6H_5 \longrightarrow CH_3CH=NNHC_6H_5 + H_2O$$

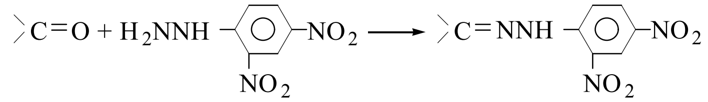
Acetaldehyde
phenyl hydrazone



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O + H_2N.NHC_6H_5 \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=NNHC_6H_5 + H_2O$$

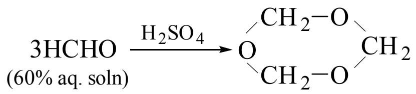
acetone phenyl hydrazone

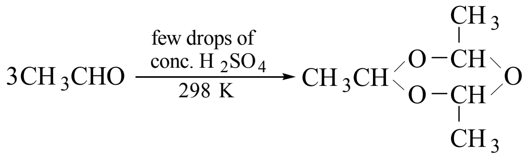
- Substituted phenyl hydrazines, like 2, 4-dinitrophenyl hydrazine reacts similarly yielding hydrazones which are coloured solids with specific melting points and useful in identification of the carbonyl compounds, *e.g.*

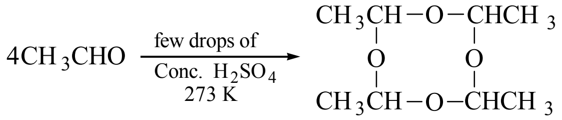


(Hydrazone)

Polymerisation Reactions

- Lower aldehydes, like formaldehyde and acetaldehyde undergo polymerisation under special conditions to yield commercially important polymers, *e.g.*
- $n\ HCHO(aq) \xrightarrow{373\ K} (CH_2O)_n . H_2O$
  Paraformaldehyde
  (n = 6 to 50)
- 

  Trioxan or metaformaldehyde
- 

  Paraldehyde
- 

  Metaldehyde
- Ketones do not show polymerisation.

TESTS USED TO DIFFERENTIATE ALDEHYDES AND KETONES

- **Fehling solution**

  It is alkaline solution of copper sulphate containing some sodium potassium tartrate (Roschelle salt). It consists of two parts. Part (A) is copper sulphate solution and part (B) is alkaline solution of sodium potassium tartrate. When equivalent quantities of these two parts are mixed a deep blue solution is formed. It is because of copper tartrate complex. Aldehyde reduces Fehling's solution and forms a red precipitate of cuprous oxide.

  $$\underset{\text{Fehling soln.}}{RCHO + 2Cu^{++} + 3OH^-} \longrightarrow \underset{\text{(Red precipitate)}}{R—COO^- + 2Cu^+ + 2H_2O}$$

  Aromatic aldehyde and ketone do not give this test.
- **Benedict solution**

  It is an alkaline solution of Cu^{2+} ion complexed with citrate ions (sodium citrate). It reacts in same way as Fehling solution.

Note: Fehling and Benedict solutions are used to detect reducing sugars *e.g.* glucose and fructose.

- **Tollen's reagent**

  It is ammoniacal silver nitrate solution. When aldehyde is added to Tollen's reagent, silver oxide is reduced to metallic silver which deposits as a mirror.

  $$RCHO + \underset{\text{Amm. silver nitrate solution}}{2[Ag(NH_3)_2]^+} + 3OH^- \longrightarrow RCOO^- + \underset{\text{silver mirror}}{2Ag} + 4NH_3 + 2H_2O$$

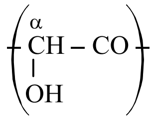
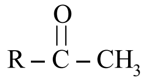
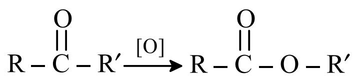
Ketones do not give this test.

- **Schiff's base test**

  It is a colourless solution of rosaniline hydrochloride, a magenta dye and sulphur dioxide. Also called as Schiff's reagent.

  Aldehydes restore the red colouration of Schiff's reagent while ketones do not.

Comparison between aldehydes and ketones

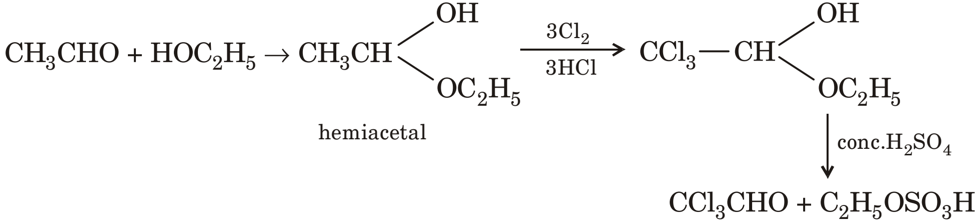
S.No.	Test	RCHO	RCOR
1.	Schiff's reagent	Pink colour is given by RCHO	no reaction
2.	Tollen's reagent	is reduced by RCHO	is not reduced
3.	Fehling's solution	is reduced by RCHO (except C_6H_5CHO)	is not reduced; α-hydroxy ketones reduce Tollen's reagent and Fehling's solution.  $\left(-\overset{\alpha}{\underset{OH}{\underset{\vert}{CH}}}-CO-\right)$
4.	Benedict's solution	is reduced by RCHO	is not reduced
5.	$K_2Cr_2O_7 + H_2SO_4$	is oxidised to RCOOH	alkyl group adjacent to keto group and with smaller number of H-atoms is oxidised (denoted by *) $CH_3\overset{*}{C}OCH_2CH_3 \xrightarrow{[O]} 2CH_3COOH$
6.	Iodoform test (haloform test)	only CH_3CHO gives this test	 $R-\overset{\overset{O}{\Vert}}{C}-CH_3$ (all ketones containing acetyl group CH_3CO) give this test
7.	With NaOH	give brown resinous mass (except HCHO)	no reaction
8.	With sodium nitroprusside + NaOH	a deep red colour (except HCHO)	red colour which changes to orange
9.	Peroxy acid (Caro's acid, peroxy benzoic acid) Baeyer-Villiger oxidation	acid is formed $RCHO \xrightarrow{[O]} RCOOH$	ester is formed  $R-\overset{\overset{O}{\Vert}}{C}-R' \xrightarrow{[O]} R-\overset{\overset{O}{\Vert}}{C}-O-R'$
10.	Acetal with alcohol	formed	not formed

Competitions Window

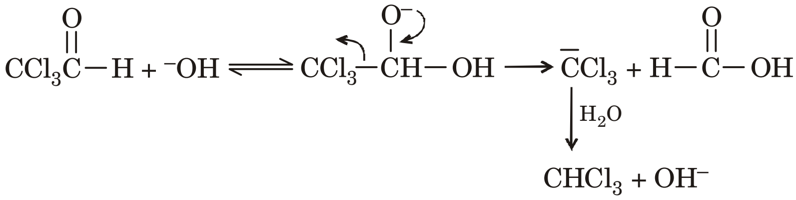
- **Chloral $CCl_3—CH═O$**

  Chloral (trichloroacetaldehyde) is prepared industrially by the chlorination of ethanol. Chlorine is first passed into cold ethyl alcohol and then at 60°C, till no further absorption of chlorine takes place. The final product is chloral alcoholate which separates out as a crystalline solid. This on distillation with concentrated H_2SO_4 gives chloral.

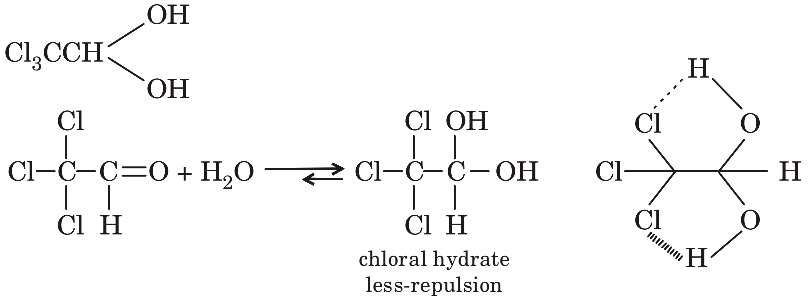
  $CH_3CH_2OH + Cl_2 \rightarrow CH_3CHO$



  Reaction with Alkali : with conc. KOH, it yields pure chloroform.

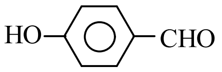


  In acids, most aldehydes form nonisolable unstable gem-diols but chloral hydrate is stable.

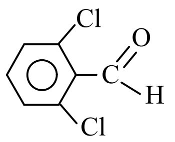


  Strong electron withdrawing group on α-C destabilizes an adjacent carbonyl group because of repulsion of adjacent positive charges. Hydrate formation overcomes the forces of repulsion.

- **The following aldehyde does not contain any α-hydrogen but still fails to undergo Cannizzaro reaction.**

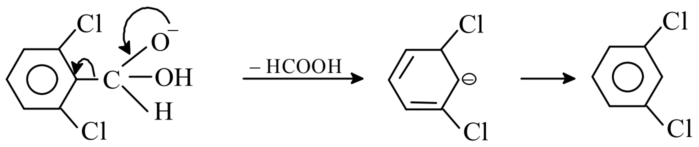


  Because the corresponding hydroxide is strongly stabilized by –R effect of – CHO. Consequently, the electrophilicity of the carbonyl carbon is reduced and the OH^- does not attack the carbonyl group. The inertness towards Cannizzaro reaction is also observed in some other aliphatic and aromatic aldehydes as well because of various reasons. Consider few cases:

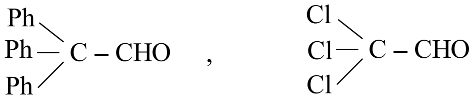


  fails to give Cannizzaro reaction.

Because the intermediate formed due to attack of OH cleaves to give a stable anion. The stability of the anion is due to the electron withdrawing Cl-atoms at *ortho* positions.

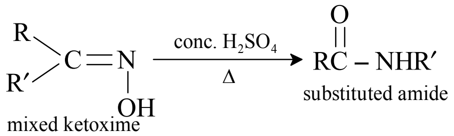


Similarly, the following aldehydes also do not give Cannizzaro reaction.

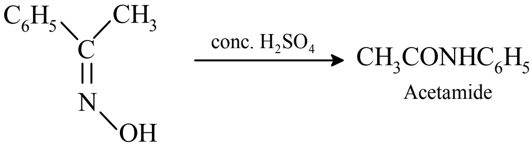


Ph_3C-CHO , Cl_3C-CHO

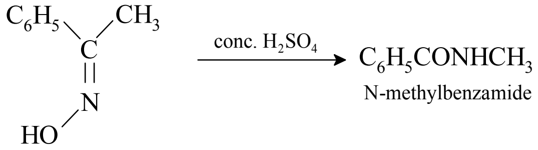
- **Beckmann rearrangement**
The reaction of NH_2OH with ketones gives ketoxime. Ketoximes when heated with certain inorganic reagents (such as conc. H_2SO_4, PCl_5, H_3PO_4, $SOCl_2$ or $C_6H_5SO_2Cl$, etc.) undergo rearrangements to form amides, This is known as Beckmann rearrangement.



mixed ketoxime

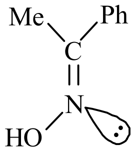


anti-phenyl acetophenone oxime

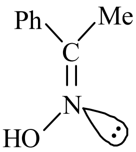


syn-phenyl acetophenone oxime

In ketoximes, the prefixes syn and anti are related to the position of the –R group named with respect to the – OH group whether lying on the same side or opposite side of the double bond respectively.

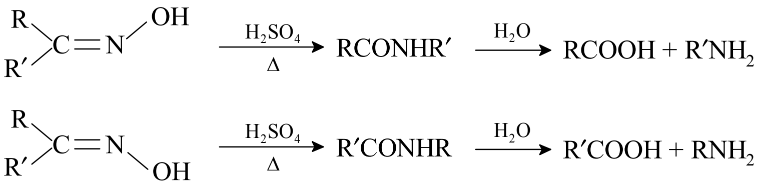


syn-methylphenylketoxime



anti-methylphenylketoxime

Note : During Beckmann rearrangement, it is always the anti group with respect to – OH group which migrates. Therefore this rearrangement is used to determine the configuration of ketoximes.



- **Comparison of the reactions of benzaldehyde and acetaldehyde**

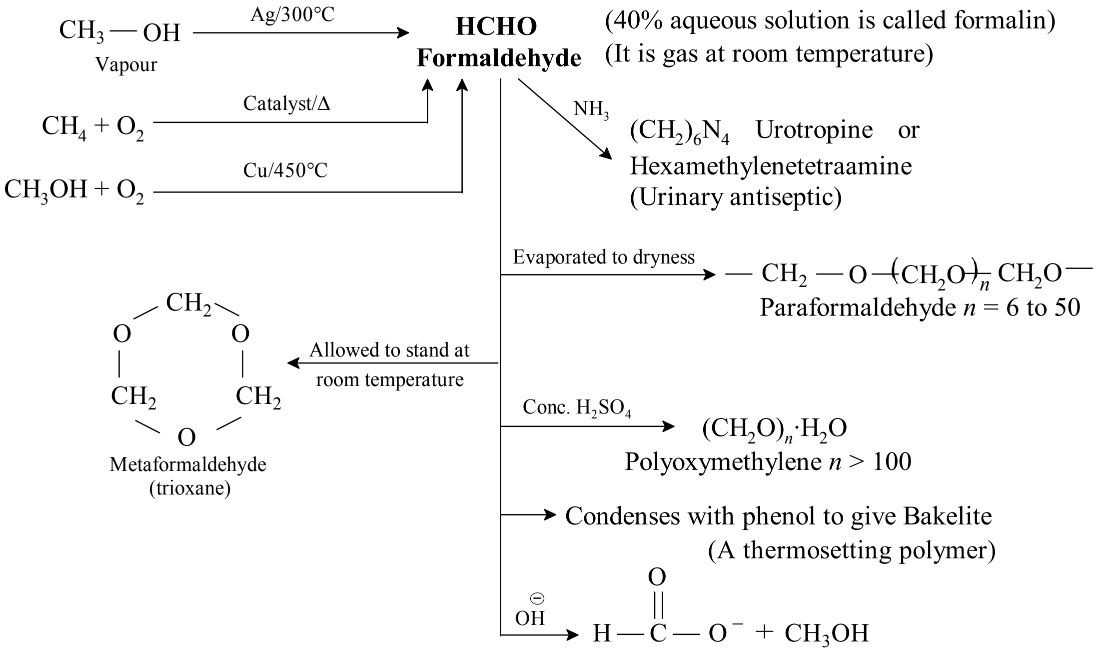
  In the following reactions, benzaldehyde and acetaldehyde behave in a similar way towards the same reagent.

  (1) Addition of HCN, $NaHSO_3$ and $RMgX$
  (2) Reaction with NH_2OH, NH_2NH_2 and $C_6H_5NHNH_2$
  (3) Oxidation with $K_2Cr_2O_7$ or $KMnO_4$
  (4) Reduction with $LiAlH_4$
  (5) Reaction with Tollen's reagent.

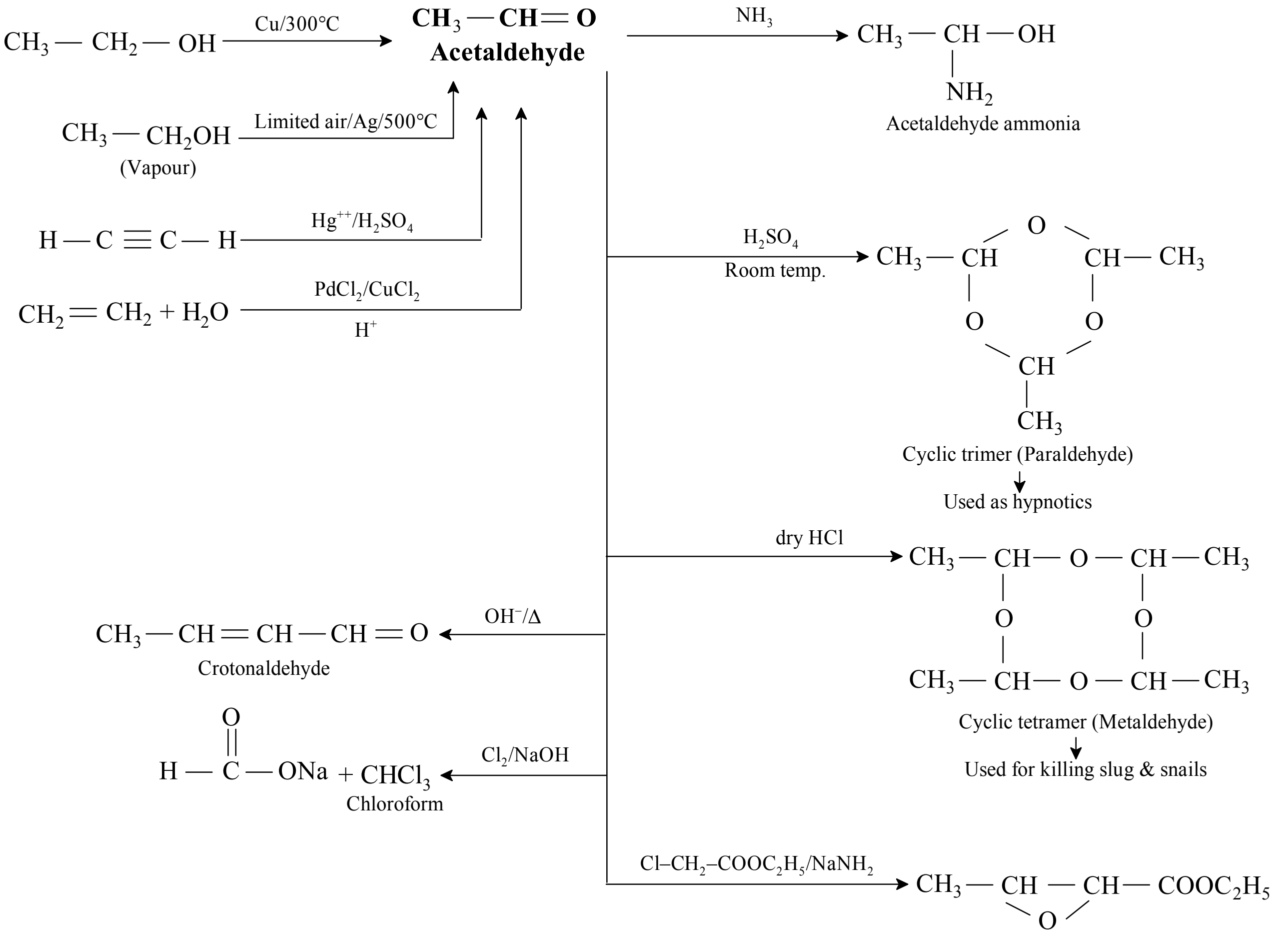
  Benzaldehyde and acetaldehyde behave differently towards the same reagent in the following reactions :

  (1) Iodoform reaction : given by acetaldehyde and not by benzaldehyde.
  (2) Aldol condensation : given by acetaldehyde and not by benzaldehyde.
  (3) Cannizzaro reaction : given by acetaldehyde and not by benzaldehyde.
  (4) Reaction with NH_3 : benzaldehyde condenses with it whereas acetaldehyde gives addition reaction.
  (5) Reaction with Fehling's solution : given by acetaldehyde and not by benzaldehyde.

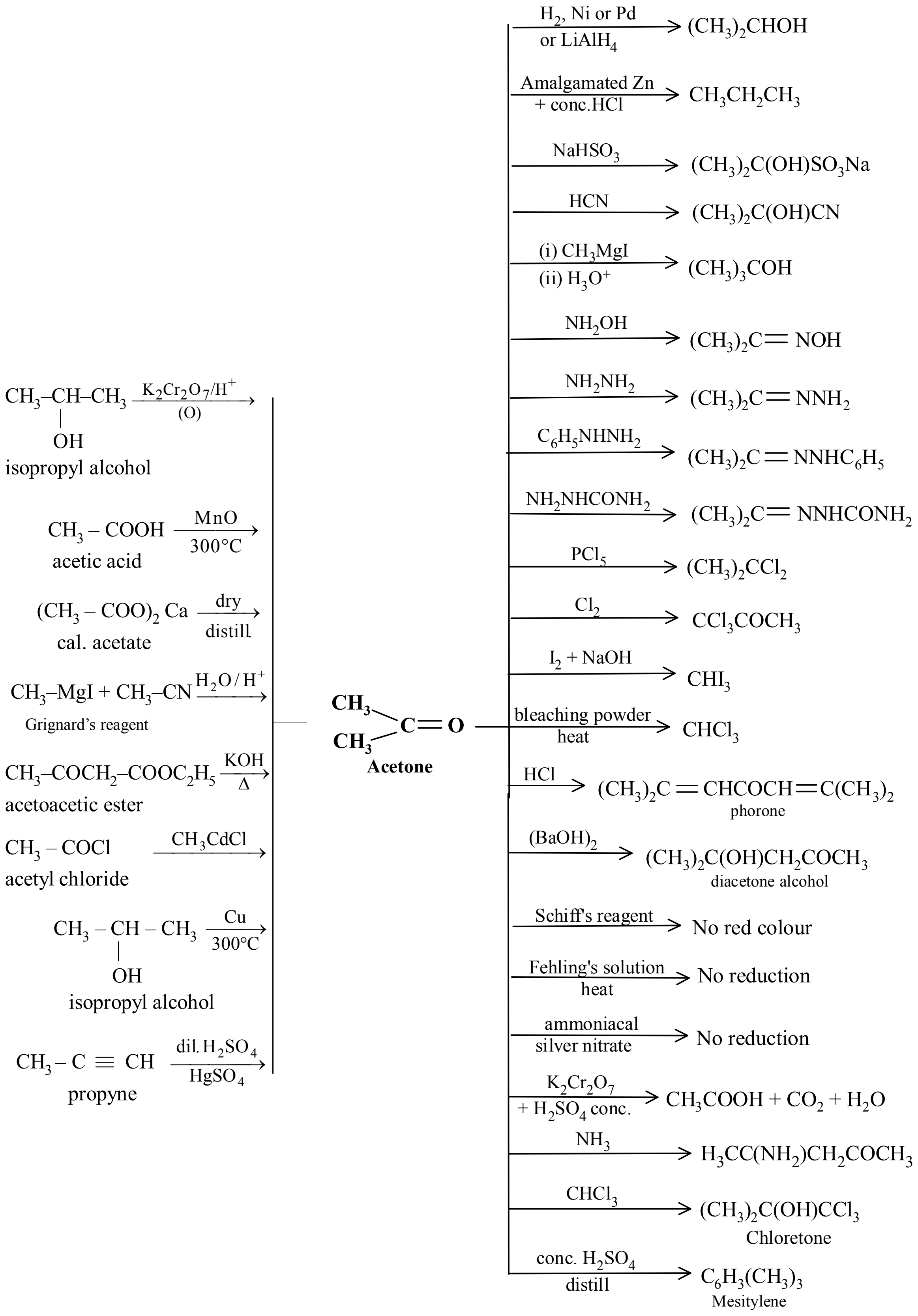
FLOW CHART OF FORMALDEHYDE



FLOW CHART OF ACETALDEHYDE



FLOW CHART OF ACETONE



$CH_3-\underset{|}{CH}-CH_3 \xrightarrow[(O)]{K_2Cr_2O_7/H^+}$ with OH on the CH

isopropyl alcohol

$CH_3-COOH \xrightarrow[300°C]{MnO}$

acetic acid

$(CH_3-COO)_2Ca \xrightarrow[distill]{dry}$

cal. acetate

$CH_3-MgI + CH_3-CN \xrightarrow{H_2O/H^+}$

Grignard's reagent

$CH_3-COCH_2-COOC_2H_5 \xrightarrow[\Delta]{KOH}$

acetoacetic ester

$CH_3-COCl \xrightarrow{CH_3CdCl}$

acetyl chloride

$CH_3-\underset{|}{CH}-CH_3 \xrightarrow[300°C]{Cu}$ with OH on the CH

isopropyl alcohol

$CH_3-C\equiv CH \xrightarrow[HgSO_4]{dil.\,H_2SO_4}$

propyne

$(CH_3)_2C=O$

Acetone

$\xrightarrow[\text{or } LiAlH_4]{H_2,\ Ni \text{ or } Pd} (CH_3)_2CHOH$

$\xrightarrow[+\text{ conc.}HCl]{\text{Amalgamated Zn}} CH_3CH_2CH_3$

$\xrightarrow{NaHSO_3} (CH_3)_2C(OH)SO_3Na$

$\xrightarrow{HCN} (CH_3)_2C(OH)CN$

$\xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } CH_3MgI} (CH_3)_3COH$

$\xrightarrow{NH_2OH} (CH_3)_2C=NOH$

$\xrightarrow{NH_2NH_2} (CH_3)_2C=NNH_2$

$\xrightarrow{C_6H_5NHNH_2} (CH_3)_2C=NNHC_6H_5$

$\xrightarrow{NH_2NHCONH_2} (CH_3)_2C=NNHCONH_2$

$\xrightarrow{PCl_5} (CH_3)_2CCl_2$

$\xrightarrow{Cl_2} CCl_3COCH_3$

$\xrightarrow{I_2 + NaOH} CHI_3$

$\xrightarrow[\text{heat}]{\text{bleaching powder}} CHCl_3$

$\xrightarrow{HCl} (CH_3)_2C=CHCOCH=C(CH_3)_2$

phorone

$\xrightarrow{(BaOH)_2} (CH_3)_2C(OH)CH_2COCH_3$

diacetone alcohol

$\xrightarrow{\text{Schiff's reagent}}$ No red colour

$\xrightarrow[\text{heat}]{\text{Fehling's solution}}$ No reduction

$\xrightarrow[\text{silver nitrate}]{\text{ammoniacal}}$ No reduction

$\xrightarrow[+H_2SO_4\text{ conc.}]{K_2Cr_2O_7} CH_3COOH + CO_2 + H_2O$

$\xrightarrow{NH_3} H_3CC(NH_2)CH_2COCH_3$

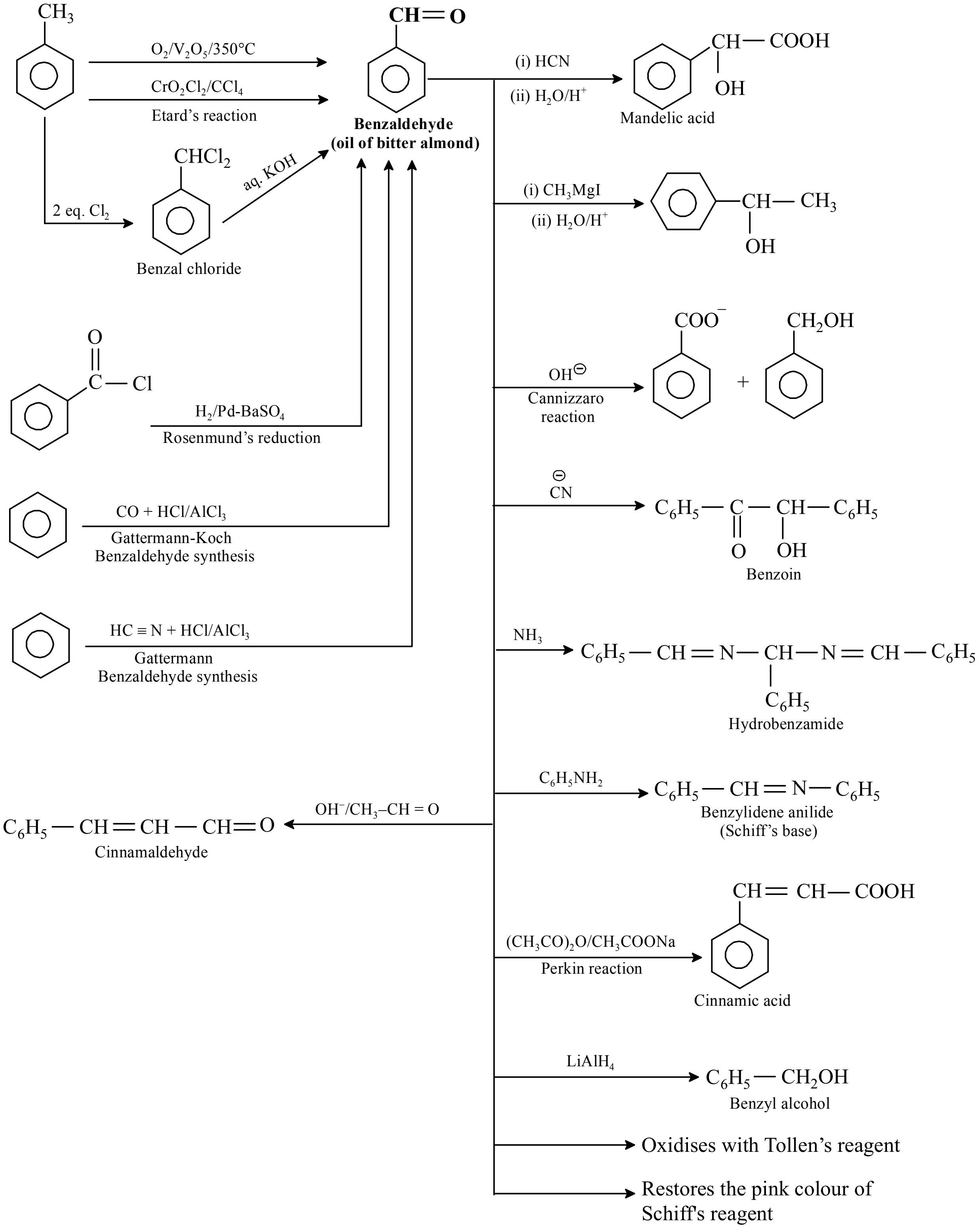
$\xrightarrow{CHCl_3} (CH_3)_2C(OH)CCl_3$

Chloretone

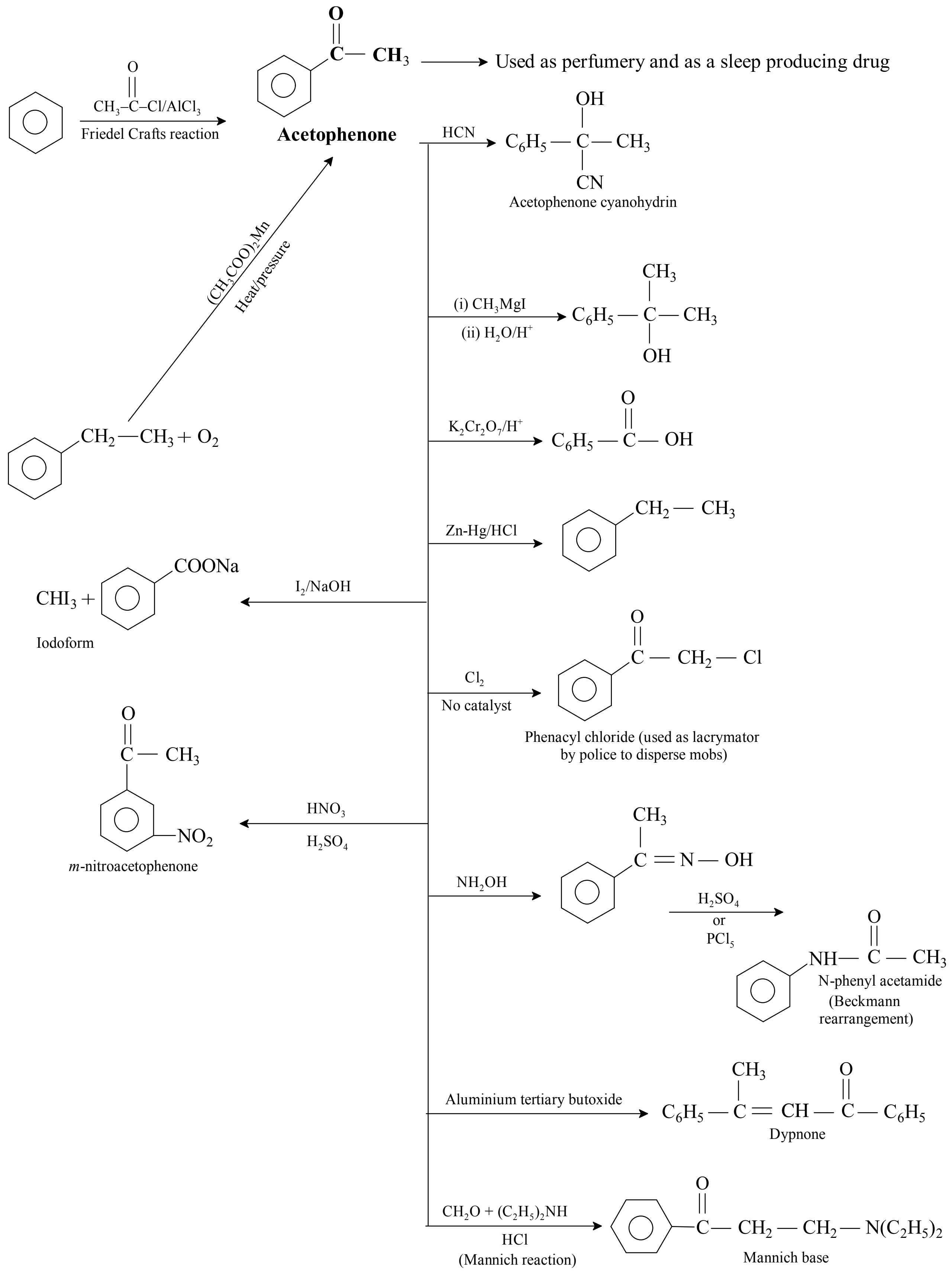
$\xrightarrow[\text{distill}]{\text{conc. } H_2SO_4} C_6H_3(CH_3)_3$

Mesitylene

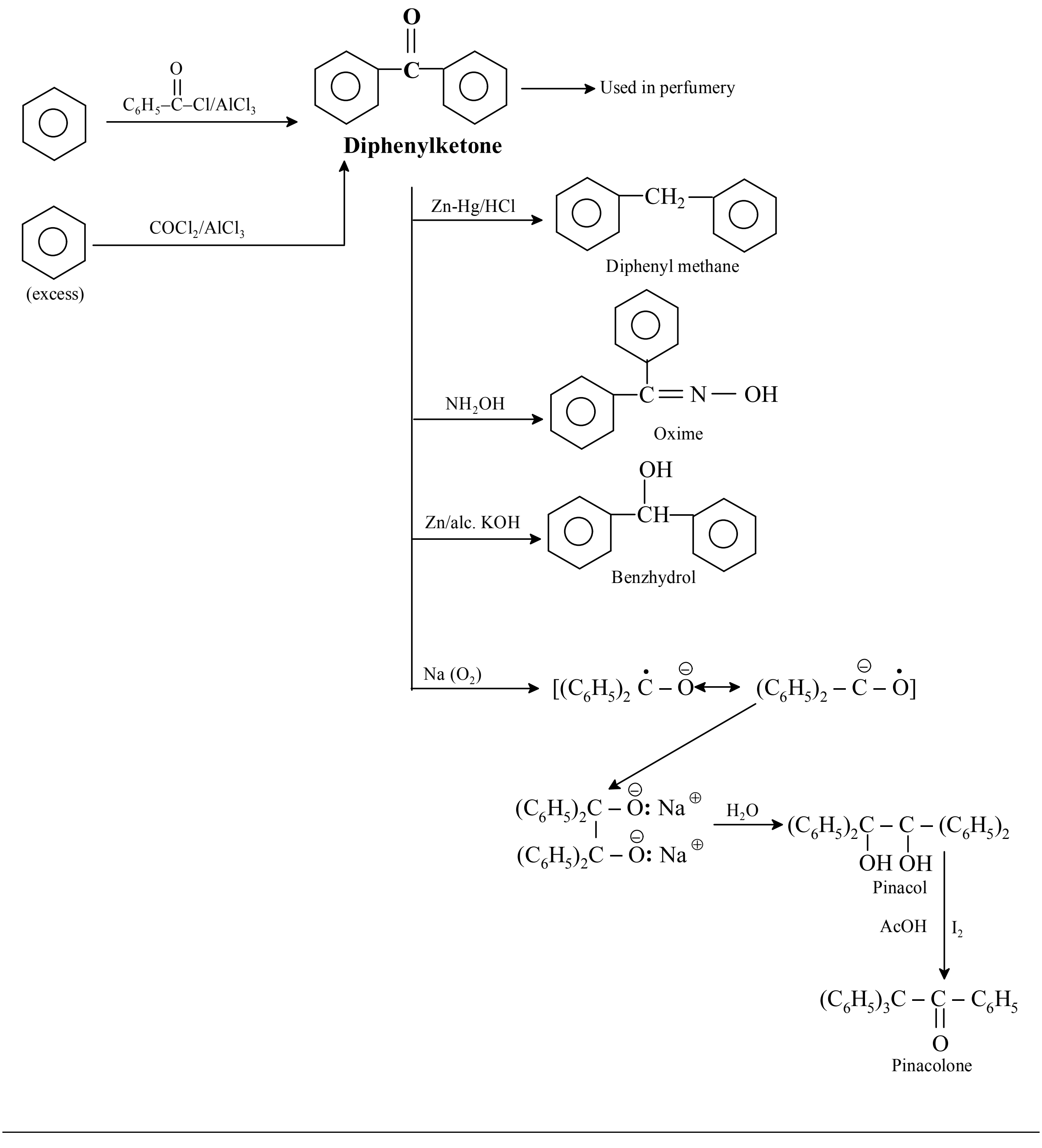
FLOW CHART OF BENZALDEHYDE



FLOW CHART OF ACETOPHENONE



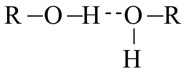
FLOW CHART OF DIPHENYLKETONE



Miscellaneous Examples

1. Account for the boiling points of 2-propanol, propanone and 2-methylpropene (their molecular masses are approximately same), 82°C, 57°C and –7°C respectively.

Soln.: The higher boiling point of 2-propanol is due to H-bonding.



$R-O-H\cdots\underset{H}{\underset{|}{O}}-R$

The higher boiling point of propanone is due to dipole-dipole attractive forces due to carbonyl group, which are absent in alkenes.

---

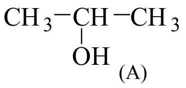
2. An organic compound (*A*) having molecular formula, C_3H_8O on treatment with copper at 300°C gives (*B*). (*B*) does not reduce Tollen's reagent but gives positive iodoform test. Give structures of *A* and *B*.

Soln.: (1) Since (*B*) does not reduce Tollen's reagent so it is not an aldehyde.

(2) (*B*) gives iodoform test, a characteristic of methyl ketones, hence (*B*) is acetone.

$$\underset{(B)}{CH_3-CO-CH_3}$$

(3) Acetone can be obtained by dehydrogenation of a secondary alcohol, therefore structure of *A* could be:



$CH_3-\underset{OH}{\underset{|}{CH}}-CH_3$ (A) (C_3H_8O)

Conclusion:

(*A*) is isopropyl alcohol and (*B*) is acetone.

---

3. An organic compound (*A*) with molecular formula, C_3H_6O is not readily oxidised. It gives on reduction (*B*), C_3H_8O, which reacts with HBr to give (*C*). Grignard reagent obtained from (*C*) reacts with (*A*) to give $C_6H_{14}O$ (*D*). Identify (*A*) to (*D*).

Soln.: (1) Since (*A*) is not readily oxidised, it should be a ketone which on reduction yields a secondary alcohol (*B*). Thus structures for (*A*) and (*B*) are:

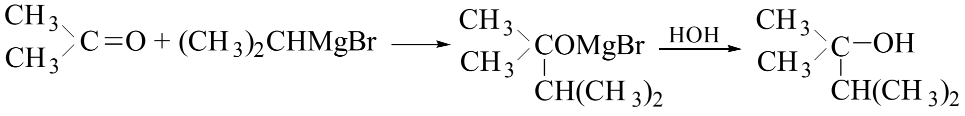
$$\underset{(A)}{CH_3COCH_3} \xrightarrow{[H]} \underset{(B)}{CH_3CHOH\,CH_3}$$

(2) (*B*) reacts with HBr to yield (*C*) which should be an alkyl bromide as it forms a Grignard reagent.

$$\underset{(B)}{CH_3CHOHCH_3} \xrightarrow{HBr} \underset{(C)}{CH_3CHBrCH_3}$$

$$\underset{(C)}{(CH_3)_2CHBr} + Mg \longrightarrow \underset{\text{Grignard reagent}}{(CH_3)_2CHMgBr}$$

(3) Grignard reagent reacts with (*A*) to yield (*D*), $C_6H_{14}O$. The reaction can be written as:



(*D*) $C_6H_{14}O$

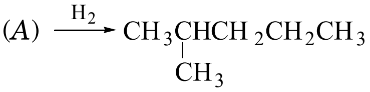
---

4. An organic compound (*A*) does not react with sodium but reacts with PCl_5. (*A*) also undergoes haloform reaction and gives 3-methylbut-2-enoic acid on acidification of products. On hydrogenation (*A*) gives 2-methylpentane. Identify *A*.

Soln.: (1) (*A*) does not react with sodium but reacts with PCl_5, hence it should be a carbonyl compound.

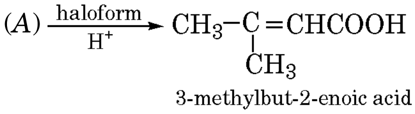
(2) Also, (*A*) undergoes haloform reaction, hence it must have a CH_3CO- unit.

(3) Reduction of (*A*) gives 2-methylpentane.



$(A) \xrightarrow{H_2} CH_3\underset{CH_3}{\underset{|}{C}}HCH_2CH_2CH_3$

(4) During haloform reaction an acid salt is formed which yields acid on acidification:



$$(A) \xrightarrow[H^+]{\text{haloform}} CH_3-\underset{\underset{CH_3}{|}}{C}=CHCOOH$$

3-methylbut-2-enoic acid

Conclusion: On the basis of above reactions structure of (*A*) will be:

$(CH_3)_2\,C = CH\,COCH_3$

(4-methylpent-3-en-2-one)

---

5. The double bond in carbonyl compounds is reactive towards nucleophilic reagents, *e.g.* CN^-:, whereas in alkenes, it is not. Why?

Soln.: Carbonyl group ($>C = O$) polarises completely on demand of the reagent (electromeric effect) forming $> \overset{+}{C} - \overset{-}{\ddot{O}}$ form, which when attacked by a nucleophile forms an intermediate anion $> \overset{CN}{\overset{|}{C}} - \overset{-}{\ddot{O}}$ with negative charge on more electronegative oxygen, hence stable. On the other hand, addition of a nucleophile to $> C = C <$ (alkene) will result in the formation of an anion $> \overset{CN}{\overset{|}{C}} - \overset{-}{\ddot{C}}$ with carbon (not electronegative) carrying the negative charge, hence unstable and thus not reactive to nucleophilic reagents.

---

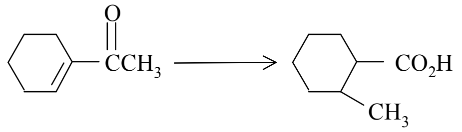
6. Both formaldehyde and benzaldehyde, do not contain α-H atom while formaldehyde reduces Fehling's solution, benzaldehyde does not. Explain, why?

Soln.: Both formaldehyde and benzaldehyde undergo Cannizzaro's reaction in presence of NaOH present in Fehling's solution. Formaldehyde produces formic acid as one of the products, which reduces the Fehling's solution. While benzaldehyde produces both non-reducing compounds benzyl alcohol and benzoic acid.

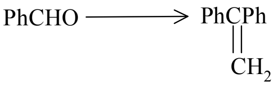
---

7. Suggest a synthesis of each product from the indicated starting material.

(a)

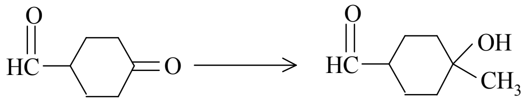


(b)

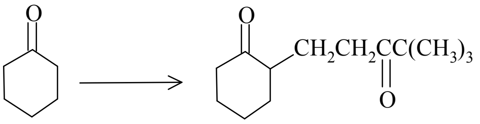


$$PhCHO \longrightarrow Ph\underset{\underset{CH_2}{||}}{C}Ph$$

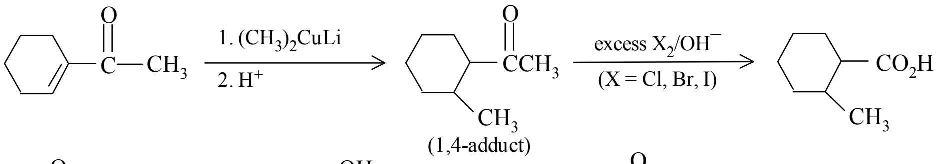
(c)



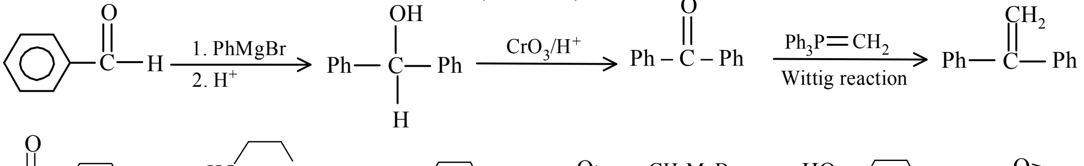
(d)



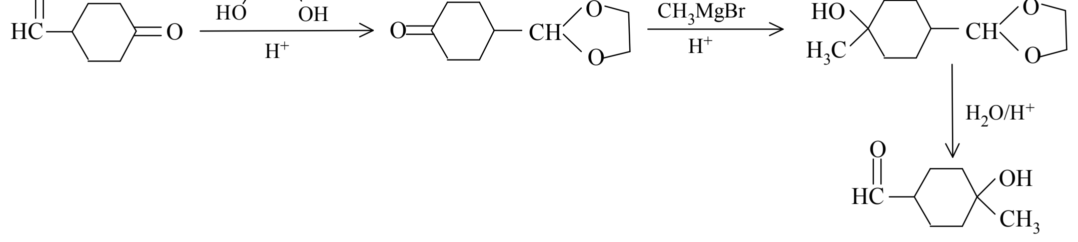
Soln.: (a)

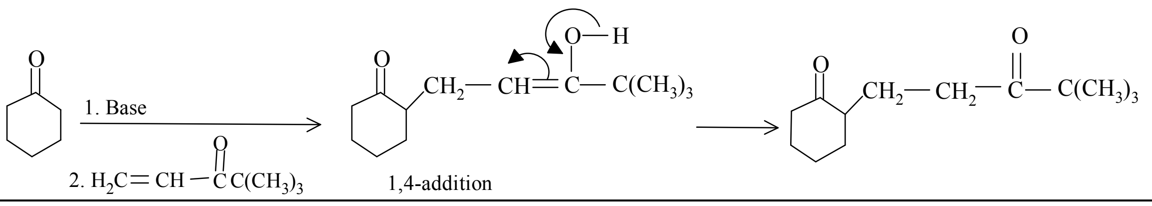


(b)

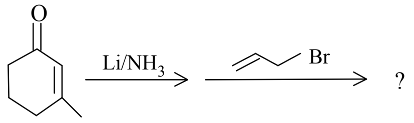


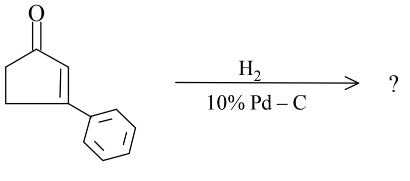
(c)

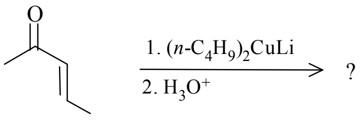


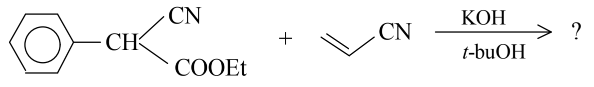
(d) 

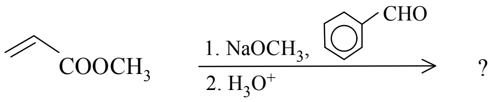
8. Write the products of the following reactions.

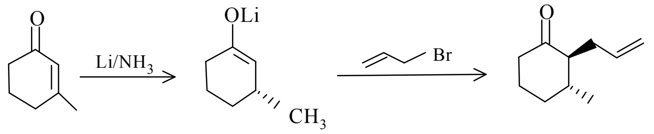
(a) 

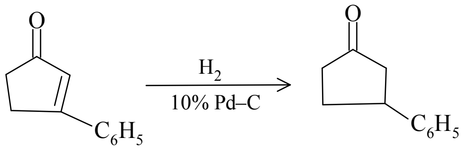
(b) 

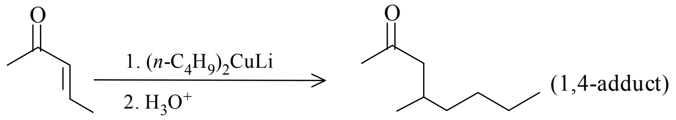
(c) 

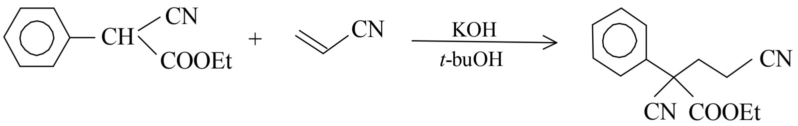
(d) 

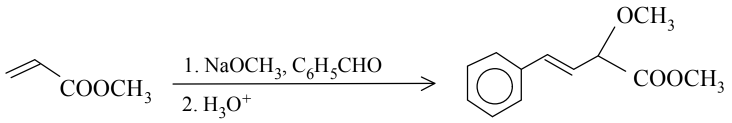
(e) 

Soln.: (a) 

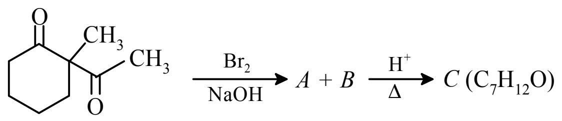
(b) 

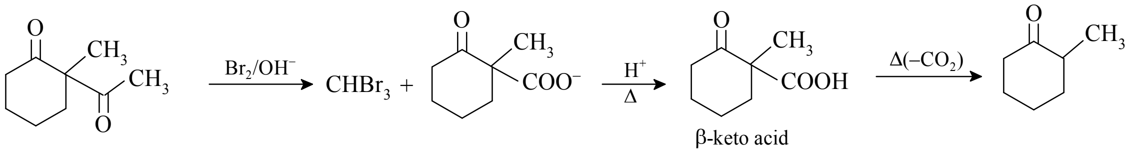
(c) 

(d) 

(e) 

9. Identify *A*, *B* and *C* and give their structures.



Soln.: 

10. In the following identify the compounds and reaction conditions represented by the alphabets *A*, *B* and *C*.

$$H_3C-CH{=}CH-CHO \xrightarrow{NaBH_4} A \xrightarrow[ZnCl_2]{HCl} B \xrightarrow[H^+]{KCN} C$$

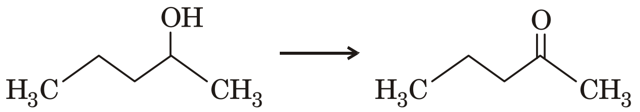
Soln.: $$CH_3-CH=CH-CHO \xrightarrow[\text{or } LiAlH_4]{NaBH_4} \underset{(A)}{CH_3-CH=CH-CH_2OH} \xrightarrow[ZnCl_2]{HCl} \underset{(B)}{CH_3-CH=CH-CH_2Cl} \xrightarrow[H^+]{KCN}$$
$$CH_3-CH=CH-CH_2CN \xrightarrow{H_2O/H^+} \underset{(C)}{CH_3-CH=CH-CH_2COOH}$$

---

11. Suggest suitable reagents for the following conversions :

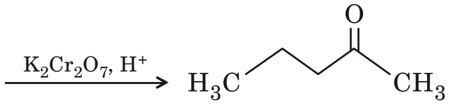
(a) $CH_3CH_2CH_2CH_2CH_2OH \longrightarrow CH_3CH_2CH_2CH_2CHO$

(b)



Soln.: (a) $\xrightarrow[\Delta]{\text{Cu or CuO}} CH_3CH_2CH_2CH_2CHO$

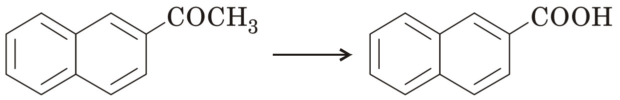
(b)



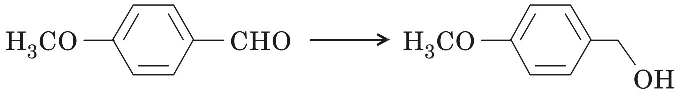
---

12. Suggest reagents to obtain the following products

(a)



(b)

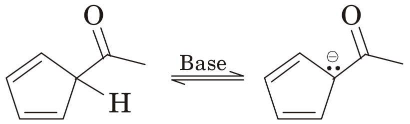


Soln.: (a) $NaOH/Cl_2$ **(b)** $NaBH_4/CH_3OH$

---

13. Which of the following ketones is more acidic ? Give a reason.

Soln.:

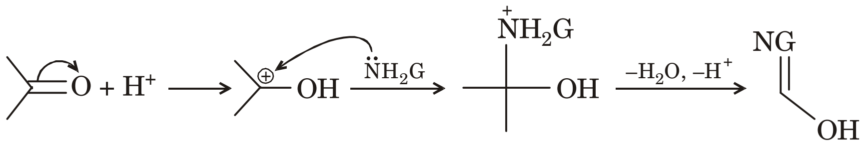


This ketone is more acidic because the resulting enolate ion obeys Huckel's rule of aromaticity and is thus more stable.

---

14. How would you account for the following ?
During the preparation of ammonia derivatives from aldehydes and ketones, pH of the reaction is fully controlled.

soln.: Action of ammonia derivatives, $\ddot{N}H_2G$ on aldehydes and ketones is the nucleophilic addition reaction in which ammonia derivatives act as nucleophiles. Addition of acid is helpful in developing +ve charge on the carbon of carbonyl group. Due to this positive charge, nucleophile can attack easily on carbonyl group. Thus acid (H^+) is required for these reactions.



On the other hand, if we increase the concentration of H^+ (*i.e.*, decrease the pH), it will react wit ammonia derivative to form the salt.

$$\ddot{N}H_2G + H^+ \longrightarrow \ddot{N}H_3G$$

This salt can no more act as a nucleophile, thus the reaction stops. Due to the above reasons the pH should neither be more nor be less or it should be fully controlled (≈ 3.5)

15. A ketone *A* which undergoes a haloform reaction gives compound *B* on reduction. *B* on heating with sulphuric acid gives compound *C*, which forms mono-ozonide *D*. The compound *D* on hydrolysis in presence of zinc dust gives only acetaldehyde. Identify *A*, *B* and *C*. Write down the reactions involved.

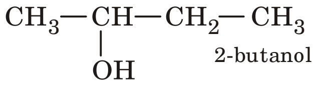
Soln.: We are given that $A \xrightarrow{\text{reduction}} B$; $B \xrightarrow{H_2SO_4} C$

C forms mono-ozonide, *D*. $D \xrightarrow{H_2O/Zn} CH_3CHO$

The compound *A* gives a haloform reaction; it must contain CH_3CO group. The compound *C* contains a double bond as it forms mono-ozonide *D*. Since, the compound *D* on hydrolysis gives only CH_3CHO, the structure of *C* would be

$$\underset{(C)}{CH_3CH{=}CHCH_3} \text{ 2-butene}$$

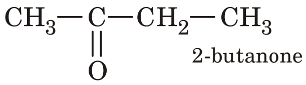
The compound *C* is obtained by dehydration of *B*, thus the latter should be



$$CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CH_3 \quad \text{2-butanol}$$

(*B*)

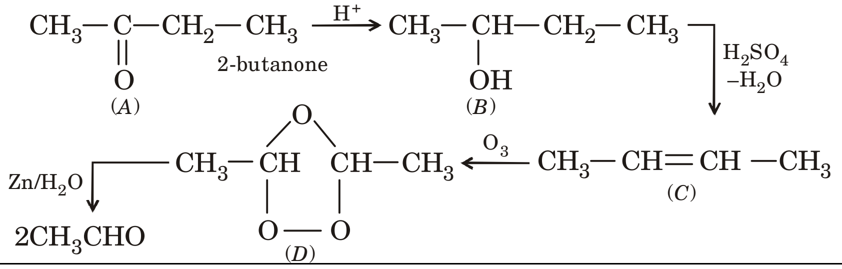
Finally, *B* is obtained by the reduction of *A*. Hence, the compound *A* should be



$$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_3 \quad \text{2-butanone}$$

(*C*)

The equations involved are as follows

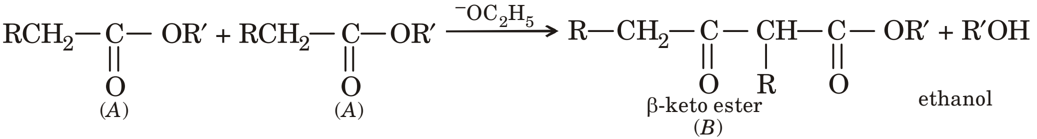


---

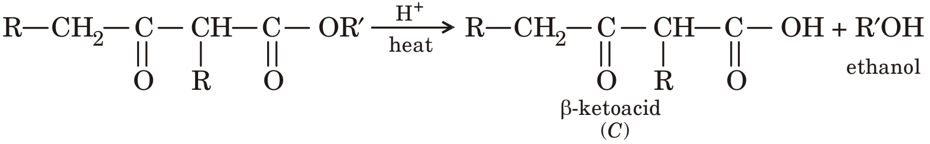
16. Two moles of an ester *A* are condensed in the presence of sodium ethoxide to give a β-keto ester, *B* and ethanol. On heating in an acidic solution, *B* gives ethanol and a β-keto acid, *C*. On decarboxylation *C* gives 3-pentanone. Identify *A*, *B* and *C* with proper reasoning.

Soln.: The reaction of 2 mol of an ester giving β-keto ester and alcohol in the presence of sodium ethoxide is known as Claisen condensation.

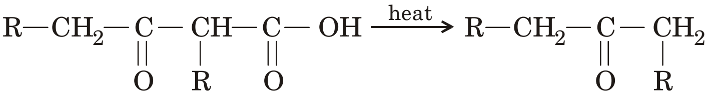
Let the given reactions may be depicted as shown in the following.



$$\underset{(A)}{RCH_2-\underset{\underset{O}{\|}}{C}-OR'} + \underset{(A)}{RCH_2-\underset{\underset{O}{\|}}{C}-OR'} \xrightarrow{^-OC_2H_5} \underset{\beta\text{-keto ester }(B)}{R-CH_2-\underset{\underset{O}{\|}}{C}-\underset{\underset{R}{|}}{CH}-\underset{\underset{O}{\|}}{C}-OR'} + \underset{\text{ethanol}}{R'OH}$$



$$R-CH_2-\underset{\underset{O}{\|}}{C}-\underset{\underset{R}{|}}{CH}-\underset{\underset{O}{\|}}{C}-OR' \xrightarrow[\text{heat}]{H^+} \underset{\beta\text{-ketoacid }(C)}{R-CH_2-\underset{\underset{O}{\|}}{C}-\underset{\underset{R}{|}}{CH}-\underset{\underset{O}{\|}}{C}-OH} + \underset{\text{ethanol}}{R'OH}$$



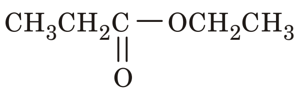
$$R-CH_2-\underset{\underset{O}{\|}}{C}-\underset{\underset{R}{|}}{CH}-\underset{\underset{O}{\|}}{C}-OH \xrightarrow{\text{heat}} R-CH_2-\underset{\underset{O}{\|}}{C}-\underset{\underset{R}{|}}{CH_2}$$

From these reactions, it is obvious that

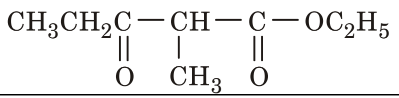
$R' \equiv -CH_2CH_3$

$R \equiv -CH_3$

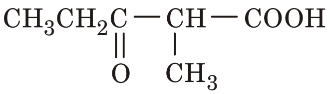
Hence, the compounds *A*, *B* and *C* are

A : 

$CH_3CH_2\underset{\underset{O}{\|}}{C}-OCH_2CH_3$

B : 

$CH_3CH_2\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{O}{\|}}{C}-OC_2H_5$

C : 

$CH_3CH_2\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-COOH$

---

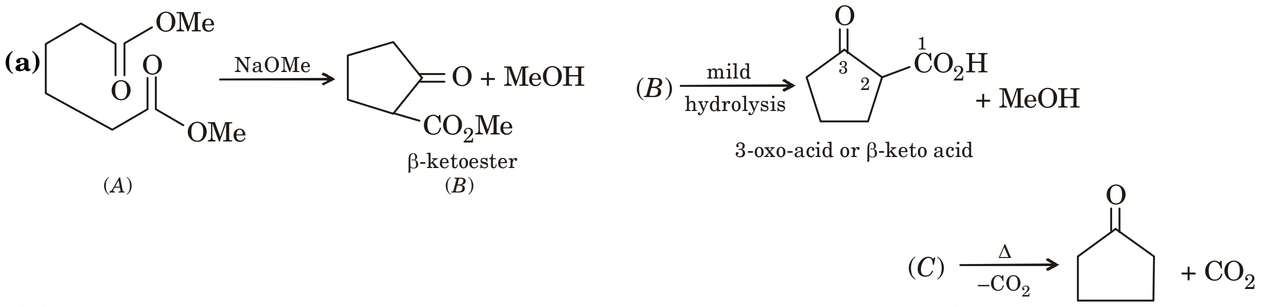
17. An ester (*A*) is condensed in the presence of sodium methoxide to give a β-keto ester (*B*) and Methanol. On mild hydrolysis with cold conc. HCl, (*B*) gives methanol and 3-oxo-acid (*C*). (*C*) underwent readily decarboxylation to give cyclopentanone.

(a) Identify (*A*), (*B*) and (*C*).

(b) Name the reaction involved in conversion of (*A*) to (*B*).

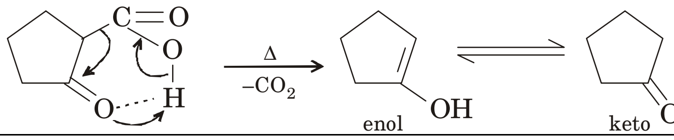
(c) Give the mechanism of decarboxylation.

Soln.:



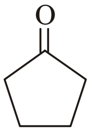
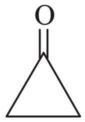
(b) Dieckmann condensation (intramolecular Claisen ester condensation)

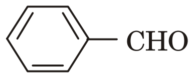
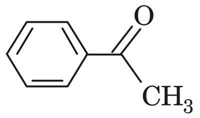
(c) Mechanism of decarboxylation



---

18. Within each pair which compound will react faster in carbonyl addition reactions ?

(a)  or 

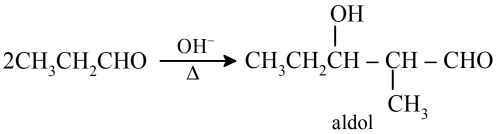
(b)  or 

Soln.: (a) Cyclopropanone (b) Benzaldehyde.

---

19. Write down the main product of the following reaction: Propanal $\xrightarrow[\text{heat}]{\text{NaOH}}$

Soln.: This reaction is an example of aldol condensation.

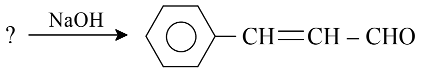


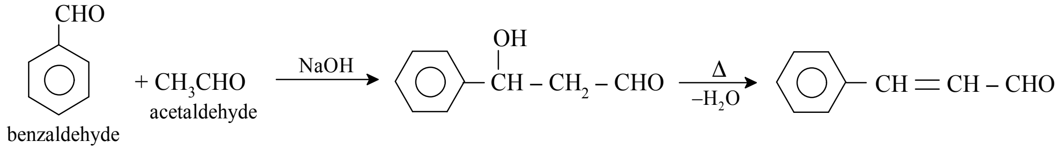
$$2CH_3CH_2CHO \xrightarrow[\Delta]{OH^-} CH_3CH_2\overset{\overset{OH}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CHO$$

aldol

---

20. Complete the following with appropriate structures?

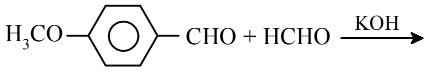


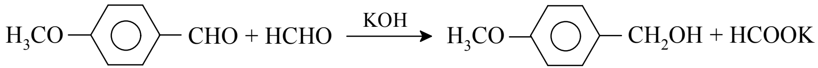
Soln.: 

This is an example of crossed-aldol condensation.

---

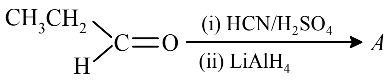
21. Write the structure of the major organic product expected from the following reaction.



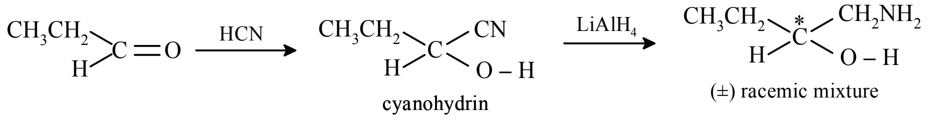
Soln.: 

This is a crossed Cannizzaro reaction.

22. Complete the following reaction with appropriate structure:

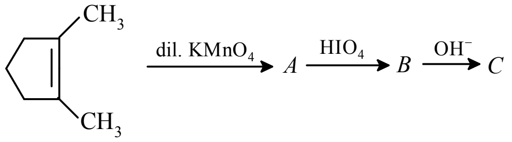


Soln.:

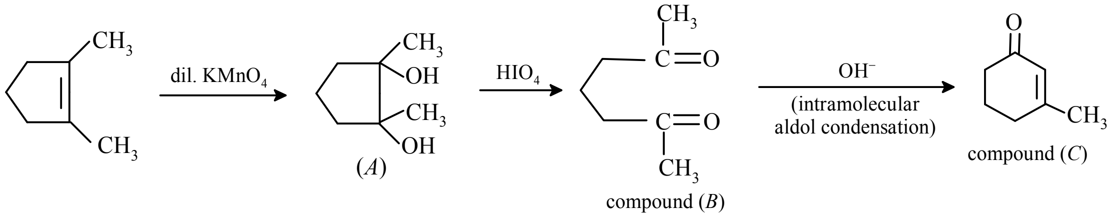


---

23. Suggest appropriate structures for the missing compounds.
The number of carbon atoms remains the same throughout the reaction.



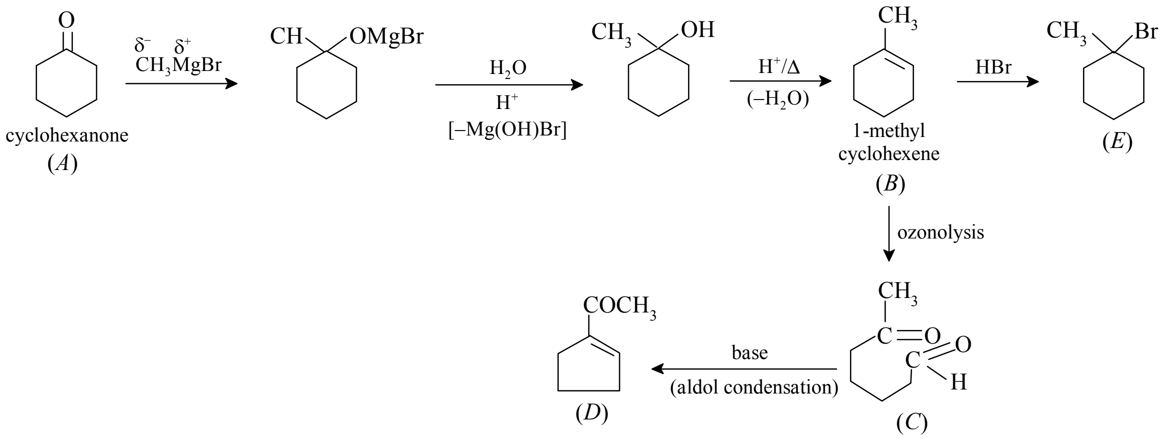
Soln.:



---

24. An organic compound A ($C_6H_{10}O$), on reaction with CH_3MgBr followed by acid treatment gives compound B. The compound B on ozonolysis gives compound C, which in presence of a base gives 1-acetyl cyclopentane, D. The compound B on reaction with HBr gives compound E. Write the structures of A, B, C, D and E. Show how D is formed from C.

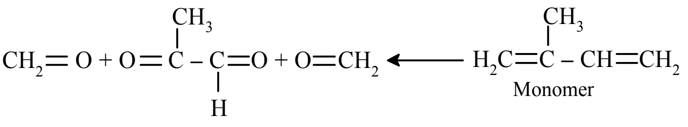
Soln.:



---

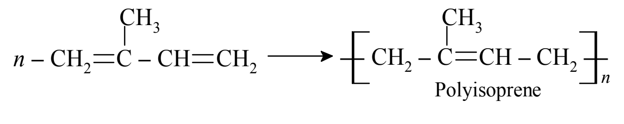
25. A monomer of a polymer on ozonoloysis gives two moles of CH_2O and one mole of CH_3COCHO. Write the structure of monomer and write all – '*cis*' configuration of polymer chain.

Soln.:



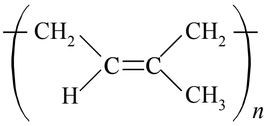
$$CH_2{=}O + O{=}\overset{\displaystyle CH_3}{\overset{|}{C}}-\underset{\displaystyle H}{\underset{|}{C}}{=}O + O{=}CH_2 \longleftarrow \underset{\text{Monomer}}{H_2C{=}\overset{\displaystyle CH_3}{\overset{|}{C}}-CH{=}CH_2}$$

Thus the possible polymer should be



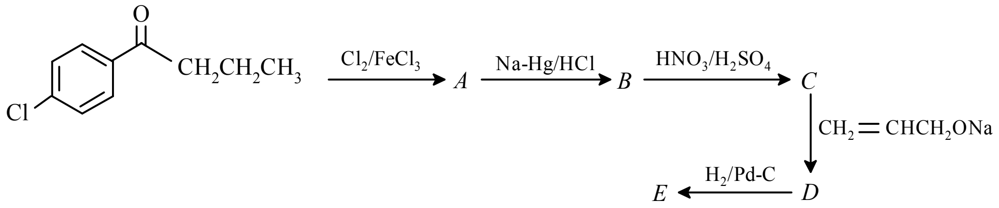
$$n - CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}-CH{=}CH_2 \longrightarrow \underset{\text{Polyisoprene}}{\left[CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH-CH_2 \right]_n}$$

The polymer so obtained has *cis*-configuration all through

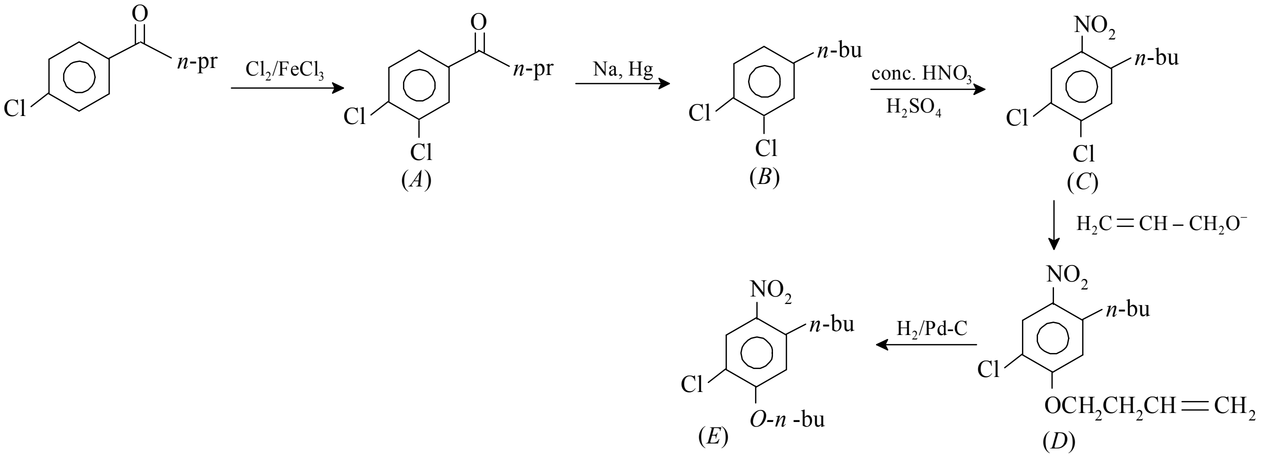


.

26. Write structures of the products *A*, *B*, *C*, *D* and *E* in the following scheme:



Soln.:



EXERCISE

MCQs One Correct Option

1. Which of the following does not undergo benzoin condensation ?
(a) C_6H_5CHO
(b) *p*-Methoxybenzaldehyde
(c) *o*-Tolualdehyde (d) $C_6H_5CH_2CHO$.

2. One mole of an organic compound requires 0·5 mole of oxygen to produce an acid. The compound may be
(a) Alcohol (b) Ether
(c) Ketone (d) Aldehyde.

3. Benzyl alcohol is obtained from benzaldehyde by
(a) Fittig's reaction (b) Cannizzaro's reaction
(c) Kolbe's reaction (d) Wurtz's reaction.

4. $C_6H_6 + CO + HCl \xrightarrow[Cu_2Cl_2]{Anhyd.AlCl_3} X + HCl$. Compound X is
(a) $C_6H_5CH_3$ (b) $C_6H_5CH_2Cl$
(c) C_6H_5CHO (d) C_6H_5COOH.

5. Ethylidene chloride on treatment with aq. KOH gives
(a) CH_3CHO (b) $CH_2OH.CH_2OH$
(c) HCHO (d) CHO.CHO

6. Formalin is an aqueous solution of
(a) Fluorescein (b) Formic acid
(c) Formaldehyde (d) Furfuraldehyde.

7. Benzene reacts with CH_3COCl in the presence of $AlCl_3$ to give
(a) C_6H_5COCl (b) C_6H_5Cl
(c) $C_6H_5CH_3$ (d) $C_6H_5COCH_3$.

8. Toluene on treatment with CrO_2Cl_2 gives
(a) Chlorotoluene (b) Benzyl chloride
(c) Benzaldehyde (d) Benzoic acid.

9. Ethanal reacts with alkali to give 3-hydroxybutanal. The reaction is
(a) Polymerisation (b) Claisen condensation
(c) Aldol condensation
(d) Reimer-Tiemann reaction.

10. Methyl ketones are usually characterized through
(a) The Tollen's reagent
(b) The iodoform test
(c) The Schiff's test
(d) The Benedict's reagent.

11. Carbonyl compounds undergo nucleophilic addition because of
(a) Electronegativity difference of carbon and oxygen atoms
(b) Electromeric effect
(c) More stable anion with negative charge on oxygen atom and less stable carbocation
(d) None of these.

12. Aldol condensation is a characteristic reaction of
(a) All aldehydes and ketones
(b) Only those aldehydes and ketones which contain α-hydrogen atoms
(c) Only those aldehydes and ketones which do not contain α-hydrogen atoms
(d) Only aromatic aldehydes and ketones.

13. Which of the following will not give the iodoform test?
(a) Acetophenone (b) Ethanal
(c) Benzophenone (d) Ethanol.

14. The general order of reactivity of carbonyl compounds towards nucleophilic addition reactions is ?
(a) $H_2C = O > RCHO > ArCHO > R_2C = O > Ar_2C = O$
(b) $ArCHO > Ar_2C = O > RCHO > R_2C = O > H_2C = O$
(c) $Ar_2C = O > R_2C = O > ArCHO > RCHO > H_2C = O$
(d) $H_2C = O > R_2C = O > Ar_2C = O > RCHO > ArCHO$.

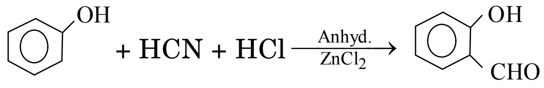
15. Paraldehyde is formed by polymerisation of
(a) CH_3CHO (b) HCHO
(c) CH_3OH (d) CH_3CH_2OH.

16. Which of the following does not undergo aldol condensation ?
(a) HCHO (b) CH_3CHO
(c) CH_3COCH_3 (d) C_2H_5CHO.

17. 1-phenylethanol can be prepared by reaction of benzaldehyde with
(a) Methyl bromide
(b) Ethyl iodide and magnesium
(c) Methyl bromide and aluminium bromide
(d) Methyl iodide and magnesium.

18. Formaldehyde upon reaction with methyl magnesium bromide gives
(a) C_2H_5OH (b) CH_3COOH
(c) CH_3CHO (d) HCHO.

19. The following reaction



is known as

(a) Perkin reaction

(b) Gattermann aldehyde synthesis

(c) Kolbe's reaction

(d) Gattermann-Koch reaction.

20. The reaction of $C_6H_5CH = CHCHO$ with $NaBH_4$ gives

(a) $C_6H_5CH_2CH_2CH_2OH$

(b) $C_6H_5CH = CHCH_2OH$

(c) $C_6H_5CH_2CH_2CHO$

(d) $C_6H_5CH_2CHOHCH_3$.

21. Which of the following compounds will not give Cannizzaro reaction ?

(a) CH_3CHO (b) $HCHO$

(c) Me_3CCHO (d) C_6H_5CHO.

22. The cyanohydrin of a compound *X* on hydrolysis gives lactic acid. The *X* is

(a) $HCHO$ (b) CH_3CHO

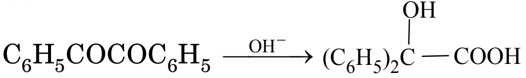
(d) $(CH_3)_2CO$ (d) $C_6H_5CH_2CHO$.

23. Benzophenone can be converted into benzene using

(a) Fused alkali (b) Anhydrous $AlCl_3$

(c) Sodium amalgam in water

(d) Acidified dichromate.

24. 

$C_6H_5COCOC_6H_5 \xrightarrow{OH^-} (C_6H_5)_2\overset{OH}{C}-COOH$

The above reaction is known as

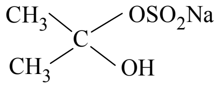
(a) Beckmann rearrangement

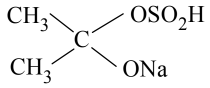
(b) Benzilic acid rearrangement

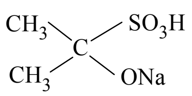
(c) Benzoin condensation

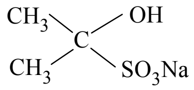
(d) Aldol condensation.

25. The structure of the addition product formed when acetone reacts with a concentrated aqueous solution of sodium bisulphite is

(a) 

(b) 

(c) 

(d) 

26. Which one of the following can be oxidised to the corresponding carbonyl compound?

(a) 2-hydroxypropane

(b) *o*-nitrophenol (c) phenol

(d) 2-methyl-2-hydroxypropane.

27. Which one of the following undergoes reaction with 50% sodium hydroxide solution to give the corresponding alcohol and acid?

(a) Phenol (b) Benzaldehyde

(c) Butanol (d) Benzoic acid.

28. Acetone is mixed with bleaching powder to give

(a) Chloroform (b) Acetaldehyde

(c) Ethanol (d) Phosgene.

29. In which of the following disproportionation takes place?

(a) Aldol condensation

(b) Cannizzaro reaction

(c) Benzoin condensation

(d) Wittig's reaction

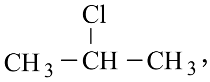
30. The reagent with which both acetaldehyde and acetone react easily is

(a) Fehling's solution

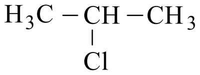
(b) Grignard reagent

(c) Schiff's reagent (d) Tollen's reagent

31. Identify the set from the following which contains the two compounds each of which can form propanone in a single step reaction.

(a)  $CH_3-\overset{Cl}{CH}-CH_3$, $(CH_3)_2C = CH_2$

(b) $(CH_3COO)_2Ca$, $(CH_3)_2C = CH_2$

(c) $H_3C - C \equiv CH$,  $H_3C-\underset{Cl}{CH}-CH_3$

(d) $(CH_3COO)_2Ca$, $H_3C - C \equiv CH$

32. Which of the following compounds will give a yellow precipitate with iodine and alkali?

(a) 2-hydroxypropane

(b) acetophenone

(c) both of these (d) none of these

33. An organic compound C_3H_6O does not give a precipitate with 2,4-dinitrophenylhydrazine reagent and does not react with metallic sodium. It could be

(a) CH_3CH_2CHO (b) $CH_2 = CHCH_2OH$

(c) CH_3COCH_3 (d) $CH_2 = CHOCH_3$

34. The reaction which is used to prepare β-hydroxy esters is called

(a) Wittig reaction (b) Cannizzaro's reaction

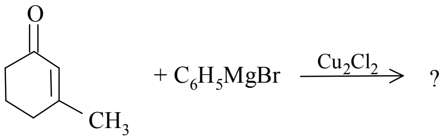
(c) Reformatsky reaction

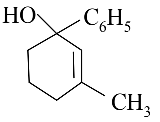
(d) Claisen condensation

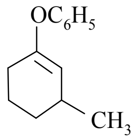
35. A keto ester (*A*) with molecular formula $C_6H_{10}O_3$ on treatment with NaOH and I_2 does not give iodoform but on boiling with dilute KOH gives a compound (*B*) with molecular formula $C_4H_5O_3K$ which upon acidification followed by heating undergoes decarboxylation to give acetone. The keto ester (*A*) is

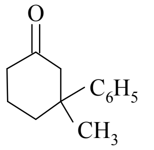
(a) $CH_3CO\ CH_2CH_2COOCH_3$
(b) $CH_3COCH_2COOC_2H_5$
(c) $CH_3CH_2OCH_2COOCH_3$
(d) $CH_3COCH(CH_3)COOCH_3$

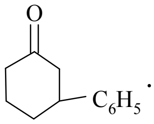
36. The major product of the following reaction is



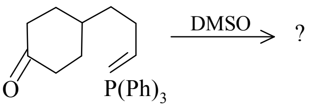
(a)


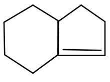
(b)


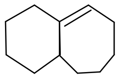
(c)


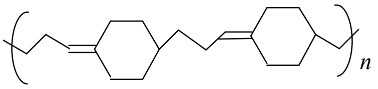
(d)


37. The major product of the following reaction is



(a)


(b)


(c)


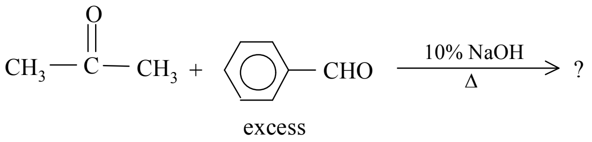
(d) none of these.

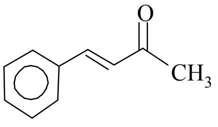
38. The major product of the following reaction is

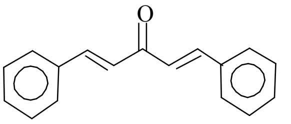
$$(CH_3O)_2CO \xrightarrow[\text{hydrolysis}]{C_2H_5MgBr\ \text{excess}} ?$$

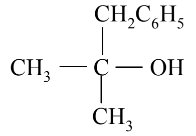
(a) $(C_2H_5)_3COH$ (b) $(CH_3)_3COH$
(c) $C_2H_5COC_2H_5$ (d) $HCOOH$.

39. The major product of the following reaction is

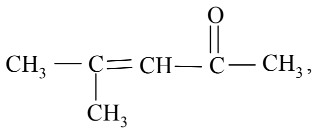


(a)


(b)


(c)


$$CH_3-\underset{CH_3}{\overset{CH_2C_6H_5}{C}}-OH$$

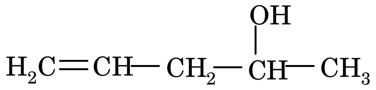
(d)


$$CH_3-\underset{CH_3}{C}=CH-\overset{O}{\overset{\|}{C}}-CH_3,$$

$C_6H_5CH_2OH$, $C_6H_5COO^-$

40. An organic liquid has an empirical formula $C_5H_{10}O$. This liquid gives a pale yellow precipitate on warming with iodine in alkaline KI solution. The resulting salt upon acidification gives an acid which easily undergoes decarboxylation on mild heating. The structural formula of the organic liquid could be

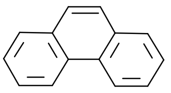
(a) $CH_3COCH_2CH_2CH_3$

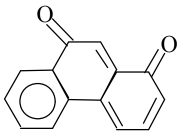
(b)


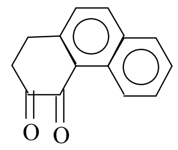
$$H_2C=CH-CH_2-\overset{OH}{CH}-CH_3$$

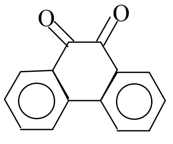
(c) $H_3CCH_2CH_2CH_2CHO$
(d) $CH_3\ CH_2\ CH_2OCH=CH_2$.

41. Which of the following diketone is obtained when the following compound is strongly oxidized with $K_2Cr_2O_7/H_2SO_4$?

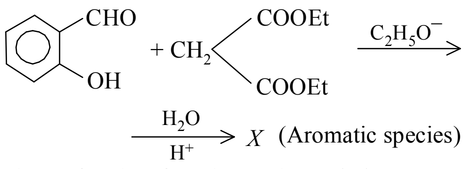


(a)


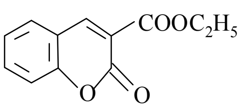
(b)


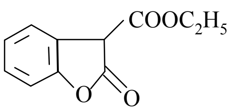
(c)


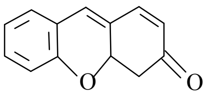
(d) no oxidation.

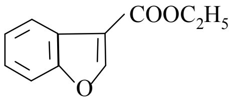
42.


Identify the final product (*X*)

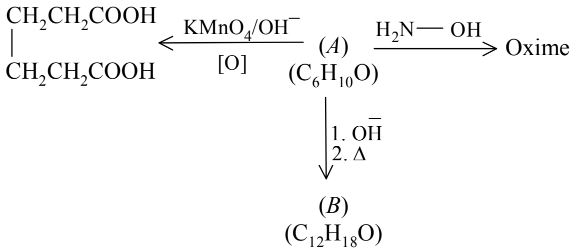
(a)


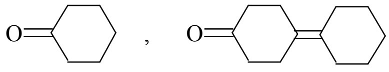
(b)


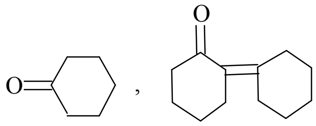
(c)


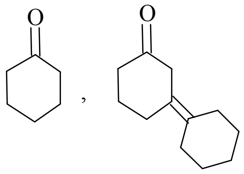
(d)


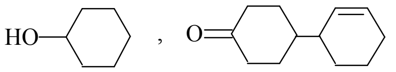
43. Identify (*A*) and (*B*) based on the following reaction scheme



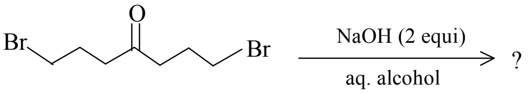
(a) 

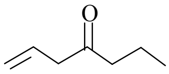
(b) 

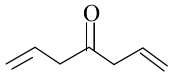
(c) 

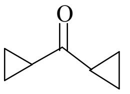
(d) 

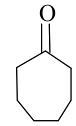
44. Which of the following product is obtained when



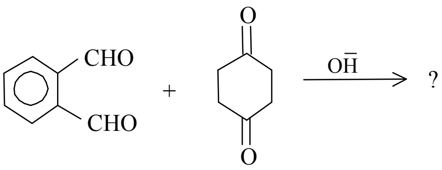
(a) 

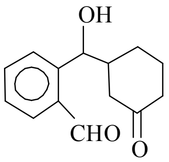
(b) 

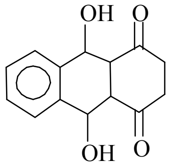
(c) 

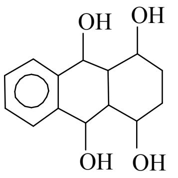
(d) .

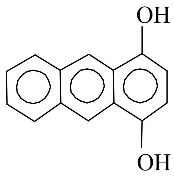
45. Which of the following product is the result of the reaction



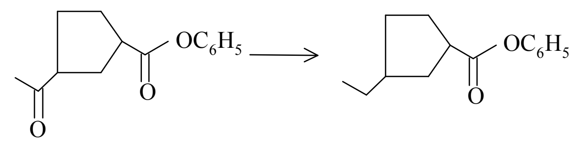
(a) 

(b) 

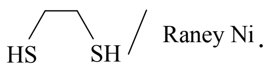
(c) 

(d) .

46. The following transformation can be best effected by



(a) B_2H_6/THF (b) $LiAlH_4$

(c) Zn·Hg/HCl (d) 

47. Decreasing order of boiling points of

(1) CH_3CH_2CHO (2) $CH_3CH_2CH_2OH$

(3) $CH_3OCH_2CH_3$ (4) $CH_3CH_2CH_3$

(a) 1 > 2 > 3 > 4 (b) 2 > 1 > 3 > 4

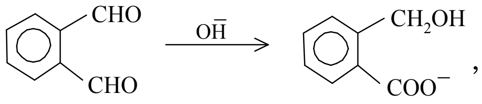
(c) 3 > 2 > 1 > 4 (d) 2 > 3 > 1 > 4.

48. A ketone reacted with ethyl magnesium bromide (Grignard reagent) followed by hydrolysis gave a product which on dehydration gave an alkene. The alkene on ozonolysis gave diethyl ketone and acetaldehyde. The ketone is

(a) dimethyl ketone (b) ethyl methyl ketone

(c) diethyl ketone (d) ethyl propyl ketone.

49. In Cannizzaro reaction given below,



, the key step (slowest step) is

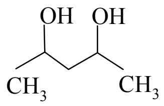
(a) the attack of OH^- on carbonyl group

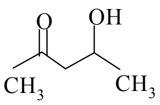
(b) the intramolecular proton transfer

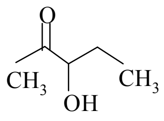
(c) the transfer of H^- to another carbonyl group

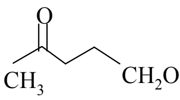
(d) all the three steps.

50. Which of the following compound will be most easily dehydrated?

(a) 

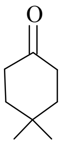
(b) 

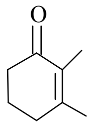
(c) 

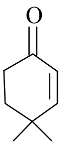
(d) .

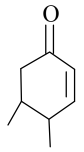
51. The major product of the following reaction after acidification is

$Me_2CHCHO + H_2C = CH — COCH_3 \xrightarrow{\overline{OH}}$

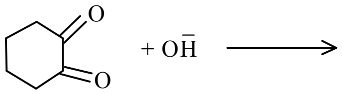
(a) 

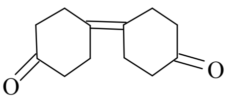
(b) 

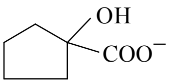
(c) 

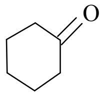
(d) .

52. The product of the following reaction is



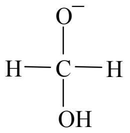
(a) 

(b) 

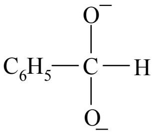
(c) 

(d) none of these.

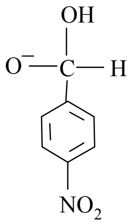
53. In a Cannizzaro reaction, the intermediate that is the best hydride donor is

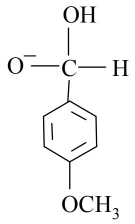
(a) 

$H-\overset{O^-}{\underset{OH}{C}}-H$

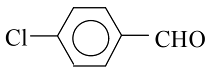
(b) 

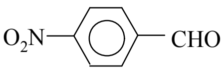
$C_6H_5-\overset{O^-}{\underset{O^-}{C}}-H$

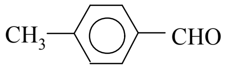
(c) 

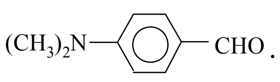
(d) .

54. Which of the following aldehyde does not undergo Cannizzaro reaction?

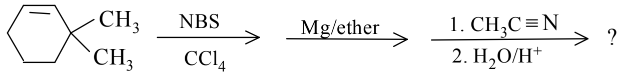
(a) 

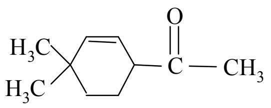
(b) 

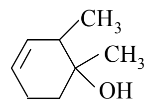
(c) 

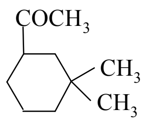
(d) .

55. The final product in the following reaction sequence is

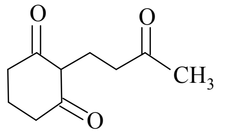


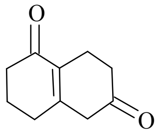
(a) 

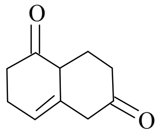
(b) 

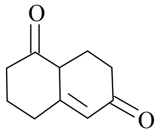
(c) 

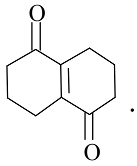
(d) no reaction.

56.  on aldol condensation followed by heating gives

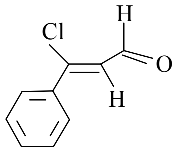
(a) 

(b) 

(c) 

(d) .

57. The IUPAC name of the following compound is



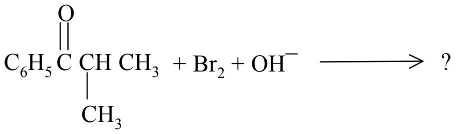
(a) Z-2-chloro-1-phenylpropenal

(b) Z-3-chloro-3-phenyl-2-propenal

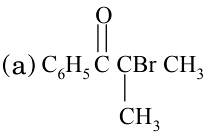
(c) E-2-chloro-3-phenylpropenal

(d) E-3-chloro-3-phenyl-2-propenal.

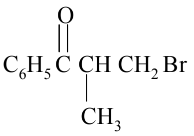
58. What would be the major product of the following reaction



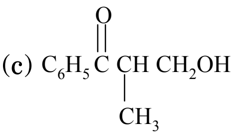
$C_6H_5\overset{O}{\overset{\|}{C}}\underset{CH_3}{CH}CH_3 + Br_2 + OH^- \longrightarrow ?$

(a) 

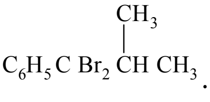
$C_6H_5\overset{O}{\overset{\|}{C}}\underset{CH_3}{CBr}CH_3$

(b) 

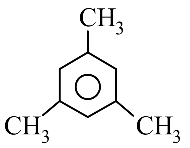
$C_6H_5\overset{O}{\overset{\|}{C}}\underset{CH_3}{CH}CH_2Br$

(c) 

$C_6H_5\overset{O}{\overset{\|}{C}}\underset{CH_3}{CH}CH_2OH$

(d) .

$C_6H_5CBr_2\overset{CH_3}{CH}CH_3$

59. 

The above compound describes a condensation polymer which can be obtained in two ways: either treating 3 molecules of acetone

(CH_3COCH_3) with conc. H_2SO_4 or passing propyne ($CH_3C\equiv CH$) through a red hot tube. The polymer is

(a) Phorone (b) Mesityl oxide

(c) Diacetonyl alcohol

(d) Mesitylene

60. The correct order of reactivity of $>C=O$ group in the following compounds is

(a) $CH_3CHO > (CH_3)_2CO > C_2H_5COCH_3$

(b) $C_2H_5COCH_3 > (CH_3)_2CO < CH_3CHO$

(c) $(CH_3)_2CO > CH_3CHO > C_2H_5COCH_3$

(d) $(CH_3)_2CO > C_2H_5COCH_3 > CH_3CHO$

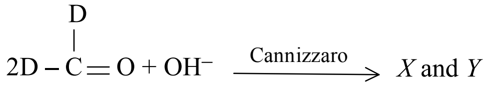
61. Clemmensen reduction of a ketone is carried out in presence of

(a) H_2 with Pd as catalyst

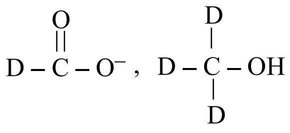
(b) $NH_2NH_2.H_2O$/glycol with KOH

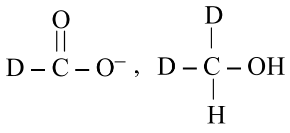
(c) $LiAlH_4$ in ether

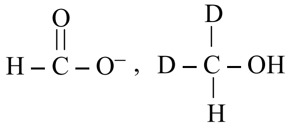
(d) Zn-Hg and HCl

62. 
$2D-\overset{\overset{\displaystyle D}{|}}{C}=O+OH^- \xrightarrow{\text{Cannizzaro}} X \text{ and } Y$

(Y is alcohol, D is deuterium & X is an acid)

(a) 
$D-\overset{\overset{\displaystyle O}{||}}{C}-O^-,\ D-\underset{\underset{\displaystyle D}{|}}{\overset{\overset{\displaystyle D}{|}}{C}}-OH$

(b) 
$D-\overset{\overset{\displaystyle O}{||}}{C}-O^-,\ D-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle D}{|}}{C}}-OH$

(c) 
$H-\overset{\overset{\displaystyle O}{||}}{C}-O^-,\ D-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle D}{|}}{C}}-OH$

(d) none is correct.

63. Which one of the statements about $HOH_2CCH(OH)CHO$ is not correct? It

(a) is an isomer of 1, 3-dihydroxypropanone

(b) contains a tertiary alcoholic group

(c) has the same empirical formula as glucose

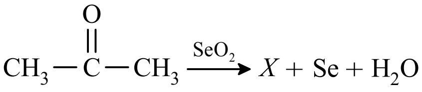
(d) can show optical isomerism.

64. Treatment of furfural with NaOH yields

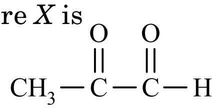
(a) Furoin (b) Furoic acid

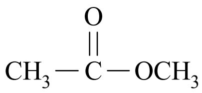
(c) Furfuryl alcohol and sodium salt of furan-2-carboxylic acid

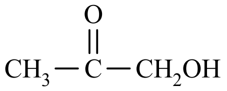
(d) No reaction

65. 
$CH_3-\overset{\overset{\displaystyle O}{||}}{C}-CH_3 \xrightarrow{SeO_2} X+Se+H_2O$

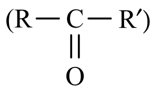
Here X is

(a) 
$CH_3-\overset{\overset{\displaystyle O}{||}}{C}-\overset{\overset{\displaystyle O}{||}}{C}-H$

(b) 
$CH_3-\overset{\overset{\displaystyle O}{||}}{C}-OCH_3$

(c) 
$CH_3-\overset{\overset{\displaystyle O}{||}}{C}-CH_2OH$

(d) None of these

66. Ketones  $(R-\underset{\underset{\displaystyle O}{||}}{C}-R')$, where R = R′ = alkyl group, can be obtained in one step by

(a) Hydrolysis of esters

(b) Oxidation of 1° alcohol

(c) Oxidation of 2° alcohol

(d) Reaction of alkyl halide with alcohols

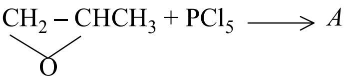
67. The conversion, $PhCN \longrightarrow PhCOCH_3$, can be achieved most conveniently by reaction with

(a) CH_3MgBr followed by hydrolysis

(b) I_2-NaOH, CH_3I

(c) Dil. H_2SO_4 followed by reaction with CH_2N_2

(d) LAH followed by reaction with CH_3I

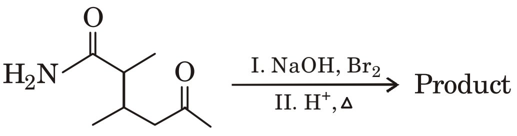
68. 

$CH_3CH_2CHO + PCl_5 \longrightarrow B$, A and B are

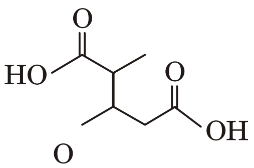
(a) *vic* halides (b) *gem* halides

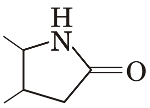
(c) A *gem* halide, B *vic* halide

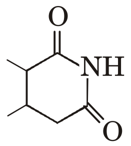
(d) A *vic* halide, B *gem* halide.

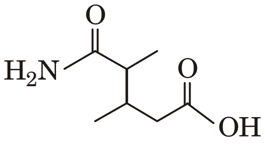
69. 

The main product is

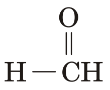
(a) 

(b) 

(c) 

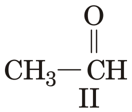
(d) 

70. Mark the correct order of dipole moment of the following molecules :



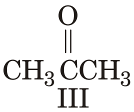
$H-\overset{\overset{\large O}{\|}}{C}H$

I



$CH_3-\overset{\overset{\large O}{\|}}{C}H$

II



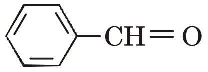
$CH_3\overset{\overset{\large O}{\|}}{C}CH_3$

III

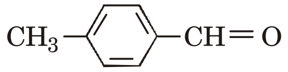
(a) I > II > III (b) III > II > I

(c) III > I > II (d) I > III > II

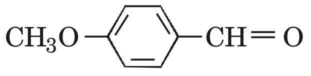
71. Choose the correct decreasing order of rate of Cannizzaro reaction :



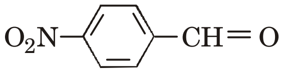
I



II



III

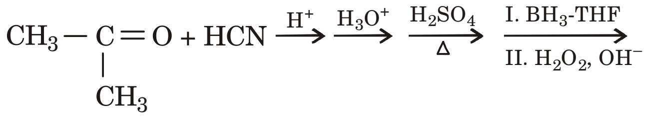


IV

(a) III > II > I > IV (b) I > II > III > IV

(c) IV > I > II > III (d) II > I > III > IV

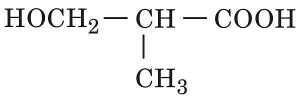
72.



$$CH_3-\underset{\underset{\large CH_3}{|}}{C}=O + HCN \xrightarrow{H^+} \xrightarrow{H_3O^+} \xrightarrow[\Delta]{H_2SO_4} \xrightarrow[\text{II. } H_2O_2,\ OH^-]{\text{I. } BH_3\text{-THF}}$$

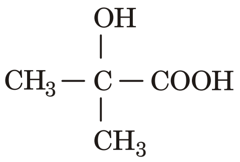
The final predominant product

(a)



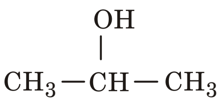
$HOCH_2-\underset{\underset{\large CH_3}{|}}{C}H-COOH$

(b)



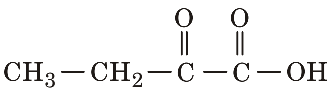
$CH_3-\overset{\overset{\large OH}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-COOH$

(c)



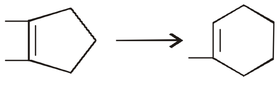
$CH_3-\overset{\overset{\large OH}{|}}{C}H-CH_3$

(d)



$CH_3-CH_2-\overset{\overset{\large O}{\|}}{C}-\overset{\overset{\large O}{\|}}{C}-OH$

73.



Which of the following set of reagents is the most appropriate to perform the above conversion?

(a) HIO_4; OH^-; Zn – Hg, HCl

(b) Cold alkaline $KMnO_4$;$Pb(OAc)_4$; OH^-;Li/Liq. NH_3

(c) O_3; $(CH_3)_2S$; OH^-;Li/Liq. NH_3

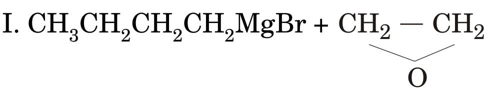
(d) $KMnO_4$; H^+; OH^-; NH_2-NH_2; OH^-; 150°C

74. Which sequence represents the best synthesis of hexanal? $CH_3CH_2CH_2CH_2CH_2CH = O$

(a) I. $CH_3CH_2CH_2CH_2Br + NaC \equiv CH$
II. H_2O, H_2SO_4, $HgSO_4$

(b) I. $CH_3CH_2CH_2CH = CH_2 + CH_3CO_3H$
II. CH_3MgBr, diethyl ether
III. H_3O^+ IV. PCC, CH_2Cl_2

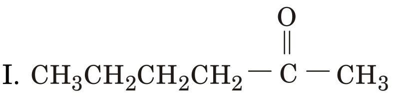
(c)



I. $CH_3CH_2CH_2CH_2MgBr + CH_2-CH_2$ (O bridging)

II. $H_3\overset{+}{O}$ III. PCC, CH_2Cl_2

(d)



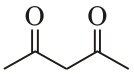
I. $CH_3CH_2CH_2CH_2-\overset{\overset{\large O}{\|}}{C}-CH_3$

II. CH_3CO_3H III. $LiAlH_4$

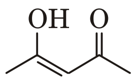
IV. H_2O V. PCC, CH_2Cl_2

75. Which structure is the most stable?

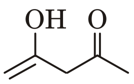
(a)



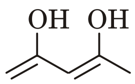
(b)



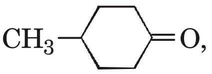
(c)

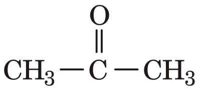


(d)



76. Terpineol ($C_{10}H_{18}O$) is an optically active compound with one chiral centre. Reaction of terpineol with H_2/Pt forms an optically inactive compound ($C_{10}H_{20}O$). Heating the reduced compound in acid followed by ozonolysis and work-up under reducing condition produces the following compounds:

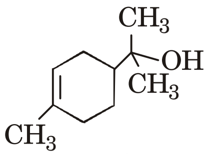




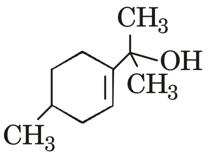
$CH_3-\overset{\overset{\large O}{\|}}{C}-CH_3$

The structure of terpineol which is not in accordance with the information, is

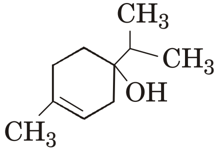
(a)

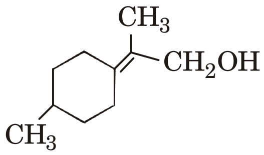


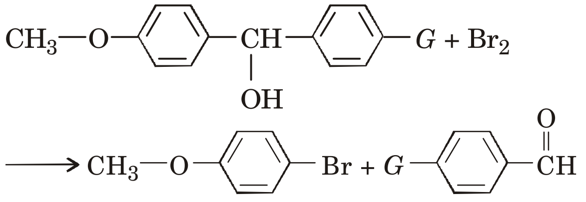
(b)



(c)



(d) 

77. 

The rate of reaction is moderately affected by the nature of *G*. Choose the correct order decreasing rate of reaction with various substituents as *G*.

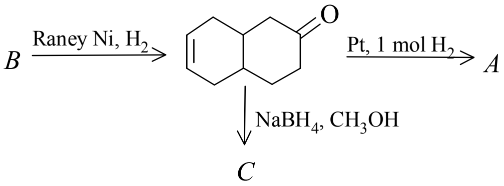
(a) $—NO_2 > —Br > — H > — CH_3 > —OCH_3$

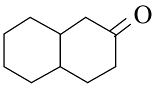
(b) $—OCH_3 > —CH_3 >—H >—Br > —NO_2$

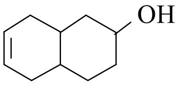
(c) $—OCH_3 > —Br > —CH_3 >—H > —NO_2$

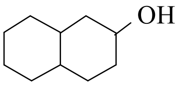
(d) $—NO_2 > —OCH_3 > —Br > —H > —CH_3$

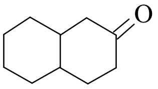
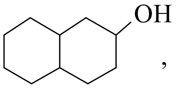
78. What are *A*, *B* and *C* in the following?

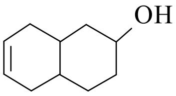


(a)  in all cases

(b)  in all cases

(c)  in all cases

(d) *A* :  , *B* :  ,

C : 

79. Which one of the following reaction is a method for the conversion of a ketone into a hydrocarbon?

(a) Aldol condensation

(b) Reimer-Tiemann reaction

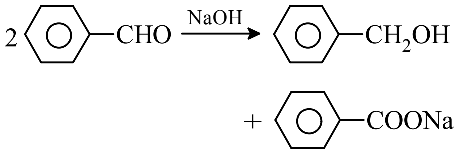
(c) Cannizzaro reaction

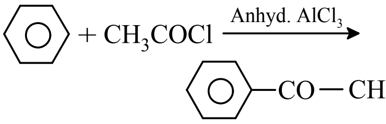
(d) Wolf-Kishner reduction

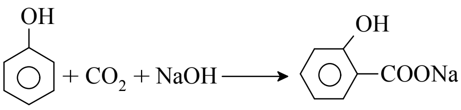
80. Match List I (Reaction) with List II (Name) and select the correct answer using the codes given below the lists:

List I

(I) $R-CO-CH_3 \xrightarrow{Zn-Hg/HCl} R-CH_2-CH_3$

(II) 

(III) 

(IV) 

List II

A. Friedel-Crafts reaction

B. Kolbe's reaction

C. Clemmensen's reaction

D. Cannizzaro's reaction

Codes:

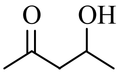
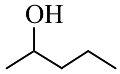
(a) I-A, II-B, III-C, IV-D

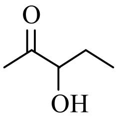
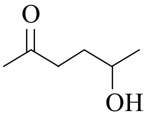
(b) I-B, II-A, III-C, IV-D

(c) I-C, II-D, III-A, IV-B

(d) I-D, II-C, III-A, IV-B

81. Which of the following be most readily dehydrated in acidic conditions?

(a)  (b) 

(c)  (d) 

82. Rearrangement of an oxime to an amide in presence of strong acid is called

(a) Curtius rearrangement

(b) Fries rearrangement

(c) Beckmann rearrangement

(d) Sandmeyer reaction

83. $(CH_3)_2CO \xrightarrow[HCl]{NaCN} A \xrightarrow[\Delta]{H_3O^+} B$

In the above sequence of reactions *A* and *B* are

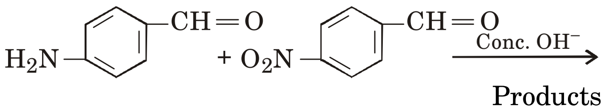
(a) $(CH_3)_2C(OH)CN, (CH_3)_2C(OH)COOH$

(b) $(CH_3)_2C(OH)CN, (CH_3)_2C(OH)_2$

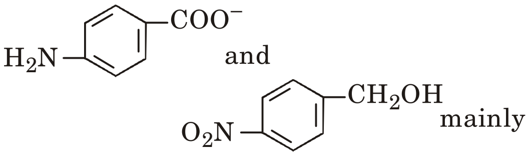
(c) $(CH_3)_2C(OH)CN, (CH_3)_2CHCOOH$

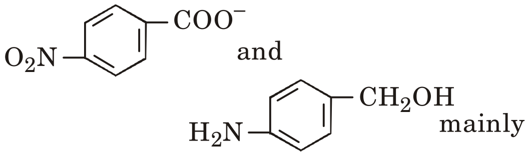
(d) $(CH_3)_2C(OH)CN, (CH_3)_2C=O$

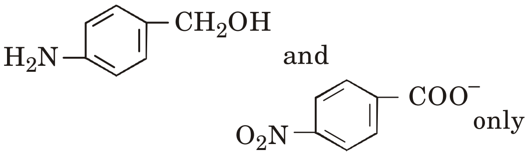
84.

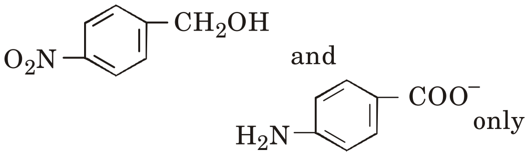


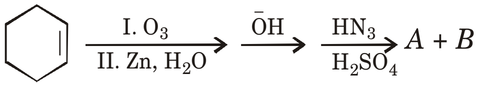
The products are

(a)


(b)


(c)


(d)


85.


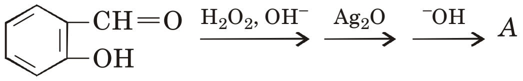
the final product is a mixture of *A* and *B*. *A* and *B* are functionally

(a) amine and amide, respectively

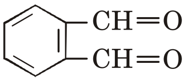
(b) acid and amide, respectively

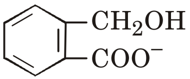
(c) amide and nitrile, respectively

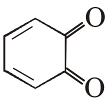
(d) 1° and 2° amides, respectively

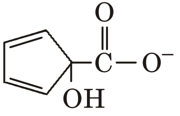
86.


The final product '*A*', is

(a)


(b)


(c)


(d)


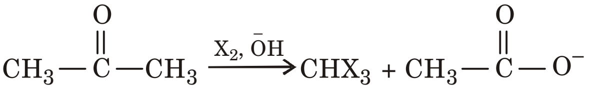
87. $A \xleftarrow[\text{II. } H_2O]{\text{I. PhCH=O}} \text{PhMgBr} \xrightarrow[\text{II. } H_2O]{\text{I. 2PhCH=O}} B$

(a) Product *A* contains benzhydrol (Ph—CH(OH)—Ph and product *B* contains mixture of benzophenone (Ph—CO—Ph) and benzyl alcohol ($PhCH_2OH$).

(b) Product *A* contains benzhydrol and product *B* contains benzyl alcohol only.

(c) Product *A* and *B*, both contain benzhydrol, but *B* contains much larger amount of benzhydrol.

(d) Product *A* and *B* both contain benzophenone only.

88.


$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{X_2,\ \bar{O}H} CHX_3 + CH_3-\overset{O}{\overset{\|}{C}}-O^-$

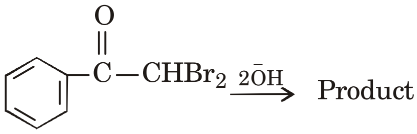
The rate of haloform reaction is found the fastest with

(a) $X_2 = Cl_2$

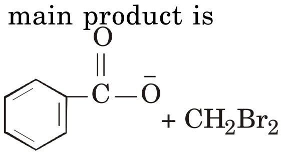
(b) $X_2 = Br_2$

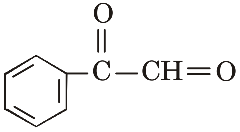
(c) $X_2 = I_2$

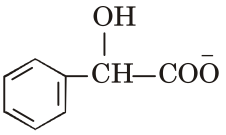
(d) All at the same rate, $r_{Cl_2} = r_{Br_2} = r_{I_2}$

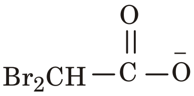
89.


The main product is

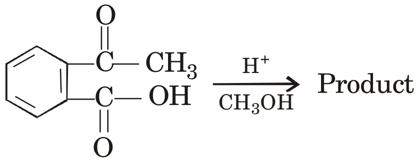
(a)


(b)


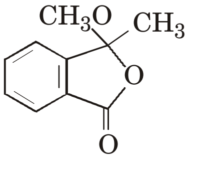
(c)


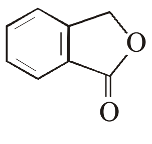
(d)


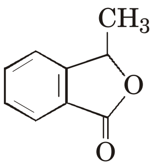
$Br_2CH-\overset{O}{\overset{\|}{C}}-\bar{O}$

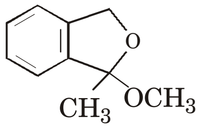
90.


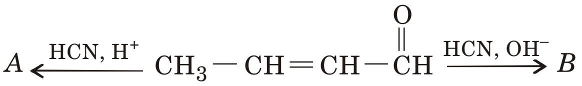
Which of the following is the most suitable product?

(a)


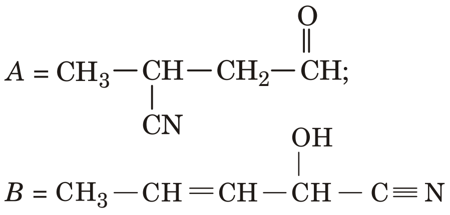
(b)


(c)


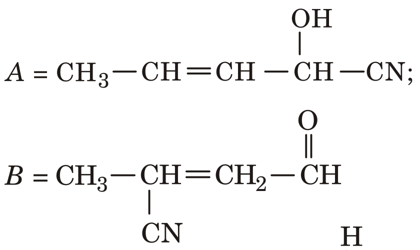
(d)


91.


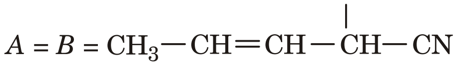
$A \xleftarrow{HCN,\ H^+} CH_3-CH=CH-\overset{O}{\overset{\|}{CH}} \xrightarrow{HCN,\ OH^-} B$

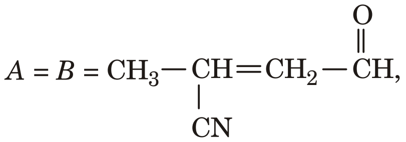
(a) 
$A = CH_3-\underset{\underset{CN}{|}}{C}H-CH_2-\overset{\overset{O}{\|}}{C}H;$

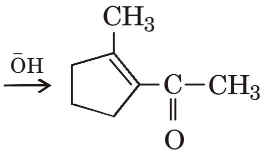
$B = CH_3-CH=CH-\overset{\overset{OH}{|}}{C}H-C\equiv N$

(b) 
$A = CH_3-CH=CH-\overset{\overset{OH}{|}}{C}H-CN;$

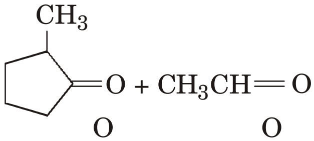
$B = CH_3-\underset{\underset{CN}{|}}{C}H=CH_2-\overset{\overset{O}{\|}}{C}H$

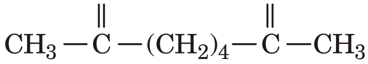
(c) 
$A = B = CH_3-CH=CH-\overset{\overset{H}{|}}{C}H-CN$

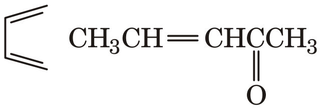
(d) 
$A = B = CH_3-\underset{\underset{CN}{|}}{C}H=CH_2-\overset{\overset{O}{\|}}{C}H,$

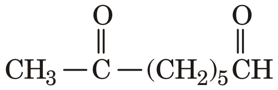
92. Reactant(s) 

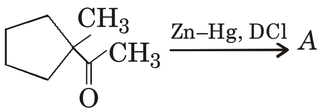
The suitable reactant(s) is/are

(a) 

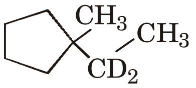
(b) 
$CH_3-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-CH_3$

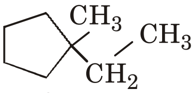
(c) 
$CH_3CH=CH\underset{\underset{O}{\|}}{C}CH_3$

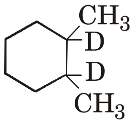
(d) 
$CH_3-\overset{\overset{O}{\|}}{C}-(CH_2)_5\overset{\overset{O}{\|}}{C}H$

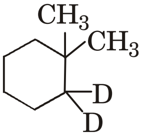
93. 

The main product '*A*', is

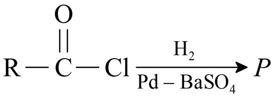
(a) 

(b) 

(c) 

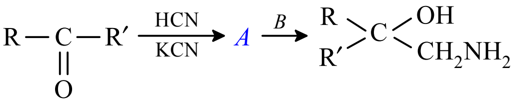
(d) 

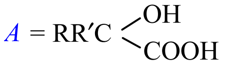
94. In the following reaction, product '*P*' is


$R-\overset{\overset{O}{\|}}{C}-Cl \xrightarrow[\text{Pd - BaSO}_4]{H_2} P$

(a) RCH_2OH (b) $RCOOH$
(c) $RCHO$ (d) RCH_3

95. *A* and *B* in the following reactions are:


$R-\underset{\underset{O}{\|}}{C}-R' \xrightarrow[KCN]{HCN} A \xrightarrow{B} \begin{matrix}R\\R'\end{matrix}\!>C<\!\begin{matrix}OH\\CH_2NH_2\end{matrix}$

(a) 
$A = RR'C<\!\begin{matrix}OH\\COOH\end{matrix}$, $B = NH_3$

(b) 
$A = RR'C<\!\begin{matrix}CN\\OH\end{matrix}$, $B = H_3O^+$

(c) $A = RR'CH_2CN$, $B = NaOH$

(d) 
$A = RR'C<\!\begin{matrix}CN\\OH\end{matrix}$, $B = LiAlH_4$

96. A compound *X* having molecular formula, $C_4H_{10}O$ on oxidation gave a ketone, C_4H_8O. Which of the following is the structure of *X* ?
(a) $CH_3CH_2CH_2CH_2OH$
(b) $CH_3CHOHCH_2CH_3$
(c) $(CH_3)_2CHCH_2OH$
(d) $(CH_3)_3COH$.

97. Which of the following statements is not true about the following reaction?

$$RCOCl + H_2 \xrightarrow[\text{Boiling xylene}]{\text{Pd/BaSO}_4} RCHO + HCl$$

(a) All aldehydes can be obtained by reduction of the corresponding acid chlorides
(b) This reaction is called Rosenmund reduction
(c) Here $BaSO_4$ is used to poison the catalyst so that further reduction of aldehyde cannot occur
(d) None of the above.

98. Which one of the following is the best method for the preparation of acetophenone ?
(a) $PhCOOEt + CH_3MgBr$
(b) $PhCOCl + CH_3MgBr$
(c) $PhCONH_2 + CH_3MgBr$
(d) $PhCN + CH_3MgBr$.

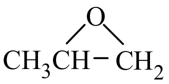
99. Which of the following statements is not true about C=O group ?
(a) The carbon atom of the carbonyl group is sp^2-hybridized

(b) The C═O bond length is longer than C═C bond length

(c) The dipole moments of aldehydes and ketones lie in the range 2.3–2.8 D

(d) The portion of the molecule immediately surrounding the carbonyl group is planar.

100. The most probable structural formula for the compound whose empirical formula is C_3H_6O, and which can react with Benedict's reagent is

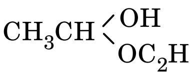
(a) 

(b) CH_3CH_2CHO

(c) $CH_3OCH=CH_2$

(d) $CH_2=CHCH_2OH$.

101. The product formed by the reaction of acetaldehyde with excess of ethanol in the presence of sulphuric acid is

(a) 

$CH_3CH\begin{smallmatrix}OH\\OC_2H_5\end{smallmatrix}$

(b) $CH_3CH(OH)_2$

(c) $CH_3CH(OC_2H_5)_2$

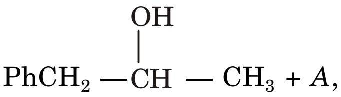
(d) $H_5C_2OCH_2CH_2OC_2H_5$.

102. A compound which gives a yellow solid on adding to an alcoholic solution of 2,4-dinitrophenylhydrazine but does not reduce Fehling's solution and ammoniacal silver nitrate solution, is

(a) $CH_3CHOHCH_3$ (b) CH_3COCH_3

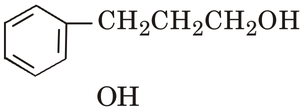
(c) CH_3CHO (d) CH_3COOH.

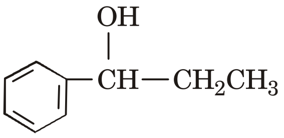
103. $PhCH_2MgBr + CH_3CH=O \rightarrow$

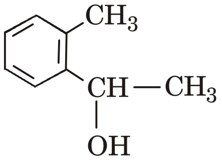


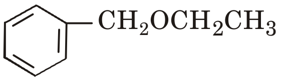
$PhCH_2-\overset{OH}{\underset{|}{C}H}-CH_3 + A$,

A is the isomer of other given product. The by-product *A*, is

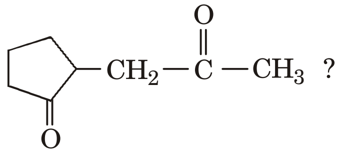
(a) 

(b) 

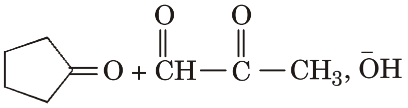
(c) 

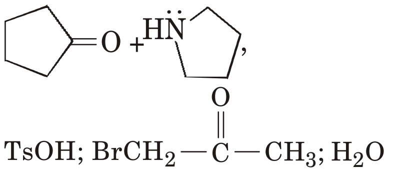
(d) 

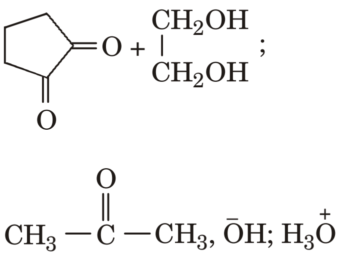
104. Which of the following set of reagents is the most appropriate to synthesise the compound

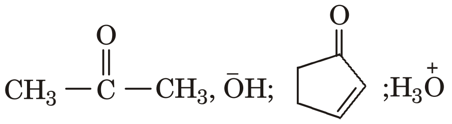


?

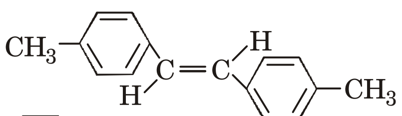
(a) 

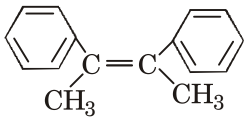
(b) 

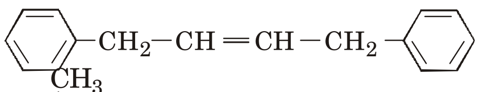
(c) 

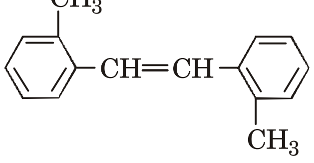
(d) 

105. An alkene $(A)C_{16}H_{16}$ on ozonolysis gives only one product $B(C_8H_8O)$. Compound (*B*) on reaction with NH_2OH, H_2SO_4, Δ gives N-methyl benzamide. The compound '*A*', is

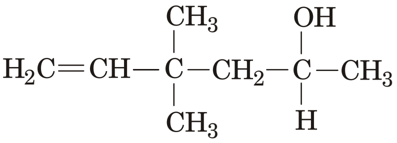
(a) 

(b) 

(c) 

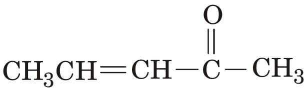
(d) 

106. $A \xrightarrow[\text{2. }H^+,\,H_2O]{\text{1. }(CH_2=CH)_2CuLi} B \xrightarrow[\text{2. }H^+,\,H_2O]{\text{1. }CH_3Li}$

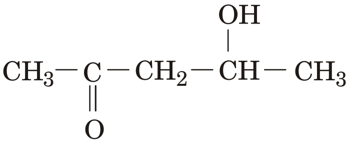


$$H_2C{=}CH{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2{-}\underset{H}{\overset{OH}{C}}{-}CH_3$$

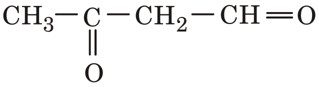
The reactant '*A*' is

(a) 

$CH_3CH{=}CH{-}\overset{\overset{O}{\|}}{C}{-}CH_3$

(b) 

$CH_3{-}\underset{\underset{O}{\|}}{C}{-}CH_2{-}\overset{OH}{CH}{-}CH_3$

(c) 

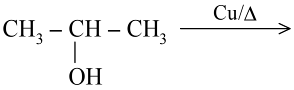
$CH_3{-}\underset{\underset{O}{\|}}{C}{-}CH_2{-}CH{=}O$

(d) $(CH_3)_2C{=}CH{-}CH{=}O$

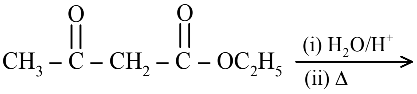
MCQs More than One Correct Option

1. Which of the following will give acetone?

(a) $CH_3-C{\equiv}N \xrightarrow[\text{(ii) } H_2O/H^+]{\text{(i) } CH_3MgBr}$

(b) 

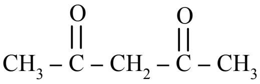
$CH_3-\underset{OH}{CH}-CH_3 \xrightarrow{Cu/\Delta}$

(c) 

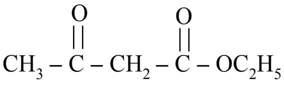
$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-OC_2H_5 \xrightarrow[\text{(ii) } \Delta]{\text{(i) } H_2O/H^+}$

(d) $CH_3-COOH \xrightarrow{MnO/300^\circ C}$

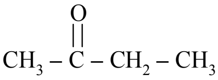
2. Enolic form of which compounds contain intramolecular H-bonding?

(a) 

$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$

(b) 

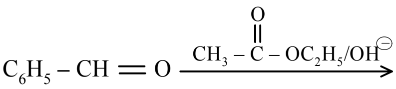
$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-OC_2H_5$

(c) 

$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$

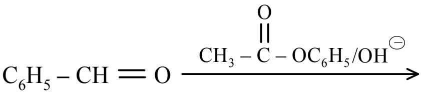
(d) $CH_3 - CH_2 - CH = O$

3. Which reactions are Claisen condensation?

(a) 

$C_6H_5-CH=O \xrightarrow{CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5/OH^\ominus}$

(b) $C_6H_5-CH=O \xrightarrow{CH_3-COOC_2H_5/OH^\ominus}$

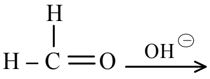
(c) 

$C_6H_5-CH=O \xrightarrow{CH_3-\overset{\overset{O}{\|}}{C}-OC_6H_5/OH^\ominus}$

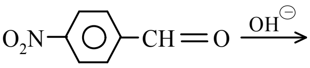
(d) $C_6H_5-CH=O \xrightarrow{OH^\ominus}$

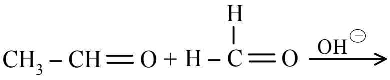
4. Which of the following is not an aldol condensation?

(a) $Cl_3CCH=O \xrightarrow{OH^\ominus}$

(b) 

$H-\overset{H}{C}=O \xrightarrow{OH^\ominus}$

(c) 

(d) 

$CH_3-CH=O + H-\overset{H}{C}=O \xrightarrow{OH^\ominus}$

5. Which of the following will give cinnamic acid?

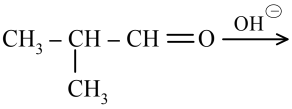
(a) $C_6H_5CH = O \xrightarrow{(CH_3CO)_2O/CH_3COONa}$

(b) $C_6H_5CH = O \xrightarrow{CH_3CH=O/OH^\ominus}$

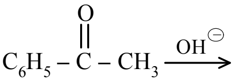
(c) $C_6H_5CH = O \xrightarrow{CH_2(COOC_2H_5)_2/pyridine}$

(d) all of these.

6. Cannizzaro reaction is not observed in

(a) 

$CH_3-\underset{CH_3}{CH}-CH=O \xrightarrow{OH^\ominus}$

(b) 

$C_6H_5-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{OH^\ominus}$

(c) $Cl_3C-CH=O \xrightarrow{OH^\ominus}$

(d) $CH_3-CH_2-CH = O \xrightarrow{OH^\ominus}$

7. Which of the following will give an aldehyde only?

(a) Ozonolysis of alkene

(b) Rosenmund's reaction

(c) Stephen's reaction

(d) Hydration of alkyne.

8. Acetaldehyde and formaldehyde during crossed aldol will produce

(a) 2-butanal

(b) β-hydroxypropanal

(c) Tetrahydroxymethyl methane and sodium formate

(d) Trihydroxymethyl acetaldehyde.

9. Hypnotics are

(a) Chloretone (b) Paraldehyde

(c) Metaldehyde (d) Phorone.

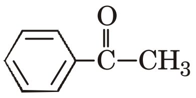
10. Which of the following will give +ve test for the aldehyde?

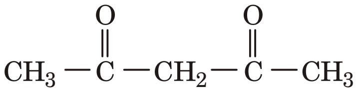
(a) Schiff's base (b) Tollen's reagent

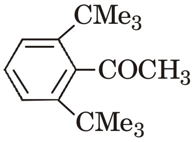
(c) Fehling solution

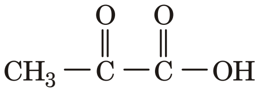
(d) Benedict's solution.

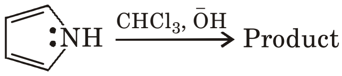
11. Iodoform reaction is given by

(a)


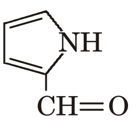
(b)

$CH_3-CO-CH_2-CO-CH_3$

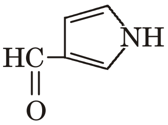
(c)


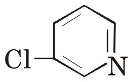
(d)

$CH_3-CO-CO-OH$

12.


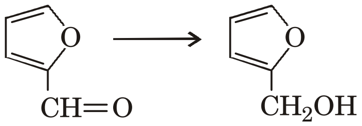
Which of the following is/are possible products (in significant amounts)?

(a)


(b)


(c)


(d)


13.


Which of the following reagents can perform this conversion successfully?

(a) H_2, Raney Ni, Δ

(b) Mg, THF; H_2O

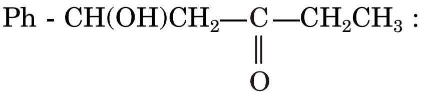
(c) $NaBH_4$, C_2H_5OH; H^+, H_2O

(d) HCH= O, OH^-

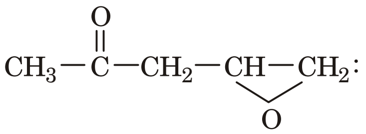
14. Select the correct combination of compound(s) and the reducing agent(s) (to reduce the >C=O group only).

(a) $BrCH_2CH_2CH = O$; Desulphurisation ($HSCH_2CH_2SH$; H_2, Ni)

(b) $BrCH_2CH_2—CH=O$; Clemmensen's reduction (Zn-Hg, HCl)

(c)

$Ph - CH(OH)CH_2—CO—CH_2CH_3$:

Wolff-Kishner reduction

(d)


Wolff-Kishner reduction

15. $R — CH=O + NaHSO_3 \rightarrow \underset{\text{Sodium bisulphite adduct}}{R—CH(OH)SO_3^-Na^+}$

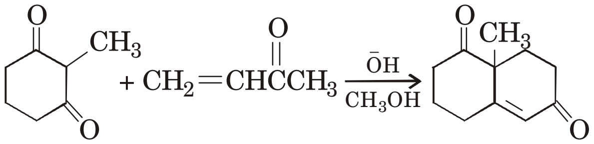
Choose the correct statement(s) about the above reaction.

(a) SO_3^{2-} is a large nucleophile and reacts only with less sterically hindered > C = O groups *e.g.*, $RCH = O$, CH_3COCH_3 and $RCOCH_3$.

(b) SO_3^{2-} is an ambidient nucleophile, on addition form C — O bond instead of C — S bond.

(c) The resultant sodium bisulphite adduct is a solid adduct in ethyl alcohol.

(d) Carbonyl compounds can be regenerated from the adducts on acidic hydrolysis—not in basic hydrolysis.

16.


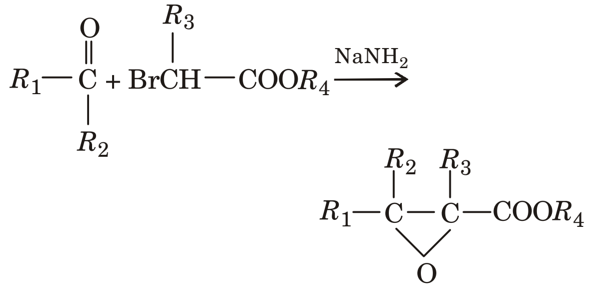
Select the reaction(s) involved in the above reaction.

(a) Dehydration

(b) Aldol condensation

(c) Michael addition

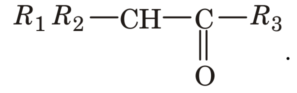
(d) Knoevenagel condensation

17.


Choose the correct statement(s) regarding the above reaction.

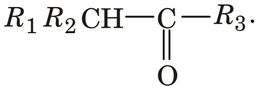
(a) The reaction is called Darzen's glycidic ester synthesis.

(b) On alkaline hydrolysis of the product followed by warming with dilute acid, a new ketone forms *i.e.*,



$R_1R_2\text{—CH—}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\text{—}R_3$.

(c) If $R_4 = \mathrm{CMe_3}$, heating of the product molecule gives a new ketone *i.e.*,



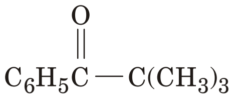
$R_1R_2\mathrm{CH}\text{—}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\text{—}R_3$.

(d) The mentioned reaction may proceed more precisely if conc. $\mathrm{OH^-}$ is used.

18. Which of the following molecule(s) contain(s) deuterium after reaction with NaOD in D_2O?

(a) $C_6H_5CH = O$

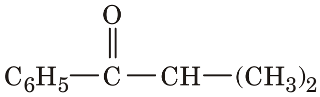
(b)



$C_6H_5\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}—C(CH_3)_3$

(c) $C_6H_5CH_2CH = O$

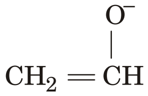
(d)



$C_6H_5—\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}—CH—(CH_3)_2$

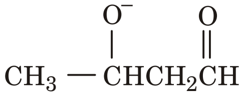
19. Which of the following species is/are not intermediate(s) in the aldol condensation of acetaldehyde in aqueous base?

(a)



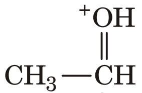
$CH_2 = \overset{\overset{\mathrm{O^-}}{|}}{\mathrm{CH}}$

(b)



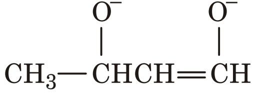
$CH_3 — \overset{\overset{\mathrm{O^-}}{|}}{\mathrm{C}}HCH_2\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}H$

(c)



$CH_3—\overset{\overset{\mathrm{^+OH}}{\|}}{\mathrm{CH}}$

(d)



$CH_3—\overset{\overset{\mathrm{O^-}}{|}}{\mathrm{C}}HCH{=}\overset{\overset{\mathrm{O^-}}{|}}{\mathrm{C}}H$

20. Which of the following statements about benzaldehyde are true?

(a) Reduces Tollen's reagent

(b) Undergoes Aldol condensation

(c) Undergoes Cannizzaro reaction

(d) Does not form an addition compound with sodium hydrogen sulphite.

21. Which of the following compounds will give a yellow precipitate with iodine and alkali?

(a) 2-hydroxypropane

(b) Acetophenone

(c) Methyl acetate (d) Acetamide.

22. Keto-enol tautomerism are observed in

(a) C_6H_5CHO (b) $C_6H_5COCH_3$

(c) $C_6H_5COOC_6H_5$ (d) $C_6H_5COCH_2COCH_3$

23. Which of the following are examples of aldol condensation?

(a) $2CH_3CHO \xrightarrow{\text{dil. NaOH}} CH_3CHOHCH_2CHO$

(b) $2CH_3COCH_3 \xrightarrow{\text{dil. NaOH}}$

$CH_3C(OH)(CH_3)CH_2COCH_3$

(c) $2HCHO \xrightarrow{\text{dil. NaOH}} CH_3OH + HCOOH$

(d) $C_6H_5CHO + HCHO \xrightarrow{\text{dil. NaOH}} C_6H_5CH_2OH$

24. Under Wolf-Kishner reduction conditions the conversions which may be brought about are

(a) Benzophenone into diphenyl methane

(b) Benzaldehyde into benzyl alcohol

(c) Cyclohexanone into cyclohexane

(d) Cyclohexanone into cyclohexanol.

25. The compound (*A*) obtained by the reaction,

$$CH_3CH_2CHO + 2HCHO \xrightarrow{\overline{\mathrm{O}}\mathrm{H}} (A)$$

(a) gives Cannizzaro product

(b) reduces Tollen's solution

(c) reacts with Na

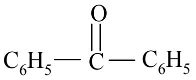
(d) reacts with Lucas reagent.

26. Which of the following compounds does not undergo Cannizzaro reaction?

(a) $(CH_3)_2CHCHO$

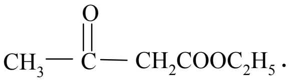
(b) CH_3COCH_2CHO

(c)



$C_6H_5—\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}—C_6H_5$

(d)

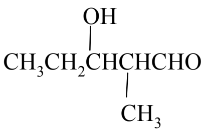


$CH_3—\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}—CH_2COOC_2H_5$.

27. What are all the possible products in the reaction,

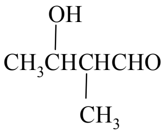
$$CH_3CHO + CH_3CH_2CHO \xrightarrow[25°\mathrm{C}]{\overline{\mathrm{O}}\mathrm{H}} ?$$

(a)



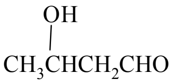
$CH_3CH_2\overset{\overset{\mathrm{OH}}{|}}{\mathrm{C}}H\underset{\underset{\mathrm{CH_3}}{|}}{\mathrm{C}}HCHO$

(b)



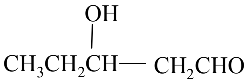
$CH_3\overset{\overset{\mathrm{OH}}{|}}{\mathrm{C}}H\underset{\underset{\mathrm{CH_3}}{|}}{\mathrm{C}}HCHO$

(c)



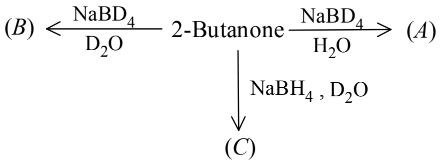
$CH_3\overset{\overset{\mathrm{OH}}{|}}{\mathrm{C}}HCH_2CHO$

(d)



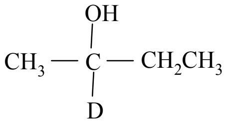
$CH_3CH_2\overset{\overset{\mathrm{OH}}{|}}{\mathrm{C}}H— CH_2CHO$

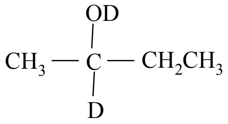
28. Consider the reduction of 2-butanone,

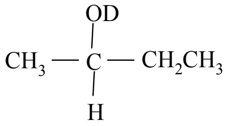


$$(B) \xleftarrow[D_2O]{NaBD_4} \text{2-Butanone} \xrightarrow[H_2O]{NaBD_4} (A)$$
$$\text{2-Butanone} \xrightarrow{NaBH_4,\ D_2O} (C)$$

Which of the following statements are true about the products?

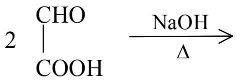
(a) Compound (*A*) is  $CH_3-\overset{OH}{\underset{D}{C}}-CH_2CH_3$

(b) Compound (*B*) is  $CH_3-\overset{OD}{\underset{D}{C}}-CH_2CH_3$

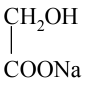
(c) Compound (*C*) is  $CH_3-\overset{OD}{\underset{H}{C}}-CH_2CH_3$

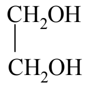
(d) None is correct.

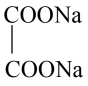
29. The products obtained in the following reaction are



$$2\ \begin{matrix}CHO\\|\\COOH\end{matrix} \xrightarrow[\Delta]{NaOH}$$

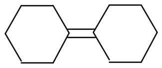
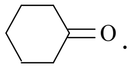
(a)  $\begin{matrix}CH_2OH\\|\\COONa\end{matrix}$

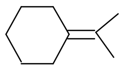
(b)  $\begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix}$

(c)  $\begin{matrix}COONa\\|\\COONa\end{matrix}$

(d) all the above.

30. Which of the following statements are correct?

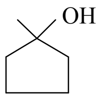
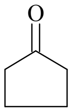
(a) Ozonolysis of  gives only  .

(b)  upon ozonolysis gives formic acid.

(c) $H_2C=CH-CH=CH_2$ upon ozonolysis gives glyoxal.

(d) Cyclopentene upon ozonolysis gives only one product.

31. Which of the following statements are correct?

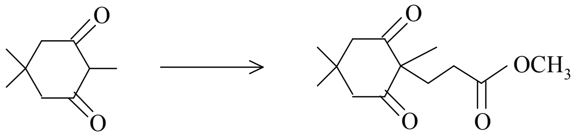
(a)  can be oxidized to  using $K_2Cr_2O_7/H_2SO_4$

(b) The above reaction can be made effective first by dehydration and then by ozonolysis

(c) $C_6H_5CH(OH)CH_2OH$ can be selectively oxidized to $C_6H_5COCH_2OH$ using MnO_2

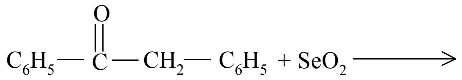
(d) $CH_3COCH_2CH_2COCH_3$ can be dehydrogenated to $CH_3COCH=CHCOCH_3$ using SeO_2/Δ.

32. Which of the following reagents are used in the following synthetic conversion?



(a) *t*-buOK
(b) $H_2C=CHCOOCH_3$
(c) H^+/H_2O
(d) CH_3MgBr.

33. The product of the following reaction undergoes



$$C_6H_5-\overset{O}{\overset{\|}{C}}-CH_2-C_6H_5 + SeO_2 \longrightarrow$$

(a) Benzilic acid rearrangement
(b) Cannizzaro reaction
(c) Claisen rearrangement
(d) Cyclic imine formation.

34. Which of the following statements regarding semicarbazide formation from cyclohexanone and benzaldehyde are incorrect?

(a) Both forms nearly have the same amount of semicarbazide.
(b) Semicarbazide of benzaldehyde is more stable.
(c) Semicarbazide of cyclohexanone is more stable.
(d) Semicarbazide formation from benzaldehyde is faster.

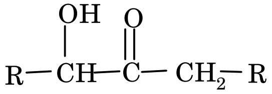
35. Which of the following statements are incorrect?

(a) $2C_6H_5CHO \xrightarrow{\overline{OH}} C_6H_5COO^- + C_6H_5CH_2OH$ is an example of disproportionation reaction.
(b) Benzaldehyde reduces Fehling's solution.
(c) *p*-Hydroxy benzaldehyde is major product obtained when phenol is treated with $CHCl_3/OH^-$.
(d) Gattermann-Koch reaction involves electrophilic aromatic substitution.

36. In the context of Beckmann rearrangement, which of the following statements are correct?

(a) It is *trans*-hydrocarbon radical with respect to –OH group migrates on to nitrogen.
(b) N-substituted amides are major product.
(c) This rearrangement is induced by electron deficient species.
(d) This rearrangement is induced by electron rich species.

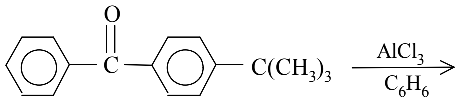
37. Which of the following compounds will give red precipitate when heated with Fehling's solution?

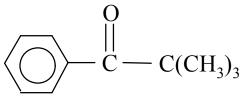
(a) 
$R-\overset{OH}{\overset{|}{C}H}-\overset{O}{\overset{||}{C}}-CH_2-R$

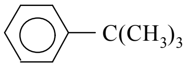
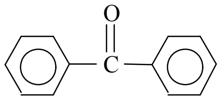
(b) C_6H_5CHO

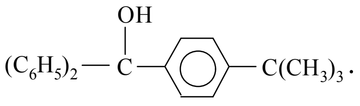
(c) HCOOH (d) $CH_3COCH_2COCH_3$.

38. The products of the following reaction are



(a) 

(b)  (c) 

(d) 

Assertion Reason

Each question contains Statement-1 (Assertion) and Statement-2 (Reason). Of these Statements, mark correct choice if

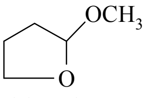
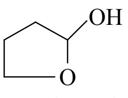
(a) Statements-1 and 2 are true and Statement-2 is a correct explanation for Statement-1

(b) Statements-1 and 2 are true and Statement-2 is not a correct explanation for Statement-1

(c) Statement-1 is true, Statement-2 is false

(d) Statement-1 is false, Statement-2 is true.

1. **Statement-1 :** Acetaldehyde is more reactive than trichloroacetaldehyde.
Statement-2 : Chlorine atom exhibits –I effect in trichloroacetaldehyde.

2. **Statement-1 :**  and  can be distinguished by the reaction with sodium.
Statement-2 : Na reduces cyclic ethers.

3. **Statement-1 :** Formaldehyde condenses with phenol to give resin.
Statement-2 : Formaldehyde contains no alkyl group in its molecule.

4. **Statement-1 :** 2, 2-Dimethylpropanal undergoes Cannizzaro reaction with concentrated NaOH.
Statement-2 : Cannizzaro reaction is a dispropor-tionation reaction.

5. **Statement-1 :** Reduction of 3-phenylprop-2-en-1-al with $LiAlH_4$ gives 3-phenylpropan-1-ol.
Statement-2 : Only aldehyde group of α, β-unsaturated aldehydes are reduced by $LiAlH_4$.

6. **Statement-1 :** Acetaldehyde undergoes aldol condensation with dilute NaOH.
Statement-2 : Aldehydes which do not contain α-hydrogen undergo aldol condensation.

7. **Statement-1 :** In formaldehyde, all the four atoms are in the same plane.
Statement-2 : The carbon atom in formaldehyde is sp^2-hybridised.

8. **Statement-1 :** α-Hydrogen atoms in aldehydes and ketones are acidic.
Statement-2 : Anions formed after loss of α-hydrogens are stabilised due to inductive effect.

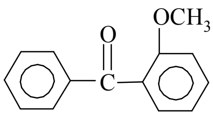
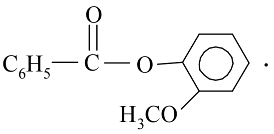
9. **Statement-1 :** RCHO, $RCOCH_3$ and cyclic ketones react with sodium bisulphite.
Statement-2 : Crystalline solid derivatives are formed when aldehydes or ketones are shaken with saturated aqueous solution of sodium bisulphite.

10. **Statement-1 :** Aldehydes can be prepared by the action of Grignard reagents on ethyl formate.
Statement-2 : Aldehydes and ketones are functional isomers of each other.

11. **Statement-1 :** HCHO and HCOOH can be distinguished by Tollen's test.
Statement-2 : Silver mirror is formed when ammoniacal $AgNO_3$ is reduced.

12. **Statement-1 :** $CH_3COCH_2COCH_3$ does not respond to the iodoform test with I_2/OH^-.
Statement-2 : Presence of active methylene group attracts the base.

13. **Statement-1 :** Acrolein containing aldehyde group undergoes aldol condensation with alkali.
Statement-2 : The double bond breaks when treated with NaOH.

14. **Statement-1 :** The Baeyer-Villiger oxidation of  predominantly gives mainly  .

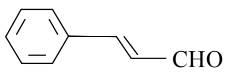
Statement-2 : Migratory aptitude of $-C_6H_5$ is greater than *o*-anisyl.

15. Statement-1 : $(CH_3)_2CHCHO$ mainly undergoes Cannizzaro reaction when heated with strong alkali.
Statement-2 : Steric hindrance prevents aldol condensation.

16. Statement-1 : The acetal formation with ketones does not respond to base catalysis.
Statement-2 : The dehydration step has to be acid-catalysed.

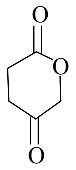
17. Statement-1 : $(CH_3)_3CCOC(CH_3)_3$ and acetone can be distinguished by the reaction with $NaHSO_3$.
Statement-2 : SO_3^{2-} is the nucleophile in bisulphite addition.

18. Statement-1 :



upon treatment with CH_3MgBr followed by hydrolysis gives 1-phenylbutadiene as major product.
Statement-2 : 1,4-adduct is formed in conjugated system.

19. Statement-1 : The products obtained in the reduction of



using $LiAlH_4$ and $NaBH_4$ are different.

Statement-2 : $LiAlH_4$ is a stronger reducing agent than $NaBH_4$.

20. Statement-1 : HCHO facilitates better nucleophilic attack than acetone, CH_3COCH_3.
Statement-2 : Formaldehyde is more polar than acetone.

21. Statement-1 : Like other haloforms, fluoroform (CHF_3) is not obtained on treatment of alkali over 1,1,1-trifluoroacetone.
Statement-2 : $^{-}CF_3$ is much less stable in comparison to $-CCl_3$.

22. Statement-1 : The bisulphite compounds of aldehydes are crystalline solids in alcohol.
Statement-2 : Aldehydes can be separated out from the alcoholic mixture by treating with $NaHSO_3$.

23. Statement-1 : The oxidation of ketone by perbenzoic acid gives ester.
Statement-2 : Perbenzoic acid oxidises because of nascent oxygen released on the dissociation.

24. Statement-1 : Reimer-Tiemann reaction is used to prepare benzaldehyde from benzene.
Statement-2 : Reimer-Tiemann reaction involves electrophilic substitution.

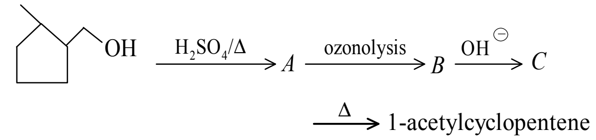
25. Statement-1 : Toluene is oxidized to benzaldehyde on treatment with CrO_3 in acetic anhydride.
Statement-2 : The oxidation of toluene by CrO_3 gives ester, benzylidene acetate as the instant product.

26. Statement-1 : Chloroform, bromoform and iodoform form at the same rate in the alkaline medium from acetone.
Statement-2 : Cl_2, Br_2 and I_2 all are having same electrophilicity.

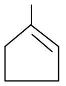
27. Statement-1 : Benzaldehyde gives benzyl alcohol on treatment with HCHO and ^{-}OH.
Statement-2 : Formaldehyde is a better reducing agent than benzaldehyde.

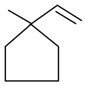
Passage Comprehension

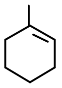
PASSAGE 1: See the following sequence of reactions.

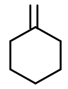


1. In given reaction (*A*) is

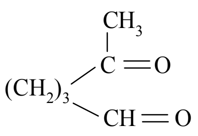
(a)


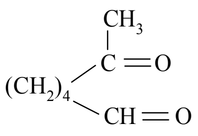
(b)


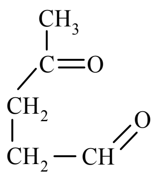
(c)


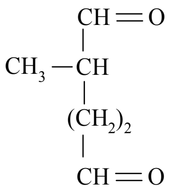
(d)


2. Structure of (*B*) is

(a)


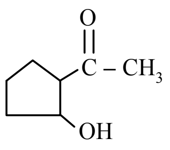
(b)


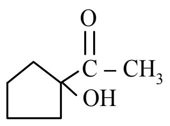
(c)


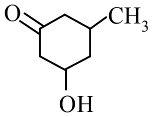
(d)


$$\begin{array}{l} \quad\;\; CH{=}O \\ \quad\;\; | \\ CH_3-CH \\ \quad\;\; | \\ \quad\;\; (CH_2)_2 \\ \quad\;\; | \\ \quad\;\; CH{=}O \end{array}$$

3. Structure of (*C*) is

(a)


(b)


(c)  (d) none of these.

PASSAGE 2 : Aldehydes and ketones are characterised by the addition of nucleophilic reagents to the carbonyl group, especially derivatives of ammonia. An aldehyde or ketone will, for example, react with 2,4-dinitrophenylhydrazine to form an insoluble yellow or red solid. Aldehydes are characterised, and in particular are differentiated from ketones, through their ease of oxidation, aldehydes give a positive test with Tollen's reagent; ketones do not. A positive Tollen's test is also given by a few other kinds of easily oxidisable compounds, *e.g.* certain phenols and amines; these compounds do not, however, give positive tests with 2,4-dinitrophenylhydrazine. Aldehydes are also, of course, oxidised by many other oxidising agents: by cold, dilute, neutral $KMnO_4$ and by CrO_3 in H_2SO_4. A highly sensitive test for aldehydes is the Schiff's test. Aliphatic aldehydes and ketones having an α-hydrogen react with Br_2 in CCl_4. This reaction is generally too slow to be confused with a test of unsaturation, and moreover, it liberates HBr. Aldehydes and ketones are generally identified through the melting points of derivatives like 2,4-dinitrophenylhydrazones, oximes and semicarbazones. Methyl ketones are characterised by the iodoform test.

1. Clemmensen reduction of ketone is carried out in presence of
(a) H_2 with Pd as catalyst
(b) $NH_2NH_2 \cdot H_2O$/glycol with KOH
(c) $LiAlH_4$ in ether (d) Zn-Hg and HCl

2. An organic compound *A* has the molecular formula C_3H_6O. It gives positive iodoform test. When saturated with HCl it gives *B* of molecular formula $C_9H_{14}O$. *A* and *B* respectively are
(a) Propanal and mesitylene
(b) Propanone and mesityl oxide
(c) Propanone and 2,6-dimethyl-2,5-heptadien-4-one
(d) Propanone and mesitylene oxide.

3. Compound *A* (molecular formula C_3H_8O) is treated with acidified potassium dichromate to form a product *B* (molecular formula C_3H_6O). *B* forms a shining silver mirror on warming with ammoniacal silver nitrate. *B* when treated with an aqueous solution of $H_2NCONHNH_2 \cdot HCl$ and sodium acetate gives a product *C*. Identify the structure of *C*.
(a) $CH_3CH_2CH = NNHCONH_2$
(b) $Me - C(Me) = NNHCONH_2$
(c) $Me - C(Me) = NCONH_2$
(d) $CH_3CH_2CH = NCONHNH_2$.

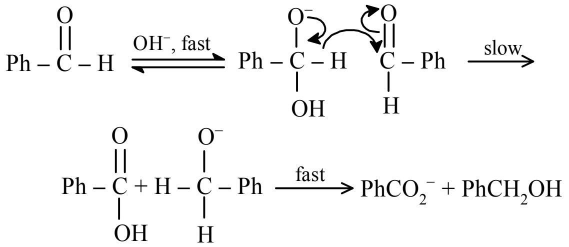
PASSAGE 3: For haloform reaction there must be presence of CH_3CO- group as all the hydrogen atoms are replaced by halogen in alkaline media to give trihalogenated ketone which subsequently undergoes base hydrolysis to form haloform. Aldehydes give Ag- mirror test with Tollen's reagent but not ketones. It also gives red precipitate with Fehling's solution. Being strong oxidising agents aliphatic and aromatic aldehydes both give +ve Ag-mirror test but red precipitate with Fehling's solution is obtained with aldehydes only.

1. Iodoform test is observed with
(a) $C_6H_5CH = O$ (b) $C_6H_5COCH_3$
(c) $C_6H_5CH_2 - COOH$
(d) CH_3COCl

2. Fehling solution will oxidise
(I) $C_6H_5 - CH = O$ (II) $C_6H_5CH(OH)CH_3$
(III) $C_6H_5 - CH_2 - CH{=}O$
(IV) $CH_3 - CH{=}O$
(a) II & IV (b) I & II
(c) I & III (d) III & IV

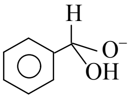
3. Fehling solution gives red precipitate from
(a) Aliphatic aldehyde
(b) Aromatic aldehyde
(c) Aliphatic ketone
(d) All of these.

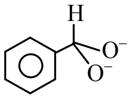
PASSAGE 4 : Aldehydes which do not have any α-hydrogen atoms when treated with a concentrated solution of NaOH or KOH, undergo a simultaneous oxidation and reduction forming a salt of carboxylic acid and an alcohol. This reaction is known as Cannizzaro reaction.

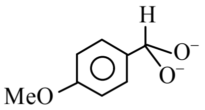


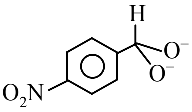
1. The Cannizzaro reaction is not given by
(a) Trimethylacetaldehyde
(b) Acetaldehyde
(c) Benzaldehyde (d) All of these.

2. In a Cannizzaro reaction, the intermediate that will be best hydride donor is

(a) 

(b) 

(c) 

(d) 

PASSAGE 5 : Aldol condensation is a chemical reaction in which two or more molecules of same or different carbonyl compounds containing α-hydrogen atom unite together in the presence of dilute base such as NaOH, $Ba(OH)_2$ or K_2CO_3 etc. to form compounds called aldols. The term aldol is derived from the combination of words aldehyde and alcohol, the two functional groups present in the product. In such a condensation, the hydrogen of one molecule in α-position with respect to the carbonyl group enters into combination with the oxygen of the carbonyl group of the other molecule forming a hydroxy group. Formaldehyde, though contains no α-hydrogen atom, yet undergoes aldol condensation. In aldol condensation

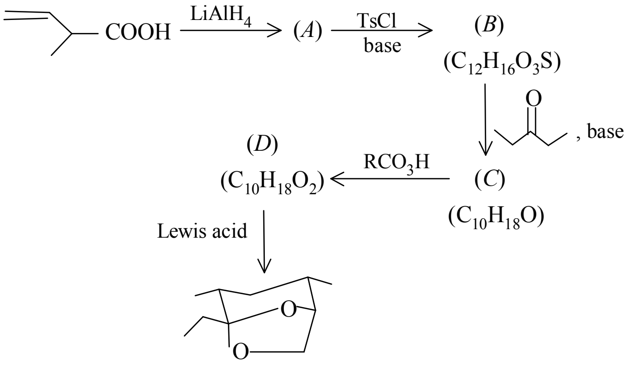
(i) New carbon to carbon linkage is formed.

(ii) The condensation product *i.e.*, aldol loses a molecule of water to form an unsaturated aldehyde or ketone.

1. Aldol condensation of aldehyde and ketone takes place through the formation of
(a) Carbene (b) Nucleophile
(c) Electrophile (d) Free radical.

2. Aldol condensation between which of the following compounds followed by dehydration gives methyl vinyl ketone.
(a) HCHO and CH_3COCH_3
(b) HCHO and CH_3CHO
(c) Two molecules of CH_3CHO
(d) Two molecules of CH_3COCH_3.

PASSAGE 6 : Shown below is a synthesis of *elm bark beetle pheromone*, *multistriatin*

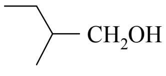


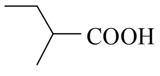
multistriatin

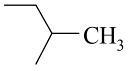
Based on the above synthesis, answer the following questions.

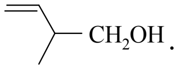
1. Which of the following reagent cannot be used for the first step in the conversion?
(a) $NaBH_4$ (b) B_2H_6/THF
(c) H_2/Pd-$BaSO_4$ (d) Both b and c.

2. The structural formula of compound (*A*) is

(a) 

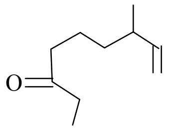
(b) 

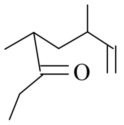
(c) 

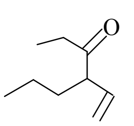
(d) 

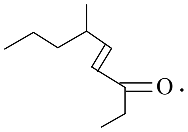
3. Tosylation is done in conversion of *A* to *B* in order to
(a) easily remove the –OH group of *A*
(b) reduce the –OH group
(c) oxidise the –OH group
(d) condense alcohols.

4. Structural formula of (*C*) is

(a) 

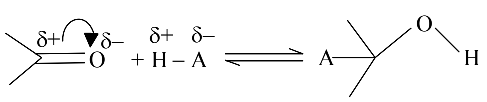
(b) 

(c) 

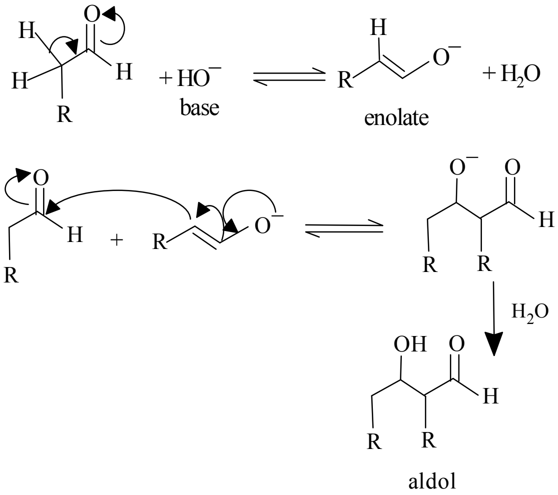
(d) 

5. Conversion of (*C*) to (*D*) involves
(a) epoxidation
(b) Baeyer-Villiger oxidation
(c) trans hydroxylation
(d) dehydrogenation.

PASSAGE 7 : Aldehydes and ketones are polar molecules. Nucleophiles usually attack $>C=O$ at carbon (positively charged) and electrophiles are attacked by oxygen. The characteristic reaction of aldehydes and ketones is nucleophilic addition to the carbon of carbonyl group.

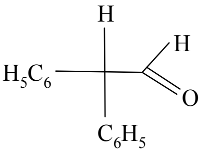


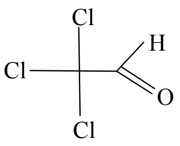
Aldehydes and ketones undergo condensation when they consist of a α-hydrogen atom. This reaction is aldol type. The reaction takes place with dilute alkali and one aldehyde molecule is partially converted to its enolate anion by the base. The enolate ion undergoes nucleophilic addition to the carbonyl group. The alkoxide formed in nucleophilic addition step, abstracts a proton from the solvent to give aldol, which consists of an aldehydic and a hydroxyl group.

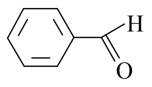


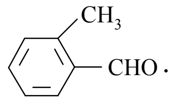
The reactivity of carbonyl compounds towards nucleophilic addition reaction is inversely proportional to electron releasing effects (+I, +M) of the groups attached to the carbonyl carbon.

1. Which of the following undergoes aldol condensation?

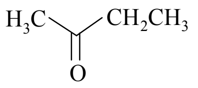
(a) 

(b) 

(c) 

(d) 

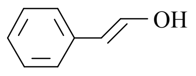
2. Which one is most reactive for addition of alcohol on carbonyl group?
(a) C_6H_5CHO (b) HCHO

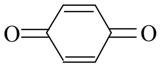
(c) 

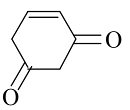
(d) CH_3CH_2CHO.

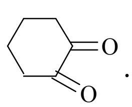
3. How many aldol products can be formed when 2-butanone and propanaldehyde reacts in presence of dilute base?
(a) 4 (b) 5
(c) 6 (d) 7.

4. Tautomerism is not exhibited by

(a) 

(b) 

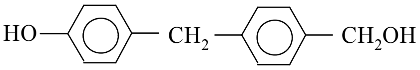
(c) 

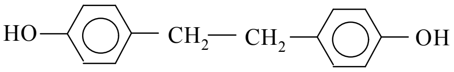
(d) .

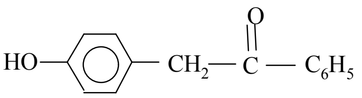
PASSAGE 8 : An organic compound (*A*), C_7H_6O gives positive test with Tollen's reagent, on treatment with alcoholic CN^-, (*A*) yields the compound (*B*), $C_{14}H_{12}O_2$. Compound (*B*) on reduction with Zn·Hg/conc. HCl and dehydration gives an unsaturated compound (*C*), which adds one mole of Br_2/CCl_4. The compound (*B*) can be oxidized with HNO_3 to a compound (*D*), $C_{14}H_{10}O_2$. Compound (*D*) on heating with KOH undergoes rearrangement and subsequent acidification of rearranged products yields an acidic compound (*E*), $C_{14}H_{12}O_3$.

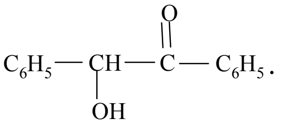
1. Compound (*A*) cannot undergo
(a) Fehling's test (b) Aldol condensation
(c) Cannizzaro reaction
(d) Benzoin condensation.

2. Structural formula of (*B*) is

(a) 

(b) 

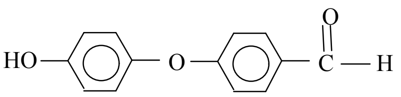
(c) 

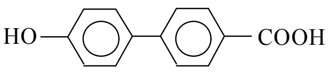
(d) 

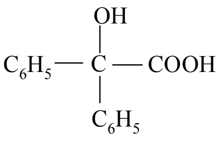
$C_6H_5-CH(OH)-C(=O)-C_6H_5$.

3. The common name of compound (*D*) is
(a) benzil (b) benzilic acid
(c) benzophenone (d) none of these.

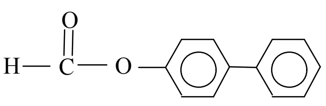
4. The structural formula of compound (*E*) is

(a) 

(b) 

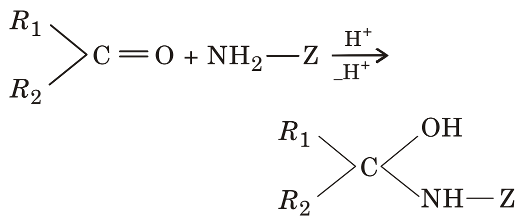
(c) 

$C_6H_5-C(OH)(C_6H_5)-COOH$

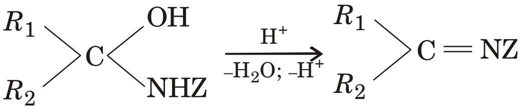
(d) .

PASSAGE 9 :

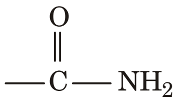
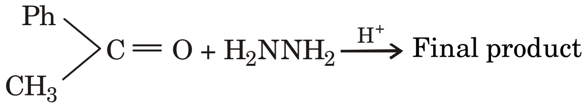
Step-I :



Step II:

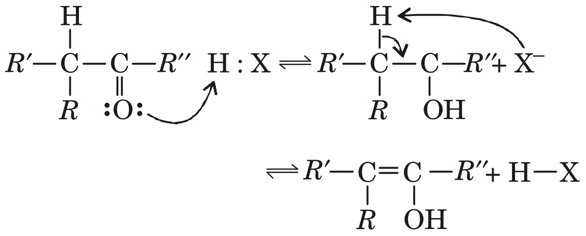


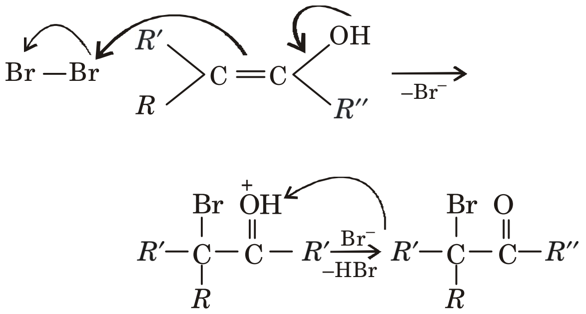
R_1 and R_2 may be —H, — R (alkyl) or —Ar

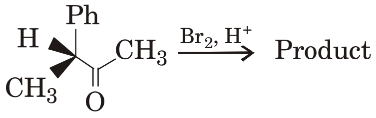
1. Rate of reaction is observed the fastest when Z is
   - (a) —CH_3
   - (b) —NH_2
   - (c) 
     $—\overset{\overset{O}{\|}}{C}—NH_2$
   - (d) —OH
2. If the medium of reaction is fairly alkaline in the beginning of the reaction and pH of the solution is made to decrease gradually,
   - (a) the rate of reaction decreases throughout
   - (b) the rate of reaction increases throughout
   - (c) the rate of reaction reaches maximum at a particular pH, and then decreases
   - (d) the rate of reaction reaches minimum at a particular pH, and then increases
3. 

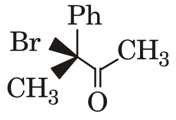
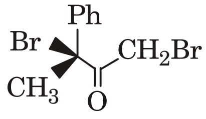
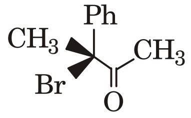
   Which of the following isomers are not expected in the final product?
   - (a) Functional isomers
   - (b) Tautomers
   - (c) Geometrical isomers
   - (d) Metamers

PASSAGE 10 :



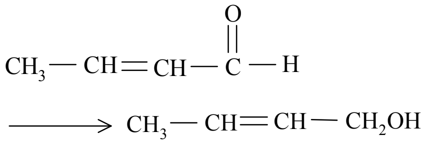
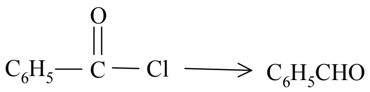
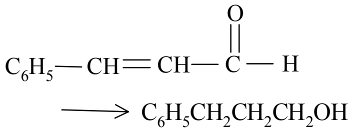


1. Bromination of carbonyl compound at α-position is
   - (a) a nucleophilic substitution
   - (b) a nucleophilic addition
   - (c) an electrophilic substitution
   - (d) an electrophilic addition
2. 

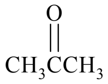
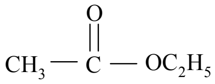
   Choose the correct product.
   - (a) 
   - (b) 
   - (c) 
   - (d) Both (a) and (c)
3. Reaction of 1 mole each of Br_2 and $PhCOCH_2CH_3$ in a basic solution yield 0.5 mole of $PhCOCBr_2CH_3$ and 0.5 mole of unreacted $PhCOCH_2CH_3$. It suggests that
   - (a) bromination further decreases the rate of bromination
   - (b) bromination further increases the rate of bromination
   - (c) bromination decreases the rate of tautomerisation
   - (d) bromination increases the reactivity of carbonyl carbon due to bigger size.

Matrix Match Type

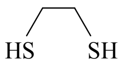
1.

Column I	**Column II**
(A)  $CH_3-CH=CH-\overset{O}{\overset{\|}{C}}-H \longrightarrow CH_3-CH=CH-CH_2OH$	(P) $H_2/Pd\text{-}BaSO_4$
(B) $C_6H_5-C\equiv N \longrightarrow C_6H_5CHO$	(Q) $LiAlH_4$
(C)  $C_6H_5-\overset{O}{\overset{\|}{C}}-Cl \longrightarrow C_6H_5CHO$	(R) $SnCl_2/HCl$, H_2O/H^+
(D)  $C_6H_5-CH=CH-\overset{O}{\overset{\|}{C}}-H \longrightarrow C_6H_5CH_2CH_2CH_2OH$	(S) $NaBH_4$

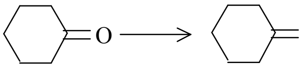
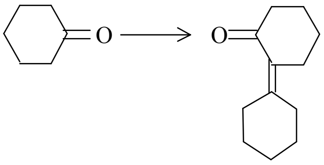
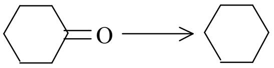
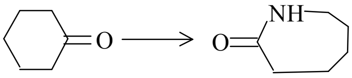
2.

Column I	**Column II**
(A) C_6H_5CHO	(P) Aldol condensation
(B)  $CH_3\overset{O}{\overset{\|}{C}}CH_3$	(Q) Reformatsky reaction
(C)  $CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5$	(R) Perkin's reaction
(D) $BrZnCH_2COOC_2H_5$	(S) Claisen condensation

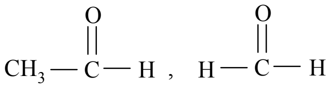
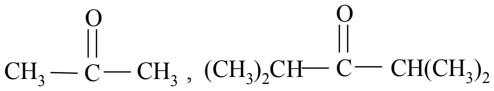
3.

Column I	**Column II**
(A) $HIO_4 \cdot 2H_2O$	(P) Mozingo reaction
(B)  / Raney Ni	(Q) Malaprade reaction
(C) $CO + HCl + CuCl_2/AlCl_3$	(R) Fries rearrangement
(D) $AlCl_3/CS_2$	(S) Gattermann-Koch reaction

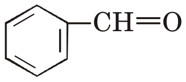
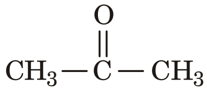
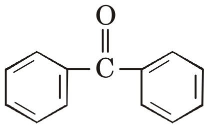
4.

Column I	**Column II**
(A) 	(P) Aldol condensation
(B) 	(Q) Beckmann rearrangement
(C) 	(R) Clemmensen's reaction
(D) 	(S) Wittig reaction

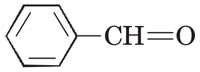
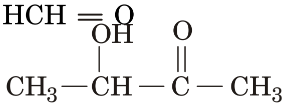
5.

Column I (Pair of compounds)	Column II (Tests to distinguish)
(A) C_6H_5CHO, HCHO	(P) $NaHCO_3$
(B) HCOOH, HCHO	(Q) $NaHSO_3$
(C)  $CH_3-\overset{O}{\overset{\parallel}{C}}-H$, $H-\overset{O}{\overset{\parallel}{C}}-H$	(R) Fehling's test
(D)  $CH_3-\overset{O}{\overset{\parallel}{C}}-CH_3$, $(CH_3)_2CH-\overset{O}{\overset{\parallel}{C}}-CH(CH_3)_2$	(S) Iodoform test

6.

Column I	Column II
(A) 	(P) Aldol condensation
(B)  $CH_3-\overset{O}{\overset{\parallel}{C}}-CH_3$	(Q) Cannizzaro reaction
(C) H — CH = O	(R) Benzoin condensation
(D) 	(S) Claisen-Schmidt reaction

7.

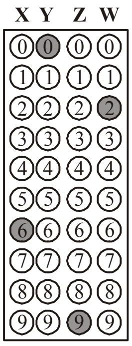
Column I	Column II
(A) 	(P) Positive Iodoform test
(B) CH_3 — CH = O	(Q) Reduces Fehling's solution
(C) HCH = O	(R) Positive Tollen's test
(D)  $CH_3-\underset{}{\overset{OH}{\overset{\vert}{CH}}}-\overset{O}{\overset{\parallel}{C}}-CH_3$	(S) Brady's reagent turns red

8.

Column I	Column II
(A) Darzens Glycidic ester synthesis	(P) Electrophilic substitution
(B) Haloform reaction	(Q) Nucleophilic substitution
(C) Cyanohydrin formation	(R) Disproportionation
(D) Cannizzaro reaction	(S) Nucleophilic addition

Integer Answer Type

In this section the answer to each of the questions is a single-digit integer, ranging from 0 to 9. If the correct answers to question numbers X, Y, Z and W (say) are 6, 0, 9 and 2, respectively, then the correct darkening of bubbles will look like the following.



1. An organic compound $A(C_6H_{12}O)$ forms an oxime but does not reduce Tollen's reagent. *A* on reduction with sodium-amalgam forms an alcohol *B*, which on dehydration forms chiefly a single alkene *C*. The ozonolysis of *C* produces *D* and *E*. The compound *D* reduces Tollen's reagent but does not answer iodoform test whereas *E* answers iodoform test. The position of double bond in compound *C* is

2. 5.26 g mixture of ethanol and acetaldehyde when heated with Fehling's solution gave 1.2 g of a red ppt. What is the percentage of acetaldehyde in the mixture ?

3. The total number of products obtained when propanal and ethanal react in the presence of dil.NaOH are

4. Total number of DBE present in the product obtained when cyclohexanone reacts with 2,4-DNP is

5. In the formation of phorone starting form acetone, the number of aldol condensation reactions participated is

6. When pentan-3-one reacts with excess Cl_2 in aqueous base, the number of Cl atoms which get inserted are

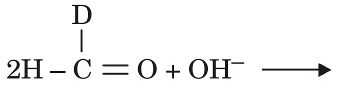
7. The total number of possible stereoisomers obtained during complete reduction of benzil with $LiAlH_4$ are

8. An unknown compound of carbon, hydrogen and oxygen contains 69.77% C and 11.63% H and has a molecular weight of 86. It does not reduce Fehling's solution but forms a bisulphite addition product and gives a positive iodoform test. The number of probable structures for this compound is

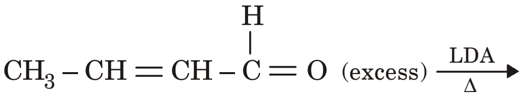
9. A compound *A* $(C_5H_8O_2)$ is reduced to pentane with Zn-Hg/HCl. It forms a dioxime with NH_2OH and also gives positive iodoform and Tollen's tests. The number of ketonic groups present in *A* is

10. The number of carbocation intermediates in Tischenko reaction is

11. The number of products in the given reaction will be deuterated is



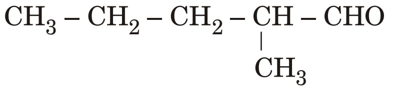
$$2H-\overset{\overset{\textstyle D}{|}}{C}=O+OH^- \longrightarrow$$

12. 

$$CH_3-CH=CH-\overset{\overset{\textstyle H}{|}}{C}=O \text{ (excess)} \xrightarrow[\Delta]{LDA}$$

The DBE of the product in the above reaction is

13. The number of position isomers for



$$CH_3-CH_2-CH_2-\underset{\underset{\textstyle CH_3}{|}}{CH}-CHO$$

is

14. $xCH_3CH=O \xrightarrow{\text{dry HCl gas}}$ Metaldehyde
The value of *x* is

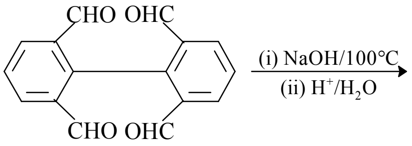
QUESTIONS FROM PREVIOUS YEARS IIT-JEE/JEE Advanced

MCQs : One Correct Option

1. A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives
(a) benzyl alcohol and sodium formate
(b) sodium benzoate and methyl alcohol
(c) sodium benzoate and sodium formate
(d) benzyl alcohol and methyl alcohol

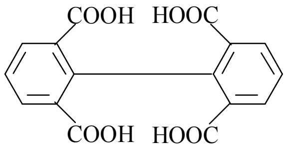
(2001)

2.

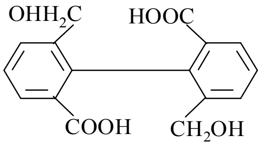


Major product is

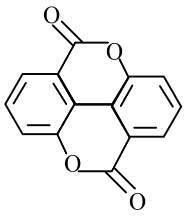
(a)



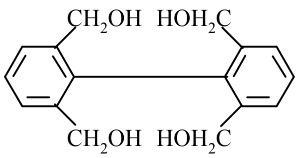
(b)



(c)

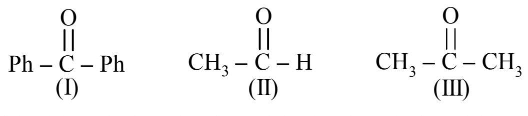


(d)



(2003)

3. The correct order of reactivity of PhMgBr with

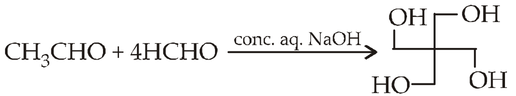


$\underset{\text{(I)}}{Ph-\overset{\overset{\displaystyle O}{||}}{C}-Ph}$ $\quad \underset{\text{(II)}}{CH_3-\overset{\overset{\displaystyle O}{||}}{C}-H}$ $\quad \underset{\text{(III)}}{CH_3-\overset{\overset{\displaystyle O}{||}}{C}-CH_3}$ is

(a) (I) > (II) > (III) (b) (III) > (II) > (I)
(c) (II) > (III) > (I) (d) (I) > (III) > (II)

(2004)

4. The number of aldol reaction(s) that occurs in the given transformation is

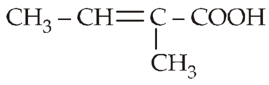


(a) 1 (b) 2
(c) 3 (d) 4 **(2012)**

5. The major product H of the given reaction sequence is

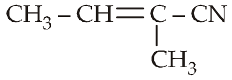
$$CH_3-CH_2-CO-CH_3 \xrightarrow{\overset{\ominus}{C}N} G \xrightarrow[\text{Heat}]{95\%\ H_2SO_4} H$$

(a)



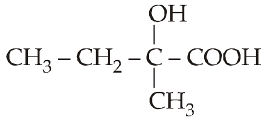
$CH_3-CH{=}\underset{\displaystyle CH_3}{\underset{|}{C}}-COOH$

(b)



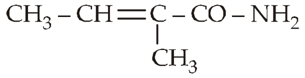
$CH_3-CH{=}\underset{\displaystyle CH_3}{\underset{|}{C}}-CN$

(c)



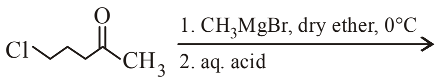
$CH_3-CH_2-\overset{\displaystyle OH}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-COOH$

(d)

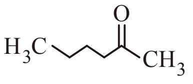


$CH_3-CH{=}\underset{\displaystyle CH_3}{\underset{|}{C}}-CO-NH_2$ **(2012)**

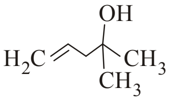
6. The major product in the following reaction is



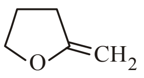
(a)



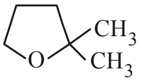
(b)



(c)



(d)

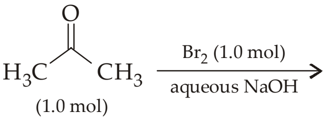


(JEE Advanced 2014)

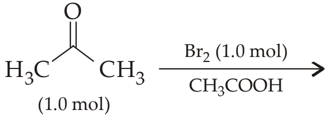
MCQs : More Than One Correct Option

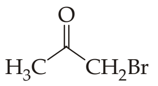
7. After completion of the reactions (I and II), the organic compound(s) in the reaction mixtures is(are)

Reaction I :

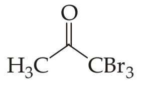


Reaction II :

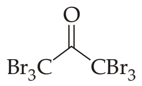




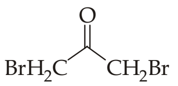
P



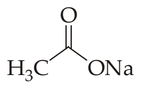
Q



R



S



T

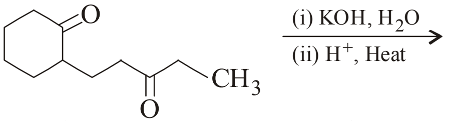
$CHBr_3$

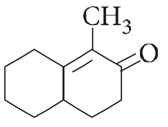
U

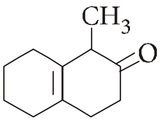
(a) Reaction I : *P* and Reaction II : *P*
(b) Reaction I : *U*, acetone and Reaction II : *Q*, acetone
(c) Reaction I : *T*, *U*, acetone and Reaction II : *P*
(d) Reaction I : *R*, acetone and Reaction II : *S*, acetone

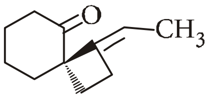
(JEE Advanced 2013)

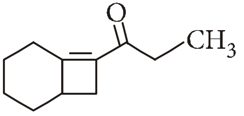
8. The major product of the following reaction is



(a)


(b)


(c)


(d)


(JEE Advanced 2015)

Assertion and Reason

Each question contains Statement-1 (Assertion) and Statement-2 (Reason). Of these Statements, mark correct choice if

(a) Statements-1 and 2 are true and Statement-2 is a correct explanation for Statement-1
(b) Statements-1 and 2 are true and Statement-2 is not a correct explanation for Statement-1
(c) Statement-1 is true, Statement-2 is false
(d) Statement-1 is false, Statement-2 is true.

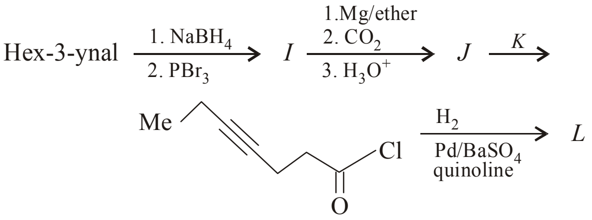
9. Statement-1: Dimethylsulphide is commonly used for the reduction of an ozonide of an alkene to get the carbonyl compounds.

Statement-2 : It reduces the ozonide giving water soluble dimethyl sulphoxide and excess of it evaporates. **(2001)**

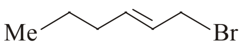
Passage Comprehension

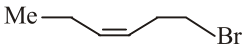
Comprehension-1

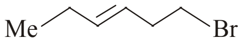
In the following reaction sequence products *I*, *J* and *L* are formed. *K* represents a reagent.

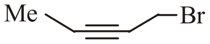


10. The structure of the product *I* is

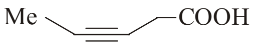
(a)


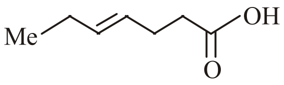
(b)


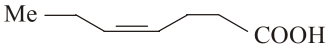
(c)


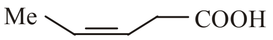
(d)


11. The structures of compounds *J* and *K*, respectively, are

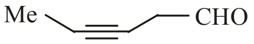
(a)

and $SOCl_2$

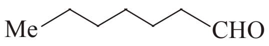
(b)

and SO_2Cl_2

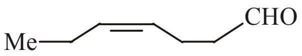
(c)

and $SOCl_2$

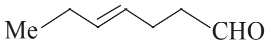
(d)

and CH_3SO_2Cl

12. The structure of product *L* is

(a)


(b)


(c)


(d)


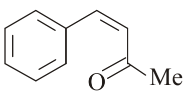
(2008)

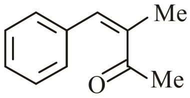
Comprehension-2

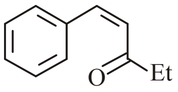
A carbonyl compound *P*, which gives positive iodoform test, undergoes reaction with MeMgBr followed by dehydration to give an olefin *Q*. Ozonolysis of *Q* leads to a dicarbonyl compound *R*, which undergoes intramolecular aldol reaction to give predominantly *S*.

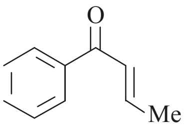
$$P \xrightarrow[\substack{2.\ H^+,\ H_2O \\ 3.\ H_2SO_4,\ \Delta}]{1.\ MeMgBr} Q \xrightarrow[2.\ Zn,\ H_2O]{1.\ O_3} R \xrightarrow[2.\ \Delta]{1.\ OH^-} S$$

13. The structure of the carbonyl compound *P* is

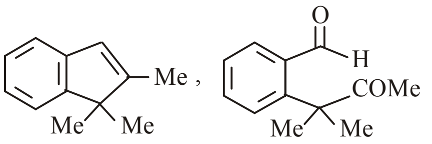
(a)


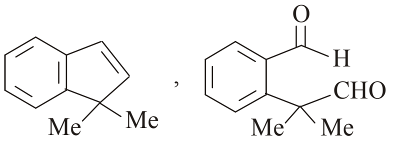
(b)


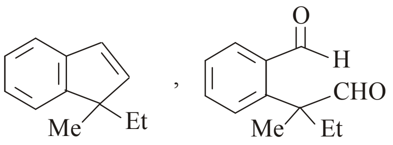
(c)


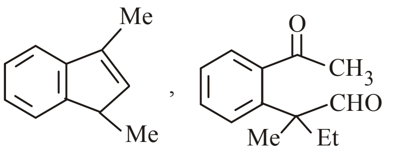
(d)


14. The structure of the products *Q* and *R*, respectively are

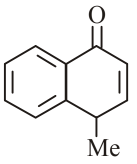
(a)


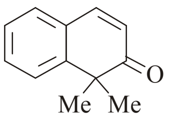
(b)


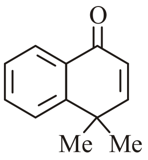
(c) 

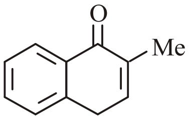
(d) 

15. The structure of product S is

(a) 

(b) 

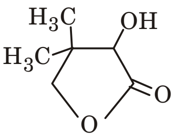
(c) 

(d) 

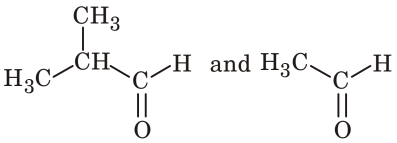
(2009)

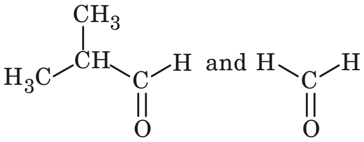
Comprehension-3

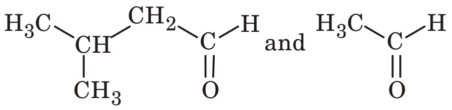
Two aliphatic aldehydes P and Q react in the presence of aqueous K_2CO_3 to give compound R, which upon treatment with HCN provides compound S. On acidification and heating, S gives the product shown below :

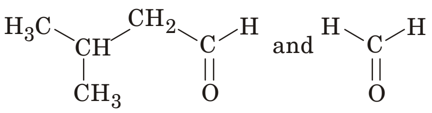


16. The compounds P and Q respectively are

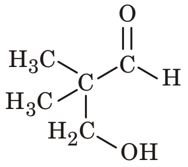
(a) 

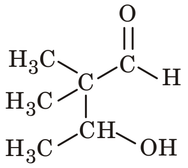
(b) 

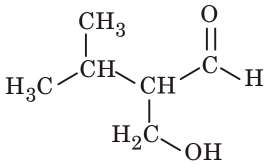
(c) 

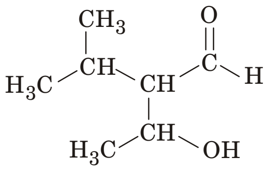
(d) 

17. The compound R is

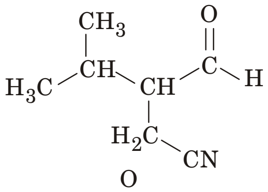
(a) 

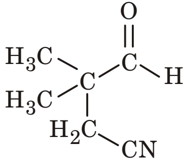
(b) 

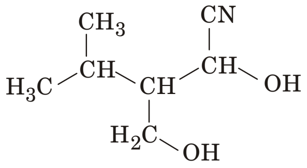
(c) 

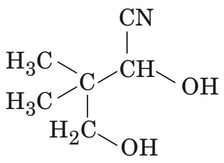
(d) 

18. The compound S is

(a) 

(b) 

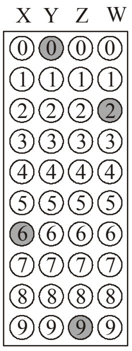
(c) 

(d) 

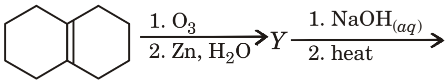
(2010)

Integer Type Questions

In this section answer to each of the questions is a single digit integer, ranging from 0 to 9. If the correct answers to question numbers X, Y, Z and W (say) are 6, 0, 9 and 2 respectively, then the correct darkening of bubbles will look like the following



19. In the scheme given below, the total number of intramolecular aldol condensation products formed from 'Y' is

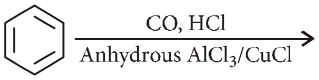


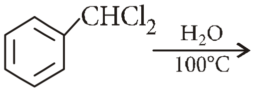
(2010)

20. Consider all possible isomeric ketones, including stereoisomers of MW = 100. All these isomers are independently reacted with $NaBH_4$ (NOTE : stereoisomers are also reacted separately). The total number of ketones that give a racemic product(s) is/are

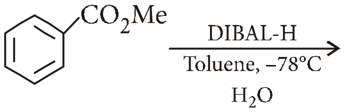
(JEE Advanced 2014)

21. Among the following, the number of reaction(s) that produce(s) benzaldehyde is

I. 

II. 

III. 

IV. 

(JEE Advanced 2015)

HINTS & SOLUTIONS

MCQs : One Option Correct

1. **(d) :** $C_6H_5CH_2CHO$ is not an aromatic aldehyde and hence, does not undergo benzoin condensation.
2. **(d) :** Each mole of an aldehyde requires 0.5 mole of O_2 for oxidation to give the corresponding acid, *i.e.*, $RCHO + 1/2\ O_2 \longrightarrow RCOOH$
3. **(b) :** Benzyl alcohol is obtained from benzaldehyde by Cannizzaro's reaction.

$$2C_6H_5CHO + KOH \longrightarrow \underset{\text{benzyl alcohol}}{C_6H_5CH_2OH} + \underset{\text{potassium benzoate}}{C_6H_5COOK}$$

4. **(c) :** $C_6H_6 + CO + HCl \xrightarrow{\text{anhyd. AlCl}_3} \underset{X}{C_6H_5CHO} + HCl$

This reaction is called *Gattermann-Koch aldehyde* synthesis.

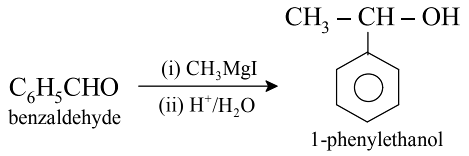
5. **(a) :** $\underset{\text{ethylidene chloride}}{CH_3-CHCl_2} + 2KOH \xrightarrow[-2KCl]{} CH_3-CH(OH)_2 \longrightarrow \underset{\text{acetaldehyde}}{CH_3CHO} + H_2O$
6. **(c) :** Formalin is an aqueous solution (40%) of formaldehyde.
7. **(d) :** $C_6H_6 \xrightarrow[\text{anhyd. AlCl}_3]{CH_3COCl} C_6H_5COCH_3$ (Friedel-Craft's acylation)
8. **(c) :** The reaction is called Etard reaction.
9. **(c) :** $\underset{\text{ethanal}}{2CH_3CHO} \xrightarrow{\text{alkali}} \underset{\text{3-hydroxybutanal}}{CH_3CHOHCH_2CHO}$

This is called aldol condensation.

10. **(b) :** Methyl ketones ($RCOCH_3$) are generally characterized by iodoform test.

$RCOCH_3 \xrightarrow{I_2/NaOH} CHI_3 + RCOONa$

11. **(c) :** Due to more stable anion with negative charge on oxygen atom and less stable carbocation.
12. **(b)**
13. **(c) :** Benzophenone ($C_6H_5COC_6H_5$) does not contain the group CH_3CO or CH_3CHOH - linked to carbon and hence, does not give iodoform test.
14. **(a) :** Reactivity decreases as the magnitude of +ve charge on the carbonyl carbon decreases, $H_2C=O > RCHO > ArCHO > R_2C=O > Ar_2C=O$
15. **(a) :** Paraldehyde is a trimer of acetaldehyde.
16. **(a) :** HCHO does not contain α-hydrogen and hence, does not undergo aldol condensation.
17. **(d) :** $CH_3I + Mg \longrightarrow CH_3MgI$



18. **(a) :** $HCHO \xrightarrow[\text{(ii) H}^+/H_2O]{\text{(i) CH}_3\text{MgBr}} CH_3CH_2OH$
19. **(b)**
20. **(b) :** $NaBH_4$ reduces only $>\!=O$ group and double bond remains unaffected.

$$C_6H_5CH=CHCHO \xrightarrow{NaBH_4} C_6H_5CH=CHCH_2OH$$

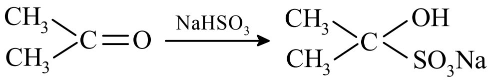
21. (a) : CH_3CHO contains α-hydrogens and hence, does not undergo Cannizzaro reaction.

22. (b) : $$\underset{\text{acetaldehyde}}{CH_3CHO} \xrightarrow{HCN} CH_3CH(OH)CN \xrightarrow{H^+/H_2O} \underset{\text{lactic acid}}{CH_3CHOHCOOH}$$

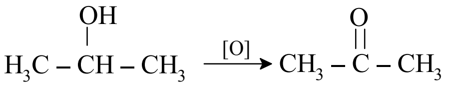
23. (a) : $$\underset{\text{benzophenone}}{C_6H_5COC_6H_5} + KOH \xrightarrow{\text{fusion}} C_6H_6 + \underset{\text{pot. benzoate}}{C_6H_5CO_2K}$$

24. (b)

25. (d) :



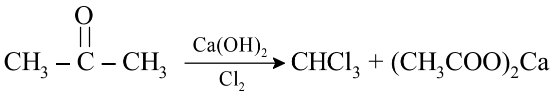
26. (a) :



$$H_3C-\overset{OH}{\overset{|}{CH}}-CH_3 \xrightarrow{[O]} CH_3-\overset{O}{\overset{||}{C}}-CH_3$$

27. (b) : C_6H_5CHO, due to lack of α-hydrogen, undergoes Cannizzaro reaction.

28. (a) :

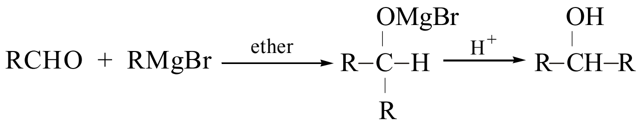


$$CH_3-\overset{O}{\overset{||}{C}}-CH_3 \xrightarrow[Cl_2]{Ca(OH)_2} CHCl_3 + (CH_3COO)_2Ca$$

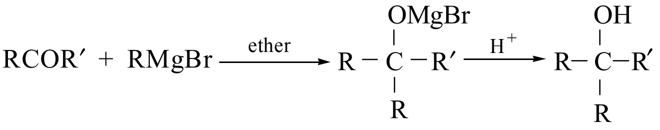
29. (b): The aldehydes which do not have α-hydrogen atoms when heated with concentrated alkali show disproportionation reaction in which one molecule of aldehyde is oxidised while other one is reduced. This is also known as Cannizzaro reaction.

$$2HCHO + NaOH \xrightarrow{\Delta} \underset{\text{Sodium formate}}{HCOONa} + \underset{\text{Methyl alcohol}}{CH_3OH}$$

30. (b): Fehling's solution, Schiff's reagent and Tollen's reagent react only with aldehydes but Grignard's reagent reacts with both aldehydes and ketones.

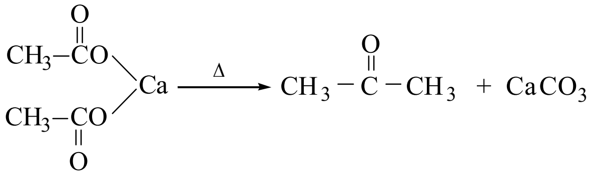


$$RCHO + RMgBr \xrightarrow{\text{ether}} R-\underset{\underset{R}{|}}{\overset{\overset{OMgBr}{|}}{C}}-H \xrightarrow{H^+} R-\overset{\overset{OH}{|}}{C}H-R$$

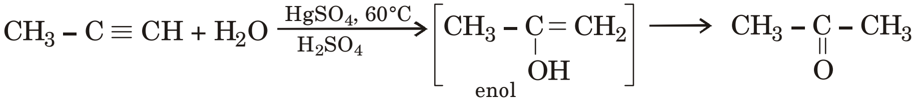


$$RCOR' + RMgBr \xrightarrow{\text{ether}} R-\underset{\underset{R}{|}}{\overset{\overset{OMgBr}{|}}{C}}-R' \xrightarrow{H^+} R-\underset{\underset{R}{|}}{\overset{\overset{OH}{|}}{C}}-R'$$

31. (d):



$$(CH_3COO)_2Ca \xrightarrow{\Delta} CH_3-\overset{O}{\overset{||}{C}}-CH_3 + CaCO_3$$



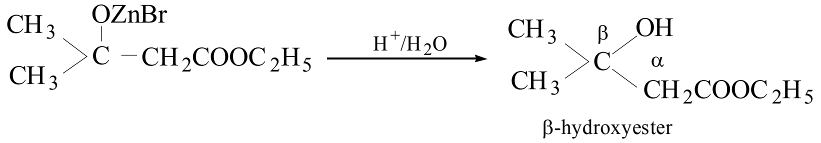
$$CH_3-C\equiv CH + H_2O \xrightarrow[H_2SO_4]{HgSO_4,\ 60°C} \underset{\text{enol}}{\left[CH_3-\underset{\underset{OH}{|}}{C}=CH_2\right]} \longrightarrow CH_3-\underset{\underset{O}{||}}{C}-CH_3$$

32. (c): The compounds having $CH_3-\underset{\underset{O}{||}}{C}-R$ give positive iodoform test (yellow precipitate with iodine and alkali), so $CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$ and $CH_3-\underset{\underset{O}{||}}{C}-C_6H_5$ both will give a yellow precipitate with iodine and alkali.

33. (d): Since the compound does not give a precipitate with 2,4-dinitrophenylhydrazine, it cannot be an aldehyde or a ketone. Further since it does not react with metallic sodium, therefore, it cannot be an alcohol. Thus, the compound C_3H_6O must be an ether.

34. **(c):** Reformatsky reaction involves the condensation of aldehydes or ketones with α-bromoesters in presence of zinc to give β-hydroxy esters, *i.e.*,

$$BrCH_2COOC_2H_5 + Zn \xrightarrow{\text{dry ether}} BrZnCH_2COOC_2H_5 \xrightarrow{(CH_3)_2C=O}$$



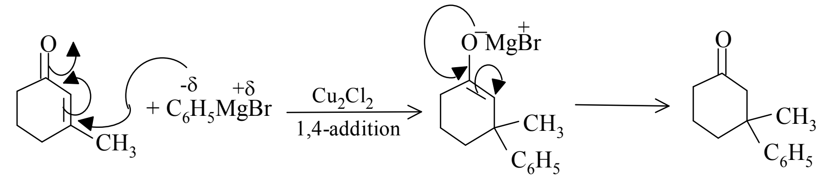
35. **(b):** Since compound (*B*) with molecular formula $C_4H_5O_3K$ containing four C-atoms is obtained from keto ester (*A*) with molecular formula $C_6H_{10}O_3$ containing six C-atoms, therefore, the ester (*A*) must be ethyl ester. Further since the compound (*B*) on acidification followed by heating undergoes decarboxylation to give acetone, therefore, (*B*) must be the potassium salt of a β-ketoacid. If this is so then (*A*) must be ethyl aceto acetate as explained below.

$$\underset{(A)}{CH_3COCH_2COOC_2H_5} \xrightarrow{KOH} \underset{(B)}{CH_3COCH_2COOK} \xrightarrow{HCl}$$

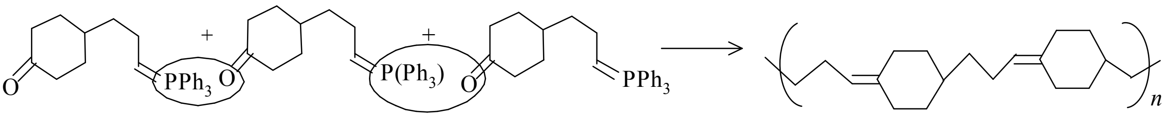
$$[CH_3COCH_2COOH] \xrightarrow{\Delta} CH_3COCH_3 + CO_2\uparrow$$

It may be noted here that although $CH_3COCH_2COOC_2H_5$ contains a $-COCH_3$ group, it does not undergo iodoform reaction. The reason being that H-atoms of CH_2 group are more acidic than those of CH_3 since it is flanked on either side by electron withdrawing $C=O$ groups. As a result, iodination occurs preferentially at CH_2 rather than at CH_3. Since iodination does not occur at CH_3, therefore iodoform is not formed.

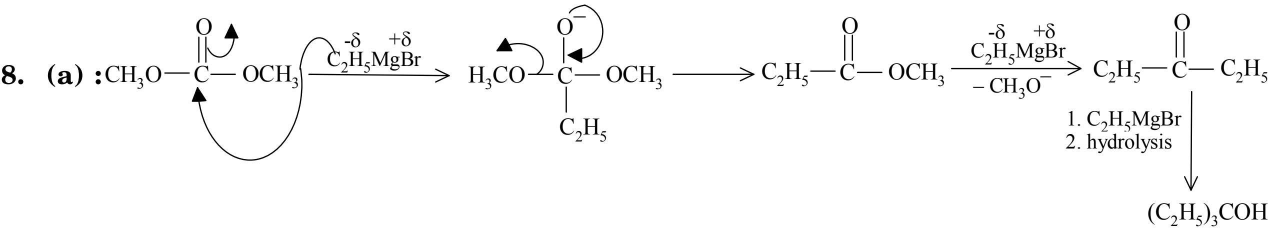
36. **(c) :**



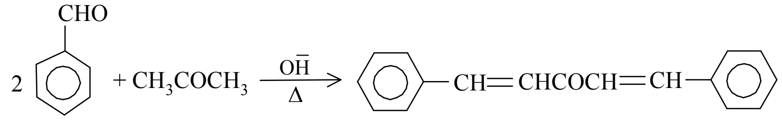
37. **(c) :** This is an example of Wittig reaction.



38. **(a) :**

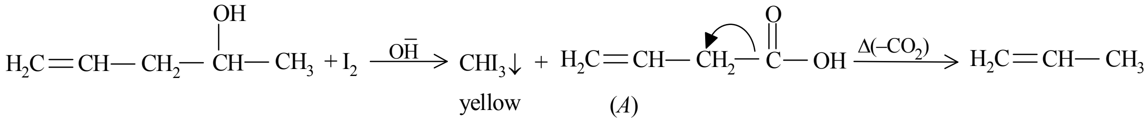


39. **(b) :** This is an example of crossed aldol condensation



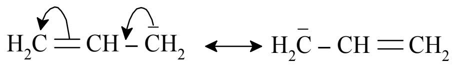
The Cannizzaro products are also observed but are minor in yield.

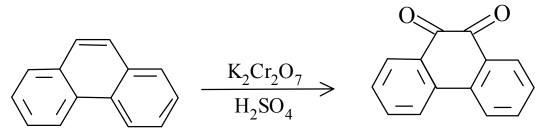
40. **(b) :**

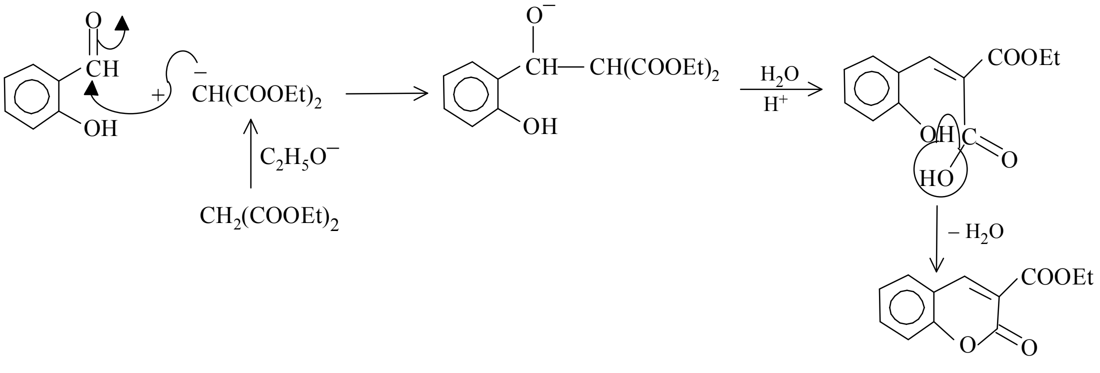


$$H_2C=CH-CH_2-\overset{OH}{CH}-CH_3 + I_2 \xrightarrow{\bar{O}H} \underset{\text{yellow}}{CHI_3\downarrow} + \underset{(A)}{H_2C=CH-CH_2-\overset{O}{\overset{\|}{C}}-OH} \xrightarrow{\Delta(-CO_2)} H_2C=CH-CH_3$$

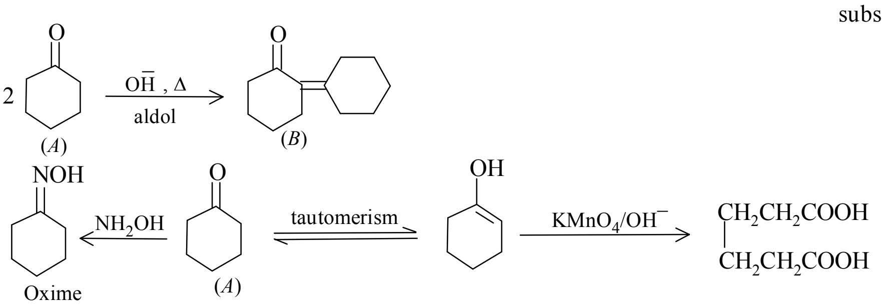
Acid (*A*) is β,γ-unsaturated acid easily undergoes decarboxylation, due to the stabilization of carbanion.

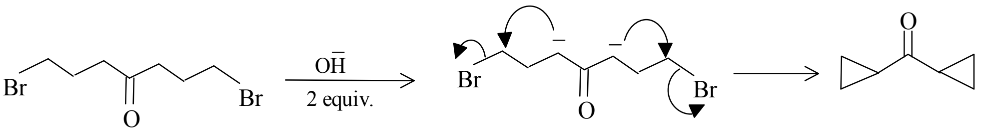


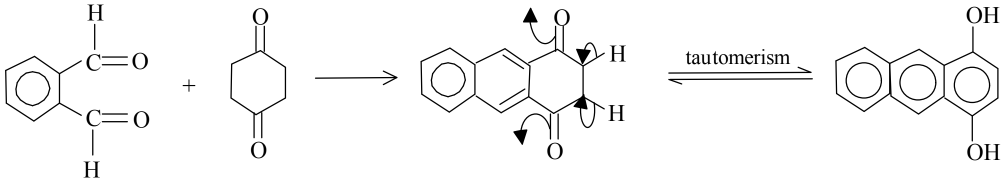
41. (c) : 

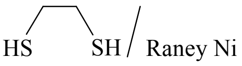
42. (a) : 

substituted coumarins

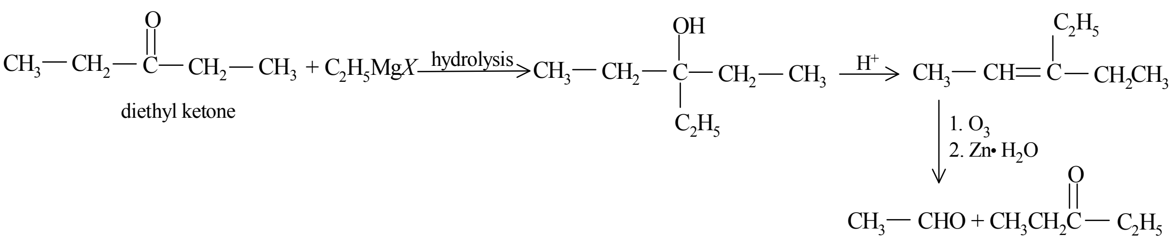
43. (b) : 

44. (c) : 

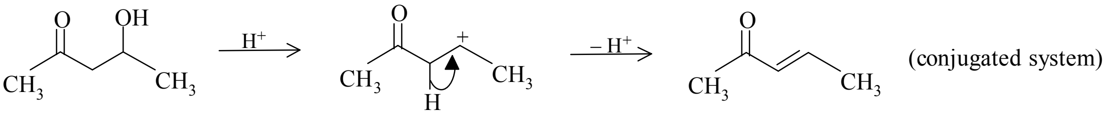
45. (d) : 

46. (d) :  cannot reduce ester groups effectively.

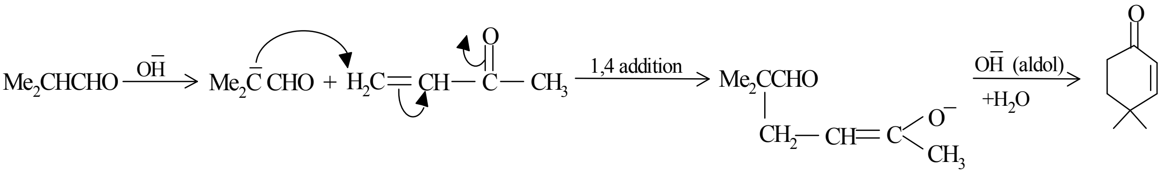
47. (b) : 2 > 1 > 3 > 4

48. (c) : 

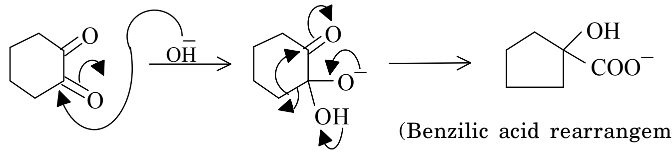
49. (c)

50. (b) : 

51. (c) :



52. (b) :

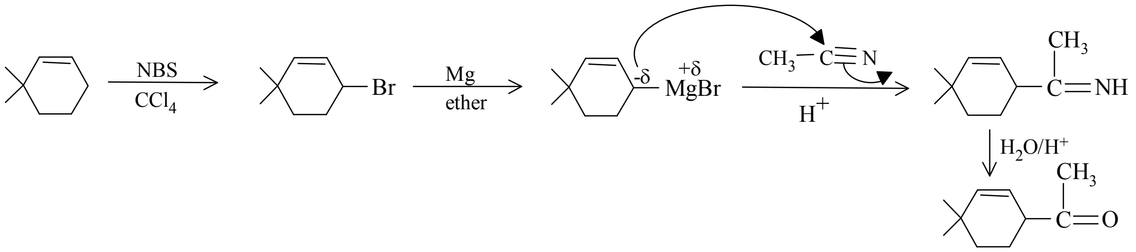


(Benzilic acid rearrangement)

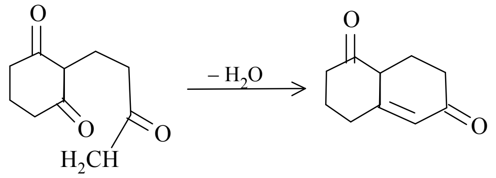
53. (c) : Electron withdrawing group enhances the rate of H^- transfer in Cannizzaro reaction.

54. (d) : Strong electron releasing groups deactivates –CHO group towards nucleophilic additions.

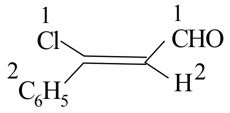
55. (a) :



56. (c) :

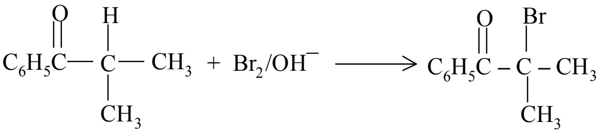


57. (b) :



Z-3-chloro-3-phenyl-2-propenal

58. (a) :



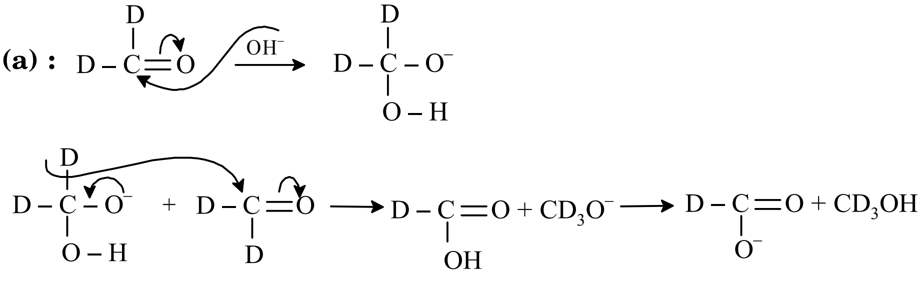
$C_6H_5\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{\overset{H}{\overset{|}{C}}}}-CH_3 + Br_2/OH^- \longrightarrow C_6H_5\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{\overset{Br}{\overset{|}{C}}}}-CH_3$

59. (d)

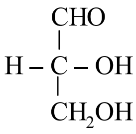
60. (a) : As the size of the alkyl groups around CO group increases, crowding increases and hence, reactivity decreases, *i.e.*
$CH_3CHO > (CH_3)_2CO > C_2H_5COCH_3$.

61. (d)

62. (a) :



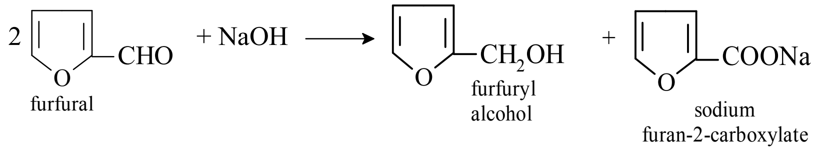
63. (b) :



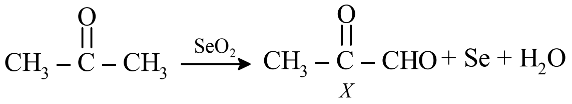
$H-\underset{CH_2OH}{\underset{|}{\overset{CHO}{\overset{|}{C}}}}-OH$

It contains one primary and one secondary alcoholic group. So, option (b) is incorrect.

64. **(c) :** Furfural does not contain an α-hydrogen and hence undergoes Cannizzaro reaction.



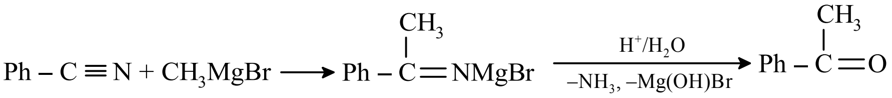
65. **(a) :** SeO_2 oxidises compounds containing active methylene (*i.e.* CH_2 next to the carbonyl group) to another CO group, *i.e.* option (a) is correct.



$$CH_3-\overset{\overset{\Large O}{||}}{C}-CH_3 \xrightarrow{SeO_2} CH_3-\underset{X}{\overset{\overset{\Large O}{||}}{C}}-CHO + Se + H_2O$$

66. **(c) :** Oxidation of secondary alcohols give ketones.

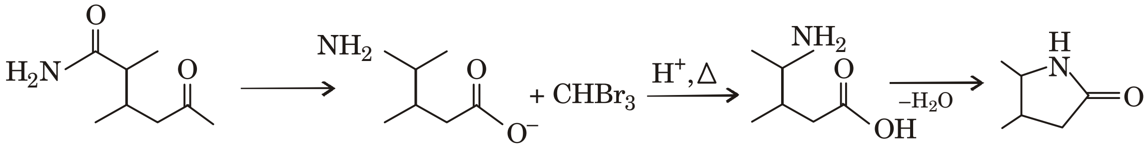
67. **(a) :** Ketones can be best prepared by the action of Grignard reagent on nitriles followed by hydrolysis.



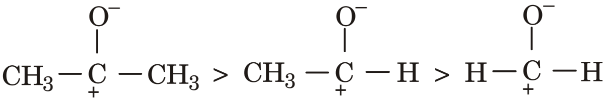
$$Ph-C\equiv N + CH_3MgBr \longrightarrow Ph-\overset{\overset{CH_3}{|}}{C}=NMgBr \xrightarrow[-NH_3,\ -Mg(OH)Br]{H^+/H_2O} Ph-\overset{\overset{CH_3}{|}}{C}=O$$

68. **(d)**

69. **(b) :** NaOH, Br_2 serves as reagents for two important reactions-Hofmann bromamide as well as bromoform.



70. **(b) :** Greater the stability of a dipolar form, greater the contribution of the dipolar form, higher the dipole moment. The stability of dipolar forms is as

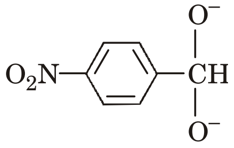


$$CH_3-\underset{+}{\overset{\overset{O^-}{|}}{C}}-CH_3 > CH_3-\underset{+}{\overset{\overset{O^-}{|}}{C}}-H > H-\underset{+}{\overset{\overset{O^-}{|}}{C}}-H$$

71. (c) :

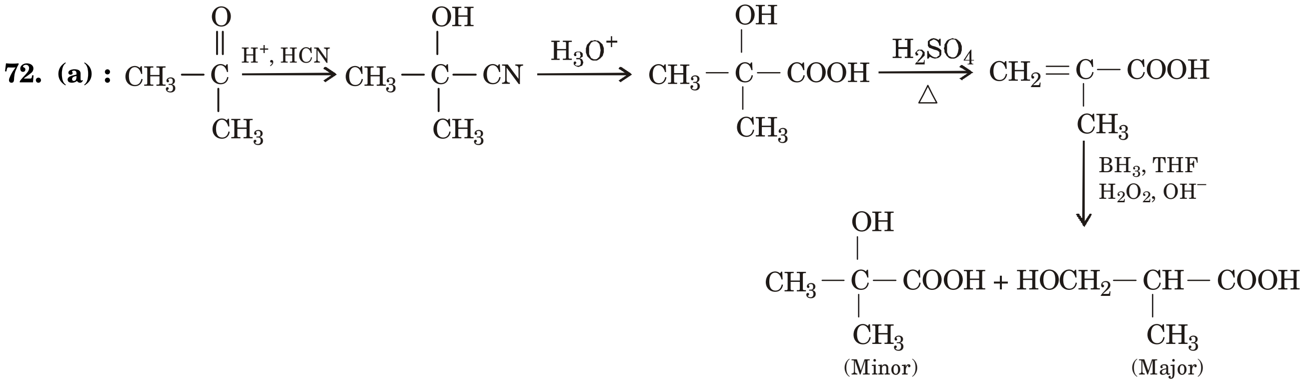
Benzaldehyde	*p*-methylbenzaldehyde	*p*-methoxybenzaldehyde	*p*-nitobenzaldehyde
Relative rates at	0.2	0.05	210

p-nitobenzaldehyde produces comparatively most stable dianion intermediate and



accepts H^- most readily.

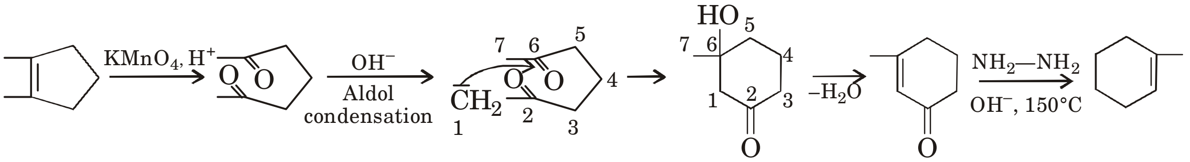
72. **(a) :**



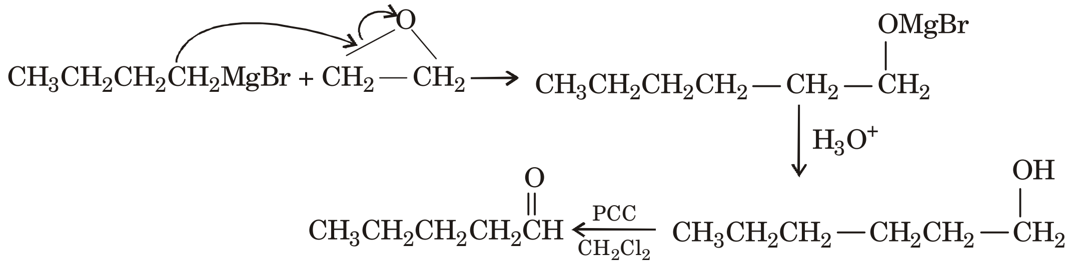
$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{O}{||}}{C}} \xrightarrow{H^+,\ HCN} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CN \xrightarrow{H_3O^+} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-COOH \xrightarrow[\Delta]{H_2SO_4} CH_2=\underset{\underset{CH_3}{|}}{C}-COOH$$

$$\xrightarrow{BH_3,\ THF;\ H_2O_2,\ OH^-} \underset{(Minor)}{CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-COOH} + \underset{(Major)}{HOCH_2-\underset{\underset{CH_3}{|}}{CH}-COOH}$$

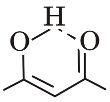
(Due to the presence of — COOH, regioselectivity of BH_3 decreases)

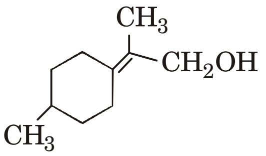
73. (d) : 

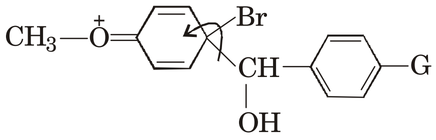
Li/liq.NH_3 selectively reduces double bond first.

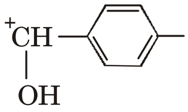
74. (c) : 

$$CH_3CH_2CH_2CH_2MgBr + \underset{\text{(epoxide)}}{CH_2-CH_2} \longrightarrow CH_3CH_2CH_2CH_2-CH_2-\overset{OMgBr}{CH_2} \xrightarrow{H_3O^+} CH_3CH_2CH_2-CH_2CH_2-\overset{OH}{CH_2} \xrightarrow[CH_2Cl_2]{PCC} CH_3CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}H$$

75. (b) :  The enol form of 1,3-diketo is more stable than diketo itself.

76. (d) :  is an optically inactive compound.

77. (b): 

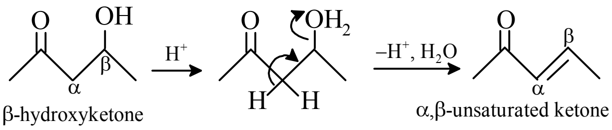
Greater the stability of  higher the leaving tendency, and higher the rate of reaction.

78. (d)

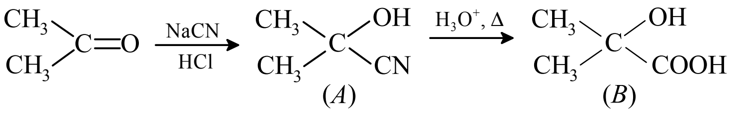
79. (d) : $>C=O \xrightarrow[-H_2O]{NH_2-NH_2} >C=N-NH_2 \xrightarrow[180°C]{KOH,\ glycol} >CH_2 + N_2$

80. (c)

81. (a) : Aldols, *i.e.*, β-hydroxyaldehydes or β-hydroxyketones readily undergo dehydration to form α,β-unsaturated aldehydes or ketones.

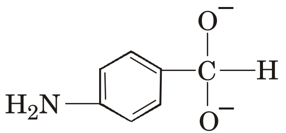


82. (c)

83. (a) : 

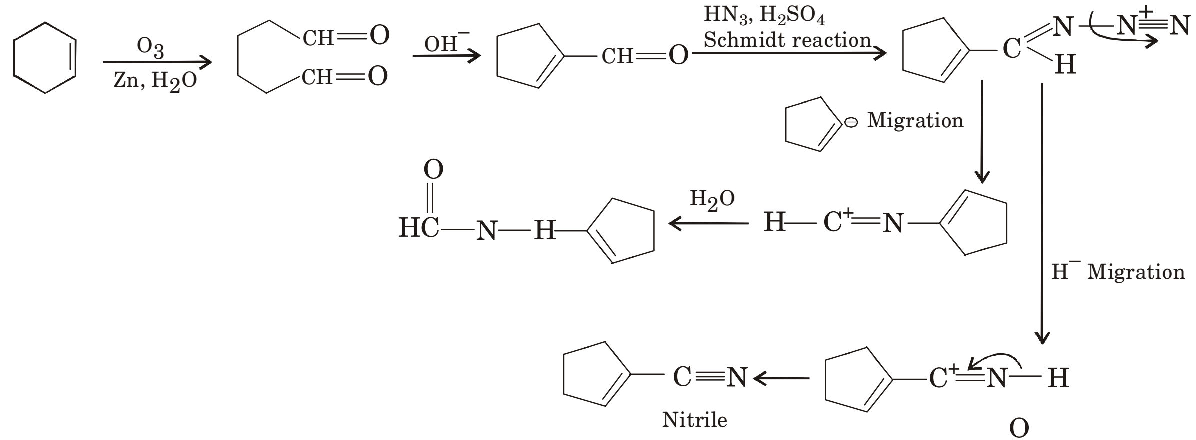
$$(CH_3)_2C=O \xrightarrow[HCl]{NaCN} \underset{(A)}{(CH_3)_2C(OH)CN} \xrightarrow{H_3O^+,\ \Delta} \underset{(B)}{(CH_3)_2C(OH)COOH}$$

84. (a) : In the Cannizzaro reaction, the rate determining step is H^- transfer.
Alongwith two $—O^-$, $— NH_2$ group is also a good e^- releasing group and promotes H^+ transfer while on the other side $— NO_2$ group at para position makes $— CH = O$ group a good H^- acceptor.

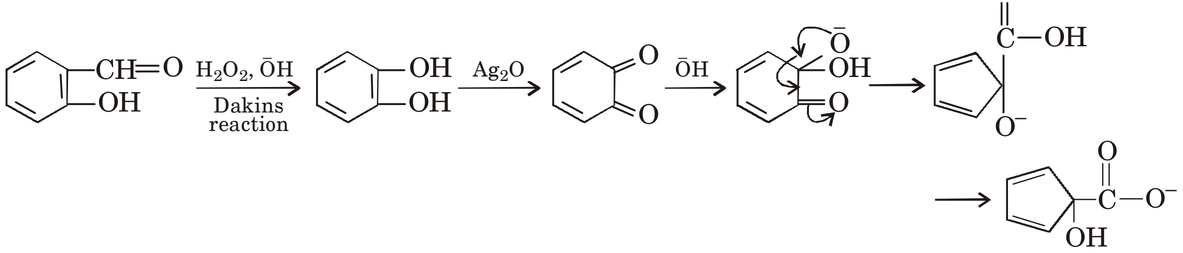


Thus, it is the best possible set to give Cannizzaro reaction effectively.

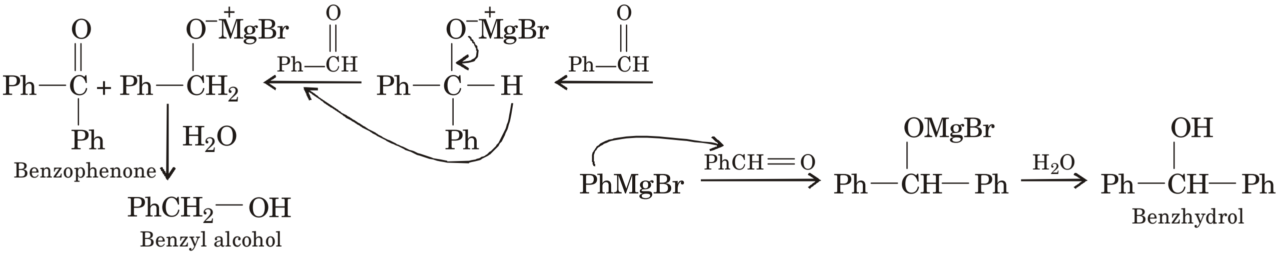
85. (c) :



86. (d) :



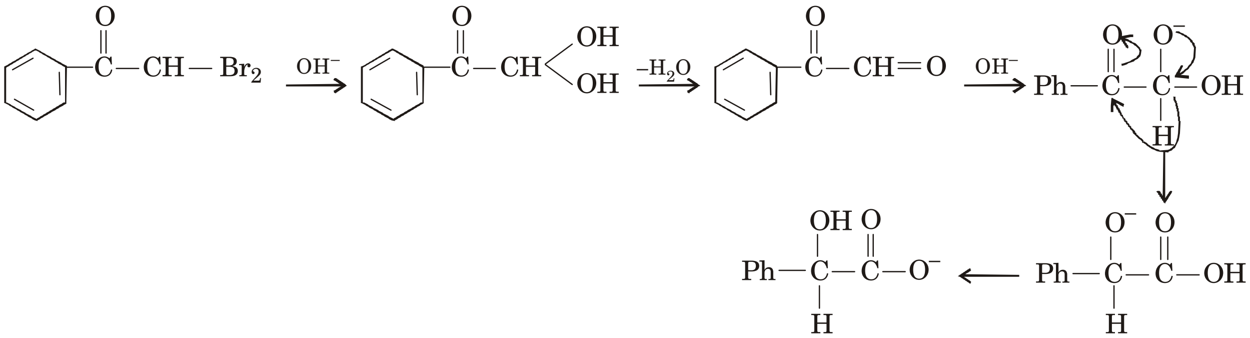
87. (a) :



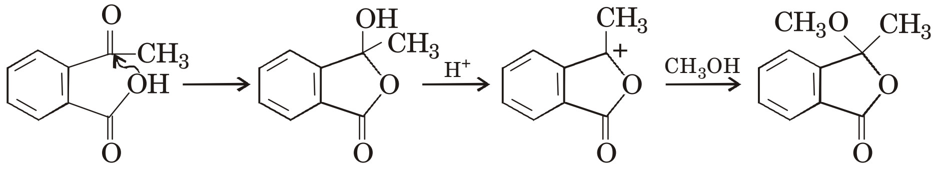
Excess of PhCH = O leads Oppenauer type of oxidation.

88. (d) : The haloform reaction rate is independent of the nature and concentration of halogens. The rate determining step is the enolate formation.

89. (c) :

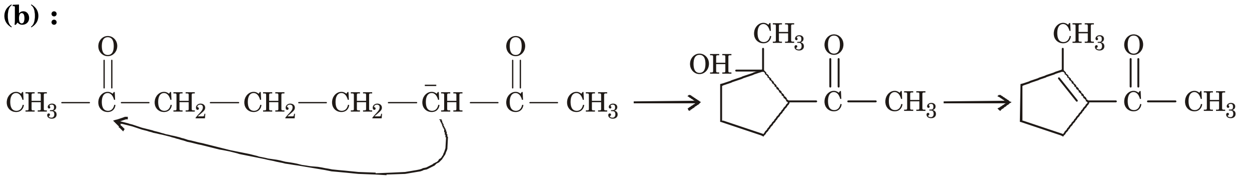


90. (a) :

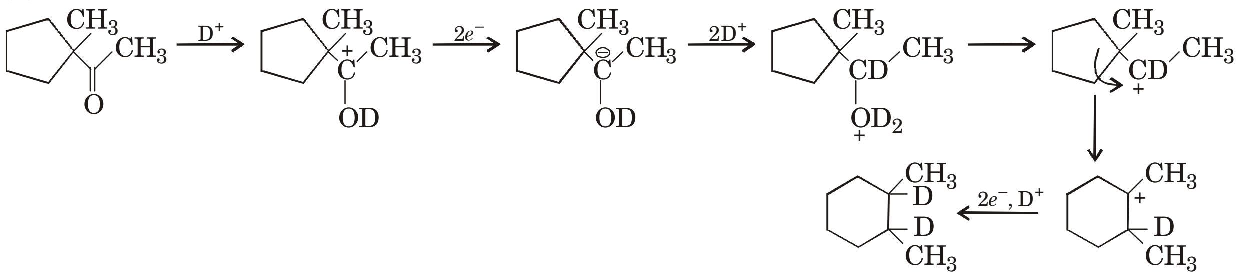


91. (a) : $HCN + \bar{O}H \rightleftharpoons H_2O + CN^-$ produces a stronger nucleophile
$HCN \rightleftharpoons H^+ + CN^-$, addition of H^+ decreases the nucleophilicity.

92. (b) :

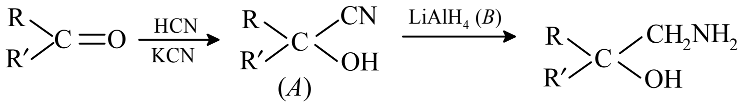


93. (c) :



94. (c) : $RCOCl + [O] \xrightarrow[\text{Pd-BaSO}_4]{H_2} RCHO + HCl$ (Rosenmund's reaction)

95. (d) :

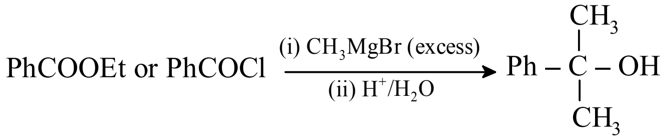


$$\begin{matrix}R\\R'\end{matrix}\!>\!C=O \xrightarrow[KCN]{HCN} \underset{(A)}{\begin{matrix}R\\R'\end{matrix}\!>\!C\!<\!\begin{matrix}CN\\OH\end{matrix}} \xrightarrow{LiAlH_4\ (B)} \begin{matrix}R\\R'\end{matrix}\!>\!C\!<\!\begin{matrix}CH_2NH_2\\OH\end{matrix}$$

96. (b) : $CH_3CHOHCH_2CH_3 \xrightarrow{[O]} CH_3COCH_2CH_3$
Oxidation of a secondary alcohol gives ketone.

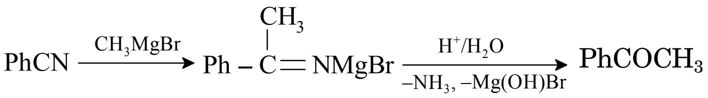
97. (a) : Since formyl chloride is unstable so, formaldehyde cannot be prepared by Rosenmund reduction. Therefore, statement (a) is wrong.

98. (d) : Esters and acid chlorides react with Grignard reagents to form 3° alcohols while amides form alkanes.



$$PhCOOEt \text{ or } PhCOCl \xrightarrow[\text{(ii) } H^+/H_2O]{\text{(i) } CH_3MgBr \text{ (excess)}} Ph-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-OH$$

and $PhCONH_2 + CH_3MgBr \rightarrow PhCONHMgBr + CH_4$
Thus, action of CH_3MgBr on PhCN is the best method.

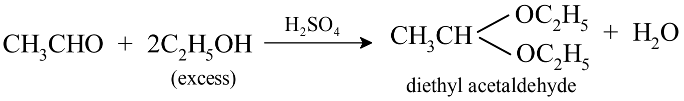


$$PhCN \xrightarrow{CH_3MgBr} Ph-\overset{CH_3}{\overset{|}{C}}=NMgBr \xrightarrow[-NH_3,\,-Mg(OH)Br]{H^+/H_2O} PhCOCH_3$$

99. (b) : Due to smaller size of oxygen than carbon, $C=O$ double bond is shorter (1.23 Å) than $C=C$ double bond (1.34 Å).

100. (b) : Aldehydes reduce Benedict's solution of $CuSO_4$ containing Rochelle salt.

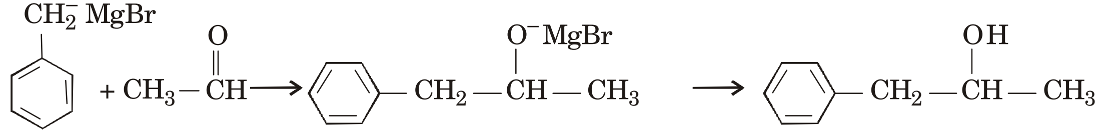
101. (c) :

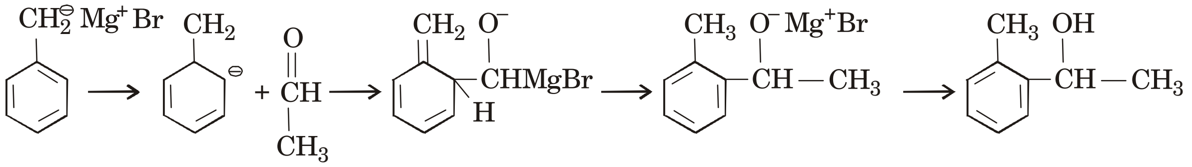


$$CH_3CHO + \underset{\text{(excess)}}{2C_2H_5OH} \xrightarrow{H_2SO_4} \underset{\text{diethyl acetaldehyde}}{CH_3CH\!<\!\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}} + H_2O$$

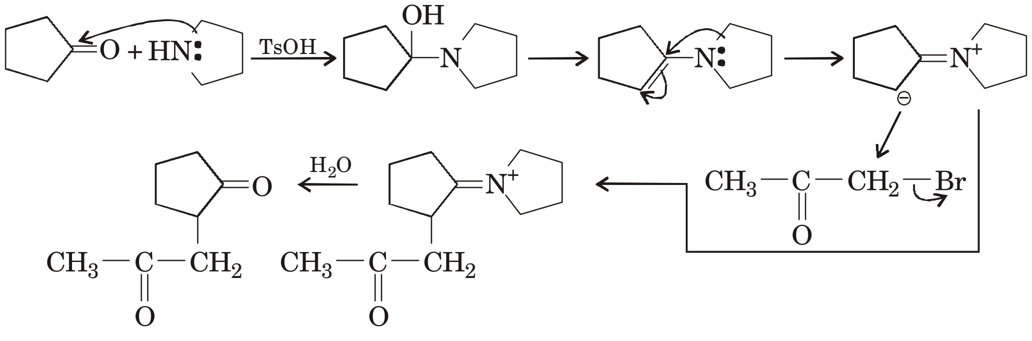
102. (b) : Since the compound forms a yellow solid on adding an alcoholic solution of 2,4-DNP and does not reduce ammoniacal $AgNO_3$ solution, it must be a ketone, *i.e.*, CH_3COCH_3.

103. (c) :



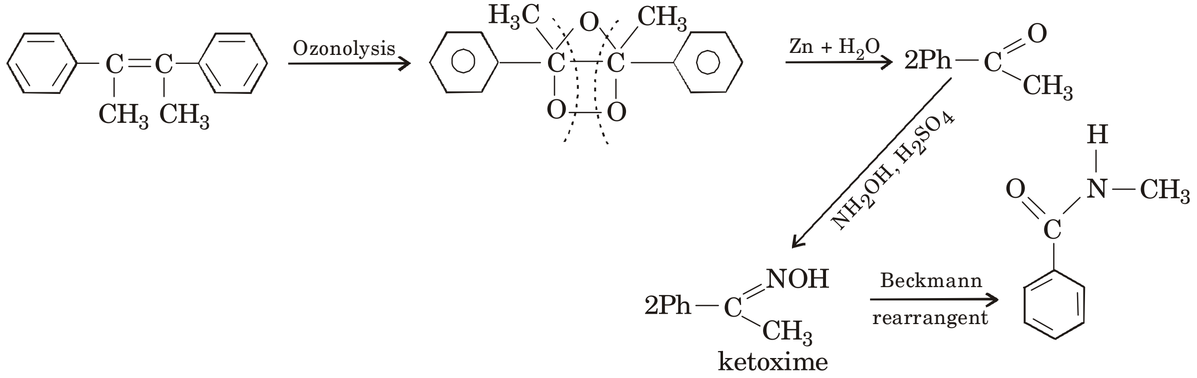


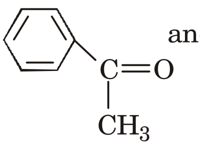
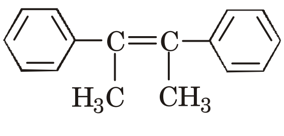
104. (b) :



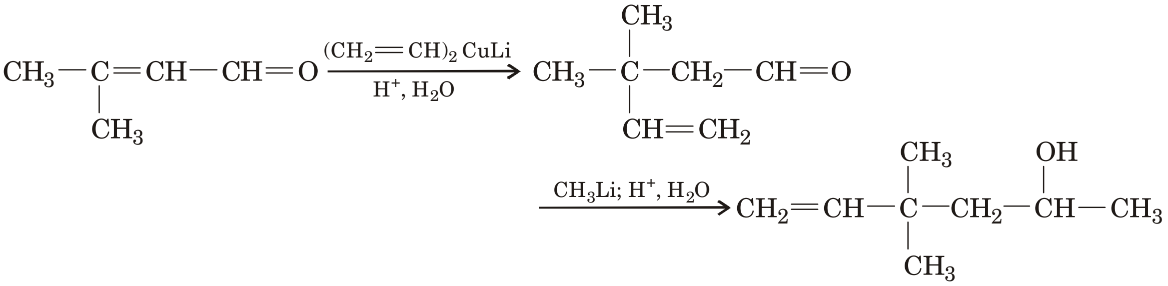
Stork-enamine synthesis

105.(b):



So, *B* is  and *A* is 

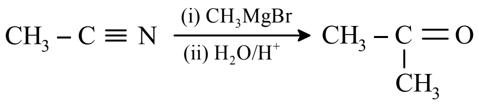
106. (d) :



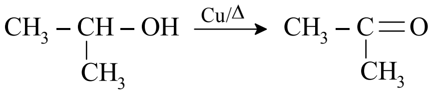
$CH_3-\underset{CH_3}{\underset{|}{C}}=CH-CH=O \xrightarrow[H^+,\ H_2O]{(CH_2=CH)_2CuLi} CH_3-\overset{CH_3}{\overset{|}{\underset{CH=CH_2}{\underset{|}{C}}}}-CH_2-CH=O$

$\xrightarrow{CH_3Li;\ H^+,\ H_2O} CH_2=CH-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2-\overset{OH}{\overset{|}{CH}}-CH_3$

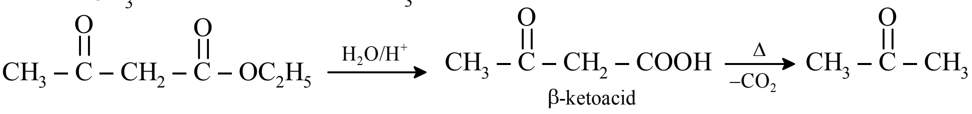
MCQs : More Than One Correct Option

1. **(a, b, c, d) :** (a) 

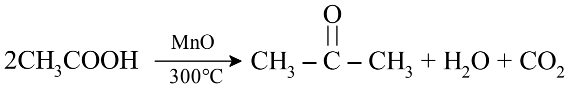
$CH_3-C\equiv N \xrightarrow[\text{(ii) } H_2O/H^+]{\text{(i) } CH_3MgBr} CH_3-\underset{CH_3}{\underset{|}{C}}=O$

(b) 

$CH_3-\underset{CH_3}{\underset{|}{CH}}-OH \xrightarrow{Cu/\Delta} CH_3-\underset{CH_3}{\underset{|}{C}}=O$

(c) 

$CH_3-\overset{O}{\overset{||}{C}}-CH_2-\overset{O}{\overset{||}{C}}-OC_2H_5 \xrightarrow{H_2O/H^+} \underset{\beta\text{-ketoacid}}{CH_3-\overset{O}{\overset{||}{C}}-CH_2-COOH} \xrightarrow[-CO_2]{\Delta} CH_3-\overset{O}{\overset{||}{C}}-CH_3$

(d) 

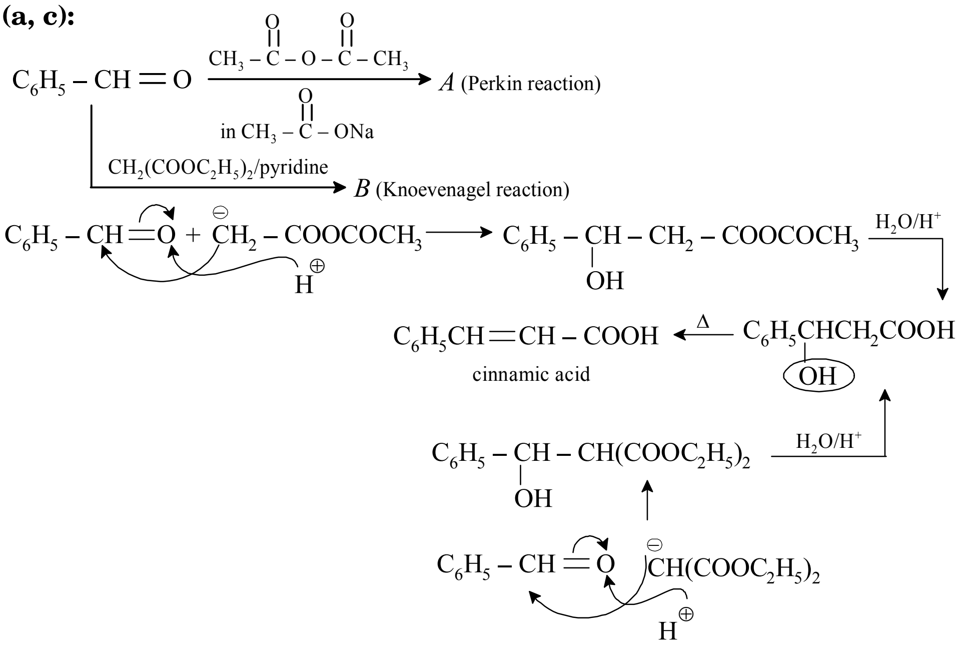
$2CH_3COOH \xrightarrow[300°C]{MnO} CH_3-\overset{O}{\overset{||}{C}}-CH_3 + H_2O + CO_2$

2. **(a, b) :** Enolic form of compound having active methylene group (Presence of electron withdrawing groups towards both side of $\rangle CH_2$) contains intramolecular H-bonding.

3. **(a, b, c) :** Benzaldehyde with carbonyl compound or ester having α-hydrogen atom undergoes Claisen condensation.

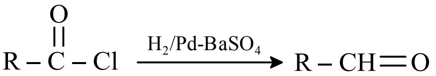
4. **(a, b, c) :** Carbonyl compounds having α-hydrogen atoms undergo aldol condensation.

5. **(a, c):**



6. **(a, c) :** Carbonyl compound not having α-hydrogen atom except 2-methylpropanol undergoes Cannizzaro reaction.

7. **(b, c) :** (a) Alkene on ozonolysis gives a mixture carbonyl compound. It is 2-butene which gives acetaldehyde only.

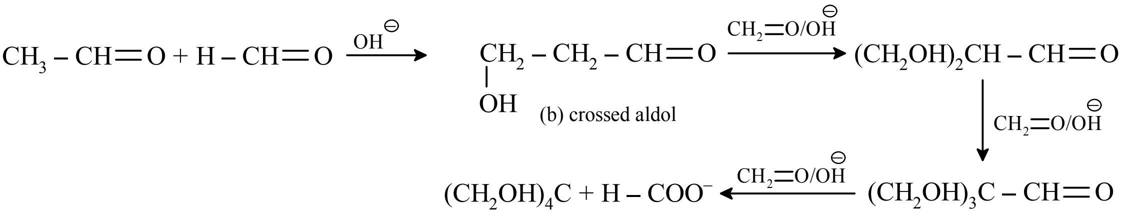
(b)  (Rosenmund's reaction)

$$R-\overset{O}{\overset{||}{C}}-Cl \xrightarrow{H_2/Pd\text{-}BaSO_4} R-CH{=}O$$

(c) $R-C{\equiv}N \xrightarrow{SnCl_2/HCl} R-CH{=}NH{\cdot}HCl \xrightarrow{H_2O} R-CH{=}O$ (Stephen's reaction)

(d) Any alkyne except acetylene on hydration gives ketone not aldehyde.

8. **(b, c, d) :**

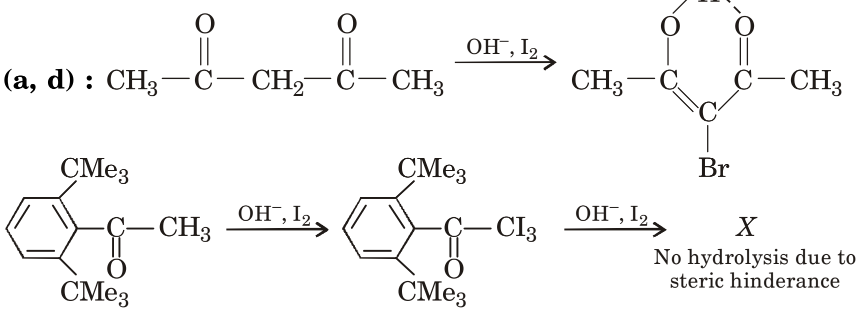


$$CH_3-CH{=}O+H-CH{=}O \xrightarrow{OH^{\ominus}} \underset{OH}{CH_2}-CH_2-CH{=}O \xrightarrow{CH_2{=}O/OH^{\ominus}} (CH_2OH)_2CH-CH{=}O$$

$$\xrightarrow{CH_2{=}O/OH^{\ominus}} (CH_2OH)_3C-CH{=}O \xrightarrow{CH_2{=}O/OH^{\ominus}} (CH_2OH)_4C+H-COO^-$$

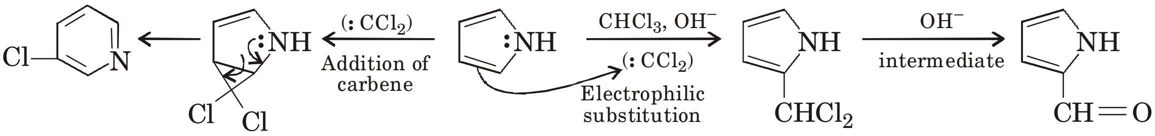
9. **(a, b)** **10.** **(a, b, c, d)**

11. **(a, d) :**



No hydrolysis due to steric hinderance

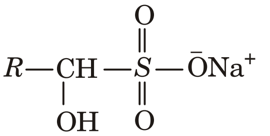
12. **(a, c):**



13. **(c, d) :** H_2 Raney Ni, Δ can reduce complete system; Mg, THF; H_2O is not effective, $NaBH_4$ can reduce effectivly HCHO, OH^- gives cross cannizaro reaction.

14. **(b, c) :** Desulphurisation method may involve displacement of –Br and Wolff-Kishner or Clemmensen or desulphurisation, all lead to ring opening in the case of option (d).

15. **(a, c) :** The adduct is

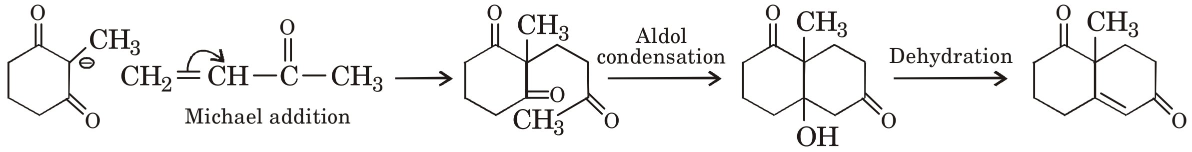


$$R-\underset{\displaystyle OH}{\underset{|}{CH}}-\overset{\displaystyle O}{\overset{\|}{\underset{\underset{\displaystyle O}{\|}}{S}}}-\bar{O}Na^+$$

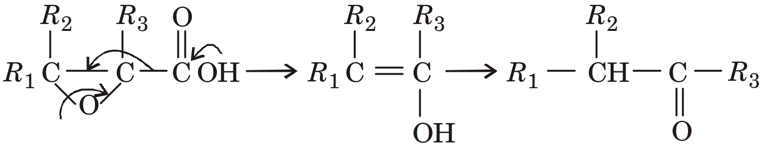
Sulphur is more nucleophilic than oxygen.

- In both H^+ and –OH, carbonyl compounds can be regenerated.

16. **(a, b, c) :**



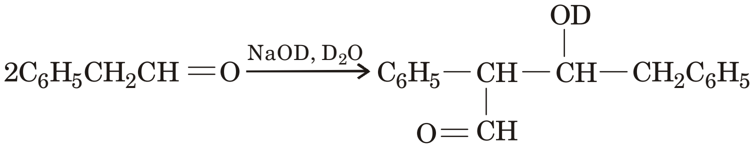
17. **(a, b, c) :**



$$R_1\overset{R_2}{\overset{|}{C}}-\overset{R_3}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}OH \longrightarrow R_1\overset{R_2}{\overset{|}{C}}=\underset{OH}{\underset{|}{\overset{R_3}{\overset{|}{C}}}} \longrightarrow R_1-\overset{R_2}{\overset{|}{CH}}-\underset{O}{\underset{\|}{C}}-R_3$$

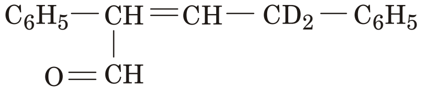
The use of OH^- is not appropriate as it is weaker amide or alkoxides are used.

18. **(c, d) :**



$$2C_6H_5CH_2CH=O \xrightarrow{NaOD,\ D_2O} C_6H_5-\underset{O=CH}{\underset{|}{CH}}-\overset{OD}{\overset{|}{CH}}-CH_2C_6H_5$$

Final product is



$$C_6H_5-\underset{O=CH}{\underset{|}{CH}}=CH-CD_2-C_6H_5$$

Similarly, with $C_6H_5COCH(CH_3)_2$

19. **(c, d) :** In the alkaline medium oxonium ion is not found and dioxyanion is also not possible.

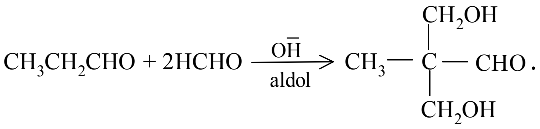
20. **(a, c)**

21. **(a, b) :** Carbonyl compounds having $CH_3-\overset{O}{\overset{\|}{C}}-$ group (except acid or acid derivatives) and $CH_3-\overset{OH}{\overset{|}{CH}}-$ group.

22. **(b, d) :** Carbonyl compounds having α-hydrogen atom undergo keto-enol tautomerism.

23. **(a, b)**

24. **(a, c) :** $\rangle C=O$ group is reduced to $\rangle CH_2$ group.

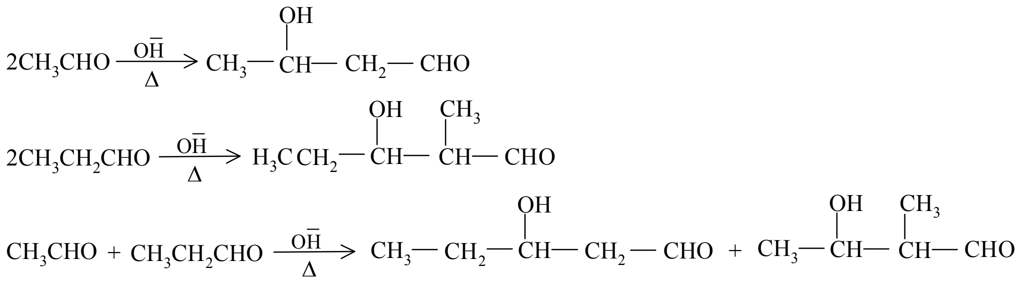
25. (a, b, c, d) : 

$$CH_3CH_2CHO + 2HCHO \xrightarrow[\text{aldol}]{\overline{O}H} CH_3-\underset{CH_2OH}{\overset{CH_2OH}{C}}-CHO$$

. Gives Cannizzaro reaction (no. α-hydrogen), reduces Tollen's reagent, reacts with Na, reacts with Lucas reagent.

26. (b, d) : Aldehyde without α-hydrogen atom undergoes Cannizzaro reaction. $(CH_3)_2CHCHO$ undergoes Cannizzaro reaction even though it has α-H atom due to steric hindrance.

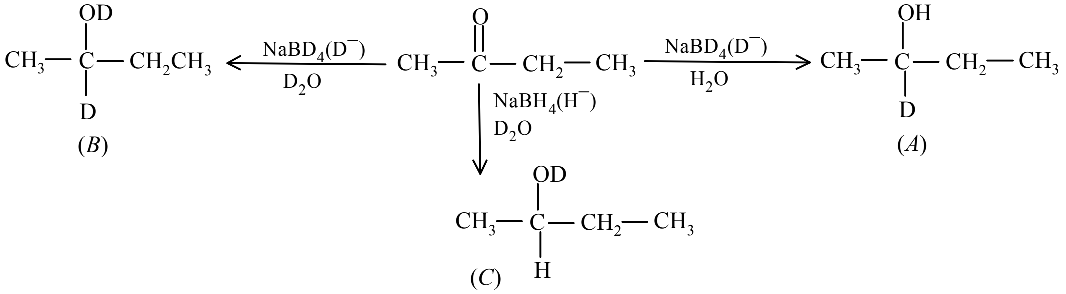
27. (a, b, c, d) : In aldol condensation,



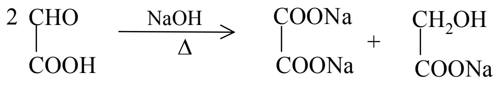
$$2CH_3CHO \xrightarrow[\Delta]{\overline{O}H} CH_3-\overset{OH}{CH}-CH_2-CHO$$

$$2CH_3CH_2CHO \xrightarrow[\Delta]{\overline{O}H} H_3CCH_2-\overset{OH}{CH}-\overset{CH_3}{CH}-CHO$$

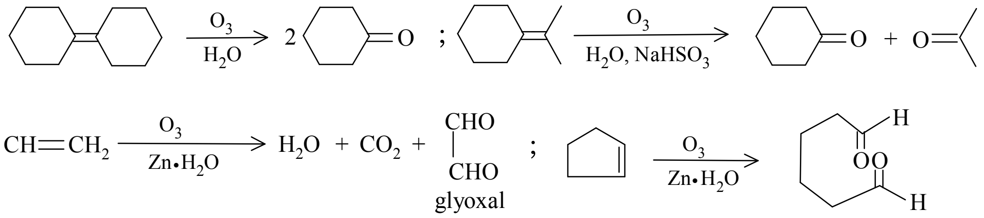
$$CH_3CHO + CH_3CH_2CHO \xrightarrow[\Delta]{\overline{O}H} CH_3-CH_2-\overset{OH}{CH}-CH_2-CHO + CH_3-\overset{OH}{CH}-\overset{CH_3}{CH}-CHO$$

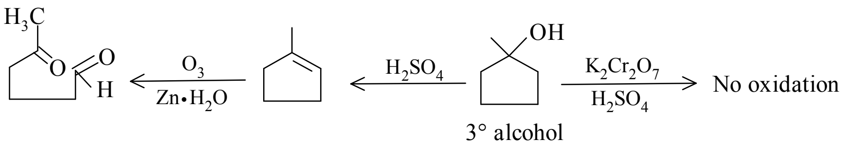
28. (a, b, c) : 

29. (a, c) : This is an example of Cannizzaro reaction.



$$2\begin{matrix}CHO\\|\\COOH\end{matrix} \xrightarrow[\Delta]{NaOH} \begin{matrix}COONa\\|\\COONa\end{matrix} + \begin{matrix}CH_2OH\\|\\COONa\end{matrix}$$

30. (a, c, d) : 

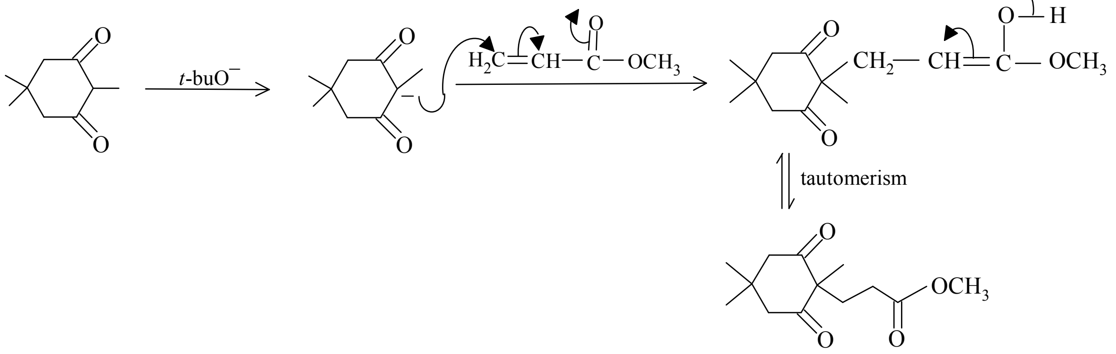
31. (c, d) : 

Allylic and benzylic alcohols are selectively oxidized by MnO_2.

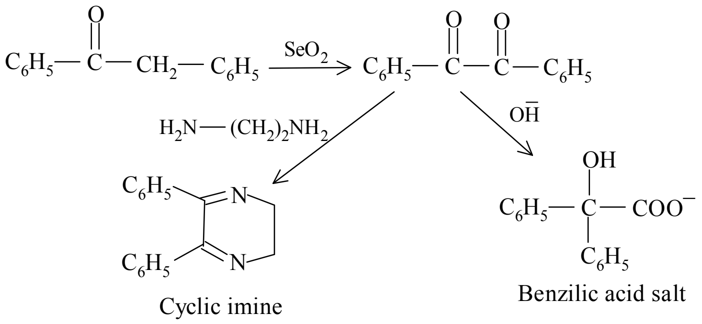
$$CH_3COCH_2CH_2COCH_3 \xrightarrow[\Delta]{SeO_2} CH_3COCH{=}CHCOCH_3$$

Small amount of SeO_2 causes dehydration.

32. (a, b, c) :

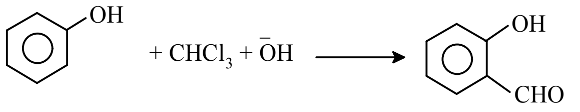


33. (a, b, d) :



34. **(a, c, d) :** Semicarbazide formation from cyclohexanone is kinetically stable but thermodynamically less stable vice versa for semicarbazide formation from benzaldehyde formation as the electronic effect activates the aldehyde group in cyclohexanone but delocalisation of electrons in benzaldehyde deactivates the aldehyde group.

35. **(b, c) :** Benzaldehyde does not reduce Fehling's solution.

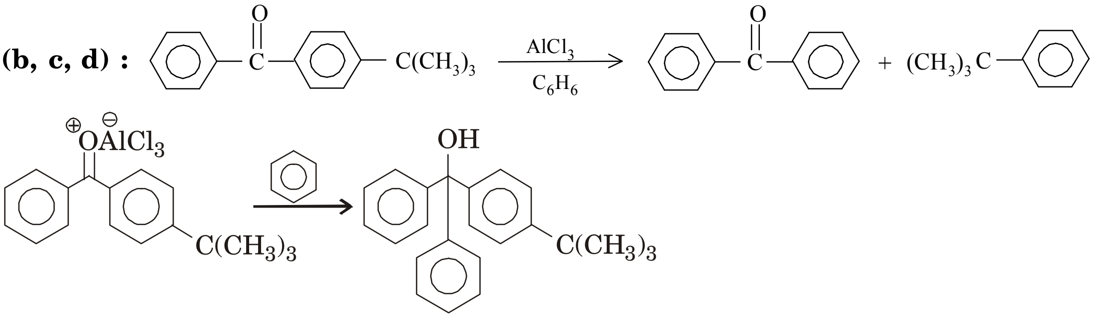


o-salicylaldehyde (*o*-hydroxybenzaldehyde)
is major product but not *p*-hydroxybenzaldehyde

36. **(a, b, c)**

37. **(a, c) :** Aldehydes (except benzaldehyde), α-hydroxy ketones, formic acid give positive Fehling's test.

38. **(b, c, d) :**



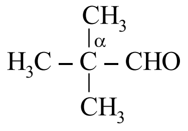
Assertion & Reason

1. **(d) :** Because of –I effect of chlorine atoms trichloroacetaldehyde undergoes nucleophilic addition more readily than acetaldehyde.

2. **(c) :** Na alone cannot reduce cyclic ethers.

3. **(b) :** Formaldehyde condenses with phenol to give a synthetic plastic, bakelite. The condensation occurs in presence of dilute NaOH or ammonia at 80-90°C.

4. **(b) :** Aldehydes which do not contain α-hydrogens undergo Cannizzaro reaction.



$$H_3C-\overset{\overset{CH_3}{|\alpha}}{\underset{\underset{CH_3}{|}}{C}}-CHO$$

2,2-dimethylpropanal (no α-H atom)

5. **(d) :** $LiAlH_4$ reduces only the $> C = O$ group leaving the double bond intact, *i.e.*, reduction gives 3-phenylprop-2-en-1-ol and not 3-phenylpropan-1-ol.

6. **(c) :** Aldehydes which do not contain α-hydrogen, do not undergo aldol condensation.

7. **(a) :** Since $C = O$ bonds utilise sp^2-hybrid orbitals, they lie in the same plane and are 120° apart. Hence, carbonyl group is planar.

8. **(c) :** The anions left after the removal of α-hydrogen are stabilized by resonance effect.

9. **(b) :** SO_3^{--} is a large ion. Its addition is possible only under the condition that $>C = O$ grouping is not sterically hindered as is the case for RCHO, $RCOCH_3$ and cyclic ketones.

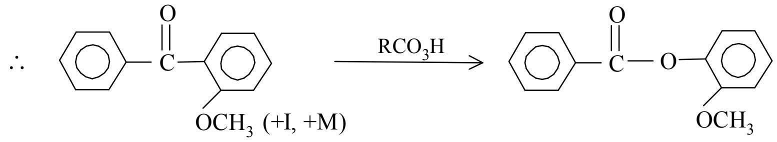
10. **(d) :** Aldehydes can be prepared by the action of Grignard reagents on ethyl ortho formate and not on ethyl formate. The reason being that during the reaction of Grignard reagents with ethyl formate, aldehydes are first formed which react further with Grignard reagent to form 3° alcohols.

11. **(d) :** HCHO and HCOOH respond positively to the Tollen's test.

12. **(a) :** $CH_3COCH_2COCH_3 \xrightarrow[\bar{O}H]{I_2} CH_3COCI_2COCH_3$

13. **(d) :** $H_2C{=}CH-CHO \xrightarrow{\bar{O}H} HCHO + CH_3CHO$

14. **(c) :** Predominantly the electron rich group migrates on to electron deficient oxygen in Baeyer Villiger oxidation.

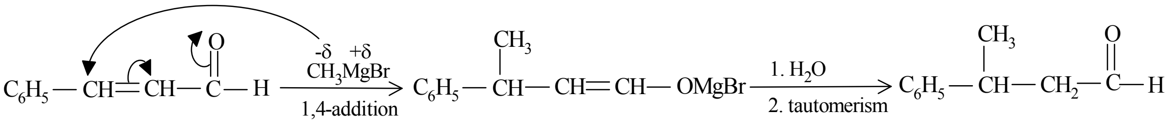


15. **(a) :** $(CH_3)_2CHCHO \xrightarrow{\bar{O}H} (CH_3)_2CHCH_2OH + (CH_3)_2CHCOO^-$

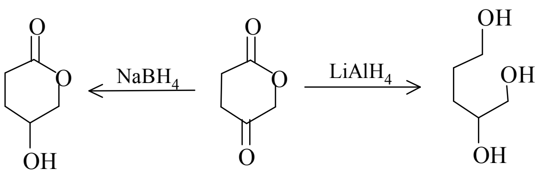
16. **(a)**

17. **(b) :** SO_3^{2-} is a bulky nucleophile, hence, cannot attack on sterically hindered ketones.

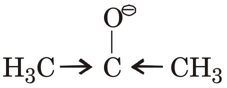
18. **(d) :**



19. **(b) :**



20. **(c) :** $-CH_3$ is electron donating species so, it will destabilize the +ve charge created on carbonyl carbon, so, formaldehyde is a better choice for nucleophilic attack.



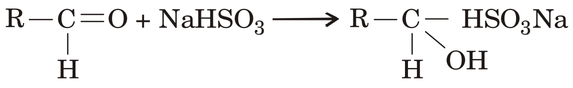
$$H_3C \rightarrow \overset{\overset{O^{\ominus}}{|}}{C} \leftarrow CH_3$$

Destabilized cation

There is no correlation of dipole moment.

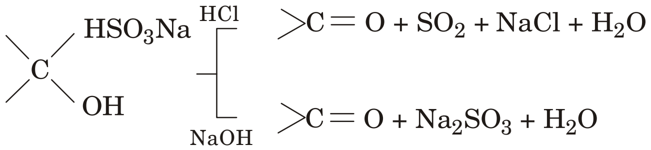
21. **(a)**

22. **(b) :**



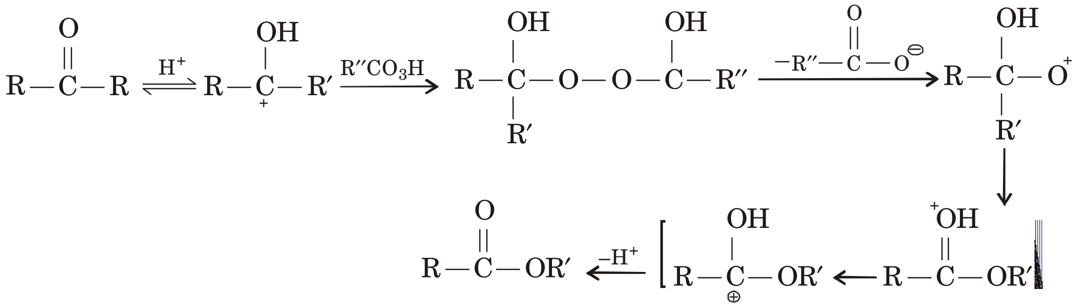
$$R-\underset{H}{\underset{|}{C}}=O + NaHSO_3 \longrightarrow R-\underset{H}{\underset{|}{C}}\begin{smallmatrix}-HSO_3Na\\ \diagdown OH\end{smallmatrix}$$

(Acetaldehyde bisulphite)

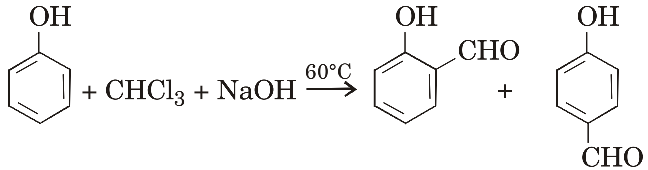


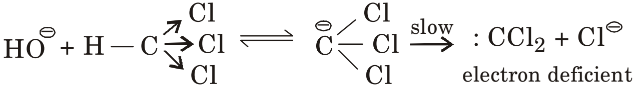
This property is used in separation and purification of aldehyde.

23. **(c) :** This is Baeyer villiger rearrangement. There is no production of nascent oxygen
Mechanism :



24. **(d) :** Reimer-Tiemann reaction – Formylation of phenols with chloroform in alkaline solution.





25. **(a) :** This is Etard reaction.

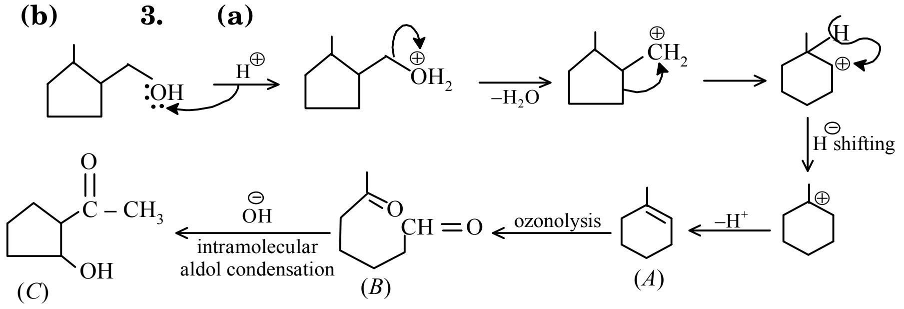
26. **(c) :** The haloform reaction is independent of the nature and concentration of halogens. The rate determining step is enolate formation.

27. **(a)**

Passage Comprehension

PASSAGE 1 :

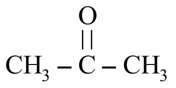
1. **(c)** **2.** **(b)** **3.** **(a)**

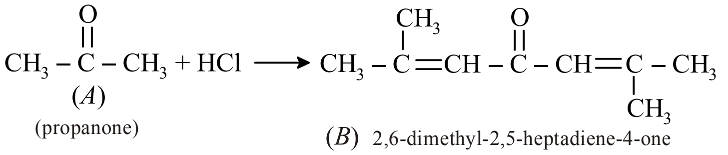


PASSAGE 2 :

It is Cannizzaro reaction.

1. **(d)**

2. **(c) :** C_3H_6O undergoes iodoform test, *i.e.* it is  $CH_3-\overset{\overset{\displaystyle O}{||}}{C}-CH_3$

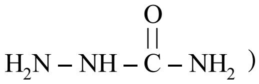


$CH_3-\overset{\overset{\displaystyle O}{||}}{C}-CH_3 + HCl \longrightarrow CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-\overset{\overset{\displaystyle O}{||}}{C}-CH=\underset{\underset{\displaystyle CH_3}{|}}{C}-CH_3$

(*A*) (propanone)

(*B*) 2,6-dimethyl-2,5-heptadiene-4-one

3. **(a) :** C_3H_8O is an alcohol which on oxidation gives a compound C_3H_6O that forms Ag-mirror with ammoniacal silver nitrate solution means C_3H_6O will be propanal.

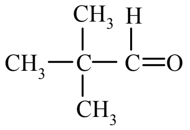
Semicarbazide ( $H_2N-NH-\overset{\overset{\displaystyle O}{||}}{C}-NH_2$) forms semicarbazone with carbonyl compound. Thus, corresponding carbazone is (a).

PASSAGE 3 :

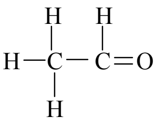
1. **(b)** 2. **(d)** 3. **(a)**

PASSAGE 4 :

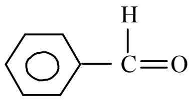
1. **(b)**



Trimethylacetaldehyde (*A*)



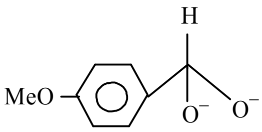
Acetaldehyde (*B*)



Benzaldehyde (*C*)

Cannizzaro reaction is given by only those aldehydes which do not have α-hydrogen atoms. So, acetaldehyde (*B*) will not give Cannizzaro reaction.

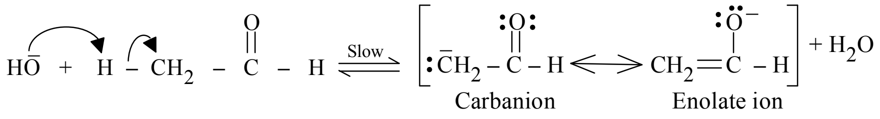
2. **(c) :**



Due to the presence of electron donating methoxy group (–OMe) at the *p*-position, the removal of hydride ion (: H^-) is facilitated.

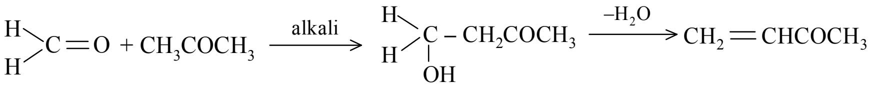
PASSAGE 5 :

1. **(b) :**



The carbanion (or the enolate ion) is a strong nucleophile.

2. **(a) :**

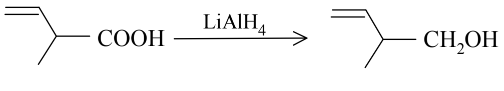


$$H_2C=O + CH_3COCH_3 \xrightarrow{alkali} H_2C(OH)-CH_2COCH_3 \xrightarrow{-H_2O} CH_2=CHCOCH_3$$

PASSAGE 6 :

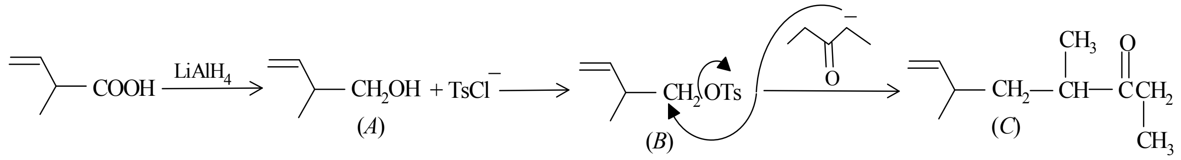
1. **(d)**

2. **(d) :**



3. **(a) :** – OTs is a good leaving group *i.e.* better than – OH group.

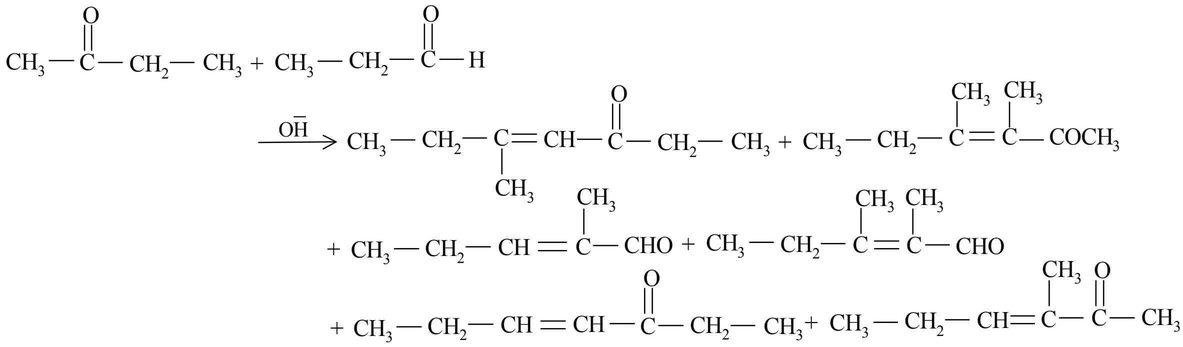
4. **(b) :**



5. **(a)**

PASSAGE 7 :

1. **(a)**
2. **(b) :** HCHO is highly reactive towards nucleophilic additions.
3. **(c) :**

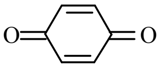


$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3 + CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H$$

$$\xrightarrow{\bar{O}H} CH_3-CH_2-\underset{CH_3}{\underset{|}{C}}=CH-\overset{O}{\overset{\|}{C}}-CH_2-CH_3 + CH_3-CH_2-\overset{CH_3}{\overset{|}{C}}=\overset{CH_3}{\overset{|}{C}}-COCH_3$$

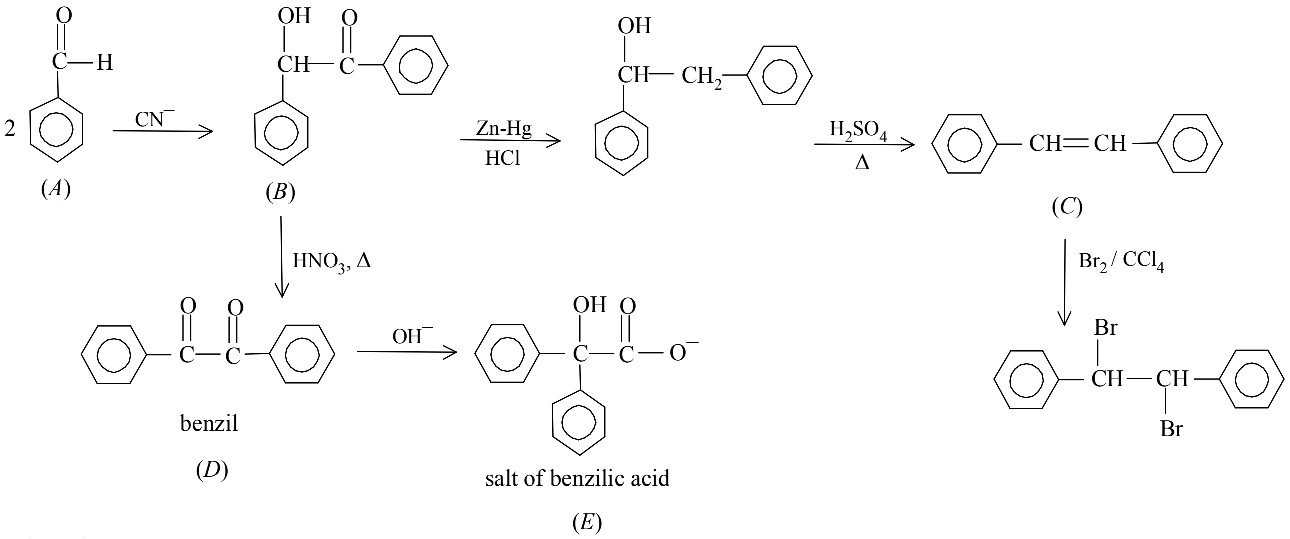
$$+ CH_3-CH_2-CH=\overset{CH_3}{\overset{|}{C}}-CHO + CH_3-CH_2-\overset{CH_3}{\overset{|}{C}}=\overset{CH_3}{\overset{|}{C}}-CHO$$

$$+ CH_3-CH_2-CH=CH-\overset{O}{\overset{\|}{C}}-CH_2-CH_3 + CH_3-CH_2-CH=\overset{CH_3}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$$

4. **(b) :**  . No enolization, occurs because there is no active α-hydrogen.

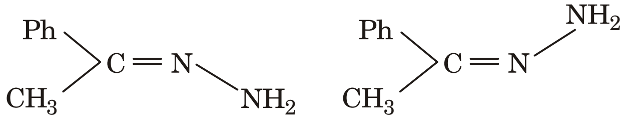
PASSAGE 8 :

1. **(b)** 2. **(d)** 3. **(a)** 4. **(c)**

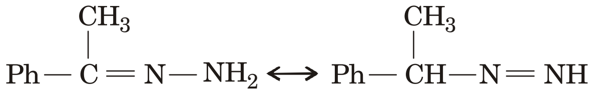


PASSAGE 9 :

1. **(c)**
2. **(c) :** Increase in H^+ promotes dehydration step. It proceeds most effectively at pH ≈ 5.
When pH is decreased most of the reagent NH_2Z gets converted into $^+NH_2$-Z and the first step slows down, that becomes rate determining step.
3. **(d) :** The product molecule is



geometrical isomers

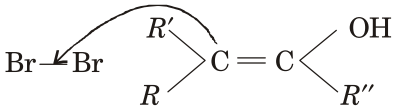


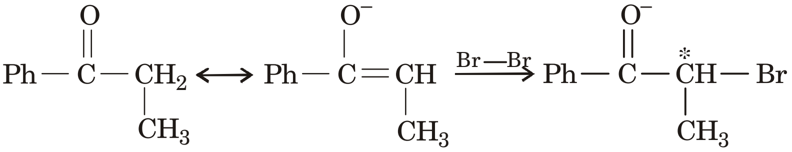
$$Ph-\overset{CH_3}{\overset{|}{C}}=N-NH_2 \longleftrightarrow Ph-\overset{CH_3}{\overset{|}{C}H}-N=NH$$

Tautomers
(functional isomers)

PASSAGE 10 :

1. **(c) :** H^+ is displaced by Br^+. Electrophilic substitution.

2. **(d) :**  The enol form picks up Br^+, and that can be done equally well from the top as well as bottom face, which leads to the formation of enantiomers.

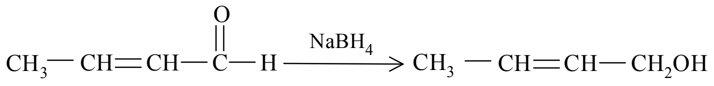
3. **(b) :** 

$$Ph-\overset{O}{\overset{||}{C}}-\underset{CH_3}{\underset{|}{CH_2}} \longleftrightarrow Ph-\overset{O^-}{\overset{|}{C}}=\underset{CH_3}{\underset{|}{CH}} \xrightarrow{Br-Br} Ph-\overset{O^-}{\overset{||}{C}}-\underset{CH_3}{\underset{|}{\overset{*}{C}H}}-Br$$

Due to monobromination (due to electronegativity of Br, acidity of α–H increases, so instead of reactant the instant monobrominated product undergoes further bromination.

Matrix Match Type

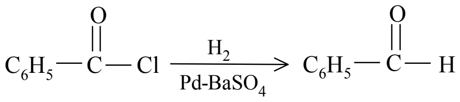
1. **A → S; B → R; C → P; D → Q :**

(A) 

$$CH_3-CH=CH-\overset{O}{\overset{||}{C}}-H \xrightarrow{NaBH_4} CH_3-CH=CH-CH_2OH$$

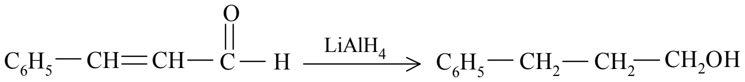
($NaBH_4$ usually reduces polar multiple bonds)

(B) $C_6H_5-C\equiv N \xrightarrow[HCl]{SnCl_2} C_6H_5-CH=NH \xrightarrow[H^+]{H_2O} C_6H_5-CHO + NH_3$ (Stephen's reduction)

(C) 

$$C_6H_5-\overset{O}{\overset{||}{C}}-Cl \xrightarrow[Pd\text{-}BaSO_4]{H_2} C_6H_5-\overset{O}{\overset{||}{C}}-H$$

(Rosenmund's reduction)

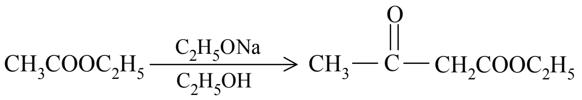
(D) 

$$C_6H_5-CH=CH-\overset{O}{\overset{||}{C}}-H \xrightarrow{LiAlH_4} C_6H_5-CH_2-CH_2-CH_2OH$$

(exception)

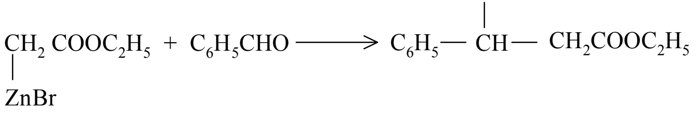
2. **A → R; B → P; C → S; D → Q :**

(A) C_6H_5CHO, an aromatic aldehyde undergoes Perkin's condensation.
(B) CH_3COCH_3 has α-H atom, hence undergoes aldol condensation.

(C) 

$$CH_3COOC_2H_5 \xrightarrow[C_2H_5OH]{C_2H_5ONa} CH_3-\overset{O}{\overset{||}{C}}-CH_2COOC_2H_5$$

(Claisen ester condensation)

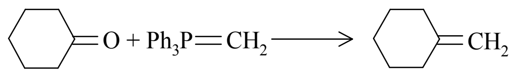
(D) 

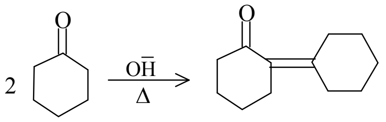
$$\underset{ZnBr}{\underset{|}{CH_2}}COOC_2H_5 + C_6H_5CHO \longrightarrow C_6H_5-\overset{OH}{\overset{|}{C}H}-CH_2COOC_2H_5$$

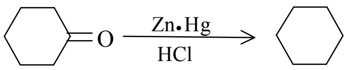
(Reformatsky reaction)

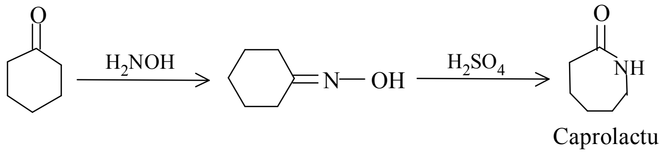
3. **A → Q; B → P; C → S; D → R**

4. **A → S; B → P; C → R; D → Q :**

(A)  $+ Ph_3P=O$ (Wittig reaction)

(B) 
(Aldol condensation)

(C) 
(Clemmensen's reaction)

(D) 

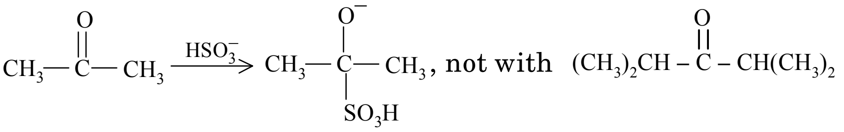
(Beckmann's rearrangement)

5. **A → R; B → P; C → S; D → Q :**

(A) C_6H_5CHO, HCHO can be distinguished by Fehling's reagent. Benzaldehyde cannot reduce Fehling's solution.

(B) $HCOOH + NaHCO_3 \longrightarrow HCOONa + CO_2 + H_2O$, not HCHO.

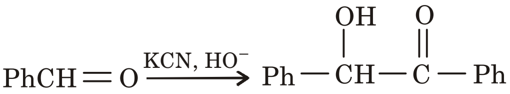
(C) $CH_3CHO + I_2 \xrightarrow{\bar{O}H} HCOO^- + \underset{\text{yellow}}{CHI_3\downarrow}$, not HCHO.

(D) 
$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{HSO_3^-} CH_3-\underset{SO_3H}{\overset{O^-}{C}}-CH_3$, not with $(CH_3)_2CH-\overset{O}{\overset{\|}{C}}-CH(CH_3)_2$ due to steric hindrance.

6. **A → Q, R, S; B → P, S; C → Q, S; D → S;**

Claisen-Schmidt reaction is basically a cross-aldol condensation where one carbonyl compound doesn't contain the enolisable hydrogen.

Benzoin condensation is specific for aromatic aldehydes.

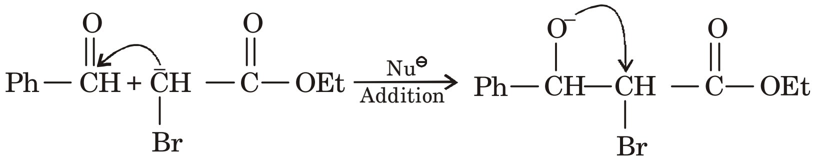

$$PhCH{=}O \xrightarrow{KCN,\ HO^-} Ph-\overset{OH}{\overset{|}{CH}}-\overset{O}{\overset{\|}{C}}-Ph$$

7. **A → R, S; B → P, Q, R, S; C → Q, R; D → P, Q, R, S;**

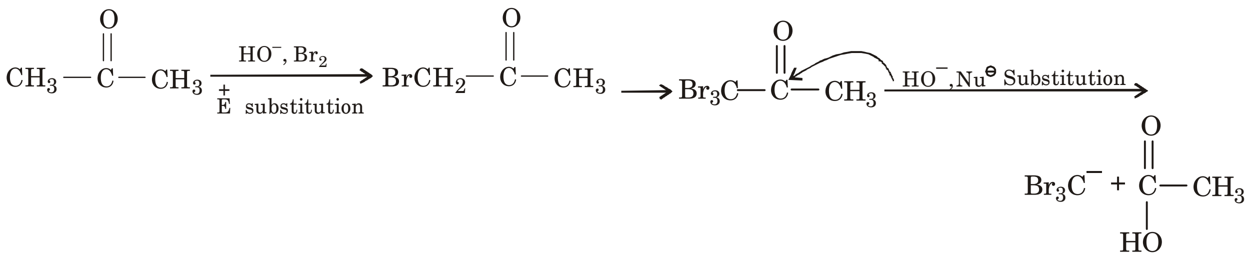
Benzaldehyde does not reduce Fehling solution, α-hydroxy ketone gives positive test with weak oxidising agent.

8. **A → Q, S; B → P, Q; C → S; D → R;**

Darzens glycidic ester synthesis :


$$Ph-\overset{O}{\overset{\|}{C}}H+\underset{Br}{\underset{|}{\bar{C}H}}-\overset{O}{\overset{\|}{C}}-OEt \xrightarrow[\text{Addition}]{Nu^\ominus} Ph-\overset{O^-}{\overset{|}{CH}}-\underset{Br}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-OEt$$

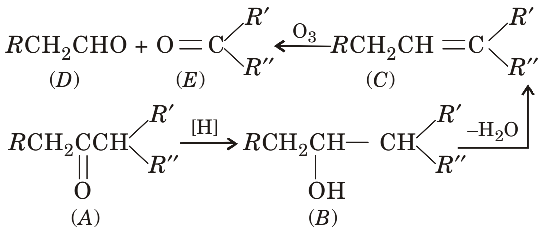
Haloform reaction


$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[\overset{+}{E}\text{ substitution}]{HO^-,\ Br_2} BrCH_2-\overset{O}{\overset{\|}{C}}-CH_3 \longrightarrow Br_3C-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{HO^-,Nu^\ominus\text{ Substitution}} Br_3C^- + \underset{HO}{\underset{|}{\overset{O}{\overset{\|}{C}}}}-CH_3$$

Integer Answer Type

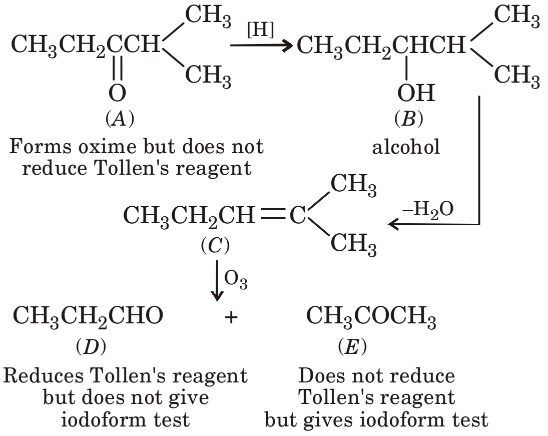
1. **(2)** The compound A must be a ketone as it forms an oxime but does not reduce Tollen's reagent. The compound D must be an aldehyde. Its structure does not include the fragment $\underset{\underset{O}{\|}}{CH_3C}—$ as it does not answer iodoform test.

   Let the compounds D and E be RCH_2CHO and $R'COR''$, respectively, where R, R' and R'' are all alkyl groups. From these, we get



   Since, the molecular formula of A is $C_6H_{12}O$, it follows that $R = R' = R'' = CH_3$.

   Hence, the structures of molecules from (A) to (E) and the reactions are as follows.



   Compound C is 2-methyl-2-pentene.

   ∴ Position of double bond is 2.

2. **(7)** Let the mixture contains acetaldehyde and ethanol of mass a and b g respectively.

   ∴ $a + b = 5.26$ g

   The mixture reacts with Fehling's solution to give a red ppt., a characteristic reaction for aldehydes, *i.e.*,

$$CH_3CHO + 2CuO \longrightarrow CH_3COOH + \underset{\text{red ppt.}}{Cu_2O}$$

   ∵ 143 g Cu_2O is formed from 44 g CH_3CHO

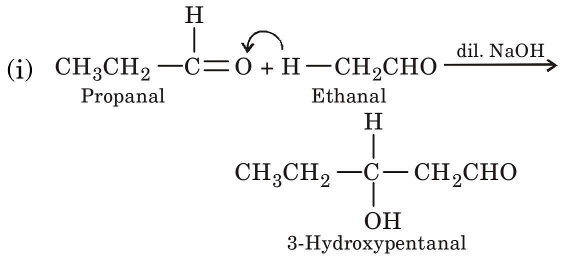
   ∴ 1.2 g Cu_2O is formed from

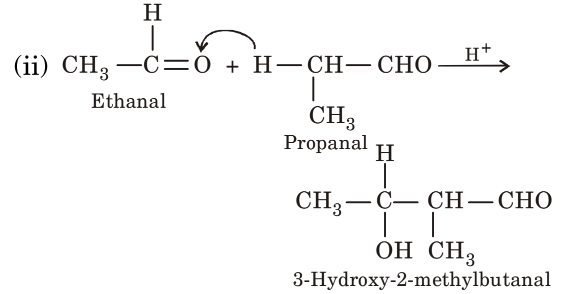
$$\frac{44 \times 1.2}{143} \text{ g } CH_3CHO = 0.369 \text{ g } CH_3CHO$$

   ∴ Wt. of aldehyde = 0.369 g

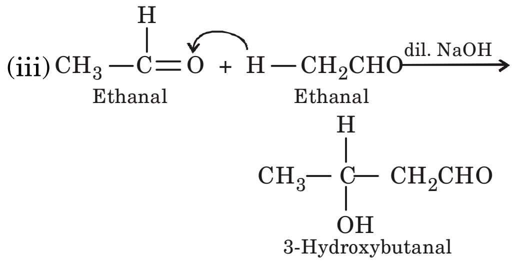
$$\text{Percentage of aldehyde} = \frac{0.369}{5.26} \times 100 \approx 7\%.$$

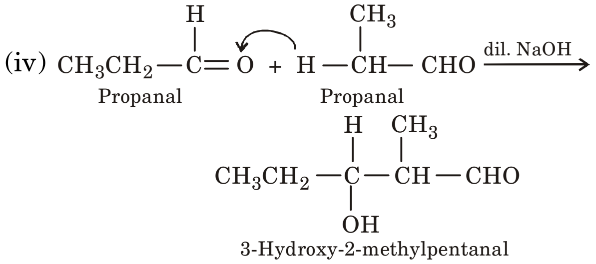
3. **(4)** The reaction is crossed aldol condensation.



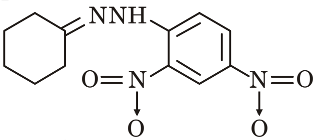


   Each of the reactants can themselves undergo aldol condensation giving the respective products.





4. **(8)** The product is



   ∴ $C_{12}H_{14}N_4O_4$

   The general formula to calculate DBE

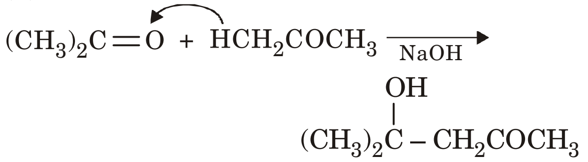
   $C_aH_bN_cO_d$, then DBE $= a + 1 - \frac{(b-c)}{2}$

   ∴ $a = 12$, $b = 14$, $c = 4$

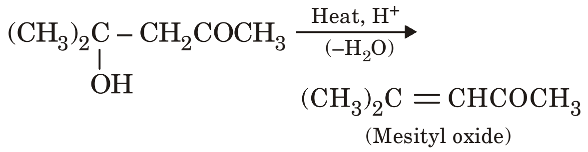
$$\Rightarrow \text{DBE} = 12 + 1 - \frac{(14-4)}{2} = 13 - \frac{10}{2} = 13 - 5$$

   DBE = 8.

5. **(2) Ist Aldol condensation**



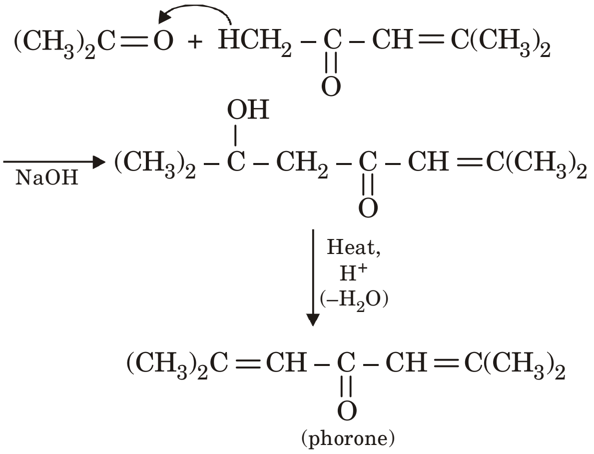
$$(CH_3)_2C{=}O + HCH_2COCH_3 \xrightarrow[\text{NaOH}]{} (CH_3)_2\overset{\overset{OH}{|}}{C}-CH_2COCH_3$$



$$(CH_3)_2\underset{\underset{OH}{|}}{C}-CH_2COCH_3 \xrightarrow[(-H_2O)]{Heat,\ H^+} (CH_3)_2C=CHCOCH_3$$

(Mesityl oxide)

2nd Aldol condensation



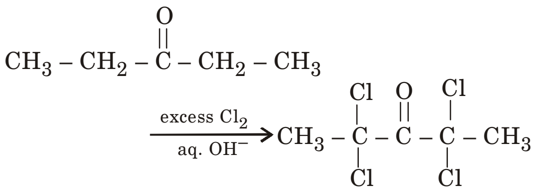
$$(CH_3)_2C=O + HCH_2-\underset{\underset{O}{||}}{C}-CH=C(CH_3)_2 \xrightarrow[NaOH]{} (CH_3)_2-\overset{\overset{OH}{|}}{C}-CH_2-\underset{\underset{O}{||}}{C}-CH=C(CH_3)_2$$

$$\xrightarrow[(-H_2O)]{Heat,\ H^+} (CH_3)_2C=CH-\underset{\underset{O}{||}}{C}-CH=C(CH_3)_2$$

(phorone)

∴ Aldol condensation takes place twice to obtain the desired product.

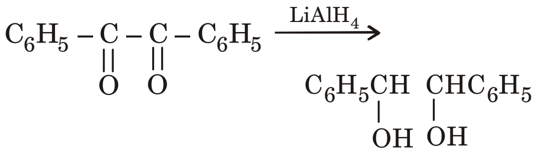
6. **(4)**



$$CH_3-CH_2-\overset{\overset{O}{||}}{C}-CH_2-CH_3 \xrightarrow[aq.\ OH^-]{excess\ Cl_2} CH_3-\underset{Cl}{\overset{Cl}{C}}-\overset{\overset{O}{||}}{C}-\underset{Cl}{\overset{Cl}{C}}-CH_3$$

∴ 4 Cl atoms get inserted.

7. **(3)**



$$C_6H_5-\underset{\underset{O}{||}}{C}-\underset{\underset{O}{||}}{C}-C_6H_5 \xrightarrow{LiAlH_4} C_6H_5\underset{\underset{OH}{|}}{CH}\ \underset{\underset{OH}{|}}{CH}C_6H_5$$

The molecule after reduction possesses two asymmetric carbons with symmetry in molecule.

Thus, $a = 2^{n-1} = 2^{2-1} = 2$

$m = 2^{n/2-1} = 2^0 = 1$

∴ No. of stereoisomers = 2 + 1 = 3.

8. **(2)** Empirical formula can be calculated as

Element	Percentage	Relative no. of atoms	Simplest ratio
C	69.77	5.81	5
H	11.63	11.63	10
O	18.60	1.16	1

∴ Empirical formula of compound is $C_5H_{10}O$ and empirical formula wt. = 86

Also molecular weight = 86

∴ Molecular formula of the compound is $C_5H_{10}O$.

Compound forms bisulphite addition product and thus, has a carbonyl group, so, it may be an aldehyde or a ketone.

It does not reduce Fehling's solution and thus, it is not aldehyde but it is a ketone.

It gives positive iodoform test and thus, it has $CH_3-\underset{\underset{O}{||}}{C}-$ unit.

The above facts reveal that the compound is

$CH_3CH_2CH_2COCH_3$ or $(CH_3)_2CHCOCH_3$

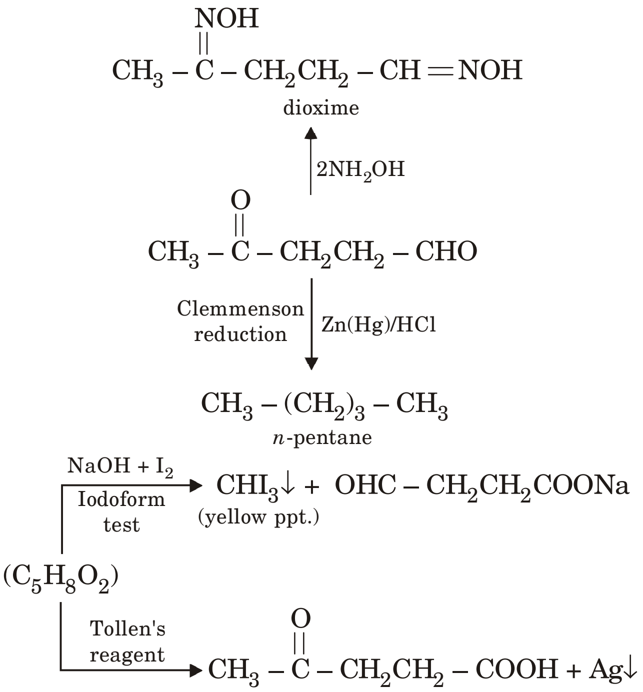
pentan-2-one 3-methylbutan-2-one

9. **(1)** (i) The compound gives positive iodoform test indicating the presence of $CH_3-\overset{\overset{O}{||}}{C}-$ group.

(ii) It also gives positive Tollen's test indicating the presence of –CHO group.

(iii)The presence of one keto and one aldehydic group in the compound is indicated by its reaction with NH_2OH forming a dioxime.

(iv)Both keto as well as aldehydic group can be reduced to hydrocarbon (alkane) through Clemmenson reduction; since, the given compound gives *n*-pentane on Clemmenson reduction, so, its structure should be written as



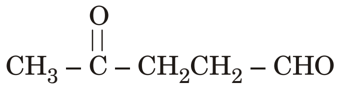
$$CH_3-\overset{\overset{O}{||}}{C}-CH_2CH_2-CHO \xrightarrow{2NH_2OH} CH_3-\overset{\overset{NOH}{||}}{C}-CH_2CH_2-CH=NOH\ \text{(dioxime)}$$

$$CH_3-\overset{\overset{O}{||}}{C}-CH_2CH_2-CHO \xrightarrow[\text{Clemmenson reduction}]{Zn(Hg)/HCl} CH_3-(CH_2)_3-CH_3\ (n\text{-pentane})$$

$$(C_5H_8O_2) \xrightarrow[\text{Iodoform test}]{NaOH + I_2} CHI_3\downarrow\ \text{(yellow ppt.)} + OHC-CH_2CH_2COONa$$

$$(C_5H_8O_2) \xrightarrow{\text{Tollen's reagent}} CH_3-\overset{\overset{O}{||}}{C}-CH_2CH_2-COOH + Ag\downarrow$$

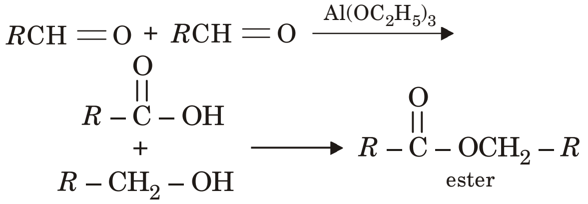
Hence, the structure of the given compound is



$$CH_3-\overset{\overset{O}{||}}{C}-CH_2CH_2-CHO$$

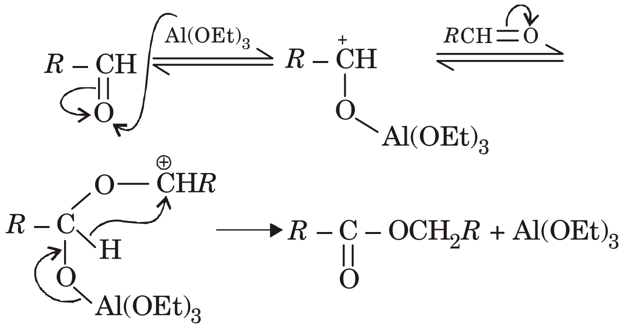
∴ The number of ketone groups is 1.

10. **(2)** Tischenko reaction can be shown as follows.



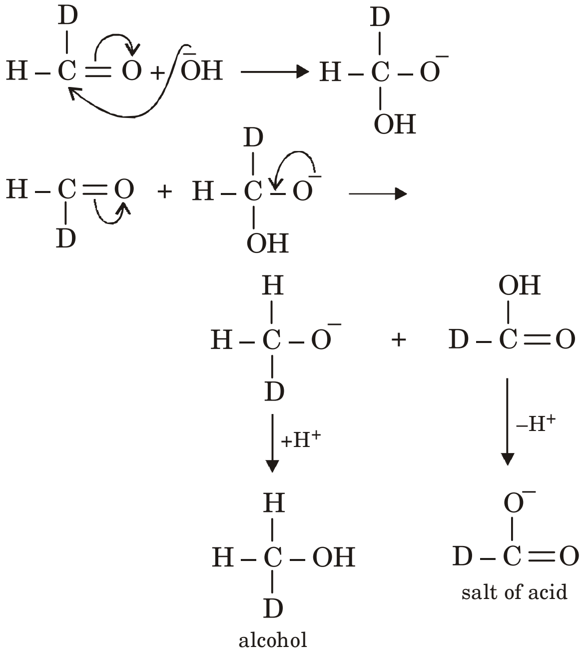
$$RCH=O + RCH=O \xrightarrow{Al(OC_2H_5)_3} \begin{matrix} R-\overset{\overset{O}{||}}{C}-OH \\ + \\ R-CH_2-OH \end{matrix} \longrightarrow R-\overset{\overset{O}{||}}{C}-OCH_2-R\ \text{(ester)}$$

The mechanism is as follows:

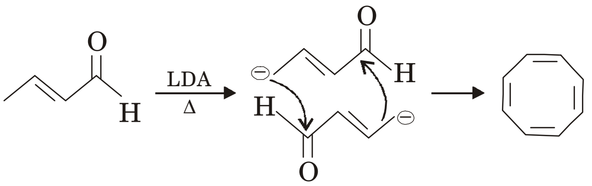


∴ The number of carbocation intermediates is 2.

11. **(2)** The given reaction is a Cannizzaro reaction. Since, bond energy of C – H < C – D, formation of H^- is easier.



12. **(5)** In the absence of α-H on saturated carbon, γ-H becomes acidic. This acidic γ-H would be abstracted by LDA to give carbanion, which condenses with another molecule to give cyclooctatetraene. The high temperature reaction condition helps in the dehydration of aldol product.



The formula of the compound is C_8H_8.

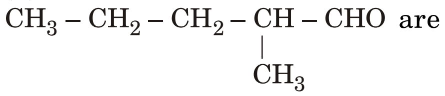
$$\text{DBE} = a+1-\frac{b}{2}$$

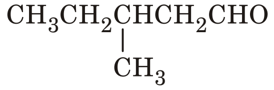
where a = number of C-atoms

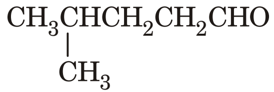
b = number of H-atoms

$$\therefore\ \text{DBE} = 8+1-\frac{8}{2} = 9-4 = 5$$

13. **(3)** Position isomer of


$CH_3-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CHO$ are

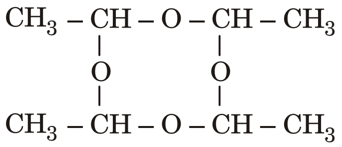
(a) 
$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CHO$

(b) 
$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_2CHO$

(c) $CH_3CH_2CH_2CH_2CH_2CHO$

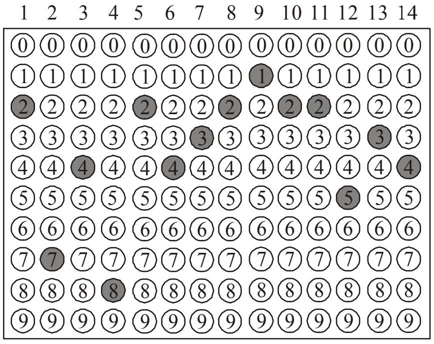
∴ 3 position isomers.

14. **(4)** $4CH_3CH=O \xrightarrow[\text{or conc. } H_2SO_4]{\text{dry HCl gas/}}$



Metaldehyde

∴ $x = 4$



	1	2	3	4	5	6	7	8	9	10	11	12	13	14
	⓪	⓪	⓪	⓪	⓪	⓪	⓪	⓪	⓪	⓪	⓪	⓪	⓪	⓪
	①	①	①	①	①	①	①	①	❶	①	①	①	①	①
	❷	②	②	②	❷	②	②	❷	②	❷	❷	②	②	②
	③	③	③	③	③	③	❸	③	③	③	③	③	❸	③
	④	④	❹	④	④	❹	④	④	④	④	④	④	④	❹
	⑤	⑤	⑤	⑤	⑤	⑤	⑤	⑤	⑤	⑤	⑤	❺	⑤	⑤
	⑥	⑥	⑥	⑥	⑥	⑥	⑥	⑥	⑥	⑥	⑥	⑥	⑥	⑥
	⑦	❼	⑦	⑦	⑦	⑦	⑦	⑦	⑦	⑦	⑦	⑦	⑦	⑦
	⑧	⑧	⑧	❽	⑧	⑧	⑧	⑧	⑧	⑧	⑧	⑧	⑧	⑧
	⑨	⑨	⑨	⑨	⑨	⑨	⑨	⑨	⑨	⑨	⑨	⑨	⑨	⑨

PREVIOUS YEARS IIT-JEE/JEE Advanced

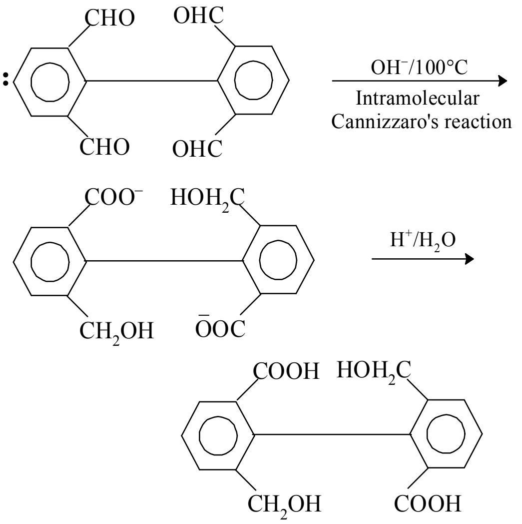
1. **(a) :** Initially OH^- attacks at carbonyl carbon atom of HCHO than that of PhCHO because of the following reason:

(i) the more electrophilic carbonyl carbon

(ii) the less steric hindrance in formation of hydroxyalkoxide that acts as hydride donor.

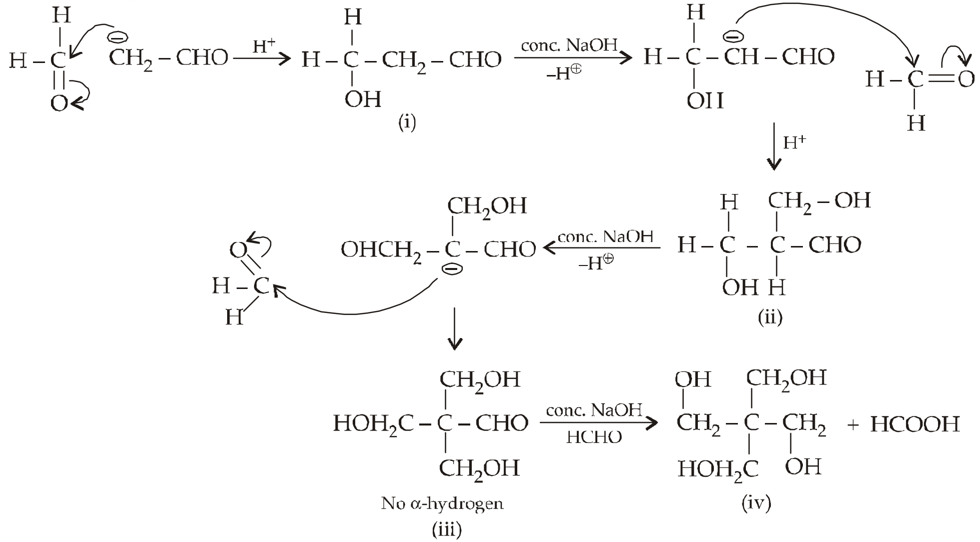
$$C_6H_5CHO + HCHO \xrightarrow{NaOH} HCOONa + C_6H_5CH_2OH$$

2. **(b) :**



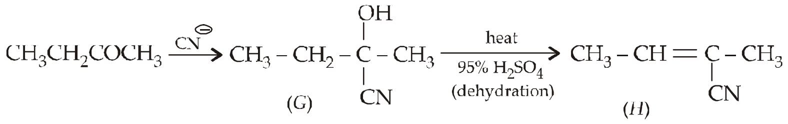
3. **(c) :** PhMgBr reacts with a carbonyl compound and the reaction is nucleophilic addition reaction which depends upon electrophilicity and steric crowding around carbonyl group. Thus CH_3CHO is most reactive and $C_6H_5COC_6H_5$ is least reactive.

4. **(c) :** $CH_3CHO \xrightarrow[-H^+]{\text{conc. NaOH}} \overset{\ominus}{C}H_2-CHO$

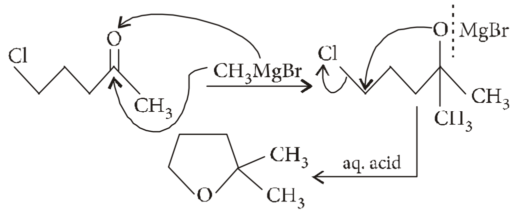


(i), (ii) and (iii) are aldol products but when two aldehydes without α-hydrogen reacts in presence of conc. NaOH they undergo cross Cannizzaro reaction not aldol reaction. Thus the final product is obtained by three cross aldol condensation processes and one cross-Cannizzaro reaction.

5. **(b) :**

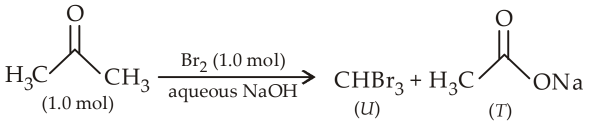


6. **(d) :**

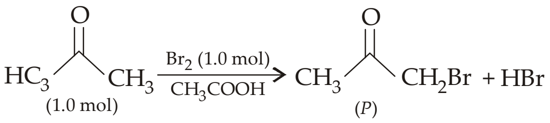


(Major product)

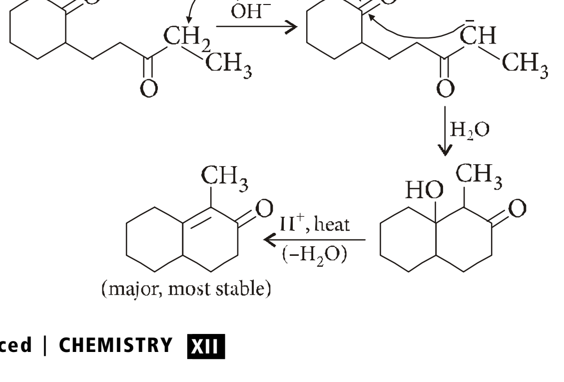
7. **(c) : Reaction I :**



Reaction II :

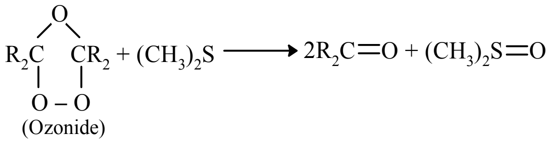


8. **(a) :**



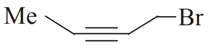
(major, most stable)

9. **(a):** We can reduce ozonides, by $(CH_3)_2S$, to yield carbonyl compounds and dimethyl sulphoxide.

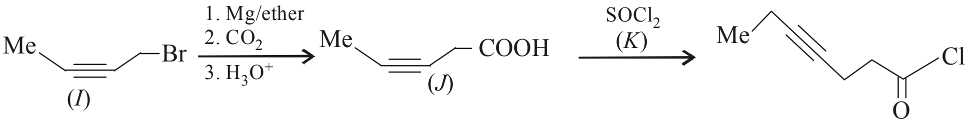


$$R_2C(O_3)CR_2 + (CH_3)_2S \longrightarrow 2R_2C{=}O + (CH_3)_2S{=}O$$

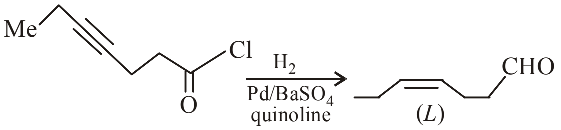
10. **(d) :** $\underset{\text{Hex-3-ynal}}{CH_3-CH_2-C\equiv C-CH_2-CHO} \xrightarrow[2.\ PBr_3]{1.\ NaBH_4} CH_3-CH_2-C\equiv \underset{I}{C}-CH_2-CH_2Br$ **or**



11. **(a) :**

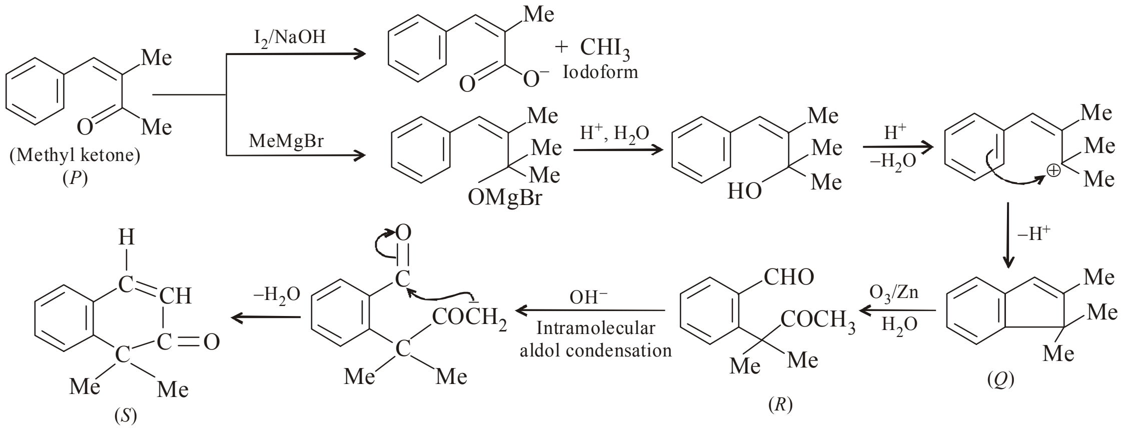


12. **(c) :**



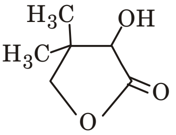
13. **(b)** **14.** **(a)** **15.** **(b)**

Hint :



16. **(b)** **17.** **(a)** **18.** **(d)**

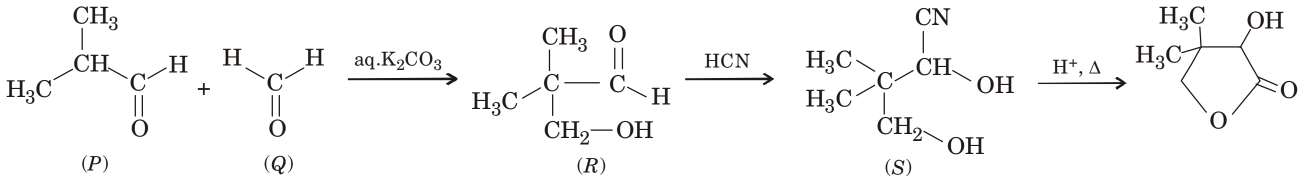
Hints : $P + Q \xrightarrow{aq.K_2CO_3} R \xrightarrow{HCN} S \xrightarrow{H^+,\ \Delta}$



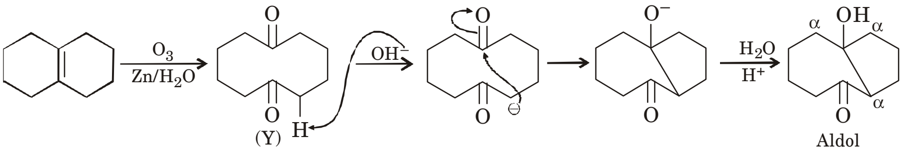
∵ R reacts with HCN, it must contain $>C{=}O$ group.

Since compound S gives the given product formed on treatment with H^+ followed by heating, thus S must have one carbon more than that in R.

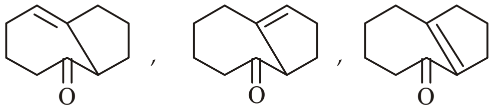
∴ P and Q are $(CH_3)_2CHCHO$ and HCHO respectively which undergo condensation in presence of *aq*. K_2CO_3 as follows :



19. **(3)**



The aldol has 3α-hydrogen atoms and hence gives three dehydration products.



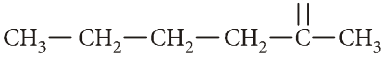
19
⓪
①
②
●
④
⑤
⑥
⑦
⑧
⑨

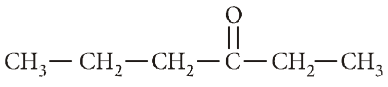
20. **(5) :** General formula of ketone; $C_nH_{2n}O$

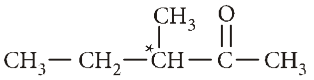
$12n + 2n + 16 = 100 \Rightarrow n = 6$

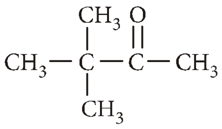
Hence, the ketone is $C_6H_{12}O$.

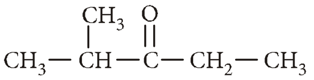
Their isomeric forms are :

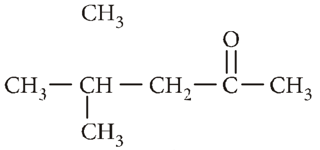
1. 
$CH_3-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

2. 
$CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$

3. 
$CH_3-CH_2-\overset{CH_3}{\overset{|}{\overset{*}{C}H}}-\overset{O}{\overset{\|}{C}}-CH_3$

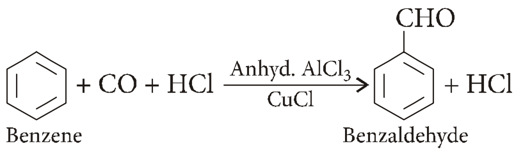
4. 
$CH_3-\underset{\underset{CH_3}{|}}{\overset{CH_3}{\overset{|}{C}}}-\overset{O}{\overset{\|}{C}}-CH_3$

5. 
$CH_3-\overset{CH_3}{\overset{|}{CH}}-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$

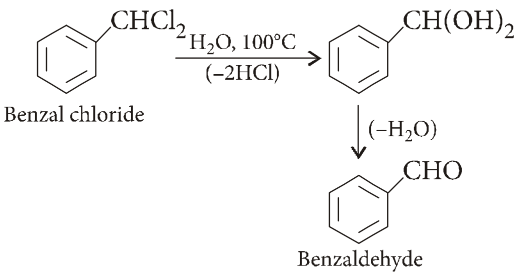
6. 
$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

Only structure (3) will not give racemic mixture on reaction with $NaBH_4$.

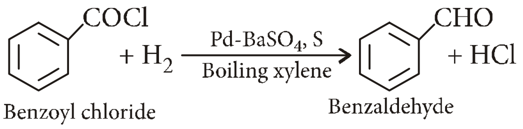
21. **(4) :** I. Gattermann-Koch aldehyde synthesis :



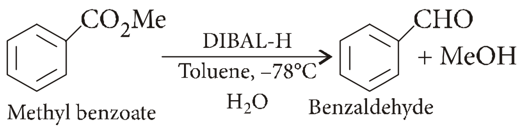
II. By hydrolysis of benzal chloride :



III. Rosenmund reduction :



IV. Esters are reduced to aldehydes with DIBAL-H :



* * *

Notes: