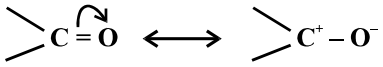
Aldehydes and Ketones

ALDEHYDES AND KETONES

C1A **Physical Properties :** 

It has high dipole moment

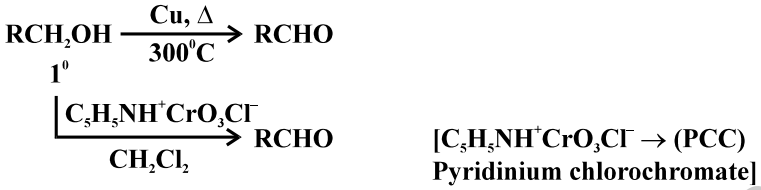
Boiling point are lower than alcohols due to their inability to form intermolecular H-bonding.

B.Pt. are higher than corresponding alkanes due to dipole-dipole interaction.

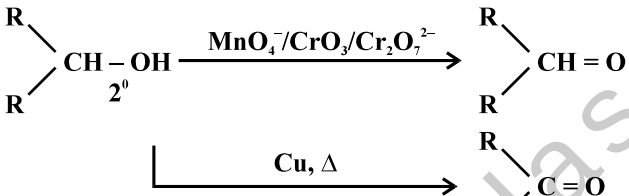
Carbonyl group can form H-bond with H_2O hence they are soluble in water to varying extent.

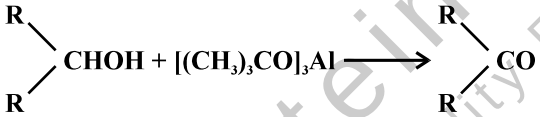
C1B **Method of Preparation :**

1. **Oxidation :**

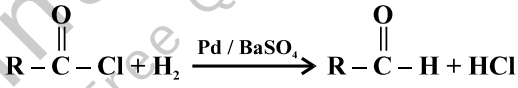
(a) 

[$C_5H_5NH^+CrO_3Cl^-$ → (PCC) Pyridinium chlorochromate]

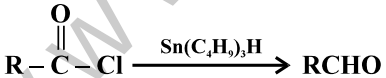
(b) 

(c) 

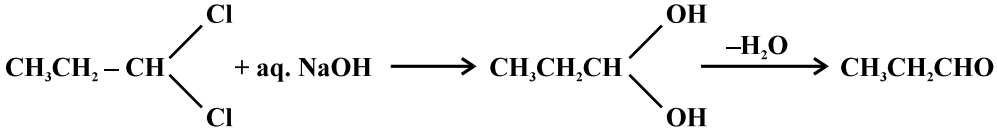
This oxidation is called as oppenauer oxidation.

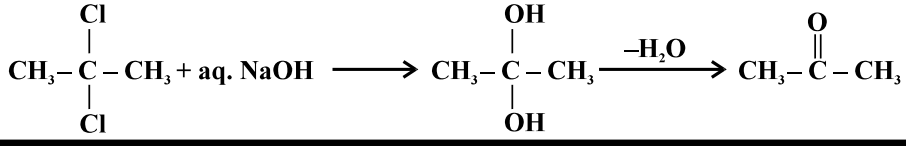
2. **Rossenmund Reduction :** 

3.  **[LiAlH $(O\text{-}t\text{-}C_4H_9)_3$ or Lithium tri-t-butoxy Aluminium hydride]**

4. 

5. **Hydrolysis of Gem-Dihalide**

(a) 

(b) 

(c) $ArCH_3 \xrightarrow{Cl_2, heat} ArCHCl_2 \xrightarrow{H_2O} ArCHO$

6. **Hydration of Alkynes :** Hydration of alkynes gives ketones (except $CH \equiv CH$ which gives CH_3CHO)

(a) $CH \equiv CH \xrightarrow[HgSO_4]{H_2O, H^+} CH_3CHO$ (b) $CH_3C \equiv CH \xrightarrow[HgSO_4]{H_2O, H^+} CH_3COCH_3$

7. **Hydroboration Oxidation :**

Hydroboration of a non-terminal alkyne followed by oxidation of the intermediate yields a ketone but terminal alkyne yield aldehyde.

$$CH_3C \equiv CH \xrightarrow{BH_3, THF} (CH_3 - \underset{H}{\underset{|}{C}} = CH)_3 - B \xrightarrow{H_2O_2, OH^-} \underset{\text{enol}}{CH_3 - \overset{H}{\overset{|}{C}} = CHOH} \rightleftharpoons \underset{\text{(keto)}}{CH_3 - CH_2 - CHO}$$

8. **Use of Grignard Reagent :**

(a) With HCN aldehyde is formed.

$$HCN \xrightarrow{RMgX} H - \underset{R}{\underset{|}{C}} = NMgX \xrightarrow{H_2O} H - \underset{R}{\underset{|}{C}} = O$$

(b) With RCN a ketone is formed.

$$R - C \equiv N \xrightarrow{R'MgX} R - \underset{R'}{\underset{|}{C}} = NMgX \xrightarrow{H_2O} R - \underset{R'}{\underset{|}{C}} = O$$

9. **With Esters**

(a) $$H - \overset{O}{\overset{\|}{C}} - OC_2H_5 + RMgX \longrightarrow H - \underset{R}{\overset{O^-}{\underset{|}{\overset{|}{C}}}} - OC_2H_5 \xrightarrow{H^+} R - \overset{O}{\overset{\|}{C}} - H + C_2H_5OH$$

(b) $$CH_3 - \overset{O}{\overset{\|}{C}} - OC_2H_5 + RMgX \longrightarrow CH_3 - \underset{R}{\overset{O^-}{\underset{|}{\overset{|}{C}}}} - OC_2H_5 \xrightarrow{H^+} CH_3 - \overset{O}{\overset{\|}{C}} - R + C_2H_5OH$$

10. **Decarboxylation of calcium salts of carboxylic acids :**

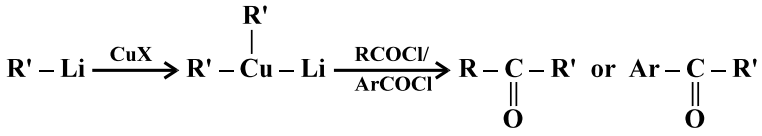
$$(R_1COO)_2Ca + (R_2COO)_2Ca \xrightarrow{\Delta} R_1 - \overset{O}{\overset{\|}{C}} - R_2 + 2CaCO_3$$

11. **Oxo Process :** $$- \underset{|}{\overset{|}{C}} = \underset{|}{\overset{|}{C}} - + CO + H_2 \xrightarrow[[CoH(CO)_4]]{100^0C, Pr.} - \underset{|}{\overset{|}{C}} - \underset{|}{\overset{|}{C}} - CHO$$

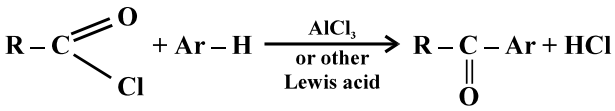
$$2\,CH_3CH = CH_2 + CO + H_2 \xrightarrow[[CoH(CO)_4]]{100^0C, Pr.} CH_3CH_2CH_2CHO + \begin{matrix} CH_3 \\ CH_3 \end{matrix} \!\!> CHCHO$$

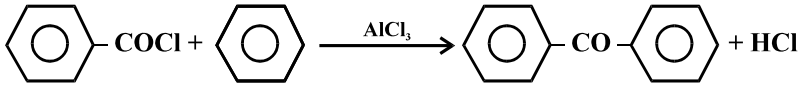
$[COH(CO)_4]$ ⟶ Cobal + Carbonyl hydride

12. **Reduction of acid chloride with organocopper compounds :**



13. **Friedel-Crafts Acylation :**

(a) 

(b) 

Benzophenone

14. **From Cadmium and Lithium Salts :**

1. $2RMgX + CdCl_2 \longrightarrow R-Cd-R + MgCl_2 + MgX_2$

$R-Cd-R + R'COCl \longrightarrow RCOR' + RCdCl$

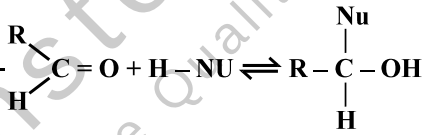
R ⟶ should be 1^0 alkyl or aryl ($-C_6H_5$)

15. Ozonylysis of Alkene (Zn/H^+) ⟶ Aldehyde/Ketone

C2 **Chemical Properties :**

1. **Nucleophilic Addition to the Carbon-Oxygen Double bond :**

The most characteristic reaction of aldehyde and ketone is nucleophilic addition to the carbon-oxygen double bond.

General Reaction : 

Relative reactivity of Aldehydes versus Ketones :

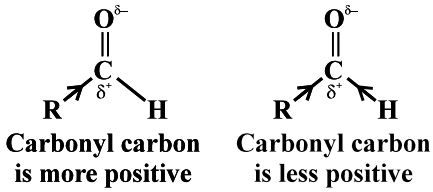
Aldehydes are more reactive than Ketones. There are two reasons for this, they are as follows :

1. Steric Factor 2. Electronic factor

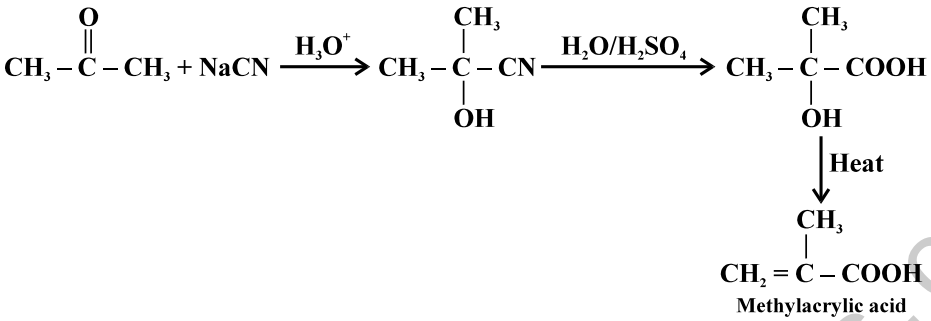
1. **Steric Factor :** With one group being the small hydrogen atom, the central carbon of the tetrahedral product formed from the aldehyde is less crowded and the product is more stable.

With ketones two alkyl groups at the carbonyl carbon causes greater steric crowding in the tetrahedral product and make it less stable. Therefore small concentration is present at equilibrium.

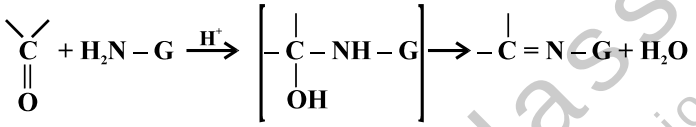
2. **Electronic Factor :** Because alkyl group are electron releasing therefore aldehydes are more reactive on electronic grounds as well. Aldehyde have one electron releasing alkyl group to stablise the partial positive charge on the carbon atom of the carbonyl group. Whereas ketones have two alkyl groups.



(a) Addition of cyanide :

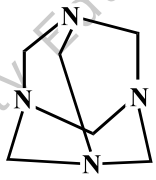


(b) Addition derivatives of ammonia :

(i) 

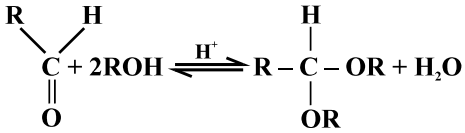
(ii) HCHO reacts with NH_3 differently forming UROTROPINE [hexamethylene tetraamine].

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



$H_2N - G$		Product	
$H_2N - OH$	Hydroxylamine	$>C = N - OH$	oxime
$H_2N - NH_2$	Hydrazine	$>C = N - NH_2$	Hydrazone
$H_2N - NHC_6H_5$	Phenylhydrazine	$>C = N - NHC_6H_5$	Phenylhydrazone
$H_2N - NHCOCH_2$	Semicarbazine	$>C = NNHCOCH_2$	Semicarbazone

(c) Addition of Alcohols : Acetal Formation

(i) 

(ii) $CH_3-\underset{\underset{H}{|}}{C}=O + 2C_2H_5OH \underset{}{\overset{HCl}{\rightleftharpoons}} CH_3-\underset{\underset{OC_2H_5}{|}}{\overset{\overset{H}{|}}{C}}-OC_2H_5 + H_2O$

Acetal

Important : $R'-\underset{\underset{OR\ (Acetal)}{|}}{\overset{\overset{H}{|}}{C}}-OR + H_2O \xrightarrow[fast]{H^+} R'-\overset{\overset{H}{|}}{C}=O + 2ROH$

(d) Addition of Grignard reagents :

$$\text{C=O} + R-MgX \longrightarrow -\underset{\underset{R}{|}}{\overset{|}{C}}-OMgX \xrightarrow{H_2O} -\underset{\underset{R}{|}}{\overset{|}{C}}-OH + Mg^{2+} + X^-$$

Formaldehyde with Grignard Reagent gives 1^0alcohol, all higher aldehydes with grignard reagent give 2^0 alcohol and ketones with grignard reagent gives the 3^0 alcohol.

C3 Other Reactions of Aldehyde and Ketones :

(a) Oxidation :

(i) $RCHO \text{ or } ArCHO \xrightarrow[K_2Cr_2O_7 \uparrow \;\; Ag(NH_3)_2^+ \uparrow]{KMnO_4} RCOOH \text{ or } ArCOOH$

Aldehydes (except) benzaldehyde reduce "Fehling's Solution" (Cu^{2+} reduced to Cu^+) which is an alkaline solution of Cu^{2+} ion complexed with tetrarate ion.

(ii) Example : Tollen's Test :

$$\underset{\text{Colourless Solution}}{CH_3CHO + 2Ag(NH_3)_2^+ + 3OH^-} \longrightarrow \underset{\text{Silver mirror}}{CH_3COO^- + 2Ag} + 4NH_3 + 2H_2O$$

Fehling Solution $CH_3CHO + 2Cu^{2+} + 3OH^- \longrightarrow CH_3COO^- + \underset{\text{Red PPt.}}{2Cu^+ \downarrow} + 2H_2O$

Tollen's test is cheifly given by aldehydes. Tollen's reagent does not attack carbon-carbon double bond. Aldehyde also reduce benedict's solution (Cu^{2+} complexed with citrate ion) to Cu^+

(b) (i) Ketones with strong oxidants and at high temperature undergo cleavage of C-C bond on either side of carbonyl group.

$$RCH_2\overset{a}{-}\underset{\underset{O}{\|}}{C}\overset{b}{-}CH_2R' \xrightarrow[drastic]{Oxidant} \underset{\text{From cleavage of bond}}{RCH_2COOH} + R'COOH$$

Carbonyl Group after bond cleavage goes with that alkyl group which is of smaller size.

(ii) Ketones are also oxidised from cleavage of bond by caro's acid (H_2SO_5) or peroxybenzoic acid ($C_6H_5CO_3H$) to esters. $RCOR' \xrightarrow[[O]]{H_2SO_5} RCOOR'$ **[Bayer's Villiger Oxidation]**

(c) Haloform Test :

(i) Methylketones :

$$R-\underset{\underset{O}{\|}}{C}-CH_3 \text{ or } Ar-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow[(NaOH)/I_2]{NaOI} RCOO^- \text{ or } ArCOO^- + CHI_3$$

Iodoform (Yellow PPt.)

(ii) <u>Hypohalite</u> **NaOX (NaOH + X_2) cannot only halogenate can also oxidise alcohols**

$$R-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-CH_3 + NaOI \longrightarrow R-\overset{\overset{O}{\|}}{C}-CH_3 + NaI + H_2O$$

(d) <u>**Reduction :**</u>

(a) Reduction to alcohol

$$>C=O \xrightarrow{H_2/Ni,\ Pt \text{ or } Pd} -\underset{|}{C}-OH$$

$$>C=O \xrightarrow[\text{then } H^+]{LiAlH_4 \text{ or } NaBH_4;} -\underset{|}{C}-OH$$

(e) <u>**Reduction to hydrocarbons :**</u>

$$>C=O \xrightarrow[HCl]{Zn(Hg)/conc.} -\underset{|}{\overset{|}{C}}-H \text{ (Clemmenson's reduction)}$$

$$>C=O \xrightarrow[base]{NH_2NH_2} -\underset{|}{\overset{|}{C}}-H \text{ (Wolff-kishner reduction)}$$

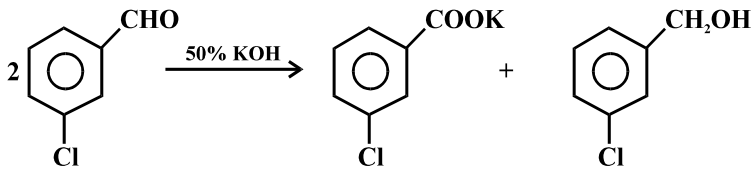
(f) Reductive Amination (Discussed under Amines)

(g) <u>**Cannizzaro reaction :**</u> **In the presence of an concentrated base i.e. alkali, aldehydes containing no α-hydrogens undergo self oxidation and reduction to yield a mixture of an alcohol.**

(i)

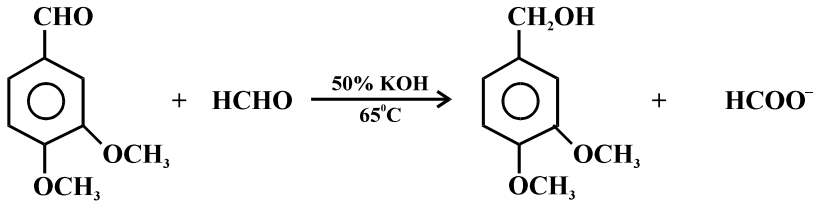
$$\underset{\text{An aldehyde with no } \alpha\text{-hydrogens}}{2H-\overset{\overset{H}{|}}{C}=O} \xrightarrow[base]{strong} \underset{\text{Acid Salt}}{HCOO^-} + \underset{\text{Alcohol}}{CH_3OH}$$

(ii)



m-chlorobenzoldehyde | **m-chloropotassium benzoate** | **m-chlorobenzylalcohol**

(h) Crossed Cannizzaro reaction :

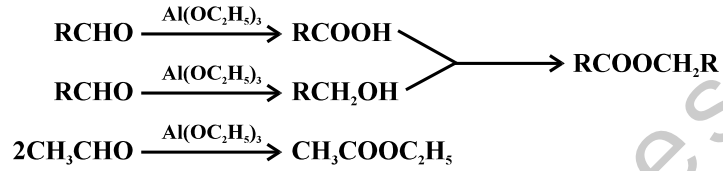


Veratraldehyde
(3, 4-Dimethoxy benzaldehyde)

(3, 4- Dimethoxybenzyl alcohol)

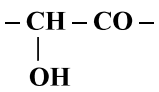
(i) Tischenko Reaction :

All aldehyde in presence of aluminium ethoxide, $Al(OC_2H5)_3$ can be simultaneously oxidised (to acid) and reduced (to alcohols) to form ester. This is called Tischenko reaction and is thus like cannizaro reaction.



(j) Distinction

Aldehyde and Ketones

S.No.	Test	RCHO	RCOR
1.	Schiffs reagent	magenta colour restored 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 reudce Tollen's re agent and Fehling's solution 

Practice Problems :

1. **Identify (Z) in the reaction series,** $CH_2 = CH_2 \xrightarrow{HBr} (X) \xrightarrow{Hydrolysis} (Y) \xrightarrow[I_2\,(excess)]{NaOH} (Z)$

   (a) C_2H_5I (b) C_2H_5OH (c) CHI_3 (d) CH_3CHO

2. **A compound (X) of the formula C_3H_8O yields a compound C_3H_6O on oxidation. To which of the following class of compounds could (X) belong**

   (a) aldehyde (b) secondard alcohol

   (c) alkene (d) tert. alcohol

3. **Which statement is incorrect in the case of acetaldehyde and acetone**

   (a) both react with hydroxylamine

   (b) both react with $NaHSO_3$

(c) both react with hydrazine

(d) both reduce ammonical silver nitrate

4. Which of the following undergoes Cannizzaro's reaction

(a) CH_3CHO (b) CH_3CH_2CHO (c) $(CH_3)_2CHCHO$ (d) HCHO

5. Urotropine is formed by the action of ammonia on

(a) acetaldehyde (b) formaldehyde (c) acetone (d) phenol

6. Hydrocarbons are formed when aldehydes and ketones are reacted with amalgamated zinc and conc. HCl. The reaction is called

(a) Cannizzaro's reaction (b) Clemmensen's reduction

(c) Rosenmund's reaction (d) Tischenko reaction

7. When acetaldehyde is treated with aluminium ethoxide, it forms

(a) ethyl acetate (b) ethyl alcohol

(c) acetic acid (d) methyl propionate

8. Chloretone is formed when chloroform reacts with

(a) formaldehyde (b) acetaldehyde (c) acetone (d) benzaldehyde

9. Which of the following reagent reacts differently with HCHO, CH_3CHO and CH_3COCH_3

(a) HCN (b) NH_2OH (c) $C_6H_5NHNH_2$ (d) NH_3

10. In the following sequence of reactions, the end product is

$$CaC_2 \xrightarrow{H_2O} (A) \xrightarrow{Hg^{2+}/H_2SO_4} (B) \xrightarrow{[O]} (C) \xrightarrow{Ca(OH)_2} (D) \xrightarrow{heat} (E)$$

(a) acetaldehyde (b) formaldehyde (c) acetic acid (d) acetone

11. In the following sequence of reactions, the end product is

$$HC \equiv CH \xrightarrow{Hg^{2+}/H_2SO_4} (A) \xrightarrow[[H_2O]]{CH_3MgX} (B) \xrightarrow{[O]} (C)$$

(a) acetaldehyde (b) isopropyl alcohol

(c) acetone (d) ethyl alcohol

12. In the following sequence of reactions, the end product is $CH_3CHO \xrightarrow{HCN} (A) \xrightarrow{H_2O} (B)$

(a) CH_3COOH (b) $CH_3CHOHCOOH$

(c) $CH_3CH_2NH_2$ (d) CH_3CONH_2

13. A compound, $C_5H_{10}O$, forms a phenyl hydrazone and gives negative Tollen's and iodoform tests. The compound on reduction gives n-pentane. The compound A is

(a) pentanal (b) pentanone-2 (c) pentanone-3 (d) amyl alcohol

14. The product Z in the series is

$$CH_2 = CH_2 \xrightarrow{HBr} X \xrightarrow{Hydrolysis} Y \xrightarrow[I_2\,(excess)]{Na_2CO_3} Z$$

(a) C_2H_5I (b) C_2H_5OH (c) CHI_3 (d) CH_3CHO

15. If formaldehyde and KOH are treated together, we get

(a) methane (b) methanol (c) ethyl acetate (d) acetylene

16. The correct order of reactivity in nucleophilic addition reaction CH_3CHO, $CH_3COC_2H_5$ and CH_3COCH_3 is

(a) $CH_3CHO > CH_3COCH_3 > CH_3COC_2H_5$

(b) $C_2H_5COCH_3 > CH_3COCH_3 > CH_3CHO$

(c) $CH_3COCH_3 > CH_3CHO > C_2H_5COCH_3$

(d) $CH_3COCH_3 > C_2H_5COCH_3 > CH_3CHO$

17. To distinguish between 2-pentanone and 3-pentanone which reagent can be used

(a) $NaOH/I_2$ (b) Tollen's reagent

(c) $K_2Cr_2O_7/H^+$ (d) Zn–Hg, HCl

18. $CH_3CH = CHCHO$ is oxidised to $CH_3 - CH = CHCOOH$, using oxidising agent as

(a) alkaline $KMnO_4$ (b) $K_2Cr_2O_7$/conc. H_2SO_4

(c) ammonical $AgNO_3$ (d) dilute HNO_3

19. m-chloro benzaldehyde on reaction with conc. KOH at room temperature gives

(a) potassium m-chloro benzoate and m-hydroxy benzaldehyde

(b) m-chloro benzyl alcohol and m-hydroxy benzaldehyde

(c) m-chloro benzyl alcohol and m-hydroxy benzyl alcohol

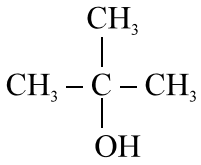
(d) m-chloro benzyl alcohol and potassium m-chloro benzoate

20. The reagent which can be used to distinguish acetophenone from benzophenone is :

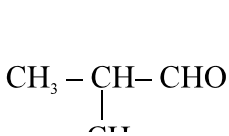
(a) 2, 4-dinitrophenyl hydrazine (b) benedict reagent

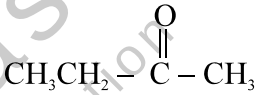
(c) I_2 and Na_2CO_3 (d) aqueous solution of $NaHSO_3$

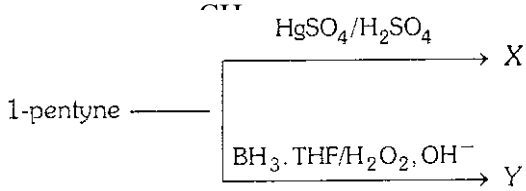
21. Best starting material to synthesize 2-methyl-2-butenoic acid is

(a) 

(b) $CH_3CH_2CH_2CHO$

(c) 

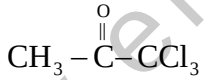
(d) 

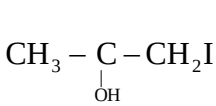
22. 

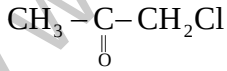
X and Y can be distinguished by :

(a) silver-mirror test (b) iodoform test (c) both (d) none

23. Which of the following will give haloform test

(a) 

(b) 

(c) 

(d) all

[Answers : (1) c (2) b (3) d (4) d (5) b (6) b (7) a (8) c (9) d (10) d (11) c (12) b (13) c (14) c (15) b (16) a (17) a (18) a (19) d (20) c (21) c (22) c (23) d]