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Organic Compounds Containing Oxygen

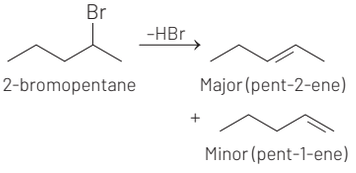
TOPIC 1
Alcohols and Phenols

01 The major product formed in dehydrohalogenation reaction of 2-bromo pentane is pent-2-ene. This product formation is based on **[NEET 2021]**

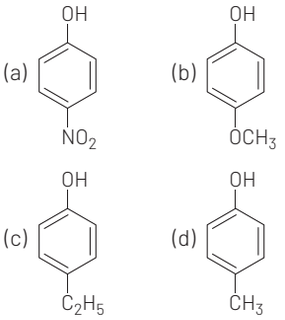
(a) Saytzeff's rule (b) Hund's rule
(c) Hoffmann rule (d) Huckel's rule

Ans. ***(a)***

Saytzeff's rule states that more substituted alkene is formed in a dehydrohalogenation reaction.
In dehydrohalogenation of 2-bromopentane, pent-2-ene is formed as major product which is a more substituted alkene.



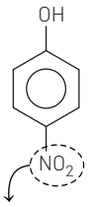
02 Which of the following substituted phenols is the strongest acid? **[NEET (Oct.) 2020]**



Ans. ***(a)***

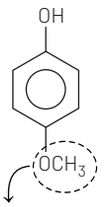
EDG (+ *R*, + *I*) decreases acidity and EWG (– *R*, – *I*) increases acidity of phenol.

(a)



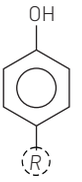
[–*R* from *para* position makes its a stronger acid]

(b)



[+*R* from *para*-position deceases its acid remarkably]

(c, d)



(*R* = CH_3, C_2H_5)

[+*I* from *para* position decreases its acidity]

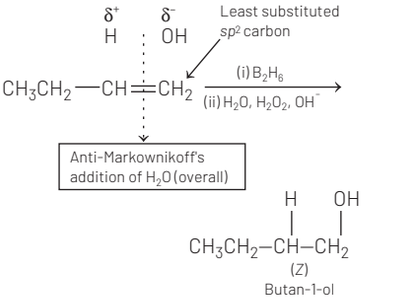
Thus, option (a) is correct.

03 $CH_3CH_2CH{=}CH_2 \xrightarrow[H_2O,H_2O_2,OH^-]{B_2H_6} Z$

what is Z? **[NEET (Oct.) 2020]**

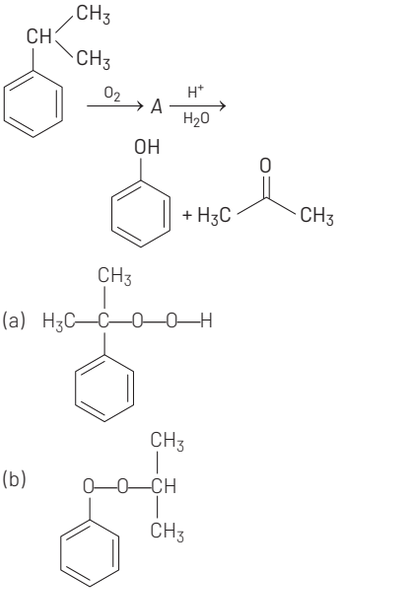
(a) $CH_3CH_2CH_2CH_2OH$
(b) $CH_3CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$
(c) $CH_3CH_2CH_2CHO$ (d) $CH_3CH_2CH_2CH_3$

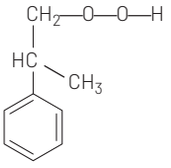
Ans. ***(a)***

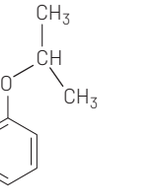


It is hydroboration-oxidation (HBO) reaction of an alkene which undergoes hydration to give an alcohol.
Here, anti-Markownikoff's addition of H_2O takes place.

04 The structure of intermediate *A* in the following reaction, is **[NEET (National) 2019]**

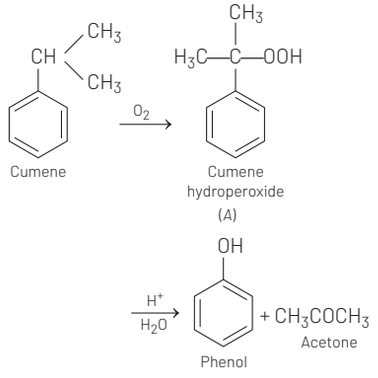


(c) 

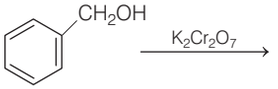
(d) 

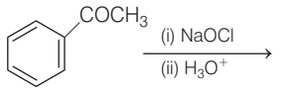
Ans. *(a)*

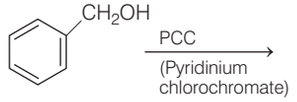
The given reaction is of cumene process for phenol production and intermediate (*A*) is cumene hydroperoxide. In the process, cumene (isopropylbenzene) is oxidised in the presence of air to cumene hydroperoxide. Which is then converted to phenol and acetone by treating with dilute acid. Acetone, a by-product of this reaction is also obtained in large quantities by this method. The reaction takes place as follows :

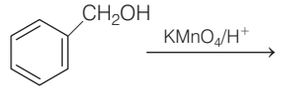


05 The reaction that does not give benzoic acid as the major product is **[NEET (Odisha) 2019]**

(a) 

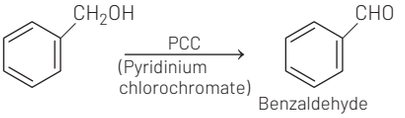
(b) 

(c) 

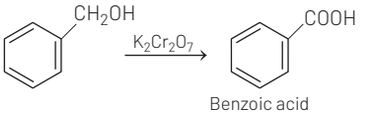
(d) 

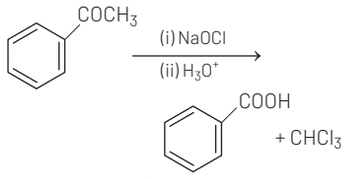
Ans. *(c)*

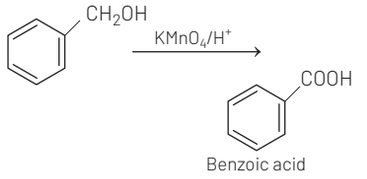
Primary aromatic alcohols on reaction with pyridinium chlorochromate (PCC) which is a mild oxidising agent forms aromatic aldehydes.



In the remaining options benzoic acid is formed as follows:

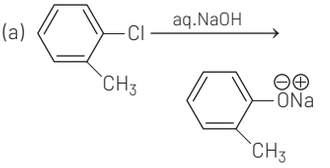


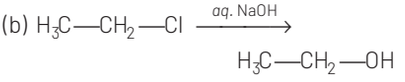


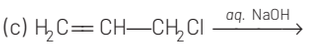


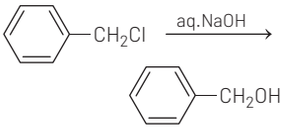
Thus, option (c) is correct.

06 The hydrolysis reaction that takes place at the slowest rate, among the following is **[NEET (Odisha) 2019]**

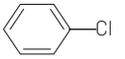
(a) 

(b) 

(c) 

(d) 

Ans. *(a)*

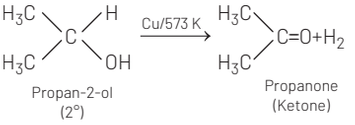
 is a benzylic halide. Thus, there is a partial double bond character between sp^3-hybridised C atom next to an aromatic ring and Cl. It is most difficult to break this bond and hence it undergoes hydrolysis reaction with slowest rate.

07 When vapours of a secondary alcohol is passed over heated copper at 573 K, the product formed is **[NEET (Odisha) 2019]**

(a) a carboxylic acid
(b) an aldehyde
(c) a ketone
(d) an alkene

Ans. *(c)*

When vapours of alcohols are passed over heated copper at 573 K, primary and secondary alcohols undergo dehydrogenation to give aldehydes and ketones, respectively. While tertiary alcohols undergo dehydration to give alkenes.



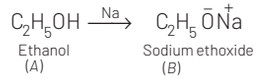
Thus, option (c) is correct.

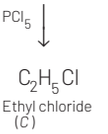
08 The compound *A* on treatment with Na gives *B*, and with PCl_5 gives *C*. *B* and *C* react together to give diethyl ether. *A*, *B* and *C* are in the order **[NEET 2018]**

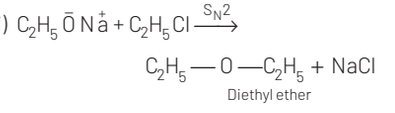
(a) C_2H_5Cl, C_2H_6, C_2H_5OH
(b) C_2H_5OH, C_2H_5Cl, C_2H_5ONa
(c) C_2H_5OH, C_2H_6, C_2H_5Cl
(d) C_2H_5OH, C_2H_5ONa, C_2H_5Cl

Ans. *(d)*

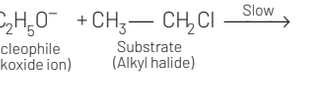
According to given question and options (*A*) must be C_2H_5OH, as it reacts with Na to give C_2H_5ONa. The reaction sequence is as follows.

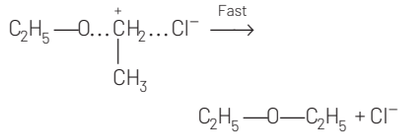
(i) 



(ii) 

The above reaction is known as Williamson's ether synthesis. It involves nucleophilic attack of alkoxide ion on alkyl halide according to S_N2 mechanism.

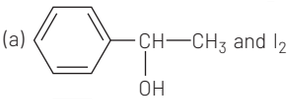


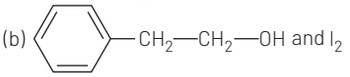


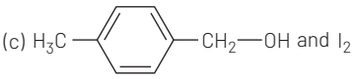
09 Compound *A*, $C_8H_{10}O$, is found to react with NaOI (produced by reacting *Y* with NaOH) and yields a yellow precipitate with characteristic smell.

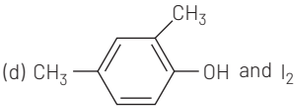
A and *Y* are respectively.

[NEET 2018]

(a) 

(b) 

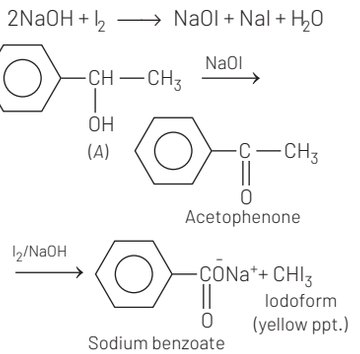
(c) 

(d) 

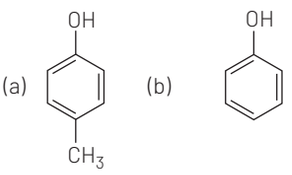
Ans. ***(a)***

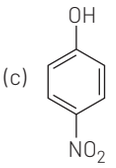
Iodoform reaction with sodium hypoiodite is used for the detection of CH_3CO group. Also compounds containing $CH_3CH(OH)$ group shows positive iodoform test as it produces CH_3CO group on oxidation.

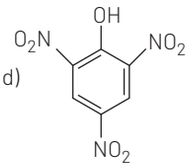
Since, among the compounds, $CH_3CH(OH)$ group is given only in the substrate of option (a) hence, it is correct. The reaction of compound *A* with NaOI is given as follows :



10 Which one is the most acidic compound? **[NEET 2017]**



(c) 

(d) 

Ans. ***(d)***

Thinking process *This problem is based on the acidic character of phenol. Electron -withdrawing group at o and p-position w.r.t. —OH group of phenol, increase the acidic strength.*

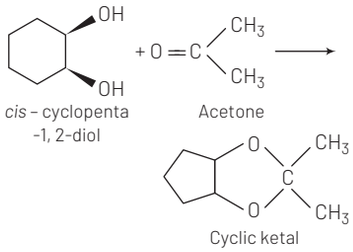
Picric acid (2, 4, 6-trinitrophenol) is extremely more acidic than given compounds because its pKa value is close to zero also due to the presence of three strong electron withdrawing group (—NO_2 group) at *ortho* and *para*-positions, picric is more acidic compound.

11 Which of the following reagents would distinguish *cis*-cyclopenta-1, 2-diol from the *trans*-isomer? **[NEET 2016, Phase II]**

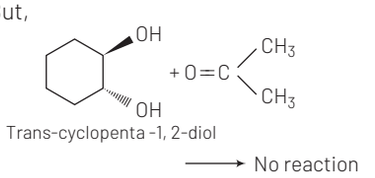
(a) Ozone
(b) MnO_2
(c) Aluminium isopropoxide
(d) Acetone

Ans. ***(d)***

cis-cyclopenta-1,2-diol when reacts with acetone, forms cyclic ketal whereas *trans*-isomer of cyclopenta-1, 2-diol can not form cyclic ketal.



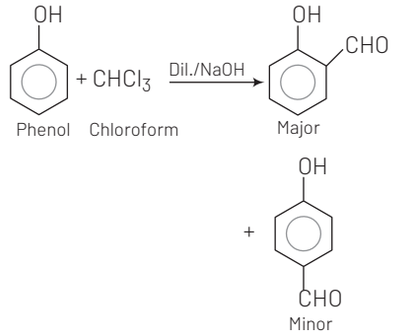
But,



12 Reaction of phenol with chloroform in the presence of dilute sodium hydroxide finally introduces, which one of the following functional group? **[CBSE AIPMT 2015]**

(a) — CH_2Cl (b) —COOH
(c) — $CHCl_2$ (d) —CHO

Ans. ***(d)***



This is Reimer-Tiemann reaction. So finally —CHO group is introduced

13 Which of the following reaction(s) can be used for the preparation of alkyl halides? **[CBSE AIPMT 2015]**

I. $CH_3CH_2OH + HCl \xrightarrow{anh.ZnCl_2}$

II. $CH_3CH_2OH + HCl \longrightarrow$

III. $(CH_3)_3COH + HCl \longrightarrow$

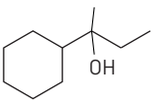
IV. $(CH_3)_2CHOH + HCl \xrightarrow{anh.ZnCl_2}$

(a) I, III and IV (b) I and II
(c) Only IV (d) III and IV

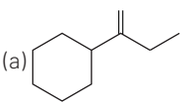
Ans. ***(a)***

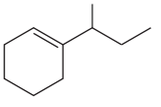
In (I) and (IV) due to the presence of Lucas reagent (HCl + anh. $ZnCl_2$) alcohols give alkyl halides while in (III) alkyl halide is formed due to S_N1 reaction.

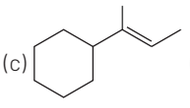
14 Which of the following is not the product of dehydration of

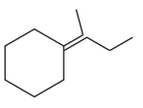


[CBSE AIPMT 2015]

(a) 

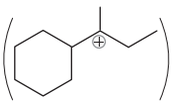
(b) 

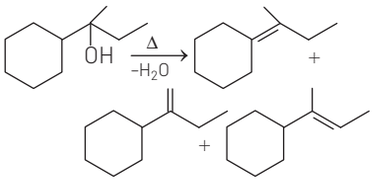
(c) 

(d) 

Ans. ***(b)***

Key Concept *When intermediate carbocation is stable, no rearrangement takes place in carbocation.*

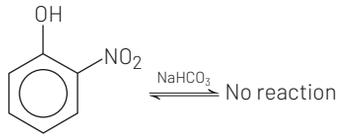




15 Which of the following will not be soluble in sodium hydrogen carbonate? **[CBSE AIPMT 2014]**

(a) 2,4,6-trinitrophenol
(b) Benzoic acid
(c) *o*-nitrophenol
(d) Benzenesulphonic acid

Ans. ***(c)***



O-nitrophenol is insoluble in sodium hydrogen carbonate. While 2,4,6-trinitrophenol, benzoic acid and benzene sulphonic acid are soluble in $NaHCO_3$.

Infact, Acid + $NaHCO_3$ ⟶ Salt + H_2CO_3

This reaction is possible in forward direction if acid is more acidic than H_2CO_3. *o*-nitrophenol is less acidic than H_2CO_3. Hence, it is not soluble in sodium hydrogen carbonate.

16 In the following sequence of reactions,

$$CH_3—Br \xrightarrow{KCN} A \xrightarrow{H_3O^+} B \xrightarrow[ether]{LiAlH_4} C$$

the end product *C* is **[CBSE AIPMT 2012]**

(a) acetone (b) methane
(c) acetaldehyde (d) ethyl alcohol

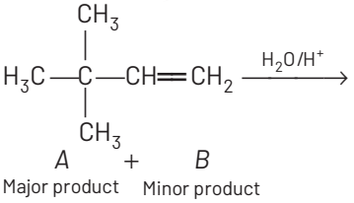
Ans. ***(d)***

CH_3Br (Methyl bromide) $\xrightarrow[-KBr]{KCN}$ CH_3CN (Ethane nitrile *A*) $\xrightarrow[\text{Complete hydrolysis}]{H_3O^+}$ CH_3COOH (Ethanoic acid *B*)

$\xrightarrow[\text{Ether}]{LiAlH_4}$ CH_3CH_2OH (Ethanol *C*)

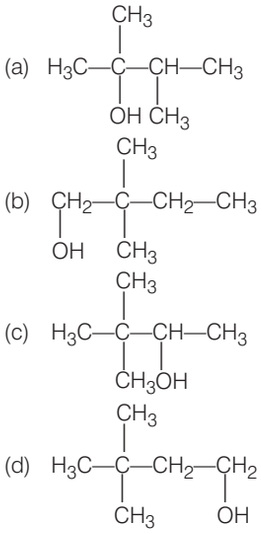
In the presence of $LiAlH_4$ carboxylic acid reduce in alcohols directly.

17 In the following reaction,

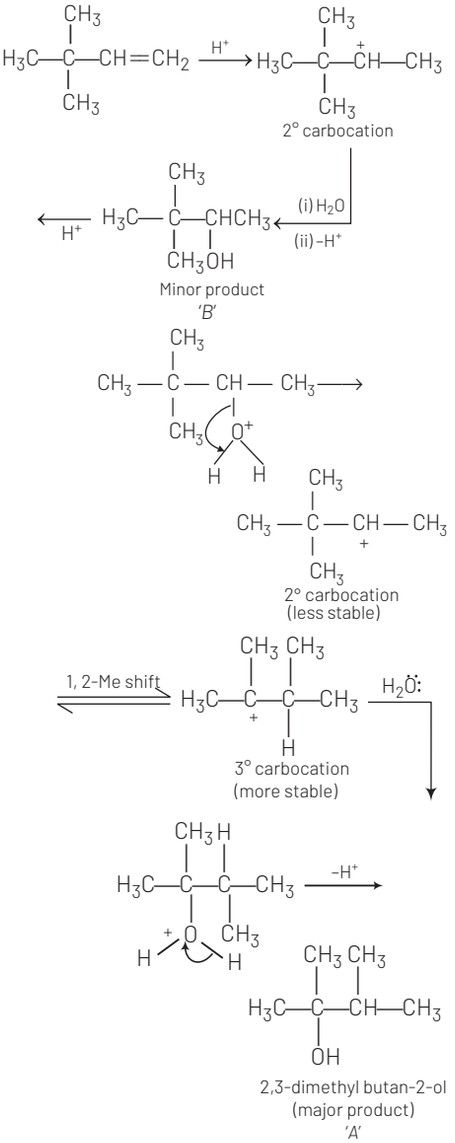


Major product + Minor product

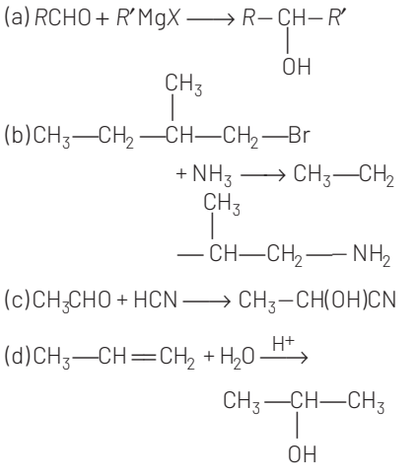
[CBSE AIPMT 2012]



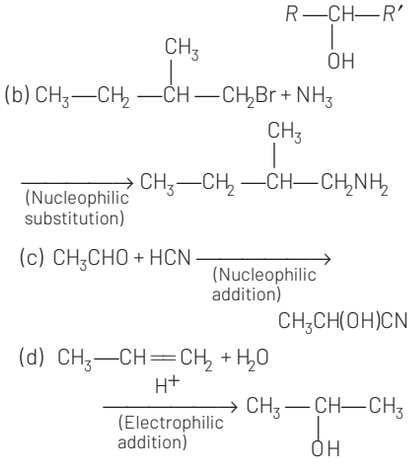
Ans. ***(a)***



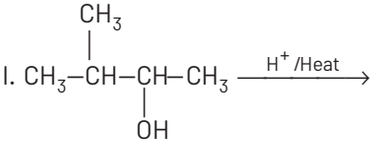
18 Which one is a nucleophilic substitution reaction among the following? **[CBSE AIPMT 2011]**

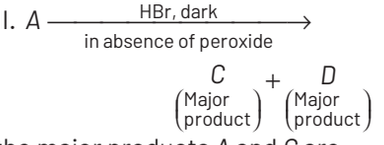


Ans. ***(b)***



19 In the following reactions, **[CBSE AIPMT 2011]**





the major products *A* and *C* are respectively

(a) $CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH_3$ and $CH_3-\underset{\underset{Br}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CH_3$

(b) $CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH_3$ and $CH_3-\underset{\underset{Br}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_3$

(c) $CH_2=\underset{\underset{CH_3}{|}}{C}-CH_2-CH_3$ and $CH_3-\underset{\underset{Br}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CH_3$

(d) $CH_2=\underset{\underset{CH_3}{|}}{C}-CH_2-CH_3$ and $CH_2-\underset{\underset{Br}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3$

Ans. *(a)*

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

$\xrightarrow[\text{Protonation and dehydration}]{H^+/\Delta} CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{\oplus}{C}-CH_3$ (2° carbocation)

$\xrightarrow[\text{shift}]{\text{1, 2-hydride}} CH_3-\underset{\underset{CH_3}{|}}{\overset{+}{C}}-CH_2-CH_3$ (More stable 3° carbonium ion)

$\xrightarrow[\text{Rearrangement}]{-H^+} CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH_3$ Major *A*

$+\ CH_3-\underset{\underset{CH_3}{|}}{CH}-CH=CH_2$ Minor *B*

A part is major because more substituted alkenes are more stable.

(II) $CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH_3$ Major *A*

$\xrightarrow[\text{In the absence of peroxide}]{HBr\,(dark)} CH_3-\underset{\underset{Br}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CH_3$ Major *C*

$+\ CH_3-\underset{\underset{H}{|}}{\underset{\underset{CH_3}{|}}{C}}-\underset{\underset{Br}{|}}{CH}-CH_3$ Minor *D*

20 Given are cyclohexanol (I), acetic acid (II), 2, 4, 6-trinitrophenol (III) and phenol (IV). In these, the order of decreasing acidic character will be **[CBSE AIPMT 2010]**

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

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

Ans. *(a)*

Key Idea *Higher the tendency to give a proton, higher is the acidic character and tendency to lose a proton depends upon the stability of intermediate, i.e. carbanion formed.*

2, 4, 6-trinitrophenol after the loss of a proton gives 2,4,6-trinitrophenoxide ion which is stabilised by resonance, $-I$-effect and $-M$-effect, thus is most acidic among the given compounds.

Phenol after losing a proton form phenoxide ion which is also stabilised by resonance, $-M$ and $-I$ effects but is less stabilised as compared to 2, 4, 6-trinitrophenoxide ions. Thus, it is less acidic as compared to 2, 4, 6-trinitrophenol. (CH_3COOH) after losing a proton gives acetate $\left(CH_3C(=O)O^-\right)$ ion (Carboxylate ion) which is stabilised by only resonance. However, it is more resonance stabilised as compared to a phenoxide ion, thus more acidic as compared to phenol. 2, 4, 6-trinitrophenol, however, is more acidic than acetic acid due to the presence of three electron withdrawing $-NO_2$ groups. Cyclohexanol gives an anion that is least stable among the given, thus, it is least acidic.

Hence, the correct order of acidic strength is

2, 4, 6-trinitrophenol > acetic acid > phenol > cyclohexanol

III > II > IV > I

21 Which of the following reactions will not result in the formation of carbon-carbon bonds? **[CBSE AIPMT 2010]**

(a) Reimer-Tiemann reaction

(b) Cannizaro reaction

(c) Wurtz reaction

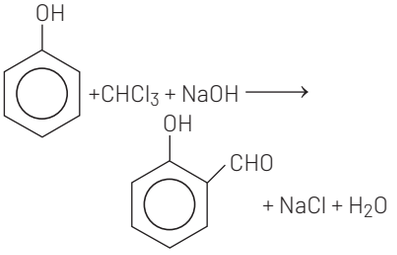
(d) Friedel-Crafts's acylation

Ans. *(b)*

(a) **Reimer-Tiemann reaction,**

(Here, a new C – C bond is formed.)

Riemer-Tiemann reaction is an electrophilic substitution reaction.



(b) **Cannizaro reaction,** (disproportionation reaction)

In this reaction, 1-molecule of HCHO convert in methanol and another molecule convert in salt.

$2\,HCHO \xrightarrow{\text{Conc. NaOH}} CH_3OH + HCOO^-N^+a$

(No new C—C bond is formed in this reaction.)

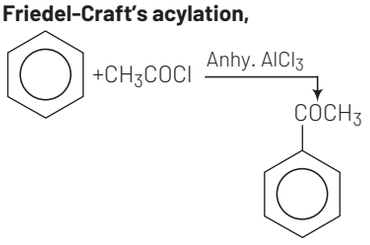
(c) **Wurtz reaction**,

$R—X + 2Na + R'X + \text{dry Na} \xrightarrow{\text{Ether}} R—R$

Here, R and R' must be equal otherwise mixture of alkanes will form

(One new C—C bond is formed).

(d) **Friedel-Craft's acylation,**



(New C—C bond is formed)

Thus, among the given reactions, only Cannizaro reaction does not involve the formation of a new C—C bond.

22 Consider the following reaction,

$\text{Ethanol} \xrightarrow{PBr_3} X \xrightarrow{\text{Alc. KOH}} Y \xrightarrow[\text{(ii) } H_2O,\ \text{heat}]{\text{(i) } H_2SO_4,\ \text{room temperature}} Z$

The product Z is **[CBSE AIPMT 2009]**

(a) $CH_2=CH_2$ (b) $CH_3CH_2OCH_2CH_3$
(c) $CH_3CH_2OSO_3H$ (d) CH_3CH_2OH

Ans. *(d)*

$C_2H_5OH \xrightarrow{PBr_3} C_2H_5Br$
Ethanol

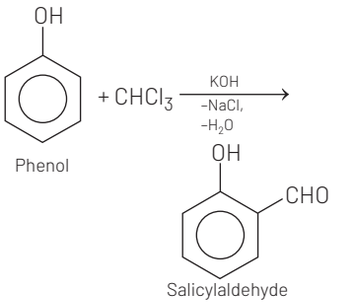
$\xrightarrow[-KBr]{\text{Alc. KOH}} CH_2=CH_2$
$-H_2O$
β- elimination

$\xrightarrow{H_2SO_4} CH_3—CH_2OSO_3H \xrightarrow[-H_2SO_4]{H_2O/\Delta} CH_3CH_2OH$
Ethanol

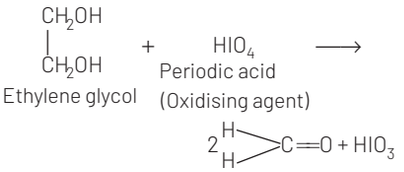
23 $H_2COH \cdot CH_2OH$ on heating with periodic acid gives

[CBSE AIPMT 2009]

(a) $2CO_2$ (b) $2HCOOH$
(c) $(CHO)_2$ (d) $2\ H_2C=O$



Ans. *(d)*



24 Consider the following reaction, Phenol

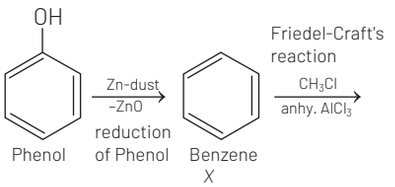
$\xrightarrow{Zn\text{-dust}} X \xrightarrow[Anhy.\ AlCl_3]{CH_3Cl} Y \xrightarrow[]{\text{Alk. } KMnO_4} Z$

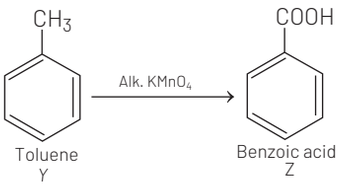
The product *Z* is

[CBSE AIPMT 2009]

(a) toluene (b) benzaldehyde
(c) benzoic acid (d) benzene

Ans. *(c)*





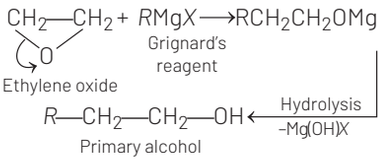
25 Ethylene oxide when treated with Grignard reagent yields

[CBSE AIPMT 2006]

(a) secondary alcohol
(b) tertiary alcohol
(c) cyclopropyl alcohol
(d) primary alcohol

Ans. *(d)*

Ethylene oxide on treatment with Grignard reagent give additive product which undergo hydrolysis to give primary alcohol as final product



26 The general molecular formula, which represents the homologous series of alkanols is **[CBSE AIPMT 2006]**

(a) $C_nH_{2n}O_2$ (b) $C_nH_{2n}O$
(c) $C_nH_{2n+1}O$ (d) $C_nH_{2n+2}O$

Ans. *(d)*

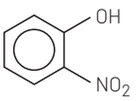
Alkanols are the derivatives of alkanes which are derived by the replacement of —H of alkanes with —OH (hydroxyl groups).

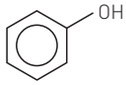
$\underset{\text{Alkanes}}{C_nH_{2n+2}} \xrightarrow[+OH]{-H} \underset{\text{Alkanols}}{C_nH_{2n+1}OH}$

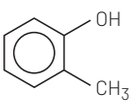
or $C_nH_{2n+2}O$

27 Which one of the following compounds is most acidic ?

[CBSE AIPMT 2005]

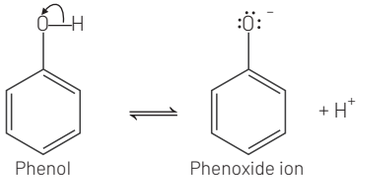
(a) $ClCH_2—CH_2OH$ (b) 

(c) 

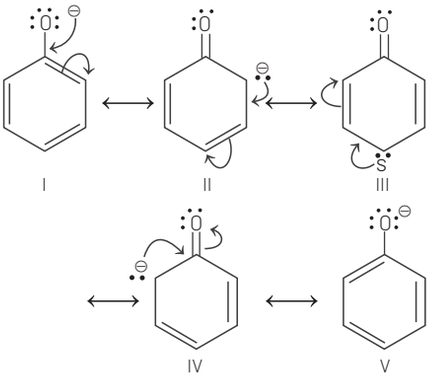
(d) 

Ans. *(c)*

Phenols are much more acidic than alcohols, due to the stabilisation of phenoxide ion by resonance



Phenoxide ion is stabilised due to following resonating structures :

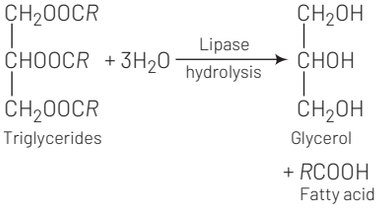


28 The enzyme which hydrolysis triglycerides into fatty acids and glycerol is called

[CBSE AIPMT 2004]

(a) maltase (b) lipase
(c) zymase (d) pepsin

Ans. *(b)*



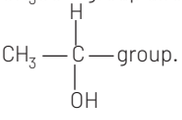
29 Which of the following will not form a yellow precipitate on heating with an alkaline solution of iodine?

[CBSE AIPMT 2004]

(a) $CH_3CH(OH)CH_3$
(b) $CH_3CH_2CH(OH)CH_3$
(c) CH_3OH
(d) CH_3CH_2OH

Ans. *(c)*

An organic compound form yellow precipitate of iodoform with I_2 in presence of alkali, if it has $CH_3CO—$ group directly or it has



(a) $CH_3CH(OH)CH_3 + I_2 \xrightarrow{NaOH} CH_3COCH_3 + 2HI + 3NaI + CH_3COO^-N^+a + 3H_2O$

$$CH_3COCH_3 + 3I_2 + 4NaOH \rightarrow \underset{\text{Yellow ppt}}{CHI_3\downarrow} + 3NaI + CH_3COO^-N^+a + 3H_2O$$

(b) $CH_3—CH_2CH(OH)CH_3 + I_2 \rightarrow CH_3—CH_2—\underset{\underset{O}{\|}}{C}—CH_3 + 2HI$

Ethyl methyl ketone

It gives iodoform test

$$CH_3CH_2—\underset{\underset{O}{\|}}{C}—CH_3 + 3I_2 + 4NaOH \longrightarrow \underset{\text{Yellow ppt}}{CHI_3\downarrow} + 3NaI + CH_3CH_2COONa + 3H_2O$$

(c) $CH_3OH + I_2 \rightarrow HCHO + 2HI$

It does not have methyl ketonic group, so it does not give yellow ppt. with I_2 in presence of alkali.

(d) $CH_3CH_2OH + I_2 \rightarrow CH_3—\underset{\underset{O}{\|}}{C}—H + 2HI$

$$CH_3—\underset{\underset{O}{\|}}{C}—H + 3I_2 + 4NaOH \rightarrow \underset{\text{Yellow ppt.}}{CHI_3} + HCOONa + 3NaI + 2H_2O$$

Due to the presence of $—COCH_3$ group, it gives Haloform test.

30 The —OH group of an alcohol or the —COOH group of a carboxylic acid can be replaced by —Cl using **[CBSE AIPMT 2004]**

(a) phosphorus pentachloride
(b) hypochlorous acid
(c) chlorine
(d) hydrochloric acid

Ans. *(a)*

The —OH group of alcohol or the —COOH group of a carboxylic acid is replaced by —Cl using phosphorus penta chloride (i.e. PCl_5)

$$\underset{\text{Alcohol}}{ROH} + PCl_5 \rightarrow RCl + POCl_3 + HCl$$

$$\underset{\text{Acid}}{RCOOH} + PCl_5 \rightarrow RCOCl + POCl_3 + HCl$$

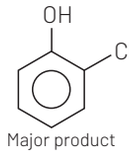
31 When phenol is treated with $CHCl_3$ and NaOH, the product formed is **[CBSE AIPMT 2002]**

(a) benzaldehyde (b) salicylaldehyde
(c) salicylic acid (d) benzoic acid

Ans. *(b)*

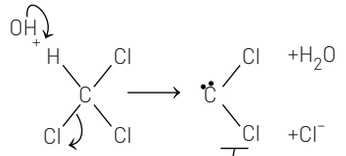
Reimer-Tiemann reaction When phenol is treated with chloroform and NaOH, salicylaldehyde is obtained.

$+ CHCl_3 + 3NaOH \longrightarrow$



$+ 3NaCl + 2H_2O$

Major product
(Salicylaldehyde)



Dichlorocarbene
(attacking species)

32 *n*-propyl alcohol and *iso*-propyl alcohol can be chemically distinguished by which reagent? **[CBSE AIPMT 2002]**

(a) PCl_5
(b) reduction
(c) oxidation with potassium dichromate
(d) ozonolysis

Ans. *(c)*

n-propyl alcohol and *iso*-propyl alcohol gives different products on oxidation with $K_2Cr_2O_7$

$$\underset{\substack{n\text{-propyl alcohol}\\1^\circ\text{ alcohol}}}{CH_3—CH_2—CH_2OH} \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} \underset{\text{Propionaldehyde}}{CH_3—CH_2—CHO}$$

$$\underset{\substack{\text{Iso-propyl alcohol}\\2^\circ\text{ alcohol}}}{CH_3—\underset{\underset{OH}{|}}{CH}—CH_3} \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} \underset{\text{Acetone}}{CH_3—\underset{\underset{O}{\|}}{C}—CH_3}$$

33 In preparation of alkene from alcohol using Al_2O_3, which is effective factor? **[CBSE AIPMT 2001]**

(a) Porosity of Al_2O_3
(b) Temperature
(c) Concentration
(d) Surface area of Al_2O_3

Ans. *(b)*

Temperature is the effective factor for dehydration of alcohol by Al_2O_3(dehydrating reagent).

$$R—CH_2—CH_2OH \xrightarrow[350^\circ - 380^\circ C]{Al_2O_3} R—CH{=}CH_2 + H_2O$$

While at 220-250°C, it forms ether.

34 Which of the following is correct? **[CBSE AIPMT 2001]**

(a) Cycloheptane is an aromatic compound
(b) Diastase is an enzyme
(c) Acetophenone is an ether
(d) All of the above

Ans. *(b)*

Diastase is an example of enzyme which is used for the conversion of starch into maltose by hydrolysis

$$\underset{\text{(starch)}}{2(C_6H_{10}O_5)_n} + nH_2O \xrightarrow[\text{enzyme}]{\text{Diastase}} \underset{\text{(maltose)}}{nC_{12}H_{22}O_{11}}$$

35 Which one of the following is correct? **[CBSE AIPMT 2001]**

(a) Reduction of any aldehyde gives secondary alcohol
(b) Reaction of vegetable oil with H_2SO_4 gives glycerine
(c) Alcoholic iodine with NaOH gives iodoform
(d) Sucrose on reaction with NaCl gives invert sugar

Ans. *(c)*

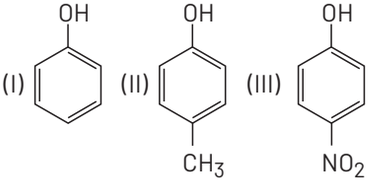
$$C_2H_5OH + 4I_2 + 6NaOH \rightarrow \underset{\text{Iodoform}}{CHI_3\downarrow} + HCOO^-N^+a + 5NaI + 5H_2O$$

Iodoform is a pale yellow solid.

36 The correct acidic order of following is **[CBSE AIPMT 2001]**

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

Ans.

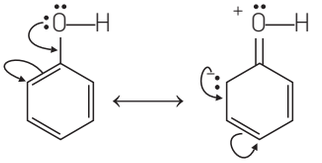


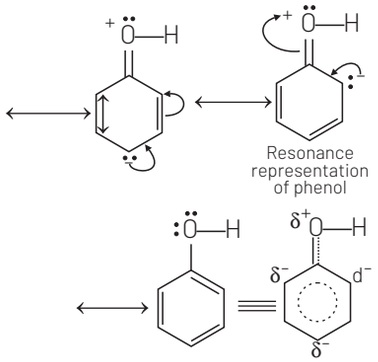
(a) I > II > III (b) III > I > II
(c) II > III > I (d) I > III > II

Ans. *(b)*

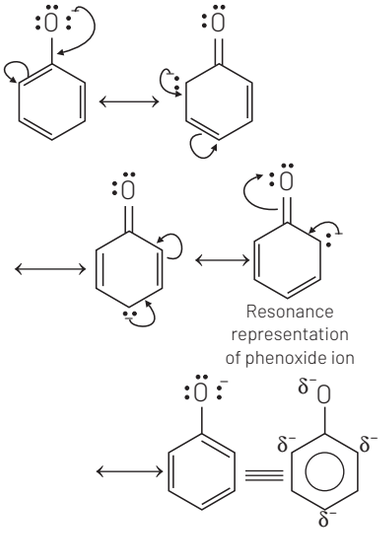
The acidic behaviour of phenols may be explained on the basis of two following reasons.

(a) Due to resonance (which is not possible in alcohols), the oxygen atom of the —OH group acquires a positive charge which helps in the release of a proton.





(b) In the dissociation of phenol to phenoxide ion and a proton the equilibrium lies mainly towards the right hand side as the resulting phenoxide ion is more stabilised by resonance as compared to phenol.



$$Ar—OH \rightleftharpoons ArO^- + H^+$$

The acidic strength of phenols depends on the nature of substituents present in the benzene nucleus.

Electron withdrawing groups like $—NO_2$, —CN, —CHO, —COOH, etc, when present at the *ortho* and *para*-positions with respect to phenolic group increases the acidity of phenol due to greater stabilisation of phenoxide ion. While the presence of electron releasing group like $—NH_2$, $—CH_3$, etc, decrease the acidity of phenols. This explains the following order of acidity

p-nitrophenol > phenol > *p*-cresol.

37 The ionisation constant of phenol is higher than that of ethanol because **[CBSE AIPMT 2000]**

(a) phenoxide ion is bulkier than ethoxide

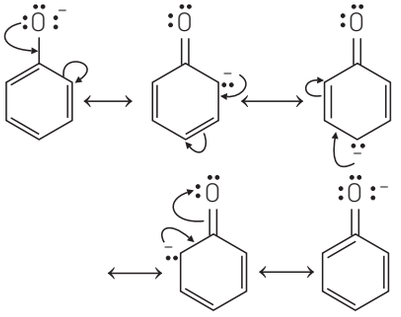
(b) phenoxide ion is stronger base than ethoxide

(c) phenoxide ion is stabilised through delocalisation

(d) phenoxide ion is less stable than ethoxide

Ans. ***(c)***

Resonance stabilisation of phenoxide ion



$$C_2H_5—O—H \rightleftharpoons C_2H_5—O^- + H^+$$

Stable — Unstable ethoxide ion (due to absence of resonance)

Phenoxide ion is more stable than ethoxide ion due to resonance. Therefore, the ionisation constant of phenol is higher than ethanol.

38 Propan-1-ol may be prepared by reaction of propene with **[CBSE AIPMT 2000]**

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

(b) H_3BO_3

(c) B_2H_6 / NaOH—H_2O_2

(d) H_2SO_4 / H_2O

Ans. ***(c)***

Hydroboration-oxidation reaction

$$6CH_3CH=CH_2 \xrightarrow{B_2H_6} 2(CH_3CH_2CH_2)_3B$$

Propene — *Tri-n*-propylborane

$$\xrightarrow[OH^-]{H_2O_2} 6CH_3CH_2CH_2OH$$

Propan-1-ol

39 Reaction of $H_2C—CH_2$ (epoxide) with $RMgX$ leads to formation of **[CBSE AIPMT 1998]**

(a) $RCHOHR$ (b) $RCHOHCH_3$

(c) RCH_2CH_2OH (d) $\begin{matrix} R \\ R \end{matrix}\!>\!CHCH_2OH$

Ans. ***(c)***

$$CH_2—CH_2 + \overset{\delta-}{R}—\overset{\delta}{Mg}X \longrightarrow$$

Ethylene oxide

$$R\,CH_2CH_2\overset{+1}{O}MgX$$

$$Mg(OH)X + R—CH_2—CH_2—OH \xleftarrow{H_2O/H^+}$$

40 The boiling point of *p*-nitrophenol is higher than that of *o*-nitrophenol because **[CBSE AIPMT 1994]**

(a) NO_2 group at *p*-position behaves in a different way from that at *o*-position

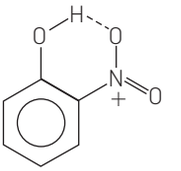
(b) intramolecular hydrogen bonding exists in *p*-nitrophenol

(c) there is intermolecular hydrogen bonding in *p*-nitrophenol

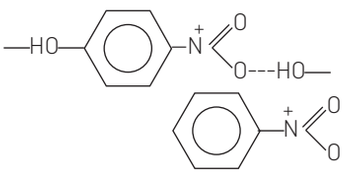
(d) *p*-nitrophenol has a higher molecular weight than *o*-nitrophenol

Ans. ***(c)***

The boiling point of *p*-nitrophenol is higher than that of *o*-nitrophenol because *p*-nitrophenol have intermolecular hydrogen bonding whereas *o*-nitrophenol have intramolecular H-bonding as given below.



o-nitrophenol easily give steam volatile



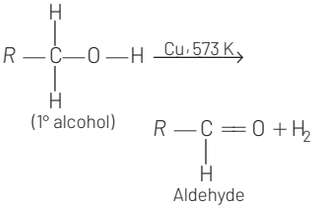
41 What is formed when a primary alcohol undergoes catalytic dehydrogenation? **[CBSE AIPMT 1993]**

(a) Aldehyde (b) Ketone

(c) Alkene (d) Acid

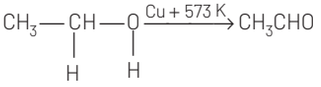
Ans. ***(a)***

Aldehydes can be prepared by the dehydrogenation of primary alcohols. It is carried out by passing the vapour of primary alcohol over reduced copper at 573 K.



1° alcohol gives aldehyde by catalytic dehydrogenation

e.g.



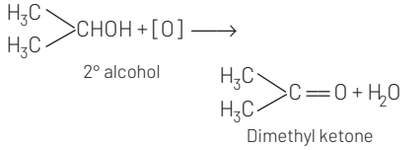
42 Which one of the following on oxidation gives a ketone?

[CBSE AIPMT 1993]

(a) Primary alcohol
(b) Secondary alcohol
(c) Tertiary alcohol (d) All of these

Ans. ***(b)***

Ketones can be prepared by the oxidation of secondary alcohols by using oxidising agent such as $K_2Cr_2O_7$ / H_2SO_4



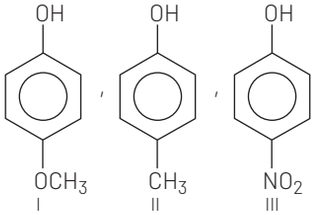
2° alcohol — Dimethyl ketone

43 Increasing order of acidic strength among *p*-methoxy phenol (I), *p*-methyl phenol (II) and *p*-nitrophenol (III) is

[CBSE AIPMT 1992]

(a) III, I, II (b) II, I, III (c) III, II, I (d) I, II, III

Ans. ***(d)***



Nitro group is an electron withdrawing group, so increases the acidic character of phenol. Whereas —CH_3 and —OCH_3 both are electron releasing groups, so it decrease the acidic character of phenol. But —CH_3 group is less electron donating or releasing, so *p*-methyl phenol is slightly more acidic as compare to *p*-methoxy phenol and *p*-nitro phenol is most acidic. So, the order of acidic character is

p-methoxy phenol < *p*-methyl phenol < *p*-nitro phenol.

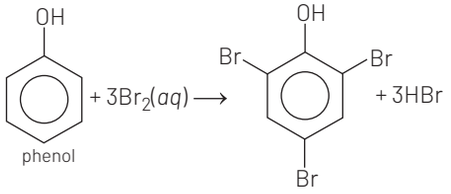
44 When phenol is treated with excess of bromine water, it gives

[CBSE AIPMT 1992]

(a) *m*-bromophenol
(b) *o*- and *p*-bromophenols
(c) 2,4-dibromophenol
(d) 2,4,6-tribromophenol

Ans. ***(d)***

Phenol reacts with bromine water (aqueous solution to give a precipitate of 2,4,6-tribromophenol) due to polar solvent.



phenol — 2,4,6-tribromophenol (White ppt)

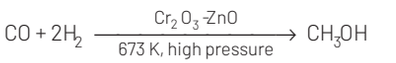
45 Methanol is industrially prepared by

[CBSE AIPMT 1992]

(a) oxidation of CH_4 by steam at 900°C
(b) reduction of HCHO using $LiAlH_4$
(c) reaction of HCHO with a solution of NaOH
(d) reduction of CO using H_2 and ZnO – Cr_2O_3

Ans. ***(d)***

Commercially methanol is prepared from water gas which is a mixture of carbon monoxide and hydrogen. In this method, CO gas is mixed with its half volume of hydrogen and is passed over heated Cr_2O_3 – ZnO catalyst at 673 K under high pressure.



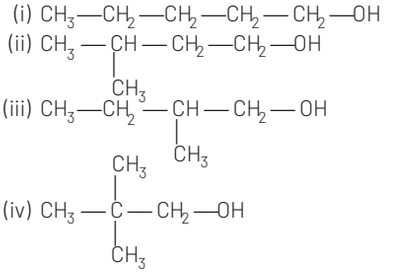
46 How many isomers of $C_5H_{11}OH$ will be primary alcohols?

[CBSE AIPMT 1992]

(a) 5 (b) 4 (c) 2 (d) 3

Ans. ***(b)***

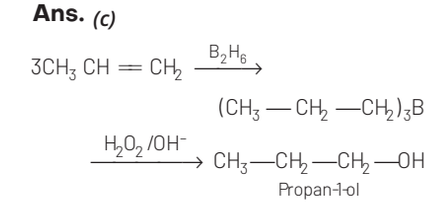
The primary alcohols isomers of $C_5H_{11}OH$ are



47 Propene, CH_3— CH═ CH_2 can be converted into 1-propanol by oxidation. Indicate which set of reagents amongst the following is ideal to affect the above conversion? **[CBSE AIPMT 1989]**

(a) $KMnO_4$ (alkaline)
(b) Osmium tetroxide (OsO_4 / CH_2Cl_2)
(c) B_2H_6 and alk H_2O_2
(d) O_3 / Zn

Ans. ***(c)***



Here, half mol of (B_2H_6) diborane react with propane by Markownikoff's addition it gives tripropyl borane called hydroboration. In presence of H_2O_2 in basic medium tripropyl borane gives alcohol. Remember that product is Anti-Markownikoff's rule that is 1-propanol. Reaction is called hydroboration oxidation.

48 The compound which reacts fastest with Lucas reagent is (at room temperature)

[CBSE AIPMT 1989]

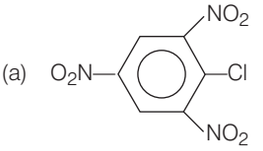
(a) butan-1-ol
(b) butan-2-ol
(c) 2-methyl propan-1-ol
(d) 2-methyl propan-2-ol

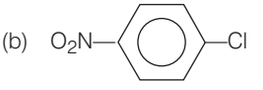
Ans. ***(d)***

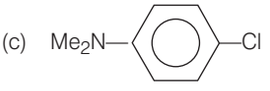
In Lucas test when Lucas reagent is treated with 1°, 2° and 3° alcohols, then turbidity appears, if turbidity is appeared immediately, then alcohol is tertiary. 2-methyl propan-2-ol is a tertiary alcohol. Hence, it reacts fastest with Lucas reagent.

49 Which chloro derivative of benzene among the following would undergo hydrolysis most readily with aq. NaOH to furnish the corresponding hydroxy derivative?

[CBSE AIPMT 1989]

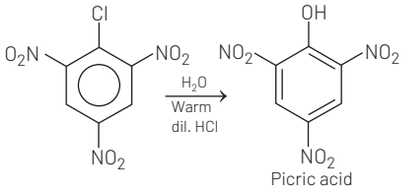


(b) 

(c) 

(d) C_6H_5—Cl

Ans. *(a)*



Picric acid

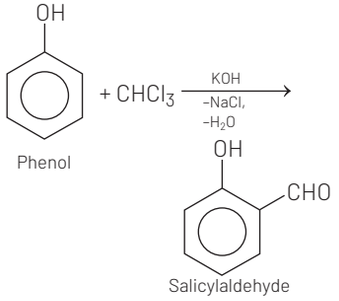
or 2, 4, 6-trinitrochlorobenzene

50 When phenol is heated with $CHCl_3$ and alcoholic KOH, salicylaldehyde is produced. This reaction is known as **[CBSE AIPMT 1989, 88]**

(a) Rosenmund's reaction
(b) Reimer-Tiemann reaction
(c) Friedel-Craft's reaction
(d) Sommelet reaction

Ans. *(b)*

When phenol is heated with chloroform ($CHCl_3$) and alcoholic KOH, salicylaldehyde is formed. This reaction is known as **Reimer-Tiemann reaction**.



Phenol

Salicylaldehyde

51 Lucas reagent is **[CBSE AIPMT 1988]**

(a) conc. HCl and anhy. $ZnCl_2$
(b) conc. HNO_3 and anhy. $ZnCl_2$
(c) conc. HCl and hydrous $ZnCl_2$
(d) conc. HNO_3 and hydrous $ZnCl_2$

Ans. *(a)*

The equimolar mixture of concentrated hydrochloric acid and anhydrous $ZnCl_2$ is called Lucas reagent. Lucas reagent is used to distinguish between 1°, 2° and 3° alcohols.

TOPIC 2
Ethers

52 The compound which shows metamerism is **[NEET 2021]**

(a) C_5H_{12} (b) C_3H_8O (c) C_3H_6O (d) $C_4H_{10}O$

Ans. *(d)*

Metamerism compound which have same molecular formula but different number of carbon atoms on either sides of functional group are known as metamers and this phenomenon is known as metamerism.

(a) C_5H_{12} contains no functional group. So, it cannot show metamerism.

(b) C_3H_8O has ether functional group in which only one arrangement is possible. So, it does not show metamerism.

$CH_3—O—CH_2—CH_3$

(c) C_3H_6O has carbonyl functional group in which following two arrangements are possible.

$CH_3—\overset{\overset{O}{\|}}{C}—CH_3$, CH_3CH_2CHO

So, it shows functional group isomerism and does not show metamerism.

(d) $C_4H_{10}O$ has ether functional group in which following two arrangements are possible. So, it shows metamerism.

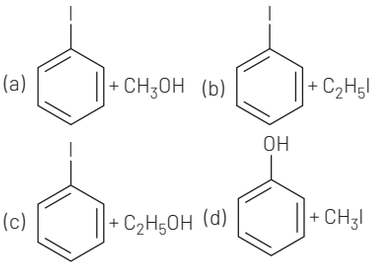
$CH_3—O—CH_2—CH_2—CH_3$

Methoxy propane

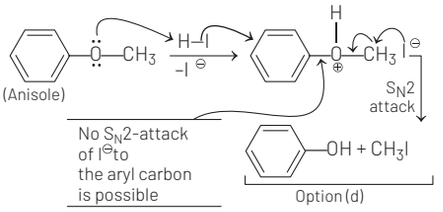
$CH_3—CH_2—O—CH_2—CH_3$

Ethoxy ethane

53 Anisole on cleavage with HI gives: **[NEET (Sep.) 2020]**



Ans. *(d)*



So, even with excess of HI anisole will give always phenol and methyl iodide (as in option-d)

54 The major products *C* and *D* formed in the following reactions respectively are **[NEET (Odisha) 2019]**

$H_3C—CH_2—CH_2—OC(CH_3)_3 \xrightarrow[\Delta]{\text{Excess HI}} C + D$

(a) $H_3C—CH_2—CH_2—I$ and $I—C(CH_3)_3$
(b) $H_3C—CH_2—CH_2—OH$ and $I—C(CH_3)_3$
(c) $H_3C—CH_2—CH_2—I$ and $HO—C(CH_3)_3$
(d) $H_3C—CH_2—CH_2—OH$ and $HO—C(CH_3)_3$

Ans. *(a)*

Ethers are readily cleaved by heating in presence of halogen acids to form alcohol and an alkyl halide. In case of unsymmetrical ethers, halogen goes preferentially with smaller alkyl group or more stable carbocation.

If excess of acid is used then only alkyl halide is formed because alcohol formed reacts further with halogen acid to form corresponding alkyl halide.

$CH_3CH_2CH_2OC(CH_3)_3 \xrightarrow[\Delta]{HI} CH_3CH_2CH_2OH + (CH_3)_3I$ *'D'*

Δ | Excess HI

$CH_3CH_2CH_2I$ *'C'*

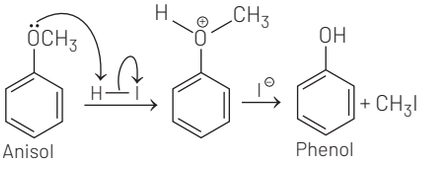
55 The heating of phenyl-methyl ethers with HI produces. **[NEET 2017]**

(a) ethyl chlorides (b) iodobenzene
(c) phenol (d) benzene

Ans. *(c)*

Thinking Process *This problem is based on the resonance stabilisation.*

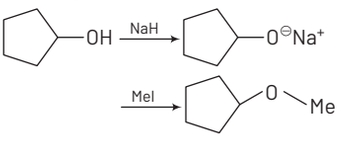
In anisol, methyl phenyl oxonium ion is formed by protonation of ether. The bond between $O—CH_3$ is weaker than the bond between $O—C_6H_5$, because the carbon of phenyl group is sp^2 -hybridised and there is a partial double bond character. Thus, the reaction yields phenol and alkyl halide.



Anisol

Phenol

56 The reaction

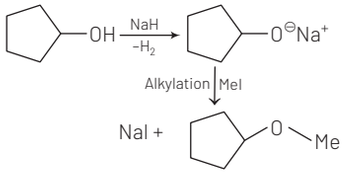


can be classified as **[NEET 2016, Phase I]**

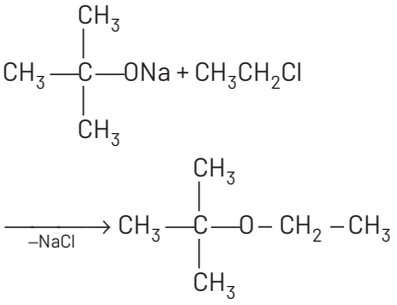
(a) Alcohol formation reaction
(b) Dehydration reaction
(c) Williamson alcohol synthesis reaction
(d) Williamson ether synthesis reaction

Ans. *(d)*

The formation of ether from alcohol in the presence of base followed by alkylation is known as Williamson ether synthesis reaction.



57 The reaction,

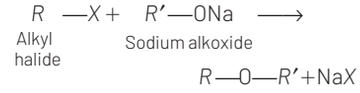


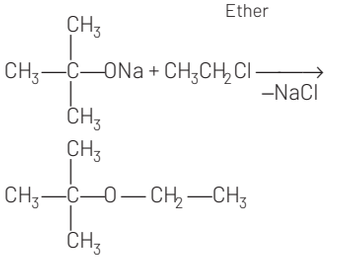
is called **[CBSE AIPMT 2015]**

(a) Williamson synthesis
(b) Williamson continuous etherification process
(c) Etard reaction
(d) Gatterman-Koch reaction

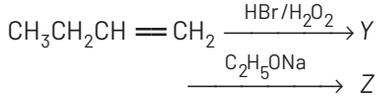
Ans. *(a)*

The reaction of alkyl halides with sodium alkoxide or sodium phenoxide to form ethers is called Williamson synthesis. Here, in this reaction alkyl halide should be primary and alkoxide, should be bulkier as shown below,





58 Identity *Z* in the sequence of reactions, **[CBSE AIPMT 2014]**



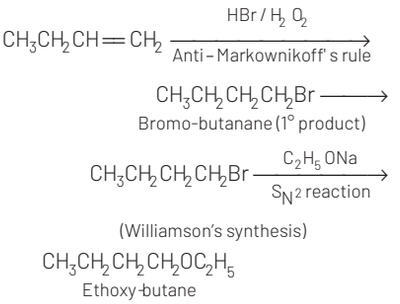
(a) $CH_3-(CH_2)_3-O-CH_2CH_3$

(b) $(CH_3)_2CH_2-O-CH_2CH_3$

(c) $CH_3(CH_2)_4-O-CH_3$

(d) $CH_3CH_2-CH(CH_3)-O-CH_2CH_3$

Ans. *(a)*



59 Among the following sets of reactants which one produces anisole? **[CBSE AIPMT 2014]**

(a) CH_3CHO, *R*MgX

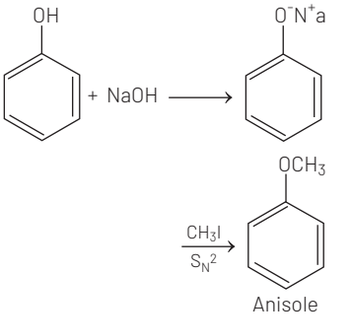
(b) C_6H_5OH, NaOH, CH_3I

(c) C_6H_5OH, neutral $FeCl_3$

(d) $C_6H_5-CH_3$, CH_3COCl, $AlCl_3$

Ans. *(b)*

Williamson's synthesis



60 Among the following ethers which one will produce methyl alcohol on treatment with hot concentrated HI? **[CBSE AIPMT 2013]**

(a) $CH_3-CH_2-CH_2-CH_2-O-CH_3$

(b) $CH_3-CH_2-C(H)(CH_3)-O-CH_3$

(c) $CH_3-C(CH_3)_2-O-CH_3$

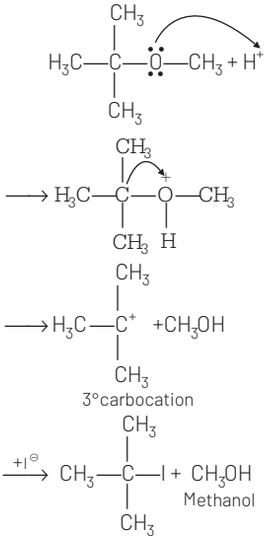
(d) $CH_3-CH(CH_3)-CH_2-O-CH_3$

Ans. *(c)*

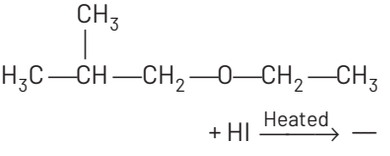
The ether which gives more stable carbocation, forms CH_3OH as one of the product with hot conc. HI. The order of stability of carbocation is

$3° > 2° > 1°$

Thus, $CH_3-C(CH_3)_2-OCH_3$ gives CH_3OH as one of the product. The reaction proceeds as



61 The reaction



Which of the following compounds will be formed? **[CBSE AIPMT 2007]**

(a) $H_3C-CH(CH_3)-CH_2-I + CH_3CH_2OH$

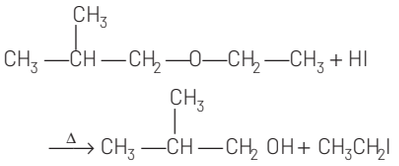
(b) $CH_3-CH(CH_3)-CH_3 + CH_3CH_2OH$

(c) $CH_3-CH(CH_3)-CH_2OH + CH_3CH_3$

(d) $H_3C-CH(CH_3)-CH_2OH + CH_3-CH_2-I$

Ans. *(d)*

When conc. HI or HBr reacts with ether, the corresponding alcohol and alkyl iodide is formed. When there is a case of mixed ethers the halogen atom attaches to the smaller alkyl group, due to steric effect.



62 The major organic product in the reaction, $CH_3OCH(CH_3)_2 + HI \longrightarrow$ Product, is/are **[CBSE AIPMT 2006]**

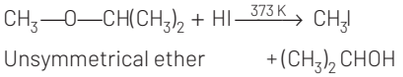
(a) $CH_3OH + (CH_3)_2CHI$

(b) $ICH_2OCH(CH_3)_2$

(c) $CH_3O\underset{|}{\overset{|}{C}}(CH_3)_2$

(d) $CH_3I + (CH_3)_2CHOH$

Ans. *(d)*



Unsymmetrical ether $+(CH_3)_2CHOH$

In case of unsymmetrical ether, the alkyl halide is always formed from smaller alkyl group. This happens, because I^- ion being larger in size approaches smaller alkyl group to avoid steric hindrance.

63 Ethanol and dimethyl ether form a pair of functional isomers. The boiling point of ethanol is higher than that of dimethyl ether due to the presence of **[CBSE AIPMT 1993]**

(a) H-bonding in ethanol

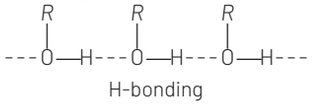
(b) H-bonding in dimethyl ether

(c) $-CH_3$ group in ethanol

(d) $-CH_3$ group in dimethyl ether

Ans. *(a)*

Alcohols have higher boiling points as compared to other organic compounds of similar molecular masses such as ethers. This is due to the presence of intermolecular hydrogen bonding in alcohols which is absent in ethers. Because of hydrogen bonding in alcohols, these exist as associated molecules rather than discrete molecules. Consequently, a large amount of energy is required to break these bonds and therefore, their boiling points are high.



H-bonding

64 Which one is formed when sodium phenoxide is heated with ethyl iodide? **[CBSE AIPMT 1988]**

(a) Phenetole

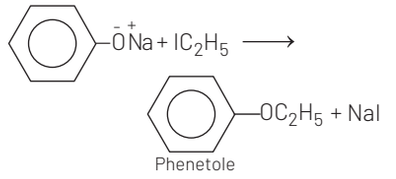
(b) Ethyl phenyl alcohol

(c) Phenol

(d) None of the above

Ans. *(a)*

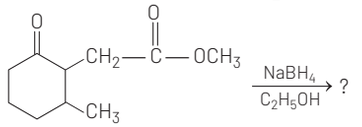
When sodium phenoxide ($C_6H_5O^-N^+a$) is heated with ethyl iodide (C_2H_5I) it form ethyl phenyl ether which is also called **phenetole**. This reaction is called **Williamson's synthesis**



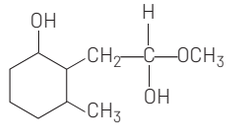
Phenetole

TOPIC 3
Aldehydes and Ketones

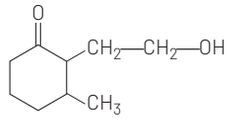
65 The product formed in the following chemical reaction is **[NEET 2021]**



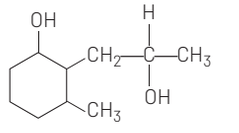
(a)



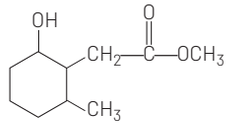
(b)



(c)

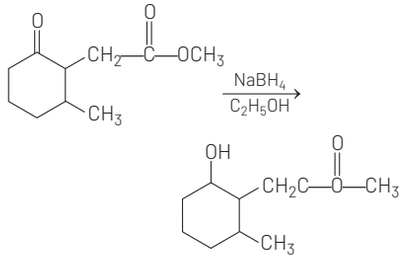


(d)

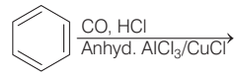
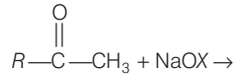
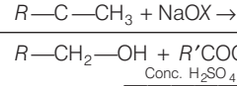
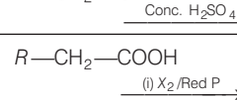


Ans. *(d)*

$NaBH_4$ is a weak reducing agent. It can reduce aldehyde/ketone to alcohol but cannot reduce ester group.



66 Match List-I with List-II.

	List-I		List-II
A.		1.	Hell-Volhard-Zelinsky reaction
B.		2.	Gattermann-Koch reaction
C.		3.	Haloform reaction
D.		4.	Esterification

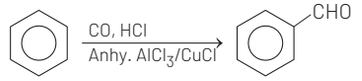
[NEET 2021]

Choose the correct answer from the options given below.

	A	B	C	D		A	B	C	D
(a)	4	1	2	3	(b)	3	2	1	4
(c)	1	4	3	2	(d)	2	3	4	1

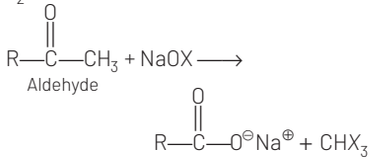
Ans. *(d)*

A. **Gattermann-Koch reaction** Benzene or its derivatives are treated with CO and HCl in presence of anhydrous $AlCl_3$/ CuCl.



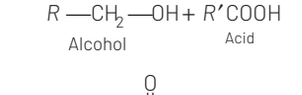
Benzene Benzaldehyde

B. **Haloform reaction** Treatment of carbonyl compound having atleast one methyl group attached to the C = O with X_2 / NaOH or NaOX.

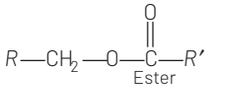


Aldehyde

C. **Esterification** Carboxylic acid reacts with an alcohol in acidic medium.

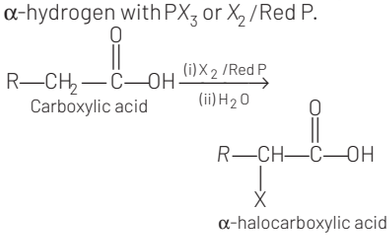


Alcohol Acid



Ester

D. Hell-Volhard Zelinsky reaction Treatment of carboxylic acid having α-hydrogen with PX_3 or X_2 / Red P.



Carboxylic acid α-halocarboxylic acid

Hence, correct match is

A → 2, B → 3, C → 4, D → 1.

67 What is the IUPAC name of the organic compound formed in the following chemical reaction?

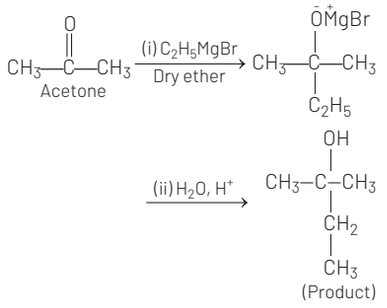
[NEET 2021]

$$\text{Acetone} \xrightarrow[(ii)\ H_2O,\ H^+]{(i)\ C_2H_5MgBr,\ \text{Dry ether}} \text{product}$$

(a) 2-methyl propan 2-ol
(b) pentan-2-ol
(c) pentan-3-ol
(d) 2-methyl butan-2-ol

Ans. *(d)*

Acetone on reaction with Grignard reagent and on further hydrolysis gives 2-methyl butan-2-ol as follows



IUPAC name of product is 2-methylbutan-2-ol.

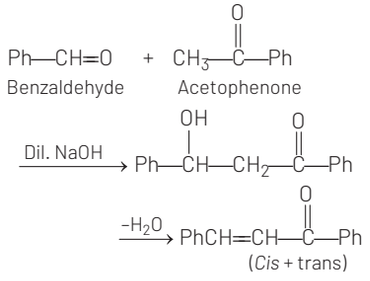
68 Reaction between benzaldehyde and acetophenone in presence of dilute NaOH is known as

[NEET (Sept.) 2020]

(a) Cannizzaro's reaction
(b) Cross Cannizzaro's reaction
(c) Cross aldol condensation
(d) Aldol condensation

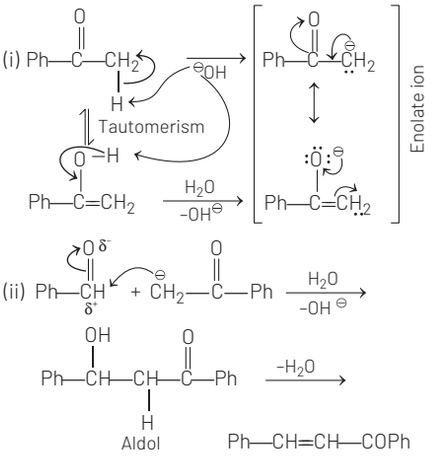
Ans. *(c)*

Dilute NaOH is the reagent for aldol condensation. Dilute NaOH process enolate ion from acetophenone which attacks benzaldehyde to give aldol.

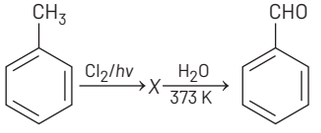


It is cross aldol condensation or Claisen-Schmidt reaction or Claisen reaction.

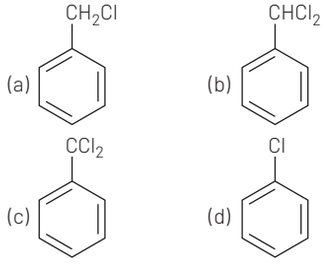
Mechanism



69 Identify compound *X* in the following sequence of reactions.

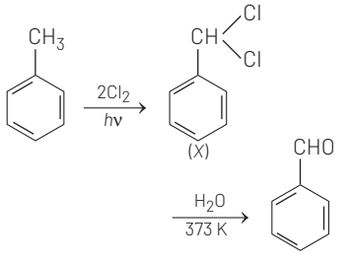


[NEET (Sept.) 2020]



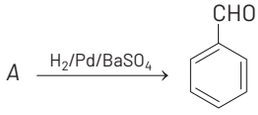
Ans. *(b)*

An 1, 1-*gem*-dihalide on hot hydrolysis (H_2O/373 K) can produce an aldehyde.



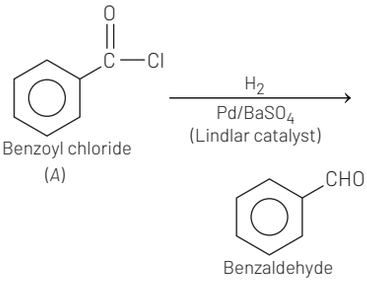
70 Identify compound (*A*) in the following reaction.

[NEET (Oct.) 2020]



(a) Benzoyl chloride (b) Toluene
(c) Acetophenone (d) Benzoic acid

Ans. *(a)*



It is Rosenmund reaction, in which an acid chloride gets converted into an aldehyde.

71 Predict the correct intermediate and product in the following reaction.

[NEET 2017]

$$H_3C—C\equiv CH \xrightarrow[HgSO_4]{H_2O,\ H_2SO_4} \underset{(A)}{\text{Intermediate}} \longrightarrow \underset{(B)}{\text{Product}}$$

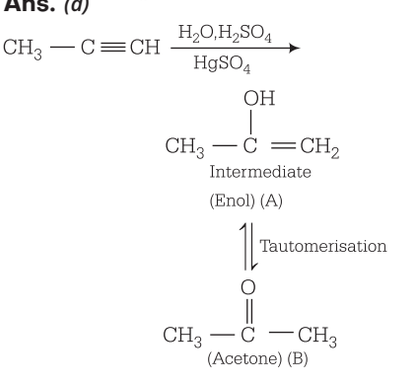
(a) $A = H_3C—C(SO_4)=CH_2$;
$B = H_3C—C(=O)—CH_3$

(b) $A = H_3C—C(OH)=CH_2$;
$B = H_3C—C(SO_4)=CH_2$

(c) $A = H_3C—C(=O)—CH_3$;
$B = H_3C—C\equiv CH$

(d) $A = H_3C—C(OH)=CH_2$;
$B = H_3C—C(=O)—CH_3$

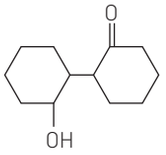
Ans. *(d)*

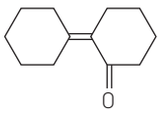


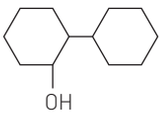
Therefore, $A = CH_3-\underset{\underset{OH}{|}}{C}=CH_2$

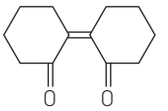
$B = CH_3-\overset{\overset{O}{||}}{C}-CH_3$

72 Of the following which is the product formed when cyclohexanone undergoes aldol condensation followed by heating? **[NEET 2017]**

(a) 

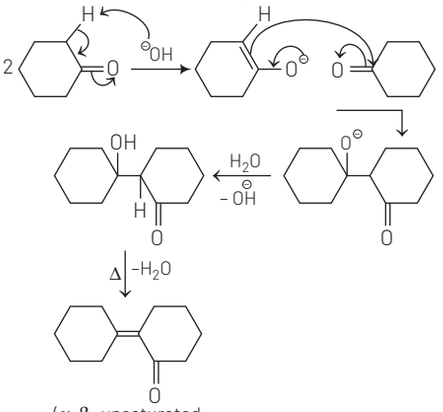
(b) 

(c) 

(d) 

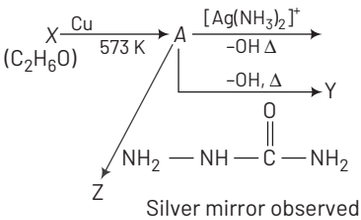
Ans. *(b)*

Aldehydes and ketones containing α—H atoms undergo aldol condensation in presence of dilute alkali as catalyst and gives α, β unsaturated compound with the elimination of H_2O molecule.



(α, β- unsaturated compound)

73 Consider the reactions,



Silver mirror observed

Identify *A*, *X*, *Y* and *Z* **[NEET 2017]**

(a) *A*-methoxymethane, *X*-ethanoic acid, *Y*-acetate ion, *Z*-hydrazine

(b) *A*-methoxymethane, *X*-ethanol, *Y*-ethanoic acid, *Z*-semicarbazide

(c) *A*-ethanal, *X*-Acetaldelyde, *Y*-but-2-enal, *Z*-semicarbazone

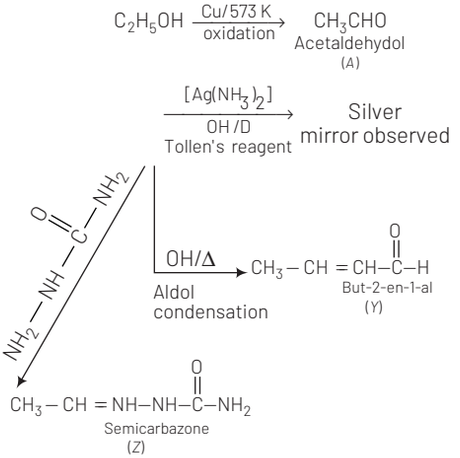
(d) *A*-ethanol, *X*-acetaldehyde, *Y*-butanone, *Z*-hydrazone

Ans. *(c)*

Aldehydes gives silver mirror test so, '*X*' may be alcohol which is oxidised by Cu gives aldehydes.

Therefore,

A is acetaldehyde (CH_3CHO)



74 The product formed by the reaction of an aldehyde with a primary amine is

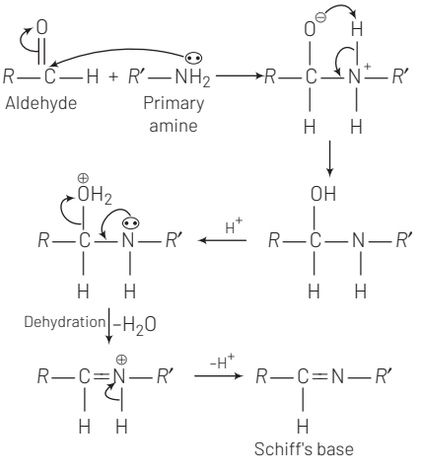
(a) Ketone **[NEET 2016, Phase I]**

(b) Carboxylic acid

(c) Aromatic acid

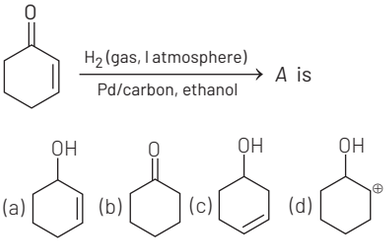
(d) Schiff base

Ans. *(d)*



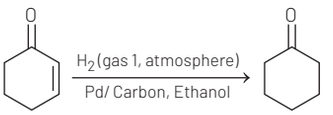
Schiff's base

75 The correct structure of the product *A* formed in the reaction **[NEET 2016, Phase II]**



Ans. *(b)*

In presence of Pd-catalyst, selective reduction of α,β-unsaturated carbonyl is observed as hydrogenation takes place of carbon-carbon double bond only.



76 Treatment of cyclopentanone

 with methyl lithium

gives which of the following species? **[CBSE AIPMT 2015]**

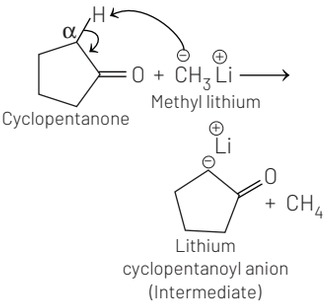
(a) Cyclopentanonyl anion

(b) Cyclopentanonyl cation

(c) Cyclopentanonyl radical

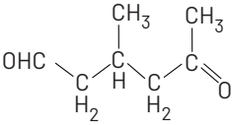
(d) Cyclopentanonyl biradical

Ans. *(a)*

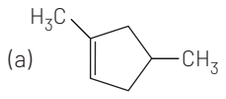
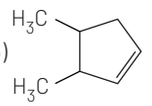


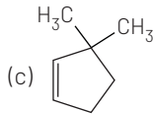
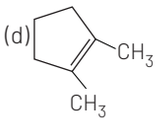
Here, CH_3Li abstract is an active proton from cyclo pentanone forming methane leaving behind an intermediate lithium cyclopentanoyl anion.

77 A single compound of the structure is

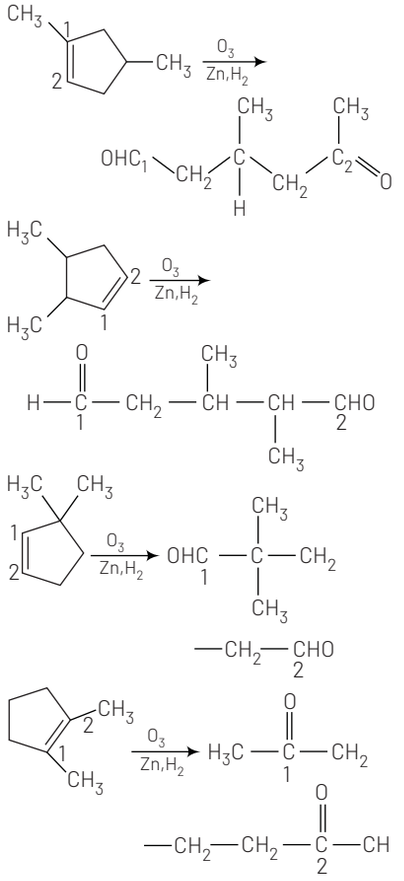


obtainable from ozonolysis of which of the following cyclic compounds? **[CBSE AIPMT 2015]**

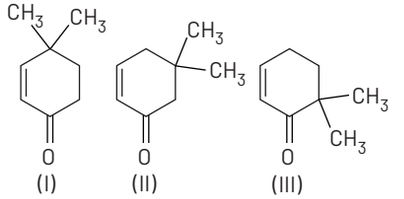
(a)  (b) 

(c)  (d) 

Ans. *(a)*



78 Given,



(I) (II) (III)

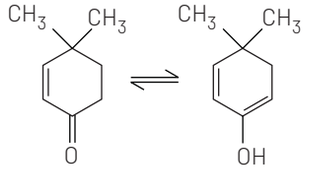
Which of the given compounds can exhibit tautomerism?

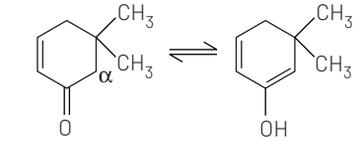
[CBSE AIPMT 2015]

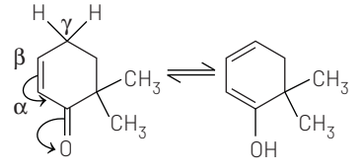
(a) I and II
(b) I and III
(c) II and III
(d) I, II and III

Ans. *(a)*

In keto-enol tautomerism keto form should have α-hydrogen (structure I and II).

I. 

II. 

III. 

Here, γ-H participates in tautomerism.

79 An organic compound *X* having molecular formula $C_5H_{10}O$ yields phenyl hydrazone and gives negative response to the iodoform test and Tollen's test. It produces *n*-pentane on reduction. *X* could be

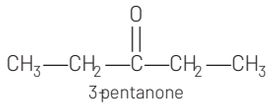
[CBSE AIPMT 2015]

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

Ans. *(c)*

Since, the compound *X* yields phenyl hydrazone and gives negative response to the iodoform test and Tollen's test , it must contain a $C=O$ group but is neither a methyl ketone nor an aldehyde.

The structure of *X* could be



3-pentanone

having molecular formula $C_5H_{10}O$.

80 Reaction of a carbonyl compound with one of the following reagents involves nucleophilic addition followed by the elimination of water. The reagents is

[CBSE AIPMT 2015]

(a) a Grignard reagent
(b) hydrazine in presence of feebly acidic solution
(c) hydrocyanic acid
(d) sodium hydrogen sulphite

Ans. *(*)*

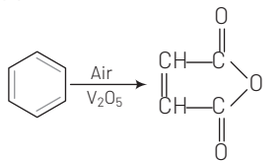
Reaction of carbonyl compounds with ammonia derivatives give addition product followed by the elimination reaction. Slightly acidic medium generate a nucleophilic centre for the attack of weak base like ammonia derivatives.

81 The oxidation of benzene by V_2O_5 in the presence of air produces

[CBSE AIPMT 2015]

(a) benzoic anhydride
(b) maleic anhydride
(c) benzoic acid
(d) benzaldehyde

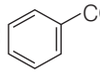
Ans. *(b)*



Maleic anhydride

82 Reaction by which benzaldehyde cannot be prepared? **[NEET 2013]**

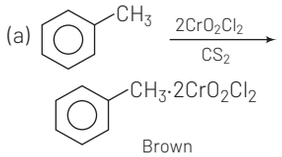
(a)  + CrO_2Cl_2 and CS_2 followed by H_3O^+

(b)  + H_2 in presence of Pd-$BaSO_4$

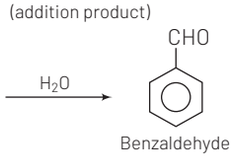
(c)  + CO + HCl in presence of anhy. $AlCl_3$

(d)  + Zn / Hg and conc. HCl

Ans. *(d)*

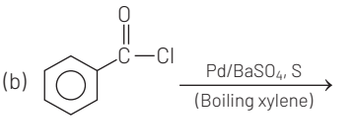
(a) 

Brown (addition product)

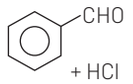


Benzaldehyde

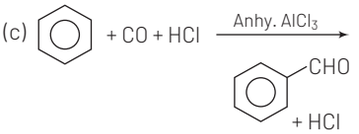
This reaction is known as **Etard reaction.**

(b) 

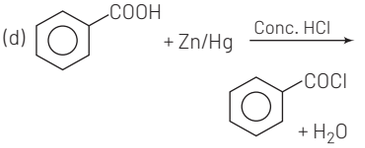
Benzoyl chloride



This reaction is called **Rosenmund reaction.**

(c) 

The above reaction is known as **Gattermann-Koch** aldehyde synthesis.

(d) 

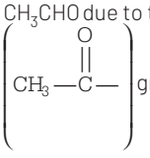
Thus, from the reactants given in option (d) benzaldehyde is not obtained.

83 CH_3CHO and $C_6H_5CH_2CHO$ can be distinguished chemically by **[CBSE AIPMT 2012]**

(a) Benedict test
(b) iodoform test
(c) Tollen's reagent test
(d) Fehling solution test

Ans. *(b)*

CH_3CHO and $C_6H_5CH_2CHO$ both being aliphatic aldehydes react with Tollen's reagent, Fehling solution and Benedict solution. So, these reagents cannot be used to distinguish them.

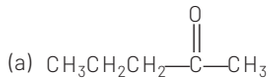
CH_3CHO due to the presence of  group reacts with NaOH and I_2 to give yellow crystals of iodoform while $C_6H_5CH_2CHO$ does not react with it.

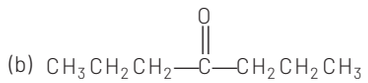
$CH_3CHO + 3I_2 + 4NaOH \longrightarrow CHI_3 + HCOONa + 3NaI + 3H_2O$

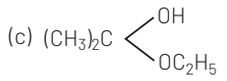
$C_6H_5CH_2CHO + I_2 + NaOH \longrightarrow$ No reaction

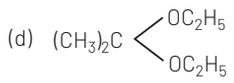
Thus, CH_3CHO and $C_6H_5CH_2CHO$ can be distinguished by iodoform test.

84 Acetone is treated with excess of ethanol in the presence of hydrochloric acid. The product obtained is **[CBSE AIPMT 2012]**

(a) 

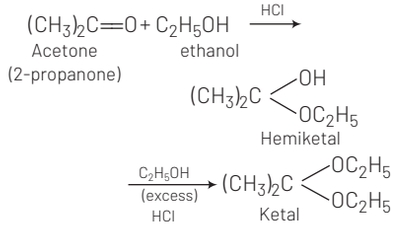
(b) 

(c) 

(d) 

Ans. *(d)*

When carbonyl compounds are treated with alcohol, they form hemiacetal (hemiketal and acetal/ketal.)



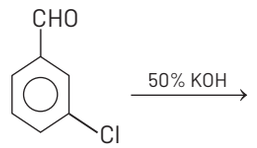
Acetone (2-propanone)

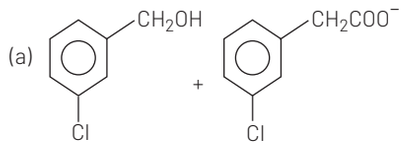
Hemiketal

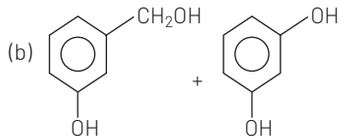
Ketal

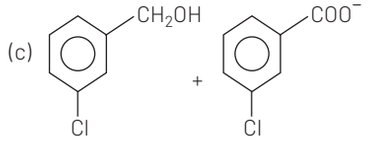
NOTE Formation of hemiketal is a nucleophilic addition reaction.

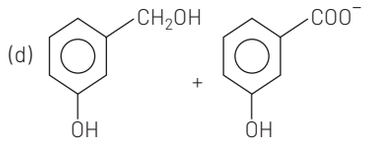
85 Predict the products in the given reaction, **[CBSE AIPMT 2012]**



(a) 

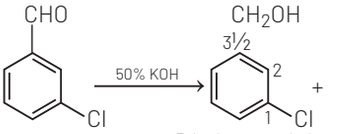
(b) 

(c) 

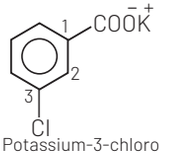
(d) 

Ans. *(c)*

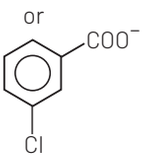
When benzaldehyde is treated with 50% alkali, it undergoes oxidation to give an acid salt as well as reduction to give an alcohol. This reaction is called Cannizaro's reaction.



3-hydroxy methyl chlorobenzene



Potassium-3-chloro benzoate

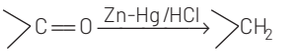
or 

86 Clemmensen reduction of a ketone is carried out in the presence of which of the following? **[CBSE AIPMT 2011]**

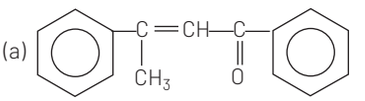
(a) Zn-Hg with HCl
(b) $LiAlH_4$
(c) H_2 and Pt as catalyst
(d) Glycol with KOH

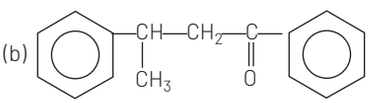
Ans. *(a)*

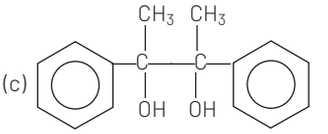
The reducing agent used in Clemmensen reduction is Zn-Hg and HCl.

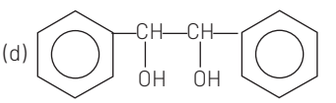


87 Acetophenone when reacted with a base, C_2H_5ONa, yields a stable compound which has the structure **[CBSE AIPMT 2008]**

(a) 

(b) 

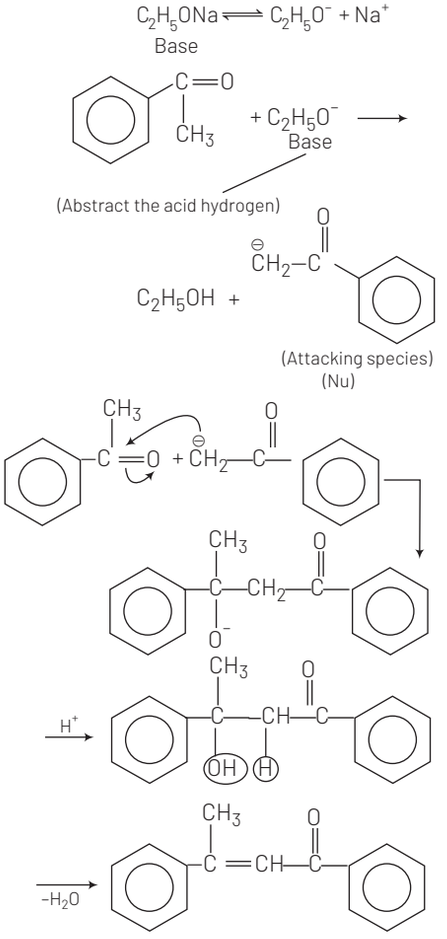
(c) 

(d) 

Ans. *(a)*

Aldehydes and ketones with α-hydrogen atom, when reacted with a base yields

aldol which on heating loses water molecule to give α, β-unsaturated aldehydes or ketones. This reaction is called aldol condensation reaction.



88 A strong base can abstract an α-hydrogen from **[CBSE AIPMT 2008]**

(a) alkene (b) amine
(c) ketone (d) alkane

Ans. *(c)*

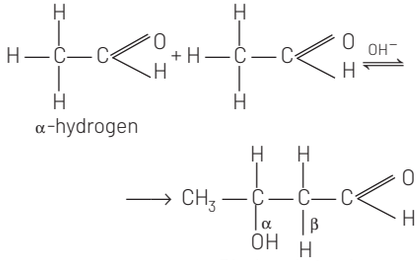
Since the carbonyl carbon is electron deficient, so most susceptible to attack by nucleophilic reagents or base. A base increases the acidity of hydrogen atom attached to the α-C of the ketones or aldehydes. That's why α-hydrogen is easily abstracted from ketones by a base, e.g. in aldol condensation reaction, α-hydrogen atom of aldehyde or ketone is abstracted by a strong base.

89 The product formed in aldol condensation is **[CBSE AIPMT 2007]**

(a) a beta-hydroxy acid
(b) a beta-hydroxy aldehyde or a beta-hydroxy ketone
(c) an alpha-hydroxy aldehyde or ketone
(d) an alpha, beta unsaturated ester

Ans. *(b)*

Condensation between two molecules of an aldehyde or a ketone having atleast one α-hydrogen atom in presence of a base to form a β-hydroxy aldehyde or β-hydroxy ketone is known as aldol condensation. Aldol condensation are divided into two parts one is self aldol condensation and another is cross-aldol condensation, when both molecules are same then it is called self aldol and *vice versa*.



90 Which one of the following on treatment with 50% aqueous sodium hydroxide yields the corresponding alcohol and acid? **[CBSE AIPMT 2007]**

(a) $C_6H_5CH_2CHO$
(b) C_6H_5CHO
(c) $CH_3CH_2CH_2CHO$
(d) $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

Ans. *(b)*

Aldehydes which do not have any α-hydrogen atom when heated with a concentrated solution of NaOH undergo a simultaneous oxidation and reduction (disproportionation) forming a salt of carboxylic acid and alcohol. This reaction is called Cannizaro reaction.

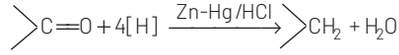
$2C_6H_5CHO + NaOH \longrightarrow \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + \underset{\text{Sodium benzoate}}{C_6H_5\overset{-}{C}OO^+Na}$

91 Reduction of aldehydes and ketones into hydrocarbons using zinc amalgam and conc. HCl is called **[CBSE AIPMT 2007]**

(a) Clemmensen reduction
(b) Cope reduction
(c) Dow reduction
(d) Wolff-Kishner reduction

Ans. *(a)*

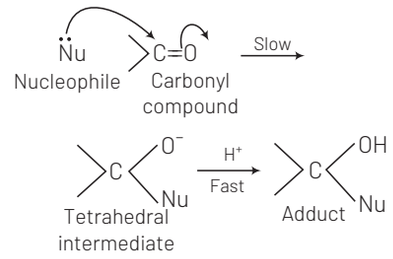
Clemmensen reduction Aldehydes and ketones are reduced to the corresponding alkanes by means of amalgamated zinc and HCl.



92 Nucleophilic addition reaction will be most favoured in **[CBSE AIPMT 2006]**

(a) $CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$
(b) $(CH_3)_2C=O$
(c) CH_3CH_2CHO
(d) CH_3CHO

Ans. *(d)*

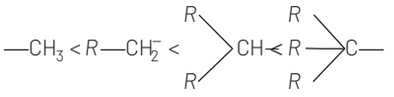


The carbonyl compounds undergo nucleophilic addition reaction because oxygen is more electronegative than carbon. As such, it withdraws shared π-electron pair towards itself and gets partial negative charge, therefore carbon get partial positive charge and becomes susceptible to nucleophilic attack.

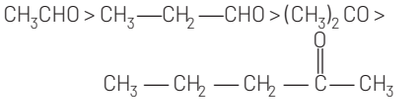
Aldehydes are more reactive than ketones towards nucleophiles. This can be explained on the basis of inductive effect as well as steric effect. The addition of nucleophiles is based upon the positive charge present on carbon atom of $>C=O$ group. In aldehyde $>C=O$ group is present with at least one alkyl group (except formaldehyde) which has +*I*-effect (electron donating effect) and which decreases the positive charge of carbon, thereby making the attack to nucleophile difficult. The nucleophilic attack becomes more difficult in ketones having minimum of two alkyl groups.

Hence, by means of attachment of alkyl groups (due to +*I*-effect) rate of nucleophilic addition decreases. That means e^- density at C-atom decreases, nucleophilic addition reaction increases.

Order of +*I*-effect in alkyl group



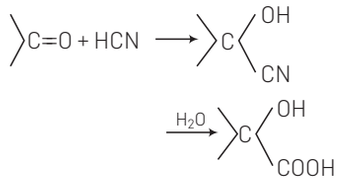
Order of nucleophilic addition in given carbonyl compound is



93 A carbonyl compound reacts with hydrogen cyanide to form cyanohydrin which on hydrolysis forms a racemic mixture of α-hydroxy acid. The carbonyl compound is **[CBSE AIPMT 2006]**

(a) acetaldehyde (b) acetone
(c) diethyl ketone (d) formaldehyde

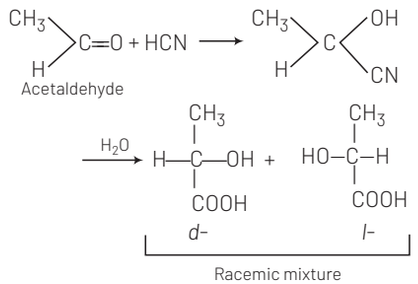
Ans. ***(a)***



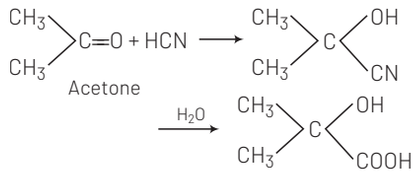
(It is α-hydroxy acid)

In this reaction, by the complete hydrolysis of cyanide gives acid and partial hydrolysis gives amide.

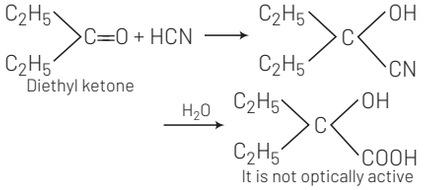
If it is racemic mixture, therefore such C-atom must be asymmertic carbon atom.



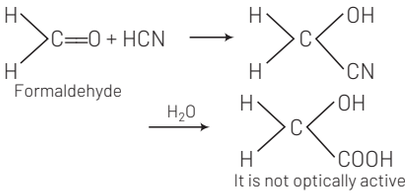
Racemic mixture



It is not optically active racemic mixture is nor formed



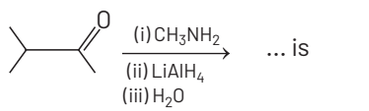
It is not optically active



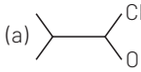
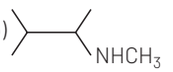
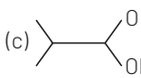
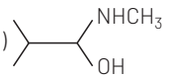
Formaldehyde

It is not optically active

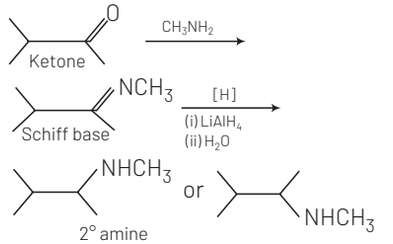
94 The major organic product formed from the following reaction **[CBSE AIPMT 2005]**



... is

(a) 
(b) 
(c) 
(d) 

Ans. ***(b)***

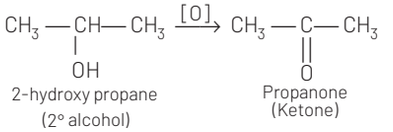


95 Which one of the following can be oxidised to the corresponding carbonyl compound ? **[CBSE AIPMT 2004]**

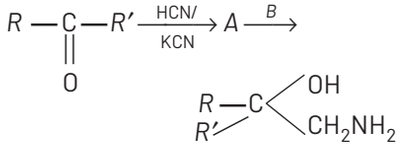
(a) 2-hydroxy propane
(b) *Ortho*-nitro phenol
(c) Phenol
(d) 2-methyl-2-hydroxy propane

Ans. ***(a)***

2-hydroxy propane or secondary alcohol is oxidised into propanone (corresponding because in 2-hydroxy propane, secondary alcoholic group is present and it is oxidised into ketone).



96 *A* and *B* in the following reactions are **[CBSE AIPMT 2003]**



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

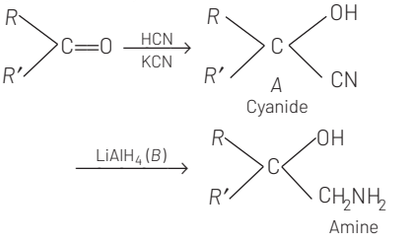
(b) $A = RR'C(OH)(COOH)$, $B = CH_3$

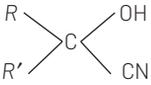
(c) $A = RR'C(CN)(COOH)$, $B = CH_3$

(d) $A = RR'C(CN)(OH)$, $B = LiAlH_4$

Ans. ***(d)***

In the presence of $LiAlH_4$, cyanide group gives amine by reduction.



Hence, *A* is  and *B* is $LiAlH_4$

97 In this reaction,

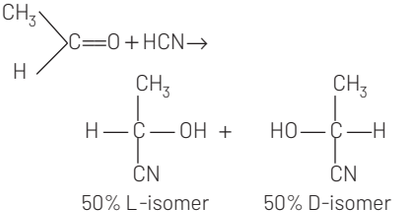
$$CH_3CHO + HCN \rightarrow CH_3CH(OH)CN \xrightarrow{H\cdot OH} CH_3CH(OH)COOH$$

an asymmetric centre is generated. The acid obtained would be **[CBSE AIPMT 2003]**

(a) 50% *D* + 50% *L*-isomer
(b) 20% *D* + 80% *L*-isomer
(c) *D*-isomer
(d) *L*-isomer

Ans. ***(a)***

Lactic acid obtained in the given reaction is an optically active compound due to the presence of chiral C-atom. It exits as *d* and *l*-forms whose ratio is 1:1.



50% L-isomer 50% D-isomer

Cyanohydrine

98 Polarisation of electrons in acrolein may be written as **[CBSE AIPMT 2000]**

(a) $\overset{\delta+}{C}H_2=CH-CH=\overset{\delta-}{O}$

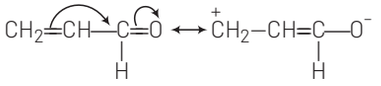
(b) $\overset{\delta+}{C}H_2=\overset{\delta+}{C}H-CH=O$

(c) $\overset{\delta+}{CH_2}=CH-CH=\overset{\delta+}{O}$

(d) $\overset{\delta-}{CH_2}=CH-\overset{\delta+}{CH}=O$

Ans. ***(a)***

In $CH_2=CH-CHO$ due to – *M*-effect of –CHO group, polarisation of electron takes place as follows :



99 During reduction of aldehydes with hydrazine and potassium hydroxide, the first is the formation of **[CBSE AIPMT 2000]**

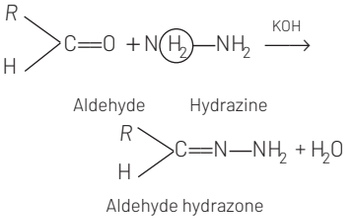
(a) $R-CH=N-NH_2$

(b) $R-C\equiv N$

(c) $R-\underset{\underset{O}{\|}}{C}-NH_2$

(d) $R-CH=NH$

Ans. ***(a)***



100 Aldol condensation will not take place in **[CBSE AIPMT 1999]**

(a) HCHO (b) CH_3CHO

(c) CH_3COCH_3 (d) CH_3CH_2CHO

Ans. ***(a)***

Aldol condensation in aldehydes is due to presence of α-hydrogen atoms. Those aldehydes which does not have α-hydrogen atom like HCHO, does not give aldol condensation reaction.

101 Iodoform test is not given by **[CBSE AIPMT 1998]**

(a) 2-pentanone

(b) ethanol

(c) ethanal

(d) 3-pentanone

Ans. ***(d)***

The compounds which contain either CH_3-CO- group or $CH_3-\underset{\underset{OH}{|}}{CH}$ group give positive iodoform test. In 2-pentanone, ($CH_3CH_2CH_2COCH_3$), CH_3CHO and C_2H_5OH, required groups are present, thus they give iodoform as follows

$$CH_3-COCH_2-CH_2CH_3 + 3I_2 + 4NaOH \rightarrow \underset{\text{Iodoform (yellow ppt.)}}{CHI_3\downarrow} + CH_3CH_2CH_2COONa + 3NaI + 3H_2O$$

$$CH_3CHO + 3I_2 + 4NaOH \longrightarrow \underset{\text{Iodoform (yellow ppt)}}{CHI_3\downarrow} + HCOONa + 3NaI + 3H_2O$$

$$C_2H_5OH \xrightarrow{I_2} CH_3CHO$$

$$CH_3CHO + 3I_2 + 4NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3\downarrow} + HCOONa + 3NaI + 3H_2O$$

But due to absence of $CH_3-\underset{\underset{OH}{|}}{CH}$ or $CH_3-\underset{|}{C}=O$ group in 3-pentanone, it does not give iodoform.

$$\underset{\text{3-pentanone}}{CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-CH_3} + I_2 + NaOH \longrightarrow \text{No reaction.}$$

102 1-phenyl ethanol can be prepared by the reaction of benzaldehyde with **[CBSE AIPMT 1997]**

(a) methyl bromide

(b) ethyl iodide and magnesium

(c) methyl iodide and magnesium

(d) methyl bromide and aluminium bromide

Ans. ***(c)***

1-phenyl ethanol is prepared by reacting benzaldehyde with methyl magnesium iodide (mixture of methyl iodide and magnesium as)

$$CH_3I + Mg \xrightarrow{\text{Dry ether}} CH_3MgI$$

$$CH_3-MgI + \underset{H}{\overset{C_6H_5}{>}}C=O \longrightarrow \underset{CH_3}{\overset{C_6H_5}{>}}CH-O-MgI$$

$$\xrightarrow[-Mg(OH)I]{H_2O} HOHC\underset{CH_3}{\overset{C_6H_5}{<}}$$

(1-phenyl ethanol)

103 Ketones $[R-\underset{\underset{O}{\|}}{C}-R_1]$, where $R = R_1$ = alkyl group, can be obtained in one step by **[CBSE AIPMT 1997]**

(a) hydrolysis of esters

(b) oxidation of primary alcohol

(c) oxidation of tertiary alcohol

(d) reaction of acid halide with alcohols

Ans. ***(c)***

By oxidation of tertiary alcohol with stronger oxidising agents, ketones may be formed along with carboxylic acid.

$$(CH_3)_3COH \xrightarrow{4[O]} CH_3COCH_3 + CO_2 + 2H_2O$$

$$(CH_3)_3COH \xrightarrow{8[O]} CH_3COOH + 2CO_2 + 3H_2O$$

104 $(CH_3)_3C-CHO$ does not undergo aldol condensation due to **[CBSE AIPMT 1996]**

(a) three electron donating methyl groups

(b) cleavage taking place between –C–CHO bond

(c) absence of alpha hydrogen atom in the molecule

(d) bulky $(CH_3)_3C-$ group

Ans. ***(c)***

$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CHO$ does not undergo aldol condensation because it does not contain α-hydrogen atom.

105 Acetone reacts with iodine (I_2) to form iodoform in the presence of **[CBSE AIPMT 1995]**

(a) $CaCO_3$ (b) NaOH

(c) KOH (d) $MgCO_3$

Ans. ***(b)***

$$\underset{\text{Acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} + 3I_2 + 4NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + CH_3COO^-Na^+ + 3NaI + 3H_2O$$

106 Which of the following compounds will undergo self aldol condensation in the presence of cold dilute alkali? **[CBSE AIPMT 1994]**

(a) $CH_2=CH-CHO$

(b) $CH\equiv C-CHO$

(c) C_6H_5CHO (d) CH_3-CH_2CHO

Ans. ***(d)***

Only those aldehyde undergoes aldol condensation which have α-hydrogen, so CH_3CH_2CHO give this reaction because it contains α-hydrogen atom. Aldol condensation proceed in presence of strong base. Aldol condensation are divided into two parts one is self aldol

condensation and another is cross-aldol condensation. When both molecules are same called as self aldol and *vice versa*.

107 Aldehydes and ketones will not form crystalline derivatives with **[CBSE AIPMT 1994]**

(a) sodium bisulphite
(b) phenyl hydrazine
(c) semicarbazide hydrochloride
(d) dihydrogen sodium phosphate

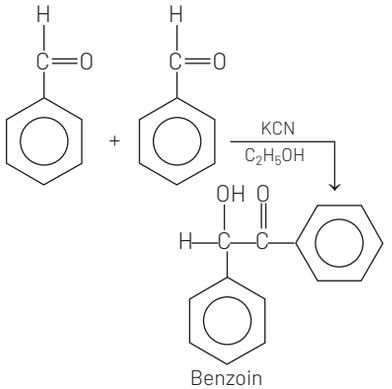
Ans. ***(d)***

Dihydrogen sodium phosphate (NaH_2PO_4) does not react with aldehydes and ketones because NaH_2PO_4 does not have any lone pair of electron on phosphorus atom, so it cannot act as a nucleophile.

108 Benzaldehyde reacts with ethanolic KCN to give **[CBSE AIPMT 1994]**

(a) $C_6H_5CHOHCN$
(b) $C_6H_5CHOHCOC_6H_5$
(c) $C_6H_5CHOHCOOH$
(d) $C_6H_5CHOHCHOHC_6H_5$

Ans. ***(b)***



Benzoin
(hydroxy ketone)

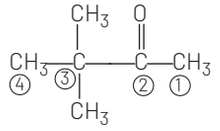
This reaction is also called benzoin condensation. Benzoin is chiral and it exists as a pair of enantiomer, i.e. *R*-benzoin and *S*-benzoin.

109 Pinacolone is **[CBSE AIPMT 1994]**

(a) 2,3-dimethyl-2,3-butanediol
(b) 3,3-dimethyl-2-butanone
(c) 1-phenyl-2-propanone
(d) 1,1-diphenyl-2-ethanediol

Ans. ***(b)***

The structure of pinacolone is



So, its IUPAC name is
3,3-dimethyl-2-butanone
(Colourless liquid)(Camphor odour)

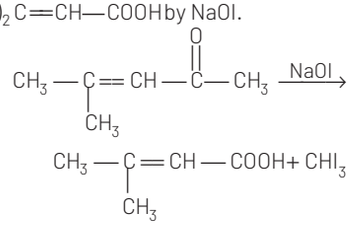
110 $(CH_3)_2C{=}CHCOCH_3$ can be oxidised to $(CH_3)_2C{=}CHCOOH$ by **[CBSE AIPMT 1993]**

(a) chromic acid (b) NaOI
(c) Cu at 300°C (d) $KMnO_4$

Ans. ***(b)***

Haloform reaction,

$(CH_3)_2C{=}CHCOCH_3$ contains $CH_3—\overset{\overset{O}{\|}}{C}—$ unit so it can be oxidised to $(CH_3)_2C{=}CH—COOH$ by NaOI.

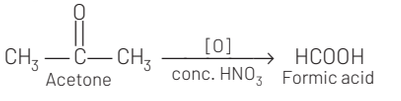


111 In which of the following the number of carbon atoms does not remain same when carboxylic acid is obtained by oxidation? **[CBSE AIPMT 1992]**

(a) CH_3COCH_3 (b) CCl_3CH_2CHO
(c) $CH_3CH_2CH_2OH$ (d) CH_3CH_2CHO

Ans. ***(a)***

Ketones are not easily oxidised. However, under drastic conditions or with powerful oxidising agents such as conc. HNO_3, $KMnO_4$ / H_2SO_4 or $K_2Cr_2O_7$ / H_2SO_4, cleavage of carbon-carbon bond takes place giving a mixture of carboxylic acids having less number of carbon atoms than the original ketone.

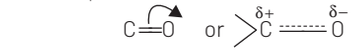


112 Acetaldehyde reacts with **[CBSE AIPMT 1991]**

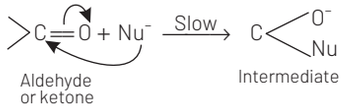
(a) only electrophiles
(b) only nucleophiles
(c) only free radicals
(d) both electrophiles and nucleophiles

Ans. ***(b)***

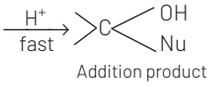
The carbonyl group is highly reactive polar group. It is polarised due to the higher electronegativity of oxygen in comparison to carbon. As a result, the electrons present between carbon and oxygen are more attracted towards oxygen atom. The actual structure may be represented as



Consequently, the carbonyl carbon is positively charged while the oxygen is negatively charged. The positively charged carbon is easily attacked by a nucleophilic reagent (Nu^-).



sp^2 hybridisation planar structure.



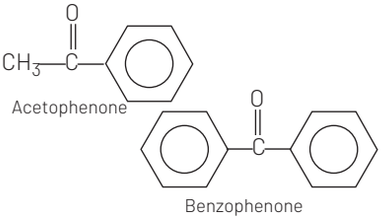
sp^3 hybridisation tetrahedral structure.

113 The reagents which can be used to distinguish acetophenone from benzophenone is (are) **[CBSE AIPMT 1990]**

(a) 2,4-dinitrophenyl hydrazine
(b) aqueous solution of $NaHSO_3$
(c) Benedict reagent
(d) I_2 and Na_2CO_3

Ans. ***(d)***

The structures of acetophenone and benzophenone are



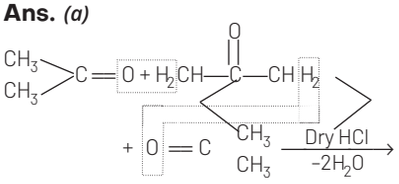
When acetophenone containing $CH_3—\overset{\overset{O}{\|}}{C}—$ unit, is treated with I_2 and Na_2CO_3 it forms yellow precipitate of CHI_3 whereas benzophenone does not give this test.Acetophenons gives iodoform test due to presence of $—COCH_3$ group.

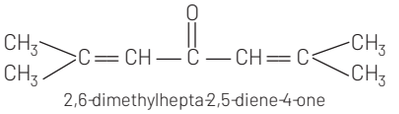
114 $\underset{(A)}{3CH_3COCH_3} \xrightarrow[-H_2O]{HCl} \underset{(B)}{(CH_3)_2C{=}CH—CO—CH{=}C(CH_3)_2}$

This polymer (*B*) is obtained when acetone is saturated with HCl gas, *B* can be **[CBSE AIPMT 1989]**

(a) phorone
(b) formose
(c) diacetone alcohol
(d) mesityl oxide

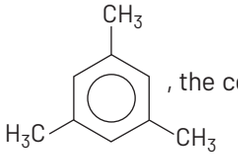
Ans. *(a)*





2,6-dimethylhepta-2,5-diene-4-one
(Phorone) (*B*)

Phorone is self condensation product of acetone. It can also be obtained from certain camphor compound. Phorone is combustible when exposed to heat or flame.

115  , the compound

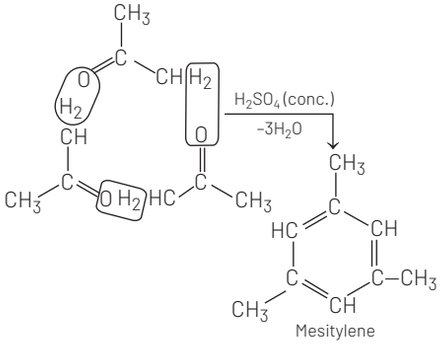
describes a condensation polymer which can be obtained in two ways, either treating 3 molecules of acetone (CH_3COCH_3) with conc. H_2SO_4 or passing propyne ($CH_3—C\equiv CH$) through a red hot tube, the polymer is

[CBSE AIPMT 1989]

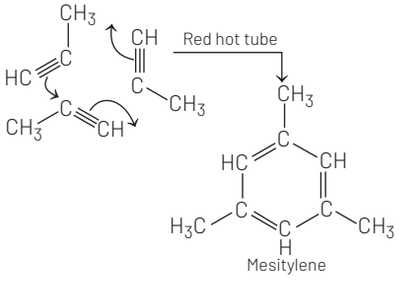
(a) phorone (b) deacetonyl alcohol
(c) mesityl oxide (d) mesitylene

Ans. *(d)*

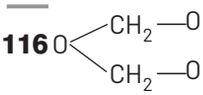
When acetone is treated with H_2SO_4, three molecules get condensed to give mesitylene,



Mesitylene



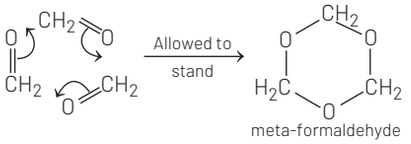
Mesitylene

116  , the shown polymer is obtained when a carbonyl compound is allowed to stand. It is a white solid. The polymer is **[CBSE AIPMT 1989]**

(a) trioxane
(b) *para*-formaldehyde
(c) formose
(d) *meta*-aldehyde

Ans. *(a)*

When formaldehyde is allowed to stand at room temperature, it slowly undergoes, polymerisation and forms a white solid called meta-formaldehyde or trioxane.



meta-formaldehyde
(Trioxane)

117 Formalin is an aqueous solution of **[CBSE AIPMT 1988]**

(a) fluorescein (b) formic acid
(c) formaldehyde (d) furfuraldehyde

Ans. *(c)*

The 40% solution of formaldehyde in water is sold in market under the name of formalin. Formaldehyde in the form of formalin (40% formaldehyde, 8% methanol and 52% water) is used for preserving biological specimens.

Formaline solution also used as a disinfectants and commonly used in hardeness and nail varnish.

118 If formaldehyde is heated with KOH, then we get **[CBSE AIPMT 1988]**

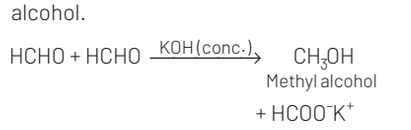
(a) methane
(b) methyl alcohol
(c) ethyl formate
(d) acetylene

Ans. *(b)*

When α-hydrogen is absent in carbonyl group, those compound gives cannizaro reaction.

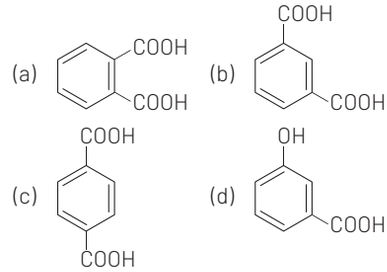
This reaction show disproportionation.

The oxidation product is salt of carboxylic acid and reduced product is alcohol.



TOPIC 4
Carboxylic Acids

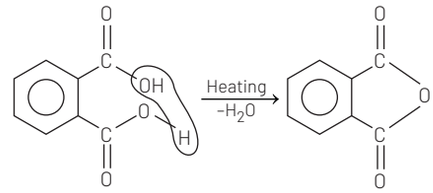
119 Which of the following acid will form an (i) anhydride on heating and (ii) acid imide on strong heating with ammonia? **[NEET (Oct.) 2020]**



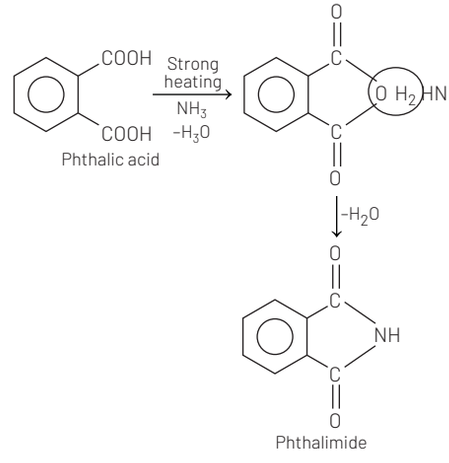
Ans. *(a)*

An α,β-dicarboxylic acid with same-side (*syn*) orientation of —COOH group is able to form anhydride (cyclic) and imide (cyclic).

Among isomeric benzene dicarboxylic acids, only benzene-1,2-dicarboxylic acid (phthalic acid) will respond to the below reactions.

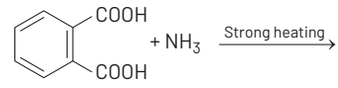


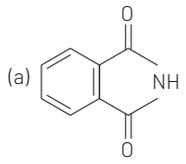
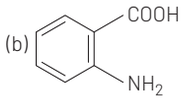
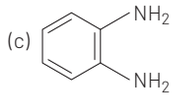
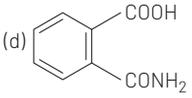
Phthalic anhydride



Phthalimide

120 The major product of the following reaction is : **[NEET (National) 2019]**

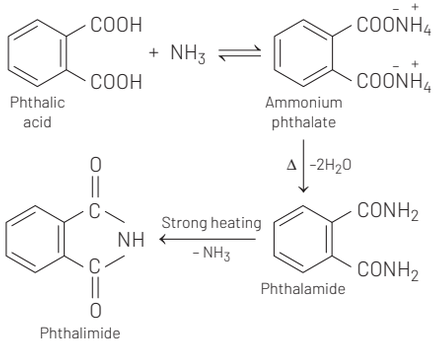


(a) 
(b) 
(c) 
(d) 

Ans. *(a)*

Carboxylic acids react with ammonia to give ammonium salt which on further heating at high temperature give amides. Further, on strong heating, ammonia is removed from phthalamide and phthalimide is formed.

The reaction takes place as follows :



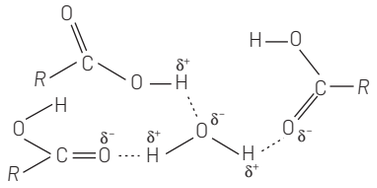
121 Carboxylic acids have higher boiling points than aldehydes, ketones and even alcohols of comparable molecular mass. It is due to their

[NEET 2018]

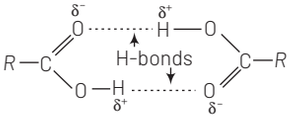
(a) more extensive association of carboxylic acid *via* van der Waals' force of attraction
(b) formation of carboxylate ion
(c) formation of intramolecular H-bonding
(d) formation of intermolecular H-bonding

Ans. *(d)*

Carboxylic acids have higher boiling points than aldehyde, ketones and even alcohols of comparable molecular mass because of the extent of intermolecular-hydrogen bonding with water, due to which they exist as associated molecules.

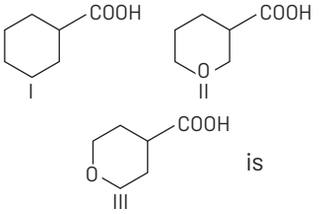


The hydrogen bonds are not completely broken in the vapour state. In fact mostly carboxylic acids exist as dimer in the vapour state or aprotic solvent.



122 The correct order of strengths of the carboxylic acids

[NEET 2016, Phase II]



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

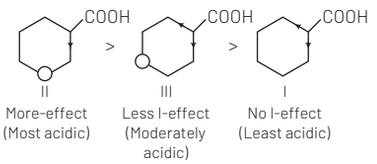
Ans. *(b)*

Key Idea *Order of strengths of the given carboxylic acids can be determined by the concept of I-effect.*

The oxygen atom present in the ring shows *I*-effect. As the distance between oxygen and —COOH group increases, –*I*-effect of oxygen decreases.

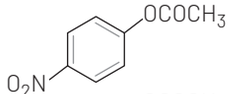
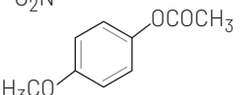
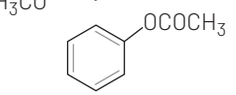
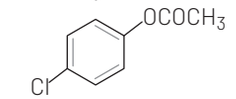
Thus, corresponding carboxylic acid will show less acidic nature.

The correct order of strengths of the carboxylic acids is



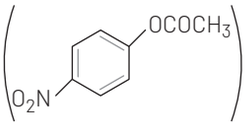
123 Which one of the following esters gets hydrolysed most easily under alkaline conditions?

[CBSE AIPMT 2015]

(a) 
(b) 
(c) 
(d) 

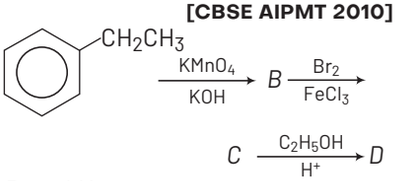
Ans. *(a)*

Electron withdrawing group attach to the benzene ring increases the reactivity towards nucleophilic sustitution reaction. Since, —NO_2 group is strong electron withdrawing group. Hence, in basic medium ester containing —NO_2 group will hydrolysed most easily.

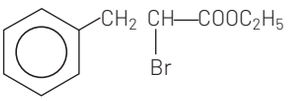
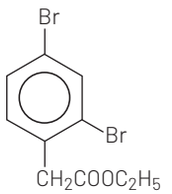
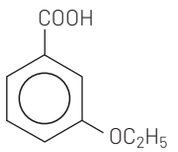
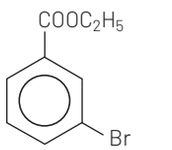


124 In a set of reactions, ethyl benzene yielded a product *D*.

[CBSE AIPMT 2010]

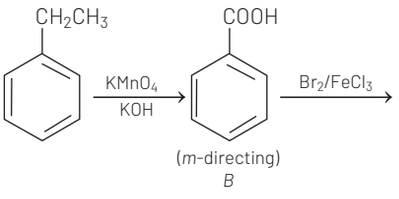


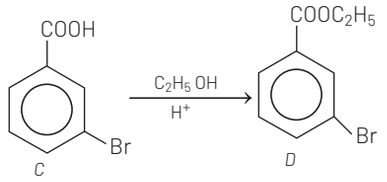
D would be

(a) 
(b) 
(c) 
(d) 

Ans. *(d)*

Alkaline $KMnO_4$ converts complete carbon chain (that is directly attached to benzene nucleus) to —COOH group. Br_2 in the presence of halogen carrier causes bromination by electrophilic substitution reaction and ethyl alcohol in acidic medium results in esterification.

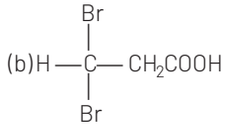




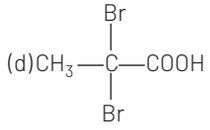
C *D*

125 Propionic acid with $Br_2 - P$ yields a dibromo product. Its structure would be **[CBSE AIPMT 2009]**

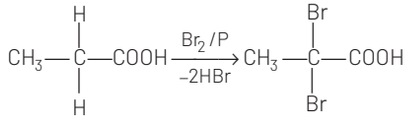
(a) $CH_2Br—CHBr—COOH$

(b) 

(c) $CH_2Br—CH_2—COBr$

(d) 

Ans. ***(d)***



Propionic acid

Carbonylic acids reacts with Cl_2 or Br_2 in presence of red P to give exclusively α-chloro or α-bromo acids.

This reaction is called Hell-Volhard-Zelinsky (HVZ) reduction. This reaction is example of α-H-substitution.

126 The relative reactivities of acyl compounds towards nucleophilic substitution are in the order of **[CBSE AIPMT 2008]**

(a) acyl chloride > acid anhydride > ester > amide

(b) ester > acyl chloride > amide > acid anhydride

(c) acid anhydride > amide > ester > acyl chloride

(d) acyl chloride > ester > acid anhydride > amide

Ans. ***(a)***

In acyl compounds (i.e. acyl chloride, acid anhydride, ester and amide) *R*CO— group is same, thus reactivity depends upon the nature of group *Z* (i.e. Cl^-, $RCOO^-$, $R'O^-$, NH_2^-, etc.)

If group *Z* is a weak base, then it is a strong leaving agent and its reactivity towards nucleophilic substitution is high.

The order of basic nature of *Z* groups is

$$Cl^- < RCOO^- < R'O^- > NH_2^-$$

Thus, order of reactivity is

$$\underset{\text{Acyl chloride}}{RCOCl} > \underset{\text{Acid anhydride}}{(RCO)_2O} > \underset{\text{Ester}}{RCOOR'} > \underset{\text{Amide}}{RCONH_2}$$

127 Which of the following represents the correct order of acidity in the given compounds? **[CBSE AIPMT 2007]**

(a) $FCH_2COOH > CH_3COOH > BrCH_2COOH > ClCH_2COOH$

(b) $BrCH_2COOH > ClCH_2COOH > FCH_2COOH > CH_3COOH$

(c) $FCH_2COOH > ClCH_2COOH > BrCH_2COOH > CH_3COOH$

(d) $CH_3COOH > BrCH_2COOH > ClCH_2COOH < FCH_2COOH$

Ans. ***(c)***

The acidity of halogenated acid increases with increase in electronegativity of the halogen present.

The electronegativity of halogen decreases in order as F > Ce > Br. Therefore correct order of given compounds is

$$FCH_2COOH > ClCH_2COOH > BrCH_2COOH > CH_3COOH$$

128 Self condensation of two moles of ethyl acetate in the presence of sodium ethoxide yields **[CBSE AIPMT 2006]**

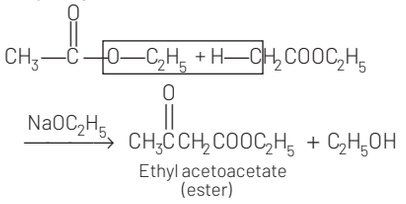
(a) ethyl butyrate (b) acetoacetic ester

(c) methyl acetoacetate

(d) ethyl propionate

Ans. ***(b)***

On condensation, two moles of ethyl acetate in the presence of sodium ethoxide, gives ethyl acetoacetate (ester). This condensation is an example of Claisen condensation because it is possible in those ester which have α-hydrogen atom.



Ethyl acetoacetate (ester)

129 In a set of reactions propionic acid yielded a compound *D*.

$$CH_3CH_2COOH \xrightarrow{SOCl_2} B \xrightarrow{NH_3} C \xrightarrow[Br_2]{KOH} D$$

The structure of *D* would be **[CBSE AIPMT 2006]**

(a) $CH_3CH_2CH_2NH_2$ (b) $CH_3CH_2CONH_2$

(c) $CH_3CH_2NHCH_3$ (d) $CH_3CH_2NH_2$

Ans. ***(d)***

For the reaction,

$$\underset{A}{CH_3CH_2COOH} \xrightarrow[-SO_2,\ -HCl]{SOCl_2} \underset{B}{CH_3CH_2COCl} \xrightarrow[-HCl]{NH_3} \underset{C}{CH_3CH_2CONH_2} \xrightarrow[(-2KBr,\ -K_2CO_3,\ -2H_2O)]{4KOH + Br_2} \underset{\substack{D\\(\text{Ethyl amine})}}{CH_3CH_2NH_2}$$

Hence, it is also called Hofmann bromamide degradation reaction.

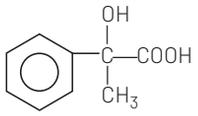
Hence, compound '*D*' is $CH_3—CH_2—NH_2$.

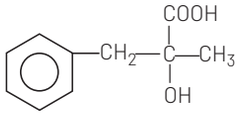
Hofmann bromamide reaction degrade the one C in amine product from amide

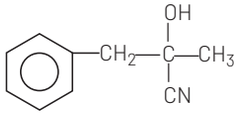
130 In a set of reactions, acetic acid yielded a product *D*.

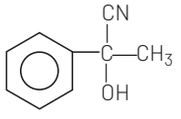
$$CH_3COOH \xrightarrow{SOCl_2} A \xrightarrow[\text{anhy. } AlCl_3]{\text{Benzene}} B \xrightarrow{HCN} C \xrightarrow{HOH} D$$

The structure of *D* would be **[CBSE AIPMT 2005]**

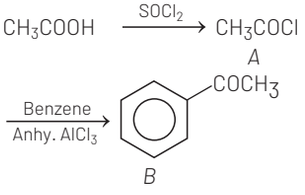
(a) 

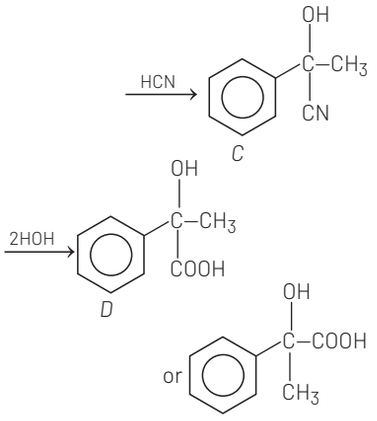
(b) 

(c) 

(d) 

Ans. ***(a)***





131 Which one of the following orders of acidic strength is correct ?

[CBSE AIPMT 2003]

(a) *R*COOH > HOH > HC ≡ CH > *R*OH

(b) *R*COOH > HC ≡ CH > HOH > *R*OH

(c) *R*COOH > *R*OH > HOH > HC ≡ CH

(d) *R*COOH > HOH > *R*OH > HC ≡ CH

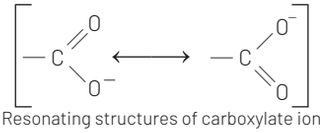
Ans. ***(d)***

Carboxylic acid is stronger than alcohol and water because after removal of proton, carboxylate ion is stabilised by resonance. Hence, correct order of acid strength is

*R*COOH > HOH > *R*OH > HC ≡ CH

Which is based upon the rate of donation of proton or strength of base, thus order of basic strength is

$\bar{C}\equiv CH > R-\bar{O} > OH^- > RCOO^-$



Resonating structures of carboxylate ion

132 In a set of the given reactions, acetic acid yielded a product *C*.

$$CH_3COOH + PCl_5 \longrightarrow A \xrightarrow[\text{anhy. } AlCl_3]{C_6H_6} B \xrightarrow[\text{Ether}]{C_2H_5MgBr} C$$

Product *C* would be

[CBSE AIPMT 2003]

(a) $CH_3CH(OH)C_6H_5$

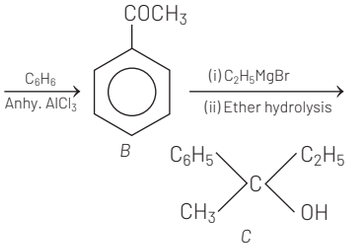
(b) $CH_3-\underset{\displaystyle C_2H_5}{\underset{|}{C}}(OH)C_6H_5$

(c) $CH_3CH(OH)C_2H_5$

(d) $CH_3COC_6H_5$

Ans. ***(b)***

$$CH_3COOH + PCl_5 \longrightarrow \underset{A}{CH_3COCl}$$



133 In the following reaction, product *P* is

$$R-\underset{\displaystyle O}{\underset{\|}{C}}-Cl \xrightarrow[Pd\text{-}BaSO_4]{H_2} P$$

[CBSE AIPMT 2002]

(a) *R*CH_2OH (b) *R*COOH

(c) *R*CHO (d) *R*CH_3

Ans. ***(c)***

The given reaction is Rosenmund reaction

$$R-\underset{\displaystyle O}{\underset{\|}{C}}-Cl \xrightarrow[Pd\text{-}BaSO_4]{H_2} R-\underset{\displaystyle O}{\underset{\|}{C}}-H + HCl$$

(*P*)

134 Benzoic acid may be converted into ethyl benzoate by reaction with

[CBSE AIPMT 2000]

(a) sodium ethoxide

(b) ethyl chloride

(c) dry HCl, C_2H_5OH

(d) ethanol

Ans. ***(c)***

Ethyl benzoate is prepared by reacting benzoic acid and ethanol in the presence of dry HCl. This reaction is known as esterification reaction.

$$\underset{\text{Benzoic acid}}{C_6H_5COOH} + \underset{\text{Ethanol}}{C_2H_5OH} \underset{HCl}{\overset{\text{Dry}}{\rightleftharpoons}} \underset{\text{Ethyl benzoate}}{C_6H_5COOC_2H_5} + H_2O$$

This reaction proceed with equilibrium. Therefore, H_2O continuously removed from reaction for preparation of ester product.

135 Reduction by $LiAlH_4$ of hydrolysed product of an ester gives

[CBSE AIPMT 2000]

(a) two acids

(b) two aldehydes

(c) one molecule of alcohol and another of carboxylic acid

(d) two alcohols

Ans. ***(d)***

$$R-COOR' \xrightarrow{H_2O} R-COOH + R'OH$$

$$\downarrow LiAlH_4 \text{ / ether}$$

$$R-CH_2OH + R'OH$$

According to the above equation, it is clear that reduction of hydrolysed product of ester by $LiAlH_4$ gives two alcohols.

136 Which one of the following esters cannot undergo Claisen self-condensation ?

[CBSE AIPMT 1998]

(a) $CH_3CH_2CH_2CH_2COOC_2H_5$

(b) $C_6H_5COOC_2H_5$

(c) $C_6H_5CH_2COOC_2H_5$

(d) $C_6H_{11}CH_2COOC_2H_5$

Ans. ***(b)***

The ester which contains α-hydrogen atom undergoes Claisen-self condensation :

(a) $CH_3(CH_2)_3\underset{\displaystyle O}{\underset{\|}{C}}-\boxed{OC_2H_5} + H-CHCOOC_2H_5$ ($CH_2CH_2CH_3$)

$$\xrightarrow{\text{Claisen Condensation}}$$

$$CH_3CH_2CH_2CH_2\underset{\displaystyle O}{\underset{\|}{C}}-CHCOOC_2H_5 \quad (CH_2CH_2CH_3) + C_2H_5OH$$

(b) $C_6H_5COOC_2H_5 + C_6H_5COOC_2H_5$

No reaction, because for Claisen condensation an ester with α-hydrogen atoms is required.

(c) $C_6H_5-CH_2CO\boxed{OC_2H_5} + H-CHCOOC_2H_5$ (C_6H_5)

$$\xrightarrow{\text{Claisen Condensation}} C_6H_5CH_2COCHCOOC_2H_5 \quad (C_6H_5)$$

(d) $C_6H_{11}CH_2CO\boxed{OC_2H_5} + H-CH-COOC_2H_5$ (C_6H_{11})

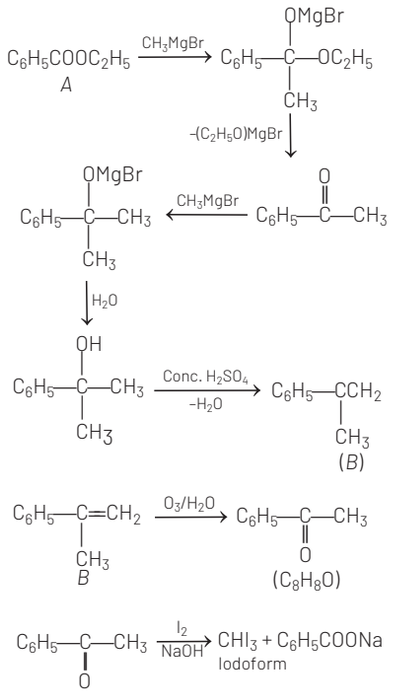
$$\xrightarrow{\text{Claisen Condensation}}$$

$$C_6H_{11}CH_2COCH-COOC_2H_5 + C_2H_5OH \quad (C_6H_{11})$$

137 An ester (*A*) with molecular formula $C_9H_{10}O_2$ was treated with excess of CH_3MgBr and the complex so formed was treated with H_2SO_4 to give an olefin (*B*). Ozonolysis of (*B*) gave a ketone with molecular formula C_8H_8O which shows positive iodoform test. The structure of (*A*) is **[CBSE AIPMT 1998]**

(a) $C_6H_5COOC_2H_5$
(b) $C_6H_5COOC_6H_5$
(c) $H_3CCOOC_6H_5$
(d) *p* - $H_3COC_6H_4COCH_3$

Ans. *(a)*



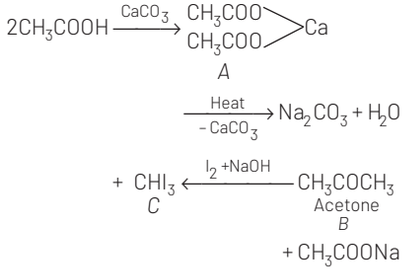
138 Consider the following transformations

$CH_3COOH \xrightarrow{CaCO_3} A \xrightarrow{Heat} B \xrightarrow[NaOH]{I_2} C$ The molecular formula of *C* is **[CBSE AIPMT 1996]**

(a) $CH_3-\underset{\underset{I}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$ (b) $ICH_2—COCH_3$

(c) CHI_3 (d) CH_3I

Ans. *(c)*



139 An ester is boiled with KOH. The product is cooled and acidified with conc. HCl. A white crystalline acid separates. The ester is **[CBSE AIPMT 1994]**

(a) methyl acetate (b) ethyl acetate
(c) ethyl formate (d) ethyl benzoate

Ans. *(d)*

$C_6H_5COOC_2H_5 \xrightarrow[Boiling]{KOH} C_6H_5COOK^+ + C_2H_5OH$

Ethyl benzoate

$C_6H_5COOK \xrightarrow{H^+/H_2O} C_6H_5COOH \downarrow$

Benzoic acid (white precipitate)

140 Schotten-Baumann reaction is a reaction of phenols with **[CBSE AIPMT 1994]**

(a) benzoyl chloride and NaOH
(b) acetyl chloride and NaOH
(c) salicylic acid and conc. H_2SO_4
(d) acetyl chloride and conc. H_2SO_4

Ans. *(a)*

Schotten-Baumann reaction

$C_6H_5COCl + C_6H_5OH \xrightarrow[pyridine]{Aq.\ NaOH} C_6H_5COOC_6H_5 + HCl$

141 The preparation of ethyl acetoacetate involves **[CBSE AIPMT 1994]**

(a) Wittig reaction
(b) Cannizaro's reaction
(c) Reformatsky reaction
(d) Claisen condensation

Ans. *(d)*

Claisen condensation

$CH_3\overset{O}{\overset{\|}{C}}OC_2H_5 + HCH_2COOC_2H_5 \xrightarrow{C_2H_5\bar{O}Na^+} CH_3\overset{O}{\overset{\|}{C}}CH_2COOC_2H_5 + C_2H_5OH$

Ethyl acetoacetate

142 Formic acid is obtained when **[CBSE AIPMT 1994]**

(a) calcium acetate is heated with conc. H_2SO_4
(b) calcium formate is heated with calcium acetate
(c) glycerol is heated with oxalic acid at 373 K
(d) acetaldehyde is oxidised with $K_2Cr_2O_7$ and H_2SO_4

Ans. *(c)*

$\underset{\text{Oxalic acid}}{COOH-COOH} \xrightarrow[Heat\ 373K]{Glycerol} \underset{\text{Formic acid}}{HCOOH} + CO_2\uparrow$

143 Among acetic acid, phenol and *n*-hexanol which one of the following compound will react with $NaHCO_3$ solution to give sodium salt and CO_2? **[CBSE AIPMT 1993, 99]**

(a) Acetic acid
(b) n-hexanol
(c) Acetic acid and phenol
(d) Phenol

Ans. *(a)*

$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Sodium carbonate}}{NaHCO_3} \longrightarrow CH_3COO\overset{+}{N}a + H_2O + CO_2\uparrow$

144 Sodium formate on heating yields. **[CBSE AIPMT 1993]**

(a) Oxalic acid and H_2
(b) Sodium oxalate and H_2
(c) CO_2 and NaOH
(d) Sodium oxalate

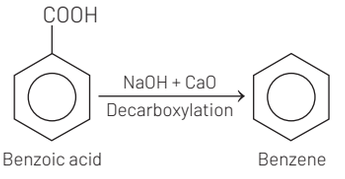
Ans. *(b)*

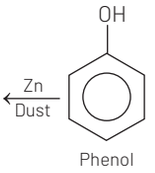
$\underset{\text{Sodium formate}}{HCOONa + HCOONa} \xrightarrow{Heat} \underset{\text{Sodium oxalate}}{\overset{+}{N}aOOC-COO\overset{+}{N}a} + \underset{\text{Hydrogen}}{H_2\uparrow}$

145 Benzoic acid gives benzene on being heated with *X* and phenol gives benzene on being heated with *Y*. Therefore, *X* and *Y* are respectively **[CBSE AIPMT 1992]**

(a) sodalime and copper
(b) Zn dust and NaOH
(c) Zn dust and sodalime
(d) sodalime and zinc dust

Ans. *(d)*





Phenol

Here x = NaOH + CaO(soda line)

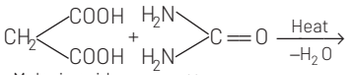
y = Zn dust

146 The compound formed when malonic acid is heated with urea, is **[CBSE AIPMT 1989]**

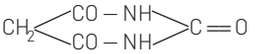
(a) cinnamic acid (b) butyric acid

(c) barbituric acid (d) crotonic acid

Ans. *(c)*



Malonic acid Urea


Barbituric acid

147 Among the following the strongest acid is **[CBSE AIPMT 1988]**

(a) CH_3COOH (b) CH_2ClCH_2COOH

(c) $CH_2ClCOOH$ (d) CH_3CH_2COOH

Ans. *(c)*

Inductance effect distance depending factor. It decreases rapidly with distance. Therefore, as the distance of Cl-atom increases the acidic character decreases.

148 Which of the following represent the correct decreasing order of acidic strength of following? **[CBSE AIPMT 1988]**

(i) Methanoic acid

(ii) Ethanoic acid

(iii) Propanoic acid

(iv) Butanoic acid

(a) (i) > (ii) > (iii) > (iv) (b) (ii) > (iii) > (iv) > (i)

(c) (i) > (iv) > (iii) > (ii) (d) (iv) > (i) > (iii) > (ii)

Ans. *(a)*

The correct order of acidic strength is methanoic acid > ethanoic acid > propanoic acid > butanoic acid because the +*I*–effect of alkyl group increases in the order.

$$CH_3 < C_2H_5 < C_3H_7 < C_4H_9$$

$$\text{Acidic Nature} \propto \frac{-I\text{-effect (EWG)}}{+I\text{-effect (ERG)}}$$

–*I*-effect increases hence, acidic nature increases.