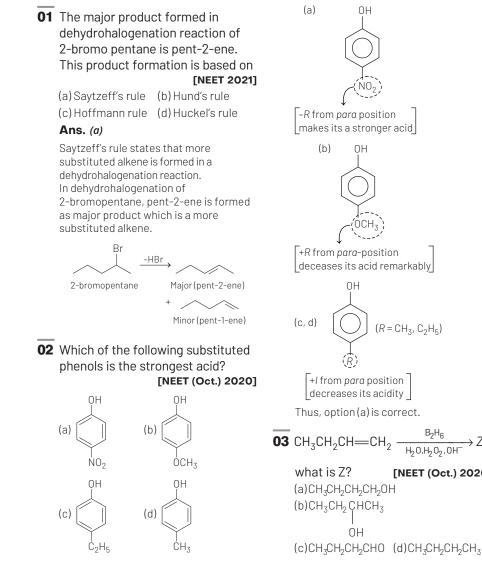
# **Organic Compounds Containing Oxygen**

#### **TOPIC 1** Alcohols and Phenols



#### Ans. (a)

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

#### (i) B<sub>2</sub>H CH = CH<sub>2</sub> (ii) H<sub>2</sub>0, H<sub>2</sub>0<sub>2</sub>, OH CH<sub>z</sub>CH<sub>2</sub> Anti-Markownikoff's addition of H<sub>2</sub>O (overall) ∩н́–СН₂ (Z)Butan-1-ol It is hydroboration-oxidation (HBO) reaction of an alkene which undergoes hydration to give an alcohol. Here, anti-Markownikoff's addition of H<sub>2</sub>O takes place. **04** The structure of intermediate A in the following reaction, is [NEET (National) 2019] CH<sub>3</sub> CH CH₄ (a) H<sub>3</sub>C--0-[NEET (Oct.) 2020] CH<sub>3</sub> (b) ĊН ĊH<sub>3</sub>

Ans. (a)

Least substituted

ОH

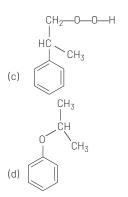
<sup>2</sup> carbon

δ

ΛH

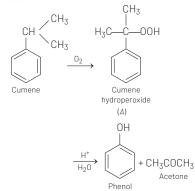
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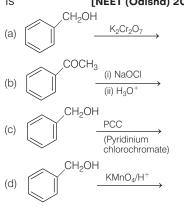


#### Ans. (a)

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]



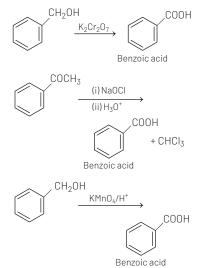
#### Ans. (c)

Primary aromatic alcohols on reaction with pyridinium chlorochromate (PCC)

which is a mild oxidising agent forms aromatic aldehydes.



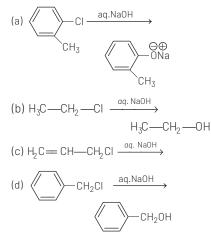
In the remaining options benzoic acid is formed as follows:



Thus, option (c) is correct.

**06** The hydrolysis reaction that takes place at the slowest rate, among the following is

#### [NEET (Odisha) 2019]



#### **Ans.** (a)

Cl 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.

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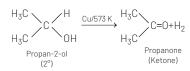
#### 07 When vapours of a secondary alcohol is passed over heated copper at 573 K, the product formed is [NEET (Odisha) 2019]

(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 PCI<sub>5</sub> gives C. B and C react together to give diethyl ether. A, B and C are in the order [NEET 2018]

 $\begin{array}{l} \text{(a)} \ C_2H_5\text{CI}, C_2H_6, C_2H_5\text{OH} \\ \text{(b)} \ C_2H_5\text{OH}, C_2H_5\text{CI}, C_2H_5\text{ONa} \\ \text{(c)} \ C_2H_5\text{OH}, C_2H_6, C_2H_5\text{CI} \\ \text{(d)} \ C_2H_5\text{OH}, C_2H_5\text{ONa}, C_2H_5\text{CI} \\ \end{array}$ 

#### 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) 
$$C_2H_5OH \xrightarrow{Na} C_2H_5\bar{O}Na$$
  
Ethanol Sodium ethoxide  
 $(A)$   $(B)$   
 $PCI_5 \downarrow$   
 $C_2H_5CI$ 

Ethyl chloride (C)

(ii) 
$$C_2H_5 \overline{O} Na^+ + C_2H_5CI \xrightarrow{S_N^2}$$

 $C_2H_5 - 0 - C_2H_5 + NaCl$ Diethyl ether

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The above reaction is known as Williamson's ether synthesis. It involves nucleophilic attack of alkoxide ion on alkyl halide according to S $_{\rm N}2$  mechanism.

 $\begin{array}{c} C_2H_5O^- + CH_3 \longrightarrow CH_2CI \xrightarrow{Slow} \\ \text{Nucleophile} & \text{Substrate} \\ (Alkoxide ion) & (Alkyl halide) \end{array}$ 

$$\begin{array}{c} C_2H_5 \longrightarrow C_1H_2 \ldots CI^- \xrightarrow{Fast} \\ & & \\ CH_3 \end{array}$$

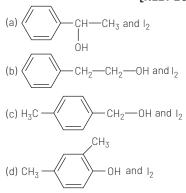
$$C_2H_5 \longrightarrow C_2H_5 + C_$$

**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]

CI-

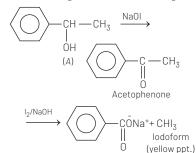


#### Ans. (a)

lodoform 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.

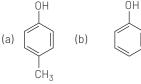
Since, among the compounds,  $CH_3CH(OH)$  group is given only in the substrate of option (a) hence, it is correct. The reaction of compound A with NaOI is given as follows :

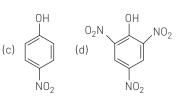
 $2NaOH + I_2 \longrightarrow NaOI + NaI + H_2O$ 



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

Sodium benzoate





#### **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]

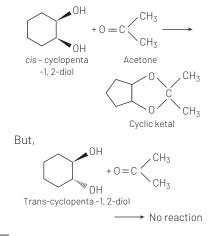
(a) Ozone

(b)  $MnO_2$ 

(c) Aluminium isopropoxide (d) Acetone

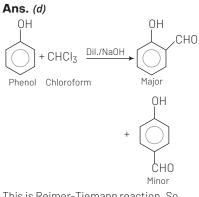
#### Ans. (d)

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.



**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<sub>2</sub>CI (c) — CHCI<sub>2</sub> (b)—C00H (d)—CH0



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.  $CH_3CH_2OH + HCI \xrightarrow{anh.ZnCl_2}$ 

in ongoing on their

II.  $CH_3CH_2OH + HCI \longrightarrow$ 

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

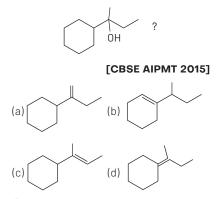
IV.  $(CH_3)_2$ CHOH + HCI  $\xrightarrow{anh.ZnCl_2}$ 

(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 (HCI+ anh.  $ZnCI_2$ ) alcohols give alkyl halides while in (III) alkyl halide is formed due to  $S_N 1$  reaction.

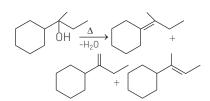
## **14** Which of the following is not the product of dehydration of



Ans. (b) Key Concept When intermediate carbocation is stable, no rearrangement takes place in carbocation.



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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<sub>3</sub>.

Infact, Acid + NaHCO<sub>3</sub>  $\longrightarrow$  Salt + H<sub>2</sub>CO<sub>3</sub> This reaction is possible in forward direction if acid is more acidic than H<sub>2</sub>CO<sub>3</sub>. *o*-nitrophenol is less acidic than  $H_2^{-}CO_3^{-}$ . Hence, it is not soluble in sodium hydrogen carbonate.

#### **16** In the following sequence of reactions,

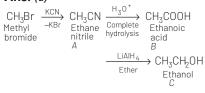
$$CH_3 \longrightarrow Br \xrightarrow{KCN} A \xrightarrow{H_3O^+} B \xrightarrow{\text{LiAlH}_4} C$$

the end product C is

#### [CBSE AIPMT 2012]

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

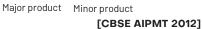
Ans. (d)



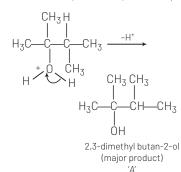
In the presence of LiAIH<sub>4</sub> carboxylic acid reduce in alcohols directly.



$$H_{3}C \xrightarrow[]{CH_{3}} C \xrightarrow[]{CH_{3}} CH \xrightarrow[]{CH_{2}} CH_{2} \xrightarrow[]{H_{2}O/H^{+}} A \xrightarrow[]{CH_{3}} B$$



(a) 
$$H_{3}C$$
 — CH<sub>3</sub>  
 $H_{3}C$  — CH—CH<sub>3</sub>  
 $H_{3}C$  — CH<sub>2</sub>—CH<sub>3</sub>  
(b)  $CH_{2}$  — CH<sub>2</sub>—CH<sub>3</sub>  
 $H_{3}C$  — CH<sub>2</sub>—CH<sub>3</sub>  
 $CH_{3}$   
(c)  $H_{3}C$  — C — CH—CH<sub>3</sub>  
 $H_{3}C$  — CH—CH<sub>3</sub>  
 $H_{3}C$  — CH<sub>2</sub>—CH<sub>2</sub>  
 $H_{3}C$  — CH<sub>3</sub> — CH<sub>3</sub>  
 $H_{3}C$  — CH<sub>3</sub> — CH<sub>3</sub>



**18** Which one is a nucleophilic  
substitution reaction among the  
following? [CBSE AIPMT 2011]  
(a) 
$$RCHO + R'MgX \longrightarrow R - CH - R'$$
  
(b)  $CH_3 \longrightarrow CH_2 - CH - CH_2 - Br$   
 $+ NH_3 \longrightarrow CH_3 - CH_2$   
(b)  $CH_3 - CH_2 - CH - CH_2 - Br$   
 $+ OH_3 \longrightarrow CH_3 - CH_2$   
(c)  $CH_3CHO + HCN \longrightarrow CH_3 - CH(OH)CN$   
(d)  $CH_3 - CH = CH_2 + H_2O \xrightarrow{H^+}$   
 $CH_3 - CH - CH_3$   
(d)  $CH_3 - CH = CH_2 + H_2O \xrightarrow{H^+}$   
 $CH_3 - CH - CH_3$   
 $OH$ 

.

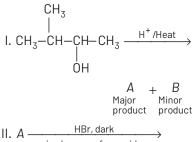
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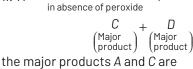
.

#### Ans. (b)

(a) 
$$RCHO + R'MgX \xrightarrow{(Nucleophilic) addition)} R \xrightarrow{-CH-R'} CH_3 OH$$
  
(b)  $CH_3 \longrightarrow CH_2 \longrightarrow CH \longrightarrow CH_2Br + NH_3$   
 $(DH_3 \longrightarrow CH_2 \longrightarrow CH_2 - CH \longrightarrow CH_2NH_2$   
 $(DH_3CHO + HCN \xrightarrow{(Nucleophilic)} CH_3CH(OH)CN$   
(c)  $CH_3CHO + HCN \xrightarrow{(Nucleophilic)} CH_3CH(OH)CN$   
(d)  $CH_3 \longrightarrow CH \longrightarrow CH_2 + H_2O$   
 $\xrightarrow{(Electrophilic)} CH_3 \longrightarrow CH_3 \longrightarrow CH \longrightarrow CH_3$ 

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





respectively



$$\begin{array}{c} CH_{3} \\ (a)CH_{3} \\ -C \\ = CH \\ CH_{3} \\ CH_{3} \\ -C \\ -C \\ -CH_{2} \\ -CH_{3} \\ CH_{3} \\ -C \\ -CH \\ -CH_{3} \\ -CH \\ -CH \\ -CH_{3} \\ -CH_{$$

Ans. (a)

(I) 
$$CH_{3} \longrightarrow CH \longrightarrow CH_{-}CH \longrightarrow CH_{3}$$
  
 $\xrightarrow{H^{+}/\Delta} OH \longrightarrow CH_{3} \xrightarrow{C} CH \longrightarrow CH_{3}$   
 $\xrightarrow{Protonation} CH_{3} \xrightarrow{C} CH \longrightarrow CH_{3}$   
 $\xrightarrow{Protonation} CH_{3} \xrightarrow{C} CH \longrightarrow CH_{3}$   
 $\xrightarrow{Protonation} CH_{3} \xrightarrow{C} CH_{2} \longrightarrow CH_{3}$   
 $\xrightarrow{H^{+}} CH_{3} \xrightarrow{C} CH_{2} \longrightarrow CH_{3}$   
 $\xrightarrow{H^{+}} CH_{3} \xrightarrow{-C} CH_{-}CH_{2} \longrightarrow CH_{3}$   
 $\xrightarrow{H^{+}} CH_{3} \xrightarrow{-C} CH \longrightarrow CH_{3}$   
 $\xrightarrow{H^{+}} CH_{3} \longrightarrow CH_{3} \xrightarrow{-C} CH \longrightarrow CH_{3}$   
 $\xrightarrow{H^{+}} CH_{3} \longrightarrow CH_{3} \longrightarrow CH_{3} \longrightarrow CH_{3}$   
 $\xrightarrow{H^{+}} CH_{3} \longrightarrow CH_{3} \longrightarrow CH_{3} \longrightarrow CH_{3}$   
 $\xrightarrow{H^{+}} CH_{3} \longrightarrow CH_{3} \longrightarrow CH_{3} \longrightarrow CH_{3} \longrightarrow CH_{3}$   
 $\xrightarrow{H^{+}} CH_{3} \longrightarrow CH_{3$ 

$$\xrightarrow{HBr(dark)} CH_3 \xrightarrow{HBr(dark)} CH_3 \xrightarrow{HBr(dark)} CH_3 \xrightarrow{H} CH_2 \xrightarrow{H} CH_3$$

$$\xrightarrow{H} CH_2 \xrightarrow{H} CH_3$$

$$\xrightarrow{H} CH_3 \xrightarrow{H} CH_3$$

$$\xrightarrow{H} CH_3 \xrightarrow{H} CH_3$$

$$\xrightarrow{H} CH_3 \xrightarrow{H} CH_3$$

$$\xrightarrow{H} CH_$$

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 > 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. ( $CH_{3}COOH$ ) after losing

a proton gives acetate  $\begin{bmatrix} CH_3C \\ 0 \end{bmatrix}$  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

 $||| > || > |\vee > |$ 

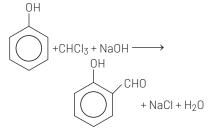
21 Which of the following reactions will not result in the formation of carbon-carbon bonds? [CBSE AIPMT 2010]

- (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 <u>Conc. NaOH</u> CH<sub>3</sub>OH

+ HC00<sup>-</sup>N<sup>+</sup>a

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

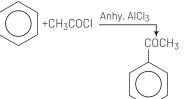
#### (c) Wurtz reaction,

R - X + 2Na + R'X + dry Na

$$\xrightarrow{\text{Ether}} R \longrightarrow R$$

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,

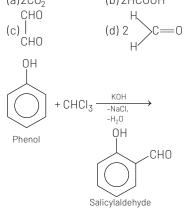
Ethanol  $\xrightarrow{\text{PBr}_3} X \xrightarrow{\text{Alc. KOH}} Y$ 

$$\xrightarrow{(i) H_2 SO_4, \text{ room temperature}} (ii) H_2 O, \text{ heat} \rightarrow Z$$

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  $\xrightarrow{Alc. KOH} CH_2 = CH_2$   
 $\xrightarrow{-KBr} -H_2O$   
 $\xrightarrow{-KBr} -H_2O$   
 $\xrightarrow{-H_2O}$   
 $\xrightarrow{-H_2O}$   
 $\xrightarrow{-H_2OA} CH_3 - CH_2OSO_3H \xrightarrow{-H_2OA} CH_3CH_2OH$   
Ethanol  
Ethanol  
  
H\_2COH · CH\_2OH on heating with  
periodic acid gives  
[CBSE AIPMT 2009]  
(a) 2CO\_2 (b) 2HCOOH



CH<sub>2</sub>OH | + HIO<sub>4</sub> ----CH<sub>2</sub>OH Periodic acid Ethylene glycol (Oxidising agent)

$$2 H C = 0 + HIO_3$$

24 Consider the following reaction, Phenol

$$\xrightarrow{Zn-dust} X \xrightarrow{CH_3CI} Y \xrightarrow{Alk. KMnO_4} Z$$

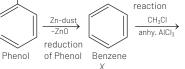
The product Z is

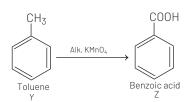
#### [CBSE AIPMT 2009]

Friedel-Craft's









#### 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

 $\begin{array}{c} CH_2 - CH_2 + RMgX \longrightarrow RCH_2CH_2OMg \\ Grignard's \\ reagent \\ Ethylene oxide \\ R - CH_2 - CH_2 - OH \xleftarrow{Hydrolysis}{-Mg(OH)X} \\ Primary alcohol \end{array}$ 

**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)  $C_n H_{2n+1}^{-1}$ **Ans.** (d)

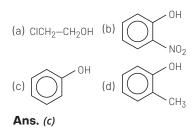
Alkanols are the derivatives of alkanes which are derived by the replacement of -H of alkanes with -OH (hydroxyl groups).

 $(d)C_{n}H_{2n+2}O$ 

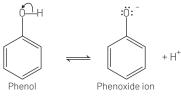
$$\begin{array}{c} C_n H_{2n+2} \xrightarrow{-H} C_n H_{2n+1} OH\\ Alkanes \end{array}$$

or  $C_nH_{2n+2}O$ 

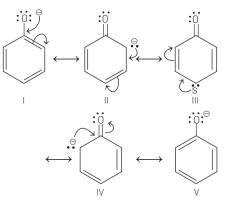
27 Which one of the following compounds is most acidic ? [CBSE AIPMT 2005]



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) CH <sub>2</sub> OOCR   CHOOCR + 3H <sub>2</sub>   CH <sub>2</sub> OOCR Triglycerides	$0 \xrightarrow{\text{Lipase}} \begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{hydrolysis} \end{array} \xrightarrow{\text{CHOH}} \begin{array}{c} \text{CHOH} \\   \\ \text{CHOH} \\ \text{CH}_2\text{OH} \\ \text{Glycerol} \\ + RCOOH \\ \text{Fatty acid} \end{array}$

29 Which of the following will not form a yellow precipitate on heating with an alkaline solution of iodine? [CBSE AIPMT 2004]

(a) CH<sub>3</sub>CH(OH)CH<sub>3</sub>

(b)  $CH_{3}CH_{2}CH(OH)CH_{3}$ (c)  $CH_{3}OH$ (d)  $CH_{3}CH_{2}OH$ 

#### **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  $H_3CH_3-CC-group$ .

(a) CH<sub>3</sub>CH(OH)CH<sub>3</sub> +  $I_2 \xrightarrow{\text{NaOH}} \text{CH}_3\text{COCH}_3$ + 2HI + 3NaI + CH<sub>3</sub>COO<sup>-</sup>N<sup>+</sup>a + 3H<sub>2</sub>O





 $CH_{3}COCH_{3} + 3I_{2} + 4NaOH \rightarrow CHI_{3} \downarrow$ Yellow ppt + 3Nal + CH<sub>3</sub>COO<sup>-</sup>N<sup>+</sup> a + 3H<sub>2</sub>O (b) CH<sub>2</sub> —CH<sub>2</sub>CH(OH)CH<sub>3</sub> +  $I_2 \rightarrow$ -CH<sub>3</sub> + 2HI CH\_-Ethyl methyl ketone It gives iodoform test  $-CH_3 + 3I_2 + 4NaOH$ CHI,↓  $+3Nal+CH_3CH_2COONa+3H_2O$ Yellow ppt (c)  $CH_{3}OH + I_{2} \rightarrow HCHO + 2HI$ It does not have methyl ketonic group, so it does not give yellow ppt. with I<sub>2</sub> in presence of alkali. (d)  $CH_3CH_2OH + I_2 \rightarrow CH_3$ -H + 2HICHI<sub>3</sub> Yellow ppt. + HCOONa + 3Nal + 2H<sub>2</sub>O Due to the presence of -COCH<sub>7</sub> 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.  $PCI_5$ )  $ROH + PCI_5 \rightarrow RCI + POCI_3 + HCI$ Alcohol

 $\begin{array}{c} R\text{COOH} + \text{PCI}_5 \rightarrow R\text{COCI} + \text{POCI}_3 + \text{HCI}\\ \text{Acid} \end{array}$ 

**31** When phenol is treated with  $CHCI_3$  and NaOH, the product formed is

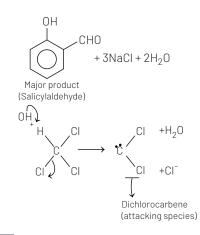
#### [CBSE AIPMT 2002]

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

#### Det....

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

+ CHCl<sub>3</sub> + 3NaOH 
$$\longrightarrow$$



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

#### (a)PCI₅

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

#### Ans. (c)

*n*-propyl alcohol and *iso*-propyl alcohol gives different products on oxidation with  $K_2 Cr_2 O_7$ 

$$\begin{array}{c} \text{CH}_{3} & -\text{CH}_{2} & -\text{CH}_{2}\text{OH} & \xrightarrow{[0]}{\text{K}_{2}\text{Cr}_{2}\text{O}_{7}/\text{H}_{2}\text{SO}_{4}} \\ \xrightarrow[1^{\circ} \text{ alcohol} & \text{CH}_{3} - \text{CH}_{2} - \text{CH} \end{array}$$

$$\begin{array}{c} CH_{3} & \hline CH_{-}CH_{-}CH_{3} & \hline 0 \\ | \\ OH \\ lsopropyl alcohol \\ 2^{\circ} alcohol \end{array}$$

**33** In preparation of alkene from alcohol using  $Al_2O_3$ , which is effective factor?

[CBSE AIPMT 2001]

(a) Porosity of Al<sub>2</sub>O<sub>3</sub>
(b) Temperature
(c) Concentration
(d) Surface area of Al<sub>2</sub>O<sub>3</sub>

#### Ans. (b)

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

$$R - CH_2 - CH_2OH \xrightarrow{Al_2O_3} 350^\circ - 380^\circ C$$

**CLICK HERE** 

R—CH==CH<sub>2</sub> + H<sub>2</sub>O 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

 $\begin{array}{c} 2(C_6H_{10}O_5)_n + nH_2O \xrightarrow[]{\text{Diastase}} \\ (\text{starch}) & nC_{12}H_{22}O_{11} \\ (\text{maltose}) \end{array}$ 

## **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  $\rm H_2SO_4$  gives glycerine
- (c) Alcoholic iodine with NaOH gives iodoform
- (d) Sucrose on reaction with NaCl gives invert sugar

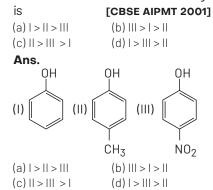
#### Ans. (c)

 $C_2H_5OH + 4I_2 + 6NaOH \rightarrow CHI_3 ↓$ Iodoform

+ HCOO<sup>-</sup>N<sup>+</sup> a + 5Nal + 5H<sub>2</sub>O

lodoform is a pale yellow solid.

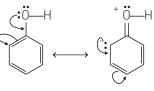
#### **36** The correct acidic order of following



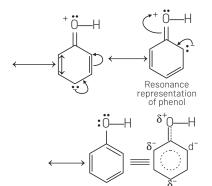
#### Ans. (b)

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

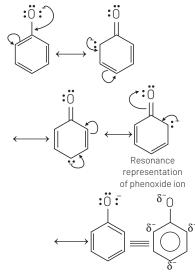
(a) Due to resonance (which is not possible in alcohols), the oxygen atom of the — OH group acquires a positive charge which helps in the release of a proton.



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(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.



 $Ar -OH \implies ArO^- + H^+$ 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.

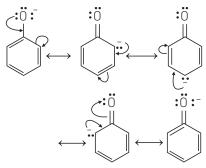
**37** The ionisation constant of phenol is higher than that of ethanol because [CBSE AIPMT 2000]

- (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



 $C_2H_5 \longrightarrow 0 \longrightarrow H \iff C_2H_5 \longrightarrow 0^- + H^+$ 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]

$$\begin{array}{c} 0 \\ || \\ (a) CH_3 - C - 0 - 0 - H \\ (b) H_3 BO_3 \\ (c) B_2 H_6 / NaOH - H_2 O_2 \\ (d) H_2 SO_4 / H_2 O \\ \textbf{Ans. (c)} \end{array}$$

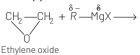
Hydroboration-oxidation reaction

 $6CH_{3}CH = CH_{2} \xrightarrow{B_{2}H_{6}} 2(CH_{3}CH_{2}CH_{2})_{3} B$ Propene Tri-n-propylborane  $\downarrow H_{2}O_{2} / OH^{-}$   $6CH_{3}CH_{2}CH_{2}OH$ Propan-t-ol

**39** Reaction of  $H_2 C - CH_2$  with RMgX

0 leads to formation of [CBSE AIPMT 1998] (a) RCH0HR (b) RCH0HCH<sub>3</sub> (c) RCH<sub>2</sub>CH<sub>2</sub>OH (d) CHCH<sub>2</sub>OH

#### Ans. (c)



$$\begin{array}{c} \mathsf{Mg(OH)}X + \\ R - CH_2 - CH_2 - OH \leftarrow \\ H_2 O/H^+ \end{array}$$

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

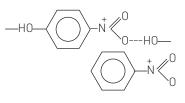
- (a) NO<sub>2</sub> group at *p*-position behaves in a different way from that at *o*-position
- (b) intramolecular hydrogen bonding exists in *p*-nitrophenol
- (c) there is intermolecular hydrogen bonding in *p*-nitrophenol
- (d) *p*-nitrophenol has a higher molecular weight than *o*-nitrophenol

#### 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



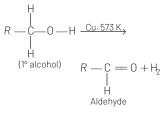
**41** What is formed when a primary alcohol undergoes catalytic dehydrogenation?

#### [CBSE AIPMT 1993]

(a) Aldehyde (c) Alkene (b) Ketone (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.



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R CH<sub>2</sub>CH<sub>2</sub><sup>+1</sup>OMgX

1° alcohol gives aldehyde by catalytic dehydrogenation

e.g.

$$\begin{array}{c} CH_{3} \longrightarrow CH \longrightarrow O \xrightarrow{Cu + 573 \text{ K}} CH_{3}CHC \\ | & | \\ H & H \end{array}$$

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  $K_2 Cr_2 O_7 / H_2 SO_4$ 

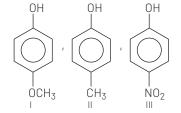
 $\begin{array}{c} H_{3}C \\ H_{3}C \\ \end{array} \xrightarrow{2^{\circ} \text{ alcohol}} H_{3}C \\ H_{3}C \\ H_{3}C \\ \end{array} \xrightarrow{2^{\circ} \text{ alcohol}} C = 0 + H_{2} \\ H_{3}C \\ \end{array}$ 

**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

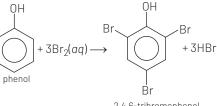
#### 44 When phenol is treated with excess of bromine water, it gives [CBSE AIPMT 1992]

(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.



2,4,6-tribromophenol (White ppt)

#### 45 Methanol is industrially prepared by [CBSE AIPMT 1992]

- (a) oxidation of  $CH_4$  by steam at  $900^{\circ}C$
- (b) reduction of HCHO using LiAIH<sub>4</sub>
- (c) reaction of HCHO with a solution of NaOH
- (d) reduction of CO using  $\rm H_2$  and  $\rm ZnO-Cr_2O_3$

#### 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.

$$CO + 2H_2 \xrightarrow{Cr_2O_3-ZnO} CH_3OH$$

#### **46** How many isomers of C<sub>5</sub>H<sub>11</sub>OH will

be primary alcohols? [CBSE AIPMT 1992] (a) 5 (b) 4 (c) 2 (d) 3

#### Ans. (b)

The primary alcohols isomers of C<sub>5</sub>H<sub>11</sub>OH are

(i) 
$$CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - OH$$
  
(ii)  $CH_3 - CH - CH_2 - CH_2 - OH$   
(iii)  $CH_3 - CH_2 - CH_2 - OH$   
(iii)  $CH_3 - CH_2 - CH - CH_2 - OH$   
 $CH_3 - CH_3 - CH_3 - CH_3$ 

47 Propene, CH<sub>3</sub> — CH == CH<sub>2</sub> 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<sub>4</sub> (alkaline) (b)Osmium tetroxide (OsO<sub>4</sub> / CH<sub>2</sub>Cl<sub>2</sub>) (c)B<sub>2</sub>H<sub>6</sub> and alk H<sub>2</sub>O<sub>2</sub> (d)O<sub>3</sub>/Zn

#### Ans. (c)

$$3CH_{3} CH = CH_{2} \xrightarrow{B_{2}H_{6}} (CH_{3} - CH_{2} - CH_{2})_{3}B$$

$$\xrightarrow{H_{2}O_{2}/OH^{-}} CH_{3} - CH_{2} - CH_{2} - OH$$
Propan-1-ol
Propan-1-ol

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

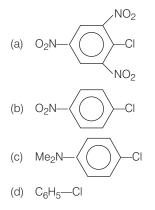
(d)2-methyl propan-2-ol

#### 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.

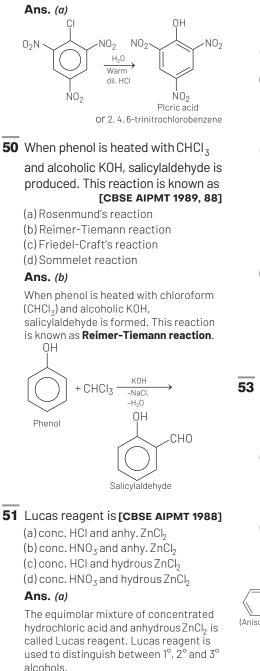
**49** Which chloro derivative of benzene among the following would undergo hydrolysis most readily with aq. NaOH to furnish the corresponding hydroxy derivative?

#### [CBSE AIPMT 1989]



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#### TOPIC 2 Ethers

**52** The compound which shows metamerism is [NEET 2021] (a) $C_5H_{12}$  (b) $C_3H_80$  (c) $C_3H_60$  (d) $C_4H_{10}0$ 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.

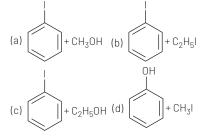
- (a) C<sub>5</sub>H<sub>12</sub> contains no functional group. So, it cannot show metamerism.
- (b)  $C_3H_8O$  has ether functional group in which only one arrangement is possible. So, it does not show metamerism.
- CH<sub>3</sub>—0—CH<sub>2</sub>—CH<sub>3</sub> (c) C<sub>3</sub>H<sub>6</sub>O has carbonyl functional group in which following two arrangements are possible.

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

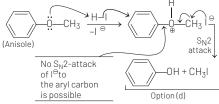
(d)  $C_4H_{10}O$  has ether functional group in which following two arrangements are possible. So, it shows metamerism.

$$Ethoxy ethane$$

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







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]

$$\begin{array}{c} \mathsf{H}_{3}\mathsf{C} - \mathsf{C}\mathsf{H}_{2} - \mathsf{C}\mathsf{H}_{2} - \mathsf{O}\mathsf{C}(\mathsf{C}\mathsf{H}_{3})_{3} \\ \xrightarrow{\mathsf{Excess}\,\mathsf{H} !}{\Delta} \; \mathcal{C} + \mathcal{D} \end{array}$$

(a)
$$H_3C$$
— $CH_2$ — $CH_2$ —I and I— $C(CH_3)_3$ 

(b)H<sub>3</sub>C—CH<sub>2</sub>—CH<sub>2</sub>—OH and  

$$I = C(CH_3)_3$$
  
(c)H<sub>3</sub>C—CH<sub>2</sub>—CH<sub>2</sub>—H and  
HO—C(CH<sub>3</sub>)<sub>3</sub>  
(d)H<sub>3</sub>C—CH<sub>2</sub>—CH<sub>2</sub>—OH and  
HO—C(CH<sub>3</sub>)<sub>3</sub>

#### Ans. (a)

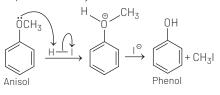
Ethers are readily cleaved by heating in presence of halogen acids to form alcohol and an alkyl halide. In case of unsymmetrical ethers, halogen goes preferentially with smaller alkyl group or more stable carbocation.

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.

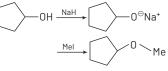
$$\begin{array}{c} \mathsf{CH}_3\mathsf{CH}_2\mathsf{CH}_2\mathsf{OC}(\mathsf{CH}_3)_3 \xrightarrow[]{\mathsf{H}} \\ \mathsf{CH}_3\mathsf{CH}_2\mathsf{CH}_2\mathsf{OH} + (\mathsf{CH}_3)_3 | \\ \Delta \\ \downarrow_{\mathsf{H}}^{\mathsf{Excess}} & D' \\ \mathsf{CH}_3\mathsf{CH}_2\mathsf{CH}_2\mathsf{H}_2\mathsf{H} \\ \mathsf{CH}_3\mathsf{CH}_2\mathsf{CH}_2\mathsf{H}_2\mathsf{H} \end{array}$$

# 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.



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

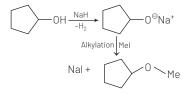
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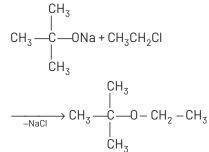


#### Ans. (d)

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



#### 57 The reaction,

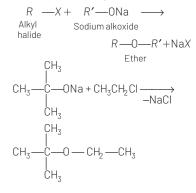


#### is called [CBSE AIPMT 2015]

- (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]**  $CH_{3}CH_{2}CH \Longrightarrow CH_{2} \xrightarrow{HBr/H_{2}O_{2}} Y$  $\xrightarrow{C_{2}H_{5}ONa} Z$ (a) $CH_{3}$ —  $(CH_{2})_{3}$ — 0— $CH_{2}CH_{3}$ 

(b)(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub> — 0 — CH<sub>2</sub>CH<sub>3</sub>

(d) CH<sub>3</sub>CH<sub>2</sub>—CH(CH<sub>3</sub>)—O—CH<sub>2</sub>CH<sub>3</sub>  
**Ans.** (a)  
CH<sub>3</sub>CH<sub>2</sub>CH=CH<sub>2</sub>
$$\xrightarrow{HBr/H_2 O_2}$$
  
CH<sub>3</sub>CH<sub>2</sub>CH=CH<sub>2</sub> $\xrightarrow{HBr/H_2 O_2}$   
CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br $\longrightarrow$   
Bromo-butanane(1° product)  
CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br $\xrightarrow{C_2H_5 ONa}$   
(Williamson's synthesis)  
CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CC<sub>2</sub>H<sub>5</sub>  
Ethoxy-butane  
**59** Among the following sets of  
reactants which one produces  
anisole? [CBSE AIPMT 2014]  
(a) CH<sub>3</sub>CHO, RMgX

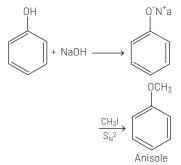
(b)C<sub>6</sub>H<sub>5</sub>OH, NaOH, CH<sub>3</sub>I

 $(c)CH_3(CH_2)_4 - 0 - CH_3$ 

- (c)C<sub>6</sub>H<sub>5</sub>OH, neutral FeCl<sub>3</sub>
- $(d)C_6H_5-CH_3, CH_3COCI, AICI_3$

#### 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<sub>3</sub>—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—O—CH<sub>3</sub>
(b)CH<sub>3</sub>—CH<sub>2</sub>—C H—O—CH<sub>3</sub>

$$\begin{array}{c} & & & \\ & & & \\ & & & \\ CH_{3} \\ (c)CH_{3} \\ - & C \\ & & \\ & CH_{3} \\ (d)CH_{3} \\ - & CH \\ - & CH_{2} \\ - & O \\ - & CH_{3} \end{array}$$

#### **Ans.** (c)

The ether which gives more stable carbocation, forms  $CH_3OH$  as one of the

CLICK HERE

product with hot conc. HI. The order of stability of carbocation is 3°>2°>1°  $CH_3$ — OCH<sub>3</sub> gives CH<sub>3</sub>OH as Thus, CH<sub>3</sub>. CHone of the product. The reaction proceeds as CH-CH2 CH<sub>3</sub> H CH₃ . C⁺ +CH₂OH ĊH3 3° carbocation CH<sub>3</sub> -C----I + CH<sub>3</sub>OH | Methanol ĊH₄ 61 The reaction CH<sub>3</sub>  $H_3C - CH - CH_2 - O - CH_2 - CH_3$ Which of the following compounds will be formed? [CBSE AIPMT 2007] CH<sub>2</sub>  $(a)H_3C$  — CH —  $CH_2$  —  $I + CH_3CH_2OH$ (b)CH<sub>3</sub> ----CH----CH<sub>3</sub> + CH<sub>3</sub>CH<sub>2</sub>OH  $CH_3$ (c)CH<sub>3</sub>--CH -----CH<sub>2</sub>OH + CH<sub>3</sub>CH<sub>3</sub> CH<sub>3</sub>

#### CH<sub>3</sub> | (d)H<sub>3</sub>C —CH— CH<sub>2</sub>OH + CH<sub>3</sub>—CH<sub>2</sub>—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.

$$CH_{3} \longrightarrow CH_{2} \longrightarrow C$$

**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)  $CH_3OC_1(CH_3)_2$ 

 $(d) CH_3 + (CH_3)_2 CHOH$ 

#### Ans. (d)

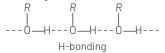
 $CH_3 \longrightarrow CH(CH_3)_2 + HI \xrightarrow{373 \text{ K}} CH_3I$ 

Unsymmetrical ether  $+(CH_3)_2$  CHOH In case of unsymmetrical ether, the alkyl halide is always formed from smaller alkyl group. This happens, because I<sup>-</sup> 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.



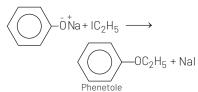
64 Which one is formed when sodium phenoxide is heated with ethyl iodide? [CBSE AIPMT 1988] (a) Phenetole

(b) Ethyl phenyl alcohol

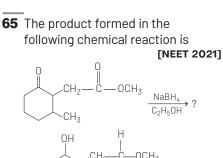
(c) Phenol(d) None of the above

#### **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** 



#### **TOPIC 3** Aldehydes and Ketones

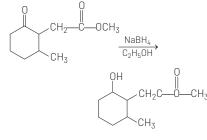


(b)  

$$\begin{array}{c}
 & CH_{3} & CH_{2} \\
 & CH_{2} & CH_{2} \\
 & CH_{3} \\$$

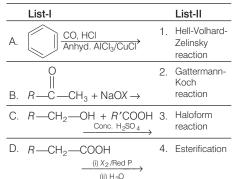
#### Ans. (d)

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



**CLICK HERE** 

#### 66 Match List-I with List-II.



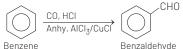
#### [NEET 2021]

Choose the correct answer from the options given below.

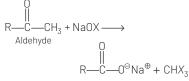
	А	В	С	D	А	В	С	D	
(a)	4	1	2	3	(b) 3	2	1	4	
(c)	1	4	3	2	(d) 2	3	4	1	

#### Ans. (d)

A. Gattermann-Koch reaction Benzene or its derivatives are treated with CO and HCl in presence of anhydrous  $AICI_3/CuCl$ .



B. Haloform reaction Treatment of carbonyl compound having atleast one methyl group attached to the C=0 with  $X_2$  / NaOH or NaOX.

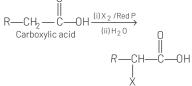


C. **Esterification** Carboxylic acid reacts with an alcohol in acidic medium.

R — CH<sub>2</sub> — OH + R'COOH Alcohol Acid

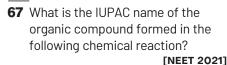
R-CH<sub>2</sub>-0-C-R'

D. Hell-Volhard Zelinsky reaction Treatment of carboxylic acid having  $\alpha$ -hydrogen with PX<sub>3</sub> or X<sub>2</sub>/Red P.



 $\alpha$ -halocarboxylic acid

Hence, correct match is  $A \rightarrow 2$ ,  $B \rightarrow 3$ ,  $C \rightarrow 4$ ,  $D \rightarrow 1$ .

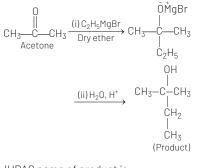


Acetone  $\frac{(i) C_2 H_5 MgBr, Dry \text{ ether}}{(ii) H_2 0, H^+}$  product

(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.

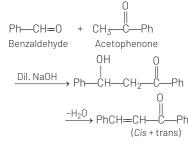
**68** Reaction between benzaldehyde and acetophenone in presence of dilute NaOH is known as

#### [NEET (Sept.) 2020]

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

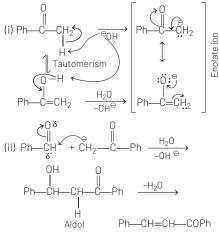
#### Ans. (c)

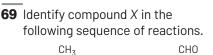
Dilute NaOH is the reagent for aldol condensation. Dilute NaOH process enolate ion from acetophenone which attacks benzaldehyde to give aldol.

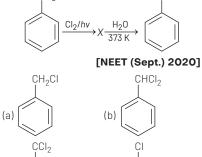


It is cross aldol condensation or Claisen-Schmidt reaction or Claisen reaction.





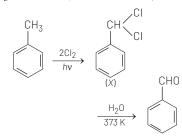




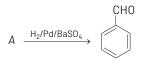


An 1, 1-gem-dihalide on hot hydrolysis (H<sub>2</sub>O/373 K) can produce an aldehyde.

(d)

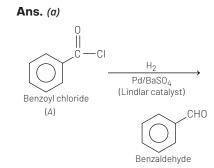


**70** Identify compound (A) in the following reaction. [NEET (Oct.) 2020]



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

**CLICK HERE** 



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]

$$H_{3}C \longrightarrow C \equiv CH \xrightarrow{H_{2}O, H_{2}OO_{4}}_{HgSO_{4}} \rightarrow$$
Intermediate  $\longrightarrow$  Product
$$(A) \qquad (B)$$

a) 
$$A = H_{3}C - C = CH_{2};$$
  
 $SO_{4}$   
 $B = H_{3}C - C - CH_{3}$   
 $O$   
b)  $A = H_{3}C - C = CH_{2};$   
 $OH$   
 $B = H_{3}C - C = CH_{2}$   
 $SO_{4}$   
c)  $A = H_{3}C - C - C - CH_{3};$   
 $O$ 

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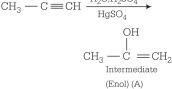
$$B = H_3C - C \equiv CH$$
(d) 
$$A = H_3C - C \equiv CH_2;$$

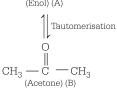
$$|$$

$$OH$$

$$B = H_3C - C - CH_3$$

Ans. (d) 
$$H_2O, H_2SO$$

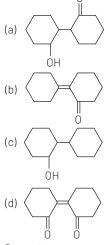




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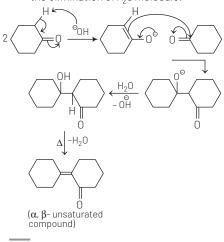
ОH Therefore,  $A = CH_{3}$ -Ċ == CH.  $B = CH_{\tau}$ CH-

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

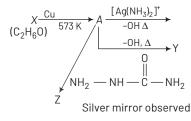


#### Ans. (b)

Aldehydes and ketones containing  $\alpha$ —H atoms undergo aldol condensation in presence of dilute alkali as catalyst and gives  $\alpha$ ,  $\beta$  unsaturated compound with the elimination of H<sub>2</sub>O molecule.



73 Consider the reactions,



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

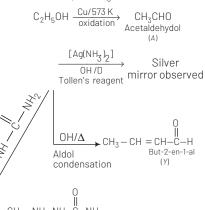
- (a) A-methoxymethane, X-ethanoic acid, Y-acetate ion, Z-hydrazine
- (b) A-methoxymethane, X-ethanol, Y-ethanoic acid, Z-semicarbazide
- (c) A-ethanal, X-Acetaldelyde, Y-but-2-enal, Z-semicarbazone
- (d) A-ethanol, X-acetaldehyde, Y-butanone, Z-hydrazone

#### Ans. (c)

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

Therefore,

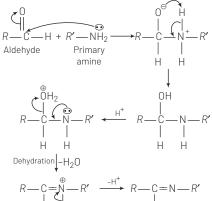
A is acetaldehyde (CH<sub>3</sub>CHO)



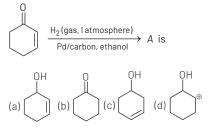
 $CH_3 - CH = NH - NH - C - NH_2$ Semicarbazone (Z)

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)

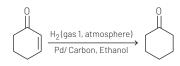


Н Н Н Schiff's base 75 The correct structure of the product A formed in the reaction [NEET 2016, Phase II]



#### Ans. (b)

In presence of Pd-catalyst, selective reduction of  $\alpha$ ,  $\beta$ -unsaturated carbonyl is observed as hydrogenation takes place of carbon-carbon double bond only.

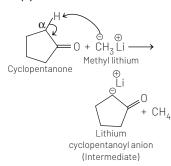


#### 76 Treatment of cyclopentanone

0 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)



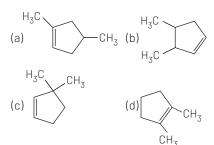
Here, CH<sub>3</sub>Li abstract is an active proton from cyclo pentanone forming methane leaving behind an intermediate lithium cyclopentanoyl anion.

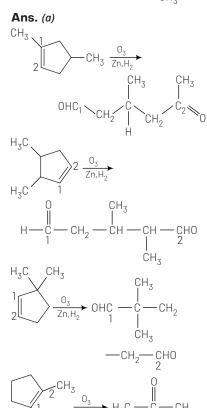
**77** A single compound of the structure is

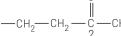
$$\begin{array}{c} CH_3 & CH_3 \\ | \\ OHC \\ C \\ H_2 \\ H_2 \\ H_2 \end{array}$$

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

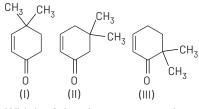
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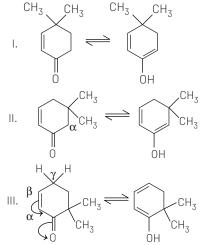
Which of the given compounds can exhibit tautomerism?

#### [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  $\alpha\text{-hydrogen}$  (structure I and II).



Here,  $\gamma$ -H participates in tautomerism.

**79** An organic compound *X* having molecular formula C <sub>5</sub>H<sub>10</sub>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 = 0 group but is neither a methyl ketone nor an aldehyde. The structure of X could be

having molecular formula  $C_{E}H_{10}O$ .

**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. (\*)

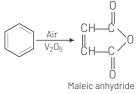
Reaction of carbonyl compounds with ammonia derivatives give addition product followed by the elimination reaction. Slightly acidic medium generate a nucleophilic centre for the attack of weak base like ammonia derivatives.

#### **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

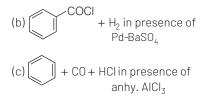
#### Ans. (b)



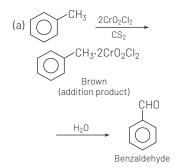
## 82 Reaction by which benzaldehyde cannot be prepared? [NEET 2013]

(a) 
$$CH_3 + CrO_2CI_2$$
 and  $CS_2$ 

followed by H<sub>3</sub>O<sup>+</sup>



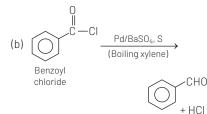
Ans. (d)



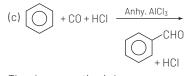
This reaction is known as **Etard** reaction.



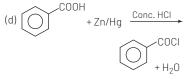




This reaction is called **Rosenmund** reaction.







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]

(b) iodoform test

(c) Tollen's reagent test

(d) Fehling solution test

#### Ans. (b)

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

$$CH_3CHO due to the presence of
 $\begin{vmatrix} O \\ | | \\ CH_3 - C - \\ \end{vmatrix}$  group reacts with NaOH$$

and  $l_2$  to give yellow crystals of iodoform while  $C_6H_5CH_2CHO$  does not react with it.  $CH_3CHO + 3l_2 + 4NaOH \longrightarrow CHI_3$ 

+ HCOONa + 3Nal + 
$$3H_2O$$
  
 $C_6H_5CH_2CHO + I_2 + NaOH \longrightarrow$   
No reaction

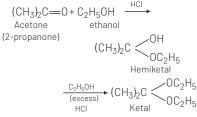
Thus,  $CH_3CHO$  and  $C_6H_5CH_2CHO$  can be distinguished by iodoform test.

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

(a) 
$$CH_{3}CH_{2}CH_{2}$$
 —  $C$  —  $CH_{3}$   
(b)  $CH_{3}CH_{2}CH_{2}$  —  $C$  —  $CH_{2}CH_{2}CH_{3}$   
(c)  $(CH_{3})_{2}C$   $< OH \\ OC_{2}H_{5}$   
(d)  $(CH_{3})_{2}C$   $< OC_{2}H_{5}$   
 $OC_{2}H_{5}$ 

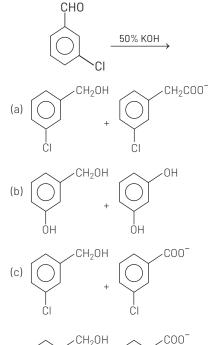
Ans. (d)

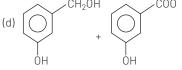
When carbonyl compounds are treated with alcohol, they form hemiacetal (hemiketal and acetal/ketal.)



**NOTE** Formation of hemiketal is a nucleophilic addition reaction.

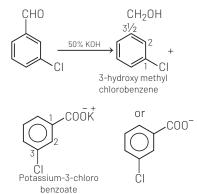
85 Predict the products in the given reaction, [CBSE AIPMT 2012]





#### 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.



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

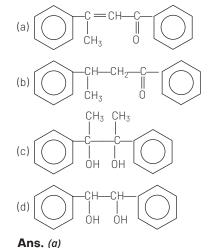
(a) Zn-Hg with HCl
(b)LIAIH<sub>4</sub>
(c)H<sub>2</sub> and Pt as catalyst
(d) Glycol with KOH

#### **Ans.** (a)

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

$$> C = 0 \xrightarrow{Zn-Hg/HCl} > CH_2$$

87 Acetophenone when reacted with a base, C<sub>2</sub>H<sub>5</sub>ONa, yields a stable compound which has the structure [CBSE AIPMT 2008]



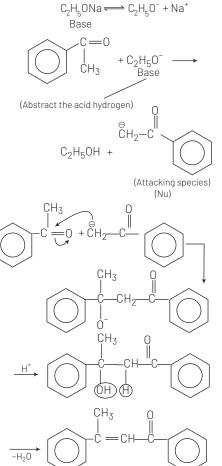
Aldehydes and ketones withα-hydrogen atom, when reacted with a base yields

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aldol which on heating loses water molecule to give  $\alpha,\,\beta$ -unsaturated aldehydes or ketones. This reaction is called aldol condensation reaction.



**88** A strong base can abstract an  $\alpha$ -hydrogen from

[CBSE AIPMT 2008]

(b) amine

(d) alkane

(a) alkene (c) ketone

#### 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  $\alpha$ -C of the ketones or aldehydes. That's why  $\alpha$ -hydrogen is easily abstracted from ketones by a base, e.g. in aldol condensation reaction,  $\alpha$ -hydrogen atom of aldehyde or ketone is abstracted by a strong base.

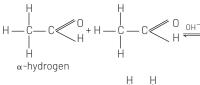
## 89 The product formed in aldol condensation is [CBSE AIPMT 2007]

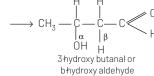
- (a) a beta-hydroxy acid
- (b) a beta-hydroxy aldehyde or a beta-hydroxy ketone

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

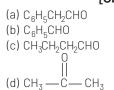
#### **Ans.** (b)

Condensation between two molecules of an aldehyde or a ketone having atleast one  $\alpha$ -hydrogen atom in presence of a base to form a  $\beta$ -hydroxy aldehyde or  $\beta$ -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]



#### Ans. (b)

Aldehydes which do not have any  $\alpha$ -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.  $2C_6H_5CHO + NaOH \longrightarrow C_6H_5CH_2OH$ Benzyl alcohol

> + C<sub>6</sub>H<sub>5</sub>COONa Sodium benzoate

**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

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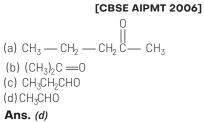
- (c) Dow reduction
- (d) Wolff-Kishner reduction

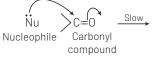
#### Ans. (a)

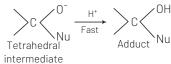
**Clemmensen reduction** Aldehydes and ketones are reduced to the corresponding alkanes by means of amalgamated zinc and HCl.

$$C = 0 + 4[H] \xrightarrow{Zn-Hg/HCl} CH_2 + H_20$$

## **92** Nucleophilic addition reaction will be most favoured in







The carbonyl compounds undergo nucleophilic addition reaction because oxygen is more electronegative than carbon. As such, it withdraws shared  $\pi$ -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

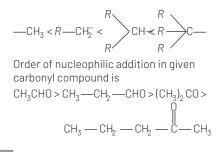
atom of C=0 group. In aldehyde

>C==0 group is present with at least

one alkyl group (except formaldehyde) which has +/-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.

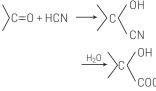
Hence, by means of attachment of alkyl groups (due to +/-effect) rate of nucleophilic addition decreases. That means e<sup>-</sup> density at C-atom decreases, nucleophilic addition reaction increases. Order of +/-effect in alkyl group

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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)

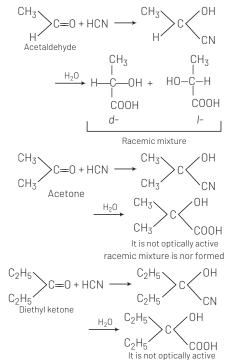


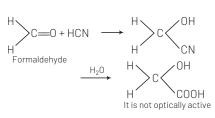




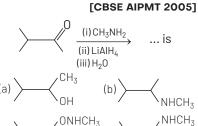
In this reaction, by the complete hydrolysis of cyanide gives acid and partial hydrolysis gives amide.

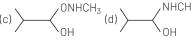
If it is racemic mixture, therefore such C-atom must be asymmetric carbon atom.

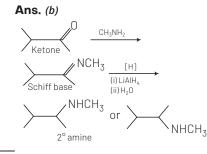




**94** The major organic product formed from the following reaction







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

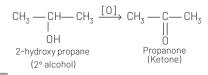
(a) 2-hydroxy propane(b) Ortho-nitro phenol

(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

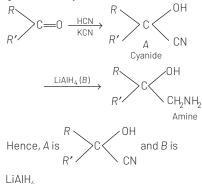
$$R - C - R' \xrightarrow{HCN/}{KCN} A \xrightarrow{B} 0$$

$$R - C \xrightarrow{OH}{R} \xrightarrow{C} OH$$

(a) 
$$A = RR'CH_2CN$$
,  $B = NaOH$   
(b)  $A = RR'C \checkmark OH COOH$ ,  $B = CH_3$   
(c)  $A = RR'C \checkmark CN COOH$ ,  $B = CH_3$   
(d)  $A = RR'C \checkmark OH B = LiAIH_4$ 

#### Ans. (d)

In the presence of  $\mbox{LiAlH}_4,$  cyanide group gives amine by reduction.



#### **97** In this reaction, $CH_3CHO + HCN \rightarrow CH_3CH(OH)CN$

an asymmetric centre is

generated. The acid obtained would be [CBSE AIPMT 2003]

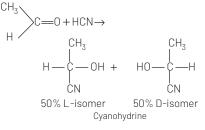
(a) 50% D + 50% L-isomer (b) 20% D + 80% L-isomer

(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.



**98** Polarisation of electrons in acrolein may be written as

 $[ \underset{\delta_{-}}{\text{CBSE AIPMT 2000} } ]$ 

(a) 
$$CH_2 = CH - CH = 0$$
  
(b)  $CH_2 = CH - CH = 0$ 

84

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(c) 
$$\stackrel{\delta_{+}}{CH_{2}=CH_{-}CH=0} \stackrel{\delta_{+}}{O}$$
  
(d)  $\stackrel{\delta_{-}}{CH_{2}=CH_{-}CH=0}$   
**Ans.** (a)  
In  $CH_{2}=CH_{-}CHO$  due to - *M*-effect of -CHO group, polarisation of electron takes place as follows :  
 $CH_{2}=CH_{-}C=0 \leftrightarrow \stackrel{+}{C}H_{2}-CH=C_{-}O^{-}$   
H  
**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)  $R-C=N$   
(c)  $R-C=NH_{2}$   
(d)  $R-CH=NH$   
**Ans.** (a)  
 $R \rightarrow C=0 + NH_{2}-NH_{2} \xrightarrow{KOH}$   
Aldehyde Hydrazine  
 $R \rightarrow C=N-NH_{2} + H_{2}O$ 

Aldehyde hydrazone

## **100** Aldol condensation will not take place in

#### [CBSE AIPMT 1999]

(a) HCHO (b) CH<sub>3</sub>CHO (c) CH<sub>3</sub>COCH<sub>3</sub> (d) CH<sub>3</sub>CH<sub>2</sub>CHO

#### **Ans.** (a)

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

#### **101** lodoform 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  $CH_3 - CO - group \text{ or } CH_3 - CH group give positive | iodoform test. In 2-pentanor <math>R_{+}^{H}$  ( $CH_3CH_2CH_2COCH_3$ ),  $CH_3CHO$  and  $C_2H_5OH$ , required groups are present, thus they give iodoform as follows

$$\begin{array}{c} CH_{3} & --COCH_{2} & --CH_{2} CH_{3} + 3I_{2} + 4NaOH \rightarrow \\ CHI_{3} \downarrow + CH_{3}CH_{2}CH_{2}COONa \\ lodoform + 3NaI + 3H_{2}O \\ (yellow ppt.) \end{array}$$

$$\begin{array}{c} CH_{3} CHO + 3I_{2} + 4NaOH \longrightarrow \\ CHI_{3} \downarrow + HCOONa + 3NaI + 3H_{2}O \\ lodoform \\ (yellow ppt) \end{array}$$

$$\begin{array}{c} C_{2}H_{5}OH \xrightarrow{I_{2}} CH_{3}CHO \\ CH_{3}CHO + 3I_{2} + 4NaOH \longrightarrow CHI_{3} \downarrow \\ lodoform \end{array}$$

$$\begin{array}{c} +HCOONa + 3NaI + 3H_{2}O \\ lodoform \end{array}$$

$$\begin{array}{c} +HCOONa + 3NaI + 3H_{2}O \\ lodoform \end{array}$$

$$\begin{array}{c} 0 \\ +HCOONa + 3NaI + 3H_{2}O \\ 0 \\ \end{array}$$
But due to absence of CH\_{3} - CH \\ 0 \\ OH \\ Or CH\_{3} - C = 0 \\ 0 \\ CH\_{3} - CH\_{2} - CH\_{2} - CH\_{3} + I\_{2} + NaOH \\ 3 - pentanone \end{array}
$$\begin{array}{c} 0 \\ \longrightarrow No \ reaction. \end{array}$$

#### **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 )

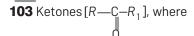
$$CH_3I + Mg \xrightarrow{Dry ether} CH_3MgI$$
  
 $C_6H_5 \searrow$ 

$$CH_3 - MgI + H > C = 0 - H$$

$$\begin{array}{c} C_6H_5 \\ CH_3 \end{array} \xrightarrow{} CH \longrightarrow O \longrightarrow MgI \\ \hline H_2O \\ \hline -Mg(OH)I \xrightarrow{} HOHC \xrightarrow{} C_6H_5 \\ CH \end{array}$$



 $\rightarrow$ 



 $R = R_1$  = alkyl group, can be obtained in one step by [CBSE AIPMT 1997]

CL

#### (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.

$$(CH_3)_3COH \xrightarrow{4[0]} CH_3COCH_3 + CO_2 + 2H_2O$$

$$8[0] \rightarrow CH_2COOH + 2CO_2 + 3H_2O$$

#### 104 (CH<sub>3</sub>)<sub>3</sub>C — 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 
$$(CH_3)_3 C$$
 — group

#### Ans. (c)

CH<sub>3</sub> | CH<sub>3</sub>—C — CHO does not undergo aldol | CH<sub>4</sub>

condensation because it does not contain  $\alpha\text{-hydrogen}$  atom.

#### **105** Acetone reacts with iodine (I<sub>2</sub>) to

#### form iodoform in the presence of [CBSE AIPMT 1995] (a)CaCO<sub>3</sub> (b) NaOH (c) KOH (d)MgCO<sub>3</sub>

(c)KOH **Ans.** *(b)* 

$$CH_3 \xrightarrow[Acetone]{} CH_3 + 3I_2 + 4NaOH \longrightarrow$$

 $CHI_3 + CH_3COONa + 3NaI + 3H_2O$ lodoform

# **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 = C - CHO(c)  $C_6H_5CHO$  (d)  $CH_3 - CH_2CHO$ 

#### **Ans.** (d)

Only those aldehyde undergoes aldol condensation which have  $\alpha$ -hydrogen, so CH<sub>3</sub>CH<sub>2</sub>CHO give this reaction because it contains  $\alpha$ -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

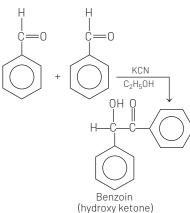
(d) dihydrogen sodium phosphate

#### 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]

#### Ans. (b)



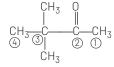
This reaction is also called benzoin condensation. Benzoin is chiral and it exists as a pair of enantiomer, i.e. *R*-benzoin and *S*-benzoin.

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

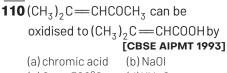
(a) 2,3-dimethyl-2,3-butanediol
(b) 3,3-dimethyl-2-butanone
(c) 1-phenyl-2-propanone
(d) 1,1-diphenyl-2-ethanediol

#### Ans. (b)

The structure of pinacolone is



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



(c) Cu at  $300^{\circ}$ C (d) KMnO<sub>4</sub>

#### Ans. (b)

Haloform reaction,

 $(CH_3)_2 C = CHCOCH_3 \text{ contains } CH_3 - C$ unit so it can be oxidised to  $(CH_3)_2 C = CH - COOH by NaOI.$ 

$$CH_{3} - C = CH - C - CH_{3} \xrightarrow{NaOI} CH_{3} - C = CH - COOH + CH_{3}$$

$$CH_{3} - C = CH - COOH + CH_{3}$$

**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] (b)CCI<sub>2</sub>CH<sub>2</sub>CH0

(c)CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH (d)CH<sub>3</sub>CH<sub>2</sub>CHO

**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.

$$CH_{3} \xrightarrow{0}_{Acetone} CH_{3} \xrightarrow{[0]}_{conc. HNO_{3}} HCOOH$$

+ CH<sub>3</sub>COOH Acetic acid

#### **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

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oxygen atom. The actual structure may be represented as

$$C \stackrel{\frown}{=} 0$$
 or  $\sum_{c}^{\delta_{+}} \frac{\delta_{-}}{0}$ 

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<sup>-</sup>).

$$>$$
 C  $=$  0 + Nu<sup>-</sup>  $\xrightarrow{\text{Slow}}$  C  $\xrightarrow{\text{O}^-}$  Nu  
Aldehyde  
or ketone

 $sp^2$  hybridisation planar structure.

$$H^+$$
  $\to$   $C$   $H^+$   $H^$ 

Addition product

*sp*<sup>3</sup> 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

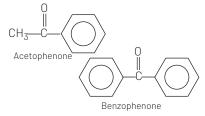
(b) aqueous solution of  $NaHSO_3$ 

(c) Benedict reagent

(d)  $\rm I_2$  and  $\rm Na_2CO_3$ 

#### Ans. (d)

The structures of acetophenone and benzophenone are

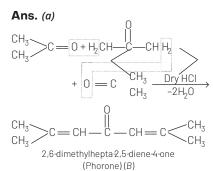


When acetophenone containing

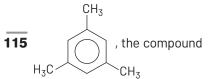
CH<sub>3</sub> — Ċ—unit, is treated with I<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub> it forms yellow precipitate of CHI<sub>3</sub> whereas benzophenone does not give this test.Acetophenons gives iodoform test due to presence of —COCH<sub>3</sub> group.

$$114 \operatorname{3CH}_{3} \operatorname{COCH}_{3} \xrightarrow{HCI}_{-H_{2}^{0}}$$

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



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.



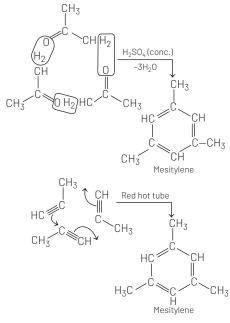
describes a condensation polymer which can be obtained in two ways, either treating 3 molecules of acetone ( $CH_3COCH_3$ ) with conc.  $H_2SO_4$  or passing propyne ( $CH_3 - C \equiv CH$ ) through a red hot tube, the polymer is

#### [CBSE AIPMT 1989]

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

#### Ans. (d)

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



**116** 
$$O \subset CH_2 = O \\ CH_2 = O \\ CH_2 = O$$
  $CH_2$ , 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

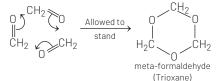
(c)formose

(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.



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

(a) fluorescein (l (c) formaldehyde (

(b) formic acid (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  $\alpha\text{-hydrogen}$  is absent in carbonyl group, those compound gives cannizaro reaction.

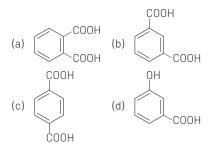
This reaction show disproportionation.

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

HCHO + HCHO  $\xrightarrow{\text{KOH(conc.)}}$  CH<sub>3</sub>OH Methyl alcohol + HCOO<sup>-</sup>K<sup>+</sup>

#### **TOPIC 4** Carboxylic Acids

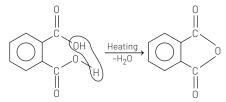
**119** Which of the following acid will form an (i) anhydride on heating and (ii) acid imide on strong heating with ammonia? **[NEET (Oct.) 2020]** 



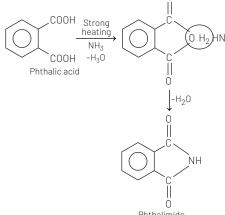
#### **Ans.** (a)

An  $\alpha$ ,  $\beta$ -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.

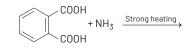




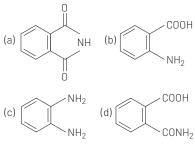


Phthalimide

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



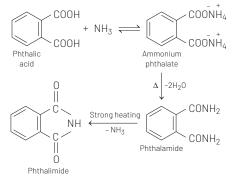
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#### Ans. (a)

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.

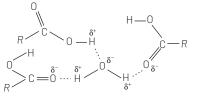
The reaction takes place as follows :



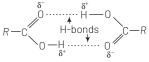
- 121 Carboxylic acids have higher boiling points than aldehydes, ketones and even alcohols of comparable molecular mass. It is due to their [NEET 2018]
  - (a) more extensive association of carboxylic acid via van der Waals' force of attraction
  - (b) formation of carboxylate ion
  - (c) formation 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.

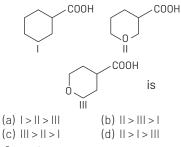


The hydrogen bonds are not completely broken in the vapour state. In fact mostly carboxylic acids exist as dimer in the vapour state or aprotic solvent.



**122** The correct order of strengths of the carboxylic acids





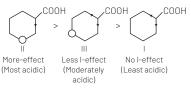
#### Ans. (b)

**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.

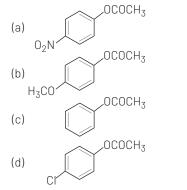
Thus, corresponding carboxylic acid will show less acidic nature.

The correct order of strengths of the carboxylic acids is



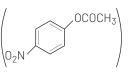
**123** Which one of the following esters gets hydrolysed most easily under alkaline conditions?

[CBSE AIPMT 2015]



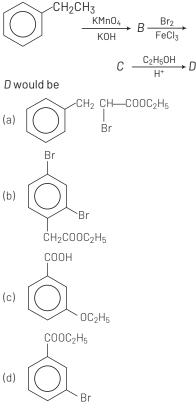
#### Ans. (a)

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.



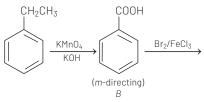
**124** In a set of reactions, ethyl benzene yielded a product *D*.





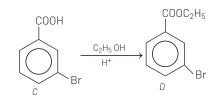
#### Ans. (d)

Alkaline KMnO<sub>4</sub> converts complete carbon chain (that is directly attached to benzene nucleus) to —COOH group. Br<sub>2</sub> in the presence of halogen carrier causes bromination by electrophilic substitution reaction and ethyl alcohol in acidic medium results in esterification.



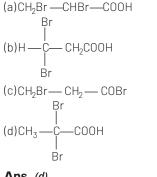
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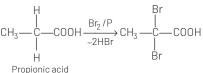


## **125** Propionic acid with Br<sub>2</sub> – P yields a dibromo product. Its structure

would be [CBSE AIPMT 2009]



#### Ans. (d)



**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)RCOgroup is same, thus reactivity depends upon the nature of group Z (i.e. Cl<sup>-</sup>,  $RCOO^-$ ,  $R'O^-$ ,  $NH_2^-$ , 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  $Z \operatorname{\mathsf{groups}}$  is

$$CI^- < RCOO^- < R'O^- > NH_2^-$$
  
Thus, order of reactivity is  
 $RCOCI > (RCO)_2O > RCOOR'$   
Acyl chloride Acid anhydride Ester

>RCONH<sub>2</sub> Amide

## **127** Which of the following represents the correct order of acidity in the given compounds?

#### [CBSE AIPMT 2007]

- (a)  $FCH_2COOH > CH_3COOH > BrCH_2COOH$ >  $CICH_2COOH$
- (b) BrCH<sub>2</sub>COOH > CICH<sub>2</sub>COOH > FCH<sub>2</sub>COOH > CH<sub>3</sub>COOH
- (c)  $FCH_2COOH > CICH_2COOH > BrCH_2COOH$  $> CH_3COOH$
- (d)  $CH_3COOH > BrCH_2COOH > CICH_2COOH$ <  $FCH_2COOH$

#### **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  $FCH_2COOH > CICH_2COOH > BrCH_2COOH$  $> CH_3COOH$ 

> CH3COO

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.

$$CH_{3} \longrightarrow C \longrightarrow C_{2}H_{5} + H \longrightarrow CH_{2}COOC_{2}H_{5}$$

$$O$$

$$MaOC_{2}H_{5} \longrightarrow CH_{3}CCH_{2}COOC_{2}H_{5} + C_{2}H_{5}OH$$

$$Ethyl acetoacetate (ester)$$

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

$$CH_{3}CH_{2}COOH \xrightarrow{SOCl_{2}} B \xrightarrow{NH_{3}} C$$
$$\xrightarrow{KOH} B_{P_{2}}$$

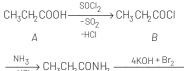
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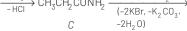
#### The structure of *D* would be [CBSE AIPMT 2006]

(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,





CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>

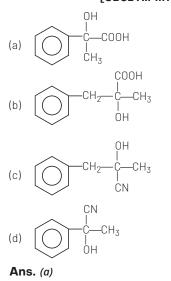
D (Ethyl amine)

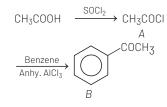
Hence, it is also called Hofmann bromamide degradation reaction. Hence, compound 'D' is  $CH_3 - CH_2 - NH_2$ . Hofmann bromamide reaction degrade the one C in amine product from amide

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

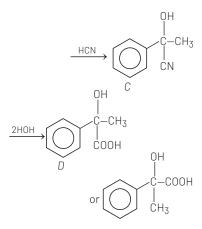
$$CH_{3}COOH \xrightarrow{SOCl_{2}} A \xrightarrow{Benzene}{anhy. AlCl_{3}} B$$
$$\xrightarrow{HCN} C \xrightarrow{HOH} D$$

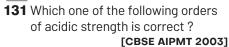
#### The structure of *D* would be [CBSE AIPMT 2005]





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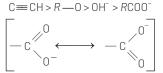


(a)  $RCOOH > HOH > HC \equiv CH > ROH$ (b)  $RCOOH > HC \equiv CH > HOH > ROH$ (c)  $RCOOH > ROH > HOH > HC \equiv CH$ (d)  $RCOOH > HOH > ROH > HC \equiv CH$ 

#### 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

 $RCOOH > HOH > ROH > HC \implies CH$ Which is based upon the rate of donation of proton or strength of base, thus order of basic strength is



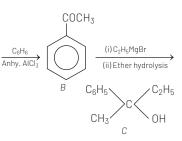
Resonating structures of carboxylate ion

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

$$CH_{3}COOH + PCI_{5} \longrightarrow A \xrightarrow{C_{6}H_{6}} B$$

$$\xrightarrow{C_{2}H_{5}MgBr}_{Ether} C$$

Product *C* would be [CBSE AIPMT 2003] (a)  $CH_3CH(OH)C_6H_5$   $C_2H_5$ | (b)  $CH_3 - C(OH)C_6H_5$ (c)  $CH_3CH(OH)C_2H_5$ (d)  $CH_3COC_6H_5$  **Ans.** (b)  $CH_3COOH + PCI_5 \longrightarrow CH_3COCI$ 



**133** In the following reaction, product *P* is

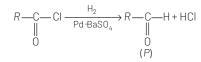
$$\begin{array}{c} \mathsf{R} - \mathsf{C} - \mathsf{C}\mathsf{I} \xrightarrow{\mathsf{H}_2} P \\ \| & \mathsf{Pd} \cdot \mathsf{BaSO}_4 \end{array} \end{array}$$

(a) RCH<sub>2</sub>OH (b) RCOOH

(d) *R*CH<sub>3</sub>

(c) RCHO Ans. (c)

The given reaction is Rosenmund reaction



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<sub>2</sub>H<sub>5</sub>OH (d) ethanol

#### Ans. (c)

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

 $C_6H_5COOH + C_2H_5OH \xrightarrow{Dry} C_6H_5COOC_2H_5$ Benzoic acid Ethanol Ethyl benzoate  $+ H_2O$ 

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

**135** Reduction by LiAlH<sub>4</sub> of hydrolysed product of an ester gives [CBSE AIPMT 2000]

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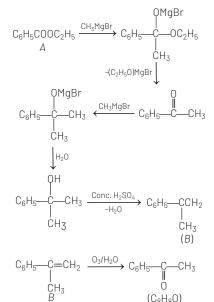
- (a) two acids(b) two aldehydes
- (c) one molecule of alcohol and
- another of carboxylic acid
- (d) two alcohols

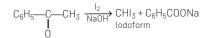
R—COOR' - COOH + R'OH LiAlH<sub>4</sub> / ether  $R - CH_0H + R'OH$ According to the above equation, it is clear that reduction of hydrolysed product of ester by LiAIH<sub>4</sub> gives two alcohols. **136** Which one of the following esters cannot undergo Claisen self-condensation? [CBSE AIPMT 1998] (a)CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>COOC<sub>2</sub>H<sub>5</sub>  $(b)C_6H_5COOC_2H_5$  $(c)C_6H_5CH_2COOC_2H_5$ (d)C<sub>6</sub>H<sub>11</sub>CH<sub>2</sub>COOC<sub>2</sub>H<sub>5</sub> Ans. (b) The ester which contains  $\alpha$ -hydrogen atom undergoes Claisen-self condensation : (a) CH3(CH2)3 C +OC<sub>2</sub>H<sub>5</sub> + H-CHCOOC<sub>2</sub>H<sub>5</sub> CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> Claisen Condensation CH3CH2CH2CH2CH2C CHCOOC<sub>2</sub>H<sub>5</sub> ĊH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>+C<sub>2</sub>H<sub>5</sub>OH (b)  $C_6H_5COOC_2H_5 + C_6H_5COOC_2H_6$ No reaction, because for Claisen condensation an ester with α-hydrogen atoms is required.  $(c)C_{6}H_{5}$ — $CH_{2}CO:OC_{2}H_{5} + H:CHCOOC_{2}H_{5}$ C<sub>6</sub>H<sub>5</sub> Claisen → C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>COCHCOOC<sub>2</sub>H<sub>5</sub> Condensation C<sub>6</sub>H<sub>F</sub> (d)  $C_6H_{11}CH_2COOC_2H_5 + H_1$ -COOC<sub>2</sub>H<sub>5</sub>  $C_{6}H_{11}$ Claisen Condensation C<sub>6</sub>H<sub>11</sub>CH<sub>2</sub>COCH- $-COOC_2H_5 + C_2H_5OH$ Ċ<sub>6</sub>H<sub>11</sub>

Ans. (d)

**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]** 

#### Ans. (a)





## **138** Consider the following transformations

 $\xrightarrow{\text{CaCO}_3} A -$ CH<sub>3</sub>COOH -I<sub>2</sub>  $\rightarrow$  C The molecular formula of NaOH C is [CBSE AIPMT 1996] ОH (a)CH<sub>3</sub> — Ç – CH<sub>3</sub> (b)ICH<sub>2</sub> — COCH<sub>3</sub> (d)CH<sub>3</sub>I (c)CHI<sub>3</sub> Ans. (c) CaCO3 CH3COO 2CH3COOH CH<sub>z</sub>COO/ Heat -CaCO<sub>3</sub> L2 +NaOH CH3COCH3 Acetone B

+ CH<sub>3</sub>COONa

# **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)

 $\begin{array}{c} C_6H_5COOC_2H_5 \xrightarrow{KOH} & C_6H_5COOK^+\\ Ethyl benzoate \end{array}$ 

 $\begin{array}{c} C_{6}H_{5}COOK \xrightarrow{H^{+}/H_{2}O} & C_{6}H_{5}COOH \downarrow \\ & Benzoic acid \\ (white precipitate) \end{array}$ 

## **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<sub>2</sub>SO<sub>4</sub>
(d) acetyl chloride and conc. H<sub>2</sub>SO<sub>4</sub>

#### **Ans.** (a)

Schotten-Baumann reaction

$$C_6H_5COCI + C_6H_5OH \xrightarrow{Aq. NaOH}{pyridine}$$

 $C_6H_5COOC_6H_5 + HCI$ 

## **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

#### $\rightarrow Na_2CO_3 + H_2O$ **142** Formic acid is obtained when

#### [CBSE AIPMT 1994]

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- (a) calcium acetate is heated with conc.  $\rm H_2SO_4$
- (b) calcium formate is heated with calcium acetate

- (c) glycerol is heated with oxalic acid at 373 K
- (d) acetaldehyde is oxidised with  $\rm K_2Cr_2O_7$  and  $\rm H_2SO_4$

#### **Ans.** (c)

 $\begin{array}{c} \text{COOH} \\ | \\ \text{COOH} \end{array} \xrightarrow[\text{Heat 373K}]{} = \begin{array}{c} \text{HCOOH} \\ \text{Formic acid} \end{array} + \begin{array}{c} \text{CO}_2 \uparrow \\ \end{array}$ 

143 Among acetic acid, phenol and *n*-hexanol which one of the following compound will react with NaHCO<sub>3</sub> solution to give sodium salt and CO<sub>2</sub>?[CBSE AIPMT 1993, 99]
(a) Acetic acid
(b) n-hexanol
(c) Acetic acid and phenol
(d) Phenol

#### **Ans.** (a)

 $\begin{array}{c} \mathsf{CH}_3\mathsf{COOH} + \mathsf{N}\mathsf{a}\mathsf{H}\mathsf{CO}_3 & \longrightarrow \mathsf{CH}_3\mathsf{COON}\overset{\scriptscriptstyle +}{\mathsf{a}}\\ \mathsf{Acetic} \ \mathsf{acid} & \overset{\mathsf{Sodium}}{\mathsf{carbonate}} & + \mathsf{H}_2\mathsf{O} + \mathsf{CO}_2 \uparrow \end{array}$ 

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

#### (a) Oxalic acid and $H_2$ (b) Sodium oxalate and $H_2$ (c) CO<sub>2</sub> and NaOH (d) Sodium oxalate

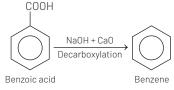
#### Ans. (b)

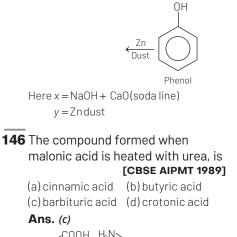
HCOONa + HCOONa Sodium formate	Heat →	COONa	+ H <sub>2</sub> ↑
		COONa Sodium oxalate	Hydrogen

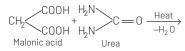
**145** Benzoic acid gives benzene on being heated with X and phenol gives benzene on being heated with Y. Therefore, X and Y are respectively [CBSE AIPMT 1992]

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

#### **Ans.** (d)







$$CH_2 \xrightarrow{CO - NH} C = 0$$
  
Barbituric acid

#### **147** Among the following the strongest

acid is (a)CH<sub>3</sub>COOH (c)CH<sub>2</sub>CICOOH [CBSE AIPMT 1988] (b)CH<sub>2</sub>CICH<sub>2</sub>COOH (d)CH<sub>3</sub>CH<sub>2</sub>COOH

#### 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

 $\begin{array}{l} (a)(i) > (ii) > (iii) > (iv)(b)(ii) > (iii) > (iv) > (i) \\ (c)(i) > (iv) > (iii) > (ii)(d)(iv) > (i) > (iii) > (ii) \end{array}$ 

#### **Ans.** (a)

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

$$\begin{split} CH_3 < C_2H_5 < C_3H_7 < C_4H_9 \\ \text{Acidic Nature} & \sim \frac{-\textit{I-effect(EWG)}}{+\textit{I-effect(ERG)}} \end{split}$$

-*l*-effect increases hence, acidic nature increases.

