25

Organic Compounds Containing Oxygen

TOPIC 1

Alcohols and Phenols

01 Given below are two statements. One is labelled as Assertion (A) and the other is labelled as Reason (R).

Assertion (A) Treatment of bromine water with propene yields 1-bromopropan-2-ol.

Reason (R) Attack of water on bromonium ion follows Markownikoff rule and results in 1-bromopropan-2-ol.

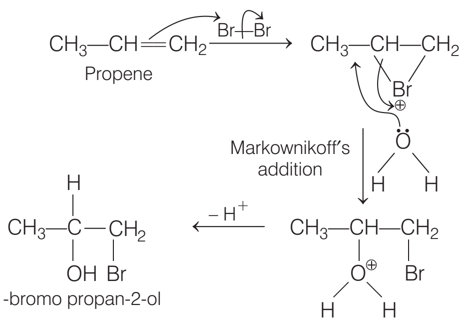
In the light of the above statements, choose the most appropriate answer from the options given below.

[2021, 31 Aug Shift-I]

(a) Both (A) and (R) are true but (R) is not the correct explanation of (A).
(b) (A) is false but (R) is true.
(c) Both (A) and (R) are true and (R) is the correct explanation of (A).
(d) (A) is true but (R) is false

Ans. ***(c)***

Propene reacts with bromine water to yield 1-bromopropan-2-ol.

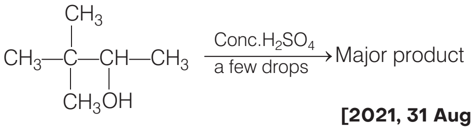


Markownikoff's rule states that in an unsymmetrical alkene the electron rich nucleophile adds to the C-atom with lesser number of hydrogen.

Hence, both A and R are true and R is the correct explanation of A.

Hence, correct option is (c).

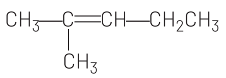
02 The major product formed in the following reaction is



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{OH}{CH}-CH_3 \xrightarrow[\text{a few drops}]{\text{Conc.}H_2SO_4} \text{Major product}$$

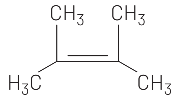
[2021, 31 Aug Shift-I]

(a)

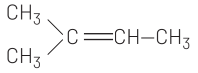


$$CH_3-\underset{CH_3}{C}=CH-CH_2CH_3$$

(b)

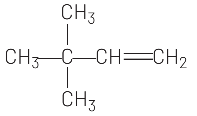


(c)



$$(CH_3)_2C=CH-CH_3$$

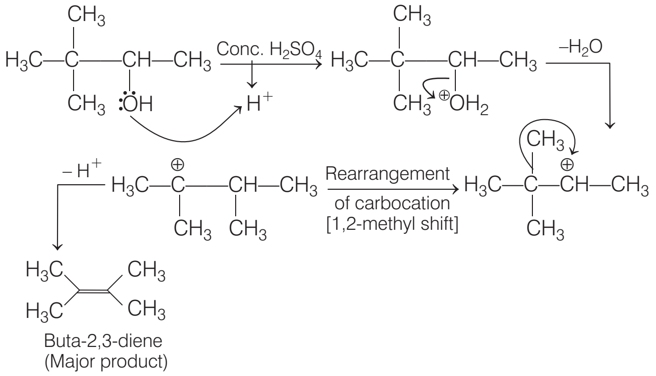
(d)



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

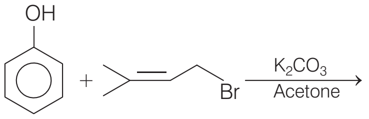
Ans. ***(b)***

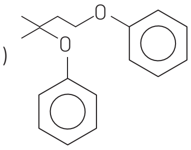
3,3-dimethylbutan-2-ol reacts with concentrated H_2SO_4 to form but-2,3-diene.

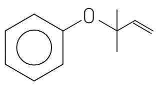


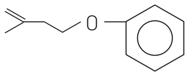
Hence, correct option is (b).

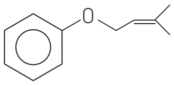
03 The major product of the following reaction, if it occurs by S_N2 mechanism is **[2021, 27 Aug Shift-II]**



(a) 

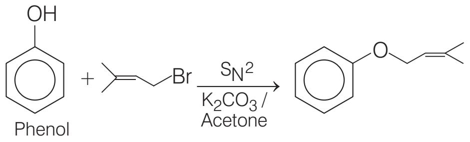
(b) 

(c) 

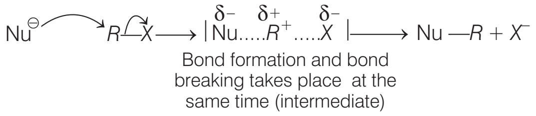
(d) 

Ans. ***(d)***

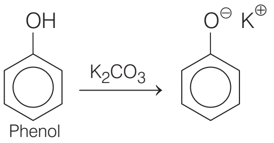
In S_N2 reaction, no formation of carbocation takes place. The nucleophile here which is phenoxide attacks from the back side to the carbon bearing the leaving group (bromide ion).

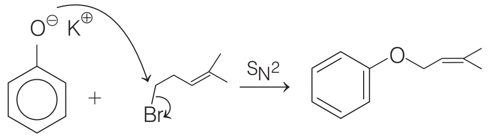


In S_N2 mechanism



Here, in the question





So, here option (d) is correct.

04 Given below are two statements.

Statement I Ethyl pent-4-yn-oate on reaction with CH_3MgBr gives a 3° alcohol.

Statement II In this reaction, one mole of ethyl pent-4-yn-oate utilizes two moles of CH_3MgBr.

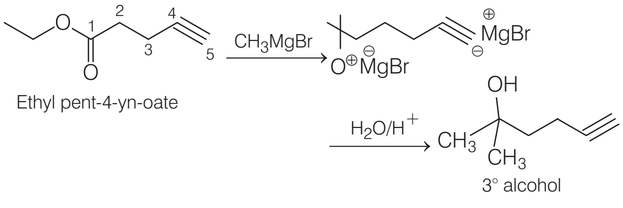
In the light of the above statements, choose the most appropriate answer from the options given below.

[2021, 27 Aug Shift-II]

(a) Both statement I and statement II are false.
(b) Statement I is false but statement II is true.
(c) Statement I is true but statement II is false.
(d) Both statement I and statement II are true.

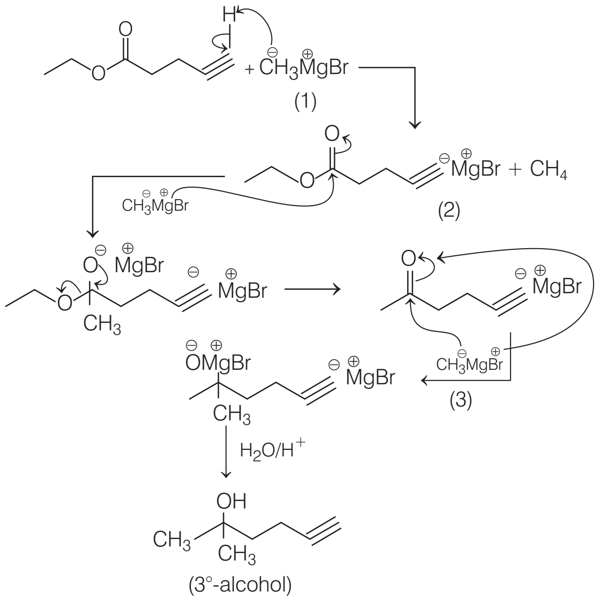
Ans. ***(c)***

Ethyl pent-4-yn-oate on reaction with CH_3MgBr gives 3° alcohol.



∴ Statement I is true.

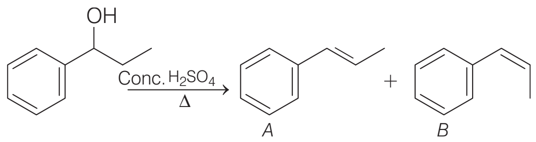
Mechanism



3 molecules of CH_3MgBr is used for this conversion.

∴ Statement II is false.

05

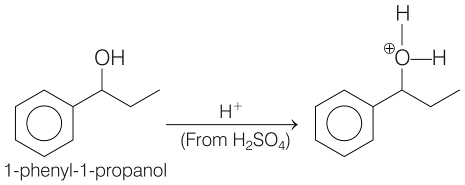


Consider the above reaction, and choose the correct statement. **[2021, 27 July Shift-II]**

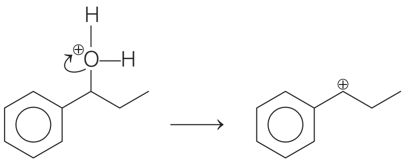
(a) The reaction is not possible in acidic medium.
(b) Both compounds *A* and *B* are formed equally.
(c) Compound *A* will be the major product.
(d) Compound *B* will be the major product.

Ans. ***(c)***

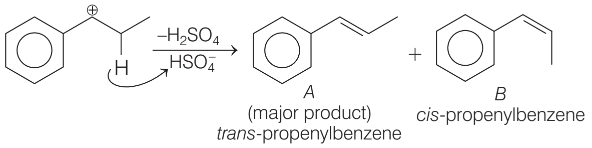
(i) Complete mechanism of given reaction is as follows: Hydrolysis process Acid catalysed hydration of alcohol group.



(ii) Removal of water molecule/formation of carbocation.

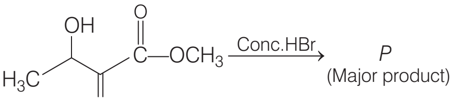


(iii) Removal of corresponding hydrogen ion by HSO_4^- and formation of *cis* and *trans* 1-phenyl-1-propene.

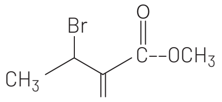


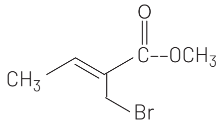
trans alkenes are more stable than *cis* alkene, so product *A* is major product formed in the reaction.

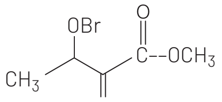
06

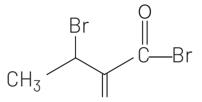


Consider the above reaction, the major product *P* formed is **[2021, 27 July Shift-II]**

(a) 

(b) 

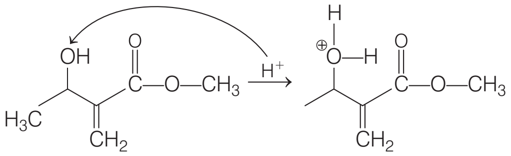
(c) 

(d) 

Ans. ***(b)***

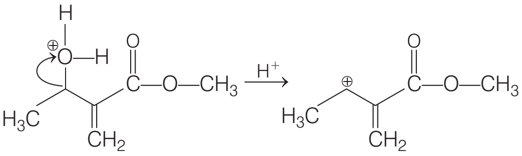
Complete reaction with mechanism is as follows

(i) Hydrolysis process Attack of H^+ on OH^- ion.



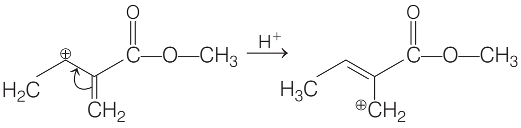
Methyl 3-hydroxy-2-methylene butanoate

(ii) Removal of water molecule/formation of carbocation.

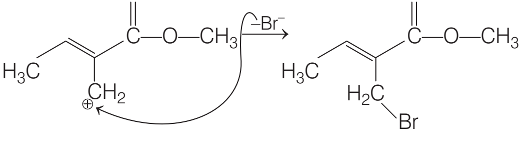


Carbocation

(iii) Resonance Movement of double bond/shifting of carbocation.

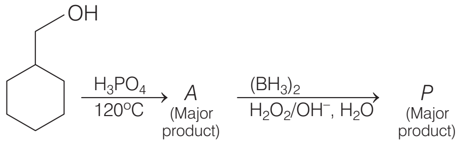


(iv) Addition of bromide ion.

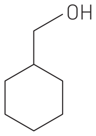


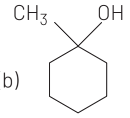
(*P*)
Major product

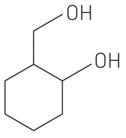
07

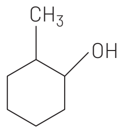


Consider the above reaction and identify the product (*P*). **[2021, 27 July Shift-I]**

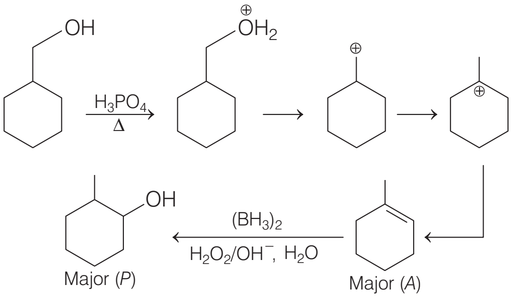
(a) 

(b) 

(c) 

(d) 

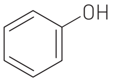
Ans. ***(d)***

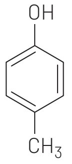


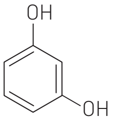
Formation of compound (*A*) takes place by dehydration of alcohol by *E′* reaction.

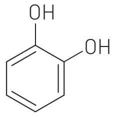
Conversion of compound *A* to compound *P* in undergoes through hydroboration-oxidation reaction that converts an alkene into an alcohol. In this process, H-attached at more hindered site while OH attached at less hindered site.

08 Which one of the following phenols does not give colour when condensed with phthalic anhydride in presence of conc. H_2SO_4 ? **[2021, 26 Aug Shift-II]**

(a) 

(b) 

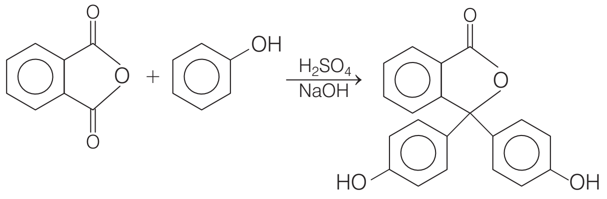
(c) 

(d) 

Ans. ***(b)***

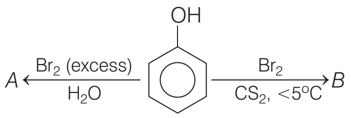
In the electrophilic substitution reaction, phenol gives *ortho* and *para* substituted product in which *para* is the major product. The electrophilic substitution reaction of phthalic anhydride with phenol is taking place at *para* position of the phenol. All the given molecules have free *para* position except in *p*-cresol. Hence, it does not give colour of phthalic anhydride.

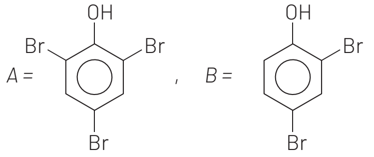
The reaction is as follows :

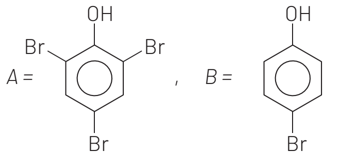


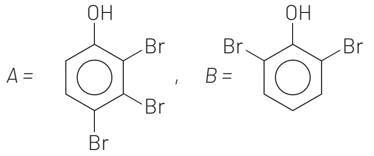
(Pink colour)

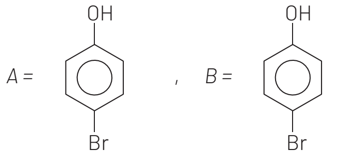
09 The correct options for the products *A* and *B* of the following reactions are **[2021, 26 Aug Shift-I]**



(a) 

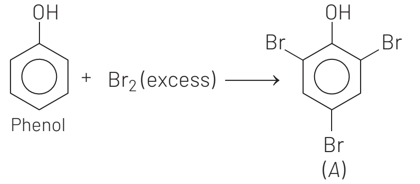
(b) 

(c) 

(d) 

Ans. ***(b)***

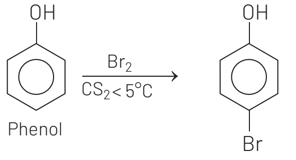
Bromination of phenol with excess of bromine and water will result in multiple substitution around ring as water ionises phenol to phenoxide ion, which activities the ring for trisubstitution, while less polar solvent, i.e. CS_2 will give mono-substituted compound.



Phenol

(*A*)

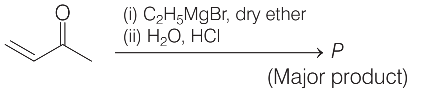
2,4,5 tribromophenol



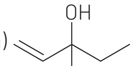
Phenol

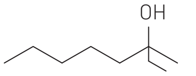
(*B*)

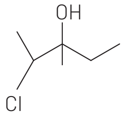
mono-substituted product

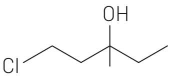
10 

Consider the above reaction, the major product *P* is **[2021, 25 July Shift-I]**

(a) 

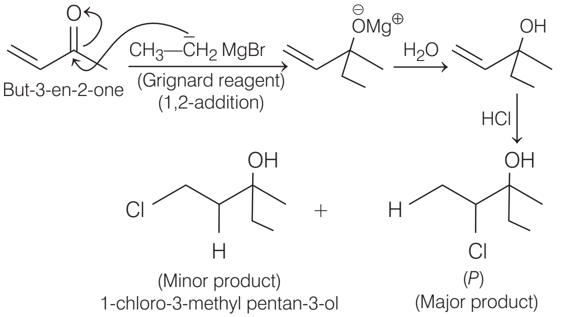
(b) 

(c) 

(d) 

Ans. ***(c)***

In the given reaction, Grignard reagent is used for 1, 2-addition in the carbonyl carbon and form alcohol as a major product.



Addition of HCl at the alkene gives 2-chloro-3-methylpentan-3-ol as major product.

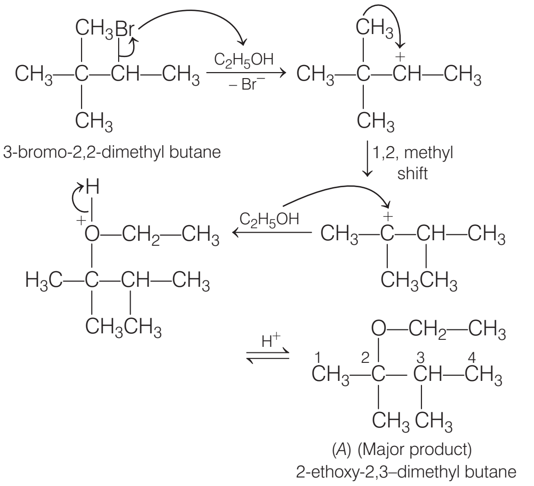
11 In the given reaction, 3-bromo-2, 2-dimethyl butane $\xrightarrow{C_2H_5OH}$ $\underset{\text{Major product}}{(A)}$.

Product *A* is **[2021, 20 July Shift-I]**

(a) 2-ethoxy-3, 3-dimethyl butane
(b) 1-ethoxy-3, 3-dimethyl butane
(c) 2-ethoxy-2, 3-dimethyl butane
(d) 2-hydroxy-3, 3-dimethyl butane

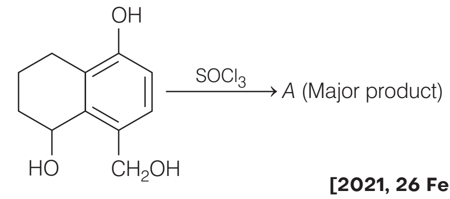
Ans. ***(c)***

The given reaction proceeds via S_N2 reaction mechanism as follows

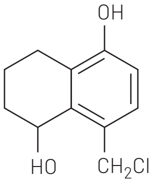


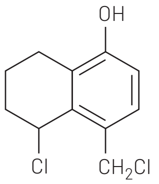
∴Therefore, product *A* is 2-ethoxy-2, 3-dimethyl butane.

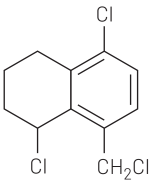
12 Identify *A* in the given reaction.



[2021, 26 Feb Shift-II]

(a)


(b)


(c)


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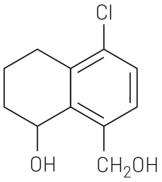
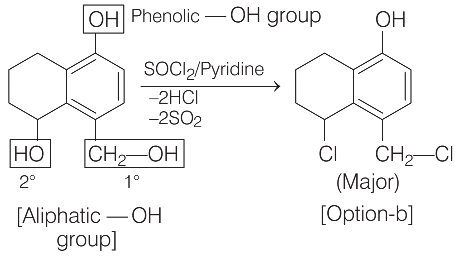


Ans. ***(b)***

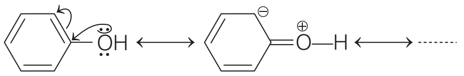
The given reaction is an application of Darzen's reaction in which an aliphatic alcohol (preferably 1° or 2°) gets converted into the respective alkyl chloride (in pure form) through S_N2 pathway when it uses

pyridine

or as organic base.

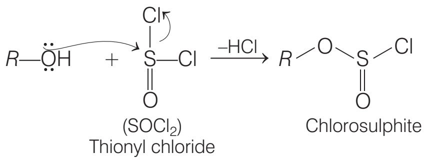


Note Phenolic —OH group does not respond to this reaction as + *R*-effect of phenolic —OH group gives double bond character to the C—O bond.

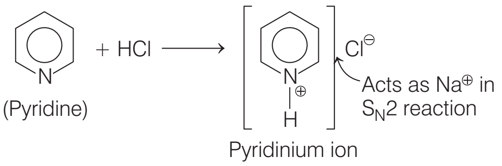


Machanism

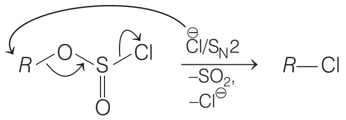
(i) Alcohol react with thionyl chloride to give chlorosulphite and HCl.



(ii) Pyridine reacts with HCl to give pyridinium chloride.



(iii) Chlorosulphite reacts with chloride ion *via*. bimolecular nucleophilic substitution reaction to give alkyl chloride.



13 Ceric ammonium nitrate and $CHCl_3$ /alc. KOH are used for the identification of functional groups present in .... and .... respectively. **[2021, 26 Feb Shift-II]**

(a) alcohol, phenol
(b) amine, alcohol
(c) alcohol, amine
(d) amine, phenol

Ans. ***(c)***

Ceric ammonium nitrate and $CHCl_3$ / alc. KOH are used for the identification of functional groups present in alcohol and amine respectively.

Ceric ammonium nitrate (CAN) test When an alcohol reacts with few drops of CAN, a red complex ammonium nitrate is developed which confirms presence of alcoholic —OH group.

$$\underset{\text{Alcohol}}{3ROH} + \underset{\text{Ceric ammonium nitrate}}{(NH_4)_2[Ce(NO_3)_6]} \xrightarrow[\text{Red colour}]{-NH_4NO_3} \underset{\text{Red complex}}{[Ce(NO_3)_4(ROH)_3]}$$

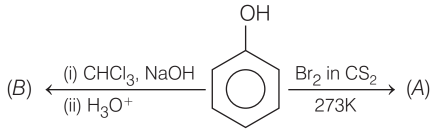
Test with $CHCl_3$ and alcoholic KOH

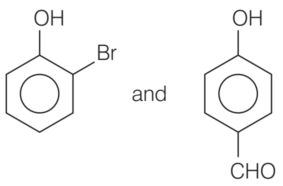
[Carbylamine test or Saytzeff's isocyanide test]

When a primary amine (aliphatic or aromatic) is heated with alcoholic KOH and chloroform ($CHCl_3$), the isocyanide (carbylamine) is formed as indicated by a foul order.

$$\underset{1^\circ\text{-amine}}{R—NH_2} + CHCl_3 + \underset{(\text{alc.})}{3KOH} \xrightarrow[-3KCl \atop -3H_2O]{\Delta} \underset{\text{Carbylamine}}{R—NC}$$

14 Identify the major products *A* and *B* respectively in the following reactions of phenol. **[2021, 26 Feb Shift-I]**



(a)


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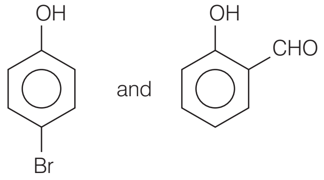
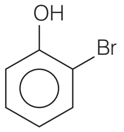
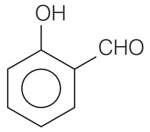
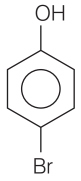
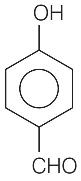
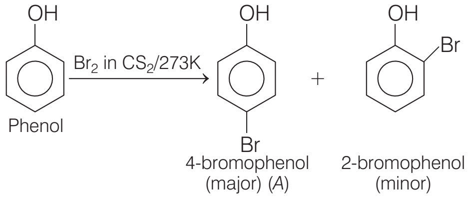


(c)  and 

(d)  and 

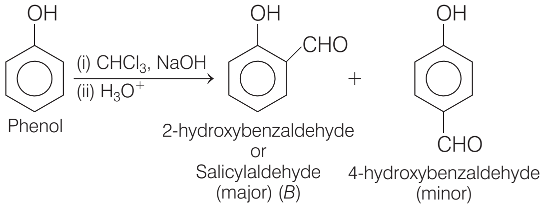
Ans. ***(b)***

Phenol on reaction with Br_2 in CS_2 / 273 K undergoes an electrophilic substitution reaction by Br^+ (electrophile) in aprotic solvent CS_2 to give 4-bromophenol as the major product.



Phenol on reaction with $CHCl_3$, NaOH followed by hydrolysis gives salicylaldehyde as a major product.

It is Reimer-Tiemann reaction. It is also an electrophilic substitution reaction of phenol by dichlorocarbene CCl_2 (electrophilic).



15 Given below are two statements:

Statement I *o*-nitrophenol is steam volatile due to intramolecular hydrogen bonding.

Statement II *o*-nitrophenol has high melting due to hydrogen bonding.

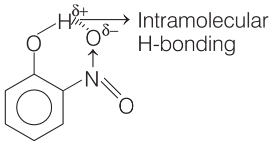
In the light of the above statements, choose the most appropriate answer from the options given below.

[2021, 26 Feb Shift-I]

(a) Statement I is false but statement II is true
(b) Both statement I and statement II are true
(c) Both statement I and statement II are false
(d) Statement I is true but statement II is false

Ans. ***(d)***

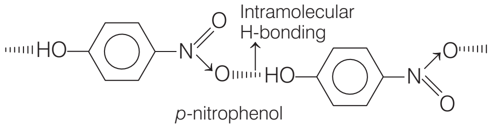
Statement I is true. Because of closer proximity (1, 2-positions) of —OH and —NO_2 groups, *o*-nitrophenol shows intramolecular hydrogen bonding.



o-nitrophenol

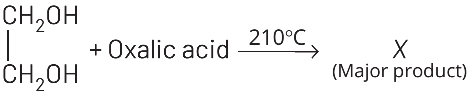
So, *o*-nitrophenol exists in monomeric state and becomes steam volatile. Statement II is false, because, due to the presence of intramolecular hydrogen bonding, boiling point and melting point of *o*-nitrophenol will be lower.

Note *p*-nitrophenol is the positional isomer of *o*-nitrophenol. *p*-nitrophenol shows intermolecular hydrogen bonding and so, it has higher boiling point, melting point and water solubility.



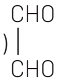
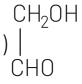
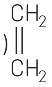
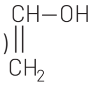
p-nitrophenol

16 What is 'X' in the given reaction?



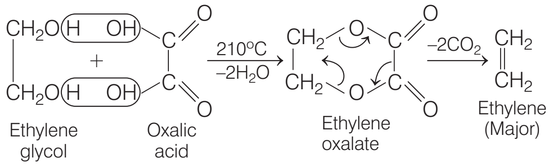
$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} + \text{Oxalic acid} \xrightarrow{210^\circ C} \underset{\text{(Major product)}}{X}$$

[2021, 25 Feb Shift-II]

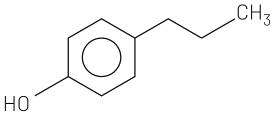
(a)  $\begin{array}{l} CHO \\ | \\ CHO \end{array}$ (b)  $\begin{array}{l} CH_2OH \\ | \\ CHO \end{array}$ (c)  $\begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array}$ (d)  $\begin{array}{l} CH—OH \\ \| \\ CH_2 \end{array}$

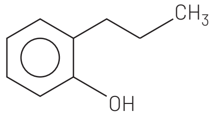
Ans. ***(c)***

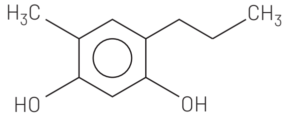
When ethylene glycol is heated with oxalic acid at 210ºC, first we get an unstable cyclic-diester (ethylene oxalate) which readily decarboxylate to give ethylene as the major product.

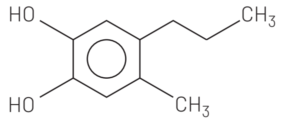


17 Which of the following compound gives pink colour on reaction with phthalic anhydride in conc. H_2SO_4 followed by treatment with NaOH? **[2021, 24 Feb Shift-I]**

(a) 

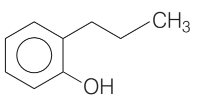
(b) 

(c) 

(d) 

Ans. ***(b)***

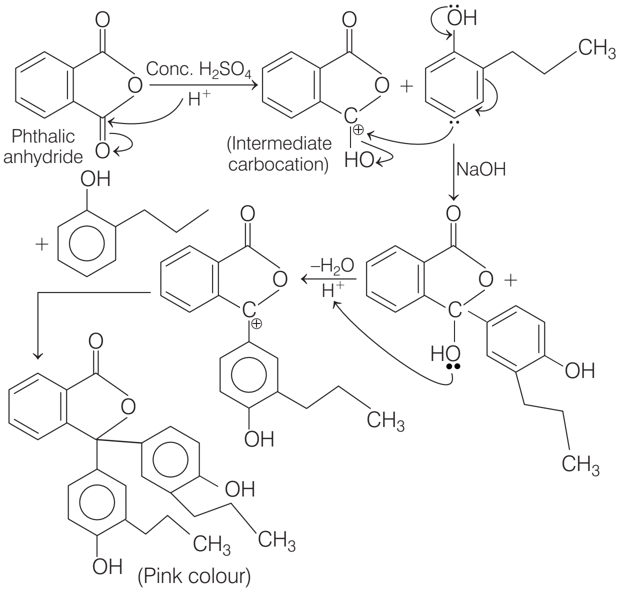
Correct answer is



2-propylphenol

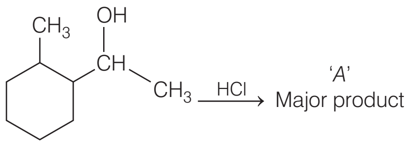
Firstly phthalic anhydride in presence of conc. H_2SO_4 undergoes protonation to give an intermediate carbocation. This carbocation reacts with 2-propylphenol in presence of NaOH to give pink colour compound.

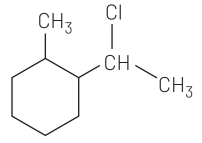
Mechanism

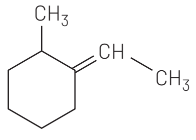


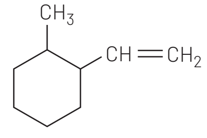
2-propylphenol gives pink colour on reaction with phthalic anhydride in conc. followed by treatment with NaOH.

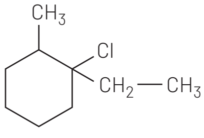
18 What is the final product (major) 'A' in the given reaction? **[2021, 24 Feb Shift-I]**



(a)


(b)


(c)


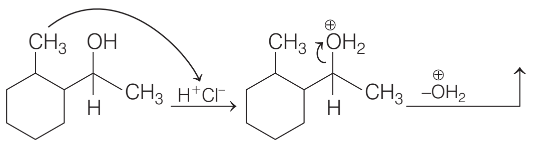
(d)


Ans. ***(d)***

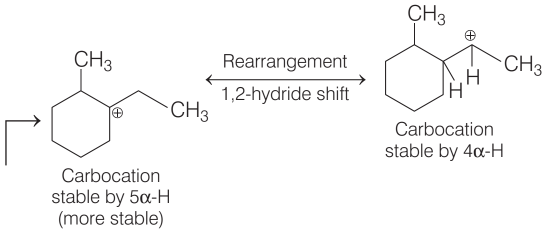
Steps involved in this reaction are as follows

Step 1 $HCl \longrightarrow H^+ + Cl^-$

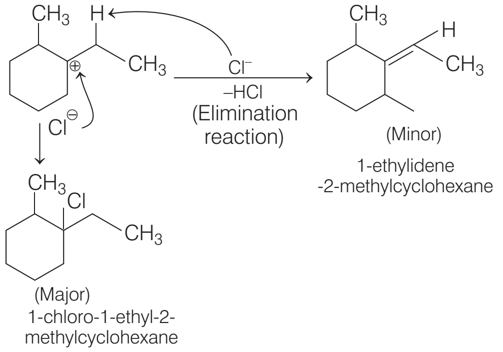
H^+ attacks on —OH (lone pair) and formed $\overset{\oplus}{O}H_2$ ion. Here, $\overset{\oplus}{O}H_2$ is the good leaving group.



1-(2-methyl cyclohexyl) ethan-1-ol



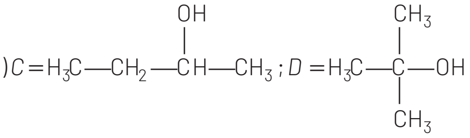
Step 2 Elimination reaction always give minor product than substitution reaction.

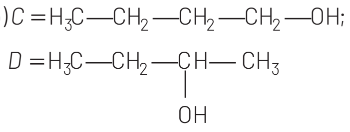


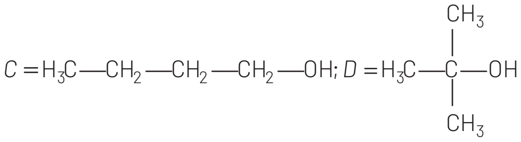
19 Two compounds *A* and *B* with same molecular formula (C_3H_6O) undergo Grignard's reaction with methylmagnesium bromide to give products *C* and *D*. Products *C* and *D* show following chemical tests.

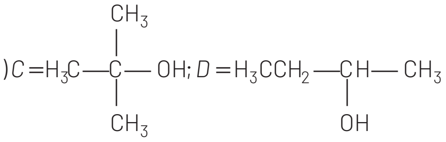
Test	*C*	*D*
Ceric ammonium nitrate test	Positive	Positive
Lucas test	Turbidity obtained after five minutes	Turbidity obtained immediately
Iodoform test	Positive	Negative

C and *D* respectively are **[2020, 2 Sep Shift-II]**

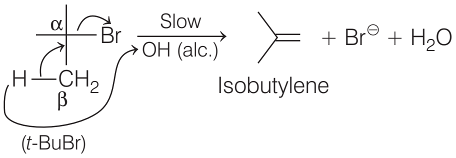
(a)

$C = H_3C—CH_2—\overset{OH}{\overset{|}{C}}H—CH_3$; $D = H_3C—\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}—OH$

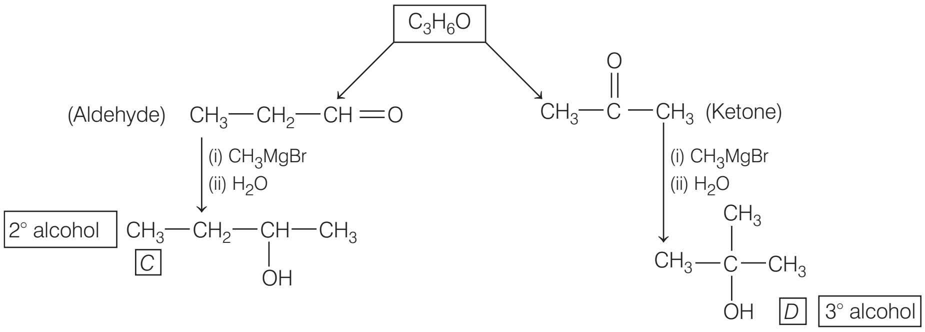
(b)

$C = H_3C—CH_2—CH_2—CH_2—OH$;
$D = H_3C—CH_2—\underset{OH}{\underset{|}{C}}H—CH_3$

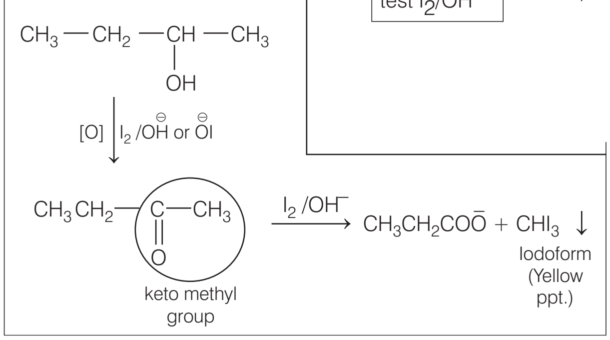
(c)

$C = H_3C—CH_2—CH_2—CH_2—OH$; $D = H_3C—\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}—OH$

(d)

$C = H_3C—\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}—OH$; $D = H_3CCH_2—\underset{OH}{\underset{|}{C}}H—CH_3$

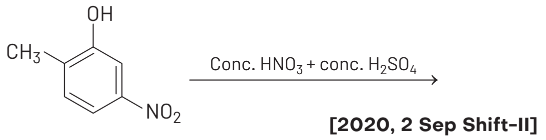
Ans. ***(a)***





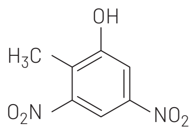
Positive Colour change: yellow → red	← Ceric ammonium nitrate test (CAN) →	Positive Colour change: yellow → red
White turbidity after 5 min	← Lucas test ZnCl$_2$ (anhyd.)/ conc. HCl/20°C →	Immediate white turbidity
Positive 	← Iodoform test I_2/OH^- →	Negative, because Ⓓ is a 3°-alcohol which is not oxidisable by halogen

20 The major product of the following reaction is

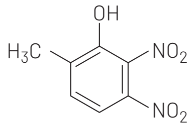


[2020, 2 Sep Shift-II]

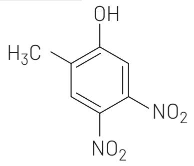
(a)



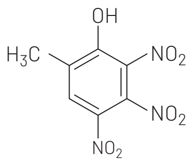
(b)



(c)



(d)



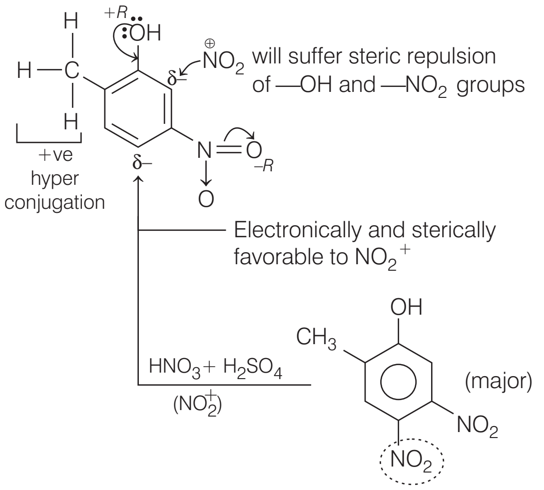
Ans. ***(c)***

The substrate undergoes nitration reaction (ArSE$_2$). The electrophile (NO_2^+) will prefer to attack benzene nucleus which is rich with electron density (by $+R$ or $+I$-effect of substituent, where $+R > +I$) as wall as sterically less crowded.

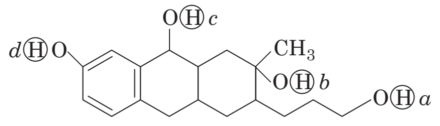
Out of three substituents, the —OH group will dominate the rate of initiation reaction, because —OH has strong ring activating property by its $+R$ or $+M$ effect.

The ring activating order is

$$\underset{(+R\text{ effect})}{-OH} > \underset{(+\text{ve hyper conjugation})}{-CH_3} > \underset{(-R\text{ effect})}{-NO_2}$$



21 Consider the following reaction :



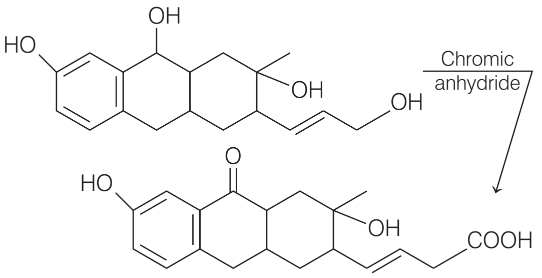
$\xrightarrow[\text{anhydride}]{\text{Chromic}}$ '*P*' The product '*P*' gives positive ceric ammonium nitrate test. This is because of the presence of which of these —OH group(s)?

[2020, 3 Sep Shift-II]

(a) (b) and (d)
(b) (d) only
(c) (b) only
(d) (c) and (d)

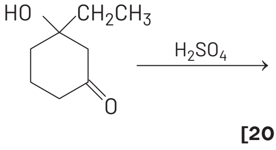
Ans. ***(c)***

Only 3° alcohol give positive ceric ammonium nitrate test.



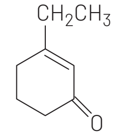
Product '*P*'
(3° alcohol gives red colour with ceric ammonium nitrate)

22 The major product of the following reaction is

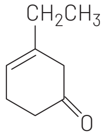


[2020, 5 Sep Shift-II]

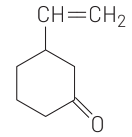
(a)



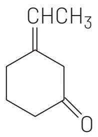
(b)



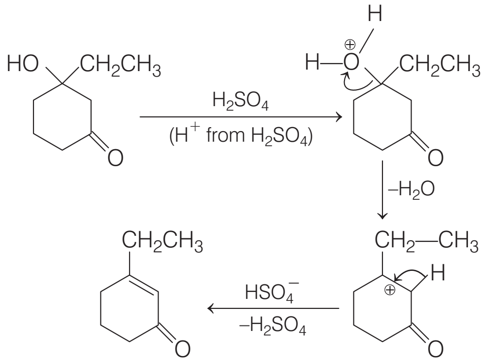
(c)



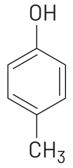
(d)



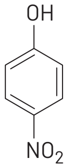
Ans. ***(a)***



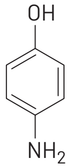
23 The increasing order of boiling points of the following compounds is



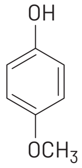
(I)



(II)



(III)

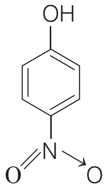


(IV)

[2020, 5 Sep Shift-II]

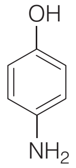
(a) I < III < IV < II
(b) I < IV < III < II
(c) IV < I < II < III
(d) III < I < II < IV

Ans. ***(b)***



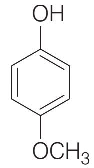
(II)

shows strongest hydrogen bonding from —OH group.



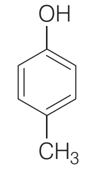
(III)

shows stronger hydrogen bonding from both side of —OH group as well as —NH_2 group.



(IV)

shows stronger hydrogen bonding from one side —OH group and another side of —OCH_3 group shows only dipole-dipole interaction.



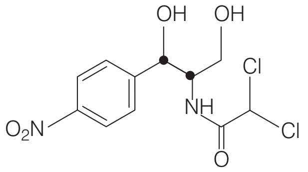
(I)

Boiling point μ dipole moment (μ). shows hydrogen bonding from —OH group only.

24 The number of chiral carbons in chloramphenicol is .... **[2020, 7 Jan Shift-I]**

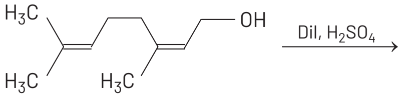
Ans. ***(2.00)***

Structure of chloramphenicol is



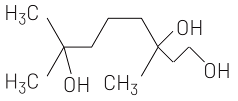
The two carbon atoms shown by black circles are chiral.

25 The major product of the following reaction is :

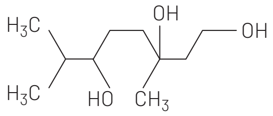


[2020, 8 Jan Shift-I]

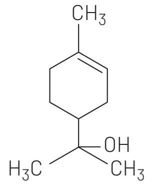
(a)



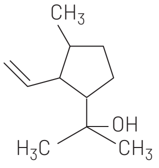
(b)



(c)

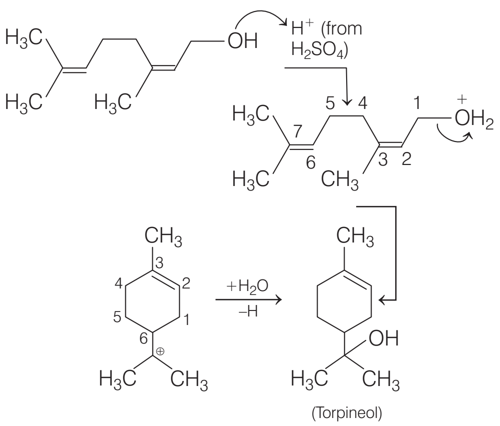


(d)



Ans. ***(c)***

The reaction proceeds as follows:



26 Arrange the following compounds in increasing order of C—OH bond length : methanol, phenol, *p*-ethoxyphenol **[2020, 8 Jan Shift-I]**

(a) phenol < methanol < *p*-ethoxyphenol
(b) phenol < *p*-ethoxyphenol < methanol
(c) methanol < *p*-ethoxyphenol < phenol
(d) methanol < phenol < *p*-ethoxyphenol

Ans. ***(b)***

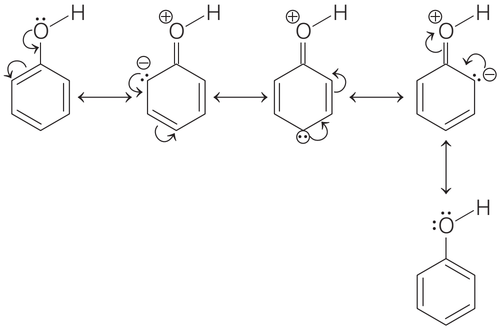
The increasing order of C—OH bond length in the given compounds is : phenol < *p*-ethoxy phenol < methanol. It is explained as follows:

Methanol has no resonance and no partial double bond character in C—OH bond.

∴ It has maximum C—OH bond length.

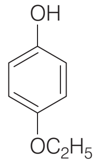
In both phenol and *p*-ethoxyphenol, resonance is involved.

∴ C—OH bond has partial double bond character and hence C—OH bond length is less than methanol.



(*p*-ethoxyphenol also exhibits similar resonating structures).

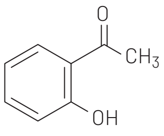
But in *p*-ethoxyphenol, there is + *R*-effect of 'OC_2H_5' group also.



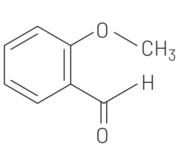
So the 'C—OH' bond has less double bond character and slightly more bond length than C—OH' bond length in phenol.

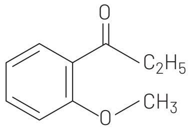
27 An organic compound neither reacts with neutral ferric chloride solution nor with Fehling solution. It however, reacts with Grignard reagent and gives positive iodoform test. The compound is **[2019, 8 April Shift-I]**

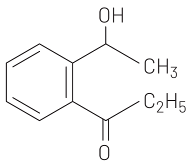
(a)



(b)



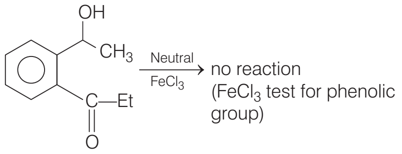
(c) 

(d) 

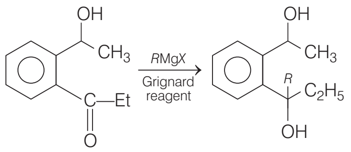
Ans. ***(d)***

According to the given conditions, compound (d) neither reacts with neutral ferric chloride solution nor with Fehling solution. It however reacts with Grignard reagent and gives positive iodoform test.

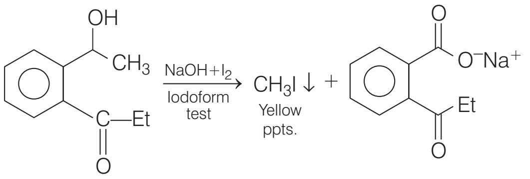
- As the compound does not contain any phenolic —OH group. Hence, it gives negative neutral $FeCl_3$ test.



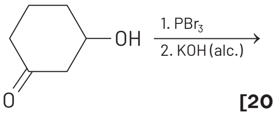
- Compound gives reaction with *R*Mg*X* as it contains $—\underset{\underset{O}{\|}}{C}—Et$.



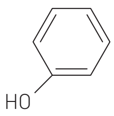
Compound with $CH_3\underset{\underset{OH}{|}}{CH}—$ group undergoes iodoform test in presence of NaOH and I_2.

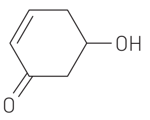


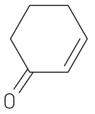
28 The major product of the following reaction is

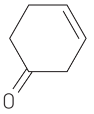


[2019, 9 April Shift-I]

(a) 

(b) 

(c) 

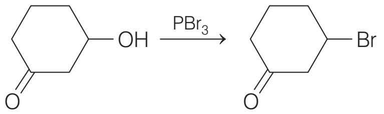
(d) 

Ans. ***(c)***

Key Idea PBr_3 reagent is used for the substitution of —Br group while alc. KOH reagent is used to carry out elimination reaction.

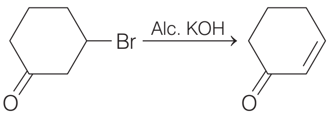
The given reaction proceed in following manner:

Step I In presence of PBr_3, alcohols undergo substitution reactions to give halides. Reagent PBr_3 is usually generated *insitu* by the reaction of red phosphorus with bromine.



3-bromohexanone

Step II 3-bromohexanone in presence of alc. KOH undergoes elimination reaction and gives cyclohex-2-en-1-one.



Cyclohex-2-en-1-one

29 The major product of the following reaction is

$CH_3CH=CHCO_2CH_3 \xrightarrow{LiAlH_4}$ **[2019, 9 April Shift-I]**

(a) $CH_3CH=CHCH_2OH$ (b) $CH_3CH_2CH_2CH_2OH$
(c) $CH_3CH_2CH_2CO_2CH_3$ (d) $CH_3CH_2CH_2CHO$

Ans. ***(a)***

Key Idea $LiAlH_4$ reagent is used for the reduction of —CHO, $—\overset{\overset{O}{\|}}{C}OCH_3$. It does not reduce double bonds.

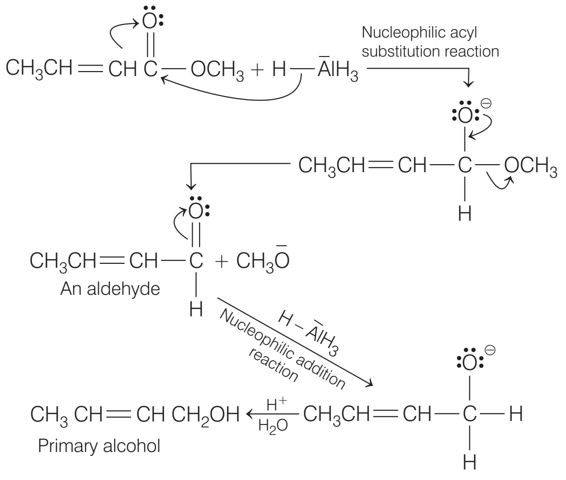
The reaction of an ester with $LiAlH_4$ produces two alcohols, one corresponding to the acyl portion of the ester and one corresponding to the alkyl portion.

$$CH_3CH=CH\overset{\overset{O}{\|}}{C}—OCH_3 \xrightarrow{LiAlH_4} \underset{\text{But-2-en-1-ol}}{CH_3CH=CHCH_2OH} + \underset{\text{Methanol}}{CH_3OH}$$

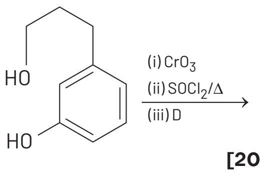
Thus, the major product of the given reactant $CH_3CH=CH\overset{\overset{O}{\|}}{C}OCH_3$ in presence of $LiAlH_4$ is $CH_3CH=CH\,CH_2OH$ and CH_3OH.

The reaction proceeds through following mechanism.

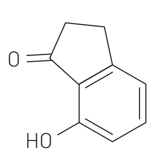
Mechanism

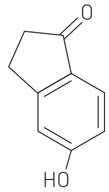


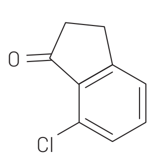
30 The major product of the following reaction is

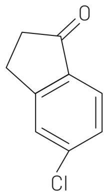


[2019, 12 April Shift-I]

(a)


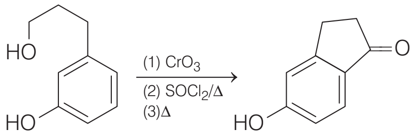
(b)


(c)


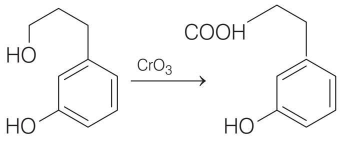
(d)


Ans. ***(b)***

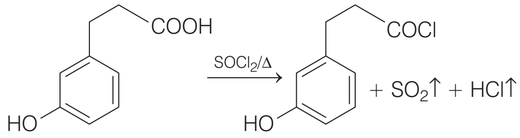
The major product formed in the reaction is as follows:



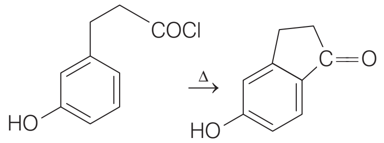
Primary alcohol readily oxidised to corresponding carboxylic acid with oxidising agent, chromium trioxide (CrO_3) in acidic medium.



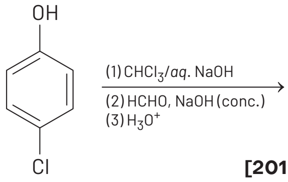
—OH group of carboxylic acid get substituted by —Cl in presence of $SOCl_2$ (Thionyl chloride).



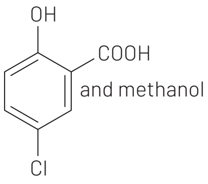
Further, heating of product leads to intramolecular cyclisation.



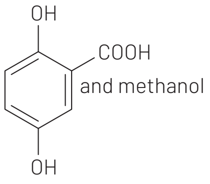
31 The major products of the following reaction are



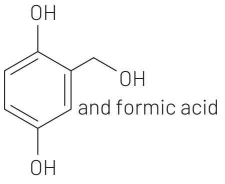
[2019, 12 April Shift-I]

(a)


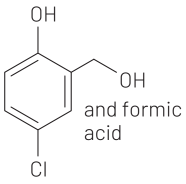
and methanol

(b)


and methanol

(c)


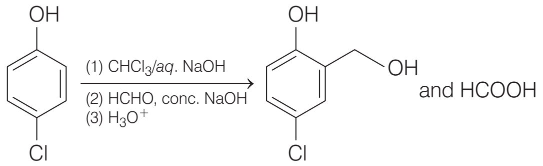
and formic acid

(d)


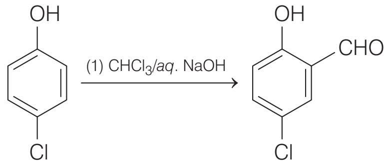
and formic acid

Ans. ***(d)***

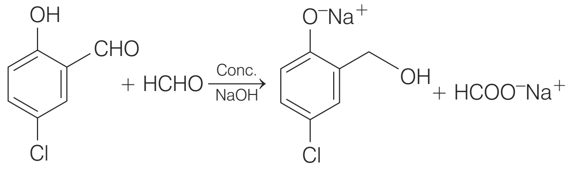
The major products of the given reaction are as follows:



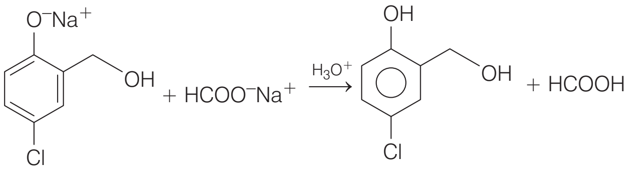
In step-I, substituted phenol undergoes Reimer- Tiemann reaction in presence of $CHCl_3$ / *aq*. NaOH



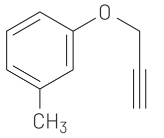
The aldehyde obtained in above equation does not possess α-hydrogen. In presence of formaldehyde and conc. NaOH it undergoes Cannizaro reaction. In this reaction, one molecule of aldehyde is reduced to alcohol while another molecule is oxidised to salt of carboxylic acid.

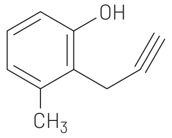


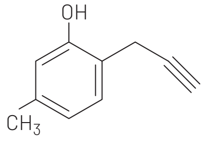
Upon hydrolysis, following reaction takes place

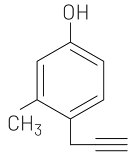


32 What will be the major product when *m*-cresol is reacted with propargyl bromide $(HC\equiv C—CH_2Br)$ in presence of K_2CO_3 in acetone? **[2019, 12 April Shift-II]**

(a) 

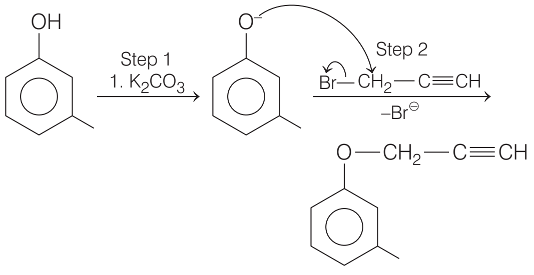
(b) 

(c) 

(d) 

Ans. ***(a)***

The major product when *m*-cresol reacts with propargyl bromide $(HC\equiv C—CH_2Br)$ in presence of K_2CO_3 in acetone is given in the following reaction:



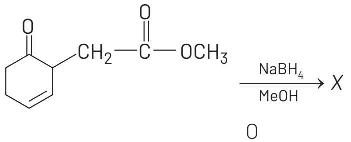
Major product

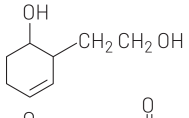
In step 1 K_2CO_3 act as a base and abstract H-atom from —OH group.

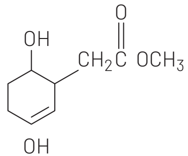
This leads to the formation of substituted phenoxide ion (highly stable).

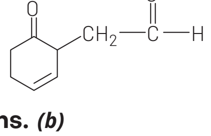
In step 2 substituted phenoxide ion on reaction with $Br—CH_2—C\equiv CH$ gives the required product.

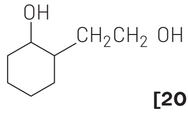
33 The major product '*X*' formed in the following reaction is



(a) 

(b) 

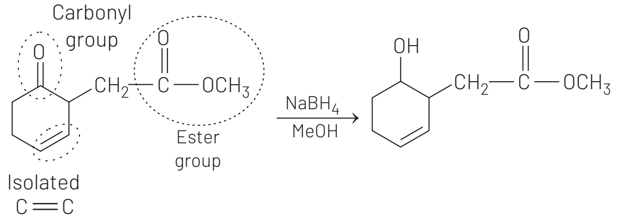
(c) 

(d) 

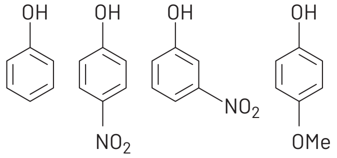
[2019, 10 Jan Shift-I]

Ans. ***(b)***

$NaBH_4$ is a selective reducing agent. It reduces carbonyl $\left(>C=O\right)$ group into an alcohol but cannot reduce an isolated $C=C$ and an ester group too.



34 The increasing order of the pK_a values of the following compounds is **[2019, 10 Jan Shift-I]**



A *B* *C* *D*

(a) $D < A < C < B$ (b) $B < C < A < D$

(c) $C < B < A < D$ (d) $B < C < D < A$

Ans. ***(b)***

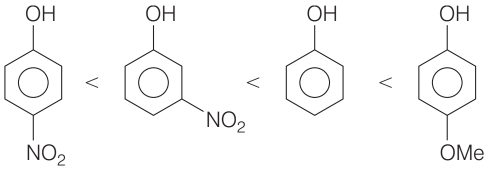
Acidic strength is inversely proportional to pK_a value. The acidity of phenols is due to greater resonance stabilisation of phenoxide ion relative to phenol.

Therefore, any substituent which stabilises the phenoxide ion more by dispersal of negative charge will tend to increase the acidity of phenol.

Electron withdrawing groups $(—NO_2)$ increases the acidic strength of phenol whereas electron donating group $(—OCH_3)$ decreases the acidic strength of phenol. In case of $—NO_2$ group attached to phenol, the dispersal of negative charge is more pronounced at *o*- and *p*-position than at *m*-position.

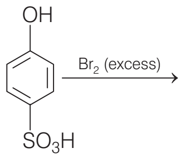
Thus, order of acidic strength of nitrophenol is:

p-nitrophenol > *o*-nitrophenol and the correct order of the pK_a values of give option is

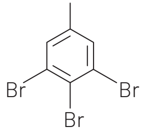


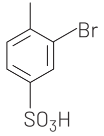
(*B*) (*C*) (*A*) (*D*)

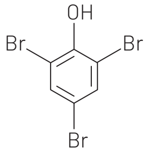
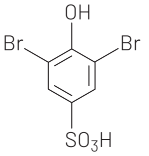
35 The major product of the following reaction is



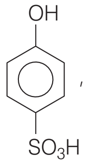
[2019, 11 Jan Shift-I]

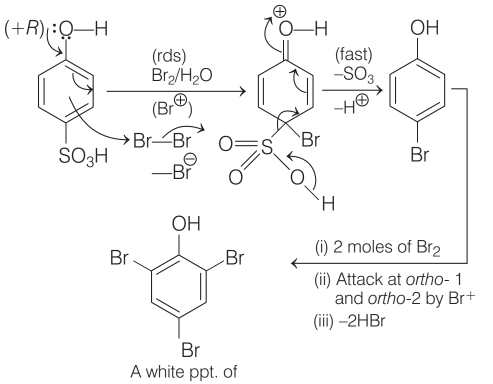
(a) 

(b) 

(c)  (d) 

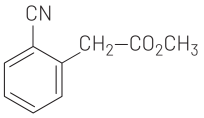
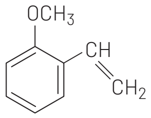
Ans. ***(c)***

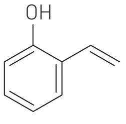
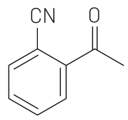
In , *ipso*-substitution takes place with the carbon bearing —SO_3H group. After the attack of the electrophilic Br^+ in the rate determining step (rds) of the ArS_E2 pathway desulphonation (—SO_3) takes place with a faster rate.



A white ppt. of 2,4,6-tribromophenol

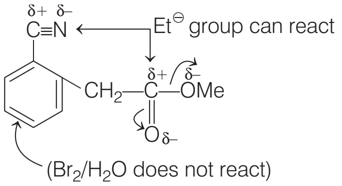
36 Which of the following compounds reacts with ethyl magnesium bromide and also decolourises bromine water solution **[2019, 11 Jan Shift-II]**

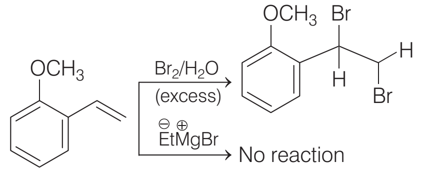
(a)  (b) 

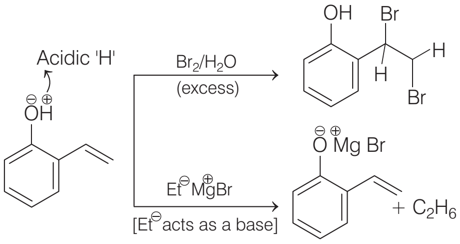
(c)  (d) 

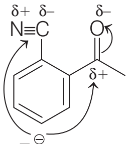
Ans. ***(c)***

Ethyl magnesium bromide is a Grignard reagent (GR), it constitutes $C_2H_5^-$ [$C_2H_5^-\overset{\oplus}{Mg}Br$ in ether/aprotic medium] which can act as nucleophile as well as strong base. Bromine water (Br_2/H_2O, red) gets decolourised with phenol derivatives (option, c), anisole derivatives (option, b) etc., as $\rangle C{=}C\langle$ is present outside the ring (aliphatic, not aromatic).

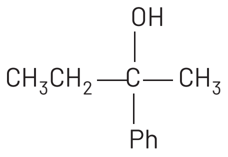
(a) 

(b) 

(c) 

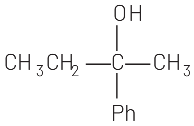
(d) 

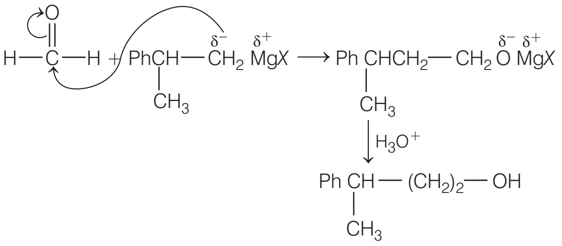
$Et^{\ominus}$ group can react but (Br_2/H_2O) does not react

37 
$CH_3CH_2-\underset{Ph}{\overset{OH}{C}}-CH_3$ cannot be prepared by **[2019, 12 Jan Shift-I]**

(a) $CH_3CH_2COCH_3 + PhMgX$ (b) $PhCOCH_3 + CH_3CH_2MgX$
(c) $PhCOCH_2CH_3 + CH_3MgX$ (d) $HCHO + PhCH(CH_3)CH_2MgX$

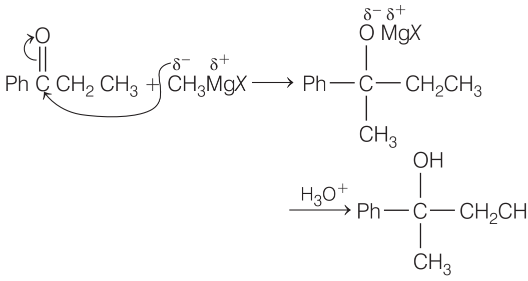
Ans. ***(d)***

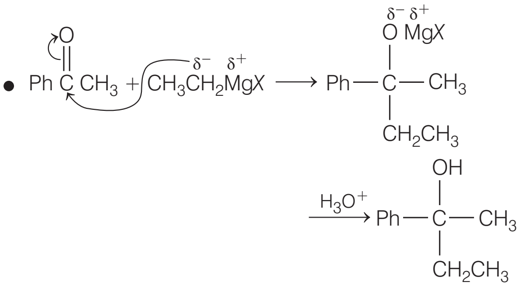

$CH_3CH_2-\underset{Ph}{\overset{OH}{C}}-CH_3$ cannot be prepared by HCHO and $PhCH(CH_3)CH_2MgX$. This can be easily illustrated by following reaction.

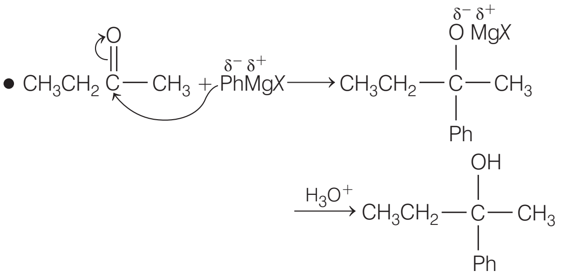


The obtained product is not the required substance. While option (a), (b) and (c) can readily prepare the required substance.

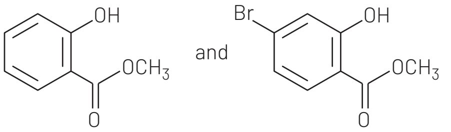
The reactions are as follows :

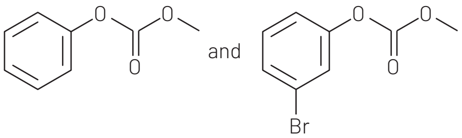
- 

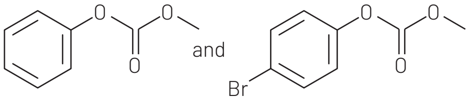


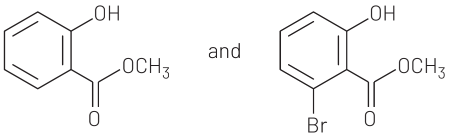


38 Phenol reacts with methyl chloroformate in the presence of NaOH to form product *A*. *A* reacts with Br_2 to form product *B*. *A* and *B* are respectively **[JEE Main 2018]**

(a) 

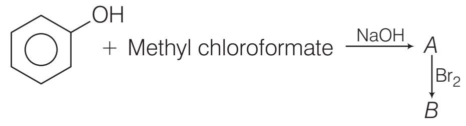
(b) 

(c) 

(d) 

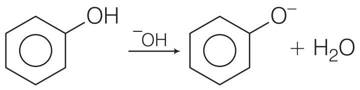
Ans. *(c)*

Given

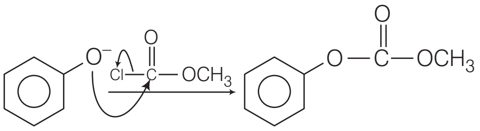


In the above road map, first reaction appears as acid base reaction followed by S_NAE (Nucleophilic substitution through Addition and Elimination). Both the steps are shown below

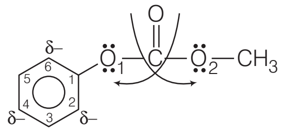
(i) **Acid base reaction**



(ii) S_NAE

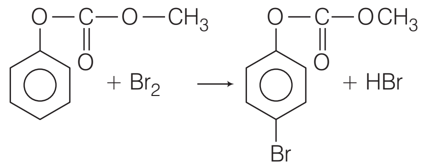


In the product of S_NAE the attached group is *ortho* and *para*-directing due to following cross conjugation

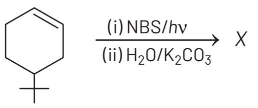


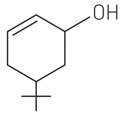
Cross conjugation due to which lone pair of oxygen 1 will be easily available to ring resulting to higher electron density at 2, 4, 6 position with respect to group. However from the stability point of view *ortho* positions are not preferred by substituents as group $-O-\underset{\underset{O}{\|}}{C}-O-CH_3$ is bulky.

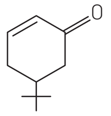
Hence, on further bromination of S_NAE product *para* bromo derivative will be the preferred product i.e.

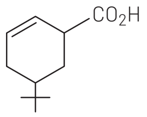


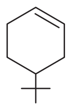
39 The product of the reaction given below is **[JEE Main 2016]**



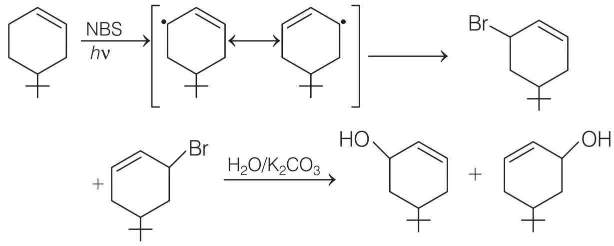
(a) 

(b) 

(c) 

(d) 

Ans. *(a)*



40 The most suitable reagent for the conversion of $R-CH_2-OH \rightarrow R-CHO$ is **[JEE Main 2014]**

(a) $KMnO_4$ (b) $K_2Cr_2O_7$

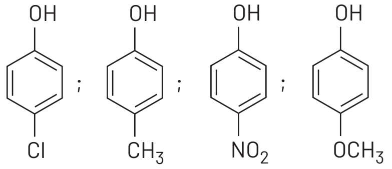
(c) CrO_3

(d) PCC [Pyridinium chlorochromate]

Ans. ***(d)***

Mild oxidising agents like PCC [Pyridinium chlorochromate] are particularly used for the conversion of $R - CH_2OH \rightarrow R - CHO$.

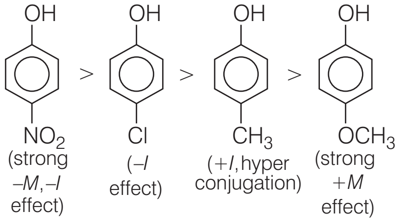
41 Arrange the following compounds in the order of decreasing acidity **[JEE Main 2013]**



I II III IV

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

Ans. ***(c)***



Electron releasing group decreases while electron withdrawing group increases acidic strength by destabilising and stabilising the phenoxide ion formed respectively.

42 An unknown alcohol is treated with the 'Lucas reagent' to determine whether the alcohol is primary, secondary or tertiary. Which alcohol reacts fastest and by what mechanism? **[JEE Main 2013]**

(a) Secondary alcohol by S_N1
(b) Tertiary alcohol by S_N1
(c) Secondary alcohol by S_N2
(d) Tertiary alcohol by S_N2

Ans. ***(b)***

The reaction of alcohol with Lucas reagent is mostly S_N1 reaction and the rate of reaction is directly proportional to the stability of carbocation formed in the reaction.

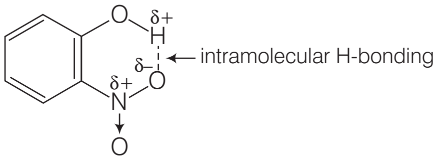
Since 3° R—OH forms 3° carbocation (most stable) hence it will react fastest by S_N1 reaction.

43 *Ortho*-nitrophenol is less soluble in water than *p*- and *m*-nitrophenols because

(a) *o*-nitrophenol is more volatile steam than those of *m*- and *p*-isomers.
(b) *o*-nitrophenol shows intramolecular H-bonding
(c) *o*-nitrophenol shows intermolecular H-bonding
(d) melting point of *o*-nitrophenol is lower than those of *m*- and *p*-isomers **[AIEEE 2012]**

Ans. ***(b)***

There is intramolecular H-bonding in *o*-nitrophenol and thus solubility in water is decreased.



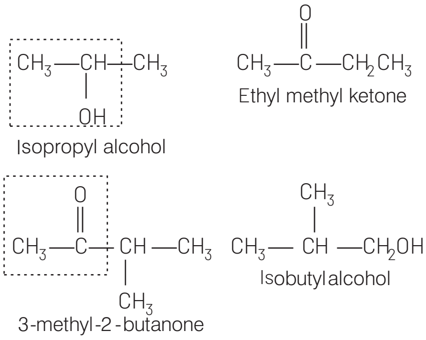
44 Iodoform can be prepared from all except

(a) ethyl methyl ketone **[AIEEE 2012]**
(b) isopropyl alcohol
(c) 3-methyl-2-butanone
(d) isobutyl alcohol

Ans. ***(d)***

Iodoform reaction is given by alcohols and ketones containing $CH_3-\underset{\underset{OH}{|}}{CH}-$ and $CH_3-\overset{\overset{O}{\|}}{C}-$ group, respectively. Thus, among the given compounds, isobutyl alcohol does not contain $CH_3-\underset{\underset{OH}{|}}{CH}-$ group.

Hence, it does not give iodoform reaction on treatment with I_2/NaOH.



Hence, compounds (*a*), (*b*) and (*c*) will give iodoform while compound (*d*) (isobutyl alcohol) does not give any iodoform reaction.

45 Phenol is heated with a solution of mixture of KBr and $KBrO_3$. The major product obtained in the above reaction is **[AIEEE 2011]**

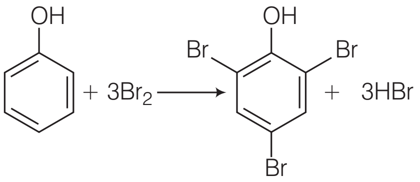
(a) 2-bromophenol
(b) 3-bromophenol
(c) 4-bromophenol
(d) 2, 4, 6-tribromophenol

Ans. ***(d)***

Br_2 is formed by a redox reaction.

$$5Br^- + BrO_3^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

—OH group is the activating group and thus activates the benzene towards electrophilic substitution reaction at *o*-and *p*-positions giving yellowish white precipitate of 2,4,6-tribromophenol.



46 The correct order of acid strength of the following compounds is **[AIEEE 2011]**

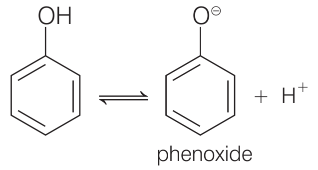
I. Phenol II. *p*-cresol

III. *m*-nitrophenol IV. *p*-nitrophenol

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

Ans. ***(b)***

I.

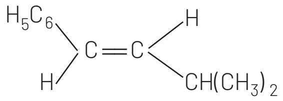


(a), (b), (d) may be formed but (c) is never formed.

47 The main product of the following reaction is

$$C_6H_5CH_2CH(OH)CH(CH_3)_2 \xrightarrow{\text{Conc. } H_2SO_4} ?$$ **[AIEEE 2010]**

(a)



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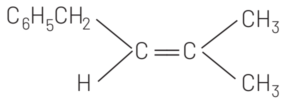
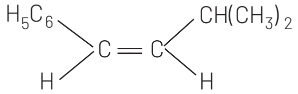
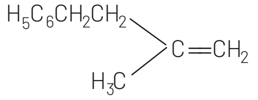


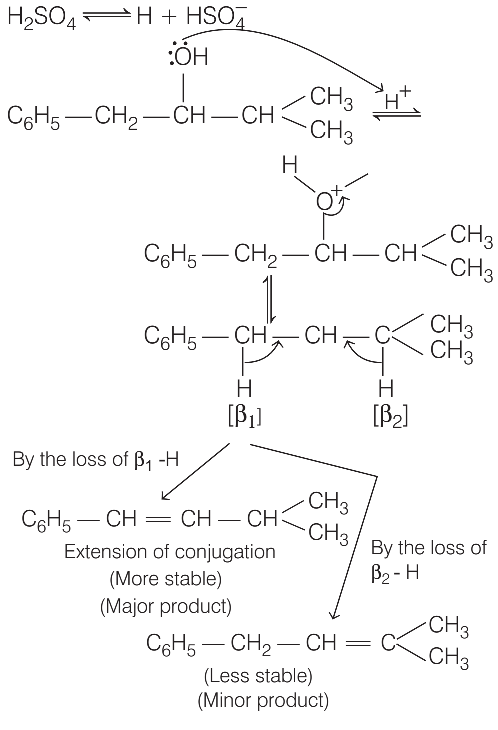
(c)



(d)



Ans. ***(a)***



48 From amongst the following alcohols the one that would react fastest with conc. HCl and anhydrous $ZnCl_2$ is

(a) 2-butanol (b) 2-methylpropan-2-l

(c) 2-methylpropanol (d) 1-butanol **[AIEEE 2010]**

Ans. ***(b)***

The reaction of alcohol with conc. HCl and anhydrous $ZnCl_2$ follows S_N1 pathway, so greater the stability of carbocation formed, faster is the reaction.2-methylpropan-2-ol gives 3° carbocation.

Hence, it reacts rapidly with conc. HCl and anhydrous $ZnCl_2$ (Lucas reagent).

49 Phenol, when it first reacts with concentrated sulphuric acid and then with concentrated nitric acid gives

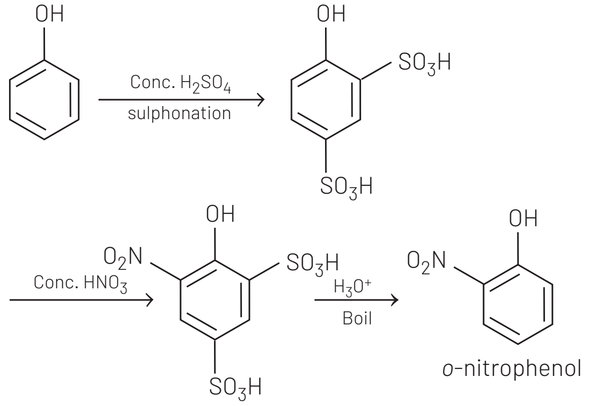
(a) 2, 4, 6-trinitrobenzene **[AIEEE 2008]**

(b) *o*-nitrophenol

(c) *p*-nitrophenol

(d) nitrobenzene

Ans. ***(b)***



First sulphonation is the means to block *para* and ortho position and to reduce the reactivity of phenolic ring against strong oxidising agent HNO_3. (The use of conc. HNO_3 over phenol cause the oxidation of ring mainly). — SO_3H groups are knocked out on boiling with H_2O.

50 In the following sequence of reactions,

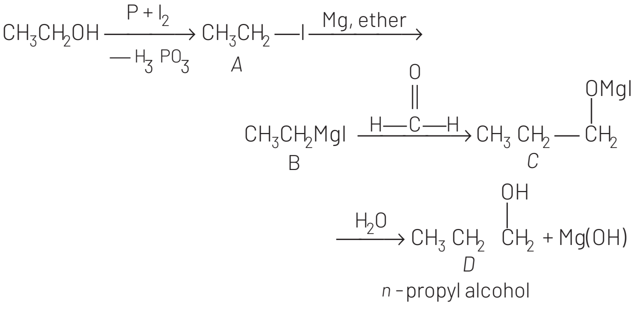
$$CH_3CH_2OH \xrightarrow{P+I_2} A \xrightarrow[\text{ether}]{\text{Mg}} B \xrightarrow{\text{HCHO}} C \xrightarrow{H_2O} D$$

the compound '*D*' is **[AIEEE 2007]**

(a) butanal (b) *n*-butyl alcohol

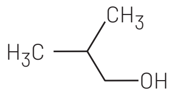
(c) *n*-propyl alcohol (d) propanal

Ans. ***(c)***



51 Among the following the one that gives positive iodoform test upon reaction with I_2 and NaOH is **[AIEEE 2006]**

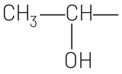
(a) $CH_3CH_2CH(OH)CH_2CH_3$ (b) $C_6H_5CH_2CH_2OH$

(c) 

(d) $PhCHOHCH_3$

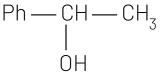
Ans. ***(d)***

For positive iodoform test, alcohol molecule must have

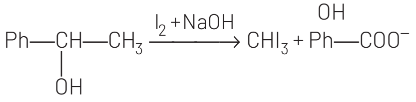


$CH_3—\underset{OH}{\underset{|}{CH}}—$ group.

Thus, iodoform test is given by only (d)



$Ph—\underset{OH}{\underset{|}{CH}}—CH_3$ while others will not give this test.



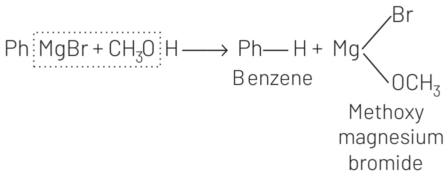
$$Ph—\underset{OH}{\underset{|}{CH}}—CH_3 \xrightarrow{I_2+NaOH} CHI_3 + Ph—COO^-$$

52 Phenyl magnesium bromide reacts with methanol to give **[AIEEE 2006]**

(a) a mixture of anisol and Mg(OH)Br
(b) a mixture of benzene and Mg(OMe)Br
(c) a mixture of toluene and Mg(OH)Br
(d) a mixture of phenol and Mg(Me)Br

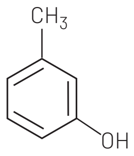
Ans. ***(b)***

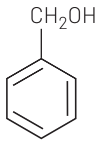
PhMgBr can be protonated by any of the protic solvent *e.g.*, CH_3OH.

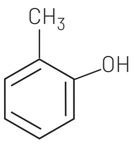


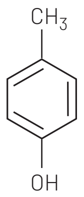
$$Ph\boxed{MgBr + CH_3O}H \longrightarrow \underset{\text{Benzene}}{Ph—H} + Mg\begin{matrix} Br \\ OCH_3 \end{matrix}$$

53 The structure of the compound that gives a tribromo derivative on treatment with bromine water is **[AIEEE 2006]**

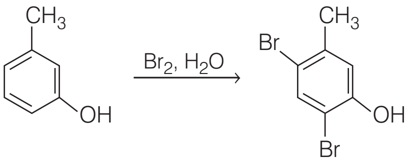
(a) 

(b) 

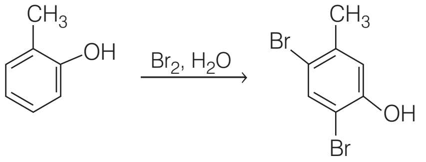
(c) 

(d) 

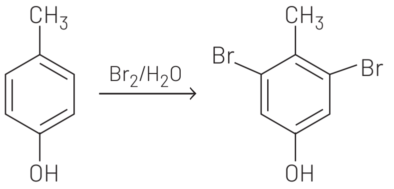
Ans. ***(a)***

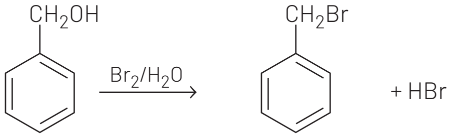


Tribromo derivative

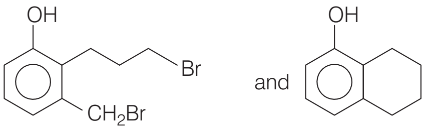


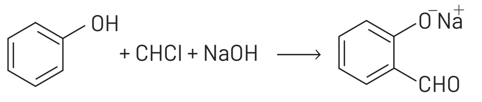
Dibromo derivative





m-cresol due to phenoxide ion in H_2O solvent, gives tribromoderivative at all *ortho and para* positions.

(d) 

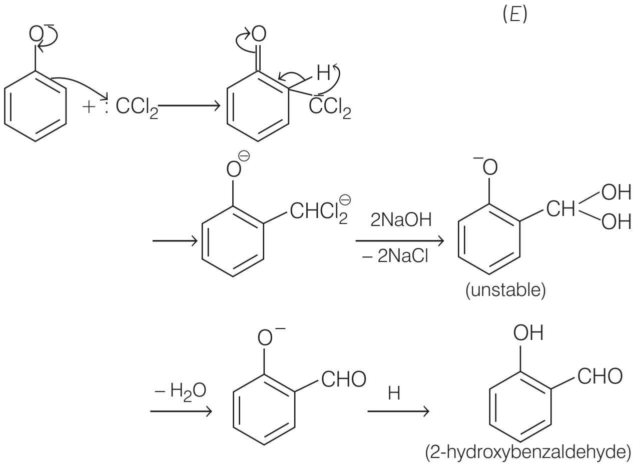
54 

The electrophile involved in the above reaction is

(a) dichloromethyl cation $(\overset{\oplus}{C}HCl_2)$ **[AIEEE 2006]**
(b) dichlorocarbene $(:CCl_2)$
(c) trichloromethyl anion $(\bar{C}Cl_3)$
(d) formyl cation $(\overset{\oplus}{C}HO)$

Ans. ***(b)***

$$\underset{[\text{from } Na^+OH^-]}{\bar{O}H + CHCl_3} \rightleftharpoons H_2O + CCl_3^- \longrightarrow \underset{\substack{\text{Dichloro}\\ \text{carbene}\\ +\\ (E)}}{:CCl_2} + Cl^-$$



55 Acid catalysed hydration of alkenes except ethene leads to the formation of **[AIEEE 2005]**

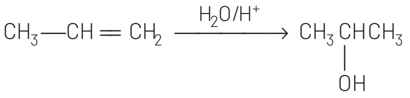
(a) mixture of secondary and tertiary alcohols
(b) mixture of primary and secondary alcohols
(c) secondary or tertiary alcohol
(d) primary alcohol

Ans. ***(c)***

Hydration of ethene gives 1° alcohol (ethanol) while all other alkenes give either 2° or 3° alcohols.

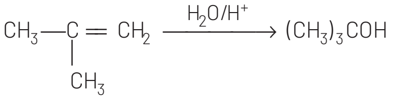
$$CH_2=CH_2 \xrightarrow{H_2O/H^+} CH_3CH_2OH$$

Ethene



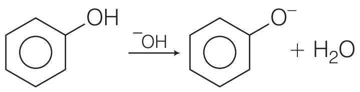
$$CH_3-CH=CH_2 \xrightarrow{H_2O/H^+} CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$$

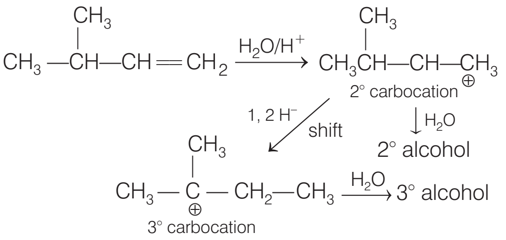
[(2° alcohol) through 2° carbocation $CH_3\overset{\oplus}{C}HCH_3$]



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2 \xrightarrow{H_2O/H^+} (CH_3)_3COH$$

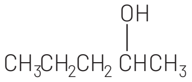
[(3° alcohol) through 3° carbocation $(CH_3)_3\overset{\oplus}{C}$]



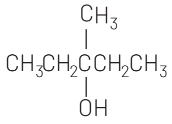


56 Among the following compounds which can be dehydrated very easily ? **[AIEEE 2004]**

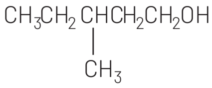
(a) $CH_3CH_2CH_2CH_2CH_2OH$

(b)


$$CH_3CH_2CH_2\overset{\displaystyle OH}{\overset{|}{C}}HCH_3$$

(c)


$$CH_3CH_2\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}CH_2CH_3$$

(d)


$$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_2OH$$

Ans. ***(c)***

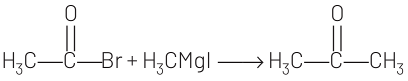
Dehydration of alcohol is in the order 1° < 2° < 3°

Thus (*c*), a 3° alcohol is dehydrated very easily.

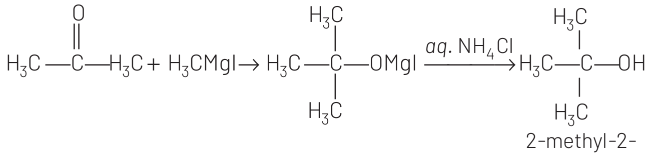
57 Acetyl bromide reacts with excess of CH_3MgI followed by treatment with a saturated solution of NH_4Cl gives **[AIEEE 2004]**

(a) acetone (b) acetamide
(c) 2-methyl-2-propanol (d) acetyl iodide

Ans. ***(c)***



$$H_3C-\overset{\displaystyle O}{\overset{||}{C}}-Br + H_3CMgI \longrightarrow H_3C-\overset{\displaystyle O}{\overset{||}{C}}-CH_3$$



$$H_3C-\overset{\displaystyle O}{\overset{||}{C}}-H_3C + H_3CMgI \rightarrow H_3C-\underset{\displaystyle H_3C}{\underset{|}{\overset{\displaystyle H_3C}{\overset{|}{C}}}}-OMgI \xrightarrow{aq.\ NH_4Cl} H_3C-\underset{\displaystyle H_3C}{\underset{|}{\overset{\displaystyle H_3C}{\overset{|}{C}}}}-OH$$

2-methyl-2-propanol

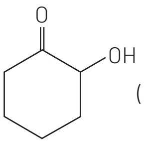
58 During dehydration of alcohols to alkenes by heating with concentrated H_2SO_4 the initiation step is **[AIEEE 2003]**

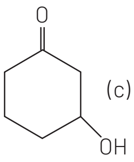
(a) protonation of alcohol molecule
(b) formation of carbocation
(c) elimination of water
(d) formation of an ester

Ans. ***(a)***

Protonation of —OH is first step. It involves conversion of poor leaving group (—OH) into good leaving group (—$\overset{+}{O}H_2$).

59 Maximum dehydration takes place in that of **[AIEEE 2002]**

(a)


(b)


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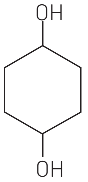

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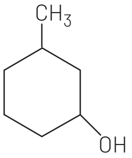
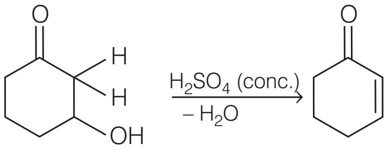


Ans. ***(b)***

Dehydration takes place with the formation of more stable carbocation. Among the given compounds, only compound (b) forms conjugated carbocation. Thus, maximum amount of dehydration takes place in compound (*b*).



TOPIC 2

Ethers

60 Given below are two statements : one is labelled as Assertion (A) and the other is labelled as Reason (R).

Assertion (A) Synthesis of ethyl phenyl ether may be achieved by Williamson synthesis.

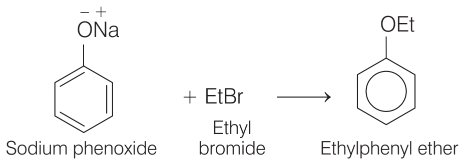
Reason (R) Reaction of bromobenzene with sodium ethoxide yields ethyl phenyl ether.

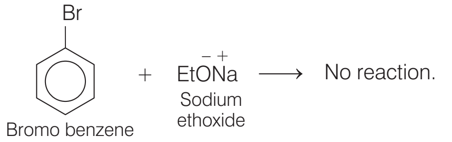
In the light of the above statements, choose the most appropriate answer from the options given below **[2021, 27 Aug Shift-I]**

(a) Both (A) and (R) are correct and (R) is the correct explanation of (A)
(b) (A) is correct but (R) is incorrect
(c) (A) is incorrect but (R) is correct
(d) Both (A) and (R) are correct but (R) is not the correct explanation of (A)

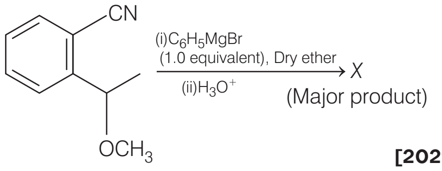
Ans. ***(b)***

Williamson's synthesis is used to prepare mixed ethers as well as simple ether. To prepare ethyl phenyl ether following reaction take place.

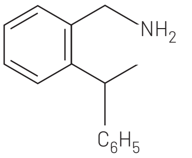


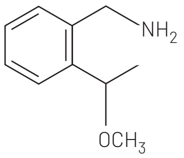


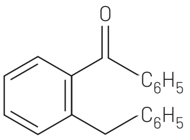
This reaction is not possible as bromine has partial double bond character with benzene ring, so it cannot be dissociated. So, Assertion is correct but Reason is not correct.

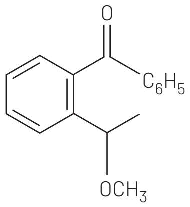
61 

[2021, 16 March Shift-II]

(a) 

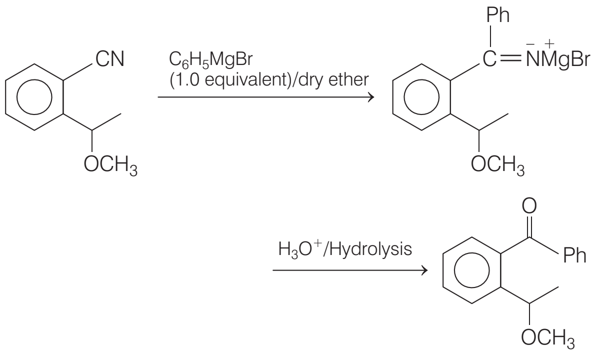
(b) 

(c) 

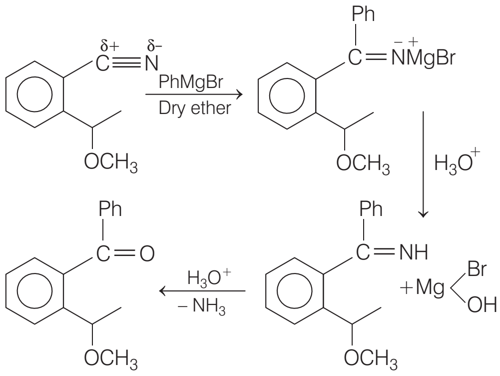
(d) 

Ans. ***(d)***

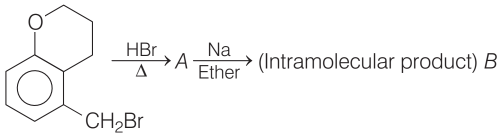
Cyanide undergoes nucleophilic addition with Grignard followed by hydrolysis to give carbonyl compound.

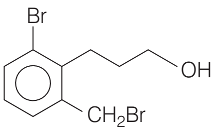
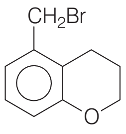


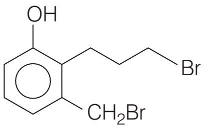
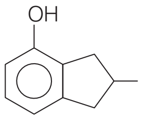
Mechanism Carbon of cyanide is electrophilic and is attacked by nucleophilic phenyl anion.

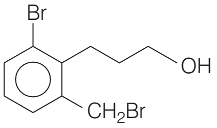
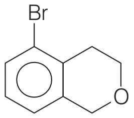


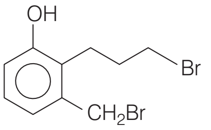
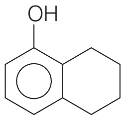
62 In the following reaction sequence, structures of *A* and *B*, respectively will be **[2020, 7 Jan Shift-II]**



(a)  and 

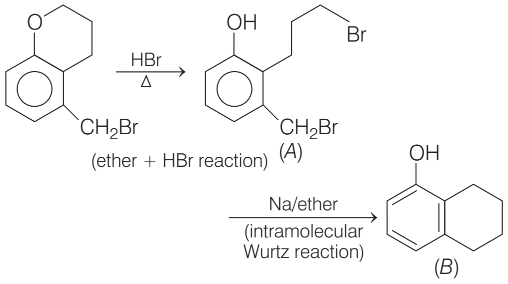
(b)  and 

(c)  and 

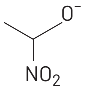
(d)  and 

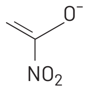
Ans. ***(d)***

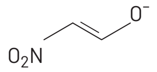
The given reaction can be completed as follows :



63 The correct order of stability for the following alkoxides is **[2020, 7 Jan Shift-II]**


(A)

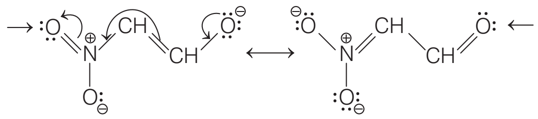

(B)


(C)

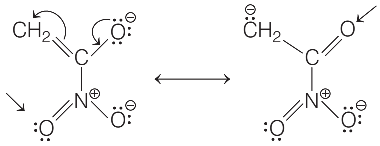
(a) (C) > (B) > (A)
(b) (B) > (C) > (A)
(c) (B) > (A) > (C)
(d) (C) > (A) > (B)

Ans. ***(a)***

(*C*) is most stable due to strong $-I$ effect as well as $-R$ (or $-M$) effect of '—NO_2' group. The negative charge is delocalised as represented by the following resonance structure :



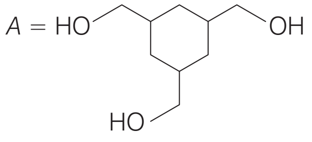
In (*A*), there is no resonance delocalisation of negative charge, and hence it is least stable. In (*B*), negative charge is delocalised by resonance as shown :

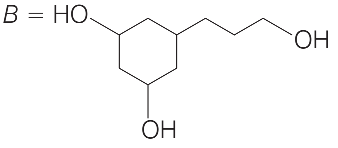


But the contribution of structure on RHS is relatively less, so stability of (*B*) is more than (*A*) but less than (*C*).

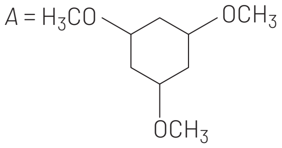
64 Among the compounds *A* and *B* with molecular formula $C_9H_{18}O_3$, *A* is having higher boiling point the *B*. The possible structures of *A* and *B* are **[2020, 8 Jan Shift-II]**

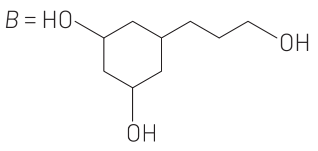
(a)



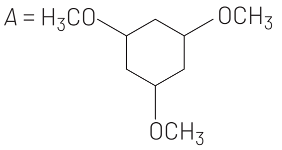


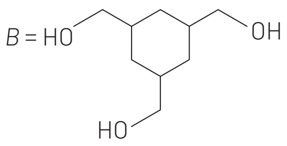
(b)



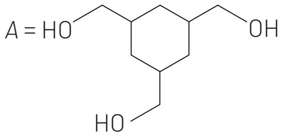


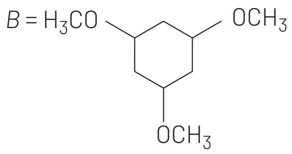
(c)





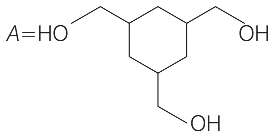
(d)

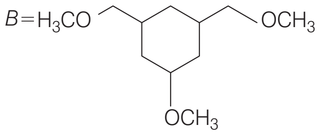




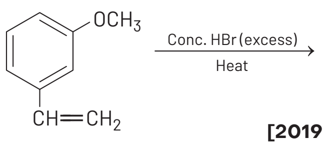
Ans. ***(d)***

Alcohols have higher boiling point than ethers of same molecular mass due to possibility of intermolecular hydrogen bonds in alcohols and not in ethers. So, *A* is alcohol derivative and *B* is ether derivative.



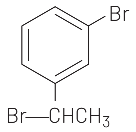


65 The major product of the following reaction is

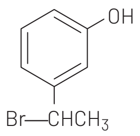


[2019, 8 April Shift-I]

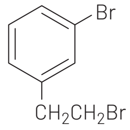
(a)



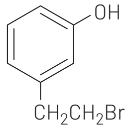
(b)



(c)



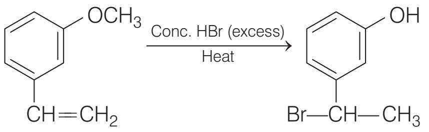
(d)



Ans. ***(b)***

Key Idea Ethers are least reactive functional groups. The cleavage of C—O bond in ethers take place under drastic conditions with excess of H*X*.

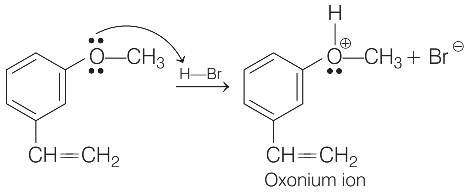
The major product obtained in the reaction is as follows:



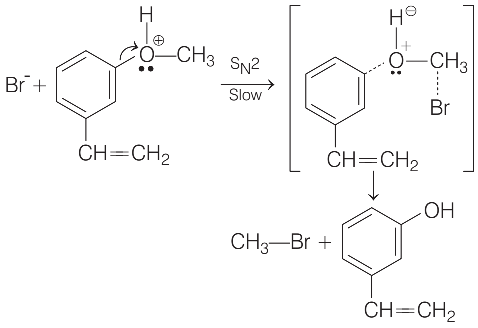
As conc. HBr is in excess. So, reaction will take place at both the substituents.

Mechanism

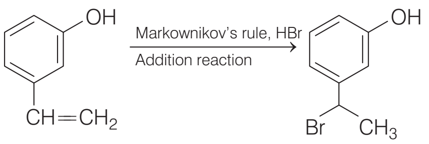
Step 1 Protonation of ether to form oxonium ion.



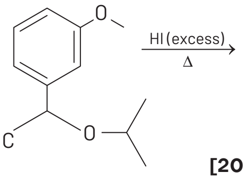
Step 2 Attack of nucleophile at the protonated ether.



Step 3 As HBr is in excess, so, reaction will also take place at alkene.

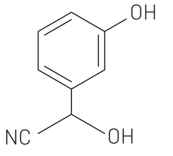


66 The major product of the following reaction is

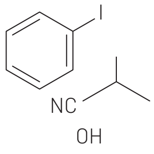


[2019, 10 April Shift-I]

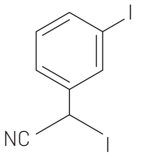
(a)



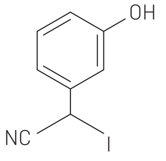
(b)



(c)

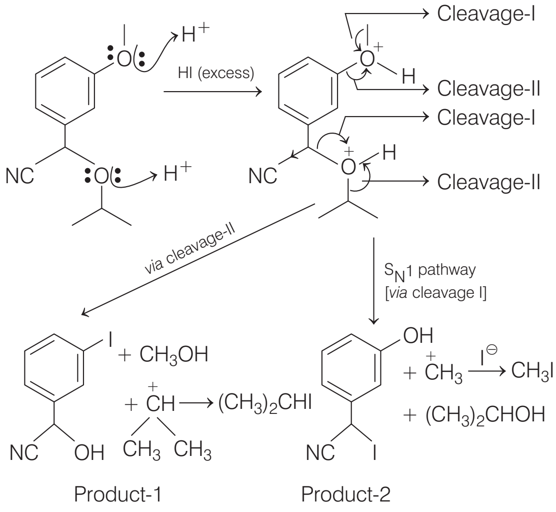


(d)



Ans. ***(d)***

The given reaction takes place as follows :

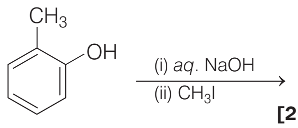


Product-2 is formed because

(i) Cleavage-I will give more stable aryl carbocation.

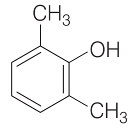
(ii) Cleavage- I will give intermediate which is in conjugation with ring.

67 The major product of the following reaction is

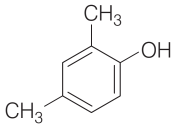


[2019, 10 Jan Shift-II]

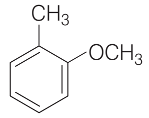
(a)



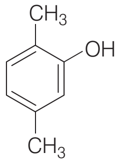
(b)



(c)

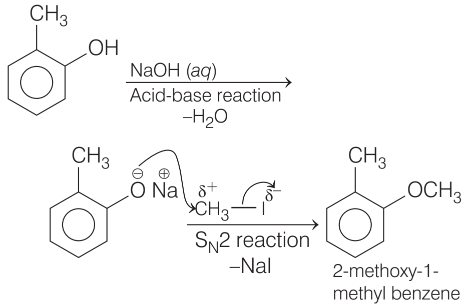


(d)

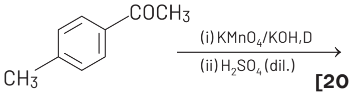


Ans. ***(c)***

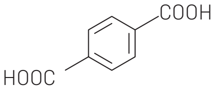
Substituted phenols react with *aq*.NaOH to form sodium phenoxides which on reaction with CH_3I undergoes S_N2 reaction to give 2-methoxy-1-methyl benzene.

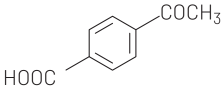


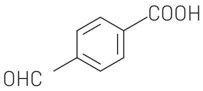
68 The major product of the following reaction is

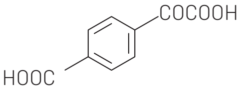


[2019, 11 Jan Shift-I]

(a) 

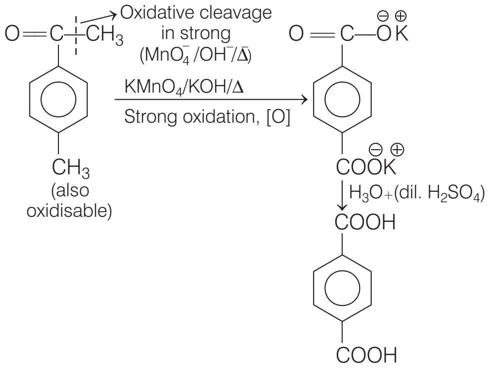
(b) 

(c) 

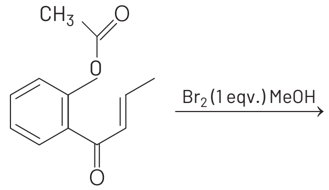
(d) 

Ans. ***(a)***

In presence of alkaline $KMnO_4$, vigorous oxidation of alkyl or acyl benzene takes place. During oxidation, aromatic nucleus remains intact but the entire chain is oxidised to —COOH group irrespective of the length of carbon chain.



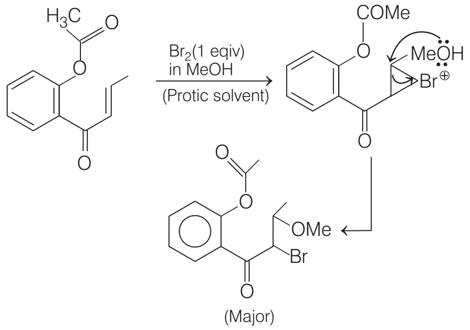
69 The major product obtained in the following conversion is



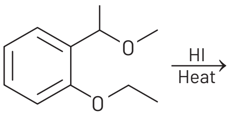
[2019, 11 Jan Shift-II]

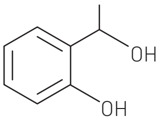
Ans. ***(b)***

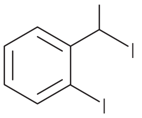
In presence of $Br_2/EtOH$, the reactant containing double bond undergoes electrophilic addition reaction *via* the formation of bromonium ion. On further attack of $—\ddot{\underset{\cdot\cdot}{O}}Me$ on bromonium ion gives the addition product.

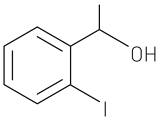


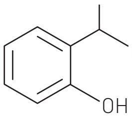
70 The major product formed in the following reaction is **[JEE Main 2018]**



(a) 

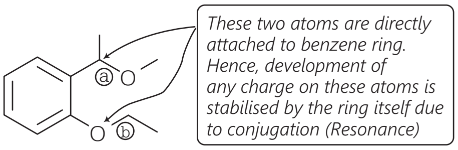
(b) 

(c) 

(d) 

Ans. ***(d)***

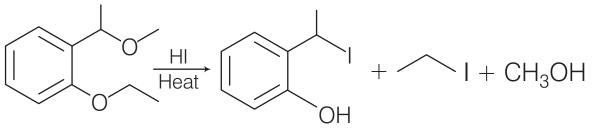
The reaction given is a nucleophilic substitution reaction in which cleavage at C—O bond is visible. The product formation can be visualised with the help of following analysis.



These two atoms are directly attached to benzene ring. Hence, development of any charge on these atoms is stabilised by the ring itself due to conjugation (Resonance)

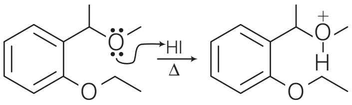
If any one properly visualise the fact written with figure above, than a conclusion can be made that C—O bonds marked (a) and (b) in the figure will undergo heterolysis during the reaction.

The reaction can be represented as



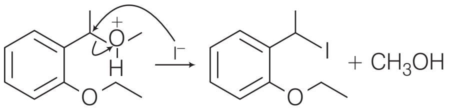
Mechanism

Step I The reaction begins with the attack of H^+ of HI on oxygen to form oxonium ion as

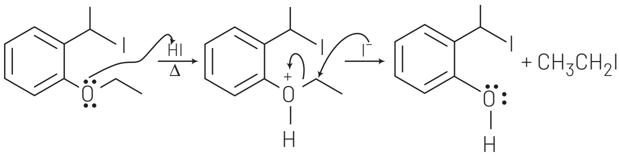


Oxonium ion

Step II This oxonium ion undergoes lysis and addition of I^- to form two products as



Step III Similar pathway is followed at the other oxygen atom, which can be visualised as



Note Mechanism of a reaction is always a logical sequencing of events which may occur simultaneously as well.

71 Consider the following reaction,

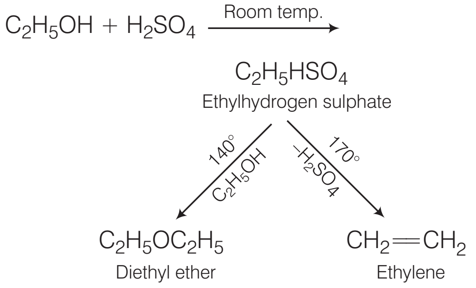
$$C_2H_5OH + H_2SO_4 \longrightarrow \text{Product}$$

Among the following, which one cannot be formed as a product under any conditions? **[AIEEE 2011]**

(a) Ethyl hydrogen sulphate (b) Ethylene
(c) Acetylene (d) Diethyl ether

Ans. ***(c)***

(a), (b), (d) may be formed but (c) is never formed.

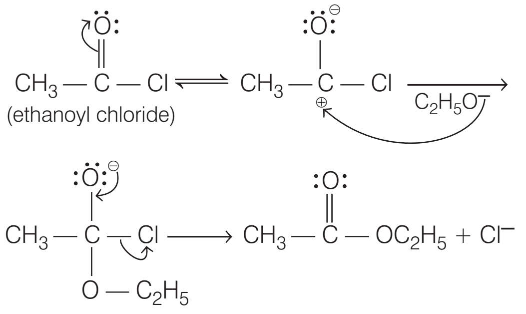


72 Sodium ethoxide has reacted with ethanoyl chloride. The compound that is produced in the above reaction is **[AIEEE 2011]**

(a) diethyl ether (b) 2-butanone
(c) ethyl chloride (d) ethyl ethanoate

Ans. ***(d)***

$$C_2H_5O^-Na^+ \rightleftharpoons C_2H_5O^- + Na^+$$



$$Na^+ + Cl^- \longrightarrow NaCl$$

This is by S_N reaction. Cl^- is a better leaving group than $C_2H_5O^-$ and the ethyl ethanoate is formed.

73 An ether is more volatile than an alcohol having the same molecular formula. This is due to **[AIEEE 2003]**

(a) dipolar character of ethers
(b) alcohols having resonance structures
(c) intermolecular hydrogen bonding in ethers
(d) intermolecular hydrogen bonding in alcohols

Ans. ***(d)***

Alcohol has polar H which makes intermolecular H-bonding possible. Ether is non-polar, hence has no H-bonding. Lack of H-bonding in ether makes it more volatile than alcohol.

TOPIC 3

Aldehydes and Ketones

74 Given below are two statements.

Statement I The nucleophilic addition of sodium hydrogen sulphite to an aldehyde or a ketone involves proton transfer to form a stable ion.

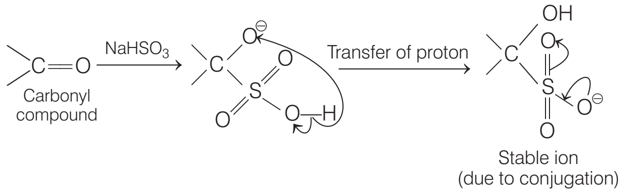
Statement II The nucleophilic addition of hydrogen cyanide to an aldehyde or a ketone yields amine as final product.

In the light of the above statements, choose the most appropriate answer from the options given below. **[2021, 1 Sep Shift-II]**

(a) Both statement I and statement II are true.
(b) Statement I is false but statement II is true.
(c) Statement I is true but statement II is false.
(d) Both statement I and statement II are false.

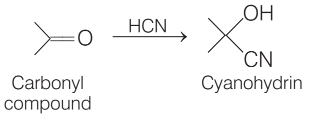
Ans. ***(c)***

Nucleophilic addition of sodium hydrogen sulphite ($NaHSO_3$) to carbonyl compound (aldehyde or ketone) involves proton transfer to form a stable ion.



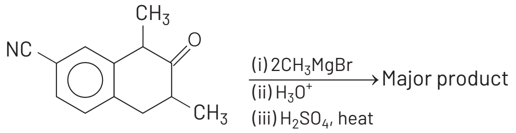
Hence, statement I is true.

Nucleophilic addition of HCN (hydrogen cyanide) to an aldehyde/ketone yield cyanohydrin as final product.

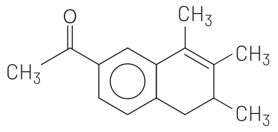


Hence, statement II is false.

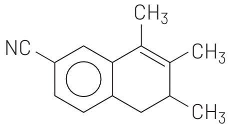
75 Which one of the following is the major product of the given reaction? **[2021, 27 Aug Shift-II]**



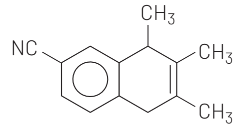
(a)



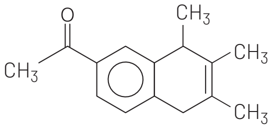
(b)



(c)

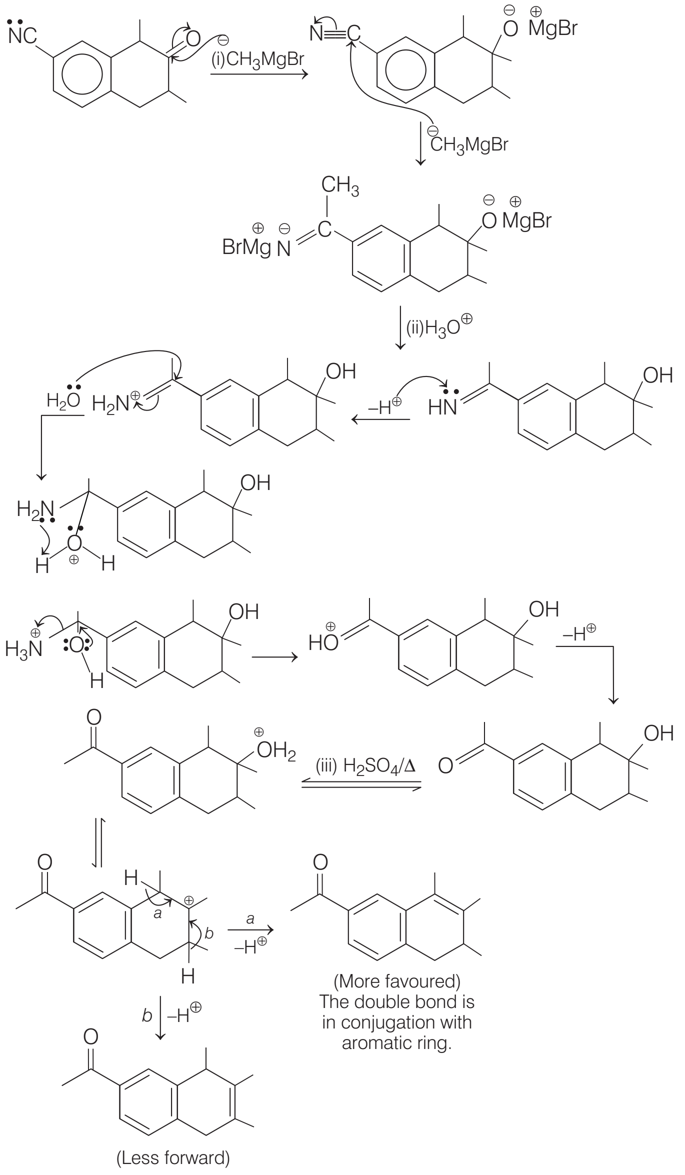


(d)



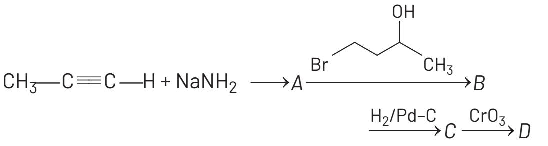
Ans. ***(a)***

The reaction of keto and cyanide group with Grignard reagent and further hydrolysis gives alcohol and keto group respectively. On further heating with H_2SO_4 at — OH group is eliminated resulting in formation of alkene.

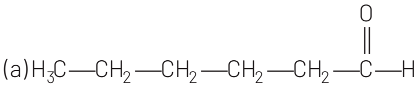


Therefore, option (a) is correct.

76 In the following sequence of reactions, the final product *D* is **[2021, 27 Aug Shift-I]**



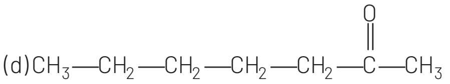
$$CH_3—C\equiv C—H + NaNH_2 \longrightarrow A \xrightarrow{Br\text{—}CH_2CH_2CH(OH)CH_3} B \xrightarrow{H_2/Pd\text{-}C} C \xrightarrow{CrO_3} D$$



(a) $H_3C—CH_2—CH_2—CH_2—CH_2—\overset{\overset{O}{\|}}{C}—H$

(b) $CH_3—CH=CH—CH_2—CH_2—CH_2—COOH$

(c) $H_3C—CH=CH—CH(OH)—CH_2—CH_2—CH_3$

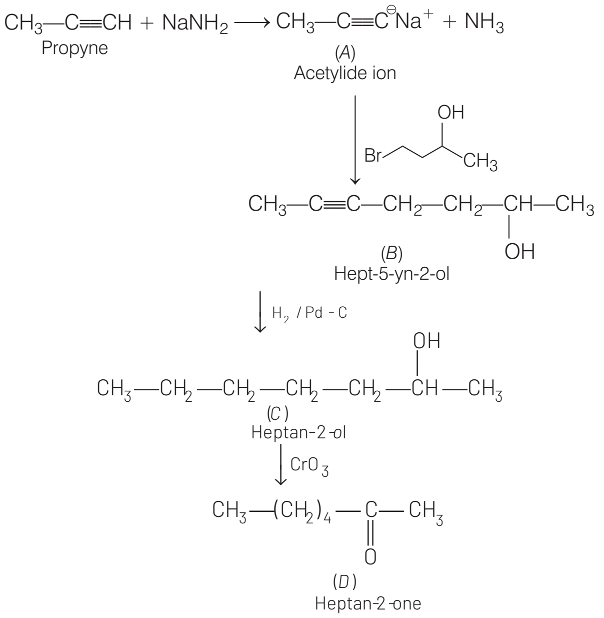


(d) $CH_3—CH_2—CH_2—CH_2—CH_2—\overset{\overset{O}{\|}}{C}—CH_3$

Ans. ***(d)***

$NaNH_2$ is a strong base that causes deprotonation of propyne and forms acetylide ion (*A*) which further combines with the carbon chain and forms hept-5-yn-2-ol (*B*) that undergoes reduction in presence of H_2/Pd-C and forms heptan-2-ol (*C*). Being a secondary alcohol (*C*), oxidises in presence of CrO_3 to give corresponding ketone i.e. heptan-2-one (*D*).

The complete reaction take place as follows.



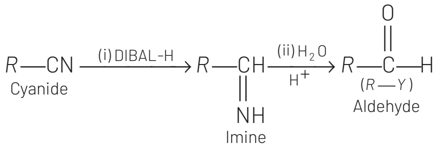
77 $R—CN \xrightarrow[\text{(ii)}\,H_2O]{\text{(i) DIBAL–H}} R—Y$

Consider the above reaction and identify *Y*. **[2021, 27 July Shift-II]**

(a) $—CH_2NH_2$ (b) $—CONH_2$ (c) — CHO (d) — COOH

Ans. ***(c)***

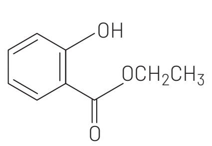
DIBAL-H, i.e. di-isobutyl aluminium hydride causes partial reduction of cyanide group and further hydrolysis forms corresponding aldehyde.

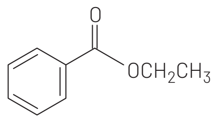


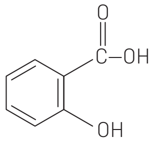
$$\underset{\text{Cyanide}}{R—CN} \xrightarrow{\text{(i) DIBAL-H}} \underset{\text{Imine}}{R—\overset{}{CH}=NH} \xrightarrow[H^+]{\text{(ii)} H_2O} \underset{\text{Aldehyde}}{\underset{(R—Y)}{R—\overset{O}{\overset{\|}{C}}—H}}$$

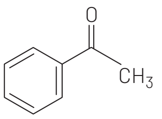
Hence, Y is —CHO group.

78 Which one of the following compounds will give orange precipitate when treated with 2, 4 dinitrophenyl hydrazine? **[2021, 27 July Shift-I]**

(a) 

(b) 

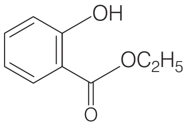
(c) 

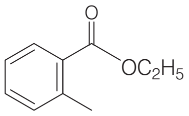
(d) 

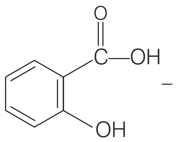
Ans. ***(d)***

2, 4-dinitrophenylhydrazine can be used for qualitative identification of ketone or aldehyde functional group.

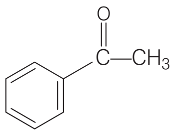
A successful test is indicated by formation of yellow, orange or red colour precipitate which is known as dinitrophenylhydrazone.

(a)  – Presence of alcohol and ester

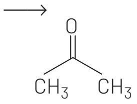
(b)  – Presence of ester group

(c)  – Presence of alcoholic and carboxylic acid group

Above compounds will not give 2, 4-DNP test due to absence of carbonyl group.

(d)  – Presence of ketone group, so it will give orange ppt. when treated with 2, 4-DNP.

79 Match List-I with List-II.

List-I (Chemical reaction)		List-II (Reagent used)	
A.	$CH_3COOC_2H_5 \longrightarrow C_2H_5OH$	1.	CH_3MgBr/H_3O^+ (1.equivalent)
B.	$CH_3COOCH_3 \longrightarrow CH_3CHO$	2.	H_2SO_4/H_2O
C.	$CH_3C\equiv N \longrightarrow CH_3CHO$	3.	DIBAL-H/H_2O
D.	$CH_3C\equiv N \longrightarrow$ 	4.	$SnCl_2$, HCl/H_2O

Choose the most appropriate option given below. **[2021, 26 Aug Shift-II]**

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

Ans. ***(c)***

(A) This reaction is reverse of esterification. As it takes place in presence of acid and the ester molecule gets hydrolysed, the reaction is called as acidic hydrolysis of ester (hydrolysis is breaking of molecule in presence of water). Acidic hydrolysis is reversible reacton, hence does not go to completion.

$$\underset{\text{Ester}}{CH_3COOC_2H_5} \xrightarrow[H_2O]{H_2SO_4} \underset{\text{Alcohol}}{C_2H_5OH}$$

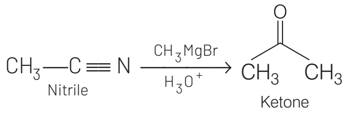
(B) Diisobutylaluminium hydride (DIBAL-H) is a reducing agent, which reduces ester to aldehyde.

$$\underset{\text{Ester}}{CH_3COOCH_3} \xrightarrow[H_2O]{\text{DIBAL-H}} \underset{\text{Aldehyde}}{CH_3CHO}$$

(C) This reaction is called Stephen aldehyde synthesis which involves preparation of aldehyde from nitrile using $SnCl_2$, HCl and quenching of resulting iminium salt ($[R—CH=NH_2]^+ Cl^-$) with H_2O.

$$\underset{\text{Nitrile}}{CH_3C\equiv N} \xrightarrow[HCl/H_2O]{SnCl_2} \underset{\text{Aldehyde}}{CH_3CHO}$$

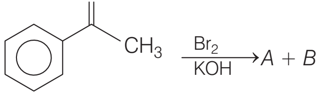
(D) Grignard reagent (CH_3MgBr) attack electrophilic carbon in the nitrile to form imine salt, this salt then gets hydrolysed to form a ketone.

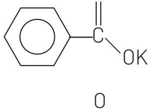


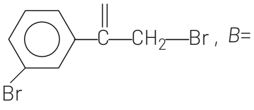
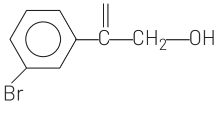
$$\underset{\text{Nitrile}}{CH_3—C\equiv N} \xrightarrow[H_3O^+]{CH_3MgBr} \underset{\text{Ketone}}{CH_3COCH_3}$$

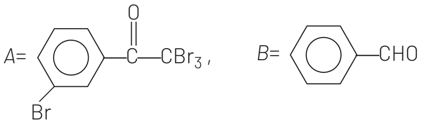
Thus, the correct match is (c) $A \rightarrow 2, B \rightarrow 3, C \rightarrow 4, D \rightarrow 1$.

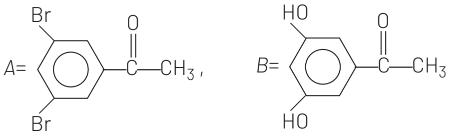
80 The major products formed in the following reaction sequence A and B are **[2021, 26 Aug Shift-I]**



(a) $A=$  , $B=CHBr_3$

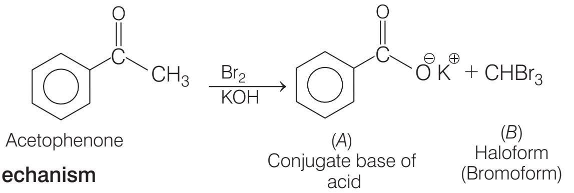
(b) $A=$  , $B=$ 

(c)


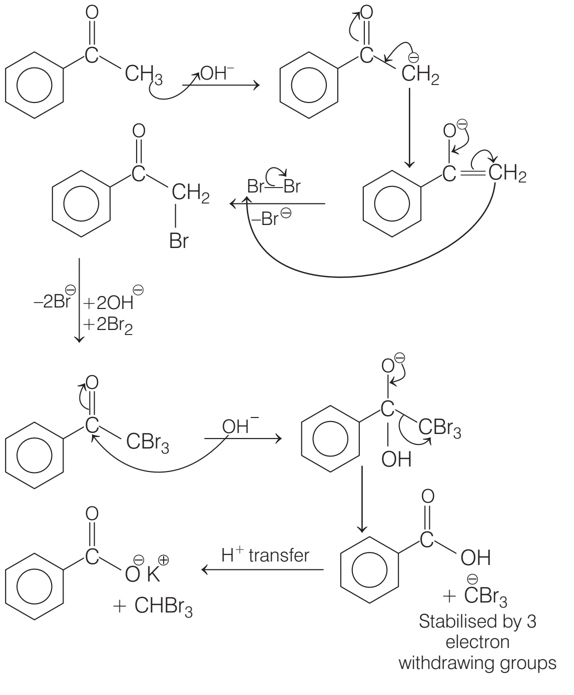
(d)


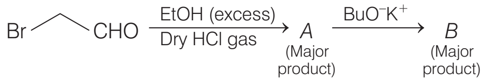
Ans. ***(a)***

Acetophenone is a methyl ketone which on reaction with Br_2 and KOH will give conjugate base of an acid and methyl group will turn into haloform. This reaction is haloform reaction.



Mechanism



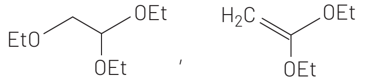
81


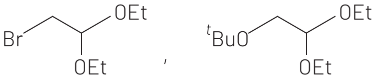
[where, $Et = C_2H_5$, $^tBu = (CH_3)_3C-$]

Consider the above reaction sequence, product *A* and product *B* formed respectively are **[2021, 25 July Shift-II]**

(a)


(b)

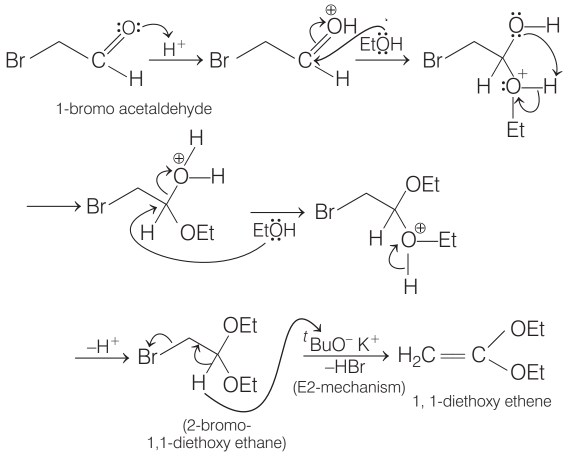

(c)


(d)


Ans. ***(a)***

In reaction t-BuO$^{\ominus}$H^{+} is used as a base to remove HBr and form alkene as a major product (*B*) *via* E2 elimination mechanism.

Machanism Firstly, 1-bromoacetaldehyde undergoes protonation which is then react with t-BuO$^{\ominus}$H^{+}. (t- BuO$^{\ominus}$ act as nucleophile and attack on carbonyl carbon). In next step, t-BuO$^{\ominus}$H^{+} act as base and accepts proton and at last alkene is formed as major product.

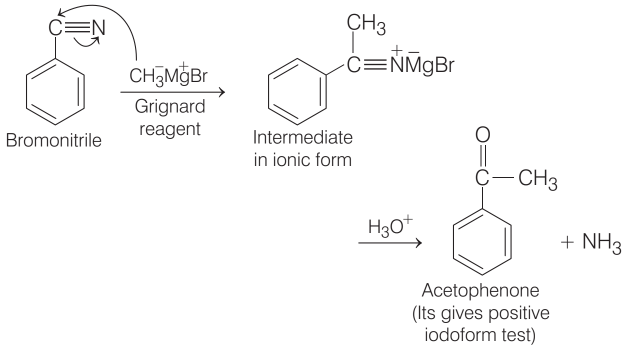


82 A reaction of benzonitrile with one equivalent CH_3MgBr followed by hydrolysis produces a yellow liquid *P*. The compound *P* will give positive **[2021 25 July Shift-II]**

(a) iodoform test	(b) Schiff's test
(c) ninhydrin's test	(d) Tollen's test

Ans. ***(a)***

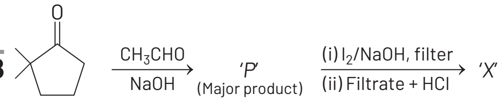
Treatment of benzonitrile with Grignard reagent followed by acid hydrolysis gives acetophenone product.



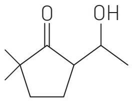
Iodoform test is used to check the presence of carbonyl compound with the structure R—CO—CH_3 or alcohols with the structure R—CH(OH)—CH_3 in a given unknown substance. The reaction of iodine, a base and a methyl ketone gives a yellow precipitate along with an "antiseptic" smell.

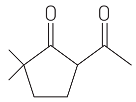
$$C_6H_5 - CO - CH_3 + I_2 + NaOH \longrightarrow C_6H_5COONa + CHI_3\downarrow$$

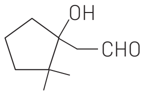
This conclude that acetophenone give iodof form test.

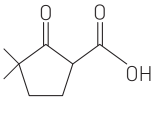
83 

Consider the given reaction, the product *X* is **[2021, 22 July Shift-I]**

(a) 

(b) 

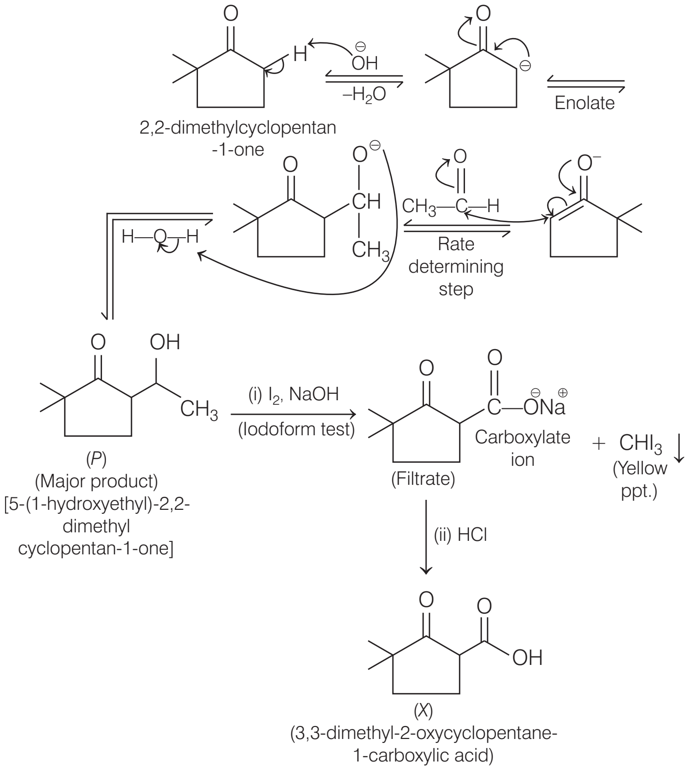
(c) 

(d) 

Ans. ***(d)***

In first step, aldol reaction is involved in reaction mechanism and in second step, (I_2, NaOH) is used for iodoform test, which gives CHI_3 (yellow precipitate) as by product.

Reaction Mechanism

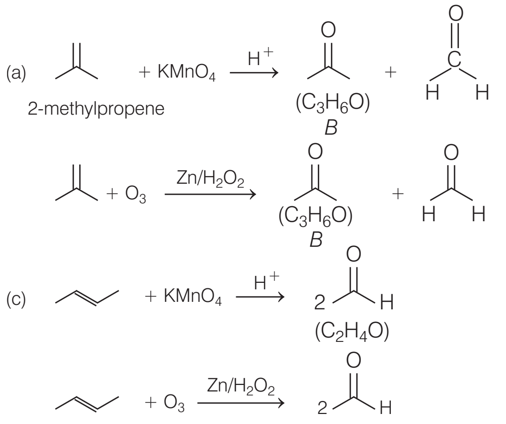


84 An organic compound 'A' C_4H_8 on treatment with $KMnO_4$ /H^+ yield's compound 'B' C_3H_6O. Compound 'A' also yields compound 'B' an ozonolysis. Compound 'A' is **[2021, 25 July Shift-I]**

(a) 2-methylpropene
(b) 1-methylcyclopropane
(c) but-2-ene
(c) cyclobutane

Ans. ***(a)***

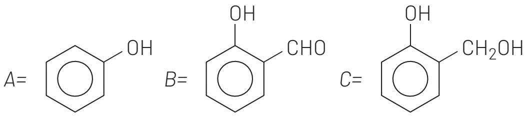
Alkenes react with $KMnO_4$ / H^+ and O_3 to give carbonyl compound.

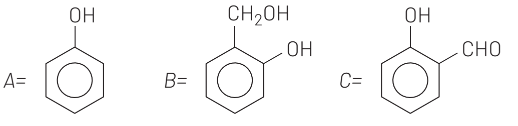


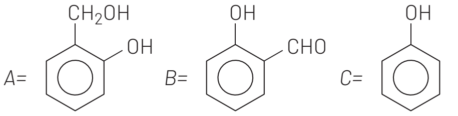
So, only 2-methylpropene gives compound *B* with molecular formula, C_3H_6O.

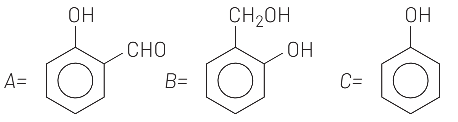
Therefore, compound *A* is 2-methylpropene.

85 An organic compound *A* (C_6H_6O) gives dark green colouration with ferric chloride. On treatment with $CHCl_3$ and KOH, followed by acidification gives compound *B*. Compound *B* can also be obtained from compound *C* on reaction with pyridinium chlorochromate (PCC). Identify *A*, *B* and C. **[2021, 22 July Shift-II]**

(a) 

(b) 

(c) 

(d) 

Ans. ***(a)***

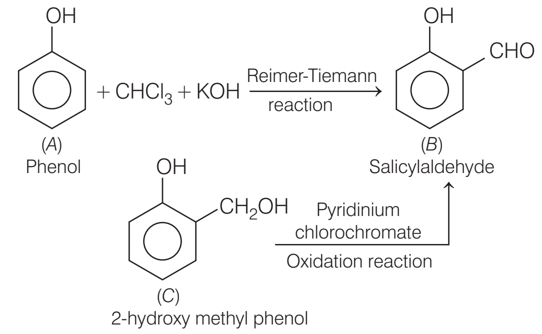
Compound *A* is phenol, compound *B* is salicylaldehyde and compound *C* is 2-hydroxy methyl phenol.

When phenols react with ferric chloride solution to give blue, violet or green colouration due to the formation of ferric phenoxide which gives different coloured water soluble complex compounds.

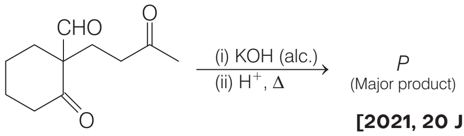
Phenol reacts with chloroform and alcoholic KOH to give salicylaldehyde. This reaction is called Reimer-Tiemann reaction.

Salicylaldehyde also obtained on reaction of 2-hydroxy methyl phenol with pyridinium chlorochromate (PCC).

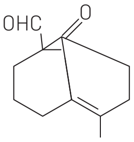
Chemical reactions are as follows :

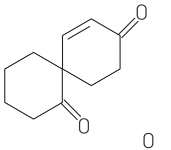


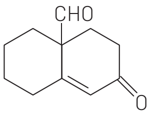
86 The major product *P* in the following reaction is

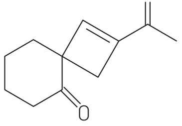


[2021, 20 July Shift-II]

(a)


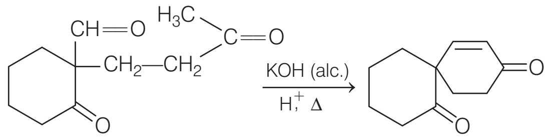
(b)


(c)


(d)


Ans. ***(b)***

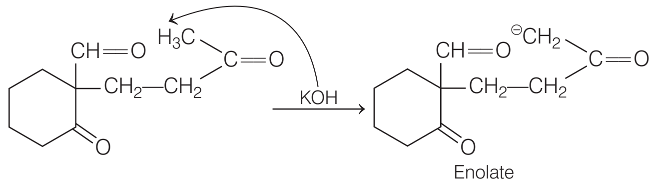
Given reaction is aldol condensation.



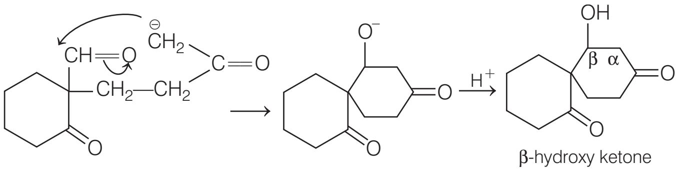
In this reaction, substrate undergoes intramolecular aldol condensation in which condensation reaction of two aldehyde groups or ketone groups occur in same molecule.

Mechanism

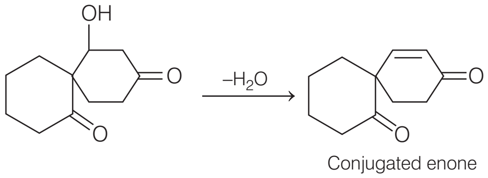
Step I Abstraction of proton by base KOH to form enolate.

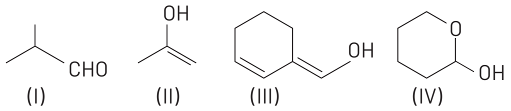


Step II Reaction of enolate and aldehyde group on substrate to form β-hydroxy ketone.



Step III β-hydroxy ketone undergoes dehydrate to form a conjugated enone.



87


Which among the above compound/s does/do not form silver mirror when treated with Tollen's reagent?

[2021, 20 July Shift-I]

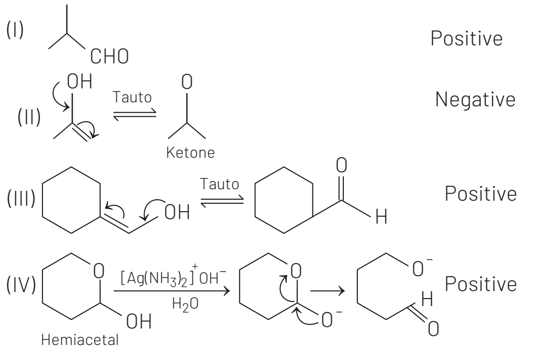
(a) (I), (III) and (IV) only
(b) Only (IV)
(c) Only (II)
(d) (III) and (IV) only

Ans. ***(c)***

Only compound (II) which has ketonic group does not form silver mirror when treated with Tollen's reagent.

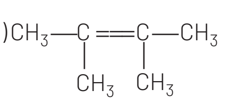
Because Tollen's reagent oxidises an aldehyde into the corresponding carboxylic acid. Ketones are not oxidised by Tollen's reagent, so the treatment of a ketone with Tollen's reagent in a glass test tube does not result in a silver mirror.

Aldehydes give positive Tollen's test (silver mirror test).

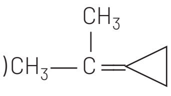


88 An unsaturated hydrocarbon *X* on ozonolysis gives *A*. Compound *A* when warmed with ammonical silver nitrate forms a bright silver mirror along the sides of the test tube. The unsaturated hydrocarbon *X* is

[2021, 17 March Shift-II]

(a)


$CH_3—\underset{CH_3}{\underset{|}{C}}=\underset{CH_3}{\underset{|}{C}}—CH_3$

(b)


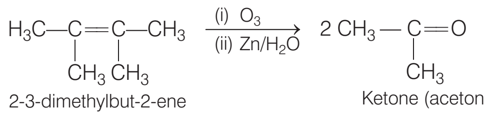
(c) $HC\equiv C—CH_2—CH_3$

(d) $CH_3—C\equiv C—CH_3$

Ans. ***(c)***

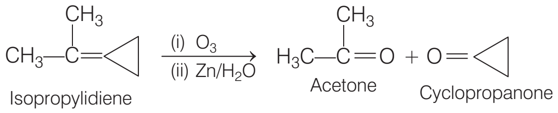
On ozonolysis, unsaturated hydrocarbon *X* will form carbonyl compound, which gives positive Tollen's test. So, it should be aldehyde.

(a) 2, 3-dimethylbut-2-ene undergoes ozonolysis reaction to give 2 molecules of acetone.



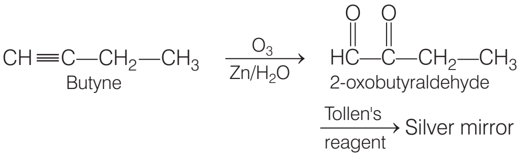
$$\mathrm{H_3C{-}\underset{CH_3}{\overset{|}{C}}{=}\underset{CH_3}{\overset{|}{C}}{-}CH_3 \xrightarrow[\text{(ii) Zn/H}_2\text{O}]{\text{(i) O}_3} 2\,CH_3{-}\underset{CH_3}{C}{=}O}$$

(b) Isopropylidiene undergoes ozonolysis reaction to give acetone along with cyclopropanone.



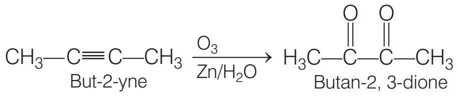
(c) Butyne reacts with O_3 and Zn/H_2O to give 2-oxobutyraldehyde. The aldehyde will give Tollen's test to give silver mirror.

Note Tollen's reagent contain silver nitrate ($AgNO_3$), ammonia and sodium hydroxide (NaOH) which react with aldehydes to give Ag (silver mirror).



$$CH{\equiv}C{-}CH_2{-}CH_3 \xrightarrow[Zn/H_2O]{O_3} H\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}CH_3 \xrightarrow[\text{reagent}]{\text{Tollen's}} \text{Silver mirror}$$

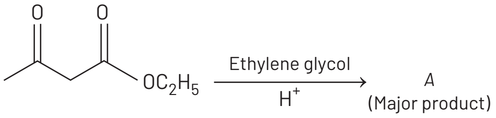
(d) But-2-yne undergoes ozonolysis to give butan-2, 3-dione.



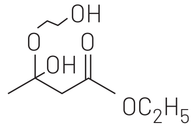
$$CH_3{-}C{\equiv}C{-}CH_3 \xrightarrow[Zn/H_2O]{O_3} H_3C{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}CH_3$$

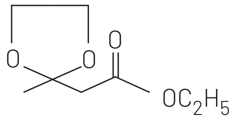
Only product of option (c) contains aldehyde group.

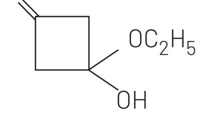
89

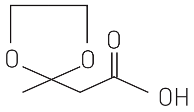


The product in the above reaction is **[2021, 16 March Shift-I]**

(a)


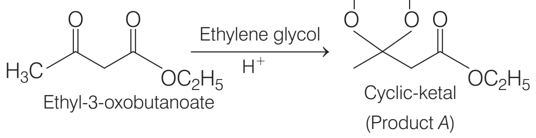
(b)


(c)


(d)


Ans. ***(b)***

Nucleophilic addition of ethylene glycol in ketone to give ketal.



Addition of one molecule of alcohol on ketone give hemiketal and addition of two molecules give ketal.

90 **Assertion (A)** Enol form of acetone $[CH_3COCH_3]$ exists in < 0.1% quantity. However, the enol form of acetyl acetone $[CH_3COCH_2OCCH_3]$ exists in approximately 15% quantity.

Reason (R) Enol form of acetyl acetone is stabilised by intramolecular hydrogen bonding, which is not possible in enol form of acetone.

Choose the correct statement. **[2021, 16 March Shift-I]**

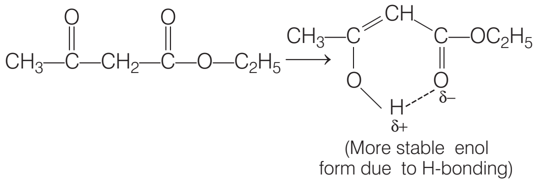
(a) A is false but R is true.
(b) Both A and R are true and R is the correct explanation of A.
(c) Both A and R are true but R is not the correct explanation of A.
(d) A is true but R is false.

Ans. ***(b)***

Enol form of acetone $[CH_3COCH_3]$ exists in < 0.1% quantity as monocarbonyl are more stable in keto form due to high bond energy.

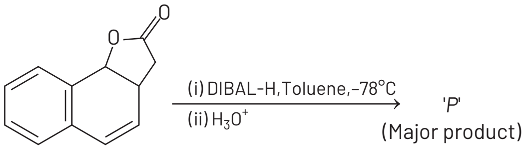
$$CH_3{-}\overset{O}{\overset{\|}{C}}{-}CH_3 \xrightarrow{\text{Tautomerisation}} CH_3{-}\overset{OH}{\overset{|}{C}}{=}CH_2$$

The enol form of acetyl acetone $[CH_3COCH_2OCCH_3]$ exists in approximately 15% quantity as it is stabilised by intramolecular hydrogen bonding, which is not possible in enol form of acetone.

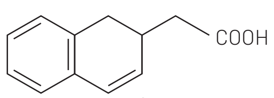


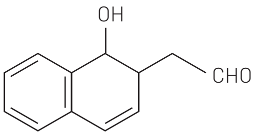
So, both A and R are true and R is the correct explanation of A.

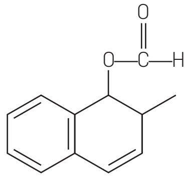
91

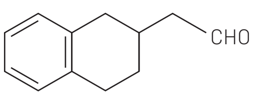


The product *P* in the above reaction is **[2021, 16 March Shift-I]**

(a)


(b)


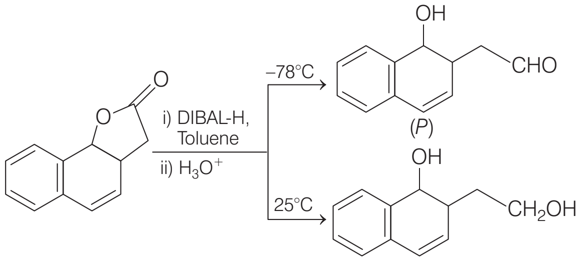
(c)


(d)


Ans. ***(b)***

DIBAIL is added to produce aldehyde from ester by keeping the temperature low while at higher temperature it can perform different conversions.

Complete reaction is as follows:



Diisobutyl aluminium hydride (DIBAL-H) is parallel to LAH (Lithium aluminium hydride) as a reducing agent but it is more selective.

It forms different product at different temperature.

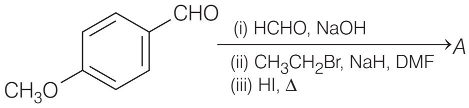
Role of DIBAL-H is shown below

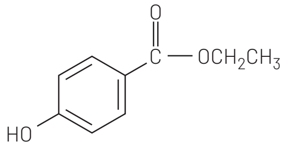
Reagent	**DIBAL-H** (− 78°C)	**DIBAL-H** (25° C)	**DIBAL-H** (−78°C)
Reactant	Ester	Ester	Cyanide
Product	Aldehyde	Alcohol	Aldehyde

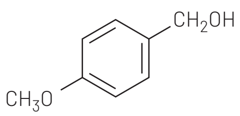
Note : DIBAL-H does not reduce double bond.

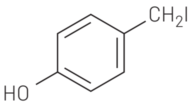
92 Identify *A* in the following chemical reaction.

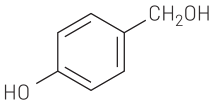
[2021, 26 Feb Shift-II]



(a)


(b)


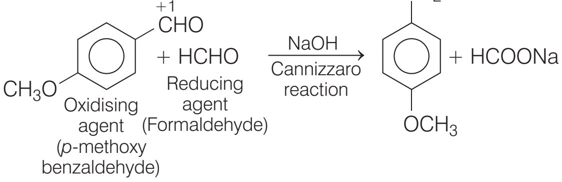
(c)


(d)


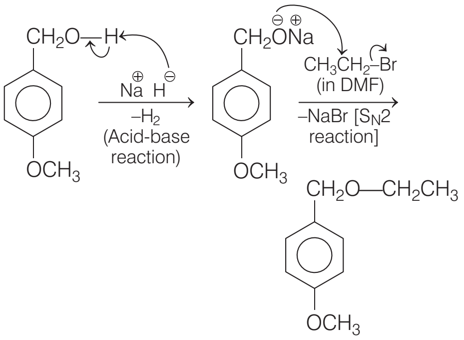
Ans. ***(c)***

Here, 4-methoxybenzaldehyde in series of reaction finally forms 4-(iodomethyl) phenol (*A*). Let us compute the reaction step by step with mechanism as follows

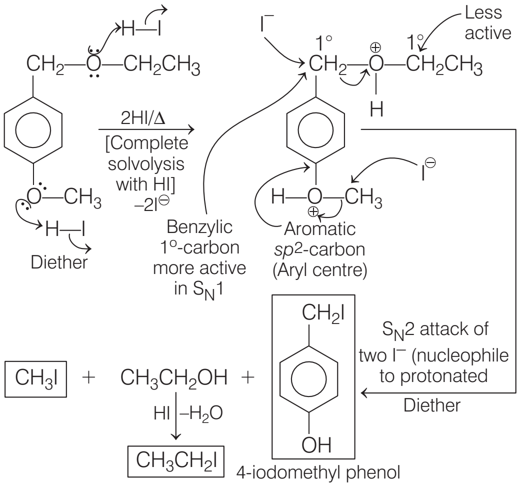
(i) In first step, oxidising agent (*p*-methoxybenzaldehyde) reacts with formaldehyde in presence of strong base NaOH to give *p*-methoxybenzyl alcohol along with sodium salt of methanoic acid. It is known as Cannizzaro's reaction.



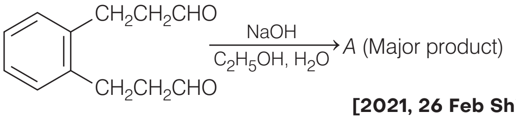
(ii) In second step, deprotonation of *p*-methoxybenzyl alcohol in presence of sodium hydride (NaH) to form alkoxide which further react with bromoethane in presence of DMF to give 1-ethoxymethyl-4-methoxybenzene.



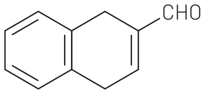
(iii) In last step, 1-ethoxymethyl-4-methoxybenzene undergoes solvolysis reaction followed by S_N2 attack of two iodide ion (I^-) to give 4-iodomethyl phenol, iodoform and iodoethane.

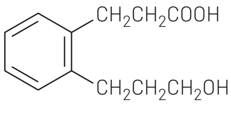


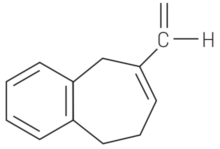
93 Identify *A* in the given chemical reaction,



[2021, 26 Feb Shift-II]

(a)


(b)


(c)


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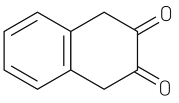
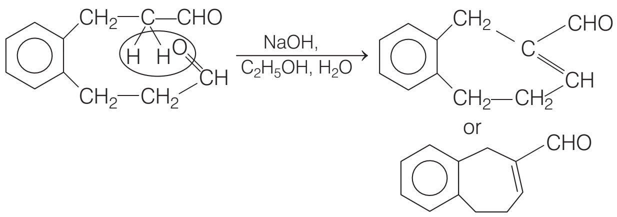
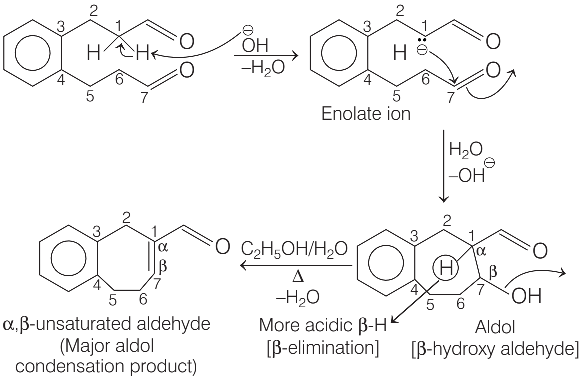


Ans. ***(c)***



It is an example of intramolecular aldol condensation.
α - hydrogen atom of one — CHO group gets abstracted by NaOH form enolate ion which then attacks of another — CHO group to form aldol or β - hydroxy aldehyde. The aldol on heating C_2H_5OH/H_2O forms the final product (α,β-unsaturated aldehyde) as the major product.

Mechanism

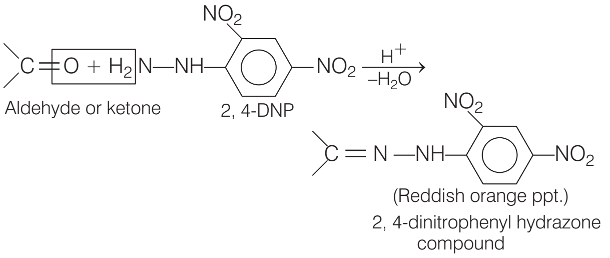


94 2,4-DNP test can be used to identify **[2021, 26 Feb Shift-II]**

(a) amine (b) aldehyde
(c) ether (d) halogens

Ans. ***(b)***

2, 4 - DNP test is used to detect the presence of carbonyl group (aldehyde or ketone) in organic compound. The test is carried out with 2, 4- dinitro phenyl hydrazine or 2, 4 - DNP (Brady's reagent) to give a reddish orange precipitate.



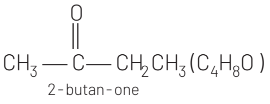
95 $\underset{(C_4H_8Cl_2)}{A} \xrightarrow[373\text{ K}]{\text{Hydrolysis}} \underset{(C_4H_8O)}{B}$

B reacts with hydroxyl amine but does not give Tollen's test. Identify *A* and *B*. **[2021, 26 Feb Shift-I]**

(a) 1,1-dichlorobutane and 2-butanone
(b) 2,2-dichlorobutane and butanal
(c) 1,1-dichlorobutane and butanal
(d) 2,2-dichlorobutane and 2-butan-one

Ans. ***(d)***

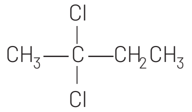
Compound $B(C_4H_8O)$ reacts with hydroxylamine (NH_2OH). So, compound *B* is an aldehyde or a ketone. Again, *B* does not give Tollen's test which indicates that *B* is a ketone but not an aldehyde. So, *B* is



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2CH_3\ (C_4H_8O)$$

2-butan-one

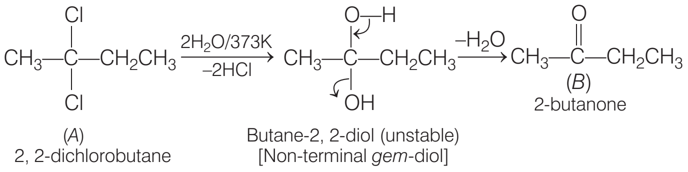
Compound $A(C_4H_8Cl_2)$ is a dihalide which undergoes hot hydrolysis ($H_2O/373$ K) to give *B*, a ketone. So, *A* is a non-terminal *geminal* or *gem* dichloride and *A* is



$$CH_3-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-CH_2CH_3 \quad (C_4H_8Cl_2)$$

2,2-dichlorobutane

The reaction can be computed as,

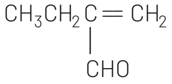


96 The major product of the following reaction is

$$CH_3CH_2CH=CH_2 \xrightarrow[\text{Rh catalyst}]{H_2/CO}$$

[2021, 25 Feb Shift-II]

(a) $CH_3CH_2CH_2CH_2CHO$ (b) $CH_3CH_2CH_2CHO$
(c) $CH_3CH_2CH=CH-CHO$ (d)



$CH_3CH_2\underset{\underset{CHO}{|}}{C}=CH_2$

Ans. ***(a)***

The major product of the reaction is $CH_3CH_2CH_2CH_2CHO$. Here, electrophilic addition of $H-\overset{+}{C}=O$ (formylation) take place to the alkene through Markownikoff addition.

(i) $H_2 + :C{=}\ddot{O}: \xrightarrow[\text{(Catalyst)}]{\text{Rh}} [H-\overset{\oplus}{C}=O]H^S$
Water gas

(ii) $\underset{\text{But-1-ene}}{CH_3CH_2-CH=CH_2} \xrightarrow[\text{Slow}]{H-\overset{\oplus}{C}=O}$

$CH_3CH_2-\overset{\oplus}{C}H-CH_2-CHO \xrightarrow[\text{Fast}]{H^{\ominus}} \underset{\text{Pentanal}}{CH_3CH_2CH_2CH_2CHO}$ (major)

97 Which one of the following reactions will not form acetaldehyde? **[2021, 25 Feb Shift-I]**

(a) $CH_2=CH_2 + O_2 \xrightarrow[H_2O]{Pd(II)/Cu(II)}$

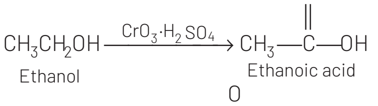
(b) $CH_3CH_2OH \xrightarrow{CrO_3-H_2SO_4}$

(c) $CH_3CN \xrightarrow[(ii)\,H_2O]{(i)\,DIBAL-H}$

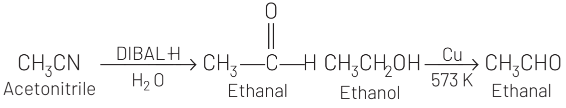
(d) $CH_3CH_2OH \xrightarrow[573\text{ K}]{Cu}$

Ans. ***(b)***

$$\underset{\text{Ethene}}{CH_2=CH_2} + O_2 \xrightarrow[H_2O]{Pd(II)/Cu(II)} \underset{\text{Ethanal}}{CH_3CHO}$$



$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{CrO_3 \cdot H_2SO_4} \underset{\text{Ethanoic acid}}{CH_3-\overset{\overset{O}{\|}}{C}-OH}$$



$$\underset{\text{Acetonitrile}}{CH_3CN} \xrightarrow[H_2O]{DIBAL\text{-}H} \underset{\text{Ethanal}}{CH_3-\overset{\overset{O}{\|}}{C}-H} \quad \underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[573\text{ K}]{Cu} \underset{\text{Ethanal}}{CH_3CHO}$$

Since, $CrO_3 \cdot H_2SO_4$ behave as strong oxidising agent and it converts alcohol directly to carboxylic acid. Thus, reaction (b) will not form acetaldehyde.

98 The major product of the following chemical reaction is

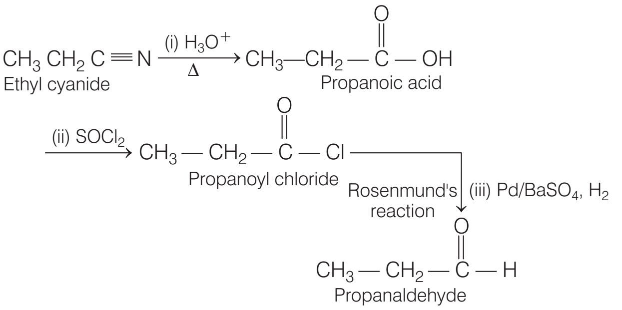
$$CH_3CH_2CN \xrightarrow[\text{(iii) } Pd/BaSO_4,\, H_2]{\text{(i) } H_3O^+,\, \Delta \quad \text{(ii) } SOCl_2} ?$$

[2021, 25 Feb Shift-I]

(a) $CH_3CH_2CH_2OH$ (b) $(CH_3CH_2CO)_2O$
(c) $CH_3CH_2CH_3$ (d) CH_3CH_2CHO

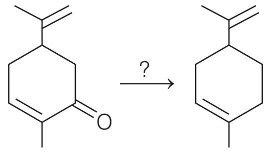
Ans. *(d)*

The complete reaction take place as follows



Final product of reaction is propanaldehyde.

99



Which of the following reagent is suitable for the preparation of the product in the above reaction?

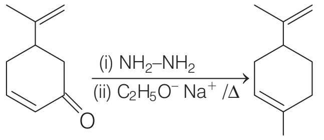
[2021, 24 Feb Shift-II]

(a) $NaBH_4$ (b) $NH_2—NH_2 / C_2H_5\overset{\ominus\oplus}{O}Na$
(c) Ni/H_2 (d) Red P + Cl_2

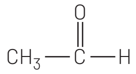
Ans. *(b)*

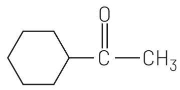
To reduce the carbonyl groups into alkane, wolff-Kishner reduction is used, without affecting the double bond.

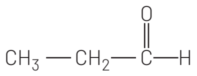
Wolff-Kishner reagent It utilises hydrazine $(NH_2—NH_2)$ as the reducing agent in the presence of strong base KOH or $C_2H_5\bar{O}Na^+$ in a high boiling protic solvent. The driving force for the reaction is the conversion of hydrazine to nitrogen gas.

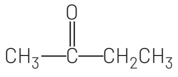


100 Which one of the following carbonyl compounds cannot be prepared by addition of water on an alkyne in the presence of $HgSO_4$ and H_2SO_4? **[2021, 24 Feb Shift-II]**

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

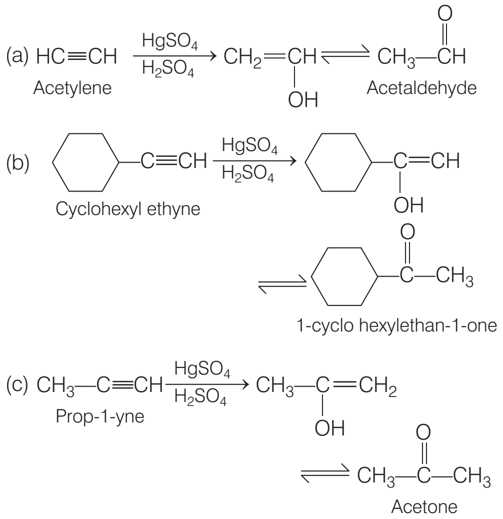
(b) 

(c) 
$CH_3—CH_2—\overset{O}{\overset{||}{C}}—H$

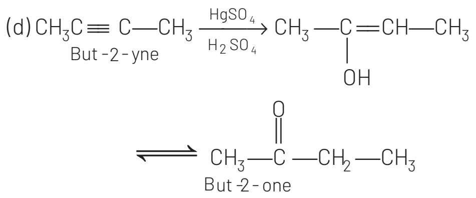
(d) 
$CH_3—\overset{O}{\overset{||}{C}}—CH_2CH_3$

Ans. *(c)*

Reaction of $HgSO_4$/dil. H_2SO_4 with alkyne result in addition of water as per Markownikoff's rule.



Hence $CH_3—CO—CH_3$ cannot be form.



101 Match List-I with List-II.

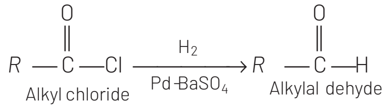
	List-I	List-II
A.	$R—\overset{O}{\overset{\Vert}{C}}—Cl \longrightarrow R—CHO$	1. Br_2 /NaOH
B.	$R—CH_2—COOH \longrightarrow R—\underset{Cl}{\underset{\vert}{CH}}—COOH$	2. H_2 /Pd - $BaSO_4$
C.	$R—\overset{O}{\overset{\Vert}{C}}—NH_2 \longrightarrow R—NH_2$	3. Zn(Hg) / Conc.HCl
D.	$R—\overset{O}{\overset{\Vert}{C}}—CH_3 \longrightarrow R—CH_2—CH_3$	4. Cl_2 / Red P, H_2O

Choose the correct answer from the options given below. **[2021, 24 Feb Shift-II]**

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

Ans. *(c)*

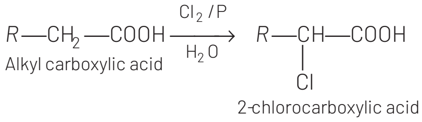
(A) Alkyl chloride reacts with H_2/Pd-$BaSO_4$ and reduced to alkyl aldehyde. This is known as Rosenmund reduction.



$$\underset{\text{Alkyl chloride}}{R-\overset{\overset{O}{\|}}{C}-Cl} \xrightarrow[\text{Pd-BaSO}_4]{H_2} \underset{\text{Alkylal dehyde}}{R-\overset{\overset{O}{\|}}{C}-H}$$

(Rosenmund reduction)

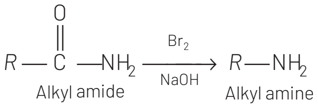
(B) Carboxylic acid reacts with Cl_2 /P in aqueous medium to form 2-chlorocarboxylic acid. This reaction is known as HVZ reaction.



$$\underset{\text{Alkyl carboxylic acid}}{R-CH_2-COOH} \xrightarrow[H_2O]{Cl_2/P} \underset{\text{2-chlorocarboxylic acid}}{R-\underset{\underset{Cl}{|}}{CH}-COOH}$$

[Hell-Volhard-Zelinsky (HVZ) reaction]

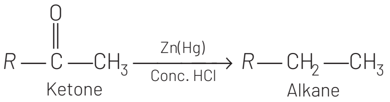
(C) Alkyl amide reacts with Br_2 in presence of NaOH to give alkyl amine. This reaction is known as Hofmann bromide reaction,



$$\underset{\text{Alkyl amide}}{R-\overset{\overset{O}{\|}}{C}-NH_2} \xrightarrow[NaOH]{Br_2} \underset{\text{Alkyl amine}}{R-NH_2}$$

(Hofmann bromide reaction)

(D) Ketone reacts with Zn-Hg in presence of conc.HCl to give alkane. This reaction is known as clemmensen reduction.



$$\underset{\text{Ketone}}{R-\overset{\overset{O}{\|}}{C}-CH_3} \xrightarrow[\text{Conc. HCl}]{Zn(Hg)} \underset{\text{Alkane}}{R-CH_2-CH_3}$$

(Clemmenson reduction)

Hence, correct match is (A)–2, (B)–4, (C)–1, (D)–3.

102 Which of the following reagent is used for the following reaction ?

$$CH_3CH_2CH_3 \xrightarrow{?} CH_3CH_2CHO$$

[2021, 24 Feb Shift-I]

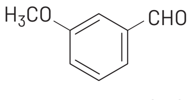
(a) Copper at high temperature and pressure
(b) Molybdenum oxide
(c) Manganese acetate
(d) Potassium permanganate

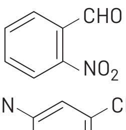
Ans. ***(b)***

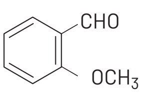
Molybdenum oxide (Mo_2O_3) is used for oxidising alkanes to aldehyde. It used to manufacture molybdenum metal, which serves as an additive to steel and corrosive resistant alloys.

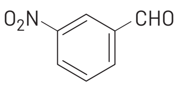
$$\underset{\text{Propane}}{CH_3-CH_2-CH_3} \xrightarrow[\text{Oxidising agent}]{Mo_2O_3} \underset{\text{Propanal}}{CH_3-CH_2-CHO}$$

103 The increasing order of the following compounds towards HCN addition is **[2020, 2 Sep Shift-I]**

(i) 

(ii) 

(iii) 

(iv) 

(a) (i) < (iii) < (iv) < (ii)
(b) (iii) < (iv) < (i) < (ii)
(c) (iii) < (iv) < (ii) < (i)
(d) (iii) < (i) < (iv) < (ii)

Ans. ***(d)***

Addition of HCN to $>C=O$ group of a carbonyl compound follows nucleophilic addition mechanism.

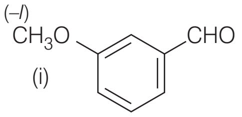
Rate of nucleophilic addition ∝ Polarity of the $>\overset{\delta^+}{C}=\overset{\delta^-}{O}$ group ∝ Attachment of electron withdrawing group (EWG), i.e., $-R$ and $-I$ groups, where $-R > -I$

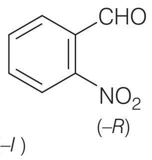
$$\propto \frac{1}{\text{Attachment of electron donating group (EDG)}}$$

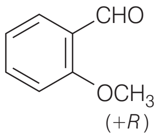
i.e., $+R$ and $+I$ groups

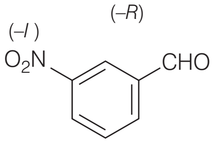
In substituted benzaldehyde, $-NO_2$ (EWG) shows $-R$ effect from *ortho*-and *para*-positions and $-I$ effect (only) from *meta*-positions. The group $-OCH_3$ (EDG) shows $+R$ effect from *ortho*-and *para*-position but $-I$ effect from *meta*-positions.

EWG ($-R > -I$) increases '$\delta+$' character of sp^2 carbon of the $>C=O$ group and hence attack of the nucleophile (CN^-) will be easier.









So, the increasing order of HCN addition is :

$$\underset{\textcircled{+R}}{(iii)} < \underbrace{\underset{\textcircled{-I}}{(i)} < \underset{\textcircled{-I}}{(iv)}}_{-I\text{ effect : }NO_2 > OCH_3} < \underset{\textcircled{-R}}{(ii)}$$

104 The increasing order of the reactivity of the following compounds in nucleophilic addition reaction is :

Propanal, Benzaldehyde, Propanone, Butanone

[2020, 3 Sep Shift-II]

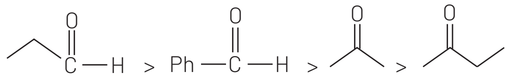
(a) Benzaldehyde < Butanone < Propanone < Propanal
(b) Butanone < Propanone < Benzaldehyde < Propanal
(c) Propanal < Propanone < Butanone < Benzaldehyde
(d) Benzaldehyde < Propanal < Propanone < Butanone

Ans. ***(b)***

Reactivity order toward nucleophilic addition reaction is aldehydes > ketones. Due to the following reasons aldehydes are more reactive than ketones.

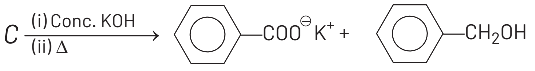
(i) Inductive effect An alkyl group has electron donating ($+I$) inductive effect. Hence, greater the number of alkyle group attached to carbonyl group, greater the electron density on carbonyl carbon. Thus, it lowers the attack of nucleophile and hence, reactivity decreases.
(ii) Steric effect Increase in the number of alkyl group attached to carbon results in the attack of nucleophile on carbonyl group becomes more and more difficult due to steric hinderance. Therefore, due to two bulky R groups, ketones are less reactive than aldehydes.

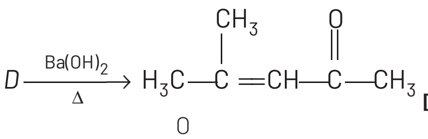
So, the correct reactivity order is



105 The compound, *A* in the following :

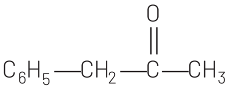
$$A \xrightarrow[\text{(ii) Conc. } H_2SO_4/\Delta]{\text{(i) } CH_3MgBr/H_2O} B \xrightarrow[\text{(ii) } Zn/H_2O]{\text{(i) } O_3} C + D$$

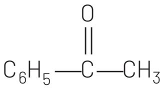


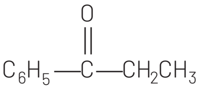


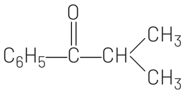
$$D \xrightarrow[\Delta]{Ba(OH)_2} H_3C-\overset{CH_3}{\overset{|}{C}}=CH-\overset{O}{\overset{\|}{C}}-CH_3$$

[2020, 3 Sep Shift-II]

(a) 
$C_6H_5-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

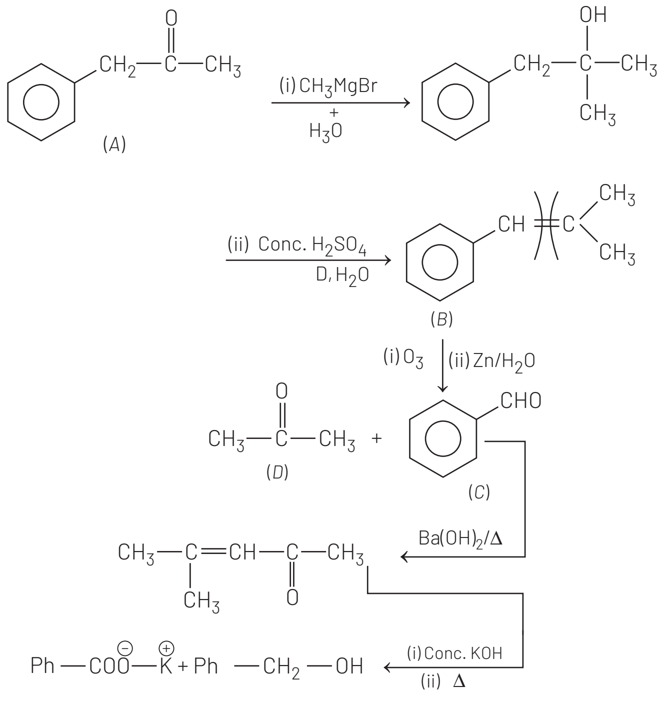
(b) 
$C_6H_5-\overset{O}{\overset{\|}{C}}-CH_3$

(c) 
$C_6H_5-\overset{O}{\overset{\|}{C}}-CH_2CH_3$

(d) 
$C_6H_5-\overset{O}{\overset{\|}{C}}-CH(CH_3)_2$

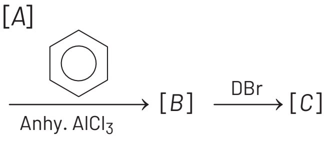
Ans. ***(a)***

Complete reaction is as follows :

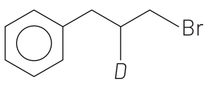


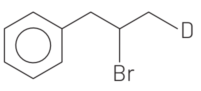
106 The major product [*C*] of the following reaction sequence will be

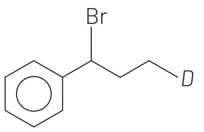
$$CH_2=CH-CHO \xrightarrow[\text{(ii) } SOCl_2]{\text{(i) } NaBH_4} [A]$$

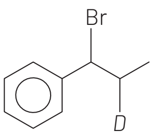


[2020, 4 Sep Shift-II]

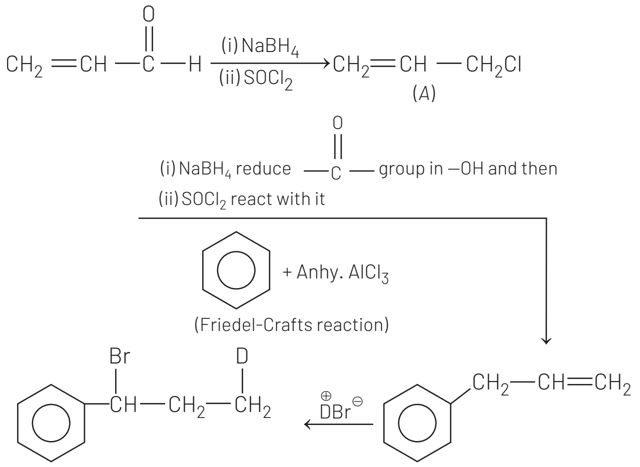
(a) 

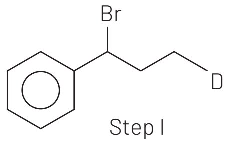
(b) 

(c) 

(d) 

Ans. ***(c)***



Hence (C) will be 

Step I

In the above reaction,

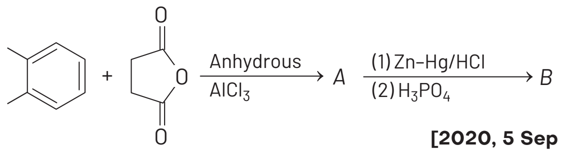
Step I $NaBH_4$ reduce $-\overset{O}{\overset{\|}{C}}-H$ group into alcohol.

Step II $SOCl_2$ react with this alcohol and form *R* —*X*.

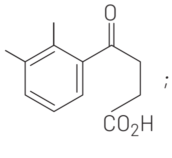
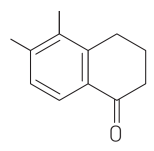
Step III This *R* —*X* react with benzene in the presence of anhydrous $AlCl_3$ *via* Friedel-Crafts reaction and form product.

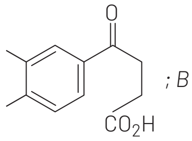
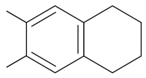
Step IV DBr react with this product and form rearranged product.

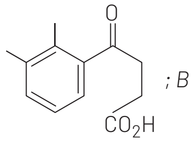
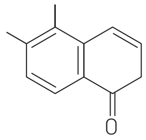
107 In the following reaction sequence the major products *A* and *B* are

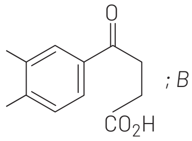
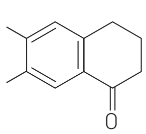


[2020, 5 Sep Shift-I]

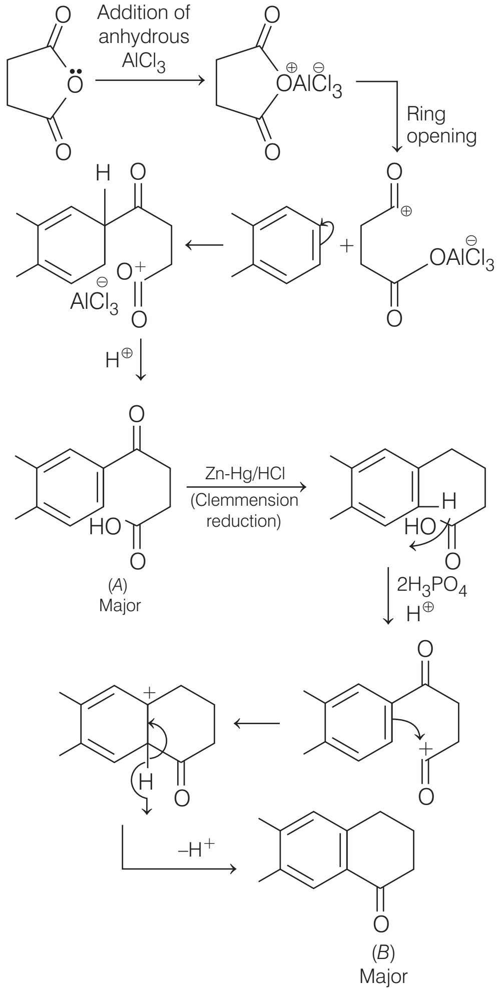
(a) *A* =  ; *B* = 

(b) $A =$  ; $B =$ 

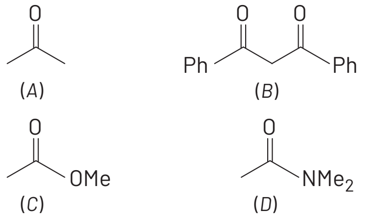
(c) $A =$  ; $B =$ 

(d) $A =$  ; $B =$ 

Ans. ***(d)***

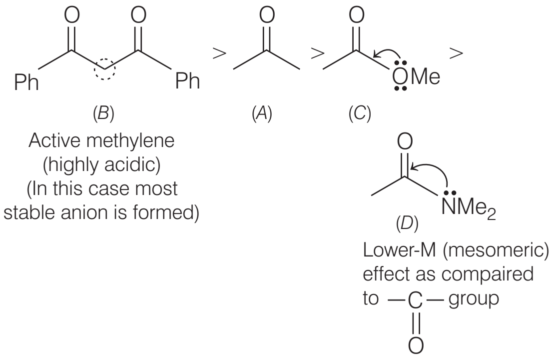


108 The increasing order of the acidity of the α-hydrogen of the following compounds is **[2020, 5 Sep Shift-I]**



(a) $(D) < (C) < (A) < (B)$ (b) $(C) < (A) < (B) < (D)$
(c) $(A) < (C) < (D) < (B)$ (d) $(B) < (C) < (A) < (D)$

Ans. ***(a)***



Compound (B) is a active methylene compound is highly resonance stabilised. This compound possessing a methylene bridge located between two strong electron withdrawing groups (such as carbonyl group). So, it is highly acidic in nature.

Compounds (C) and (D) having electron donating group. Which decreases the acidity and compound (A) is more acidic than (C) and (D) because it does not contain any electron releasing group.

Hence option (a) is correct.

$$(D) < (C) < (A) < (B)$$

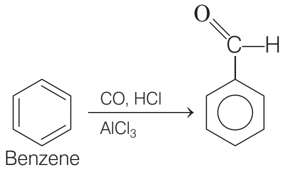
109 The correct match between Item-I (starting material) and Item-II (reagent) for the preparation of benzaldehyde is **[2020, 6 Sep Shift-II]**

	Item - I		Item - II
I	Benzene	(P)	HCl and $SnCl_2$, H_3O^+
II	Benzonitrile	(Q)	H_2, Pd-$BaSO_4$, S and quinoline
III	Benzoyl chloride	(R)	CO, HCl and $AlCl_3$

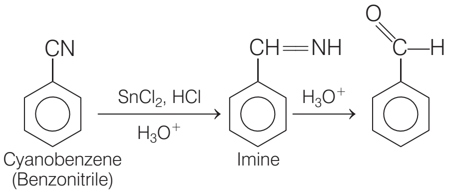
(a) (I) - (Q), (II) - (R) and (III) - (P) (b) (I) - (P), (II) - (Q) and (III) - (R)
(c) (I) - (R), (II) - (P) and (III) - (Q) (d) (I) - (R), (II) - (Q) and (III) - (P)

Ans. ***(c)***

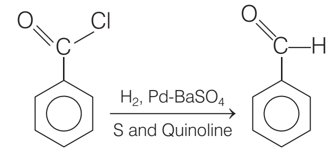
(I) Given, reaction is Gattermann -Koch reaction involves the formation of an aryl aldehyde using CO and HCl as reactants. The reaction catalysed by $AlCl_3$.



(II) Given, reaction is Stephen reduction reaction involves the preparation of aldehydes from nitriles using tin (II) chloride, hydrochloric acid and quenching the resulting minimum salt with water.



(III) Given, reaction is Rosenmund reduction is a hydrogenation process in which an acyl chloride is selectively reduced to an aldehyde.



Benzoyl chloride

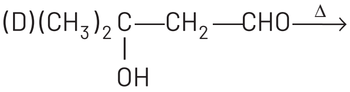
Correct match of Item-I and Item-II will be (I) - (R), (II) - (P) and (III) - (Q).

110 Consider the following reactions :

(A) $(CH_3)_3CCH(OH)CH_3 \xrightarrow{\text{Conc. } H_2SO_4}$

(B) $(CH_3)_2CHCH(Br)CH_3 \xrightarrow{\text{Alc. KOH}}$

(C) $(CH_3)_2CHCH(Br)CH_3 \xrightarrow{(CH_3)_3O^{\ominus}K^{\oplus}}$

(D) 
$(CH_3)_2\underset{OH}{C}-CH_2-CHO \xrightarrow{\Delta}$

Which of these reaction(s) will not produce Saytzeff product? **[2020, 7 Jan Shift-I]**

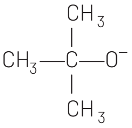
(a) (A), (C) and (D)
(b) (B) and (D)
(c) Only (C)
(d) Only (D)

Ans. ***(c)***

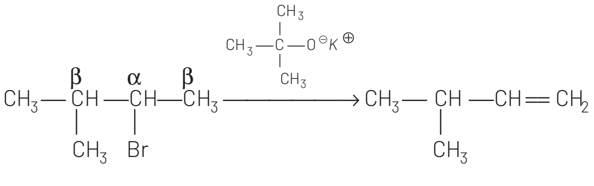
In a β-elimination reaction, a leaving group (like Cl$^-$) leaves along with a hydrogen (as H$^+$) from a β-position. Among available β-positions, H$^+$ removal is preferred to take place from the β-position having least H atoms according to Saytzeff's rule.

But in reaction (c),

the major product is not Saytzeff 's product

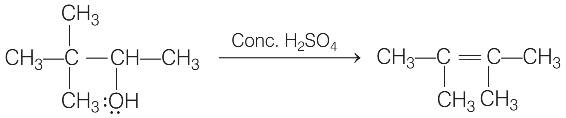
because the given base,  $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O^-$ is bulky and ∴ due to steric hinderance removes H$^+$ from —CH$_3$ group.

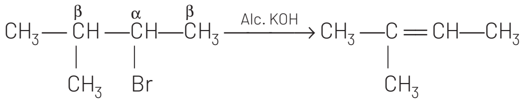
In this case reaction occurs as :

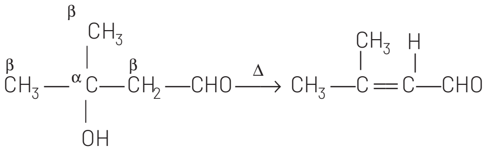

$CH_3-\underset{CH_3}{\overset{\beta}{CH}}-\underset{Br}{\overset{\alpha}{CH}}-\overset{\beta}{CH_3} \xrightarrow{CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O^{\ominus}K^{\oplus}} CH_3-\underset{CH_3}{CH}-CH=CH_2$

The major product is called Hofmann product.

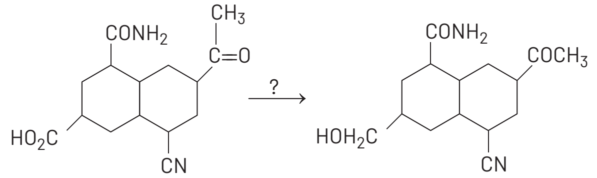
The rest of the given reactions produce Saytzeff products as follows :

(a) 
$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{:\ddot{O}H}{CH}-CH_3 \xrightarrow{\text{Conc. } H_2SO_4} CH_3-\underset{CH_3}{C}=\underset{CH_3}{C}-CH_3$

(b) 
$CH_3-\underset{CH_3}{\overset{\beta}{CH}}-\underset{Br}{\overset{\alpha}{CH}}-\overset{\beta}{CH_3} \xrightarrow{\text{Alc. KOH}} CH_3-\underset{CH_3}{C}=CH-CH_3$

(d) 
$\overset{\beta}{CH_3}-{}^{\alpha}\underset{OH}{\overset{\overset{\beta}{CH_3}}{C}}-\overset{\beta}{CH_2}-CHO \xrightarrow{\Delta} CH_3-\overset{CH_3}{C}=\overset{H}{C}-CHO$

111 The most suitable reagent for the given conversion is

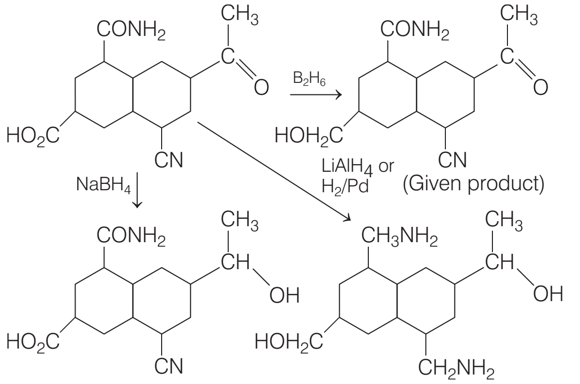


[2020, 8 Jan Shift-I]

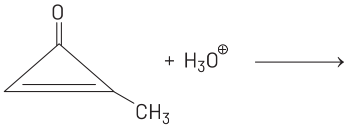
(a) B$_2$H$_6$
(b) LiAlH$_4$
(c) NaBH$_4$
(d) H$_2$ / Pd

Ans. ***(a)***

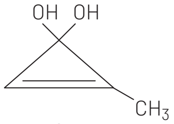
The most suitable reagent for the given conversion is B_2H_6.

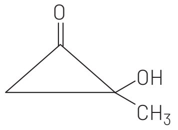


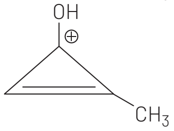
112 The major product in the following reaction is

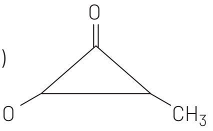


[2020, 8 Jan Shift-II]

(a) 

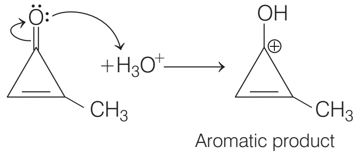
(b) 

(c) 

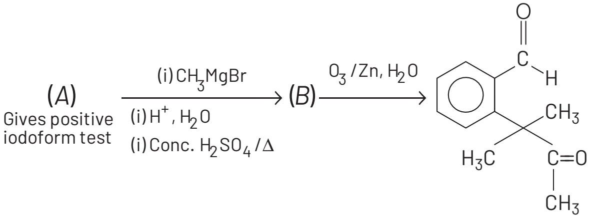
(d) 

Ans. ***(c)***

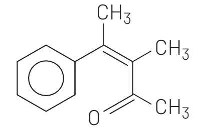
Option (c) is the major product formed.

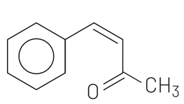


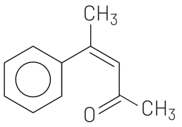
113 Identify (*A*) in the following reaction sequence :

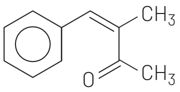


[2020, 9 Jan Shift-I]

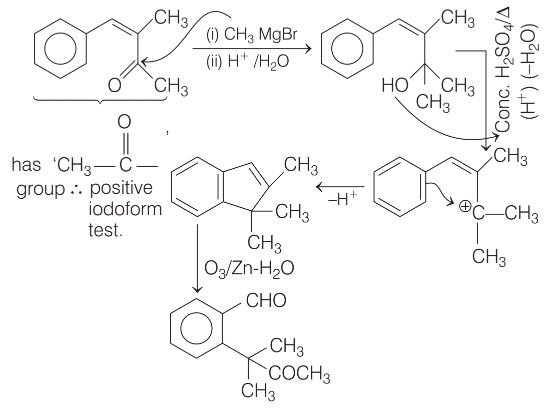
(a) 

(b) 

(c) 

(d) 

Ans. ***(d)***



114 Consider the following reactions :

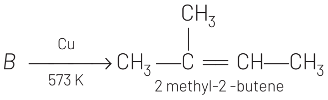
$$A \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } CH_3MgBr} B \xrightarrow[573\text{ K}]{Cu} \text{2-methyl- 2- butene}$$

The mass percentage of carbon in *A* is ......

[2020, 9 Jan Shift-II]

Ans. ***(66.67)***

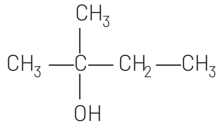
On reversing the given reaction we can get the *A* and *B*.



$$B \xrightarrow[573\text{ K}]{Cu} \underset{\text{2 methyl-2 -butene}}{CH_3-\overset{\overset{CH_3}{|}}{C}=CH-CH_3}$$

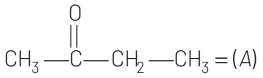
∴ *B* must be a 3° alcohol that, on oxidation produces alkene.

So, the structure of *B* is



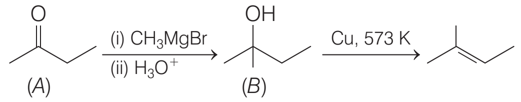
$$CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_3$$

To get *B* (alcohol) CH_3MgBr must react with a ketone.



$$CH_3-\overset{\overset{O}{||}}{C}-CH_2-CH_3=(A)$$

Complete reaction is as follows :

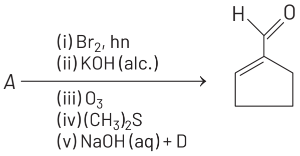


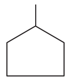
% C by mass

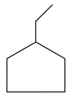
$$=\frac{\text{mass of C}(=4\times 12)\times 100}{\text{total molar mass}[=4\times 12+(16)+(8\times 1)]}$$

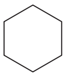
$$=\frac{48\times 100}{72}=66.67\%$$

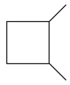
115 In the following reaction *A* is **[2020, 9 Jan Shift-II]**



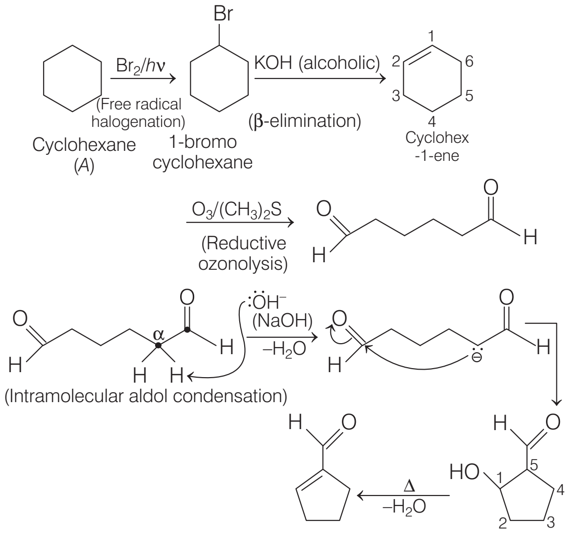
(a) 

(b) 

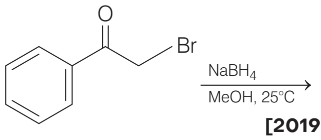
(c) 

(d) 

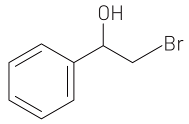
Ans. ***(c)***

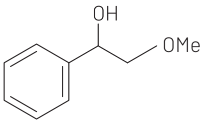


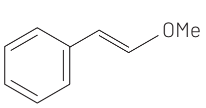
116 The major product of the following reaction is

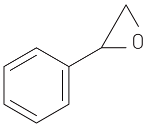


[2019, 8 April Shift-I]

(a) 

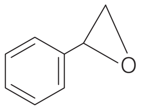
(b) 

(c) 

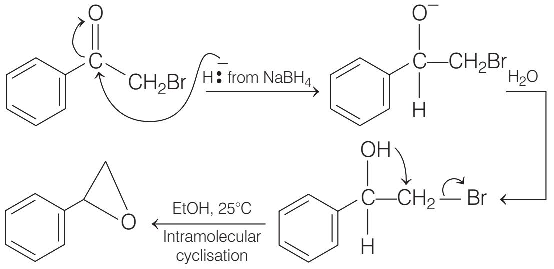
(d) 

Ans. ***(d)***

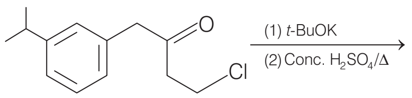
Major product obtained in the given reaction is



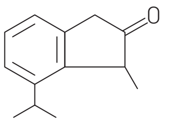
$NaBH_4$ in the reaction is used for the reduction by addition of a hydride ion and a proton. Carbon-oxygen double bonds are easily reduced by sodium borohydride. The actual reducing agent in these reductions is hydride ion(H^-). Hydride ion adds to the carbonyl carbon and the alkoxide ion that is formed is subsequently protonated by water. In other words, the carbonyl group is reduced by adding an H^- followed by an H^+. The mechanism of the given reaction is as follows :

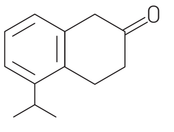


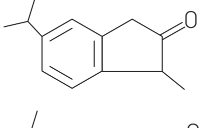
117 The major product of the following reaction is

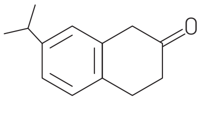


[2019, 8 April, Shift-II]

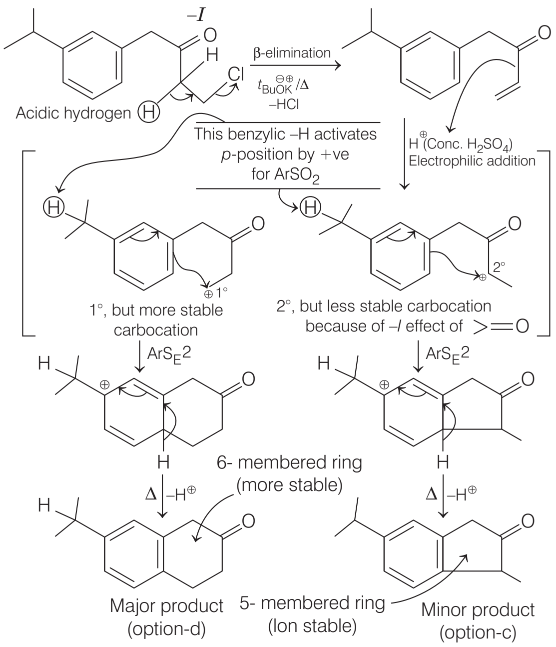
(a) 

(b) 

(c) 

(d) 

Ans. ***(d)***



118 In the following reaction,

Carbonyl compound + MeOH $\xrightleftharpoons{HCl}$ acetalRate of the reaction is the highest for:

(a) Acetone as substrate and methanol in excess

(b) Propanal as substrate and methanol in stoichiometric amount

(c) Acetone as substrate and methanol in stoichiometric amount

(d) Propanal as substrate and methanol in excess

[2019, 9 April Shift-II]

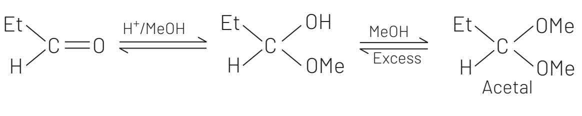
Ans. ***(d)***

Key Idea Aldehydes are more reactive than ketones in nucleophilic addition reactions.

For the reaction,

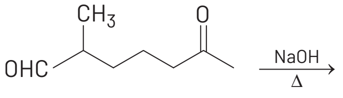
Carbonyl compound + MeOH $\xrightleftharpoons{HCl}$ Acetal

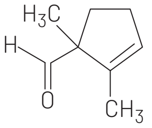
Rate of reaction is the highest for propanal as substrate and methanol in excess. Propanal is an aldehyde and more reactive than ketones. When MeOH is taken in excess then reaction moves in the forward direction that results in the formation of acetal. Reaction involved is as follows :

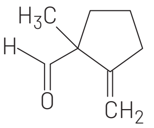


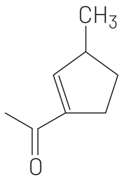
119 The major product obtained in the following reaction is

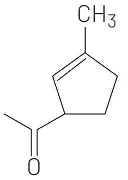
[2019, 8 April Shift-II]



(a) 

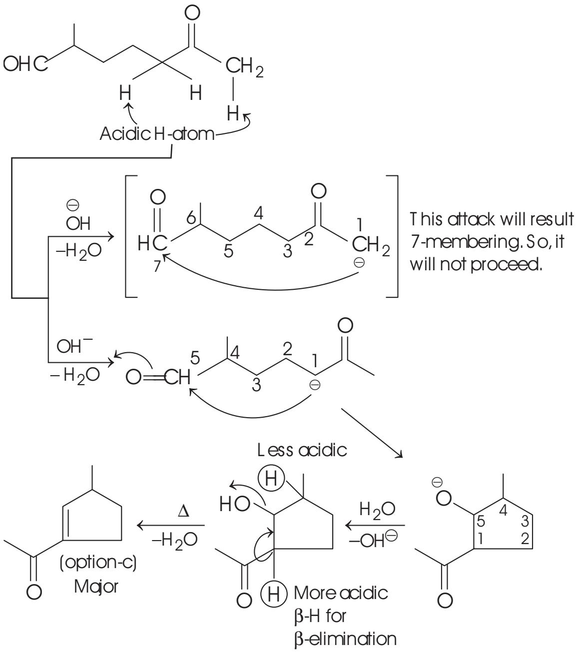
(b) 

(c) 

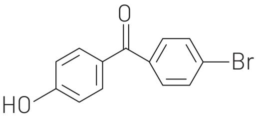
(d) 

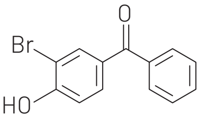
Ans. ***(c)***

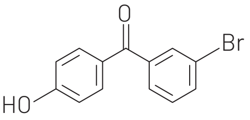
It is in intermolecular aldol condensation reaction.

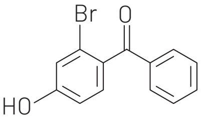


120 *p*-hydroxybenzophenone upon reaction with bromine in carbon tetrachloride gives **[2019, 9 April Shift-II]**

(a) 

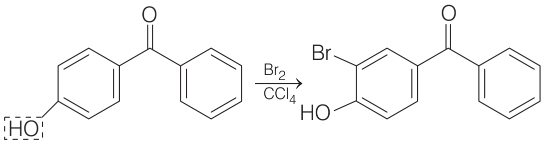
(b) 

(c) 

(d) 

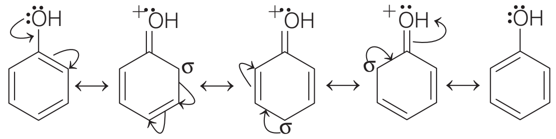
Ans. ***(b)***

p-hydroxy benzophenone upon reaction with bromine in carbon tetrachloride gives 3-bromo-4-hydroxy benzophenone.

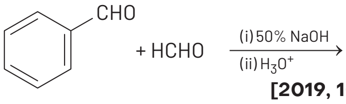


—OH group attached on the benzene ring direct the incoming group at *ortho* and *para*-positions due to increase in electron density at *o* and *p*-positions. —OH group also exhibit –I group that reduces the electron density to some extent at *o* and *p*-positions. But overall electron density increases at these positions of the ring due to resonance. Hence, attack of —Br occur at *ortho-position*.

Resonating structures are as follows:

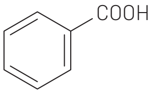


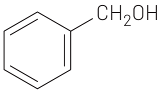
121 Major products of the following reaction are

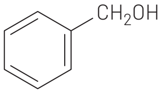
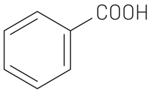


[2019, 10 April Shift-I]

(a) CH_3OH and HCO_2H

(b) CH_3OH and 

(c) HCOOH and 

(d)  and 

Ans. ***(c)***

The given reaction is a crossed Cannizzaro reaction which is a redox reaction too. Oxidation number of carbon atom of the —CHO groups of Ph—CHO and H—CHO are +1 and zero respectively. So, HCHO is the stronger reducing agent than PhCHO. As a result, HCHO is oxidised to HCOONa (by donation of hydride, H^-) and PhCHO (H^- acceptor) is reduced to $PhCH_2OH$.

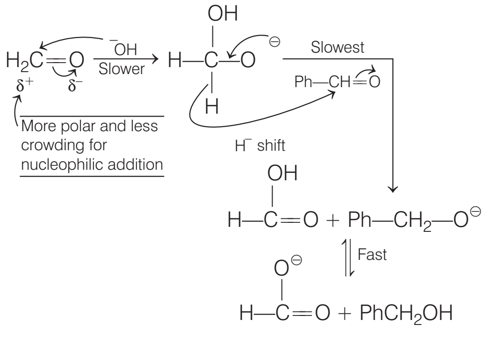
$$\text{Ph—}\overset{+1}{\text{C}}\text{HO} + \text{H}\overset{0}{\text{C}}\text{HO} \xrightarrow{50\%\ \text{NaOH}} \text{Ph—}\overset{-1}{\text{C}}\text{H}_2\text{OH} + \text{H}\overset{+2}{\text{C}}\text{O}\overset{-}{\text{O}}\overset{+}{\text{N}}\text{a}$$

$$\downarrow H_3O^+$$

$$PhCH_2OH + HCOOH$$

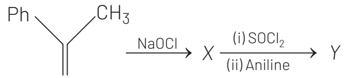
(Major products)

The reaction proceed *via* following mechanism.

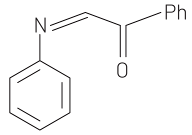


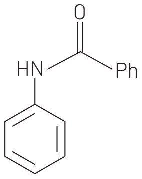
Thus, the correct option is (c).

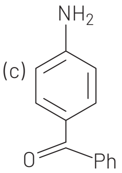
122 The major product *Y* in the following reaction is

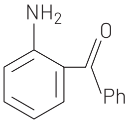


[2019, 10 April Shift-II]

(a)


(b)


(c)


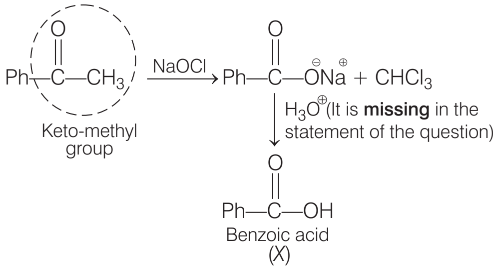
(d)


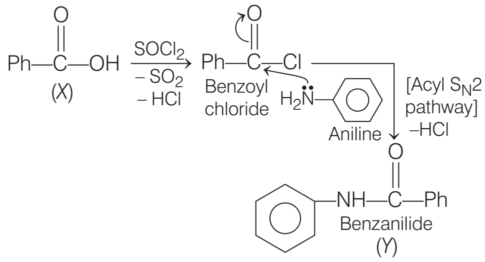
Ans. ***(b)***

NaOCl (sodium hypochlorite) is the reagent of haloform (chloroform formation) reaction.

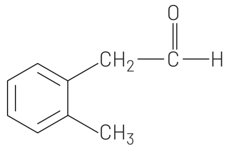
$$2NaOH + Cl_2 \longrightarrow NaOCl + NaCl + H_2O$$

The given reaction takes place as follows :





123 Compound *A*($C_9H_{10}O$) shows positive iodoform test. Oxidation of *A* with $KMnO_4$ / KOH gives acid *B* ($C_8H_6O_4$). Anhydride of *B* is used for the preparation of phenolphthalein. Compound *A* is **[2019, 10 April Shift-II]**

(a)


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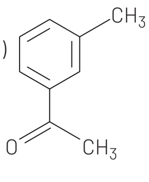
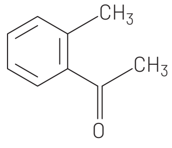
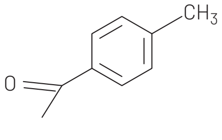


(c)


(d)


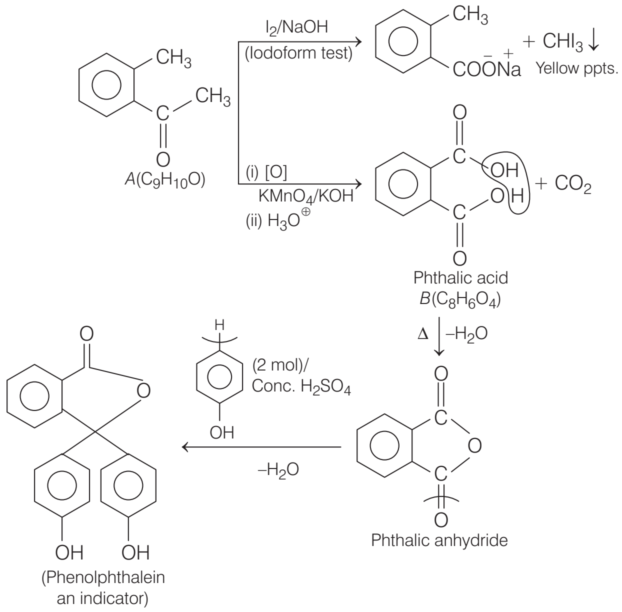
Ans. ***(c)***

(i) $C_9H_{10}O$ shows positive iodoform test thus, $-\underset{\underset{O}{\|}}{C}-CH_3$ group is present.

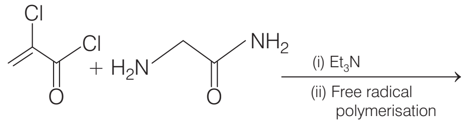
(ii) $C_9H_{10}O$ on strong oxidation ($KMnO_4$ /KOH), gives acid ($C_8H_6O_4$), indicating it can be a dicarboxylic acid. So, '*A*' contains $-COCH_3$ and one $-CH_3$ group which get oxidised into $-COOH$ and $-COOH$ respectively.

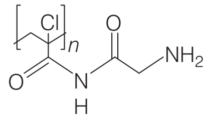
(iii) In the preparation of phenolphthalein from phenol, phthalic anhydride is used. So, '*B*' can be phthalic acid (benzene-1,2-dicarboxylic acid) which readily forms anhydride.

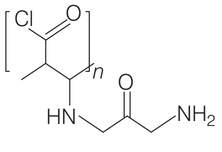
Thus, the reaction sequence is as follows :

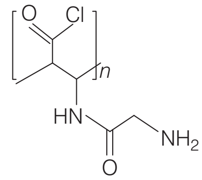


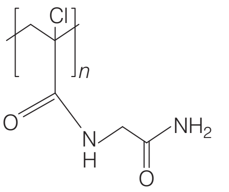
124 Major product of the following reaction is



(a)


(b)


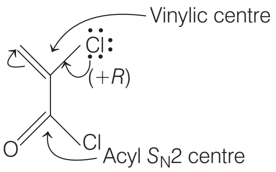
(c)


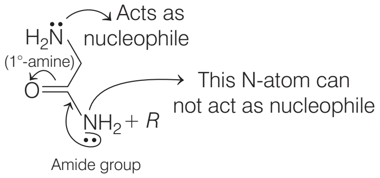
(d)


[2019, 9 Jan Shift-I]

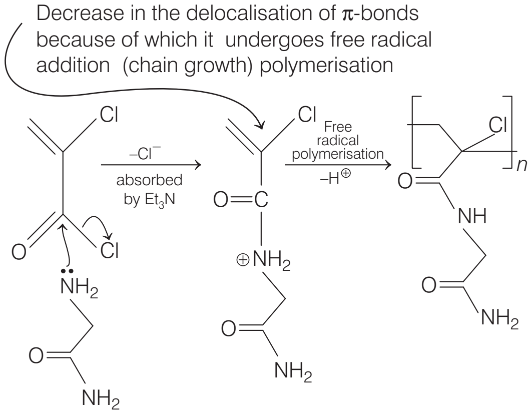
Ans. ***(d)***

The analysis of both the substrates :

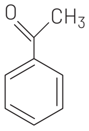


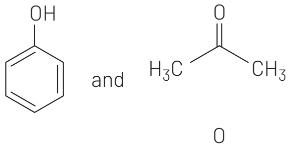


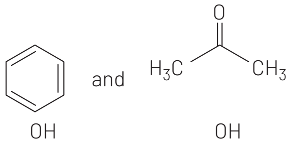
So, the reaction can take place as follows :

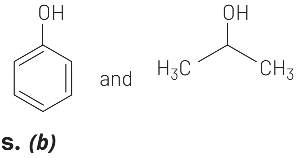

Decrease in the delocalisation of π-bonds because of which it undergoes free radical addition (chain growth) polymerisation

125 The products formed in the reaction of cumene with O_2 followed by treatment with dil. HCl are

(a)  and CH_3-OH

(b) 

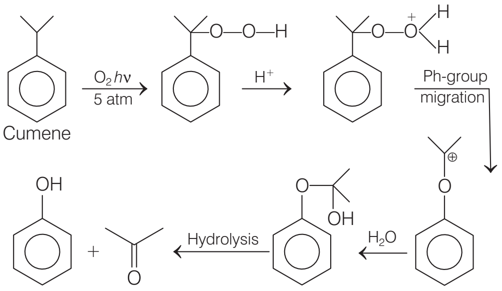
(c) 

(d) 

[2019, 9 Jan Shift-I]

Ans. ***(b)***

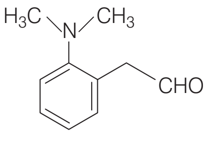
The given process is cumene process (Hock process) to synthesise phenol and acetone industrially. In Hock p rocess, Ph— group migrate and release H_2O.

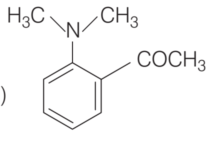


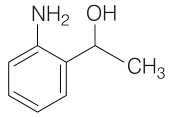
126 The tests performed on compound *X* and their inferences are :

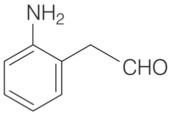
	Test	Inference
(a)	2, 4- DNP test	Coloured precipitate
(b)	Iodoform test	Yellow precipitate
(c)	Azo-dye test	No dye formation

Compound '*X*' is

(a) 

(b) 

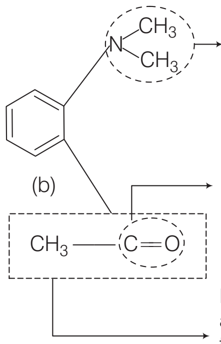
(c) 

(d) 

[2019, 9 Jan Shift-II]

Ans. ***(b)***

Let us study the chemical nature of the functional groups present in the following compound (b).



It is a 3°-amino group (—NMe_2) though aromatic which will not respond to diazotisation ($NaNO_2$ + dil. HCl/5°C). So, formation of diazonium ion and its further reaction with alkaline phenol or β-napthol at 5-10°C to produce a precipitate of azo-dye will not take place.

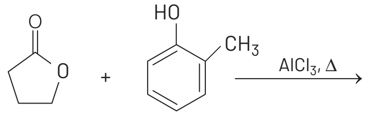
It is a keto group $>C=O$ and so it responds to 2, 4-DNP test with Brady's reagent (2, 4-dinitrophenyl hydrazine) to give a reddish orange precipitate.

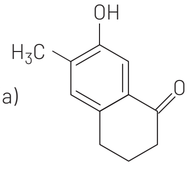
It is a keto-methyl group $-\overset{\overset{\large O}{\|}}{C}-CH_3$ and hence, it responds to iodoform test to give a yellow precipitate of iodoform (CHI_3).

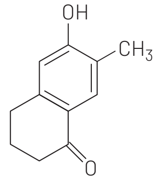
Compound (c) is an alcohol and does not give positive 2,4-DNP test. Hence, eliminated.

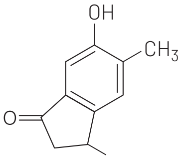
(a) and (d) does not have $-CH_3CO$ group and does not give iodoform test. Hence, eliminated.

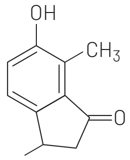
127 The major product of the following reaction is



(a)


(b)


(c)


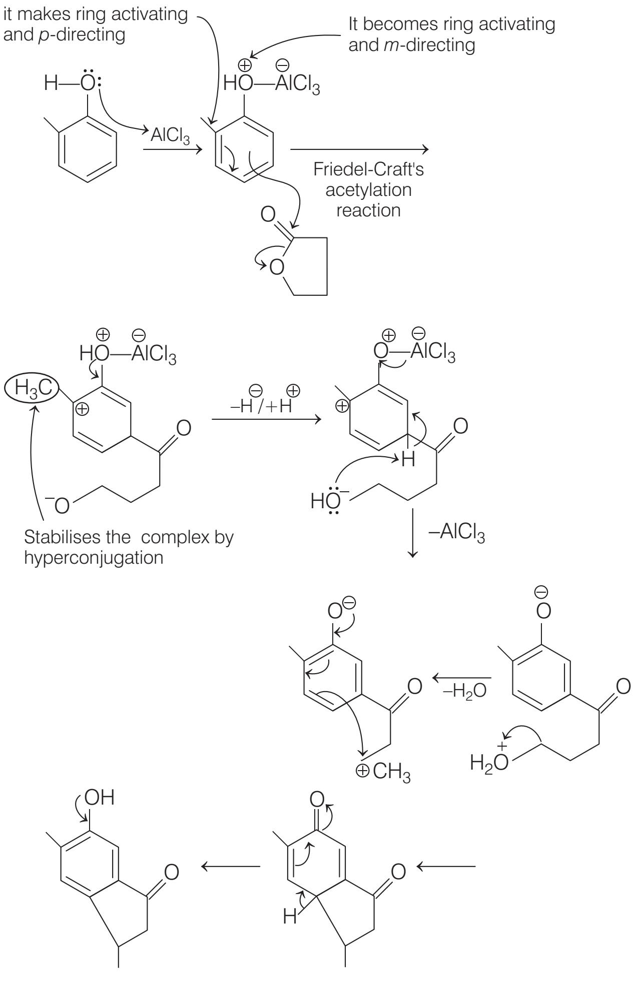
(d)


[2019, 9 Jan Shift-II]

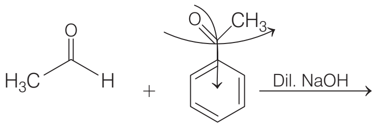
Ans. ***(c)***

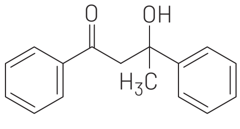
It is an aromatic electrophilic substitution reaction (Ar S_E2).

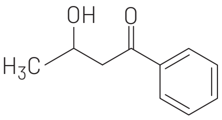
The reaction follows Ar S_E2 (Aromatic electrophlic substitution pathway) as shown below :

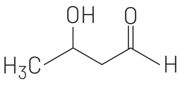


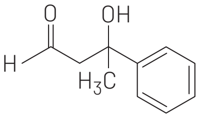
128 The major product formed in the following reaction is



(a)


(b)


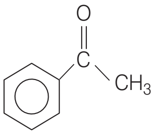
(c)


(d)


[2019, 9 Jan Shift-II]

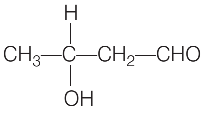
Ans. ***(c)***

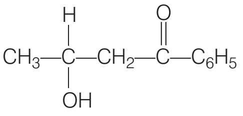
In aldol condensation, generally aldehydes react at a faster rate than ketones towards base. In the given case CH_3CHO will lose α-hydrogen faster than

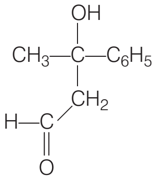


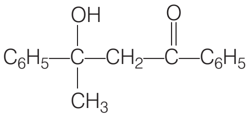
to one more reason, i.e. conjugation between benzene ring and $>C=O$ group. Along with sterically less hindered nucleophile of CH_3CHO will also add to the major product formation.

Following four products are possible in the reaction:

(i)

$CH_3-\underset{OH}{\overset{H}{C}}-CH_2-CHO$ (Self Aldol condensation of CH_3CHO)

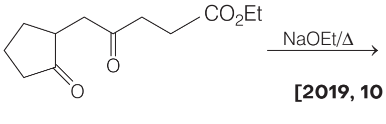
(ii)

$CH_3-\underset{OH}{\overset{H}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-C_6H_5$ (Cross Aldol condensation of CH_3CHO and $CH_3COC_6H_5$ in which $>C=O$ group of CH_3CHO is carbanion acceptor).

(iii)

$CH_3-\underset{CH_2-\overset{O}{\overset{\|}{C}}-H}{\overset{OH}{C}}-C_6H_5$ (Cross Aldol condensation of CH_3CHO and $CH_3COC_6H_5$ in which $>C=O$ group of $C_6H_5COCH_3$ is carbanion acceptor).

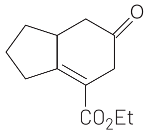
(iv)

$C_6H_5-\underset{CH_3}{\overset{OH}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-C_6H_5$ (Self Aldol condensation product of $C_6H_5COCH_3$)

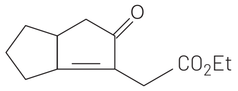
$\overset{-}{O}H$ of base will prefer to attack on $-CH_3$ group of CH_3CHO for the formation of carbanion and as among the $>C=O$ groups available, the $>C=O$ group of CH_3CHO is the best carbanion acceptor. Hence, self condensation product of CH_3CHO will be the major product.

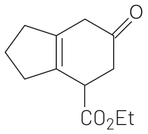
129 The major product obtained in the following reaction is

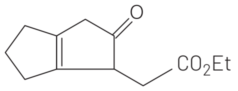


[2019, 10 Jan Shift-II]

(a)


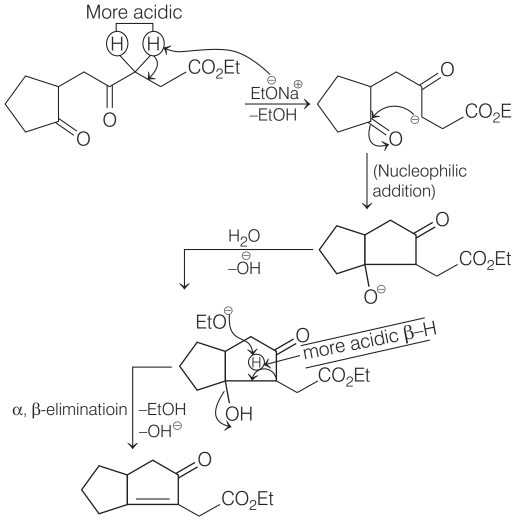
(b)


(c)


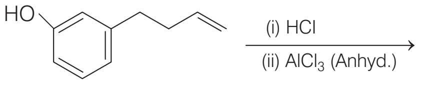
(d)


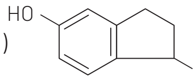
Ans. ***(b)***

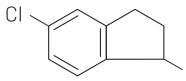
In presence of strong base, acidic H can easily be removed that result in formation of anion. The resulting anion undergoes intramolecular nucleophilic addition which on hydrolysis followed by heating gives the required product.

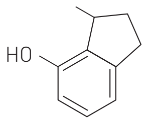


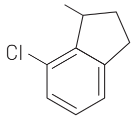
130 The major product of the following reaction is



(a)


(b)


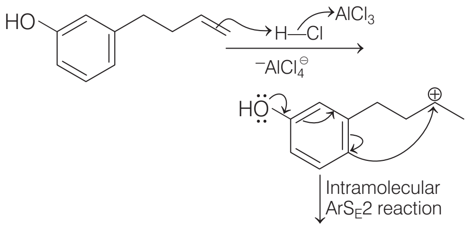
(c)


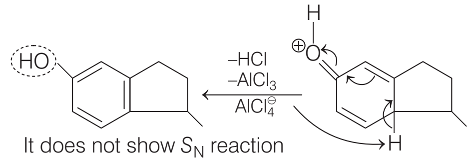
(d)


[2019, 11 Jan Shift-II]

Ans. ***(a)***

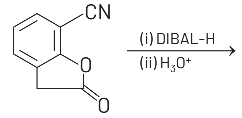
In the given reaction, $AlCl_3$ helps in the generation of electrophile that further undergoes ArS_E2 reaction to give the required product.

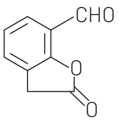


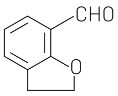


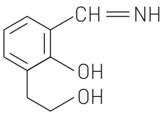
It does not show S_N reaction with HCl because of double bond nature of the O—C bond, (due to $+R$-effect of the —OH group.)

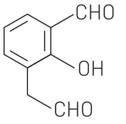
131 The major product of the following reaction is



(a)


(b)


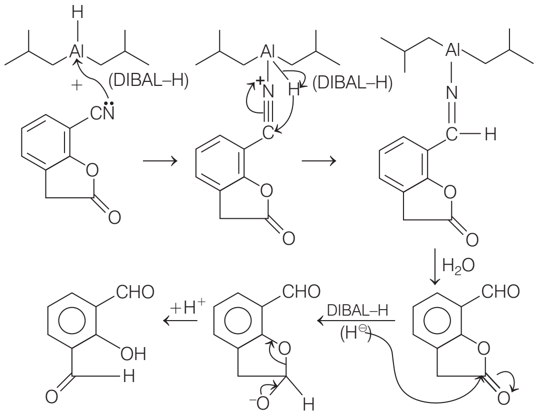
(c)


(d)


[2019, 12 Jan Shift-I]

Ans. ***(d)***

DIBAL-H (Diisobutylaluminium hydride) is a reducing agent with formula [λ-Bu_2AlH]. At ordinary temperatures, nitriles give imines which are readily converted in aldehydes by hydrolysis whereas lactones are reduced directly to aldehydes.



132 In the following reaction,

$$\text{Aldehyde} + \text{Alcohol} \xrightarrow{\text{HCl}} \text{Acetal}$$

Aldehyde	Alcohol	Aldehyde	Alcohol
HCHO	^{t}BuOH	CH_3CHO	MeOH

The best combination is **[2019, 12 Jan Shift-I]**

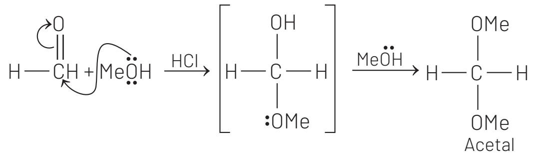
(a) CH_3CHO and MeOH
(b) CH_3CHO and ^{t}BuOH
(c) HCHO and MeOH
(d) HCHO and ^{t}BuOH

Ans. ***(c)***

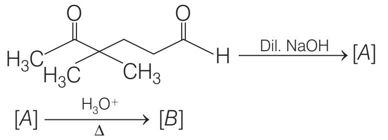
Acetal formation is nucleophilic addition reaction due to the addition of alcohols on aldehydes. The reactivity of nucleophilic addition depends on following two factors.

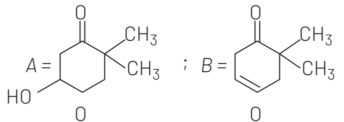
- Inductive effect Greater the number of alkyl group attached to carbonyl group, greater is the electron density on carbonyl carbon. Thus, lowers the attack of nucleophile. Hence, reactivity decreases.
- Steric effect As the number of alkyl group attached to carbonyl carbon increases, the attack of nucleophile on carbonyl group becomes more difficult due to steric hinderance.

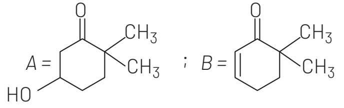
Thus, the best combination is HCHO and MeOH. The reaction is as follows:

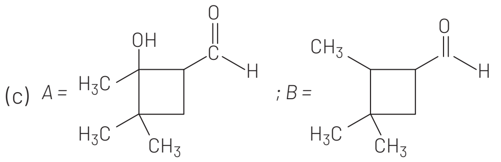


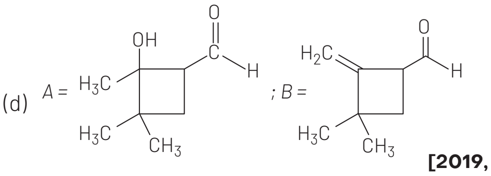
133 In the following reactions, products *A* and *B* are



(a) 

(b) 

(c) 

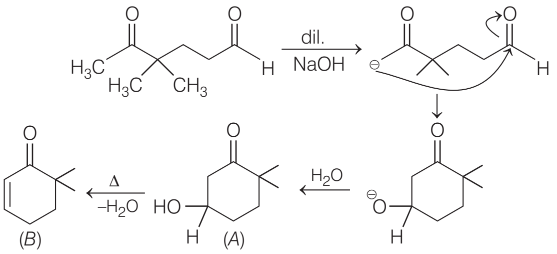
(d) 

[2019, 12 Jan Shift-I]

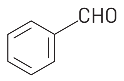
Ans. ***(b)***

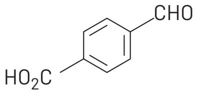
The reactant in presence of Dil. NaOH undergoes intramolecular aldol condensation reaction.

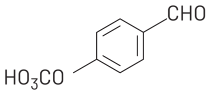
As a result of this, β-hydroxyketone (*A*) is obtained which on hydrolysis followed by heating produces α, β-unsaturated ketone (B)

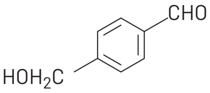


134 The aldehydes which will not form Grignard product with one equivalent Grignard reagents are

(*A*) 

(*B*) 

(*C*) 

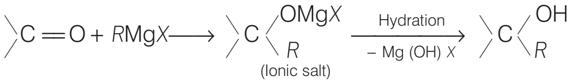
(*D*) 

(a) (*C*), (*D*)
(b) (*B*), (*D*)
(c) (*B*), (*C*), (*D*)
(d) (*B*), (*C*)

[2019, 12 Jan Shift-II]

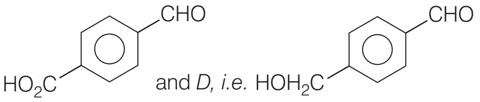
Ans. ***(b)***

Key Idea Grignard reagent usually attacks on $>C=O$ group as $>C^2=O$

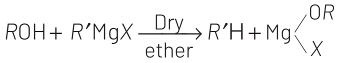


The question is related to above reaction only with the condition that the consumption of *R*MgX will be more than 1 equivalent in some of the given cases.

Among the given compounds *B*, i.e.



contain additional groups which can give active hydrogens. Grignard reagents produce alkanes whenever come in contact with any group or compound which can give active hydrogen as:

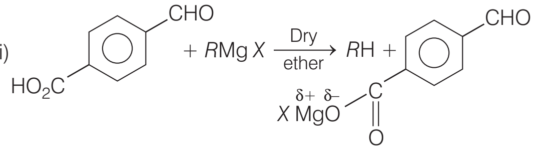


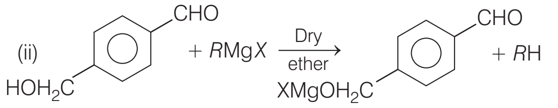
$$ROH + R'MgX \xrightarrow[\text{ether}]{\text{Dry}} R'H + Mg\begin{matrix} OR \\ X \end{matrix}$$

These reactions are equivalent to acid-base reactions. So, in both of these compounds more than one equivalent will be required to form Grignard products. Remember these compounds will give 2 type of products as:

(i) from the $>C=O$ group
(ii) from the group which release active hydrogen

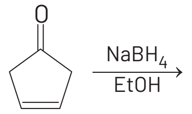
The additional reactions involved are:

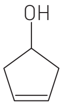
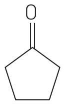
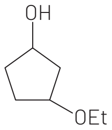
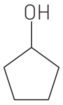
(i) 

(ii) 

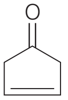
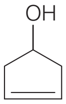
135 The major product of the following reaction is

[2019, 12 Jan Shift-II]

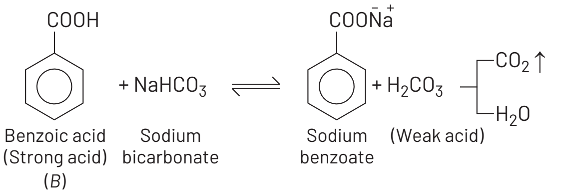


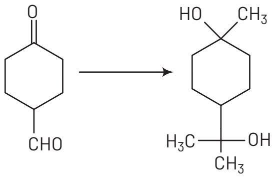
(a)  (b)  (c)  (d) 

Ans. ***(a)***

Reducing agents like $LiAlH_4$, $NaBH_4$, i.e. complex hydrides usually does not affect olifenic or π-bonds. Thus, if $NaBH_4$ is applied to a compound like  then its $\rangle C{=}O$ bond will be reduced only and we get  as the final product.

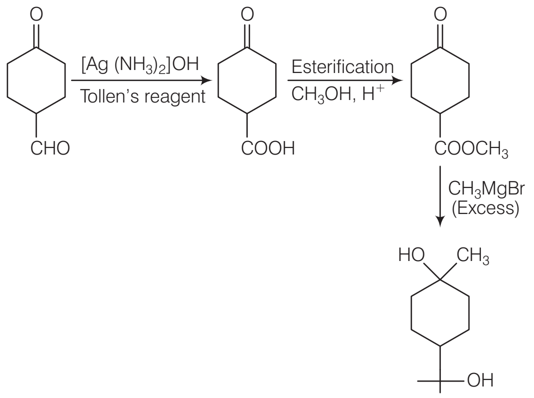
136 The correct sequence of reagents for the following conversion will be **[JEE Main 2017]**



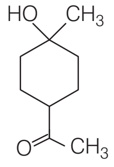


(a) $[Ag(NH_3)_2]^+$ OH^-, H^+ / CH_3OH, CH_3MgBr
(b) CH_3MgBr, H^+ / CH_3OH, $[Ag(NH_3)_2]^+$ OH^-
(c) CH_3MgBr, $[Ag(NH_3)_2]^+$ OH^-, H^+ / CH_3OH
(d) $[Ag(NH_3)_2]^+$ OH^-, CH_3MgBr, H^+ / CH_3OH

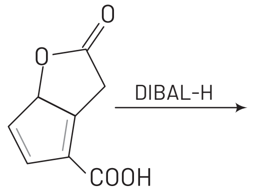
Ans. ***(a)***



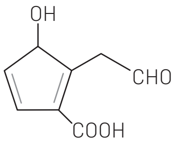
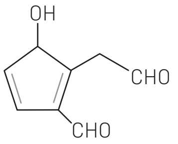
Before final product is formed, intermediate is

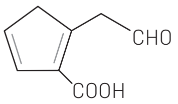
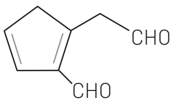


137 The major product obtained in the following reaction is



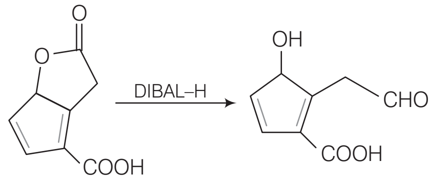
[JEE Main 2017]

(a)  (b) 

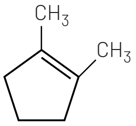
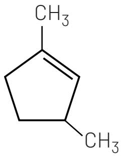
(c)  (d) 

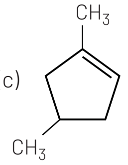
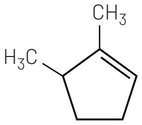
Ans. ***(a)***

DIBAL-H (Di-isobutyl aluminium hydride) is a reducing agent with formula. This is generally used for the preparation of aldehydes. Using DIBAL –H, Lactones are reduced directly to aldehydes.

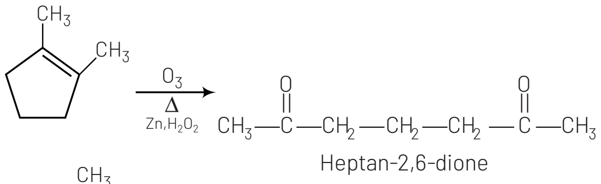


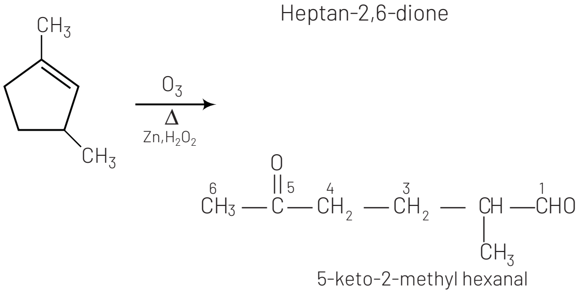
138 Which compound would give 5-keto-2-methyl hexanal upon ozonolysis? **[JEE Main 2015]**

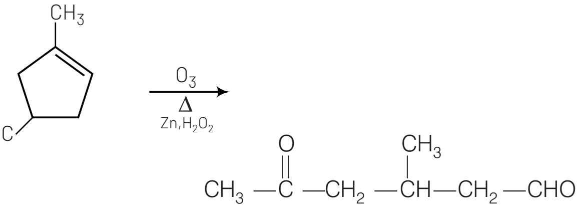
(a)  (b) 

(c)  (d) 

Ans. ***(b)***

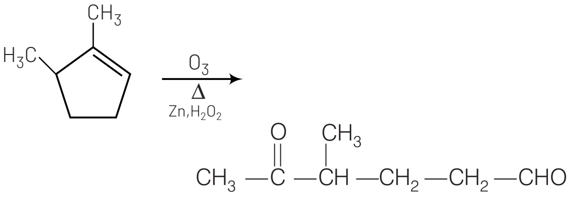


(b) 

(c) 

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

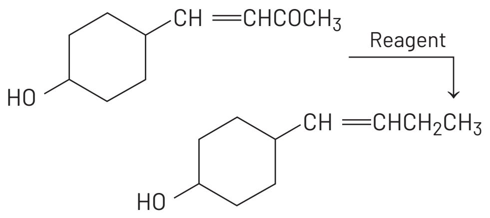
5-keto-3-methyl hexanal

(d) 

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

5-keto-4-methyl hexanal

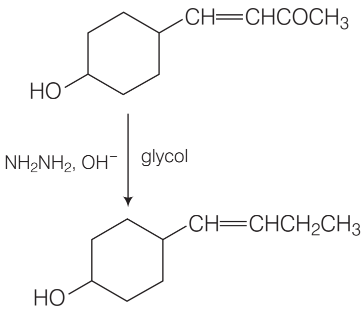
139 In the given transformation, which the following is the most appropriate reagent? **[AIEEE 2012]**



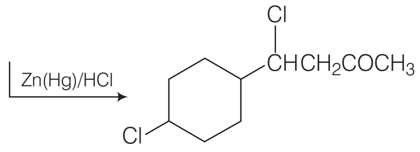
(a) $NH_2NH_2, \overset{\ominus}{O}H$ (b) Zn -Hg / HCl

(c) Na, Liq. NH_3 (d) $NaBH_4$

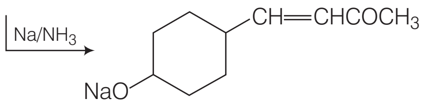
Ans. ***(a)***

(a) 

(Wolff-Kishner)

(b) 

HCl attacks 2° alcohol as well as (C═C) bond.

(c) 

(d) $\xrightarrow{NaBH_4}$ Low yield

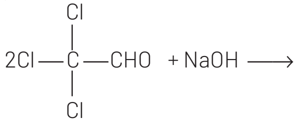
140 Trichloroacetaldehyde was subjected to Cannizzaro's reaction by using NaOH. The mixture of the products contains sodium trichloroacetate ion and another compound. The other compound is **[AIEEE 2011]**

(a) 2, 2, 2-trichlorethanol (b) trichloromethanol

(c) 2, 2, 2-trichloropropanol (d) chloroform

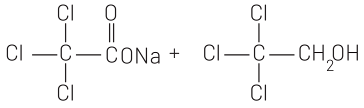
Ans. ***(a)***

Cannizzaro's reaction is given by aldehydes (RCHO) lacking H at α-carbon or lacking α-carbon (as in HCHO). With NaOH, there is formation of acid salt ($RCOO^-$) by oxidation and alcohol (RCH_2OH) by reduction.



$$2Cl-\overset{Cl}{\overset{|}{\underset{Cl}{\underset{|}{C}}}}-CHO + NaOH \longrightarrow$$

a-carbon without H



$$Cl-\overset{Cl}{\overset{|}{\underset{Cl}{\underset{|}{C}}}}-\overset{O}{\overset{\|}{C}}ONa + Cl-\overset{Cl}{\overset{|}{\underset{Cl}{\underset{|}{C}}}}-CH_2OH$$

(By oxidation) (By reduction 2, 2, 2, trichloroethanol)

141 Silver mirror test is given by which one of the following compounds? **[AIEEE 2011]**

(a) Acetaldehyde (b) Acetone

(c) Formaldehyde (d) Benzophenone

Ans. ***(a, c)***

All aldehydes including reducing sugar (as glucose, fructose) gives Silver-mirror test (with Tollen's reagent)

$$RCHO + 2[Ag(NH_3)_2]^+ + 3OH^- \xrightarrow{\Delta} RCOO^- + 2Ag\downarrow + 4NH_3 + 2H_2O$$

Silver mirror (R=H, CH_3)

Thus, acetaldehyde and formaldehyde give silver-mirror test.

142 Ozonolysis of an organic compound A produces acetone and propionaldehyde in equimolar mixture. Identify A from the following compounds. **[AIEEE 2011]**

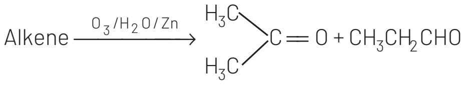
(a) 2-methyl-1-pentene

(b) 1-pentene

(c) 2-pentene

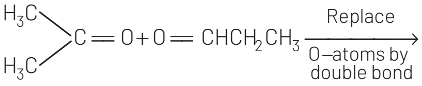
(d) 2-methyl-2-pentene

Ans. ***(d)***

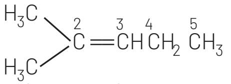


Acetone Propionaldehyde

To identify alkene (from ozonolysis products) place these products with O-atoms face to face.
Replace O-atoms by ═ (double) bond.



O-atom face to face



2-methyl-2-pentene

143 One mole of a symmetrical alkene on ozonolysis gives two moles of an aldehyde having a molecular mass of 44 u. The alkene is **[AIEEE 2010]**

(a) propene (b) 1-butene (c) 2-butene (d) ethene

Ans. ***(c)***

The general molecular formula for carbonyl compound is $C_nH_{2n}O$.

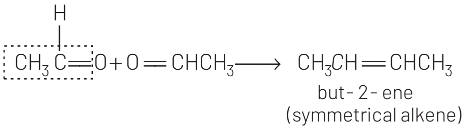
$\Rightarrow \quad C_nH_{2n}O = 44\,u$

$\Rightarrow \quad C_nH_{2n} = 44 - 16$

$\Rightarrow \quad C_nH_{2n} = 28\,u \Rightarrow n = 2$

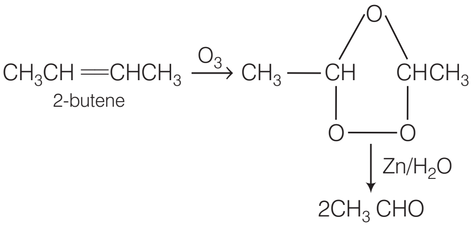
Thus, the aldehyde comes out to be C_2H_4O or CH_3CHO. In order to identify an alkene, place 2 molecules of CH_3CHO with O–atom face to face.

Then, replace O atom by doube bond.



$$\boxed{CH_3\overset{H}{\overset{|}{C}}=}O + O=CHCH_3 \longrightarrow \underset{\substack{\text{but-2-ene}\\\text{(symmetrical alkene)}}}{CH_3CH=CHCH_3}$$

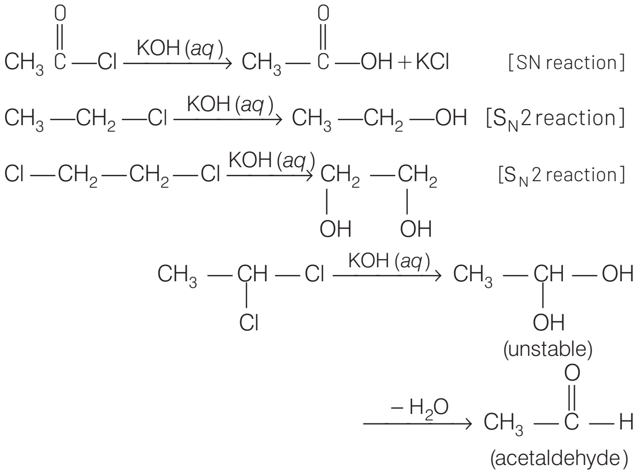
Hence,



144 Which of the following on heating with aqueous KOH, produces acetaldehyde? **[AIEEE 2009]**

(a) CH_3COCl (b) CH_3CH_2Cl (c) CH_2ClCH_2Cl (d) CH_3CHCl_2

Ans. ***(d)***



$$CH_3\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{KOH\,(aq)} CH_3-\overset{O}{\overset{\|}{C}}-OH + KCl \quad [\text{SN reaction}]$$

$$CH_3-CH_2-Cl \xrightarrow{KOH\,(aq)} CH_3-CH_2-OH \quad [S_N2\,\text{reaction}]$$

$$Cl-CH_2-CH_2-Cl \xrightarrow{KOH\,(aq)} \underset{OH}{\underset{|}{CH_2}}-\underset{OH}{\underset{|}{CH_2}} \quad [S_N2\,\text{reaction}]$$

$$CH_3-\underset{Cl}{\underset{|}{CH}}-Cl \xrightarrow{KOH\,(aq)} \underset{\text{(unstable)}}{CH_3-\underset{OH}{\underset{|}{CH}}-OH}$$

$$\xrightarrow{-H_2O} \underset{\text{(acetaldehyde)}}{CH_3-\overset{O}{\overset{\|}{C}}-H}$$

145 In Cannizzaro reaction given below

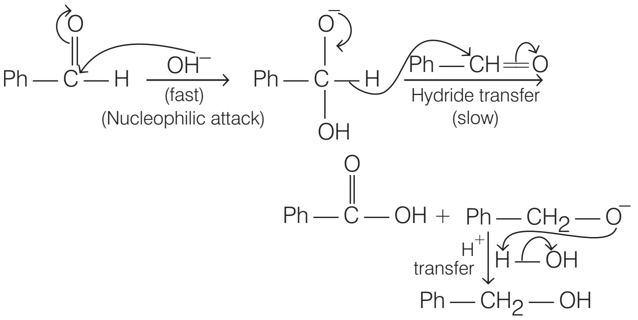
$$2PhCHO \xrightarrow{OH^{\ominus}} PhCH_2OH + PhCO_2^{\ominus}$$

the slowest step is **[AIEEE 2009]**

(a) the attack of : : $OH^{\ominus}$ at the carboxyl group
(b) the transfer of hydride to the carbonyl group
(c) the abstraction of proton from the carboxylic group
(d) the deprotonation of $PhCH_2OH$

Ans. ***(b)***

In Cannizzaro reaction, the transfer of H^- to a carbonyl group is a slowest step of the reaction and hence, it is a rate determining step of the reaction.



146 The increasing order of the rate of HCN addition to compounds A-D is **[AIEEE 2006]**

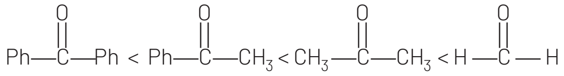
(A) HCHO (B) CH_3COCH_3
(C) $PhCOCH_3$ (D) PhCOPh

(a) A < B < C < D (b) D < B < C < A
(c) D < C < B < A (d) C < D < B < A

Ans. ***(c)***

Addition of HCN is a nucleophilic reaction. Greater the electron deficiency of C atom of carbonyl group, higher the rate of reaction.

Hence,

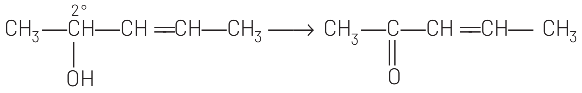


$$Ph-\overset{O}{\overset{\|}{C}}-Ph < Ph-\overset{O}{\overset{\|}{C}}-CH_3 < CH_3-\overset{O}{\overset{\|}{C}}-CH_3 < H-\overset{O}{\overset{\|}{C}}-H$$

147 The best reagent to convert pent-3-en-2-ol into pent-3-en-2-one is **[AIEEE 2005]**

(a) pyridinium chloro-chromate
(b) chromic anhydride in glacial acetic acid
(c) acidic dichromate
(d) acidic permanganate

Ans. ***(b)***



$$CH_3-\underset{OH}{\underset{|}{\overset{2^\circ}{CH}}}-CH=CH-CH_3 \longrightarrow CH_3-\underset{O}{\underset{\|}{C}}-CH=CH-CH_3$$

Only suitable reagent is chromic anhydride in glacial acetic acid. Other will also effect $(C=C)$ bond.

148 Which one of the following undergoes reaction with 50% sodium hydroxide solution to give the corresponding alcohol and acid? **[AIEEE 2004]**

(a) Phenol (b) Benzaldehyde
(c) Butanal (d) Benzoic acid

Ans. ***(b)***

$$A + NaOH \rightarrow \text{alcohol} + \text{acid}$$

Thus, it is Cannizzaro reaction.

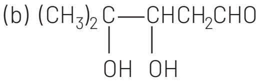
A is thus aldehyde without H at α-carbon.

(as C_6H_5CHO, HCHO)

$$2C_6H_5CHO + NaOH \longrightarrow C_6H_5CH_2OH + C_6H_5COONa$$

149 On vigorous oxidation by permangnate solution $(CH_3)_2C{=}CHCH_2CHO$ gives **[AIEEE 2002]**

(a) $(CH_3)_2CO$ and $OHCCH_2CHO$

(b)

$(CH_3)_2\underset{OH}{C}{-}\underset{OH}{C}HCH_2CHO$

(c) $(CH_3)_2CO$ and $OHCCH_2COOH$

(d) $(CH_3)_2CO$ and $CH_2(COOH)_2$

Ans. ***(d)***

$C{=}C$ bond is cleaved and oxidised to —COOH,—CHO group is also oxidised to —COOH.

$$(CH_3)_2C{=}CHCH_2CHO \longrightarrow (CH_3)_2\ C{=}O + HOOC{-}CH_2{-}COOH$$

TOPIC 4

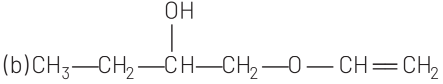
Carboxylic Acids

150 In the following sequence of reactions a compound *A*, (molecular formula $C_6H_{12}O_2$) with a straight chain structure gives a C_4 carboxylic acid. *A* is

$$A \xrightarrow[H_3O^+]{LiAlH_4} B \xrightarrow{\text{Oxidation}} C_4 \text{ carboxylic acid}$$

[2021, 01 Sep Shift-II]

(a) $CH_3{-}CH_2{-}COO{-}CH_2{-}CH_2{-}CH_3$

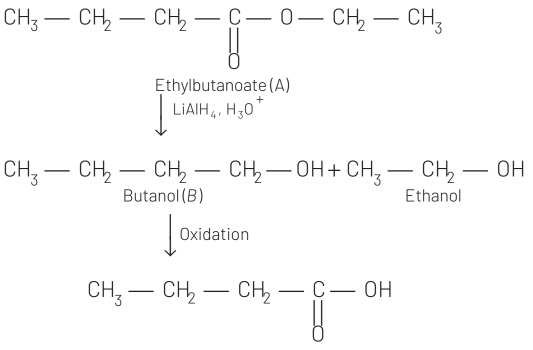
(b)

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

(c) $CH_3{-}CH_2{-}CH_2{-}COO{-}CH_2{-}CH_3$

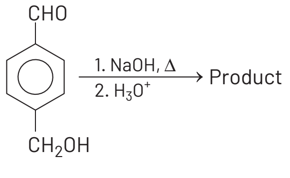
(d) $CH_3{-}CH_2{-}CH_2{-}O{-}CH{=}CH{-}CH_2{-}OH$

Ans. ***(c)***

Ethylbutanoate on reduction with $LiAlH_4$ and hydrolysis gives butanol and ethanol. Butanol on further oxidation gives butanoic acid which has four carbon atoms. The complete reaction is as follows



151 For the reaction given below.



The compound which is not formed as a product in the reaction is a **[2021, 31 Aug Shift-II]**

(a) compound with both alcohol and acid functional groups

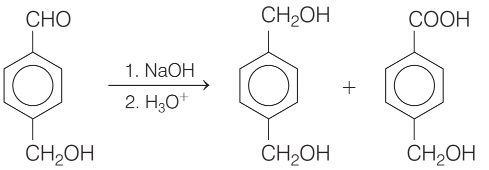
(b) monocarboxylic acid

(c) dicarboxylic acid

(d) diol

Ans. ***(c)***

In this reaction, one compound having alcohol and acid functional group and another one having two alcohol groups are formed.

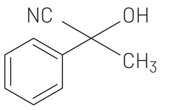


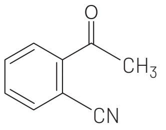
∴ Dicarboxylic acid not formed as a product.

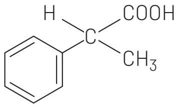
152 The structure of product *C*, formed by the following sequence of reactions is

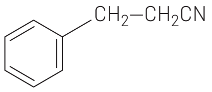
$$CH_3COOH + SOCl_2 \longrightarrow A \xrightarrow[AlCl_3]{\text{Benzene}} B \xrightarrow[-OH]{KCN} C$$

[2021, 31 Aug Shift-I]

(a)


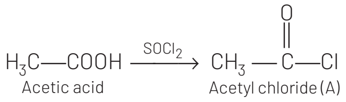
(b)


(c)


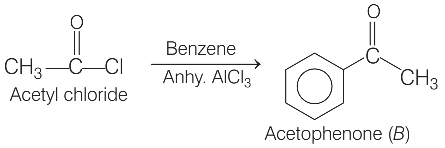
(d)


Ans. ***(a)***

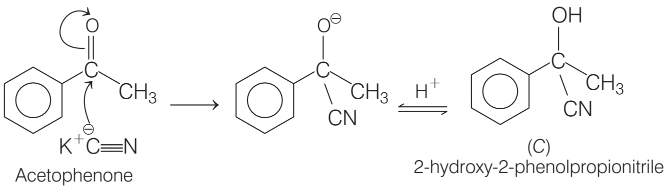
Acetic acid on reaction with $SOCl_2$ gives acetyl chloride (*A*).


$H_3C{-}COOH \xrightarrow{SOCl_2} CH_3{-}\overset{O}{\overset{\|}{C}}{-}Cl$

Acetyl chloride undergoes Friedel-Craft acylation in presence of anhyd. $AlCl_3$ and benzene to form acetophenone (*B*).

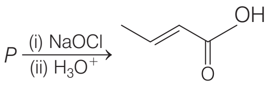


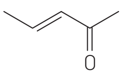
Acetophenone reacts with KCN to give (*C*) the final product, i.e. 2-hydroxy-2-phenolpropionitrile.

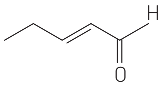


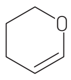
Hence, correct option is (a).

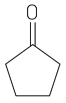
153 The structure of the starting compound *P* used in the reaction given below is **[2021, 27 Aug Shift-I]**



(a) 

(b) 

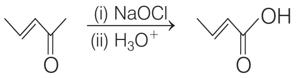
(c) 

(d) 

Ans. ***(a)***

Sodium hypochlorite (NaOCl) is a strong oxidising agent that will convert ketone to carboxylic acid.

Since, product is carboxylic acid, therefore reactant (*P*) would be ketone.



(*P*)
Pent-3-en-2-one

But-2-enoic acid

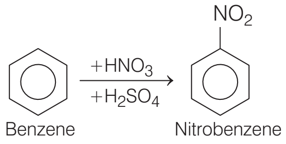
154 The correct sequential addition of reagents in the preparation of 3-nitrobenzoic acid from benzene is **[2021, 26 Aug Shift-I]**

(a) Br_2 /$AlBr_3$, HNO_3 /H_2SO_4, Mg /ether, CO_2, H_3O^+
(b) Br_2 / $AlBr_3$, NaCN, H_3O^+, HNO_3 / H_2SO_4
(c) Br_2 /$AlBr_3$, HNO_3 /H_2SO_4, NaCN, H_3O^+
(d) HNO_3 /H_2SO_4, Br_2 / $AlBr_3$, Mg/ether, CO_2, H_3O^+

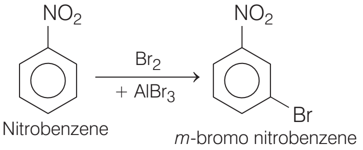
Ans. ***(d)***

The preparation of 3-nitrobenzoic acid from benzene is as follows

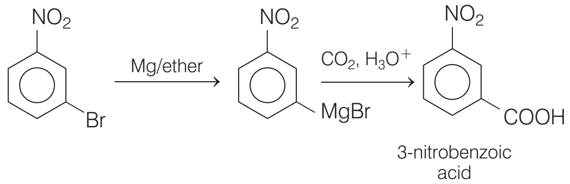
- Nitration of benzene



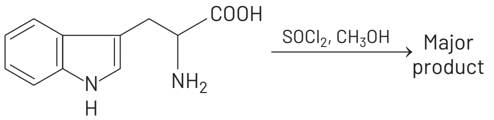
- Electrophilic substitution of nitrobenzene

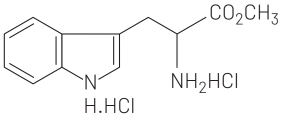


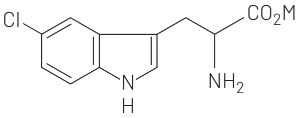
- m-bromo nitrobenzene is converted to 3-nitrobenzoic acid.

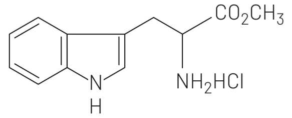


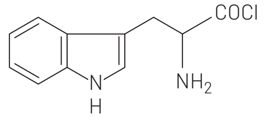
155 The major product formed in the following reaction is **[2021, 26 Aug Shift-I]**



(a) 

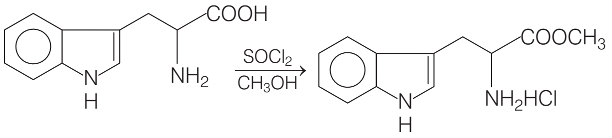
(b) 

(c) 

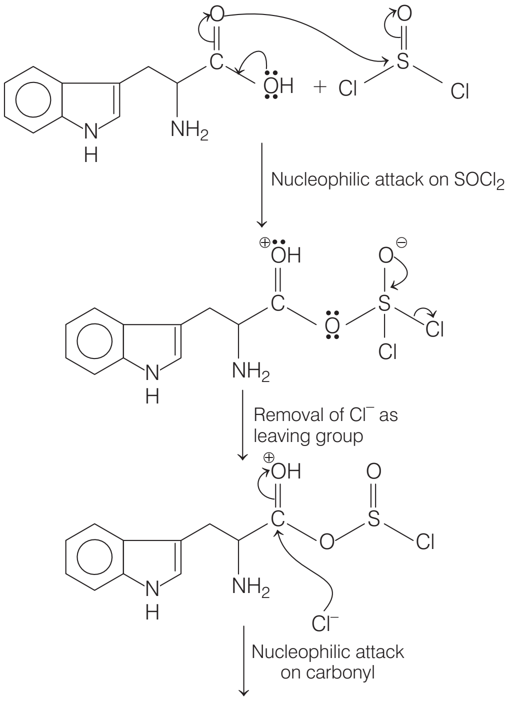
(d) 

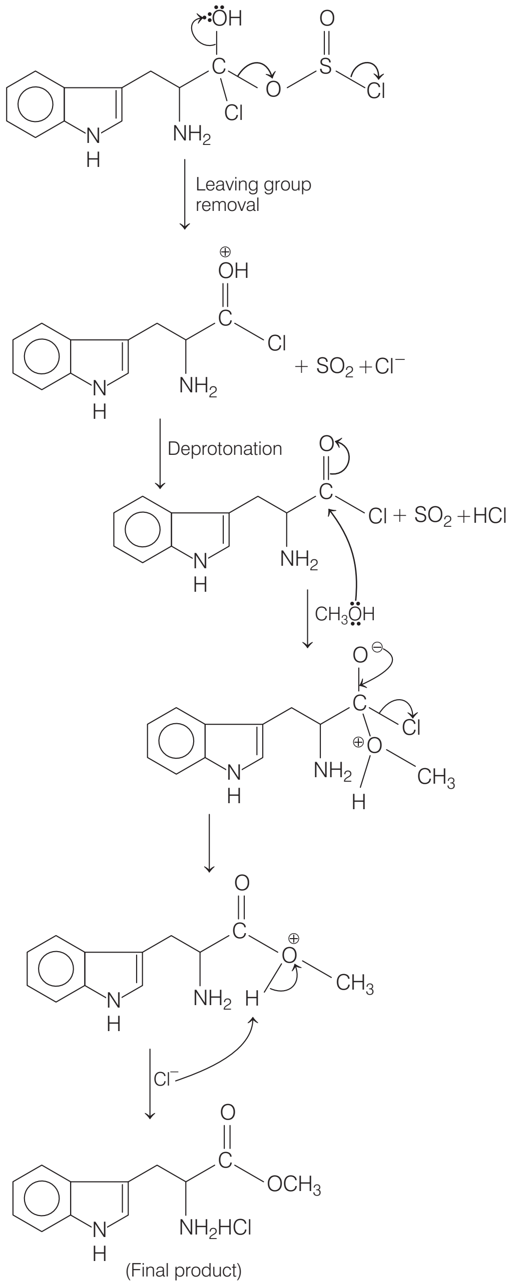
Ans. ***(c)***

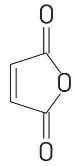
Esterification of carboxylic group (—COOH) take place in presence of $SOCl_2$ and CH_3OH as follows



Mechanism





156 

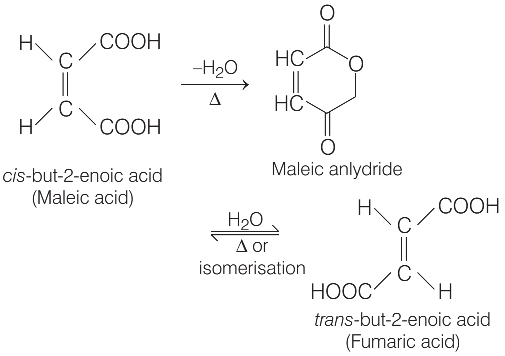
(Maleic anhydride)

Maleic anhydride can be prepared by **[2021, 25 July Shift-II]**

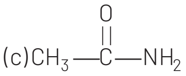
(a) heating *trans*-but-2-enedioic acid
(b) heating *cis*-but-2-enedioic acid
(c) treating *cis*-but-2-enedioic acid with alcohol and acid
(d) treating *trans*-but-2-enedioic acid with alcohol and acid

Ans. ***(b)***

Maleic acid is an organic compound that is a dicarboxylic acid. It mainly used as a precursor to fumaric acid, and relative to its parent maleic anhydride. Maleic anhydride can be prepared by heating *cis*-but-2-enedioic acid.



157 Which one of the following compounds will liberate CO_2, when treated with $NaHCO_3$? **[2021, 25 July Shift-I]**

(a) $(CH_3)_3\overset{\oplus}{N}H\overset{\ominus}{Cl}$
(b) $(CH_3)_3\overset{\oplus\ominus}{NO}H$
(c)  $CH_3-\overset{\overset{O}{||}}{C}-NH_2$
(d) CH_3NH_2

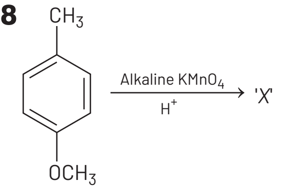
Ans. ***(a)***

Compound (*A*), reacts with sodium bicarbonate to form carbonic acid which further dissociate to liberate CO_2 effervescence.

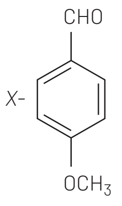
Bicarbonate test

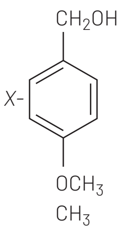
$$(CH_3)_3\overset{\oplus}{N}HCl^- + \underset{\text{Sodium bicarbonate}}{NaHCO_3} \longrightarrow \underset{\text{Carbonic acid}}{H_2CO_3} + \underset{\text{Trimethyl-amine}}{(CH_3)_3N} + NaCl$$

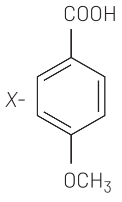
$$H_2CO_3 \longrightarrow \underset{\substack{\text{Carbon dioxide}\\\text{(effervescence)}}}{CO_2} + H_2O$$

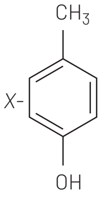
158 

Considering the above chemical reaction, identify the product '*X*'. **[2021, 18 March Shift-I]**

(a) 

(c) 

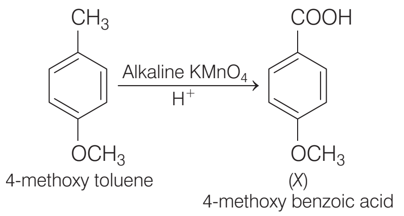
(c) 

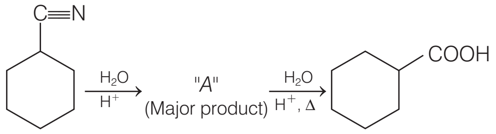
(d) 

Ans. ***(c)***

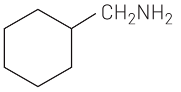
4-methoxy toluene in the presence of alkaline $KMnO_4$ to give 4-methoxy benzoic acid.

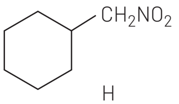
Chemical reaction is as follows :

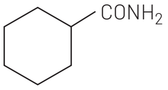


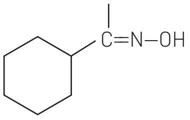
159 

Consider the above chemical reaction and identify product "A" **[2021, 18 March Shift-I]**

(a) 

(b) 

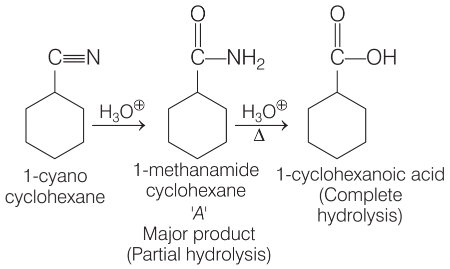
(c) 

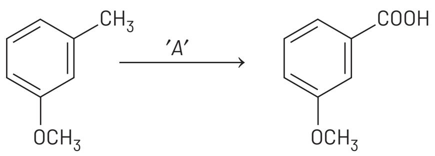
(d) 

Ans. ***(c)***

1-cyano cyclo hexane on complete hydrolysis gives 1-cyclo hexanoic acid. Intermediate 1- methanamide cyclohexane(A) is formed by partial hydrolysis.

Complete reaction is as follows



160 

In the above reaction, the reagent 'A' is **[2021, 16 March Shift-II]**

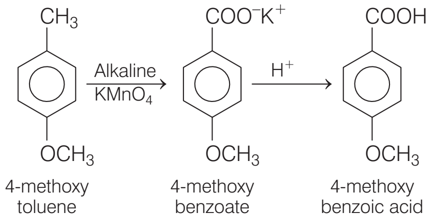
(a) $NaBH_4$, H_3O^+ (b) $LiAlH_4$

(c) Alkaline $KMNO_4$,H^+ (d) HCl, Zn - Hg

Ans. ***(c)***

In the given reaction, A is alkaline $KMnO_4$, H^+.

Alkaline $KMnO_4$ /H^+ is a strong oxidising agent and oxidises alkyl benzene to benzoic acid. While $NaBH_4$, $LiAlH_4$ and Zn-Hg/HCl are reducing agent.



161 The number of compound(s) given below which contain(s) — COOH group is ....

(i) Sulphanilic acid

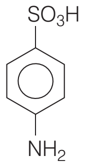
(ii) Picric acid

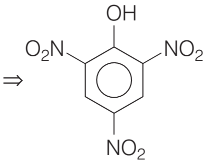
(iii) Aspirin

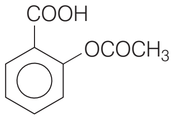
(iv) Ascorbic acid **[2021, 25 Feb Shift-II]**

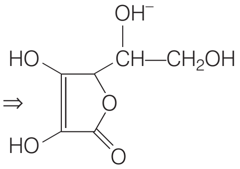
Ans. ***(1)***

Structure of given compounds are as follows

(i) (Sulphanilic acid) ⇒ 

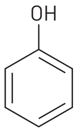
(ii) (Picric acid) ⇒ 

(iii) (Aspirin) ⇒ 

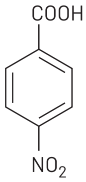
(iv) (Ascorbic acid) ⇒ 

Only one compound (iii) contains —COOH group.

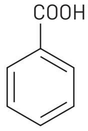
162 The correct order of acid character of the following compounds is **[2021, 25 Feb Shift-II]**



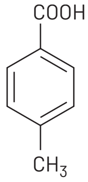
I



II



III



IV

Options

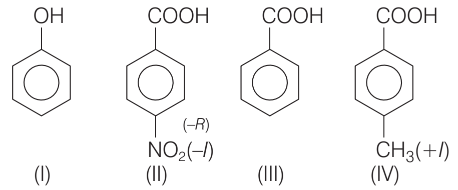
(a) I > II > III > IV

(b) III > II > I > IV

(c) II > III > IV > I

(d) IV > III > II > I

Ans. ***(c)***

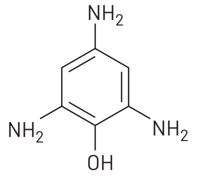


Acidity of phenol (I) is weaker than any carboxylic acid. Electron withdrawing nature (–*R*, –*I*), of $—NO_2$ group at *para* position increases acidic strength of (II), whereas + *I* effect of $—CH_3$ group at *para* position decreases acidic strength of (IV).

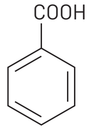
So, the order of acid character is II > III > IV > I.

163 Compound(s) which will liberate carbon dioxide with sodium bicarbonate solution is/are **[2021, 25 Feb Shift-I]**

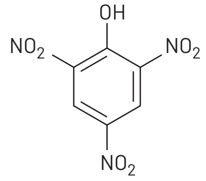
A =



B =



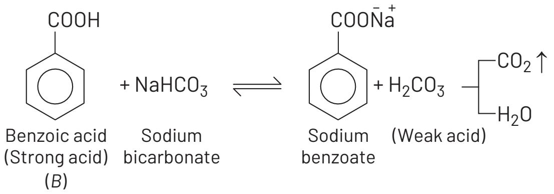
C =



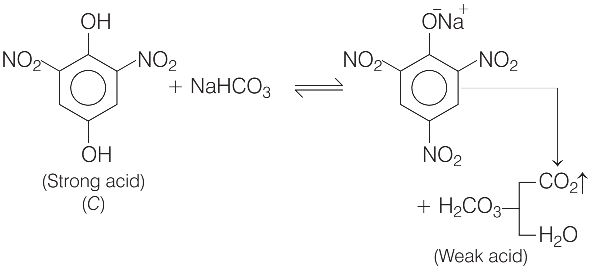
(a) *A* and *B*
(b) *C* only
(c) *B* and *C*
(d) *B* only

Ans. ***(c)***

The reactions of given compound with sodium bicarbonate solution are as follows

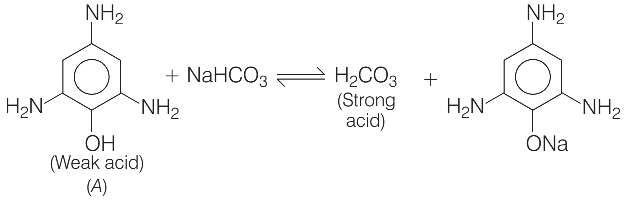


As H_2CO_3 is weak acid it dissociate to liberate CO_2 gas and H_2O.



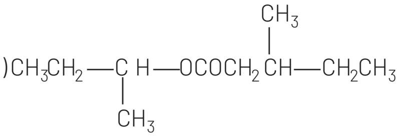
Equilibrium favours forward direction and CO_2 is liberated. In the above two reactions, H_2CO_3 is comparatively weak acid.

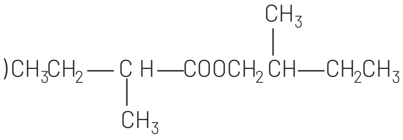
∴ CO_2 gas is liberated



Equilibrium favours backward direction and CO_2 is not liberated. Thus, only *B* and *C* will liberate carbon dioxide with sodium bicarbonate solution.

164 An organic compound [*A*], molecular formula $C_{10}H_{20}O_2$ was hydrolysed with dilute sulphuric acid to give a carboxylic acid [*B*] and an alcohol [*C*]. Oxidation of [*C*] with $CrO_3—H_2SO_4$ produced [*B*]. Which of the following structures are not possible for [*A*]? **[2020, 3 Sep Shift-I]**

(a) 
$CH_3CH_2—\underset{CH_3}{C}H—OCOCH_2\overset{CH_3}{C}H—CH_2CH_3$

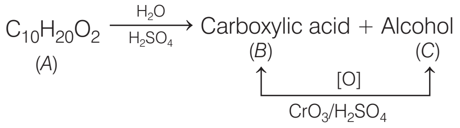
(b) 
$CH_3CH_2—\underset{CH_3}{C}H—COOCH_2\overset{CH_3}{C}H—CH_2CH_3$

(c) $CH_3CH_2CH_2COOCH_2CH_2CH_2CH_3$

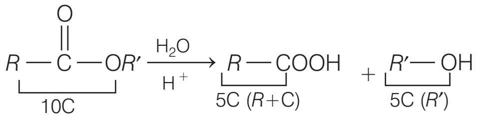
(d) $(CH_3)_3—C—COOCH_2C(CH_3)_3$

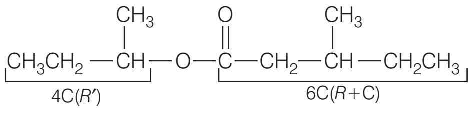
Ans. ***(a, c)***

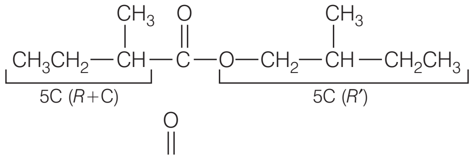
A can be written as : $(CH_3)_3C—COOCH_2C(CH_3)_3]$

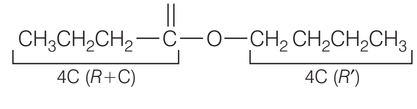


From the informations given, it is clear that *A* is an ester which contain 10 carbon atoms. Again, *C* on oxidation gives *B*. It indicates *B* and *C* contains equal number of carbon atom, i.e. each of *B* and *C* contains 5 carbon atom.

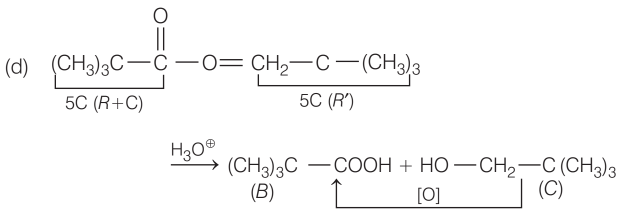


(a) 

(b) 

(c) 

Note It is not having the molecular formula of $A(C_{10}H_{20}O_2)$. Its molecular formula $(C_8H_{16}O_2)$.

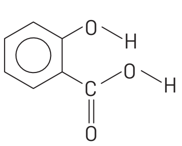


$$\text{(d)}\ \underbrace{(CH_3)_3C-\overset{\overset{O}{\|}}{C}}_{5C\ (R+C)}-O=\underbrace{CH_2-C-(CH_3)_3}_{5C\ (R')}$$

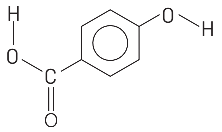
$$\xrightarrow{H_3O^{\oplus}} \underset{(B)}{(CH_3)_3C-COOH} + \underset{(C)}{HO-CH_2-C(CH_3)_3}\qquad (C)\xrightarrow{[O]}(B)$$

165 Consider the following molecules and statements related to them

(A)



(B)



(I) (B) is more likely to be crystalline than (A).

(II) (B) has higher boiling point than (A).

(III) (B) dissolves more readily than (A) in water.

Identify the correct option from below :

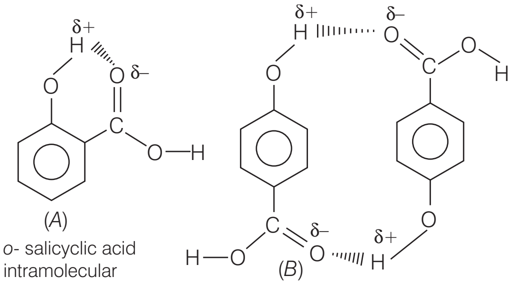
[2020, 3 Sep Shift-II]

(a) (I) and (III) are true (b) Only (I) is true

(c) (II) and (III) are true (d) (I) and (II) are true

Ans. ***(c)***

Given, molecules (A) and (B) undergoes intramolecular H-bonding and intermolecular H-bonding respectively. It is shown as follows :



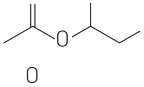
(A)
o- salicyclic acid
intramolecular
H-bonding

(B)
p-salicyclic acid
intermolecular H-bonding

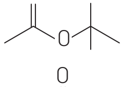
Among the given statements, II and III are true whereas I is false. Corrected statement I, (A) is more likely to crystalline than (B).

166 An organic compound (A) (molecular formula $C_6H_{12}O_2$) was hydrolysed with dil. H_2SO_4 to give a carboxylic acid (B) and an alcohol (C). 'C' gives white turbidity immediately when treated with anhydrous $ZnCl_2$ and conc. HCl. The organic compound (A) is **[2020, 4 Sep Shift-I]**

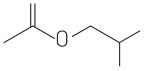
(a)



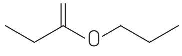
(b)



(c)



(d)

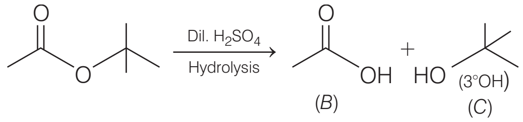


Ans. ***(b)***

$$ZnCl_2 + HCl \longrightarrow \text{Lucas reagent}$$

(C) give precipitate with Lucas reagent (immediately ppt.). It mean C will be 3° alcohol So, according to the given hints option (b) fits the category.

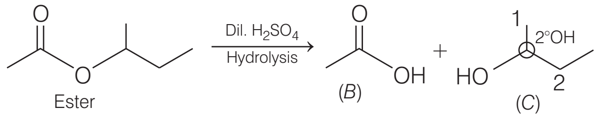
(b)



is 3°OH. In 3°OH, it gives immediate ppt. then this is correct option.

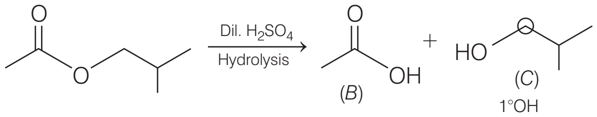
Explanation of other options are as follows :

(a)



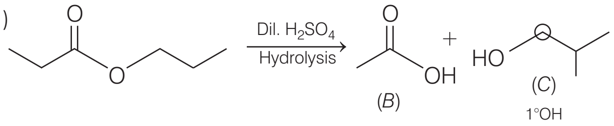
C is 2° alcohol, we want 3° alcohol then that this is incorrect option.

(c)



C is 1°OH, it does not give ppt. immediately then that this is incorrect option.

(d)



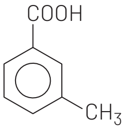
C is 1°OH that does not give test immdiately.

According to the question, compound

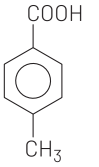
(A) gives carboxylic acid and alcohol on hydrolysis. So, A must be an ester.

167 [P] on treatment with $Br_2/FeBr_3$ in CCl_4 produced a single isomer $C_8H_7O_2$ Br while heating [P] with sodalime gave toluene. The compound [P] is **[2020, 4 Sep Shift-I]**

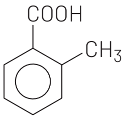
(a)



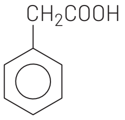
(b)



(c)



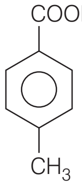
(d)



Ans. ***(b)***

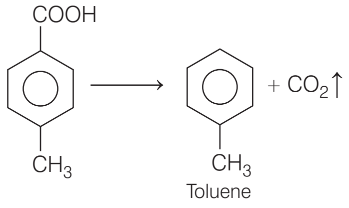
The compound [P] is 4-methyl benzoic acid.

Option (b)



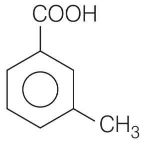
Here, —CH_3 group is *o*-and *p*-directing but *p*-position is already acquired by —COOH group. So, only one single product is formed.

On treatment option (b) with sodalime, CO_2 gas is released COOH.



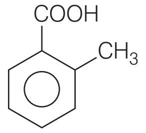
Other given options does not satisfy the condition.

Option (a)



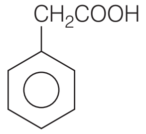
On promination 2 possible isomers will form.

Option (c)



In respect of COOH, bromination occurs at *ortho* but in *ortho* is blocked by CH_3 and in respect of CH_3 bromination not possible.

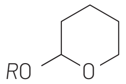
Option (d)



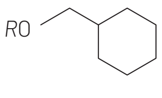
In respect of CH_2COOH bromination is done at *ortho* and *para*, then single isomer not possible.

168 Which of the following derivative of alcohols is unstable in an aqueous base? **[2020, 5 Sep Shift-I]**

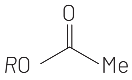
(a)



(b)



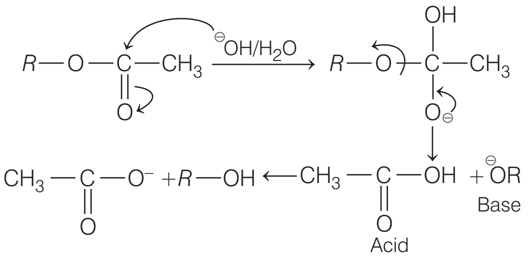
(c)



(d) *RO*—CMe_3

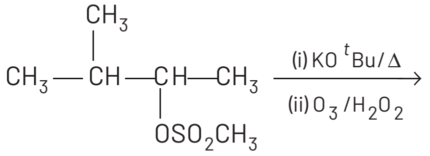
Ans. ***(c)***

Derivative of alcohols is unstable in an aqueous basic solution and undergoes hydrolysis to give alcohol and carboxylate.



(It is a hydrolysis of ester in basic medium).

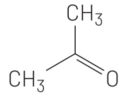
169 The major products of the following reaction are



$$CH_3-\underset{|}{\overset{CH_3}{\overset{|}{C}H}}-\underset{\underset{OSO_2CH_3}{|}}{CH}-CH_3 \xrightarrow[\text{(ii) } O_3/H_2O_2]{\text{(i) } KO^tBu/\Delta}$$

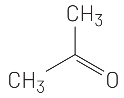
[2020, 6 Sep Shift-I]

(a)



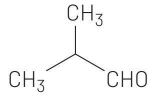
+ CH_3CHO

(b)



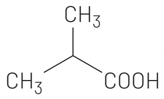
+ CH_3COOH

(c)



+ HCHO

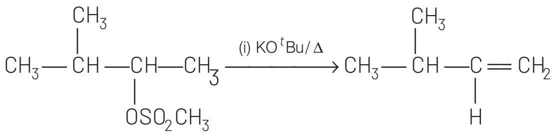
(d)



+ HCOOH

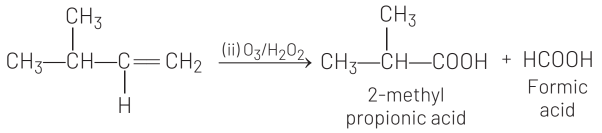
Ans. ***(d)***

Tertiary butoxide is a bulky base, which favour elimination to form less substituted alkenes (Hofmann-product).



$$CH_3-\overset{CH_3}{\overset{|}{C}H}-\underset{\underset{OSO_2CH_3}{|}}{CH}-CH_3 \xrightarrow{\text{(i) } KO^tBu/\Delta} CH_3-\overset{CH_3}{\overset{|}{C}H}-\underset{\underset{H}{|}}{C}=CH_2$$

Now, alkene in presence of O_3/H_2O_2 undergoes oxidative ozonloysis to produce 2-methyl propionic acid and formic acid.



$$CH_3-\overset{CH_3}{\overset{|}{C}H}-\underset{\underset{H}{|}}{C}=CH_2 \xrightarrow{\text{(ii) } O_3/H_2O_2} \underset{\text{2-methyl propionic acid}}{CH_3-\overset{CH_3}{\overset{|}{C}H}-COOH} + \underset{\text{Formic acid}}{HCOOH}$$

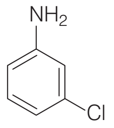
170 A solution of *m*-chloroaniline, *m*-chlorophenol and *m*-chlorobenzoic acid in ethyl acetate was extracted initially with a saturated solution of $NaHCO_3$ to give fraction *A*.

The left over organic phase was extracted with dilute NaOH solution to give fraction *B*. The final organic layer was labelled as fraction *C*. Fractions *A*, *B* and *C* contain respectively **[2020, 7 Jan Shift-I]**

(a) *m*-chlorobenzoic acid, *m*-chloroaniline and *m*-chlorophenol
(b) *m*-chlorophenol, *m*-chlorobenzoic acid and *m*-chloroaniline
(c) *m*-chlorobenzoic acid, *m*-chlorophenol and *m*-chloroaniline,
(d) *m*-chlorobenzoic acid and *m*-chlorophenol

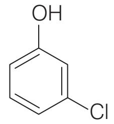
Ans. ***(c)***

m-chloroaniline,



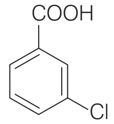
doesn't dissolve in $NaHCO_3$ or NaOH solutions because it has no considerable acidity and therefore can't form salt with bases.

In *m*-chlorophenol;



which is substituted phenol is very weakly acidic which is sufficient to form their salt with NaOH. Therefore, these dissolve in dil. NaOH solution. But not acidic enough to form a salt with saturated $NaHCO_3$ solution.

Carboxylic acids such as



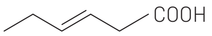
are strongly acidic. Their acidity is sufficient to form salt with *aq*.NaOH or *aq*. $NaHCO_3$.

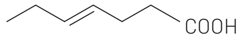
Therefore, *m*-chlorobenzoic acid (layer *A*) can be extracted by *aq*. $NaHCO_3$, then from the left over, *m*-chlorophenol (layer *B*) can be extracted by *aq*. NaOH. While the final organic layer (*C*) is of *m*-chloroaniline.

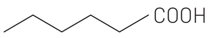
171 What is the product of following reaction?

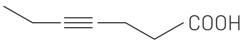
$$\text{Hex-3-ynal} \xrightarrow[\substack{\text{(ii) PBr}_3 \\ \text{(iii) Mg/ether} \\ \text{(iv) CO}_2/\text{H}_3\text{O}^+}]{\text{(i) NaBH}_4} ?$$

[2020, 7 Jan Shift-I]

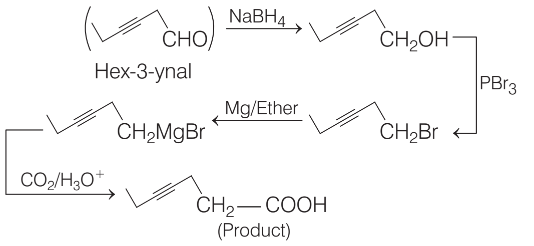
(a)


(b)


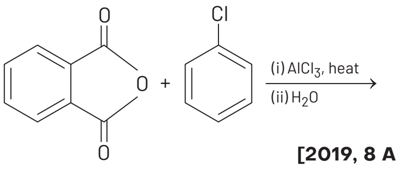
(c)


(d)


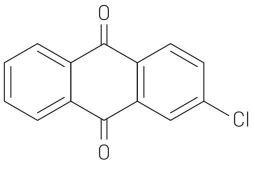
Ans. ***(d)***

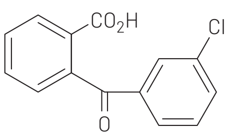


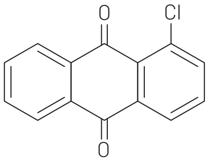
172 The major product of the following reaction is

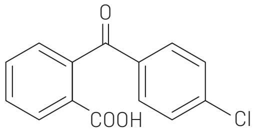


[2019, 8 April Shift-I]

(a)


(b)


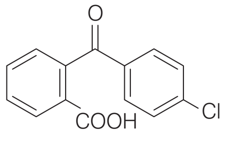
(c)


(d)


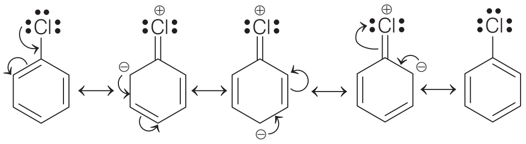
Ans. ***(d)***

The major product of the given reaction is (d).

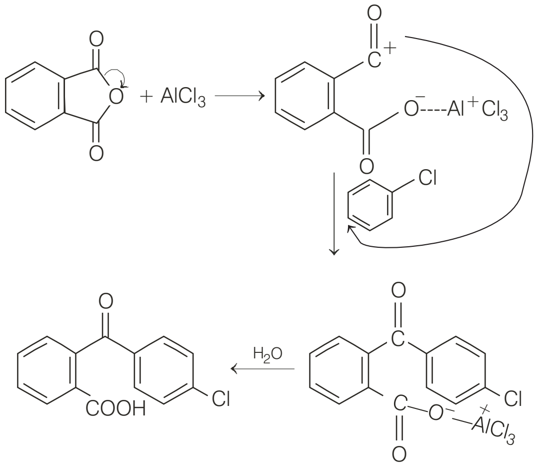
This reaction proceed *via* Friedel-Craft acylation. Here, —Cl group present on chlorobenzene is *ortho* and *para*-directing. It can be easily understood by resonating structures of chlorobenzene.



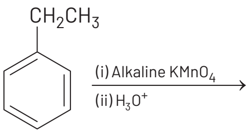
(d)



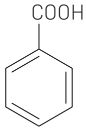
The given reaction proceed as follows :

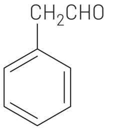


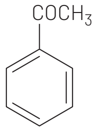
173 The major product of the following reaction is

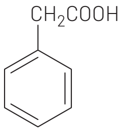


[2019, 9 April Shift-I]

(a)


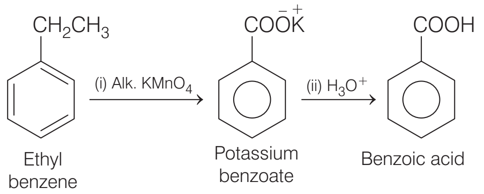
(b)


(c)


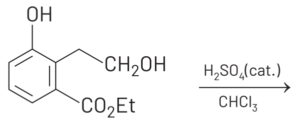
(d)


Ans. ***(a)***

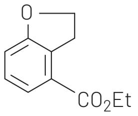
The major product of the given reaction is benzoic acid (C_6H_5COOH). On vigorous oxidation of alkyl benzene with acidic or alkaline $KMnO_4$, aromatic acids are obtained. During oxidation of alkyl benzene, the aromatic nucleus remains intact and the entire chain is oxidised to —COOH group irrespective of the length of carbon chain.

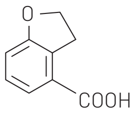


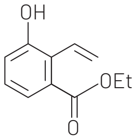
174 The major product of the following reaction is

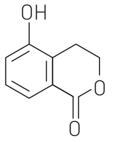


[2019, 9 April Shift-II]

(a)


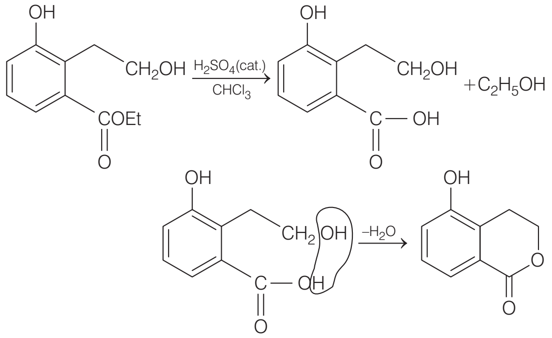
(b)


(c)


(d)


Ans. ***(d)***

Given reaction involves acidic hydrolysis of esters followed by the intramolecular cyclisation. The chemical equation is as follows:



175 The correct decreasing order for acid strength is

(a) $FCH_2COOH > NCCH_2COOH > NO_2CH_2COOH > ClCH_2COOH$

(b) $CNCH_2COOH > O_2NCH_2COOH > FCH_2COOH > ClCH_2COOH$

(c) $NO_2CH_2COOH > NCCH_2COOH > FCH_2COOH > ClCH_2COOH$

(d) $NO_2CH_2COOH > FCH_2COOH > CNCH_2COOH > ClCH_2COOH$

[2019, 9 Jan Shift-I]

Ans. ***(c)***

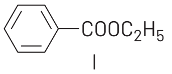
All the given compounds are α-monosubstituted acetic acid derivatives and the α-substitutions have been made by strong $-I$ groups/atoms. More powerful the $-I$ group, stronger will be the acid. $-I$ power of different groups is as follows :

$$—NO_2 > —CN > —F > — Cl.$$

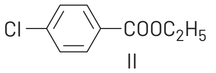
Thus, the correct decreasing order for acid strength is:

$NO_2CH_2COOH > NCCH_2COOH > FCH_2COOH > ClCH_2COOH$.

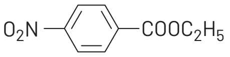
176 The decreasing order of ease of alkaline hydrolysis for the following esters is **[2019, 10 Jan Shift-I]**



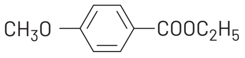
I



II



III

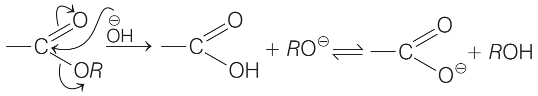


IV

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

Ans. ***(b)***

Alkaline hydrolysis of an ester (carboxylic acid derivative) follows acyl S_N2 mechanism.

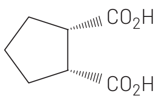


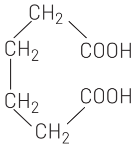
Rate of S_N2 mechanism depends on the polarity of group of —COOR group. Electron withdrawing group ($-R > -I$) increases the rate of S_N2 reaction whereas electron donating group ($+R > +I$) decreases the rate of S_N2 reaction.

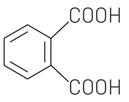
Here, the nature of functional groups attached *para* to the benzene ring are: $\underset{(-R)}{—NO_2} > \underset{(-I)}{— Cl} > \underset{(+R)}{— OCH_3}$

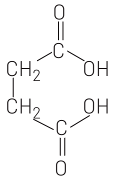
So, the order of hydrolysis will be, $\underset{(-R)}{III} > \underset{(-I)}{II} > I > \underset{(+R)}{IV}$

177 Which dicarboxylic acid in presence of a dehydrating agent is least reactive to give an anhydride? **[2019, 10 Jan Shift-I]**

(a)


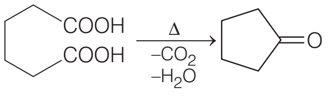
(b)


(c)


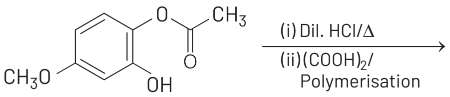
(d)


Ans. ***(b)***

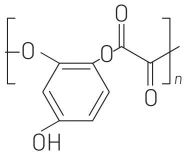
Heating of $(CH_2)_4 \begin{matrix} COOH \\ COOH \end{matrix}$ (adipic acid) with a dehydrating agent, decarboxylates ($—CO_2$) to give a ketone (cyclopentanone), not an anhydride.



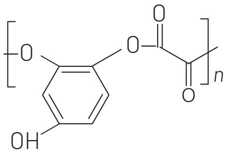
178 The major product of the following reaction is



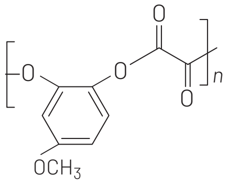
(a)



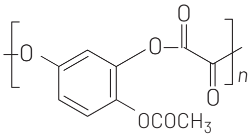
(b)



(c)



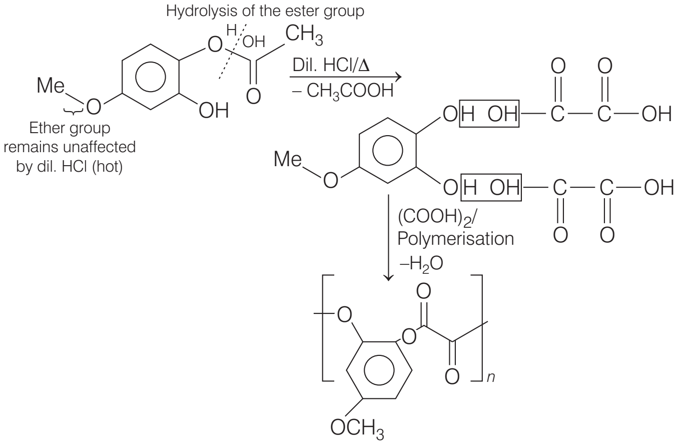
(d)



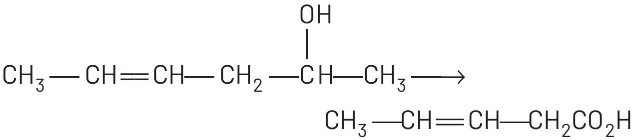
[2019, 10 Jan Shift-II]

Ans. *(c)*

In the given reaction, ester get cleaved in presence of dil. HCl and readily forms alcohol. This alcohol on reaction with oxalic acid undergoes polymerisation reaction.



179 Which is the most suitable reagent for the following transformation ?



$$CH_3-CH=CH-CH_2-\overset{OH}{\overset{|}{C}}H-CH_3\longrightarrow CH_3-CH=CH-CH_2CO_2H$$

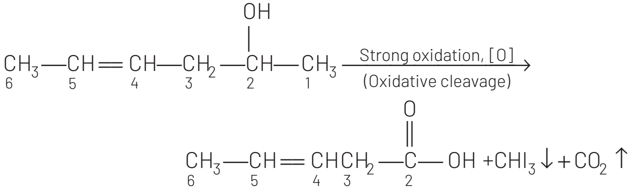
[2019, 10 Jan Shift-II]

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

(c) Alkaline $KMnO_4$ (d) CrO_2Cl_2 / CS_2

Ans. *(b)*

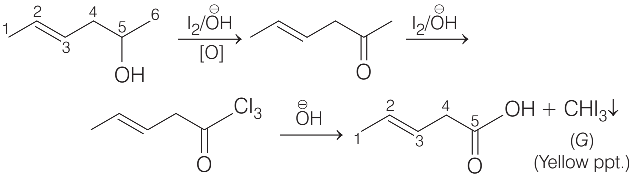
The most suitable reagent to carry out given transformation is I_2/NaOH



$$\underset{6}{CH_3}-\underset{5}{CH}=\underset{4}{CH}-\underset{3}{CH_2}-\underset{2}{\overset{OH}{\overset{|}{CH}}}-\underset{1}{CH_3}\xrightarrow[\text{(Oxidative cleavage)}]{\text{Strong oxidation, [O]}}$$

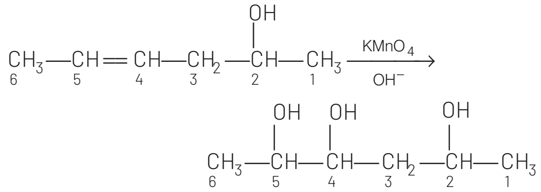
$$\underset{6}{CH_3}-\underset{5}{CH}=\underset{4}{CH}\underset{3}{CH_2}-\underset{2}{\overset{O}{\overset{\|}{C}}}-OH+CHI_3\downarrow+CO_2\uparrow$$

Here, the haloform reaction will give following reaction:



(i) Tollen's reagent ($AgNO_3$ + NH_4OH) is a mild oxidising agent. It does not react with $-\underset{OH}{\underset{|}{CH}}-CH_3$ group (2°-alcohol).

(ii) Alkaline $KMnO_4$ cannot perform the oxidative cleavage, rather it will hydroxylate the C=C.

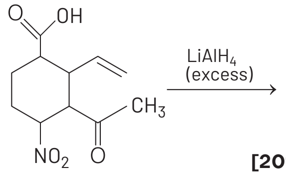


$$\underset{6}{CH_3}-\underset{5}{CH}=\underset{4}{CH}-\underset{3}{CH_2}-\underset{2}{\overset{OH}{\overset{|}{CH}}}-\underset{1}{CH_3}\xrightarrow[OH^-]{KMnO_4}$$

$$\underset{6}{CH_3}-\underset{5}{\overset{OH}{\overset{|}{CH}}}-\underset{4}{\overset{OH}{\overset{|}{CH}}}-\underset{3}{CH_2}-\underset{2}{\overset{OH}{\overset{|}{CH}}}-\underset{1}{CH_3}$$

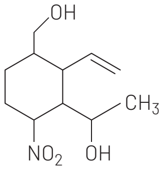
(iv) CrO_2Cl_2 / CS_2 will not react here.

180 The major product obtained in the following reaction is

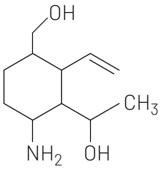


[2019, 11 Jan Shift-II]

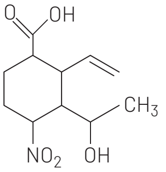
(a)



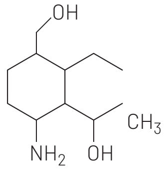
(b)



(c)

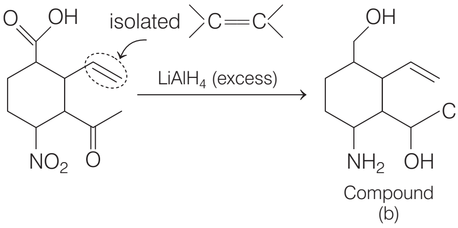


(d)



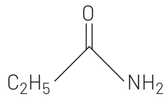
Ans. *(b)*

$LiAlH_4$ acts as a nucleophilic reducing agent that can reduce —COOH to —CH_2OH, $-\underset{|}{C}=O$ into $-\underset{|}{CH}-OH$ and —NO_2 into —NH_2, but it cannot reduce isolated $>C=C<$

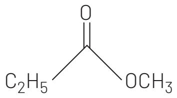


181 The increasing order of the reactivity of the following with $LiAlH_4$ is **[2019, 12 Jan Shift-II]**

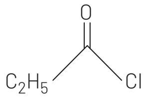
(A)



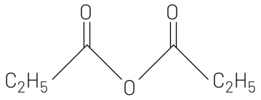
(B)



(C)



(D)



(a) $(A) < (B) < (D) < (C)$ (b) $(A) < (B) < (C) < (D)$

(c) $(B) < (A) < (D) < (C)$ (d) $(B) < (A) < (C) < (D)$

Ans. ***(a)***

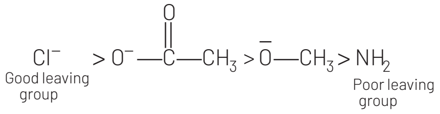
All the given compounds are acid derivatives, thus contain carbonyl group in them. $LiAlH_4$ reduces these compounds through nucleophilic substitution *via* addition elimination $(S_{N_A} E)$ reaction. The rate of reaction depends upon the following factors :

(i) Size of alkyl group.

(ii) Steric hinderance around the $> C{=}O$ group.

(iii) (+) ve charge on the C-atom of $> C{=}O$ group.

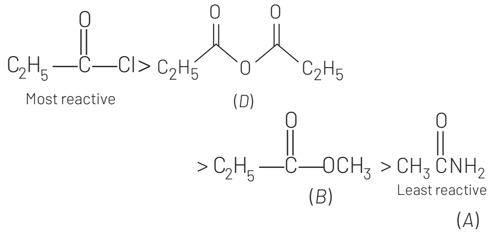
The alkyl groups are more or less same in the given compounds. Thus, the reactivity order of given compounds depends upon 2nd and 3rd factor written above. The cumulative effect of these two factors results to leaving group ability (LGA) of the substituents in the following order :



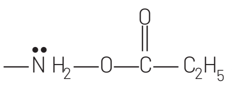
$$\underset{\text{Good leaving group}}{Cl^-} > O^-—\overset{\overset{O}{\|}}{C}—CH_3 > \bar{O}—CH_3 > \underset{\text{Poor leaving group}}{NH_2}$$

This leaving group ability (weak conjugate base) corresponds directly to the reactivity order.

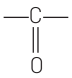
Hence, the correct reactivity order is:



Note The –*I*-effect of —Cl and + *m*-effects of



$\ddot{N}H_2—O—\overset{\overset{O}{\|}}{C}—C_2H_5$ and — OCH_3 groups while attached to

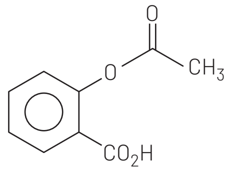


$—\underset{\underset{O}{\|}}{C}—$ group to be reduced

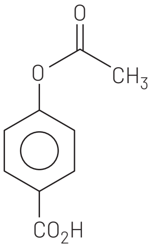
Also, add to the group leaving ability.

182 Phenol on treatment with CO_2 in the presence of NaOH followed by acidification produces compound *X* as the major product. *X* on treatment with $(CH_3CO)_2O$ in the presence of catalytic amount of H_2SO_4 produces: **[JEE Main 2018]**

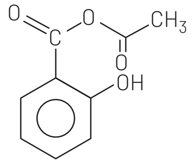
(a)



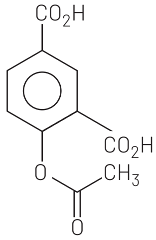
(b)



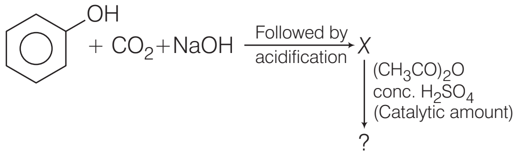
(c)



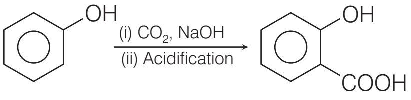
(d)



Ans. ***(a)***

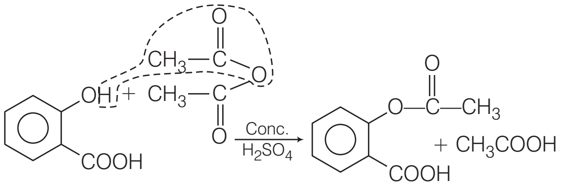


The very first reaction in the above road map looks like Kolbe's reaction which results to salicylic acid as



Salicylic acid
(*X*)

The salicylic acid with acetic anhydride $[(CH_3CO)_2O]$ in the presence of catalytic amount of conc. H_2SO_4 undergoes acylation to produce aspirin as



Acetyl salicylic acid (Aspirin)

Aspirin is a non-narcotic analgesic (Pain killer).

183 In the following sequence of reaction,

$$\text{Toluene} \xrightarrow{KMnO_4} A \xrightarrow{SOCl_2} B \xrightarrow[BaSO_4]{H_2/Pd} C$$

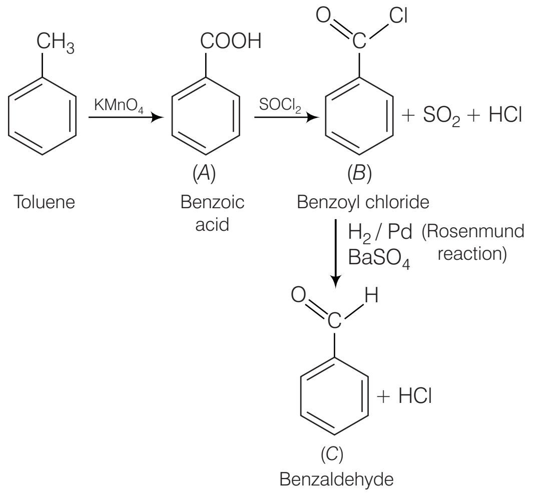
The product C is **[JEE Main 2015]**

(a) C_6H_5COOH (b) $C_6H_5CH_3$ (c) $C_6H_5CH_2OH$ (d) C_6H_5CHO

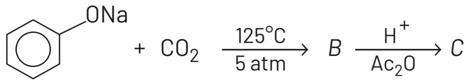
Ans. ***(d)***

Toluene undergoes oxidation with $KMnO_4$, forms benzoic acid. In this conversion, alkyl part of toluene converts into carboxylic group. Further, benzoic acid reacts with thionyl chloride $(SOCl_2)$ to give benzoyl chloride which upon reduction with H_2/Pd or $BaSO_4$ forms benzaldehyde (Rosenmund Reduction).

The conversion look like,

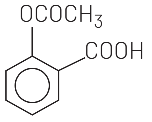


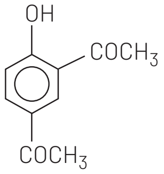
184 Sodium phenoxide when heated with CO_2 under pressure at 125°C yields a product which on acetylation produces *C*. **[JEE Main 2014]**

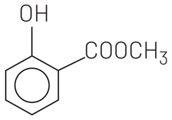


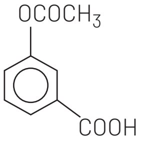
$$C_6H_5ONa + CO_2 \xrightarrow[5\text{ atm}]{125^\circ C} B \xrightarrow[Ac_2O]{H^+} C$$

The major product *C* would be

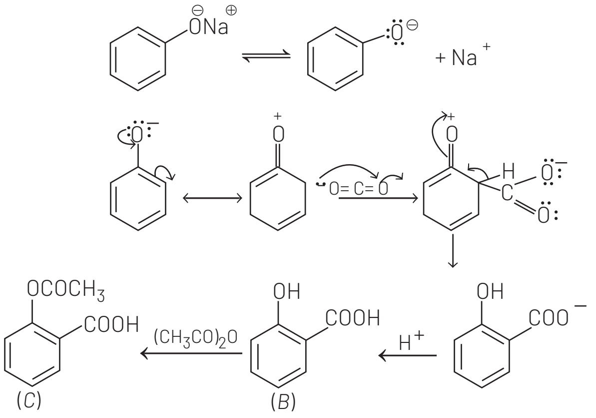
(a) 

(b) 

(c) 

(d) 

Ans. ***(a)***



185 In the reaction,

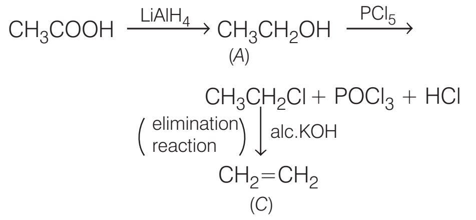
$$CH_3COOH \xrightarrow{LiAlH_4} A \xrightarrow{PCl_5} B \xrightarrow{alc.\ KOH} C$$

the product *C* is **[JEE Main 2014]**

(a) acetaldehyde (b) acetylene
(c) ethylene (d) acetylchloride

Ans. ***(c)***

The complete series of reaction can be represented as



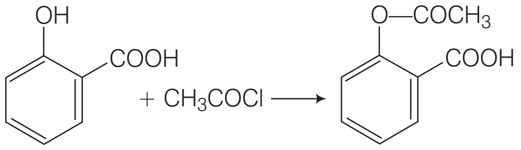
$$\underset{}{CH_3COOH} \xrightarrow{LiAlH_4} \underset{(A)}{CH_3CH_2OH} \xrightarrow{PCl_5} CH_3CH_2Cl + POCl_3 + HCl \xrightarrow[\text{(elimination reaction)}]{alc.KOH} \underset{(C)}{CH_2{=}CH_2}$$

186 Aspirin is known as **[AIEEE 2012]**

(a) acetyl salicylic acid (b) phenyl salicylate
(c) acetyl salicylate (d) methyl salicylic acid

Ans. ***(a)***

Aspirin is acetyl derivative of salicylic acid.



Acetyl salicylic acid

187 Which of the following reagents may be used to distinguish between phenol and benzoic acid ? **[AIEEE 2011]**

(a) Aqueous NaOH (b) Tollen's reagent
(c) Molisch reagent (d) Neutral $FeCl_3$

Ans. ***(d)***

	Reagent	Phenol	Benzoic acid	Conclusion
(a)	Aqueous NaOH	Salt formation	Salt formation	No specific colour change
(b)	Tollen's reagent	No effect	No effect	
(c)	Molisch reagent	No effect	No effect	
(d)	Neutral $FeCl_3$	Violet colour	Buff-coloured precipitate	Thus, $FeCl_3$ can be used to make distinction

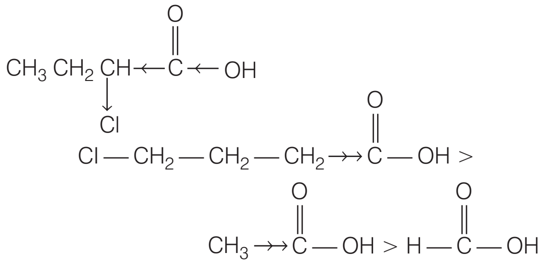
188 The strongest acid amongst the following compounds is **[AIEEE 2011]**

(a) CH_3COOH (b) $HCOOH$
(c) $CH_3CH_2CH(Cl)CO_2H$ (d) $ClCH_2CH_2CH_2COOH$

Ans. ***(c)***

– *I* effect exerting (electron withdrawing) groups increases the acidic strength of an acid by withdrawing electron density towards itself, they weakning O—H bond and thus, the release of H^+ ion by an acid becomes easier.

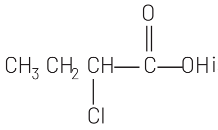
Whereas +*I* effect excerting (e^- releasing) groups decreases the acidic strength by donating electron density to O-atom. Further, – *I* effect decreases with distance. Thus, the acidic strength of the given acids would be



$$\mathrm{CH_3\,CH_2\,\underset{\underset{\displaystyle Cl}{\downarrow}}{CH}\leftarrow\overset{\overset{\displaystyle O}{\|}}{C}\leftarrow OH}$$

$$\mathrm{Cl-CH_2-CH_2-CH_2\twoheadrightarrow\overset{\overset{\displaystyle O}{\|}}{C}-OH >}$$

$$\mathrm{CH_3\twoheadrightarrow\overset{\overset{\displaystyle O}{\|}}{C}-OH > H-\overset{\overset{\displaystyle O}{\|}}{C}-OH}$$



Hence, $\mathrm{CH_3\,CH_2\,\underset{\underset{\displaystyle Cl}{|}}{CH}-\overset{\overset{\displaystyle O}{\|}}{C}-OH}$ is most acidic and strongest acid than other given compounds.

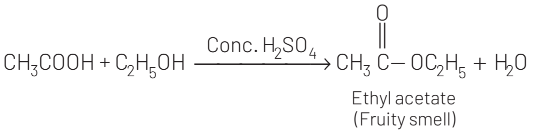
189 A liquid was mixed with ethanol and a drop of concentrated H_2SO_4 was added. A compound with a fruity smell was formed. The liquid was **[AIEEE 2009]**

(a) CH_3OH (b) HCHO (c) CH_3COCH_3 (d) CH_3COOH

Ans. ***(d)***

$$\text{A liquid} + C_2H_5OH \xrightarrow{\text{Conc. } H_2SO_4} \underset{\text{(Fruity smell)}}{\text{Compound}}$$

Fruity smell is the characteristic property of ester, thus the above reaction leads to the formation of ester.



$$CH_3COOH + C_2H_5OH \xrightarrow{\text{Conc. } H_2SO_4} \underset{\substack{\text{Ethyl acetate}\\ \text{(Fruity smell)}}}{CH_3\overset{\overset{\displaystyle O}{\|}}{C}-OC_2H_5} + H_2O$$

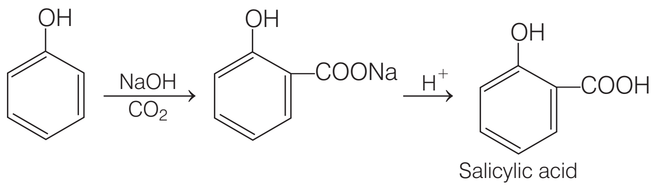
This reaction is called esterification.

190 The major product obtained on interaction of phenol with sodium hydroxide and carbon dioxide is **[AIEEE 2009]**

(a) benzoic acid (b) salicylaldehyde

(c) salicylic acid (d) phthalic acid

Ans. ***(c)***



The above reaction is called Kolbe's reaction.

191 The compound formed as a result of oxidation of ethyl benzene by $KMnO_4$ is **[AIEEE 2007]**

(a) benzophenone

(b) acetophenone

(c) benzoic acid

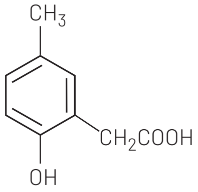
(d) benzyl alcohol

Ans. ***(c)***

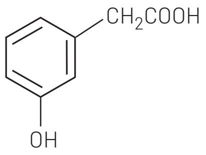
Any aliphatic carbon with hydrogen attached to it, in combination with benzene ring, will be oxidised to benzoic acid by $KMnO_4$ / H^+.

192 *p*-cresol reacts with chloroform in alkaline medium to give the compound *A* which adds hydrogen cyanide to form the compound *B*. The latter, on acidic hydrolysis gives chiral carboxylic acid. The structure of the carboxylic acid is **[AIEEE 2005]**

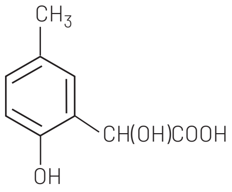
(a)



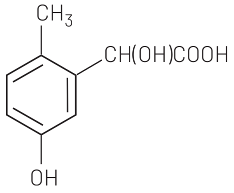
(b)



(c)



(d)



Ans. ***(c)***