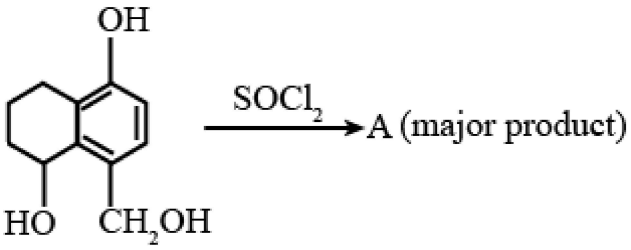
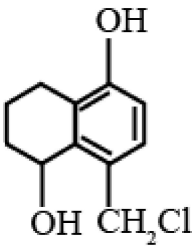
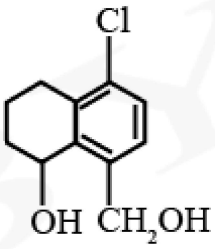
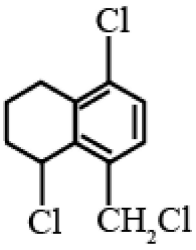
Halo compounds + Compounds containing Oxygen

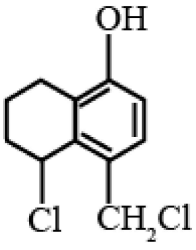
1. Identify A in the given reaction,



A. 

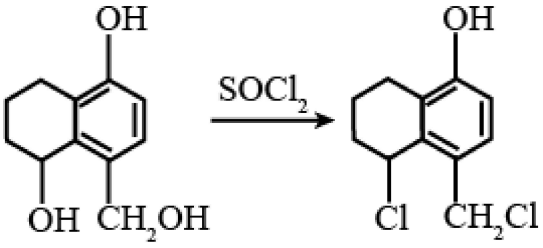
B. 

C. 

D. 

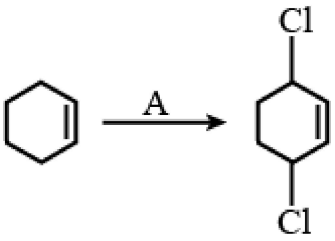
Halo compounds + Compounds containing Oxygen

$SOCl_2$ does not chlorinate the aromatic alcohols because it goes by S_N2 reaction.



Hence, option (d) is correct.

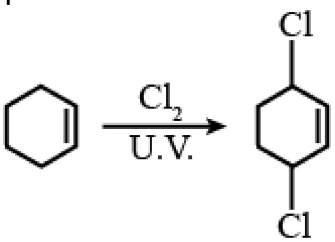
2.



Identify the reagent(s) 'A' and condition(s) for the reaction.

- ✗ **A.** $A = HCl$; $Anhydrous\ AlCl_3$
- ✓ **B.** $A = Cl_2$; $UV\ light$
- ✗ **C.** $A = Cl_2$; $dark,\ Anhydrous\ AlCl_3$
- ✗ **D.** $A = HCl,\ ZnCl_2$

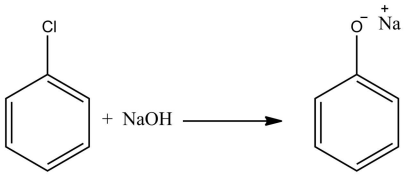
In presence of U.V. light, free radical substitution reaction occurs, at allylic position.



With all other reagents, Cl will get add to the alkene.

Hence, option (b) is correct.

Halo compounds + Compounds containing Oxygen

3. 

The above reaction requires which of the following reaction condition?

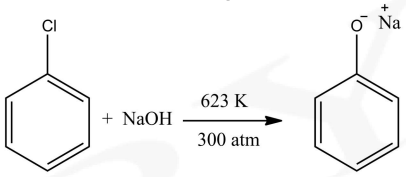
A. $573\ K,\ 300\ atm$

B. $623\ K,\ Cu,\ 300\ atm$

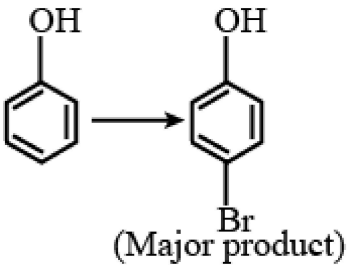
C. $573\ K,\ Cu,\ 300\ atm$

D. $623\ K,\ 300\ atm$

Chlorobenzene is fused with $NaOH$ at $623\ K$ and 300 atmospheric pressure to get sodium phenoxide. This is called Dow process. In this process, formed sodium phenoxide is acidified to get phenol.



Halo compounds + Compounds containing Oxygen

4. 

(Major product)

The given reaction can occur in the presence of

(a) Bromine water

(b) Br_2 in $CS_2,\ 273\ K$

(c) $Br_2/FeBr_3$

(d) Br_2 in $CHCl_3,\ 273\ K$

Choose the correct answer from the options given below

A. (a) and (c) only

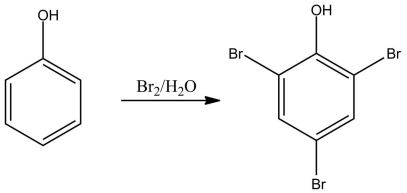
B. (a), (b) and (d) only

C. (b) and (d) only

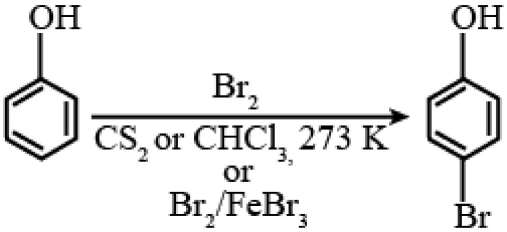
D. (b), (c) and (d) only

Reaction of phenol and water with bromine is known as bromination of phenol. Solvent has a great influence on the reaction. In different solvents, different products are obtained.

In the water solvent when phenol treated with Br_2 gives a polybromo derivative in which all hydrogen atoms at ortho, meta, and para positions with respect to the $-OH$ group are replaced by bromine atoms. It is so because in aqueous medium phenol ionises to form peroxide ion. Due to the presence of negative ions, the ring gets highly activated and tri substitution occurs and the formation of 2,4,6 – tribromophenol takes place.



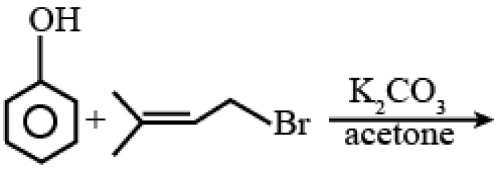
In all other case it form para-bromo as the major product.

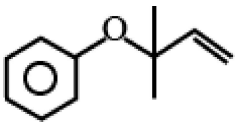


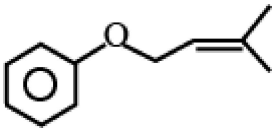
hence, option (d) is correct.

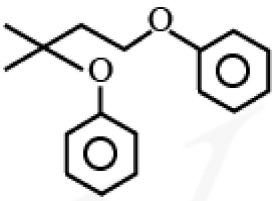
Halo compounds + Compounds containing Oxygen

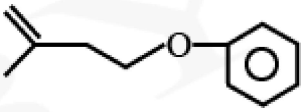
5. The major product of the following reaction, if it occurs by S_N2 mechanism is :



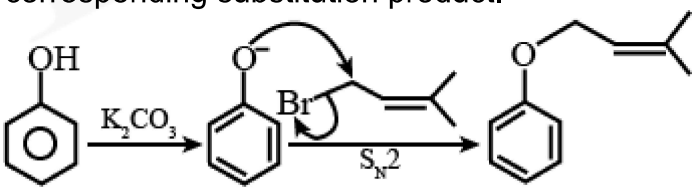
✗ **A.** 

✓ **B.** 

✗ **C.** 

✗ **D.** 

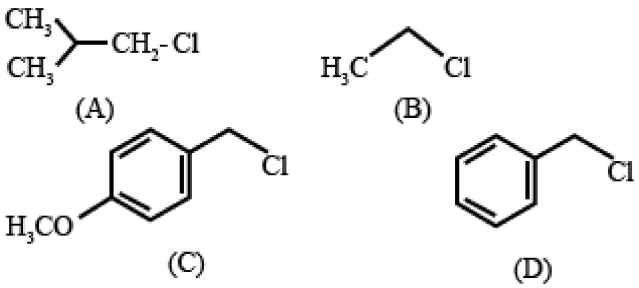
It is mentioned that above reaction undergoes S_N2 reaction. Thus, the phenoxide formed in the basic medium attacks alkyl halide to give corresponding substitution product.



(Attack is on least hindered position)

Halo compounds + Compounds containing Oxygen

6. Increasing order of reactivity of the following compunds for $S_N\,1$ substitution is:

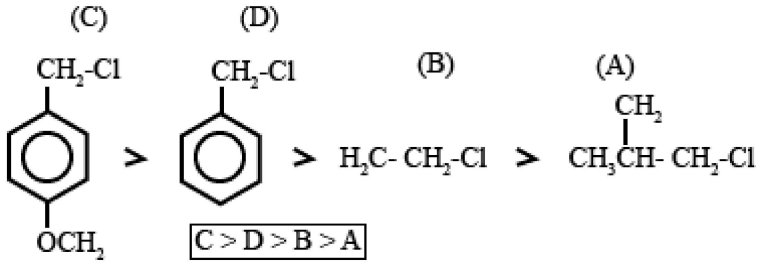


- **A.** $(A) < (B) < (D) < (C)$
- **B.** $(B) < (C) < (D) < (A)$
- **C.** $(B) < (C) < (A) < (D)$
- **D.** $(B) < (A) < (D) < (C)$

In S_N1 reaction mechanism, formation of carbocation is the rate determining step.
Thus,
$\text{Rate of reaction} \propto \text{stability of carbocation}$

Carbocation formed from (C) abnd (D) are more stable because they are benzyl carbocation. They are resonance stabilised.
Comparing (C) and (D), carbocation formed from (C) is more stable because it is extra stabilised by the +I effect of $-OCH_3$ group.

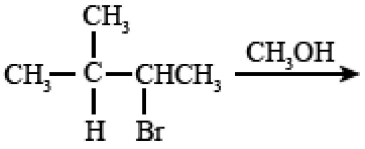
Both (B) and (A) forms primary carbocation, but (B) has more α-hydrogen compared to (A). So, by conjugation effect carbocation of B is more stable than A.

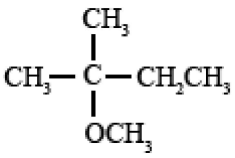


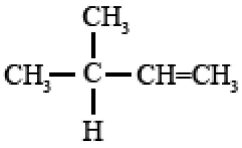
Hence, option (a) is correct.

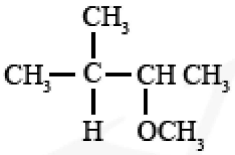
Halo compounds + Compounds containing Oxygen

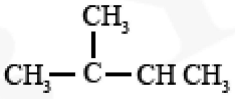
7. The major product of the following reaction is :



(✔) **A.** 

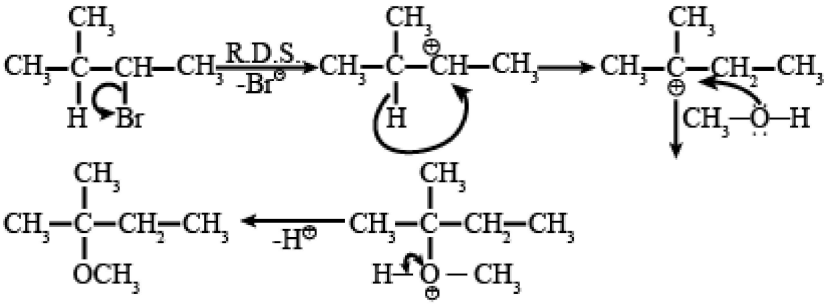
(✘) **B.** 

(✘) **C.** 

(✘) **D.** 

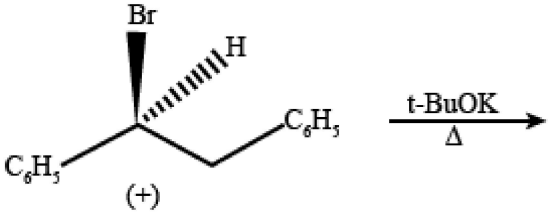
(✘) **E.** Answer not mention

CH_3OH can act as weak nucleophile or weak base.
Substrate forms secondary carbocation which can undergoes H-shift to form tertiary carbocation so S_N1 is prefered over S_N2.
CH_3OH is smaller in size so in this case substitution is preferred over elimination.
Hence, the major product will be the product of S_N1 reaction mechanism which includes rearrangement.



Halo compounds + Compounds containing Oxygen

8. The major product obtained in the following reaction is :



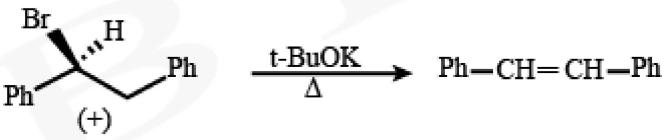
A. $C_6H_5CH = CHC_6H_5$

B. $(+)C_6H_5CH(O^tBu)CH_2C_6H_5$

C. $(-)C_6H_5CH(O^tBu)CH_2C_6H_5$

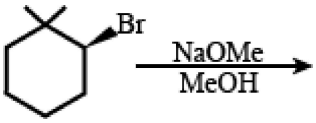
D. $(\pm)C_6H_5CH(O^tBu)CH_2C_6H_5$

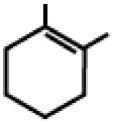
Potassium tertiary butoxide is a bulky base, thus, it will favour elimination reaction.
Heating of reaction also favour elimination reaction.
There is only one possible way for $\beta-$ elimination and it is the major product.

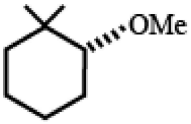


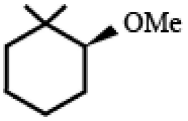
Halo compounds + Compounds containing Oxygen

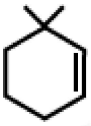
9. The major product of the following reaction is :



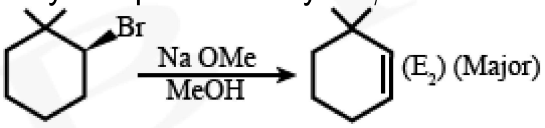
✗ **A.** 

✗ **B.** 

✗ **C.** 

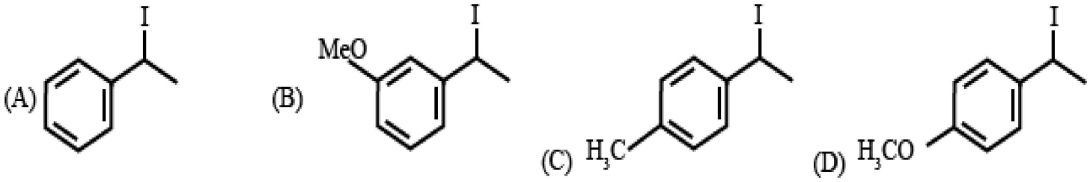
✓ **D.** 

$NaOMe$ is a strong base so it undergoes E2 elimination reaction. There is only one possible way for $\beta-$ elimination and it is the major product.



Halo compounds + Compounds containing Oxygen

10. Increasing rate of S_N1 reaction in the following compunds is :



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

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

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

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

In S_N1 reaction mechanism, formation of carbocation is the rate determining step.
Thus,
$\text{Rate of reaction} \propto \text{stability of carbocation}$

All the given compound forms benzylic carbocation.
Among them, carbocation of (D) is more stabilised by the +R effect of $-OCH_3$ followed by (C) due to hyperconjugation effect of $-CH_3$.

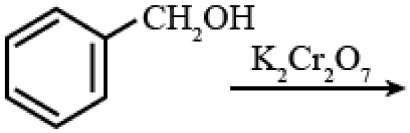
Carbocation of (B) is least stabilised due to presence of carbon cation at meta position and it is also destabilised by -I effect of $-OCH_3$.

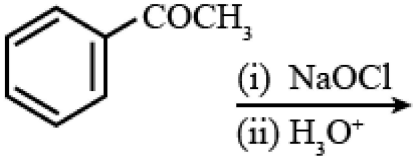
Hence, correct order of stability of carbocation formed is
$B < A < C < D$

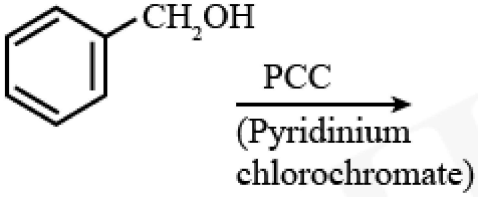
Hence, increasing rate of S_N1 reaction follows the order
$B < A < C < D$

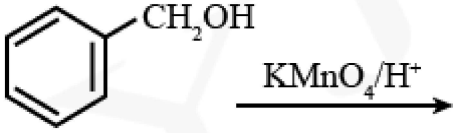
Halo compounds + Compounds containing Oxygen

11. The reaction that does not give benzoic acid as the major product is:

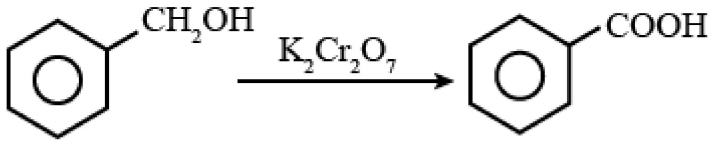
✗ **A.** 

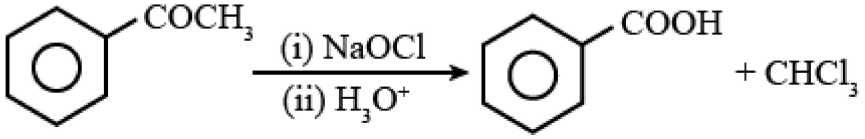
✗ **B.** 

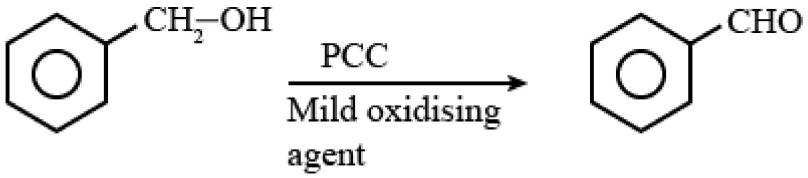
✓ **C.** 

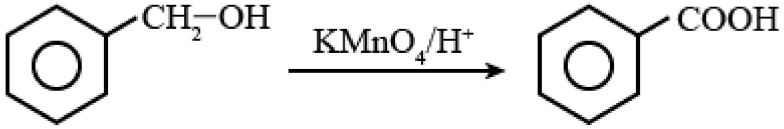
✗ **D.** 

PCC is a mild oxidising agent so it will oxidise primary alcohol to aldehyde. $K_2Cr_2O_7$ and $KMnO_4/H^+$ are strong oxidising agent, they will oxidise primary alcohol to carboxylic acid.
Sodium hypochlorite will also oxidise terminal $CH_3 - CO$ into acid salt and on hydrolysis it gives carboxylic acid.

(1) 

(2) 

(3) 

(4) 

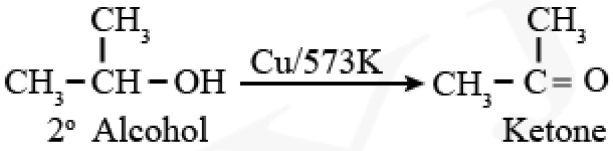
Hence, option (c) is correct.

Halo compounds + Compounds containing Oxygen

12. When vapours of a secondary alcohol is passed over heated copper at $573\ K$, the product formed is:

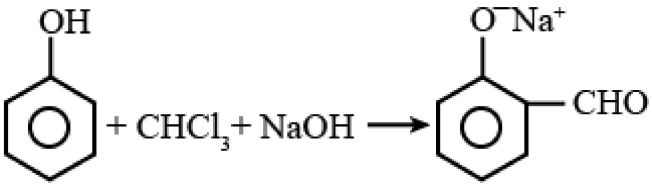
- **A.** a carboxylic acid
- **B.** an aldehyde
- **C.** a ketone
- **D.** an alkene

When vapours of primary, secondary and tertiary alcohols are passed over heated copper at $573\ K$, dehydrogenation of primary and secondary alcohol takes place to form aldehyde and ketone respectively while tertiary alcohols undergo dehydration to given an alkene.



Halo compounds + Compounds containing Oxygen

13. In the reaction



The electrophile involved is

A. Dichloromethyl cation ($\overset{\oplus}{C}HCl_2$)

B. Formyl cation ($\overset{\oplus}{C}HO$)

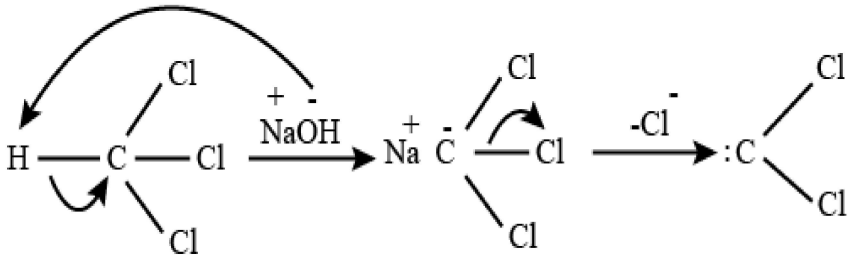
C. Dichlorocarbene (: CCl_2)

D. Dichloromethyl anion ($\overset{\oplus}{C}HCl_2$)

It is Reimer- Tiemann reaction. The electrophile formed is,
: CCl_2 (Dichlorocarbene) according to the following reaction.

The mechanism of Riemer-Tiemann reaction involves 3 steps.

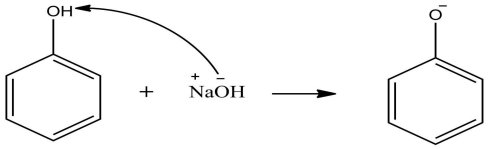
Step-1:
Formation of carbene



DCC

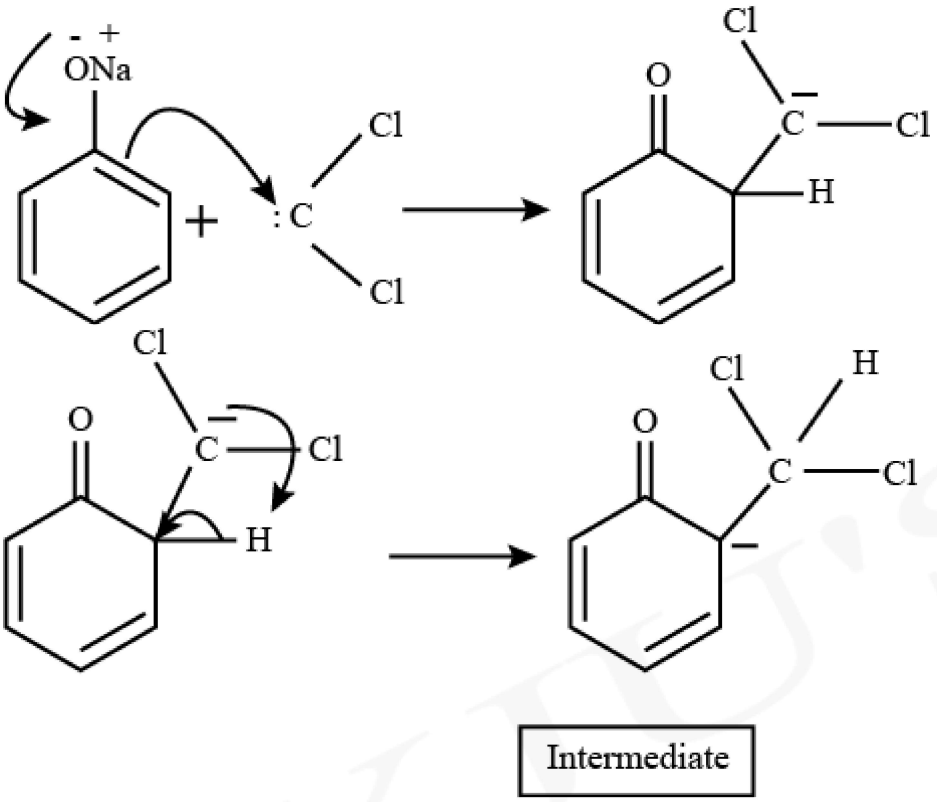
Electrophile

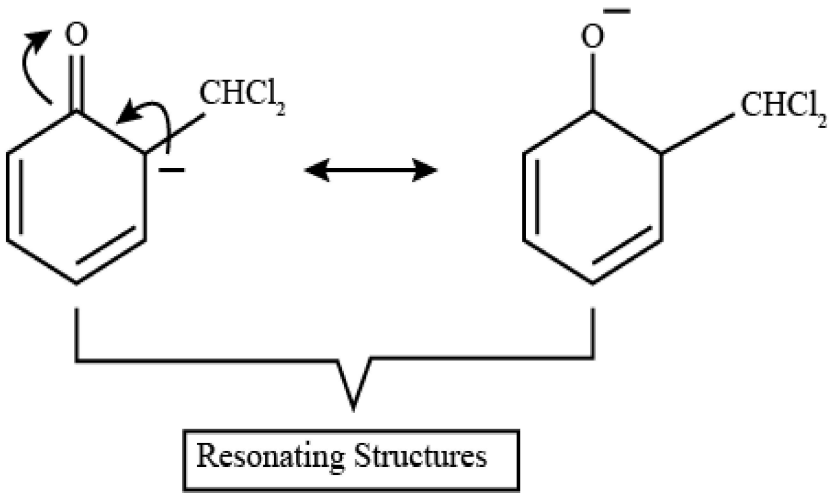
Step-2:
Formation of intermediate



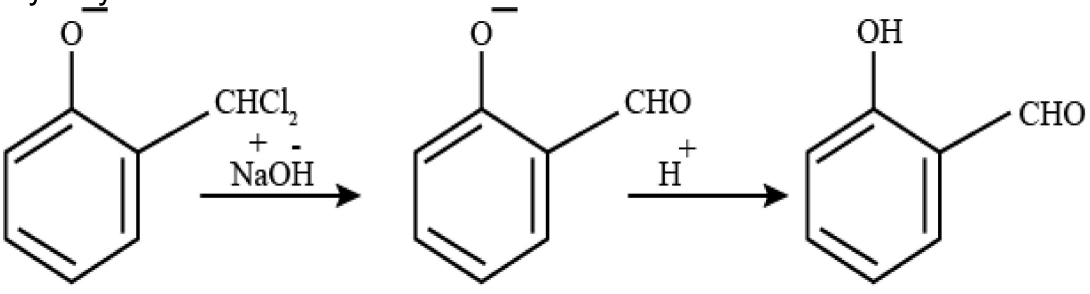
Phenoxide ion

Halo compounds + Compounds containing Oxygen





Step-3:
Hydrolysis of intermediate

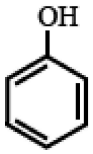


Hence, option (c) is the correct amswer.

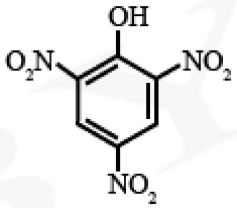
Halo compounds + Compounds containing Oxygen

14. Which one is the most acidic compound?

A. 

B. 

C. 

D. 

Due to the presence of three strong electron withdrawing groups (-M effect) at ortho and para positions, picric acid (2, 4, 6-trinitrophenol) is more acidic compound than (b) and (c).

$-CH_3$ group increases electron density on OH group by hyperconjugation effect, thus it is less acidic.

Hence, option (d) is correct.

Halo compounds + Compounds containing Oxygen

15. Which of the following reagents would distinguish $\text{cis-cyclopenta-1, 2-diol}$ from the trans-isomer?

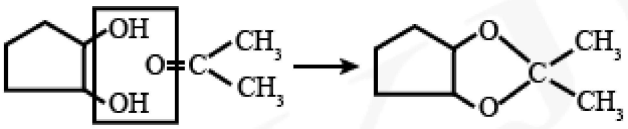
A. Aluminium isopropoxide

B. Acetone

C. Ozone

D. MnO_2

When cis diols reacts with keto group, forms acetal. This happens only when both $-OH$ group are at syn position.
This is a reaction of protection of diols by keto group by forming cyclic acetals.



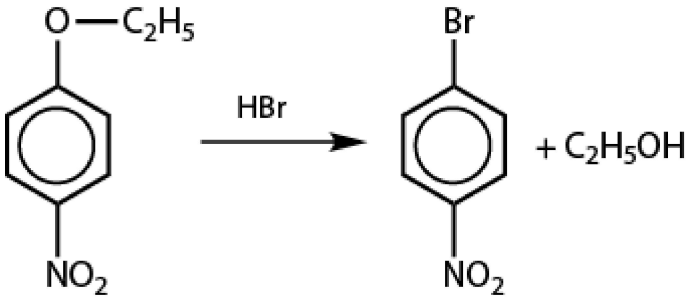
If the $-OH$ at trans position, then the above mentioned reaction does not take place, so alcohol will be free to undergo its respective reactions.

All other reagents does not distinguish the cis and trans isomers.

Hence, option (b) is correct answer.

Halo compounds + Compounds containing Oxygen

16. **Assertion:**



Reason: Due to formation of highly stable carbocation.

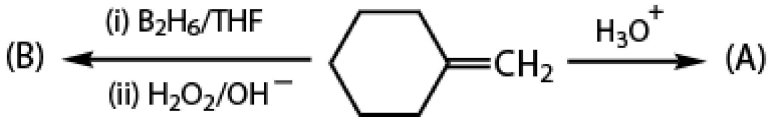
- **A.** Both assertion and reason are true and reason is the correct explanation of assertion
- **B.** Both assertion and reason are true and reason is not the correct explanation of assertion
- **C.** Assertion is true but reason is false
- **D.** Both assertion and reason are false

In case of alkyl aryl ethers, the products are always phenol and alkyl halide and never an aryl halide and alcohol. This is due to the fact that $O-C_6H_5$ bond has partial double bond character and is stronger than $O-C_2H_5$ bond. Therefore, halide ion exclusively breaks the $O-C_2H_5$ bond forming alkyl halide and phenol.

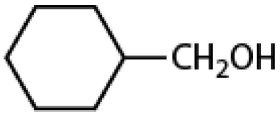
Hence, option (d) is the correct answer.

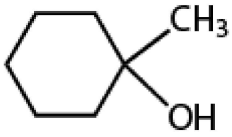
Halo compounds + Compounds containing Oxygen

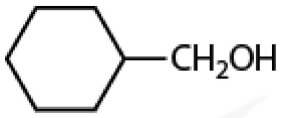
17. In the following reaction,

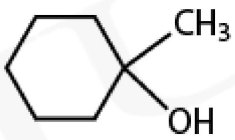


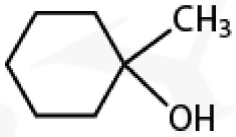
(A) and (B) respectively, are

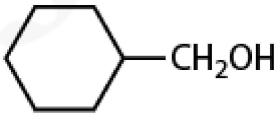
A. Both are 

B. Both are 

C. 

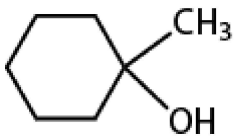
and 

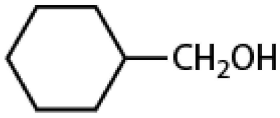
D. 

and 

When methylenecyclohexane undergoes hydrolysis, 1-methylcyclohexanol (A) is formed by Markovnikov addition.

When methylenecyclohexane reacts with reagents such as B_2H_6/THF, a product is formed which further undergoes reaction with hydrogen peroxide to form cyclohexylmethanol (B).
This reagent is particularly used to get alcohol product by anti-markovnikov addition.
Thus, products (A) and (B) respectively are:



and 

Hence, option (d) is correct answer.

Halo compounds + Compounds containing Oxygen

18. Consider the following reaction:

$$\text{Phenol} \xrightarrow{\text{Zn dust}} X \xrightarrow[\text{Anhydrous } AlCl_3]{CH_3Cl} Y \xrightarrow{\text{Alkaline } KMnO_4} Z$$

The product Z is

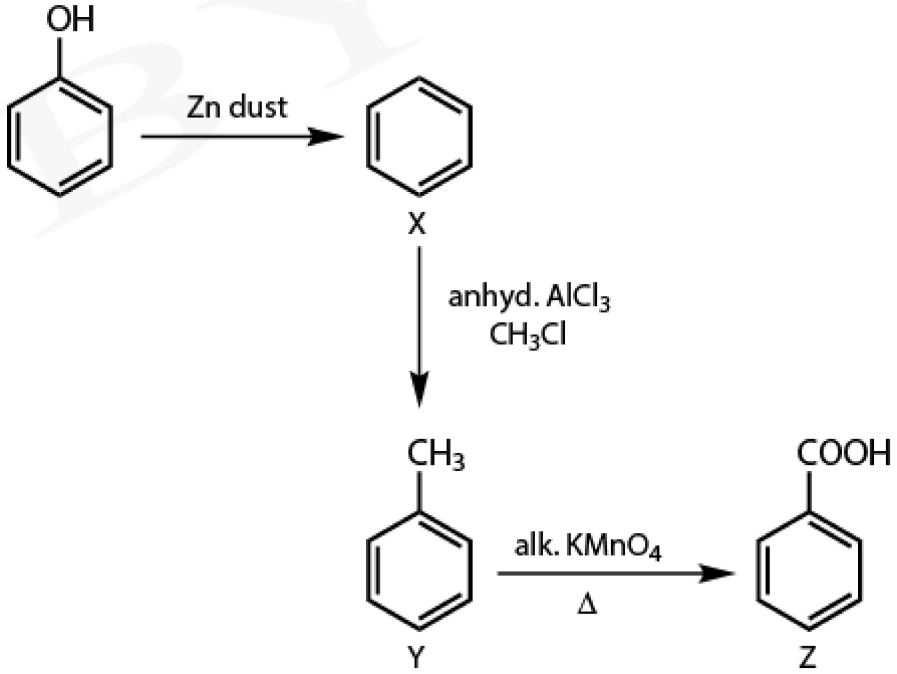
A. Benzene

B. Toluene

C. Benzaldehyde

D. Benzoic acid

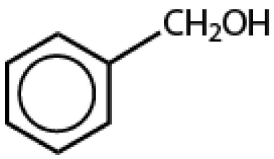
Phenol will reduce to benzene in presence of Zinc dust.
In next step, benzene undergoes Friedel Crafts alkylation to form toluene.
The methyl group in toluene get oxidised to carboxylic acid in presence of alkaline $KMnO_4$.

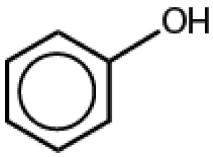


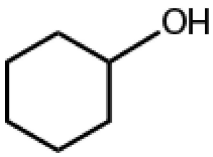
Hence, option (d) is correct.

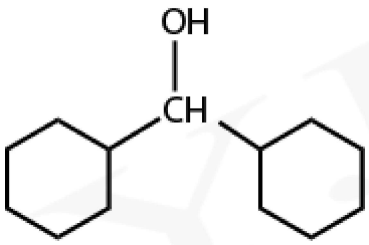
Halo compounds + Compounds containing Oxygen

19. Which one of the following compound has the most acidic nature?

A. 

B. 

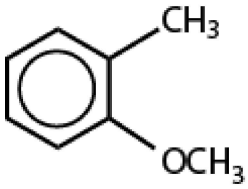
C. 

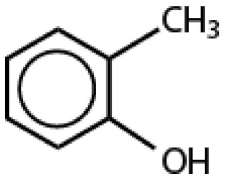
D. 

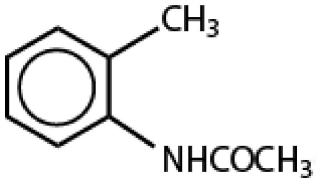
Acidic nature is directly proportional to the stability of conjugate base formed when acidic H is removed. Since negative charge formed on phenol will be delocalised in the whole ring. Hence, it will be most stable. So, phenol will be most acidic compound.
Hence, option (b) is correct answer.

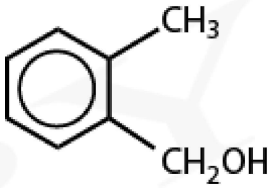
Halo compounds + Compounds containing Oxygen

20. Which one of the following is most reactive towards electrophilic reagent?

A. 

B. 

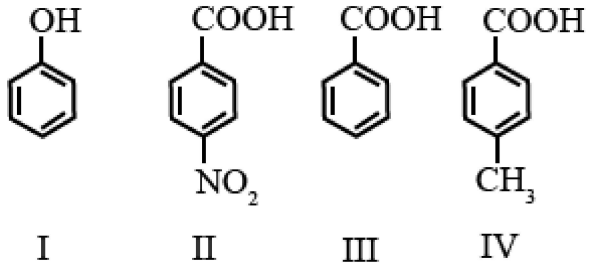
C. 

D. 

CH_2OH group shows -I effect and it deactivates benzene ring.
Order of +M effect:
$-OH > -OR > -NHCOR$
Thus, $-OH$ will increase the electron density at ortho/para position to greater extent and hence, compound (b) is the most reactive towards electrophilic aromatic substitution.

Halo compounds + Compounds containing Oxygen

21. The correct order of acid character of the following compounds is :



I II III IV

A. $IV > III > II > I$

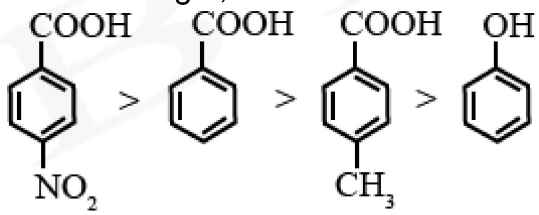
B. $II > III > IV > I$

C. $I > II > III > IV$

D. $III > II > I > IV$

Carboxylic acids are more acidic than phenols .
$-I$ and $-R$ effect increase the acidic strength where as $+I$ and $+R$ effect decreases the acidic strength of carboxylic acids.

Acidic strength,



Hence, option (b) is correct.

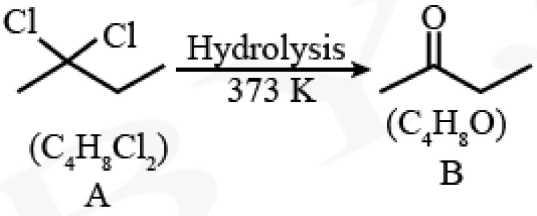
Halo compounds + Compounds containing Oxygen

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

B reacts with Hydroxyl amine but does not give Tollen's test. Identify A and B.

- **A.** 2, 2-Dichlorobutane and Butanal
- **B.** 1, 1-Dichlorbutane and Butanal
- **C.** 1, 1-Dichlorobutane and Butan-2-one
- **D.** 2, 2-Dichlorobutane and Butan-2-one

Carbonyl groups reacts with hydroxyl amine but only ketone does not give Tollen's test.
Hence, compound (B) should be a ketone.
Thus, only secondary dihalide (geminal) on hydrolysis gives keto group.



$(C_4H_8Cl_2)$ A

(C_4H_8O) B

Hence,
A$\rightarrow$ 2, 2-Dichlorobutane
B $\rightarrow$ Butan-2-one

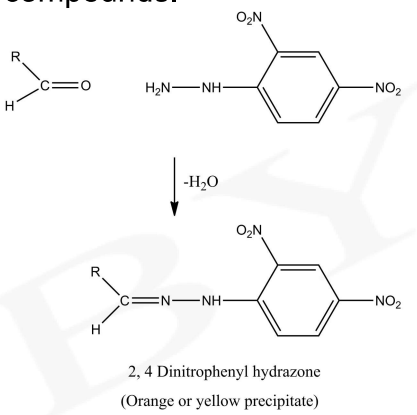
So correct option should be (d).

Halo compounds + Compounds containing Oxygen

23. 2, 4-DNP test can be used to identity

- ✔ **A.** Aldehyde
- ✘ **B.** Amine
- ✘ **C.** Ether
- ✘ **D.** Halogens

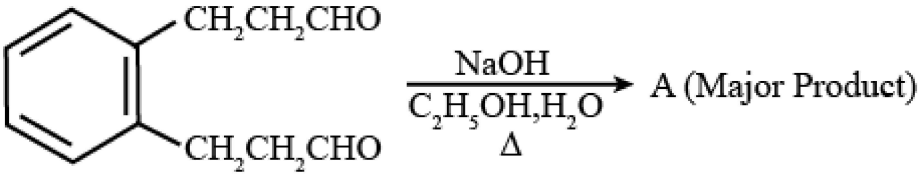
2,4 DNP test to identify $-\overset{\overset{O}{\|}}{C}-$ group. It gives condensation reaction with carbonyl compounds. So, it can be used to identify aldehyde in the given option. It gives yellow/orange precipitate with carbonyl containing compounds.

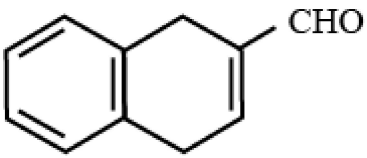


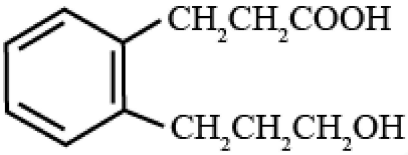
2, 4 Dinitrophenyl hydrazone
(Orange or yellow precipitate)

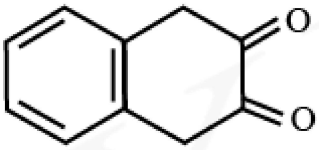
Halo compounds + Compounds containing Oxygen

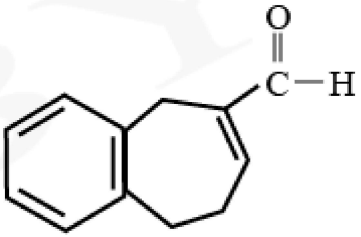
24. Identify A in the given chemical reaction.



✗ **A.** 

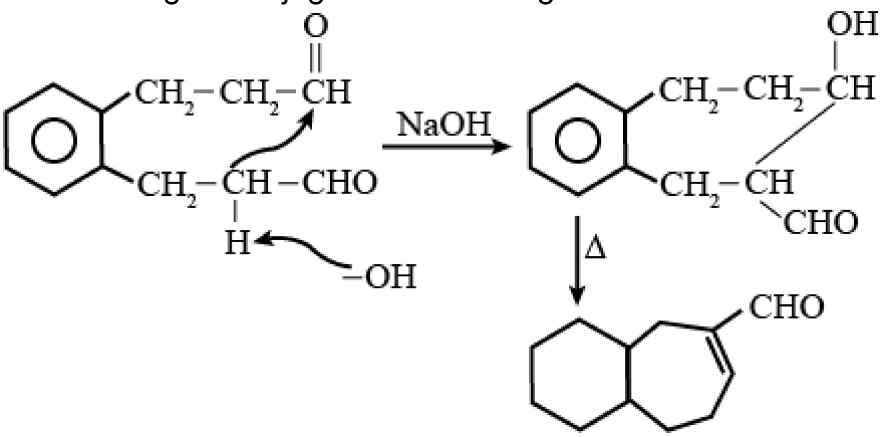
✗ **B.** 

✗ **C.** 

✓ **D.** 

Aldehyde with alpha hydrogens undergoes aldol condensation in presence of dilute base followed by removal of water molecule during heating.

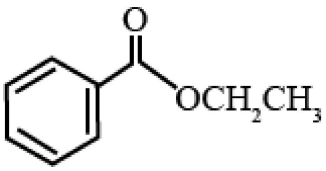
In the given molecule, there are two symmetrical aldehyde group so it will undergoes intramolecular aldol condensation followed by condensation reaction to give conjugated enone as given below:

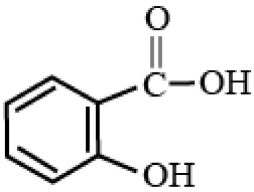


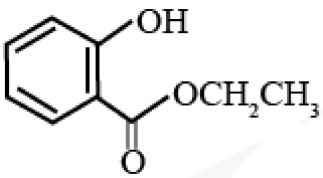
Hence, option (d) is correct.

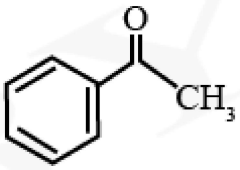
Halo compounds + Compounds containing Oxygen

25. Which one of the following compounds will give orange percipitate when treated with 2, 4-dinitrophenyl hydrazine?

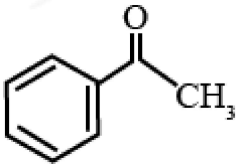
A. 

B. 

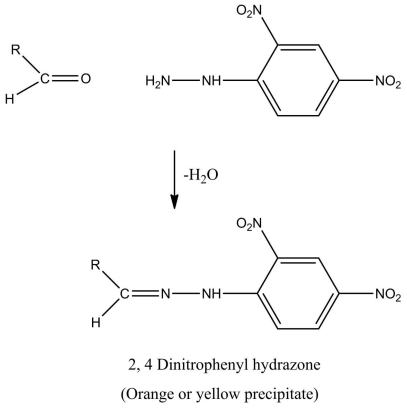
C. 

D. 

2, 4 DNP (2,4-dinitrophenyl hydrazine) test is used to identify aldehyde and ketone group. It gives condensation reaction with carbonyl compounds. It gives yellow/orange precipitate with carbonyl containing compounds.

 give orange ppt with 2,4-dinitrophenyl hydrazine.

General reaction:

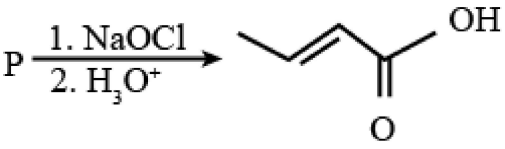


2, 4 Dinitrophenyl hydrazone
(Orange or yellow precipitate)

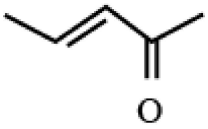
Hence, option (d) is correct.

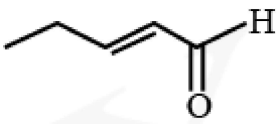
Halo compounds + Compounds containing Oxygen

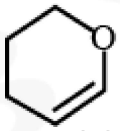
26. The structure of the starting compound P used in the reaction given below is:



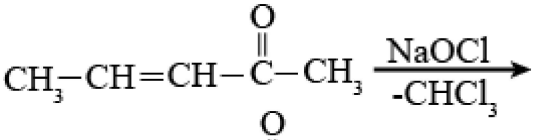
A. 

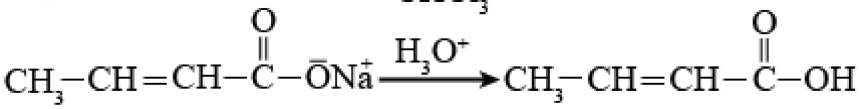
B. 

C. 

D. 

The reagent 'NaOCl' undergoes haloform reaction to give carbocylate ion followed by hydrolysis to give carboxylic acid.
Aldehydes and ketones having 3 α-hydrogen atoms undergo haloform reaction with $NaOCl$.

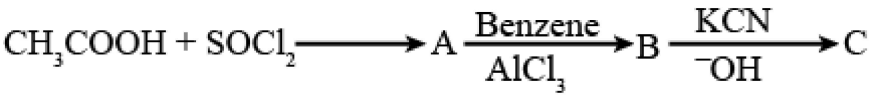


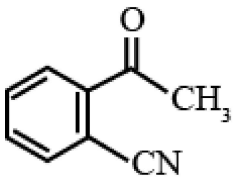


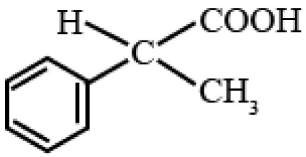
Hence, option (b) is the correct answer.

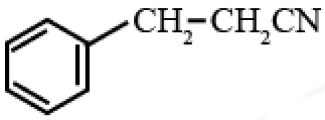
Halo compounds + Compounds containing Oxygen

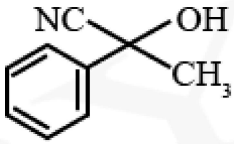
27. The structure of product C, formed by the following sequence of reaction is :



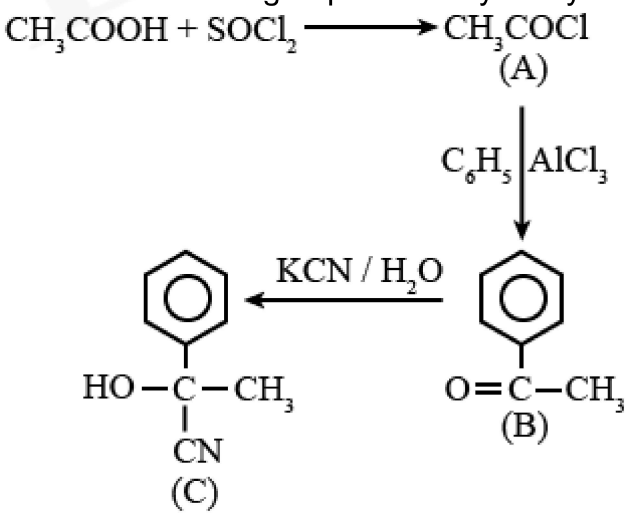
A. 

B. 

C. 

D. 

Carboxylic acid with $SOCl_2$ gives acid chloride.
Acid chloride with benzene and lewis acid $(AlCl_3)$ undergoes Friedel craft acylation reaction. In final step, CN^- undergoes nucleophilic addition reaction with keto group to form cyanohydrin.



Hence, option (d) is the correct answer.

Halo compounds + Compounds containing Oxygen

28. $\mathrm{R - CN} \xrightarrow[(ii)\ \mathrm{H_2O}]{(i)\ \mathrm{DIBAL\text{-}H} } \mathrm{R - Y}$ Consider the above reaction and identify "Y"

A. $-CH_2NH_2$

B. $-CHO$

C. $COOH$

D. $-CONH_2$

H^- from DIBAL-H undergoes nucleophilic addition reaction with nitrile followed by hydrolysis to give aldehyde group.

$$\mathrm{R - CN} \xrightarrow[(ii)\ \mathrm{H_2O}]{(i)\ \mathrm{DIBAL\text{-}H} } \mathrm{R - CHO}$$

Hence, option (b) is correct.

Halo compounds + Compounds containing Oxygen

29. Match List-I with List-II

List-I (Chemical reaction)	List-II (Reagent used)
(a)$CH_3COOCH_2CH_3 \rightarrow CH_3CH_2OH$	(i)CH_3MgBr/H_3O^+ (1 equivalent)
(b) $CH_3COOHCH_3 \rightarrow CH_3CHO$	(ii)H_2SO_4/H_2O
(c) $CH_3C \equiv N \rightarrow CH_3CHO$	(iii)$DIBAL - H/H_2O$
(d) $CH_3C \equiv N \rightarrow CH_3COCH_3$	(iv) $SnCl_2, HCl/H_2O$

Choose the most appropriate match.

A. $(a)-(ii), (b)-(iii), (c)-(iv), (d)-(i)$

B. $(a)-(iii), (b)-(ii), (c)-(i), (d)-(iv)$

C. $(a)-(ii), (b)-(iv), (c)-(iii), (d)-(i)$

D. $(a)-(iv), (b)-(ii), (c)-(iii), (d)-(i)$

Halo compounds + Compounds containing Oxygen

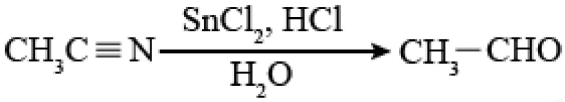
(a) Ester get hydrolysed to respective acid and alcohol in presence of sulphuric acid.

$$CH_3COOCH_2CH_3 \xrightarrow[H_2O]{H_2SO_4} CH_3COOH + CH_3CH_2OH$$

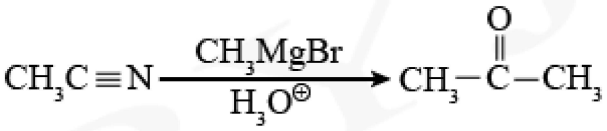
(b) DIBAL-H will reduce esther group to aldehyde.

$$CH_3COOCH_3 \xrightarrow[H_2O]{DIBAL-H} CH_3 - CHO + CH_3OH$$

(c)
This reaction is called stephen reaction. It involves the preparation of aldehydes from nitriles using tin(II) chloride, hydrochloric acid and quenching the resulting iminium salt with water. During the synthesis, ammonium chloride is also produced.



(d) When nitriles react with grignard reagent R^- from the grignard will undergo nulceophilic addtion reaction to form imine product.
Imine will undergo hydrolysis to form keto product.

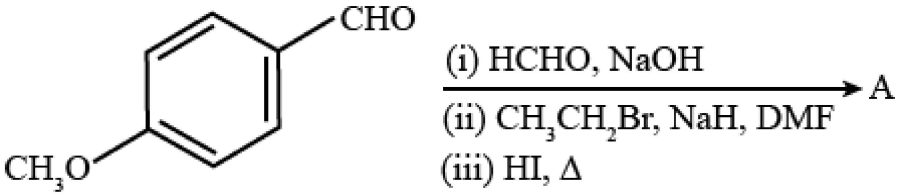


So, the correct match is
$(a) - (ii), (b) - (iii), (c) - (iv), (d) - (i)$

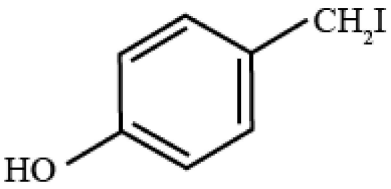
Cyanides can also be converted to aldehydes by $DIBAL - H/H_2O$ as well.

Halo compounds + Compounds containing Oxygen

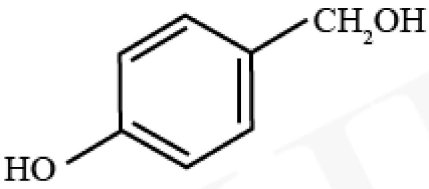
30. Identify A in the following chemical reaction.



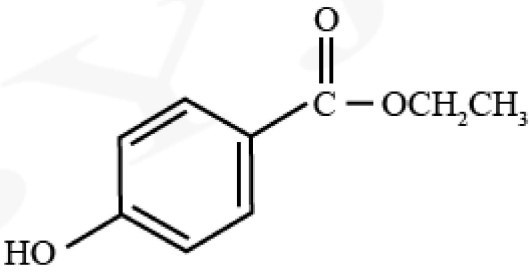
✔ **A.**



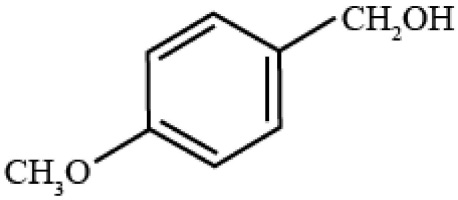
✘ **B.**



✘ **C.**



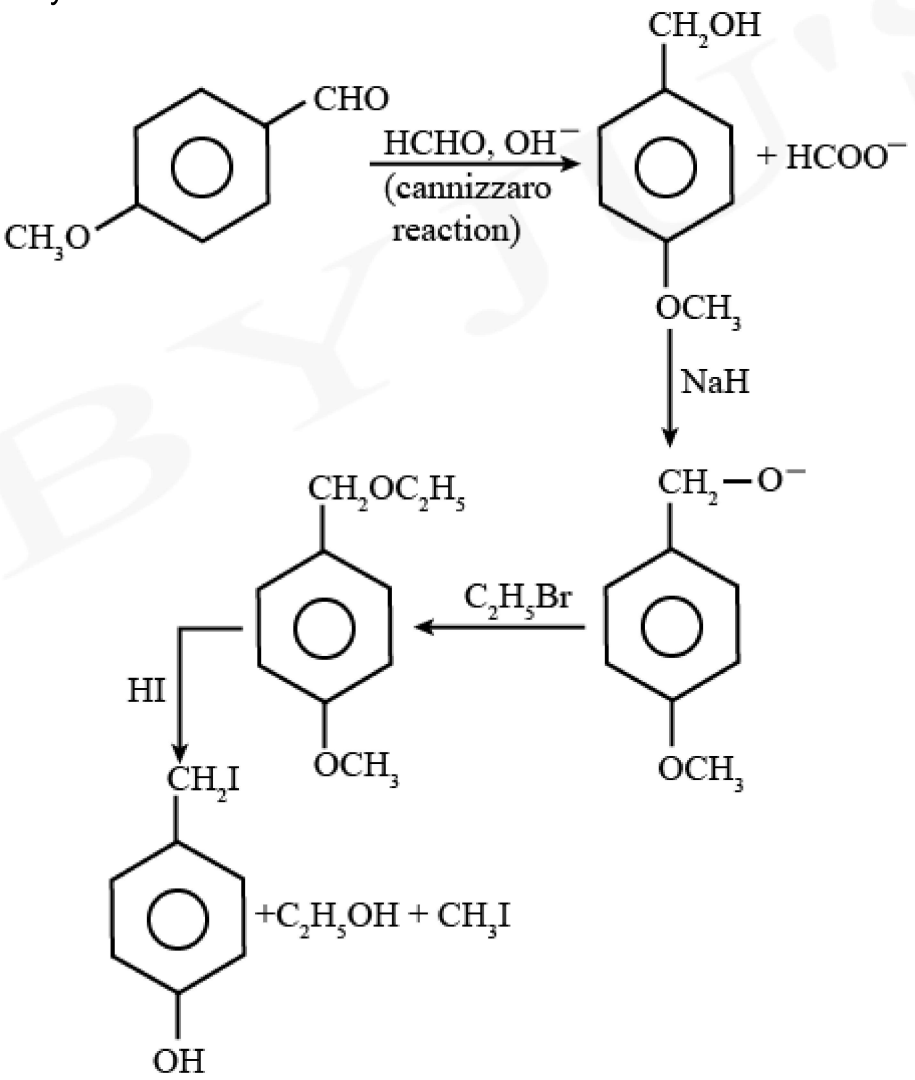
✘ **D.**



Halo compounds + Compounds containing Oxygen

Aldehydes which does not have α-Hydrogen undergoes cannizzaro reaction.
In crossed cannizzaro reaction, aldehyde which has less steric and highly positive carbonyl carbon undergoes oxidation and other will undergo reduction.
In second step, the alcohol group gets depronated by H^- from NaH and followed by S_N2 reaction to form ether compound.

In final step, ether on reaction with HI undergoes S_N2 or S_N1 reaction depends on the nature substrate.
Benzylic cation is highly stable so it undergoes S_N1 to form the major product.
Also, at another position, ether cleavage occurs by S_N2 reaction since, phenyl cation is unstable.



Hence, option (a) is correct.