

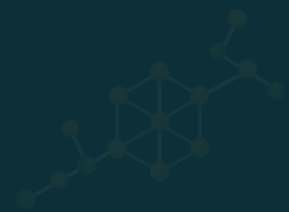
CRACK JEE 2023

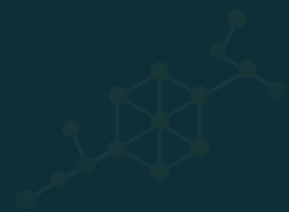


**ALCOHOLS, PHENOLS
AND ETHERS - L4**

**CHEMICAL
PROPERTIES**

GRADE 12 | CHEMISTRY

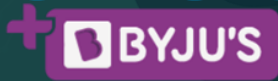




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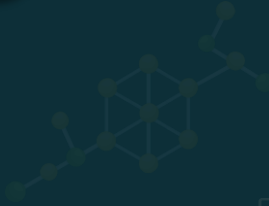
Acidity of Phenols

Reaction with **metals**



Phenols release **H₂** gas on reaction with sodium or potassium or other alkali metals.

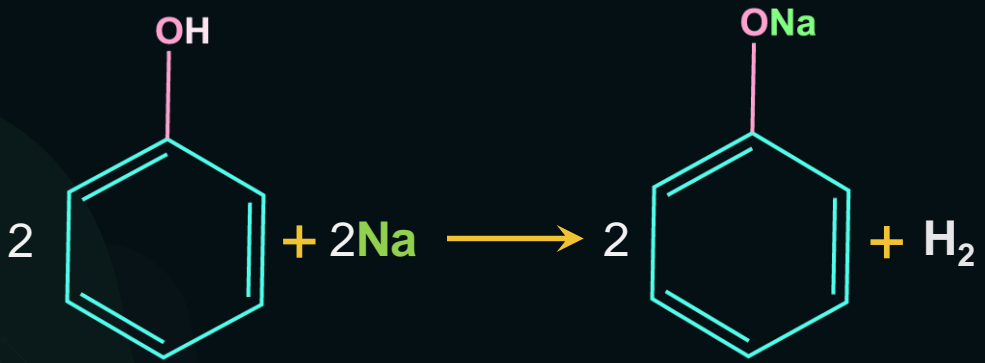
This reflects the **presence** of **acidic** hydrogen.



n=0



Acidity of Phenols



Polarization of the **O-H** bond makes the **hydrogen** partially positive and makes them **weak acid**.



Comparison of Acidity of Phenol and Alcohols



Acidity of Phenol and Alcohols



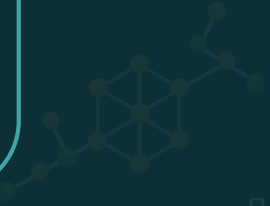
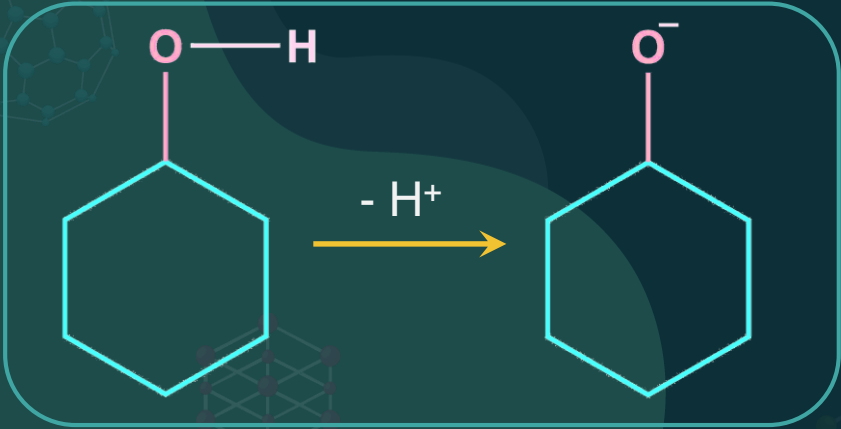
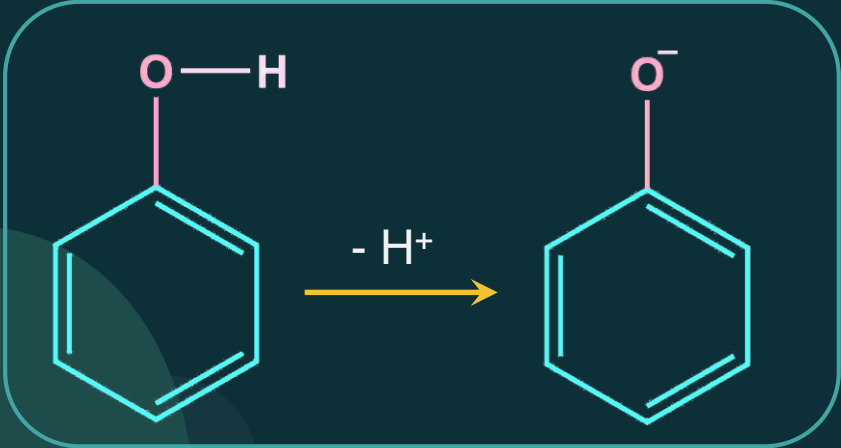
Although phenols are **structurally similar** to alcohols, they are much **stronger acids**.



Cyclohexanol
 $\text{pK}_a = 18$



Phenol
 $\text{pK}_a = 9.89$

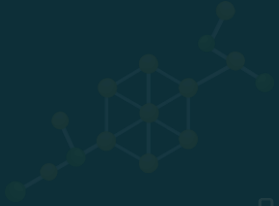




Acidity of Phenol



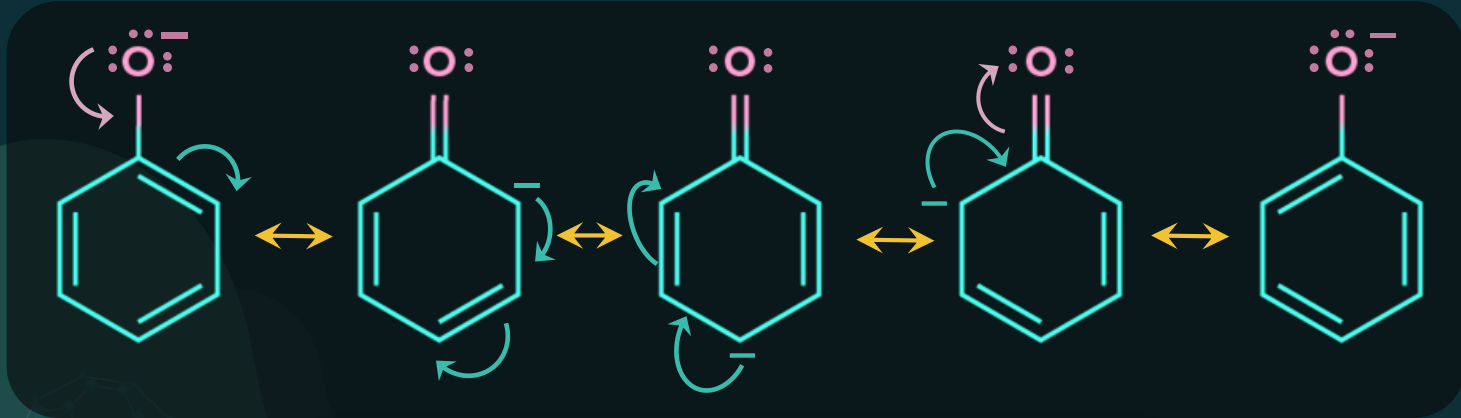
The hydroxyl group in phenol is directly attached to the **sp² hybridised carbon** of benzene ring, that acts as an **electron withdrawing** group because of more 's' character in it and thus, **stabilising** the negative charge of **oxygen** atom.



n=0



Acidity of Phenol

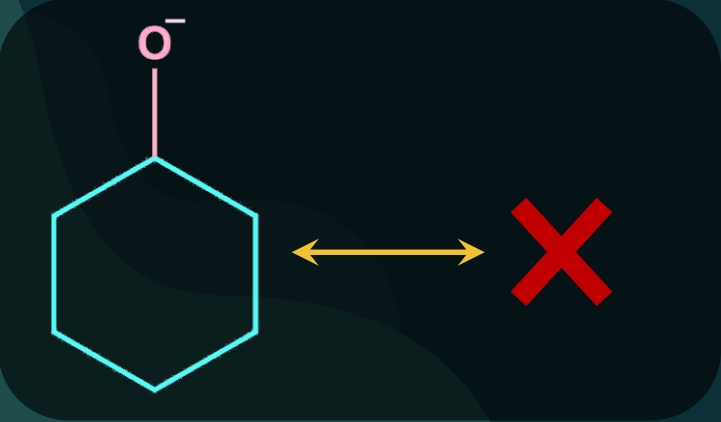


Phenoxide ion (conjugate base of phenol) is **resonance stabilised**



Acidity of Phenol

No stabilisation by resonance





Acidity of Phenols

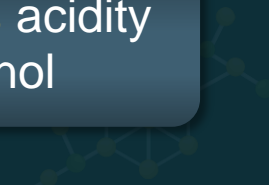
-I, -M
groups

Increase acidity
of phenol

They effectively **disperse** the
-ve charge on phenoxide ion.

+I, +M
groups

Decreases acidity
of phenol



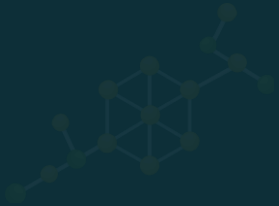


The **order of pK_a** values for the following compounds is:

m-Nitrophenol

o-Nitrophenol

p-Nitrophenol



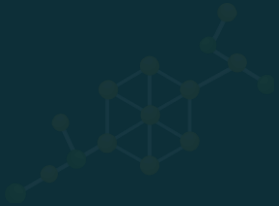


The **order of pK_a** values for the following compounds is:

o-Cresol

m-Cresol

Phenol



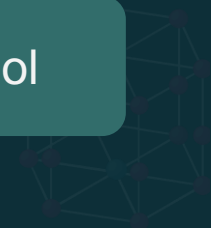
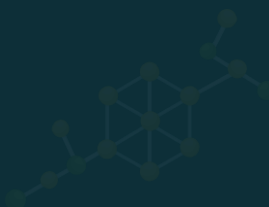


The **order of pK_a** values for the following compounds is:

Ethanol

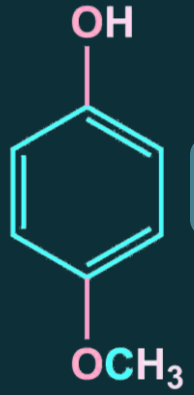
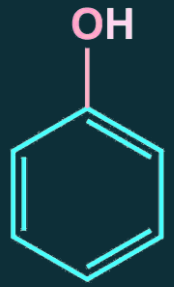
p-Cresol

m-Cresol





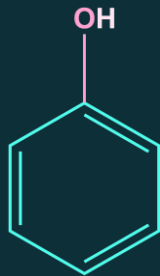
The order of pK_a values for the following compounds is:





Which one is the **most acidic** compound?

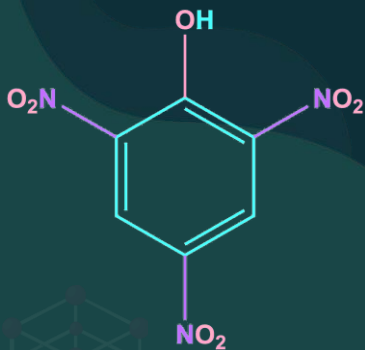
a)



b)



c)



d)



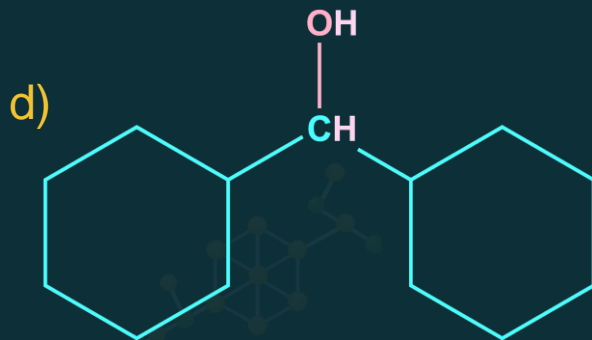
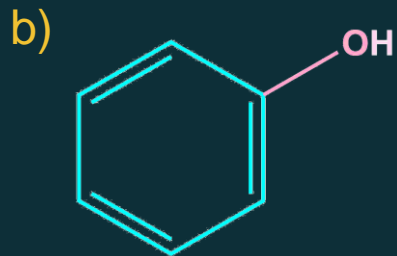
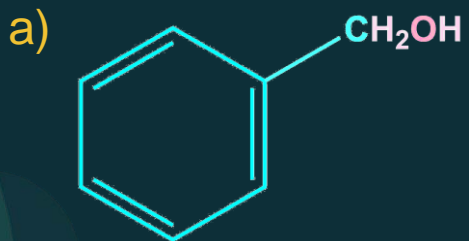
NEET
2017





Which of the following compounds has the **most acidic nature**?

AIPMT
2010





Which of the following fact(s) explain(s) as to why **p-nitrophenol is more acidic than phenol?**

AIIMS 2015

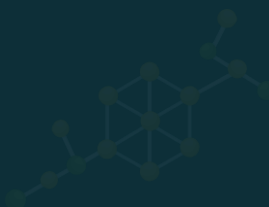
- (i) -I Effect of nitro group.
- (ii) Greater resonance effect of p-nitrophenoxy group
- (iii) Steric effect of bulky nitro group



Which of the following fact(s) explain(s) as to why **p-nitrophenol** is more acidic than phenol?

AIIMS 2015

- a) (i) and (ii)
- b) (i) and (iii)
- c) (ii) and (iii)
- d) (ii) alone





Reactions of phenol

1

Oxidation

2

Electrophilic aromatic substitution

3

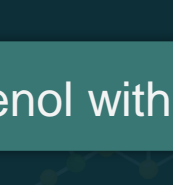
Kolbe reaction

4

Reimer-Tiemann reaction

5

Reaction of phenol with zinc dust





Reactions of phenol

1

Oxidation

2

Electrophilic aromatic substitution

3

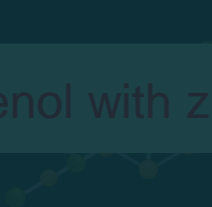
Kolbe reaction

4

Reimer-Tiemann reaction

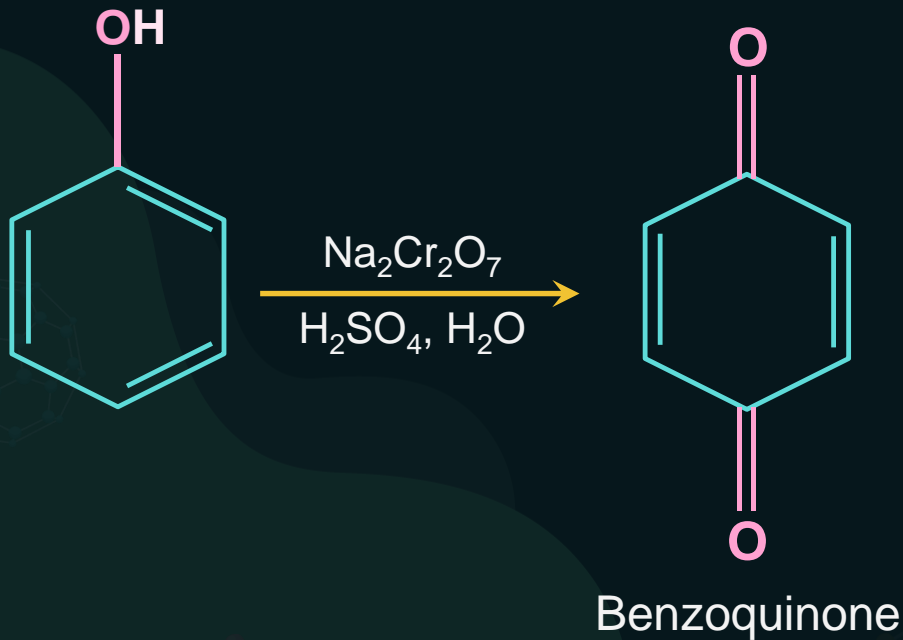
5

Reaction of phenol with zinc dust





Oxidation of Phenol





Reactions of phenol

1

Oxidation

2

Electrophilic aromatic substitution

3

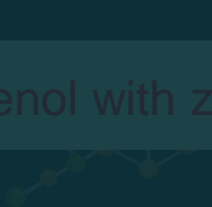
Kolbe reaction

4

Reimer-Tiemann reaction

5

Reaction of phenol with zinc dust



n=0

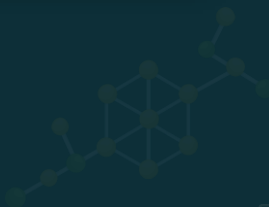


Electrophilic Aromatic Substitution

In electrophilic aromatic substitution, **-OH group** act as

A powerful **activating** group (**+M**)

An **ortho-para** director

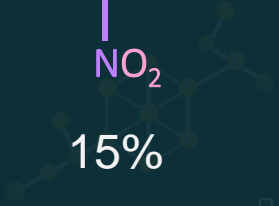
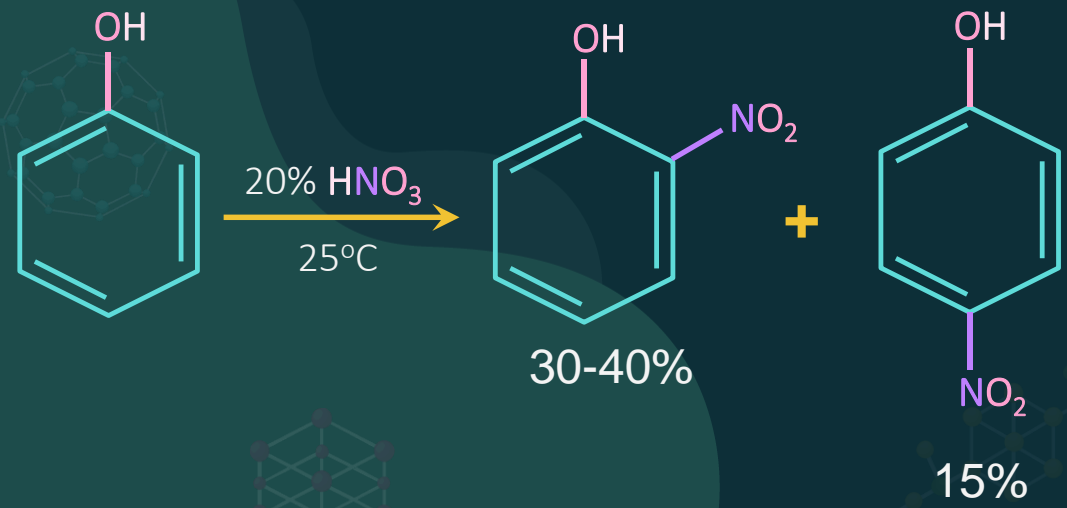


7=0



Nitration

Phenol reacts with dilute nitric acid to yield a mixture of **o-** and **p-Nitrophenol**





Nitration

o-Nitrophenol

p-Nitrophenol

Intramolecular
H-bonding

Intermolecular
H-bonding

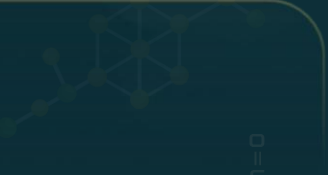
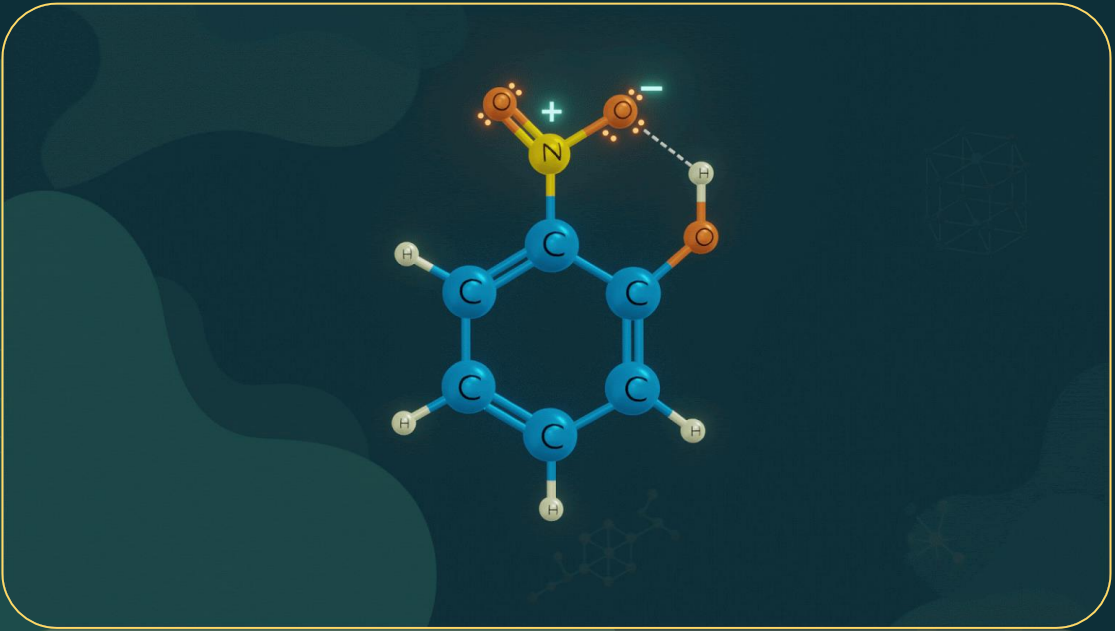
More volatile

Less volatile

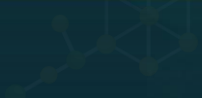
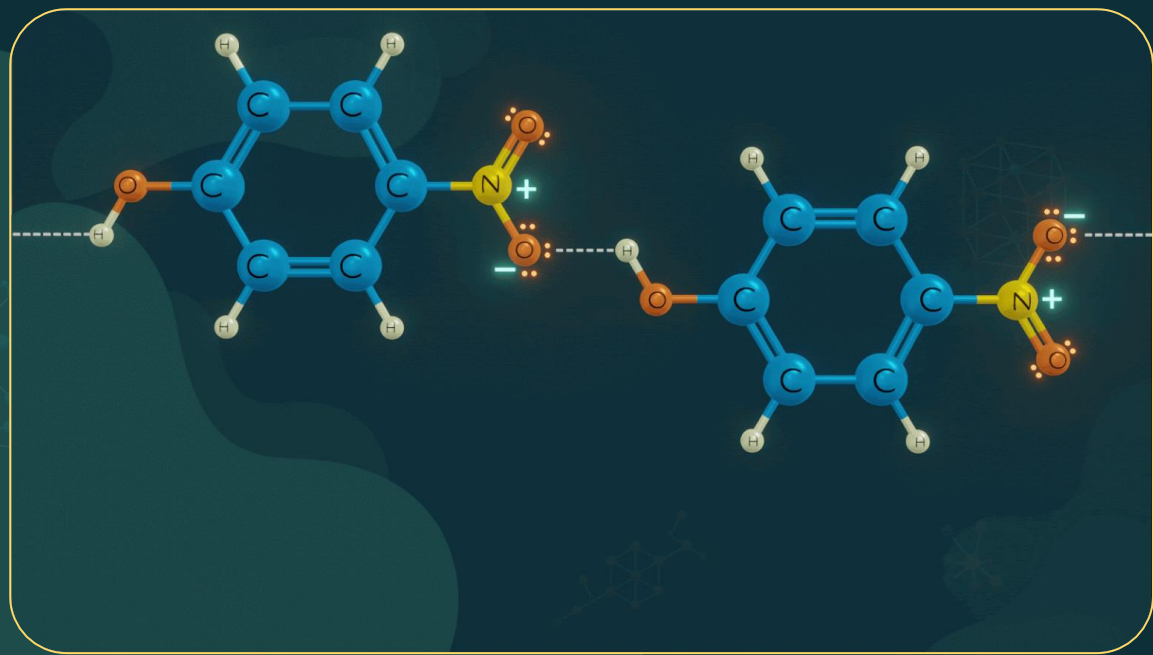
Passes over
with the steam

Remains in the
distillation flask





n=0

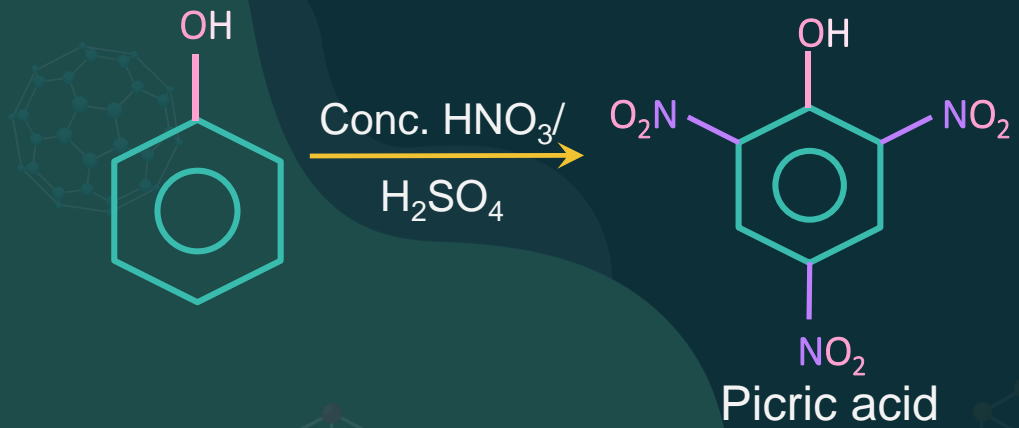


$n=0$



Nitration

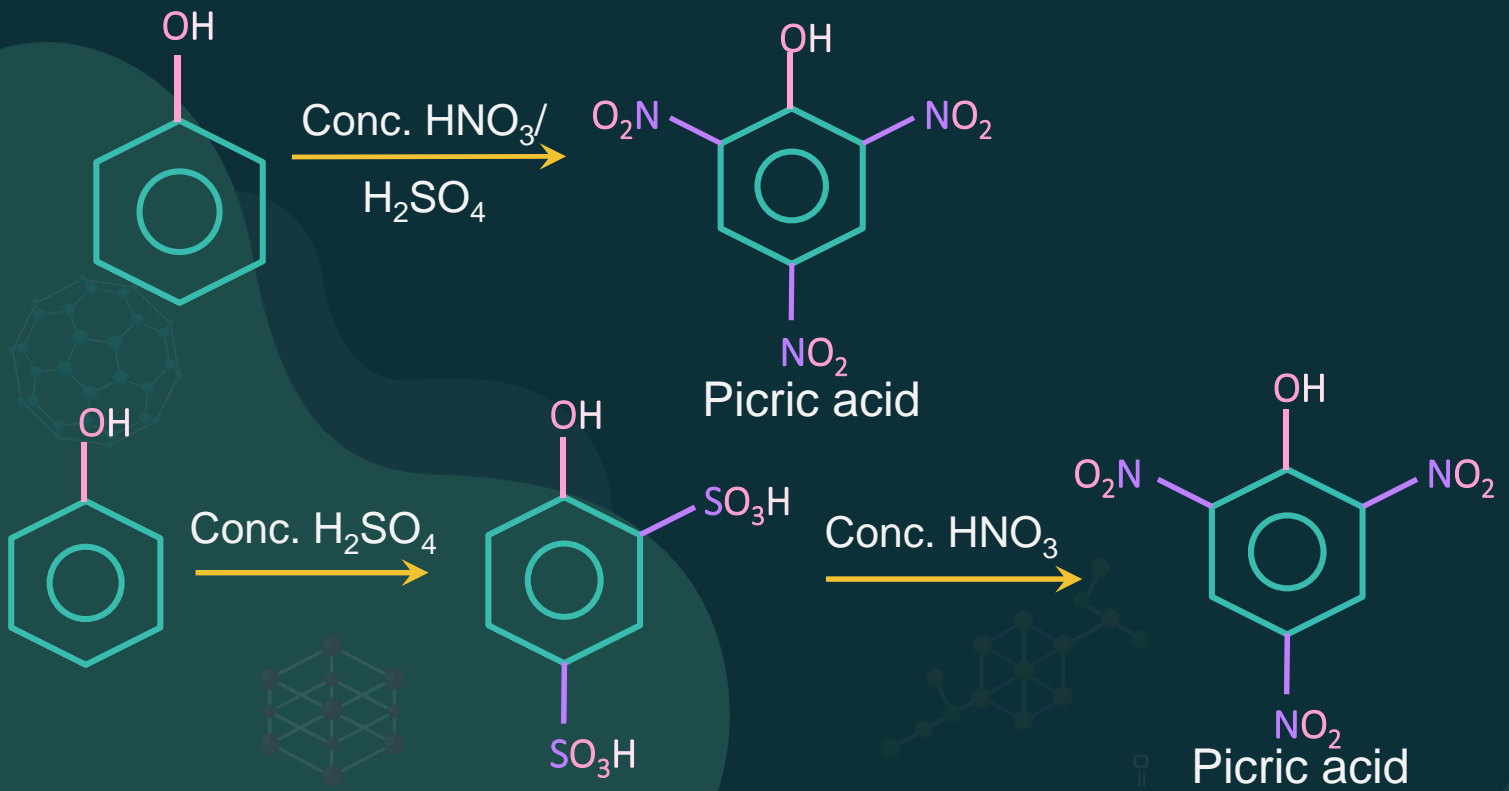
Phenol with conc. nitric acid gives picric acid in **low yield** (because of oxidation of ring).





Nitration

Phenol with conc. nitric acid gives picric acid in **low yield** (because of oxidation of ring).

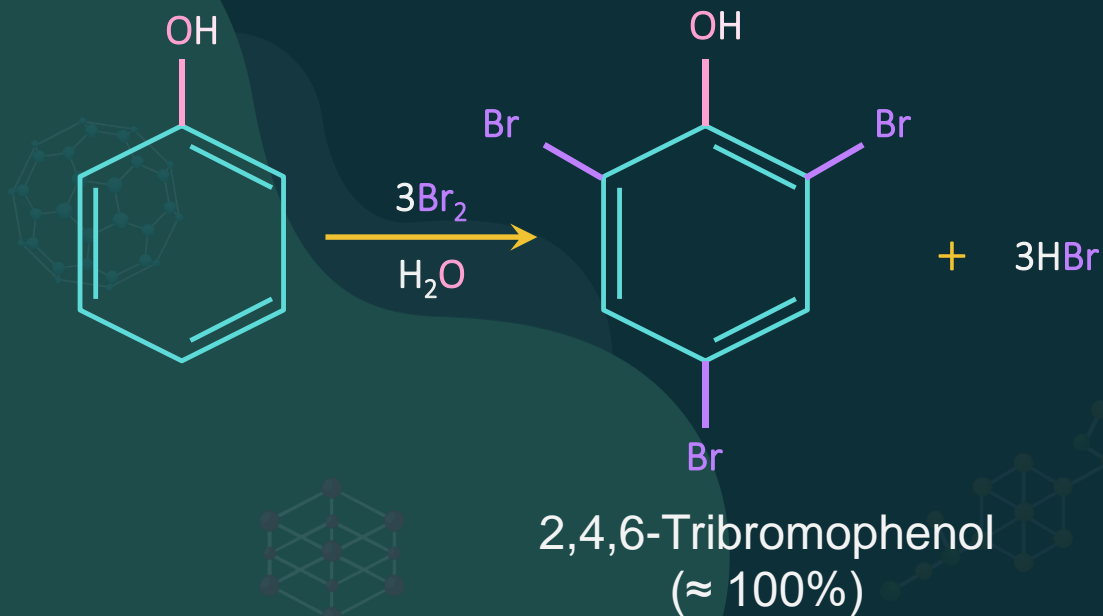




Bromination

Phenol reacts with **bromine** in aqueous solution to yield **2,4,6-Tribromophenol**.

A Lewis acid is **not required** for the bromination of this highly activated ring.

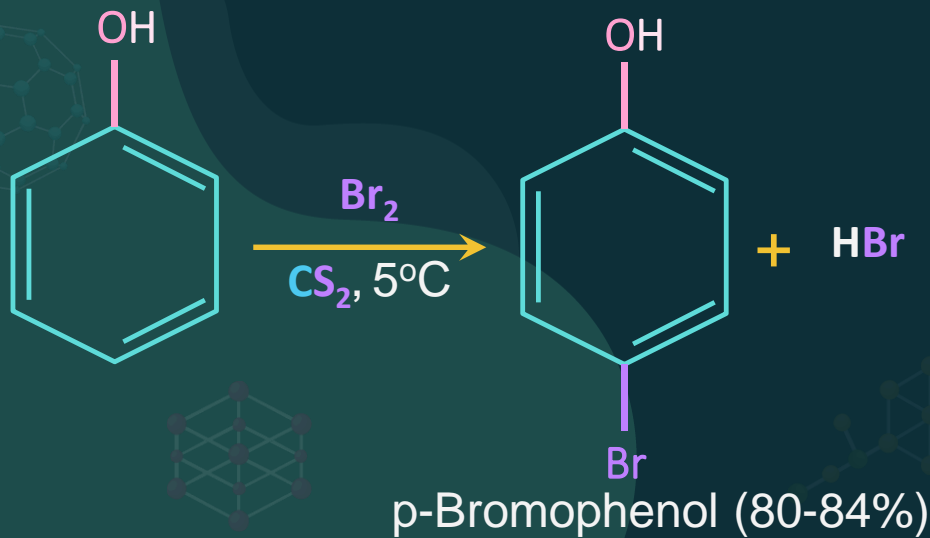




Bromination

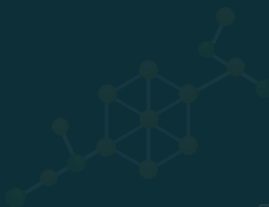
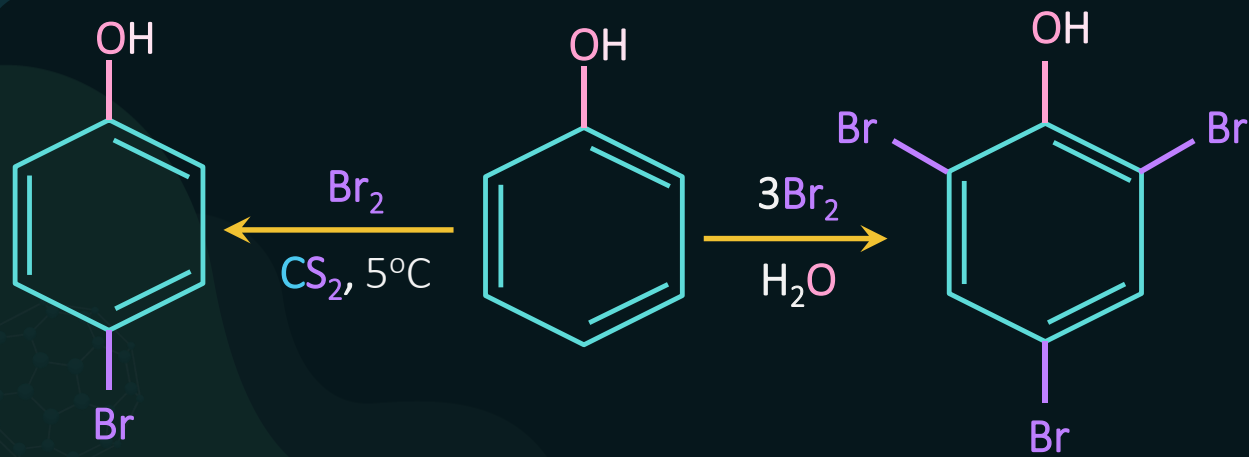
Monobromination of phenol can be achieved by carrying out the reaction in carbon disulfide at a low temperature, conditions that **reduce** the **electrophilic reactivity** of bromine.

The **major product** is the **para isomer**.





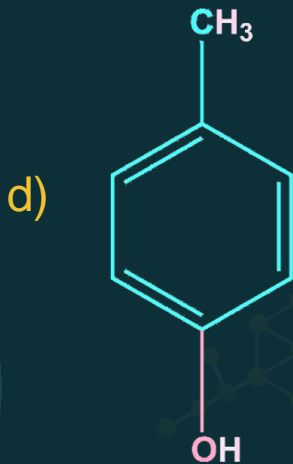
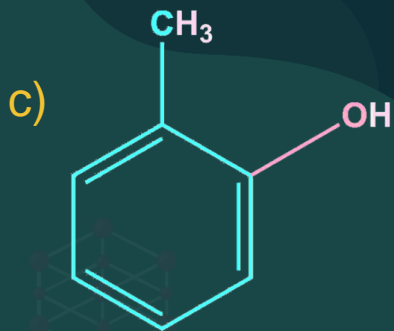
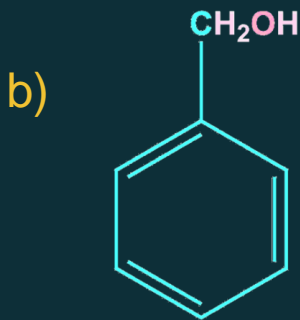
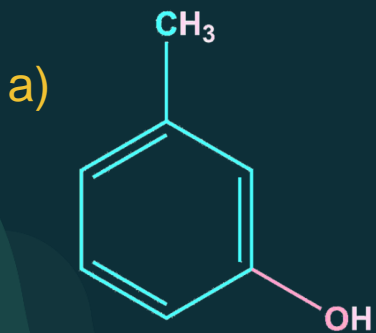
Bromination of Phenol



n=0



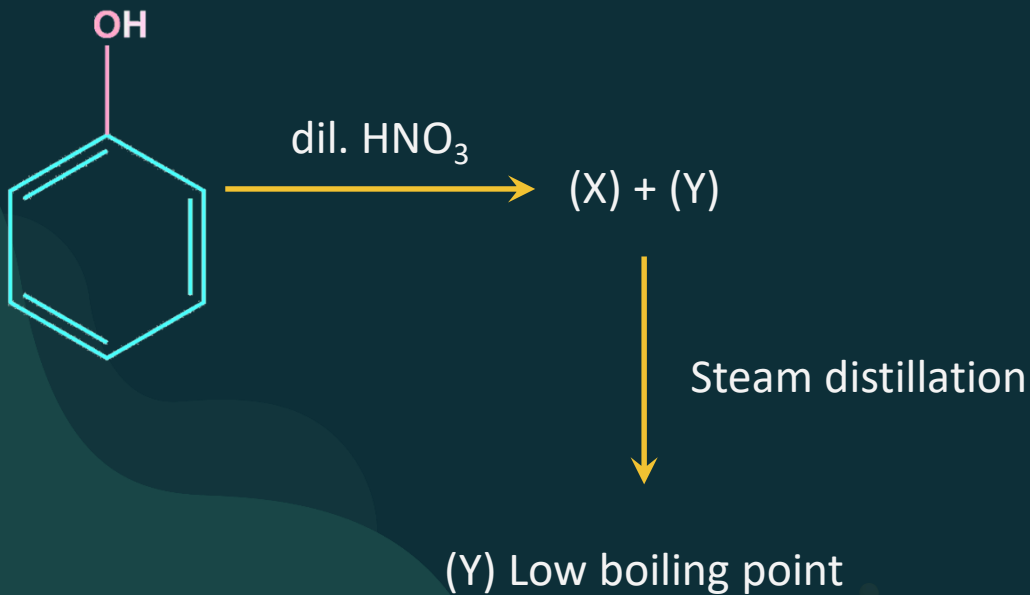
The structure of the compound that gives a **tribromo derivative** on treatment with **bromine water** is:

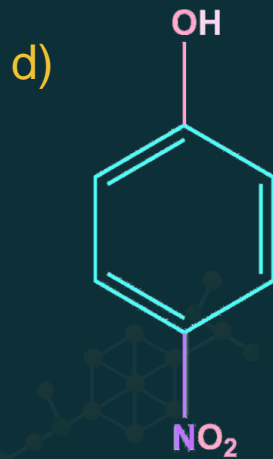
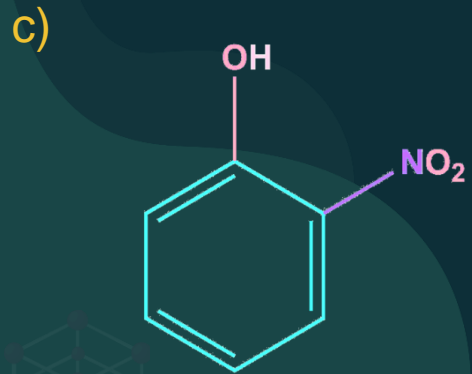
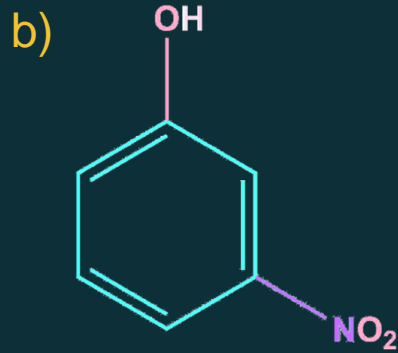
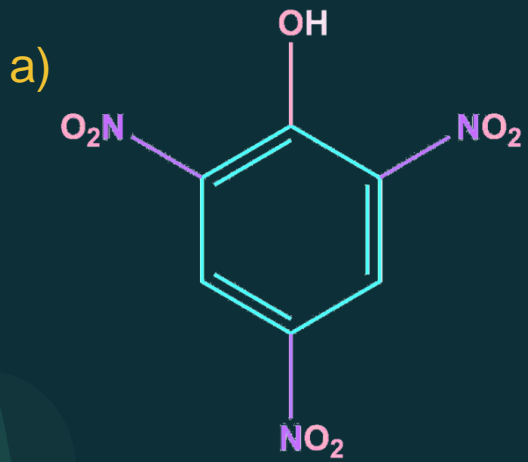




Observe the following reaction.

Y is:







Reactions of phenol

1

Oxidation

2

Electrophilic aromatic substitution

3

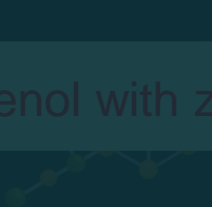
Kolbe reaction

4

Reimer-Tiemann reaction

5

Reaction of phenol with zinc dust





Kolbe Reaction



Kolbe reaction is carried out by allowing **sodium phenoxide** to absorb **carbon dioxide**. Acidification of the resulting mixture produces **salicylic acid**



The phenoxide ion is even **more susceptible** to electrophilic aromatic substitution than phenol itself.

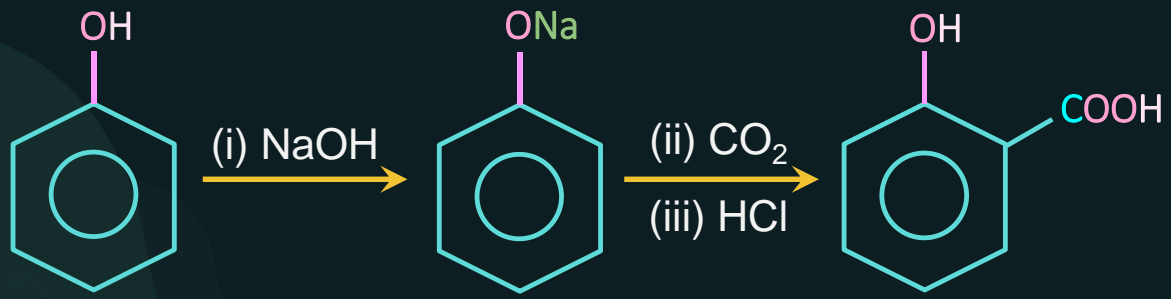


In the Kolbe reaction, CO_2 acts as an **electrophile**.





Kolbe Reaction





Reactions of phenol

1

Oxidation

2

Electrophilic aromatic substitution

3

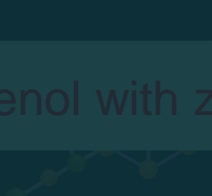
Kolbe reaction

4

Reimer-Tiemann reaction

5

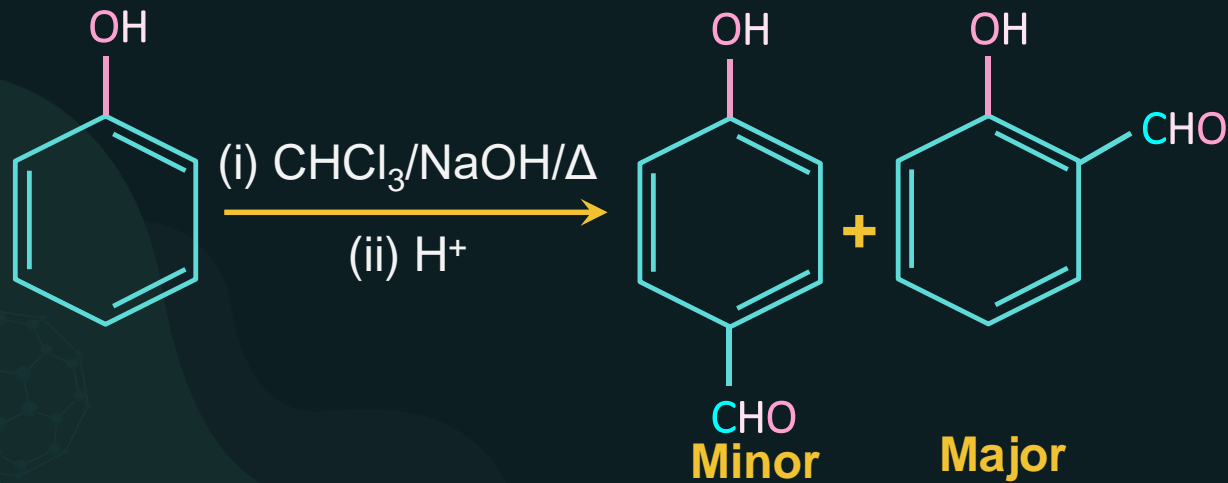
Reaction of phenol with zinc dust



n=0



Reimer-Tiemann Reaction





Reactions of phenol

1

Oxidation

2

Electrophilic aromatic substitution

3

Kolbe reaction

4

Reimer-Tiemann reaction

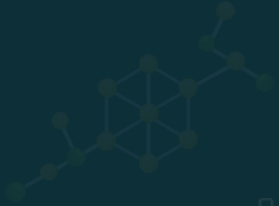
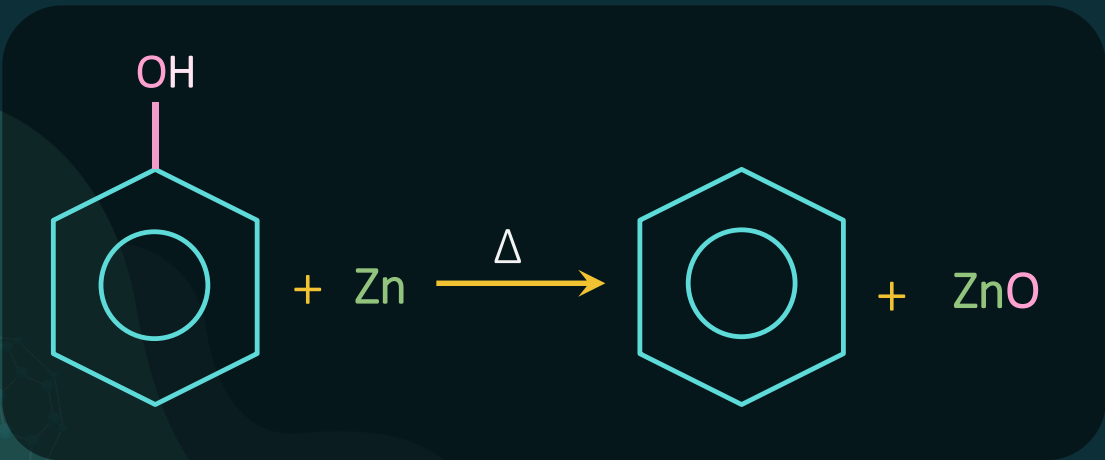
5

Reaction of phenol with zinc dust



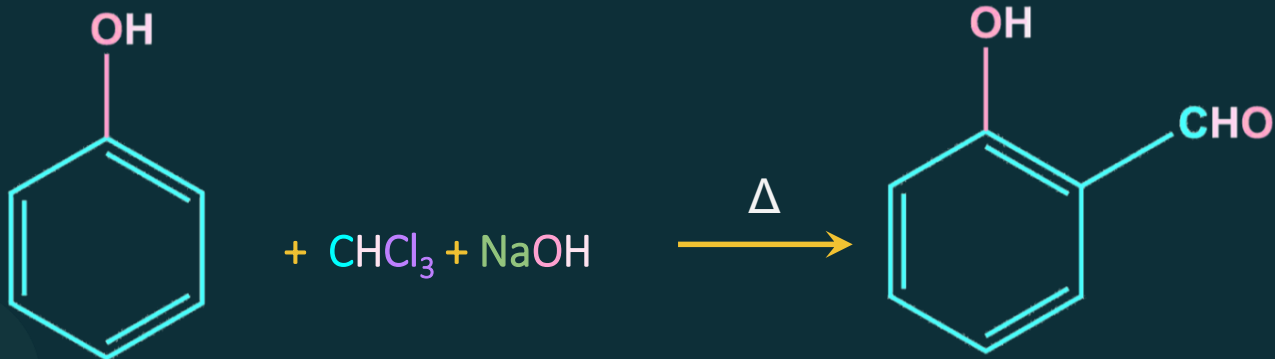


Reaction of Alcohol with Zinc Dust



n=0

Identify the **intermediates** of the following reaction.

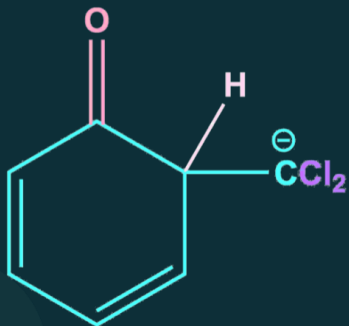




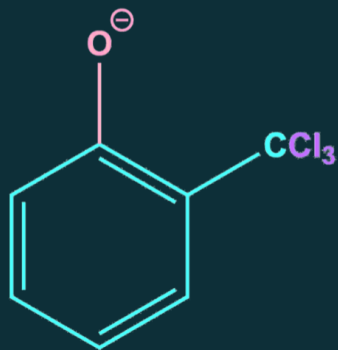
Identify the **intermediates** of the given reaction.



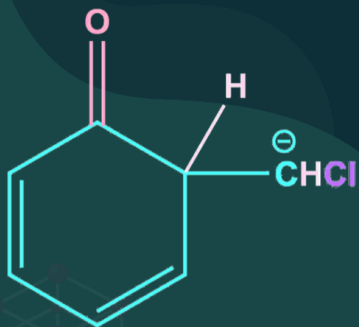
a)



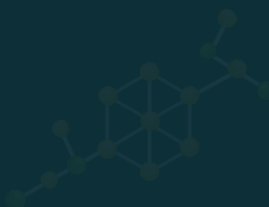
b)



c)



d) All of these

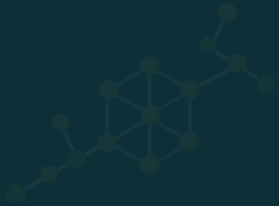




Reaction of phenol with chloroform in presence of dilute sodium hydroxide, finally introduces which one of the following functional group?

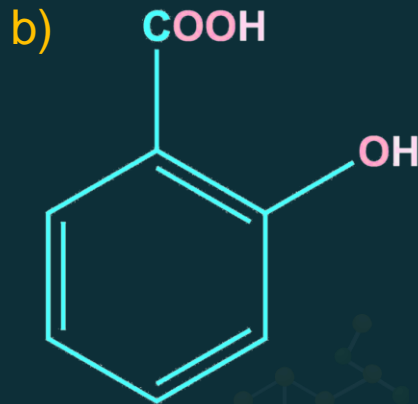
NEET
2015

- a) $-\text{CH}_2\text{Cl}$
- b) $-\text{COOH}$
- c) $-\text{CHCl}_2$
- d) $-\text{CHO}$



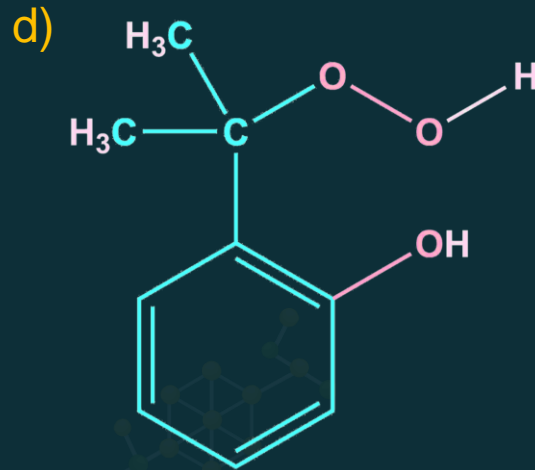
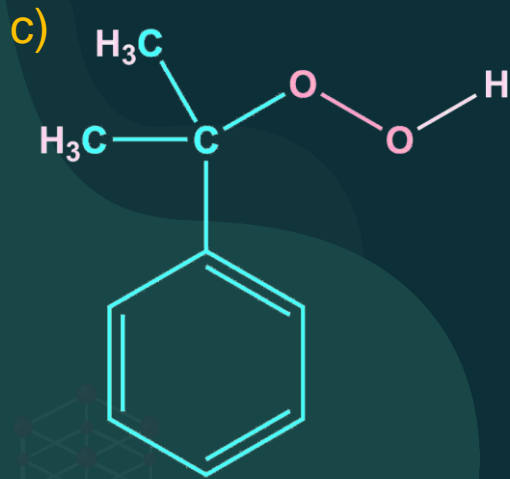


Phenol is distilled with Zn dust followed by Friedel craft alkylation with propyl chloride in presence of $AlCl_3$ to give a compound (B). B is oxidized in presence of air to form compound C. The structural formula of C is:



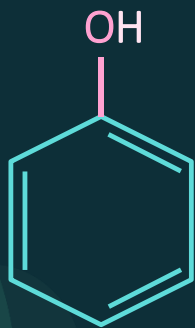


Phenol is distilled with Zn dust followed by Friedel craft alkylation with propyl chloride in presence of $AlCl_3$ to give a compound (B). B is oxidized in presence of air to form compound C. The structural formula of C is:





The **product** obtained from the reaction is:



(i) NaOH

(ii) CO₂



(iii) Hydrolysis

AIIMS 1998,
2017

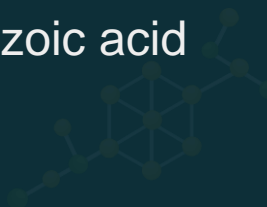


a) Benzene

b) Toluene

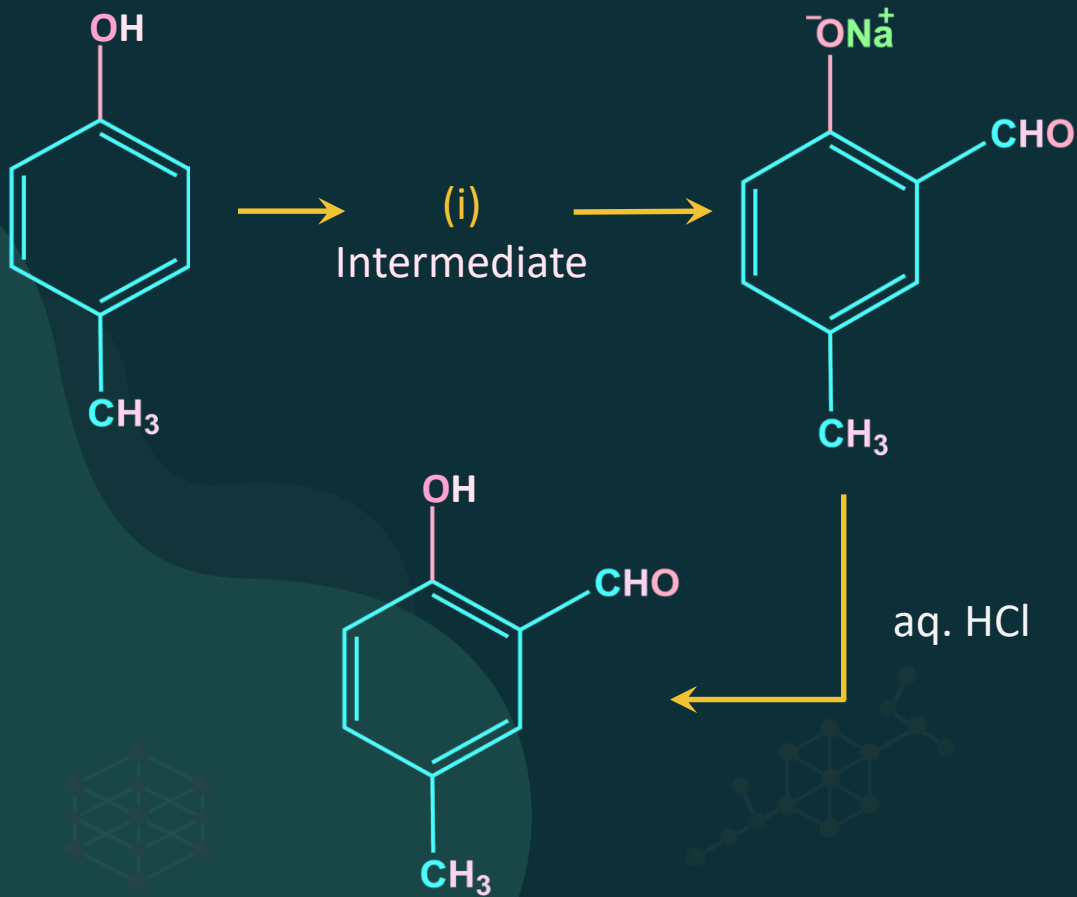
c) Salicylic acid

d) Benzoic acid



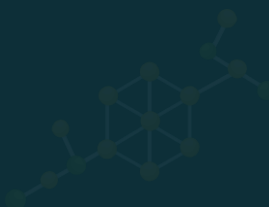


Which one of the following reagents is used in the above reaction?





Which one of the following **reagents** is used in the above reaction?





“Stay Positive, Work Hard. Make It Happen!”

THANK YOU