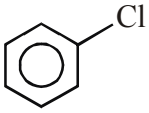
AROMATIC COMPOUNDS

❑ INTRODUCTION

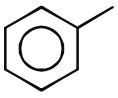
Aromatic hydrocarbons are known generally as arenes. An aryl group is one derived from an arene by removal of a hydrogen atom and its symbol is Ar—. Thus, arenes are designated ArH just as alkanes are designated RH.

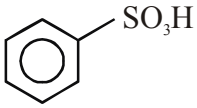
❑ SOME IMPORTANT AROMATIC COMPOUNDS

1. 
Benzene

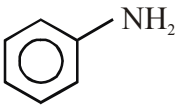
2. 

Chlorobenzene

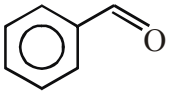
3. 
Toluene

4. 

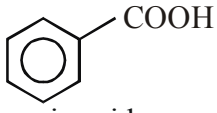
Benzene sulphonic acid

5. 

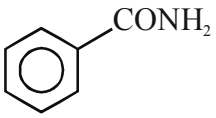
Aniline

6. 

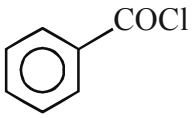
Benzaldehyde

7. 

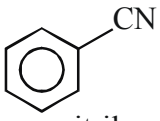
Benzoic acid

8. 

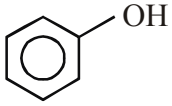
Benzamide

9. 

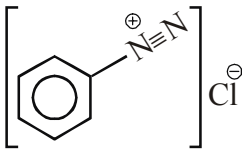
Benzoyl chloride

10. 

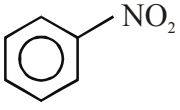
Benzonitrile

11. 

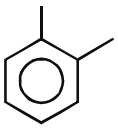
Phenol

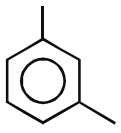
12. 

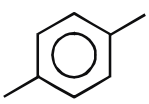
Benzene diazonium salt

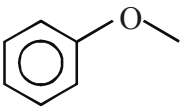
13. 

Niterobenzene

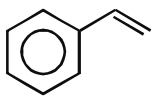
14. 
o-Xylene

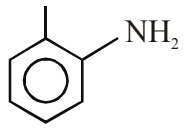
15. 
m-Xylene

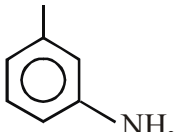
16. 
p-Xylene

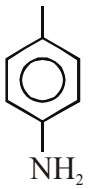
17. 

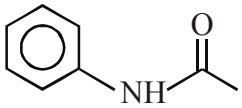
Anisole

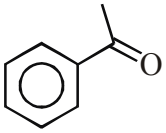
18. 
Styrene

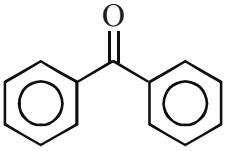
19. 
o-Toluidine

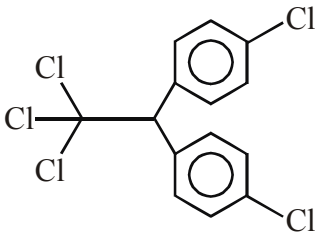
20. 
m-Toluidine

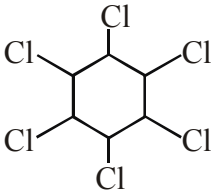
21. 
p-Toluidine

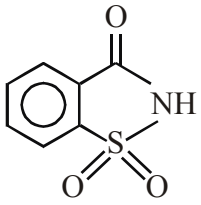
22. 
Acetanialide

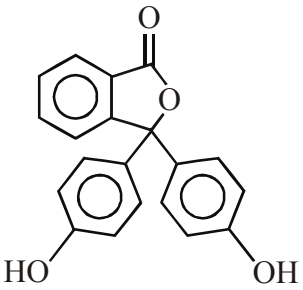
23. 
Acetophenone

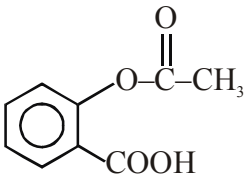
24. 
Acetophenone

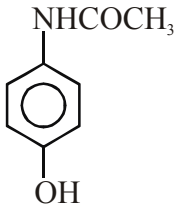
25. 
DDT
(Dihlorodiphynl trichloroethane)

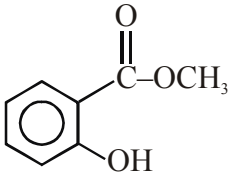
26. 
BHC
(Benzene Hexachloride)

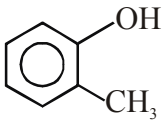
27. 
Saccharin

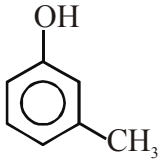
28. 
Phenolphtlalein

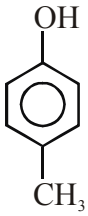
29. 
Aspirine

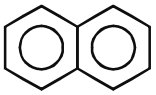
30. 
Paracetamol

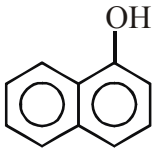
31. 
Oil of wintergreen

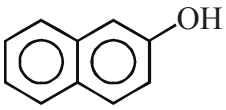
32. 
o-Cresol

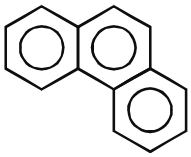
33. 
m-Cresol

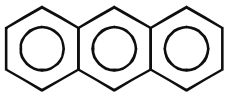
34. 
p-Cresol

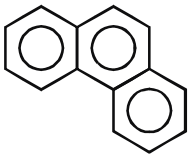
35. 
Napthalene

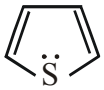
36. 
α-napthol

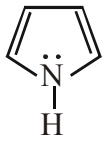
37. 
β-napthol

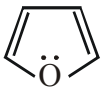
38. 
Phenonthracene

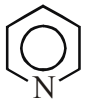
39. 
Anthracene

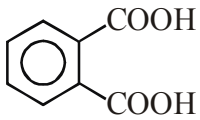
40. 
Phenonthracene

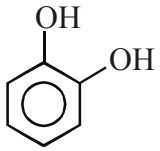
41. 
Thiphene

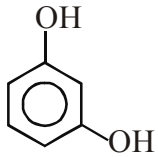
42. 
Pyrole

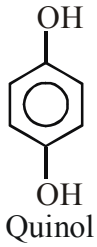
43. 
Furan

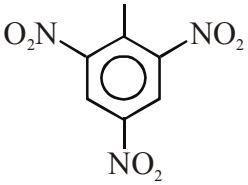
44. 
Pyridine

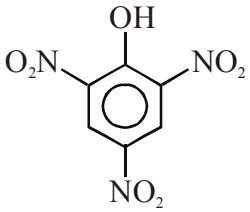
45. 
Pthalic acid

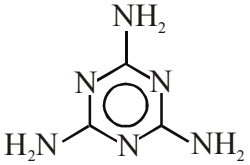
46. 
Catechol

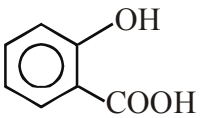
47. 
Resorcinol

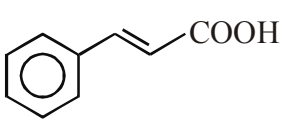
48. 
Quinol

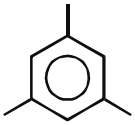
49. 
TNT

50. 
Picric acid

51. 
Melamine

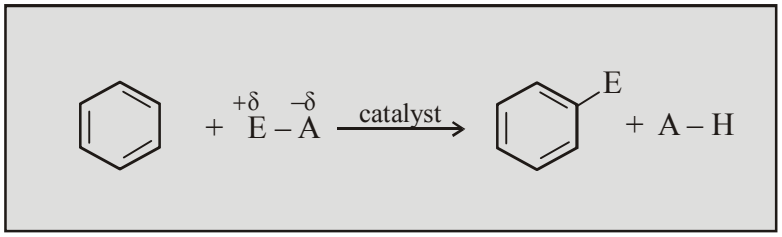
52. 
Salicylic acid

53. 
Cinnamic acid

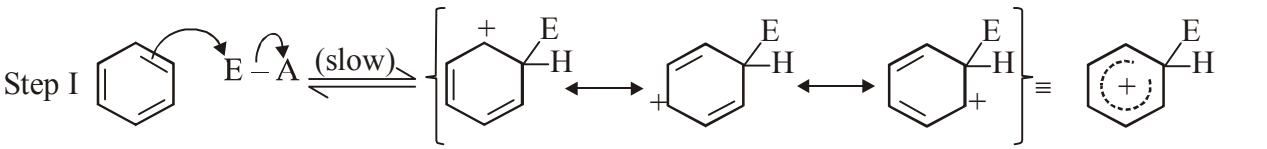
54. 
Mesitylene

❑ REACTION OF AROMATIC COMPOUNDS

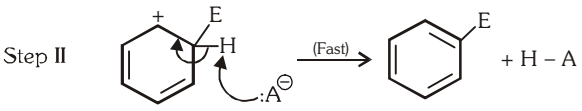
(A) Electrophilic substitution reaction :

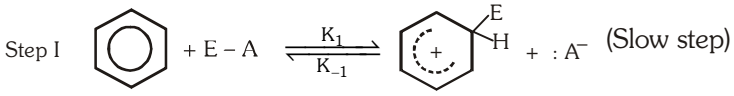


(1) General Mechanism for electrophilic Aromatic substitution :

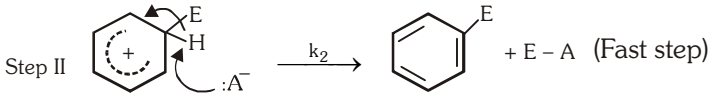


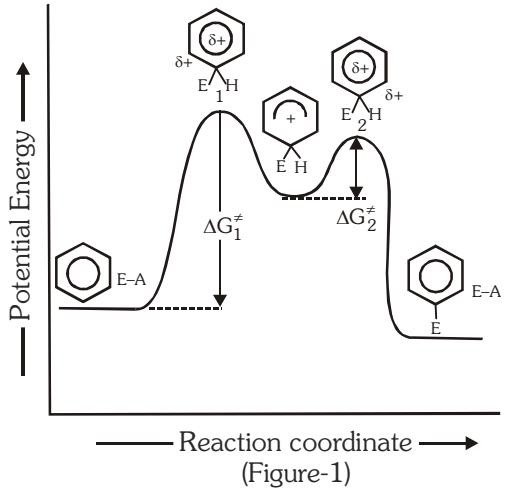
Arenium ion (σ-complex)





Arenium ion (σ-complex)





(Figure-1)

The effects of various substituents on the reactivity of a benzene ring toward electrophilic substituion:

Strong activating groups : —NH_2, —NHR, —NR_2, —OH, —OR.

Moderately activating groups : —NHCR, —OCR,

Weakly activating groups :—R, —Ar, —$CH=CR_2$

Weakly deactivating groups :—F, —Cl, —Br, —I

Ortho/para directing

Moderately deactivating groups : —CHO, —COR, —COOR, —COOH, —COCl

Strong deactivating groups : —C≡N, —SO_3H, —$\overset{+}{N}H_3$, —$\overset{+}{N}H_2R$, —$\overset{+}{N}HR_2$, —$\overset{+}{N}R_3$, —NO_2

Meta directing

❑ NITRATION

Nitration reaction is generally carried out with a mixture of concentrated nitric acid and sulphuric acid. The reagents which is used for nitration are called nitrating agents.

Other nitrating agents which are commonly used are :

(a) N_2O_5 in CCl_4 in the presence of P_2O_5 is used when anhydrous conditions are required.

(b) Ethyl nitrate ($C_2H_5ONO_2$) is used to carry out nitration in alkaline medium.

(c) In the case of polycyclic hydrocarbons N_2O_5 and nitronium salts such as $NO_2^+BF_4^-$, $NO_2^+PF_6^-$, $NO_2^+SO_3^-$, can be used.

The electrophile involved in nitration reaction is nitronium ion $\left(NO_2^{\oplus}\right)$.

Mechanism :

Generation of electrophile from nitrating agent.

Step 1 :

(a) In a mixture of nitric acid and sulphuric acid an acid base reaction takes place in which nitric acid acts as the base.

$$\underset{\text{Base}}{HO{-}NO_2} + H_2SO_4 \longrightarrow H{-}\overset{\oplus}{O}(H){-}NO_2 + HSO_4^{\ominus}$$

$$H{-}\overset{\oplus}{O}(H){-}NO_2 \longrightarrow \overset{\oplus}{N}O_2 + H_2O$$

$$H_2O + H_2SO_4 \longrightarrow H_3O^{\oplus} + HSO_4^{\ominus}$$

$$HNO_3 + 2H_2SO_4 \longrightarrow \overset{\oplus}{N}O_2 + H_3O^{\oplus} + 2\,HSO_4^{\ominus}$$

(b) N_2O_5 in CCl_4 when used, results in a spontaneous dissociation reaction.

$$N_2O_5 \rightleftharpoons \overset{\oplus}{N}O_2 + NO_3^-$$

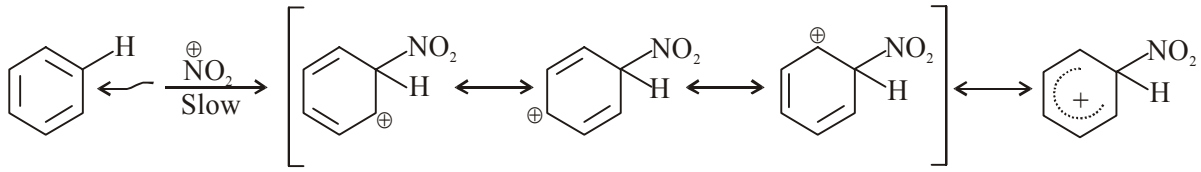
(c) With concentrated HNO_3 alone

$$2HNO_3 \rightleftharpoons NO_2^{\oplus} + NO_3^- + H_2O$$

The electrophile generated in this case is obtained by the behaviour of one nitric acid as the base and other molecule as the acid, but the equilibrium lies in the reactant side.

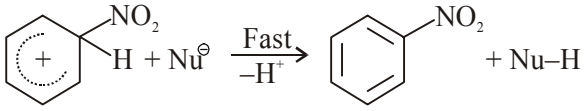
Step 2 :

Attack of electrophile on aromatic System :



Step 3 :

Transfer of Proton to a base/nucleophile



KEY POINTS:

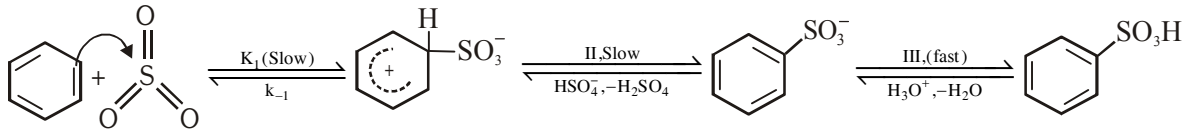
- In nitration, electrophile is NO_2^+
- Conc. (H_2SO_4 + HNO_3) is known as nitrating mixture.
- In nitrating mixture (HNO_2) work as bronsted base and H_2SO_4 as bronsted acid.

❑ SULPHONATION

Sulphonation is another synthetically important reaction. It is often accomplished with concentrated sulphuric acid or fuming sulphuric acid containing excess of SO_3 or chlorosulphonic acid, $ClSO_2OH$.

H_2SO_4 (SO_3 + H_2O) or $H_2S_2O_7$)

$$2H_2SO_4 \rightleftharpoons HSO_4^- + H_3O^+ + SO_3$$



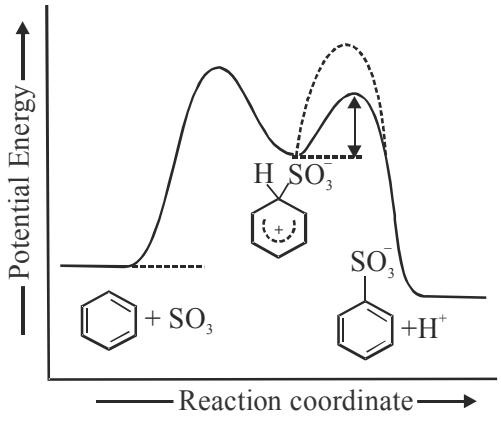


Figure-2

KEY POINTS:

- In sulphonation, SO_3 is electrophile.
- $ClSO_3H$ in CCl_4 can also be used for sulphonation in some cases.
- Kinetic isotopic effect occurs here on rate of reaction. Hence benzene reacts more fast than C_6D_6 than C_6T_6.

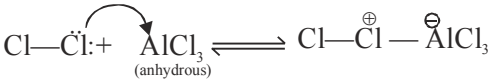
❑ HALOGENATION

Halogenation is catalysed by a Lewis acid like $AlCl_3$, or $FeCl_3$, Reactivity of halogens has the following order,

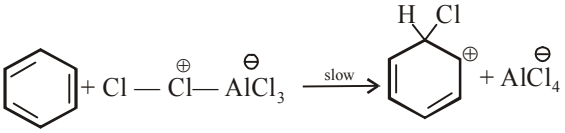
$$I_2 < Br_2 < Cl_2$$

Let us take chlorination as a representative reaction to understand the mechanism of halogenation. Chlorine, in the presence of $AlCl_3$ or $FeCl_3$ forms a complex, Cl_2—$AlCl_3$. This complex can itself be the reactive electrophile or it may dissociate to give Cl^+.

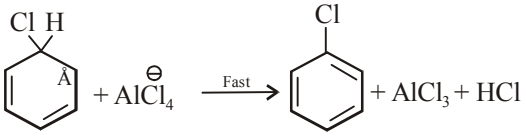
Step 1 :

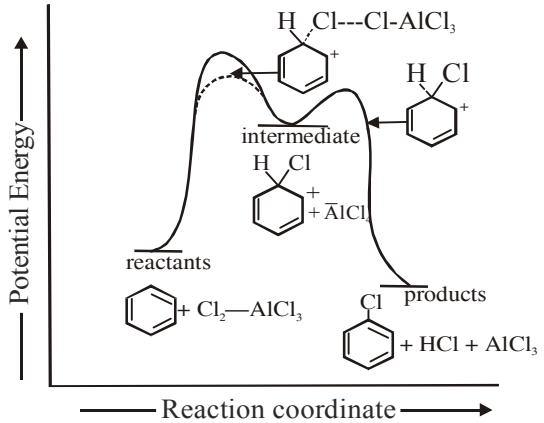


Step 2 :



Step 3 :

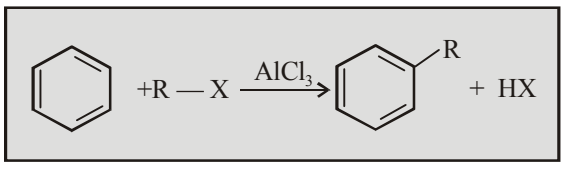




Schematic potential energy diagram for chlorination of benzene with Cl_2, $AlCl_3$ as the electrophile

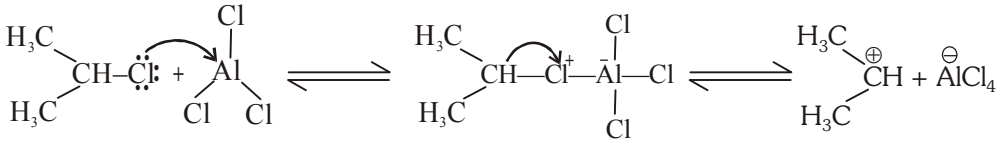
(Figure-3)

FRIDEL-CRAFT'S ALKYLATION

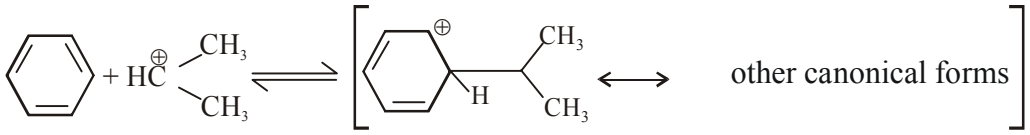


Mechanism for the Reaction :

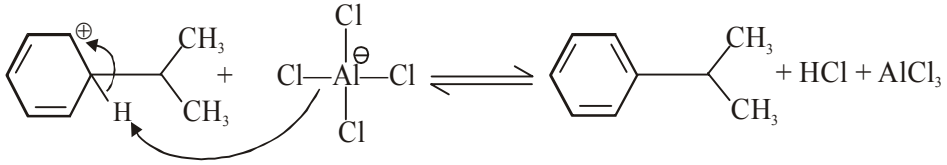
Step I :



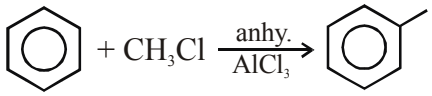
Step II



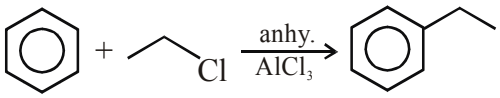
Step III :

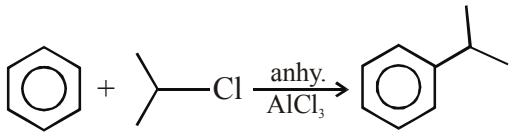


Some examples of Friddel-Craft's Alcylation :

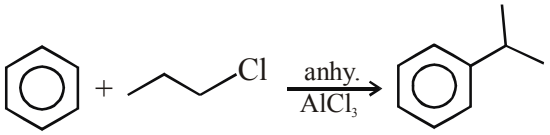
1. 

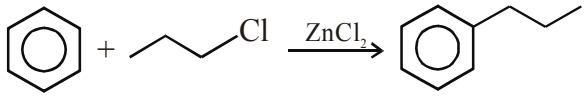
(Toluene)

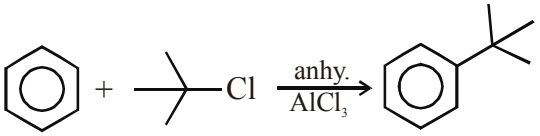
2. 

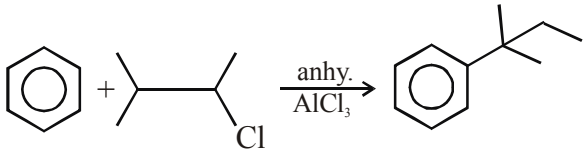
3. 

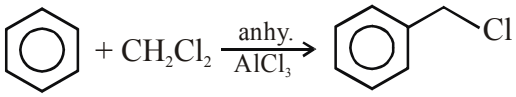
(Cumene)

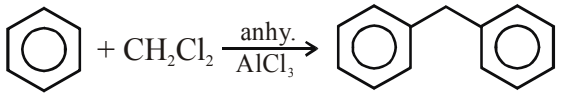
4. 

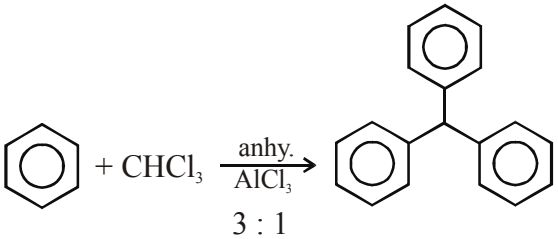
5. 

6. 

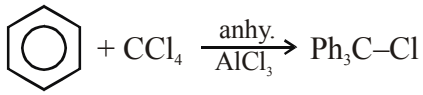
7. 

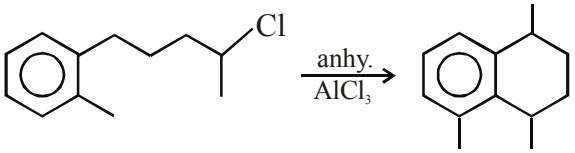
8. 

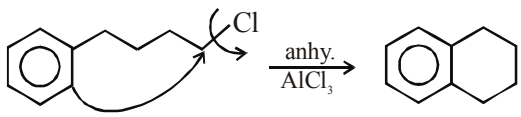
9. 

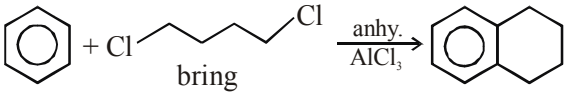
10. 

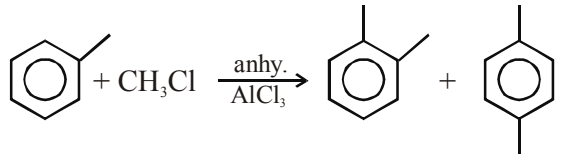
3 : 1

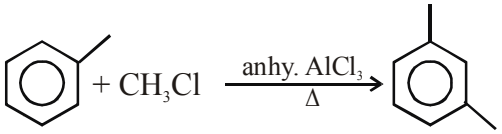
11. 

12. 

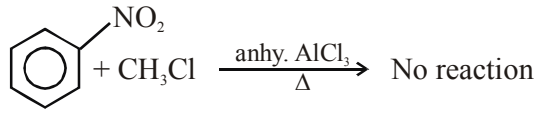
13. 

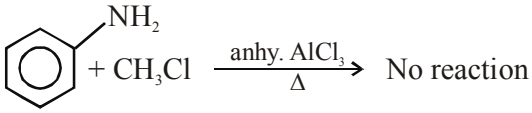
14. 

15. 

16. 

m-xylene
(most stable)

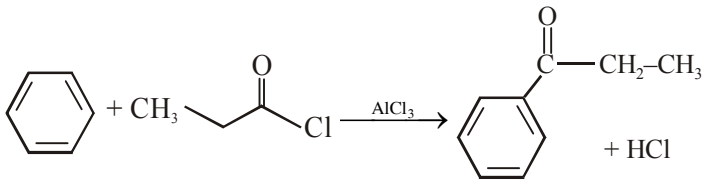
17. 

18. 

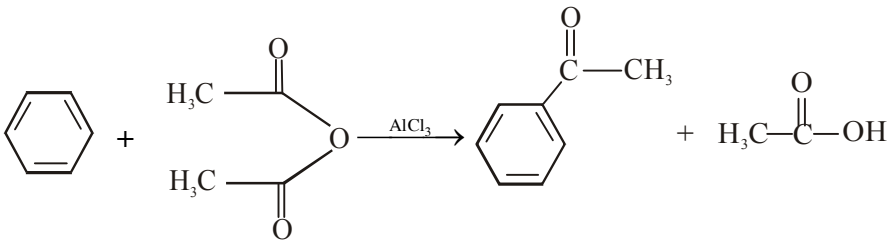
FRIEDEL-CRAFTS ACYLATION

The reaction where an acyl group is introduced into an aromatic compound compound is called an acylation reaction.

The Friedel-Crafts acylation reaction is an effective means of introducing an acyl group into an aromatic ring. The reaction is often carried out by treating the aromatic compound with an acyl halide.

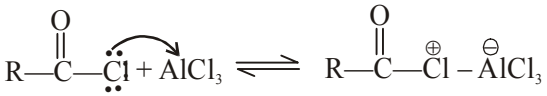


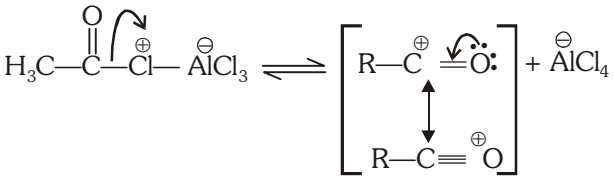
Friedel-Crafts acylations can also be carried out using carboxylic acid anhydrides. eg.

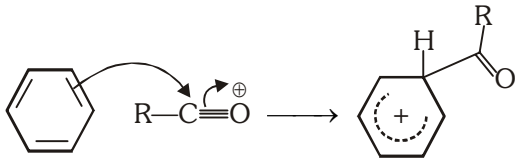


Mechanism of the Reaction :

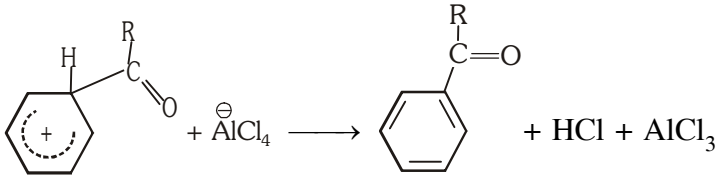
In most Friedel-Crafts acylation reactions the electrophile appears to be an acylium ion formed from an acyl halide in the following way.

Step I : 

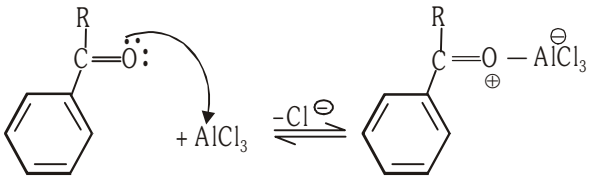
Step II : 

Step III : 

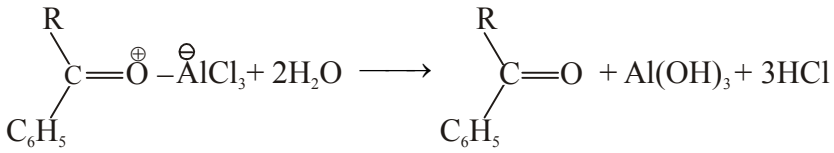
Step IV :



Step V :



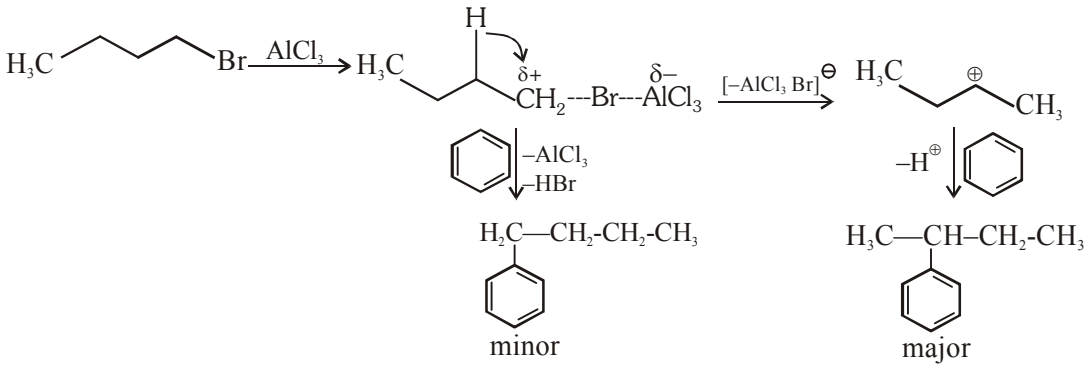
In the last step, $AlCl_3$ (a Lewis acid) forms a complex with the ketone (a Lewis base). After the reaction is over, treating the complex with water liberates the ketone.



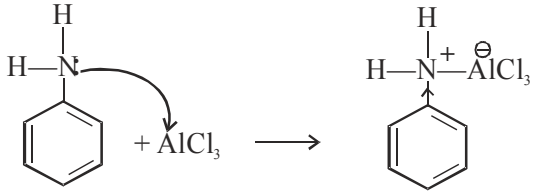
Limitations of Friedel - Crafts Reactions :

(a) When the carbocation formed from an alkyl halide, alkene, or alcohol can rearrange to a more stable carbocation, it usually does so and the major product obtained from the reaction is usually the one from the more stable carbocation.

When benzene is alkylated with butyl bromide, for example, some of the developing butyl cations rearrange by a hydride shift-some developing 1° carbocations (see following reactions) become more stable 2° carbocations. The benzene reacts with both kinds of carbocations to form both butylbenzene and sec-butylbenzene.

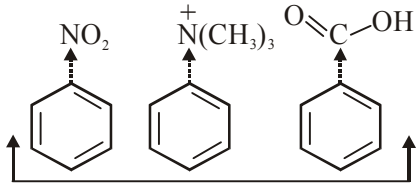


(b) Aromatic ring containing $-NH_2$, $-NHR$, $-NR_2$, groups do not undergo Friedal-Craft's alkylation due to formation of anilinum complex which is meta directing and has more electron withdrawing power than halogen in benzene ring.



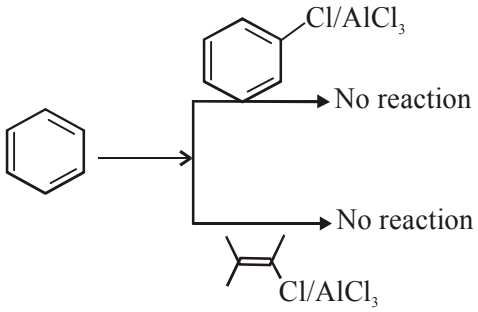
Meta directing group
and does not undergo
Friedal Craft's reaction

(c) Friedel-Crafts reactions (alkylationi and acylation) do not occur when powerful electron-withdrawing groups are (like $-NO_2$, $-\overset{\oplus}{N}R_3$ etc) present on the aromatic ring.

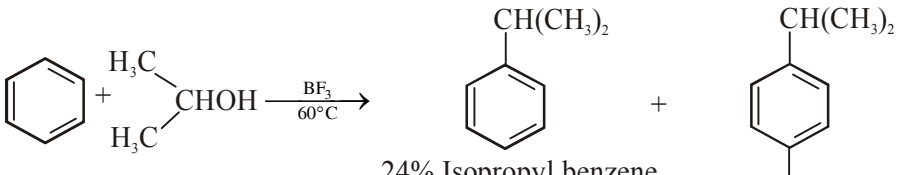


These do not undergo Friedel -Crafts reactions

(d) Aryl and vinylic halides can not be used as the halide component because they do not form carbocations readily.



(e) Polyalkylations often occur because alkyl groups are electron releasing groups, and once one is introduced into the benzene ring it activates the ring towards further substitution.

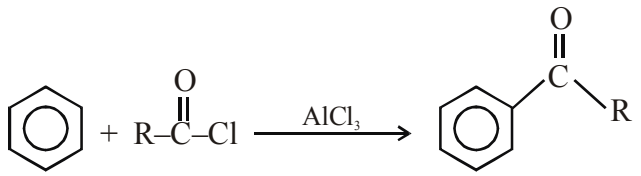


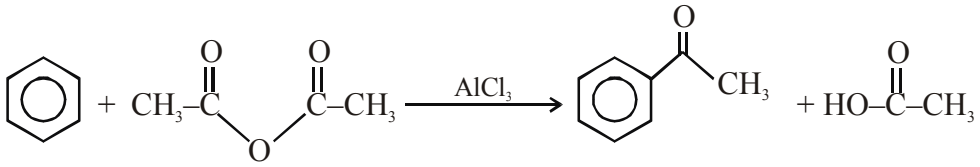
24% Isopropyl benzene

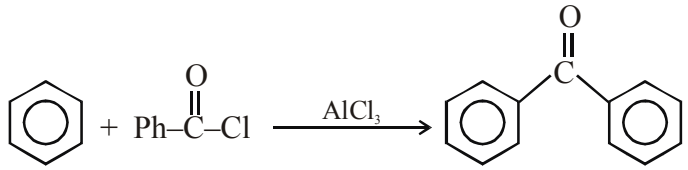
14% diisopropylbenzene

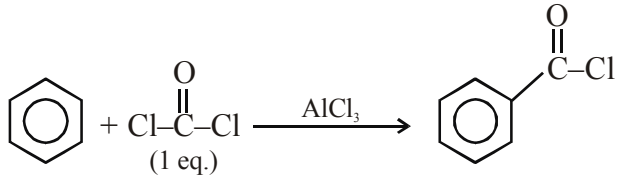
Polyacylations are not a problem in Friedel-Crafts acylations. The acyl group (RCO–) by itself is an electron-withdrawing group, and when it forms a complex with $AlCl_3$ in the last step of the reaction, it is made even more electron withdrawing. This strongly inhibits further substitution and makes monoacylation easy.

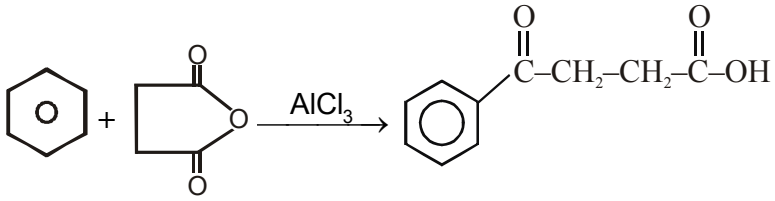
Some examples of Friedel-Craft's Acylation reaction

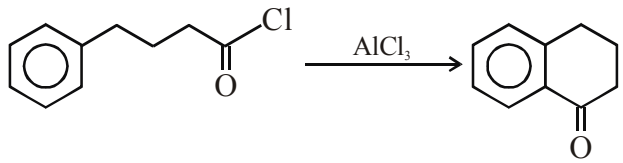
Q.1 

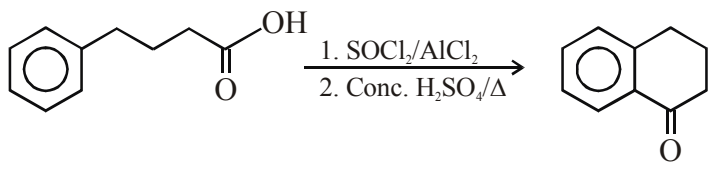
Q.2 

Q.3 

Q.4 

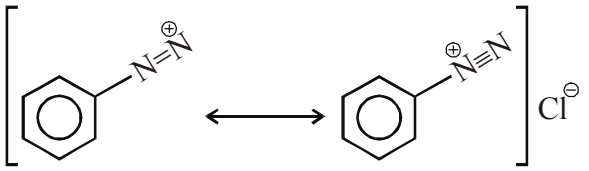
Q.5 

Q.6 

Q.7 

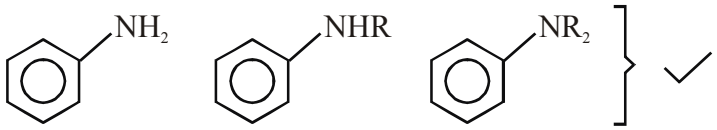
❑ COUPLING REACTION

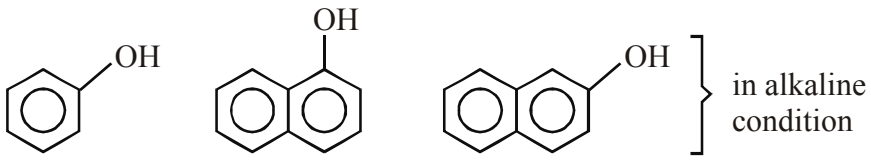
Coupling reaction is used for formation of coloured compound dye & indicator. In this reaction benzene diazonium salt is electrophile.

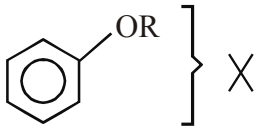


Resonating structures of Benzene diazonium chloride.

Since PhN_2^+ is weak electrophile hence couples only with highly activated ring.







There are two kinds of coupling :

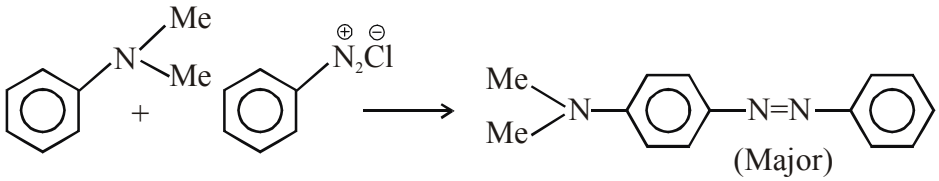
(a) C–N coupling :

The reaction in which coupling occurs between carbon & nitrogen is called C–N coupling.

(b) N–N coupling :

The reaction in which coupling occurs between nitrogen & nitrogen is called N–N coupling.

1.



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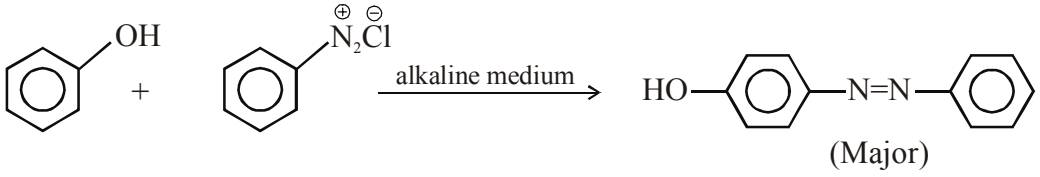
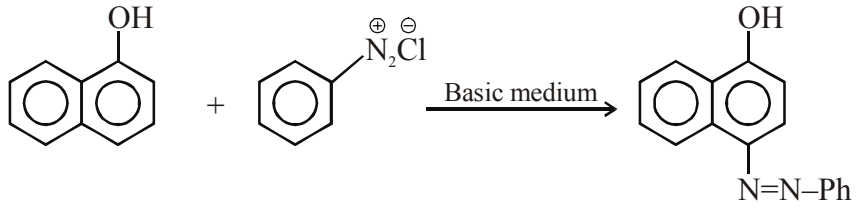
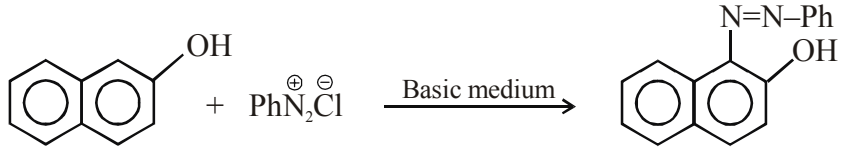


3.

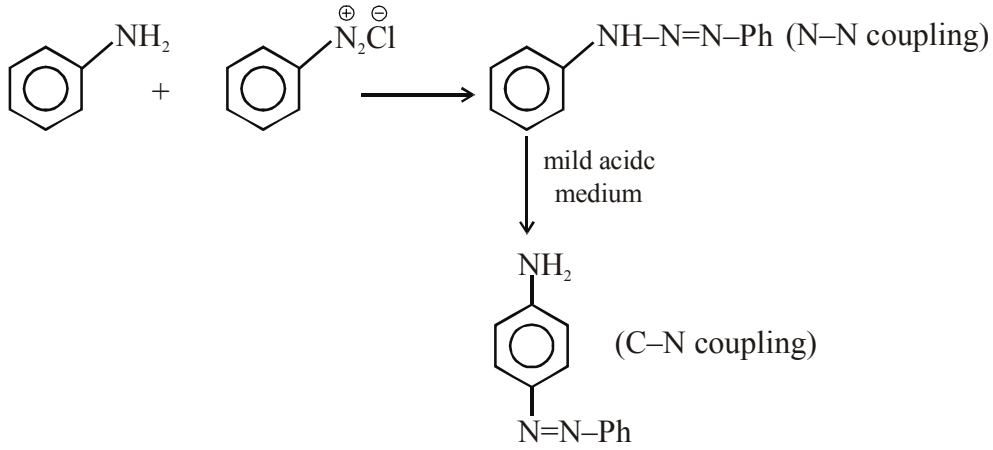


4.



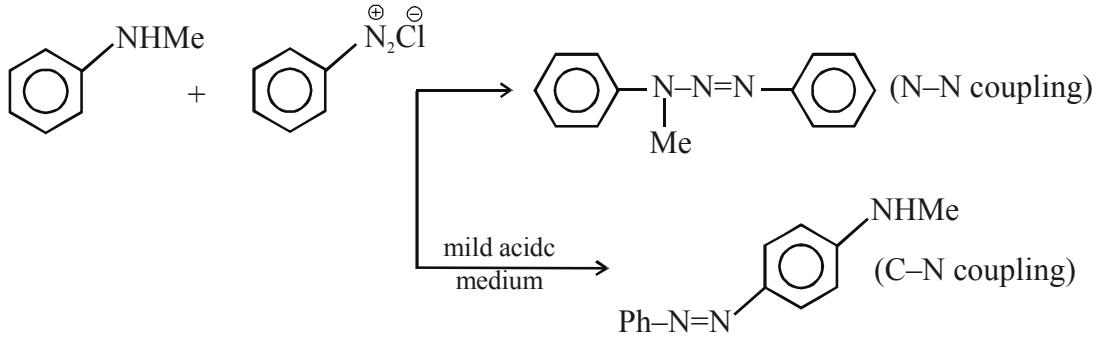
(Red colour dye)

5.



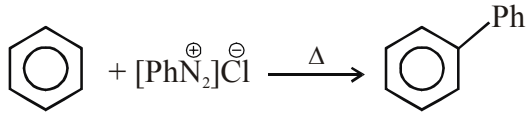
(C–N coupling)

6.



C–N coupling takes place in acidic medium on the other hand N–N coupling takes place in absence of acidic medium.

7.



[Gomerb reaction] + Na_2 (↑) + HCl

❑ NUCELOPHILIC AROMATIC SUBSTITUTION

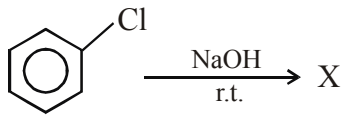
Possible mechanism for nucleophilic aromatic substitution.

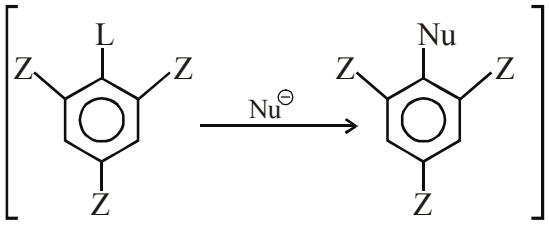
(i) SN^2–Ar/SN_{AE}–mechanism

(ii) SN^1–Ar/Aryl cation mechanism

(iii) S_{NEA}/Sine substitution/Benzyme mechanism.

SN^2–Ar mechanism : (Biomolecular nucleophilic substitution on aromatic ring mechanism)



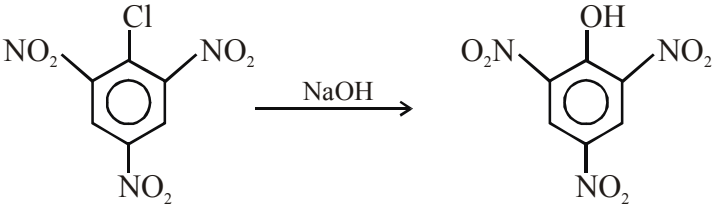


where, L, Z, $N_4^{\ominus}$ / Na may be

–L	–Z	$-Nu^{\ominus}$/ $\dot{N}u$
–F	–CN	NaOH
–Cl	–CHO	KOH
–Br	–COR	H_2O
–I	$-NO_2$	NH_3
–OR	–F	N_2H_4
$-NO_2$	–Cl	$RO^{\ominus}$
	–Br	ROH

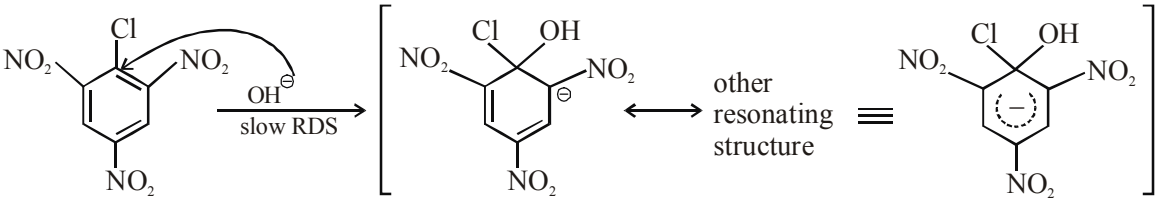
❑ Some examples of SN^2–Ar reaction :

1.



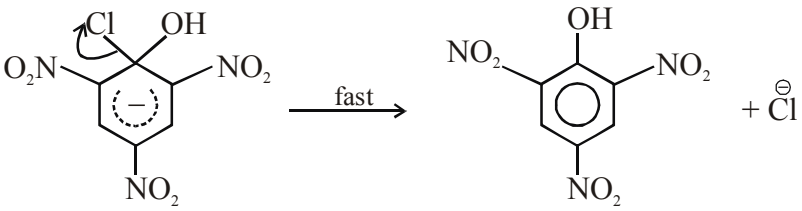
Mechanism :

Step-1



Carbanion intermediate / m-complex

Step-2 :



Note :

(i) Carbanion intermediate (M-complex)

(ii) Step-1 is rate determining step / slow step.

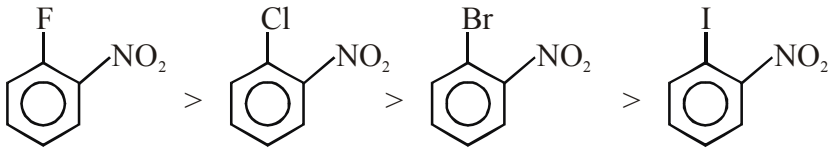
(iii) Rate of SN^2–Ar depends on stability of M-complex.

(iv) M-complex can be stabilized by

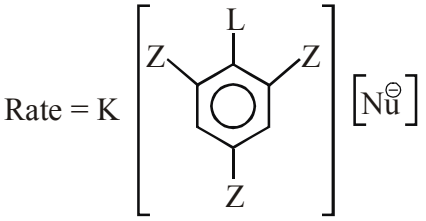
(a) EWG at ortho & para position.

(b) –I effect of leaving group.

(v) Order of substitution in following

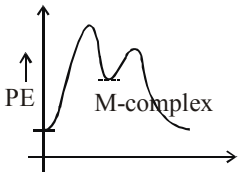


(vi) Rate expression for above reaction is



(vii) Bimolecular II[nd] order

(viii)



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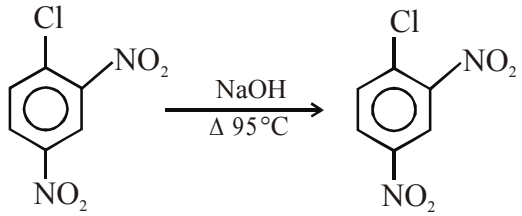
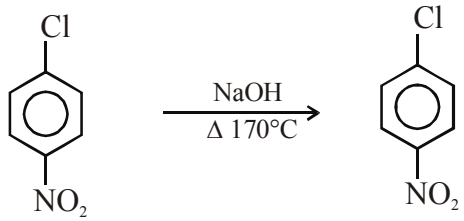
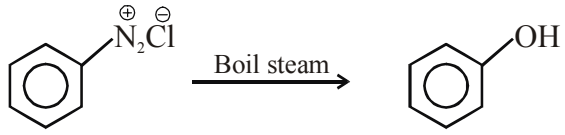


3.



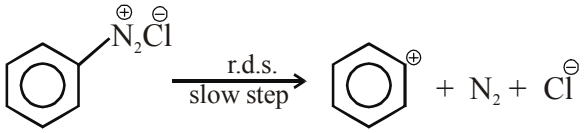
❑ **SN^1–Ar mechanism :**

1.

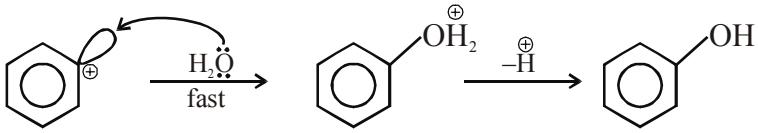


Mechanism :

Step-1 :



Step-2 :



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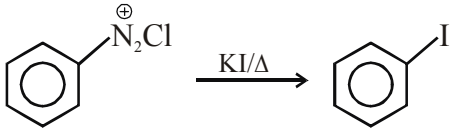

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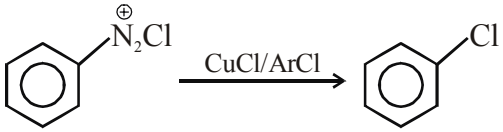
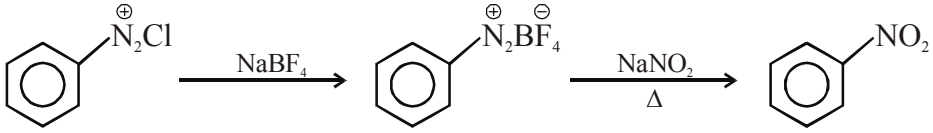


Sandmayer reaction

4.

Sandmayer reaction

5.



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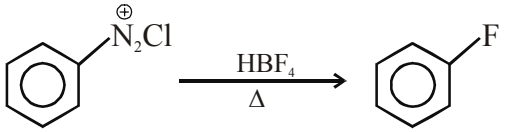
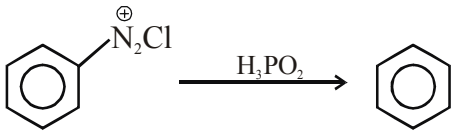


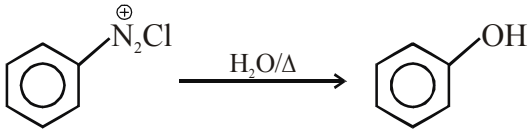
(Boltz scheimern reaction)

7.



+ H_3PO_3

8.



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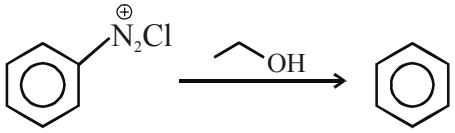
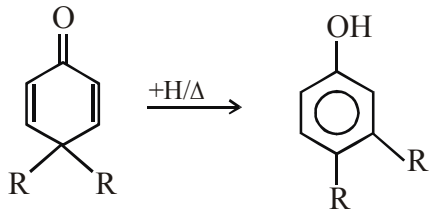


+ $CH_3–CH=O$ + HCl

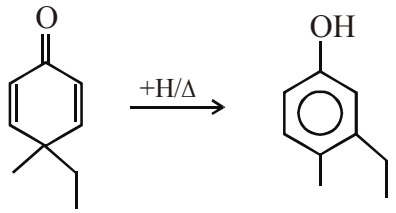
❑ AROMATIC REARRANGEMENTS

1. Dienone-phenol rearrangement :

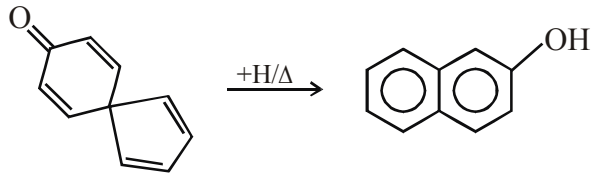
(i)



(ii)

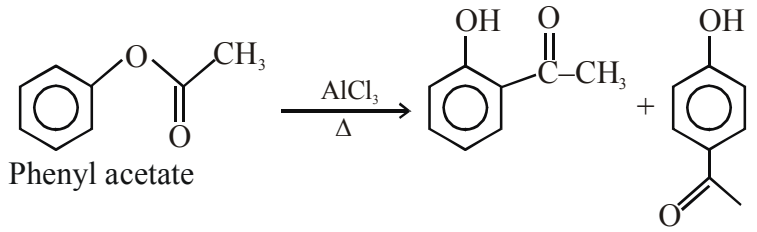


(iii)

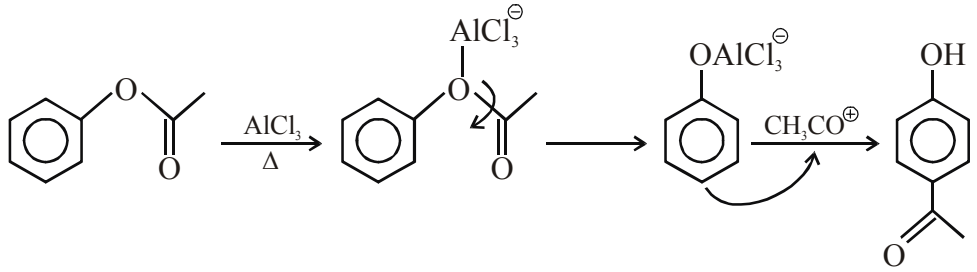


2. Fries rearrangement

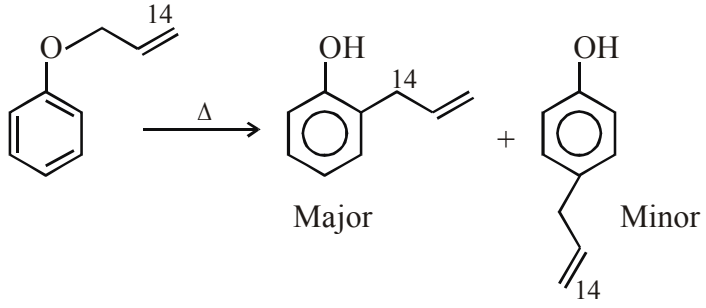
(i)



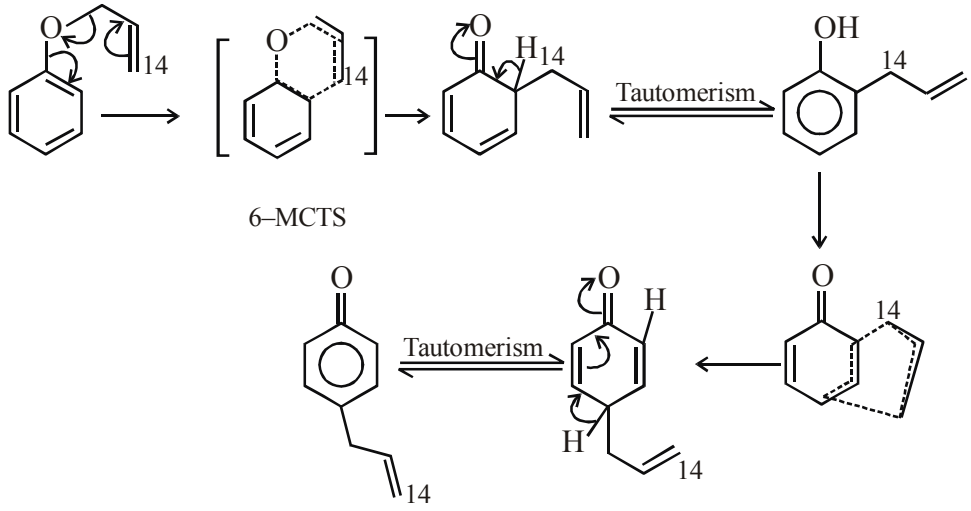
Mechanism :



3. Claisen rearrangement



Mechanism :



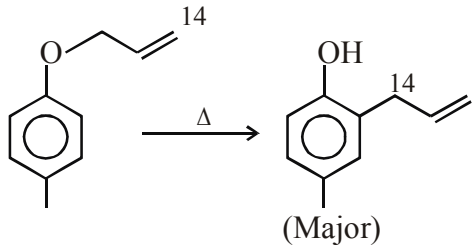
Note :

(i) Ortho is major as latter MCTS is strained

(ii) Reaction occure 6-MCTS

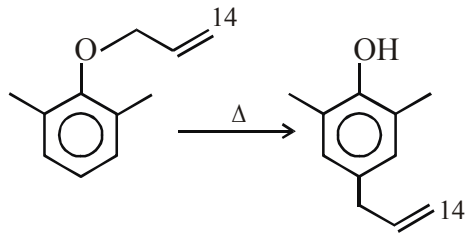
(iii) Para dominates when both ortho are blocked.

(i)



(Major)

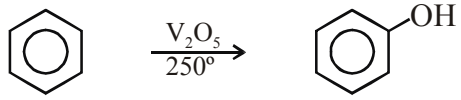
(i)



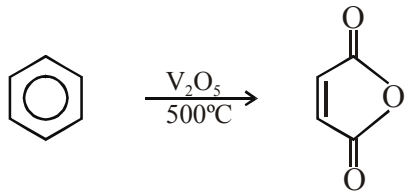
Oxidation of some aromatic compounds

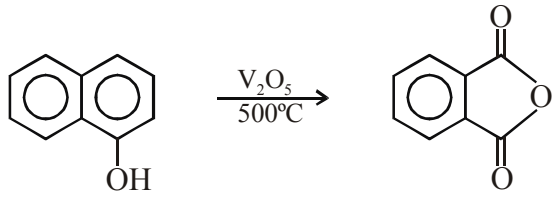
1. By V_2O_5

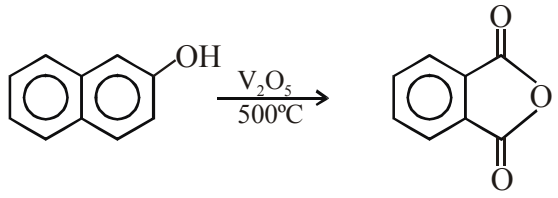
(i)



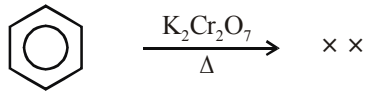
(ii)

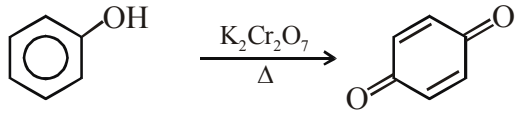


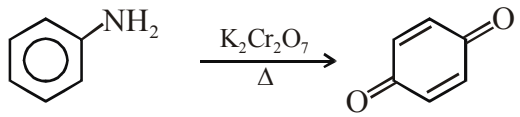
(iii) 

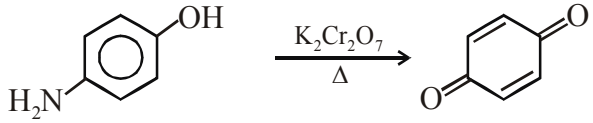
(iv) 

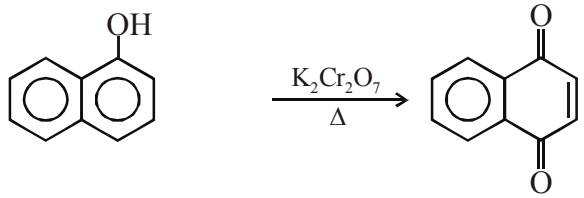
2. By $K_2Cr_2O_4$

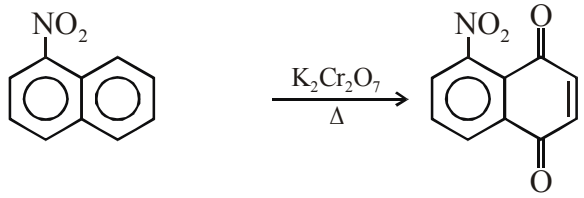
(v) 

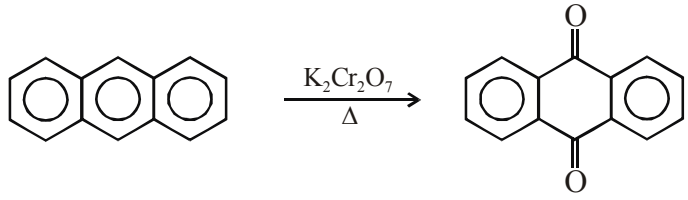
(vi) 

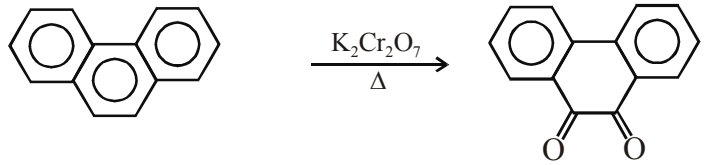
(vii) 

(viii) 

(ix) 

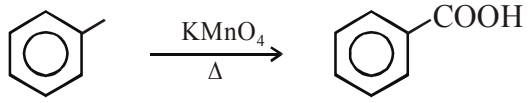
(x) 

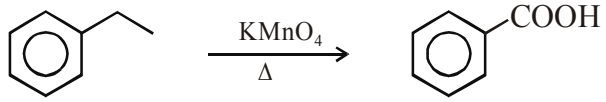
(xi) 

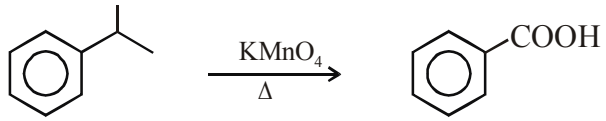
(xii) 

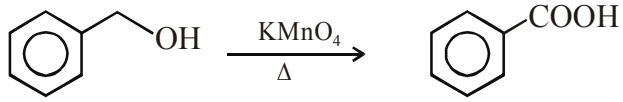
3. By $KMnO_4$

(xiii) 

(xiv) 

(xv) 

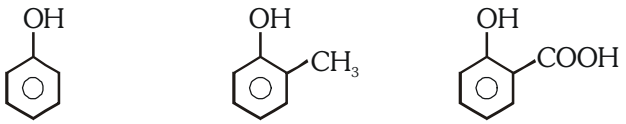
(xvi) 

(xvii) 

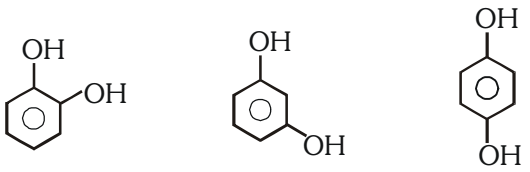
AROMATIC HYDROXY DERIVATIVES

❑ **Phenolic compounds :**

Compounds in which —OH group is directly attached to sp^2 carbon of benzene ring



Phenol o-cresol Salicylic acid



catechol resorcinol quinol

All phenolic compounds give characteristic colour with neutral $FeCl_3$.

$Ph—OH \xrightarrow{\text{neutral } FeCl_3}$ Violet colour

$CH_3CH_2—OH \xrightarrow{\text{neutral } FeCl_3}$ No colour

PHENOL (C_6H_5OH)

Phenol is also known as carbolic acid or Benzenol or hydroxy benzene or carbinol.In phenol —OH group is attached with sp^2 hybridised carbon.It was discovered by Runge in the middle oil fraction of coaltar distillation and named it carbolic acid (carbo = coal; oleum = oil) .It is also present in traces in human urine.

❑ **General Methods of preparation :**

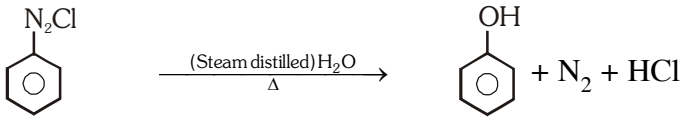
(1) From benzene sulphonic acid :

When sodium salt of benzene sulphonic acid is fused with NaOH, phenol is obtained.

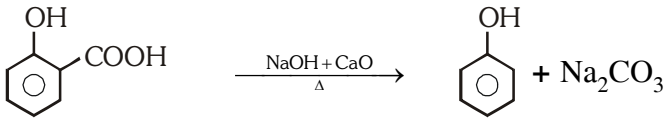
$$C_6H_5SO_3Na \xrightarrow[(ii)\ H^{\oplus}]{(i)\ NaOH} C_6H_5OH + Na_2SO_3$$

(2) From benzene diazonium chloride :

When benzene diazonium chloride solution is warmed, phenol is obtained with evolution of nitrogen.

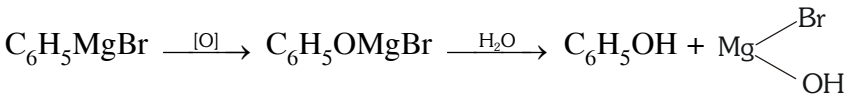


(3) By distilling a phenolic acid with sodalime (decarboxylation):

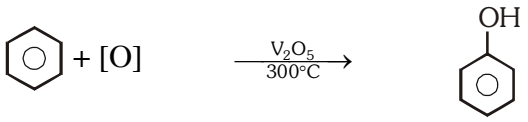


Salicylic acid

(4) From Grignard reagent : (The Grignard reagent on reaction with oxygen and subsequent hydrolysis by acid yields phenol)



(5) From benzene :



(6) From chloro benzene :

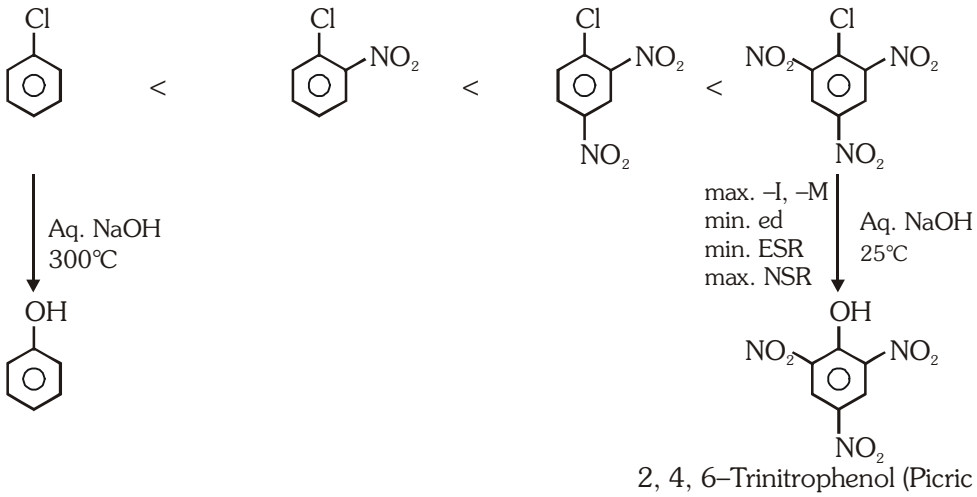
Ph—Cl $\xrightarrow{\text{Aq. NaOH}}$ No NSR at normal condition

Stable by resonance

R—Cl $\xrightarrow{\text{Aq. NaOH}}$ R—OH [NSR]

Ph—Cl $\xrightarrow[300^\circ C]{\text{Aq. NaOH}}$ Ph—ONa

Order of NAS (Nucleophilic Aromatic substitution, ArSN or NSR) :



2, 4, 6–Trinitrophenol (Picric acid)

(7) Industrial preparation of phenol:

Phenol can be prepared commercially by **:**

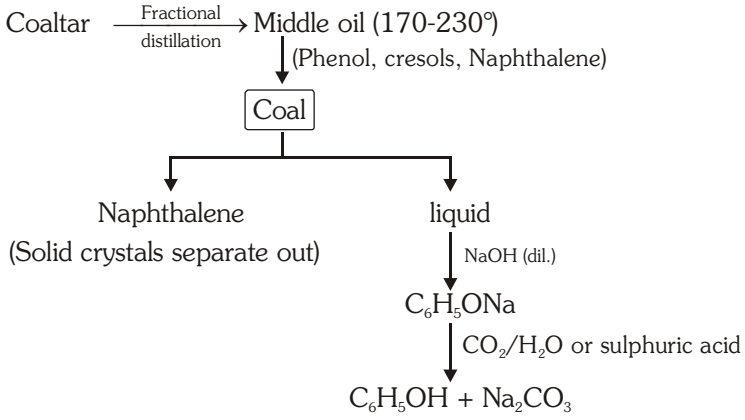
(a) Middle oil fraction of coaltar distillation

(b) Cumene

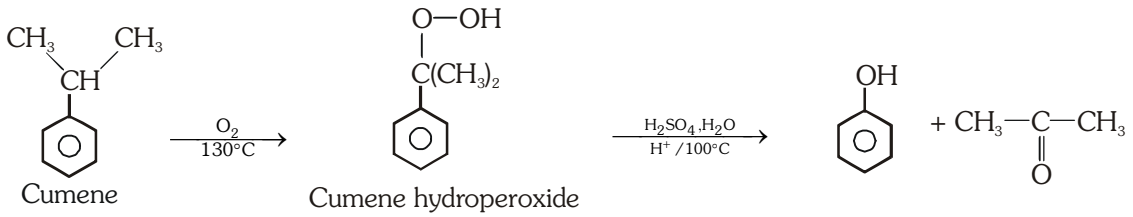
(c) Raschig process

(d) Dow's process

(a) Middle oil fraction of coaltar:



(b) From cumene (Isopropyl benzene) : Cumene is oxidised with oxygen into cumene hydroperoxide in presence of a catalyst. This is decomposed by dil. H_2SO_4 into phenol and acetone.



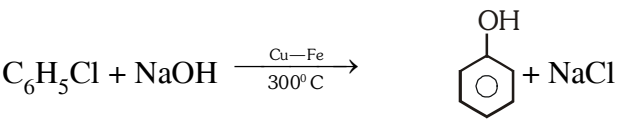
(c) Raschig process : Chlorobenzene is formed by the interaction of benzene, HCl and air at 300°C in presence of catalyst $CuCl_2 + FeCl_3$. It is hydrolysed by superheated steam at 425° C to form phenol and HCl.

$$C_6H_6 + HCl + \frac{1}{2}O_2 \xrightarrow[300^0\,C]{CuCl_2/FeCl_3} C_6H_5Cl + H_2O$$

$$C_6H_5Cl + H_2O \xrightarrow{425^0\,C} C_6H_5OH + HCl$$

(super heated steam)

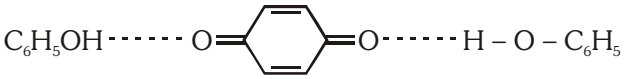
(d) Dow process : This process involves alkaline hydrolysis of chloro benzene-(large quantities of phenol formed).



❑ **Physical properties :**

(i) Phenol is a colourless, hygroscopic crystalline solid.

(ii) It attains pink colour on exposure to air and light. (slow oxidation)



Phenoquinone (pink colour)

(iii) It is poisonous in nature but acts as antiseptic and disinfectant.

(iv) Phenol is slightly soluble in water , readily soluble in organic solvents.

(v) Solublity of phenol in water is much lower than alcohols because of larger hydrocarbon part in the molecule.

(vi) Due to intermolecular H-Bonding, phenol has relatively high boiling point than the corresponding hydrocarbons, aryl halides etc. but intermolecular H-bonding in o–derivatives is used in the preparation of dyes, drugs, bakelite and it's melting point (MP) is 43° C and boiling point (BP) is 182° C .

❑ **Chemical Properties :**

(A) Reactions due to –OH group :

◆ **Acidic Nature :** Phenol is a weak acid. The acidic nature of phenol due to formation of stable phenoxide ion in solution. The phenoxide ion is stable due to resonance. The negative charge is spread through out the benzene ring which is stabilising factor in the phenoxide ion. Electron withdrawing groups ($-NO_2$, –Cl) increase the acidity of phenol while electron releasing groups ($-CH_3$ etc.) decrease the acidity of phenol.

$$C_6H_5OH \rightleftharpoons C_6H_5\overset{\ominus}{O} + H_3\overset{\oplus}{O}$$

Phenol is stronger acid than alcohols but weaker than the carboxylic acids and even carbonic acid

The acidic nature of phenol is observed in the following:

(i) Phenol changes blue litmas to red.

(ii) Highly electro positive metals react with phenol.

$$2C_6H_5OH + 2Na \longrightarrow 2C_6H_5ONa + H_2$$

(iii) Phenol reacts with strong alkalies to form phenoxides.

$$C_6H_5OH + NaOH \longrightarrow C_6H_5\overset{\ominus}{O}\overset{\oplus}{N}a + H_2O$$

(iv) However phenol does not decompose Na_2CO_3 or $NaHCO_3$ because phenol is weaker than carbonic acid.

$$C_6H_5OH + Na_2CO_3 \text{ or } NaHCO_3 \longrightarrow \text{No reaction}$$

$$\underset{\text{Acid-I}}{Ph—OH} + \underset{\text{Base-I}}{NaHCO_3} \rightleftharpoons \underset{\text{Base-II}}{Ph—ONa} + \underset{\text{Acid-II}}{H_2CO_3}$$

Acid-I < Acid-II
Base-I < Base-II } Reaction in reverse direction.

(v) Phenol does not react with $NaHCO_3$.

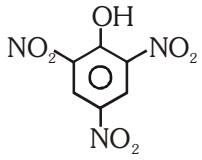
$$CH_3-\underset{\underset{O}{\|}}{C}-OH + NaHCO_3 \rightleftharpoons CH_3-\underset{\underset{O}{\|}}{C}-ONa + H_2CO_3 \quad [H_2O + CO_2\uparrow]$$

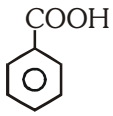
Acid-I Base-I Base-II Acid-II

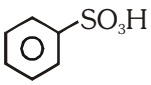
Acid-I > Acid-II
Base-I > Base-II
} Reaction in forward direction.

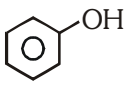
(vi) Acetic acid reacts with $NaHCO_3$ and gives effervesence of CO_2.

Q. Identify the compound which release CO_2 with $NaHCO_3$?

(A) 

(B) 

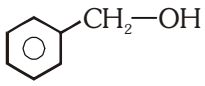
(C) 

(D) 

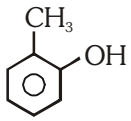
Ans. (A, B, C)

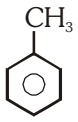
◆ **Reaction with Zn dust:** When phenol is distilled with zinc dust benzene is obtained.

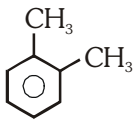
$$C_6H_5OH + Zn \longrightarrow C_6H_6 + ZnO$$

Q.  $\xrightarrow{Zn}$?

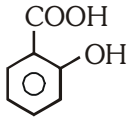
Sol. No reaction

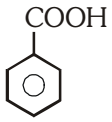
Q.  $\xrightarrow{Zn}$?

Sol. 

Q.  $\xrightarrow{Zn}$?

Sol. No reaction

Q.  $\xrightarrow{Zn}$?

Sol. 

- **Reaction with NH_3(Bucherer reaction):** Phenol reacts with NH_3 in presence of anhydrous $ZnCl_2$ to form aniline.

$$C_6H_5OH + NH_3 \xrightarrow[300°C]{\text{Anhydrous } ZnCl_2 \text{ or } (NH_4)_2SO_3 / NH_3\, 150°C} C_6H_5NH_2 + H_2O$$

- **Reaction with $FeCl_3$:** Phenol gives violet colouration with $FeCl_3$ solution (neutral) due to formation of a complex.

$$C_6H_5OH + FeCl_3 \longrightarrow \text{Voilet colour}$$

This reaction is used to differentiate phenol from alcohols.

- **Acetylation (Schotten-Baumann reaction) :** Phenol reacts with acid chlorides or acid anhydrides in alkali solution to form phenyl esters.

$$C_6H_5OH + ClCOCH_3 \xrightarrow[-HCl]{NaOH} C_6H_5O{-}\overset{\overset{O}{\|}}{C}{-}CH_3$$

$$C_6H_5OH + Cl{-}\overset{\overset{O}{\|}}{C}{-}C_6H_5 \xrightarrow[-HCl]{NaOH} C_6H_5O{-}\overset{\overset{O}{\|}}{C}{-}C_6H_5$$

- **Ether formation (Alkylation) :** Phenol reacts with alkyl halides in alkali solution to form phenyl ethers. **(Williamson's synthesis)**

$$C_6H_5OH + NaOH \xrightarrow{\text{alkali solution}} C_6H_5ONa \xrightarrow[-NaX]{RX} C_6H_5OR$$

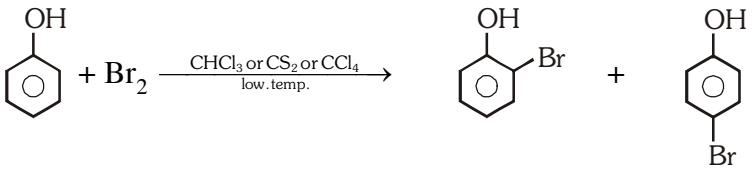
Sodium phenoxide

- Ether can also be formed when phenol react with diazomethane.

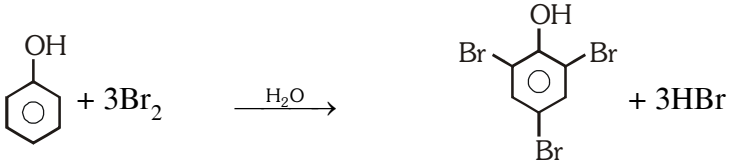
$$C_6H_5OH + CH_2N_2 \longrightarrow C_6H_5OCH_3 + N_2 \uparrow$$

(B) Reaction of Benzene Ring : The —OH group is ortho and para directing. It activates the benzene nucleus.

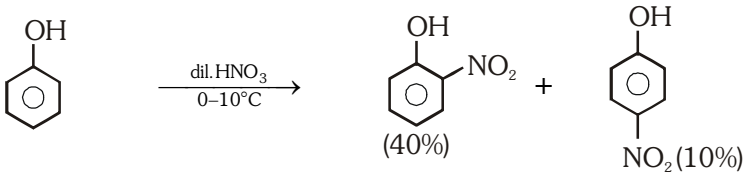
- **Halogenation :** Phenol reacts with bromine in CCl_4 to form mixture of ortho–and para–bromo phenol.



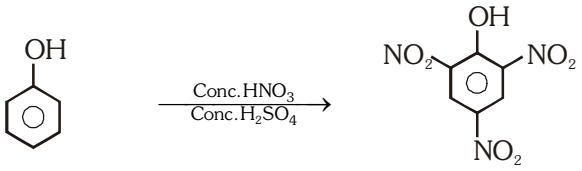
Phenol reacts with bromine water to form a white ppt. of 2,4,6 tribromo phenol.



- **Nitration :** Phenol reacts with dil. HNO_3 at 0°–10° C to form ortho- and para- nitro phenols.

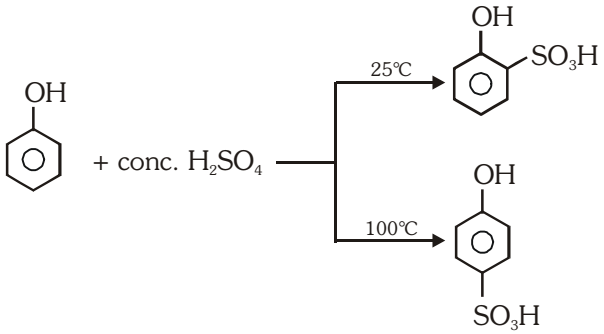


When phenol is treated with nitrating mixture to form 2,4,6- trinitro phenol (picric acid)

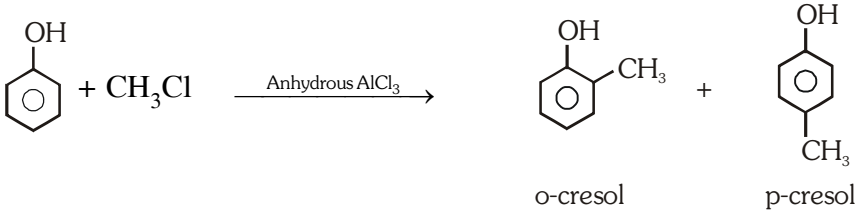


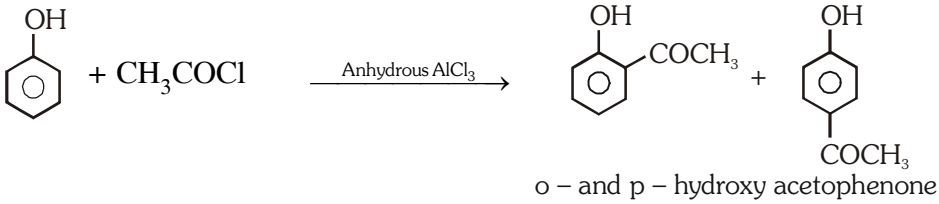
[2, 4, 6–Trinitrophenol (Picric acid)]

- **Sulphonation:** Phenol reacts with fuming H_2SO_4 to form ortho–and para–hydydroxy benzene sulphonic acid at different temperatures.



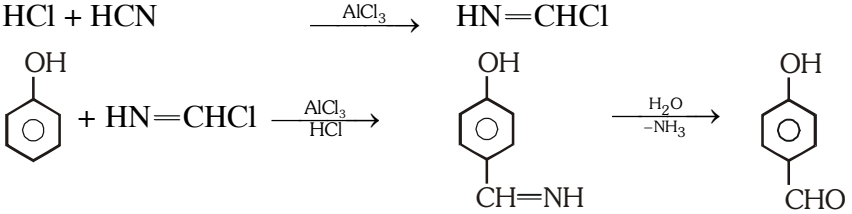
- **Friedel-Craft's reaction :** Phenol when treated with methyl chloride in presence of anhydrous $AlCl_3$, p-cresol is main product.



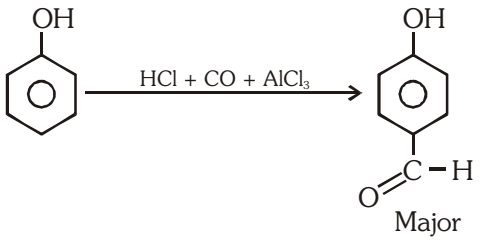


o – and p – hydroxy acetophenone

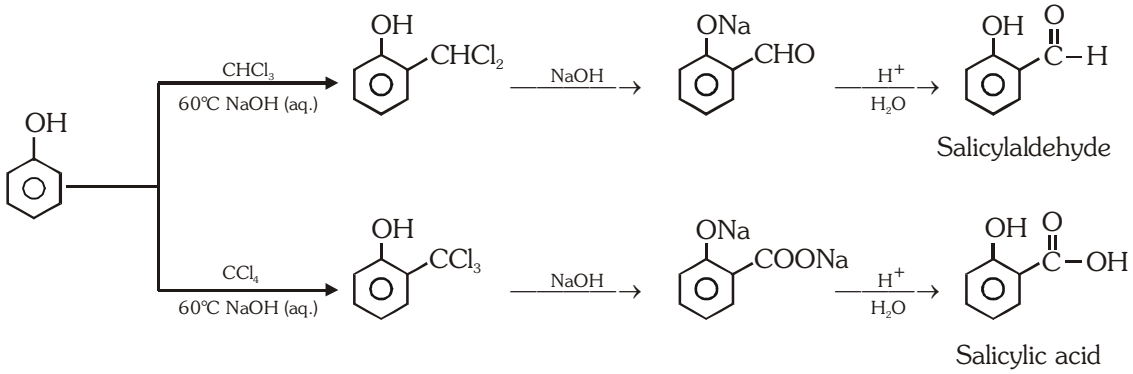
- **Gattermann aldehyde synthesis :** When phenol is treated with liquid HCN and HCl gas in presence of anhydrous $AlCl_3$ yields mainly p- hydroxy benzaldehyde (formylation)



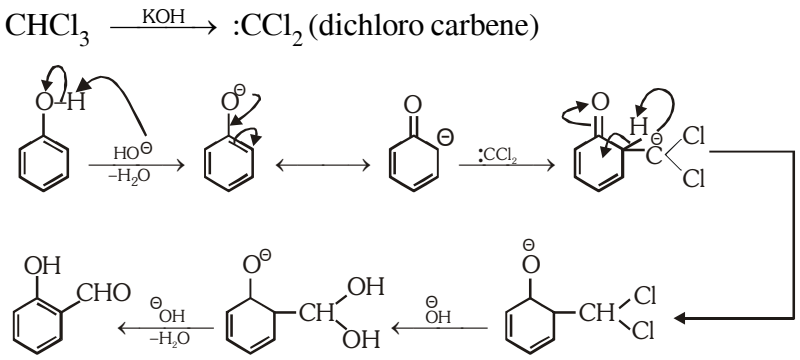
◆ **Gatterman Koch reaction :**



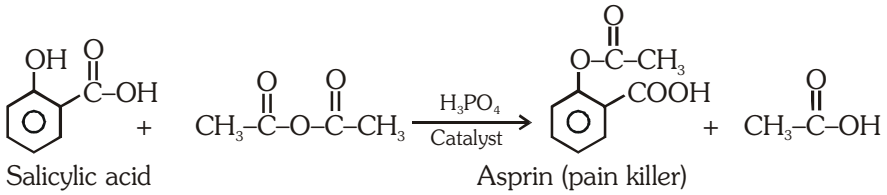
◆ **Riemer-Tiemann reaction :** Phenol on refluxing with chloroform and NaOH (aqueous) followed by acid hydrolysis yields o–hydroxy benzaldehyde (As major product). When CCl_4 is used salicylic acid is formed.



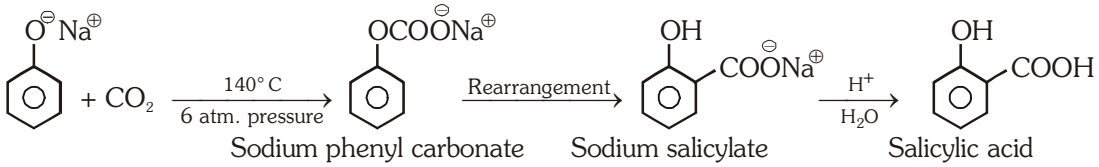
Mechanism : CCl_2 is neutral attacking electrophile (formed by α– elimination reaction)



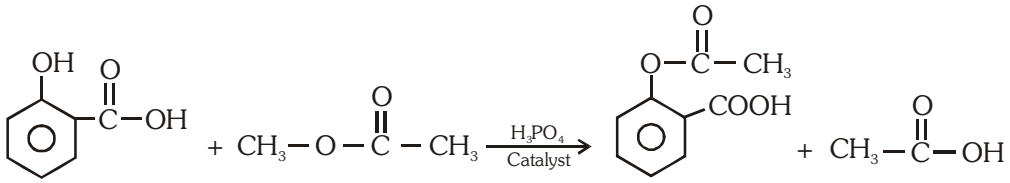
Asprin formation :



◆ **Kolbe 's Schmidt reaction :** This involves the reaction of C_6H_5ONa with CO_2 at 140^0 C followed by acid hydrolysis salicylic acid is formed followed.

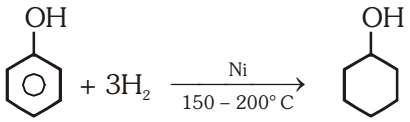


- **Asprin fomation**



Salicylic acid Asprin (pain killer)

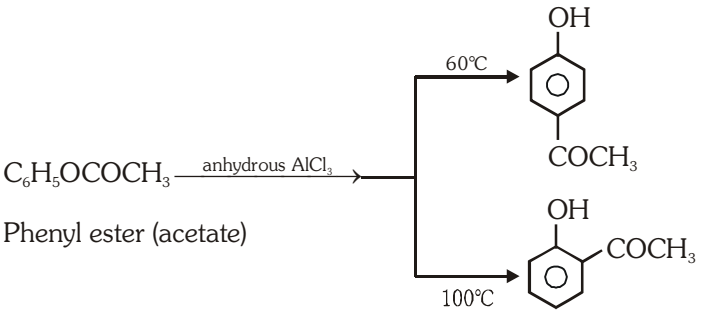
- **Hydrogenation:** Phenol when hydrogenated in presence of Ni at 150-200^{0}C forms cyclohexanol.



Cyclohexanol. ($C_6H_{11}OH$)
(used as a good solvent)

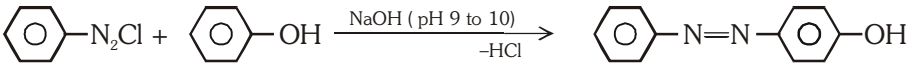
- **Fries rearrangement reaction :**

$C_6H_5OH + CH_3COCl \xrightarrow{\text{Anhydrous } AlCl_3} C_6H_5OCOCH_3$

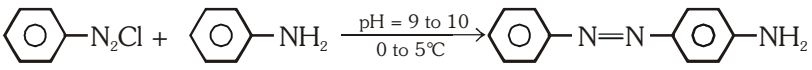


Phenyl ester (acetate)

- **Coupling reactions:** Phenol couples with benzene diazonium chloride in presence of an alkaline solution to form a dye (p- hydroxy azobenzene) red only.

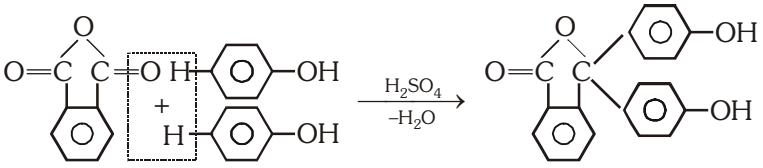


p–hydroxy azobenzene (Orange dye or Red dye)



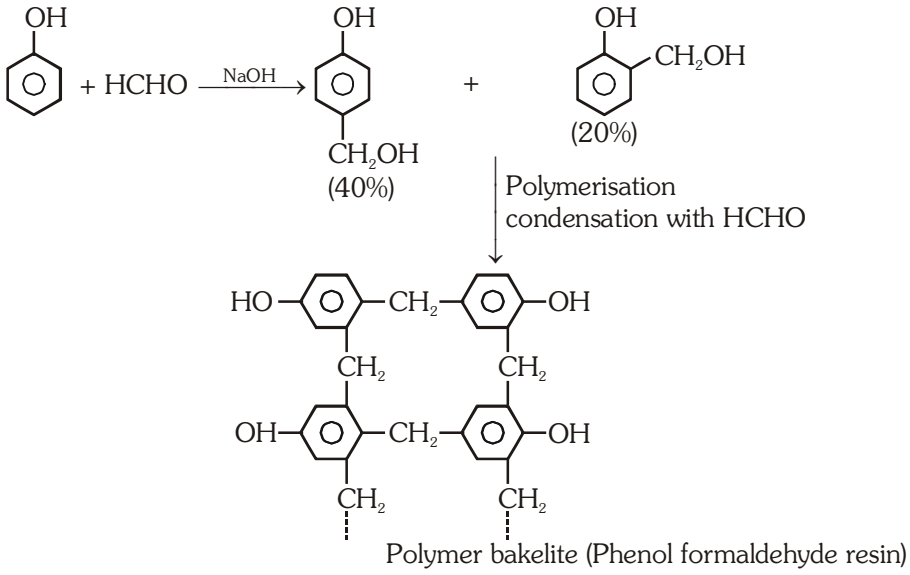
p–amino azobenjene (orange dye)

Phenol couples with phthalic anhydride in presence of conc. H_2SO_4 to form a dye (phenolphthalien) used as an indicator.



Phenol (2 molecules) Phenolphthalien (Colourless in acidic medium and pink in alkaline medium)

◆ **Lederer Manasse (Condensation with formaldehyde) :** Phenol condenses with HCHO (excess) in presence of NaOH or weak acid (H^+) to form a polymer known as bakelite (a resin).

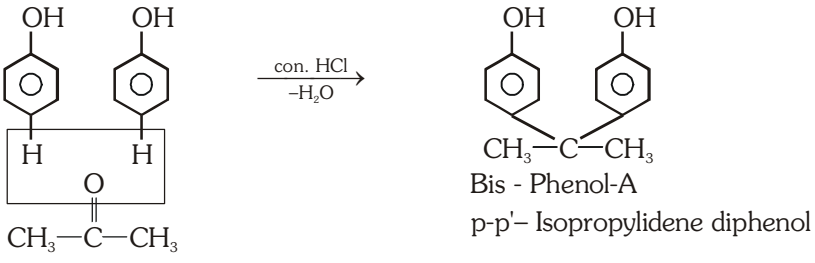


◆ **Leibermann's nitroso reaction :** When phenol is reacted with $NaNO_2$ and conc. H_2SO_4 it gives a deep green or blue colour which changes to red on dilution with water. When made alkaline with NaOH original green or blue colour is restrored.

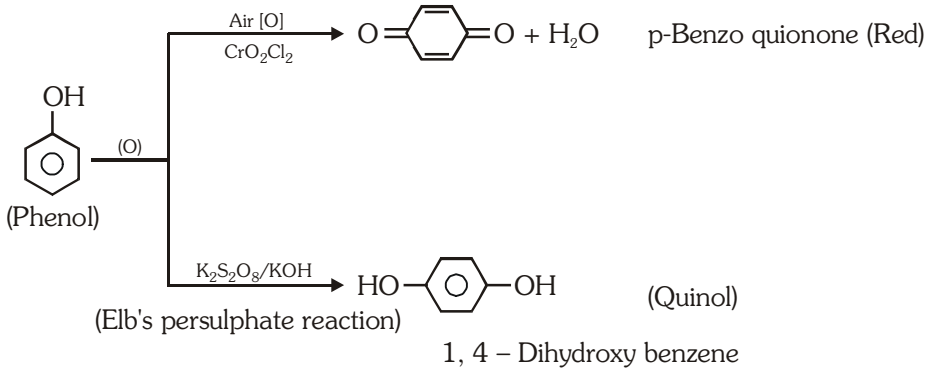
This reaction is used as a test of phenol.

$2NaNO_2 + H_2SO_4 \longrightarrow 2HNO_2 + Na_2SO_4$

◆ **Reaction with acetone:** (Condensation with acetone)



◆ **Oxidation:**



❑ **Test of Phenol :**

(i) Phenol turns blue litmus to red.

(ii) Aqeous solution of phenol gives a violet colour with a drop of ferric chloride.

(iii) Phenol gives Lieber mann 's nitroso test.

$$\text{Phenol in conc. } H_2SO_4 \xrightarrow[\text{excess of water}]{NaNO_2} \text{Red colour} \xrightarrow{NaOH\ excess} \text{Blue colour}$$

(iv) Aqeous solution of phenol gives a white ppt. of 2,4,6 tribromophenol with bromine water.

(v) Phenol combines with phthalic anhydride in presence of conc. H_2SO_4 to form phenolphthalein which gives pink colour with alkali.

(vi) With ammonia and sodium hypochlorite , phenol gives blue colour.

❑ **Differences between phenol and alcohol (C_2H_5OH) :**

(i) Phenol is more acidic than aliphatic alcohol due to resonance in phenoxide ion.

(ii) Phenol gives violet colour with $FeCl_3$ while aliphatic alcohol does not give.

(iii) Phenol gives triphenyl phosphate with PCl_5 while aliphatic alcohol gives alkyl chloride.

(iv) Phenol has phenolic odour whereas alcohol has pleasent odour.

(v) Phenol on oxidation gives quinone while alcohol gives aldehyde or ketone and acids.

❑ **Uses of Phenol :** Phenol is used :

(a) As an antiseptic in soaps and lotions. "Dettol" (2,4-Dichloro-3,5-dimethyl phenol)

(b) In manufacture of azodyes, phenolphthalein , picric acid (explosive), cyclohexanol (Solvent for rubber), plastics (bakelite) etc.

(c) In manufacture of drugs like aspirin salol, phenacetin etc.

(d) As preservative for ink.

ANILINE ($C_6H_5NH_2$)

Aniline is also called aminobenzene or phenyl amine. Aniline was first prepared by **Unverdon** 1826 by the distillation of indigo which is called **anil** in spanish and hence the name aniline. In aniline — NH_2 group is directly attached to benzene ring.

❑ **General Methods of Preparation :**

(1) Lab method : Aniline is prepared in the lab by reduction of $C_6H_5NO_2$ with Sn + HCl.

$$C_6H_5NO_2 \xrightarrow[(ii)NaOH]{(i)Sn+HCl} C_6H_5NH_2 + H_2O$$

(2) Industrial method : Aniline is obtained by reduction of nitrobenzene in presence of Fe/HCl.

$$C_6H_5—NO_2 \xrightarrow[(ii)NaOH]{(i)\ Fe+HCl} C_6H_5—NH_2 + H_2O$$

(3) From Phenol : Aniline is obtained when phenol is treated with ammonia in presence of $ZnCl_2$ at 300°C.

$$C_6H_5OH + NH_3 \xrightarrow[300°C]{ZnCl_2} C_6H_5NH_2 + H_2O$$

(4) From benzamide (Hofmann's reaction)**:** Aniline is formed when benzamide is treated with Br_2 and KOH.

$$C_6H_5CONH_2 + Br_2 + 4KOH \longrightarrow C_6H_5NH_2 + K_2CO_3 + 2KBr + 2H_2O$$

(5) From benzoic acid (Schmidt reaction) **:** Benzoic acid is dissolved in conc. H_2SO_4 and hydrazoic acid is dissolved in chloroform. When both solutions are mixed aniline obtained.

$$\underset{\text{(Hydrazoic acid)}}{C_6H_5COOH + N_3H} \xrightarrow[H_2SO_4]{Conc.} C_6H_5NH_2 + N_2\uparrow + CO_2\uparrow$$

(6) From chloro benzene : Aniline can be manufactured by the action of ammonia on chloro benzene in presence of cuprous oxide (Cu_2O).

$$2C_6H_5Cl + Cu_2O + 2NH_3 \longrightarrow 2\,C_6H_5NH_2 + 2CuCl + H_2O$$

(7) From Grignard reagent :

$$C_6H_5MgBr + ClNH_2 \longrightarrow C_6H_5NH_2 + Mg\begin{matrix}Br\\Cl\end{matrix} + C_6H_6$$

(8) From Benzene:

$$C_6H_6 + NH_2OH \xrightarrow{FeCl_3} C_6H_5NH_2 + H_2O$$

(9) From phenyl isocyanide :

$$C_6H_5N{\equiv}C + 2H_2O \longrightarrow C_6H_5NH_2 + HCOOH$$

(10) From phenyl isocyanate:-

$$C_6H_5N{=}C{=}O + 2KOH \longrightarrow C_6H_5NH_2 + K_2CO_3$$

❑ **Physical Properties :**

(i) Fresh, aniline is a colourless oily liquid. On standing the colour becomes dark brown due to action of air and light.

(ii) It's B.P. is 183° C.

(iii) It is heavier than water.

(iv) It has characteristic unpleasent odour. It is toxic in nature.

❑ **Similarities and Differences between Aromatic and Aliphatic amines :**

(A) Similarities :

(i) Both are basic, although aliphatic amines are more basic than the aromatic amines.

(ii) Both form salts with acids, however salts of aromatic amines are easily hydrolysed.

(iii) Both undergoes alkylation and acylation.

(iv) Both react with Grignard reagents forming hydrocarbons.

(v) Both forms schiff's bases.

(B) Differences :

(i) Aniline is insoluble in water while aliphatic amines are soluble in water (due to H-bonds)

(ii) Aniline gives diazonium salt with HNO_2 while aliphatic amines gives alcohol and nitrogen (except CH_3NH_2)

(iii) Aniline undergoes coupling and electrophilic substitution reactions in benzene ring while aliphatic is not.

(iv) Aniline has characteristic aromatic smell while aliphatic amines have smell like ammonia

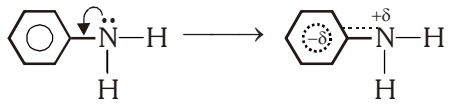
(v) Aniline gives aniline black dye with acidic $K_2Cr_2O_7$ while aliphatic does not form dye.

❑ **Chemical Properties :**

(i) Aniline is a primary amine it shows properties of both of benzene nucleus and —NH_2 group.

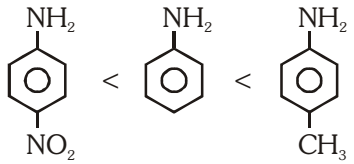
(ii) Aniline has weak basic nature as compared to aliphatic amine.

(ii) Weaker basic nature of aniline as compared to aliphatic amines can be explained on the basis of resonance. In aniline the non-bonding electron pair of N is delocalised in to benzene ring by resonance. Thus electron density is less on N atom due to which aniline is less basic than aliphatic amines



Order of basic strength : $RNH_2 > NH_3 > C_6H_5NH_2$

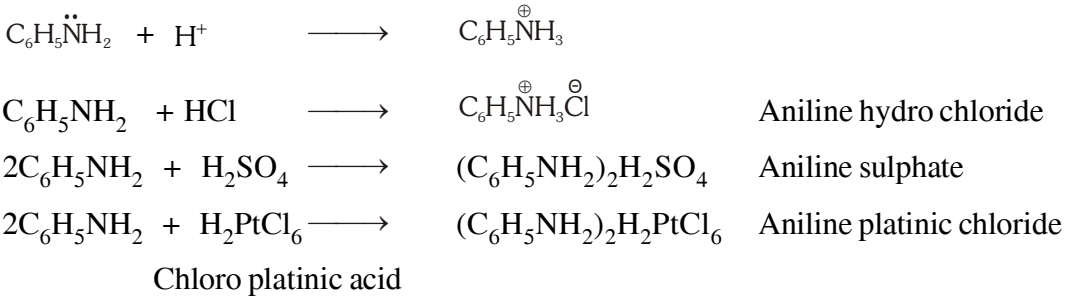
(iv) Electron withdrawing group decreases the basic strength where as electron donating groups increases the basic strength



(v) Aqueous solution of aniline is neutral to litmus

(A) Reactions due to —NH_2 group :

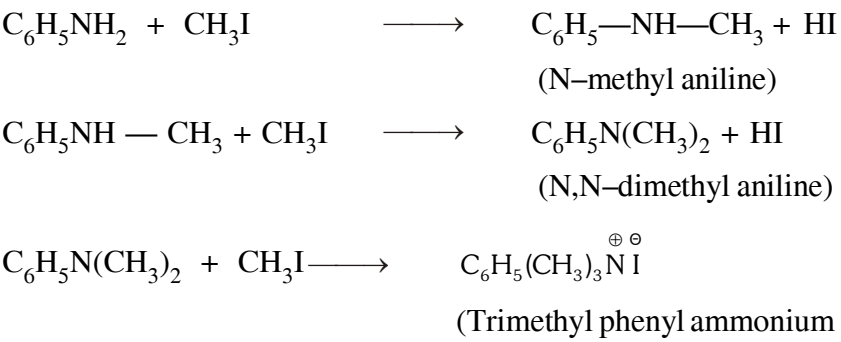
(1) Basic nature : Aniline is weak base but it forms salt with strong acids. It a accepts a proton.



Chloro platinic method : This is used to determination of molecular weight of organic compounds.

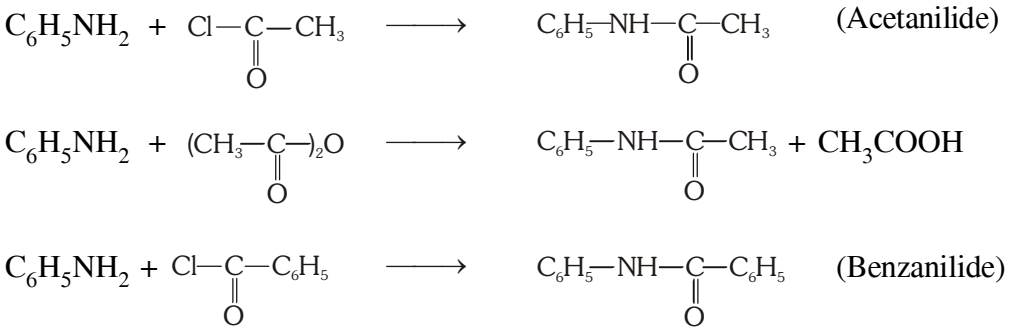
(2) Alkylation :

Aniline reacts with alkyl halides forming secondary, tertiary and quaternary ammonium salts depending on the concentration of alkyl halides.

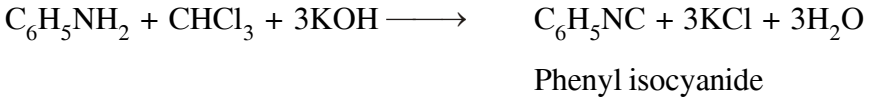


(3) Acylation :

Aniline reacts with acid chlorides or anhydrides to form corresponding amides called anilides. The reaction of $C_6H_5NH_2$ with benzoyl chloride is called **"Schotten Baumann reaction"**.



(4) Carbylamine reaction : When aniline is heated with $CHCl_3$ and KOH it gives isocyanide having unpleasent smell which can be easily detected.



◆ **Note :** (i) Intermediate species is dichloro carbene [**:** CCl_2].

(ii) This is a test of aniline and other primary amines and is known as **isocyanide test.**

(5) Hoffmann's mustard oil reaction :

When aniline is heated with alc. CS_2 and excess of $HgCl_2$ phenyl isothiocyanate having a characteristic smell of mustard oil is formed.

$$C_6H_5NH_2 + S{=}C{=}S \xrightarrow[-H_2S]{HgCl_2} C_6H_5N{=}C{=}S$$

Phenyl isothiocyanate

If the above reaction is carried out in presence of solid KOH diphenyl thiourea is formed (Used as accelerator for vulcanisation of rubber).

$$\begin{matrix} C_6H_5NH_2 \\ C_6H_5NH_2 \end{matrix} + S{=}C{=}S \longrightarrow \begin{matrix} C_6H_5NH \\ C_6H_5NH \end{matrix}\!\!>C{=}S + H_2S$$

When diphenyl thiourea is treated with HCl it gives phenyl isothiocyanate.

$$\begin{matrix} C_6H_5NH \\ C_6H_5NH \end{matrix}\!\!>C{=}S + HCl \longrightarrow C_6H_5{-}N{=}C{=}S + C_6H_5\overset{\oplus}{N}H_3\overset{\ominus}{Cl}$$

(6) Reaction with aldehydes : Aniline condenses with aldehydes to form schiff's base.

$$C_6H_5NH_2 + H{-}\underset{\underset{O}{\|}}{C}{-}C_6H_5 \xrightarrow{H^{\oplus}} C_6H_5N{=}CHC_6H_5 + H_2O$$

Benzylidene aniline
(schiff's base)

(7) Reaction with Heinsberg's reagent :

$$C_6H_5{-}SO_2Cl + HNHC_6H_5 \xrightarrow{-HCl} C_6H_5SO_2NHC_6H_5$$

(N– Phenylbenzene sulphonamide)

(8) Acidic nature :

$$C_6H_5NH_2 + Na \longrightarrow C_6H_5NHNa + 1/2H_2$$

N-Phenyl sodamide

(9) Diazotisation :

Diazotisation is a reaction in which ice cooled solution of aniline in a inorganic acid with sodium nitrite solution leading to the formation of diazonium salt.

$$C_6H_5NH_2 + NaNO_2 + HCl \xrightarrow[-H_2O]{0^\circ-5^\circ C} C_6H_5N_2Cl$$

$$C_6H_5NH_2 + HCl \longrightarrow C_6H_5\overset{\oplus}{N}H_3\overset{\ominus}{Cl}$$

$$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$$

$$C_6H_5\overset{\oplus}{N}H_3\overset{\ominus}{Cl} + HNO_2 \longrightarrow C_6H_5N_2Cl + 2H_2O$$

Benzene diazonium chloride

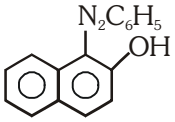
Benzene diazonium chloride is a useful synthetic reagent. It is used in the preparation of many organic compounds

◆ **Note :**

Coupling between arenediazonium cations and amines take place most rapidly in slightly acidic solution (pH 5 to 7). Under these conditions the concentration of the arenediazonium cation is at a maximum ; at the same time an excessive amount of the amine has not been converted to an unreactive aminium salt.

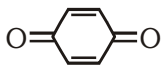
$C_6H_5N_2Cl \xrightarrow{C_6H_5OH} C_6H_5N{=}NC_6H_4OH$ [p-hydroxy azobenzene (orange dye)]

$C_6H_5N_2Cl \xrightarrow{C_6H_5NH_2} C_6H_5N{=}NC_6H_4NH_2$ [p-amino azobenzene (aniline yellow)]

$C_6H_5N_2Cl \xrightarrow[10\%NaOH]{\beta\text{–Naphthol}}$  (Red colour)

(10) Oxidation : Aniline forms a number of products depending upon the nature of oxidising agent:-

$-NH_2 \xrightarrow{[O]} -NHOH \xrightarrow{[O]} -NO \xrightarrow{[O]} -NO_2$

S.N.	Oxidant	Product
1.	Acidic $KMnO_4$	Aniline black (a dye)
2.	Alkaline $KMnO_4$	Azobenzene $C_6H_5N = NC_6H_5$
3.	Neutral $KMnO_4$	Azobenzene + Nitro benzene
4.	Caro's acid (H_2SO_5)	Nitrobenzene + Nitroso benzene
5.	CF_3COOOH	Nitrobenzene
6.	$K_2Cr_2O_7$ + conc. H_2SO_4	p–Benzo quinone 
7.	NaOCl	p- Amino Phenol (Violet colour)
8.	HNO_3	Decomposes
9.	Aniline $\xrightarrow[\text{\& light}]{\text{Atmospheric air}}$	Dark red colour

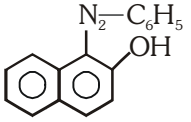
$C_6H_5N_2Cl$

- $\xrightarrow{C_2H_5OH}$
- $\xrightarrow{H_3PO_2}$
- $\xrightarrow{HCOOH}$
- $\xrightarrow{Na/NaOH,\ 2H}$

$\}$ C_6H_6 Benzene

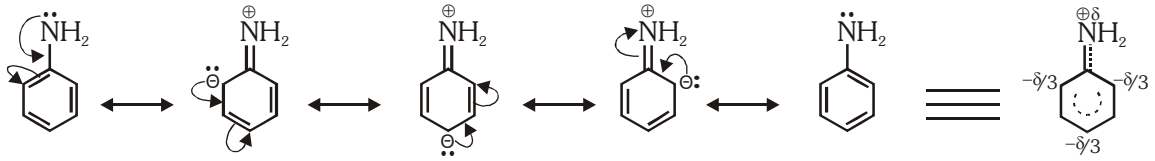
- $\xrightarrow{Cu_2Cl_2/HCl}$ $C_6H_5Cl + N_2 + HCl$
- $\xrightarrow{Cu_2Br_2/HBr}$ $C_6H_5Br + N_2 + HCl$
- $\xrightarrow{Cu_2(CN)_2/HCN}$ $C_6H_5CN + N_2 + HCl$

$\}$ Sandmeyer reactions

- $\xrightarrow{KI\ (aq.)}$ $C_6H_5I + N_2 + KCl$
- $\xrightarrow[\text{Sodium tetrafluoro borate}]{NaBF_4/\Delta}$ $C_6H_5F + BF_3 + NaCl$ — Balz–Schiemann reaction
- $\xrightarrow[\Delta]{H_2O}$ C_6H_5OH
- $\xrightarrow{Cu}$ C_6H_5Cl — Gattermann reactions
- $\xrightarrow[SnCl_2 + HCl]{+4H}$ $C_6H_5NHNH_2$ (Phenyl hydrazine)
- $\xrightarrow[10\%\ NaOH]{\beta\text{–Naphthol}}$  (Red colour)
- $\xrightarrow{SnCl_2/NaOH}$ C_6H_6
- $\xrightarrow{C_6H_5OH}$ $C_6H_5N{=}N{-}C_6H_4OH$, p-Hydroxy azobenzene (Orange dye)
- $\xrightarrow{C_6H_5NH_2}$ $C_6H_5N{=}N{-}C_6H_4NH_2$, p-Amino azobenzene (aniline yellow)

$\}$ Coupling reactions

(B) Reactions due to benzene ring :



Resonance hybrid

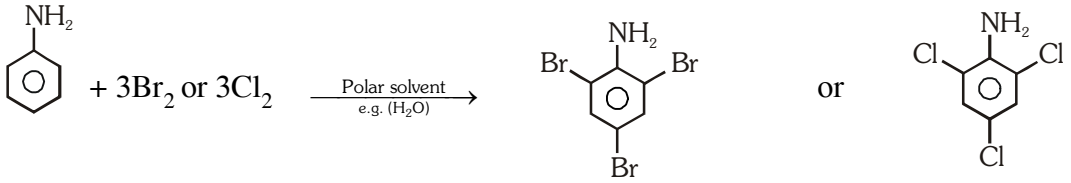
◆ **Note :**

(i) In aniline 2, 4, 6 or ortho and para positions are electron rich so electrophile attacks here.In aniline 3, 5, or meta position is electron deficient so nucleophile attacks here.

(ii) The benzene ring of aniline undergoes halogenation, sulphonation and nitration.

(iii) The NH_2 group is o-, p-directing.

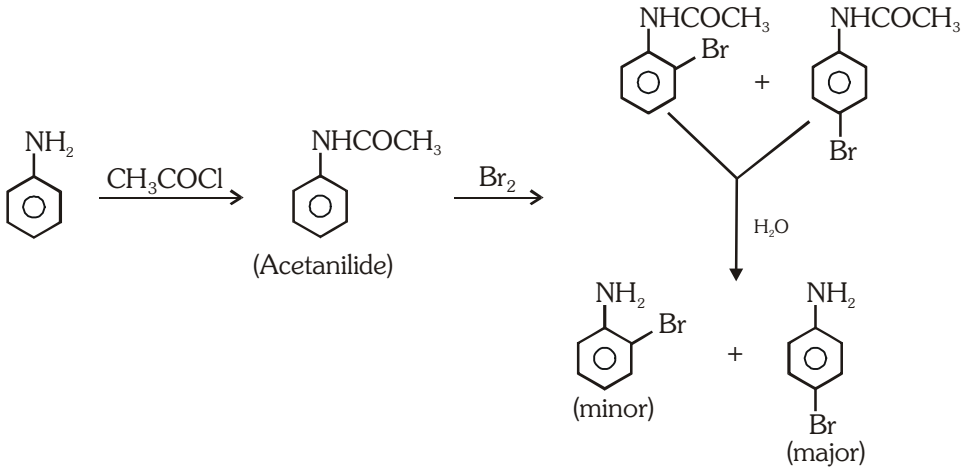
(1) Halogenation : Chlorine and bromine react with aniline and form trichloro and tribromo aniline respectively



2,4,6– Tribromo aniline
(white ppt.)

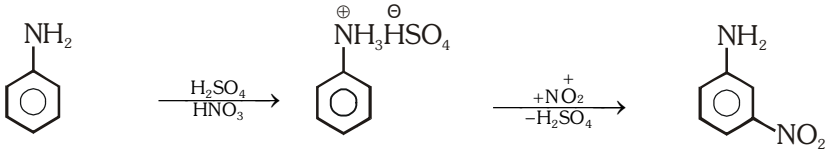
◆ **Note :**

However, monobromo or chloro derivative of aniline can be prepared if -NH_2 group is first protected by acetyl group. Here the reactivity decreases due to -I effect of acetyl group.

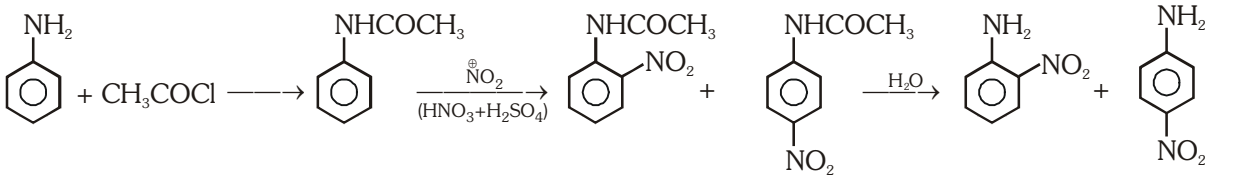


(2) Nitration :

(a) Direct nitration : The direct nitration of aniline by conc. HNO_3 and conc. H_2SO_4 give meta-nitroaniline. Due to positively charged N, m-position becomes electron rich as compared to o, p–position.



(b) Indirect nitration : In indirect nitration amino group is protected by acetylation to give acetanilide, which on nitration and subsequent hydrolysis give o- and p- nitro-aniline.



(major)

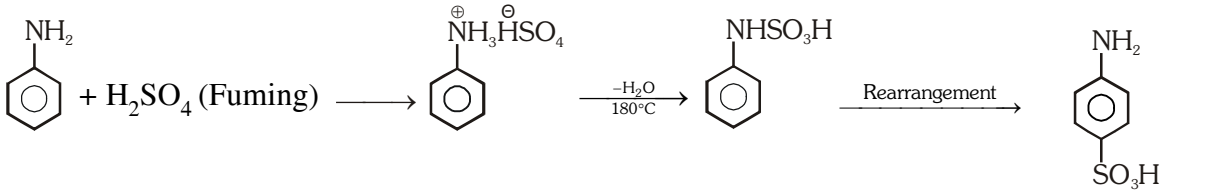
Ex. Azo dye test is given by

(A) All amines (B) Only secondary amine

(C) Only primary aliphatic amine (D) Only primary aromatic amine

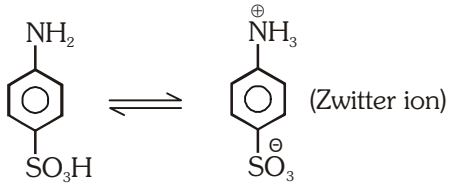
Sol. (D)

(3) Sulphonation : Aniline reacts with fuming H_2SO_4 to give sulphanilic acid.(p-Amino-benzene sulphonic acid)



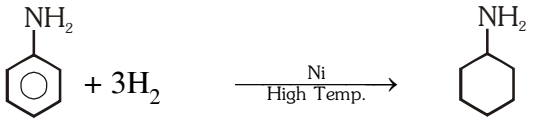
Sulphanilic acid

◆ **Note :** (i) The compounds in which both proton donating & proton accepting groups present are called ampholite (dipolar ion).

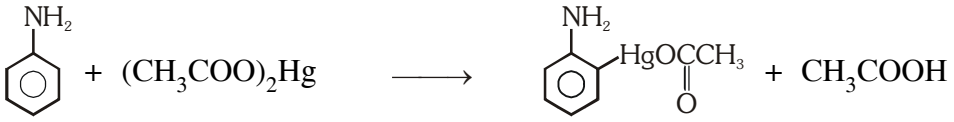


(4) Catalytic hydrogenation :

Aniline undergoes hydrogenation in presence of Ni at high temp. to form amino cyclohexane.



(5) Mercuration : When treated with alc. solution of mercuric acetate aniline undergoes mercuration.



o– Amino phenyl mercuric acetate

❑ **Tests of aniline :**

◆ **Carbylamine test :** Aniline gives carbylamine test or Isocyanide test.

$$C_6H_5NH_2 + CHCl_3 + KOH \longrightarrow \underset{\text{(Bad smelling)}}{C_6H_5NC}$$

◆ **Dye test :** Aniline is first diazotised. On adding alkaline soln. of β-naphthol to the diazotised product a scarlet red dye is formed.

◆ On heating with bromine water, a ppt. is formed.

❑ **Uses of Aniline :** Aniline is used in

(i) The manufacture of dyes and dye intermediates

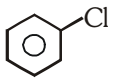
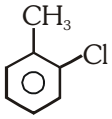
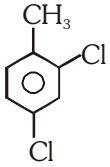
(ii) The manufacture of accelerators and antioxidants in rubber industry.

(iii) The manufacture of acetanilide, sulphuric acid and indigo

(iv) The Manufacture of sulpha drugs.

ARYL HALIDE

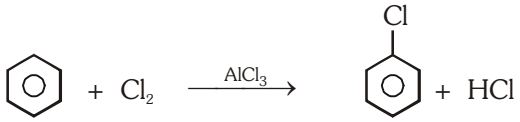
If halogen atom is directly attached to the benzene ring, then compound is called as Haloarene.

Example :   

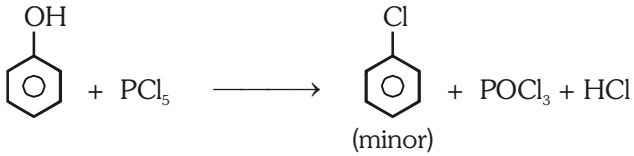
(Chlorobenzene) (2–Chlorotoluene) (2,4–Dichlorotoluene)

❑ GENERAL METHODS OF PREPARATION

◆ **Halogenation of Benzene :**



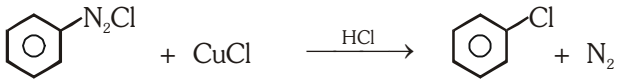
◆ **From Phenol :**

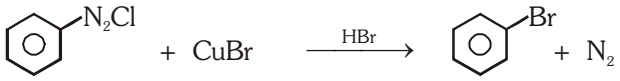


$$3C_6H_5OH + POCl_3 \longrightarrow (C_6H_5)_3PO_4 + 3HCl$$

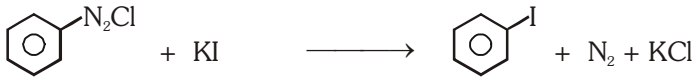
(major)

◆ **Sandmeyer's reaction :**

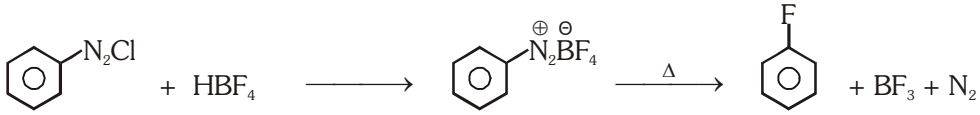




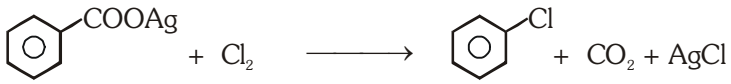
◆ **Reaction with KI :**



◆ **Balz-schiemann's reaction :**

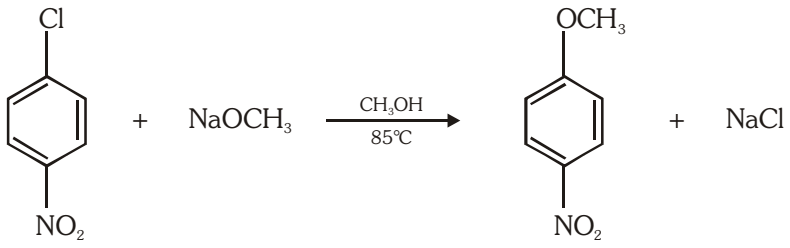


◆ **Hunsdicker reaction :**



Nucleophilic Aromatic Substitution by the addition Elimination Mechanism :

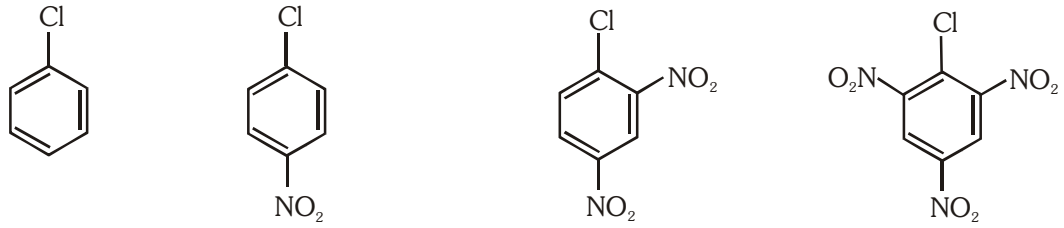
(i) The generally accepted mechanism for nucleophilic aromatic substitution in nitro-substituted aryl halides.



p-Chloronitrobenzene p-Nitroanisole

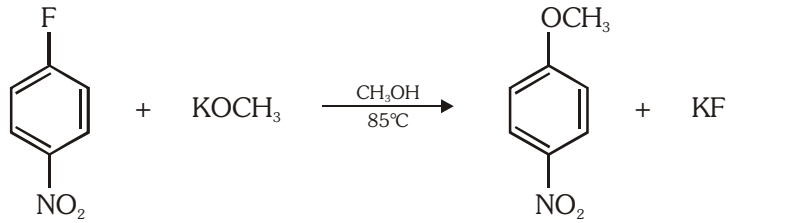
(ii) An ortho - nitro group exert a comparable rate-enhancing effect, m-chloronitrobenzyne while much more reactive than chlorobenzyne itself, is thousand of times less reactive than either o-or p-chloronitrobenzene.

(iii) The effect of o- & p-nitro substituents is cummulative, as the rate data for substitution with methoxide ion in a series of nitro-substituted chlorobenzene derivative demostrate increasing rate of reaction as :



	Chlorobenzene	1-Chloro-4-nitrobenzene	1-Chloro-2, 4-dinitrobenzene	2-Chloro-1, 3, 5-trinitrobenzene
Relative rate :	1.0	7×10^{10}	2.4×10^{15}	(too fast to measure)

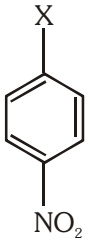
(iv) In contrast to nucleophilic substitution in alkyl halides, where alkyl fluorides are exceedingly unreactive, aryl fluorides undergo nucleophilic substitution readily when the ring bears an o- or a p-nitro group.



p-Fluoro nitrobenzene | Potassium methoxide | p-Nitroanisole (93%) | Potassium fluoride

(v) Indeed, the order of leaving group reactivity in nucleophilic aromatic substitution is the opposite of that seen in alphatic substitution.

(vi) Fluoride is the best reactive leaving group in nucleophilic aromatic substitution, iodide the least reactive.



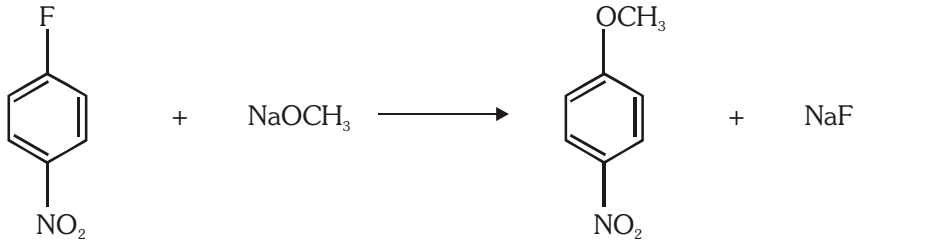
Relative reactivity towards sodium methoxide in methanol (50°C)

X =	F	Cl	Br	I
	312	1.0	0.8	0.4

(vii) Kinetic studies of many of the reactions described in teh section have demostrated that they follow a second-order rate law.

Rate = k[aryl halide] [nucleophile]

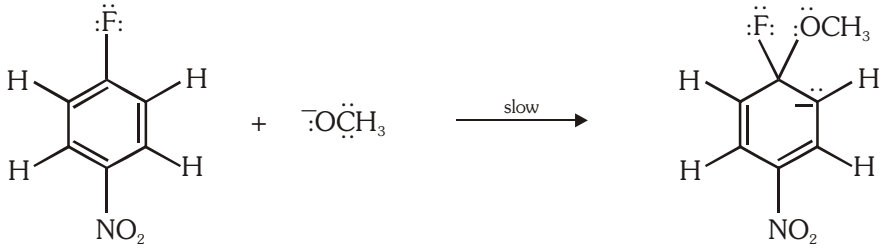
(viii) Second order kinetics is usually interpreated in terms of a bimolecular rate determining step.



p-Fluoronitrobenzene Sodium methoxide p-Nitroanisole Sodium Fluoride

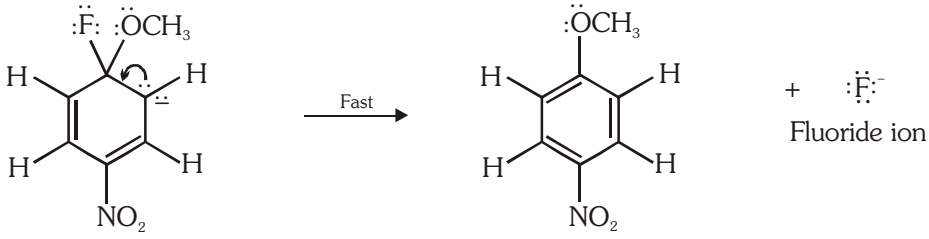
Mechanism :

Step -1 - Addition stage. The nucleophile, in this case methoxide ion, adds to the carbon atom that bears the leaving group to give a cyclohexadienyl anion intermediate.



p-Fluoronitrobenzene Methoxide ion Cyclohexadienyl anion intermediate

Step -2 - Elimination stage. Loss of halide form the cyclohexadienyl intermediate restores the aromaticity of the ring and gives the product of nucleophilic aromatic substitution.

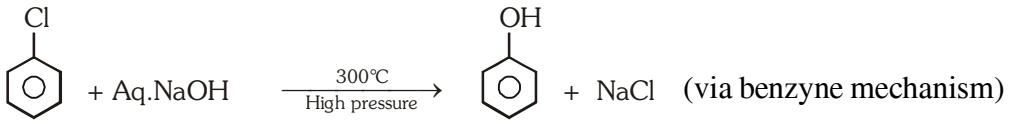


Fluoride ion

Cyclohexadienyl anion intermediate

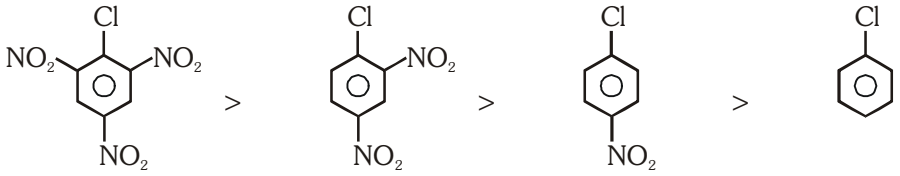
p-Nitroanisole

(a) Dow process :

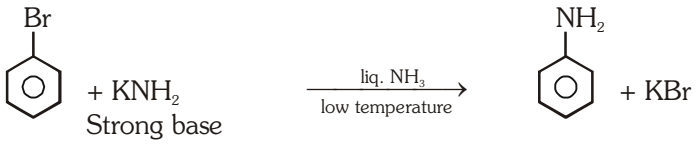


Presence of deactivating group in ortho and para position makes the nucleophilic substitution easier.

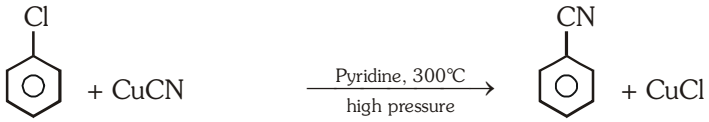
Reactivity Order : (Towards nucleophilic substatitution)



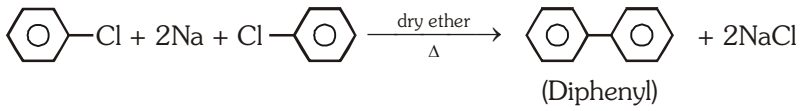
(b)



(c)

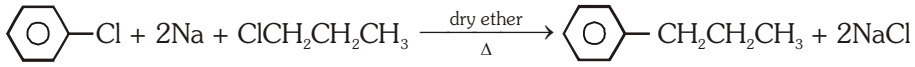


- **Fitting reaction :**

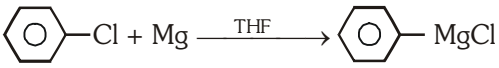


(Diphenyl)

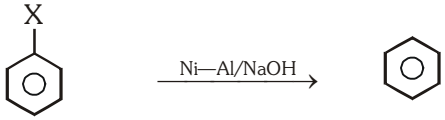
- **Wurtz fitting reaction :**



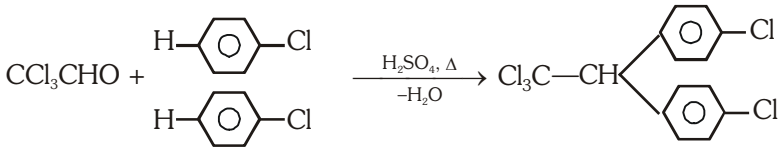
- **Formation of aryl megnisium halide :**



- **Reduction :**

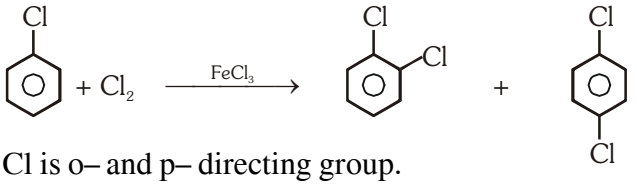


- **With Chloral :**

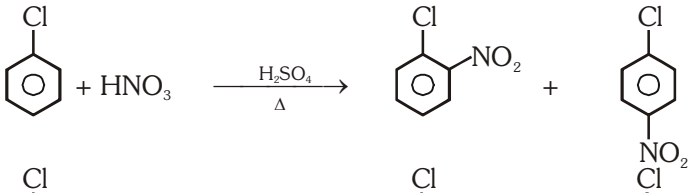


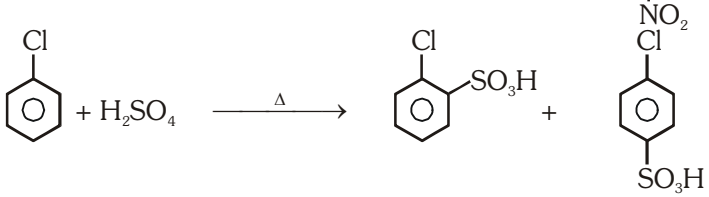
DDT (insecticide)
p,p–Dichloro diphenyl trichloroethane

◆ **Electrophilic Substitution Reaction :**

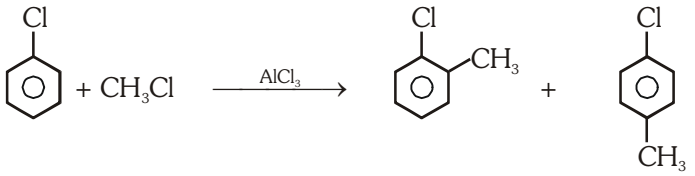
(i) 

Cl is o– and p– directing group.

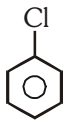
(ii) 

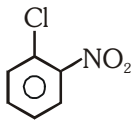
(iii) 

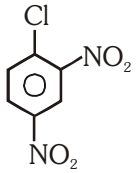
(iv) Friedal Craft Reaction :

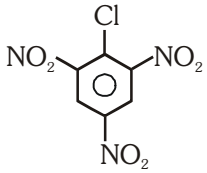


Q.1 Which of the following undergoes Hydrolysis most easily :

(A) 

(B) 

(C) 

(D) 

Ans. (D)

Sol. If there is more m-directing group then there will be more nuclephilic substitution reaction.

Q.2 The product in the following reaction is :

$Ph - Cl + Fe / Br_2 \longrightarrow$ Product

(A) o– bromo-chloro benzene (B) p– bromo-chloro benzene

(C) (A) and (B) both (D) 2, 4, 6-tribromo chloro benzene

Ans. (C)

Q.3 Since – Cl group is deactivating and o/p directing group so only o– and p– products are formed.

Q.4 The most reactive towards SN^1 is :

(A) $PhCH_2Cl$ (B) Ph–Cl (C) $CH_3CHCl(CH_3)$ (D) $p\text{–}NO_2\text{—}Ph\text{—}CH_2\text{—}Cl$

Ans. (A)

Q.5 S_{N^1} the intermediate carbocation is formed.

$C_6H_5\text{—}CH_2Cl \longrightarrow C_6H_5\overset{\oplus}{C}H_2$ is maximum stable due to resonance.

Q.6 Which of the following is used as insecticide :

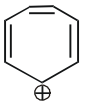
(A) D.D.T. (B) Chloritone (C) Chloropicrin (D) (A) and (C) both

Ans. (D)

AROMATIC COMPOUNDS

EXERCISE # O-I

1. Which of the following is not an aromatic compound :

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

AH0001

2. Which of the following group is divalent:

(A) Benzoyl (B) Benzyl (C) Benzal (D) p-Tolyl

AH0002

3. Benzene is a resonance hybrid mainly of two Kekule structures. Hence :

(A) Half of the molecules correspond to one structure, and half of the second structure

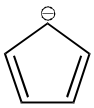
(B) At low temperatures benzene can be separated into two structures

(C) Two structures make equal contribution to resonance hybrid

(D) An individual benzene molecule changes back and forth between two structures

AH0003

4. How many π electron are there in the following species :



(A) 2 (B) 4 (C) 6 (D) 8

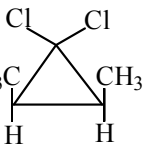
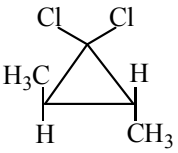
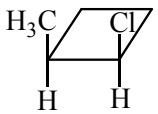
AH0004

5. The number of benzylic hydrogen atoms in ethylbenzene is:

(A) 3 (B) 5 (C) 2 (D) 7

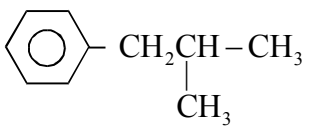
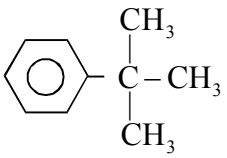
AH0005

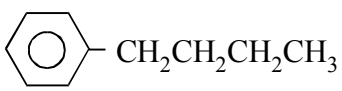
6. Trans-Butene-2 $\xrightarrow[\text{Solvent}]{CHCl_3 / KOH}$ Product

(A)  (B)  (C)  (D) Both (A) & (B)

AH0006

7.  + $CH_3CH_2CH_2CH_2Cl \xrightarrow{AlCl_3}$ hydrocarbon (X) major product X is:

(A)  (B) 

(C)  (D) None is correct

AH0007

8. In the sulphonation, acetylation and formylation of benzene the group of effective electrophiles would be :

(A) $SO_3^+, CH_3C \equiv \overset{+}{O}, H\overset{+}{C}O$ (B) $SO_3, CH_3 - C \equiv \overset{+}{O}, H\overset{+}{C}O$

(C) SO_3, CH_3CHO, CO + HCl (D) HSO_3, CH_3CO, HCO

AH0008

9. o/p ratio in highest for nitration of which of the following compound ?

(A) Ethyl benzene (B) Toluene

(C) Isopropyl benzene (D) Tertiarybutyl benzene

AH0009

10. Which can be used to generate NO_2^+ in nitration of benzene ring

(A) $HNO_3 + H_2SO_4$ (B) $HNO_3 + HClO_4$ (C) N_2O_5 (D) All

AH0010

11. For the electrophilic substitution reaction involving nitration, which of the following sequence regarding the rate of reaction is true?

(A) $k_{C_6H_6} > k_{C_6D_6} > k_{C_6T_6}$ (B) $k_{C_6H_6} < k_{C_6D_6} < k_{C_6T_6}$

(C) $k_{C_6H_6} = k_{C_6D_6} = k_{C_6T_6}$ (D) $k_{C_6H_6} > k_{C_6D_6} < k_{C_6T_6}$

AH0011

12. For the electrophilic substitution reaction involving sulphonation, which of the following sequence regarding the rate of reaction is true?

(A) $k_{C_6H_6} > k_{C_6D_6} > k_{C_6T_6}$ (B) $k_{C_6H_6} < k_{C_6D_6} < k_{C_6T_6}$

(C) $k_{C_6H_6} = k_{C_6D_6} = k_{C_6T_6}$ (D) $k_{C_6H_6} > k_{C_6D_6} < k_{C_6T_6}$

AH0012

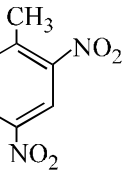
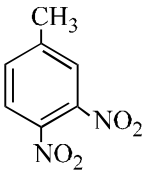
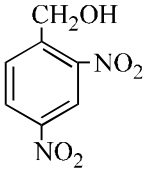
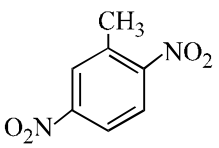
13. $C_6H_6 \xrightarrow[AlCl_3]{CH_3COCl} A \xrightarrow[HCl]{Zn-Hg} B$

The end product in the above sequence is:

(A) Toluene (B) Ethyl benzene (C) Both the above (D) None

AH0013

14. p-Nitrotoluene on further nitration gives:

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

AH0014

15. Reaction of SO_3 is easier in:

(A) Benzene (B) Toluene (C) Nitrobenzene (D) chlorobenzene

AH0015

16. Which order is correct for the decreasing reactivity to ring monobromination of the following compounds:

(I) $C_6H_5CH_3$ (II) C_6H_5COOH (III) C_6H_6 (IV) $C_6H_5NO_2$

(A) I > II > III > IV (B) I > III > II > IV (C) II > III > IV > I (D) III > I > II > IV

AH0016

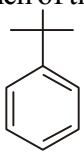
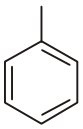
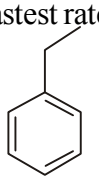
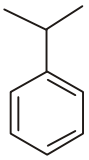
17. The highest yield of m-product is possible by the electrophilic substitution of the following:

(A) $C_6H_5CH_3$ (B) $C_6H_5CH_2COOC_2H_5$

(C) $C_6H_5CH(COOC_2H_5)_2$ (D) $C_6H_5C(COOC_2H_5)_3$

AH0017

18. Which of the following will undergo sulphonation at fastest rate ?

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

AH0018

19. Aniline under acidic medium, when chlorinated, produces:

(A) o-Chloro aniline (B) m-Chloro aniline

(C) p-Chloro aniline (D) Mixture of ortho and para-chloro aniline

AH0019

20. When sulphonilic acid (p-$H_2NC_6H_4SO_3H$) is treated with excess of bromine water, the product is:

(A) Tribromo product (B) Dibromo product

(C) Monobromo product (D) Tetrebromo product

AH0020

21. In a reaction of C_6H_5Y, the major product (>60%) is m-isomer, so the group Y is:

(A) –COOH (B) –Cl (C) –OH (D) $-NH_2$

AH0021

22. An aromatic compound of molecular formula $C_6H_4Br_2$ was nitrated then three isomers of formula $C_6H_3Br_2NO_2$ were obtained. The original compound is:

(A) o-Dibromobenzene (B) m-Dibromobenzene

(C) p-Dibromobenzene (D) Both A & C

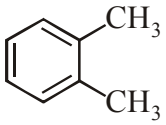
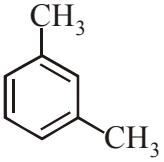
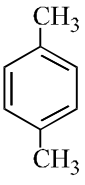
AH0022

23. Which of the following is most reactive towards sulphonation?

(A) m-Xylene (B) o-Xylene (C) Toluene (D) p-Xylene

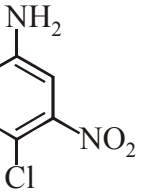
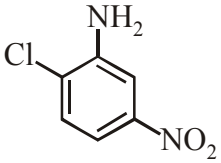
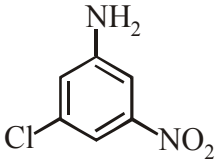
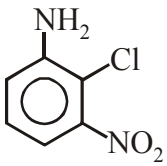
AH0023

24. Ring nitration of dimethyl benzene results in the formation of only one nitro dimethyl benzene. The dimethyl benzene is :

(A)  (B)  (C)  (D) None of these

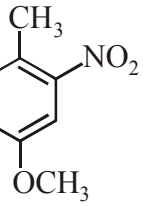
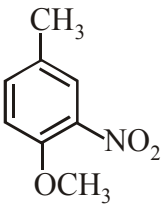
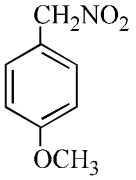
AH0024

25. If meta-nitroaniline is chlorinated, the major product is:

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

AH0025

26. If p-methoxy toluene is nitrated, the major product is:

(A)  (B)  (C)  (D) No reaction

AH0026

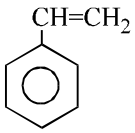
27. $C_6H_5CH_3 \xrightarrow{CrO_2Cl_2} A \xrightarrow{H_2O} B$

The functional group present in B and name of the reaction would be

(A) –CHO, Gattermann aldehyde synthesis (B) –CHO, Etard reaction

(C) $-COCH_3$, Friedel Crafts reaction (D) –CHO, Oxo reaction

AH0027

28. A $\xleftarrow{Br_2}$  $\xrightarrow{KMnO_4}$ B

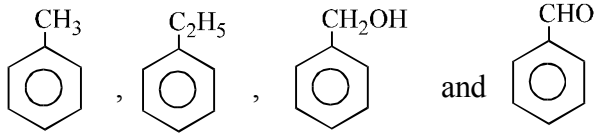
Compound A and B respectively are:

(A) o-Bromostyrene, benzoic acid (B) p-Bromostyrene, benzaldehyde

(C) m-Bromostyrene, benzaldehyde (D) Styrene dibromide, benzoic acid

AH0028

29. If the mixture of the following four aromatic compounds on oxidation by strong oxidising agent gives:



(A) Mixture of $C_6H_5CH_2OH + C_6H_5COOH$ (B) Mixture of $C_6H_5CHO + C_6H_5COOH$

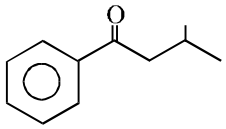
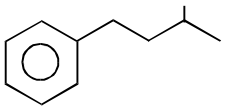
(C) Only C_6H_5COOH (D) None of the above

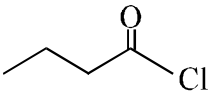
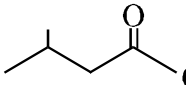
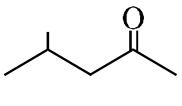
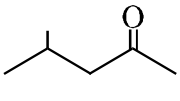
AH0029

30. Which of the following is/are produced when a mixture of benzene vapour and oxygen is passed over V_2O_5 catalyst at 775 K?

(A) Oxalic acid (B) Glyoxal (C) Fumaric acid (D) Maleic anhydride

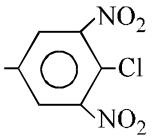
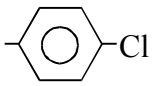
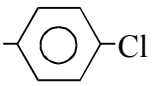
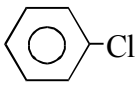
AH0030

31. Benzene on reaction with 'A' forms  which on reaction with 'B' forms 
'A' and 'B' are:

(A) Zn(Hg) + conc. HCl, 
(B) 
(C) 
(D) 

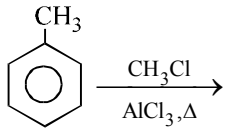
AH0031

32. Which chloroderivative of benzene among the following would undergo-hydrolysis most readily with aNaOH to furnish the corresponding hydroxy derivative.

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

AH0032

33. Major product of this reaction will be :



(A) o-Xylene (B) p-Xylene (C) Both (D) m-Xylene

AH0033

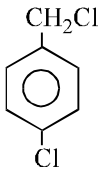
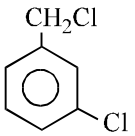
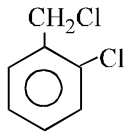
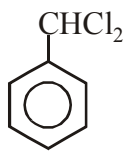
34. For preparing monoalkyl benzene, acylation process is preferred than direct alkylation because
(A) In alkylation, a poisonous gas is evolved
(B) In alkylation, large amount of heat is evolved
(C) In alkylation, polyalkylated product is formed
(D) Alkylation is very costly

AH0034

35. Phenol and ethanol are distinguished by the reaction with
(A) Red litmus (B) $NaHCO_3$ (C) $FeCl_3$ (D) Na

AH0035

36. An aromatic compound 'A' $C_7H_6Cl_2$, gives AgCl on bonding with alcoholic $AgNO_3$ solution, and yields C_7H_7OCl on treatment with sodium hydroxide. 'A' on oxidation gives a mono chlorobenzoic acid which affords only one mononitro derivative. The compound A is:

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

AH0036

37.  $+ H_2 \xrightarrow[\text{High pressure}]{\text{Ni, high temp.}}$ (A). Which of the following can be isolated as the product of this reaction.

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

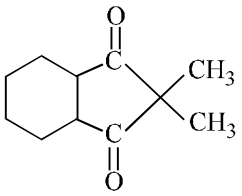
AH0037

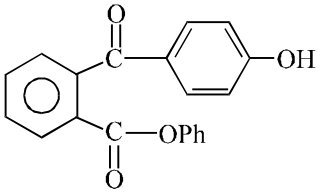
38. Chloral +  $\xrightarrow{\text{Conc.}H_2SO_4}$ product. The product is:

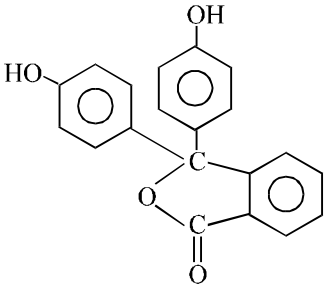
(A) Lindane (B) DDT (C) Teflon (D) Ethaneperchlorate

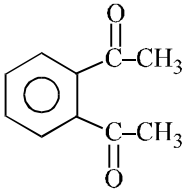
AH0038

39. Acetophenone $\xrightarrow{HCO_3H}$ A $\xrightarrow{H_3O^+}$ B + C $\xrightarrow[H^+]{\text{Pthalic Anhydride}}$ Indicator (D) ; C & D are

(A) CH_3OH & 

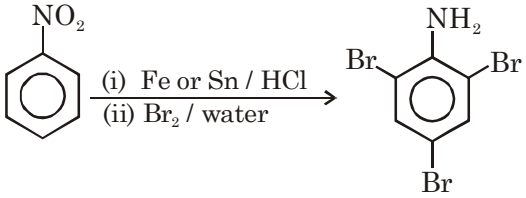
(B) PhOH & 

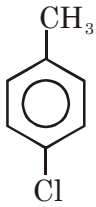
(C) PhOH & 

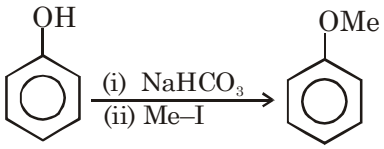
(D) CH_3OH & 

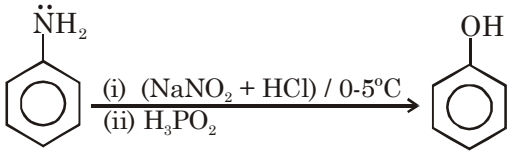
AH0039

40. Select the reaction giving correct major product :

(A) 

(B) $C_2H_2 \xrightarrow[\text{(ii) Me–Cl / } AlCl_3]{\text{(i) Red hot Fe tube}}$ 

(C) 

(D) 

AH0040

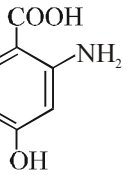
41. Phenol $\xrightarrow[\text{(ii) } CO_2 \text{ / 140°C}]{\text{(i) NaOH}}$ A $\xrightarrow{H^+ / H_2O}$ B $\xrightarrow[CH_3COOH, \Delta]{Al_2O_3}$ C

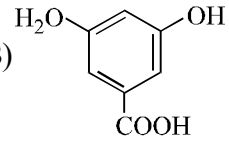
In this reaction, the end product C is:

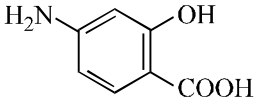
(A) Salicylaldehyde (B) Salicylic acid (C) Phenyl acetate (D) Aspirin

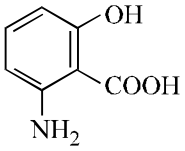
AH0041

42. m-Aminophenol on treatment with NaOH and CO_2 gives which of the following as major product?

(A) 

(B) 

(C) 

(D) 

AH0042

43. Stability order of following singlet halocarbene is

(A) $CF_2 > CCl_2 > CBr_2 > CI_2$

(B) $CI_2 > CBr_2 > CCl_2 > CF_2$

(C) $CCl_2 > CF_2 > CBr_2 > CI_2$

(D) $CF_2 > CI_2 > CCl_2 > CBr_2$

AH0043

EXERCISE # O-II

1. In which of the following reaction t-butylbenzene is formed:

(A) Benzene + iso-butyl chloride, $AlCl_3$

(B) Benzene + $(CH_3)_2C=CH_2 \xrightarrow{BF_3.HF}$

(C) Benzene + t-butyl alcohol $\xrightarrow{H_2SO_4}$

(D) Benzene + $(CH_3)_2 C= CH_2 \xrightarrow{AlCl_3}$

AH0044

2. The replacement of a hydrogen atom in benzene by alkyl group can be brought about with the following reagents :

(A) Alkyl chloride and $AlCl_3$

(B) Alkene and $AlCl_3$

(C) Alkanol and alkali

(D) Alkanol and acid

AH0045

3. Benzene reacts with n-propyl chloride in the presence of anhydrous $AlCl_3$ to give predominantly:

(A) n-Propylbenzene

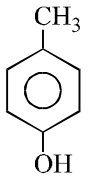
(B) Isopropylbenzene

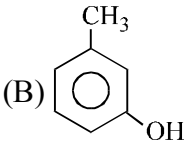
(C) 3-Propyl-1-chlorobenzene

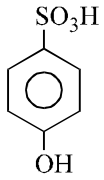
(D) Cumene

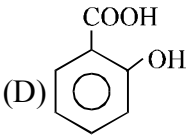
AH0046

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

(A) 

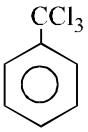
(B) 

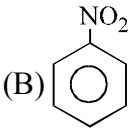
(C) 

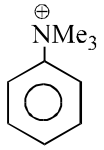
(D) 

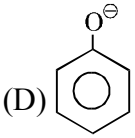
AH0047

5. Electrophilic attack of $NO_2^{\oplus}$ at meta position is observed in:

(A) 

(B) 

(C) 

(D) 

AH0048

6. The good method for converting benzene into n-propyl benzene is:

(A) $C_6H_6 + CH_3CH_2CH_2Cl$ + Anhyd. $AlCl_3$

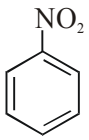
(B) $C_6H_6 + CH_3CH_2COCl$ + Anhyd. $AlCl_3$ and then treatment with Zn/Hg/HCl

(C) $C_6H_6 + CH_3CH_2COCl$ + Anhyd. $AlCl_3$ and then treatment with H_2 Ni

(D) C_6H_6 + Anhyd. $AlCl_3$ + cyclopropane

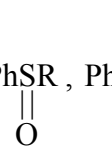
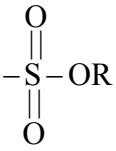
AH0049

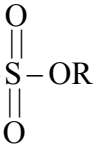
7. Which of the following can be used as reagent in Friedel Crafts reaction?

(A) 

(B) $CH_2=CH-Cl$ (C) CH_3CH_2Cl (D) $CH_2=CH-CH_2-Cl$

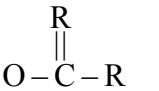
AH0050

8. Of the species PhSR,  and  the meta-substituted product is obtained from

(A) PhSR (B)  (C)  (D) 

AH0051

9. Amongst the following, the moderately activating group is

(A) —NHR (B) —$NHCOCH_3$ (C)  (D) —CH_3

AH0052

10. False statement is / are :

(A) Although benzene contains three double bonds, normally it does not undergo addition reaction.

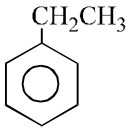
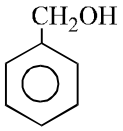
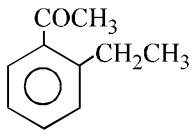
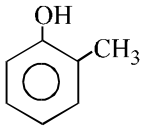
(B) m-Chlorobromobenzene is an isomer of m-bromochlorobenzene.

(C) In benzene, carbon uses all the three p orbitals for hybridization.

(D) An electron donating substitutent in benzene orients the incoming electrophilic group to the meta position.

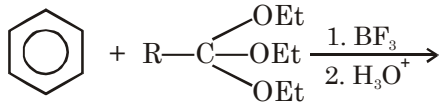
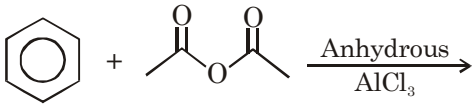
AH0053

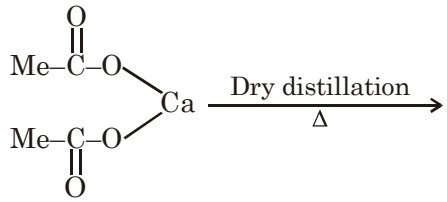
11. Benzoic acid may be prepared by the oxidation of:

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

AH0054

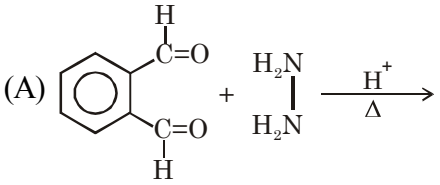
12. Identify reactions give ketone product ?

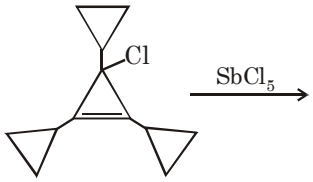
(A)  (B) 

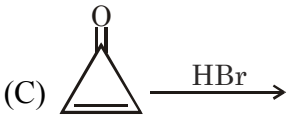
(C) $PhMgBr + Me-C\equiv N \xrightarrow{H_3O^+}$ (D) 

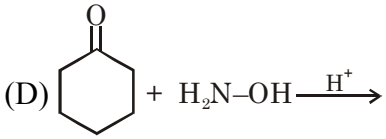
AH0055

13. Which of the following reaction(s) will give aromatic product ?

(A) 

(B) 

(C) 

(D) 

AH0056

14. Which of the following statements is/are not true?

(A) All ortho-para directing groups activates the ring towards electrophilic substitution.

(B) Halobenzene is ortho para directing but deactivating in nature

(C) All meta-directing groups have π-bond on the atom directly attached to the ring

(D) All meta directing groups are deactivating.

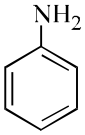
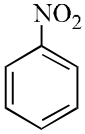
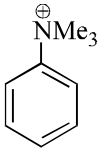
AH0057

15. Which of the following is not an ortho-para directing group?

(A) CF_3 (B) CCl_3 (C) –CH=CH–COOH (D) $-N \equiv C$

AH0058

16. Which of the following does not gives Fridel-Crafts reaction?

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

AH0059

17. Which of the following reactions of benzene proves the presence of three carbon–carbon double bonds in it :

(A) Formation of a triozonide

(B) Hydrogenation of benzene to cyclohexane

(C) Formation of $C_6H_6Cl_6$ by addition of chlorine

(D) Formation of nitrobenzene on heating benzene with a mixture of concentrated nitric acid and sulphuric acid

AH0060

18. Which of the following are classified as aromatic ?

(A) 1, 2, 3-Triphenylcyclopropenium cation (B) Cyclooctatetraenyl dianion

(C) Azulene (D) Annulene [10]

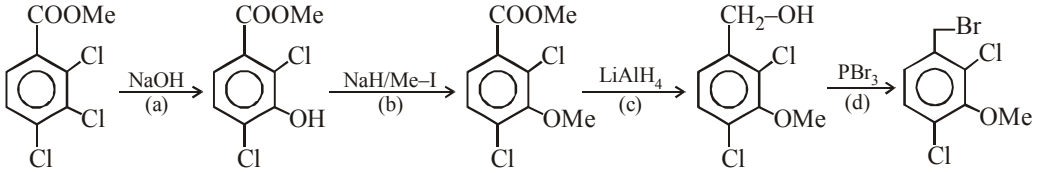
AH0061

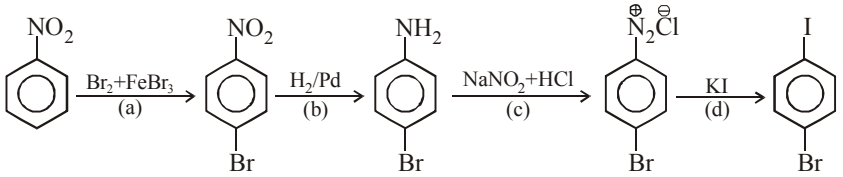
19. Which of the following is/are name of 1,2,3,4,5,6 - hexachloro cyclohexane :

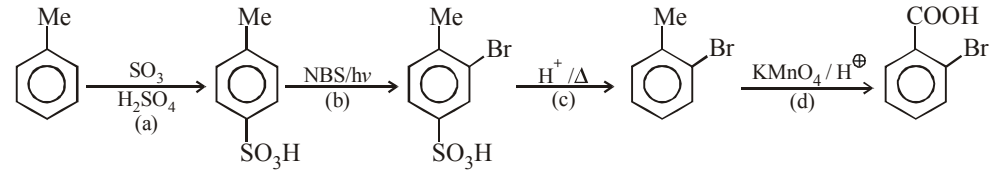
(A) Lindane (B) Gammexane (C) 666 (D) BHC

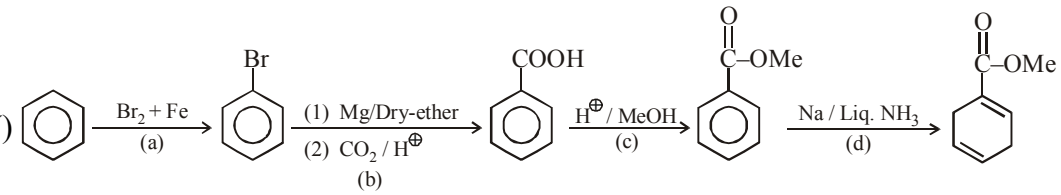
AH0062

20. Among the following reaction sequences identify incorrect step :

(I) 

(II) 

(III) 

(IV) 

(A) I–a ; II – b ; III – c ; IV – d

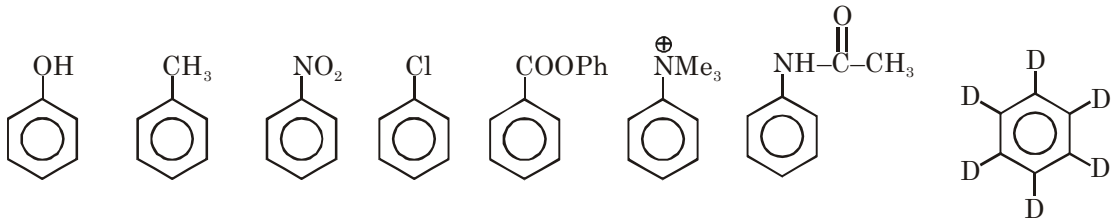
(B) I–b ; II – a ; III – d ; IV – d

(C) I–a ; II – a ; III – b ; IV – d

(D) I–b ; II – a ; III – d ; IV – c

AH0063

21. How many of following compounds are less reactive than benzene for sulphonation by conc. H_2SO_4 :



(A) 2

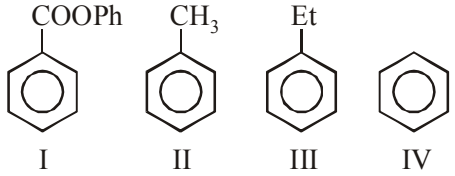
(B) 4

(C) 6

(D) 8

AH0064

22 . Decide the correct order of reactivity of following compounds towards halogenation with ($Cl_2 + AlCl_3$).



(A) I > II > III > IV

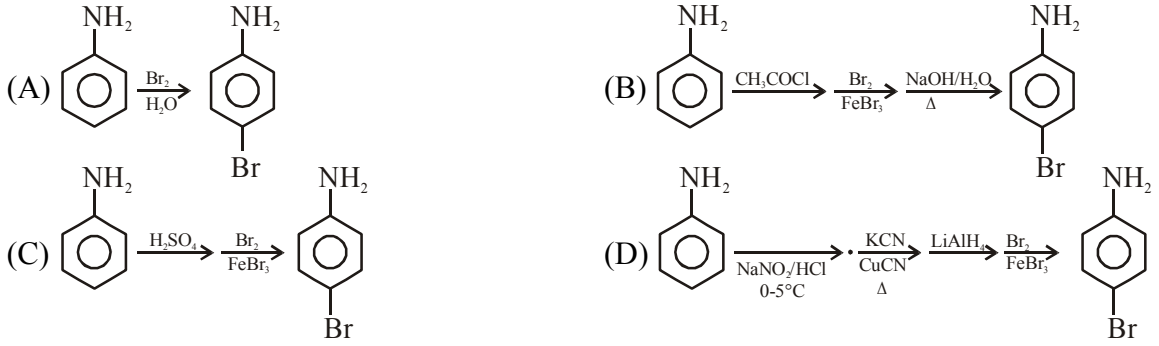
(B) II > III > IV > I

(C) III > II > IV > I

(D) II > III > I > IV

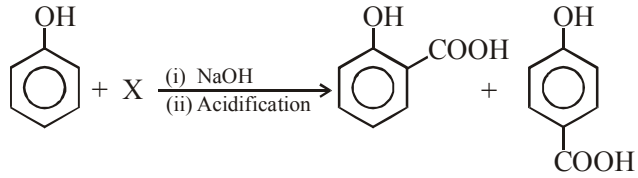
AH0065

23 Which of the following method(s) is/are not used to prepare p-bromo aniline as major product :



AH0066

24.

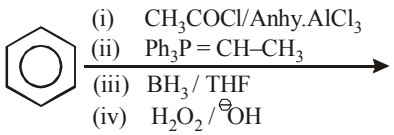


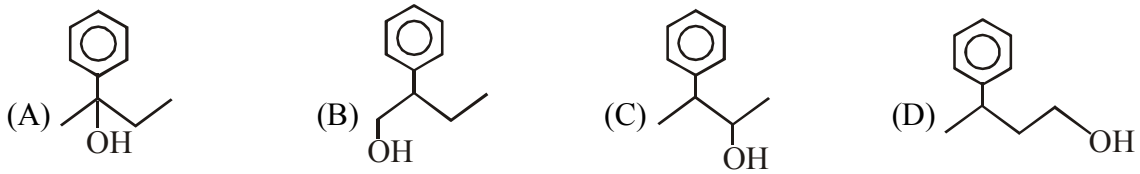
X is/are -

(A) $CHCl_3$ (B) CCl_4 (C) CO_2 (D) HCOOH

AH0067

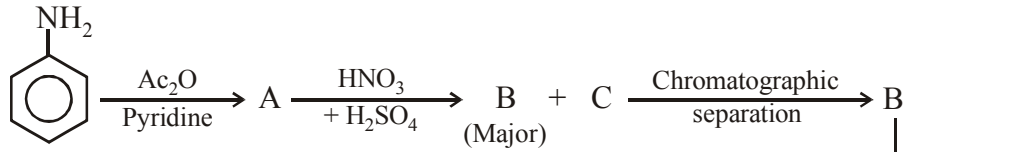
25. Which product is/are not obtained in following reaction.



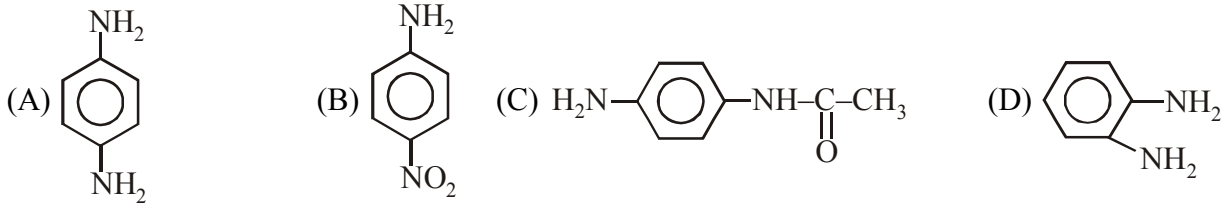


AH0068

26.

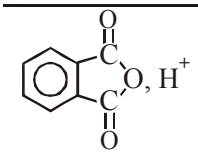


E is :



AH0069

27. Cumene $\xrightarrow[h\nu]{O_2}$ A $\xrightarrow[H_2SO_4]{conc.}$ Acetone + B $\longrightarrow$ C.



Identify correct statement :

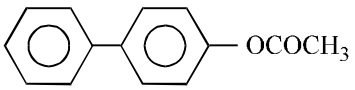
(A) Product C is phenophthalein indicater

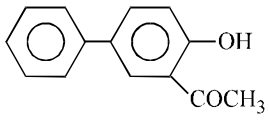
(B) Product B gives CO_2 effervescence with $NaHCO_3$

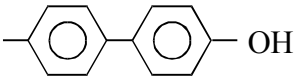
(C) Product A formation involves carbocation intermediate

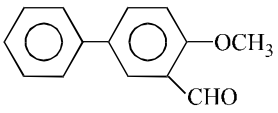
(D) Product B gives no colour with neutral $FeCl_3$

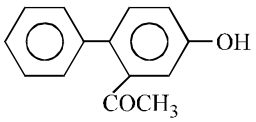
AH0070

28.  $\xrightarrow{AlCl_3}$? Major Product is :

(A) 

(B) H_3COC 

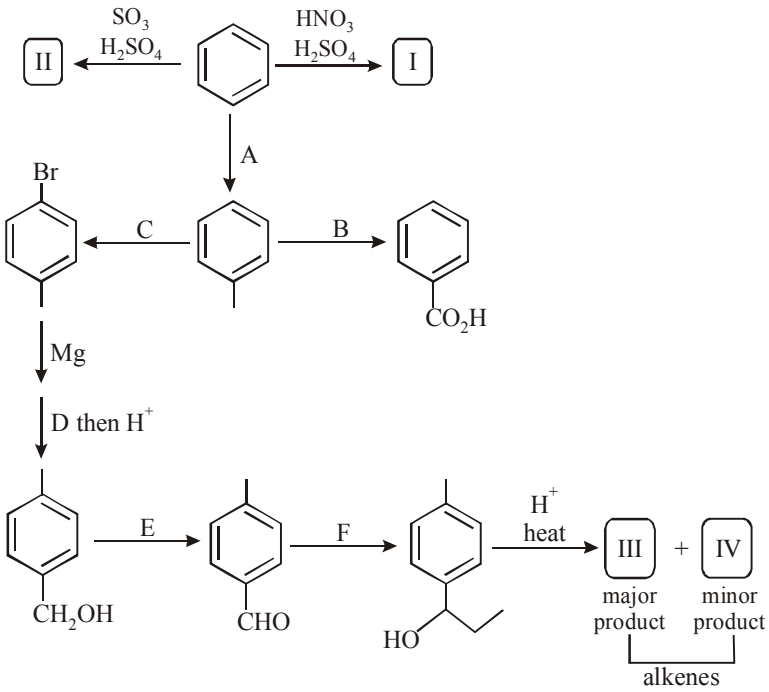
(C) 

(D) 

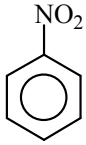
AH0071

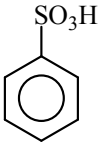
Paragraph for 29 to 30

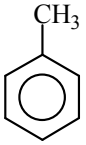
Identify reagent used and intermediate products in following conversion.

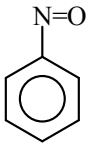


29. Identify II product -

(A) 

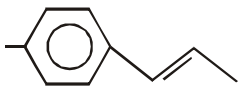
(B) 

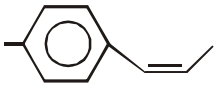
(C) 

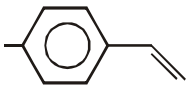
(D) 

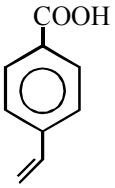
AH0072

30. (III) major product is ?

(A) 

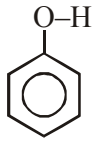
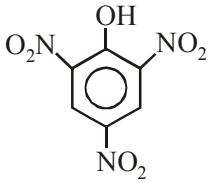
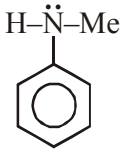
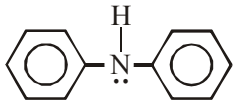
(B) 

(C) 

(D) 

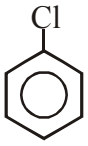
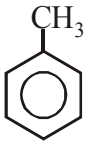
AH0072

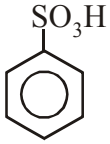
31. **Match the following :**

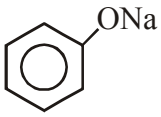
Column-I (Properties)		**Column-II (Compound)**
(A) $CO_2\uparrow$ is evolved from $NaHCO_3$	(P)	
(B) Gives libermann nitroso test	(Q)	
(C) Gives yellow oily liquid with $NaNO_2$+HCl	(R)	
(D) Evolve a colourless gas with active metals	(S)	

AH0073

32. **Match the following :**

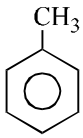
Column I (Compound)	**Column II (Properties)**
(A) 	(P) o-p directing
(B) 	(Q) m-directing

(C)  (R) Activating towards electrophile

(D)  (S) Deactivating towards electrophile

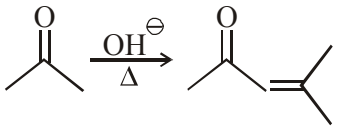
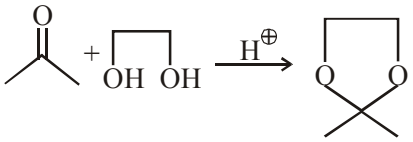
AH0074

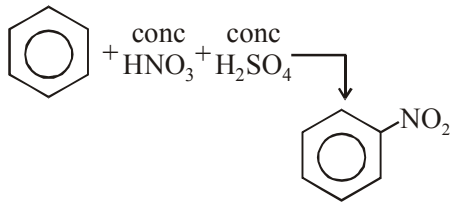
33. Match the column :

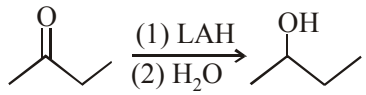
Column I (Reaction)	**Column II (Product & its property)**
(A)  + CrO_3 in $CH_3COOH \longrightarrow$?	(P) Tropylium ion
(B)  + $Ph_3C^{\oplus} \longrightarrow$?	(Q) Benzaldehyde
(C)  + n-Pr Br + $ZnCl_2 \longrightarrow$?	(R) Product can oxidise by $KMnO_4/H^+$
(D) $C_6H_6 + CO + HCl \xrightarrow{AlCl_3}$?	(S) Aromatic product obtained

AH0075

34.

Column - I (Reactions	**Column - II (Intermediate formed or type of reaction)**
(A) 	(P) Product obtained as racemic mixture
(B) 	(Q) Substitution reaction

(C) 

(D) 

(R) $Nu^{\ominus}$ Addition takes place during reaction

(S) Carbocation intermediate

(T) Carbanion intermediate

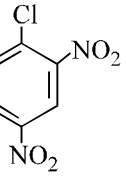
AH0076

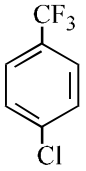
EXERCISE # S-I

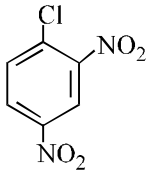
1. Write the most stable resonating structure for the cyclohexadienyl anion formed by reaction of methoxide ion with o-fluoronitrobenzene.

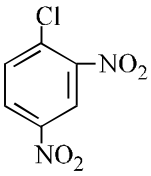
AH0077

2. Write the principal organic product in each of the following reactions:

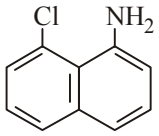
(i)  $\xrightarrow[\text{triethylene glycol}]{H_2NNH_2}$ B

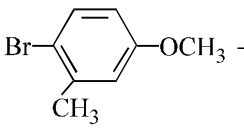
(ii)  $\xrightarrow[(ii)\,NaOCH_3,CH_3OH]{(i)\,HNO_3,H_2SO_4}$ C

(iii)  $+ CH_3CH_2ONa \longrightarrow$ D

(iv)  $+ C_6H_5CH_2SNa \longrightarrow$ E

AH0078

3. (i)  $\xrightarrow[(ii)\,CuBr]{(i)\,NaNO_2,HBr}$ E

(ii)  $\xrightarrow[(ii)\,NaSCH_3]{(i)\,NBS,Benzoyl\ peroxide,CCl_4,heat}$ F

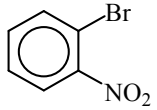
AH0079

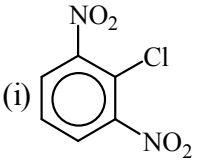
4. Reaction of 1,2,3-tribromo-5-nitrobenzene with sodium ethoxide in ethanol gave a single product, $C_8H_7Br_2NO_3$, in quantitative yield. Suggest a reasonable structure for this compound.

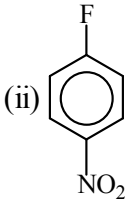
AH0080

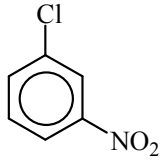
5. Compare the given characteristics of aniline and cyclohexanamine :
(i) Both are primary amine
(ii) Both can be acylated by RCOCl
(iii) Both reacts with $CHCl_3$/KOH
(iv) Both reacts with $NaNO_2$ + HCl at 0-5°C
(v) Both reacts with $PhSO_2Cl$ to give a compound which is soluble in KOH
(vi) Both gives coupling reaction with phenol
(vii) Both gives electrophilic substitution reaction
How many of the given characteristics are correct?

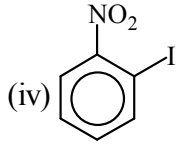
AH0081

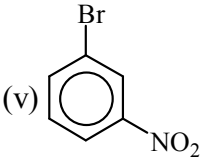
6. Number of compounds which can show faster rate of nucleophilic substitution of halogen than  :

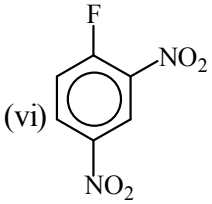
(i) 

(ii) 

(iii) 

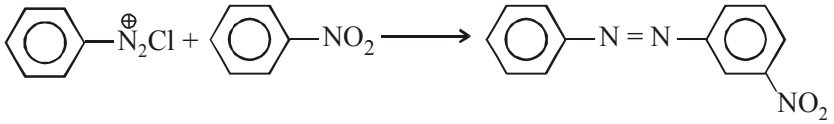
(iv) 

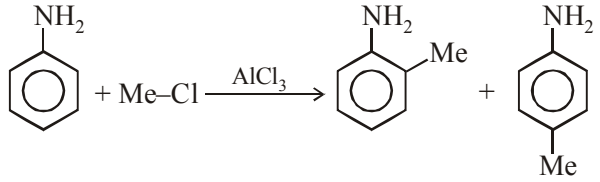
(v) 

(vi) 

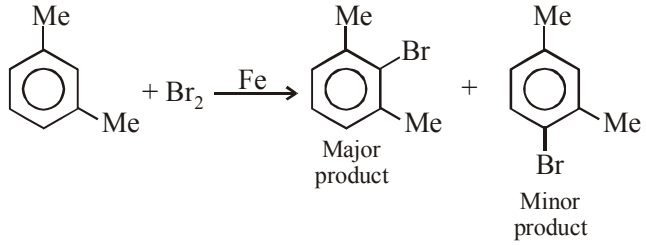
AH0082

7. Identify total number of reactions incorrectly match with its product ?

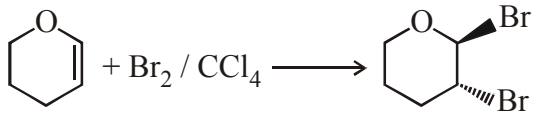
(a) 

(b) 

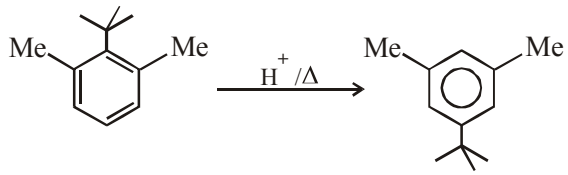
(c) $Et–OH + NaI \xrightarrow[H_2SO_4]{conc.} Et - I$

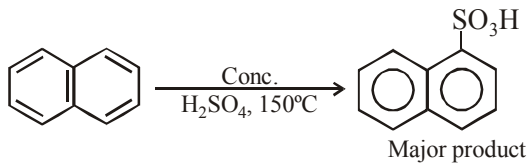
(d) 

(e) $Me–C\equiv CH + Na/Liq\ NH_3 \longrightarrow Me–CH = CH_2$

(f) 

100 % product [Stereo specific reactions] / 100 % उत्पाद [त्रिविम् विशिष्ट अभिकिया]

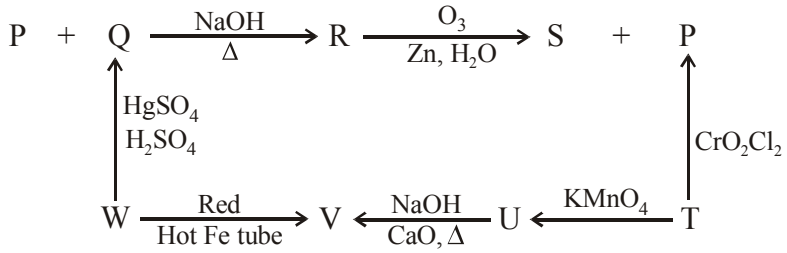
(g) 

(h) 

AH0083

Paragraph for No. 8 to 9

For given reaction sequence molecular formula for compound 'U' is $C_7H_6O_2$ & P gives negative Fehling test.

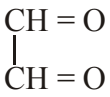
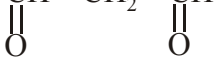


8. Compound which is not a hydrocarbon

(A) W (B) R (C) T (D) V

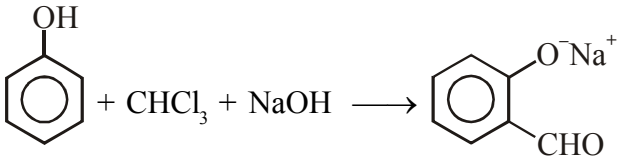
AH0084

9. Compound S is :

(A) $CH_3 - CH = O$ (B) $Ph - CH = O$ (C)  (D) 

AH0084

EXERCISE # (MAINS)

1. 

The electrophile involved in the above reaction is **[AIEEE-2006]**

(1) dichlorocarbene ($:CCl_2$)

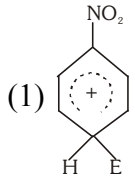
(2) trichloromethyl anion ($\overset{\ominus}{(}CCl_3$)

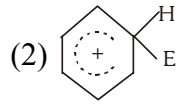
(3) formyl cation ($\overset{\oplus}{(}CHO$)

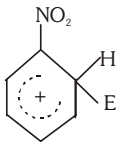
(4) dichloromethyl cation ($\overset{\oplus}{(}CHCl_2$)

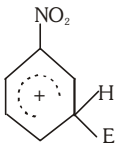
AH0085

2. The electrophile, $E^{\oplus}$ attacks the benzene ring to generate the intermediate σ–complex. Of the following, which σ–complex is of lowest energy ? **[AIEEE-2008]**

(1) 

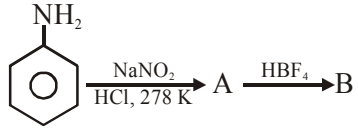
(2) 

(3) 

(4) 

AH0086

3. In the chemical reactions, **[AIEEE-2010]**



the compounds 'A' and 'B' respectively are :-

(1) Nitrobenzene and chlorobenzene

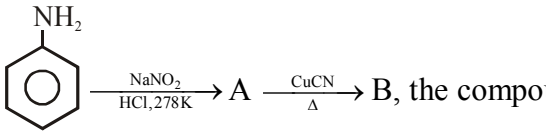
(2) Nitrobenzene and fluorobenzene

(3) Phenol and benzene

(4) Benzene diazonium chloride and fluorobenzene

AH0087

4. In the chemical reactions



, the compounds A and B respectively are : **[AIEEE-2011]**

(1) Fluorobenzene and phenol

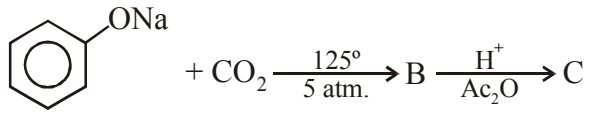
(2) Benzene diazonium chloride and benzonitrile

(3) Nitrobenzene and chlorobenzene

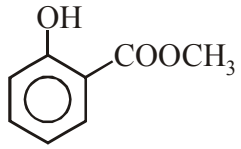
(4) Phenol and bromobenzene

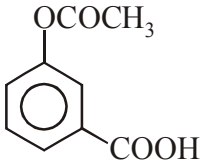
AH0088

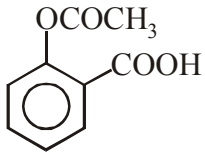
5. Sodium phenoxide when heated with CO_2 under pressure at 125ºC yields a product which on acetylation produces C. **[JEE(Main)-2014]**

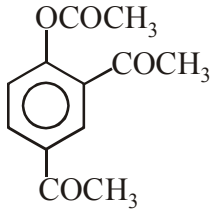


The major product C would be :

(1) 

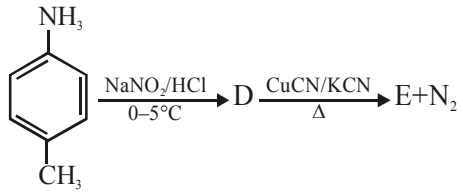
(2) 

(3) 

(4) 

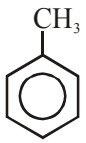
AH0089

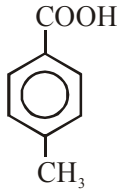
6. In the reaction **[IIT-2015]**

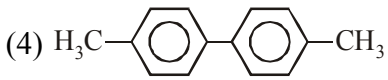


the product E is :-

(1) 

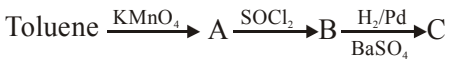
(2) 

(3) 

(4) 

AH0090

7. In the following sequence of reactions : **[IIT 2015]**

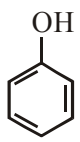


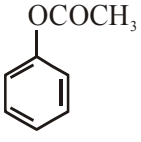
the product C is :-

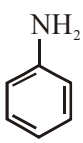
(1) $C_6H_5CH_2OH$ (2) C_6H_5CHO (3) C_6H_5COOH (4) $C_6H_5CH_3$

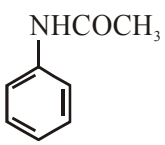
AH0091

8. Which of the following compounds will significant amont of meta product during mono-nitration reaction ? **[JEE(Main)-2017]**

(1) 

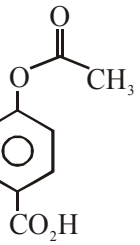
(2) 

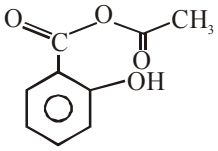
(3) 

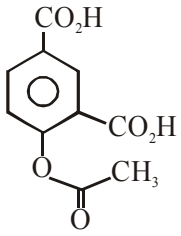
(4) 

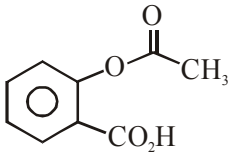
AH0092

9. 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]**

(1) 

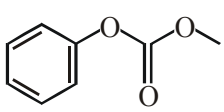
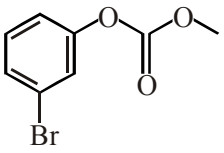
(2) 

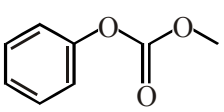
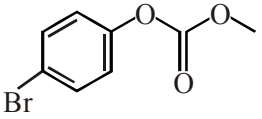
(3) 

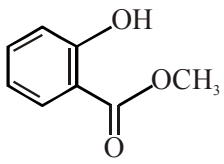
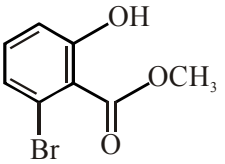
(4) 

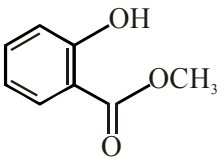
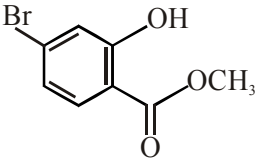
AH0093

10. 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]**

(1)  and 

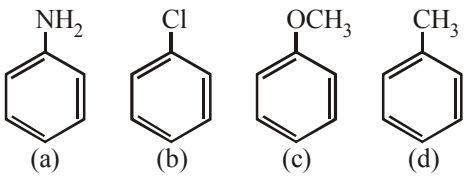
(2)  and 

(3)  and 

(4)  and 

AH0094

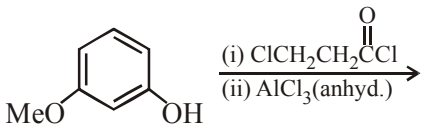
11. The increasing order of nitration of the following compound is :-**[JEE(Main)-2018(ONLINE)]**

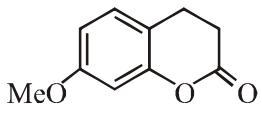


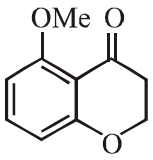
(1) (b) < (a) < (c) < (d)
(2) (b) < (a) < (d) < (c)
(3) (a) < (b) < (c) < (d)
(4) (a) < (b) < (d) < (c)

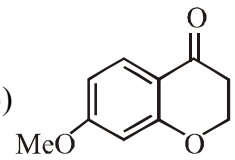
AH0095

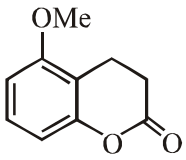
12. The major product of the following reaction is : **[JEE(Main)-2018(ONLINE)]**



(1) 

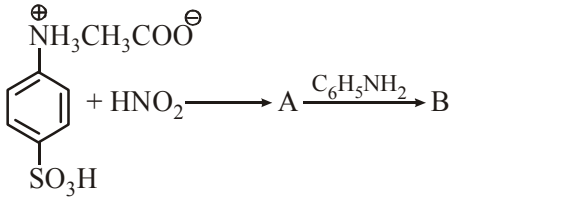
(2) 

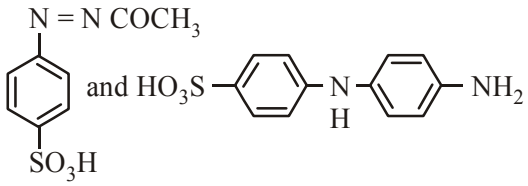
(3) 

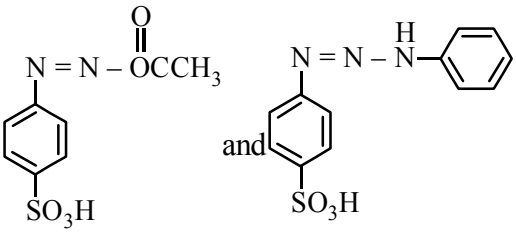
(4) 

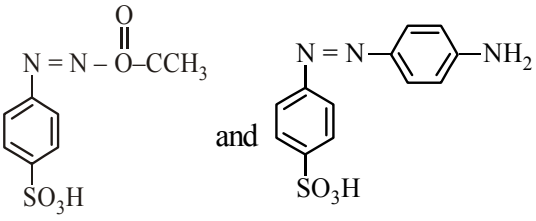
AH0096

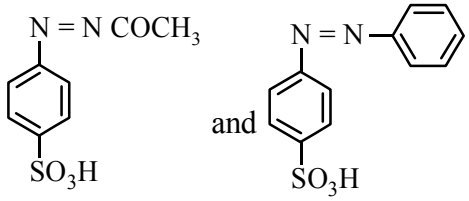
13. Products A and B formed in the following reactions are respectively : **[JEE(Main)-2018(ONLINE)]**



(1) 

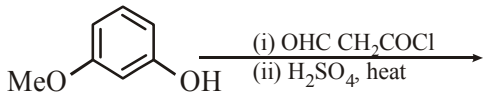
(2) 

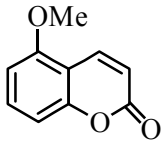
(3) 

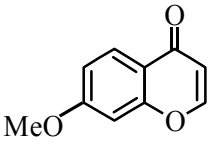
(4) 

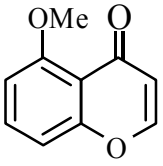
AH0097

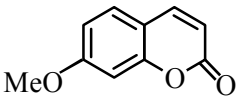
14. The major product of the following reaction is : **[JEE(Main)-2018(ONLINE)]**



(1) 

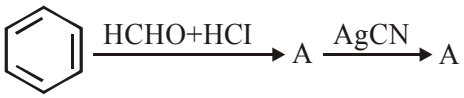
(2) 

(3) 

(4) 

AH0098

15. The compounds A and B in the following reaction are, respectively: **[JEE-Mains (JAN)-2019]**



(1) A = Benzyl alcohol, B = Benzyl isocyanide

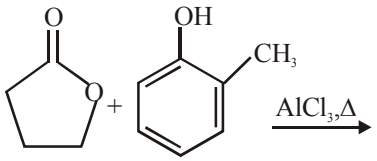
(2) A = Benzyl alcohol, B = Benzyl cyanide

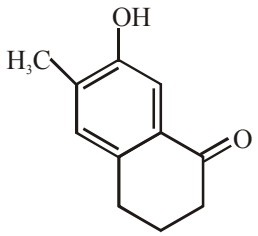
(3) A = Benzyl chloride, B = Benzyl cyanide

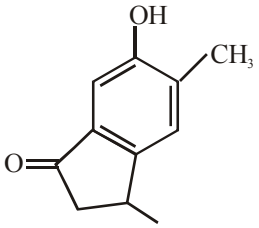
(4) A = Benzyl chloride, B = Benzyl isocyanide

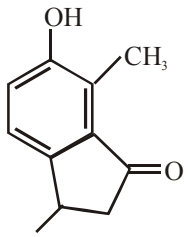
AH0099

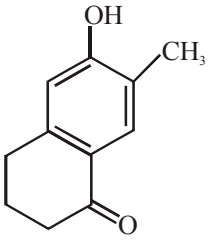
16. The major product of the following reaction is: **[JEE-Mains (JAN)-2019]**



(1) 

(2) 

(3) 

(4) 

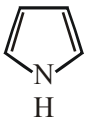
AH0100

17. Which of the following compounds is not aromatic ? **[JEE-Mains (JAN)-2019]**

(1) 

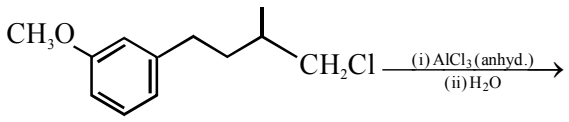
(2) 

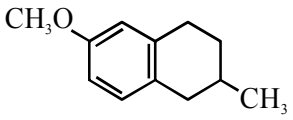
(3) 

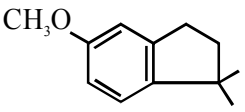
(4) 

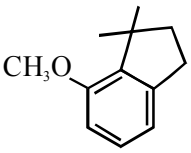
AH0101

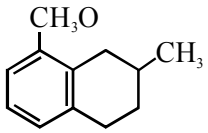
18. The major product of the following reaction is: **[JEE-Mains (JAN)-2019]**



(1) 

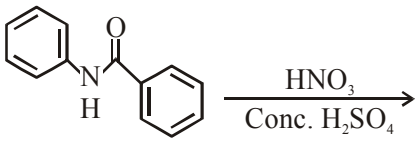
(2) 

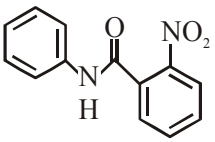
(3) 

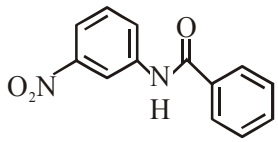
(4) 

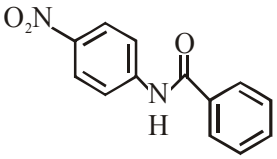
AH0102

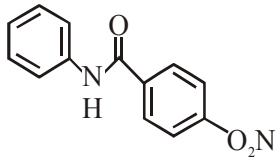
19. What will be the major product in the following mononitation reaction ? **[JEE-Mains (JAN)-2019]**



(1) 

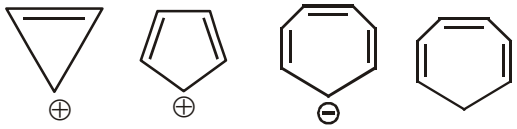
(2) 

(3) 

(4) 

AH0103

20. Which compound(s) out of the following is/are not aromatic ? **[JEE-Mains (JAN)-2019]**

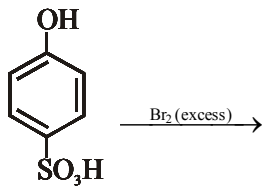


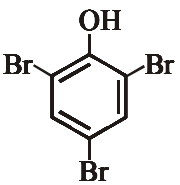
(A) (B) (C) (D)

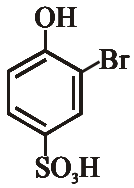
(1) C and D (2) B, C and D (3) A and C (4) B

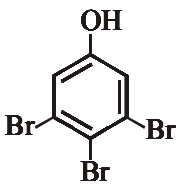
AH0104

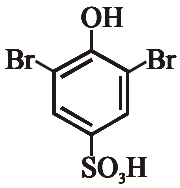
21. The major product of the following reaction is : **[JEE-Mains (JAN)-2019]**



(1) 

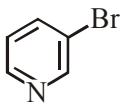
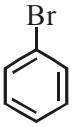
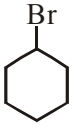
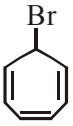
(2) 

(3) 

(4) 

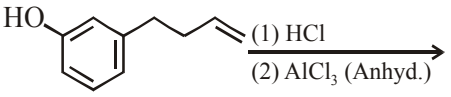
AH0105

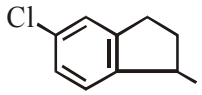
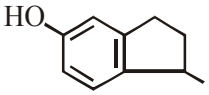
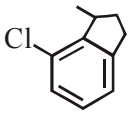
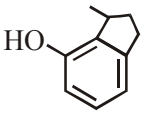
22. Which of the following compounds will produce a precipitate with $AgNO_3$?
[JEE-Mains (JAN)-2019]

(1) 
(2) 
(3) 
(4) 

AH0106

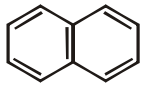
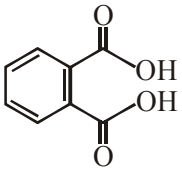
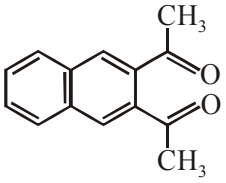
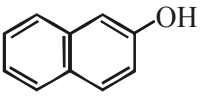
23. The major product of the following reactionis :- **[JEE-Mains (JAN)-2019]**



(1) 
(2) 
(3) 
(4) 

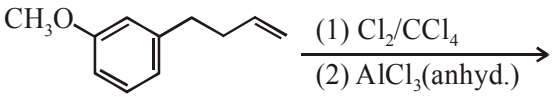
AH0107

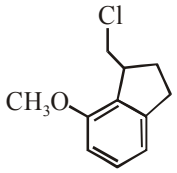
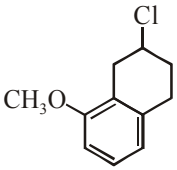
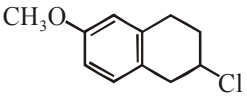
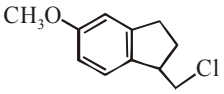
24. Among the following four aromatic compounds, which one will have the lowest melting point ?
[JEE-Mains (JAN)-2019]

(1) 
(2) 
(3) 
(4) 

AH0108

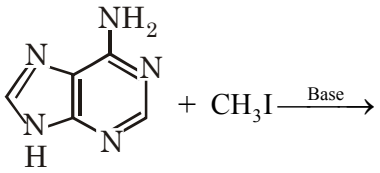
25. The major product of the following reaction is : **[JEE-Mains (JAN)-2019]**

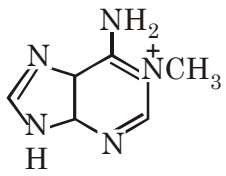
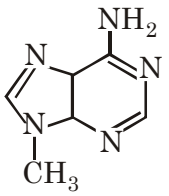
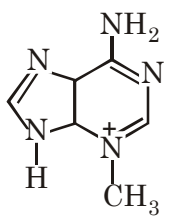
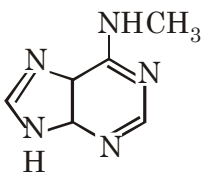


(1) 
(2) 
(3) 
(4) 

AH0109

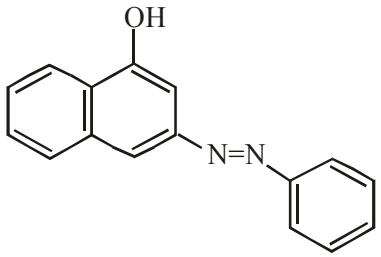
26. The major product in the following reaction is : **[JEE-Mains (April)-2019]**

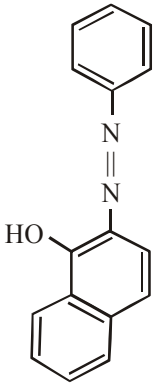


(1) 
(2) 
(3) 
(4) 

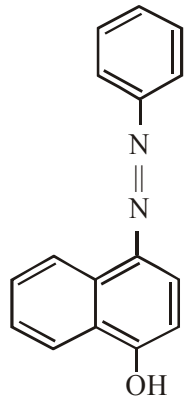
AH0110

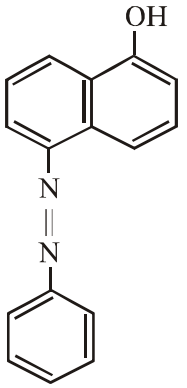
27. Coupling of benzene diazonium chloride with 1-napthol in alkaline medium will give

(1) 

(2) 

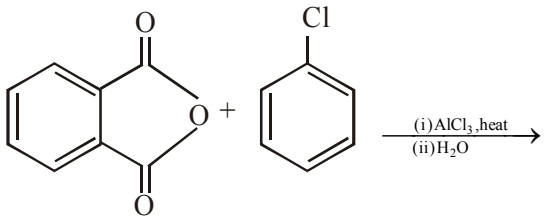
[JEE-Mains (April)-2019]

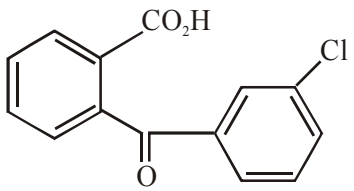
(3) 

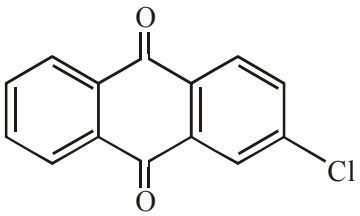
(4) 

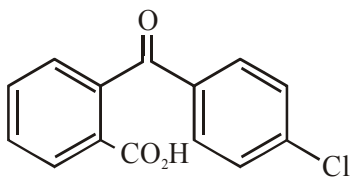
AH0111

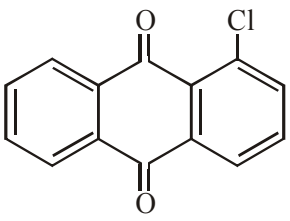
28. The major product of the following reaction is: **[JEE-Mains (April)-2019]**



(1) 

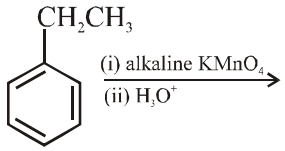
(2) 

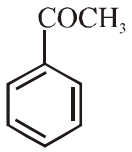
(3) 

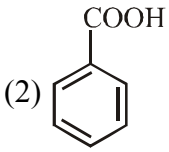
(4) 

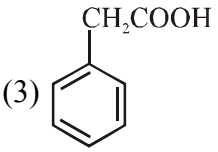
AH0112

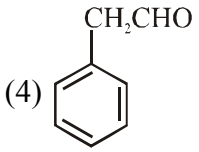
29. The mojor product of the following reaction is : **[JEE-Mains (April)-2019]**



(1) 

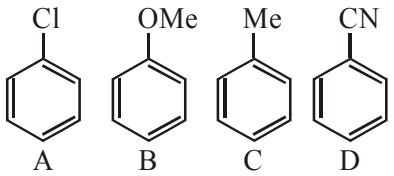
(2) 

(3) 

(4) 

AH0113

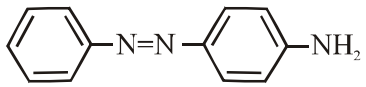
30. The increasing order of reactivity of the following compounds towards aromatic electrophilic substitution reaction is : **[JEE-Mains (April)-2019]**

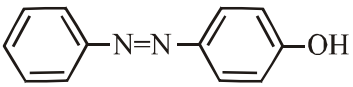


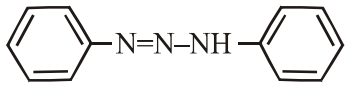
(1) D < B < A < C (2) A < B < C < D (3) D < A < C < B (4) B < C < A < D

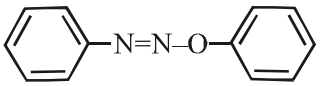
AH0114

31. Aniline dissolved in dilute HCl is reacted with sodium nitrite at 0ºC. This solution was added dropwise to a solution containing equimolar mixture of aniline and phenol in dil. HCl. The structure of the major product is : **[JEE-Mains (April)-2019]**

(1) 

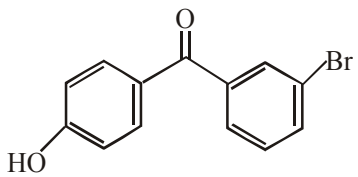
(2) 

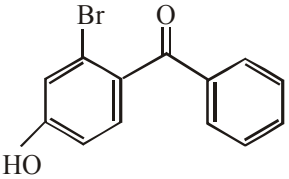
(3) 

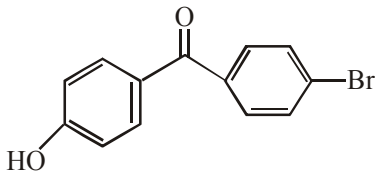
(4) 

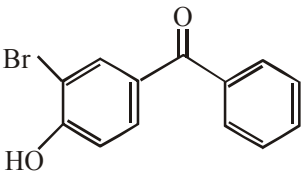
AH0115

32. p-Hydroxybenzophenone upon reaction with bromine in carbon tetrachloride gives: **[JEE-Mains (April)-2019]**

(1) 

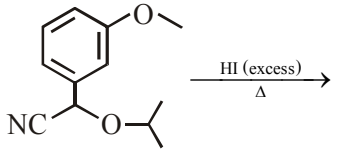
(2) 

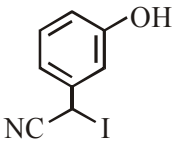
(3) 

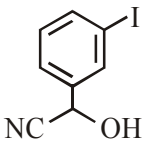
(4) 

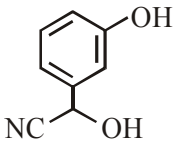
AH0116

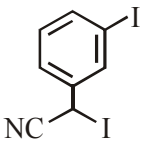
33. The major product of the following reaction is : **[JEE-Mains (April)-2019]**



(1) 

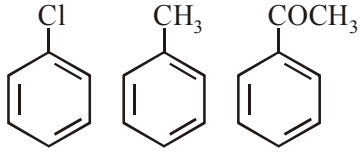
(2) 

(3) 

(4) 

AH0117

34. The increasing order of the reactivity of the following compounds towards electrophilic aromatic substitution reactions is :- **[JEE-Mains (April)-2019]**



(1) I < III < II (2) II < I < III (3) III < I < II (4) III < II < I

AH0118

35. Which of the following is NOT a correct method of the preparation of benzylamine from cyanobenzene ? **[JEE-Mains (April)-2019]**

(1) (i) HCl/H_2O (ii) $NaBH_4$

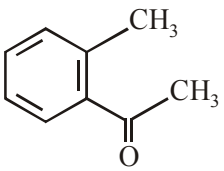
(2) (i) $LiAlH_4$ (ii) H_3O^+

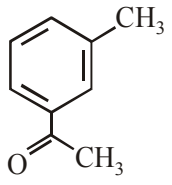
(3) (i) $SnCl_2$+HCl(gas) (ii) $NaBH_4$

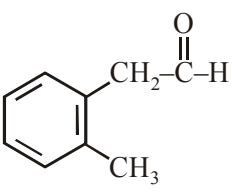
(4) H_2/Ni

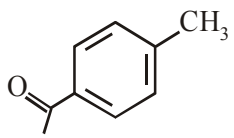
AH0119

36. 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 :- **[JEE-Mains (April)-2019]**

(1) 

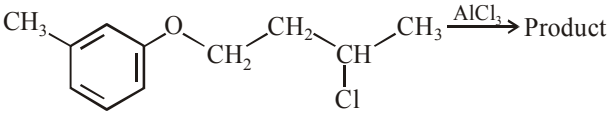
(2) 

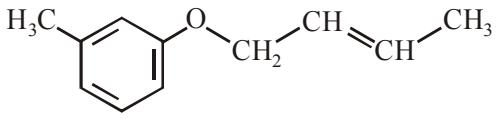
(3) 

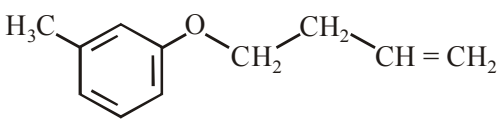
(4) 

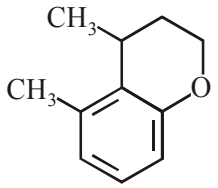
AH0120

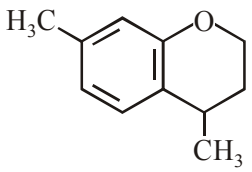
37. The major product obtained in the given reaction is :- **[JEE-Mains (April)-2019]**



(1) 

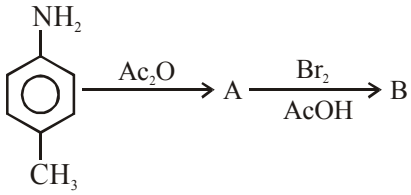
(2) 

(3) 

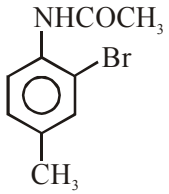
(4) 

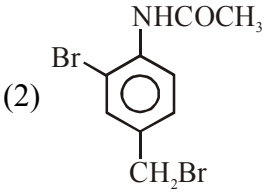
AH0121

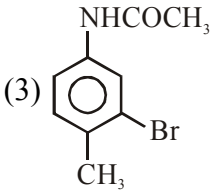
38. In the following reaction sequence **[JEE-Mains (Jan)-2020]**

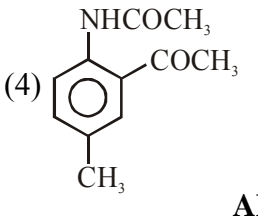


the major products B is -

(1) 

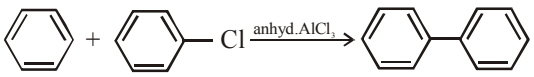
(2) 

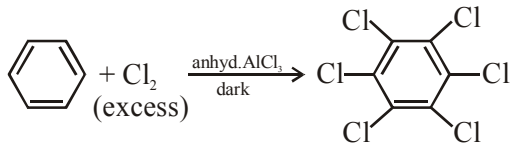
(3) 

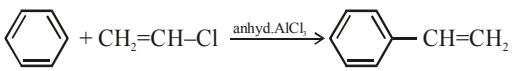
(4) 

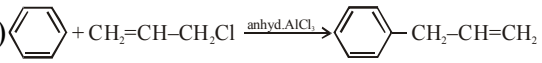
AH0122

39. Consider the following reactions : **[JEE-Mains (Jan)-2020]**

(a) 

(b) 

(c) 

(d) 

Which of these reactions are possible ?

(1) (a) and (d)
(2) (b) and (d)
(3) (a) and (b)
(4) (b) , (c) and (d)

AH0123

40. 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 : **[JEE-Mains (Jan)-2020]**

(1) m-chlorobenzoic acid, m-chloroaniline and m-chlorophenol

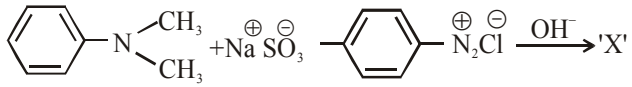
(2) m-chloroaniline, m-chlorobenzoic acid and m-chlorophenol

(3) m-chlorobenzoic acid, m-chlorophenol and m-chloroaniline

(4) m-chlorophenol, m-chlorobenzoic acid and m-chloroaniline

AH0124

41. Consider the following reaction : **[JEE-Mains (Jan)-2020]**



The product 'X' is used :

(1) in acid base titration as an indicator

(2) in protein estimation as an alternative to ninhydrin

(3) in laboratory test for phenols

(4) as food grade colourant

AH0125

42. In the following sequence of reactions the maximum number of atoms present in molecule 'C' in one plane is _____. **[JEE-Mains (Jan)-2020]**

$$A \xrightarrow[\text{Cu tube}]{\text{Red hot}} B \xrightarrow[\text{Anhydrous } AlCl_3]{CH_3Cl(1.eq.)} C$$

(A is a lowest molecular weight alkyne)

AH0126

EXERCISE # (ADVANCE)

1. The chlorination of toluene in presence of ferric chloride gives predominatly: **[JEE 1986]**

(A) Benzyl chloride (B) m-Chlorotoluene (C) Benzal chloride (D) *o*-and *p*-Chlorotoluene

AH0127

2. The most basic compound among the following is: **[JEE 1990]**

(A) Benzylamine (B) Aniline (C) Acetaniline (D) p-Nitro aniline

AH0128

3. When nitrobenzene is treated with Br_2 in presence of $FeBr_3$ the major product formed is m-bromonitrobenzene. Correct statements are : **[JEE 1992]**

(A) The electron density on meta carbon is more than on ortho and para position.

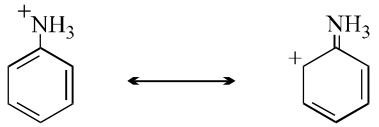
(B) The intermediate carbonium ion formed after initial attack of Br^+ attack the meta position is least destabilized.

(C) Loss of aromaticity when Br^+ attacks at the ortho and para positions and not at meta position

(D) Easier loss of H^+ to regain aromaticity form the meta position than from ortho and para position.

AH0129

4. Choose the correct statement from the ones given below for two aniline in: **[JEE 1993]**



(I) (II)

(A) II is not an acceptable canonical structure because carbonium ions are less stable than ammonium ions

(B) II is not an acceptable canonical structure because it is non aromatic

(C) II is not an acceptable canonical structure because the nitrogen has 10 valence electrons

(D) II is an acceptable canonical structure

AH0130

5. Most stable carbonium ion is: **[JEE 1995]**

(A) $p - NO_2 - C_6H_4 - {}^+CH_2$ (B) $C_6H_5{}^+CH_2$

(C) $p - Cl - C_6H_4 - {}^+CH_2$ (D) $p - CH_3O - C_6H_4 - {}^+CH_2$

AH0131

6. Arrange in order of decreasing trend towards S_E reactions: **[JEE 1995]**

(I) Chlorobenzene (II) Benzene (III) Anilinium chloride (IV) Toluene

(A) II > I > III > IV (B) III > I > II > IV (C) IV > II > I > III (D) I > II > III > IV

AH0132

7. Among the following statements on the nitration of aromatic compounds, the false one is:

(A) The rate of benzene is almost the same as that of hexadeuterobenzene **[JEE 1997]**

(B) The rate of nitration of toluene is greater than that of benzene.

(C) The rate of nitration of benzene is greater than that of hexadeuterobenzene

(D) Nitration is an electrophilic substitution reaction

AH0133

8. Nitrobenzene can be prepared from benzene by using a mixture of conc. HNO_3 and conc. H_2SO_4. In the nitrating mixture HNO_3 acts as a: **[JEE 1997]**

(A) Base (B) Acid (C) Reducing agent (D) Catalyst

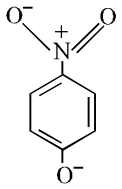
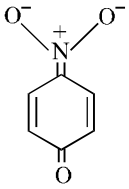
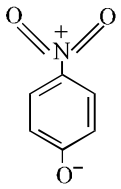
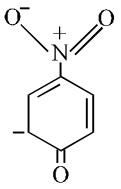
AH0134

9. Benzyl chloride ($C_6H_5CH_2Cl$) can be prepared from toluene by chlorination with: **[JEE 1998]**

(A) $SO_2Cl_2h\nu$ (B) $SOCl_2$ (C) $Cl_2\ h\nu$ (D) NaOCl

AH0135

10. The most unlikely representation of resonance structure of p-nitrophenoxide ion is: **[JEE 1998]**

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

AH0136

11. Benzenediazonium chloride on reaction with phenol in weakly basic medium gives: **[JEE 1998]**

(A) Diphenyl ether (B) p-hydrooxyazobenzene

(C) Chlorobenzene (D) Benzene

AH0137

12. Toluene, when treated with Br_2/Fe, gives p-bromotoluene as the major product, because the CH_3 group:

(A) is para directing (B) is meta directing **[JEE 1999]**

(C) activates the ring by hyperconjugation (D) deactivates the ring

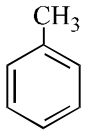
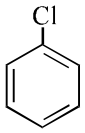
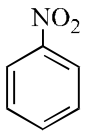
AH0138

13. Amongst the following the strongest base is: **[JEE 2000]**

(A) $C_6H_5NH_2$ (B) p-$O_2NC_6H_4NH_2$ (C) m-$O_2NC_6H_4NH_2$ (D) $C_6H_5CH_2NH_2$

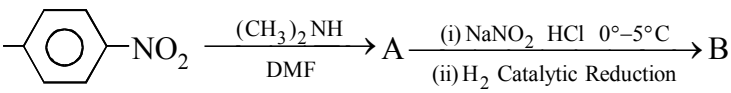
AH0139

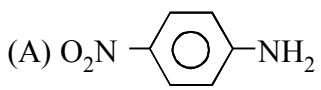
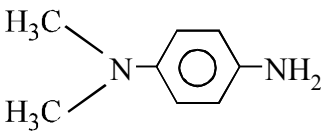
14. Identify the correct order of reactivity in electrophilic substitution reactions of the following compounds:

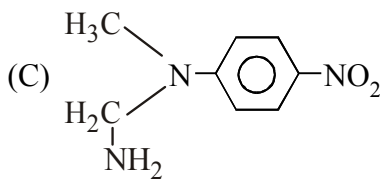
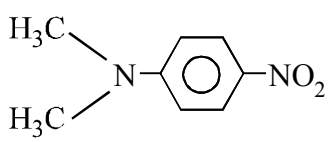
(I)  (II)  (III)  (IV)  **[JEE 2002]**

(A) I > II > III > IV (B) IV > III > II > I (C) II > I > III > IV (D) II > III > I > IV

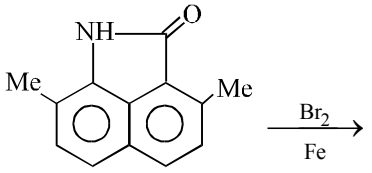
AH0140

15.  **[JEE 2003]**

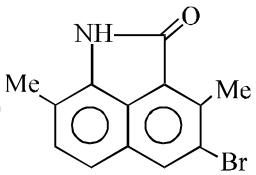
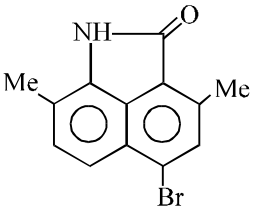
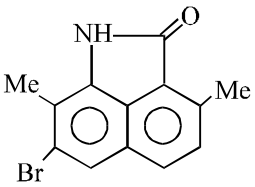
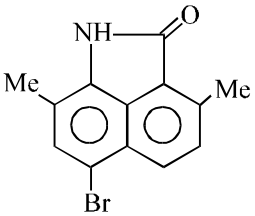
(A)  (B) 

(C)  (D) 

AH0141

16.  **[JEE 2004]**

Major product of above reaction is:

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

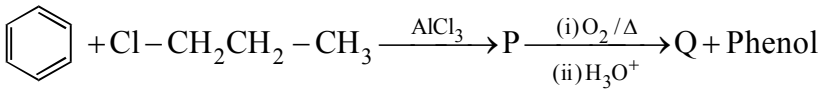
AH0142

17. Which of the following is obtained when 4-Methylbenzenesulphonic acid is hydrolysed with excess of sodium acetate? **[JEE 2005]**

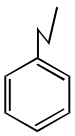
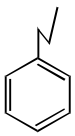
(A) $CH_3-C_6H_4-CO\overset{-}{O}\overset{+}{N}a$ (B) $CH_3-C_6H_4+SO_3$

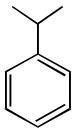
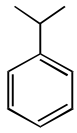
(C) $CH_3-C_6H_4-SO_3^-\overset{+}{N}a + CH_3COOH$ (D) $CH_3-C_6H_4-SO_2O.\,COCH_3 + NaOH$

AH0143

18.  **[JEE 2006]**

The major products P and Q are

(A)  and CH_3CH_2CHO (B)  and CH_3COCH_3

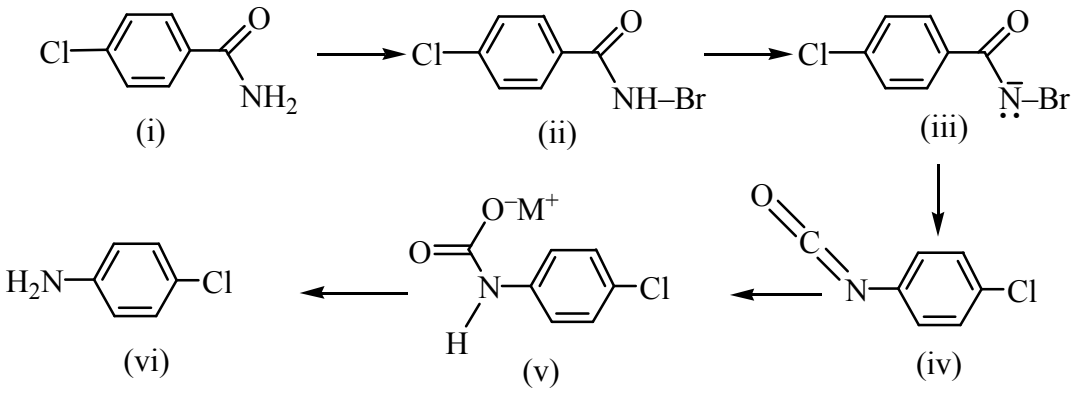
(C)  and CH_3COCH_3 (D)  and CH_3CH_2CHO

AH0144

Question No. 19 to 21 (3 questions)

Comprehension I

$RCONH_2$ is converted into RNH_2 by means of Hofmann bromamide degradation.



In this reaction, RCONHBr is formed from which this reaction has derived its name. Electron donating group at phenyl activates the reaction. Hofmann degradation reaction is an intramolecular reaction.

19. How can the conversion of (i) to (ii) be brought about? **[JEE 2006]**

(A) KBr (B) KBr + CH_3ONa (C) KBr + KOH (D) Br_2 + KOH

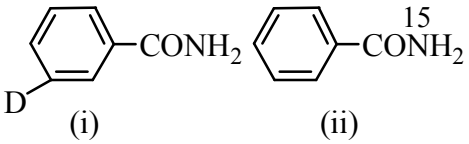
AH0145

20. Which is the rate determining step in Hofmann bromamide degradation? **[JEE 2006]**

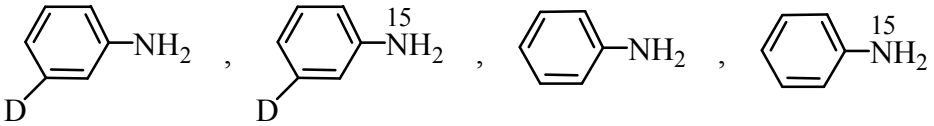
(A) Formation of (i) (B) Formation of (ii) (C) Formation of (iii) (D) Formation of (iv)

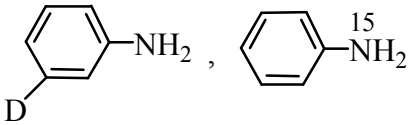
AH0145

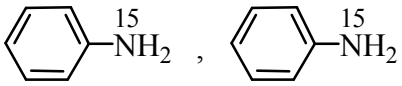
21. What are the constituent amines formed when the mixture of (i) and (ii) undergoes Hofmann bromamide degradation ? **[JEE 2006]**

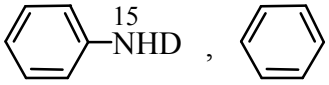


(i) (ii)

(A) 

(B) 

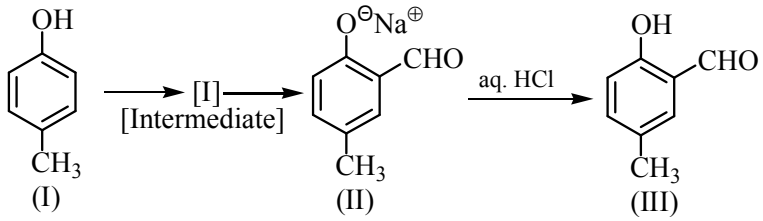
(C) 

(D) 

AH0145

Paragraph for Question Nos. 22 to 25 (4 questions)

Riemer-Tiemann reaction introduces an aldehyde group, on to the aromatic ring of phenol, ortho to the hydroxyl group. This reaction involves electrophilic aromatic substitution. This is a general method for the synthesis of substituted salicylaldehydes as depicted below.



22. Which one of the following reagents is used in the above reaction ? **[JEE 2007]**

(A) a NaOH + CH_3Cl (B) a NaOH + CH_2Cl_2

(C) a NaOH + $CHCl_3$ (D) aNaOH + CCl_4

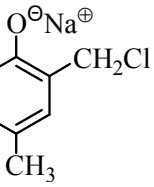
AH0146

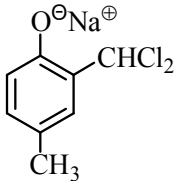
23. The electrophile in this reaction is **[JEE 2007]**

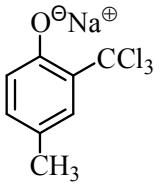
(A) $:CHCl$ (B) $^{+}CHCl_2$ (C) $:CCl_2$ (D) $\bullet CCl_3$

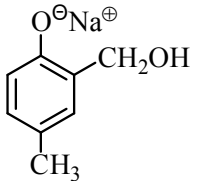
AH0146

24. The structure of the intermediate I is **[JEE 2007]**

(A) 

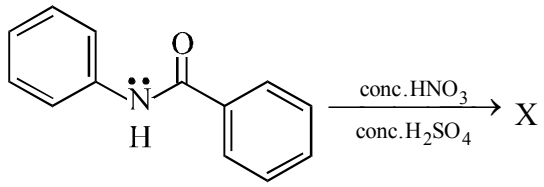
(B) 

(C) 

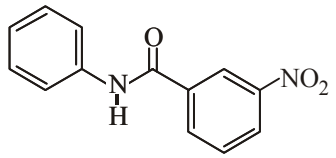
(D) 

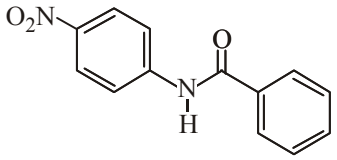
AH0146

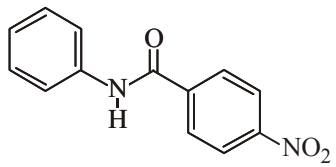
25. In the following reaction, **[JEE 2007]**

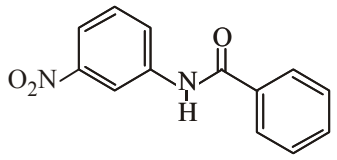


the structure of the major product 'X' is

(A) 

(B) 

(C) 

(D) 

AH0147

26. **Statement - 1 :** Bromobenzene upon reaction with Br_2 / Fe gives 1, 4-dibromobenzene as the major product.

and

Statement-2 : In bromobenzene, the inductive effect of the bromo group is more dominant than the mesomeric effect in directing the incoming electrophile.

(A) Statement-1 is True, Statement-2 is True ; Statement-2 is a correct explanation for Statement-1

(B) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement1

(C) Statement-1 is True, Statement-2 is False

(D) Statement-1 is False, Statement-2 is True **[JEE 2008]**

AH0148

27. **Statement-1 :** Aniline on reaction with $NaNO_2$ / HCl at 0°C followed by coupling with β-naphthol gives a dark **blue** coloured precipitate.

and

Statement-2 : The colour of the compound formed in the reaction of aniline with $NaNO_2$ / HCl at 0° followed by coupling with β-naphthol is due to the extended conjugation.

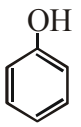
(A) Statement-1 is True, Statement-2 is True ; Statement-2 is a correct explanation for Statement-1

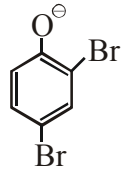
(B) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement1

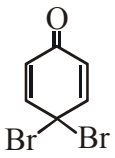
(C) Statement-1 is True, Statement-2 is False

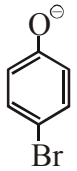
(D) Statement-1 is False, Statement-2 is True **[JEE 2008]**

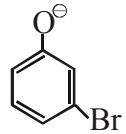
AH0149

28. In the reaction  $\xrightarrow{NaOH(aq)/Br_2}$ the intermediate(s) is(are) – **[JEE 2009]**

(A) 

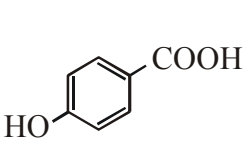
(B) 

(C) 

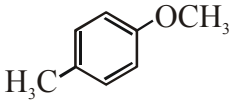
(D) 

AH0150

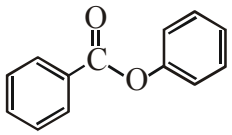
29. The compounds P, Q and S **[JEE 2009]**



P

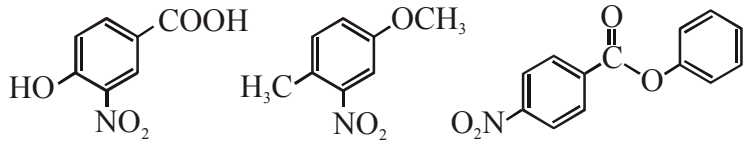


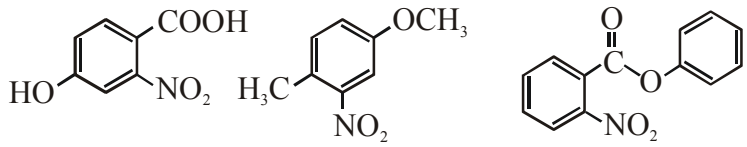
Q

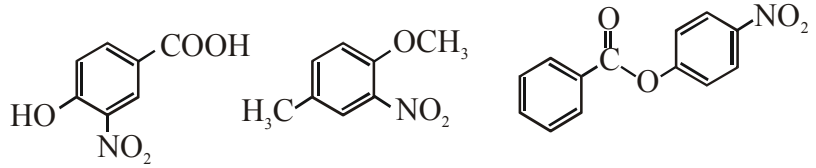


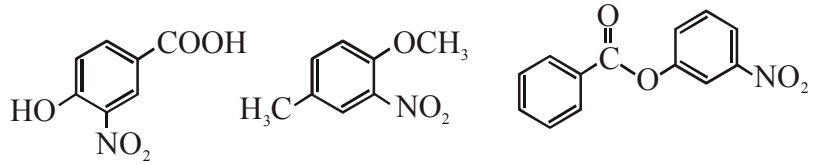
S

were separately subjected to nitration using HNO_3 / H_2SO_4 mixture. The product formed in each case respectively, is

(A) 

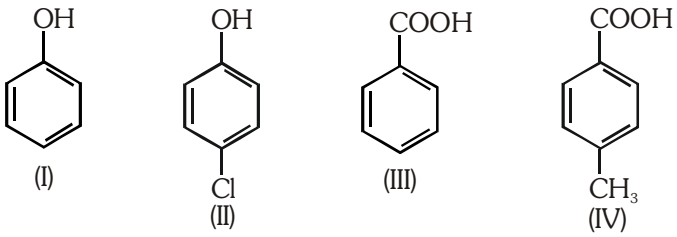
(B) 

(C) 

(D) 

AH0151

30. The correct acidity order of the following is : **[JEE 2009]**

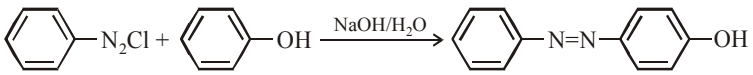


(A) (III) > (IV) > (II) > (I)
(B) (IV) > (III) > (I) > (II)
(C) (III) > (II) > (I) > (IV)
(D) (II) > (III) > (IV) > (I)

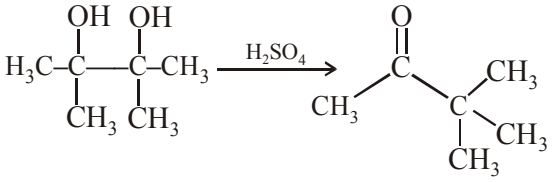
AH0152

31. Match the reactions in Column–I with appropriate options in Column–II.

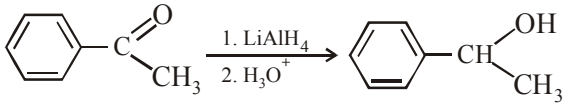
Column–I **Column–II** **[IIT-JEE-2010]**

(A) 

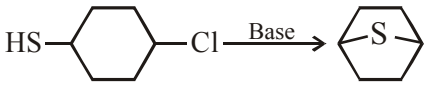
(P) Racemic mixture

(B) 

(Q) Addition reaction

(C) 

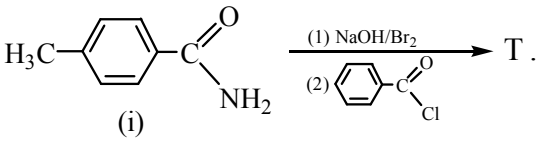
(R) Substitution reaction

(D) 

(S) Coupling reaction

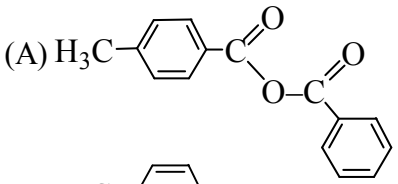
(T) Carbocation intermediate

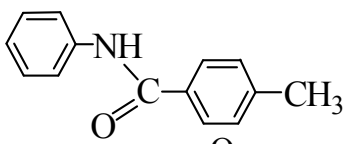
AH0153

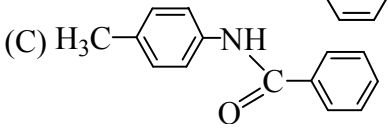
32. In the reaction 

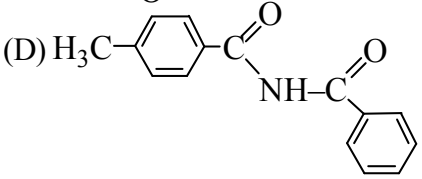
T .

The structure of the Product T is : **[JEE 2010]**

(A) 

(B) 

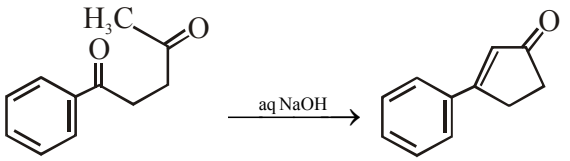
(C) 

(D) 

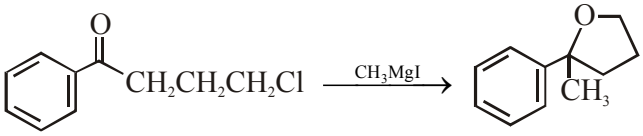
AH0154

33. Match the reactions in **Column-I** with appropriate types of step/reactive intermediate involved in these reactions as given in **Column-II**

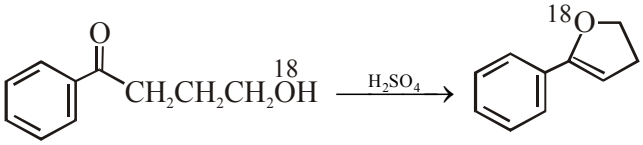
Column-I **Column-II** **[IIT-JEE-2012]**

(A) 

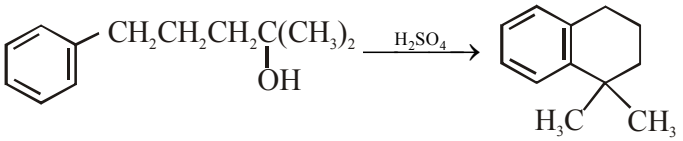
(P) Nucleophilic substitution

(B) 

(Q) Electrophilic substitution

(C) 

(R) Dehydration

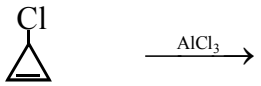
(D) 

(S) Nucleophilic addition

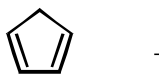
(R) Carbanion

AH0155

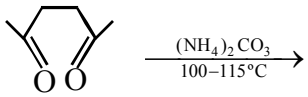
34. Among P, Q, R and S, the aromatic compound(s) is / are : **[JEE 2013]**



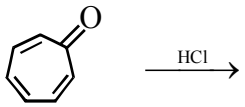
P



Q



R

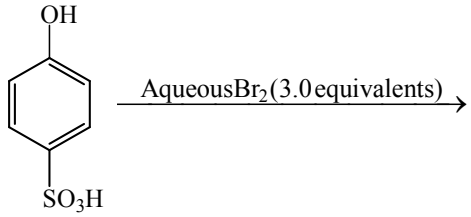


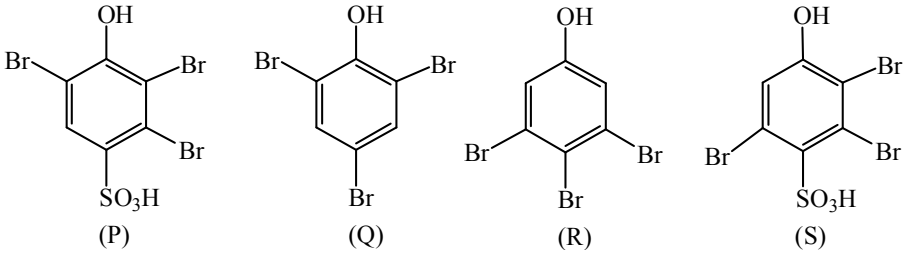
S

(A) P (B) Q (C) R (D) S

AH0156

35. The major product(s) of the following reaction is (are) - **[JEE 2013]**

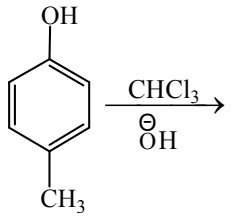


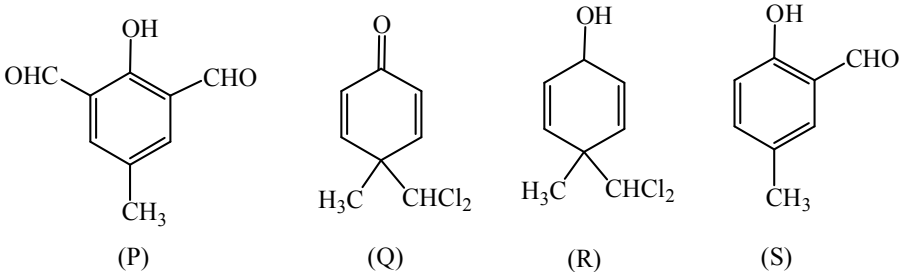


(A) P (B) Q (C) R (D) S

AH0157

36. In the following reaction, the product (s) formed is (are) **[JEE 2013]**





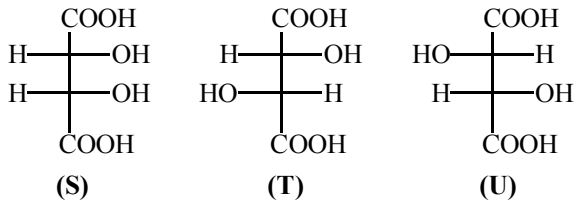
(A) P (major) (B) Q (minor) (C) R (minor) (D) S (major)

AH0158

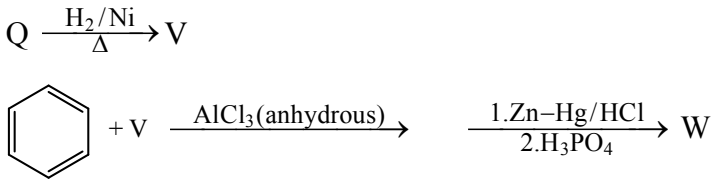
Paragraph for Question 37 and 38

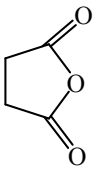
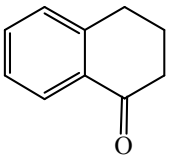
P & Q are isomers of dicarboxylic acid $C_4H_4O_4$. Both decolourize Br_2/H_2O, On heating P forms the cyclic anhydride.

Upon treatment with dilute alkaline $KMnO_4$, P as well as Q could produce one or more than one from S, T and U. **[JEE 2013]**

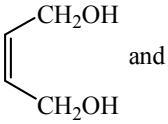
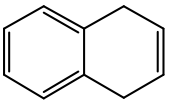


37. In the following reaction sequences V and W are , respectively -

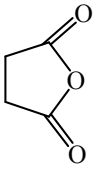
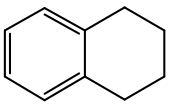


(A)  and 

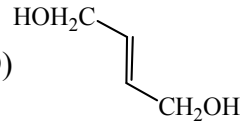
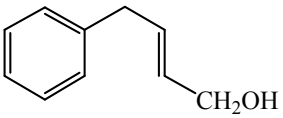
(V) (W)

(B)  and 

(V) (W)

(C)  and 

(V) (W)

(D)  and 

(V) (W)

AH0159

38. Compounds formed from P and Q are respectively

(A) Optically active S and optically active pair (T, U)

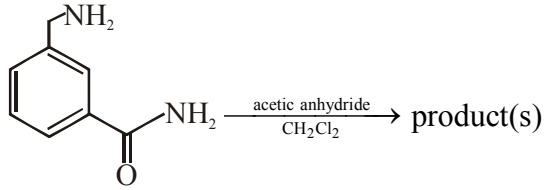
(B) Optically inactive S and optically inactive pair (T, U)

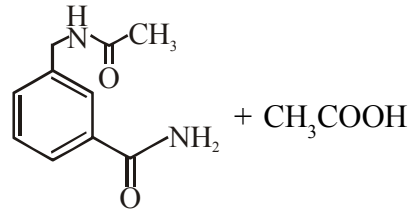
(C) Optically active pair (T, U) and optically active S

(D) Optically inactive pair (T, U) and optically inactive S

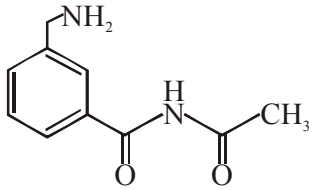
AH0159

39. In the reaction shown below, the major product(s) formed is / are : **[JEE 2014]**

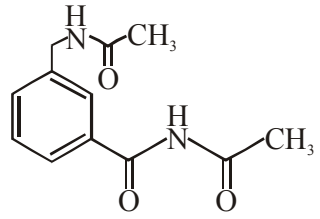


(A) 

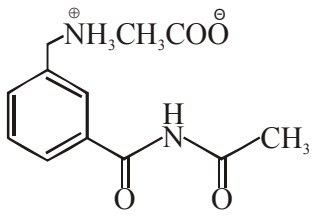
+ CH_3COOH

(B) 

+ CH_3COOH

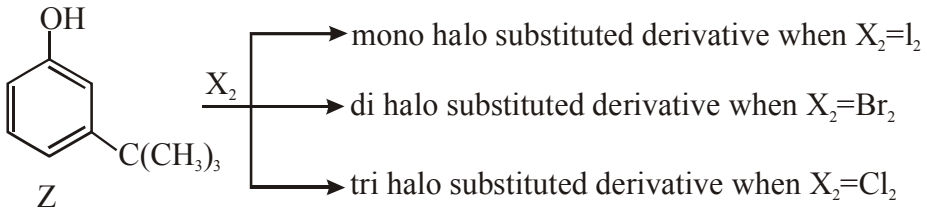
(C) 

+ H_2O

(D) 

AH0160

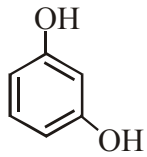
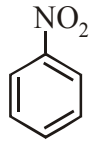
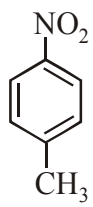
40. The reactivity of compound Z with different halogens under appropriate conditions is given below : **[JEE 2014]**



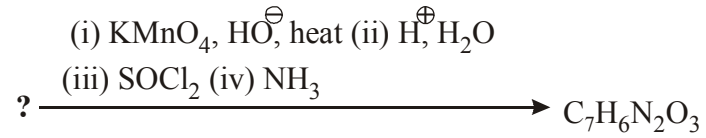
The observed pattern of electrop hilic substitution can be explained by -
(A) The steric effect of the halogen
(B) The steric effect of the tert-butyl group
(C) The electronic effect of the phenolic group
(D) The electronic effect of the turt-butyl group

AH0161

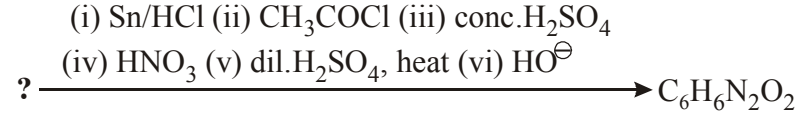
41. Match the four starting materials (P , Q, R, S) given in List I with the corresponding reaction scheme (I, II, III, IV) provided in List - II and select the correct answer using the code given below in lists. **[JEE 2014]**

List - I	**List - II**
(P) H—≡—H	**(1) Scheme I**
(Q) 	**(2) Scheme II**
(R) 	**(3) Scheme III**
(S) 	**(4) Scheme IV**

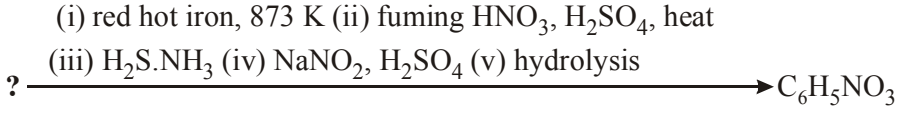
Scheme I



Scheme II



Scheme III



Scheme IV

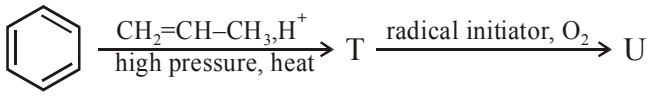
$$? \xrightarrow[\text{(ii) conc. } HNO_3, \text{ conc. } H_2SO_4 \text{ (iii) dil. } H_2SO_4, \text{ heat}]{\text{(i) conc. } H_2SO_4,\ 60^\circ C} C_6H_5NO_4$$

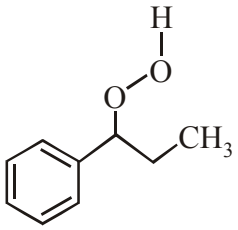
Code :

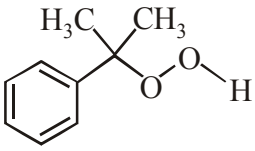
	P	Q	R	S
(A)	1	4	2	3
(B)	3	1	4	2
(C)	3	4	2	1
(D)	4	1	3	2

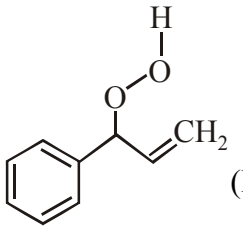
AH0162

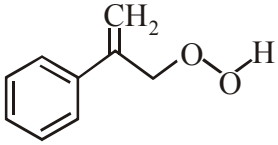
42. The major product U in the following reactions is : **[IIT 2015]**



(A) 

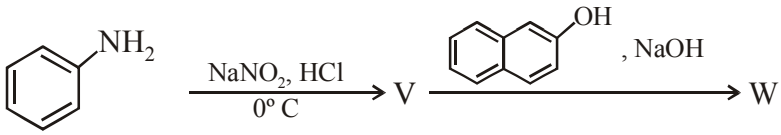
(B) 

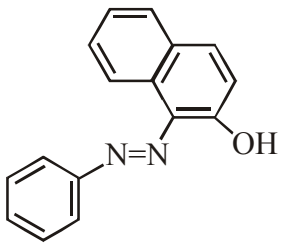
(C) 

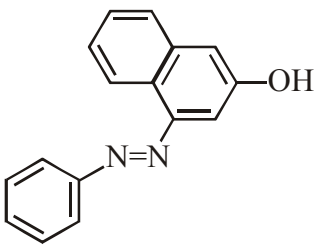
(D) 

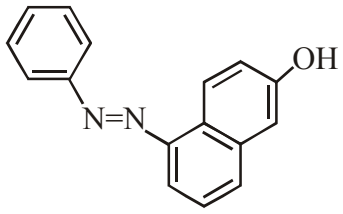
AH0163

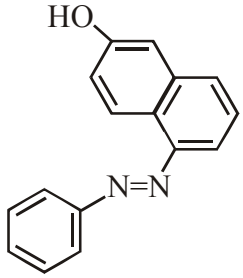
43. In the following reactions, the major product **W** is : **[IIT 2015]**



(A) 

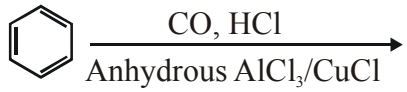
(B) 

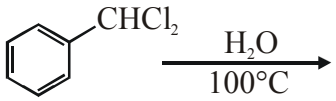
(C) 

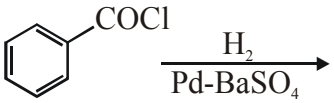
(D) 

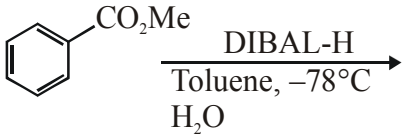
AH0164

44. Among the following the number of reaction(s) that produce(s) benzaldehyde is : **[IIT 2015]**

I. 

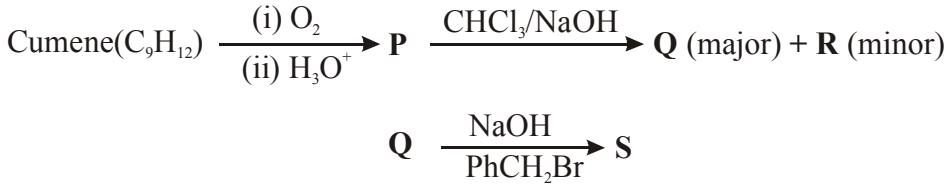
II. 

III. 

IV. 

AH0165

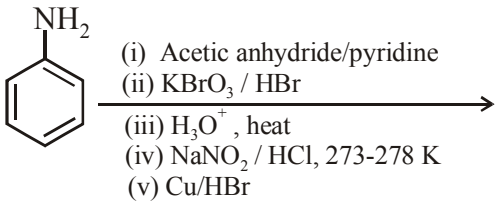
45. The correct statements(s) about of the following reaction sequence is(are) **[IIT 2016]**

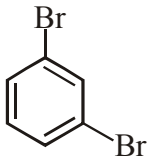


(A) **R** is steam volatile
(B) **Q** gives dark violet coloration with 1% aqueous $FeCl_3$ solution
(C) **S** gives yellow precipitate with 2, 4,-dinitrophenylhydrazine
(D) **S** gives dark violet coloration with 1% aqueous $FeCl_3$ solution

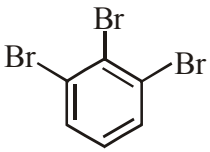
AH0166

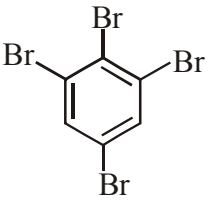
46. The product(s) of the following reaction sequence is(are) **[IIT 2016]**



(A) 

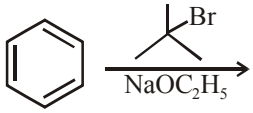
(B) 

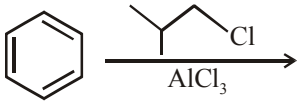
(C) 

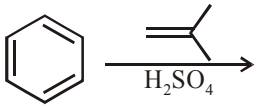
(D) 

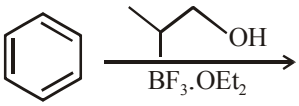
AH0167

47. Among the following reaction(s) which gives (give) tert-butyl benzene as the major product is(are) **[IIT 2016]**

(A) 

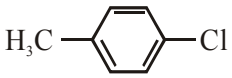
(B) 

(C) 

(D) 

AH0168

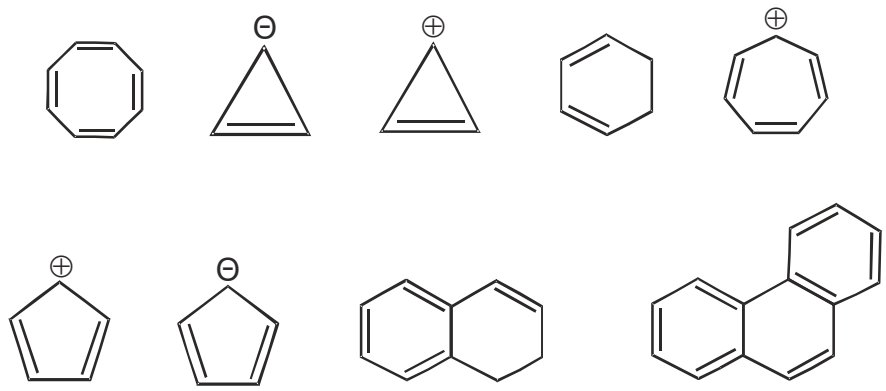
48. The IUPAC name(s) of the following compound is(are) : **[IIT 2017]**



(A) 4-methylchlorobenzene (B) 4-chlorotoluene
(C) 1-chloro-4-methylbenzene (D) 1-methyl-4-chlorobenzene

AH0169

49. Among the following, the number of aromatic compound (s) is : **[IIT 2017]**



Answer 50, 51 and 52 by appropriately matching the information given in the three columns of the following table.

Columns 1, 2 and 3 contains starting materials, reaction conditions, , and type of reactions, respectively.

Column 1	Column 2	Column 3
(I) Toluene	(i) $NaOH/Br_2$	(P) Condensation
(II) Acetophenone	(ii) Br_2 / hν	(Q) Carboxylation
(III) Banzaldehyde	(iii)$(CH_3CO)_2O/CH_3COOK$	(R) Substitution
(IV) Phenol	(iv) $NaOH/CO_2$	(S) Haloform

AH0170

50. For the synthesis of benzoic acid, the only CORRECT combination is

(A) (III) (iv) (R) (B) (IV) (ii) (P) (C) (I) (iv) (Q) (D) (II) (i) (S)

AH0171

51. The only CORRECT combination in which the reaction proceeds through radical mechanism is

(A) (I) (ii) (R) (B) (II) (iii) (R) (C) (III) (ii) (P) (D) (IV) (i) (Q)

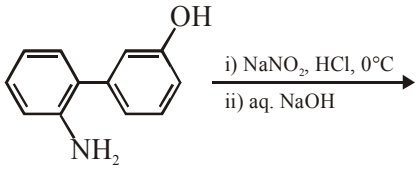
AH0171

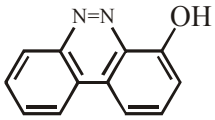
52. The only CORRECT combination that gives two different carboxylic acids is

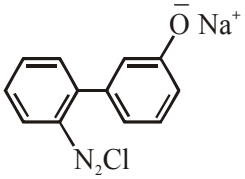
(A) (IV) (iii) (Q) (B) (III) (iii) (P) (C) (II) (iv) (R) (D) (I) (i) (S)

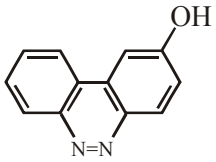
AH0171

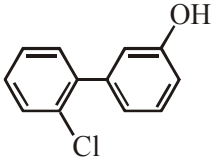
53. The major product of the following reaction is :



(A) 

(B) 

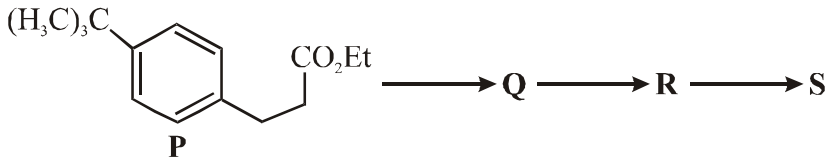
(C) 

(D) 

AH0172

Paragraph for 54 & 55

The reaction of compound P with CH_3MgBr (excess) in $(C_2H_5)_2O$ followed by addition of H_2O gives **Q**, The compound **Q** on treatment with H_2SO_4 at 0ºC gives **R**. The reaction of **R** with CH_3COCl in the presence of anhydrous $AlCl_3$ in CH_2Cl_2 followed by treatment with H_2O produces compounds S. [Et it compounds **P** is ethyl group] **[IIT 2017]**



54. The reactions, **Q** to **R** and **R** to **S**, are -

(A) Dehydration and Friedel -Crafts acylation

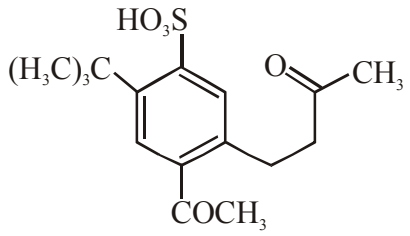
(B) Friedel-Crafts alkylation, dehydration and Friedel-Crafts acylation

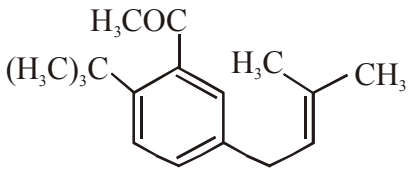
(C) Aromatic sulfonation and Friedel-Crafts acylation

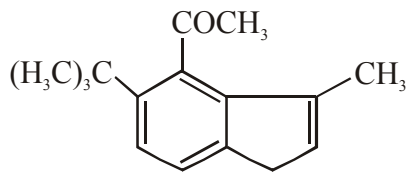
(D) Friedel-Crafts alkylation and Fridel-Crafts acylation

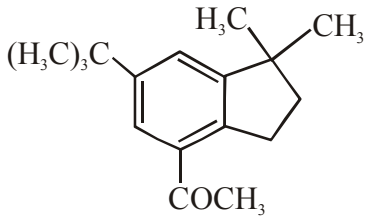
AH0173

55. The product **S** is -

(A) 

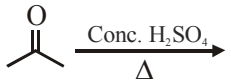
(B) 

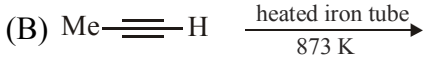
(C) 

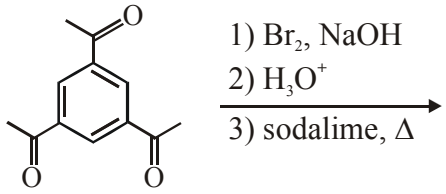
(D) 

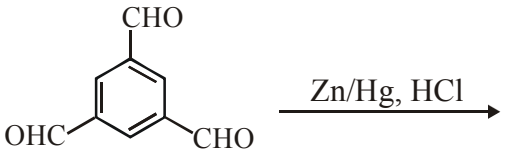
AH0173

56. The reaction(s) leading to the formation of 1,3,5-trimethylbenzene is (are) **[IIT 2018]**

(A) 

(B) 

(C) 

(D) 

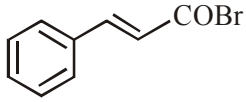
AH0174

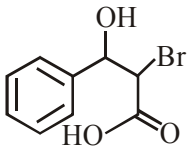
Paragraph "X"

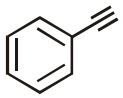
Treatment of benzene with CO/HCl in the presence of anhydrous $AlCl_3$/CuCl followed by reaction with Ac_2O/NaOAc gives compound X as the major product. Compound X upon reaction with Br_2/Na_2CO_3, followed by heating at 473 K with moist KOH furnishes Y as the major product. Reaction of X with H_2/Pd-C, followed by H_3PO_4 treatment gives Z as the major product. **[IIT 2018]**

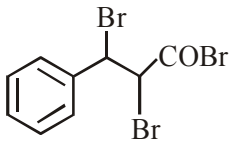
(There are two questions based on PARAGRAPH "X", the question given below is one of them)

57. The compound Y is :-

(A) 

(B) 

(C) 

(D) 

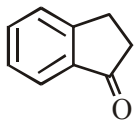
AH0175

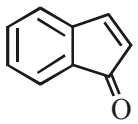
Paragraph "X"

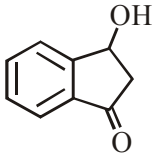
Treatment of benzene with CO/HCl in the presence of anhydrous $AlCl_3$/CuCl followed by reaction with Ac_2O/NaOAc gives compound X as the major product. Compound X upon reaction with Br_2/Na_2CO_3, followed by heating at 473 K with moist KOH furnishes Y as the major product. Reaction of X with H_2/Pd-C, followed by H_3PO_4 treatment gives Z as the major product.

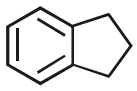
(There are two question based on PARAGARAPH "X", the question given below is one of them)

58. The compound Z is :-

(A) 

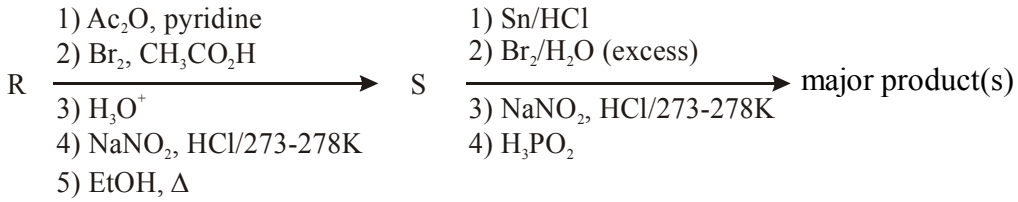
(B) 

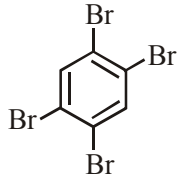
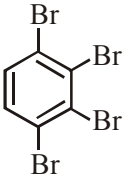
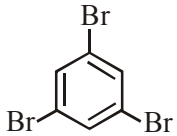
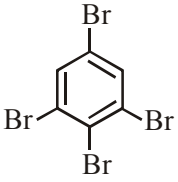
(C) 

(D) 

AH0175

59. Aniline reacts with mixed acid (conc. HNO_3 and conc. H_2SO_4) at 288 K to give P (51%), Q (47%) and R (2%). The major product(s) the following reaction sequence is (are) :- **[IIT 2018]**



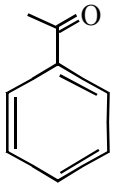
(A)  (B)  (C)  (D) 

AH0176

60. In the following reaction sequence, the amount of D (in g) formed from 10 moles of acetophenone is____.

[IIT 2018]

(Atomic weight in g mol^{-1}: H = 1, C = 12, N = 14, O = 16, Br = 80. The yield (%) corresponding to the product in each step is given in the parenthesis)

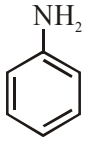


$\xrightarrow[H_3O^+]{NaOBr}$ A (60%) $\xrightarrow{NH_3,\Delta}$ B (50%) $\xrightarrow{Br_2/KOH}$ C (50%) $\xrightarrow[AcOH]{Br_2(3\ equiv)}$ D (100%)

AH0177

61. Scheme 1 and 2 describe the conversion of **P** to **Q** and **R** to **S**, respectively. Scheme 3 describes the synthesis of **T** from **Q** and **S**. The total number of Br atoms in a molecule of **T** is _____

Scheme 1 : **[IIT 2019]**



P

$\xrightarrow[\text{(iii) CuCN/KCN}]{\text{(i) } Br_2 \text{ (excess), } H_2O,\ \text{(ii) } NaNO_2, HCl, 273\ K}$ **Q** (major)

$\xrightarrow{\text{(iv) } H_3O^+,\Delta,\ \text{(v) } SOCl_2, \text{pyridine}}$

Scheme 2 :

R

$\xrightarrow[\text{(iii) } H^+]{\text{(i) Oleum, (ii) NaOH, } \Delta}$ **S** (major)

$\xrightarrow{\text{(iv) } Br_2, CS_2\ 273\ K}$

Scheme 3 :

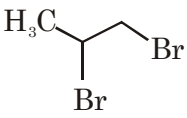
S $\xrightarrow[\text{(ii) Q}]{\text{(i) NaOH}}$ **T** (major)

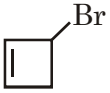
AH0178

62. Choose the correct option(s) that give(s) an aromatic compound as the major product.

[IIT 2019]

(1)  + Cl_2(excess) $\xrightarrow{UV,\ 500K}$

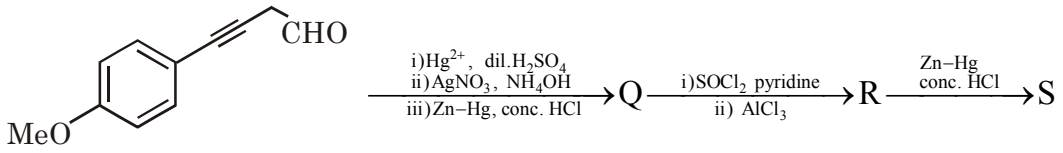
(2)  $\xrightarrow[\text{iii) red hot iron tube, 873 K}]{\text{i) alc.KOH, ii) } NaNH_2}$

(3)  $\xrightarrow{NaOEt}$

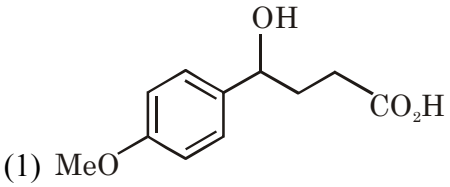
(4)  $\xrightarrow{NaOMe}$

AH0179

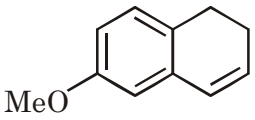
63. Choose the correct option(s) for the following reaction sequence **[IIT 2019]**



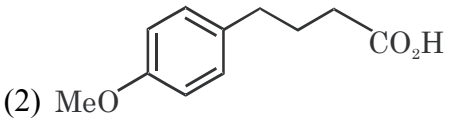
Consider Q, R and S as major products

(1) 

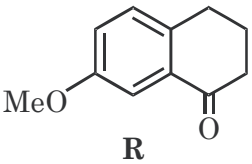
Q



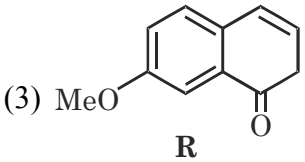
S

(2) 

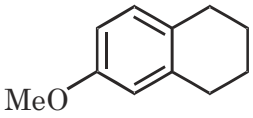
Q



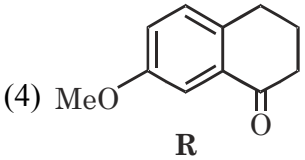
R

(3) 

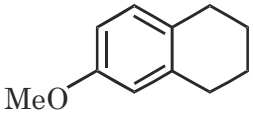
R



S

(4) 

R



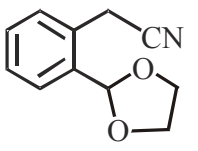
S

AH0180

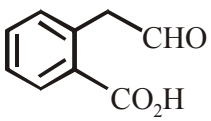
64. Answer the following by appropriately matching the lists based on the information given in the paragraph

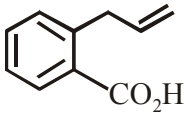
List-I includess starting materials and reagents of selected chemical reactions. List-II gives structures of compounds that may be formed as intermediate products and/or final products from the reactions of List-I **[IIT 2019]**

List-I **List-II**

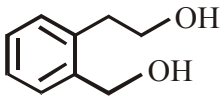
(I) 

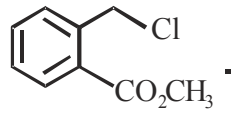
i) DlBAL-H
ii) dil, HCl
iii) $NaBH_4$
iv) conc. H_2SO_4

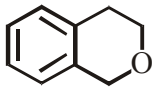
(P) 

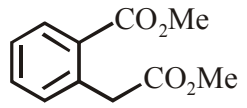
(II) 

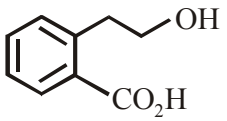
i) O_3
ii) Zn, H_2O
iii) $NaBH_4$
iv) conc. H_2SO_4

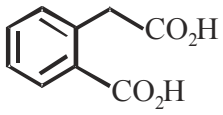
(Q) 

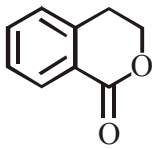
(III) 

i) KCN
ii) H_3O^+, Δ
iii) $LiAlH_4$
iv) conc. H_2SO_4
(R) 

(IV) 

i) $LiAlH_4$
ii) conc. H_2SO_4
(S) 

(T) 

(U) 

Which of the following options has correct combination considering List-I and List-II?

(1) (III), (S), (R) (2) (IV), (Q), (R)

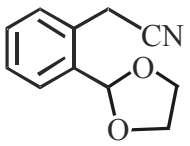
(3) (III), (T), (U) (4) (IV), (Q), (U)

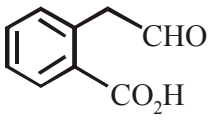
AH0181

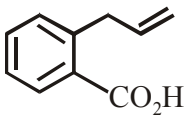
65. Answer the following by appropriately matching the lists based on the information given in the paragraph

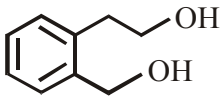
List-I includess starting materials and reagents of selected chemical reactions. List-II gives structures of compounds that may be formed as intermediate products and/or final products from the reactions of List-I **[IIT 2019]**

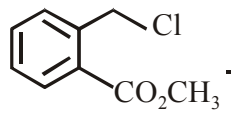
List-I **List-II**

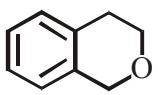
(I) 

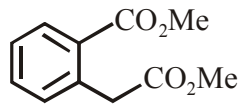
i) DlBAL-H
ii) dil, HCl
iii) $NaBH_4$
iv) conc. H_2SO_4
(P) 

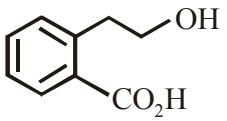
(II) 

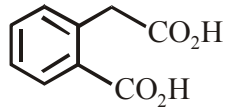
i) O_3
ii) Zn, H_2O
iii) $NaBH_4$
iv) conc. H_2SO_4
(Q) 

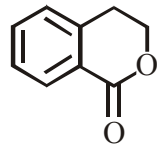
(III) 

i) KCN
ii) H_3O^+, Δ
iii) $LiAlH_4$
iv) conc. H_2SO_4
(R) 

(IV) 

i) $LiAlH_4$
ii) conc. H_2SO_4
(S) 

(T) 

(U) 

Which of the following options has correct combination considering List-I and List-II?

(1) (I), (Q), (T), (U)
(2) (II), (P), (S), (U)
(3) (II), (P), (S), (T)
(4) (I), (S), (Q), (R)

AH0182

AROMATIC COMPOUNDS _ ANSWER KEY

EXERCISE # O-I

1	**Ans. (B)**	2	**Ans. (C)**	3	**Ans. (C)**	4	**Ans. (C)**	5	**Ans. (C)**
6	**Ans. (B)**	7	**Ans. (D)**	8	**Ans. (B)**	9	**Ans. (B)**	10	**Ans. (D)**
11	**Ans. (C)**	12	**Ans. (A)**	13	**Ans. (B)**	14	**Ans. (A)**	15	**Ans. (B)**
16	**Ans. (B)**	17	**Ans. (D)**	18	**Ans. (B)**	19	**Ans. (B)**	20	**Ans. (A)**
21	**Ans. (A)**	22	**Ans. (B)**	23	**Ans. (A)**	24	**Ans. (C)**	25	**Ans. (B)**
26	**Ans. (B)**	27	**Ans. (B)**	28	**Ans. (D)**	29	**Ans. (C)**	30	**Ans. (D)**
31	**Ans. (D)**	32	**Ans. (A)**	33	**Ans. (D)**	34	**Ans. (C)**	35	**Ans. (C)**
36	**Ans. (A)**	37	**Ans. (A)**	38	**Ans. (B)**	39	**Ans. (C)**	40	**Ans. (A)**
41	**Ans. (D)**	42	**Ans. (C)**	43	**Ans. (A)**				

EXERCISE # O-II

1	**Ans. (A,B,C,D)**	2	**Ans. (A,B,D)**	3	**Ans. (B,D)**	4	**Ans. (B,C,D)**
5	**Ans. (A,B,C)**	6	**Ans. (B,D)**	7	**Ans. (C,D)**	8	**Ans. (C,D)**
9	**Ans. (B,C)**	10	**Ans. (B,C,D)**	11	**Ans. (A,B)**	12	**Ans. (A,B,C,D)**
13	**Ans. (A,B,C)**	14	**Ans. (A,C)**	15	**Ans. (A,B,D)**	16	**Ans. (B,C,D)**
17	**Ans. (A,B,C)**	18	**Ans. (A,B,C)**	19	**Ans. (A,B,C,D)**	20	**Ans. (C)**
21	**Ans. (B)**	22	**Ans. (A)**	23	**Ans. (A,C,D)**	24	**Ans. (B,C)**
25	**Ans. (A,B,D)**	26	**Ans. (A)**	27	**Ans. (A)**	28	**Ans. (A)**
29	**Ans. (B)**	30	**Ans. (A)**	31	**Ans. (A)-Q, (B)-P,R,S, (C)-R,S, (D)-P,Q,R,S**		

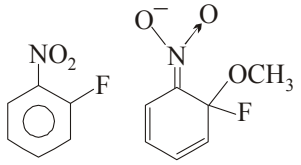
32 **Ans. (A)-P, S ; (B)- P, R ; (C)-Q, S ; (D)-P, R**

33 **Ans. (A)→Q,R,S ; (B)→P,R,S ; (C)→R,S ; (D)→Q,R,S**

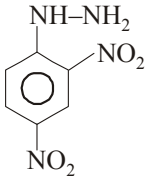
34 **Ans. (A) → R, T ; (B) → R, S ; (C) → Q, S ; (D) → P, R**

EXERCISE # S-I

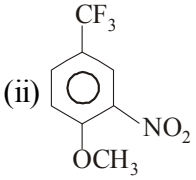
1 **Ans.**



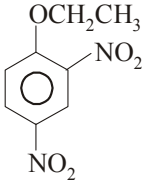
2 **Ans.** (i)



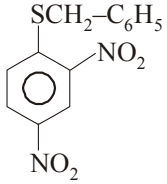
(ii)



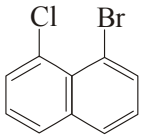
(iii)



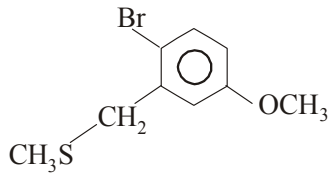
(iv)



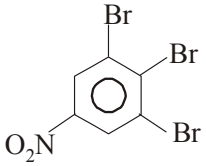
3 **Ans.** (i)

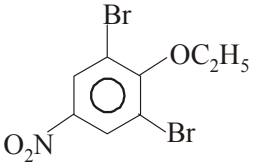


(ii)

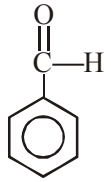


4 **Ans.**



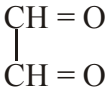


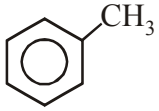
Solution for No. 8 & 9

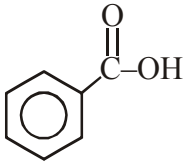
P = 

Q = $CH_3-\overset{O}{\overset{\|}{C}}-H$

R = Ph–CH = CH–CHO

S = 

T = 

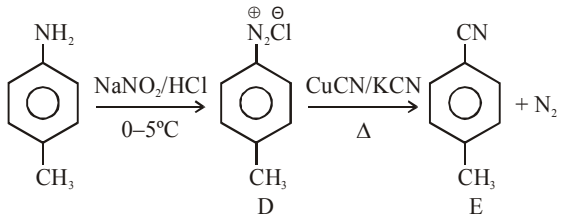
U = 

V = 

W = HC ≡ CH

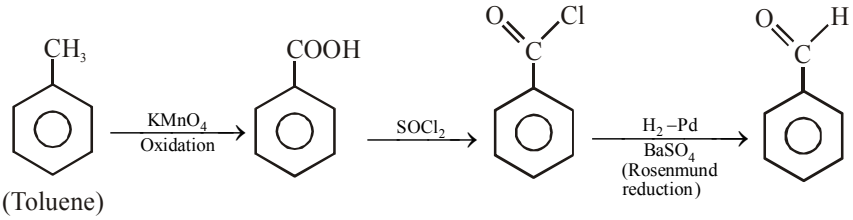
EXERCISE # (MAINS)

1	**Ans. (1)**	2	**Ans. (2)**	3	**Ans. (4)**	4	**Ans. (2)**
5	**Ans. (3)**	6	**Ans. (1)**				

Sol. 

Formation of D is example of Diazotisation
Formation of E from D is example of Sandmayer's Reaction

7 **Ans. (2)**

Sol. 

(Toluene)

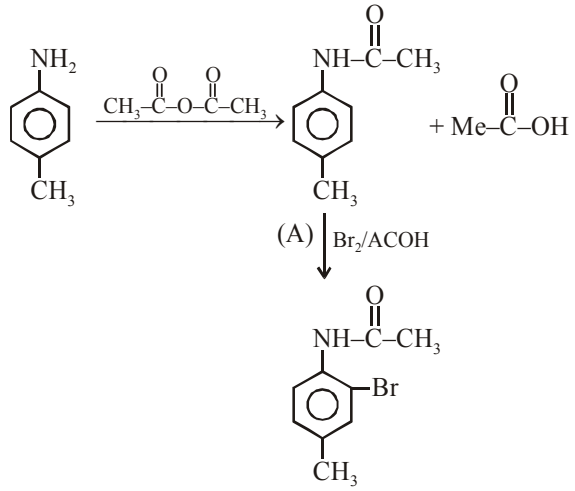
8	**Ans. (3)**	**9.**	**Ans.(4)**	**10.**	**Ans.(2)**	**11.**	**Ans.(4)**
12.	**Ans.(1)**	**13.**	**Ans.(3)**	**14.**	**Ans.(4)**	**15.**	**Ans. (4)**
16.	**Ans. (1)**	**17.**	**Ans. (3)**	**18.**	**Ans. (2)**	**19.**	**Ans. (3)**
20.	**Ans. (2)**	**21.**	**Ans. (1)**	**22.**	**Ans. (4)**	**23.**	**Ans. (2)**
24.	**Ans. (1)**	**25.**	**Ans.(4)**	**26.**	**Ans. (Bonus)**	**27.**	**Ans. (3)**
28.	**Ans. (3)**	**29.**	**Ans. (2)**	**30.**	**Ans. (3)**	**31.**	**Ans. (1)**

32. Ans. (4) **33. Ans. (1)** **34. Ans.(3)** **35. Ans. (1)**

36. Ans. (1) **37. Ans. (4)**

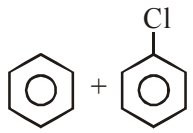
38. Ans. (1)

Sol.



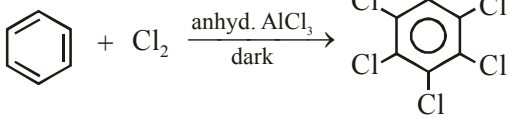
39. Ans. (2)

Sol. (a)



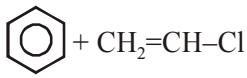
No reaction

(b)

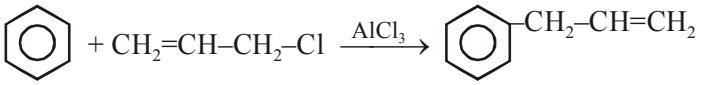


(electrophilic substitution)

(c)

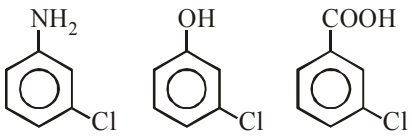


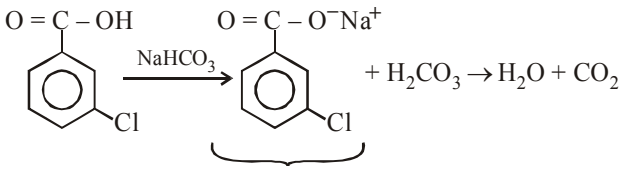
No reaction (d)



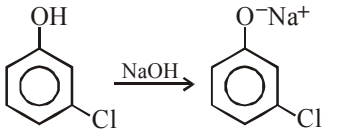
40. Ans. (3)

Sol.

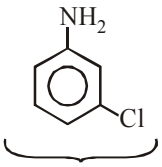




Fraction-A



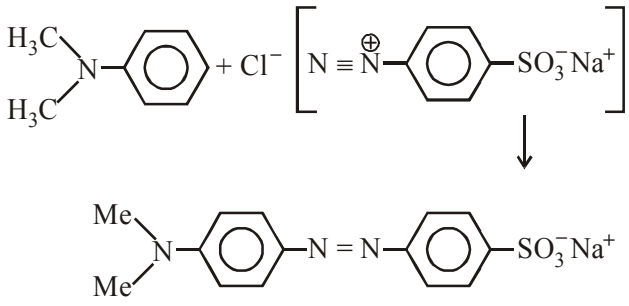
Fraction-B



Fraction-C

41. Ans. (1)

Sol.

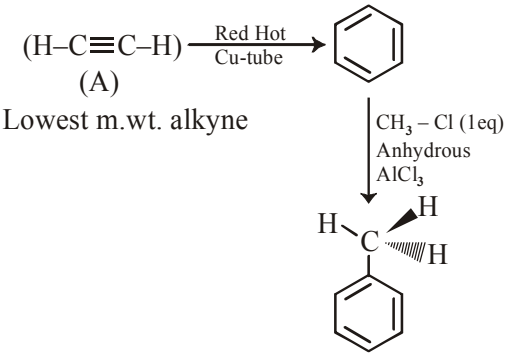


(Methyl orange)

It is an acid base indicator

42 Ans. (13)

Sol.



Lowest m.wt. alkyne

Total 13 atom are present in same plane (7 carbon & 6 hydrogen atoms.)

EXERCISE # (ADVANCE)

1	**Ans. (D)**	2	**Ans. (A)**	3	**Ans. (A,B)**	4	**Ans. (C)**
5	**Ans. (D)**	6	**Ans. (C)**	7	**Ans. (C)**	8	**Ans. (A)**
9	**Ans. (A,C)**	10	**Ans. (C)**	11	**Ans. (B)**	12	**Ans. (A,C)**
13	**Ans. (D)**	14	**Ans. (C)**	15	**Ans. (B)**	16	**Ans. (D)**
17	**Ans. (C)**	18	**Ans. (C)**	19	**Ans. (D)**	20	**Ans. (D)**
21	**Ans. (B)**	22	**Ans. (C)**	23	**Ans. (C)**	24	**Ans. (B)**
25	**Ans. (B)**	26	**Ans. (C)**	27	**Ans. (D)**	28	**Ans. (A,B,C)**
29	**Ans. (C)**	30	**Ans. (A)**				
31	**Ans. (A)→R, S, T ; (B)→T ; (C)→P, Q ; (D)→R**					32	**Ans. (C)**
33	**Ans. (A)→(R,S,T) ; (B)→(P, S) ; (C)→(R, S) ; (D)→(Q, R)**						
34	**Ans. (A,B,C,D)**	35	**Ans. (B)**	36	**Ans. (B,D)**	37	**Ans. (A)**
38	**Ans. (B)**	39	**Ans. (A)**	40	**Ans. (A,B,C)**	41	**Ans. (C)**
42	**Ans. (C)**	43	**Ans. (A)**	44	**Ans. (4)**	**45.**	**Ans. (B,C)**
46.	**Ans. (B)**	**47.**	**Ans. (B,C,D)**	**48.**	**Ans. (B,C)**	**49.**	**Ans. (5)**
50.	**Ans. (D)**	**51.**	**Ans. (A)**	**52.**	**Ans. (B)**	**53.**	**Ans. (C)**
54.	**Ans. (B)**	**55.**	**Ans. (D)**	**56.**	**Ans.(A,B,D)**	**57.**	**Ans.(C)**
58.	**Ans.(A)**	**59.**	**Ans.(D)**	**60.**	**Ans.(495)**	**61.**	**Ans. (4.00)**
62.	**Ans. (2,4)**	**63.**	**Ans. (2,4)**	**64.**	**Ans. (2)**	**65.**	**Ans. (2)**