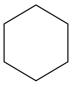
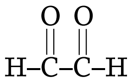
CHAPTER 7

Aromatic Hydrocarbon (Arenes)

INTRODUCTION

- Aromatic hydrocarbons are also called arenes
- General formula of arenes is C_nH_{2n-6y} where y is the number of benzene ring in molecule
- Following reactions are important in the determination of the structure of benzene

(i) $C_6H_6 \xrightarrow[Pt]{H_2/\Delta}$ 

(ii) $C_6H_6 \xrightarrow[2.\ H_2O/Zn]{1.\ O_3}$ 

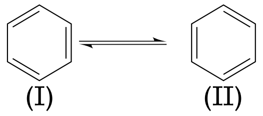
$H-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-H$

(iii) $C_6H_6 \xrightarrow[\text{Cold \& dil.}]{KMnO_4}$ No reaction (no decolourisation)

(iv) $C_6H_6 \xrightarrow{Br_2CCl_4}$ No reaction

(v) $C_6H_6 \xrightarrow{HCl}$ No reaction

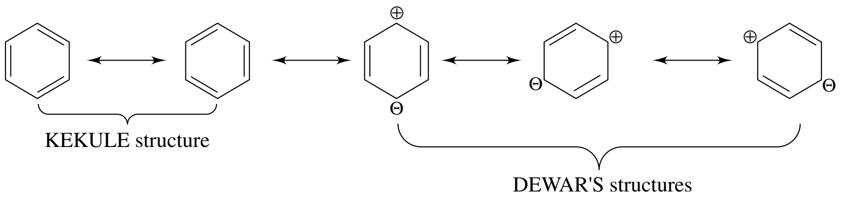
On the basis of (i) and (ii) reactions Kekule in 1865 suggested that benzene is equilibrium mixture of cyclohexatrienes [(I) and (II)] as follows



But reaction (iii), (iv) and (v) cannot be explained by Kekule's structure.

THE RESONANCE HYBRID STRUCTURE

According to the resonance theory, benzene is a resonance hybrid of the following canonical forms.



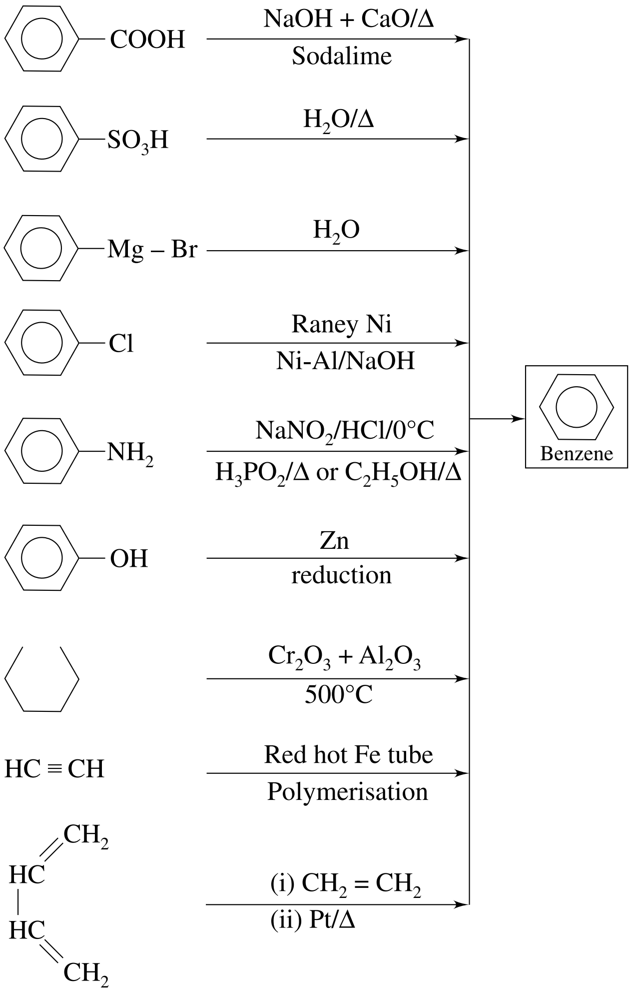
Contribution:	Total 80%	Total 20%
	40% each	i.e., $\frac{20}{3}$% contribution by each

It should be noted that the concept of resonance is imaginary and the canonical forms mentioned above actually do not exist. It is the hybrid structure which is a reality.

Physical Properties of Benzene

- Benzene is a colourless volatile liquid; it has characteristic smell
- Its boiling point is 80°C and freezing point is 5.5°C
- It is highly inflammable and burns with sooty flame
- It is lighter than water; its specific gravity at 20°C is 0.8788
- It is immiscible with water but miscible with organic solvents such as alcohol and ether
- It is a non-polar compound and its dipole moment is zero
- It is extremely poisonous substance. Inhalation of vapours or absorption though skin has a toxic effect.

METHODS OF PREPARATION OF BENZENE



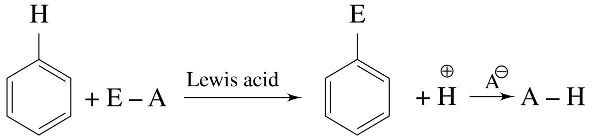
CHEMICAL PROPERTIES OF BENZENE

Aromatic Electrophilic Substitution Reactions

The most characteristic reactions of benzenoid arenes are the substitution reactions that occur when they react with electrophilic reagents.

The reactions in which one or more hydrogen atoms of the benzene ring are replaced by an electrophile are called electrophilic aromatic substitution reactions.

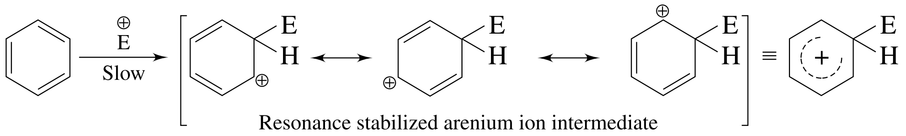
These reactions are of the general type shown below:



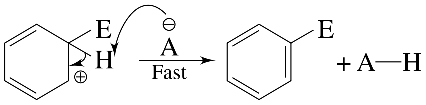
benzenoid arenes undergoes electrophilic substitution reactions because it has an electron rich system due to delocalized -electron.

General Mechanism

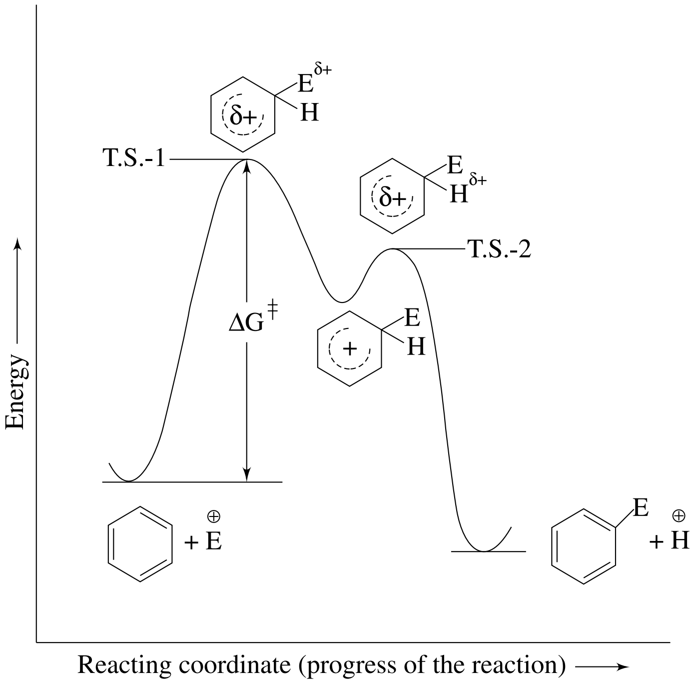
Step 1.



Step 2.



Energy profile for a typical aromatic electrophilic substitution reaction: A more detailed picture of the arenium ion mechanism may be represented by its energy profile.



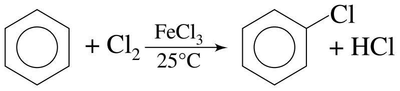
Important Points

- Benzene is a poor nucleophile because it losses its aromaticity
- First step is RDS where Wheeland intermediate or σ complex is formed
- σ complex has 4 e^- non-aromatic resonance stabilized carbocation
- Breaking of C–H bond takes place in fast step it means no isotopic effect thus rate of reaction is $C_6H_6 \approx C_6D_6 \approx C_6T_6$

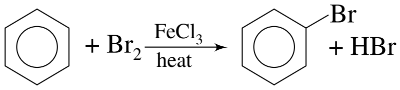
Note: In sulphonation and iodination isotopic effect considered because difference between TS_1 and TS_2 is very less.

Thus rate of reaction is $C_6H_6 > C_6D_6 > C_6T_6$

Halogenation of Benzene



Chlorobenzene (90%)

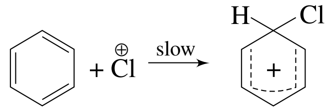


Bromobenzene (75%)

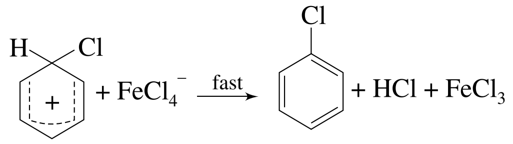
The mechanism for aromatic chlorination is as follows.

Step-1 $\text{Cl–Cl} + \text{FeCl}_3 \rightleftharpoons \text{Cl–}\overset{\oplus}{\text{Cl}} - \overset{\ominus}{\text{FeCl}_3} \longrightarrow \overset{\oplus}{\text{Cl}} + \overset{\ominus}{\text{FeCl}_4}$

Step-2



Step-3



Some facts

(i) The function of Lewis acid is to convert weaker electophile (Cl_2) into stronger electrophile ($\overset{\oplus}{Cl}$)

(ii) The Lewis acids most commonly used to effect chlorination and bromination reactions are $FeCl_3$, $FeBr_3$, and $AlCl_3$ all in the anhydrous form.

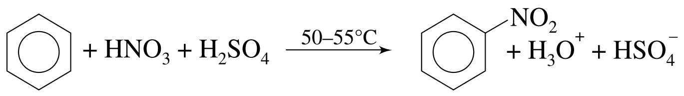
(iii) Ferric chloride and ferric bromide are usually generated in the reaction mixture by adding iron to it. The iron then reacts with halogen to produce the ferric halide.

$$2Fe + 3X_2 \rightarrow 2FeX_3$$

(iv) The Lewis acids behave as a halogen carrier.

Nitration of Benzene

A mixture of nitric acid and sulphuric acid is the nitrating reagent.



(85%)

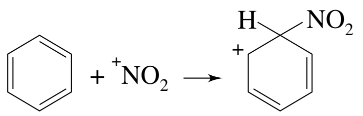
The steps involved in the mechanisms are as follows.

Step-1 Formation of nitronium ion

$$HONO_2 + 2H_2SO_4 \rightleftharpoons H_3O^+ + 2HSO_4^- + {}^+NO_2$$

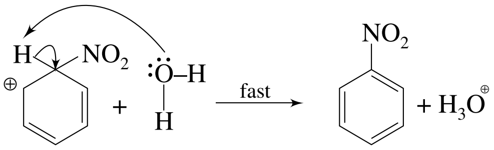
Nitronium ion

Step-2 Electrophilic attack by nitronium ion



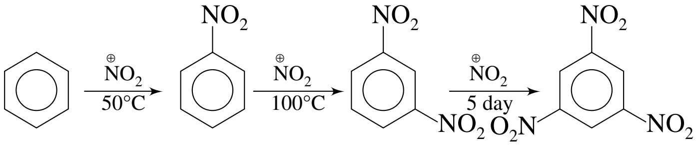
Arenium ion

Step-3 Removal of proton



Some facts

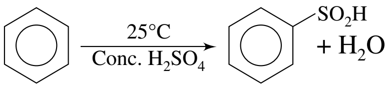
(i) In nitration HNO_3 behave as bronsted base and H_2SO_4 as a bronsted acid.
(ii) For formation of 1 mol NO_2^+ 2 : 1 ratio for H_2SO_4 and HNO_3 is used.
(iii) The rate determining step is the formation of carbocation (σ complex).
(iv) Breaking of C–H bond takes place in fast stape so that there is no isotopic effect.
(v) NO_2 is a deactivating group it means for further nitration, rate of reaction decreases.



1, 3, 5-tri nitro benzene (T.N.B)
(explosive)

Sulfonation of Benzene

Benzene reacts with fuming sulphuric acid at room temperature to produce benzene-sulfonic acid. Fuming sulphuric acid is sulphuric acid that contains added sulphur trioxide (SO_3). Sulfonation also takes place in concentrated sulphuric acid alone, but more slowly.

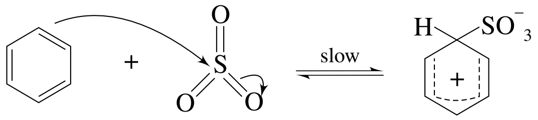


Benzenesulfonic acid
(56%)

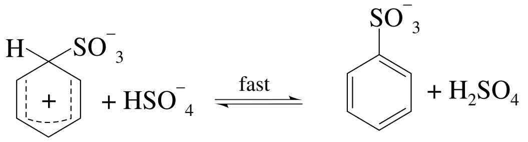
The steps involved in the mechanisms are as follows :

Step-1 $2H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^- + SO_3$

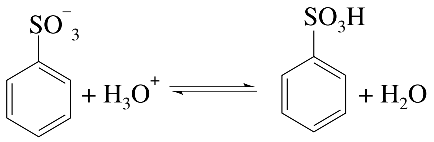
Step-2



Step-3



Step-4



Some Facts

(i) The entire sulphonation process is an equilibrium process

$C_6H_6 + H_2SO_4 \overset{H^+}{\rightleftharpoons} C_6H_5SO_3H + H_2O$

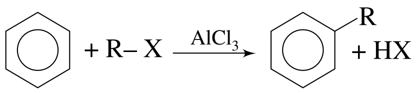
For sulphonation, we require excess of H_2SO_4 along with SO_3 and for desulphonation we use excess of H_2O along with heating (100–175°C).

(ii) Sulphonation is a reversible reaction because different between $T.S_1$ and $T.S_2$ is very less.

(iii) Order of reactivity in isotopic benzene is $C_6H_6 > C_6D_6 > C_6T_6$.

Friedel–Crafts Alkylation

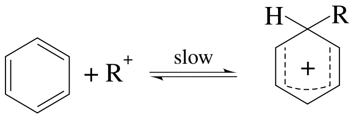
A general equation for a Friedel–Crafts alkylation reaction is the following:



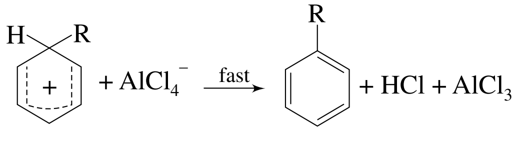
The steps involved in the mechanisms are as follows:

Step-1 $RCl + AlCl_3 \rightleftharpoons AlCl_4^- + R^+$

Step-2

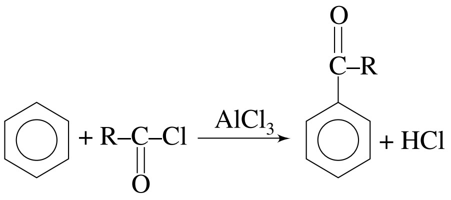


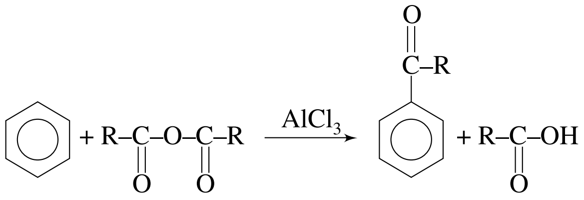
Step-3



Here $AlCl_3$ acts as a Lewis acid.

Friedel–Crafts Acylaction

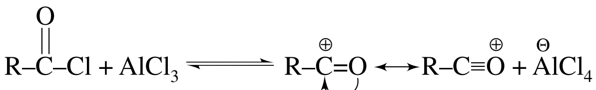




The steps involved in the mechanisms are as follows:

In most Friedel –Crafts acylation the electrophile appears to be an acylium ion formed from an acyl halide in the following ways:

Step-1

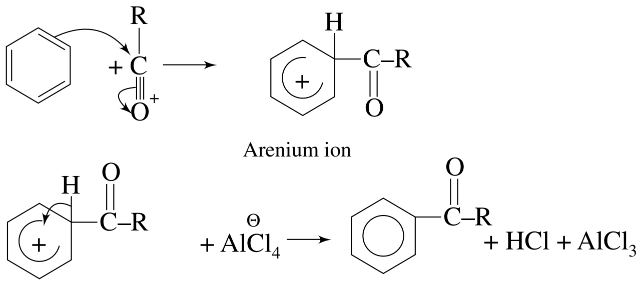


$R\overset{\overset{O}{\|}}{C}Cl + AlCl_3 \rightleftharpoons R–\overset{\oplus}{C}=O \longleftrightarrow R–C{\equiv}\overset{\oplus}{O} + \overset{\ominus}{AlCl_4}$

An acylium ion
(a resonance hybrid)

Step-2

Step-3



Limitation of Friedel-Crafts Reactions:

(i) 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.

(ii) Vinyl halides and aryl halides do not react in Friedel-Crafts alkylation because carbocation derived from vinyl halide and aryl halide are highly unstable.

(iii) Friedel-Crafts reaction usually give poor (almost no yields) yields when powerful electron withdrawing groups are present on the aromatic ring due instability of σ complex.

(iv) When the ring bears an – NH_2, $–NHR$, or $–NR_2$ group, these groups are changed into powerful electron– withdrawing groups by the Lewis acids used to catalyze Friedel-Crafts reaction so that $–NH_2$, $–NHR$, and $–NR_2$ groups are not give Friedel-Crafts reaction.

(v) Another limitation of Friedel-Crafts alkylation arises because of polyalkylation as an alkyl substituted benzene is more reactive than benzene. However no Polyacylation takes place.

EFFECT OF SUBSTITUENTS ON REACTIVITY AND ORIENTATION

When substituted benzene undergo electrophilic attack, groups already on the ring affect both the rate of the reaction and the site of attack therefore substituent groups affect both reactivity and orientation in electrophilic aromatic substitutions.

We can divide substituent groups into two classes according to their influence on the reactivity of the ring. Those that cause the ring to be more reactive than benzene itself we call activating groups. Those that cause the ring to be less reactive than benzene we call deactivating groups.

Theory of Orientation

A group attached to benzene has a directing influence on the electrophilic substitution reaction. Two types of groups have been classified based on their orientation effects.

Activating Group

A group that releases electrons to benzene ring is an activating group. It directs the incoming electrophile to *ortho* or *para* position. Examples include

Strongly activating: $–NH_2$, $–NHR$, $–NR_2$, $–OH$, $–OCH_3$

Moderately activating: $–NHCOCH_3$, $–OCOCH_3$

Weakly activating: $–CH_3$, $–CH{=}CH_2$, $–C_6H_5$

Deactivating Group

A group that withdraws electrons from benzene is a deactivating group. It directs the incoming electrophile to *meta* position. Examples include

Strongly deactivating: $–\overset{+}{N}(CH_3)_3$,$–NO_2$, $–CN$, $–SO_3H$

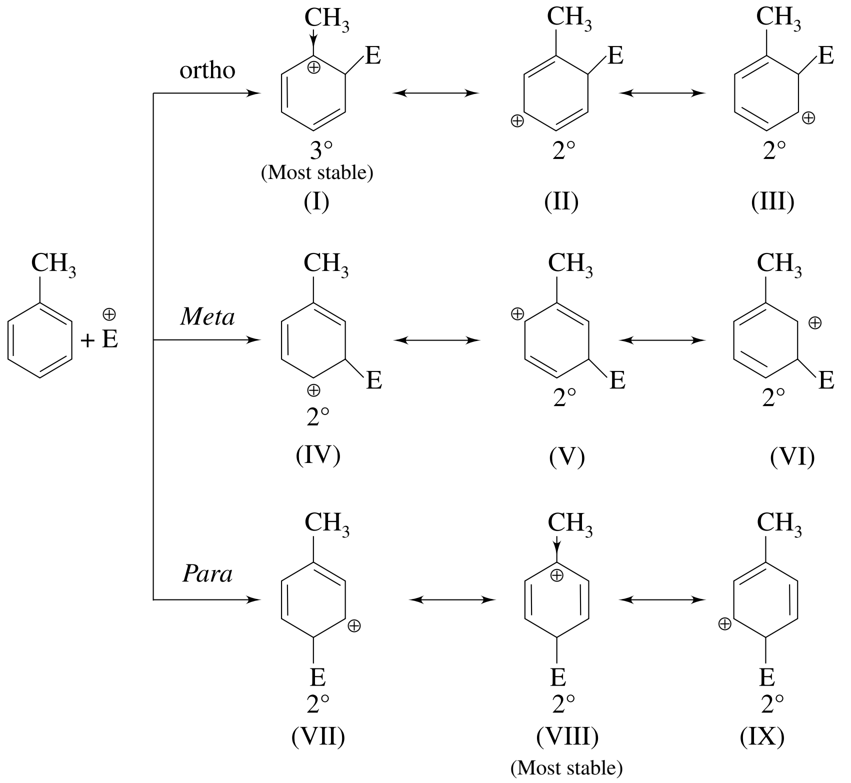
Moderately deactivating $–CHO$, $–COR$, $–COOR$, $–COOH$, $–COCl$

*Weakly deactivating: F, –Cl, –Br, –I (*o*/*p* director)

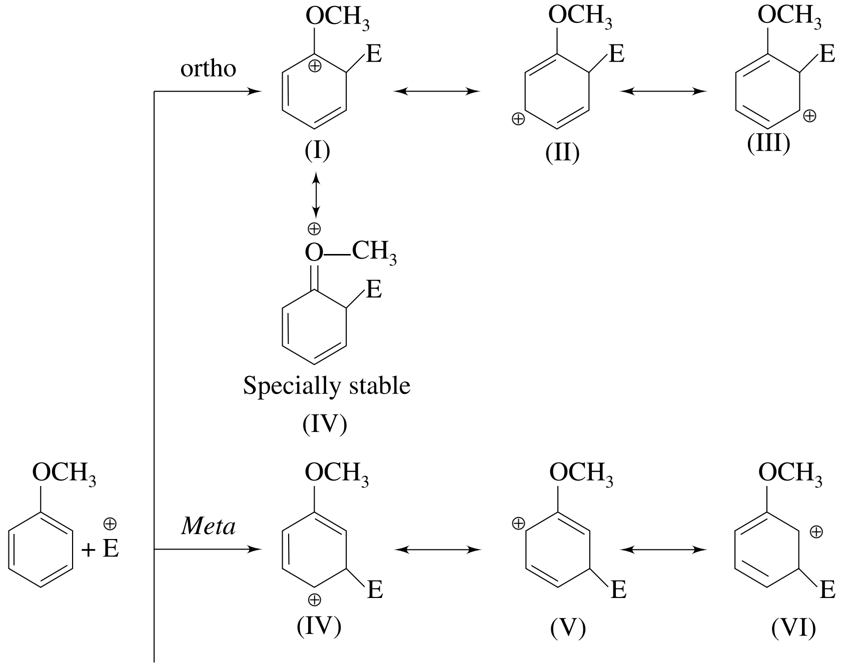
Orientation Based on Sigma Complex Stability

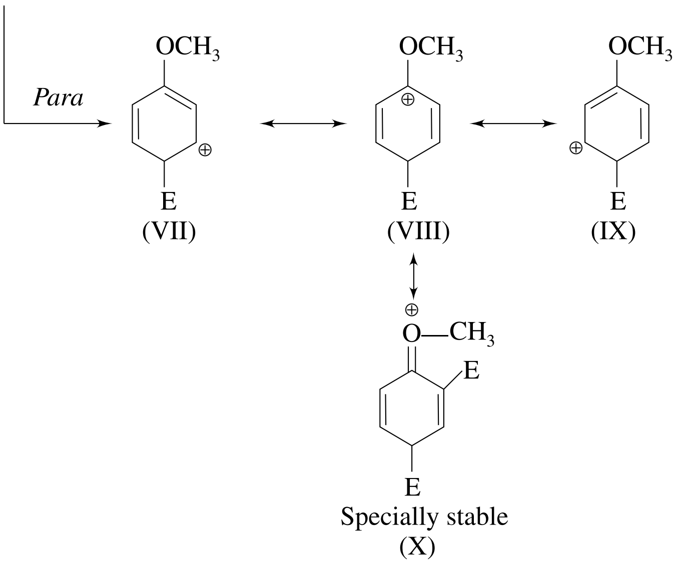
Case-I: Activating Groups : Ortho para Directors

(a) **When group is +H/+I group only, i.e., Alkyl group:** Structures of the carbocation intermediates formed from the reaction of an electrophile with toluene at the otrtho, at the ortho, meta and para position



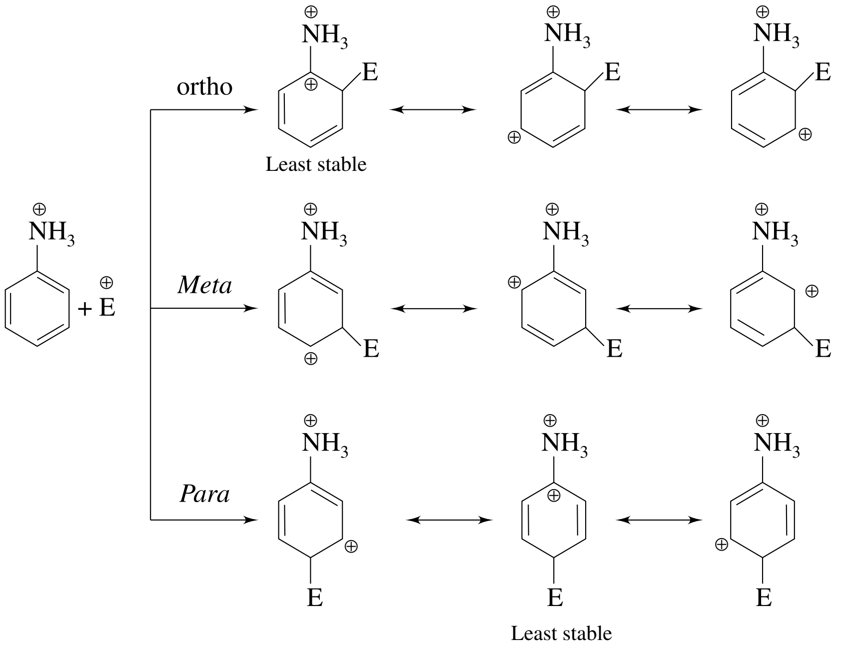
(b) **When group +M/–I group:** The structures of the carbocation intermediates formed from the reaction of an electrophile with anisole at the ortho, meta and para positions.



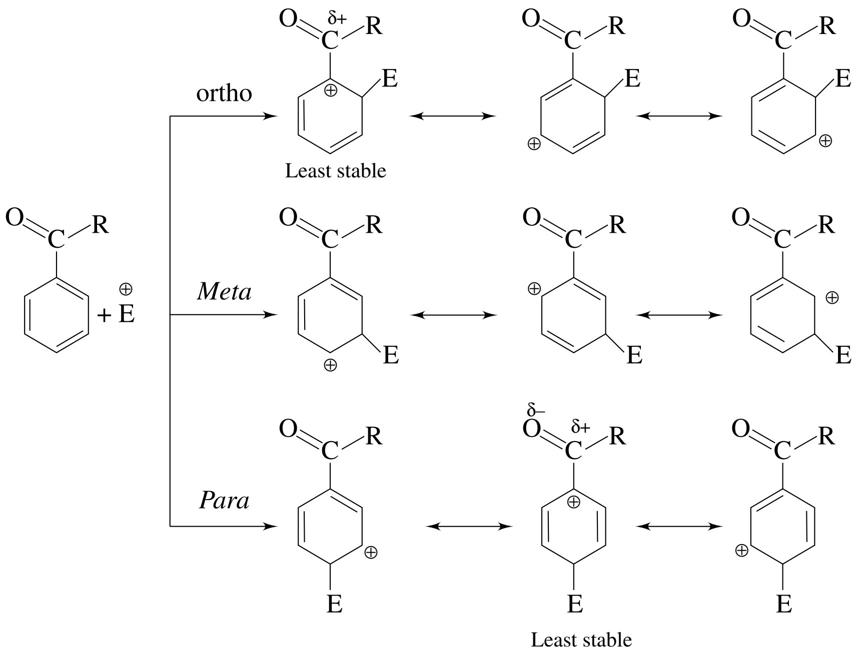


Case-II: Deactivating Groups : Meta Directors

(a) When group is –I group: Structure of the carbocatoin intermediates formed from the reaction of an electrophile with protonated aniline (–I group) at the ortho, meta and para positions

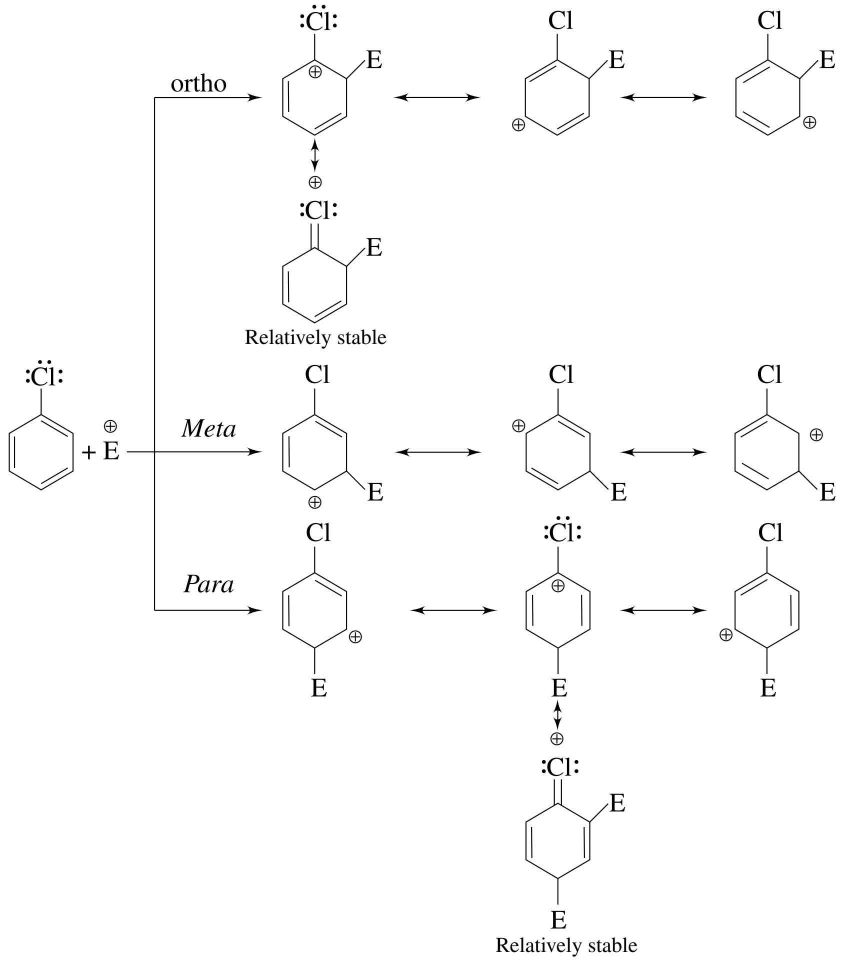


(b) When group is –M/–I group: Structures of the carbocation intermediates formed from the reaction of an electrophile with a substrate, having an –M group, at the ortho, meta and para position



Case-III: Halo Substituents : Deactivating Ortho-Para Directors

Structures of the carbocation intermediates formed from the reaction of an electrophile with a halogenated benzene at the ortho, meta and para position



EFFECT OF SUBSTITUTENTS ON REACTIVITY:

In presence of different substituents on benzene ring, rate of reaction increased or decreased is known as substitution effect.

$$\boxed{\text{Reactivity of ArsE} \propto \text{Activating power} \propto \frac{1}{\text{Deactivating power}}}$$

Classification of Substituents

ORTHO-PARA DIRECTIORS	META DIRECTORS
Strongly activating $-NR_2$, $-NHR$, $-NH_2$, $-OH$, $-O^-$ Moderately activating $-NHCOR$,$-OCOR$,$-OR$ Weakly activiating $-CH_3$, $-C_2H_5$, $-C_6H_5$ Weakly deactivating $-F$, $-Cl$, $-Br$, $-I$	Moderately Deativating $-C{\equiv}N$, $-SO_3H$, $-CO_2H$, $-CO_2R$, $-CHO$, $-COR$ Strongly deactivating $-NO_2$, $-\ NR_3^+$, $-CF_3$, $-CCl_3$

Summary of Substituent Effects on orientation

We can summarize the effect that groups have on orientation and reacvtivity in the following way.

<table>
<tr><td rowspan="2">Full or partial (+) charge on directly attached atoms</td><td colspan="2">At least one nonbonding pair on directly attached atom</td><td rowspan="2">Alkyl or aryl</td></tr>
<tr><td>Halogen</td><td>$-\ddot{N}H_2$,$-\ddot{\underset{..}{O}}H$, etc.</td></tr>
<tr><td colspan="4">← meta directing ——————→×←—————— ortho-para directing ——————→</td></tr>
<tr><td colspan="4">←—— deactivating ——————————→×←—————activating ——————→</td></tr>
</table>

Aromatic Electrophilic Substitution Reactions of Polysubstituted Benzene

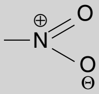
What happens when two or more substituent groups are attached to the benzene ring ? Where is the electrophile likely to attack? Some qualitative rules have been formulated to answer this question.

(i) The most activating group will control orientation.

(ii) No substitution occurs between two meta substituents because of crowding.

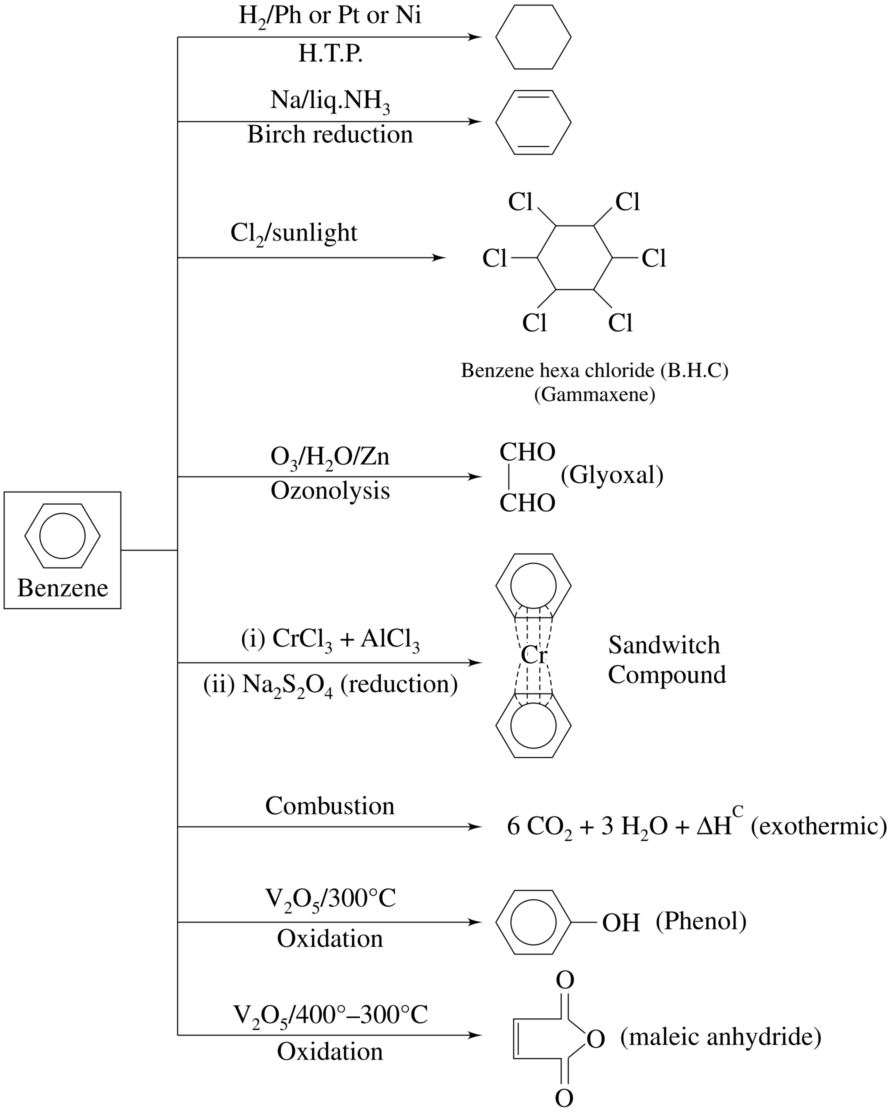
(iii) When both groups are meta directors, it is difficult to introduce third group.

Summary of main electrophilic substitutions on benzene

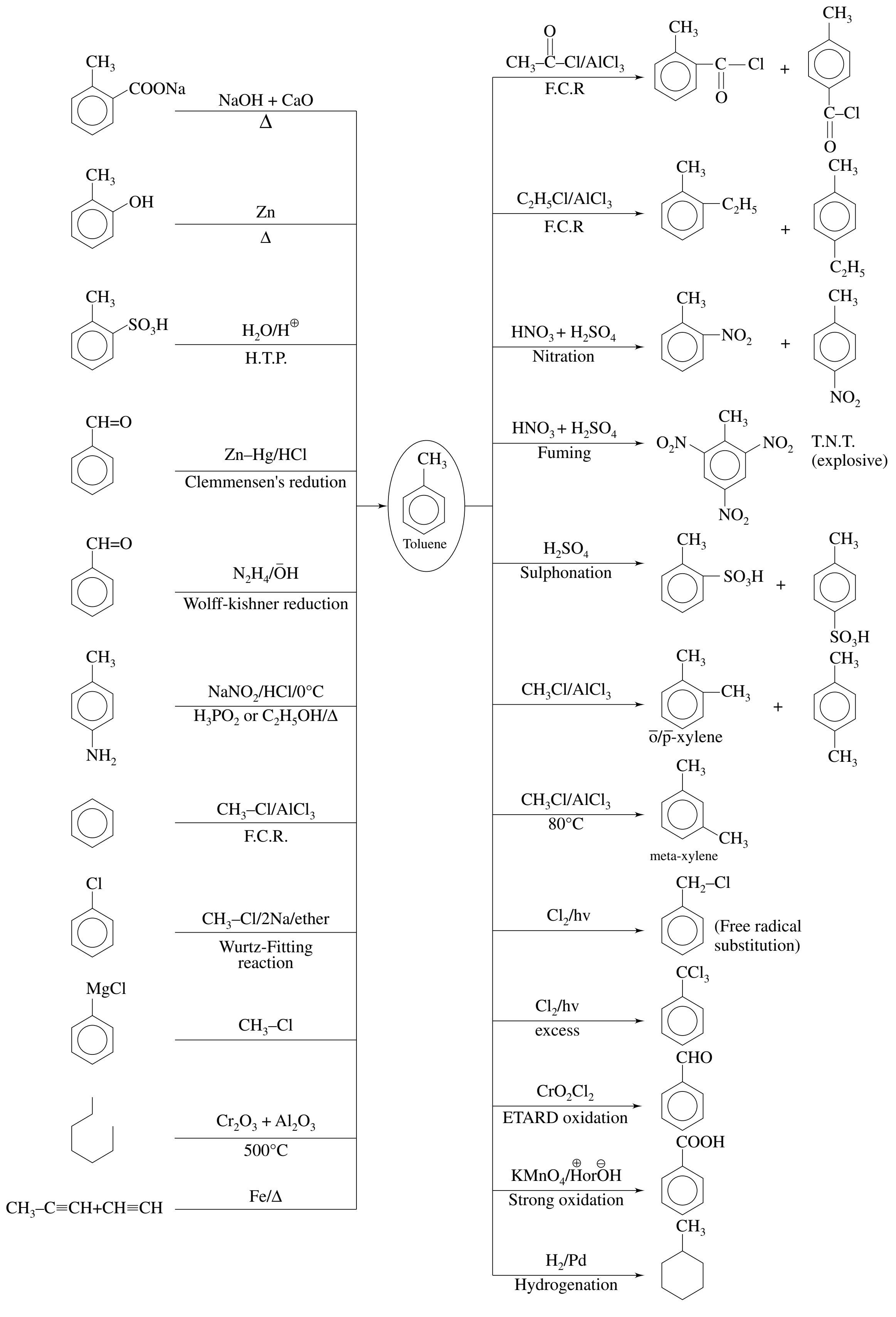
Reaction	Reagents	Electrophile	Products
Bromination	Br_2 and Lewis acid, e.g., $AlCl_3$, $FeBr_3$, Fe Powder, I_2	$Br—\overset{\oplus}{Br}—\overset{\ominus}{AlCl_3}$ $Br—\overset{\oplus}{Br}—Fe$	$C_6H_5—Br$
Nitration	$HNO_3 + H_2SO_4$		$C_6H_5—NO_2$
Sulphonation	Concentrated H_2SO_4 or $H_2SO_4 + SO_3$(oleum)	$\overset{\oplus}{S}O_3H$ or SO_3	$C_6H_5—SO_3H$
Friedel–Crafts alkylation	R—X + Lewis acid usually $AlCl_3$	$R^{\oplus}$	$C_6H_5—R$
Friedel–Crafts acylation	$RCOCl + AlCl_3$	$R—C{\equiv}\overset{\oplus}{O}$	$C_6H_5—\overset{\overset{\displaystyle O}{\Vert}}{C}—R$

Gatterman–Koch	CO, HCl, $AlCl_3$, Cu_2Cl_2	$H-C\equiv\overset{\oplus}{O} \leftrightarrow H-\underset{\oplus}{C}=O$	C_6H_5-CHO
Gatterman aldehyde	HCN, $HCl/AlCl_3$, H^+	$H-C\equiv\overset{\oplus}{N}H \leftrightarrow H-\underset{\oplus}{C}=NH$	C_6H_5-CHO
Chloromethylation	CH_2O, HCl $ZnCl_2$	$\overset{\oplus}{C}H_2OH$	$C_6H_5-CH_2OH$
Mercuration	$Hg(OAc)_2/\Delta$	$\overset{\oplus}{Hg}(OAc)$	$C_6H_5-HgOAc$
Thallunation	$Tl(OCOCF_3)_3/\Delta$	$\overset{\oplus}{Tl}(OCOCF_3)_2$	$C_6H_5-Tl(OCOCF_3)_2$

Some other Reactions of benzene

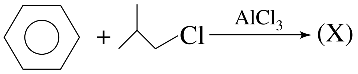


METHODS OF PREPARATION AND CHEMICAL PROPERIES OF TOLUENE:

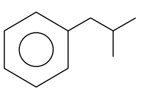


SOLVED EXAMPLE

1. In the reaction



The major product (X) is

(1)


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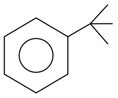

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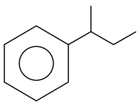

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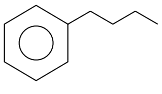
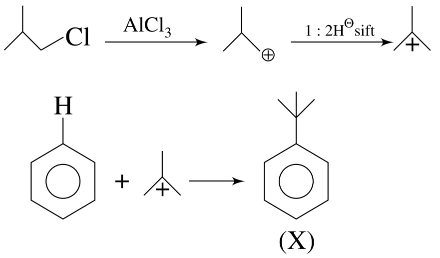


Sol. **[2]**



Friedel–Craft Reaction

2. Is nitrated and the resulting product is reduced with tin and hydrochloric acid. The product so obtained is diazotized and then heated with potassium iodide. The reaction mixture so formed contains:

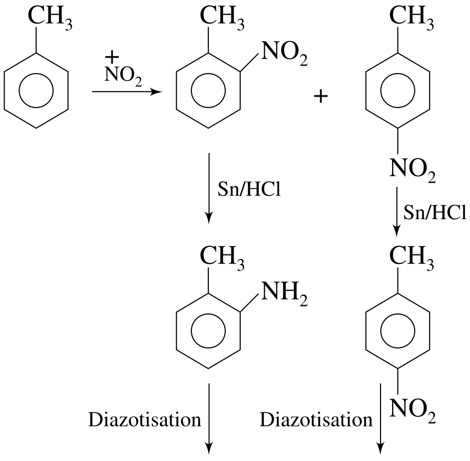
(1) Mixture of *o*– and *p*–iodotoluenes

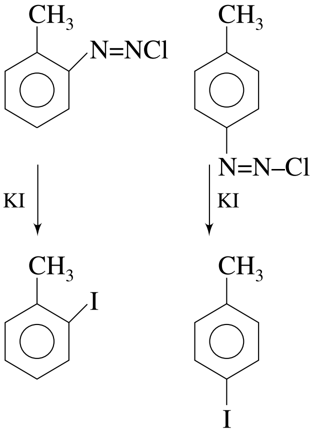
(2) Mixture of *o*– and *p*–diiodobenzenes

(3) Mixture of *o*– and *p*–iodoanilintes

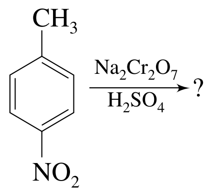
(4) Mixture of *o*– and *m*–iodotoluenes

Sol. **[1]**





3. What is the product of the following reaction?



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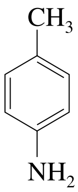

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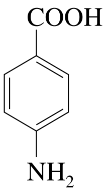

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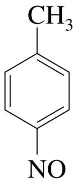

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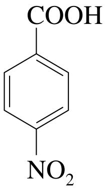
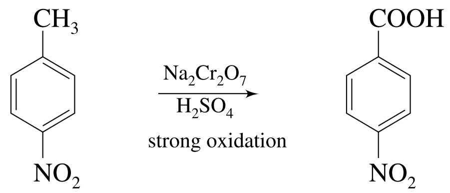
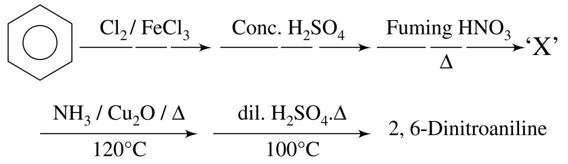
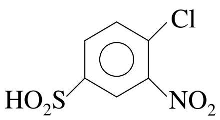


Sol. **[4]**



4. The intermediate product 'X' of following synthesis is identified as:



(1)


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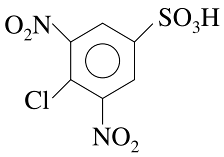

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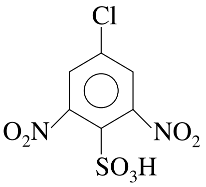

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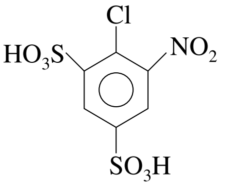
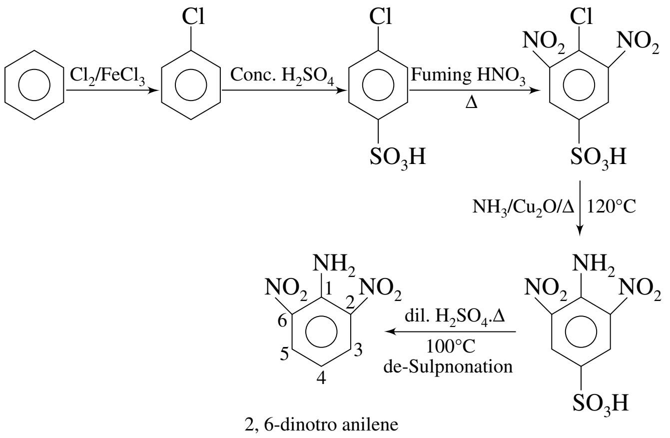
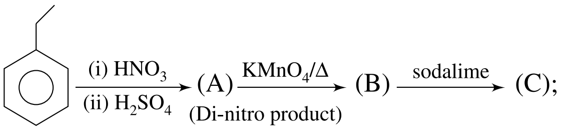


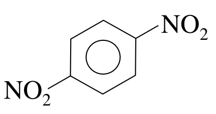
Sol. **[2]**



2, 6-dinotro anilene

5.


Product (C) of this reaction is:

(1)


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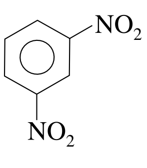

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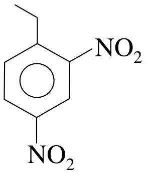

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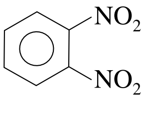
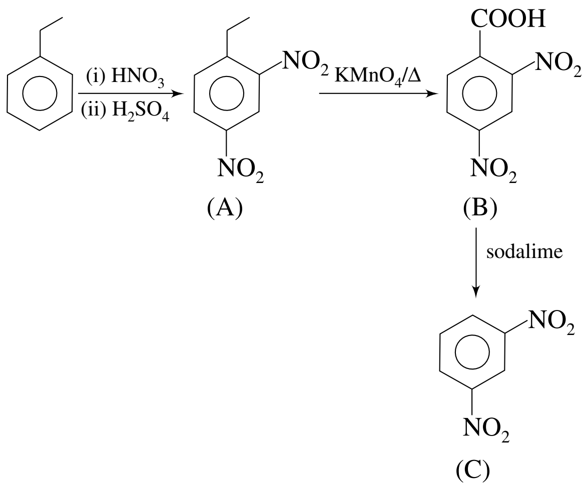
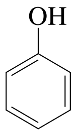


Sol. **[2]**



6. Each of the following compounds gives a Friedel–Crafts alkylation, except:

(1)


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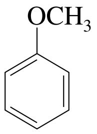

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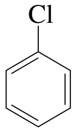

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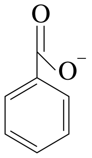
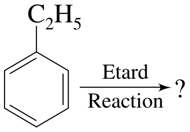
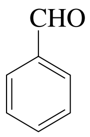


Sol. **[4]**

Due to presence of de-activating group Friedel–Craft reaction does not take place because σ complex is unstable

7.


(1)


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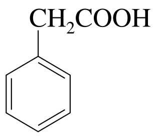

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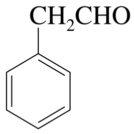

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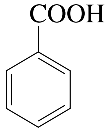
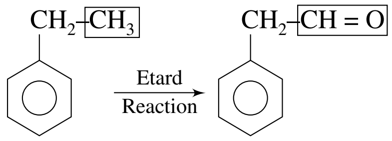


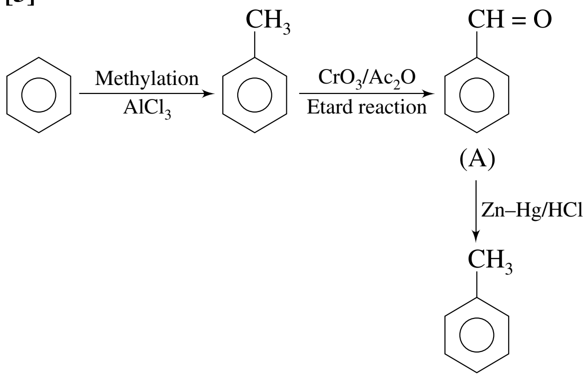
Sol. **[3]**



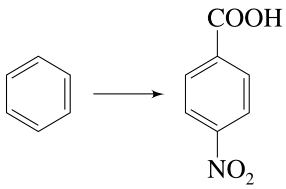
8. Benzene undergoes methylation in presence of $AlCl_3$ followed by oxidation with CrO_3 in the presence of $(CH_3CO)_2O$. It gives a product 'A' which on treatment with Zn-Hg/HCl produces:

(1) C_6H_5COOH
(2) C_6H_6
(3) $C_6H_5–CH_3$
(4) $C_6H_5–CH=O$

Sol. **[3]**

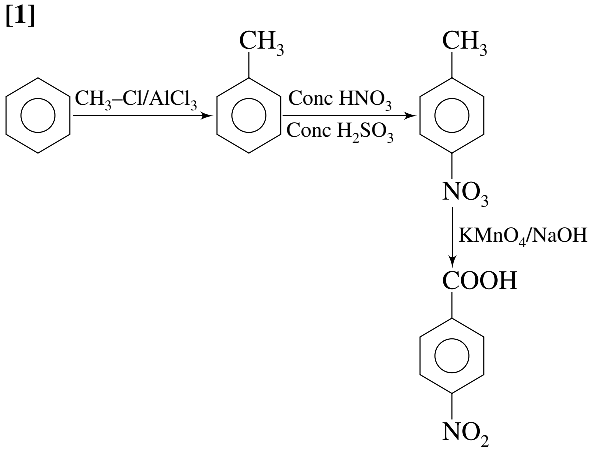


9. Provide the appropriate sequence of reagents that can bring about the following:

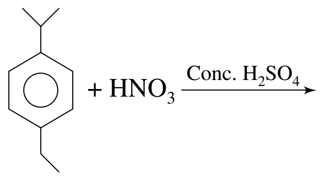


(1) $CH_3Cl/AlCl_3$ then conc. HNO_3/conc. H_2SO_4 then $KMnO_4/NaOH$
(2) Conc. HNO_3/Conc. H_2SO_4 then $CH_3Cl/AlCl_3$ then $KMnO_4/NaOH$
(3) $CH_3Cl/AlCl_3$ then $KMnO_4/NaOH$ then conc. HNO_3/Conc. H_2SO_4
(4) Conc. H_2SO_4/conc. HNO_3 then $CH_3COCl/AlCl_3$ then $KMnO_4/NaOH$

Sol. **[1]**



10. The major product formed in the reaction



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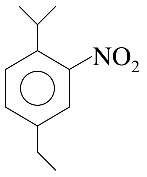

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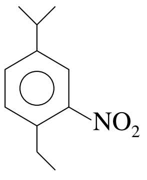

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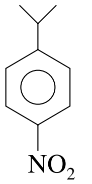

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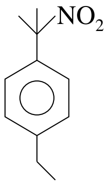
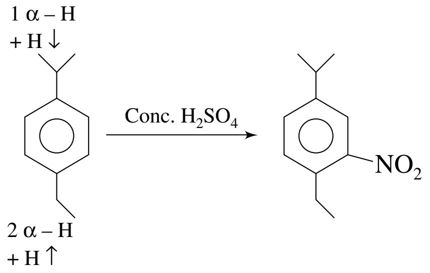


Sol. **[2]**



11. The reactivites of $C_6H_5CH_3$ (I), $C_6H_5CH_2Cl$ (II), $C_6H_5CHCl_2$ (III), $C_6H_5CCl_3$ (IV) toward nitration are in the order

(1) I > II > III > IV
(2) II > I > III > IV
(3) IV > III > II > I
(4) III > I > II > IV

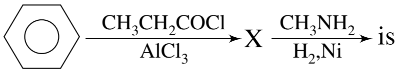
Sol. [1]

Nitration ≡ Ar–SE ∝ activating power

$$\propto \frac{1}{\text{De-activating power}}$$

+ H (CH_3 > $–CH_2–Cl$ > $–CHCl_2$ > $–CCl_3$)

12. The final product obtained in the reaction



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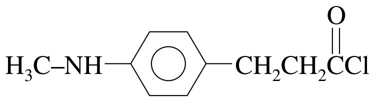

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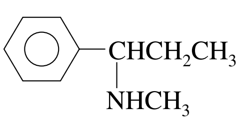
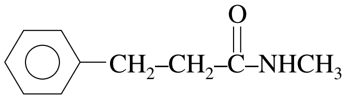
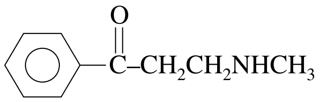
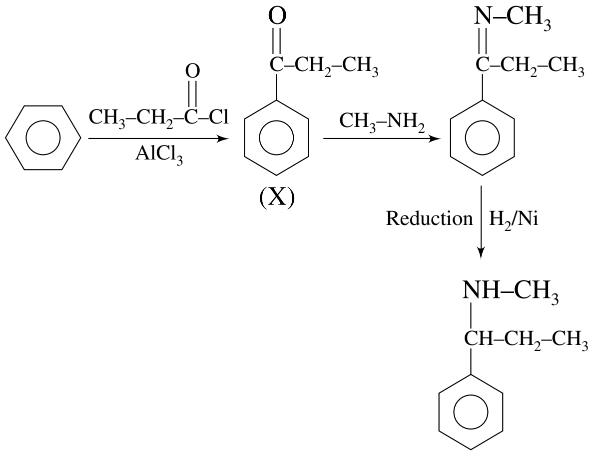


(3) 

(4) 

Sol. **[2]**



13. m-Nitrobenzoic acid can be obtained by

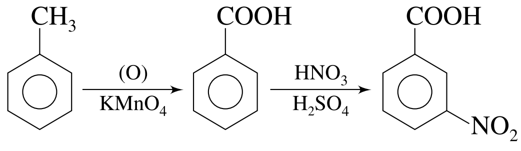
(1) toluene $\xrightarrow[\text{KMnO}_4]{[\text{O}]}$ A $\xrightarrow[\text{H}_2\text{SO}_4]{\text{HNO}_3}$

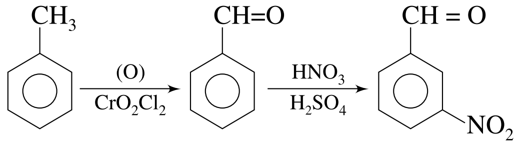
(2) toluene $\xrightarrow[\text{CrO}_2\text{Cl}_2]{[\text{O}]}$ A $\xrightarrow[\text{H}_2\text{SO}_4]{\text{HNO}_3}$

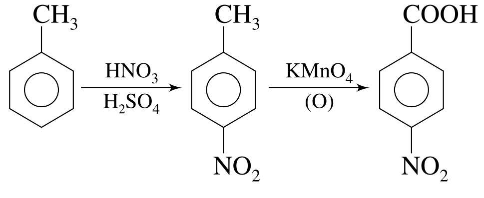
(3) toluene $\xrightarrow[\text{HNO}_3 + \text{H}_2\text{SO}_4]{\text{nitration}}$ A $\xrightarrow[\text{KMnO}_4]{[\text{O}]}$

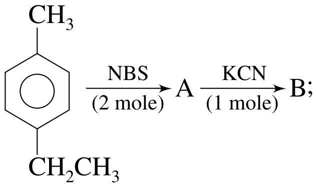
(4) All these methods

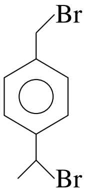
Sol. **[1]**

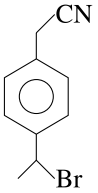
(1) 

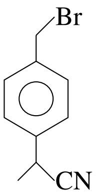
(2) 

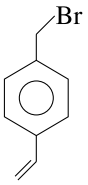
(3) 

14.  B; Product B is

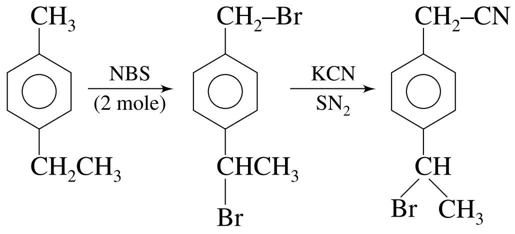
(1) 

(2) 

(3) 

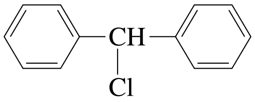
(4) 

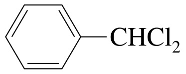
Sol. **[2]**

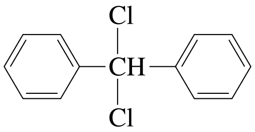


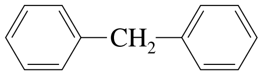
1° halide predominantly gives SN_2 reaction

15. Which of the following structures correspond to the product expected, when excess of C_6H_6 reacts with CH_2Cl_2 in presence of anhydrous $AlCl_3$?

(1) 

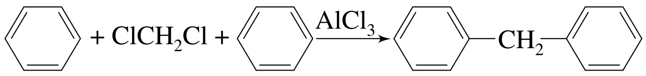
(2) 

(3) 

(4) 

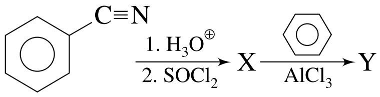
Sol. **[4]**

The reaction takes place as follows:

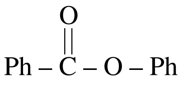


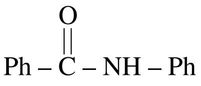
Diphenyhmethane

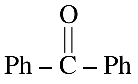
EXERCISE 1

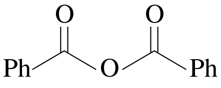
1. 

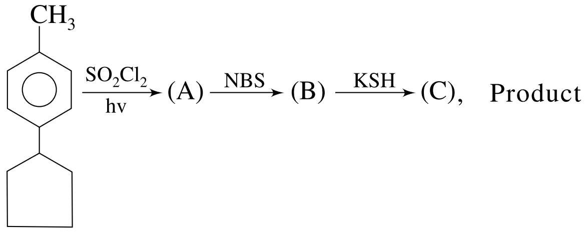
The structure of compound:

(1) 
$\mathrm{Ph-\overset{O}{\overset{\|}{C}}-O-Ph}$

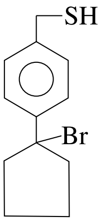
(2) 
$\mathrm{Ph-\overset{O}{\overset{\|}{C}}-NH-Ph}$

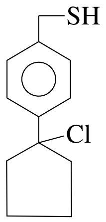
(3) 
$\mathrm{Ph-\overset{O}{\overset{\|}{C}}-Ph}$

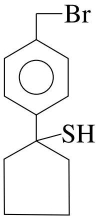
(4) 

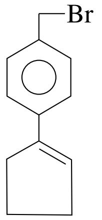
2. 

(B) is:

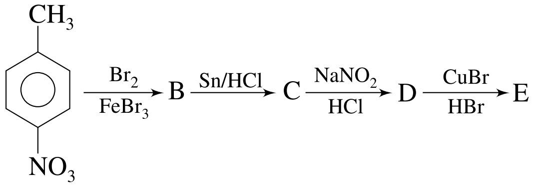
(1) 

(2) 

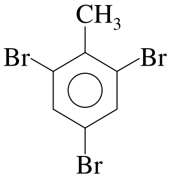
(3) 

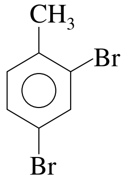
(4) 

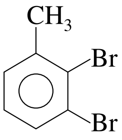
3. In a set of reactions, *p*–nitrotoluene yielded a product E

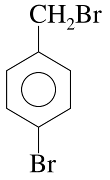


The product E would be:

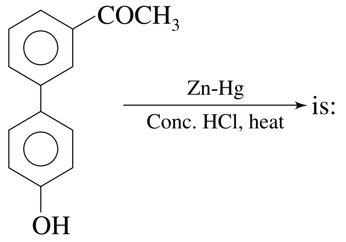
(1) 

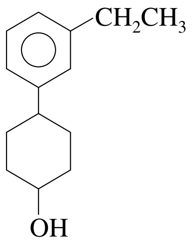
(2) 

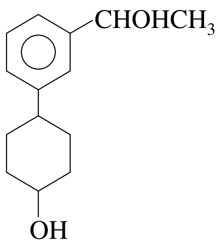
(3) 

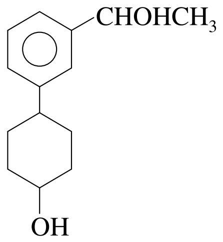
(4) 

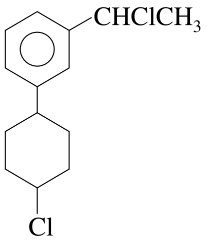
4. The major product formed in the reaction



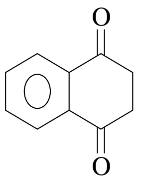
(1) 

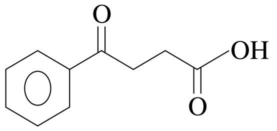
(2) 

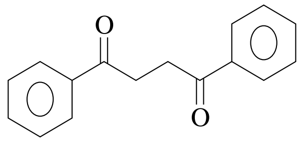
(3) 

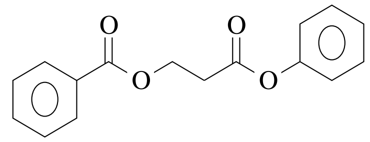
(4) 

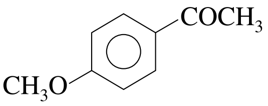
5. Benzene is allowed to react with succinic anhydride in the presence of anhydrous $AlCl_3$ and subsequently treated with dilute HCl. The product formed is:

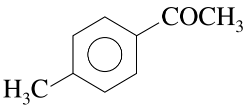
(1) 

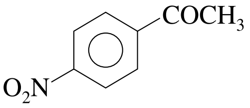
(2) 

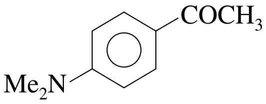
(3) 

(4) 

6. (I) 

(II) 

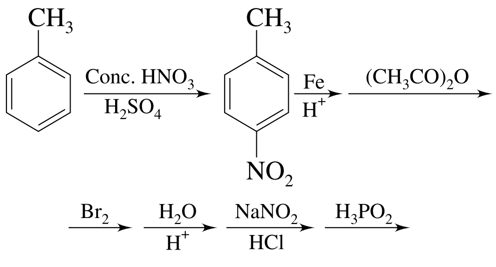
(III) 

(IV) 

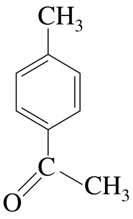
Friedel–Craft acylation reaction can be used to obtain the compounds

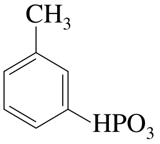
(1) II, III, and IV (2) I, III and IV
(3) I and II (4) II and III

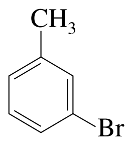
7. Consider the following reaction sequence:

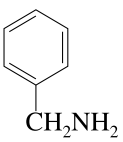


The final product of this reaction sequence is:

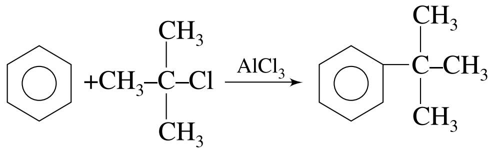
(1) 

(2) 

(3) 

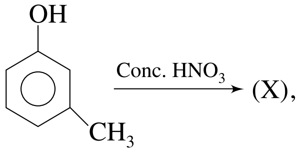
(4) 

8. In the given reaction, the intermediate formed and name of the reaction is:

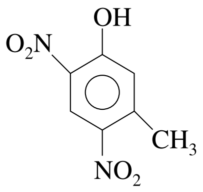


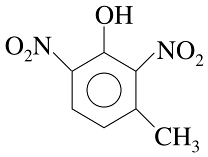
(1) Free Radical, Friedel–Craft alkyaltion
(2) Carbocation, Friedel–Craft alkyaltion
(3) Carbocation, Friedel–Craft acylation
(4) Carbanion, Friedel–Craft alkylation

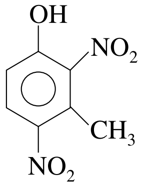
9. In the reaction for dinitration,

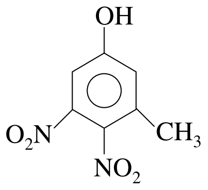


The major dinitrated product (X) is:

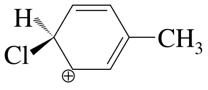
(1) 

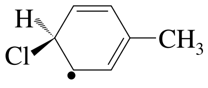
(2) 

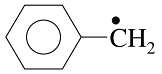
(3) 

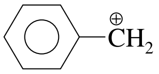
(4) 

10. Which represents an intermediate formed in the reaction of toluene and chlorine at elevated temperature in sunlight?

(1) 

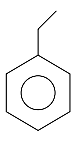
(2) 

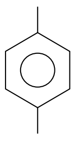
(3) 

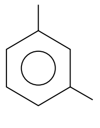
(4) 

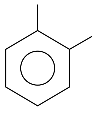
11. Deduce structure of (A) is:

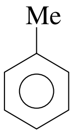
(A) $C_8H_{12} \xrightarrow{KMnO_4}$ (B) $C_8H_6O_4 \xrightarrow[Fe]{Br_2} C_8H_5BrO_4$ (C)
(One-product only)

(1) 

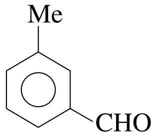
(2) 

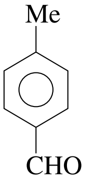
(3) 

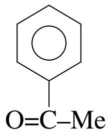
(4) 

12.  + HN = CH – Cl $\xrightarrow{AlCl_3}$ (A) $\xrightarrow{H_3O^+}$ (B),

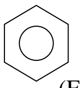
Product (B) of this reaction is:

(1) 

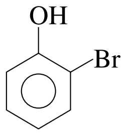
(2) 

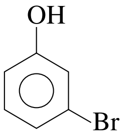
(3) 

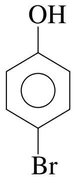
(4) No-reaction

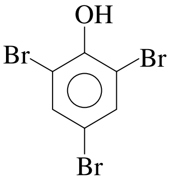
13.  $\xrightarrow[H_2O_2]{Fe^{+2}}$ (A) $\xrightarrow[H_2O]{Br_2}$ (B);
(Fenton's reagent) (≡100%)

Major product (B) of this reaction is:

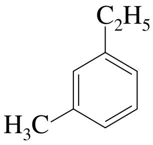
(1) 

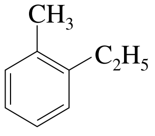
(2) 

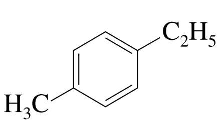
(3) 

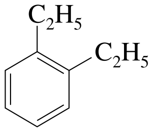
(4) 

14. Which of the following produces isophthalic acid upon oxidation?

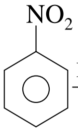
(1) 

(2) 

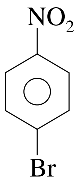
(3) 

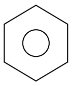
(4) 

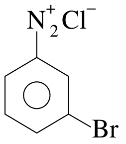
15. Consider the following sequence of reaction:

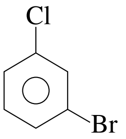
 $\xrightarrow{Br_2, FeBr_3}$ A $\xrightarrow{H_2, Ni}$ B $\xrightarrow[\text{dil. HCl, 0°C}]{NaNO_2}$ C $\xrightarrow{H_3PO_2}$ D $\xrightarrow{\text{Raney Ni}}$ E

The end product (E) is:

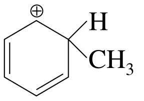
(1) 

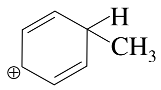
(2) 

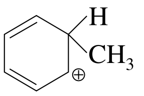
(3) 

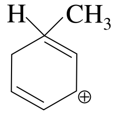
(4) 

16. In the alkylation of benzene, unstable σ-complex can be:

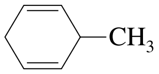
(1) 

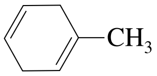
(2) 

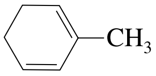
(3) 

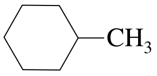
(4) 

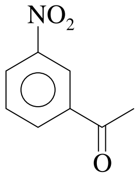
17. The Birch reduction of toluene gives

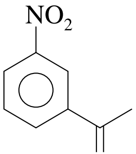
(1) 

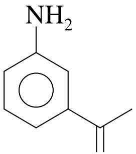
(2) 

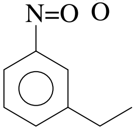
(3) 

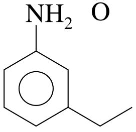
(4) 

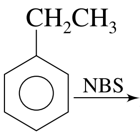
18.  $\xrightarrow{Zn\text{–}Hg/HCl}$ Product:

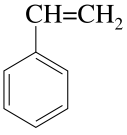
(1) 

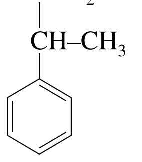
(2) 

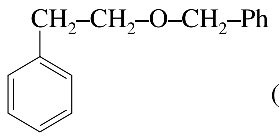
(3) 

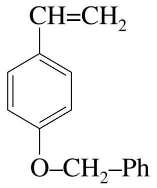
(4) 

19.  $\xrightarrow{NBS}$ X $\xrightarrow{\text{Alc. KOH}}$ Y $\xrightarrow[NaBH_4,\text{–}OH]{Hg(OAc)_2,\ Ph\text{–}CH_2OH}$ Z; 'Z' is:

(1) 

(2) 

(3) 

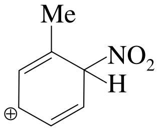
(4) 

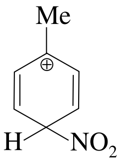
20. When an aromatic compound undergoes ozonolysis followed by treatment with H_2O/Zn, it produces glyoxal, monomethylglyoxal and dimethylglyoxal. It could be

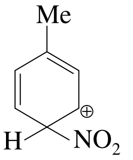
(1) benzene (2) toluene
(3) *o*-xylene (4) *m*-xylene

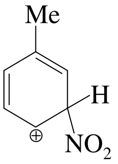
EXERCISE 2

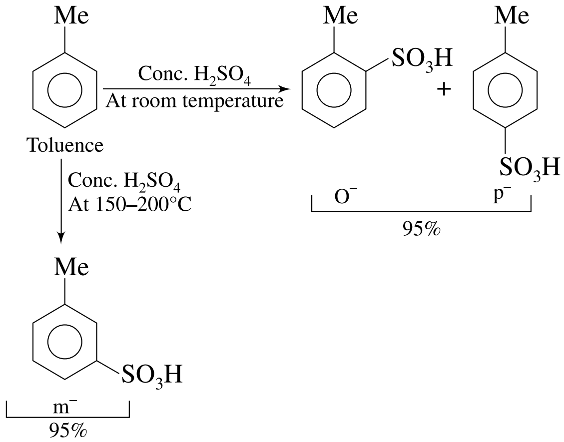
1 Which of the following is the most stable arenium or benzenium ion?

(1) 

(2) 

(3) 

(4) 

2. 

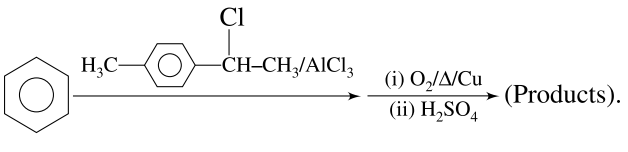
Which of the following statements is wrong about the reaction?

(1) At lower temperature, the reaction is kinetically controlled and *o*/*p* directive effects of the (Me) group operate.

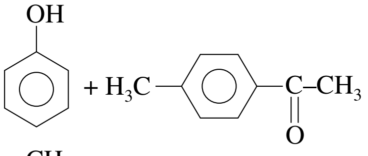
(2) At a higher temperature, the reaction is thermodynamically controlled, and longer reaction times are employed for equilibrium to be reached. The most stable form of m-toluene sulphonic acid is obtained.

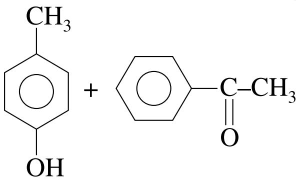
(3) (Me–) group is activated by +I effect, and *o*⁻, *p*⁻ directing.

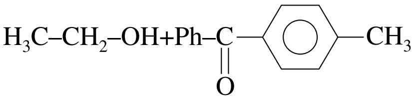
(4) (Me–) group is deactivating by hyperconjugation and is m directing

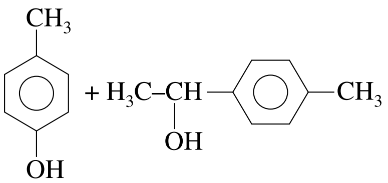
3. 

The final product is:

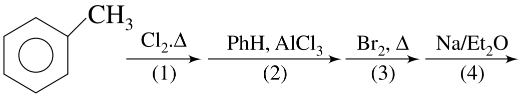
(1) 

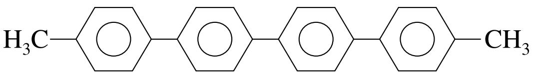
(2) 

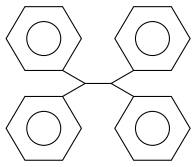
(3) 

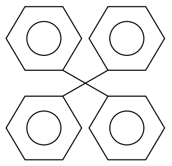
(4) 

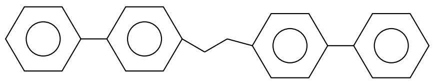
4. The end product of following sequence of reactions is:



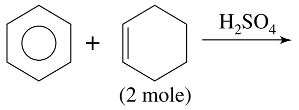
(1) 

(2) 

(3) 

(4) 

5. Major product obtained in given reaction is:



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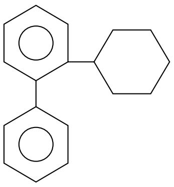

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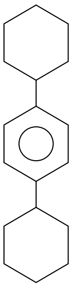

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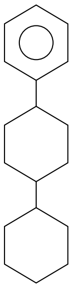
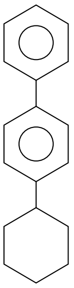


(4)


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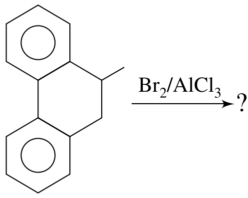
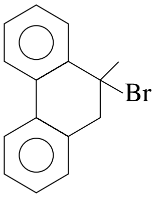


?, The most appropriate product is:

(1)


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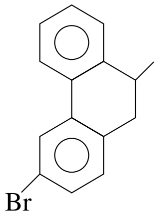
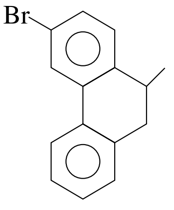


(3)


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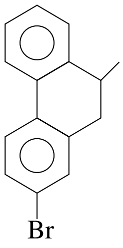
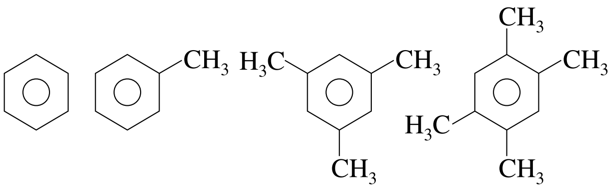


7. Arrange the following in order of decreasing boiling point.

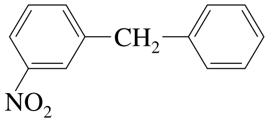


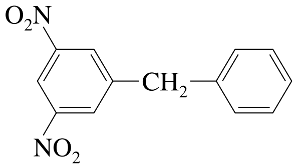
I II III IV

(1) I > II > III > IV (2) IV > III > II > I
(3) I > III > IV > II (4) II > III > I > IV

8. Which of the following statements is correct?

(1) Monobromination of *p*-toluenesulphonic acid followed by treatment with acid and superheated steam gives *m*-bromotoluene.

(2) The mononitration of


gives the product


(3) The reactivity towards ring nitration of 2, 4-dinitrotoluene is greater than that of *m*-dinitrobenzene.

(4) The reactivity towards ring nitration of 2, 4-dinitrophenol is smaller than that of 2, 4-dinitrochlorobenzene.

9. Which of the following statements is not correct?

(1) In electrophilic aromatic substitution reaction, the formation of intermediate arenium cation is the rate-determining step.

(2) The C–H bond in benzene is slightly stronger than the C–D bond in deuterated benzene (C_6D_6).

(3) The overall rate of an electrophilic substitution reaction, except sulphonation in benzene and deuterated benzene, are identical.

(4) The sulphonation reaction involving benzene is a reversible reaction.

10. Which of the following statements is correct?

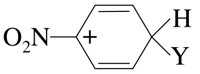
(1) The oxidation of naphthalene with $KMnO_4$ in acid gives phthalic acid.

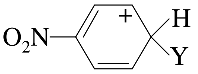
(2) The oxidation of naphthalene with O_2/V_2O_5 gives 1, 4-naphthaquinone.

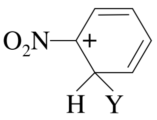
(3) Treatment of *p*-chlorotoluene with NaOH (aq.) at 340°C exclusively gives *p*-hydroxyoluene.

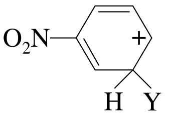
(4) Chlorine in *p*-chlorotoluene is replaced by OH when taken in NaOH (aq.) at 340°C. No such replacement occurs for 2,6-dimethylchlorobenzene.

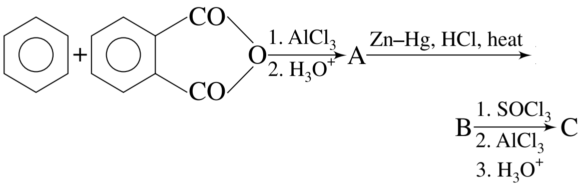
11. Which of the following carbocation is expected to be most stable?

(1) 

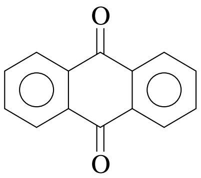
(2) 

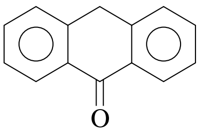
(3) 

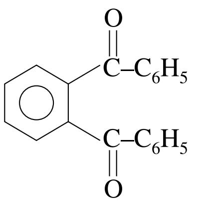
(4) 

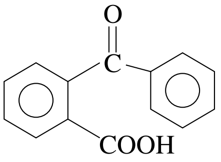
12. 

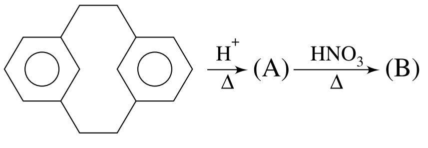
The end product (C) is:

(1) 

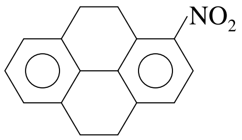
(2) 

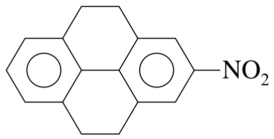
(3) 

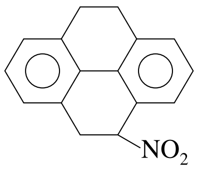
(4) 

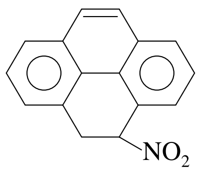
13. 

Product (B) in the above reactions is:

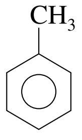
(1) 

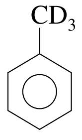
(2) 

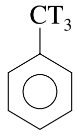
(3) 

(4) 

14. Arrange the following in decreasing order of reactivity towards EAS (electrophilic aromatic substitution)


(a)


(b)

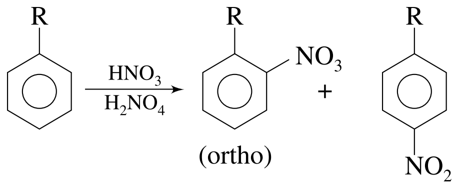

(c)

(1) a > b > c

(2) c > b > a

(3) a > c > b

(4) c > a > b

15. 

In the above reaction *o*/*p* ratio will be highest when:

(1) R = $-CH_3$

(2) R = $-CH_2-CH_3$

(3) R = $-CHMe_2$

(4) R = $-CMe_3$

EXERCISE 3

One and More Than One Option Correct Type Question

1. $\underset{\text{(n-hexane)}}{C_6H_{14}} \xrightarrow{Al_2O_3/\Delta} (A) \xrightarrow{(CO + HCl)/AlCl_3} (B)$

Select the correct statement among following:

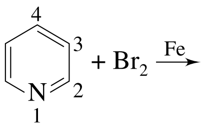
(1) Compound 'B' form silver mirror on reaction with $[Ag(NH_3)_2]OH$

(2) Compound 'B' can also be obtained by the reaction of toluene with chromyl chloride

(3) Compound 'A' can also be synthesised by reaction of benzene diazonium chloride with H_3PO_2

(4) Compound 'B' gives grey colour with aq. $HgCl_2$ solution

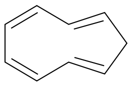
2. Consider the following reaction,



The correct statement(s) is/are

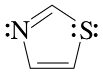
(1) Major bromination occur at C–2
(2) Major bromination occur at C–3
(3) Bromination at C–3 and C–4 are equally probable
(4) Bromination occur at a rate slower than that at benzene

3. What makes the following compound aromatic?



(1) Add one electron to π-bond to give $C_9H_{10}^{-}$
(2) Add two electrons to π-bond to give $C_9H_{10}^{2-}$
(3) Remove an ion, H^+, from sp^3 carbon
(4) Remove an ion, H^+ from sp^2 carbon

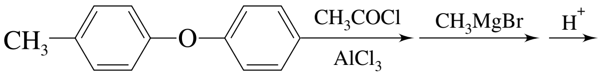
4. What is/are regarding sulphathiazole?

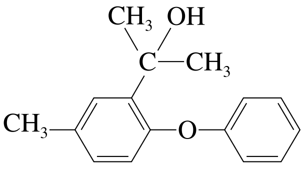


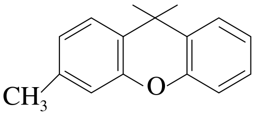
Sulphathiazole

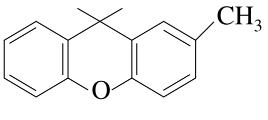
(1) It is an aromatic
(2) It has six delocalised pi-electrons
(3) Extent of delocalisation is equivalent to benzene
(4) It absorb Br_2 when reacted with Br_2-CCl_4

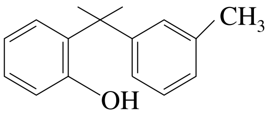
5. Predict major product of the reaction below.



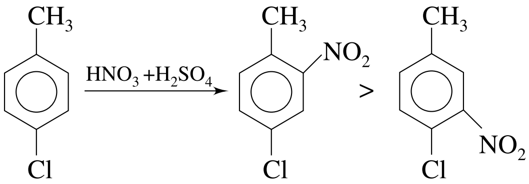
(1)


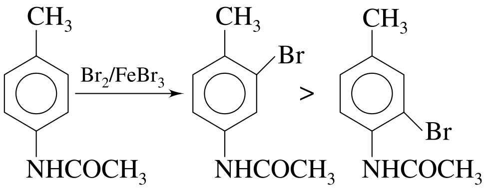
(2)


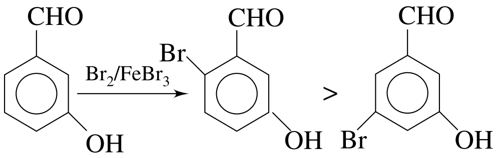
(3)


(4)


6. Select the reaction in which the correct orientations have been mentioned in the major products.

(1)


(2)


(3)


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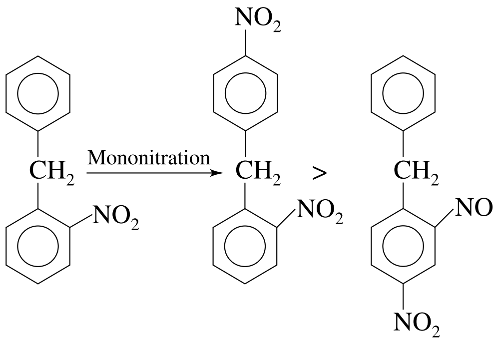
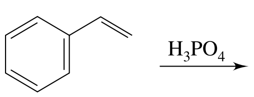
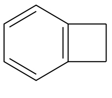
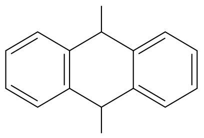
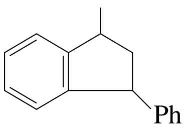


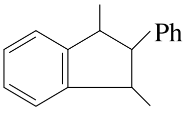
7. What is/are the principal products of the following reaction?



(1)


(2)


(3)


(4)


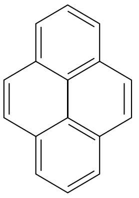
Assertion and Reason Type Question

(1) If both (A) and (R) are correct and (R) is the correct explanation for (A)
(2) If both (A) and (R) are correct and (R) is not the correct explanation
(3) If (A) is correct and (R) is incorrect
(4) If (A) is incorrect and (R) is correct

8. **Assertion:** Sulphonation of benzene is reversible in nature.

Reason: Deuterated benzene reacts slower than benzene in sulphonation with hot conc. H_2SO_4.

9. **Assertion:** Pyrene, although aromatic, decolourise brown colour of bromine water.



Pyrene

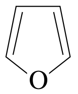
Reason: It has one pi-bond extra which is not the part of aromatic system.

10. **Assertion:** Both toluene and iso-propyl benzene give the same product on oxidation with $KMnO_4$.

Reason: $KMnO_4$ oxidises side aliphatic chain of arenes to –COOH group.

11. **Assertion:** Furan is an aromatic system, has resonance energy comparable to that of benzene.

Reason: Furan decolourises the brown colour of bromine water solution.

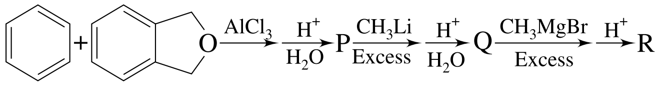


(Furan)

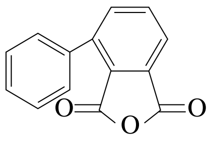
Comprehension Type Question

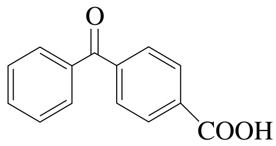
Comprehension (Q. 12-14)

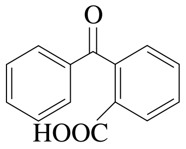
Consider the following road-map reaction,

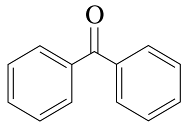


12. The most likely structure of P is

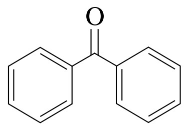
(1) 

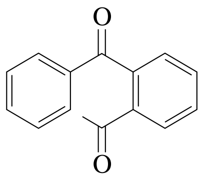
(2) 

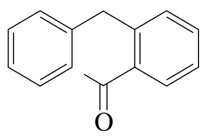
(3) 

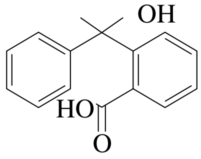
(4) 

13. What is Q?

(1) 

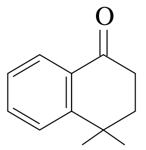
(2) 

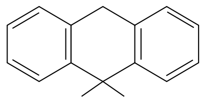
(3) 

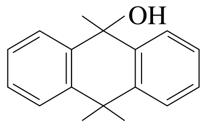
(4) 

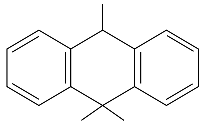
Sol. **[2]**

14. What is R?

(1) 

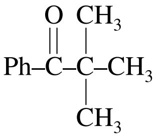
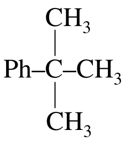
(2) 

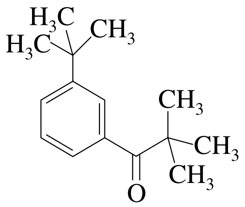
(3) 

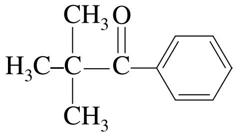
(4) 

Column Matching Type Question

15. Consider the compounds on left column and match with reactions form right column by

Column-I	*Column-II*
(A)  $\mathrm{Ph{-}\overset{\overset{\displaystyle O}{\Vert}}{C}{-}\underset{\underset{\displaystyle CH_3}{\vert}}{\overset{\overset{\displaystyle CH_3}{\vert}}{C}}{-}CH_3}$	(P) $C_6H_6 + (CH_3)_3CCl \xrightarrow{AlCl_3}$
(B)  $\mathrm{Ph{-}\underset{\underset{\displaystyle CH_3}{\vert}}{\overset{\overset{\displaystyle CH_3}{\vert}}{C}}{-}CH_3}$	(Q) $C_6H_6 + (CH_3)_2\,C{=}CH_2 \xrightarrow{H_3PO_4}$

(C) 

(D) 

(R) $C_6H_6 + (CH_3)_3\ CCOCl \xrightarrow{AlCl_3}$

(S) $CH_6H_6 + (CH_3)_3\ COH \xrightarrow{HF}$

(T) $CH_6H_6 + \{(CH_3)_3CCO\}_2O \xrightarrow{AlCl_3}$

Code

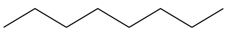
	A	B	C	D
(1)	P, Q	Q	R, T	R, S
(2)	S	R, S	Q	P, Q
(3)	S	R	P, T	Q
(4)	R, T	P, Q, R, S, T	R, T	R, T

16. Match the reactions from Column-I with expected product(s) from Column-I

Column-I

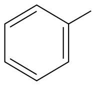
(A) $CH_6H_6 + CH_3Cl \xrightarrow{AlCl_3}$

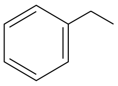
(B) $CH_6H_6 + CH_3CH_2\ Cl \xrightarrow{AlCl_3}$

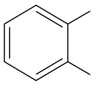
(C)  $\xrightarrow[Cr_2O_2/\Delta]{Al_2O_3}$

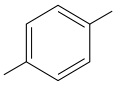
(D) $C_6H_6 + CH_3COCl \xrightarrow{Al_2O_3} \xrightarrow[NaOH/\Delta]{N_2H_4}$

Column-II

(P) 

(Q) 

(R) 

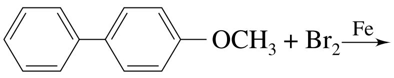
(S) 

Code

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

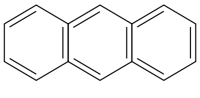
Single Digit Integer Type Question

17. If the following compound is treated with Br_2–Fe, how many mono bromination products are formed in principle?



18. How many isomers of C_8H_{10} when reacts with hot alkaline $KMnO_4$ give only aromatic dicarboxylic acid.

19. How many monobromo derivatives exist for anthracene?



Anthracene

20. How many isomers of C_7H_8O exists that has a phenyl ring?

EXERCISE 4

1. Phenyl magnesium bromide reacts with methanol to give **[JEE Main-2006]**

(1) a mixture of benzene and Mg(OMe)Br

(2) a mixture of toluene and Mg(OH)Br

(3) a mixture of phenol and Mg(Me)Br

(4) a mixture of anisole and Mg(OH)Br

2. The reaction of toluene with Cl_2 in presence of $FeCl_3$ gives predominantly **[JEE Main-2007]**

(1) benzoyl chloride (2) benzyl chloride

(3) *o*-and p-chlorotoluene (4) *m*-chlorotoluene

3. Presence of a nitro group in a benzene ring **[JEE Main-2007]**

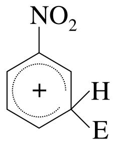
(1) activates the ring towards electrophilic substitution

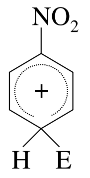
(2) renders the ring basic

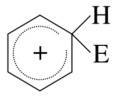
(3) deactivates the ring towards nucleophilic substitution

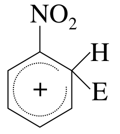
(4) deactivates the ritng towards electrophilic substitution

4. The electrophile E^+ attacks the benzene ring to generate the intermediate σ-complex. Of the following which σ-complex is of lowest energy? **[JEE Main-2008]**

(1)


(2)


(3)


(4)


5. Toluene is nitrated and the resulting product is reduced with Sn and hydrochloric acid. The product so obtained is diazotised and the heated with cuprous bromide. The reaction mixture so formed contains **[JEE Main-2008]**

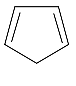
(1) mixture of *o*- and *m*-bromotoluenes

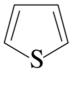
(2) mixture of *o*- and *p*-bromotoluenes

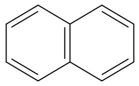
(3) mixture of *o*- and *p*-dibromobenzenes

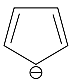
(4) mixture of *o*- and *p*-bromoanilines

6. The nonaromatic compound along the following is **[JEE Main-2011]**

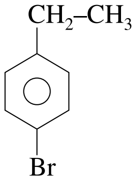
(1)


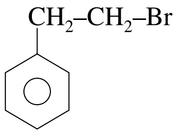
(2)


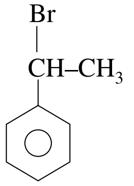
(3)


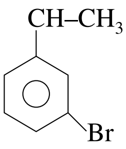
(4)


7. The product of the reaction between ethyl benzene and N-bromo succinamide is: **[JEE Main Online-2012]**

(1)


(2)


(3)


(4)


8. Which of the following would not give 2-phenylbutane as the major product in a Friedel–Crafts alkylation reaction? **[JEE Main Online-2013]**

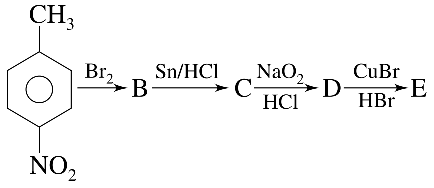
(1) 1-butene + HF

(2) 2-butanol + H_2SO_4

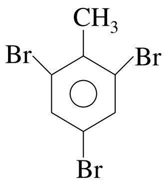
(3) butanoylchloride + $AlCl_3$ then Zn, HCl

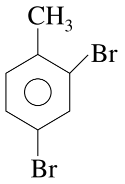
(4) Butyl chloride + $AlCl_3$

9. In a set of reactions p-nitrotoluene yielded a product E **[JEE Main Online-2014]**



The product E would be:

(1)


(2)


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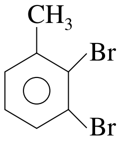

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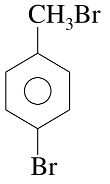


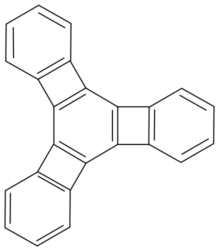
10. In the following sequence of reaction

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

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

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

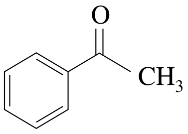
11. The compound below has four phenyl rings, but very less stable due to an opposing factor of stability. Therefore, this compound absorbs bromine in dark. How many bromine molecules, when added to this molecule, would make it stable and prevent further bromine addition? **[IIT-JEE 2005]**

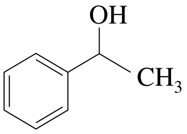


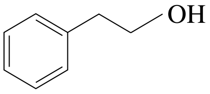
Comprehension (12 and 13)

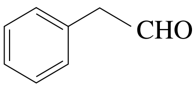
$$\begin{tikzcd}
C_8H_6 \arrow[r, "\text{Pd-BaSO}_4"] \arrow[d, "\begin{array}{l}H_2O\\ HgSO_4{,}H_2SO_4\end{array}"] & C_8H_8 \arrow[r, "\text{i. }B_2H_6", "\text{ii. }B_2H_2\text{, NaOH, }H_2O"'] & X \\
C_8H_8O \arrow[r, "\text{1. EtMgBr}", "\text{ii }H^+\text{, heat}"'] & Y &
\end{tikzcd}$$

12. Compound X is **[JEE Adv.-2015]**

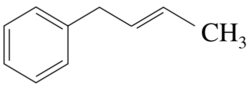
(1) 

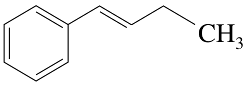
(2) 

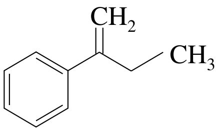
(3) 

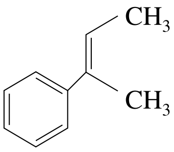
(4) 

13. The major compound Y is **[JEE Adv.-2015]**

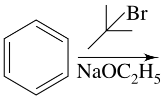
(1) 

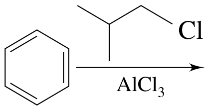
(2) 

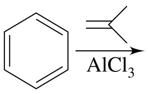
(3) 

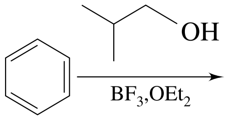
(4) 

14. Among the following reactions(s) which gives (give) tert-butyl benzene as the major product? **[JEE Adv.-2016]**

(1) 

(2) 

(3) 

(4) 

ANSWER KEY

EXERCISE # 1

1. (3) 2. (2) 3. (2) 4. (1) 5. (1)
6. (3) 7. (3) 8. (2) 9. (1) 10. (3)
11. (2) 12. (2) 13. (4) 14. (1) 15. (2)
16. (4) 17. (2) 18. (4) 19. (2) 20. (3)

EXERCISE # 2

1. (2) 2. (4) 3. (2) 4. (2) 5. (2)
6. (2) 7. (2) 8. (3) 9. (2) 10. (4)
11. (4) 12. (2) 13. (2) 14. (1) 15. (1)

EXERCISE # 3

1. (1,2,3,4) 2. (2,4) 3. (3) 4. (1,2,4) 5. (3)
6. (1,3,4) 7. (2,3) 8. (2) 9. (1) 10. (1)
11. (4) 12. (3) 13. (2) 14. (3) 15. (4)
16. (1) 17. (5) 18. (3) 19. (3) 20. (5)

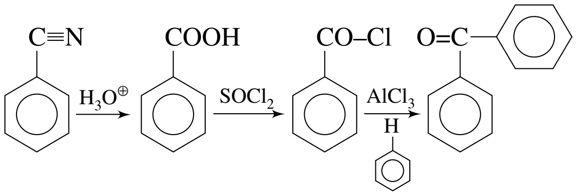
EXERCISE # 4

1. (1) 2. (3) 3. (4) 4. (3) 5. (2)
6. (2) 7. (3) 8. (3) 9. (2) 10. (4)
11. (3) 12. (3) 13. (4) 14. (2,3,4)

HINT AND SOLUTION

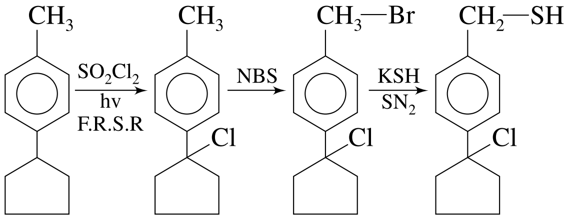
EXERCISE # 1

1. [3]

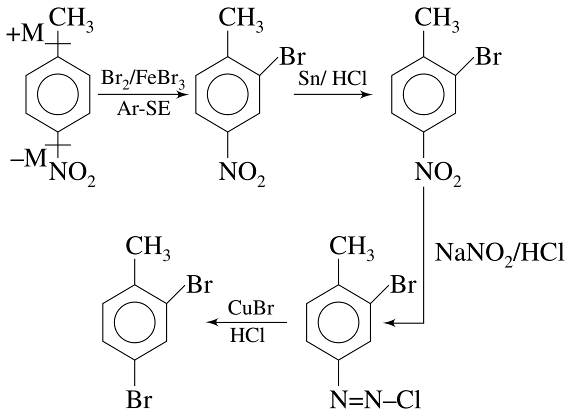


Friedel–Cracft acetylation

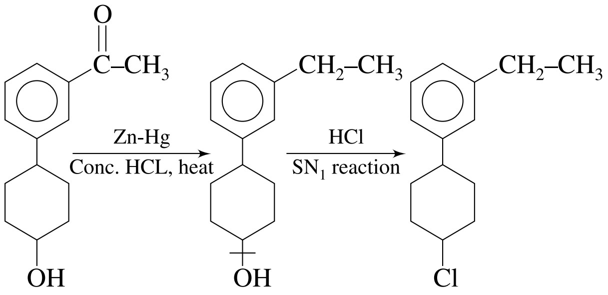
2. [2]



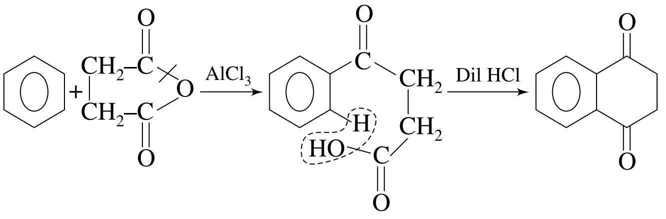
3. [2]



4. [1]



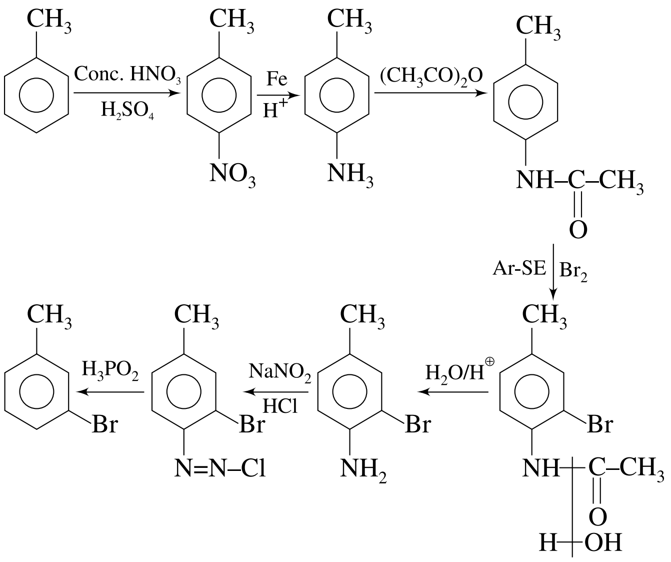
5. [1]



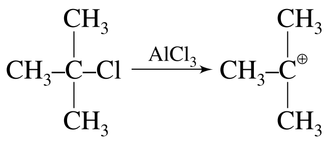
6. [3]

- De-activating group (–M) containing benzene ring do not give Friedel–Craft acylation due to instability of σ complex.
- $-NH_2$, its derivative containing benzene ring also does not give Friedel–Craft acylation because they form salt by acid base reaction with Lewis acid ($AlCl_3$)

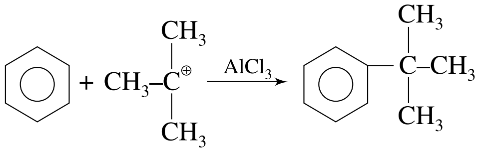
7. [3]



8. [2]



carbocation

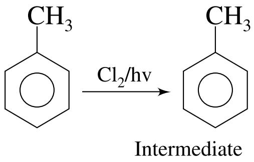


Friedel–Craft alkylation

9. [1]

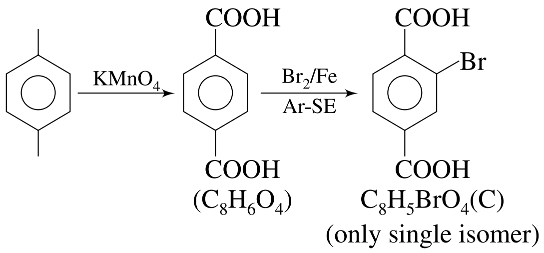
The most activating group will control orientation at least stericly hindred ortho and para position.

10. [3]



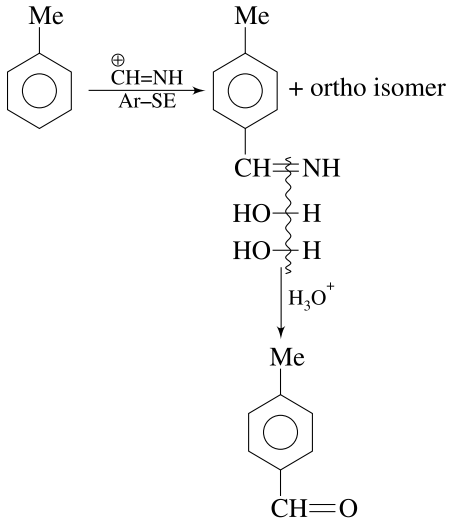
Free radical substitution reaction

11. [2]

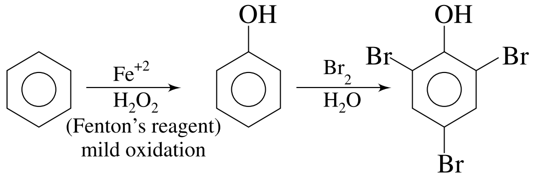


12. [2]

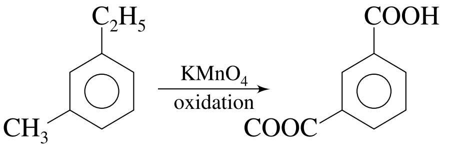
$$\mathrm{NH = CH{-}Cl \xrightarrow[\text{Electrophile}]{AlCl_3} NH = \overset{\oplus}{C}H + Al\overset{\ominus}{Cl_4}}$$



13. [4]

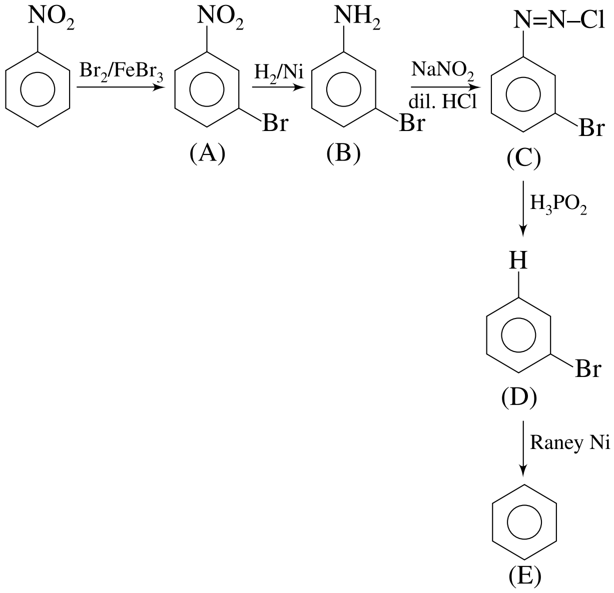


14. [1]



Isophthalic acid

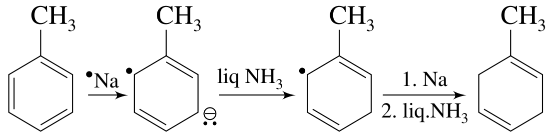
15. [2]



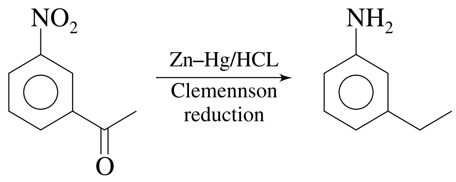
16. [4]

Resonance do not take place at mea position so that +ve charge is not occurred at meta position thus σ complex unstable at meta position.

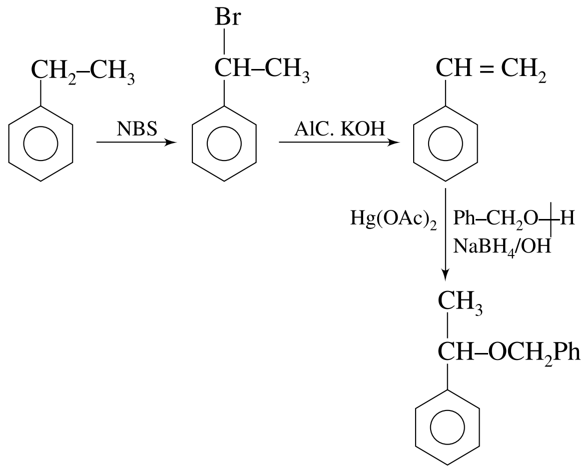
17. [2]



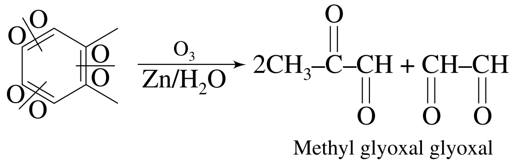
18. [4]

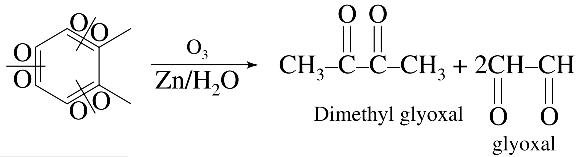


19. [2]



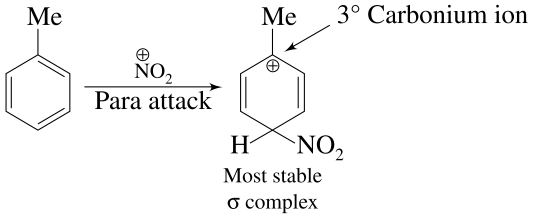
20. [3]





EXERCISE # 2

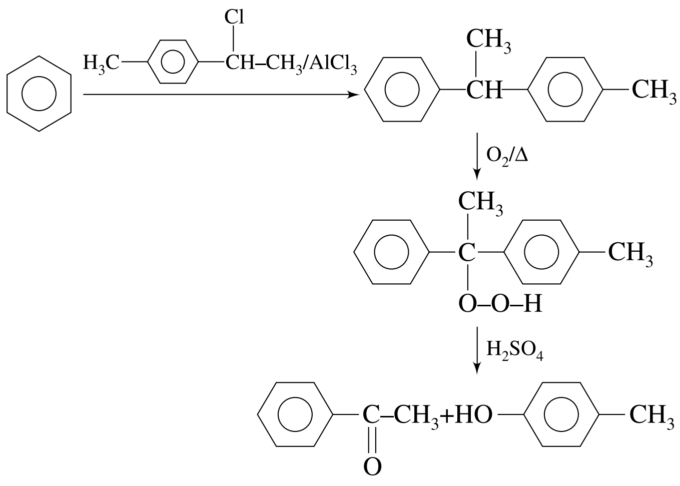
1. [2]



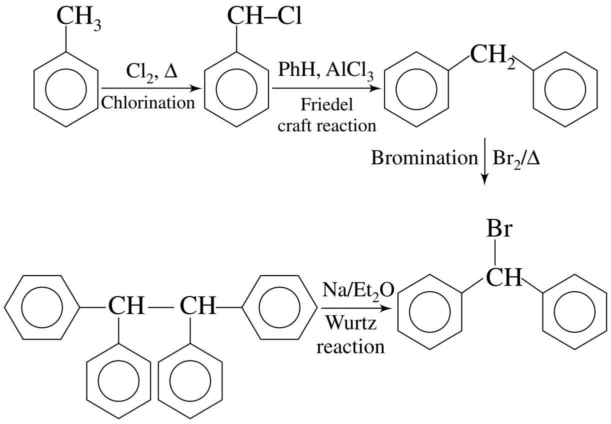
2. [4]

Due to hyperconjugation, Methyl group is activating and o/p director.

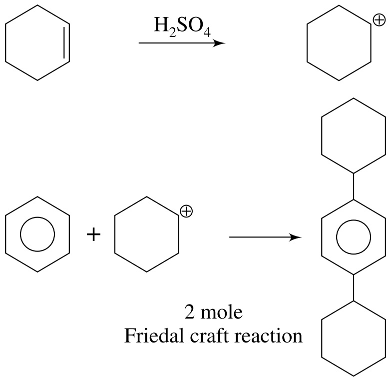
3. [2]



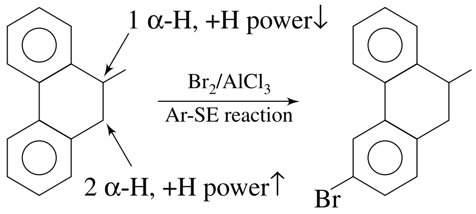
4. [2]



5. [2]



6. [2]

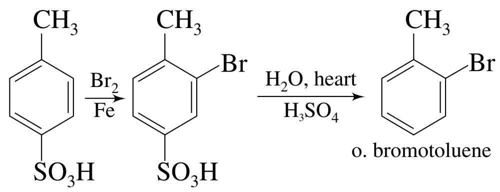


7. [2]

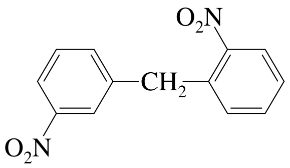
Boiling point α molecular weight

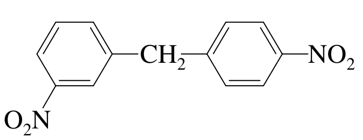
8. [3]

(1) The product is o-bromotoluene



(2) Substitution is faster in the ring that is not deactivated by $-NO_2$. Thus, the compounds obtained will be





(3) In 2,4-dinitrotoluene, there are two deactivating (NO_2) groups and one activating (CH_3) group while in m-dinitrobenzene, there are only two deactivating groups.

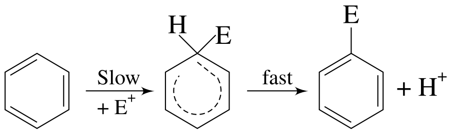
(4) 2,4-dinitrophenol contains a strongly activating group (–OH) while 2, 4 dinitrochlorobenzene contains weak deactivating group (–CL)

9. [2]

(1) The formation of intermediate arenium cation is slow while the elimination of H^+ from this cation is fast. The former involves the removal of aromaticity while the latter restores aromaticity

(2) The C–D bonds are stronger than C–H bonds. In fact, the bond with the heavier isotope is slightly stronger than that with the lighter isotope

(3) In electrophilic substitution reaction, the rate-determining step is the formation of arenium cation



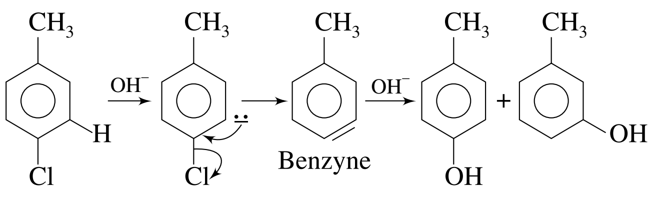
In this step, E^+ bonds to the aromatic ring without cleavage of a C–H bond. The latter is broken in the second step, which is fast as it restores the stable aromatic system. Since C–H or C–D bond is not broken in the rate-determining step, the overall rates of reaction are identical.

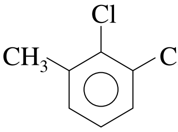
10. [4]

(1) The product is 1,4-naphthaquinone.

(2) The product is phthalic acid.

(3) Two products namely *p*-hydroxytoluene and *m*-hydroxytoluene are obtained. This reaction proceeds through the formation of benzyne and is known as elimination-addition reaction

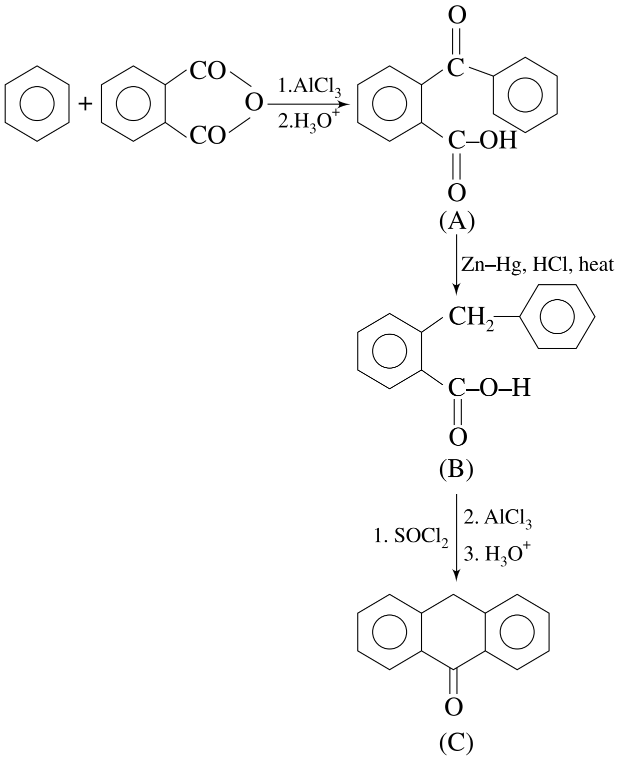


(4) , there is no *Roth*-H, thus benzyne cannot form.

11. [4]

$-NO_2$ group is benzene deactivator, it is meta directing.

12. [2]



13. [2]

Intramolecular electrophilic aromatic substitution then nitration with respect to phenyl ring.

14. [1]

$-CH_3 > -CD_3 > -CT_3$

Order of hyperconjugation on the basis of bond energy

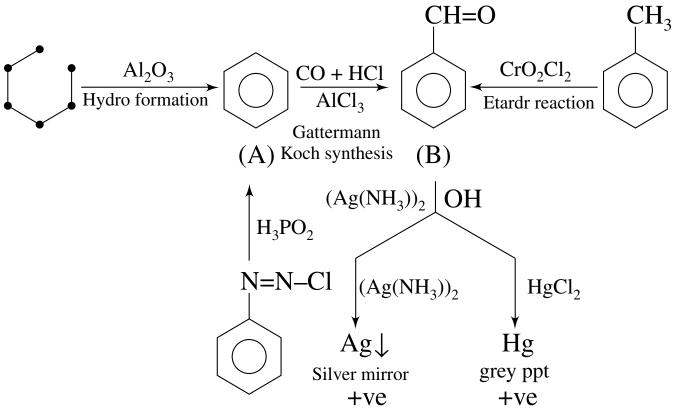
15. [1]

The steric demand of $H^{\ominus}$ is, however, extremely small, and when attack on C_6H_5Y is by any other electrophile, $E^{\oplus}$, which will necessarily be larger, there will be increasing interaction between E and Y in the transition state for attack at the position o- to Y (57 b, R = E) as attacking electrophile and substituent increase in size; there can be no such interaction in the transition state for p- attack (57 a, R = E). This will be reflected in an increasing ΔG^+ for o-attack, a consequently slower reaction, and the relative proportion of o-product will thus fall as the size of E and / or Y increase. This is illustrated by the falling f_{o-}/f_{p-} ration which are observed for the nitration of alkylbenzenes (Y – $CH_3 \rightarrow CMe_3$) under comparable condition;

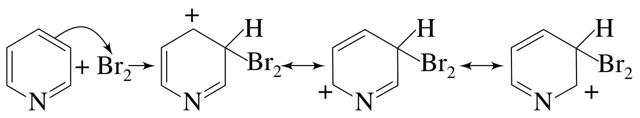
	Y	%o^-	%p^-
Increase in size of Y ↓	CH_3	58	37
	CH_2Me	45	49
	$CHMe_2$	30	62
	CMe_3	16	73

EXERCISE # 3

1. **[1, 2, 3, 4]**

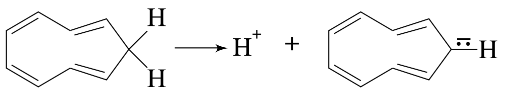


2. **[2,4]**



No such stabilisation of intermediate carbocation occurs by attack of Br^+ at C–2 or C–4 carbon. Electron withdrawing–I effect of nitrogen destabilises carbocation to some extent. Hence, pyridine is less reactive than benzene towards electrophilic substitution reaction.

3. **[3]**

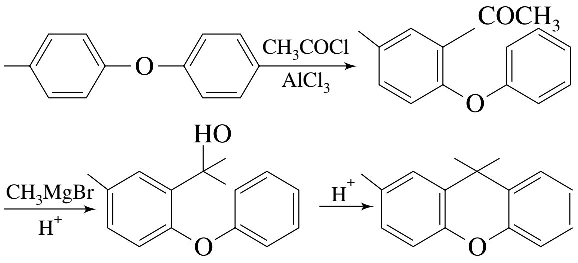


10 π -electrons
(aromatic)

4. **[1, 2, 4]**

It is aromatic, has six delocalised pi electrons but not as aromatic as benzene because 3p orbitals of S do not overlaps effectively with 2p orbitals of carbon. Hence, it does show reactions of alkenes to some extent.

5. **[3]**



6. **[1, 3, 4]**

When two group attach with benzene ring, then major product at the *o*/*p*-position of strong activating group

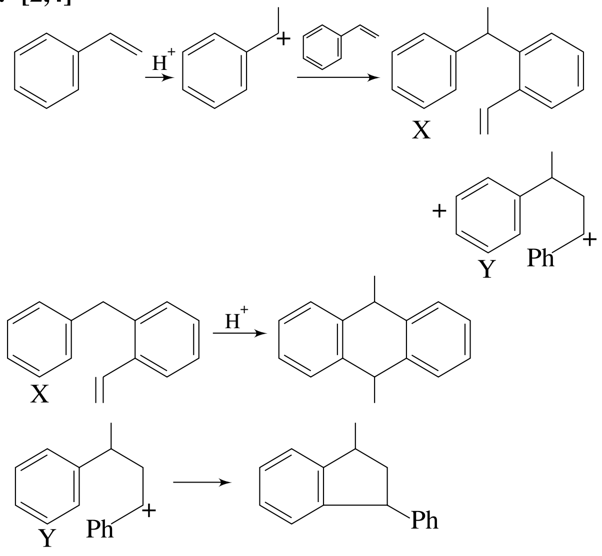
(1) + H ($-CH_3$) > +M (– Cl)

(2) + H ($-CH_3$) < + M ($-NH-CO-CH_3$)

(3) + M (–OH) > – M (–CH=O)

(4) Ring which is not de-active by $-NO_2$ group, will gives major product.

7. **[2,4]**

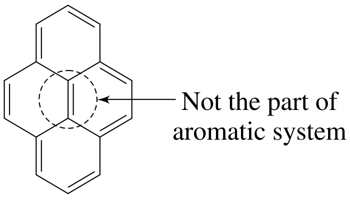


8. **[2]**

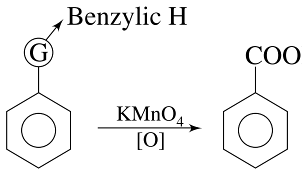
Both are correct, however, the correct explanation is small difference in the potential energies of two transition states in sulphonation reaction.

9. **[1]**

One of the resonance structure shown below indicates clearly that the central pi-bond is not involved in aromaticity, show the general reactions of a typical alkene.



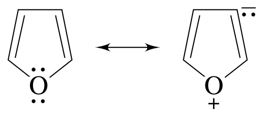
10. [1]



G → must have benzylic H

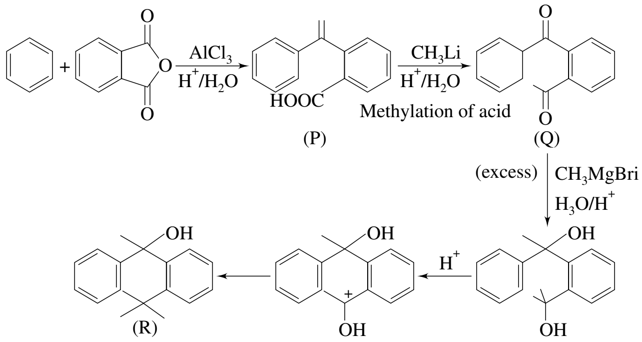
Both toluene and iso propyl have benzylic H

11. [4]



Due to abve resonance, furan acquire 6p electrons and show aromaticity but to a very small extent due to development of positive charge on electronegative oxygen atom. Hence, resonance stabilization of furan is much less than benzene. Due to this reason, furan show, to some extent, reactions of alkene.

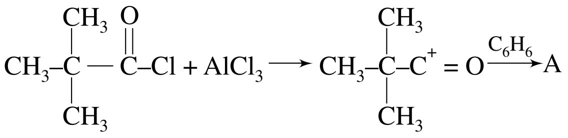
12. [3]



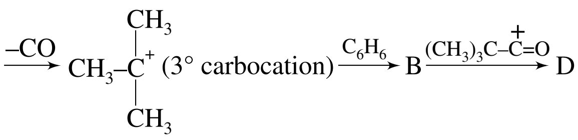
13. [2]

14. [3]

15. [4]

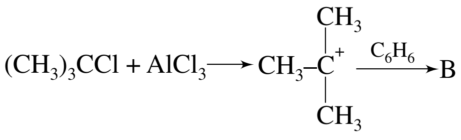


$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-Cl+AlCl_3\longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-C^+=O\xrightarrow{C_6H_6}A$$



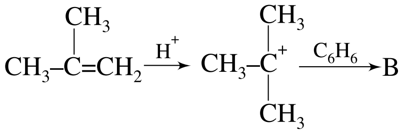
$$\xrightarrow{-CO} CH_3-\underset{CH_3}{\overset{CH_3}{C^+}}\text{ (3° carbocation)}\xrightarrow{C_6H_6}B\xrightarrow{(CH_3)_3C-\overset{+}{C}=O}D$$

(i)



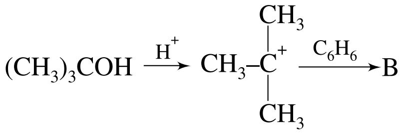
$$(CH_3)_3CCl+AlCl_3\longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C^+}}\xrightarrow{C_6H_6}B$$

(ii)



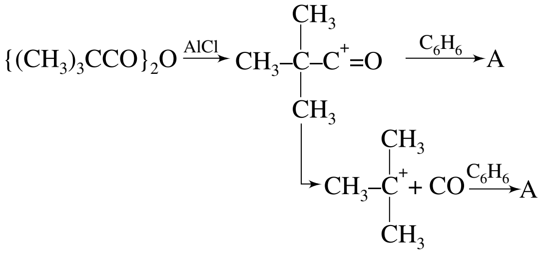
$$CH_3-\overset{CH_3}{C}=CH_2\xrightarrow{H^+}CH_3-\underset{CH_3}{\overset{CH_3}{C^+}}\xrightarrow{C_6H_6}B$$

(iii)



$$(CH_3)_3COH\xrightarrow{H^+}CH_3-\underset{CH_3}{\overset{CH_3}{C^+}}\xrightarrow{C_6H_6}B$$

(iv)



$$\{(CH_3)_3CCO\}_2O\xrightarrow{AlCl}CH_3-\underset{CH_3}{\overset{CH_3}{C}}-C^+=O\xrightarrow{C_6H_6}A$$

$$\longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C^+}}+CO\xrightarrow{C_6H_6}A$$

16. [1]

(i) Friedel–Craft methylation and dimethylation gives P, R and S,

(ii) Friedel–Craft alkylation, i.e. ethyl group is added to benzene, thus, Q is the product

(iii) Aromatisation of octane gives all P, R and S.

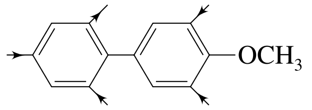
(iv) Friedel–Craft acylation produces benzophenone which on reduction produces 1-phenylethane.

(A) → P, R, S; (B) → Q; (C) → Q, R,S ;

(D) → (Q)

17. [5]

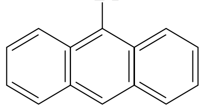
$-OCH_3$ is *ortho* and *para* directing



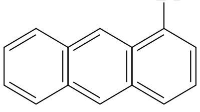
18. [3]

Ortho, meta and para xylene gives dicarboxylic acid on treatment with $KMnO_4$.

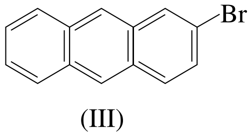
19. [3]



(I)

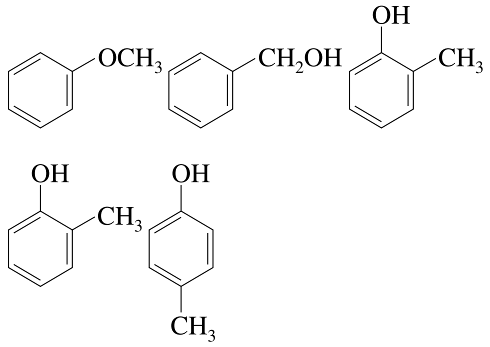


(II)



(III)

20. [5]



EXERCISE # 4

1. [1]

$Ph–MgBr \xrightarrow{Me–OH} Ph–H + Mg(OMe)Br$

2. [3]

Toluene undergoes electrophilic substitution reaction in ortho and para positions, since the methyl group attached to benzene, being ring activator, is ortho and para directing group.

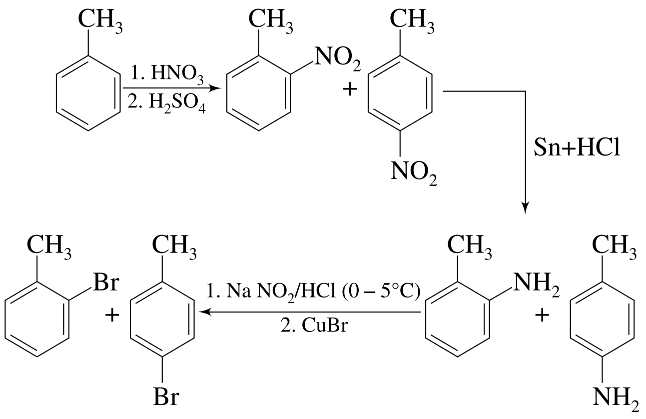
3. [4]

Nitro group is an electron-withdrawing group, thereby it deactivates the ring towards electrophilic substitution of benzene ring.

4. [3]

The nitro group is electron withdrawal group. This decreases the tendency of electrophilic substitution reaction. The intermediate σ-complex of nitrobenzene has larger energy as compared to that of benzene.

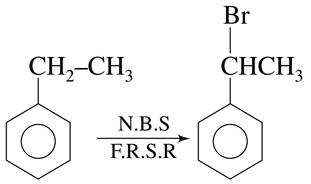
5. [2]



6. [1]

An aromatic compound has (4n + 2) π-electrons, where *n* is an integer. Cyclopentadiene has only 4π electrons and thus will be nonaromatic.

7. [3]

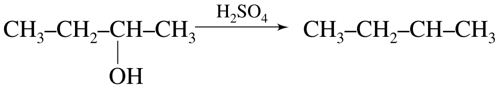


Substitution takes place at benzylic Carbon.

8. [3]

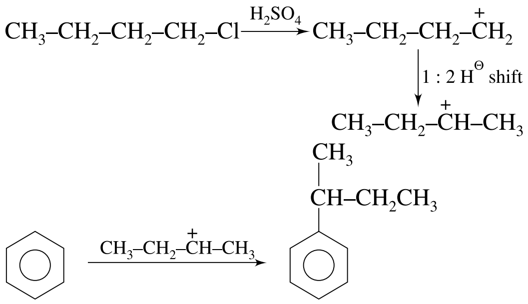
In (1), (2), (4) electrophile is alkyl carbocation which are stabilised by re-arrangement, so that 2-phenylbutane would not obtain as the major product.

(1) $CH_3–CH_2–CH=CH_2 \xrightarrow{HF} CH_3–CH_2–CH–CH_3$

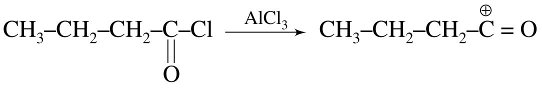
(2) 

$CH_3–CH_2–\underset{OH}{CH}–CH_3 \xrightarrow{H_2SO_4} CH_3–CH_2–CH–CH_3$

In (3) electrophile is acyl carbocation, which cannot be re-arranged.

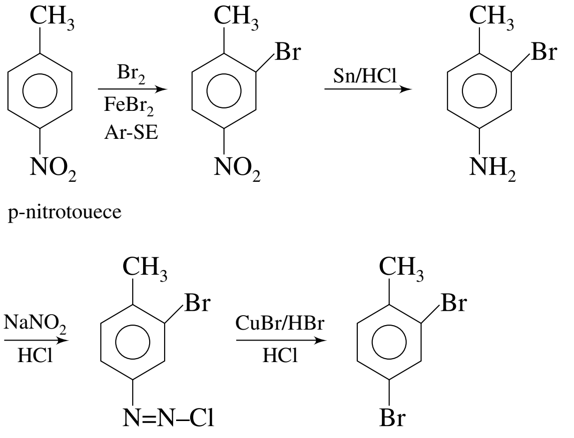
(4) 

2-phenyl butane

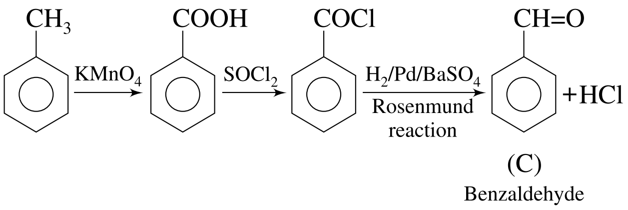
(3) 

$CH_3–CH_2–CH_2–\underset{\underset{O}{\|}}{C}–Cl \xrightarrow{AlCl_3} CH_3–CH_2–CH_2–\overset{\oplus}{C} = O$

9. [2]



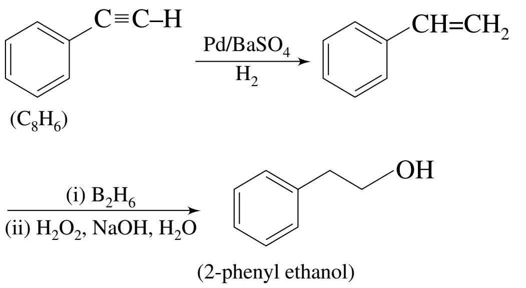
10. [4]



11. [3]

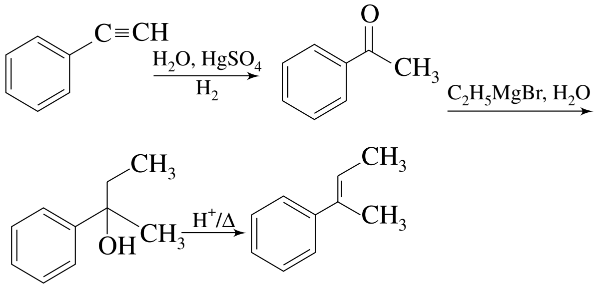
It has three anti-aromatic (cyclobutadiene) rings which makes it unstable, if 3 molecules of Br_2 are added to central benzene, anti-aromaticity would be removed completely.

12. [3]



Hydroboration oxidation brings about anti-Markownikoff's hydration of alkene.

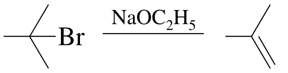
13. [4]



De-hydration takes places by syatzeff rule

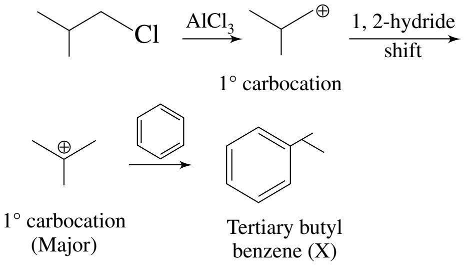
14. [2,3,4]

(1)

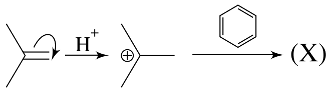


C_2HO– (a strong nucleophile causes) El reaction to form isobutene as the major product.

(2)



(3)



(4)