

Organic Reaction Mechanisms-II

- B-8. (D) B-9. (A)
 C-3. (B) C-4. (B)
 C-8. (B) C-9. (D)

- B-10. (C)
 C-5. (A)
 C-10. (A)

- C-1. (B)
 C-6. (D)

- C-2. (B)
 C-7. (C)

PART – III

1. (D) 2. (A - q, r) ; (B - p, r) ; (C - p, r) ; (D - q, s)

EXERCISE - 2**PART – I**

- | | | | | |
|----------------|----------------|--------|--------|---------|
| 1. (A) | 2. (A) | 3. (C) | 4. (C) | 5. (A) |
| 6. (D) | 7. (D) | 8. (B) | 9. (A) | 10. (C) |
| 11. (B) | 12. (A) | | | |

PART – II

- | | | | | |
|------|------|-------|------|------|
| 1. 3 | 2. 4 | 3. 23 | 4. 2 | 5. 4 |
| 6. 4 | 7. 4 | 8. 21 | | |

PART – III

- | | | | | |
|-----------|-----------|-----------|---------|----------|
| 1. (ABC) | 2. (ABC) | 3. (AC) | 4. (BD) | 5. (BCD) |
| 6. (ABCD) | 7. (ABCD) | 8. (ABCD) | 9. (AD) | 10. (AD) |

PART – IV

- | | | | | |
|--------|--------|--------|--------|--------|
| 1. (B) | 2. (B) | 3. (D) | 4. (B) | 5. (C) |
|--------|--------|--------|--------|--------|

EXERCISE – 3**PART – I**

- | | | | | |
|-------------------|------------------|---------|---------|---------|
| 1. (C) | 2. (B) | 3. (B) | 4. (C) | 5. (B) |
| 6. (A) | 7. (B) | 8. (A) | 9. (B) | 10. (B) |
| 11. (A) | 12. (A) | 13. (B) | 14. (C) | 15. (C) |
| 16. (B) | 17. 8 | 18. (A) | 19. (D) | 20. 5 |
| 21.* (BCD) | 22.* (BD) | | | |

PART – II

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

Answers**EXERCISE - 1****PART - I**

A-1. Benzene has resonance stabilization due to delocalisation of π -electrons and during electrophilic addition reactions, it loses its aromaticity. In electrophilic substitution reaction aromaticity is retained.

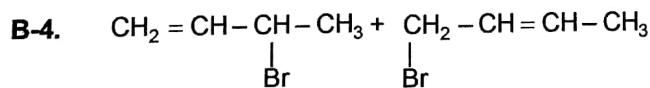
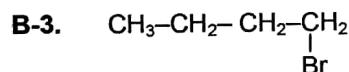
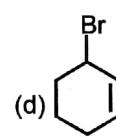
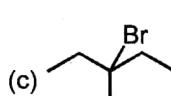
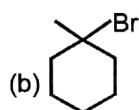
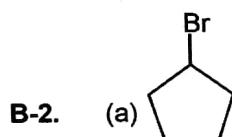
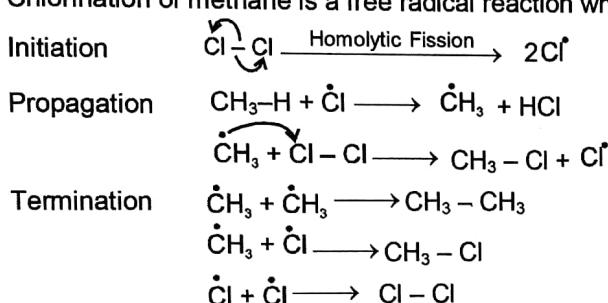
A-2. c, e, g, h

A-3. a, b, c, f, h

A-4. (a) (I) > (II) > (III) (b) (II) > (III) > (I) (c) (II) > (I) > (III) (d) (III) > (I) > (II)

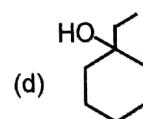
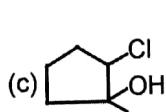
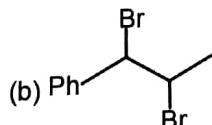
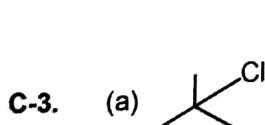
A-5. In vinyl chloride and chloro benzene lone pair on Cl atom takes part in conjugation. So, partial double bond character between C–Cl bond is developed.

B-1. Chlorination of methane is a free radical reaction which occurs by the following mechanism



C-1. IV > III > II > I

C-2. Reactivity is based on stability of intermediate carbocation.
 3° carbocation > 2° carbocation > 1° carbocation (stability order)



C-4. (a) Racemic mixture of 2,3-Dibromobutane

(b) Meso 2,3-Dibromobutane

C-5. Positional isomers

PART - II

A-1. (C)

A-2. (B)

A-3. (A)

A-4. (B)

A-5. (C)

A-6. (D)

A-7. (C)

A-8. (C)

B-1. (A)

B-2. (B)

B-3. (C)

B-4. (C)

B-5. (D)

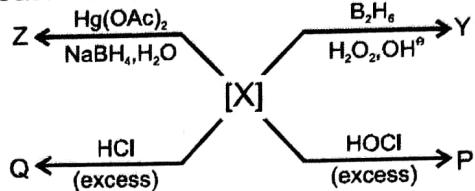
B-6. (B)

B-7. (A)

Organic Reaction Mechanisms-II

Comprehension # 2

A Hydrocarbon X (M.F. C_4H_6) produces an aldehyde Y through Hydroboration-Oxidation and a ketone Z through Oxymercuration-Demercuration. Y and Z are functional isomers. X gives P when treated with excess of HOCl and Q when treated with excess of HCl.

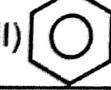
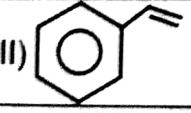
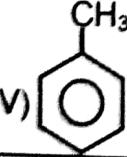


4. The structure of X is :
 (A) $CH_3-C\equiv C-CH_3$ (B) $CH_3-CH_2C\equiv CH$ (C) $CH_2=CH-CH=CH_2$ (D) $CH_2=CH-C\equiv CH$
5. The correct statement is :
 (A) P and Q are positional isomers.
 (B) Q is 1,2-Dichlorobutane.
 (C) P is 1,1-Dichlorobutan-2-one.
 (D) P and Q are identical.

Comprehension # 3

Answer Q.6, Q.7 and Q.8 by appropriately matching the information given in the three columns of the following table.

Observe the three columns in which column-1 represents reactants, column-2 represents reagents while column-3 represents reaction conditions.

Column 1	Column 2	Column 3
(I) $Ph-C\equiv CH$	(i) Hg^{++}/H_3O^+	(P) Electrophilic substitution
(II) 	(ii) $Cl_2/h\nu$	(Q) Electrophilic addition
(III) 	(iii) $CH_3-C(=O)-H/H^+$	(R) Carbocation intermediate
(IV) 	(iv) H^+/H_2O	(S) Radical intermediate

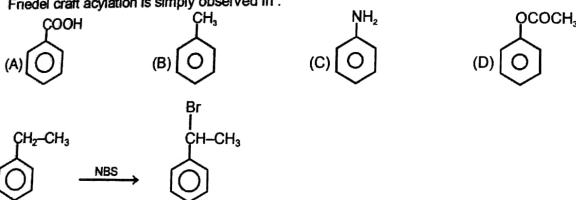
6. Ketone is formed by the reaction
 (A) (I) (i) (Q) (B) (IV) (iii) (R) (C) (III) (iv) (Q) (D) (II) (iii) (P)
7. Which of the following is non correct for substitution reaction.
 (A) (II) (iii) (R) (B) (IV) (ii) (S) (C) (III) (iv) (R) (D) (IV) (iii) (P)
8. Arenium ion is formed in the reaction.
 (A) (I) (iv) (P) (B) (II) (iii) (P) (C) (III) (iv) (R) (D) (IV) (ii) (S)

Exercise-3

Organic Reaction Mechanisms-II

3. a. Select the reactions in which the correct orientations have been mentioned in the major products.
- (A)
- (B)
- (C)
- (D)

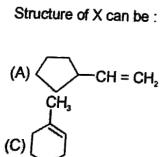
4. a. Friedel-Crafts acylation is simply observed in :



Which of the following statements are correct for above reaction.

- (A) Reaction intermediate is carbocation.
 (B) Product is mixture of two enantiomers.
 (C) Reaction intermediate is stabilized by $+I$, hyperconjugation & resonance.
 (D) Br_2 at high temperature also give same product in the place of NBS.

6. In the given reaction, $C_2H_2 \xrightarrow{(X)} \text{Product}$



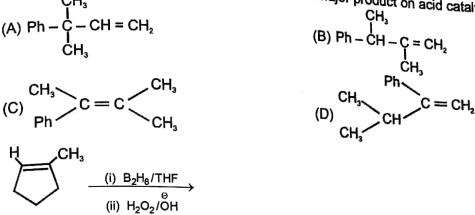
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ADV ORM II - 22

Organic Reaction Mechanisms-II

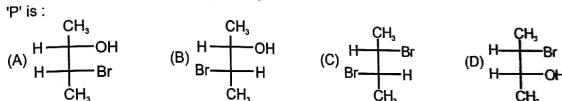
7. a. Which of the following compounds will give same major product on acid catalysed hydration?



True statement about above reaction :

- (A) Reagent involve stereospecific syn addition of H and OH species.
 (B) Product obtained is trans isomer.
 (C) Boron atom acts as electrophile.
 (D) Two stereoisomers are obtained as product.

9. Trans-2-Butene \xrightarrow{HOBr} P (product)



10. a. Identify the incorrect statement(s):

- (A) Alkynes are more reactive than alkenes towards electrophilic addition reaction
 (B) Alkynes are less reactive than alkenes towards electrophilic addition reaction
 (C) Alkynes decolorise Br_2 water
 (D) Addition of HBr to alkynes in presence of peroxide proceeds via Markownikoff's addition

PART - IV : COMPREHENSION

Read the following passage carefully and answer the questions.

Comprehension # 1

Three acyclic alkenes (x, y, z) on catalytic hydrogenation give same alkane. On reaction with HCl , (x, y, z) form same major tertiary halide product. Reductive ozonolysis of mixture of (x, y, z) gives a mixture of two moles of $CH_2=O$ one mole of $CH_3CH=O$ one mole of acetone, one mole of butanone and one mole of 2-methyl propanal. x, y and z do not have any stereoisomers.

1. a. x, y, z are

- (A) chain isomers (B) Position isomers (C) Geometrical isomers (D) Optical isomers

2. a. $(x, y, z) \xrightarrow{H_3O^+}$ addition product. The correct statement is

- (A) All three alkenes will give 3 different major hydration products
 (B) Three alkenes will give same hydration major product
 (C) Two alkenes form same product but one alkene forms different major product.
 (D) Addition of HCl and H_3O^+ both are following different regioselectivity.

3. a. What is true about x, y, z .

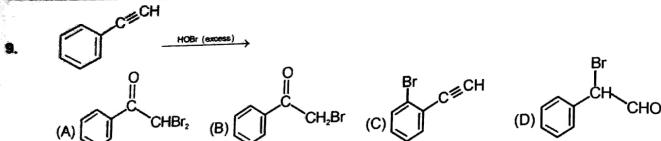
- (A) These have molecular formula C_3H_6
 (B) x, y, z on catalytic hydrogenation give chiral alkanes.
 (C) These are unbranched alkenes.
 (D) These form same carbocation intermediate on reaction with HCl to give the major product.

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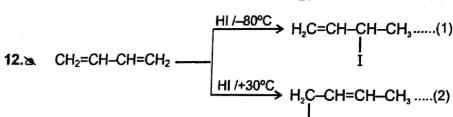
ADV ORM II - 22

Organic Reaction Mechanisms-II



10. The reaction of one equivalent of HBr with $\text{CH}_2=\text{CH}-\text{CH}_2-\text{C}\equiv\text{CH}$ gives :
- (A) $\text{CH}_2=\text{CH}-\text{CH}_2-\text{C}\equiv\text{CBr}$ (B) $\text{CH}_2=\text{CH}-\text{CH}_2-\overset{\text{Br}}{\underset{\text{Br}}{\text{C}}}=\text{CH}_2$
 (C) $\text{CH}_3-\text{CH}(\text{Br})-\text{CH}_2-\text{C}\equiv\text{CH}$ (D) $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}=\text{CHBr}$

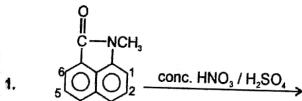
11. The reaction of one equivalent of HBr with $\text{CH}_2=\text{CH}-\text{C}\equiv\text{CH}$ gives :
- (A) $\text{CH}_2=\text{CH}-\text{C}\equiv\text{CBr}$ (B) $\text{CH}_2=\text{CH}-\overset{\text{Br}}{\underset{\text{Br}}{\text{C}}}=\text{CH}_2$ (C) $\text{CH}_3-\text{CH}(\text{Br})-\text{C}\equiv\text{CH}$ (D) $\text{CH}_2=\text{CH}-\text{CH}=\text{CHBr}$



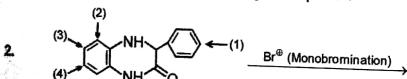
At given temperature, these reaction tell about control of reaction which is :

(1)	(2)
(A) Kinetic	Thermodynamic
(B) Thermodynamic	Kinetic
(C) Kinetic	Kinetic
(D) Thermodynamic	Thermodynamic

PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE



At which position nitration mainly takes place ?



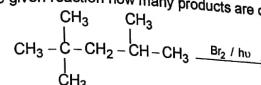
The substitution will mainly take place at position :

3. When ortho dibromobenzene is subjected to mononitration X number of product are formed and when meta dibromobenzene is subjected to mononitration, Y number of products are formed. Report your answer as XY.

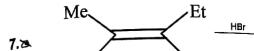
4. The number of possible enantiomer pairs that can be produced during monochlorination of 2-Methylbutane is :

Organic Reaction Mechanisms-II

5. For the given reaction how many products are optically active (all isomers) :



6. Number of structural isomers which can be obtained on monochlorination of 2-Methylbutane is :

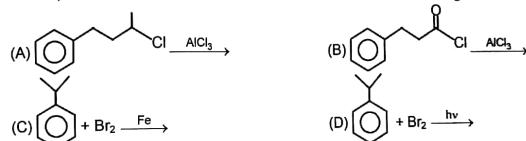


How many product will be formed in above reaction.

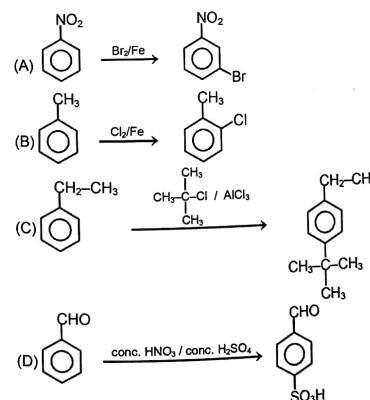
8. When trans-2-butene reacts with Br_2/CCl_4 , X number of products are formed. Whereas when trans-2-butene reacts with HBr Y number of products are formed. Report your answer as Y X .

PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

1. Electrophilic aromatic substitution can be seen in which of the following cases ?



2. In which of the following reactions correct major product is given ?



PART - III : MATCH THE COLUMN

1. Match List I (Reaction) with List II (Type of reaction) and select the correct answer using the code given below the lists :

List I		List II	
(P) $\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--CH}_3 + \text{Br}_2 \xrightarrow{\text{hv}}$		(1) Electrophilic addition	
(Q) $\text{CH}_3\text{--CH}=\text{CH--CH}_3 + \text{Br}_2 \xrightarrow{\text{CCl}_4}$		(2) Nucleophilic addition	
(R)  + $\text{Br}_2 \xrightarrow{\text{Fe}}$		(3) Free radical substitution	
(S) $\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--CHO} + \text{LiAlH}_4 \xrightarrow{\text{H}_2\text{O}}$		(4) Electrophilic substitution	

Codes :

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

2. Match the column-I with column-II :

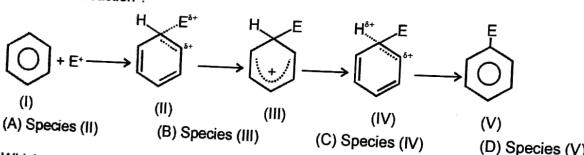
	Column-I	Column-II
	Group	Nature
(A)	$-\text{Cl}$	(p) Activating
(B)	$-\text{CH}_3$	(q) deactivating
(C)	$-\text{OH}$	(r) o,p-directing
(D)	$-\text{NO}_2$	(s) m-directing

Exercise-2

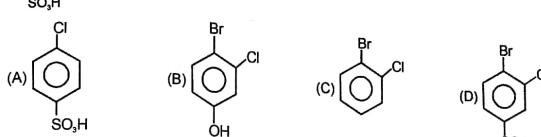
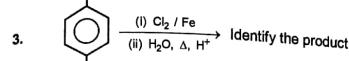
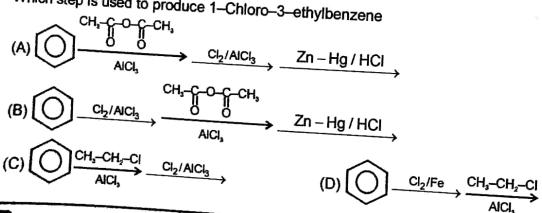
Marked Questions may have for Revision Questions.

PART - I : ONLY ONE OPTION CORRECT TYPE

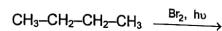
1. Which of the following species is expected to have maximum enthalpy in an electrophilic aromatic substitution reaction ?



2. Which step is used to produce 1-Chloro-3-ethylbenzene



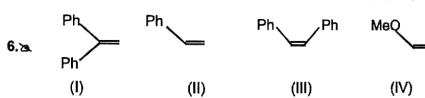
4. Which statement is correct about photochemical bromination of Butane ?



- (A) 1-Bromobutane and 2-Bromobutanes are formed in equal amounts.
 (B) 2-Bromobutane is formed with faster rate than 2-chlorobutane in the other experiment of chlorination.
 (C) The major product is an equimolar mixture of two compounds.
 (D) Major product is formed by more stable carbocation.

5. Alkynes are less reactive than alkenes towards addition of Br_2 because :

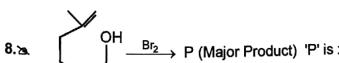
- (A) $\text{CH} = \text{CH}$ is less stable than $\text{CH}_2 = \text{CH}_2$
 (B) $\text{CH} = \text{CH}$ is more stable than $\text{CH}_2 = \text{CH}_2$
 (C) Both are equally stable
 (D) Original statement is incorrect



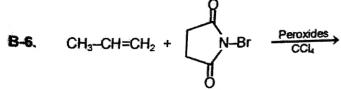
- (A) IV > I > III > II
 (B) I > II > III > IV
 (C) I > III > II > IV
 (D) IV > I > II > III

7. The correct order of reactivity of alkene towards an electrophile is mentioned in :

- (A) $\text{CH}_2=\text{CH}-\text{Cl} > \text{CH}_2=\text{CH}-\text{OCH}_3$
 (B) $\text{CH}_2=\text{CHCl} < \text{CH}_2=\text{CCl}_2$
 (C) $\text{CH}_2=\text{CH}_2 > \text{CH}_3-\text{CH}=\text{CH}_2$
 (D) $\text{CH}_2=\text{CH}-\text{OCH}_3 > \text{CH}_2=\text{CH}-\text{CH}_2-\text{OH}$



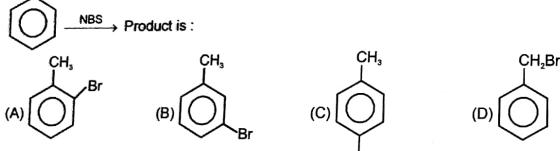
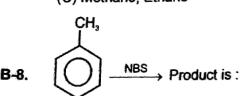
Organic Reaction Mechanisms-II



- This reaction is classified as
 (A) Electrophilic substitution reaction
 (C) Nucleophilic substitution reaction

- (B) Free radical substitution reaction
 (D) Electrophilic addition reaction

- B-7. In which of the following pairs the bromination of first member is easier than the second member ?
 (A) Isobutane, n-Butane
 (B) n-Butane, Isobutane
 (C) Methane, Ethane
 (D) None of these



- B-9. $\text{CH}_3-\text{C}=\text{CH}_2 + \text{HBr} \xrightarrow{\text{R}_2\text{O}_2} \text{Product is :}$



- B-10. Anti Markownikoff addition of HBr is not observed in :
 (A) Propene (B) 1-Butene (C) But-2-ene (D) Isobutene

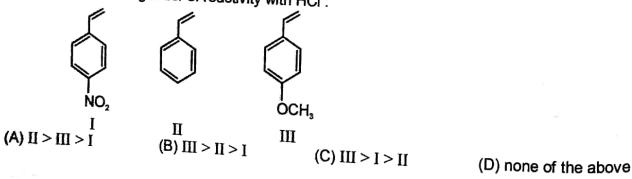
Section (C) : Electrophilic addition reaction

- C-1. What is correct order of acid catalysed hydration of following alkenes ?

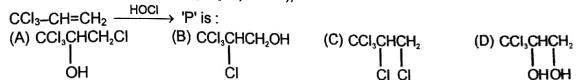
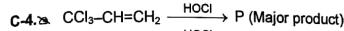
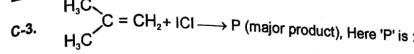
- (I) $\text{CH}_2=\text{CH}_2$ (II) $\text{CH}_3\text{CH}=\text{CH}_2$ (III) $(\text{CH}_3)_2\text{C}=\text{CH}_2$ (IV) $\text{CH}_3\text{CH}=\text{CH}-\text{CH}_3$

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

- C-2. Arrange in decreasing order of reactivity with HCl :



Organic Reaction Mechanisms-II

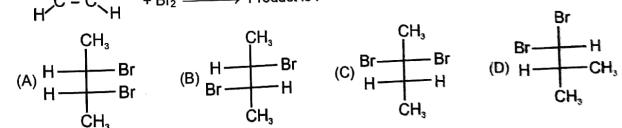
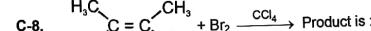
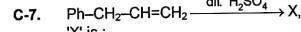


- C-5. In which reaction the product following anti markonikoff rule is observed :

- (A) $\text{CF}_3\text{CH}=\text{CH}_2 \xrightarrow{\text{HCl}}$ (B) $\text{CH}_3\text{OCH}=\text{CH}_2 \xrightarrow{\text{HCl}}$
 (C) $\text{CH}_3\text{OCH}=\text{CH}_2 \xrightarrow{\text{HCl}}$ (D) None

- C-6. Which will form 2, 2-Dibromopropane with HBr ?

- (A) $\text{CH}_2=\text{CH}-\text{CH}_3$ (B) $\text{CH}_3-\text{C}=\text{CH}$ (C) $\text{CH}_3-\text{C}=\text{CH}_2$ (D) Both B & C



- C-9. What is the product when one mole of Pent-1-yne treated with two moles of HCl ?

- (A) 1,2-Dichloropentane (B) 2,3-Dichloropentane
 (C) 1,1-Dichloropentane (D) 2,2-Dichloropentane

- C-10. The product(s) via-oxymercuration ($\text{HgSO}_4 + \text{H}_2\text{SO}_4$) of 1-Butyne would be :

- (A) $\text{CH}_3-\text{CH}_2-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_3$ (B) $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CHO}$
 (C) $\text{CH}_3-\text{CH}_2-\text{CHO} + \text{HCOOH}$ (D) $\text{CH}_3-\text{CH}_2-\text{COOH} + \text{HCOOH}$

Organic Reaction Mechanisms-II

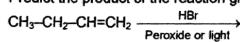
Section (B) : Free radical substitution & Free radical addition reaction

B-1. How do you account for formation of ethane during chlorination of methane?

B-2. Give the major product of monobromination of following compounds.



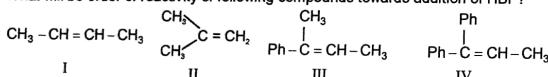
B-3. Predict the product of the reaction given below :



B-4. $\text{CH}_2=\text{CH--CH}_2\text{--CH}_3 \xrightarrow{\text{NBS}} \text{B} + \text{C}$
write structure of B and C.

Section (C) : Electrophilic addition reaction

C-1. What will be order of reactivity of following compounds towards addition of HBr?



C-2. The acid catalysed hydration follows following order $(\text{CH}_3)_2\text{C=CH}_2 > \text{CH}_3\text{CH=CH}_2 > \text{CH}_2=\text{CH}_2$
Explain this order of reactivity.

C-3. Give product of the following reactions.



C-4. What will happen when Br_2/CCl_4 react with (a) cis But-2-ene (b) trans But-2-ene.

C-5. In the reaction sequence,



What is the relationship between A & B :

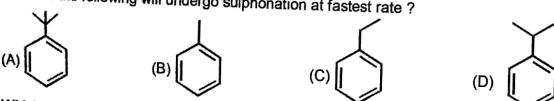
PART - II : ONLY ONE OPTION CORRECT TYPE

Section (A) : Electrophilic substitution reaction of aromatic compounds

A-1. The reagent used for Friedel-Craft's reaction is :

- (A) Dry ether (B) AlCl_3 (C) Anhydrous AlCl_3 (D) P_2O_5

A-2. Which of the following will undergo sulphonation at fastest rate?

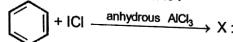


A-3. Which among the following is deactivating group?

- (A) $-\text{O}^-$ (B) $-\text{OR}$ (C) $-\text{NH}_2$ (D) $-\text{NHR}$

Organic Reaction Mechanisms-II

A-4. The compound X in the reaction is :



A-5. Toluene is o/p orienting with respect to an electrophilic substitution reaction due to

- (A) effect of the methyl group
(B) $+m$ as well as $+m$ effect of the methyl group
(C) hyperconjugation between the methyl group and the phenyl ring
(D) $+m$ effect to the methyl group.

A-6. 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 :



A-7. For preparing monoalkyl benzene, acylation process is preferred than direct alkylation because

- (A) In alkylation, a poisonous gas is evolved.
(B) In alkylation, large amount of heat is evolved.
(C) In alkylation, polyalkylated product is formed.
(D) Alkylation is very costly.

A-8. Chlorobenzene is o,p-directing in electrophilic substitution reaction. The directing influence is explained by:

- (A) $+m$ of Ph (B) $+I$ of Cl (C) $+m$ of Cl (D) $+I$ of Ph

Section (B) : Free radical substitution & Free radical addition reaction

B-1. In the free radical chlorination of methane, the chain initiating step involves the formation of

- (A) Chlorine radical (B) Hydrogen chloride (C) Methyl radical (D) Chloromethyl radical.

B-2. Which of the following cannot be considered as a step of mechanism in chain reaction of methane with Cl_2 ?

- (A) $\text{Cl}_2 \longrightarrow \text{Cl}^*$ (B) $\text{CH}_4 + \text{Cl}^* \longrightarrow \text{CH}_3\text{Cl} + \text{H}^+$
(C) $\text{Cl}^* + \text{CH}_4 \longrightarrow \text{CH}_3^* + \text{HCl}$ (D) $\text{Cl}^* + \text{CH}_3^* \longrightarrow \text{CH}_3\text{Cl}$

B-3. A gaseous hydrocarbon 'X' on reaction with bromine in light forms a mixture of two monobromo alkanes and HBr. The hydrocarbon 'X' is:

- (A) $\text{CH}_3\text{--CH}_3$ (B) $\text{CH}_2=\text{CH}_2$ (C) $\text{CH}_2=\text{CH}_2$ (D) $\text{CH}_2=\text{CHCH}_3$

B-4. The maximum ease of abstraction of a hydrogen atom by a chlorine atom is shown by:

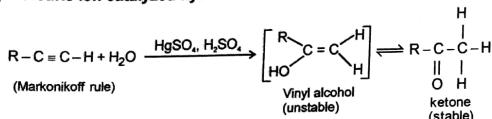
- (A) $(\text{CH}_3)_3\text{C--CH}_3$ (B) $(\text{CH}_3)_2\text{CH}_2$ (C) $\text{C}_6\text{H}_5\text{CH}_3$ (D) $\text{CH}_2=\text{CHCH}_3$

B-5. Methane reacts with excess of chlorine in diffused sunlight to give the final product as

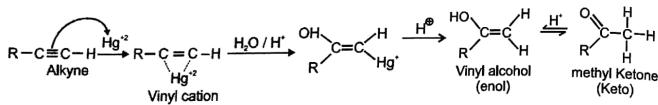
- (A) Chloroform (B) Methyl chloride.
(C) Methylene chloride (D) Carbon tetrachloride

(iv) ADDITION OF H₂O (HYDRATION REACTION) :

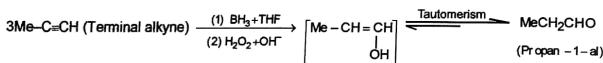
(a) Mercuric ion catalyzed hydration :



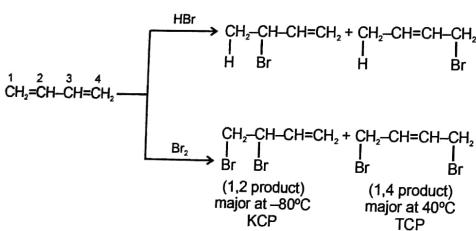
Mech.



(b) Hydroboration Oxidation of Alkynes :



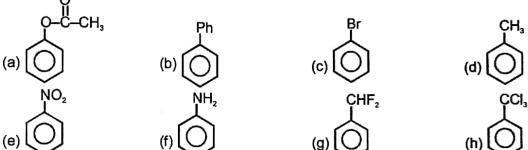
Alkadienes :

**Exercise-1**

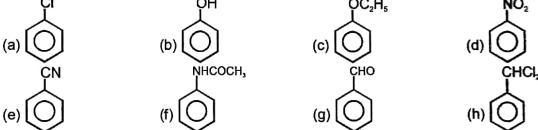
Marked Questions may have for Revision Questions.

PART - I : SUBJECTIVE QUESTIONS**Section (A) : Electrophilic substitution reaction of aromatic compounds**A-1. Δ Normally, benzene gives electrophilic substitution reaction rather than electrophilic addition reaction although it has double bonds. Explain why?

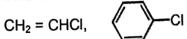
A-2. Which of the following Benzene rings contain deactivating groups ?



A-3. Which of the following Benzene rings contain o-p directing groups ?

A-4. Δ Arrange the following in decreasing order of their reactivity with an electrophile.

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

A-5. Δ Why following organic chlorides will not give a Friedel-Crafts alkylation product when heated with benzene and AlCl₃?

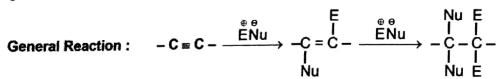
Organic Reaction Mechanisms-II

Electrophilic addition reaction of Alkynes :

Many of the reactions of alkynes are similar to the corresponding reactions of alkenes. Like the pi bond of an alkene, the pi bonds of an alkyne are electron-rich, and they readily undergo addition reaction. The bond energy of the alkyne triple bond is about 226 kJ (54 kcal) more than the bond energy of an alkene double bond.

Since sigma bonds are generally stronger than pi bonds, the reaction is usually exothermic. Alkynes have two pi bonds, so up to two molecules can add across the triple bond.

We must consider the possibility of a double addition whenever a reagent adds across the triple bond of an alkyne. Some conditions may allow the reaction to stop after a single addition, while other conditions give double addition.

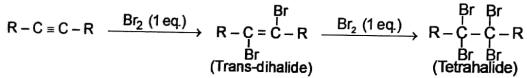


Common Reagents :

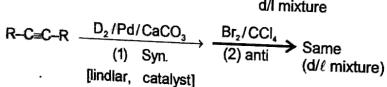
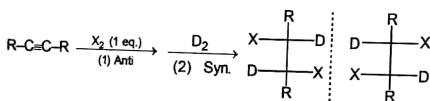


Markovnikov's rule of addition : In an electrophilic addition reaction to alkenes and alkynes the electrophile attacks in such a way that a more stable carbocation intermediate is formed on which nucleophile attacks in the next step.

(i) ADDITION OF HALOGEN (HALOGENATION) :

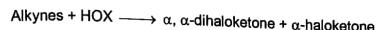


Remark : - Reaction is Anti in both step

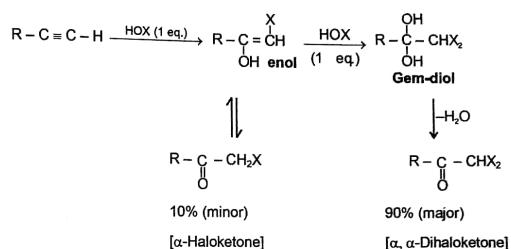


Organic Reaction Mechanisms-II

(ii) ADDITION OF HOX :



(90% major) (10% minor)

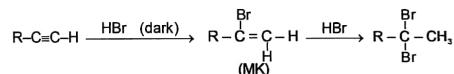


Remarks :

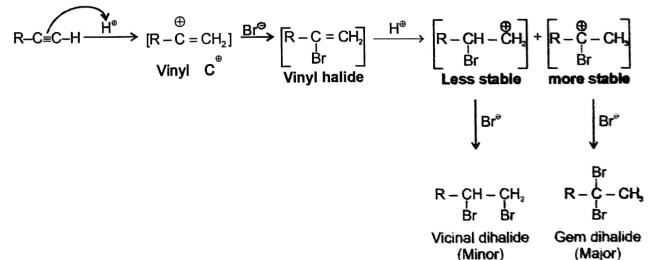
Two molecules of HOX can be added, the end product is α, α -Dihaloketone.

The intermediate product is an enol which gives a minor product α -haloketone.

(iii) ADDITION OF HYDROGEN HALIDES (+ HX) :



Mechanism :



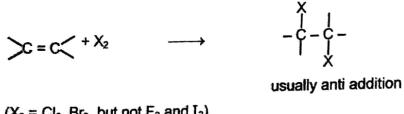
Remarks : (1) Markovnikov's Addition in both steps.

(2) If two moles of HX are added the final product is Gemdihalide.

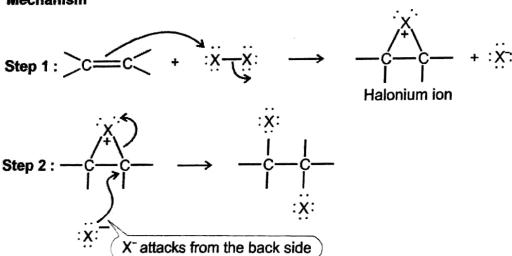
(3) Electrophilic addition to terminal alkyne is regioselective.

Organic Reaction Mechanisms-II

(i) ADDITION OF HALOGEN (HALOGENATION) :

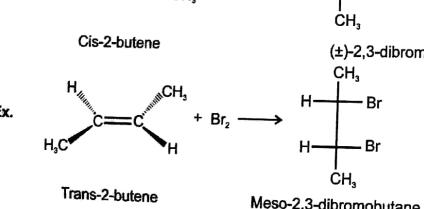
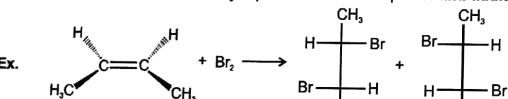


Mechanism



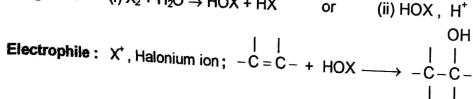
Remarks : Anti addition; No rearrangement; Bridged Carbocation; Markovnikoff's additions

The addition of bromine to cyclopentene is a stereospecific anti addition.



(ii) ADDITION OF HOX :

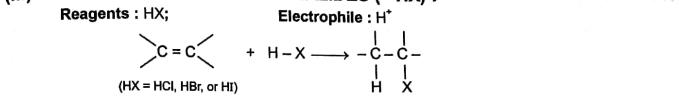
Reagents : (i) $\text{X}_2 + \text{H}_2\text{O} \rightarrow \text{HOX} + \text{HX}$ or (ii) HOX, H^+



Remarks : Anti addition; No rearrangement; Bridged Carbocation; Markovnikoff's additions

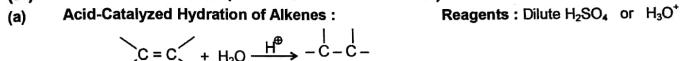
Organic Reaction Mechanisms-II

(iii) ADDITION OF HYDROGEN HALIDES (+ HX) :



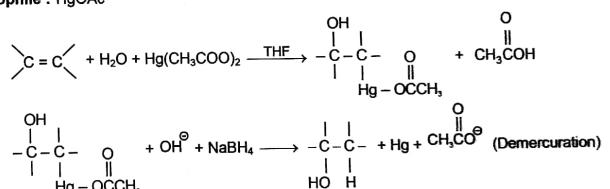
Remarks : Markovnikoff addition; Intermediate carbocation; Rearrangement may take place

(iv) ADDITION OF H_2O (HYDRATION REACTION)

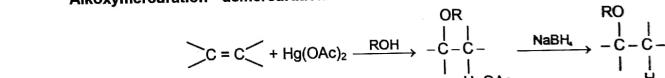


Remarks : Markovnikoff addition; Intermediate carbocation; Rearrangement may take place
Oxymercuration-Demercuration : Reagents : (i) $\text{Hg(OAc)}_2, \text{H}_2\text{O}$ (ii) NaBH_4

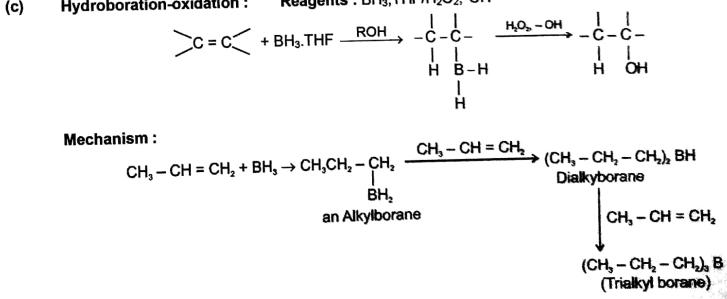
Electrophile : HgOAc



Remarks : No rearrangement; Bridged Carbocation; Markovnikoff's additions
Alkoxymercuration - demercuration

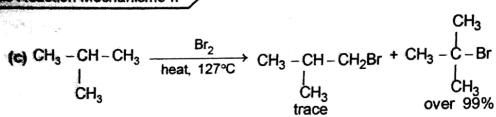


(c) Hydroboration-oxidation :



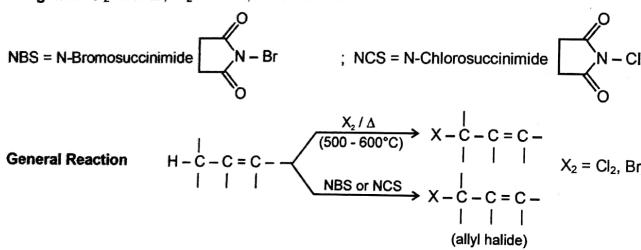
Remarks : Anti Markovnikov's addition; Syn addition.

Organic Reaction Mechanisms-II



(b) Free radical allylic and benzylic substitution reaction :

Reagents: Cl_2/hv or Δ , Br_2/hv or Δ , NBS or NCS

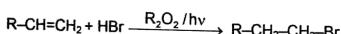


It is free radical substitution reaction.

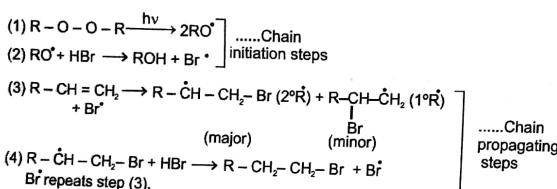
(c) Free radical addition reaction of alkene & alkyne :

Reagents : $\text{HBr}/\text{R}_2\text{O}_2, \text{hv}$ [Kharasch Effect or Peroxide Effect]

General Reaction :



Mechanism :



Remarks :

- (1) When HBr is added to an unsymmetrical alkene in presence of sunlight and peroxide. Then an Anti Markovnikov's Addition Product is obtained.
- (2) It is a free radical chain reaction.
- (3) In presence of peroxide and sunlight Br^+ is formed in chain initiation step.
- (4) Br^+ forms more stable alkyl radical by homolysis of $\text{C}=\text{C}$ π bond.
- (5) In the last step alkyl radical abstracts H^+ from HBr and Anti markownikov's product is obtained.

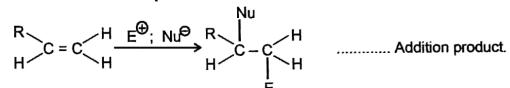
Organic Reaction Mechanisms-II

Section (C) : Electrophilic addition reaction

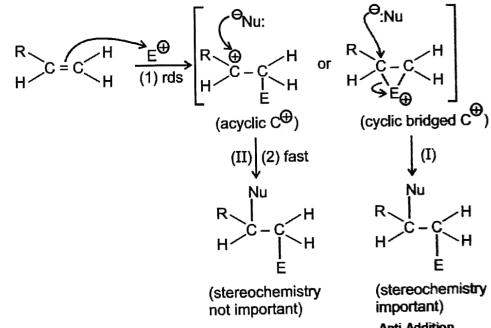
(a) Electrophilic addition reaction of Alkenes :-

Due to presence of weak π electrons in alkene and alkyne, it will go for electrophilic addition reaction. In electrophilic addition reactions one weak π -bond (251 KJ mol^{-1}) is broken and two strong σ bonds ($2 \times 347 = 694 \text{ KJ mol}^{-1}$) are formed. The overall reaction is accompanied by a release of about $694-251 = 443 \text{ KJ mol}^{-1}$ of energy.

General Reaction of electrophilic addition :



The overall reaction mechanism can be visualised as followed :



Remarks :

Alkenes, Alkynes and Alkadienes are electron rich species. So they function as Nu^{\ominus} species (due to loosely bound π -electrons)

These compounds mainly give electrophilic addition reactions. Due to nucleophilic nature of alkenes/alkynes having affinity for E^{\oplus} .

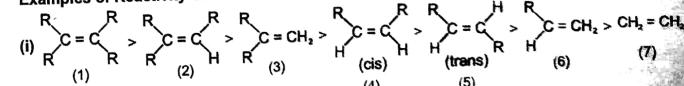
The reaction is initiated by an attack of E^{\oplus} .

Rate of reaction \propto stability of carbocation

Reactivity of an Alkene :

- (1) Presence of e^- releasing groups (+m, +I) at $\text{C}=\text{C}$ increases nucleophilicity and reactivity.
- (2) Presence of ERG stabilises the intermediate carbocation. (3) More stable C^{\oplus} , more is reactivity.

Examples of Reactivity Orders :



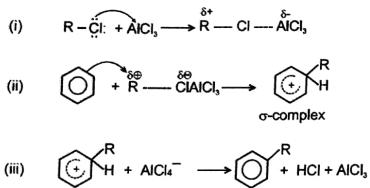
(ii) ERG - $\text{CH}=\text{CH}_2 > \text{CH}_2=\text{CH}_2 > \text{EWG}-\text{CH}=\text{CH}_2$

Organic Reaction Mechanisms-II

Some $\text{Ar}^{\oplus}\text{H}$ or $\text{Ar}^{\oplus}\text{D}$ or $\text{Ar}^{\oplus}\text{SO}_3^-$ go on to product, some revert to the starting material and decrease the rate of reaction. This effect is known as isotope effect.

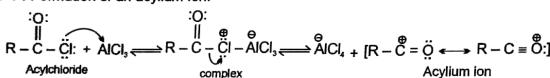
(iv) Friedel Craft's reaction

(a) Alkylation : The mechanism for Friedel Craft's reaction involves the following steps.

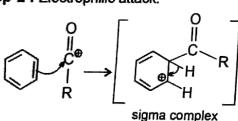


(b) Acylation : Acylation of benzene may be brought about with acid chlorides or anhydrides in presence of Lewis acids.

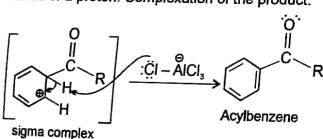
Step-1 : Formation of an acylium ion.



Step-2 : Electrophilic attack.



Step-3 : Loss of a proton. Complexation of the product.



Limitations of Friedel craft's reactions :

- (i) Highly reactive rings like aniline and highly deactivated rings like nitrobenzene, cyanobenzene do not give friedel craft reactions.
- (ii) Poly alkylation is possible but poly acylation is not possible.
- (iii) Rearranged products may form in the friedel craft alkylation reactions.
- (iv) Diketone also undergoes the Friedel Craft reaction with benzene.

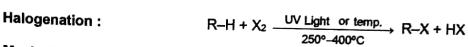
Organic Reaction Mechanisms-II

Section (B) : Free radical substitution & Free radical addition reaction

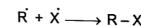
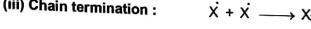
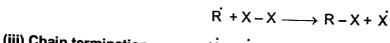
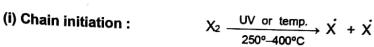
(a) Free radical substitution reaction of alkanes

Characteristic reaction of alkanes is free radical substitution reaction, these reactions are generally chain reactions which are completed in three steps :

(i) chain initiation (ii) chain propagation. (iii) chain termination



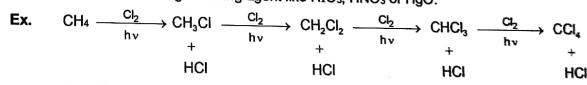
Mechanism :



Reactivity of X_2 : $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$

Reactivity of H : ${}^3\text{H} > {}^2\text{H} > {}^1\text{H}$

Remarks : With F_2 alkanes react so vigorously that even in the dark and at room temperature, reactant is diluted with an inert gas. Iodination is reversible reaction, since HI is formed as a by product and it is a strong reducing agent and reduces alkyl iodide back to alkane. Hence iodination can be done only in presence of strong oxidising agent like HIO_3 , HNO_3 or HgO .

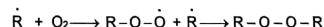


In a chain reaction following reagents are involved -

(i) Initiators : They initiate the chain reaction, Initiators are peroxide (R_2O_2), Peroxester's etc.

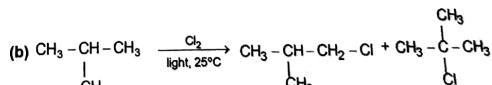
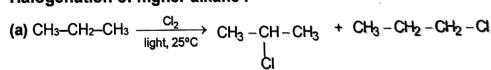
(ii) Inhibitors : A substance that slows down or stops the reaction is known as inhibitors

For example O_2 is a good inhibitor



all reactive alkyl free radicals are consumed so reaction stops for a period of time.

Halogenation of higher alkane :



Organic Reaction Mechanisms-II

(B) Ortho para directing but deactivating groups : Halogens are deactivating but ortho-para directing groups.
Reactivity of benzene decreases by $-I$ effect of halogens and ortho-para directing nature is decided by $+m$ effect of halogens.

(C) Meta directing and deactivating groups : Mostly electron withdrawing groups ($-m, -I$) are meta directing groups and deactivating towards electrophilic reactions.

	Substituent groups	Reactivity (effect on rate)	Directing nature (effect on orientation)
1.	$-O^- > -NH_2 > -NHR > -NR_2 > -OH$	Very strongly activating	Ortho-para directing
2.	$-OR > -NH-C(=O)-R > -O-C(=O)R$	Strongly activating	Ortho-para directing
3.	$-R, -Ar, -CH=CH_2$	Activating	Ortho-para directing
4.	$-X(F, Cl, Br, I), -N=O, -CH_2X, -CH_3X$	Deactivating	Ortho-para directing
5.	$-CHO, -C(=O)R, -COOH, -COOR, -COCl, -C=N, -SO_3H$	Strongly deactivating	Meta directing
6.	$-NO_2, +NR_2, -SR_2, -CF_3$	Very strongly deactivating	Meta directing

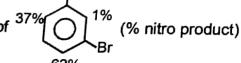
Effect of substituent groups in disubstituted benzene :

(1) If activating and deactivating both groups are present in a system then position of electrophile will be determined by activating group.

(2) If both groups present in a system are deactivator then position of electrophile will be determined by stronger deactivator.

(3) If both the groups are activating group then position of electrophile will be determined by stronger activator.

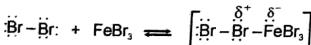
(4) There is often little substitution between two groups that are meta to each other.

Ex. Nitration product of  (% nitro product)

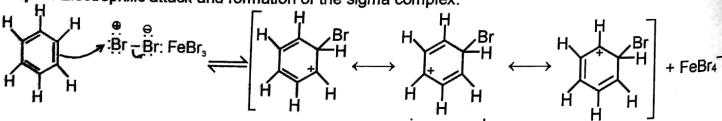
(i) Halogenation

Chlorine and bromine in presence of lewis acid (like $AlCl_3, FeCl_3$) react with benzene. Fluorination and iodination of benzene and other arenes rarely performed. Fluorine is so reactive that its reaction with benzene is difficult to control. Iodination is too slow and has an unfavourable equilibrium constant.

Step 1 : Formation of a stronger electrophile.

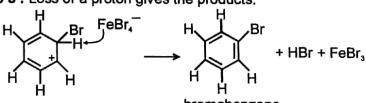


Step 2 : Electrophilic attack and formation of the sigma complex.

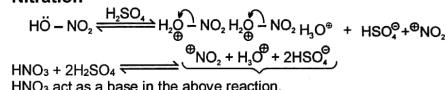


Organic Reaction Mechanisms-II

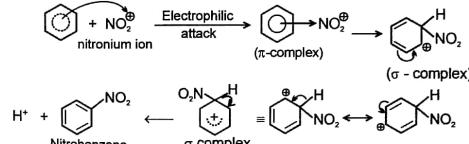
Step 3 : Loss of a proton gives the products.



(ii) Nitration

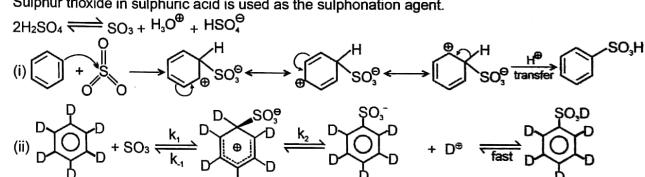


HNO₃ act as a base in the above reaction.



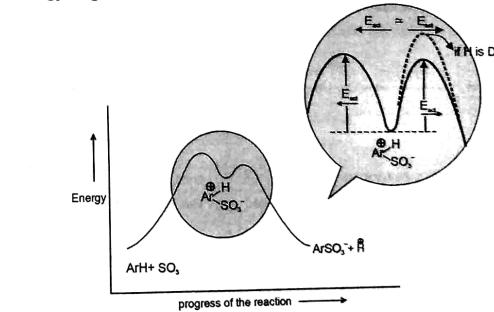
(iii) Sulphonation

Sulphur trioxide in sulphuric acid is used as the sulphonation agent.



Sulphonation, is reversible and takes place in concentrated sulphuric acid. ($K_{-1} = K_2$).

Energy Diagram



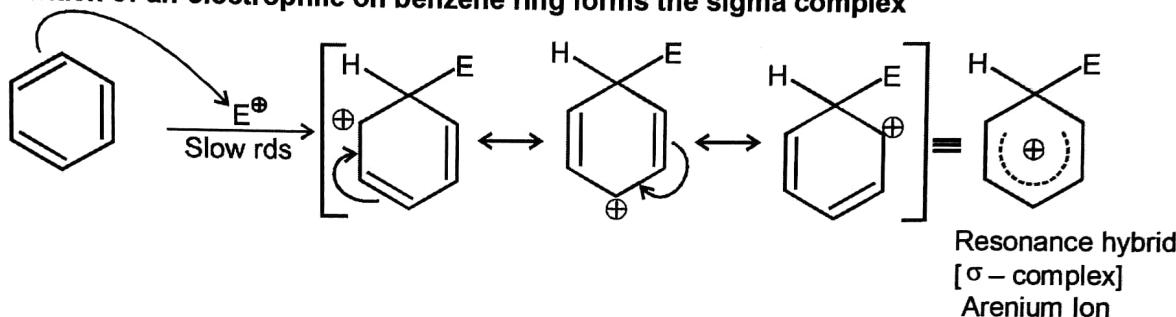
Organic Reaction Mechanisms-II

Section (A) : Electrophilic substitution reaction of aromatic compounds

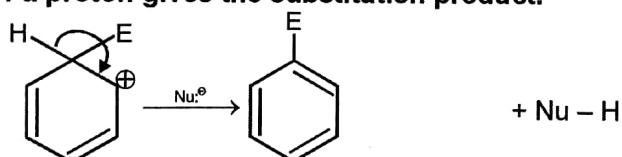
Like an alkene, benzene has cloud of pi electrons above and below its sigma bond framework. Although benzene's pi electrons are in a stable aromatic system still they are available to attack with a strong electrophile to give a carbocation. This resonance-stabilized carbocation is called a **sigma complex** because the electrophile is joined to the benzene ring by a new sigma bond. The sigma complex (also called an arenium ion) is not aromatic because the sp^3 hybrid carbon atom interrupts the ring of p orbitals. This loss of aromaticity contributes to the highly endothermic nature of thus first step. The sigma complex regains aromaticity either by a reversal of the first step (returning to the reactants) or by loss of the proton on the tetrahedral carbon atom, leading to the substitution product.

The overall reaction is the substitution of an electrophile (E^\oplus) for a proton (H^\ominus) on the aromatic ring so it is called **electrophilic aromatic substitution**.

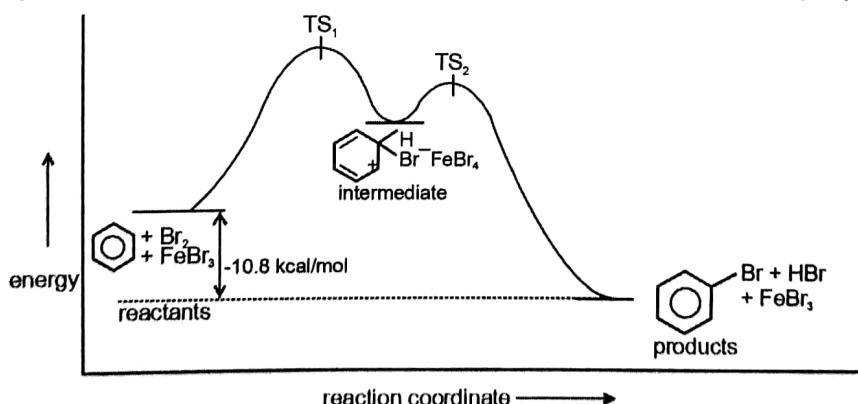
Step 1 : Attack of an electrophile on benzene ring forms the sigma complex



Step 2 : Loss of a proton gives the substitution product.



Energy diagram : For bromination reaction, electrophile is bromonium ion (Br^\oplus)



For an electrophilic aromatic substitution reaction to overcome the high activation energy that characterizes the first step, the electrophile must be a fairly reactive one. Many of the electrophilic reagents that react rapidly with alkenes do not react at all with benzene. For example peroxy acids and diborane, fall into this category, others such as bromine react with benzene only in presence of catalysts that increases their electrophilicity.

Effect of substituent groups in monosubstituted benzene :

(A) **Ortho-para directing and activating groups :** All electron releasing groups (+m, +I) are ortho-para directing groups and activating towards electrophilic reactions.