

ORGANIC REACTION MECHANISMS-II

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JEE(Advanced) Syllabus

Benzene: Electrophilic substitution reactions: halogenation, nitration, sulphonation, Friedel-Crafts alkylation and acylation; Effect of o-, m- and p-directing groups in monosubstituted benzenes.

Alkanes : Halogenation of alkanes

Alkenes : Electrophilic addition reactions of alkenes with X_2 , HX, HOX and H_2O ; Acid catalysed hydration of alkenes and alkynes (excluding the stereochemistry of addition and elimination).

Alkynes : Electrophilic addition reactions of alkynes.

JEE(Main) Syllabus

Alkanes : Chemical reactions including free radical mechanism of halogenation

Alkenes : Chemical reactions: addition of hydrogen, halogen, water, hydrogen halides (Markovnikov's addition and peroxide effect),

Alkynes : Chemical reactions: acidic character of alkynes, addition reaction of - hydrogen, halogens, hydrogen halides and water.



Organic Reaction Mechanisms-II

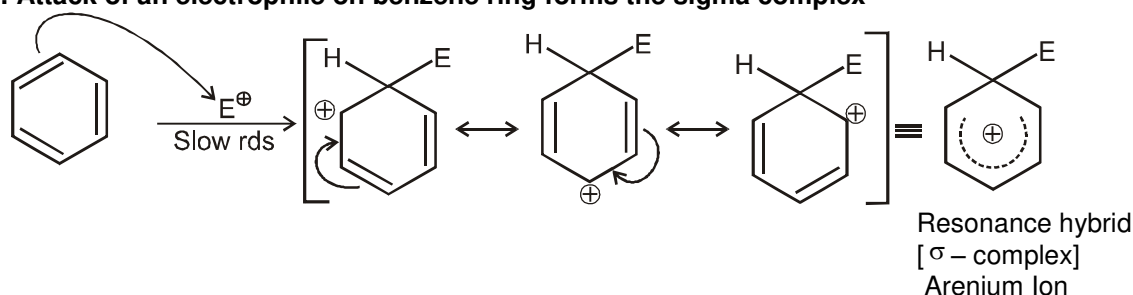
Section (A) : Electrophilic substitution reaction of aromatic compounds

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.

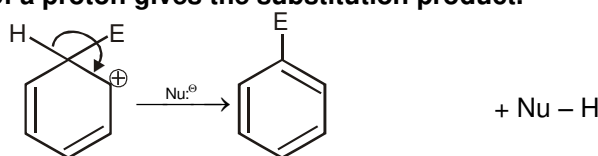
The sigma complex (also called an arenium ion) is not aromatic because the sp^3 hybrid carbon atom interrupts the ring of p orbitals. This loss of aromaticity contributes to the highly endothermic nature of this first step. The sigma complex regains aromaticity either by a reversal of the first step (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^+) for a proton (H^+) on the aromatic ring so it is called **electrophilic aromatic substitution**.

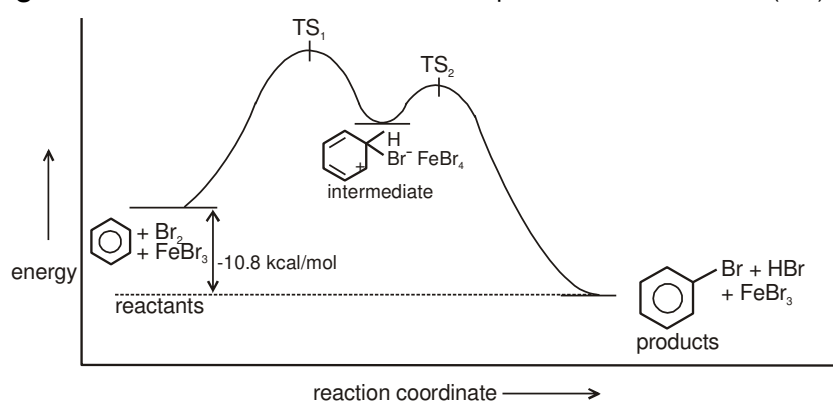
Step 1 : Attack of an electrophile on benzene ring forms the sigma complex



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



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



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.



(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.	$-X(F, Cl, Br, I), -N=O, -CH_2X, -CHX_2$	Deactivating	Ortho-para directing
5.	$-CHO, -C(=O)-R, -COOH, -COOR, -COCl, -C\equiv N, -SO_3H$	Strongly deactivating	Meta directing
6.	$-NO_2, -NR_3^+, -SR_2^+, -CF_3$	Very strongly deactivating	Meta directing

Effect of substituent groups in disubstituted benzene :

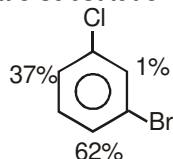
(1) If activating and deactivating both groups are present in a system then position of electrophile will be determined by activating group.

(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

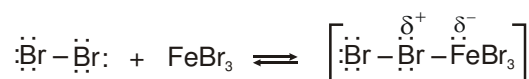


(% nitro product)

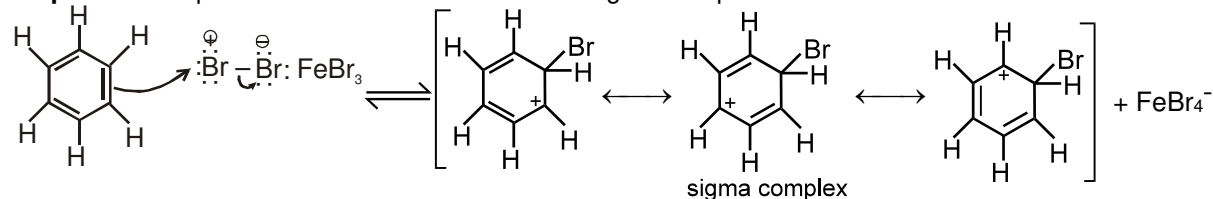
(i) Halogenation

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.

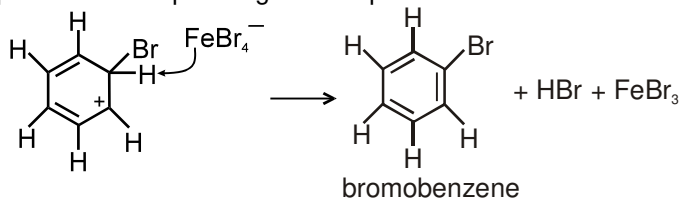


Step 2 : Electrophilic attack and formation of the sigma complex.

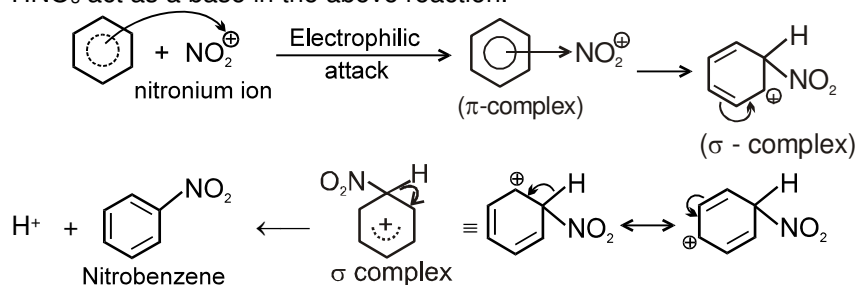
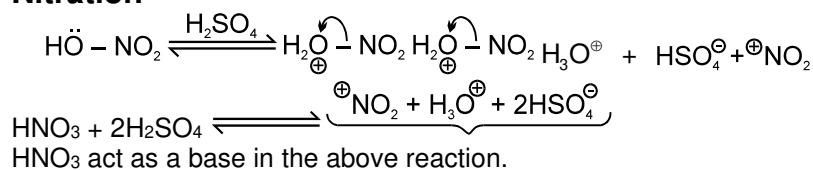




Step 3 : Loss of a proton gives the products.



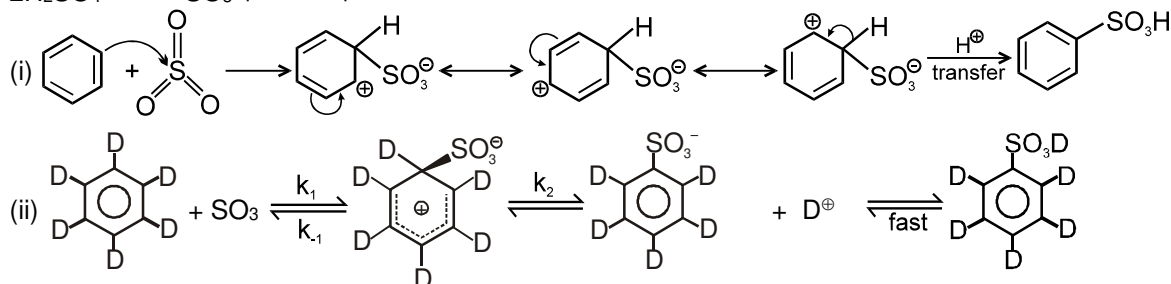
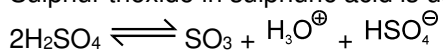
(ii) Nitration



* Purpose of sulphonic acid in the reaction is to increase the concentration of nitronium ion (NO^+_2)

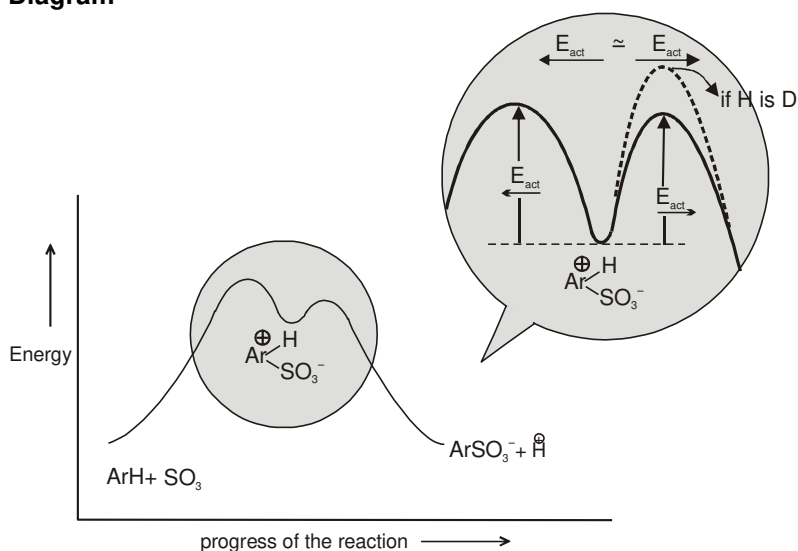
(iii) Sulphonation

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



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

Energy Diagram



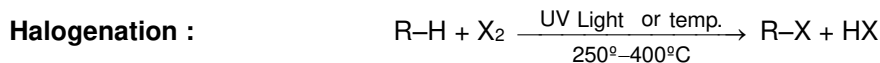


Section (B) : Free radical substitution & Free radical addition reaction

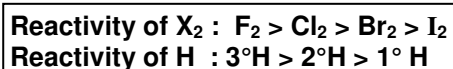
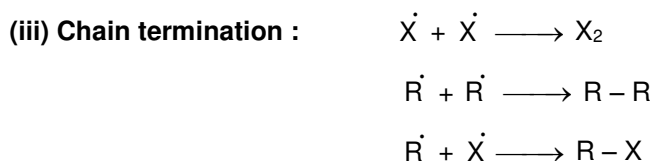
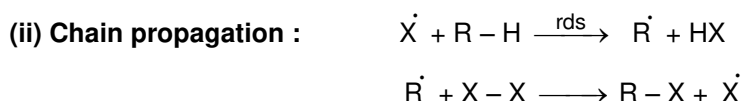
(a) Free radical substitution reaction of alkanes

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

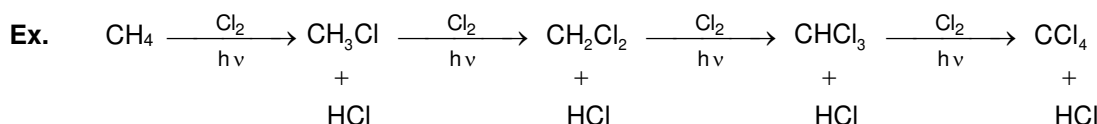
(i) chain initiation (ii) chain propagation. (iii) chain termination



Mechanism :



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 .

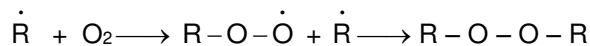


In a chain reaction following reagents are involved -

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

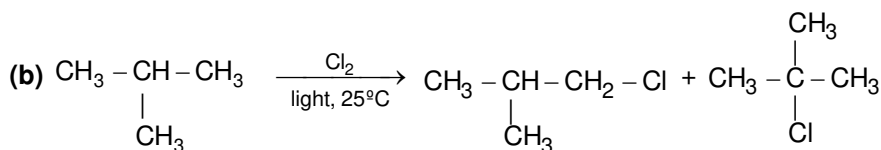
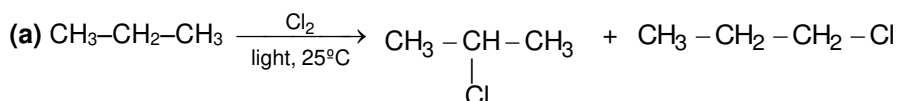
(ii) Inhibitors : A substance that slows down or stops the reaction is known as inhibitors

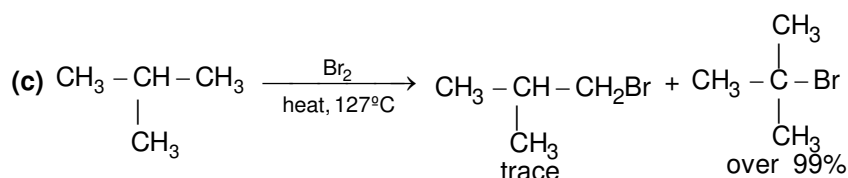
For example O_2 is a good inhibitor



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

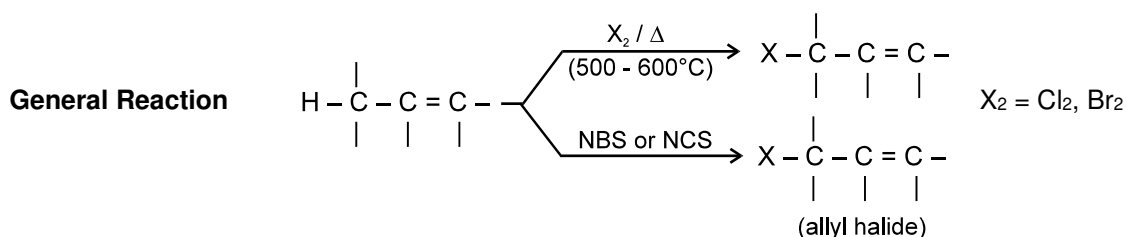
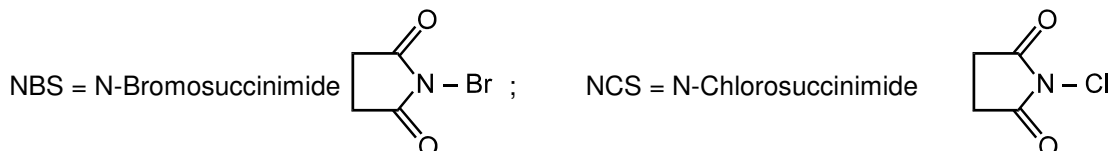
Halogenation of higher alkane :





(b) Free radical allylic and benzylic substitution reaction :

Reagents: $\text{Cl}_2/h\nu$ or Δ , $\text{Br}_2/h\nu$ or Δ , NBS or NCS

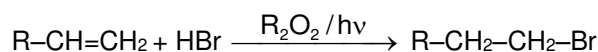


It is free radical substitution reaction.

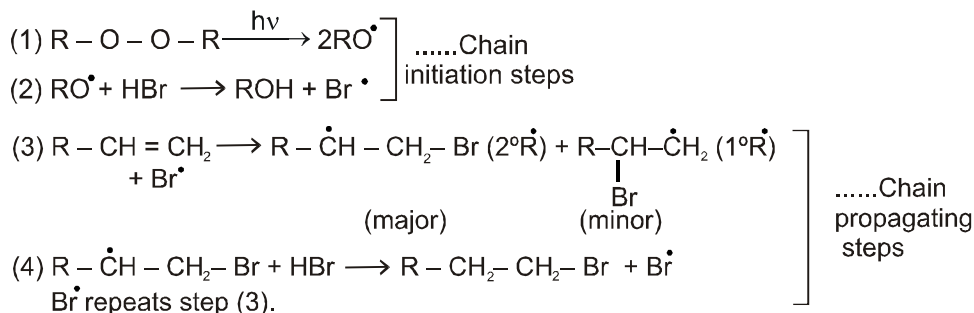
(c) Free radical addition reaction of alkene & alkyne :

Reagents : HBr / R_2O_2 , $h\nu$ [Kharasch Effect or Peroxide Effect]

General Reaction :



Mechanism :

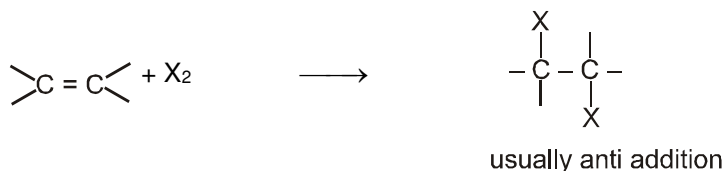


Remarks :

- (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^\bullet is formed in chain initiation step.
- (4) Br^\bullet forms more stable alkyl radical by homolysis of $\text{C}=\text{C}$ π bond.
- (5) In the last step alkyl radical abstracts H^\bullet from HBr and Anti markownikov's product is obtained.

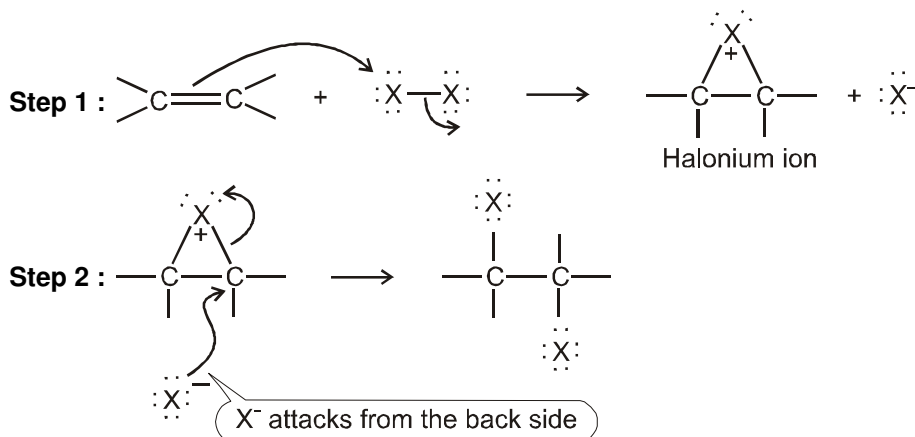


(i) ADDITION OF HALOGEN (HALOGENATION) :



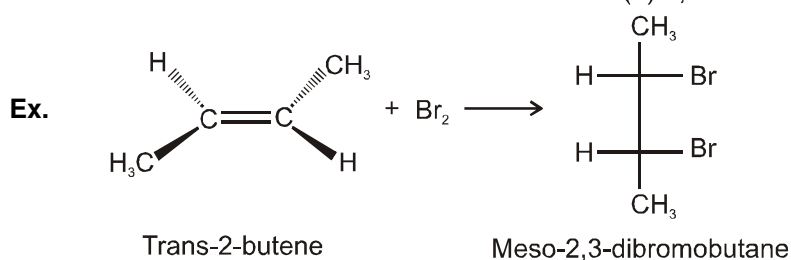
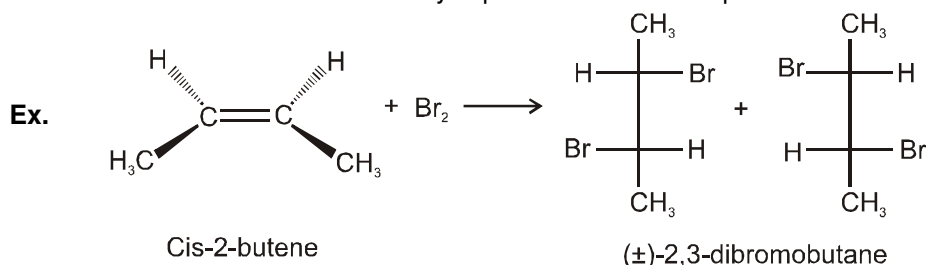
(X₂ = Cl₂, Br₂, but not F₂ and I₂)

Mechanism



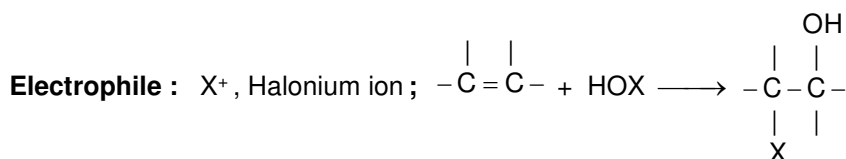
Remarks : Anti addition; No rearrangement; Bridged Carbocation; Markovnikoff's additions

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

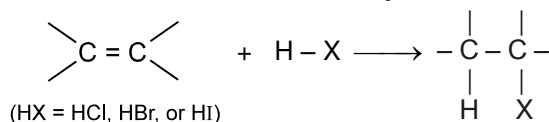
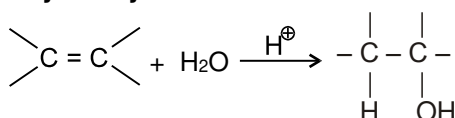
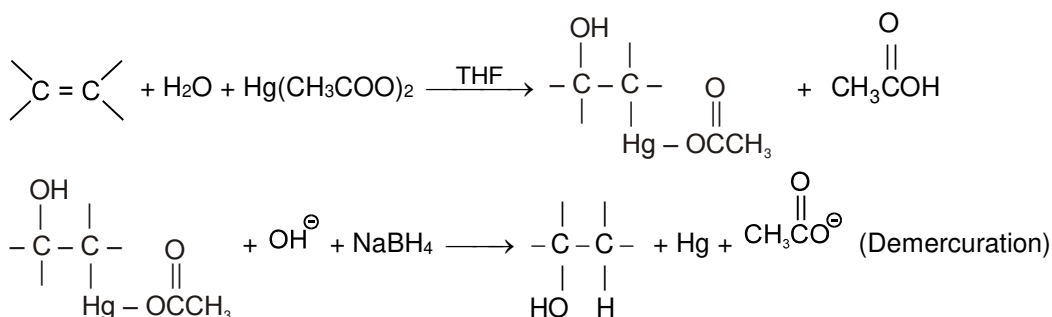
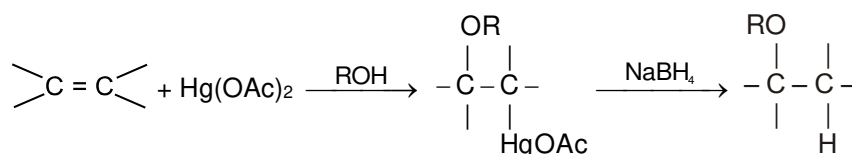
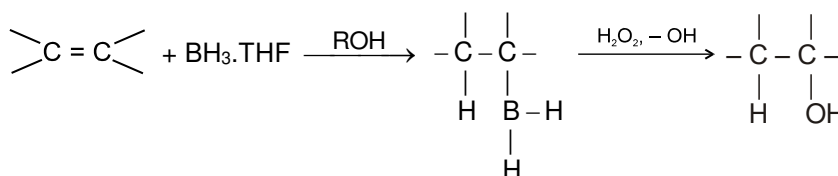
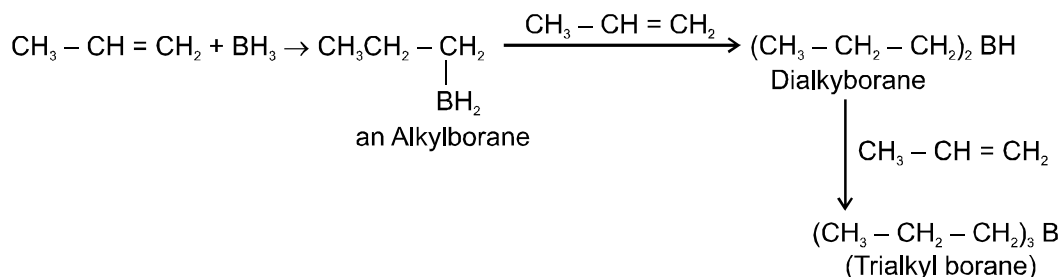


(ii) ADDITION OF HOX :

Reagents : (i) X₂ + H₂O → HOX + HX or (ii) HOX, H⁺

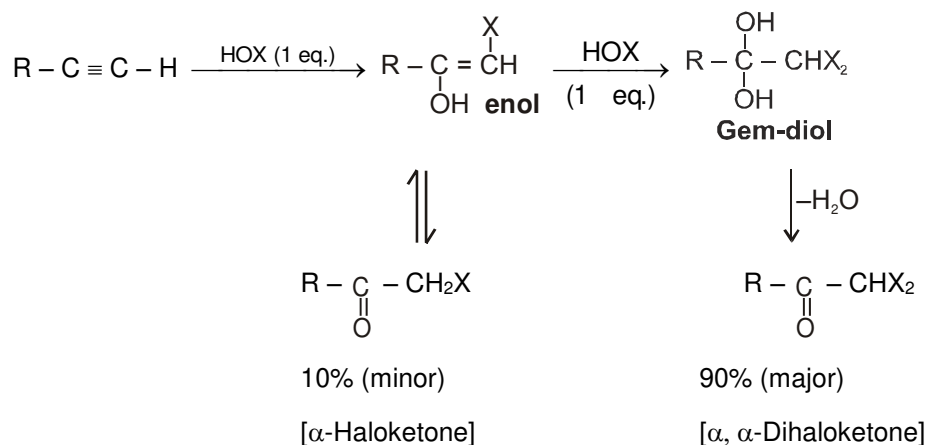


Remarks : Anti addition ; No rearrangement ; Bridged Carbocation ; Markovnikoff's additions

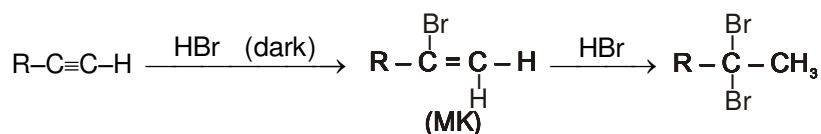
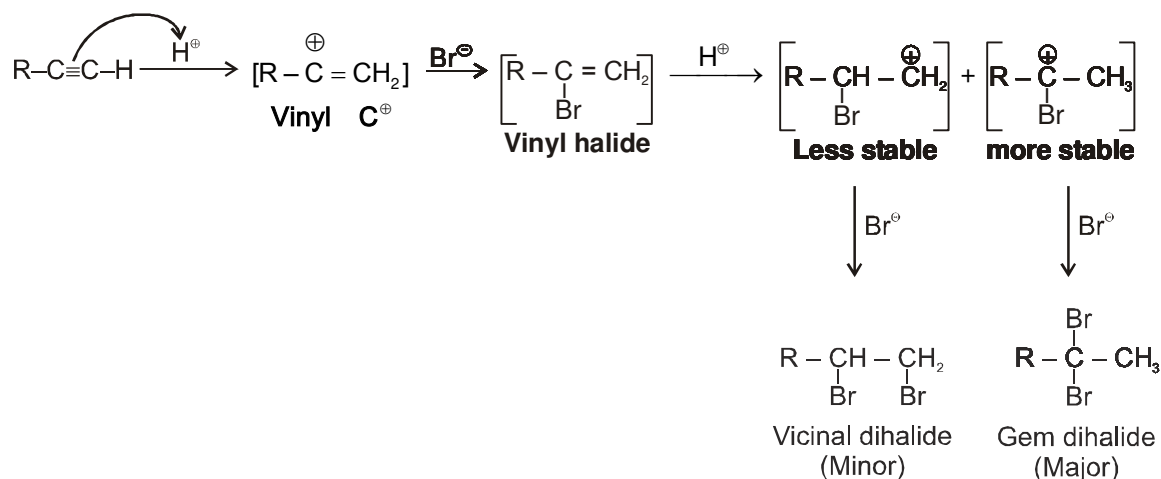
**(iii) ADDITION OF HYDROGEN HALIDES (+ HX) :****Reagents :** HX;**Electrophile :** H⁺**Remarks :** Markovnikoff addition ; Intermediate carbocation ; Rearrangement may take place**(iv) ADDITION OF H₂O (HYDRATION REACTION)****(a) Acid-Catalyzed Hydration of Alkenes :****Reagents :** Dilute H₂SO₄ or H₃O⁺**Remarks :** Markovnikoff addition ; Intermediate carbocation ; Rearrangement may take place**(b) Oxymercuration-Demercuration : Reagents :** (i) Hg(OAc)₂, H₂O (ii) NaBH₄**Electrophile :** HgOAc^+ **Remarks :** No rearrangement ; Bridged Carbocation ; Markovnikoff's additions**Alkoxymercuration - demercuration****(c) Hydroboration-oxidation : Reagents :** BH₃, THF/H₂O₂, -OH**Mechanism :****Remarks :** Anti Markovnikov's addition ; Syn addition.

**(ii) ADDITION OF HOX :**

Alkynes + HOX \longrightarrow α , α -dihaloketone + α -haloketone
 (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.

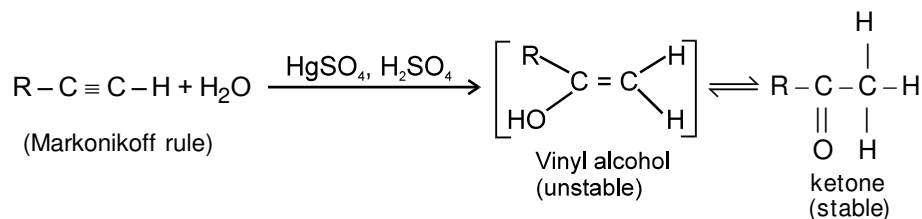
(iii) ADDITION OF HYDROGEN HALIDES (+ HX) :**Mechanism :**

- 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.**

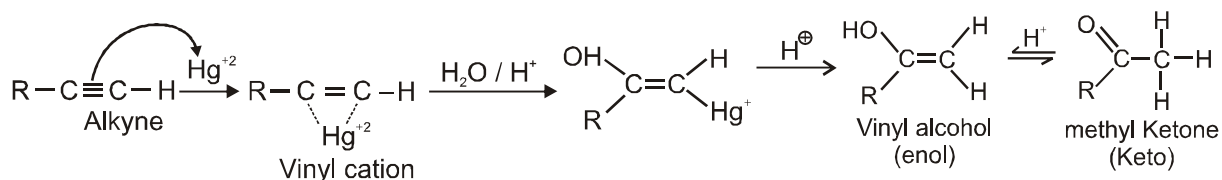


(iv) **ADDITION OF H₂O (HYDRATION REACTION) :**

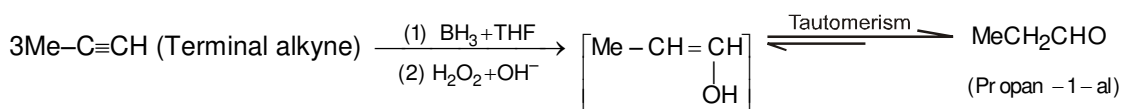
(a) **Mercuric ion catalyzed hydration :**



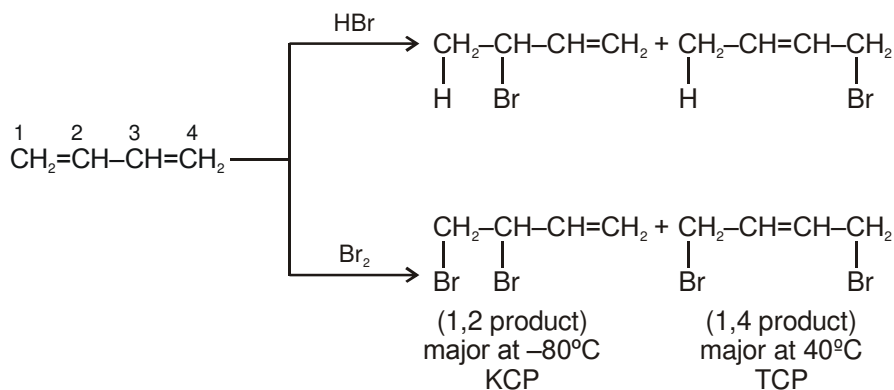
Mech.



(b) **Hydroboration Oxidation of Alkynes :**



Alkadienes :





Exercise-1

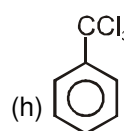
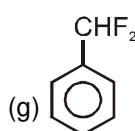
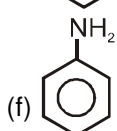
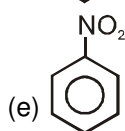
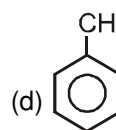
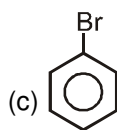
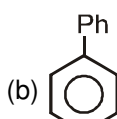
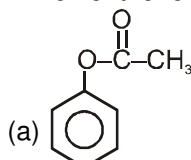
Marked questions are recommended for Revision.

PART - I : SUBJECTIVE QUESTIONS

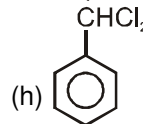
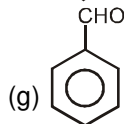
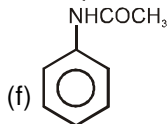
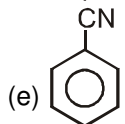
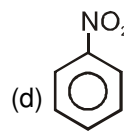
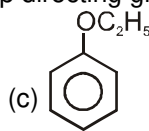
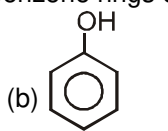
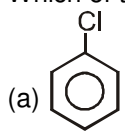
Section (A) : Electrophilic substitution reaction of aromatic compounds

A-1. 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 ?



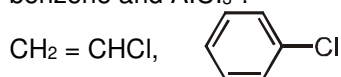
A-3. Which of the following Benzene rings contain o-p directing groups ?



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

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

A-5. Why following organic chlorides will not give a Friedel-Craft alkylation product when heated with benzene and AlCl_3 ?

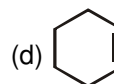
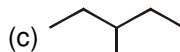
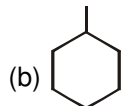
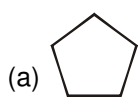




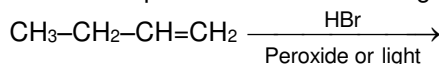
Section (B) : Free radical substitution & Free radical addition reaction

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.



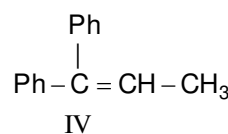
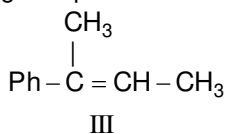
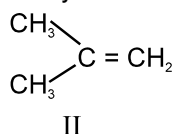
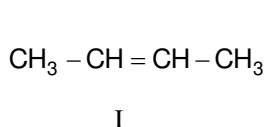
B-3. Predict the product of the reaction given below :



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.

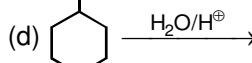
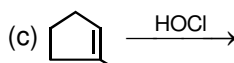
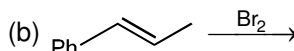
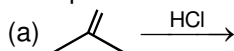
Section (C) : Electrophilic addition reaction

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



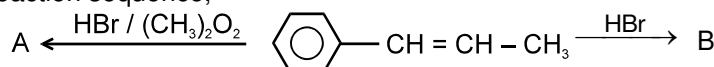
C-2. The acid catalysed hydration follows following order $(\text{CH}_3)_2\text{C=CH}_2 > \text{CH}_3\text{CH=CH}_2 > \text{CH}_2=\text{CH}_2$
Explain this order of reactivity.

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 :

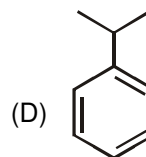
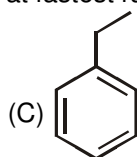
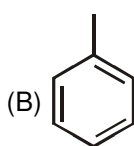
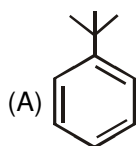
PART - II : ONLY ONE OPTION CORRECT TYPE

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 ?

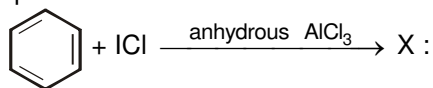


A-3. Which among the following is deactivating group ?

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



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



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

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

- (A) I effect of the methyl group
(B) I 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) (B) (C) (D)

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

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) (C) (D)

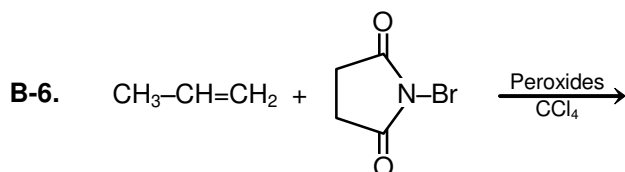
B-4. The maximum ease of abstraction of a hydrogen atom by a chlorine atom is shown by :

- (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

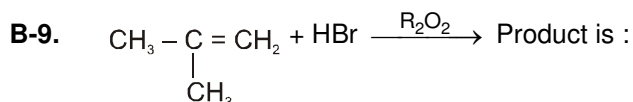
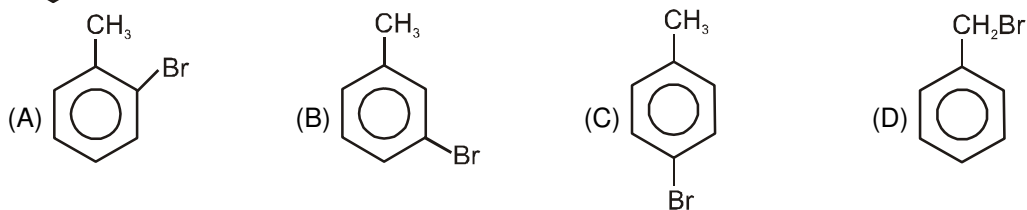
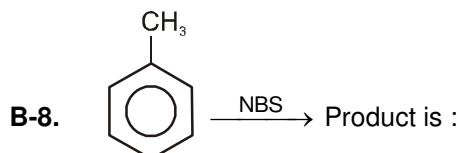




This reaction is classified as

- (A) Electrophilic substitution reaction (B) Free radical substitution reaction
(C) Nucleophilic 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



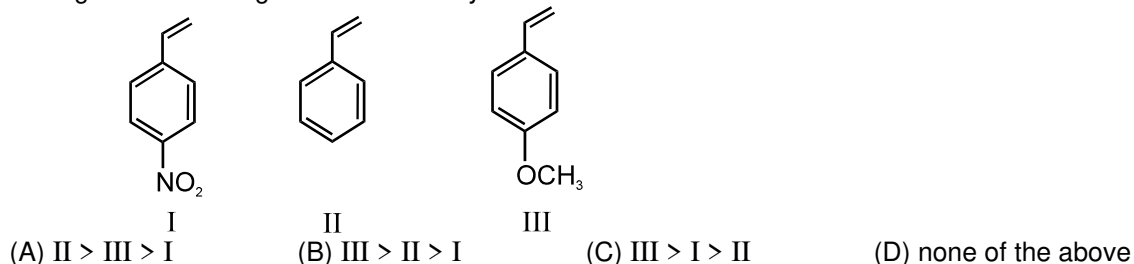
- B-10.** Anti Markownikoff addition of HBr is not observed in :
(A) Propene (B) 1-Butene (C) But-2-ene (D) Isobutene

Section (C) : Electrophilic addition reaction

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

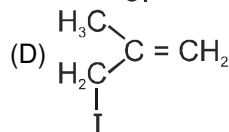
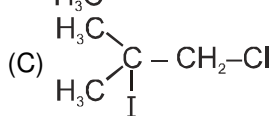
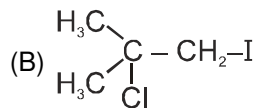
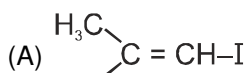
- (I) $\text{CH}_2\text{=CH}_2$ (II) $\text{CH}_3\text{--CH=CH}_2$ (III) $(\text{CH}_3)_2\text{C=CH}_2$ (IV) $\text{CH}_3\text{--CH=CH--CH}_3$
(A) III > I > II > IV (B) III > IV > II > I (C) II > IV > III > I (D) I > II > III > IV

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



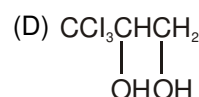
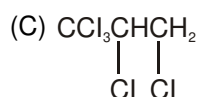
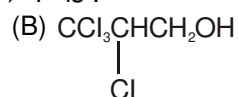
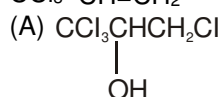


C-3. $\begin{array}{c} \text{H}_3\text{C} \\ \diagdown \\ \text{C} = \text{CH}_2 \\ \diagup \\ \text{H}_3\text{C} \end{array} + \text{ICl} \longrightarrow \text{P (major product)}, \text{ Here 'P' is :}$

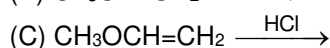
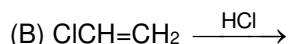
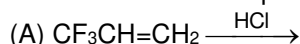


C-4. $\text{CCl}_3\text{-CH=CH}_2 \xrightarrow{\text{HOCl}} \text{P (Major product)},$

$\text{CCl}_3\text{-CH=CH}_2 \xrightarrow{\text{HOCl}} \text{'P' is :}$

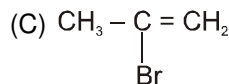
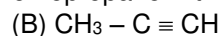
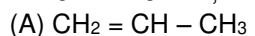


C-5. In which reaction the product following anti markonikoff rule is observed :



(D) None

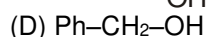
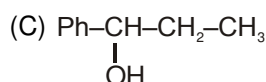
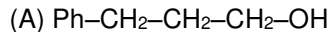
C-6. Which will form 2, 2-Dibromopropane with HBr ?



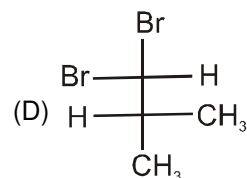
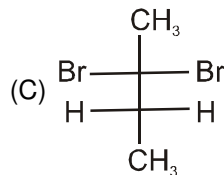
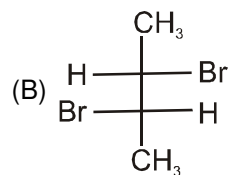
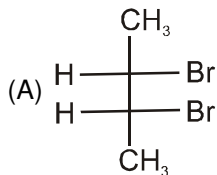
(D) Both B & C

C-7. $\text{Ph-CH}_2\text{-CH=CH}_2 \xrightarrow{\text{dil. H}_2\text{SO}_4} \text{X},$

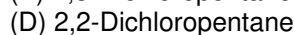
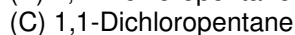
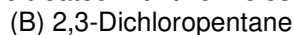
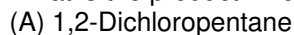
'X' is :



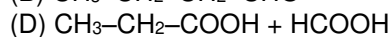
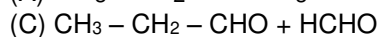
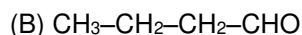
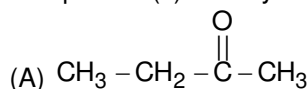
C-8. $\begin{array}{c} \text{H}_3\text{C} \\ \diagdown \\ \text{C} = \text{C} \\ \diagup \\ \text{H} \end{array} \begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C} \\ \diagdown \\ \text{H} \end{array} + \text{Br}_2 \xrightarrow{\text{CCl}_4} \text{Product is :}$



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




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





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)	$\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--CH}_3 + \text{Br}_2 \xrightarrow{h\nu}$	(1)	Electrophilic addition
(Q)	$\text{CH}_3\text{--CH=CH--CH}_3 + \text{Br}_2 \xrightarrow{\text{CCl}_4}$	(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 :

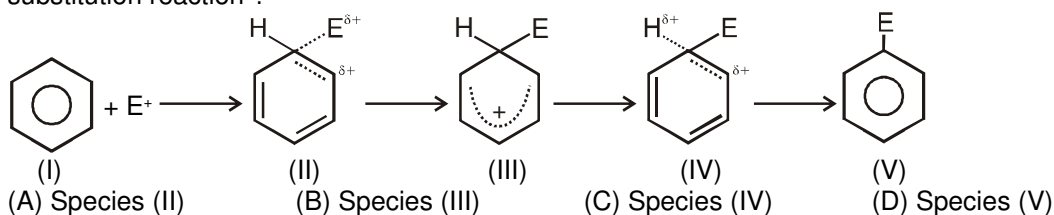
	Column-I		Column-II
	Group		Nature
(A)	$-\text{Cl}$	(p)	Activating
(B)	$-\text{CH}_3$	(q)	deactivating
(C)	$-\text{OH}$	(r)	o,p-directing
(D)	$-\text{NO}_2$	(s)	m-directing

Exercise-2

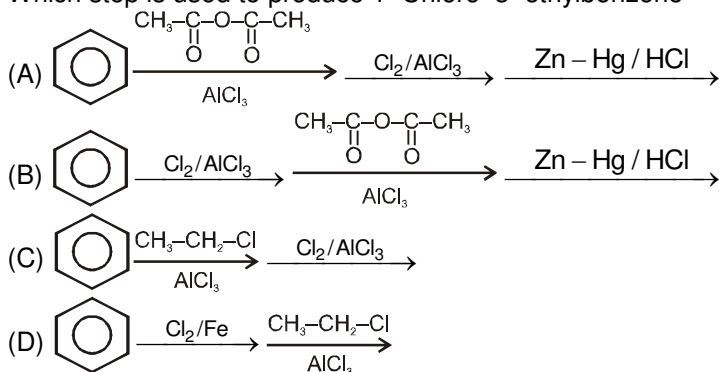
Marked questions are recommended for Revision.

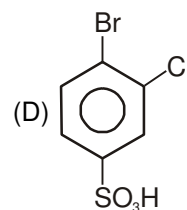
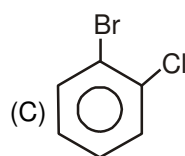
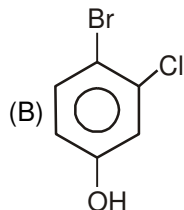
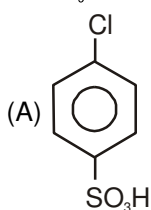
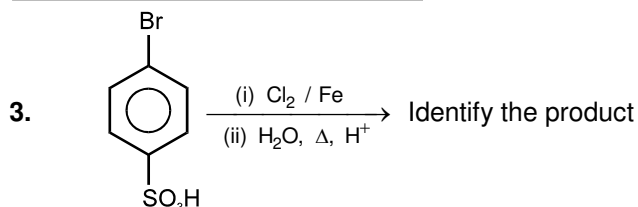
PART - I : ONLY ONE OPTION CORRECT TYPE

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



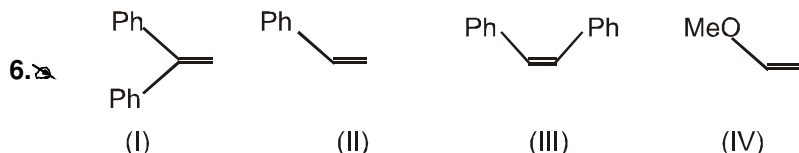


4. Which statement is correct about photochemical bromination of Butane ?

- $\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--CH}_3 \xrightarrow{\text{Br}_2, h\nu}$
- (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) is less stable than
 (B) is more stable than
 (C) Both are equally stable
 (D) Original statement is incorrect

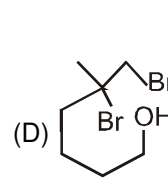
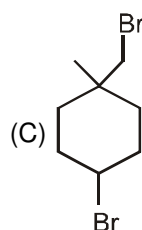
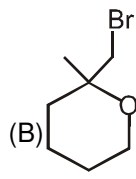
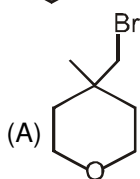
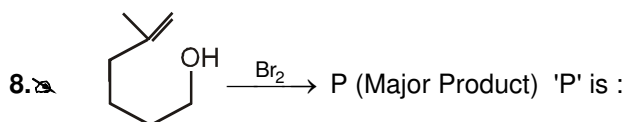


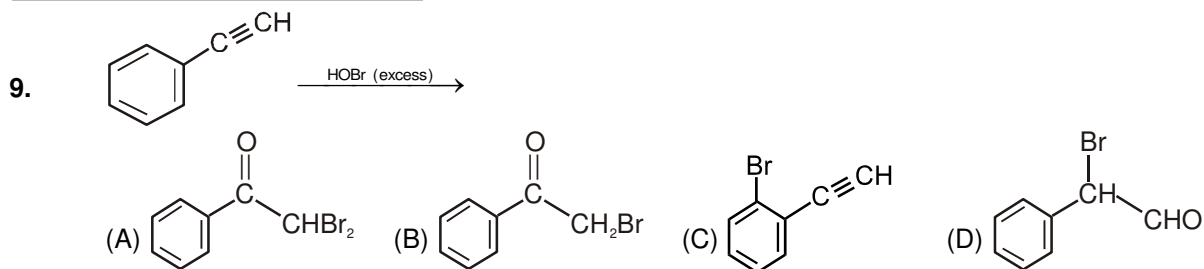
Order of rate of electrophilic addition reaction with HBr will be :

- (A) $\text{IV} > \text{I} > \text{III} > \text{II}$ (B) $\text{I} > \text{II} > \text{III} > \text{IV}$ (C) $\text{I} > \text{III} > \text{II} > \text{IV}$ (D) $\text{IV} > \text{I} > \text{II} > \text{III}$

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

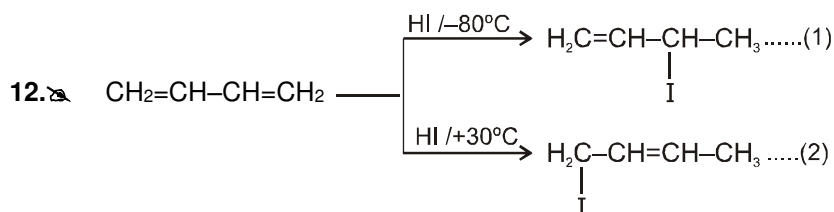
- (A) $\text{CH}_2=\text{CH--Cl} > \text{CH}_2=\text{CH--OCH}_3$
 (B) $\text{CH}_2=\text{CHCl} < \text{CH}_2=\text{CCl}_2$
 (C) $\text{CH}_2=\text{CH}_2 > \text{CH}_3\text{--CH}=\text{CH}_2$
 (D) $\text{CH}_2=\text{CH--OCH}_3 > \text{CH}_2=\text{CH--CH}_2\text{--OH}$





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

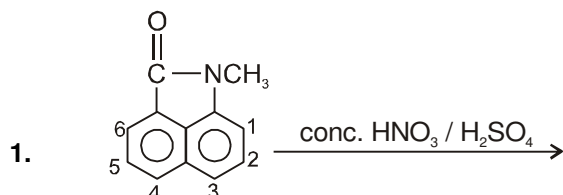
11. The reaction of one equivalent of HBr with $\text{CH}_2=\text{CH}-\text{C}\equiv\text{CH}$ gives :
 (A) $\text{CH}_2=\text{CH}-\text{C}\equiv\text{CH}$ (B) $\text{CH}_2=\text{CH}-\text{C}(\text{Br})=\text{CH}_2$
 (C) $\text{CH}_3-\text{CH}(\text{Br})-\text{C}\equiv\text{CH}$ (D) $\text{CH}_2=\text{CH}-\text{CH}=\text{CHBr}$



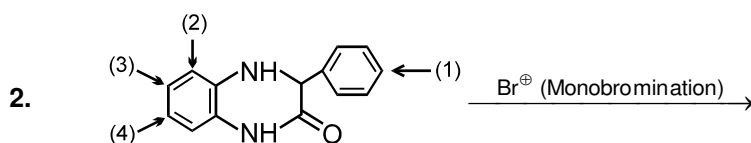
At given temperature, these reaction tell about control of reaction which is :

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

PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE



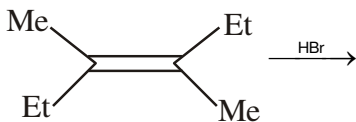
At which position nitration mainly takes place ?



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.



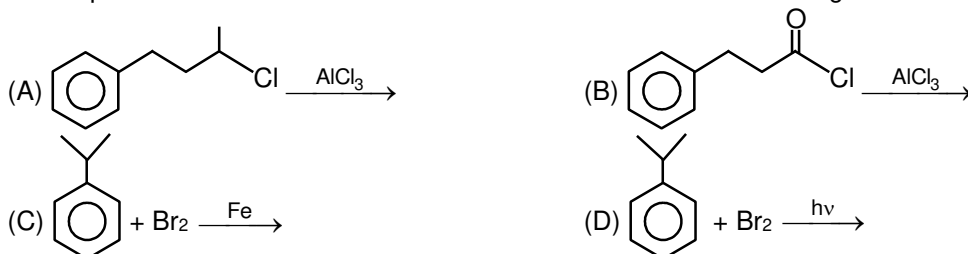
4. The number of possible enantiomer pairs that can be produced during monochlorination of 2-Methylbutane is :
5. For the given reaction how many products are optically active (all isomers) :
- $$\text{CH}_3 - \underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}} - \text{CH}_2 - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_3 \xrightarrow{\text{Br}_2 / h\nu}$$
6. Number of structural isomers which can be obtained on monochlorination of 2-Methylbutane is :
7.  $\xrightarrow{\text{HBr}}$
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
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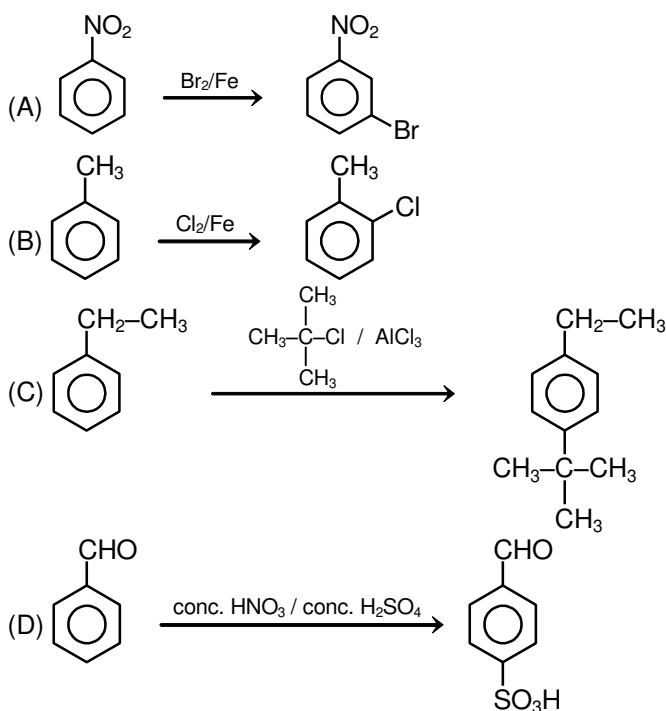
.

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

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

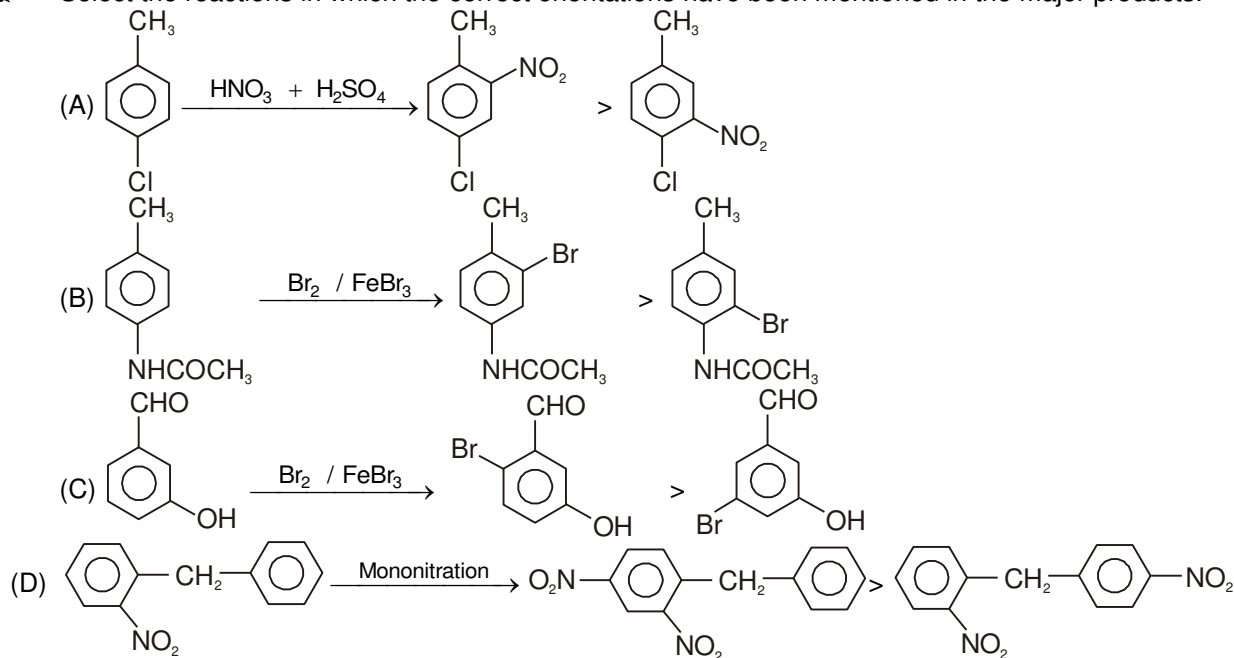


2. In which of the following reactions correct major product is given ?

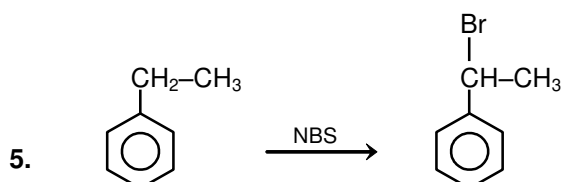
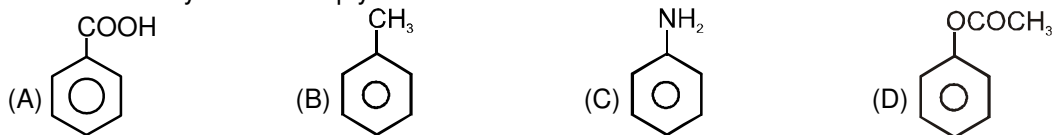




3. Select the reactions in which the correct orientations have been mentioned in the major products.

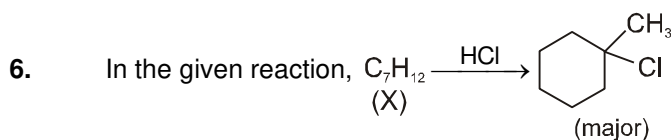


4. Friedel craft acylation is simply observed in :

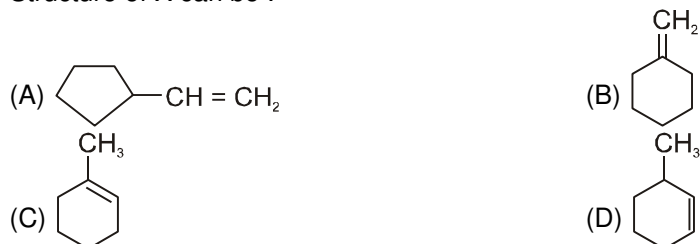


Which of the following statements are correct for above reaction.

- (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.

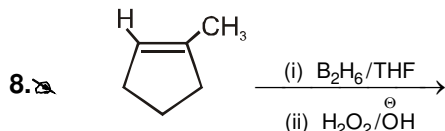
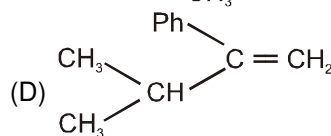
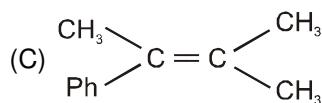
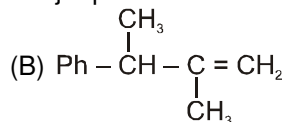
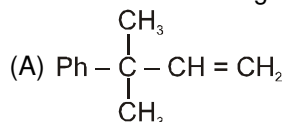


Structure of X can be :





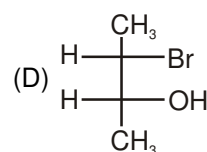
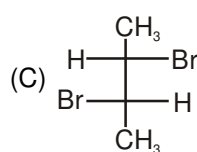
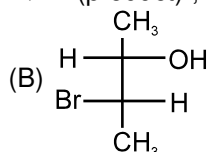
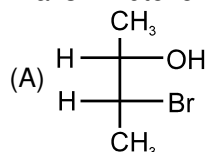
7. Which of the following compounds will give same major product on acid catalysed hydration ?



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 $\xrightarrow{\text{HOBr}}$ P (product) ; 'P' is :



10. 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 decolourise 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 $\text{CH}_2=\text{O}$ one moles of $\text{CH}_3\text{CH}=\text{O}$ 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. x, y, z are

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

2. (x, y, z) $\xrightarrow{\text{H}_3\text{O}^+}$ 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.

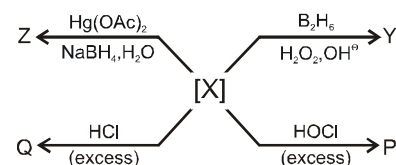
3. What is true about x, y, z.

- (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.



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 reagent 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

* Marked Questions may have more than one correct option.

PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

1. In the presence of peroxide, hydrogen chloride and hydrogen iodide do not give anti-Markovnikov addition to alkenes because :
 (A) both are highly ionic
 (B) one is oxidising and the other is reducing
 (C) one of the steps is endothermic in both the cases
 (D) all the steps are exothermic in both the cases.



2. The reaction of propene with HOCl proceeds via the addition of [IIT-JEE-2001(S), 3/135]
 (A) H^+ in the first step (B) Cl^+ in the first step
 (C) OH^- in the first step (D) Cl^+ and OH^- in a single step
3. **Assertion** : Addition of bromine to trans-2-butene yields meso-2, 3-dibromobutane.
Reason : Addition of bromine to an alkene is an electrophilic addition. [IIT-JEE-2001(S), 3/135]
 (A) Both Assertion and Reason are true and Reason is the correct explanation of Assertion.
 (B) Both Assertion and Reason are true but Reason is not correct explanation of Assertion.
 (C) Assertion is true but Reason is false.
 (D) Assertion is false but Reason is true.
4. Identify the correct order of reactivity in electrophilic substitution reactions of the following compounds [IIT-JEE-2002(S), 3/150]
- 1

2

3

4
- (A) $1 > 2 > 3 > 4$ (B) $4 > 3 > 2 > 1$ (C) $2 > 1 > 3 > 4$ (D) $2 > 3 > 1 > 4$
5. Consider the following reaction
- $$\begin{array}{c}
 H_3C - CH - CH - CH_3 + \cdot Br \rightarrow 'X' + HBr \\
 | \quad | \\
 D \quad CH_3
 \end{array}$$
- Identify the structure of the major product 'X'. [IIT-JEE-2002(S), 3/150]
- (A)
 $H_3C - CH - CH - \dot{C}H_2$
 $| \quad |$
 $D \quad CH_3$

(B)
 $H_3C - CH - \dot{C} - CH_3$
 $| \quad |$
 $D \quad CH_3$

(C)
 $H_3C - \dot{C} - CH - CH_3$
 $| \quad |$
 $D \quad CH_3$

(D)
 $H_3C - \dot{C}H - CH - CH_3$
 $|$
 CH_3
6. $Ph-C \equiv C-CH_3 \xrightarrow{Hg^{2+} / H^+} A$, A is : [JEE-2003, 3/144]
- (A)
 $Ph - C(=O) - CH_2 - CH_3$

(B)
 $Ph - C(=O) - CH_2 - CH_3$

(C)
 $Ph - CH(OH) - CH_2 - CH_3$

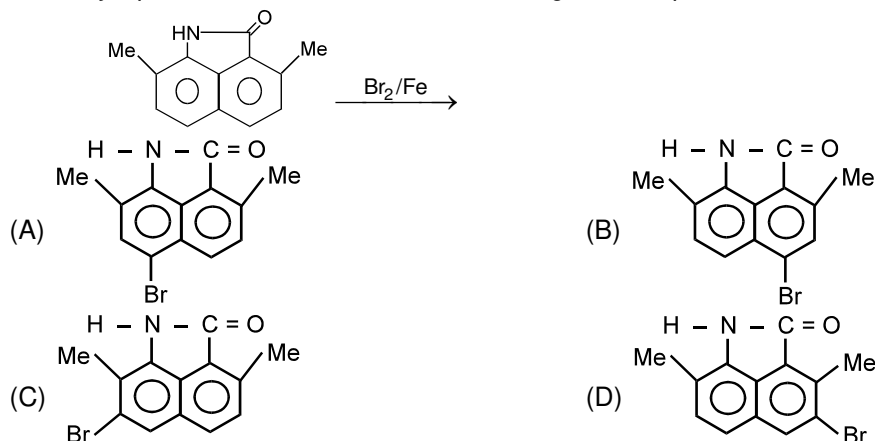
(D)
 $Ph - C(OH)=CH - CH_3$
7. The number of chiral compounds produced upon monochlorination of 2-methylbutane is : [JEE-2004, 3/144]
 (A) 2 (B) 4 (C) 6 (D) 8
8. The major product obtained on acid-catalysed hydration of 2-phenylpropene is [JEE-2004, 3/144]
 (A) 2-Phenylpropan-2-ol (B) 2-Phenylpropan-1-ol
 (C) 3-Phenylpropan-2-ol (D) 1-Phenylpropan-1-ol
9. $(CH_3)_2CH-CH_2CH_3 \xrightarrow{Cl_2 / h\nu} [N] \xrightarrow{\text{Fractional distillation}} [P]$
 The number of possible isomers [N] and number of fractions [P] are : [JEE-2006, 5/184]
 (A) (6, 6) (B) (6, 4) (C) (4, 4) (D) (3, 3)



10. $\text{CH}_2=\text{CH}-\text{CH}_3 \xrightarrow{\text{NOCl}} \text{X}$, X is : [JEE-2006, 3/184]

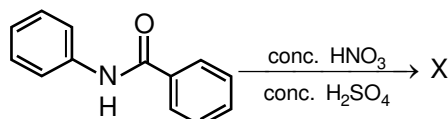


11. The major product of monobromination of the given compound with Br_2 / Fe is - [JEE-2006, 3/184]



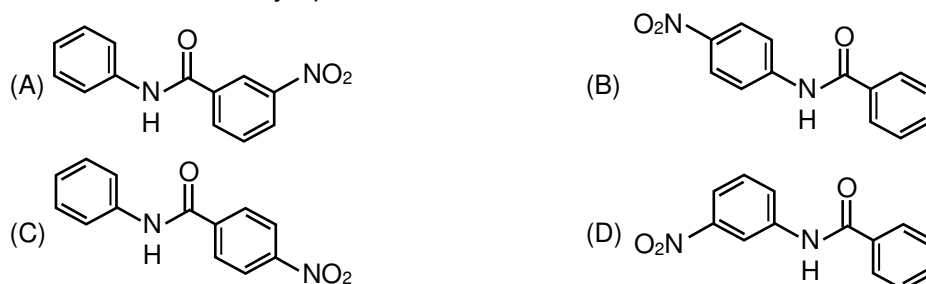
12. The number of stereoisomers obtained by bromination of trans-2-butene is : [IIT-JEE-2007, 3/162]
- (A) 1 (B) 2 (C) 3 (D) 4

13. In the following reaction,



the structure of the major product 'X' is :

[JEE 2007, 3/162]



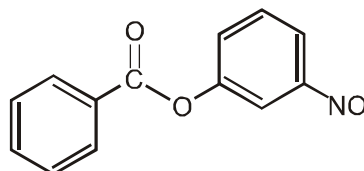
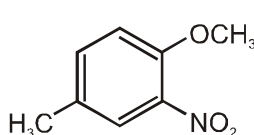
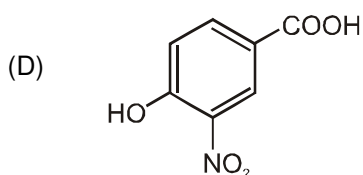
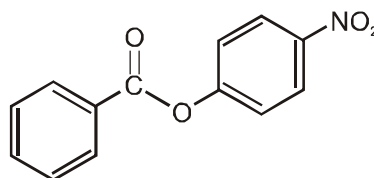
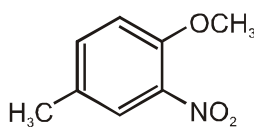
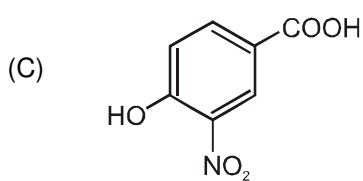
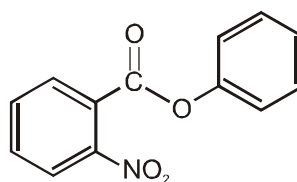
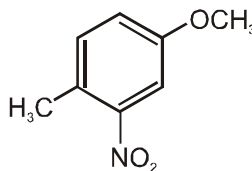
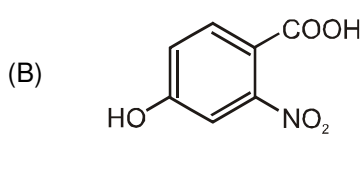
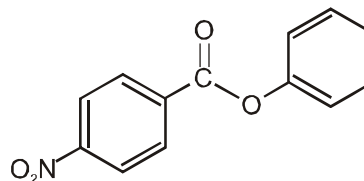
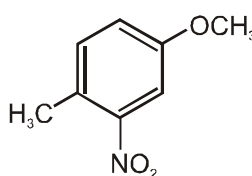
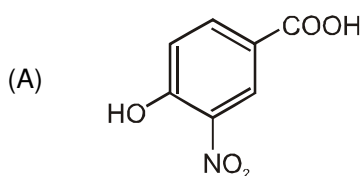
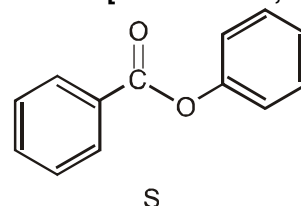
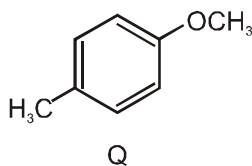
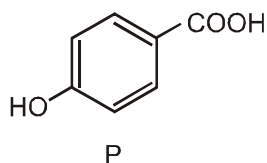
14. **Statement-1** : Bromobenzene upon reaction with Br_2/Fe gives 1,4-dibromobenzene as the major product.

Statement-2 : In bromobenzene, the inductive effect of the bromo group is more dominant than the mesomeric effect in directing the incoming electrophile. [IIT-JEE-2008, 3/162]

- (A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
 (B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1
 (C) Statement-1 is True, Statement-2 is False
 (D) Statement-1 is False, Statement-2 is True

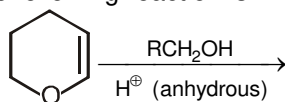


15. The compounds P, Q and S were separately subjected to nitration using $\text{HNO}_3 / \text{H}_2\text{SO}_4$ mixture. The major product formed in each case respectively, is : [IIT-JEE-2010, 5/163]



16. The major product of the following reaction is

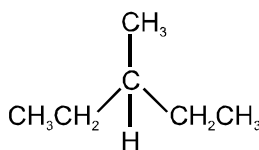
[IIT-JEE-2011, 3/160]



- (A) a hemiacetal
(C) an ether

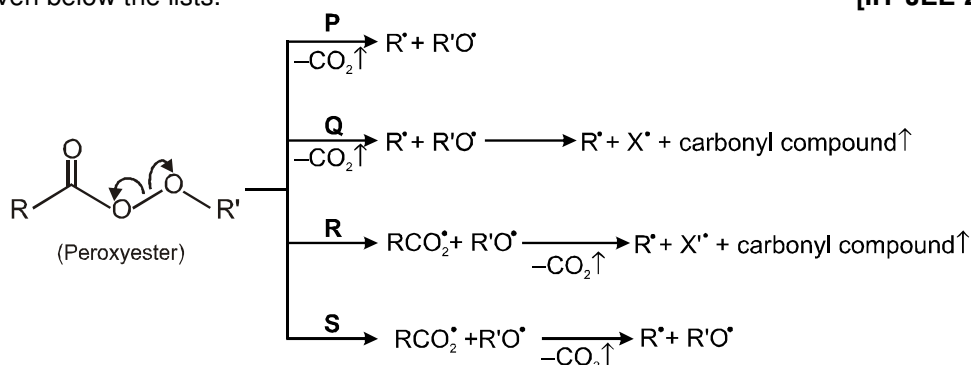
- (B) an acetal
(D) an ester

17. The maximum number of isomers (including stereoisomers) that are possible on monochlorination of the following compound, is : [IIT-JEE-2011, 4/160]





18. Different possible **thermal** decomposition pathways for peroxyesters are shown below. Match each pathway from **List I** with an appropriate structure from **List II** and select the correct answer using the code given below the lists. [IIT-JEE-2014, 3/160]



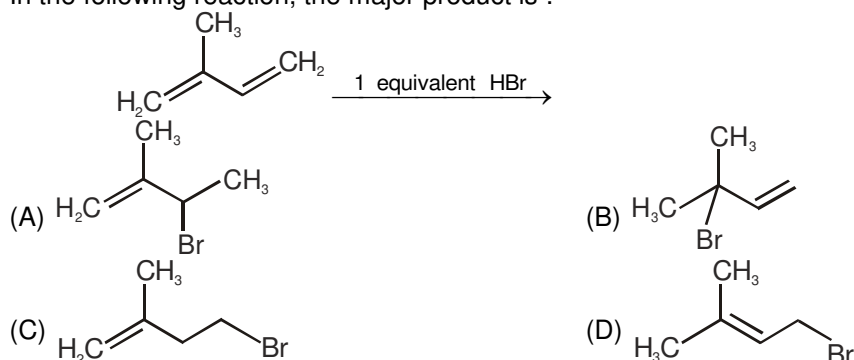
	List-I		List-II
P.	Pathway P	1.	
Q.	Pathway Q	2.	
R.	Pathway R	3.	
S.	Pathway S	4.	

Code :

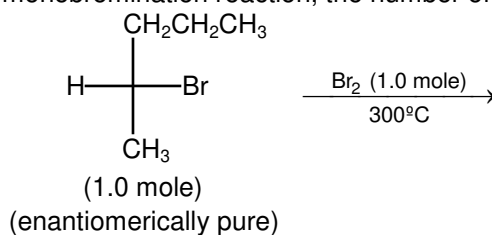
	P	Q	R	S		P	Q	R	S
(A)	1	3	4	2	(B)	2	4	3	1
(C)	4	1	2	3	(D)	3	2	1	4

19. In the following reaction, the major product is :

[JEE-2015, 4/168]



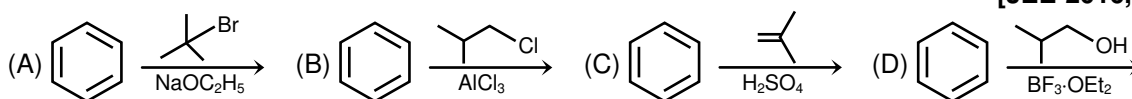
20. In the following monobromination reaction, the number of possible chiral products is [JEE-2016, 3/60]





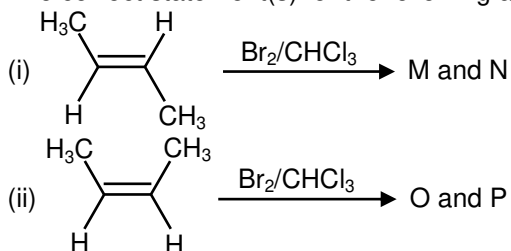
21.* Among the following, reaction(s) which gives(give) *tert*-butyl benzene as the major product is(are)

[JEE-2016, 3/60]



22.* The correct statement(s) for the following addition reactions is (are)

[JEE Advanced-2017, 4/122]



- (A) (**M** and **O**) and (**N** and **P**) are two pairs of enantiomers
 (B) Bromination proceeds through trans-addition in both the reactions
 (C) **O** and **P** are identical molecules
 (D) (**M** and **O**) and (**N** and **P**) are two pairs of diastereomers

PART - II : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

JEE(MAIN) OFFLINE PROBLEMS

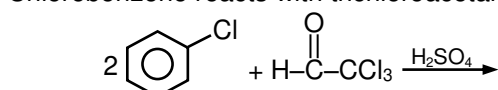
- What is the product when acetylene reacts with hypochlorous acid ? [AIEEE-2002, 3/225]
 (1) CH_3COCl (2) ClCH_2CHO (3) Cl_2CHCHO (4) ClCH_2COOH .
- Reaction of one molecule of HBr with one molecule of 1, 3-butadiene at 40°C gives predominantly [AIEEE-2005, 3/225]
 (1) 3-bromobutene under kinetically controlled conditions
 (2) 1-bromo-2-butene under thermodynamically controlled conditions
 (3) 3-bromobutene under thermodynamically controlled conditions.
 (4) 1-bromo-2-butene under kinetically controlled conditions.
- Acid catalyzed hydration of alkenes except ethene leads to the formation of [AIEEE-2005, 3/225]
 (1) Mixture of secondary and tertiary alcohols (2) Mixture of primary and secondary alcohols
 (3) Secondary or tertiary alcohol (4) Primary alcohol
- 2-Methylbutane on reacting with bromine in the presence of sunlight gives mainly? [AIEEE-2005, 3/225]
 (1) 1-Bromo-3-methylbutane (2) 1-Bromo-2-methylbutane
 (3) 2-Bromo-3-methylbutane (4) 2-Bromo-2-methylbutane
- HBr reacts with $\text{CH}_2=\text{CH}-\text{OCH}_3$ under anhydrous conditions at room temperature to give [AIEEE-2006, 3/165]
 (1) CH_3CHO and CH_3Br (2) BrCH_2CHO and CH_3Br
 (3) $\text{BrCH}_2-\text{CH}_2-\text{OCH}_3$ (4) $\text{H}_3\text{C}-\text{CHBr}-\text{OCH}_3$
- The reaction of toluene with Cl_2 in presence of FeCl_3 gives predominantly : [AIEEE-2007, 3/120]
 (1) *o*- and *p*-chlorotoluene (2) *m*-chlorotoluene
 (3) benzoylchloride (4) benzyl chloride
- Which of the following reactions will yield 2,2-dibromopropane ? [AIEEE-2007, 3/120]
 (1) $\text{CH}_3-\text{C}\equiv\text{CH} + 2\text{HBr} \rightarrow$ (2) $\text{CH}_3\text{CH}=\text{CHBr} + \text{HBr} \rightarrow$
 (3) $\text{CH}\equiv\text{CH} + 2\text{HBr} \rightarrow$ (4) $\text{CH}_3-\text{CH}=\text{CH}_2 + \text{HBr} \rightarrow$
- Presence of a nitro group in a benzene ring [AIEEE-2007, 3/120]
 (1) activates the ring towards electrophilic substitution
 (2) renders the ring basic
 (3) deactivates the ring towards nucleophilic substitution.
 (4) deactivates the ring towards electrophilic substitution.



9. The electrophile, E^+ attacks the benzene ring to generate the intermediate σ -complex. Of the following, which σ -complex is of lowest energy ? [AIEEE-2008, 3/105]
- (1) (2) (3) (4)
10. How many chiral compounds are possible on monochlorination of 2-methylbutane [AIEEE-2012, 4/120]
 (1) 8 (2) 2 (3) 4 (4) 6
11. Which branched chain isomer of the hydrocarbon with molecular mass 72u gives only one isomer of mono substituted alkyl halide ? [AIEEE-2012, 4/120]
 (1) Tertiary butyl chloride (2) Neopentane
 (3) Isohexane (4) Neohexane
12. The reaction of propene with HOCl ($Cl_2 + H_2O$) proceeds through the intermediate : [JEE-Main 2016, 4/120]
 (1) $CH_3-CH^+-CH_2-Cl$ (2) $CH_3-CH(OH)-CH_2^+$
 (3) $CH_3-CHCl-CH_2^+$ (4) $CH_3-CH^+-CH_2-OH$
13. 3-Methyl-pent-2-ene on reaction with HBr in presence of peroxide forms an addition product. The number of possible stereoisomers for the product is : [JEE-Main 2017, 4/120]
 (1) Zero (2) Two (3) Four (4) Six

JEE(MAIN) ONLINE PROBLEMS

1. In the hydroboration-oxidation reaction of propene with diborane, H_2O_2 and NaOH, the organic compound formed is : [JEE(Main) 2014 Online (09-04-14), 4/120]
 (1) CH_3CH_2OH (2) $CH_3CHOHCH_3$
 (3) $CH_3CH_2CH_2OH$ (4) $(CH_3)_3COH$
2. Chlorobenzene reacts with trichloroacetaldehyde in the presence of H_2SO_4



The major product formed is :

[JEE(Main) 2014 Online (11-04-14), 4/120]

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

3. on mercuration-demercuration produces the major product.

[JEE(Main) 2014 Online (12-04-14), 4/120]

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



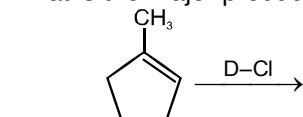
4. In the presence of peroxide, HCl and HI do not give anti-Markownikoff's addition to alkenes because: [JEE(Main) 2014 Online (12-04-14), 4/120]

(1) One of the steps is endothermic in HCl and HI.
 (2) Both HCl and HI are strong acids.
 (3) HCl is oxidizing and the HI is reducing.
 (4) All the steps are exothermic in HCl and HI.

5. The major product obtained in the photo catalyzed bromination of 2-methylbutane is : [JEE(Main) 2014 Online (12-04-14), 4/120]

(1) 1-bromo-2-methylbutane (2) 1-bromo-3-methylbutane
 (3) 2-bromo-3-methylbutane (4) 2-bromo-2-methylbutane

- 6.* What is the major product expected from the following reaction ?

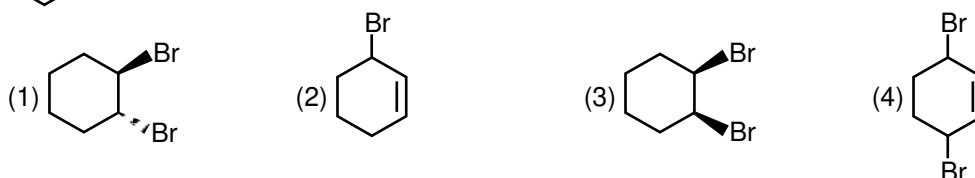
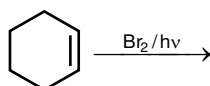


Where D is an isotope of hydrogen.

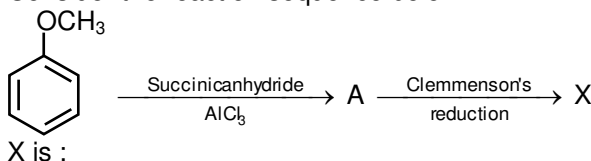
[JEE(Main) 2015 Online (11-04-15), 4/120]



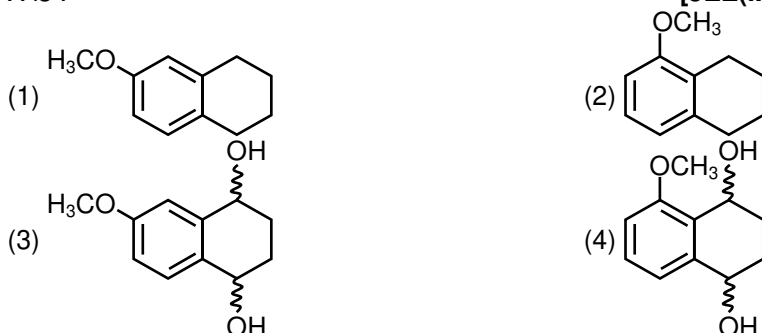
7. Bromination of cyclohexene under conditions given below yields: [JEE(Main) 2016 Online (10-04-16), 4/120]



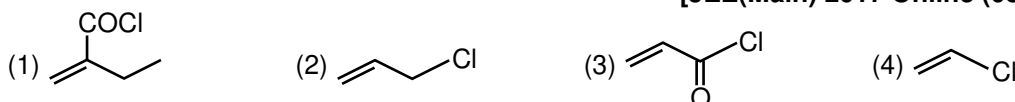
8. Consider the reaction sequence below :



[JEE(Main) 2016 Online (10-04-16), 4/120]



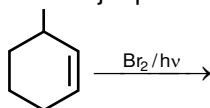
9. Which of the following compounds will not undergo Friedel Craft's reaction with benzene ? [JEE(Main) 2017 Online (08-04-17), 4/120]





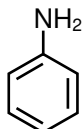
10. The major product of the following reaction is :

[JEE(Main) 2017 Online (09-04-17), 4/120]

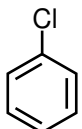


11. The increasing order of nitration of the following compounds is :

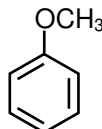
[JEE(Main) 2018 Online (15-04-18), 4/120]



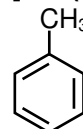
(a)



(b)



(c)



(d)

(1) (a) < (b) < (d) < (c)

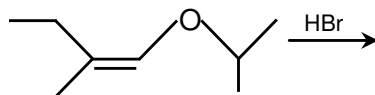
(3) (b) < (a) < (c) < (d)

(2) (a) < (b) < (c) < (d)

(4) (b) < (a) < (d) < (c)

12. The total number of optically active compounds formed in the following reaction is :

[JEE(Main) 2018 Online (15-04-18), 4/120]



(1) Two

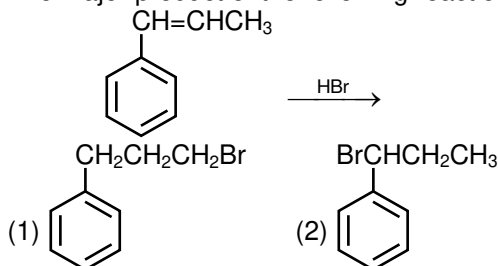
(2) Four

(3) Six

(4) Zero

13. The major product of the following reaction is :

[JEE(Main) 2018 Online (15-04-18), 4/120]



(1)

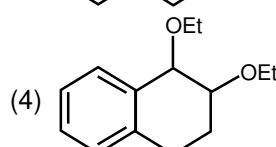
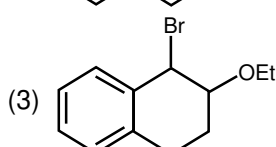
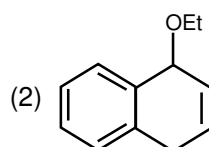
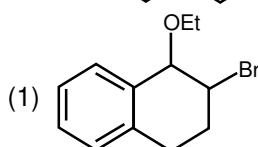
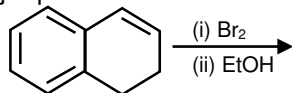
(2)

(3)

(4)

14. The major product of the following reaction is :

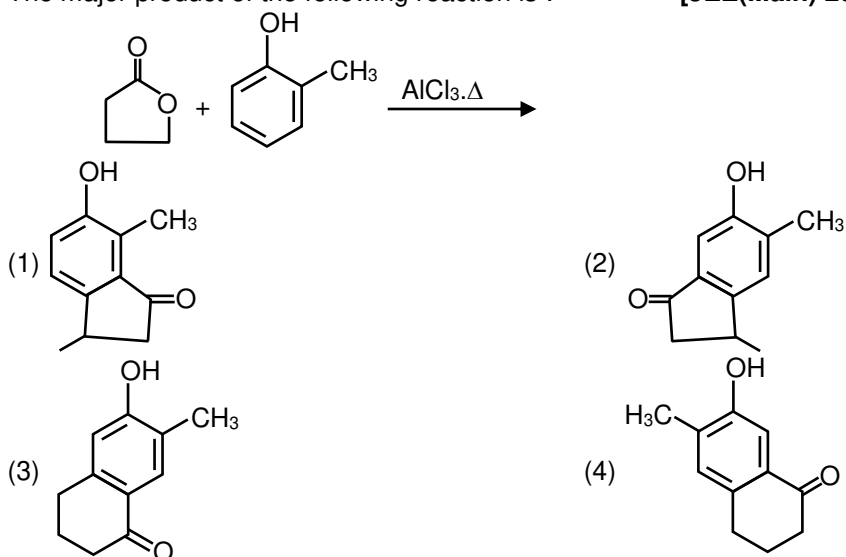
[JEE(Main) 2019 Online (09-01-19), 4/120]





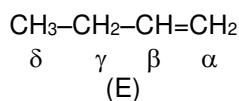
15. The major product of the following reaction is :

[JEE(Main) 2019 Online (09-01-19), 4/120]



16. Which hydrogen in compound (E) is easily replaceable during bromination reaction in presence of light?

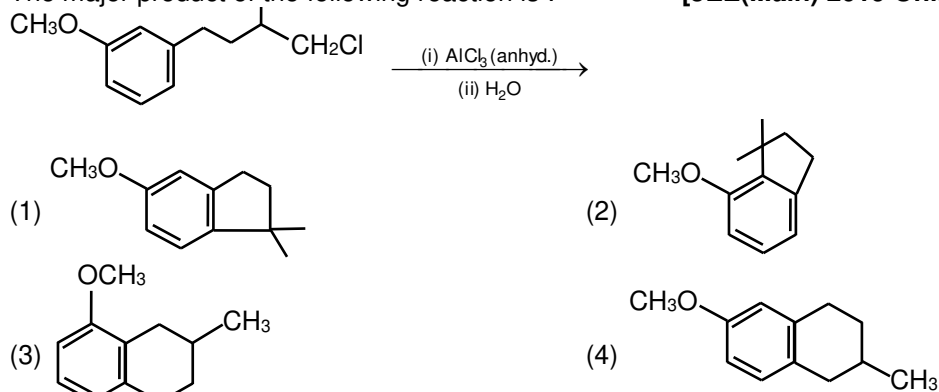
[JEE(Main) 2019 Online (10-01-19), 4/120]



- (1) α -hydrogen (2) γ -hydrogen (3) β -hydrogen (4) δ -hydrogen

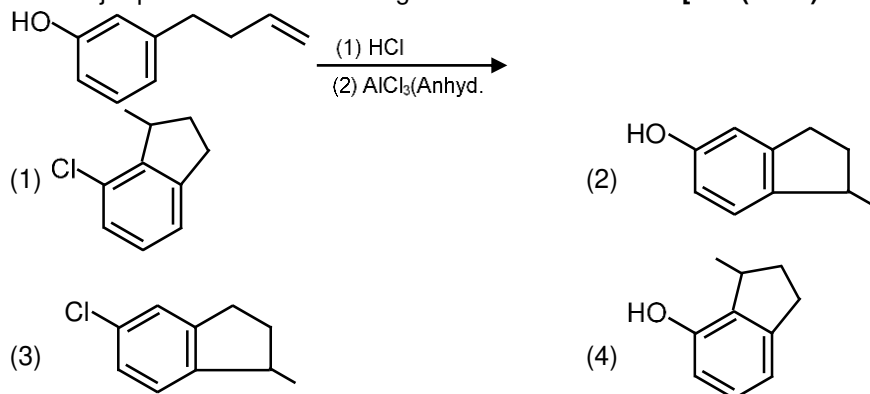
17. The major product of the following reaction is :

[JEE(Main) 2019 Online (10-01-19), 4/120]



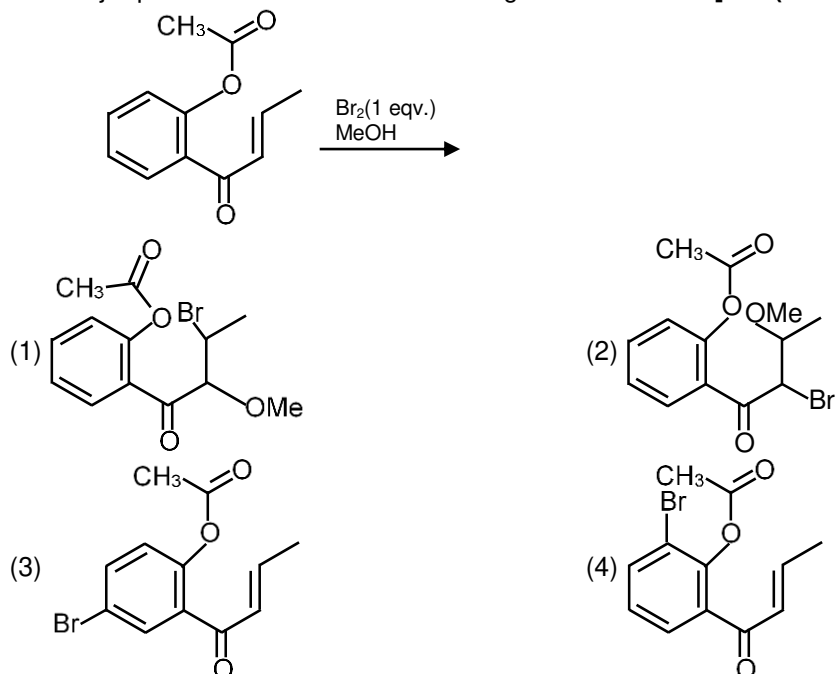
18. The major product of the following reaction is :

[JEE(Main) 2019 Online (11-01-19), 4/120]

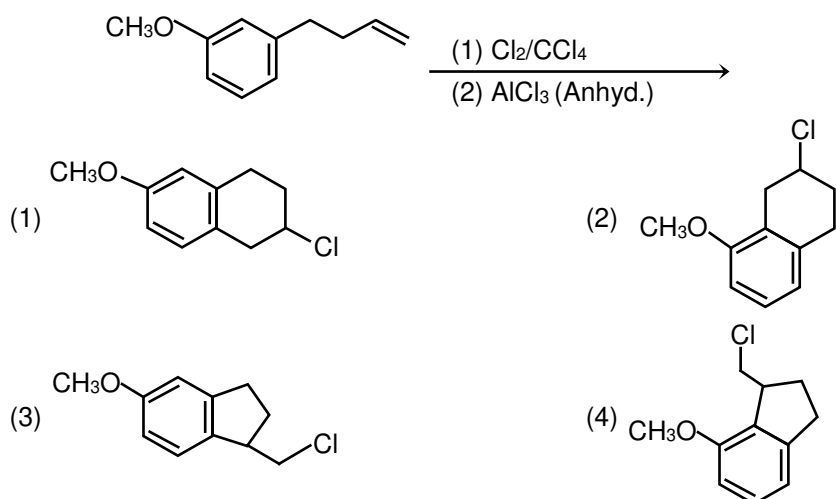




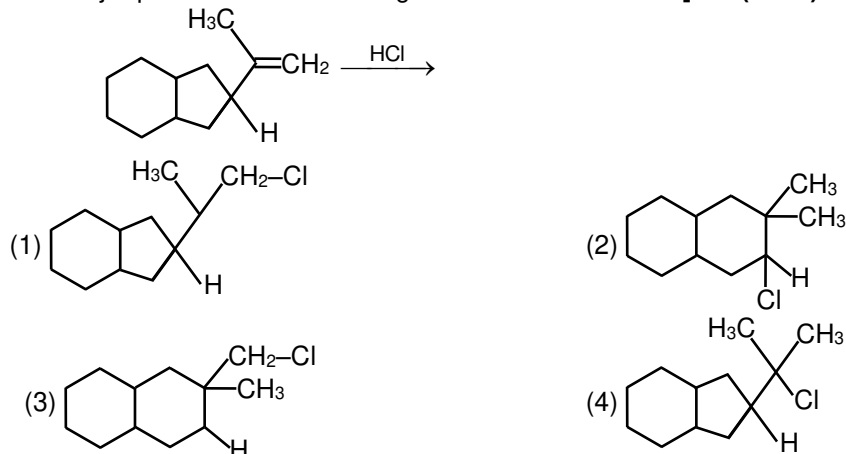
19. The major product obtained in the following conversion is: [JEE(Main) 2019 Online (11-01-19), 4/120]



20. The major product of the following reactions is: [JEE(Main) 2019 Online (12-01-19), 4/120]



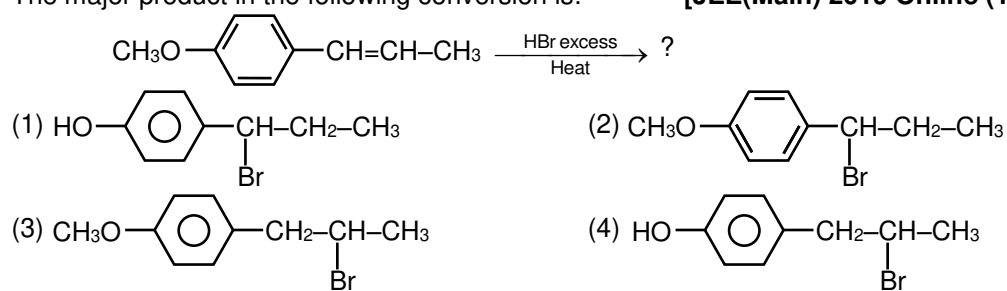
21. The major product of the following reaction is: [JEE(Main) 2019 Online (12-01-19), 4/120]





22. The major product in the following conversion is:

[JEE(Main) 2019 Online (12-01-19), 4/120]





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)

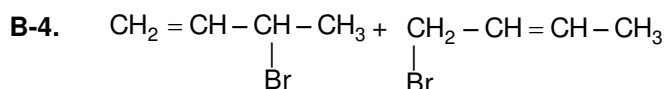
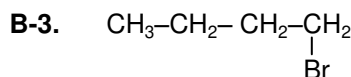
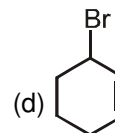
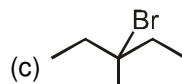
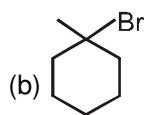
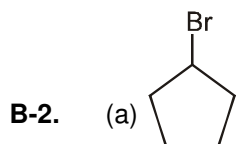
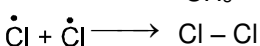
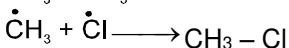
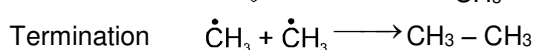
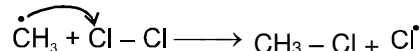
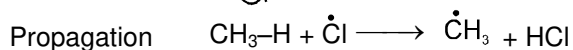
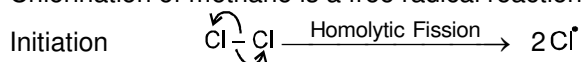
(b) (II) > (III) > (I)

(c) (II) > (I) > (III)

(d) (III) > (I) > (II)

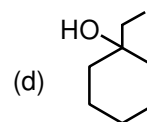
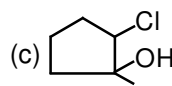
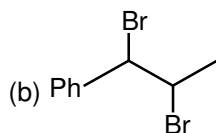
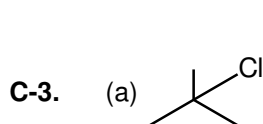
A-5. In vinyl chloride and chloro benzene lone pair on Cl atom takes part in conjugation. So, partial double bond character between C-Cl bond is developed.

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.
 $3^\circ \text{ carbocation} > 2^\circ \text{ carbocation} > 1^\circ \text{ carbocation}$ (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)
B-8. (D)	B-9. (A)	B-10. (C)	C-1. (B)	C-2. (B)
C-3. (B)	C-4. (B)	C-5. (A)	C-6. (D)	C-7. (C)
C-8. (B)	C-9. (D)	C-10. (A)		

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)
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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

JEE(MAIN) OFFLINE PROBLEMS

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)				

JEE(MAIN) ONLINE PROBLEMS

1.	(3)	2.	(3)	3.	(1)	4.	(1)	5.	(4)
6.*	(2,3)	7.	(2)	8.	(1)	9.	(4)	10.	(4)
11.	(1)	12.	(2)	13.	(2)	14.	(1)		
15.	NTA answer was (4), but correct answer is (3).					16.	(2)	17.	(1)
18.	(2)	19.	(2)	20.	(3)	21.	(4)	22.	(1)



Additional Problems For Self Practice (APSP)

✎ Marked questions are recommended for Revision.

This Section is not meant for classroom discussion. It is being given to promote self-study and self testing amongst the Resonance students.

PART - I : PRACTICE TEST-1 (IIT-JEE (MAIN Pattern))

Max. Time : 1 Hr.

Max. Marks : 120

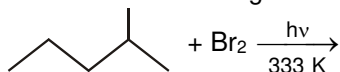
Important Instructions

- The test is of **1 hour** duration.
- The Test Booklet consists of **30** questions. The maximum marks are **120**.
- Each question is allotted **4 (four)** marks for correct response.
- Candidates will be awarded marks as stated above in Instructions No. 3 for correct response of each question. **¼ (one fourth)** marks will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
- There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted accordingly as per instructions 4 above.

- $\text{CH}_3\text{CH}=\text{CH}_2 \xrightarrow{\text{X}} \text{BrCH}_2\text{CH}=\text{CH}_2$
 x is :
 (1) $\text{Br}_2 / \text{H}_2\text{O}$ (2) HBr (3) $\text{HBr} / \text{Peroxide}$ (4) NBS
- Which of the following reactions is not an electrophilic addition reactions –
 (1) $\text{Cyclopentene} \xrightarrow[\text{CCl}_4]{\text{Br}_2}$ (2) $\text{Cyclopentene} \xrightarrow{\text{H}^+/\text{H}_2\text{O}}$
 (3) $\text{Cyclopentene} \xrightarrow[\text{R}_2\text{O}_2]{\text{HBr}}$ (4) $\text{Cyclopentene} \xrightarrow[(2) \text{NaBH}_4]{(1) \text{Hg}(\text{OAc})_2, \text{H}_2\text{O}}$
- ✎ The chlorination of Toluene in presence of ferric chloride gives predominately :
 (1) Benzyl chloride (2) m-Chlorotoluene (3) Benzal chloride (4) o- and p-Chlorotoluene
- ✎ Nitrobenzene can be prepared from benzene by using a mixture of conc. HNO_3 and conc. H_2SO_4 . In the nitrating mixture HNO_3 acts as a :
 (1) Base (2) Acid (3) Reducing agent (4) Catalyst
- Ethylbenzene + $\text{Cl}_2 \xrightarrow{\text{Light}}$ major product is :
 (1) o- & p-chloroethylbenzene (2) 1-Chloroethylbenzene
 (3) 2-Chloroethylbenzene (4) m-Chloroethylbenzene
- ✎ Which of the following is not o, p-directing group?
 (1) $-\text{NH}_2$ (2) $-\text{OH}$ (3) $-\text{X}(\text{halogens})$ (4) $-\text{CHO}$
- Presence of a cyano group in a benzene ring.
 (1) Activates the ring towards electrophilic substitution.
 (2) Renders the ring basic.
 (3) Deactivates the ring towards nucleophilic substitution.
 (4) Deactivates the ring towards electrophilic substitution.
- The relative rates of mononitration of $\text{R}-\text{C}_6\text{H}_5$, where $\text{R}=\text{CH}_3, -\text{NO}_2, -\text{OH}, -\text{Cl}$ are :
 (1) $\text{CH}_3 > \text{OH} > \text{NO}_2 > \text{Cl}$ (2) $\text{OH} > \text{Cl} > \text{CH}_3 > \text{NO}_2$
 (3) $\text{OH} > \text{CH}_3 > \text{NO}_2 > \text{Cl}$ (4) $\text{OH} > \text{CH}_3 > \text{Cl} > \text{NO}_2$
- In the free radical chlorination of Methane, the chain initiating step involves the formation of
 (1) Chlorine radical (2) Hydrogen chloride (3) Methyl radical (4) Chloromethyl radical.



10. Which of the following is the major product for the given reaction ?



- (1) 2-Bromo-2-methylpentane
(3) 4-Bromo-2-methylpentane

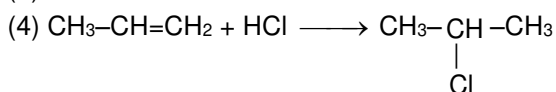
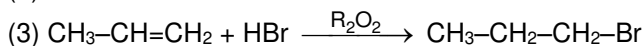
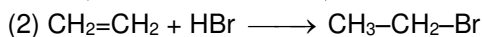
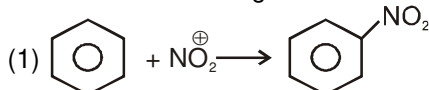
- (2) 1-Bromo-2-methylpentane
(4) 3-Bromo-2-methylpentane

11. Allylic bromination of an olefin is :

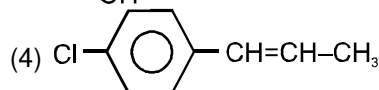
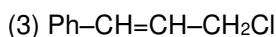
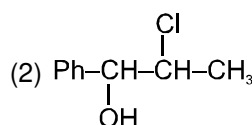
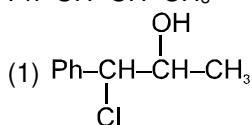
- (1) Nucleophilic substitution
(3) Free radical substitution

- (2) Electrophilic substitution
(4) Electrophilic addition.

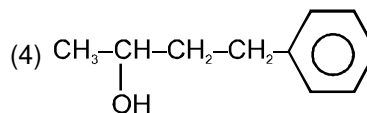
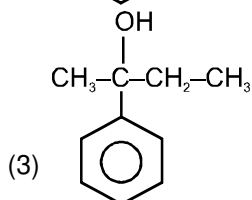
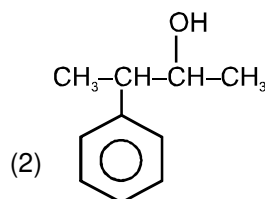
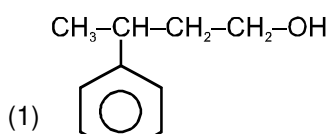
12. Which of the following is free radical addition reaction ?



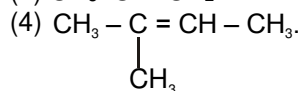
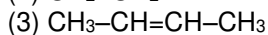
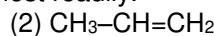
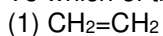
13. $\text{Ph}-\text{CH}=\text{CH}-\text{CH}_3 \xrightarrow{\text{HOCl}} \text{X}$, X is :



14. $\text{CH}_3-\underset{\text{C}_6\text{H}_5}{\text{CH}}-\text{CH}=\text{CH}_2 \xrightarrow{\text{H}_3\text{O}^+} \text{P (major)}$, P is :

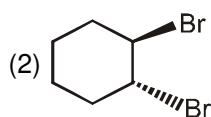
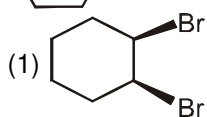


15. To which of the following compounds Br_2 adds most readily.





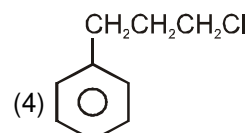
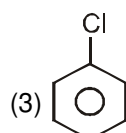
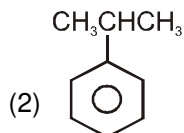
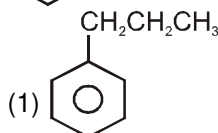
16. + Br₂ → P, P will have configuration:



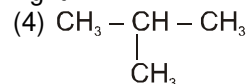
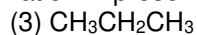
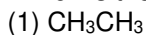
(3) both are true

(4) none is true

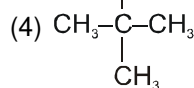
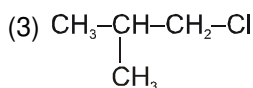
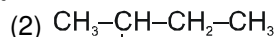
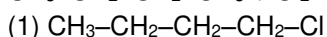
17. + CH₃CH₂CH₂Cl $\xrightarrow{\text{AlCl}_3}$ Major Product



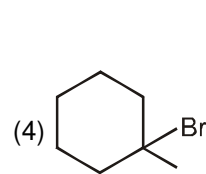
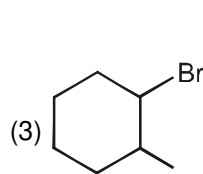
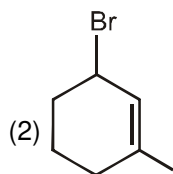
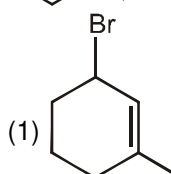
18. Which is the most reactive alkane towards bromination in presence of sunlight ?



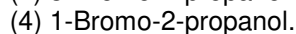
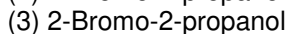
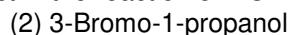
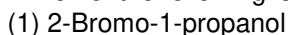
19. CH₃-CH₂-CH₂-CH₃ + Cl₂ $\xrightarrow{h\nu}$ Major product :



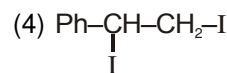
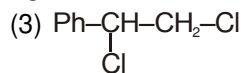
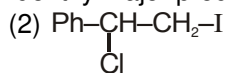
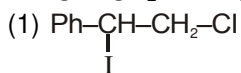
20. + HBr $\xrightarrow{\text{R}_2\text{O}_2}$ Product; Product is :



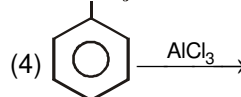
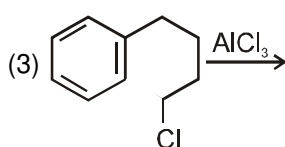
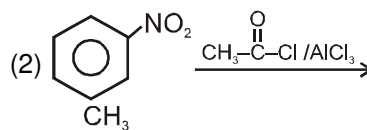
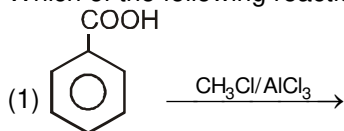
21. Which of the following is the predominant product in the reaction of HOBr with propene ?



22. Ph-CH=CH₂ $\xrightarrow{\text{ICl}}$ P, Identify major product 'P' is :



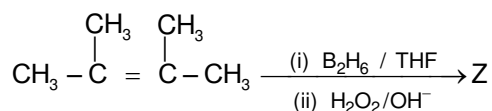
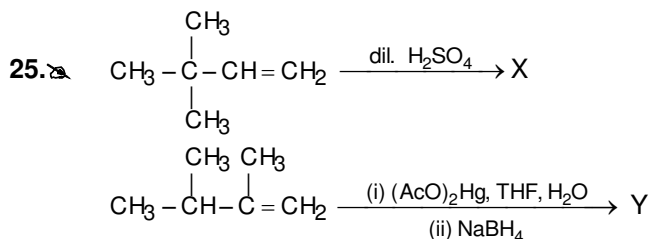
23. Which of the following reaction is feasible ?



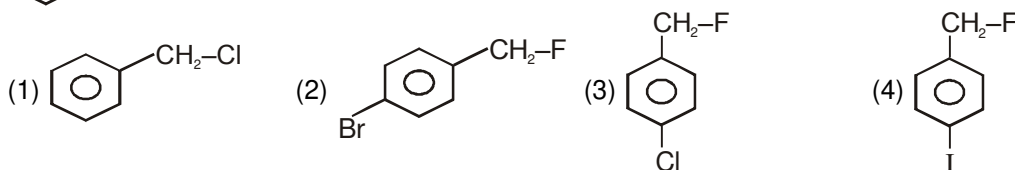
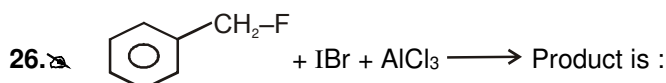


24. o,p-directing group are mostly :

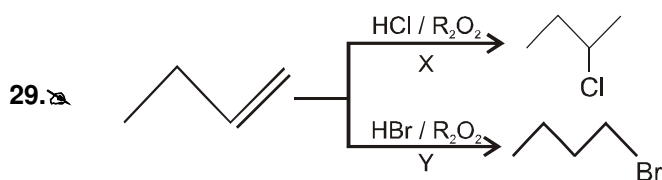
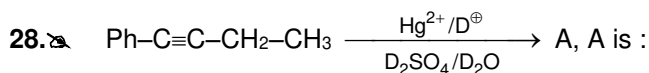
- (1) Activating group (2) Deactivating groups
(3) Neutral groups (4) None of these



- (1) All three products (X, Y, Z) are different. (2) X and Y are identical but Z is different.
(3) Y and Z are identical but X is different. (4) All three products (X, Y, Z) are identical.



27. When HBr adds to 1-Butene in the presence of benzoyl peroxide, the products is
(1) 1-Bromobutane (2) 2-Bromobutane (3) 1-Bromobutene (4) 2-Bromobutene.



Which is correct statement about X and Y.

- (1) X is product of ionic reaction and Y is product of radical reaction.
(2) X and Y both are product of ionic reaction.
(3) X and Y both are product of radical reaction.
(4) X is product of radical reaction and Y is product of ionic reaction.

30. Which of the following is the best reagent to convert 1-Methylcyclohexene into 2-methylcyclohexanol ?
(1) Dil H₂SO₄ (2) Hg(OAc)₂ / NaBH₄, H₂O
(3) B₂H₆/H₂O₂, OH^- (4) Conc. H₂SO₄

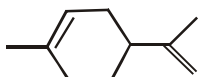


Practice Test-1 (IIT-JEE (Main Pattern))
OBJECTIVE RESPONSE SHEET (ORS)

Que.	1	2	3	4	5	6	7	8	9	10
Ans.										
Que.	11	12	13	14	15	16	17	18	19	20
Ans.										
Que.	21	22	23	24	25	26	27	28	29	30
Ans.										

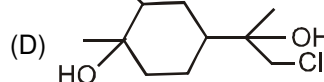
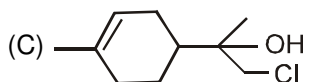
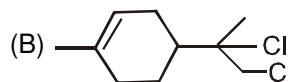
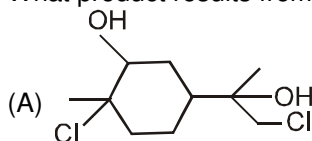
PART - II : NATIONAL STANDARD EXAMINATION IN CHEMISTRY (NSEC) STAGE-I

1. The alkene limonene has the following structure,



What product results from the reaction of limonene and chlorine water ?

[NSEC-2000]



2. An unknown compound is analyzed to have a molecular mass of 84 and elements has carbon and hydrogen only. When subjected to chlorination in the presence of light, three monochlorinated products are isolated. This compound must be

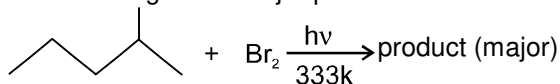
[NSEC-2000]

(A) methylcyclopentane
(C) hexane

(B) cyclohexane
(D) 1,3-dimethylcyclobutane

3. Which of the following is the major product of the following reaction ?

[NSEC-2000]



(A) 3-bromo-2-methylpentane
(C) 1-bromo-2-methylpentane

(B) 2-bromo-2-methylpentane
(D) 4-bromo-2-methylpentane

4. The peroxide effect occurs by :

[NSEC-2001]

(A) ionic mechanism
(C) heterolytic fission of double bond

(B) homolytic fission of double bond
(D) free radical mechanism

5. Benzene does not readily undergo

[NSEC-2002]

(A) halogenation
(C) sulphonation

(B) nitration
(D) oxidation.

6. Which compound amongst the following is nitrated with most difficulty ?

[NSEC-2002]

(A) nitrobenzene
(C) phenol

(B) m-dinitrobenzene
(D) quinol.

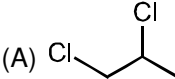
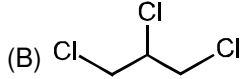
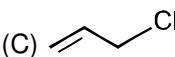
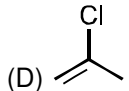
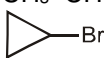
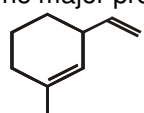
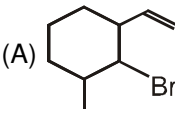
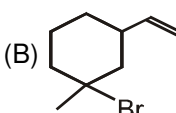
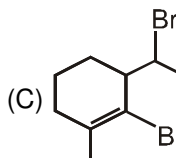
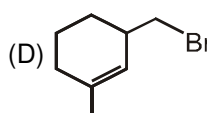

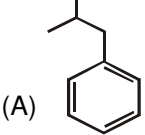
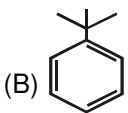
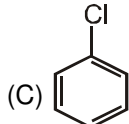
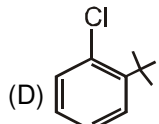
7. The reaction of toluene with chlorine in the dark and in presence of FeCl₃ gives predominantly.

[NSEC-2002]

(A) benzoyl chloride
(C) m-chlorotoluene

(B) benzyl chloride
(D) a mixture of o-and p-chlorotoluenes.

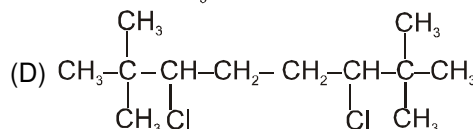
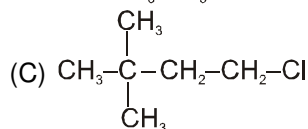
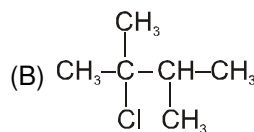
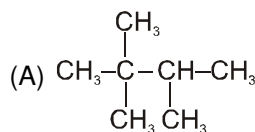
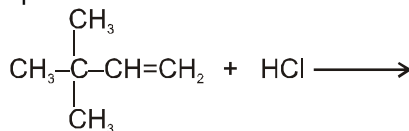


8. In the reaction of chlorine with propene at 450°C, the major product is [NSEC-2003]
- (A)  (B) 
 (C)  (D) 
9. In the nitration of an aromatic compound using a mixture of concentrated nitric acid and sulphuric acid, the acids respectively function as [NSEC-2003]
- (A) an oxidising agent and an acid (B) a Bronsted and a Lewis acid
 (C) a base and an acid (D) an acid and an oxidising agent.
10. Select the major product obtained from the addition of HBr to 1-methylcyclohexene. [NSEC-2005]
- (A) 1-bromo-2-methylcyclohexane (B) 6-bromo-1-methylcyclohex-1-ene
 (C) 3-bromo-1-methylcyclohex-1-ene (D) 1-bromo-1-methylcyclohexane.
11. Reaction of benzene with isobutylchloride ($\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{Cl}$) in the presence of anhydrous AlCl_3 yields [NSEC-2005]
- (A) tert-butylbenzene (B) iso-butylbenzene
 (C) n-butylbenzene (D) chlorobenzene.
12. The reagent system for preparing propan-1-ol from propene is [NSEC-2006]
- (A) $\text{Hg}(\text{OAc})_2/\text{H}_2\text{O}$ followed by NaBH_4 (B) $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$
 (C) B_2H_6 followed by H_2O_2 (D) $\text{HCO}_2\text{H}/\text{H}_2\text{SO}_4$.
13. In Friedel - Craft acylation, the amount of AlCl_3 that must be taken is [NSEC-2006]
- (A) in catalytic amount (B) one equivalent
 (C) more than one equivalent (D) amount does not matter.
14. For a Friedel-Craft reaction using AlCl_3 , which compound can be used as solvent, benzene or nitrobenzene? [NSEC-2006]
- (A) nitrobenzene but not benzene (B) benzene but not nitrobenzene
 (C) both benzene and nitrobenzene (D) neither benzene nor nitrobenzene.
15. The major product of the following reaction is [NSEC-2006]
- $\text{CH}_3-\text{CH}=\text{CH}_2 + \text{HBr} \xrightarrow{(\text{C}_6\text{H}_5\text{CO})_2\text{O}_2}$
- (A) $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{Br}$ (B) $\text{CH}_3-\text{CH}(\text{Br})-\text{CH}_3$
 (C) $\text{BrCH}_2-\text{CH}=\text{CH}_2$ (D) 
16. The major product formed upon addition of 1 mole of HBr in the following reactions is : [NSEC-2007]
-  $\xrightarrow{\text{HBr (1 mole)}}$ Major product ?
- (A)  (B)  (C)  (D) 
17. Predict the product formed in the following reaction [NSEC-2007]
-  $\xrightarrow[\text{AlCl}_3]{\text{2-chloro-2-methylpropane}}$ Product
- (A)  (B)  (C)  (D) 



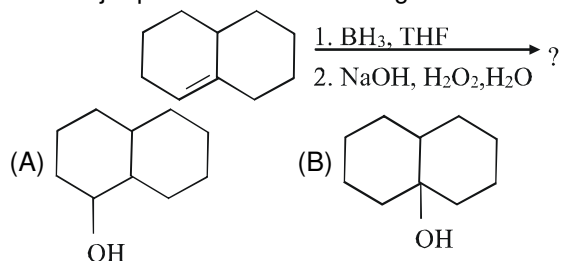
18. What is the major product that will be formed in the following reaction ?

[NSEC-2008]



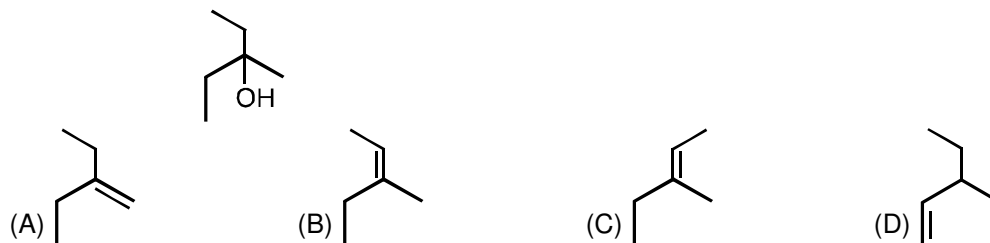
19. The major product in the following reaction is

[NSEC-2008]



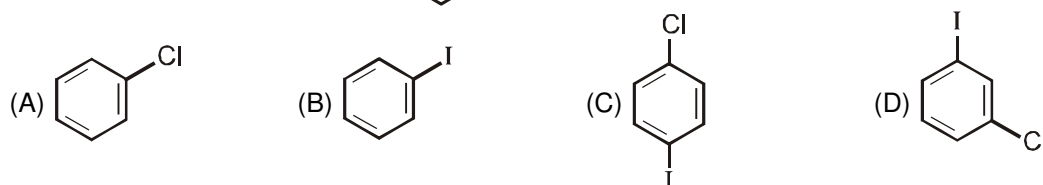
20. Identify the alkene which will not provide the following alcohol upon oxymercuration demercuration.

[NSEC-2008]



21. The compound X in the reaction, + ICl $\xrightarrow{\text{anhydrous AlCl}_3}$ X is :

[NSEC-2009]



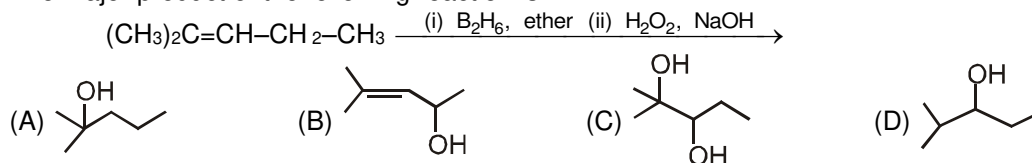
22. Cyclohexene reacts with limited amount of bromine in the presence of light to form product X ($\text{C}_6\text{H}_9\text{Br}$). The statement correct about X is :

[NSEC-2010]

- (A) It is a racemate. (B) It is a product of an addition reaction.
(C) It is formed through a cationic intermediate. (D) It is optically active.

23. The major product of the following reaction is :

[NSEC-2010]



24. The compound which does not react with bromine easily at room temperature is

[NSEC-2010]

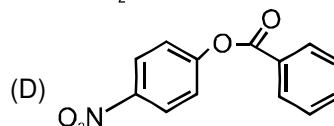
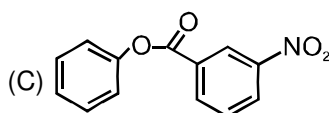
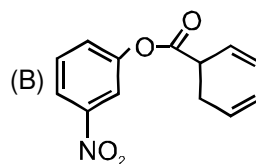
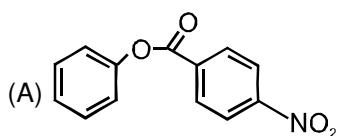
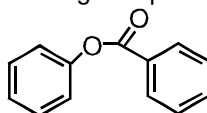
- (A) phenol (B) 2-butyne (C) chlorobenzene (D) 1-pentene





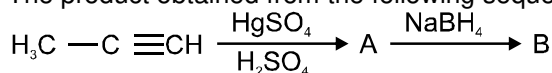
25. Major product of mononitration of the following compound is

[NSEC-2011]



26. The product obtained from the following sequence of reactions is

[NSEC-2011]



(A) propanal

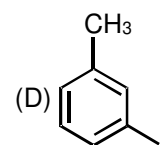
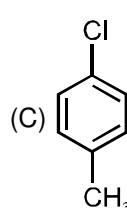
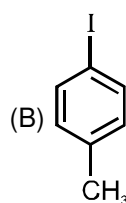
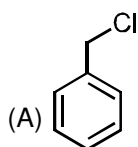
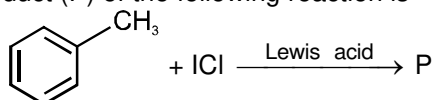
(B) 2-propanol

(C) 1-propanol

(D) propane

27. The product (P) of the following reaction is

[NSEC-2011]



28. Which isomer of xylene can give three different monochloro derivatives?

[NSEC-2012]

(A) o-xylene

(B) m-xylene

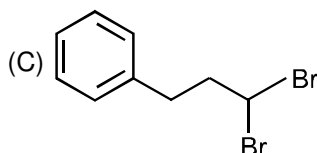
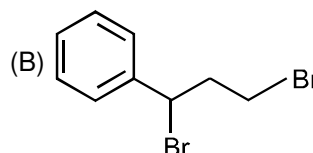
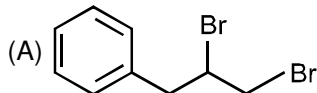
(C) p-xylene

(D) xylene cannot give a monochloro derivative

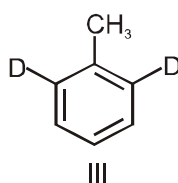
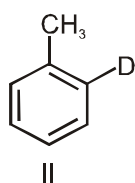
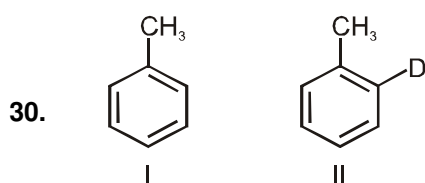
29. + HBr → Product

[NSEC-2012]

The 'product' in the above reaction is :



(D) This reaction cannot take place



[NSEC-2012]

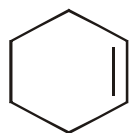
The rate of o-nitration of the above compounds, (I) toluene, (II) 2-D-toluene and (III) 2, 6-D₂-toluene are in the following order



- (A) I > II > III
(C) III > I > II

- (B) II > I > III
(D) The rate is the same for all the three compounds

31.



[NSEC-2013]

Cyclohexene

Product

The correct name of the product obtained is

- (A) cis-1,2-dibromocyclohexane (B) cis-1,4-dibromocyclohexane
(C) trans-1,2-dibromocyclohexane (D) trans-1,4-dibromocyclohexane

32.

Which of the following statements is correct ?

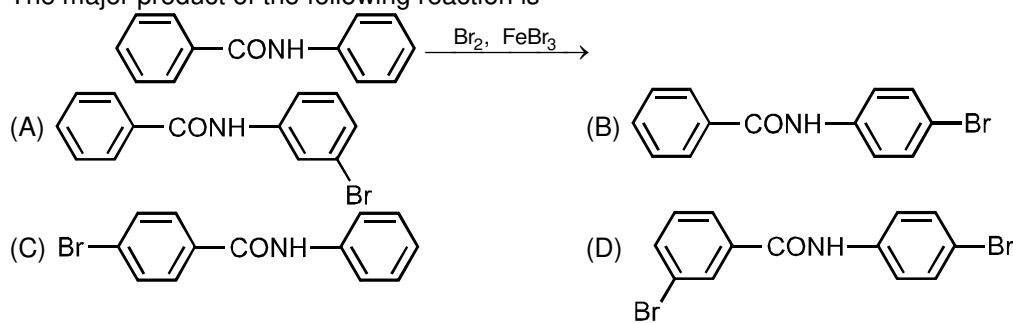
[NSEC-2013]

- (A) $-\text{NO}_2$ group activates the benzene ring for attack of electrophile at ortho and para position.
(B) $-\text{NH}_2$ group activates the benzene ring for attack of electrophile at ortho and para position.
(C) Both $-\text{NO}_2$ group as well as $-\text{NH}_2$ group activate the benzene ring for attack of electrophile at ortho and para position.
(D) Neither $-\text{NO}_2$ group nor $-\text{NH}_2$ group activate the benzene ring for attack of electrophile at ortho and para position.

33.

The major product of the following reaction is

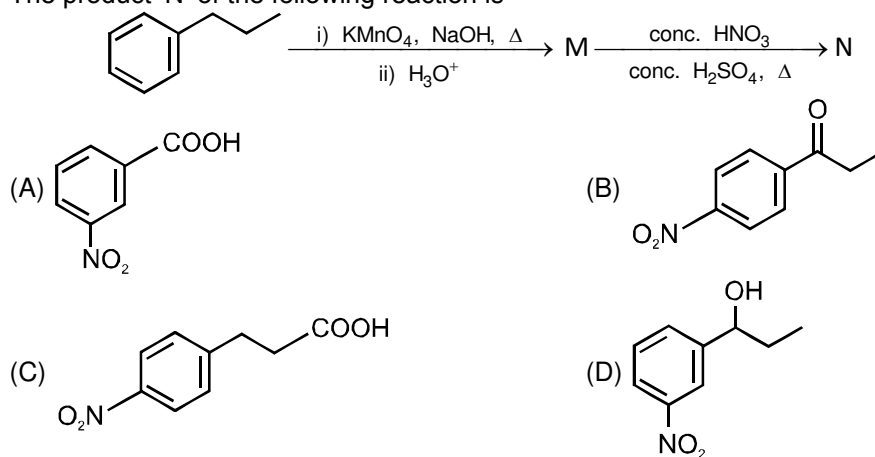
[NSEC-2014]



34.

The product 'N' of the following reaction is

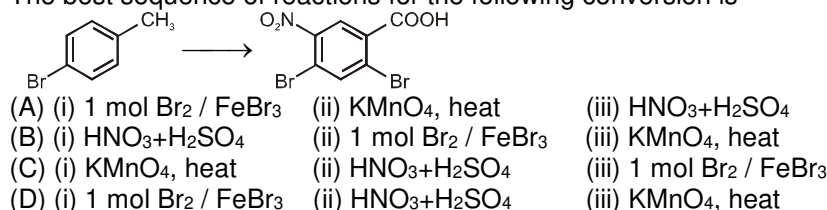
[NSEC-2014]



35.

The best sequence of reactions for the following conversion is

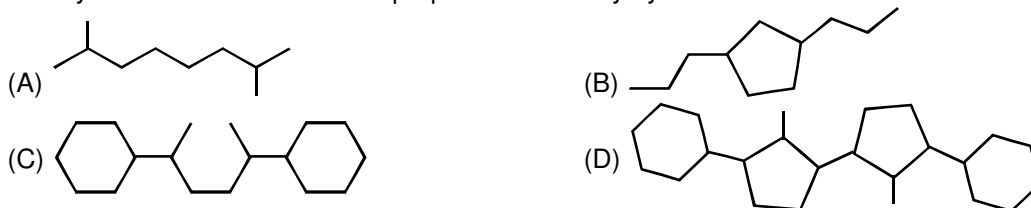
[NSEC-2015]



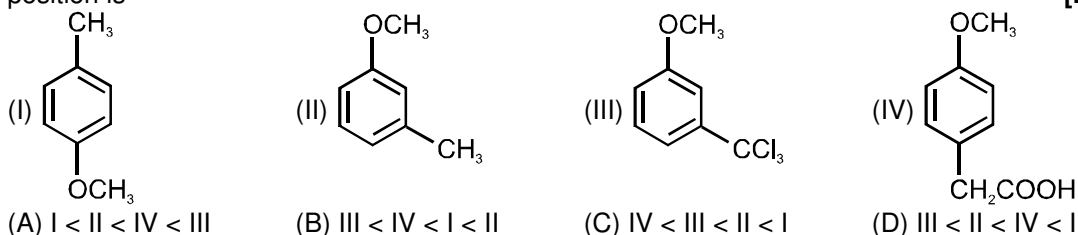


36. 1,3-pentadiene and 1,4-pentadiene are compared with respect to their intrinsic stability and reaction with HI. The correct statement is: [NSEC-2015]
 (A) 1,3-pentadiene is more stable and more reactive than 1,4-pentadiene
 (B) 1,3-pentadiene is less stable and less reactive than 1,4-pentadiene
 (C) 1,3-pentadiene is more stable but less reactive than 1,4-pentadiene
 (D) 1,3-pentadiene is less stable but more reactive than 1,4-pentadiene

37. The hydrocarbon that cannot be prepared effectively by Wurtz reaction is [NSEC-2015]



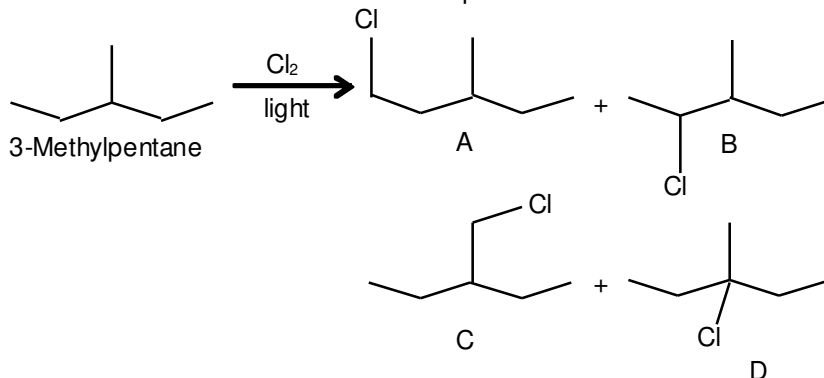
38. The order of reactivity of the following compounds in electrophilic monochlorination the most favorable position is [NSEC-2015]



39. The reaction of 1-phenylpropane with limited amount of chlorine in the presence of light gives mainly. [NSEC-2016]

- (A) 4-chloropropylbenzene (B) 1-chloro-1-phenylpropane
 (C) 3-chloro-1-phenylpropane (D) 2-chloro-1-phenylpropane

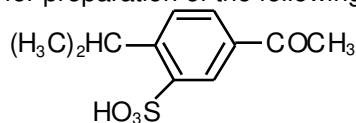
40. 3-Methylpentane on monochlorination gives four possible products. The reaction follows free radical mechanism. The relative reactivities for replacement of $-H$ are $3^\circ : 2^\circ : 1^\circ = 6 : 4 : 1$. [NSEC-2016]



Relative amounts of A, B, C and D formed are

- (A) 6/31, 16/31, 6/31, 3/31 (B) 16/31, 6/31, 6/31, 3/31
 (C) 6/31, 16/31, 3/31, 6/31 (D) 6/31, 3/31, 6/31, 16/31

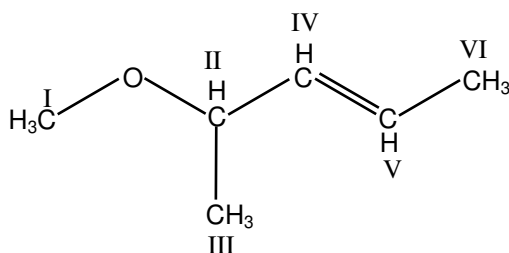
41. The best sequence of reactions for preparation of the following compound from benzene is [NSEC-2016]



- (A) (i) $CH_3COCl/AlCl_3$ (ii) Oleum (iii) $(CH_3)_2CH-Cl$ (1 mole)/ $AlCl_3$
 (B) (i) $(CH_3)_2CH-Cl$ (1 mole)/ $AlCl_3$ (ii) $CH_3COCl/AlCl_3$ (iii) Oleum
 (C) (i) Oleum (ii) $CH_3COCl/AlCl_3$ (iii) $(CH_3)_2CH-Cl$ (1 mole)/ $AlCl_3$
 (D) (i) $(CH_3)_2CH-Cl$ (1 mole)/ $AlCl_3$ (ii) Oleum (iii) $CH_3COCl/AlCl_3$



42. In the given compound the order of ease with which hydrogen atom can be abstracted from carbons I to VI is : [NSEC-2017]



- (A) I > VI > IV = V > I > III
(B) II > I > VI > III > IV = V
(C) II > I > III > VI > IV = V
(D) IV > II > I > III > IV = V
43. Addition of bromine to cis-3-hexene gives [NSEC-2017]
(A) racemic dibromide
(B) a mixture of diastereomeric dibromides
(C) optically active dibromide
(D) meso dibromide

PART - III : PRACTICE TEST-2 (IIT-JEE (ADVANCED Pattern))

Max. Time : 1 Hr.

Max. Marks : 66

Important Instructions

A. General :

- The test is of 1 hour duration.
- The Test Booklet consists of 22 questions. The maximum marks are 66.

B. Question Paper Format

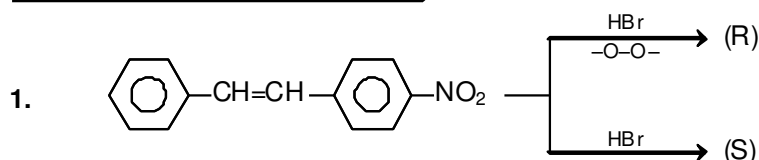
- Each part consists of five sections.
- Section-1 contains 8 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE is correct.
- Section-2 contains 6 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE OR MORE THAN ONE are correct.
- Section-3 contains 5 questions. The answer to each of the questions is a single-digit integer, ranging from 0 to 9 (both inclusive).
- Section-5 contains 1 paragraphs each describing theory, experiment and data etc. 2 questions relate to paragraph. Each question pertaining to a particular passage should have only one correct answer among the four given choices (A), (B), (C) and (D).
- Section-5 contains 1 multiple choice questions. Question has two lists (list-1 : P, Q, R and S; List-2 : 1, 2, 3 and 4). The options for the correct match are provided as (A), (B), (C) and (D) out of which ONLY ONE is correct.

C. Marking Scheme :

- For each question in Section-1, 4 and 5 you will be awarded 3 marks if you darken the bubble corresponding to the correct answer and zero mark if no bubble is darkened. In all other cases, minus one (– 1) mark will be awarded.
- For each question in Section-2, you will be awarded 3 marks. If you darken all the bubble(s) corresponding to the correct answer(s) and zero mark. If no bubbles are darkened. No negative marks will be answered for incorrect answer in this section.
- For each question in Section-3, you will be awarded 3 marks if you darken only the bubble corresponding to the correct answer and zero mark if no bubble is darkened. No negative marks will be awarded for incorrect answer in this section.

SECTION-1 : (Only One option correct Type)

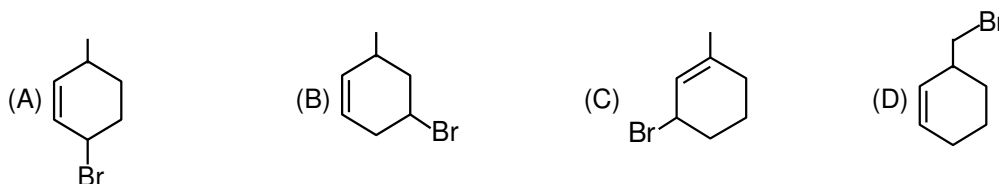
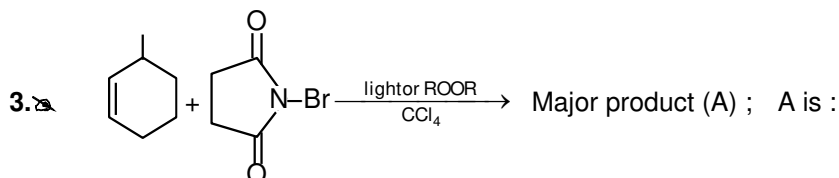
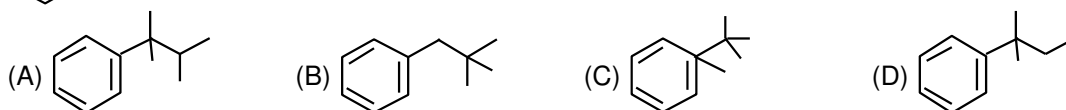
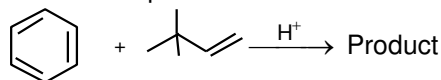
This section contains 8 multiple choice questions. Each questions has four choices (A), (B), (C) and (D) out of which Only ONE option is correct.



P & Q are :

(A) Positional isomer (B) Geometrical isomer (C) Optical isomer (D) Chain isomer

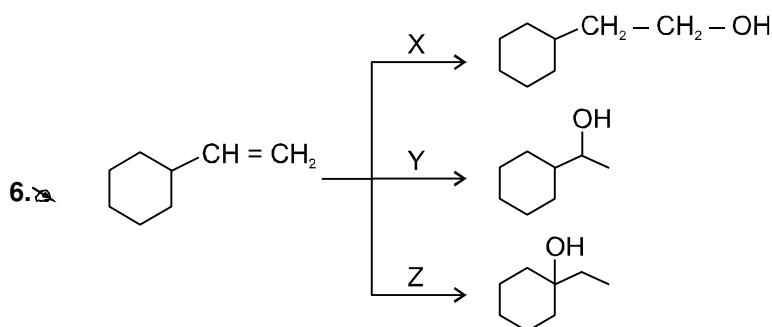
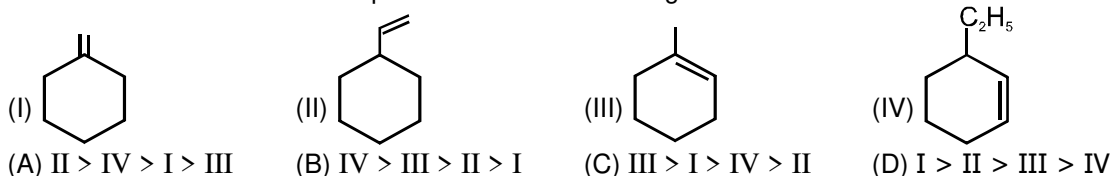
2. What is the product formed in the following reaction.



4. The reaction of toluene with Cl_2 in presence of FeCl_3 gives 'X' and reaction in presence of light gives 'Y' Thus, 'X' and 'Y' are

(A) X = Benzyl chloride, Y = m-chlorotoluene
(B) X = Benzal chloride, Y = o-chlorotoluene
(C) X = m-chlorotoluene, Y = p-chlorotoluene
(D) X = o- and p-chlorotoluene, Y = Trichloromethyl benzene

5. What is correct order of electrophilic addition of following alkene ?

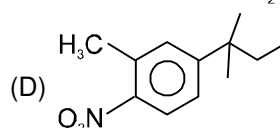
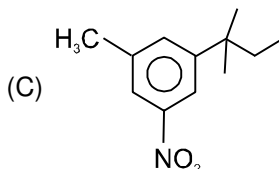
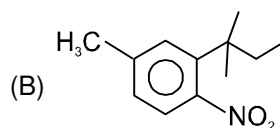
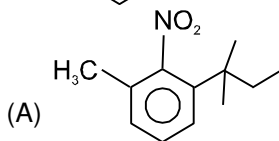
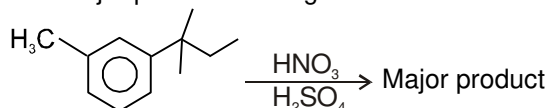


X, Y, Z reaction are :

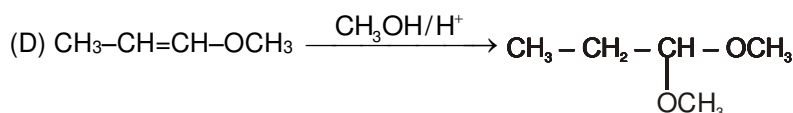
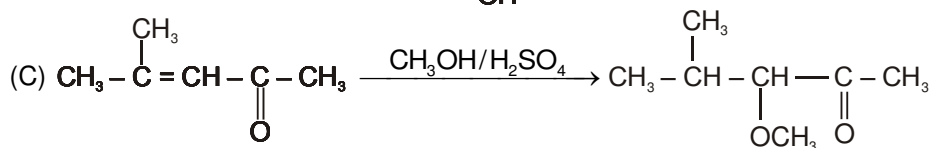
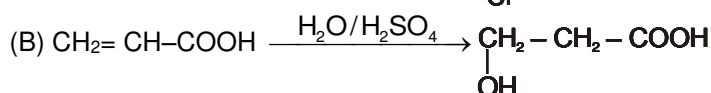
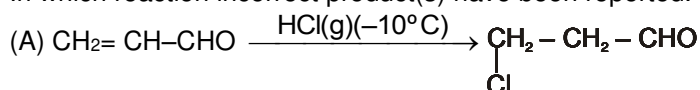
(A) Simple hydration reaction
(B) Hydroboration oxidation, hydration and oxymercuration demercuration
(C) Hydroboration oxidation, oxymercuration demercuration and hydration
(D) Oxymercuration demercuration, hydroboration oxidation and hydration



7. The major product of the given reaction is :



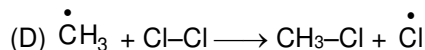
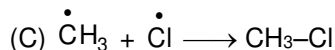
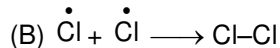
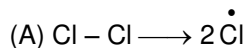
8. In which reaction incorrect product(s) have been reported.



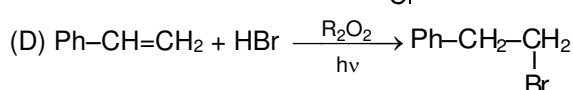
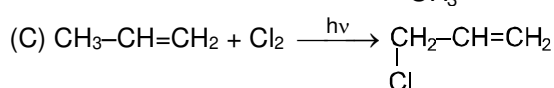
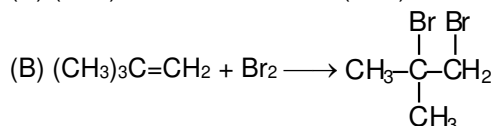
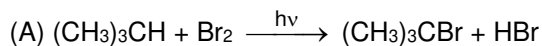
Section-2 : (One or More than one options correct Type)

This section contains 6 multiple choice questions. Each questions has four choices (A), (B), (C) and (D) out of which ONE or MORE THAN ONE are correct.

9. In the chlorination of Methane which of the following reaction involve in the chain termination step.

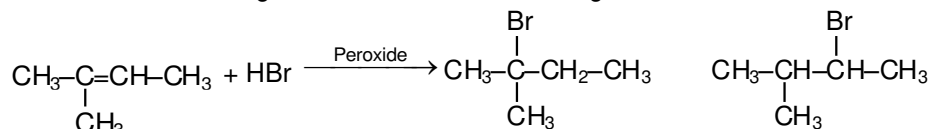


10. Which of the following reactions are completed through free radical intermediate ?

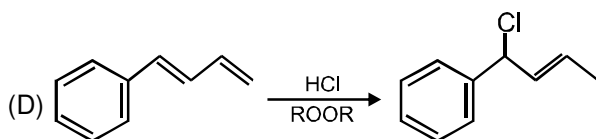
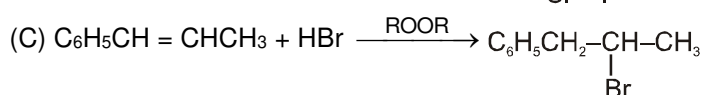
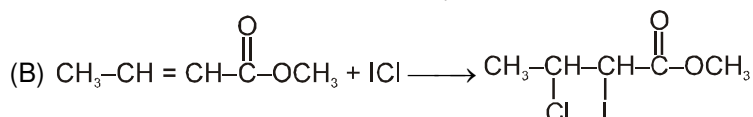
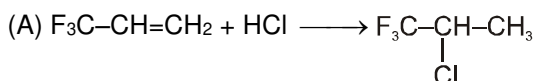




11. Which of the following statements are correct for given reaction.



- (A) Major product is mixture of two enantiomers.
 (B) Less stable carbocation give major product.
 (C) Less stable free radical give major product.
 (D) More stable free radical give major product.
12. In which of the following reaction reactants and products are correctly matched ?



13. Which statement is /are correct.

- (A) No primary kinetic isotope effect is observed during nitration of benzene
 (B) $K_H / K_D = 1$ for halogenation of benzene
 (C) $K_H / K_D = 1$ for sulphonation of benzene
 (D) K_H / K_D is > 1 for alkylation of benzene

14. Which of the following statements is/are incorrect ?

- (A) Nitrobenzene will give meta-nitrotoluene on reaction with $\text{CH}_3\text{Cl}/\text{AlCl}_3$.
 (B) Chlorobenzene will give meta-substituted product on electrophilic substitution since it exerts $-I > +M$ effect.
 (C) n-Propyl benzene can be easily obtained on Friedel crafts alkylation of benzene with n-propyl chloride.
 (D) Toluene can be obtained in better yield when excess of benzene will react with $\text{CH}_3\text{Cl}/\text{AlCl}_3$.

Section-3 : (Single/ Double Integer Value Correct Type.)

This section contains 5 questions. Each question, when worked out will result in one integer from 0 to 9 (both inclusive)

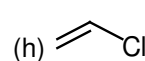
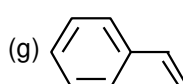
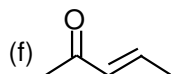
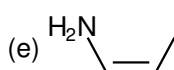
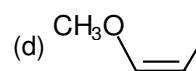
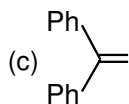
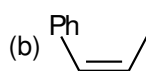
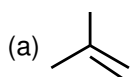
15. How many of the following substituents can cause aromatic electrophilic substitution faster than benzene ?

- (a) $-\text{NH}_2$ (b) $-\text{NR}_2$ (c) $-\text{NO}_2$ (d) $-\text{NH}_3^+$
 (e) $-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}$ (f) $-\text{NH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}$ (g) $-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl}$ (h) $-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$
 (i) $-\text{SO}_3\text{H}$ (j) $-\text{CH}_3$ (k) $-\text{CH}=\text{CR}_2$



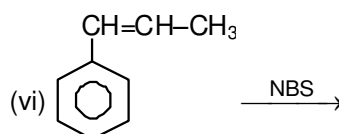
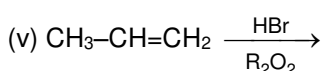
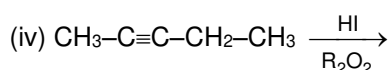
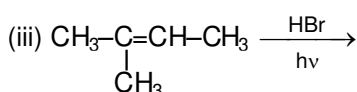
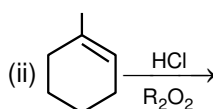
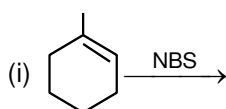


16. How many alkenes react faster than propene with $\text{dil. H}_2\text{SO}_4$?

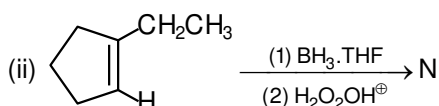
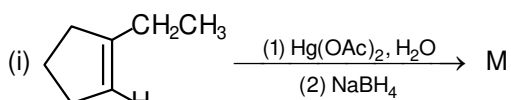


17. When addition of Br_2 was carried out in presence of aq. NaCl on ethene then total number of possible product are :

18. How many reactions will proceed through free radical addition mechanism ?



19. In the given reactions M is the number of major products obtained in Ist reaction and N number of major products obtained in IInd reaction. Report your answer as **[MN]**.



SECTION-4 : Comprehension Type (Only One options correct)

This section contains 1 paragraphs, each describing theory, experiments, data etc. 2 questions relate to the paragraph. Each question has only one correct answer among the four given options (A), (B), (C) and (D)





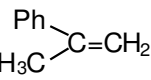
Paragraph for Question Nos. 20 to 21

Consider experimental data shown in this table :

Alkene	Relative rate	Alkene	Relative rate
$\text{CH}_2=\text{CH}_2$	1	$(\text{CH}_3)_2\text{C}=\text{CH}_2$	5,400
$\text{CH}_2=\text{CH}-\text{CH}_3$	61	$(\text{CH}_3)_2\text{C}=\text{CHCH}_3$	130,000
	1700	$(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$	1,800,000
	2600		





20. Rate of electrophilic addition on isobutylene is significantly higher than cis or trans-2-Butene chiefly due to –
- (A) Lesser stability of  (isobutylene) in comparison to  or .
- (B) Higher dipole moment of  in comparison to cis or trans-2-Butene.
- (C) Better stabilization of positive charge acquired during formation of bromonium ion intermediate by Me-groups
- (D) High angle strain in the molecule
21. Which of the following would be expected to have highest rate of electrophilic addition of Br₂ ?
- (A) Ph-CH=CH₂
- (B) 
- (C) Ph-CH=CH-CH₃
- (D) All react with the same rate, since the rate depends only on [Br₂] and not on the substrate.

SECTION-5 : Matching List Type (Only One options correct)

This section contains 1 questions, each having two matching lists. Choices for the correct combination of elements from List-I and List-II are given as options (A), (B), (C) and (D) out of which one is correct

22. Match List-I (Compounds) with List-II (% meta electrophilic substitution product) and select the correct answer using the code given below the lists:

	List-I		List-II
(P)	Ar-CH ₃	(1)	64.6
(Q)	ArCH ₂ Cl	(2)	34
(R)	ArCHCl ₂	(3)	4.5
(S)	ArCCl ₃	(4)	15

Codes :

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

Practice Test-2 ((IIT-JEE (ADVANCED Pattern))

OBJECTIVE RESPONSE SHEET (ORS)

Que.	1	2	3	4	5	6	7	8	9	10
Ans.										
Que.	11	12	13	14	15	16	17	18	19	20
Ans.										
Que.	21	22								
Ans.										



APSP Answers

PART - I

1.	(4)	2.	(3)	3.	(4)	4.	(1)	5.	(2)
6.	(4)	7.	(4)	8.	(4)	9.	(1)	10.	(1)
11.	(3)	12.	(3)	3.	(2)	14.	(3)	15.	(4)
16.	(2)	17.	(2)	18.	(4)	19.	(2)	20.	(3)
21.	(4)	22.	(2)	23.	(3)	24.	(1)	25.	(4)
26.	(4)	27.	(1)	28.	(3)	29.	(1)	30.	(3)

PART - II

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

PART - III

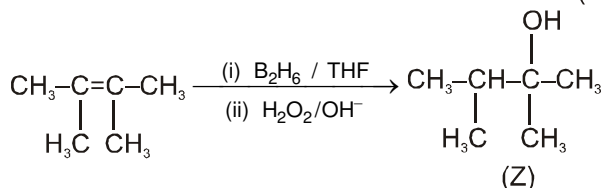
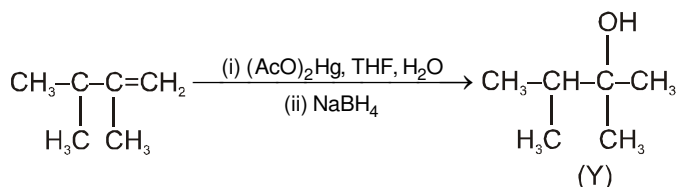
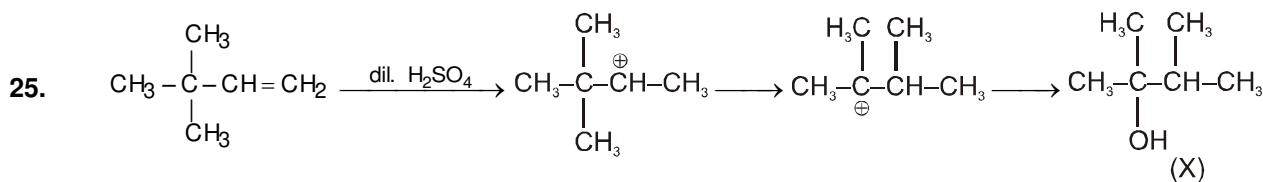
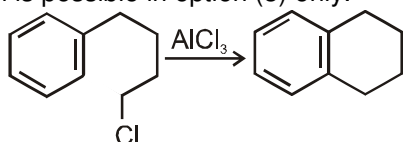
1.	(A)	2.	(A)	3.	(C)	4.	(D)	5.	(C)
6.	(C)	7.	(D)	8.	(C)	9.	(BC)	10.	(ACD)
11.	(AD)	12.	(BCD)	13.	(AB)	14.	(ABC)		
15.	6 (a, b, e, f, j, k)			16.	6 (a, b, c, d, e, g)			17.	3
18.	2	19.	12	20.	(C)	21.	(B)	22.	(B)



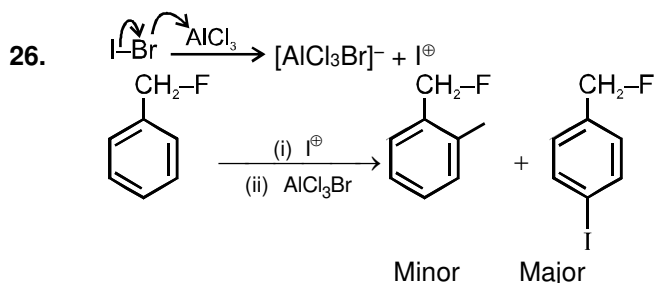
APSP Solutions

PART - I

1. It is allylic substitution reaction.
2. Reaction A is free radical addition reaction and all are electrophilic addition reactions.
7. $EAS \propto \frac{1}{EWG}$ on Benzene ring.
8. In presence of +M effect rate of mononitration increase and in presence of -M effect rate will decrease.
14. As in previous question.
23. Reaction is possible in option (3) only.



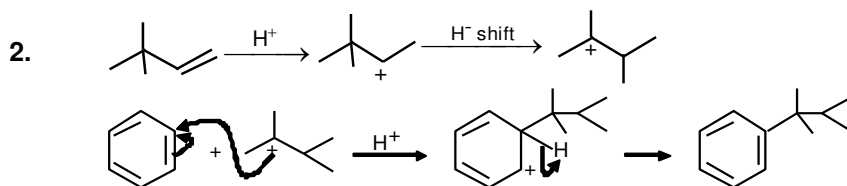
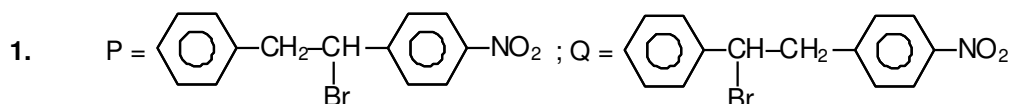
All products are identical.



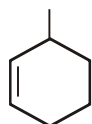
29. In the presence of peroxide, HBr undergoes free radical addition and HCl undergoes electrophilic addition, because of H-Cl bond have high bond energy.



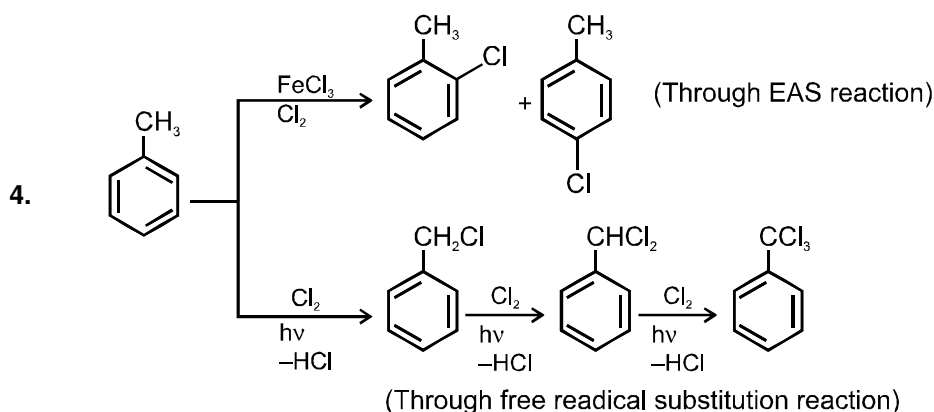
PART - III



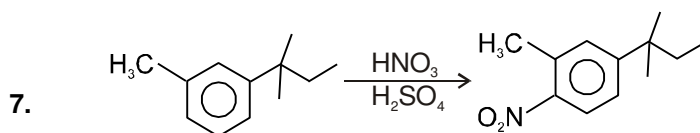
3. The given reaction occur via free radical substitution mechanism. Major product will depend on the stability of free radical.



Most stable free radical

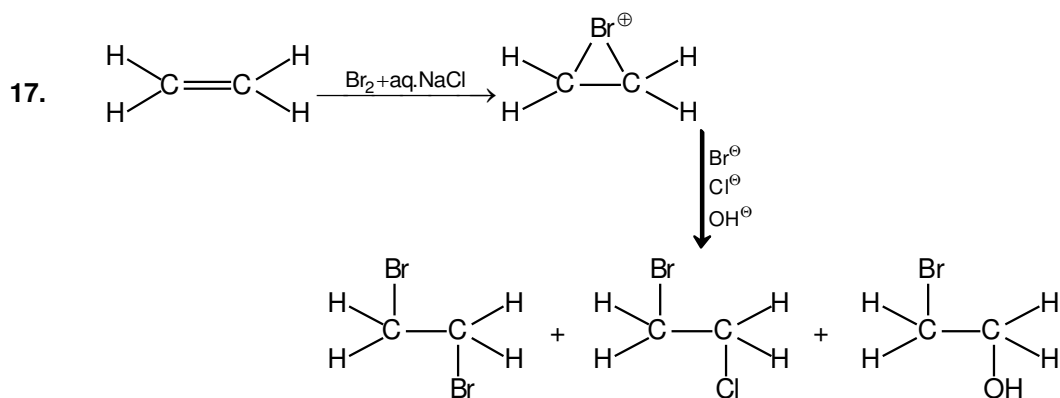


5. Electron releasing group and stability of carbocation/halonium ion will decide rate of reaction in electrophilic addition reaction.
6. X = Hydroboration oxidation, Y = oxymercuration & demercuration, Z = Simple hydration reaction



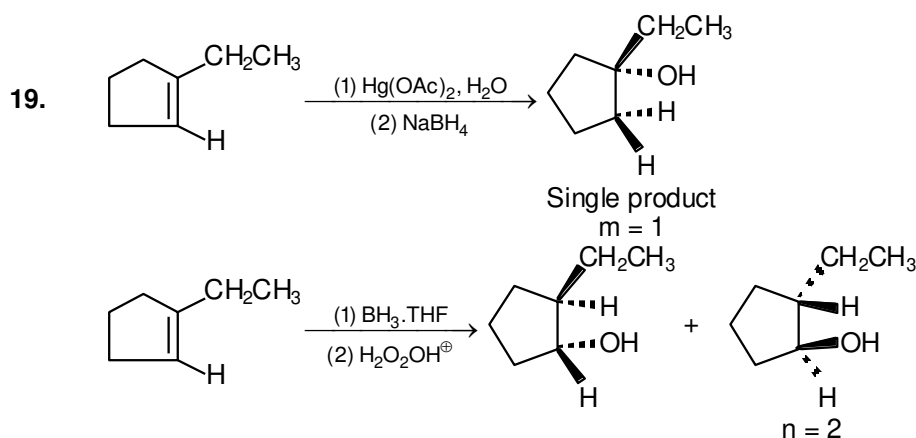
–C group is more ring activity than , para position wrt –CH₃ group is more crowded than ortho.

8. The more stable carbocation of alkene gives the major product in electrophilic addition reactions.
9. Option 'D' is chain propagating step.
14. (A) In highly de-activated ring Friedal Crafts reaction is not possible.
(B) Chloro group is ortho-para director.
(C) In Friedal Craft reaction the electrophile carbocation rearranges.
(D) To avoid polyalkylation aromatic substrate is taken in excess.
16. Rate of E⁺ addition \propto stable cation



Formation of these three products clearly indicates about formation of cyclic Bromonium ion.

18. Only (iii) & (v)



22. EWG groups are meta directing.