

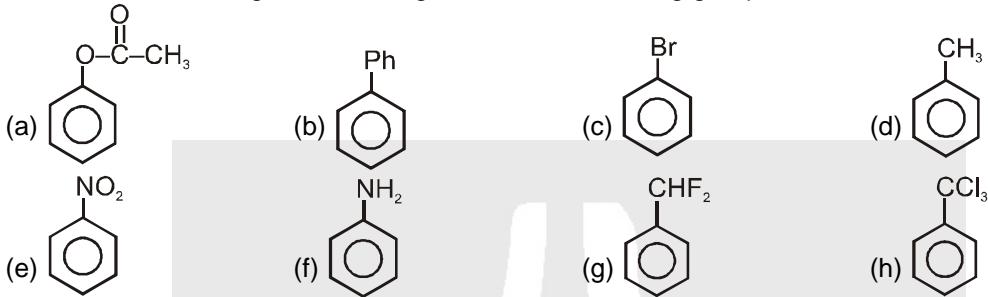
**Exercise-1**

☞ Marked questions are recommended for Revision.

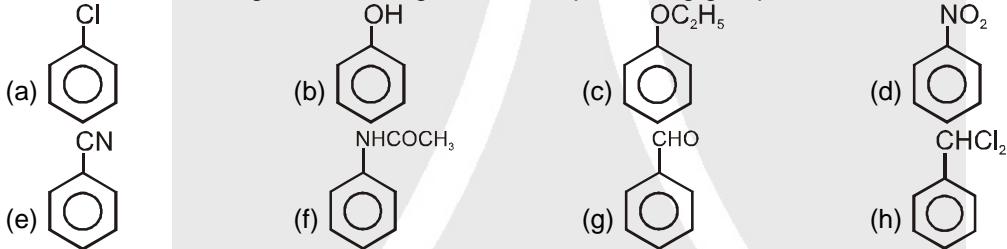
**PART - I : SUBJECTIVE QUESTIONS****Section (A) : Electrophilic substitution reaction of aromatic compounds**

**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 ?



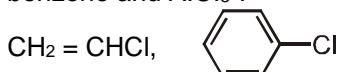
**A-3.** Which of the following Benzene rings contain o-p directing groups ?

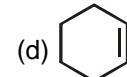
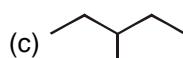
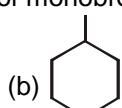
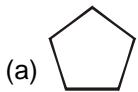
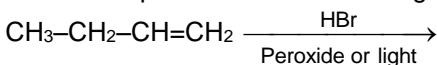
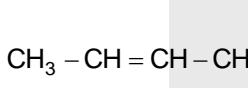


**A-4.** ☞ Arrange the following in decreasing order of their reactivity with an electrophile.

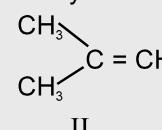
	(I)	(II)	(III)
(a)			
(b)			
(c)			
(d)			

**A-5.** ☞ Why following organic chlorides will not give a Friedel-Crafts alkylation product when heated with benzene and  $\text{AlCl}_3$  ?

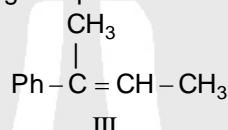


**Section (B) : Free radical substitution & Free radical addition reaction****B-1.** How do you account for formation of ethane during chlorination of methane ?**B-2.** Give the major product of monobromination of following compounds.**B-3.** Predict the product of the reaction given below :**B-4.**  $\text{CH}_2=\text{CH--CH}_2\text{--CH}_3 \xrightarrow{\text{NBS}} \text{B} + \text{C}$   
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 ?

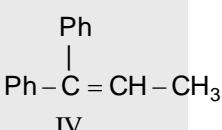
I



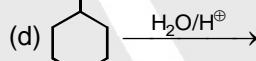
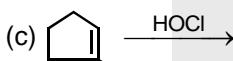
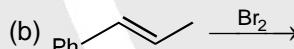
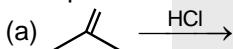
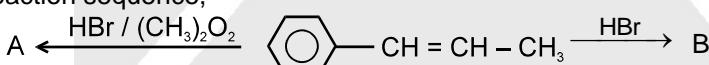
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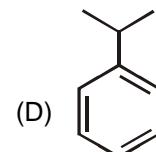
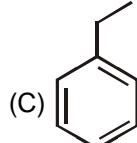
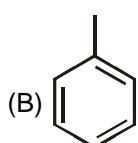
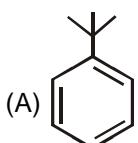
III



IV

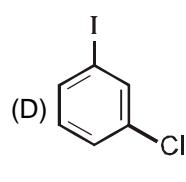
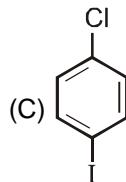
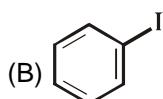
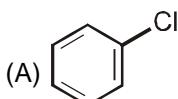
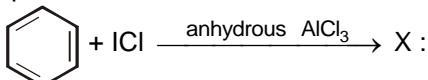
**C-2.** The acid catalysed hydration follows following order  $(\text{CH}_3)_2\text{C=CH}_2 > \text{CH}_3\text{CH=CH}_2 > \text{CH}_2=\text{CH}_2$   
Explain this order of reactivity.**C-3.** Give product of the following reactions.**C-4.** What will happen when  $\text{Br}_2/\text{CCl}_4$  react with (a) cis But-2-ene (b) trans But-2-ene.**C-5.** In the reaction sequence,

What is the relationship between A &amp; 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)  $\text{AlCl}_3$  (C) Anhydrous  $\text{AlCl}_3$  (D)  $\text{P}_2\text{O}_5$ **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)  $-\text{NHR}$



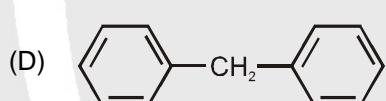
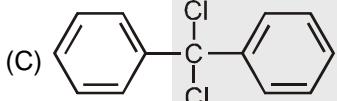
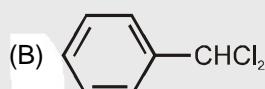
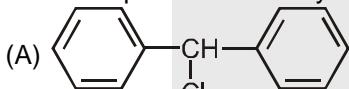
**A-4.** The compound X in the reaction is :



**A-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  $\text{C}_6\text{H}_6$  reacts with  $\text{CH}_2\text{Cl}_2$  in presence of anhydrous  $\text{AlCl}_3$ :



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

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

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

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

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

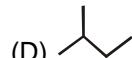
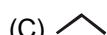
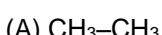
**B-1.** In the free radical chlorination of methane, the chain initiating step involves the formation of

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

**B-2.** Which of the following cannot be considered as a step of mechanism in chain reaction of methane with  $\text{Cl}_2$ ?

- (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 :

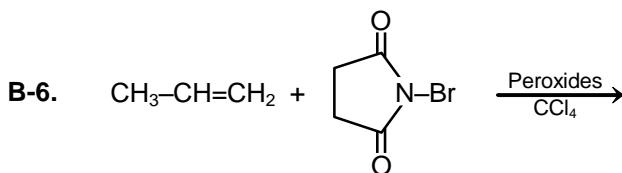


**B-4.** The maximum ease of abstraction of a hydrogen atom by a chlorine atom is shown by :

- (A)  $(\text{CH}_3)_3\text{C}-\text{CH}_3$
- (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

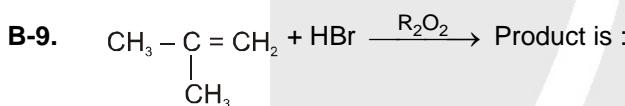
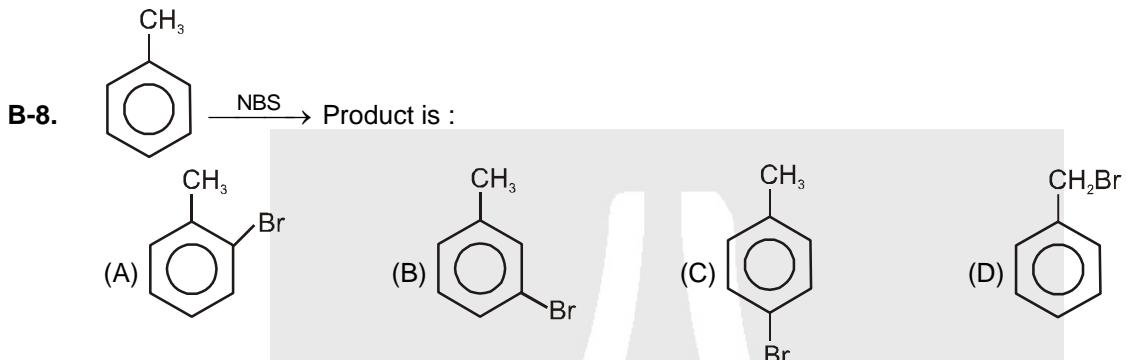
- (A) Chloroform
- (B) Methyl chloride.
- (C) Methylene chloride
- (D) Carbon tetrachloride

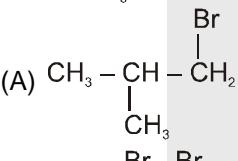
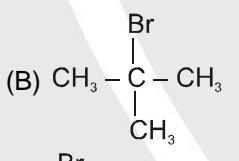
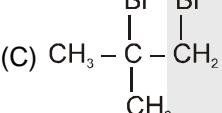
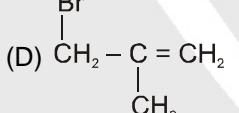


This reaction is classified as

(A) Electrophilic substitution reaction  
(C) Nucleophilic substitution reaction  
(B) Free radical substitution reaction  
(D) Electrophilic addition reaction

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



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

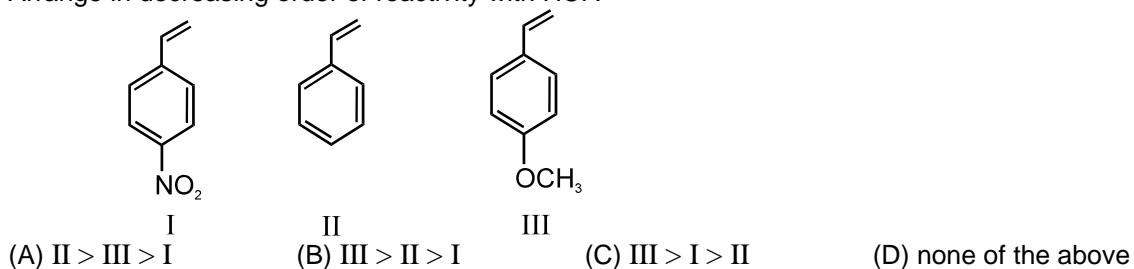
B-10. Anti Markownikoff addition of HBr is not observed in :

(A) Propene      (B) 1-Butene      (C) But-2-ene      (D) Isobutene

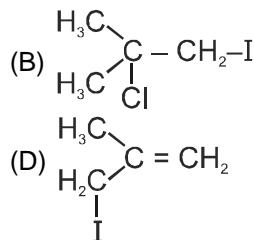
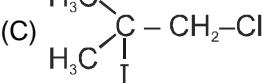
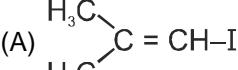
### Section (C) : Electrophilic addition reaction

C-1. What is correct order of acid catalysed hydration of following alkenes ?  
(I)  $\text{CH}_2=\text{CH}_2$       (II)  $\text{CH}_3\text{CH}=\text{CH}_2$       (III)  $(\text{CH}_3)_2\text{C}=\text{CH}_2$       (IV)  $\text{CH}_3\text{CH}=\text{CH}-\text{CH}_3$   
(A) III > I > II > IV      (B) III > IV > II > I      (C) II > IV > III > I      (D) I > II > III > IV

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

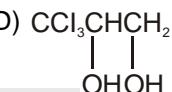
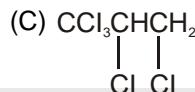
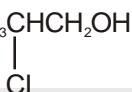
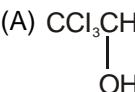


C-3.   $\text{CH}_2 + \text{ICl} \rightarrow \text{P}$  (major product), Here 'P' is :

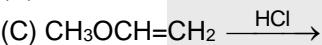
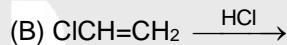
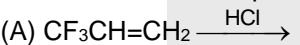


C-4.   $\xrightarrow{\text{HOCl}}$  P (Major product),

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

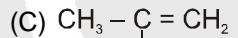


C-5. In which reaction the product following anti markonikoff rule is observed :



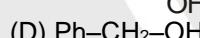
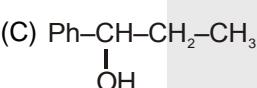
(D) None

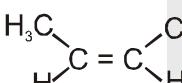
C-6. Which will form 2, 2-Dibromopropane with HBr ?

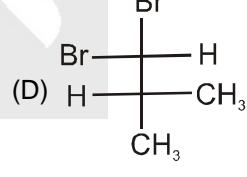
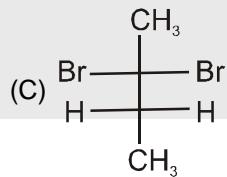
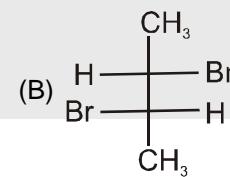
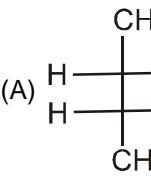


(D) Both B & C

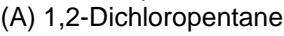
C-7.  $\text{Ph}-\text{CH}_2-\text{CH}=\text{CH}_2 \xrightarrow{\text{dil. H}_2\text{SO}_4}$  X, 'X' is :



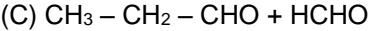
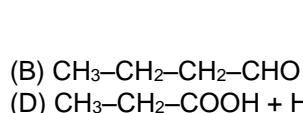
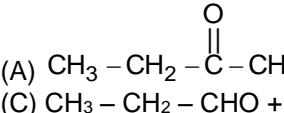
C-8.   $+ \text{Br}_2 \xrightarrow{\text{CCl}_4}$  Product is :



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-oxymercuration ( $\text{HgSO}_4 + \text{H}_2\text{SO}_4$ ) 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 :

	<b>List I</b>		<b>List II</b>
(P)	$\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--CH}_3 + \text{Br}_2 \xrightarrow{\text{h}\nu}$	(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
(A) 2	1	3	4
(C) 4	2	1	3

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

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

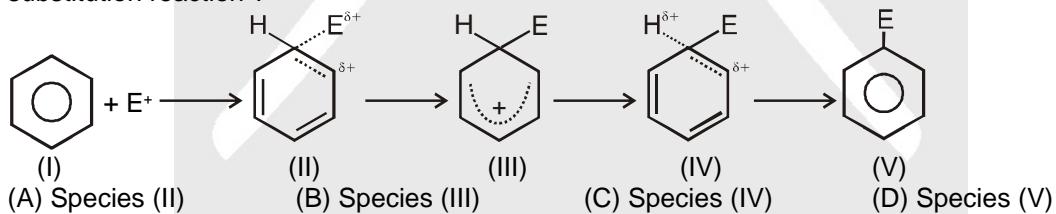
	<b>Column-I</b>		<b>Column-II</b>
	<b>Group</b>		<b>Nature</b>
(A)	$-\text{Cl}$	(p)	Activating
(B)	$-\text{CH}_3$	(q)	deactivating
(C)	$-\text{OH}$	(r)	<i>o,p</i> -directing
(D)	$-\text{NO}_2$	(s)	<i>m</i> -directing

**Exercise-2**

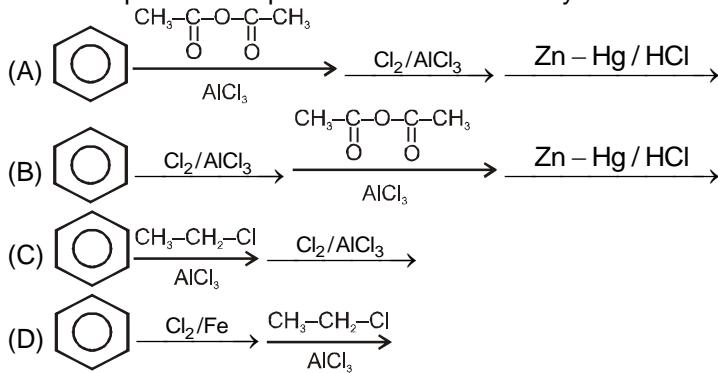
Marked questions are recommended for Revision.

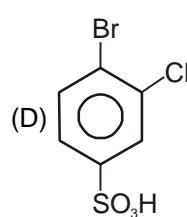
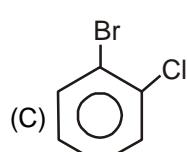
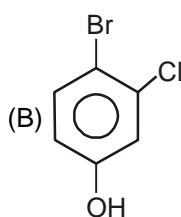
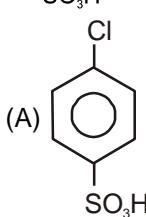
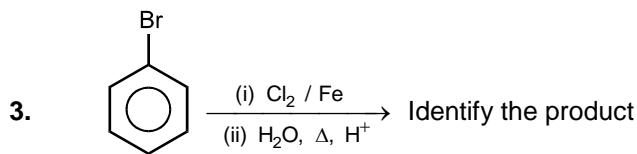
**PART - I : ONLY ONE OPTION CORRECT TYPE**

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

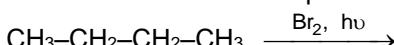


2.  Which step is used to produce 1-Chloro-3-ethylbenzene



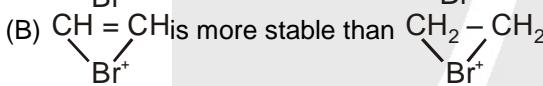
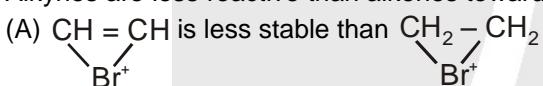


4. Which statement is correct about photochemical bromination of Butane ?



(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  $\text{Br}_2$  because :



(C) Both are equally stable

(D) Original statement is incorrect

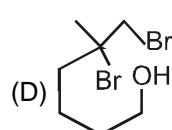
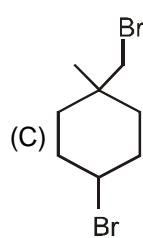
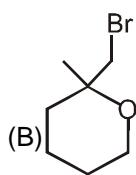
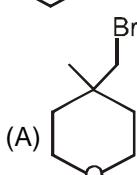
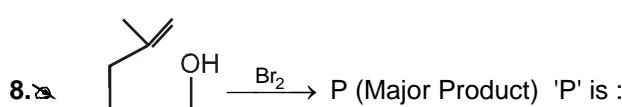


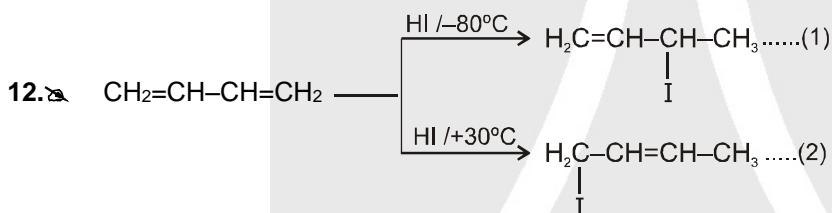
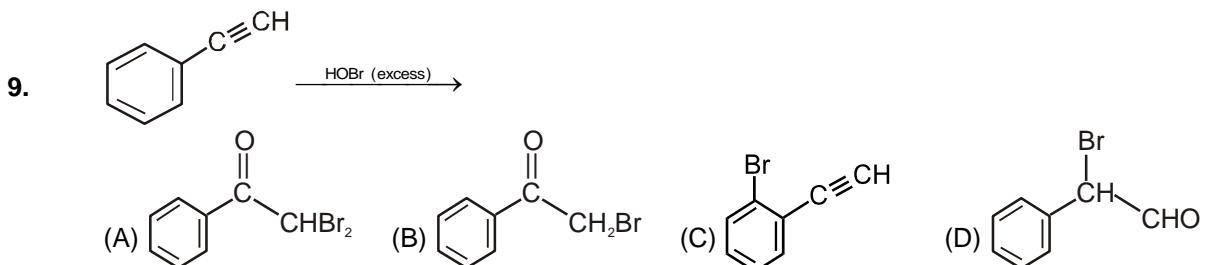
Order of rate of electrophilic addition reaction with  $\text{HBr}$  will be :

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

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

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

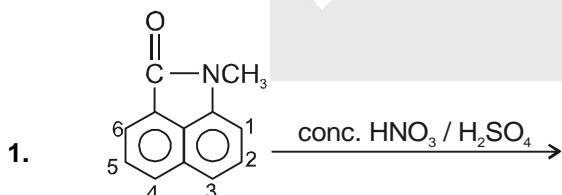




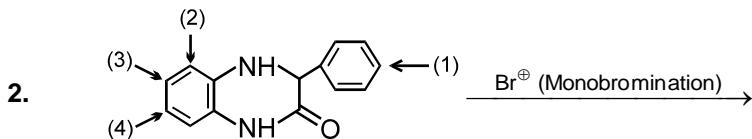
At given temperature, these reaction tell about control of reaction which is :

	(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 ?

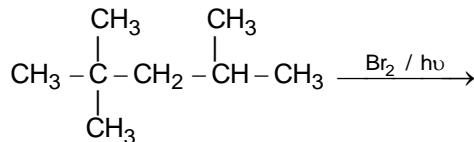


The substitution will mainly take place at position :

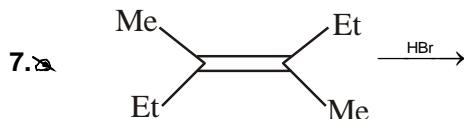
3. When ortho dibromobenzene is subjected to mononitration X number of product are formed and when meta dibromobenzene is subjected to mononitration, Y number of products are formed. Report your answer as XY.

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) :



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



How many product will be formed in above reaction.

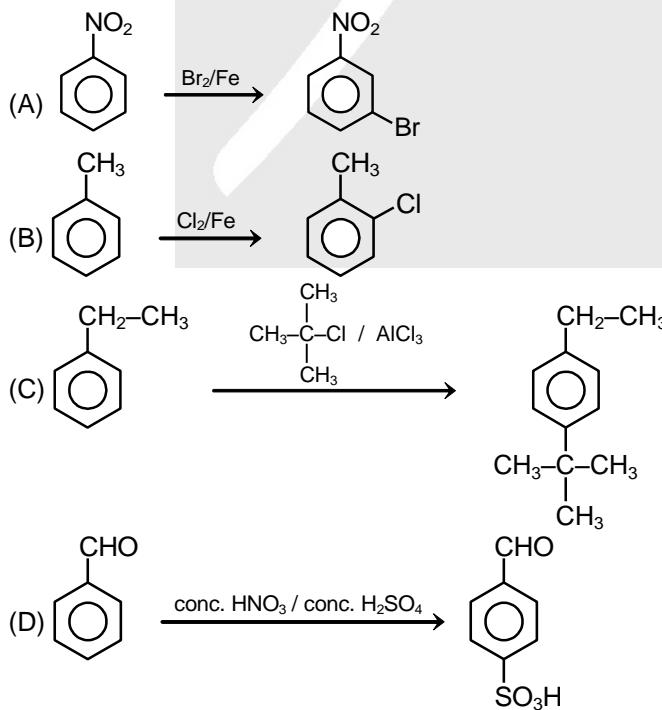
8. When trans-2-butene reacts with  $\text{Br}_2/\text{CCl}_4$ , X number of products are formed. Whereas when trans-2-butene reacts with  $\text{HBr}$  Y number of products are formed. Report your answer as Y X.

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

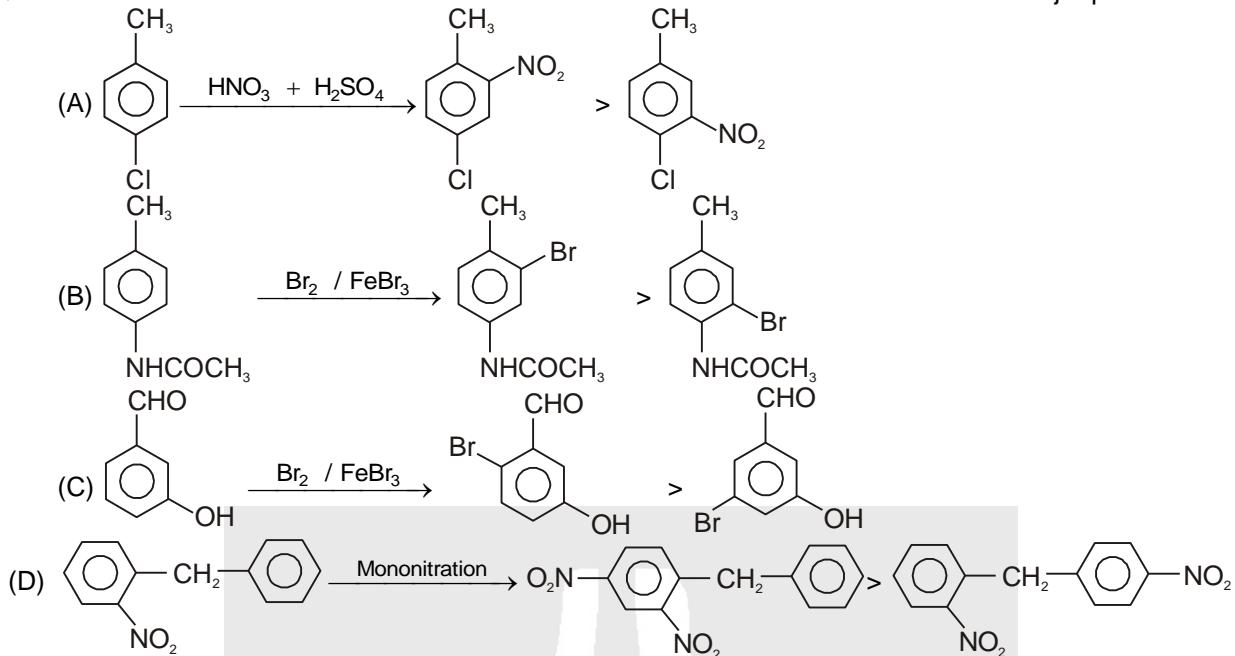
1. Electrophilic aromatic substitution can be seen in which of the following cases ?



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



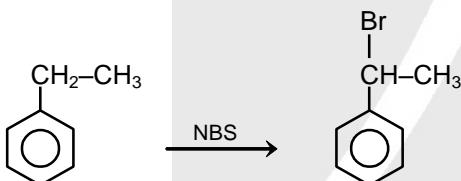
3. Select the reactions in which the correct orientations have been mentioned in the major products.



4. Friedel-Crafts Acylation is simply observed in :

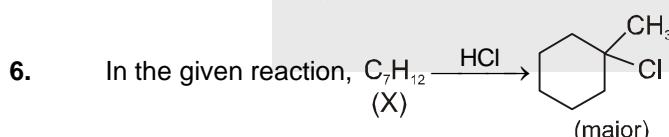


5.

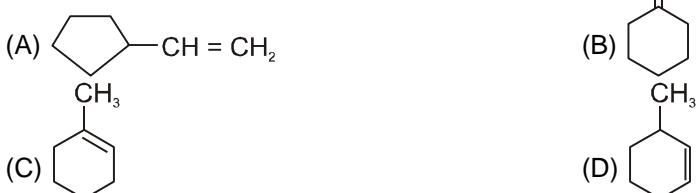


Which of the following statements are correct for above reaction.

(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.

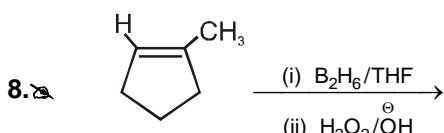
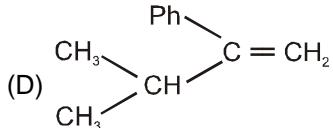
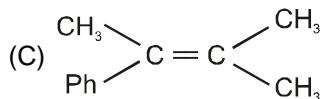
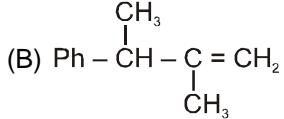
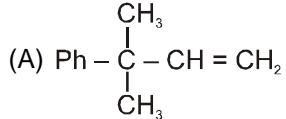


Structure of X can be :





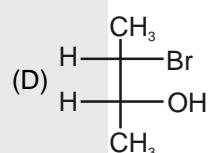
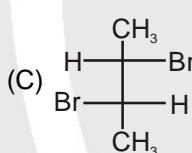
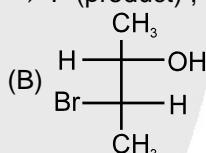
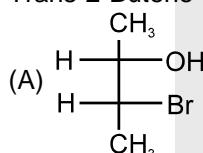
7. Which of the following compounds will give same major product on acid catalysed hydration ?



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  $\text{Br}_2$  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

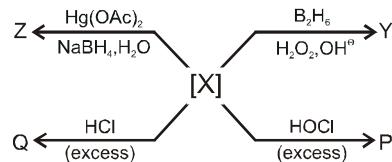
(A) All three alkenes will give 3 different major hydration products  
 (B) Three alkenes will give same hydration major product  
 (C) Two alkenes form same product but one alkene forms different major product.  
 (D) Addition of HCl and  $\text{H}_3\text{O}^+$  both are following different regioselectivity.

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

(A) These have molecular formula  $\text{C}_3\text{H}_6$   
 (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)**

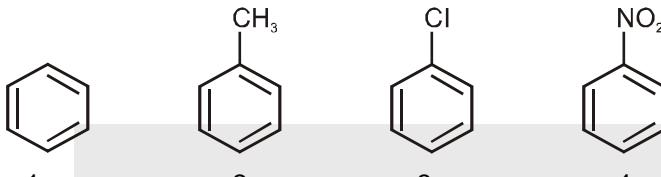
1. In the presence of peroxide, hydrogen chloride and hydrogen iodide do not give anti-Markovnikov addition to alkenes because : **[IIT-JEE-2001(S), 3/135]**  
 (A) both are highly ionic  
 (B) one is oxidising and the other is reducing  
 (C) one of the steps is endothermic in both the cases  
 (D) 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)  $\text{H}^+$  in the first step  
 (B)  $\text{Cl}^+$  in the first step  
 (C)  $\text{OH}^-$  in the first step  
 (D)  $\text{Cl}^+$  and  $\text{OH}^-$  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.

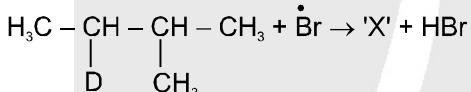
4. Identify the correct order of reactivity in electrophilic substitution reactions of the following compounds



[IIT-JEE-2002(S), 3/150]

(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



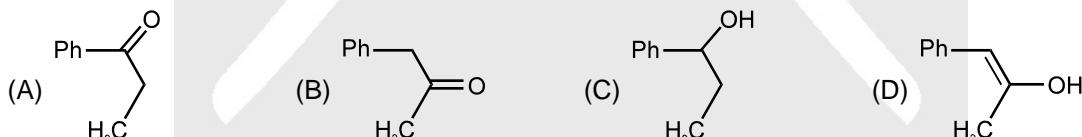
Identify the structure of the major product 'X'.

[IIT-JEE-2002(S), 3/150]

(A)  $\begin{array}{c} \text{H}_3\text{C} - \text{CH} - \text{CH} - \cdot \text{CH}_2 \\ | \qquad \qquad | \\ \text{D} \qquad \text{CH}_3 \end{array}$   
 (B)  $\begin{array}{c} \text{H}_3\text{C} - \text{CH} - \cdot \text{C} - \text{CH}_3 \\ | \qquad \qquad | \\ \text{D} \qquad \text{CH}_3 \end{array}$   
 (C)  $\begin{array}{c} \cdot \text{C} - \text{CH} - \text{CH} - \text{CH}_3 \\ | \qquad \qquad | \\ \text{D} \qquad \text{CH}_3 \end{array}$   
 (D)  $\begin{array}{c} \cdot \text{CH} - \text{CH} - \text{CH} - \text{CH}_3 \\ | \qquad \qquad | \\ \text{H}_3\text{C} \qquad \text{CH}_3 \end{array}$

6.  $\text{Ph}-\text{C}\equiv\text{C}-\text{CH}_3 \xrightarrow{\text{Hg}^{2+} / \text{H}^+} \text{A}$ , A is :

[JEE-2003, 3/144]



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

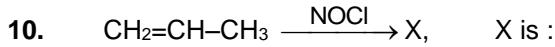
8. The major product obtained on acid-catalysed hydration of 2-phenylpropene is [JEE-2004, 3/144]

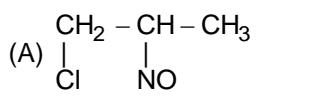
(A) 2-Phenylpropan-2-ol (B) 2-Phenylpropan-1-ol  
 (C) 3-Phenylpropan-2-ol (D) 1-Phenylpropan-1-ol

9.  $(\text{CH}_3)_2\text{CH}-\text{CH}_2\text{CH}_3 \xrightarrow{\text{Cl}_2 / \text{h}\nu} [\text{N}] \xrightarrow{\text{Fractional distillation}} [\text{P}]$

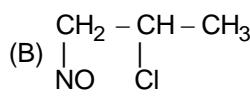
The number of possible isomers [N] and number of fractions [P] are :

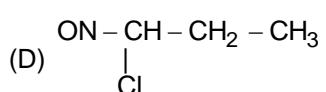
(A) (6, 6) (B) (6, 4) (C) (4, 4) (D) (3, 3)



(A) 

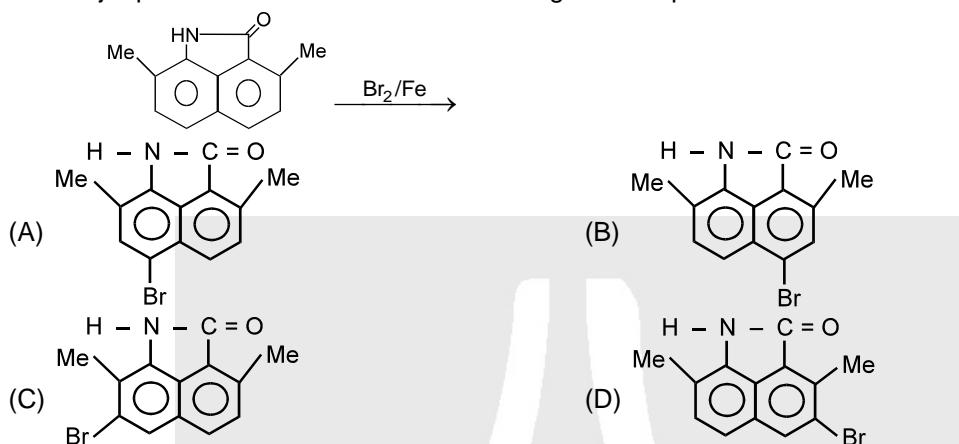
(C)  $\text{ON}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Cl}$

(B) 

(D) 

[JEE-2006, 3/184]

11. The major product of monobromination of the given compound with  $\text{Br}_2 / \text{Fe}$  is - [JEE-2006, 3/184]

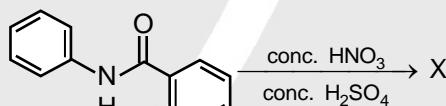


12. The number of stereoisomers obtained by bromination of trans-2-butene is :

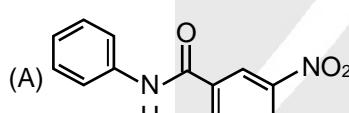
(A) 1 (B) 2 (C) 3 (D) 4

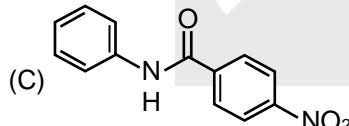
[IIT-JEE-2007, 3/162]

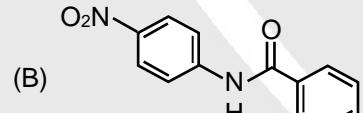
13. In the following reaction,

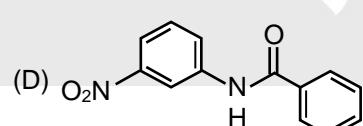


the structure of the major product 'X' is :

(A) 

(C) 

(B) 

(D) 

[JEE 2007, 3/162]

14. **Statement-1** : Bromobenzene upon reaction with  $\text{Br}_2/\text{Fe}$  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]

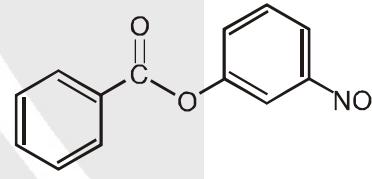
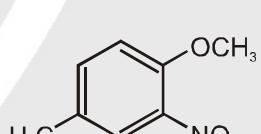
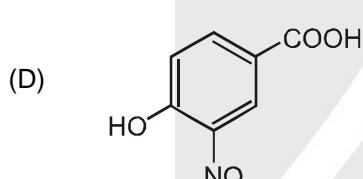
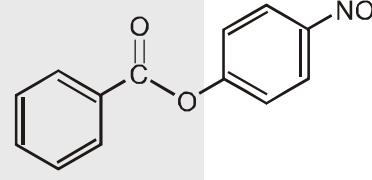
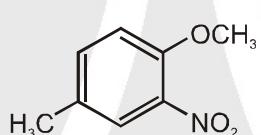
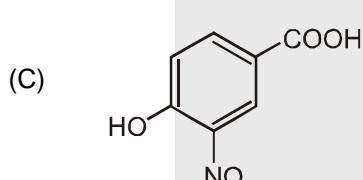
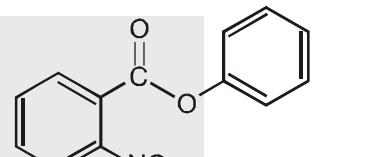
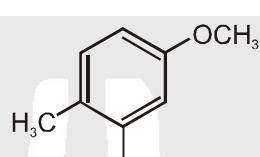
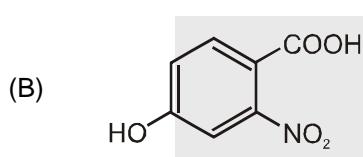
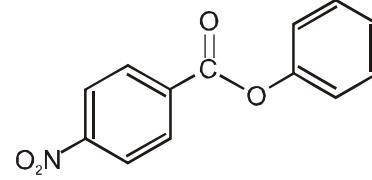
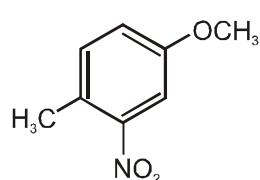
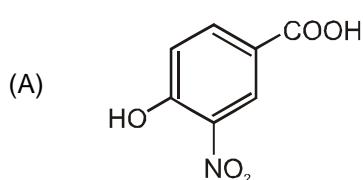
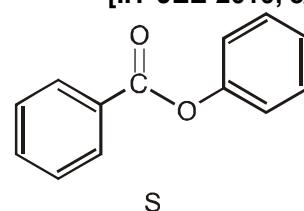
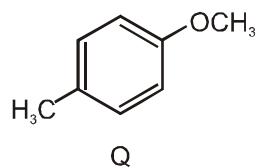
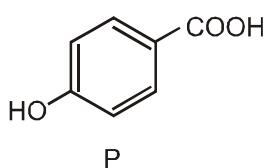
(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.

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

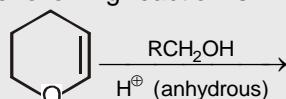
(C) Statement-1 is True, Statement-2 is False

(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]



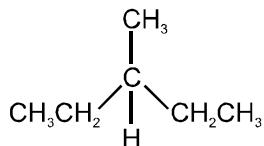
16. The major product of the following reaction is



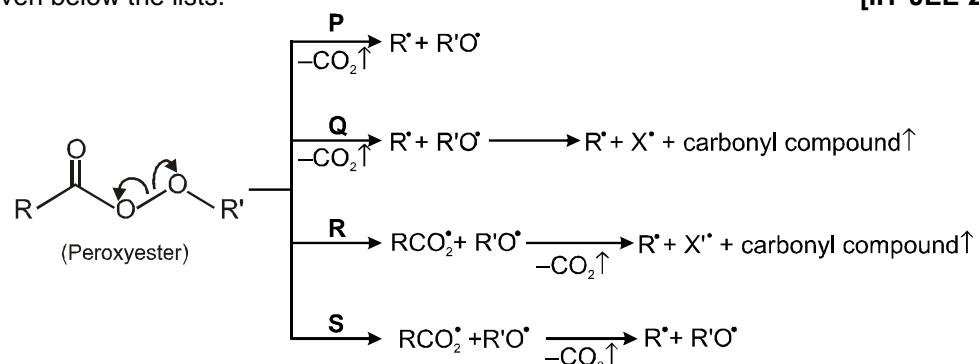
[IIT-JEE-2011, 3/160]

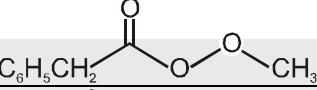
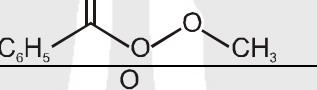
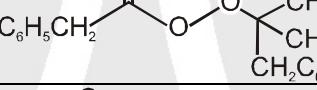
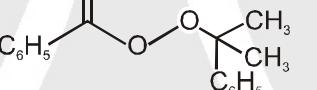
(A) a hemiacetal  
(B) an acetal  
(C) an ether  
(D) an ester

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]



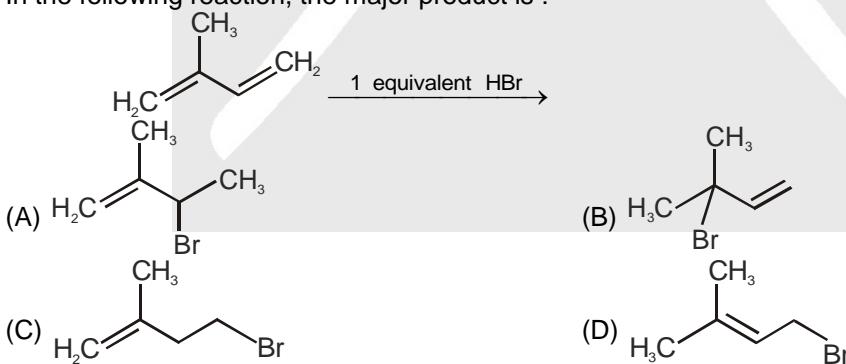
	<b>List-I</b>		<b>List-II</b>
P.	Pathway <b>P</b>	1.	
Q.	Pathway <b>Q</b>	2.	
R.	Pathway <b>R</b>	3.	
S.	Pathway <b>S</b>	4.	

Code :

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

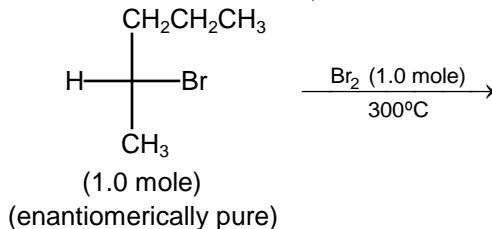
	P	Q	R	S
(B)	2	4	3	1
(D)	3	2	1	4

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



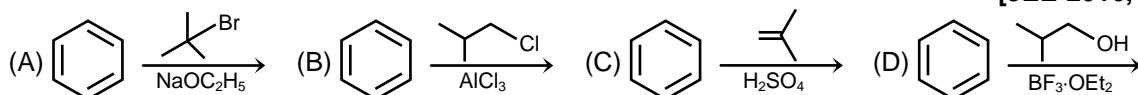
[JEE-2015, 4/168]

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

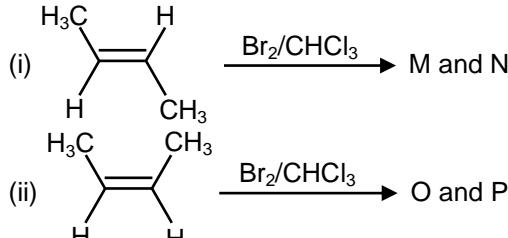




21.\* Among the following, reaction(s) which gives(give) *tert*-butyl benzene as the major product is(are) [JEE-2016, 3/60]



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

1. What is the product when acetylene reacts with hypochlorous acid ? [AIEEE-2002, 3/225]  
 (1)  $\text{CH}_3\text{COCl}$  (2)  $\text{ClCH}_2\text{CHO}$  (3)  $\text{Cl}_2\text{CHCHO}$  (4)  $\text{ClCH}_2\text{COOH}$ .

2. 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.

3. 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

4. 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

5. HBr reacts with  $\text{CH}_2=\text{CH}-\text{OCH}_3$  under anhydrous conditions at room temperature to give [AIEEE-2006, 3/165]  
 (1)  $\text{CH}_3\text{CHO}$  and  $\text{CH}_3\text{Br}$  (2)  $\text{BrCH}_2\text{CHO}$  and  $\text{CH}_3\text{Br}$   
 (3)  $\text{BrCH}_2-\text{CH}_2-\text{OCH}_3$  (4)  $\text{H}_3\text{C}-\text{CHBr}-\text{OCH}_3$

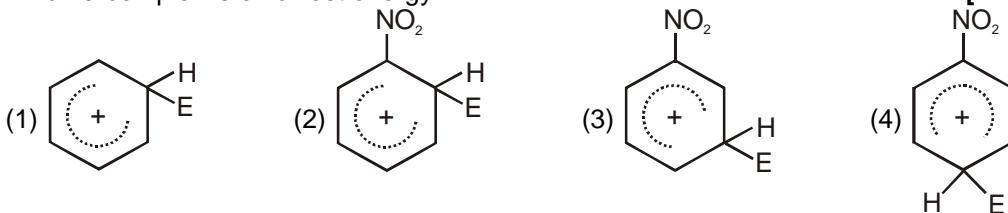
6. The reaction of toluene with  $\text{Cl}_2$  in presence of  $\text{FeCl}_3$  gives predominantly : [AIEEE-2007, 3/120]  
 (1) o- and p-chlorotoluene (2) m-chlorotoluene  
 (3) benzoylchloride (4) benzyl chloride

7. 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)  $\text{CH}_3-\text{CH}=\text{CH}_2 + \text{HBr} \rightarrow$

8. 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  $\sigma$ -complex. Of the following, which  $\sigma$ -complex is of lowest energy ? [AIEEE-2008, 3/105]



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) Neo hexane

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]

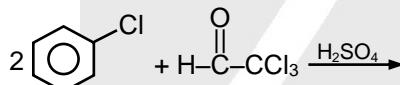
(1) Zero (2) Two (3) Four (4) Six

### 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]

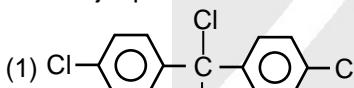
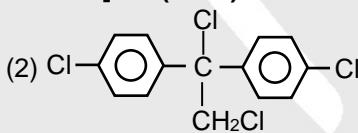
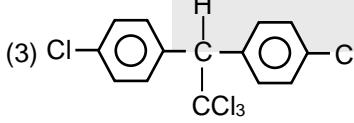
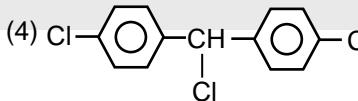
(1)  $CH_3CH_2OH$  (2)  $CH_3CHOHCH_3$   
(3)  $CH_3CH_2CH_2OH$  (4)  $(CH_3)_3COH$

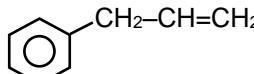
2. Chlorobenzene reacts with trichloroacetaldehyde in the presence of  $H_2SO_4$



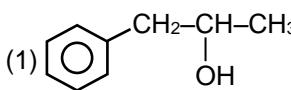
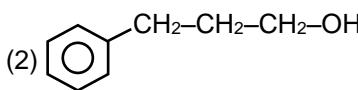
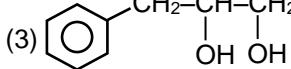
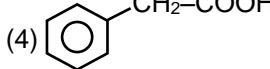
The major product formed is :

[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) 



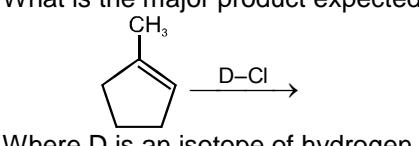
4. In the presence of peroxide, HCl and HI do not give anti-Markownikoff's addition to alkenes because:  
[JEE(Main) 2014 Online (12-04-14), 4/120]

- One of the steps is endothermic in HCl and HI.
- Both HCl and HI are strong acids.
- HCl is oxidizing and the HI is reducing.
- 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-bromo-2-methylbutane
- 1-bromo-3-methylbutane
- 2-bromo-3-methylbutane
- 2-bromo-2-methylbutane

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



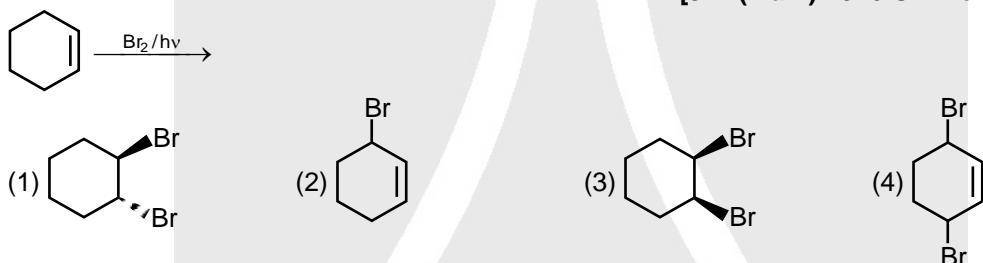
Where D is an isotope of hydrogen.

- 
- 
- 
- 

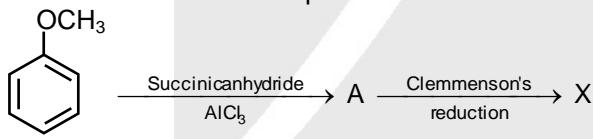
[JEE(Main) 2015 Online (11-04-15), 4/120]

7. Bromination of cyclohexene under conditions given below yields:

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



8. Consider the reaction sequence below :



X is :

- 
- 
- 
- 

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

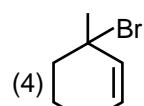
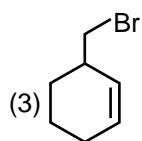
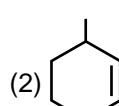
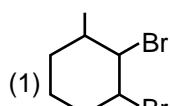
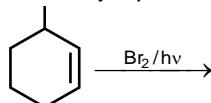
9. Which of the following compounds will not undergo Friedel Craft's reaction with benzene ?

[JEE(Main) 2017 Online (08-04-17), 4/120]

- 
- 
- 
-

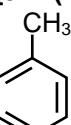
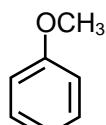
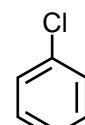
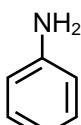
10. The major product of the following reaction is :

[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]

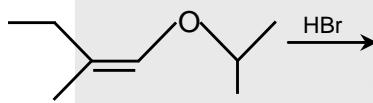


(1) (a) < (b) < (d) < (c)  
(3) (b) < (a) < (c) < (d)

(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

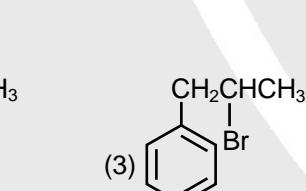
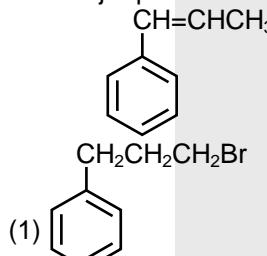
(2) Four

(3) Six

(4) Zero

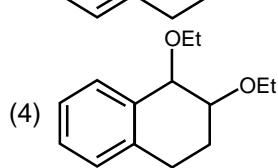
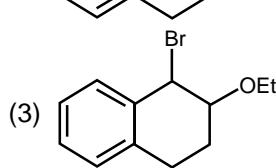
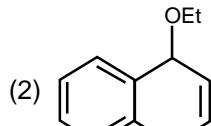
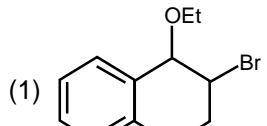
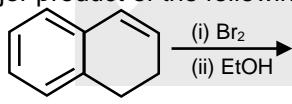
13. The major product of the following reaction is :

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



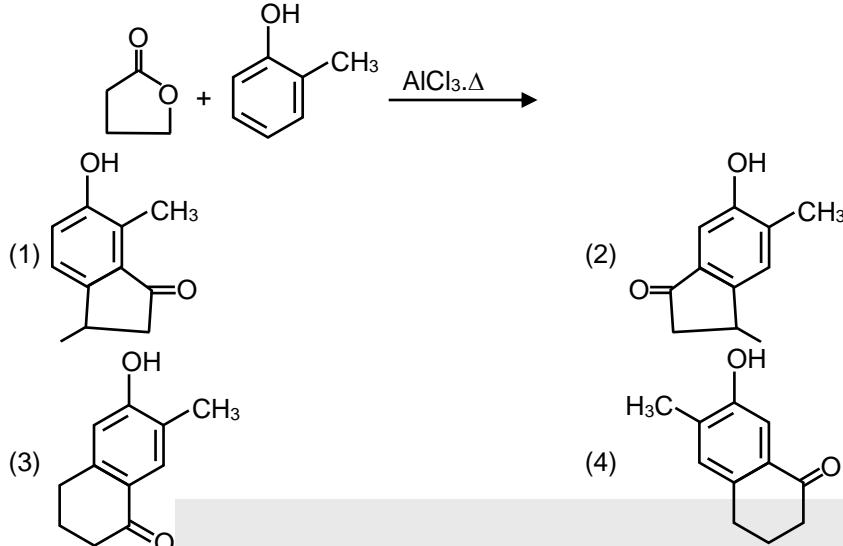
14. The major product of the following reaction is :

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



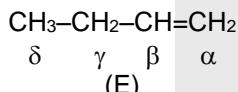
15. The major product of the following reaction is :

[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?

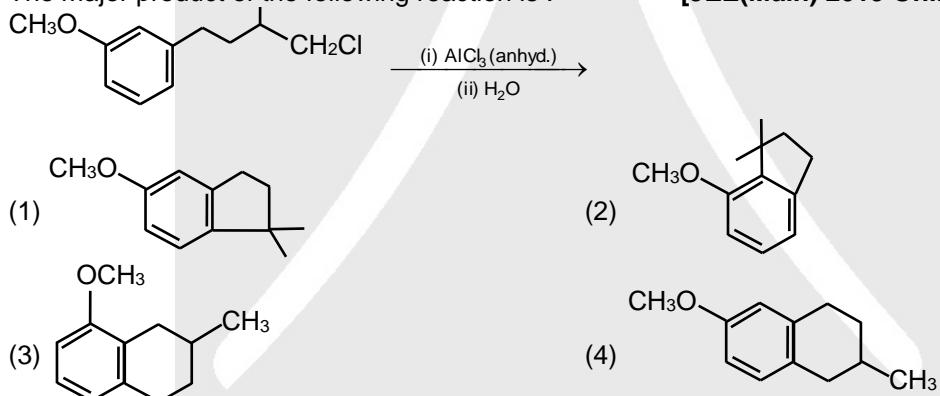
[JEE(Main) 2019 Online (10-01-19), 4/120]



(1)  $\alpha$ -hydrogen      (2)  $\gamma$ -hydrogen      (3)  $\beta$ -hydrogen      (4)  $\delta$ -hydrogen

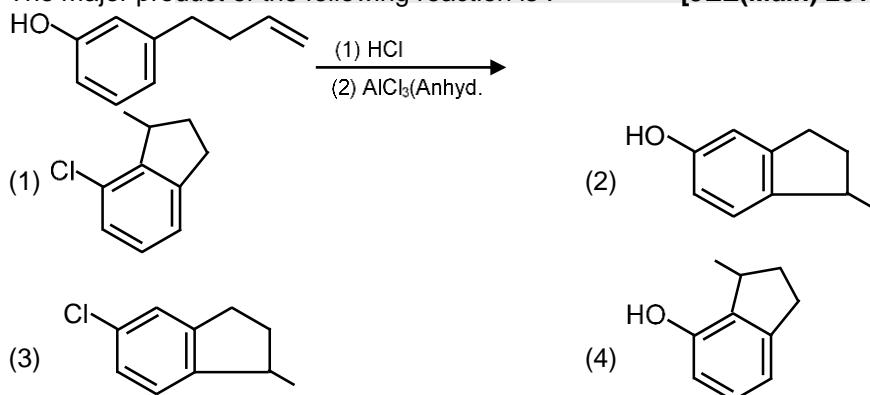
17. The major product of the following reaction is :

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

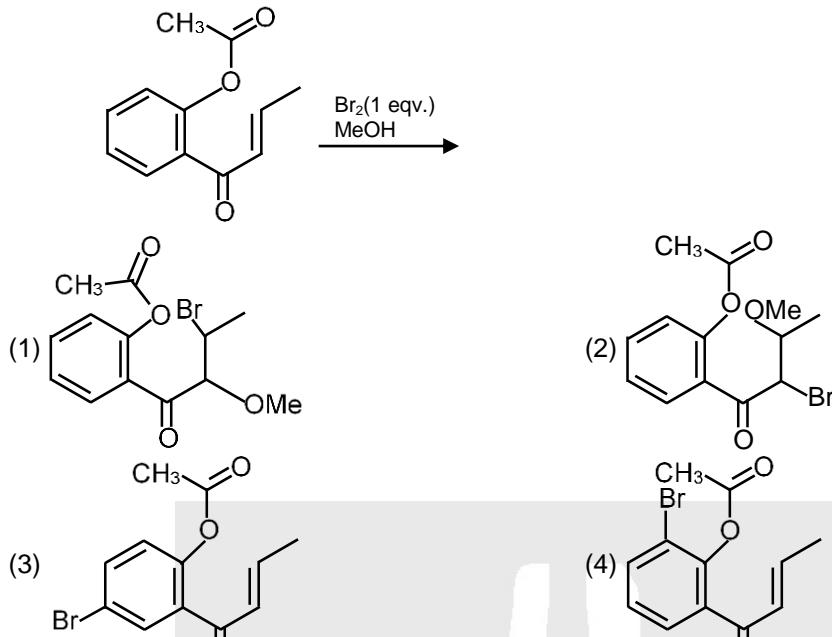


18. The major product of the following reaction is :

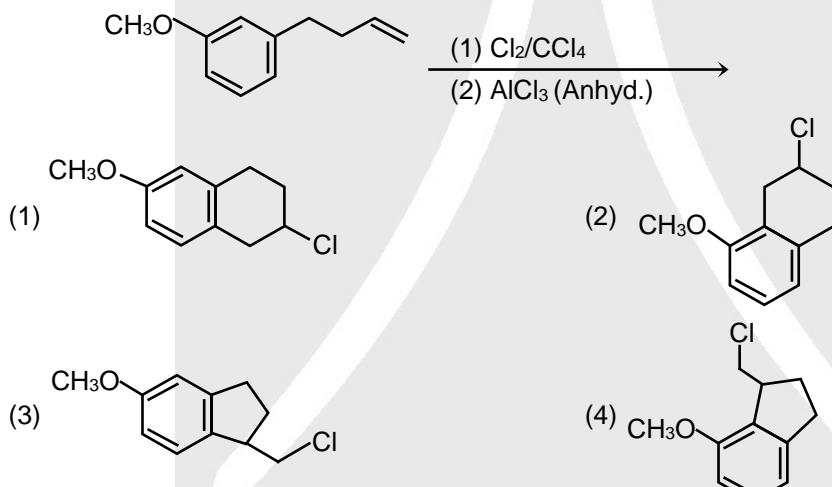
[JEE(Main) 2019 Online (11-01-19), 4/120]



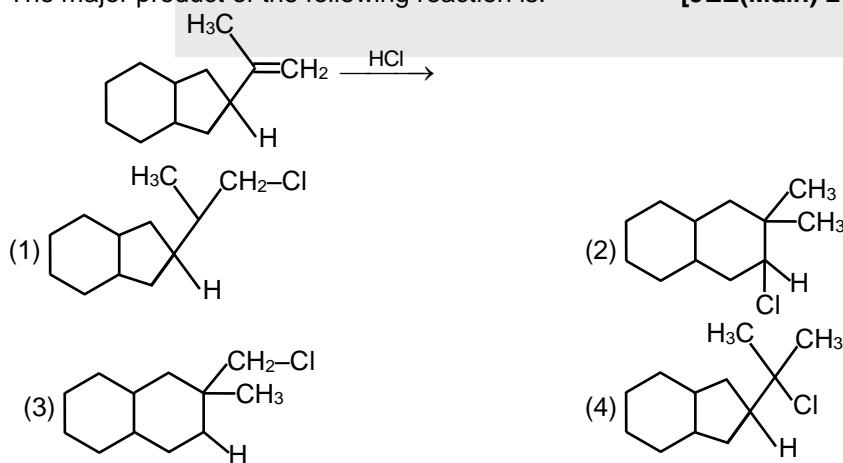
19. The major product obtained in the following conversion is: [JEE(Main) 2019 Online (11-01-19), 4/120]



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

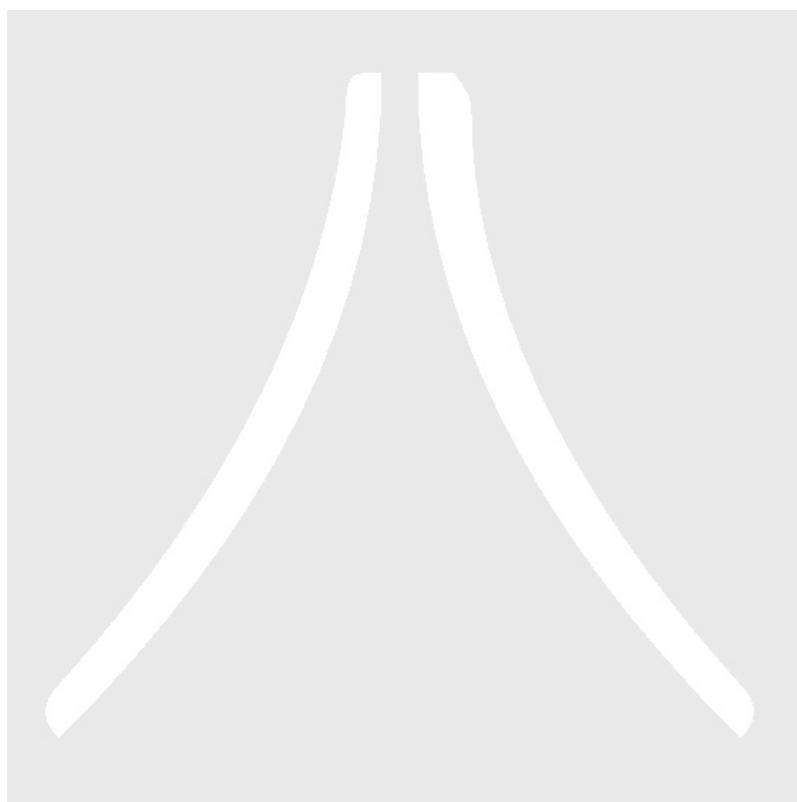
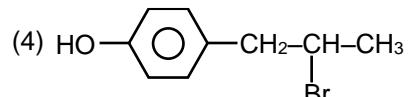
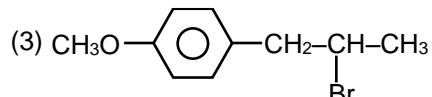
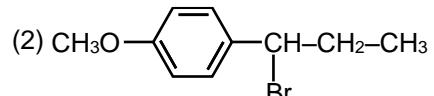
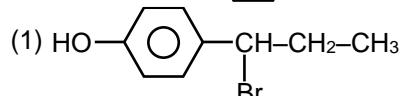
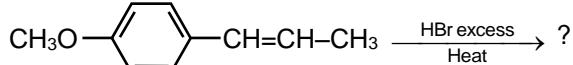


21. The major product of the following reaction is: [JEE(Main) 2019 Online (12-01-19), 4/120]



22. The major product in the following conversion is:

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





**PART – II**

<b>A-1.</b> (C)	<b>A-2.</b> (B)	<b>A-3.</b> (A)	<b>A-4.</b> (B)	<b>A-5.</b> (C)
<b>A-6.</b> (D)	<b>A-7.</b> (C)	<b>A-8.</b> (C)	<b>B-1.</b> (A)	<b>B-2.</b> (B)
<b>B-3.</b> (C)	<b>B-4.</b> (C)	<b>B-5.</b> (D)	<b>B-6.</b> (B)	<b>B-7.</b> (A)
<b>B-8.</b> (D)	<b>B-9.</b> (A)	<b>B-10.</b> (C)	<b>C-1.</b> (B)	<b>C-2.</b> (B)
<b>C-3.</b> (B)	<b>C-4.</b> (B)	<b>C-5.</b> (A)	<b>C-6.</b> (D)	<b>C-7.</b> (C)
<b>C-8.</b> (B)	<b>C-9.</b> (D)	<b>C-10.</b> (A)		

**PART – III**

<b>1.</b> (D)	<b>2.</b> (A - q, r) ; (B - p, r) ; (C - p, r) ; (D - q, s)
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**EXERCISE - 2****PART – I**

<b>1.</b> (A)	<b>2.</b> (A)	<b>3.</b> (C)	<b>4.</b> (C)	<b>5.</b> (A)
<b>6.</b> (D)	<b>7.</b> (D)	<b>8.</b> (B)	<b>9.</b> (A)	<b>10.</b> (C)
<b>11.</b> (B)	<b>12.</b> (A)			

**PART – II**

<b>1.</b> 3	<b>2.</b> 4	<b>3.</b> 23	<b>4.</b> 2	<b>5.</b> 4
<b>6.</b> 4	<b>7.</b> 4	<b>8.</b> 21		

**PART – III**

<b>1.</b> (ABC)	<b>2.</b> (ABC)	<b>3.</b> (AC)	<b>4.</b> (BD)	<b>5.</b> (BCD)
<b>6.</b> (ABCD)	<b>7.</b> (ABCD)	<b>8.</b> (ABCD)	<b>9.</b> (AD)	<b>10.</b> (AD)

**PART – IV**

<b>1.</b> (B)	<b>2.</b> (B)	<b>3.</b> (D)	<b>4.</b> (B)	<b>5.</b> (C)
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**EXERCISE – 3****PART – I**

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