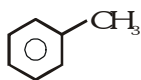


EXERCISE-01**CHECK YOUR GRASP****SELECT THE CORRECT ALTERNATIVE (ONLY ONE CORRECT ANSWER)**

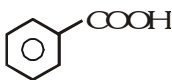
1. The correct order of reactivity towards the electrophilic substitution of the compounds aniline (I), benzene (II) and nitrobenzene (III) is :-

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

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



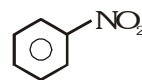
I



II



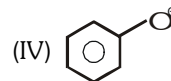
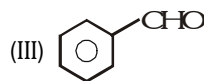
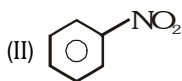
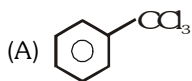
III



IV

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

3. Electrophile NO_2^+ attacks the following :



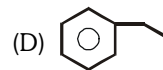
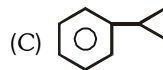
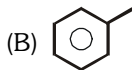
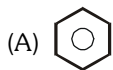
in which cases NO_2^+ will attack at meta position

(A) II and IV (B) I, II and III (C) II and IV (D) I only

4. The strongest deactivating effect on aromatic ring is

(A) $-\text{CH}_2\text{Cl}$ (B) $-\text{OCH}_3$ (C) $-\text{CH}_3$ (D) $-\text{CCl}_3$

5. Which of the following is maximum reactive for nitration is :-



6. The order of decreasing reactivity towards electrophilic reagent for the following :

(a) Benzene (b) Toluene

(c) Chloro benzene (d) Anisole

(A) b > d > a > c (B) d > c > b > a (C) d > b > a > c (D) a > b > c > d

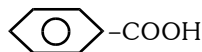
7. Increasing order of the following for electrophilic substitution reaction as -



(I)



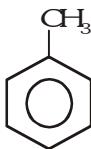
(II)



(III)

(A) I < II < III (B) III < II < I (C) II < III < I (D) I < III < II

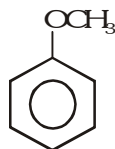
8. Among the compounds :



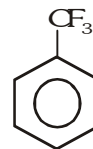
(I)



(II)



(III)



(IV)

the order of decreasing reactivity towards electrophilic substitution is :

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

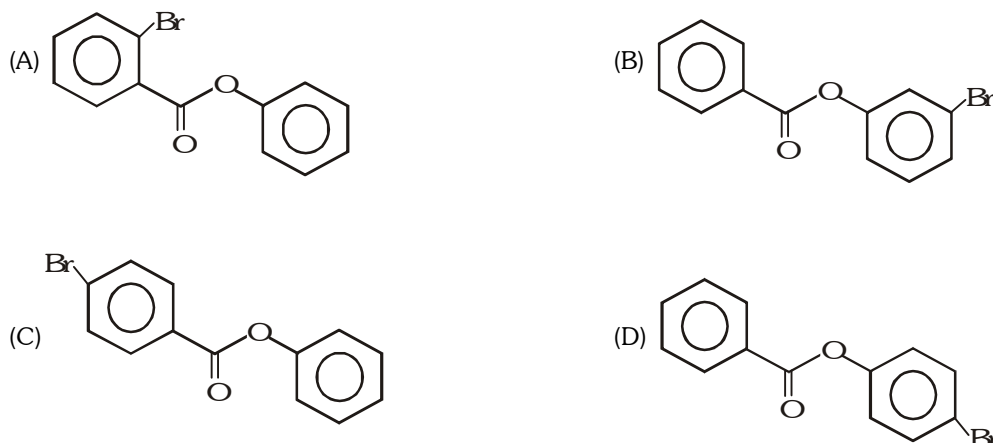
9. Choose the most reactive among the following compound :



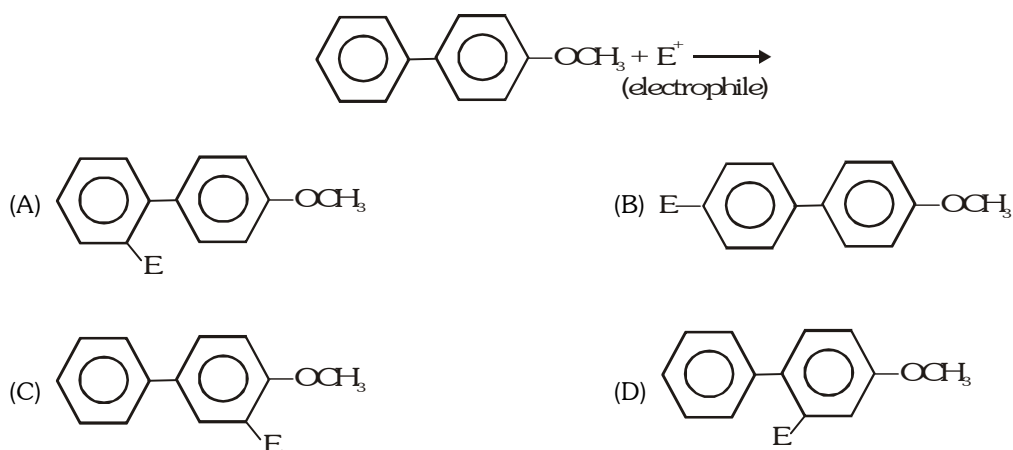
10. The number of possible dichloronitrobenzene isomers is :

- (A) 3 (B) 4 (C) 6 (D) 8

11. The major product formed on monobromination of phenylbenzoate is :



12. The major product formed in the reaction is :



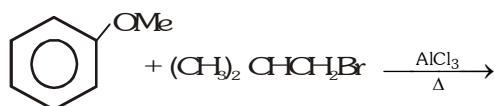
13. The electrophilic aromatic substitution of a compound C_6H_5Y produces mainly a meta-disubstituted product. Among the following which one could be the substituent Y ?

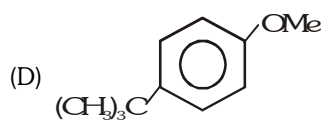
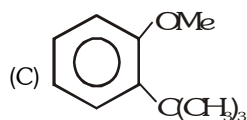
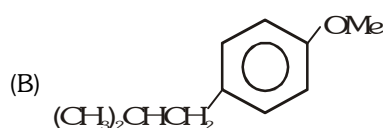
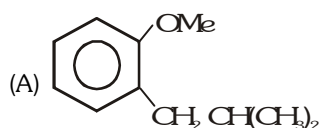
- (A) $-NH_2$ (B) $-COOH$ (C) $-CH_3$ (D) $-OCH_3$

14. Which of the following is an o-, p-directing but deactivating substituent in an electrophilic aromatic substitution :

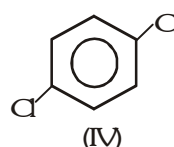
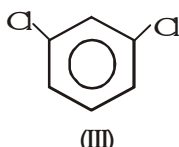
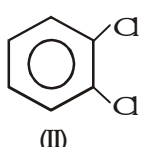
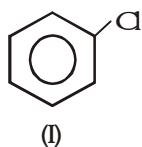
- (A) $-CCl_3$ (B) $-Cl$ (C) $-NHCOCH_3$ (D) $-OCH_3$

15. The major product formed in the reaction is :

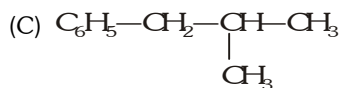
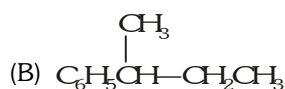
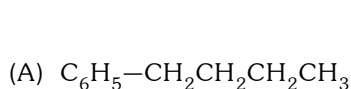




16. The dipole moment of chlorobenzene is 1.6 D. The expected dipole moment of meta-dichlorobenzene is:
 (A) 1.6 D (B) 3.2 D (C) $1.6\sqrt{2}$ D (D) 0.0 D
17. In the nitration of benzene with a mixture of concentrated HNO_3 and concentrated H_2SO_4 , the active species involved is :
 (A) NO_3^- (B) NO_2 (C) NO_2^- (D) NO_2^+
18. Which of the following substituted benzene derivatives would produce three isomeric products when one more substituent is introduced ?

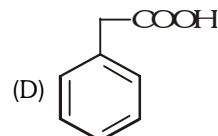
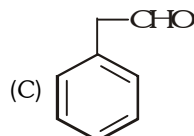
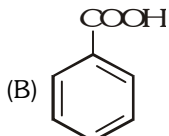
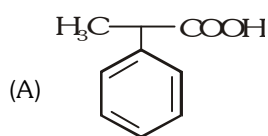


- (A) I, II and III (B) I and III (C) II and IV (D) I and IV
19. In the sulphonation of benzene, the active electrophilic species is :
 (A) SO_2 (B) SO_3 (C) SO_4^{2-} (D) HSO_4^-
20. The Friedel-Crafts reaction of benzene with n-butyl chloride at 0°C produces :

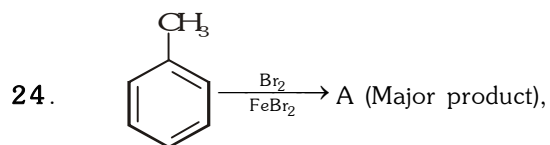


(D) all of these

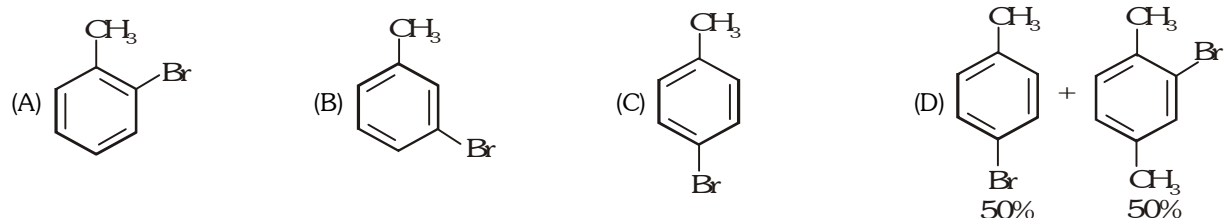
21. Sulfonation differs from most of electrophilic aromatic substitution reactions with the fact that the reaction-
 (A) is reversible (B) requires Lewis acid as catalyst
 (C) is explosive (D) takes place at high temperature
22. Cumene on treatment with KMnO_4 gives -



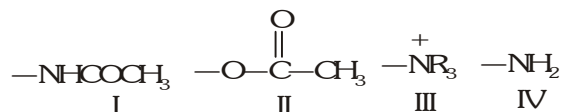
23. Benzene reacts with CH_3COCl in the presence of anhyd. AlCl_3 to give :
 (A) $\text{C}_6\text{H}_5\text{CH}_3$ (B) $\text{C}_6\text{H}_5\text{Cl}$ (C) $\text{C}_6\text{H}_5\text{O}_2\text{Cl}$ (D) $\text{C}_6\text{H}_5\text{COCH}_3$



then the major product A is -



25. Arrange the following in correct activating order towards EAS -

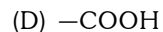
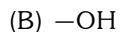
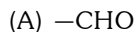


- (A) $\text{III} < \text{I} < \text{II} < \text{IV}$ (B) $\text{IV} < \text{I} < \text{II} < \text{III}$
 (C) $\text{III} < \text{II} < \text{I} < \text{IV}$ (D) $\text{II} < \text{III} < \text{I} < \text{IV}$

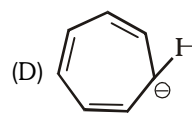
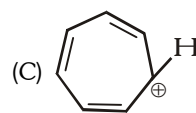
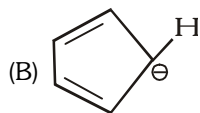
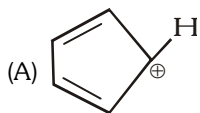
CHECK YOUR GRASP						ANSWER KEY					EXERCISE -1				
Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	D	C	B	D	B	C	B	B	B	C	D	C	B	B	D
Que.	16	17	18	19	20	21	22	23	24	25					
Ans.	A	D	B	B	A	A	B	D	A	C					

EXERCISE-02**BRAIN TEASERS****SELECT THE CORRECT ALTERNATIVES (ONE OR MORE THEN ONE CORRECT ANSWERS)**

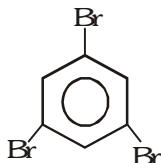
1. Which of the following groups are m-directing :



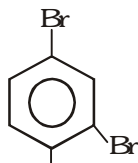
2. Amongst the ions the aromatic species are :



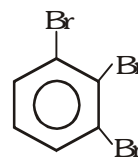
3. The following three isomeric tribromobenzenes are subjected to mononitration, which is/are given two isomers :



(I)



(II)



(III)

Which of these would produce three possible mononitrotribromobenzenes :

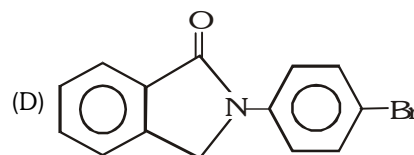
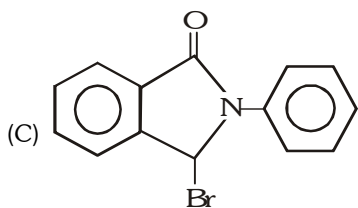
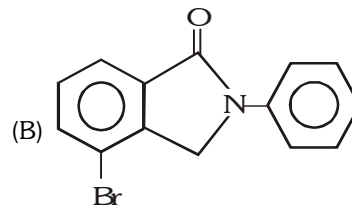
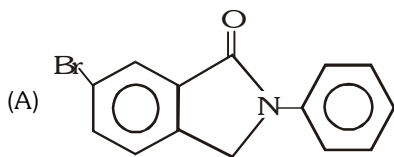
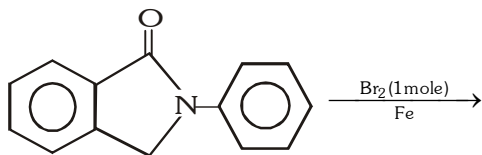
(A) II and III

(B) I and II

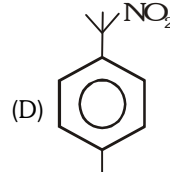
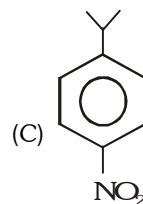
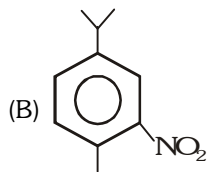
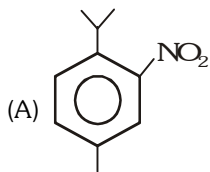
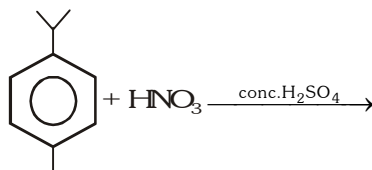
(C) II

(D) III

4. In the reaction the major product formed is :

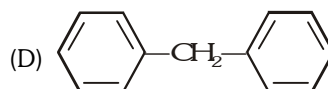
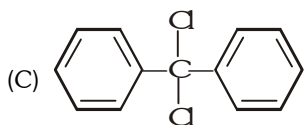
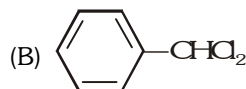
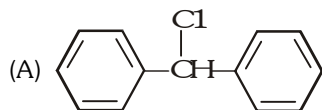


5. The major product formed in the reaction is :

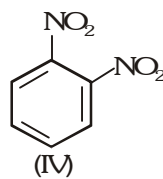
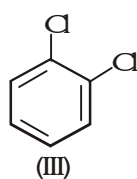
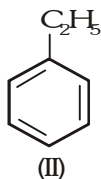
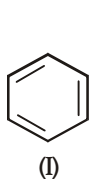


6. Nitrobenzene reacts with Br_2 in the presence of FeBr_3 to give m-bromonitrobenzene as the major product. Which of the following provides the best reason for the formation of m-bromonitrobenzene as the major product :
- The electron density at the meta position is greater than those at the ortho and para positions
 - Aromaticity is lost in the σ -complexes formed by the attack of Br^+ at the ortho and para positions but not at the meta position.
 - The σ -complex formed by the attack of Br^+ at the meta position is the least destabilized and the most stable among the three σ -complexes
 - In the final step of regeneration of benzene ring by the loss of H^+ from the σ -complexes, the meta-oriented σ -complex loses H^+ most readily
7. Isopropylbenzene can be prepared by :
- Benzene + $\text{CH}_3\text{CH}=\text{CH}_2 \xrightarrow{\text{H}_2\text{SO}_4}$
 - Benzene + $\text{CH}_3-\underset{\text{Cl}}{\underset{|}{\text{CH}}}-\text{CH}_3 \xrightarrow{\text{H}_2\text{SO}_4}$
 - Benzene + $\text{CH}_3-\underset{\text{Cl}}{\underset{|}{\text{CH}}}-\text{CH}_3 \xrightarrow{\text{AlCl}_3}$
 - Benzene + $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} \xrightarrow[\Delta]{\text{AlCl}_3}$
8. Which of the following characteristic does an aromatic compound exhibit :
- It should have $(4n + 2)$ π -electrons in the ring
 - It should be planar and conjugated
 - It should have $4n$ π -electrons in the ring
 - It should possess high resonance energy
9. Which of the following groups are meta-directing :
- $-\text{NH}_2$
 - $-\text{OH}$
 - $-\text{NO}_2$
 - $-\text{CN}$
10. Which of the following groups are ortho-and para-directing :
- $-\text{OH}$
 - $-\text{CHO}$
 - $-\text{CN}$
 - $-\text{NHCOCH}_3$
11. Which of the following statements are correct :
- An activating group is an electron-releasing group
 - An activating group activates all positions of the benzene ring
 - The effect of any group—whether activating or deactivating—is the strongest at the ortho-and para-positions in the benzene ring
 - An activating group activates only the ortho-and para-positions in the benzene ring
12. The major products formed in the reaction of toluene with chlorine in the presence of ferric chloride are:
- o-chlorotoluene
 - m-chlorotoluene
 - p-chlorotoluene
 - benzyl chloride
13. Benzene can undergo :
- substitution
 - addition
 - elimination
 - oxidation
14. Which of the following statements about the nitration of aromatic compounds are correct :
- The rate of nitration of toluene is greater than that of benzene
 - The rate of nitration of benzene is almost the same as that of hexadeutrobenzene
 - The rate of nitration of benzene is greater than that of hexadeutrobenzene
 - Nitration is an electrophilic substitution reaction

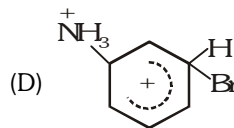
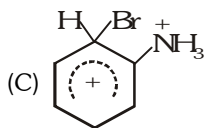
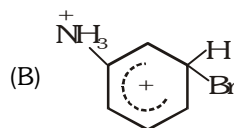
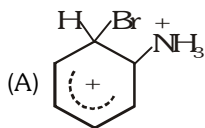
15. Halogenation of benzene in presence of AlCl_3 (anhy.) is :
 (A) nucleophilic substitution (B) nucleophilic addition
 (C) electrophilic substitution (D) free radical substitution
16. Which of the following structures correspond to the product expected, when excess of C_6H_6 reacts with CH_2Cl_2 in presence of anhydrous AlCl_3 ?



17. Select the incorrect statement among the following :
 (A) benzene undergoes predominantly electrophilic substitution reactions
 (B) toluene is more easily sulphonated than benzene
 (C) benzene reacts with CCl_4 in the presence of anhydrous AlCl_3 to give triphenyl methyl chloride
 (D) benzene reacts with chlorine (Cl_2) in presence of light to give benzyl chloride
18. Identify the correct order of reactivity in electrophilic substitution reactions of the following compounds:




- (A) $\text{I} > \text{II} > \text{III} > \text{IV}$ (B) $\text{IV} > \text{III} > \text{II} > \text{I}$
 (C) $\text{II} > \text{I} > \text{III} > \text{IV}$ (D) $\text{II} > \text{III} > \text{I} > \text{IV}$
19. The structure of Wheland intermediate obtained after the attack of Br^+ on anilinium ion is :





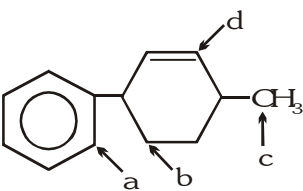
EXERCISE-03

MISCELLANEOUS TYPE QUESTIONS

TRUE OR FALSE :

1. Substitution of benzene occurs through nucleophilic attack.
2. AlCl_3 (aq.) is used as catalyst in Friedel-Crafts reaction.
3. Diphenyl methane is obtained when excess benzene is treated with dichloro methane in presence of anhydrous AlCl_3 .
4.  gives ortho-methyl aniline when treated with CH_3Cl in presence of AlCl_3 (anhydrous).
5. $-\text{CCl}_3$ and $-\text{Cl}$ are the meta director.

FILL IN THE BLANKS :

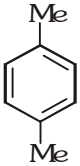
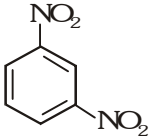

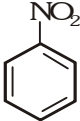
1. Give the structure of the electrophile formed as per the major product :
 - (i) $\text{FeBr}_3 + \text{Br}_2 \longrightarrow \dots\dots\dots$
 - (ii) $\text{HNO}_3 + \text{H}_2\text{SO}_4 \xrightarrow[\text{conc.}]{\text{conc.}} \dots\dots\dots$
 - (iii) $\text{SO}_3 + \text{H}_2\text{SO}_4 \xrightarrow[\text{fuming sulphuric acid}]{} \dots\dots\dots$
 - (iv) $\text{CH}_3\text{Cl} + \text{AlCl}_3 \longrightarrow \dots\dots\dots$
 - (v) $\text{CH}_3 - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_2\text{Cl} + \text{AlCl}_3 \xrightarrow{\Delta} \dots\dots\dots$
2. Write the structure of σ -complex (carbocation) in the following S_E reactions :
 - (i)  + SO_3 (neutral) $\longrightarrow \dots\dots\dots$
 - (ii)  + NO_2^+ $\longrightarrow \dots\dots\dots$
3. Write hybridisation of carbon atoms as indicated :
 - (a) $\dots\dots\dots$
 - (b) $\dots\dots\dots$
 - (c) $\dots\dots\dots$
 - (d) $\dots\dots\dots$

MATCH THE COLUMN

1. Match the column I with column II.

Column-I		Column-II	
(A)	Cyclic conjugated polyenes with $(4n + 2) \pi$ -electrons	(p)	Arenes and alkyl halides in presence of anhydrous AlCl_3
(B)	Dichlorobenzene	(q)	Aromatic compounds
(C)	Friedel crafts reaction	(r)	Delocalization of π -electrons
(D)	Meta directing group	(s)	Deactivates the ring towards electrophilic substitution

2. Match the column I with column II.

Column-I		Column-II	
	(Compounds)		(orientation of attacking electrophile)
(A)		(p)	Meta position with respect to $-\text{NO}_2$
(B)		(q)	ortho with respect to methyl group
(C)		(r)	only one mono substituted product
(D)		(s)	meta with respect to $-\text{CH}_3$

ASSERTION & REASON QUESTION :

These questions contains, Statement-I (assertion) and Statement-II (reason).

(A) Statement-I is True, Statement-II is True ; Statement-II is a correct explanation for Statement-I

(B) Statement-I is True, Statement-II is True ; Statement-II is NOT a correct explanation for Statement-I

(C) Statement-I is True, Statement-II is False.

(D) Statement-I is False, Statement-II is True.

1. **Statement-I** : In nitration H_2SO_4 is used as sulphonating agent.

Because

Statement-II : Benzene has multicentre π -bonding.

2. **Statement-I** : C_2H_5 is a meta-directing group.

Because

Statement-II : The groups which direct the incoming group to meta position are called meta-directing groups.

3. **Statement-I** : Tropylium cation is aromatic in nature.



Because

Statement-II : The only property that determines its aromatic behavior is its planar structure.

4. **Statement-I** : Benzene on heating with conc. H_2SO_4 gives benzene sulphonic acid which when heated with superheated steam under pressure gives benzene.

Because

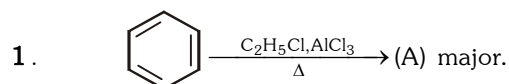
Statement-II : Sulphonation is a reversible process.

5. **Statement-I** : Chlorination of ethyl benzene with Cl_2 in presence of heat and light nearly yield 1-chloro-1-phenyl ethane as major product.
Because
Statement-II : The reaction occurs through intermediate formation of the radical $\text{C}_6\text{H}_5\dot{\text{C}}\text{H}-\text{CH}_3$.
6. **Statement-I** : Nitration of toluene is easier than benzene.
Because
Statement-II : The methyl group in toluene is electron-releasing.
7. **Statement-I** : Benzene reacts with n-propyl chloride in presence of AlCl_3/Δ to give isopropyl benzene.
Because
Statement-II : Benzene undergoes electrophilic substitution readily.
8. **Statement-I** : Most o-, p -directing substitution are deactivating.
Because
Statement-II : o-, p-directors have at least one lone pair of non-bonding electrons.
9. **Statement-I** : Nitrobenzene does not undergo Friedel-Craft's reaction.
Because
Statement-II : Nitrogroup is a deactivating group.
10. **Statement-I** : The rate of nitration of benzene is less than hexa deuterio benzene.
Because
Statement-II : Deuterium is an isotope of hydrogen.

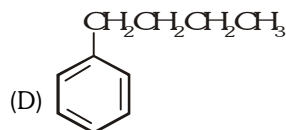
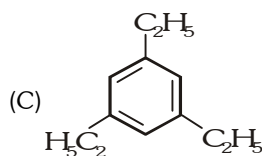
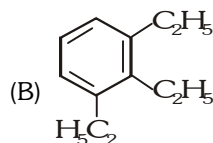
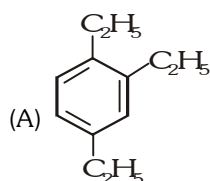
COMPREHENSION BASED QUESTIONS :

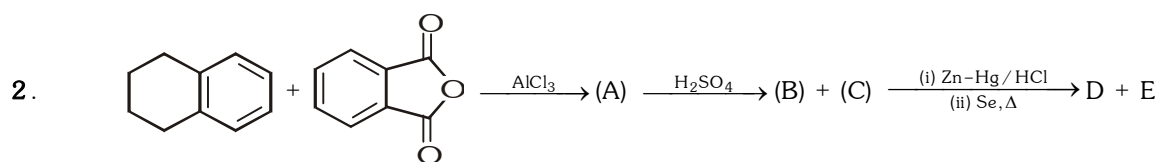
Comprehension # 1

The typical reaction of benzene and other aromatic compounds are electrophilic substitution. Presence of electron donating group activates the ring towards electrophilic substitution, while presence of electron withdrawing group deactivates the ring towards electrophilic substitution but at the same time activates the ring towards nucleophilic substitution. Some groups are predominantly meta-directing and all of these are deactivating. Except halogen, most of the o-and p-directing groups are activating groups.

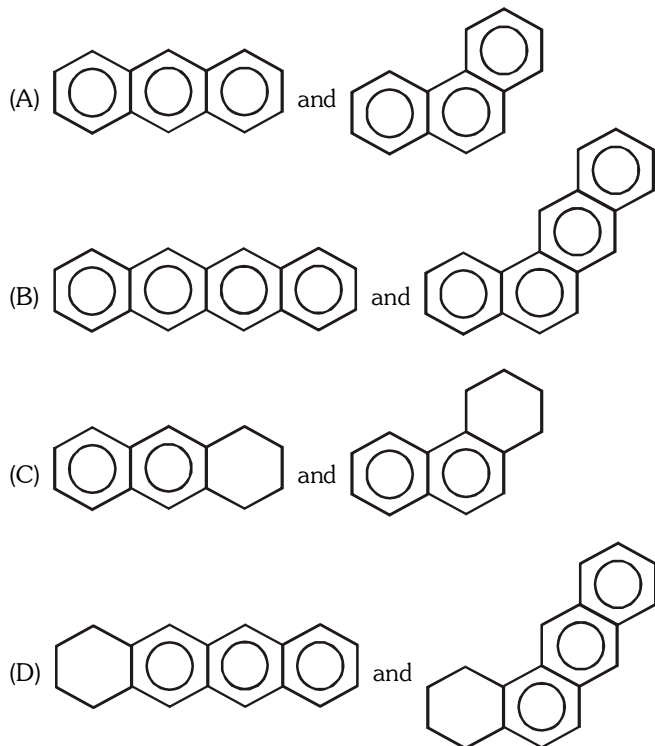


A is trisubstituted benzene. The structure of A is :

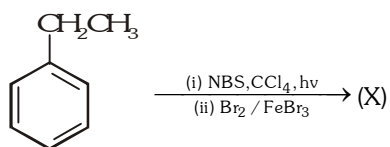




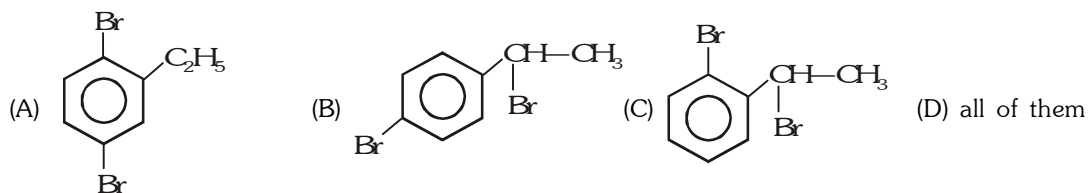
D and E are :



3. Which of the following compound is not formed.



X represents mixture of organic compounds. The mixture does not contain.



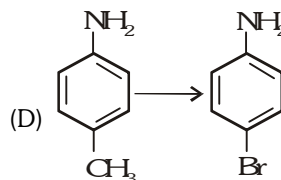
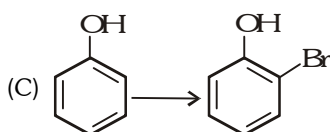
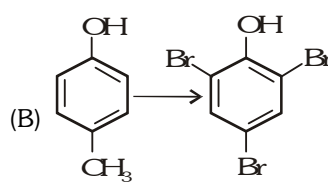
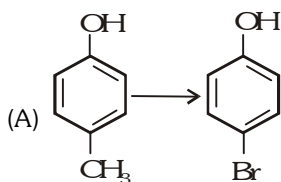
Comprehension # 2

It is not always easy to predict the position of attack on multiply substituted benzene. If the benzene ring bears different ortho/para directing group at the 1 and 4 positions, the position of further substitution is not immediately clear. Sometimes steric effects determine the outcome. In other cases, electronic factors determine the outcome, and further reaction will be at the position activated by the more strongly activating group.

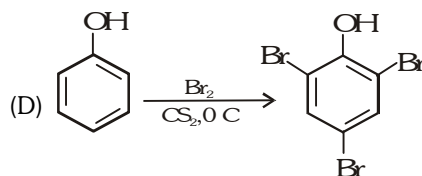
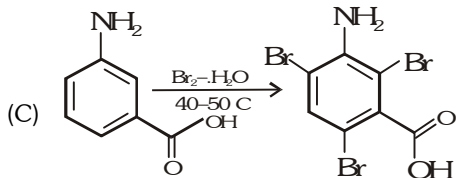
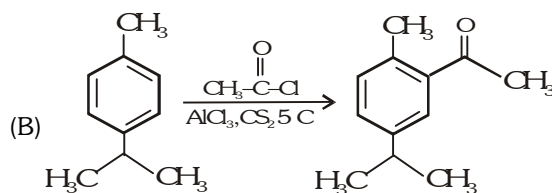
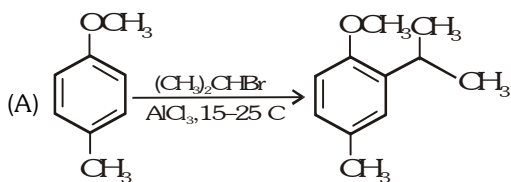
Some substituents are so strongly activating that no catalyst is needed, and it is often difficult to stop substitution after mono substitution. Mild conditions are needed to restrict the reaction to mono-substitution.

It is possible to reduce the activity such groups (by side chain reaction) so that the reaction can be stopped after mono substitution then and again by a side chain reaction the original group is restored. Effective use can sometimes be made of removable blocking groups on the ring.

1. Which of the following synthesis could be done in the ring step ?



2. Which of the following is the correct major product ?



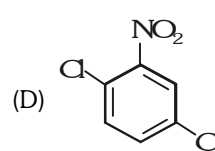
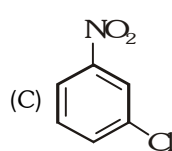
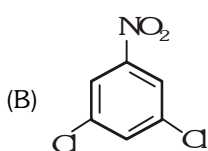
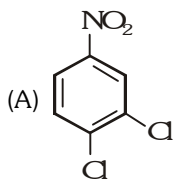
3. Which of the following side chain reaction/s can be used to reduce the activity of strongly activating groups like $-OH$?
- (A) benzylation (B) acetylation (C) both of the above (D) none of the above

Comprehension # 3

A third group is least likely to enter between two groups in the meta relationship. This is the result of steric hindrance and increases in importance with the size of the groups on the ring and with the size of the attacking species.

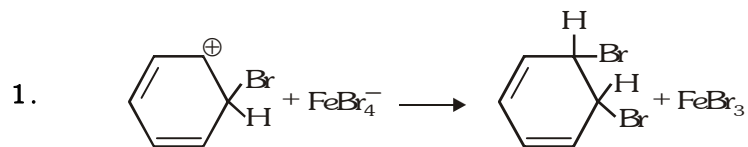
When a Meta-directing group is meta to an ortho-para directing group, the incoming group primarily goes ortho to the meta directing group rather than para.

1. Chlorination of m-chloro nitro benzene gives :



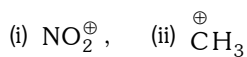
2. $\xrightarrow{E^+}$?
- (A) (B) (C) (D) all of them
3. $\xrightarrow{CH_2/CH_3COOH}$?
- (A) (B) (C) (D)
4. $\xrightarrow{HNO_3/H_2SO_4}$, unlikely to form is -
- (A) (B) (C) (D)

MISCELLANEOUS TYPE QUESTION	ANSWER KEY	EXERCISE -3
<ul style="list-style-type: none"> True / False <p>1. F 2. F 3. T 4. F 5. F</p> Fill in the Blanks <p>1. (i) Br^+; (ii) NO_2^+; (iii) SO_3; (iv) $[CH_3 - \overset{\delta+}{Cl} - \overset{\delta-}{AlCl_3}]$; (v) </p> <p>2. (i) (ii) 3. (a) sp^2; (b) sp^3; (c) sp^3; (d) sp^2</p> Match the Column <p>1. (A) \rightarrow q, r ; B \rightarrow q, r, s ; (C) \rightarrow p ; (D) \rightarrow s 2. (A) \rightarrow q, r ; (B) \rightarrow p, r ; (C) \rightarrow q, p ; (D) \rightarrow p</p> Assertion - Reason Questions <p>1. D 2. D 3. C 4. A 5. A 6. A 7. B 8. D 9. A 10. D</p> Comprehension Based Questions <p>Comprehension #1 : 1. (A) 2. (B) 3. (A) Comprehension #2 : 1. (C) 2. (D) 3. (C) Comprehension #3 : 1. (A) 2. (D) 3. (B) 4. (C)</p> 		

EXERCISE-04 [A]**CONCEPTUAL SUBJECTIVE EXERCISE**

Why does the given step does not occur

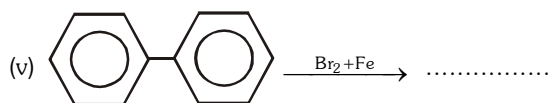
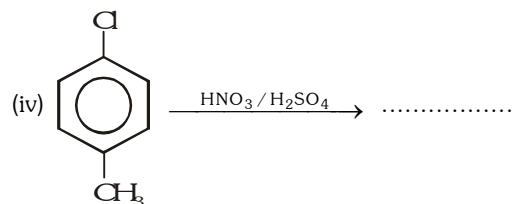
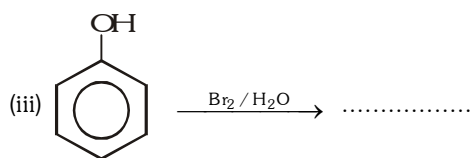
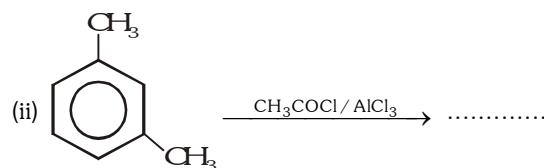
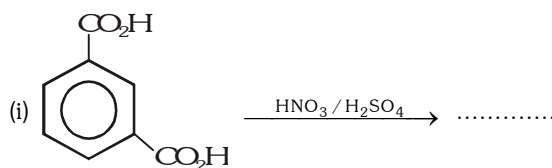
2. Write resonance structures of arenium ions with :



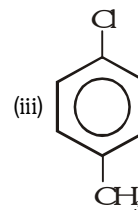
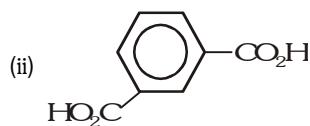
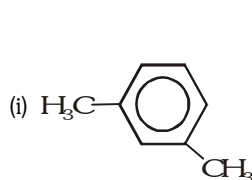
3. $\text{C}_6\text{H}_4(\text{NO}_2)\text{CH}_3$ can form different isomers. Write three isomers.

(I) (II) (III)

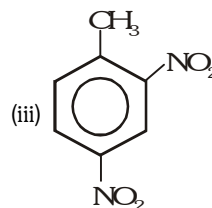
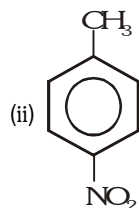
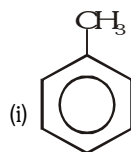
4. Write the structure of the products formed in the following S_E reactions :



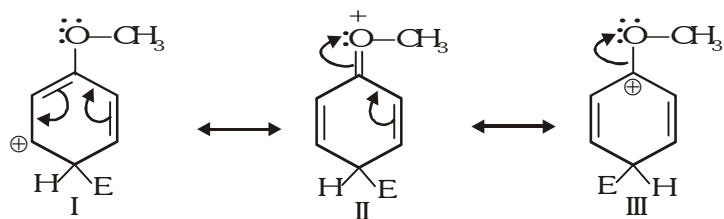
5. Indicate the position of the electrophile in the following compounds :



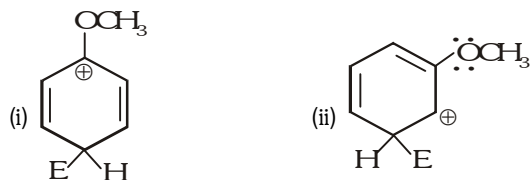
6. Indicate the compound which can be nitrated most easily :



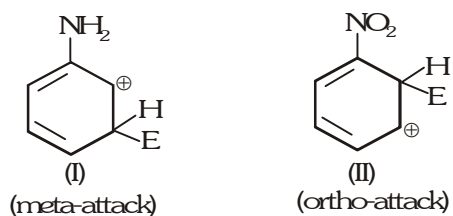
7. Indicate wrong electron-migration :



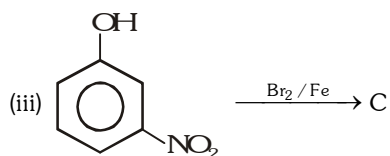
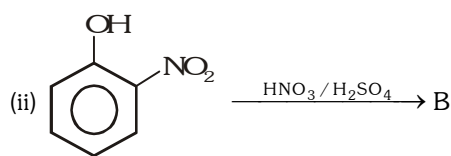
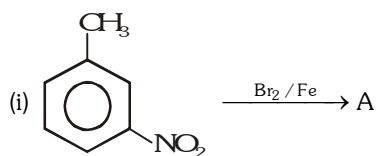
8. Indicate more stable carbocation and explain :



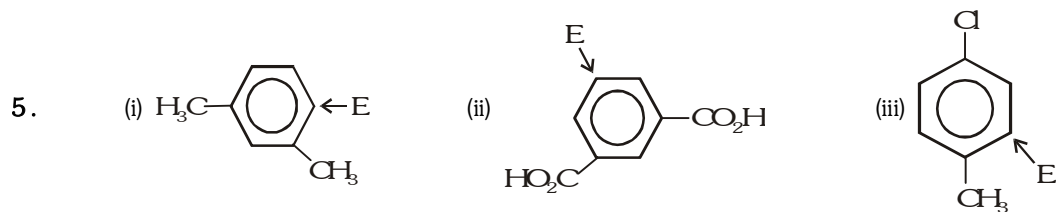
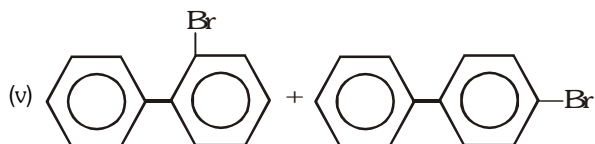
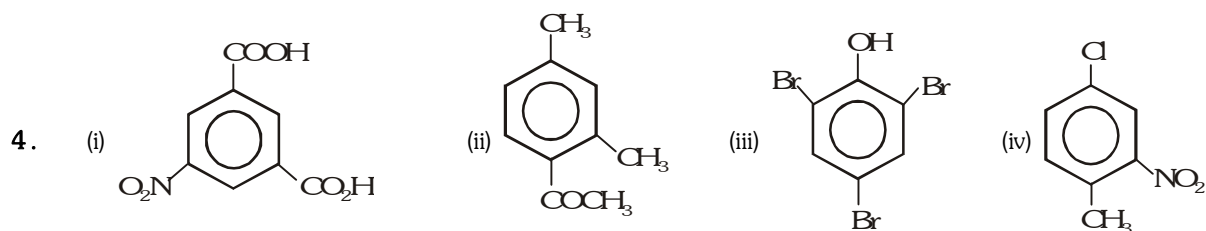
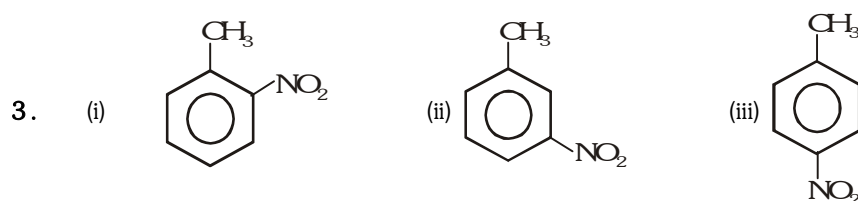
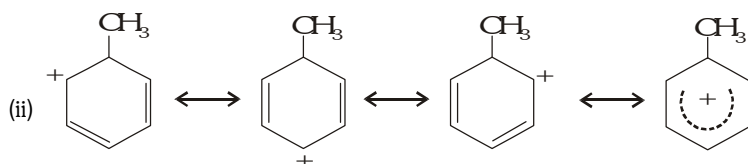
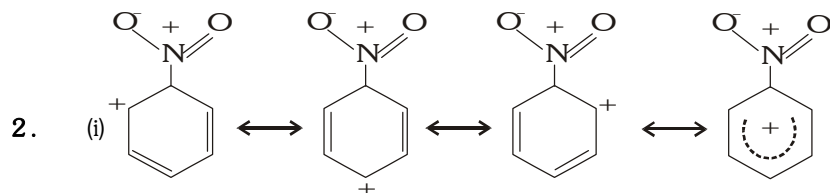
9. In case of meta- attack on aniline (where -NH_2 group is o-, p-directing) and in case of ortho-attack on nitrobenzene, resonating structures are possible. Which of them are more stable ?



10. What are the major products of the following :



1. The given reaction does not occur because on addition the ring lost its aromaticity and on deprotonation of σ -complex it retains the aromaticity hence substitution reaction takes place.

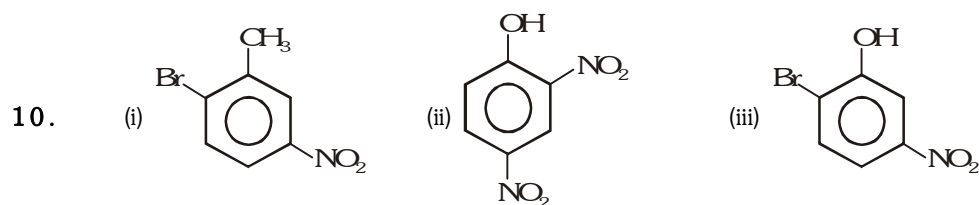


6. (i) ; because $-\text{CH}_3$ is an activating group hence toluene is most reactive.

7. (III)

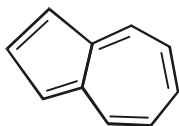
8. (I) is more stable, due to the + M effect of $-\text{OCH}_3$.

9. (I)

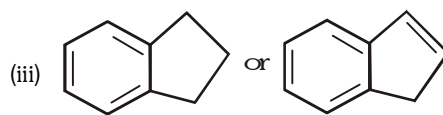
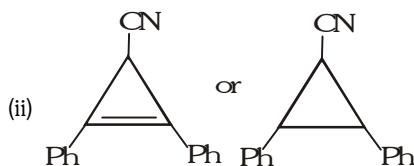
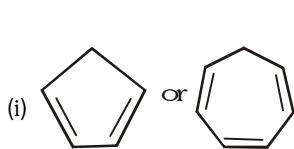


EXERCISE-04 [B]**BRAIN STORMING SUBJECTIVE EXERCISE**

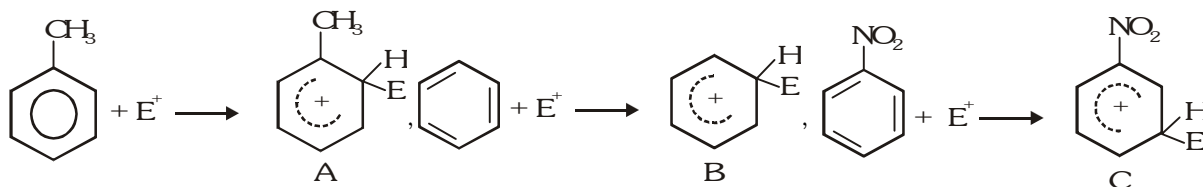
1. Unlike most hydrocarbons, azulene ($C_{10}H_8$) is highly coloured (deep blue), although its isomer, naphthalene, does not have significant zwitter-ionic character, azulene does.
- (i) Draw a resonance structure of azulene in which five-membered ring is anionic and the seven-membered ring cationic.



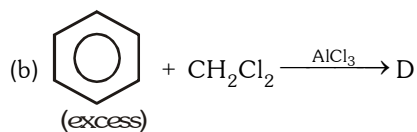
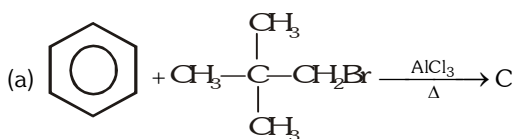
- (ii) Can azulene be considered aromatic ?
2. Explain, which of these compounds is a stronger acid. :



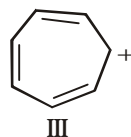
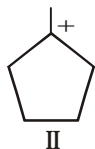
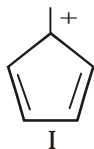
3. Arrange A, B, C in increasing potential energy :



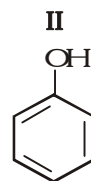
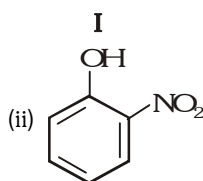
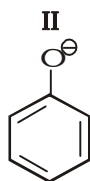
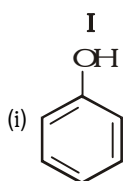
4. $C_6H_5^+$ has electron withdrawing inductive effect yet each ring of biphenyl, $C_6H_5-C_6H_5$ is more reactive than benzene towards S_E reaction and chief products are ortho and para-isomer. Show how reactivity and orientation can be accounted for on the basis of resonance.
5. What are the major products in the following reactions :

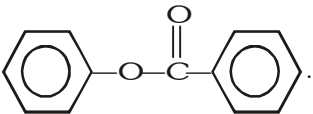


6. Arrange the following in increasing order of electrophilic strength :

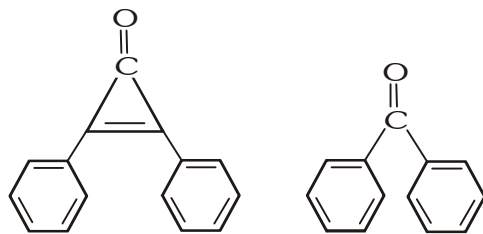


7. Which is more reactive towards S_E and explain ?

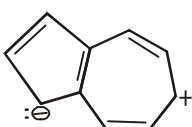



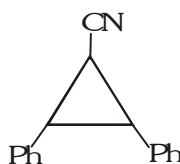
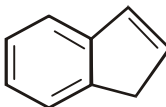
8. What are the major products when NO_2^\oplus (nitronium) reacts with .

9. Which of the following compounds has the greater dipole moment ?

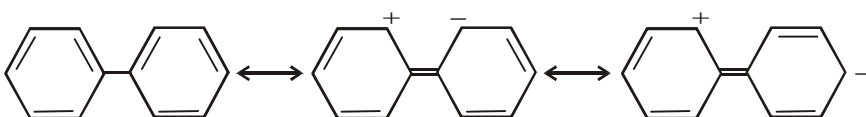


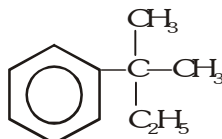
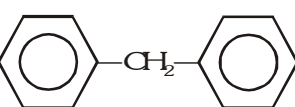
10. Explain why pyridine does not undergo Friedel-Craft's reaction ?

1. (i)  (ii) Azulene is an aromatic specie.

2. (i)  (ii)  (iii) 

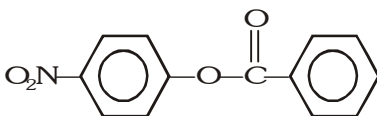
3. $A < B < C$

4. 

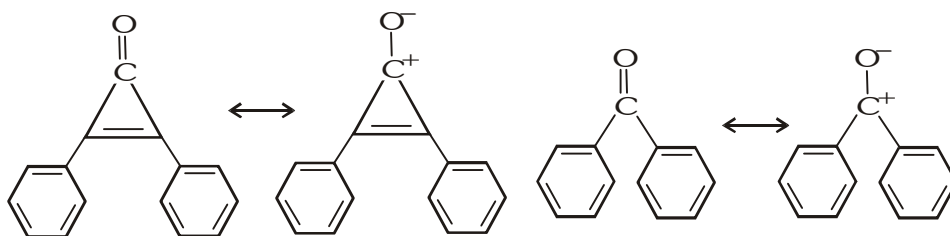
5. (a)  (b) 

6. $I > II > III$

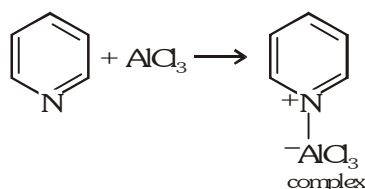
7. (i) (II) is more reactive, (ii) (II) is more reactive

8. 

9. In the case of the compound on the left, the three membered ring becomes aromatic when the charges are separated. In the case of the compound on the right, the resonance contributor with separated charges does not have any additional aromaticity. Thus, the resonance contributor with separated charges is more stable and, therefore, makes a greater contribution to the hybrid for the compound on the left than for the compound on the right. The compound on the left, therefore, has the greater dipole moment.

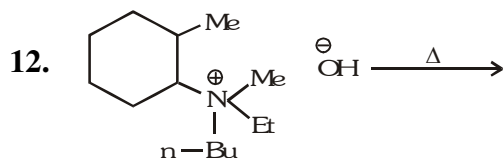


10. The Lewis acids AlCl_3 or FeCl_3 , used as catalyst in Friedel - Craft's reaction coordinate with nitrogen of the pyridine through lone pair of electrons and form a complex. The +ve charge on N greatly diminishes the reactivity towards electrophilic substitution.



EXERCISE - 05 [A]**JEE-[MAINS] : PREVIOUS YEAR QUESTIONS**

1. Which of these will not react with acetylene - [AIEEE-2002]
(A) NaOH (B) ammonical AgNO_3 (C) Na (D) HCl
2. What is the product formed when acetylene reacts with hypochlorous acid - [AIEEE-2002]
(A) CH_3COCl (B) ClCH_2CHO (C) Cl_2CHCHO (D) ClCH_2COOH
3. 1-Butene may be converted to butane by reaction with - [AIEEE-2003]
(A) Pd/H_2 (B) $\text{Zn} - \text{HCl}$ (C) $\text{Sn} - \text{HCl}$ (D) $\text{Zn} - \text{Hg/HCl}$
4. On mixing a certain alkane with chlorine and irradiating it with ultraviolet light, it forms only one monochloroalkane. This alkane could be - [AIEEE-2003]
(A) neopentane (B) propane (C) pentane (D) isopentane
5. Which one of the following is reduced with Zn-Hg/HCl to give the corresponding hydrocarbon [AIEEE-2004]
(A) Butan-2-one (B) Acetic acid (C) Acetamide (D) Ethyl acetate
6. Which one of the following has the minimum boiling point : [AIEEE-2004]
(A) isobutane (B) 1-butyne (C) 1-butene (D) n-butane
7. 2-Methylbutane on reacting with bromine in the presence of sunlight gives mainly [AIEEE-2005]
(A) 2-bromo-2-methylbutane (B) 1-bromo-2-methylbutane
(C) 1-bromo-3-methylbutane (D) 2-bromo-3-methylbutane
8. Alkyl halides react with dialkyl copper reagent to give [AIEEE-2005]
(A) alkyl copper halides (B) alkenes
(C) alkenyl halides (D) alkanes
9. Reaction of one molecule of HBr with one molecule of 1,3-butadiene at 40°C gives predominantly [AIEEE-2005]
(A) 1-bromo-2-butene under thermodynamically controlled conditions
(B) 3-bromobutene under kinetically controlled conditions
(C) 1-bromo-2-butene under kinetically controlled conditions
(D) 3-bromobutene under thermodynamically controlled conditions
10. Acid catalyzed hydration of alkenes except ethene leads to the formation of [AIEEE-2005]
(A) secondary or tertiary alcohol
(B) primary alcohol
(C) mixture of secondary and tertiary alcohols
(D) mixture of primary and secondary alcohols
11. Elimination of bromine from 2-bromobutane results in the formation of [AIEEE-2005]
(A) predominantly 2-butene (B) equimolar mixture of 1 and 2-butene
(C) predominantly 2-butyne (D) predominantly 1-butene



The alkene formed as a major product in the above elimination reaction is-

[AIEEE-2006]

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

13. Reaction of trans-2-phenyl-1-bromocyclopentane on reaction with alcoholic KOH produces-
 (A) 4-phenyl cyclopentene (B) 2-phenyl cyclopentene [AIEEE-2006]
 (C) 1-phenyl cyclopentene (D) 3-phenyl cyclopentene

14. Phenyl magnesium bromide reacts with methanol to give- [AIEEE-2006]
 (A) A mixture of anisole and $\text{Mg}(\text{OH})\text{Br}$ (B) A mixture of benzene and $\text{Mg}(\text{OMe})\text{Br}$
 (C) A mixture of toluene and $\text{Mg}(\text{OH})\text{Br}$ (D) A mixture of phenol and $\text{Mg}(\text{Me})\text{Br}$

15. Which of the following reactions will yield, 2, 2-dibromopropane [AIEEE-2007]
 (A) $\text{CH}_3-\text{C}\equiv\text{CH} + 2\text{HBr} \longrightarrow$ (B) $\text{CH}_3\text{CH}=\text{CHBr} + \text{HBr} \longrightarrow$
 (C) $\text{CH}\equiv\text{CH} + 2\text{HBr} \longrightarrow$ (D) $\text{CH}_3-\text{CH}=\text{CH}_2 + \text{HBr} \longrightarrow$

16. In the following sequence of reactions, the alkene affords the compound 'B' :- [AIEEE-2008]
 $\text{CH}_3\text{CH}=\text{CHCH}_3 \xrightarrow{\text{O}_3} \text{A} \xrightarrow[\text{Zn}]{\text{H}_2\text{O}} \text{B}.$

The compound B is

- (A) $\text{CH}_3\text{CH}_2\text{CHO}$ (B) CH_3COCH_3 (C) $\text{CH}_3\text{CH}_2\text{COCH}_3$ (D) CH_3CHO
 17. The hydrocarbon which can react with sodium in liquid ammonia is [AIEEE-2008]
 (A) $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CCH}_2\text{CH}_2\text{CH}_3$ (B) $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$
 (C) $\text{CH}_3\text{CH}=\text{CHCH}_3$ (D) $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CCH}_2\text{CH}_3$
 18. The treatment of CH_3MgX with $\text{CH}_3\text{C}\equiv\text{C}-\text{H}$ produces [AIEEE-2008]

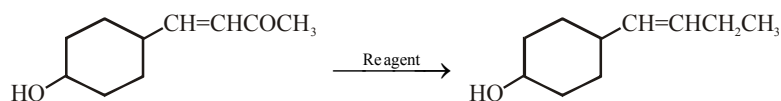
- (A) $\text{CH}_3-\text{CH}=\text{CH}_2$ (B) $\text{CH}_3\text{C}\equiv\text{C}-\text{CH}_3$ (C) $\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{CH}_3-\text{C}=\text{C}-\text{CH}_3 \end{array}$ (D) CH_4

19. The main product of the following reaction is [AIEEE-2010]
 $\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{OH})\text{CH}(\text{CH}_3)_2 \xrightarrow{\text{Conc. H}_2\text{SO}_4} ?$

- (A) $\begin{array}{c} \text{H}_5\text{C}_6\text{CH}_2\text{CH}_2 \\ \quad \quad \quad \diagdown \\ \quad \quad \quad \text{C}=\text{CH}_2 \\ \quad \quad \quad \diagup \\ \text{H}_3\text{C} \end{array}$ (B) $\begin{array}{c} \text{H}_5\text{C}_6 \quad \quad \text{H} \\ \quad \quad \diagdown \quad \diagup \\ \quad \quad \text{C}=\text{C} \\ \quad \quad \diagup \quad \diagdown \\ \text{H} \quad \quad \text{CH}(\text{CH}_3)_2 \end{array}$
 (C) $\begin{array}{c} \text{C}_6\text{H}_5\text{CH}_2 \quad \quad \text{CH}_3 \\ \quad \quad \diagdown \quad \diagup \\ \quad \quad \text{C}=\text{C} \\ \quad \quad \diagup \quad \diagdown \\ \text{H} \quad \quad \text{CH}_3 \end{array}$ (D) $\begin{array}{c} \text{C}_6\text{H}_5 \quad \quad \text{CH}(\text{CH}_3)_2 \\ \quad \quad \diagdown \quad \diagup \\ \quad \quad \text{C}=\text{C} \\ \quad \quad \diagup \quad \diagdown \\ \text{H} \quad \quad \text{H} \end{array}$

20. One mole of a symmetrical alkene on ozonolysis gives two moles of an aldehyde having a molecular mass of 44 u. The alkene is :- [AIEEE-2010]
 (A) ethene (B) propene (C) 1-butene (D) 2-butene
 21. Ozonolysis of an organic compound gives formaldehyde as one of the products. This confirms the presence of :- [AIEEE-2011]
 (A) an isopropyl group (B) an acetylenic triple bond
 (C) two ethylenic double bonds (D) a vinyl group

22. Ozonolysis of an organic compound 'A' produces acetone and propionaldehyde in equimolar mixture. Identify 'A' from the following compounds :- [AIEEE-2011]
- (A) 2 - Methyl - 1 - pentene (B) 1 - Pentene
(C) 2 - Pentene (D) 2 - Methyl - 2 - pentene
23. 2-Hexyne gives trans -2-Hexene on treatment with :- [AIEEE-2012]
- (A) LiAlH_4 (B) Pt/H_2 (C) Li/NH_3 (D) Pd/BaSO_4
24. In the given transformation, which of the following is the most appropriate reagent ? [AIEEE-2012]

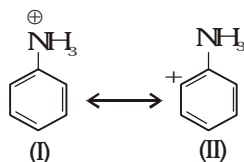


- (A) NaBH_4 (B) $\text{NH}_2\text{NH}_2, \text{OH}^-$ (C) $\text{Zn} - \text{Hg} / \text{HCl}$ (D) Na, Liq.NH_3

JEE-[MAIN] : PREVIOUS YEAR QUESTIONS							ANSWER KEY			EXERCISE -5[A]					
Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans	1	3	1	1	1	1	1	4	1	1	1	2	4	2	1
Que.	16	17	18	19	20	21	22	23	24						
Ans	4	2	4	2	4	4	4	3	2						

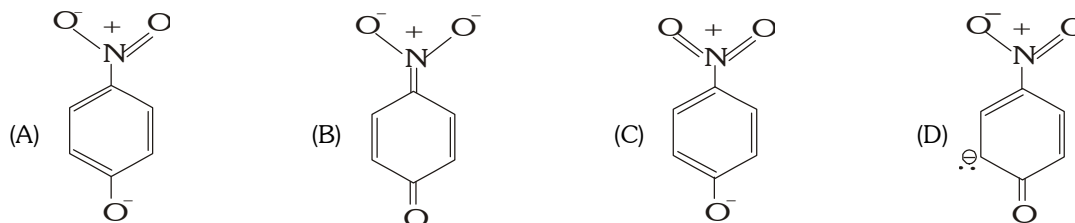
EXERCISE - 05 [B]**JEE-[ADVANCED] : PREVIOUS YEAR QUESTIONS**


1. The chlorination of toluene in presence of ferric chloride gives predominantly : [IIT-86]
(A) Benzyl chloride (B) m-chlorotoluene
(C) Benzal chloride (D) o-and-p-chlorotoluene
2. Aryl halides are less stable towards nucleophilic substitution reaction as compared to alkyl halides due to-
(A) The formation of less stable carbonium ion (B) Resonance stabilization
(C) Longer carbon-halogen bond (D) The inductive effect [IIT-90]
3. The most basic compound among the following is - [IIT-90]
(A) Benzylamine (B) Aniline (C) Acetanilide (D) p-nitro aniline
4. Excess chlorination of toluene in the presence of light and heat followed by treatment with aqueous NaOH gives :
(A) o-cresol (B) p-cresol (C) 2, 4-dihydroxytoluene (D) Benzoic acid [IIT-90]
5. Choose the correct statement from the ones given below for two anilium in - [IIT-93]

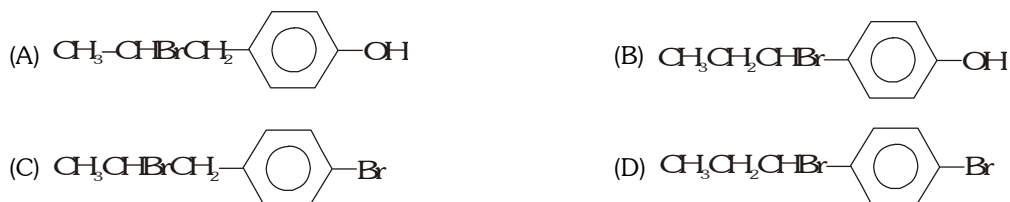


- (A) II is not an acceptable canonical structure because carbonium ions are less stable than ammonium ions
(B) II is not an acceptable canonical structure because it is aromatic
(C) II is not an acceptable canonical structure because the nitrogen has 10 valence electrons
(D) II is an acceptable canonical structure
6. The major product of nitration of benzoic acid is : [IIT-93]
(A) 3-nitrobenzoic acid (B) 4-nitrobenzoic acid
(C) 2-nitrobenzoic acid (D) 2,4-dinitrobenzoic acid
7. Most stable carbonium ion is : [IIT-95]
(A) $p\text{-NO}_2\text{-C}_6\text{H}_4\text{-}^+\text{CH}_2$ (B) $\text{C}_6\text{H}_5\text{-}^+\text{CH}_2$
(C) $p\text{-Cl-C}_6\text{H}_4\text{-}^+\text{CH}_2$ (D) $p\text{-CH}_3\text{O-C}_6\text{H}_4\text{-}^+\text{CH}_2$
8. Arrange in order of decreasing trend towards S_E reactions, [IIT-95]
Chlorobenzene, Benzene, Anilinium chloride, Toluene
I II III IV
(A) I > II > III > IV (B) III > I > II > IV (C) IV > II > I > III (D) I > II > III > IV
9. Among the following statements on the nitration of aromatic compounds, the false one is - [IIT-97]
(A) The rate of nitration of benzene is almost the same as that of hexadeuterobenzene
(B) The rate of nitration of toluene is greater than that of benzene
(C) The rate of nitration of benzene is greater than that of hexadeuterobenzene
(D) Nitration is an electrophilic substitution reaction
10. 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 - [IIT-98]
(A) Base (B) Acid (C) Reducing agent (D) Catalyst
11. Benzyl chloride ($\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$) can be prepared from toluene by chlorination with - [IIT-98]
(A) $\text{SO}_2\text{Cl}_2/h\nu$ (B) SOCl_2 (C) PCl_5 (D) NaOCl

12. The most unlikely representation of resonance structure of p-nitrophenoxide ions is - [IIT-98]



13. The reaction of $\text{CH}_3\text{-CH=CH-}$  -OH with HBr gives - [IIT-98]

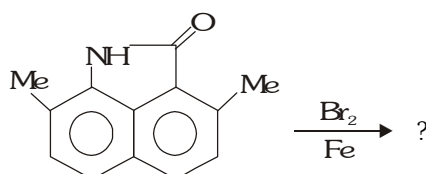


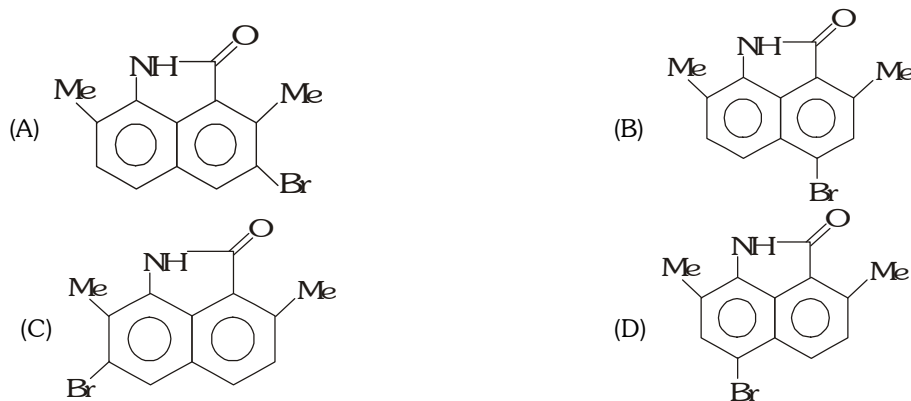
14. A new C-C bond is formed in - [IIT-98]

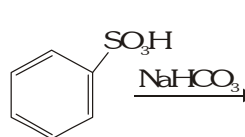
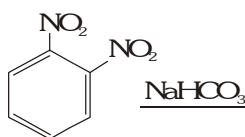
- (A) Cannizzaro' reaction (B) Friedel Crafts reaction
(C) Both (A) & (B) (D) None of these

15. Amongst the following the strongest base is - [IIT-2000]

- (A) $\text{C}_6\text{H}_5\text{NH}_2$ (B) $\text{p-O}_2\text{NC}_6\text{H}_4\text{NH}_2$ (C) $\text{m-O}_2\text{NC}_6\text{H}_4\text{NH}_2$ (D) $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$

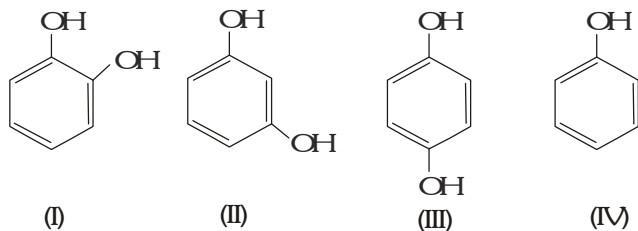
16.  Major product in this reaction is : [IIT-2004]



17. (I)  (II)  Gases released in reaction (I) and (II) are : [IIT-06]
(A) CO_2, CO_2 (B) SO_2, NO_2 (C) SO_2, CO_2 (D) SO_2, NO

18. Order of boiling point for the following compounds is -

[IIT-06]



(A) (I) < (II) < (III) < (IV)

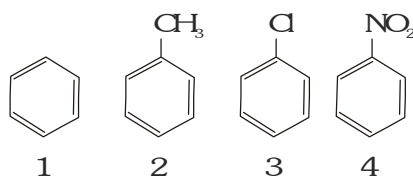
(B) (I) < (II) < (IV) < (III)

(C) (IV) < (I) < (II) < (III)

(D) (II) < (I) < (III) < (IV)

19. Identify the correct order of reactivity in electrophilic substitution reaction of the following compounds

[IIT-2002]



(A) 1 > 2 > 3 > 4

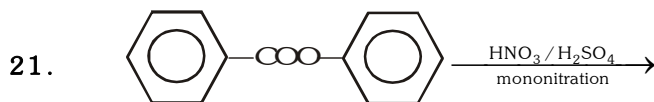
(B) 4 > 3 > 2 > 1

(C) 2 > 1 > 3 > 4

(D) 2 > 3 > 1 > 4

20. $\text{C}_6\text{H}_6 + (\text{CH}_3)_2\text{CHCH}_2\text{Cl} \xrightarrow[\Delta]{\text{AlCl}_3} ?$

[IIT 1992]

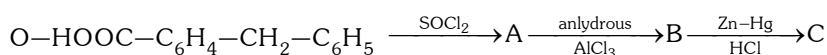


[IIT 1993]

22. $\text{C}_6\text{H}_6 + (\text{CH}_3)_2\text{CH}.\text{CH}_2\text{OH} \xrightarrow{\text{H}_2\text{SO}_4} ?$

[IIT 1994]

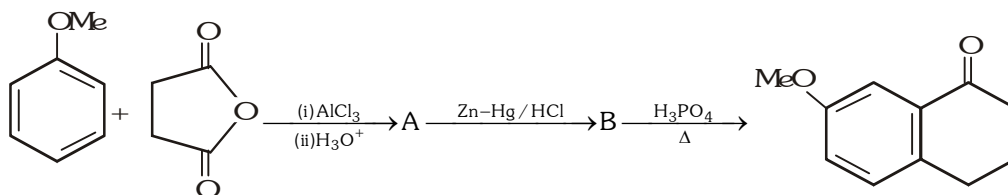
23. Fill in the blanks with appropriate structure of reaction products in the following transformation :



[IIT 1995]

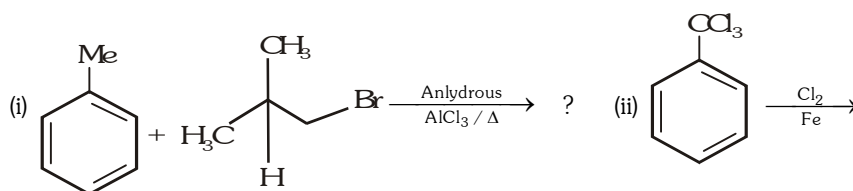
24. Predict the structures of the intermediates/products in the following reaction sequence.

[IIT 1996]



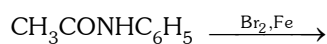
25. Predict the product

[IIT 1997]



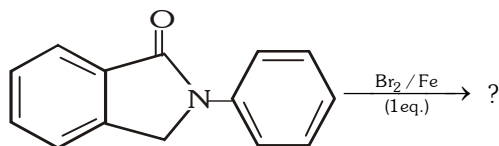
26. Each of the following reaction gives two products. Write the structure of the products :

[IIT 1998]



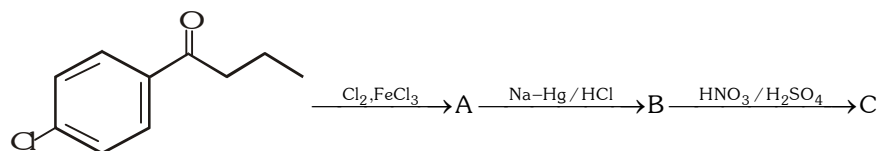
27. Predict the product

[IIT 2002]

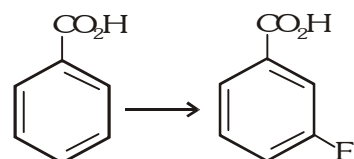


28. Predict the product

[IIT 2002]



29. Convert :

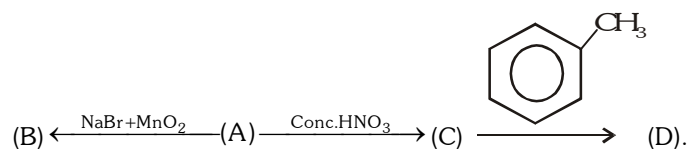


[IIT 2003]

30. 7-bromo-1, 3, 5-cycloheptatriene exists as a ionic substance whereas 5-bromo-1, 3-cyclopentadiene does not ionize even in the presence of Ag^+ ion. Explain ?

[IIT 2004]

31.



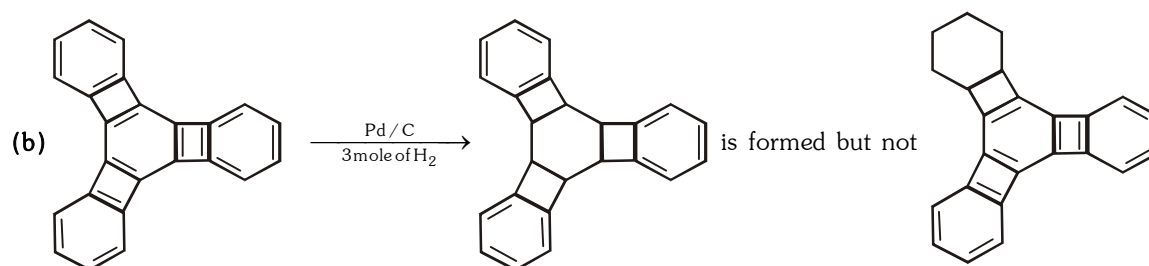
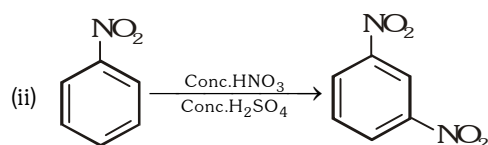
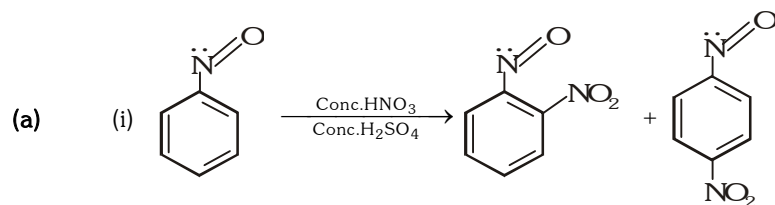
(brown fumes & Pungent smell)

(Explosive Product intermediate)

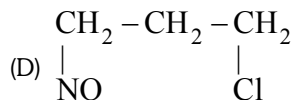
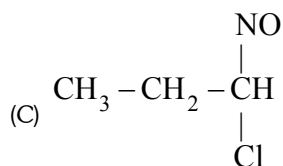
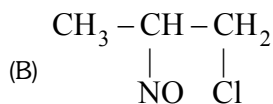
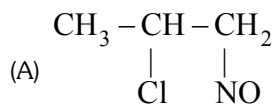
Identify the missing compounds. Give the equation from A to B and A to C.

[IIT 2005]

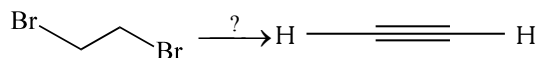
32. Give reason :



33. $\text{CH}_3\text{-CH=CH}_2 + \text{NOCl} \rightarrow \text{P}$ [IIT 2006]
Identify the adduct.



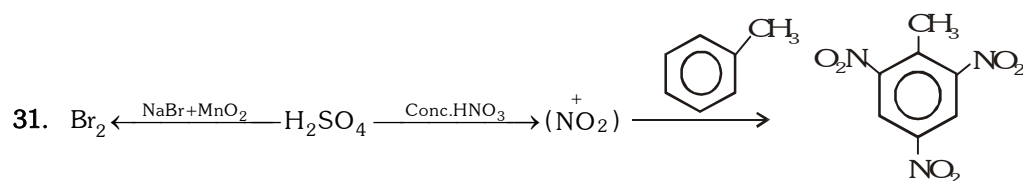
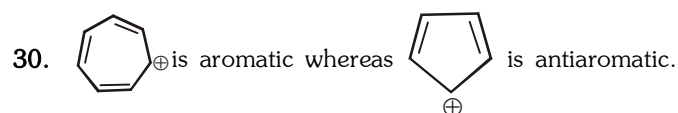
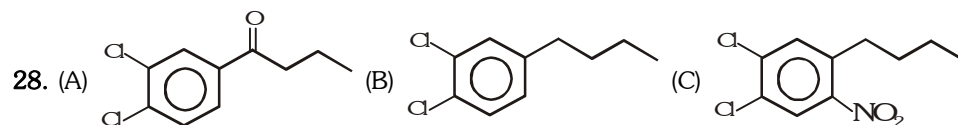
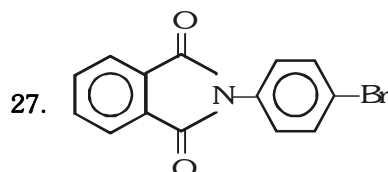
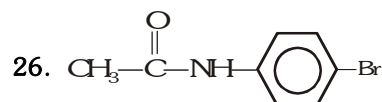
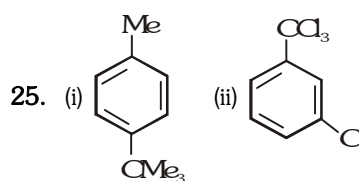
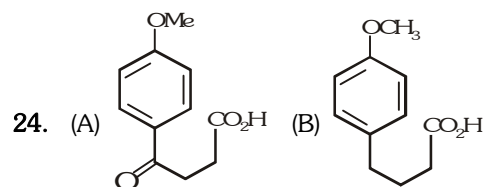
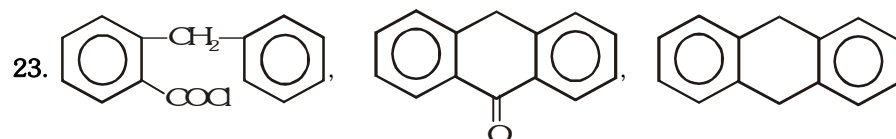
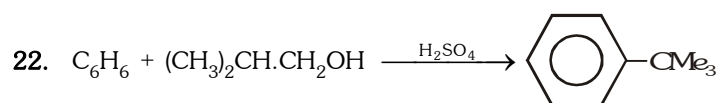
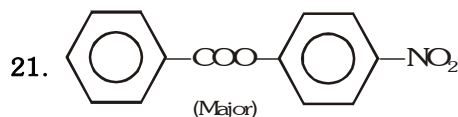
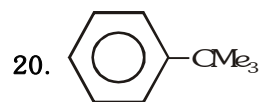
34. The number of stereoisomers obtained by bromination of trans-2-butene is [IIT 2007]
(A) 1 (B) 2 (C) 3 (D) 4
35. The number of structural isomers for C_6H_{14} is [IIT 2007]
(A) 3 (B) 4 (C) 5 (D) 6
36. The reagent(s) for the following conversion, [IIT 2007]



is / are

- (A) alcoholic KOH (B) alcoholic KOH followed by NaNH_2
(C) aqueous KOH followed by NaNH_2 (D) $\text{Zn} / \text{CH}_3\text{OH}$
37. The synthesis of 3-octyne is achieved by adding a bromoalkane into a mixture of sodium amide and an alkyne. [IIT-2010]
The bromoalkane and alkyne respectively are
(A) $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$
(B) $\text{BrCH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$
(C) $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{C}\equiv\text{CH}$
(D) $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$

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



32. (a) (i) $-\text{NO}$ is ortho and para director. (ii) $-\text{NO}_2$ is meta director.
 (b) due to high resonance energy of the product.

33. A 34. A 35. C 36. B 37. D