15 Chapter HYDROCARBONS

A SINGLE CORRECT CHOICE TYPE

Each of these questions has 4 choices (a), (b), (c) and (d) for its answer, out of which ONLY ONE is correct.

1. Isobutene is the exclusive product of dehydrohalogenation (by a strong base) of
(a) isobutyl chloride (b) *tert*-butyl bromide
(c) both (a) and (b) (d) none

2. The favourable conditions for the hydration of alkenes are
(a) low water concentration and high temperature
(b) low water concentration and low temperature
(c) high water concentration and high temperature
(d) high water concentration and low temperature

3. which of the following alkene will give same product when treated with HBr in presence and absence of benzoyl peroxide ?
(a) 1, 1-Dichloroethene
(b) *trans*-1, 2-Dichloro-2-pentene
(c) *cis*-1, 2-Dichloro-2-pentene
(d) 2-Butene

4. Which statement is true regarding following reactions

$$trans-2-\text{Butene}\xrightarrow{HCO_3H}A$$

$$cis-2-\text{Butene}\xrightarrow{HCO_3H}B$$

(a) Compounds A and B are formed by *syn* addition and they are racemic mixture and meso respectively
(b) Compounds A and B are formed by *anti* addition and are racemic mixture and meso respectively
(c) Compounds A and B are formed by *anti* addition and are meso and racemic mixture respectively
(d) Compounds A and B are formed by *syn* addition and are meso and racemic mixture respectively

5. 1-Butyne can be distinguished most easily from 2-butyne by
(a) bromine water (b) ozonolysis
(c) Tollen's reagent (d) $KMnO_4$ solution

6. 3-Methylhexane can be prepard by Corey-House synthesis using the pair

(a) $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HBr + CH_3CH_2CH_2MgBr$

(b) $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HMgCl + CH_3CH_2CH_2Br$

(c) either (a) or (b)

(d) $CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2MgBr + CH_3CH_2CH_2Br$

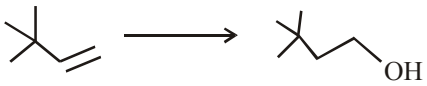
7. The probability factor for the replacement of hydrogen atom during chlorination/bromination is
(a) more important in chlorination
(b) more important in bromination
(c) equally important in chlorination/bromination
(d) not definite

8. How many conformations are possible for ethane ?
(a) 2 (b) 3
(c) infinite (d) one

9. The number of isomeric alkenes of the formula C_4H_8 is
(a) 3 (b) 4
(c) 5 (d) 2

10. E and Z forms of 2-hexene are known as
(a) stereoisomers (b) diastereomers
(c) both (d) enantiomers

MARK YOUR RESPONSE					
	1. ⓐⓑⓒⓓ	2. ⓐⓑⓒⓓ	3. ⓐⓑⓒⓓ	4. ⓐⓑⓒⓓ	5. ⓐⓑⓒⓓ
	6. ⓐⓑⓒⓓ	7. ⓐⓑⓒⓓ	8. ⓐⓑⓒⓓ	9. ⓐⓑⓒⓓ	10. ⓐⓑⓒⓓ

11. 

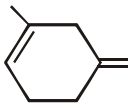
The above hydration can be carried out by

(a) acid catalyzed hydration

(b) oxymercuration-demercuration

(c) hydroboration-oxidation

(d) none of the above methods

12.  is oxidised by heating with alkaline $KMnO_4$ to give

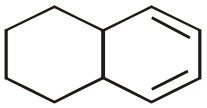
(a) $CH_2O + CH_3CO(CH_2)_4COOH$

(b) $CO_2 + CH_3COCH_2COCH_2CH_2COOH$

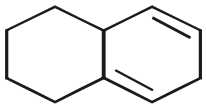
(c) $CH_2O + CH_3COCH_2COCH_2CH_2COOH$

(d) the corresponding tetrol

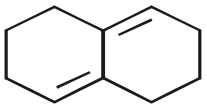
13. Which of the following hydrocarbon can react with maleic anhydride ?



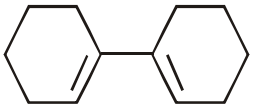
(i)



(ii)



(iii)



(iv)

(a) only (i) (b) (i) and (iv)

(c) (i), (iii) and (iv) (d) all the four

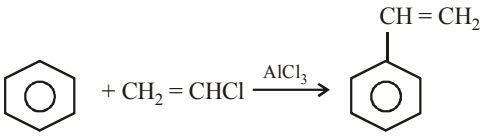
14. The two compounds A and B obtained from 1-butyne can be distinguished by

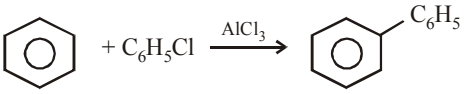
$$B \xleftarrow[(ii)\ H_2O_2/OH^-]{(i)\ BH_3} CH_3CH_2C \equiv CH \xrightarrow{H^+/Hg^{2+}} A$$

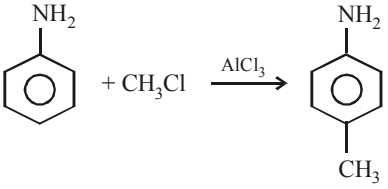
(a) $NaHSO_3$ (b) litmus solution

(c) iodoform test (d) 2, 4-DNP

15. Which of the reaction is not possible ?

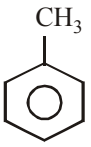
(a) 

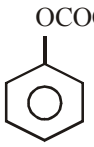
(b) 

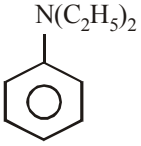
(c) 

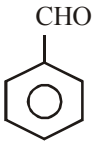
(d) All the three

16. Which of the compound undergoes electrophilic substitution most easily ?

(a) 

(b) 

(c) 

(d) 

17. $-CH_2Cl$ group is a

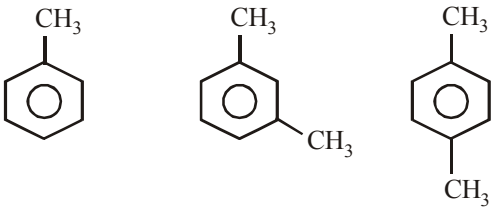
(a) weakly activating group

(b) weakly deactivating group

(c) strongly activating group

(d) strongly deactivating group

18. The ease of nitration of the following three hydrocarbons follows the order



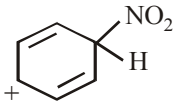
I II III

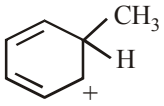
(a) II = III ≈ I (b) II > III > I

(c) III > II > I (d) I = III > I

MARK YOUR RESPONSE					
	11. ⓐⓑⓒⓓ	12. ⓐⓑⓒⓓ	13. ⓐⓑⓒⓓ	14. ⓐⓑⓒⓓ	15. ⓐⓑⓒⓓ
	16. ⓐⓑⓒⓓ	17. ⓐⓑⓒⓓ	18. ⓐⓑⓒⓓ		

19. Which of the following is an aromatic species ?

(a) 

(b) 

(c) 

(d) All of the three

20. Ethylbenzene when treated with chlorine in presence of light mainly gives

(a) β- phenylethyl chloride

(b) α - phenylethyl chloride

(c) *o* - chloroethyl benzene

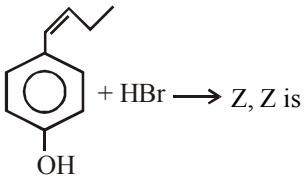
(d) *o* - and *p* - chloroethylbenzene

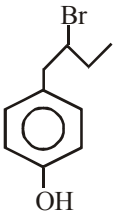
21. Predict the nature of P in the following reaction

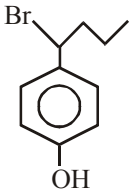
$$CH_3C \equiv CCH_3 \xrightarrow[\text{heat}]{NaNH_2 \text{ / inert solvent}} P$$

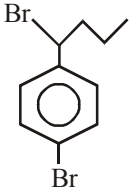
(a) CH_2=CHCH=CH_2 (b) CH_2=C=CH–CH_3

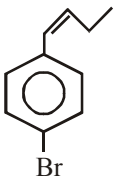
(c) $CH_3CH_2C{\equiv}CH$ (d) No reaction

22.  + HBr ⟶ Z, Z is

(a) 

(b) 

(c) 

(d) 

23. Cyclobutylethene is treated with dil. H_2SO_4 to form

(a) 2-cyclobutylethanol

(b) 1-cyclobutyl-2-ethanol

(c) 2-methylcyclopentanol

(d) 1-methylcyclopentanol

24. Which of the following statement is true regarding amount of $AlCl_3$ required during Friedel-Craft acetylation using acetyl chloride or acetic anhydride?

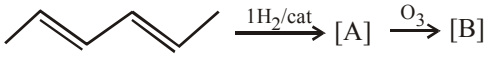
(a) Both require same amount

(b) Acetylation with acetyl chloride requires more amount

(c) Acetylation with acetic anhydride requires more amount

(d) Nothing is definite

25. The products A and B in the following reactions are



(a) 

(b) 

(c) Both a & b

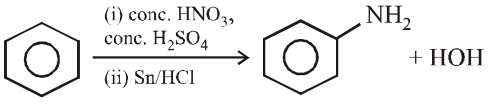
(d) 

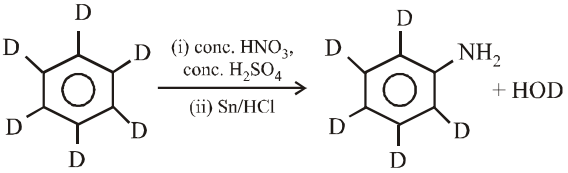
26. Which is least reactive towards addition of HCl ?

(a) $CH_3CH_2CH{=}CH_2$ (b) $CH_2{=}CH{-}CH{=}CH_2$

(c) $CH_3CH_2C{\equiv}CCH_3$ (d) $CH_3CH{=}CHCHO$

27. Which of the two reactions proceed faster ?

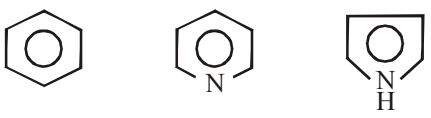
(i) 

(ii) 

(a) (i) (b) (ii)

(c) (i) = (ii) (d) Not definite

28. Arrange the following compounds in decreasing order of reactivity towards electrophilic substitution?



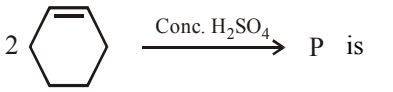
I II III

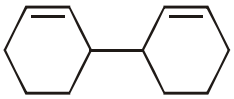
(a) I > II > III (b) I > II = III

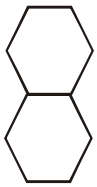
(c) III > II > I (d) III > I > II

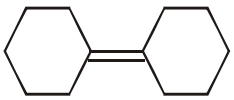
MARK YOUR RESPONSE	19. ⓐⓑⓒⓓ	20. ⓐⓑⓒⓓ	21. ⓐⓑⓒⓓ	22. ⓐⓑⓒⓓ	23. ⓐⓑⓒⓓ
	24. ⓐⓑⓒⓓ	25. ⓐⓑⓒⓓ	26. ⓐⓑⓒⓓ	27. ⓐⓑⓒⓓ	28. ⓐⓑⓒⓓ

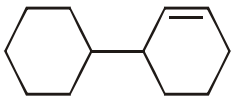
29. The most probable structure for P in the following reaction



(a) 

(b) 

(c) 

(d) 

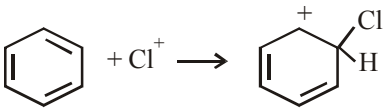
30. $HC \equiv C - COOH \xrightarrow[HgSO_4]{H_2SO_4} X$. The compound X is

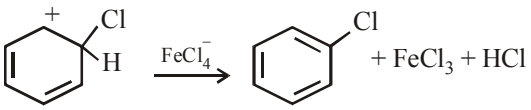
(a) $OHC.CH_2.COOH$ (b) $HOCH = CHCOOH$

(c) both (a) and (b) (d) $CH_2 = C(OH)COOH$

31. Which one is the slow step in the chlorination of benzene?

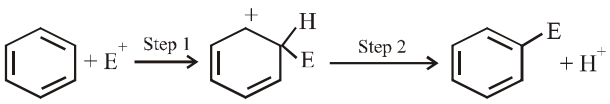
(a) $Cl_2 + FeCl_3 \rightarrow FeCl_4^- + Cl^+$

(b) 

(c) 

(d) None of the three

32. In which step of the following reaction, sp^3 carbon changes to sp^2 carbon ?



(a) Step 1 (b) Step 2

(c) Both (d) None

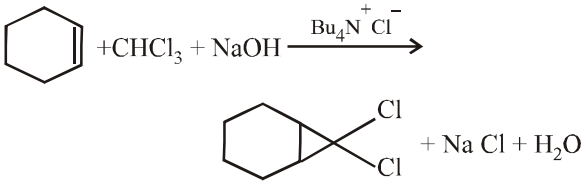
33. During nitration of benzene using a mixture of conc. HNO_3 and conc. H_2SO_4, function of conc. H_2SO_4 is to increase the rate of reaction by increasing the concentration of NO_2^+ according to following reaction.

$$HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O$$

Here nitric acid acts as

(a) a stronger acid (b) a weaker acid

(c) a base (d) none of the three

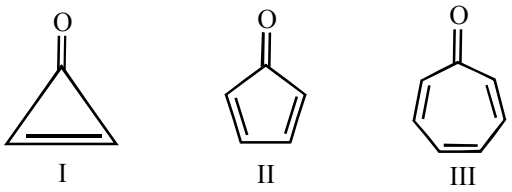
34. 

In the above reaction, $Bu_4N^+ Cl^-$ serves as a

(a) base (b) solvent

(c) catalyst (d) all the three

35. Which of the following is least stable ?

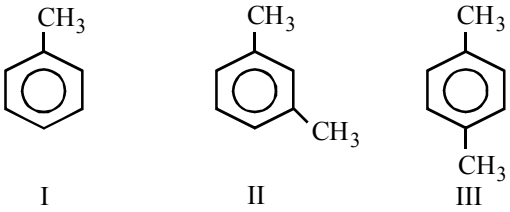


I II III

(a) I (b) II

(c) III (d) All are equally stable

36. Which of the following order is true regarding electrophilic aromatic substitution of the three given compounds?



I II III

(a) II = III > I (b) II = III = I

(c) II >>> III > I (d) II >>> III = I

37. Low concentration of bromine, provided by NBS, favours substitution (allylic bromination) rather than addition of bromine on propene

$$CH_3CH = CH_2 \xrightarrow{NBS} BrCH_2CH = CH_2$$

This reaction is due to

(a) Reversibility of the following addition reaction

$$Br^{\bullet} + CH_3CH = CH_2 \rightleftharpoons CH_3\dot{C}HCH_2Br$$

(b) Irreversibility of the following substitution reaction

$$Br^{\bullet} + CH_3CH = CH_2 \longrightarrow Br\dot{C}HCH = CH_2$$

(c) Both of the above factors

(d) NBS supplies limited amount of bromine

MARK YOUR RESPONSE					
	29. ⓐⓑⓒⓓ	30. ⓐⓑⓒⓓ	31. ⓐⓑⓒⓓ	32. ⓐⓑⓒⓓ	33. ⓐⓑⓒⓓ
	34. ⓐⓑⓒⓓ	35. ⓐⓑⓒⓓ	36. ⓐⓑⓒⓓ	37. ⓐⓑⓒⓓ	

38. $CH_2 = CH_2 + Br_2 \xrightarrow{NaCl}$ products. Which of the following product is not formed in the above reaction?

(a) $BrCH_2CH_2Br$ (b) $ClCH_2CH_2Cl$

(c) $BrCH_2CH_2Cl$ (d) All are formed

39. Tetrachloroethylene does not add chlorine quantitatively under ordinary conditions. However, when the same reaction is carried out in presence of aluminium chloride, addition occurs easily. The role of $AlCl_3$ is

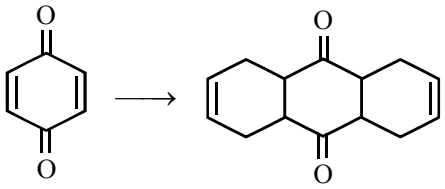
(a) to decrease the activation energy of the reaction

(b) to enhance the formation of chloronium ion

(c) to accelerate the reaction by removing impurity in the alkene

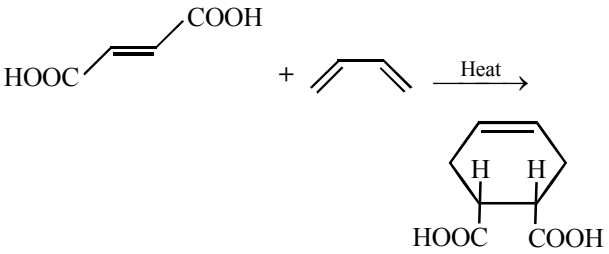
(d) to stabilize the dichloride formed by coordination

40. Pick up the nature of the reagent in the following rection



(a)  (b) 

(c) CH_2=CHCH=CH_2 (d) None

41. 

The above reaction is an example of

(a) Robinson annulation (b) Diel's-Alder reaction

(c) Dieckmann reaction (d) Reaction not possible

42. Birch reduction (reduction with metallic sodium in presence of liquid ammonia) can't be applied for

(a) $CH_3CH = C = CHCH_3$

(b) $CH_2 = CH - CH = CH_2$

(c) $CH_3CH = CHCH_3$

(d) $CH_3C \equiv CCH_2CH_3$

43. Fittig reaction between *o*-bromobenzyl bromide and metallic sodium leads to

(a) dihydroanthracene (b) dihydrophenanthrene

(c) both (a) and (b) (d) naphthalene

44. Compound X of molecular formula C_4H_6 takes up one equivalent of hydrogen in presence of Pt to form another compound Y which on ozonolysis gives only ethanoic acid. The compound X can be

(a) $CH_2 = CH - CH = CH_2$

(b) $CH_2 = C = CHCH_3$

(c) $CH_3C \equiv CCH_3$

(d) All the three

45. A hydrocarbon with molecular formula C_8H_{18} gives only one monochloro derivative, on chlorination. The compound is

(a) *n*-octane

(b) iso-octane

(c) 2,2,4-trimethylpentane

(d) 2,2,3,3-tetramethylbutane

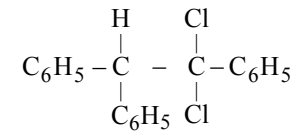
46. $2(C_6H_5)_2CCl_2 \xrightarrow[C_6H_6]{Cu} P$. Here P is

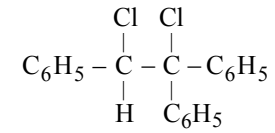
(a) $(C_6H_5)_4C$ (b) $(C_6H_5)_2C = C(C_6H_5)_2$

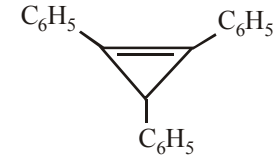
(c) Both (d) No reaction

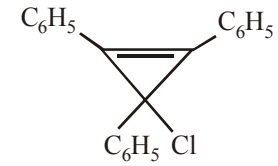
47. The product P in the given reaction is

$$C_6H_5C \equiv CC_6H_5 \xrightarrow[Me_3COK]{C_6H_5CHCl_2} [P]$$

(a) 

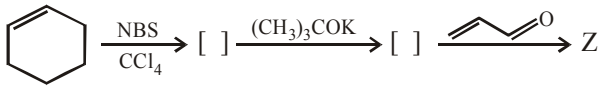
(b) 

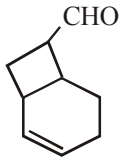
(c) 

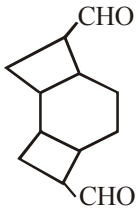
(d) 

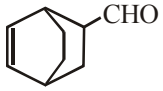
MARK YOUR RESPONSE					
	38. ⓐⓑⓒⓓ	39. ⓐⓑⓒⓓ	40. ⓐⓑⓒⓓ	41. ⓐⓑⓒⓓ	42. ⓐⓑⓒⓓ
	43. ⓐⓑⓒⓓ	44. ⓐⓑⓒⓓ	45. ⓐⓑⓒⓓ	46. ⓐⓑⓒⓓ	47. ⓐⓑⓒⓓ

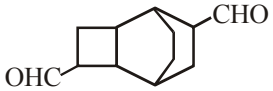
48. The final product Z in the following reaction is



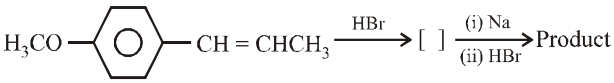
(a) 

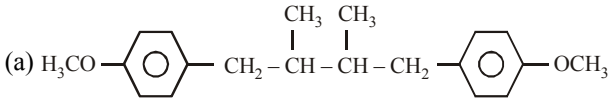
(b) 

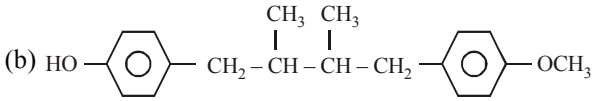
(c) 

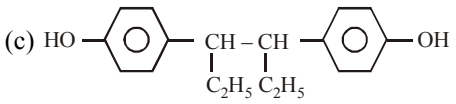
(d) 

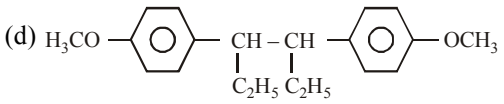
49. The final product in the following series of reactions should be



(a) 

(b) 

(c) 

(d) 

50. A compound of the molecular formula $C_{10}H_{12}O$ decolorizes bromine in CCl_4. On vigorous oxidation, it gives *p*-anisic acid (*p*-methoxybenzoic acid). The compound can exist in how many forms ?

(a) 2 (b) 3
(c) 4 (d) 5

51. Compound A reacts with carbonyl reagent and on oxidation with hot alkaline $KMnO_4$ it gives benzoic acid. The compound A can be

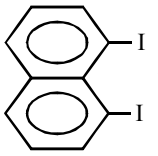
$C_6H_5COCH_2CH_3$ (I) $C_6H_5CH(CH_3)CHO$ (II)

$C_6H_5C(CH_3)_2CHO$ (III) $C_6H_5CH_2CH_2CHO$ (IV)

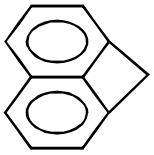
(a) I and IV (b) I, II and III
(c) I, II and IV (d) All the above

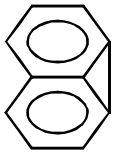
52. $CH \equiv CCOOH \xrightarrow{HgSO_4, H_2SO_4} [\ ] \xrightarrow{NH_2NH_2, OH^-} Z$;
Z is

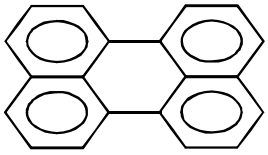
(a) $CH_3COCOOH$ (b) $CH(NNH_2).CH_2COOH$
(c) $OHCCH_2COOH$ (d) CH_3CH_2COOH

53. 

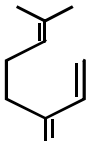
$\xrightarrow[180°C]{Cu}$ Product is

(a) 

(b) 

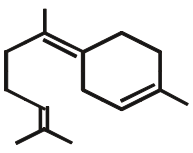
(c) 

(d) Reaction not possible

54. Reductive ozonolysis of myrcene, a terpenoid  gives how many different products?

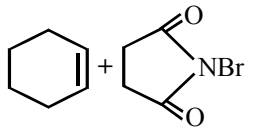
(a) 2 (b) 3
(c) 4 (d) 5

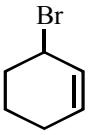
55. Reductive ozonolysis of a terpenoid of following structure

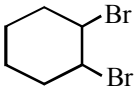
 gives how many different products ?

(a) 2 (b) 3
(c) 4 (d) 5

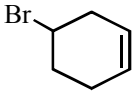
MARK YOUR RESPONSE					
	48. ⓐⓑⓒⓓ	49. ⓐⓑⓒⓓ	50. ⓐⓑⓒⓓ	51. ⓐⓑⓒⓓ	52. ⓐⓑⓒⓓ
	53. ⓐⓑⓒⓓ	54. ⓐⓑⓒⓓ	55. ⓐⓑⓒⓓ		

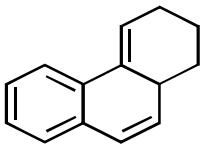
56.  $\xrightarrow{Me_4N^+Cl^-}$ Major product is

(a) 

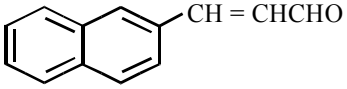
(b) 

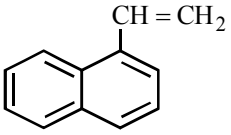
(c) Both (a) and (b)

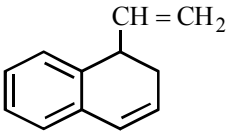
(d) 

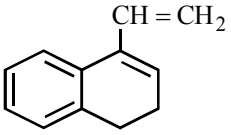
57. $[A] + CH_2 = CH_2 \longrightarrow$  Compound

[A] is

(a) 

(b) 

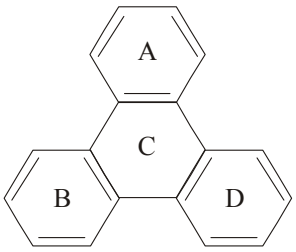
(c) 

(d) 

58. $C_6H_6 + D_2SO_4 \longrightarrow$ Product is

(a) $C_6H_5SO_3H$ (b) $C_6H_5SO_3D$

(c) C_6D_6 (d) No reaction

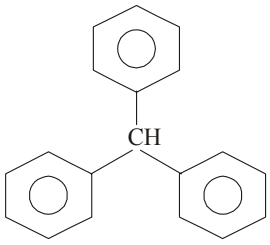
59..  + 1 mole H_2 (Pt)

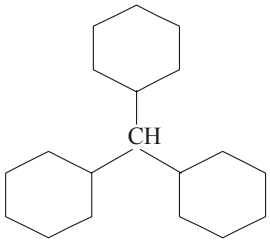
the two hydrogen atoms add on which ring?

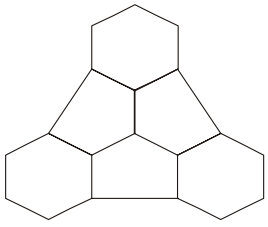
(a) A (b) B

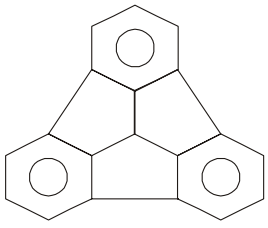
(c) C (d) none

60. Which of the following is most acidic in nature ?

(a) 

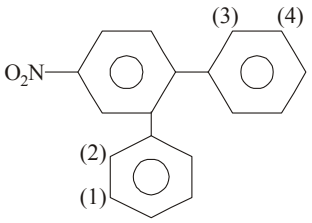
(b) 

(c) 

(d) 

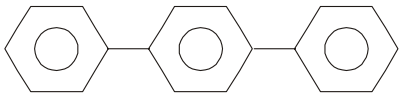
MARK YOUR RESPONSE	56. ⓐⓑⓒⓓ	57. ⓐⓑⓒⓓ	58. ⓐⓑⓒⓓ	59. ⓐⓑⓒⓓ	60. ⓐⓑⓒⓓ

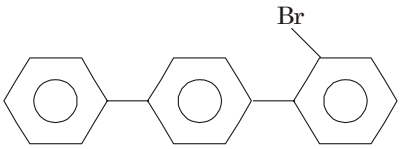
61. Which of the position in the following compound is liable to be attacked by an electrophile ?

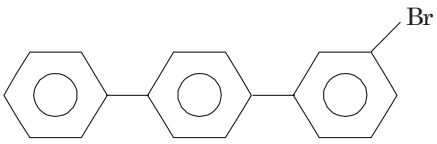


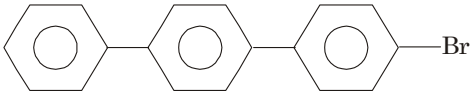
(a) 1 (b) 2
(c) 3 (d) 4

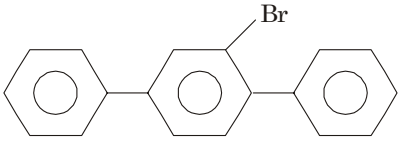
62. The major monobromo product formed on bromination of the following compound is



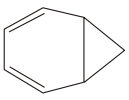
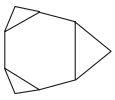
(a) 

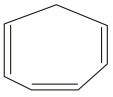
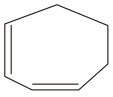
(b) 

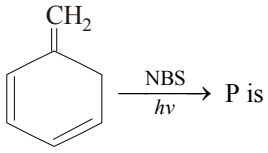
(c) 

(d) 

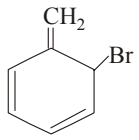
63. When diazomethane is added to but-2-ene $(CH_3CH=CHCH_3)$, $CH_3\overset{H_2C}{\diagup\diagdown}CH-CHCH_3$ is formed as the final product, what product will be formed when diazomethane is added to benzene ?

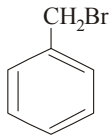
(a)  (b) 

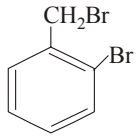
(c)  (d) 

64. 

P is

(a) 

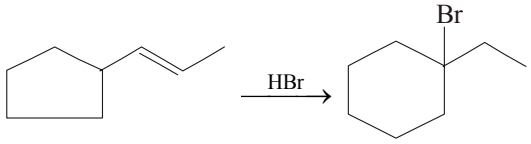
(b) 

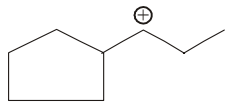
(c) 

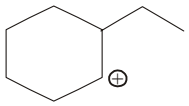
(d) All the three

65. A solution of cyclohexane in benzene is stirred at 0°C while conc. H_2SO_4 is added. After the reaction, the acid is removed and excess of benzene is removed, the product formed would be
(a) 1-cyclohexylcyclohexene
(b) cyclohexylbenzene
(c) 1, 1-diphenylcyclohexane
(d) no reaction

66. Which of the carbocation is formed in the following reaction?

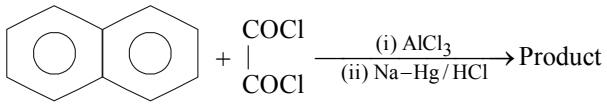


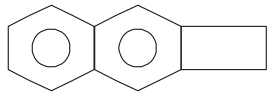
(a) 

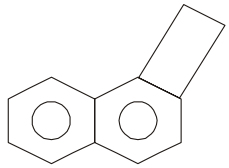
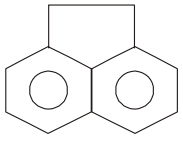
(b) 

(c) Both (d) None

67. Identify the final product in the following sequence of reactions.



(a) 

(b)  (c) 

(d) All the three

MARK YOUR RESPONSE	61. ⓐⓑⓒⓓ	62. ⓐⓑⓒⓓ	63. ⓐⓑⓒⓓ	64. ⓐⓑⓒⓓ	65. ⓐⓑⓒⓓ
	66. ⓐⓑⓒⓓ	67. ⓐⓑⓒⓓ			

B COMPREHENSION TYPE

This section contains groups of questions. Each group is followed by some multiple choice questions based on a paragraph. Each question has 4 choices (a), (b), (c) and (d) for its answer, out of which ONLY ONE is correct.

PASSAGE-1

Chlorination of methane involves three steps : chain-initiating, chain-propagating and chain-terminating.

$$Cl_2 \xrightarrow{\text{Heat or light}} 2\dot{Cl} \qquad \textbf{Chain initiating}$$

$$\left.\begin{aligned} CH_4 + \dot{Cl} &\longrightarrow \dot{C}H_3 + HCl \\ \dot{C}H_3 + Cl_2 &\longrightarrow CH_3Cl + \dot{Cl} \end{aligned}\right] \textbf{Chain propagating}$$

When oxygen is passed through the reaction mixture, chlorination of methane slows down temporarily.

1. Chain-propagating steps
- (a) consume reactive species and form another reactive species
- (b) do not produce reactive species
- (c) absorb energy and produce reactive species
- (d) are not always the part of chain-reaction mechanism.

2. Chain-terminating step may involve the formation of
- (a) Chlorine (b) Methyl chloride
- (c) Ethane (d) All the three

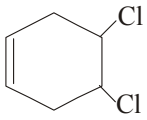
3. Although chlorination of methane is an exothermic, the reaction requires high temperature because
- (a) Activation energy is low
- (b) Heat of reaction is negative
- (c) Chain-initiating step is endothermic
- (d) Chain-terminating step is endothermic

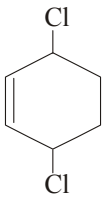
4. Temporary slow down of chlorination of methane in presence of oxygen in due to the formation of
- (a) $CH_3OO^{\bullet}$ which is highly unstable and decomposes easily
- (b) $CH_3OO^{\bullet}$ which is less reactive than $^{\bullet}CH_3$
- (c) $ClO^{\bullet}$ which is highly reactive
- (d) a diradical $\dot{Cl}\dot{O}\bullet$.

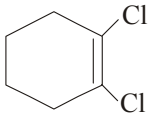
PASSAGE-2

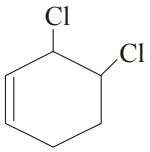
An organic compound *A* of molecular formula $C_6H_{12}O$ reacts with conc. H_2SO_4 to form compound *B* which reacts with NBS and gives compound *C* with molecular formula C_6H_9Br. Compound *C* when heated with alcoholic potash gave another compound D which reacts with 1 mole of Cl_2 at low temperature to form compound *E*, $C_6H_8Cl_2$.

5. On the basis of the above reactions, *E* ($C_6H_8Cl_2$) should be

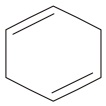
(a) 

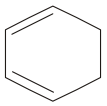
(b) 

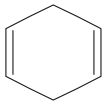
(c) 

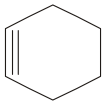
(d) 

6. Hence the compound *D* is

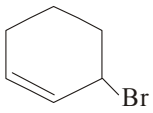
(a) 

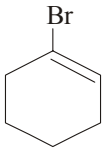
(b) 

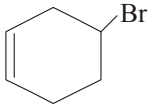
(c) 

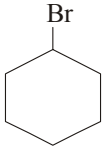
(d) 

7. The compound *C* should be

(a) 

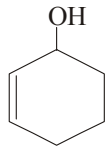
(b) 

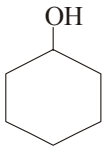
(c) 

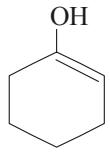
(d) 

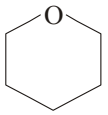
MARK YOUR RESPONSE					
	1. ⓐⓑⓒⓓ	2. ⓐⓑⓒⓓ	3. ⓐⓑⓒⓓ	4. ⓐⓑⓒⓓ	5. ⓐⓑⓒⓓ
	6. ⓐⓑⓒⓓ	7. ⓐⓑⓒⓓ			

8. The compound A is

(a) 

(b) 

(c) 

(d) 

PASSAGE-3

Halogenation of alkanes is a free radical substitution reaction and takes place in presence of light. For example,

$$CH_3CH_2CH_3 + Cl_2 \xrightarrow{light} CH_3CH_2CH_2Cl + CH_3\overset{\overset{Cl}{|}}{C}HCH_3$$

$$CH_3CH_2CH_3 + Br_2 \xrightarrow{light} CH_3CH_2CH_2Br + CH_3\overset{\overset{Br}{|}}{C}HCH_3$$

Bromination by bromine occurs at alkyl, allylic and benzylic carbon; while bromination with NBS occurs at allylic and benzylic carbon.

The relative amount of different isomers formed during halogenation depends upon three factors.

(i) ***Probability factor :*** Higher the number of each kind of hydrogen atom in the molecule, more will be the chance for its replacement by halogen

(ii) ***Reactivity of hydrogen atom :*** Higher the stability of the corresponding free radical, more will be the chance for the corresponding hydrogen to be replaced.

Benzyl $\approx$ Allyl > 3° > 2° > 1° > CH_3 > Vinyl free radical

Unlike carbocations, free radicals do not undergo rearrangement.

(iii) ***Reactivity selectivity principle :*** The more reactive chlorine free radical is less selective and hence greatly influenced by probability factor. The less reactive bromine radical is more selective and hence more influenced by the reactivity of hydrogen atom.

9. Which reagent can be used for free radical chlorination ?

(a) Cl_2 (b) SO_2Cl_2

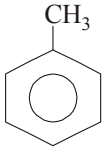
(c) Me_3COCl (d) All the three

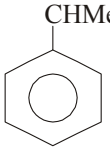
10. Which of the following will react with NBS ?

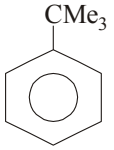
(a) $CH_3-\underset{\underset{CH_3}{|}}{CH}\,CH_3$ (b) $CH_3CH_2CH=CH_2$

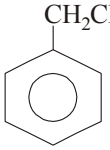
(c) $CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH=CH_2$ (d) $C_6H_5C(Me_2)CH_2CH_3$

11. Which of the following is most reactive for chlorination in the side chain ?

(a) 

(b) 

(c) 

(d) 

12. Arrange the four compounds (A to D) in order of their increasing reactivity towards NBS.

$C_6H_5CH_3$ (A) $C_6H_5CH_2CH=CH_2$ (B)

$C_6H_5CH_2CH_2CH_3$ (C) $C_6H_5\overset{\overset{CH_3}{|}}{C}HCH=CH_2$ (D)

(a) A < B < C < D (b) D < C < B < A

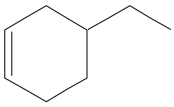
(c) C < A < D < B (d) A < C < B < D

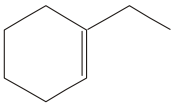
PASSAGE-4

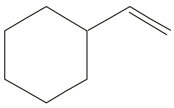
Alkenes and alkynes can be hydrogenated in presence of catalyst. In case of alkenes, less crowded alkenes are reduced at a faster rate to form alkane. In case of alkynes, hydrogenation can be used to form alkene or alkane as the final product. Further, non-terminal alkynes are reduced to *cis*-alkenes using H_2 in presence of Lindlar catalyst or to *trans*-alkenes using Na in liquid ammonia.

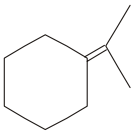
MARK YOUR RESPONSE	8. ⓐⓑⓒⓓ	9. ⓐⓑⓒⓓ	10. ⓐⓑⓒⓓ	11. ⓐⓑⓒⓓ	12. ⓐⓑⓒⓓ

13. The decreasing ease of catalytic hydrogenation of the following alkenes should be


I

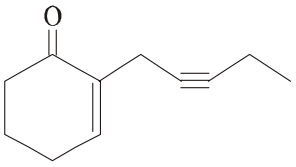

II

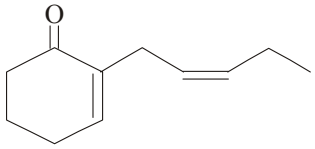

III

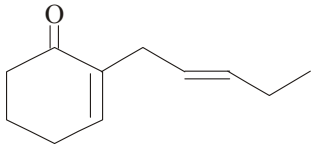

IV

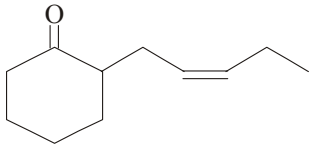
(a) II > I > III > IV (b) I = II > III = IV
(c) III > I > II > IV (d) All equal

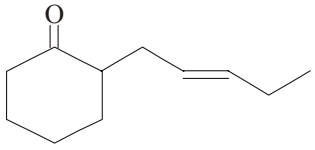
14. Hydrogenation of which of the above alkenes will be least exothermic ?
(a) I (b) II
(c) III (d) IV

15. 
$\xrightarrow[NH_3]{Na\,/\,liq.}$ Z is

(a) 

(b) 

(c) 

(d) 

16. Which of the above statement is incorrect ?
(a) Powdered catalyst provides greater surface area and hence more effective during hydrogenation.
(b) All alkynes can be converted into *cis*- or *trans*-alkene, as required
(c) All alkynes can be converted to corresponding alkane.
(d) Powdered catalyst increases the number of free valencies.

17. Butyne-2 can't be reduced by
(a) Na in liq. NH_3 (b) sodamide
(c) Li in liq. NH_3 (d) none of the three

18. Butyne-1 may react with
(a) Na in liq. NH_3 (b) sodamide
(c) H_2 in presence of Pt (d) all the three

PASSAGE-5

The acid-catalysed additions of water to the double bond of an alkene is a method for preparing alcohols. These reactions are usually regioselective since they follow Markovnikov's rule.

$$(CH_3)_2C = CH_2 + HOH \xrightarrow[25°C]{H_3O^+} (CH_3)_2\overset{OH}{\overset{|}{C}}CH_3$$

Since the acid catalyzed hydration of alkenes follows Markovnikov's rule, in majority of cases, the alcohol formed is either 2° or 3°. Further, since carbocations are formed as intermediates, which may undergo rearrangement and thus unexpected alcohol may be formed as the main product.

Answer the following questions, taking the following reactants.

$$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH=CH_2 + H_2O \xrightarrow{H_2SO_4}$$

19. The electrophile involved in the first step is
(a) H^+ (b) H_2SO_4
(c) H_3O^+ (d) $(CH_3)_3C\overset{+}{C}HCH_3$

20. The nucleophile in the first step of the reaction is
(a) OH^- (b) $^-HSO_4$
(c) $(CH_3)_3CCH=CH_2$ (d) H_2O

MARK YOUR RESPONSE					
	13. ⓐⓑⓒⓓ	14. ⓐⓑⓒⓓ	15. ⓐⓑⓒⓓ	16. ⓐⓑⓒⓓ	17. ⓐⓑⓒⓓ
	18. ⓐⓑⓒⓓ	19. ⓐⓑⓒⓓ	20. ⓐⓑⓒⓓ		

21. The electrophile in the second step of the reaction is

(a) $(CH_3)_3\overset{+}{C}CHCH_3$ (b) $(CH_3)_2\overset{+}{C}CH(CH_3)_2$

(c) H^+ (d) H_3O^+

22. The nucleophile in the second step of the reaction is

(a) OH^- (b) H_2O

(c) $(CH_3)_2\overset{-}{C}CH(CH_3)_2$ (d) HSO_4^-

23. Product formed after second step is

(a) 3° alcohol (b) protonated 3° alcohol

(c) 2° alcohol (d) protonated 2° alcohol

24. Which of the following is rate determining step?

(a) attack of electrophile H^+

(b) attack of nucleophile $(CH_3)_3CCH = CH_2$

(c) attack of electrophile $(CH_3)_2\overset{+}{C}CH(CH_3)_2$

(d) deprotonation of the protonated alcohol

25. Acid-catalyzed hydration of an alkene may form

(i) primary alcohol (ii) secondary alcohol

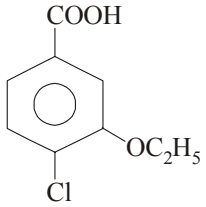
(iii) tertiary alcohol

(a) Only (ii) (b) Only (iii)

(c) (ii) and (iii) (d) (i), (ii) and (iii)

PASSAGE-6

Four isomeric compounds (A, B, C and D) of the formula $C_{11}H_{13}OCl$ give the following reactions.

$C_{11}H_{13}OCl \xrightarrow{\text{oxidation}}$ 

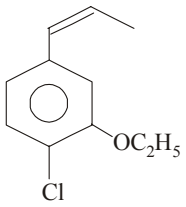
A, B or C $\xrightarrow{H_2/Ni}$ X

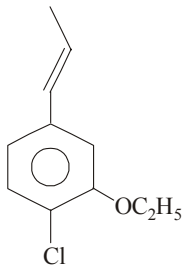
D $\xrightarrow{H_2/Ni}$ E

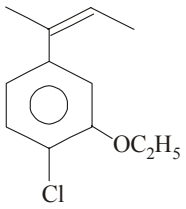
A $\xrightarrow{Br_2/CCl_4}$ Meso compound

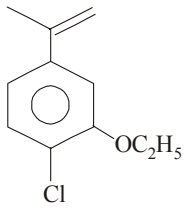
B $\xrightarrow{Br_2/CCl_4}$ (±) – Mixture

26. The compound A is

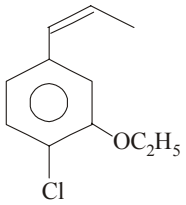
(a) 

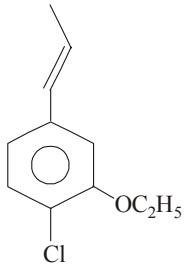
(b) 

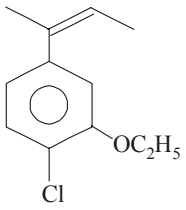
(c) 

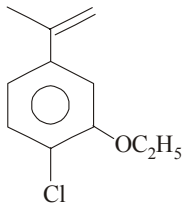
(d) 

27. The compound B is

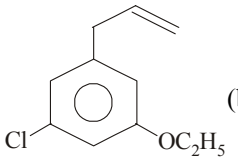
(a) 

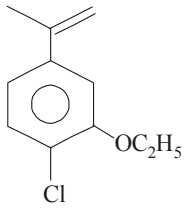
(b) 

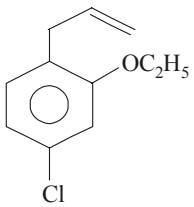
(c) 

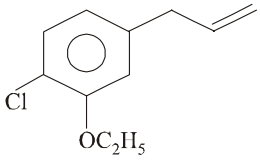
(d) 

28. The compound C is

(a) 

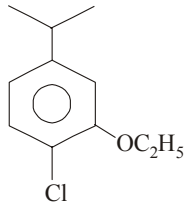
(b) 

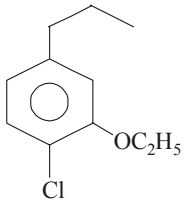
(c) 

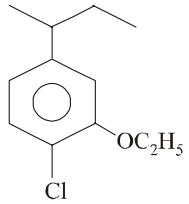
(d) 

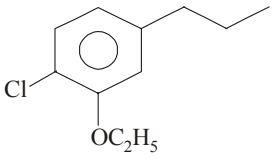
MARK YOUR RESPONSE	21. ⓐⓑⓒⓓ	22. ⓐⓑⓒⓓ	23. ⓐⓑⓒⓓ	24. ⓐⓑⓒⓓ	25. ⓐⓑⓒⓓ
	26. ⓐⓑⓒⓓ	27. ⓐⓑⓒⓓ	28. ⓐⓑⓒⓓ		

29. Compound E is

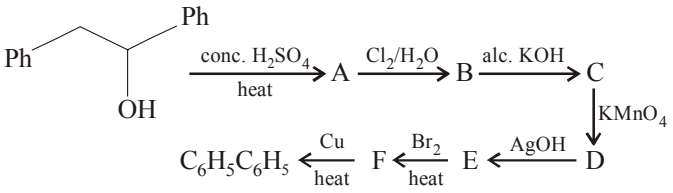
(a) 

(b) 

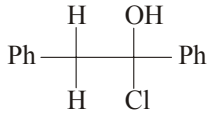
(c) 

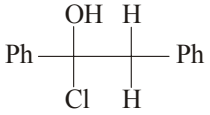
(d) 

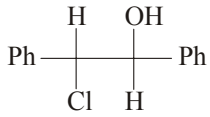
PASSAGE-7

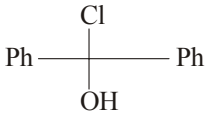


30. The compound B is

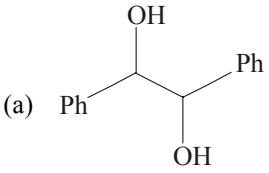
(a) 

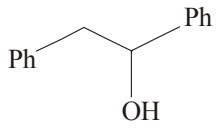
(b) 

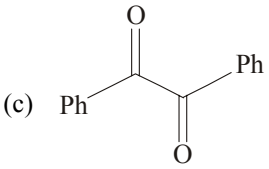
(c) 

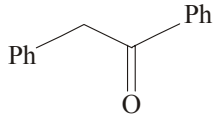
(d) 

31. Compound C is

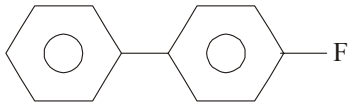
(a) 

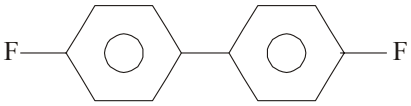
(b) 

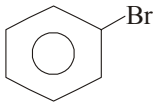
(c) 

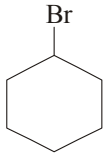
(d) 

32. Compound F is

(a) 

(b) 

(c) 

(d) 

33. The complete series of reactions involves which reaction in one or the other step ?

(a) Friedel-Craft reaction (b) Ullmann reaction

(c) Hunsdiecker reaction (d) (b) and (c) both

MARK YOUR RESPONSE	29. ⓐⓑⓒⓓ	30. ⓐⓑⓒⓓ	31. ⓐⓑⓒⓓ	32. ⓐⓑⓒⓓ	33. ⓐⓑⓒⓓ

C REASONING TYPE

In the following questions two Statement-1 (Assertion) and Statement-2 (Reason) are provided. Each question has 4 choices (a), (b), (c) and (d) for its answer, out of which ONLY ONE is correct. Mark your responses from the following options:

(a) Both Statement-1 and Statement-2 are true and Statement-2 is the correct explanation of Statement-1.
(b) Both Statement-1 and Statement-2 are true and Statement-2 is not the correct explanation of Statement-1.
(c) Statement-1 is true but Statement-2 is false.
(d) Statement-1 is false but Statement-2 is true.

1. **Statement-1** : Addition of HBr to $HC \equiv C–CH_2–CH = CH_2$ gives $HC \equiv C - CH_2 - CHBr - CH_3$ and not $H_2C = CBr - CH_2 - CH = CH_2$

Statement-2 : A triple bond is less reactive than a double bond.

2. **Statement-1** : But-2-yne on reduction with $Na/NH_3(l)$ gives *trans*-2-butene.

Statement-2 : To minimise interelectronic repulsions the addition of electrons occur on the opposite faces of the triple bond.

MARK YOUR RESPONSE	1. ⓐⓑⓒⓓ	2. ⓐⓑⓒⓓ			

3. **Statement-1** : $CH_3 - CH = CH_2 \xrightarrow{Cl_2, 773K}$

$ClCH_2 - CH = CH_2 + HCl$

Statement-2 : At high temperature Cl_2 dissociates into chlorine atoms which bring about the allylic substitution.

4. **Statement-1** : Nitration of benzene and hexadeuterobenzene occur exactly at the same rate.

Statement-2 : The cleavage of C–H bond is not the rate-determining step of the reaction.

5. **Statement-1** : 1-Butene on reaction with HBr in the presence of a peroxide produces 1-bromobutane.

Statement-2 : It involves the formation of a primary radical.

6. **Statement-1** : Friedel-Crafts reaction between benzene and acetic anhydride in the presence of anhydrous $AlCl_3$ yields acetophenone and not poly substituted products.

Statement-2 : Acetophenone formed poisons the catalyst preventing further reaction.

7. **Statement-1** : Corey-House reaction can be used to prepare both symmetrical and unsymmetrical alkanes.

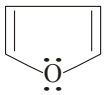
Statement-2 : It involves the interaction between lithium dialkyl-copper with an alkyl halide both of which may contain even or odd number of carbon atoms.

8. **Statement-1** : Alkylbenzene is not prepared by Friedel-Crafts alkylation of benzene.

Statement-2 : Alkyl halides are less reactive than acyl halides.

9. **Statement-1** : Melting point of neopentane is greater than that of *n*-pentane while the boiling point of neopentane is lower than *n*-pentane.

Statement-2 : Melting point depends upon packing in crystal lattice while boiling point depends upon surface area of the molecule.

10. **Statement-1** : Furan has an aromatic sextet. 

Statement-2 : The two lone pairs of electrons on oxygen and a π electron pair form an aromatic sextet.

11. **Statement-1** : Aniline becomes more reactive towards electrophilic aromatic substitution in presence of strongly acidic solution.

Statement-2 : The amino group is completely protonated in strongly acidic medium. Thus the lone pair of electrons on the nitrogen is no longer available for resonance.

12. **Statement-1** : 2-Pentyne on hydrogenation in presence of Lindlar catalyst gives *cis*-1-pentene.

Statement-2 : Addition of hydrogen in a stereospecific reaction.

13. **Statement-1** : When CH_2 = CHCOOH is treated with HBr, $CH_3\underset{|}{\overset{Br}{C}}H\,COOH$ is the main product.

Statement-2 : The carbocation, $\overset{+}{C}H_2CH_2COOH$ is more stable than $CH_3\overset{+}{C}H\,COOH$.

14. **Statement-1** : In cracking of alkanes C – C bond is broken but not C – H bonds.

Statement-2 : Bond energy of C – C bond is less than C – H bond.

15. **Statement-1** : Reduction of butyne by Na is liquid ammonia gives *trans*-butene

Statement-2 : Non-terminal alkynes when reduced by Na/liq. NH_3 gives *trans*-product.

16. **Statement-1** : Addition of HCl to butene-1 in presence of peroxide gives 1-chlorobutane.

Statement-2 : The reaction involves the formation of carbocation as an intermediate.

17. **Statement-1** : $CH \equiv CH$ is more reactive than $CH_3C \equiv CCH_3$ towards HCl.

Statement-2 : The carbocation formed from latter is more stable than that from the former.

18. **Statement-1** : Hydration of an alkene using $Hg(OAc)_2/NaBH_4$ is regioselective.

Statement-2 : There is no 1, 2-hydride/alkyl shift in the reaction.

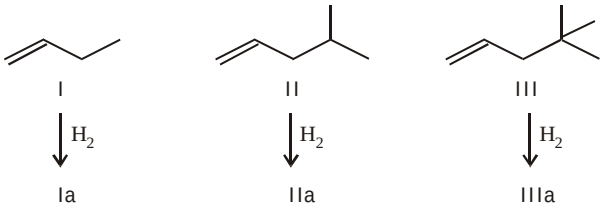
MARK YOUR RESPONSE

	3. ⓐⓑⓒⓓ	4. ⓐⓑⓒⓓ	5. ⓐⓑⓒⓓ	6. ⓐⓑⓒⓓ	7. ⓐⓑⓒⓓ
	8. ⓐⓑⓒⓓ	9. ⓐⓑⓒⓓ	10. ⓐⓑⓒⓓ	11. ⓐⓑⓒⓓ	12. ⓐⓑⓒⓓ
	13. ⓐⓑⓒⓓ	14. ⓐⓑⓒⓓ	15. ⓐⓑⓒⓓ	16. ⓐⓑⓒⓓ	17. ⓐⓑⓒⓓ
	18. ⓐⓑⓒⓓ				

D MULTIPLE CORRECT CHOICE TYPE

Each of these questions has 4 choices (a), (b), (c) and (d) for its answer, out of which ONE OR MORE is/are correct.

1. Which of the following statement is correct regarding stability of the parent alkenes and the product alkanes?



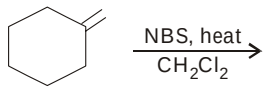
(a) All alkenes are equally stable

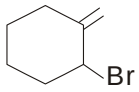
(b) Alkene III is more stable than I and II

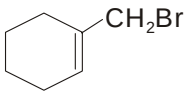
(c) All alkanes are equally stable

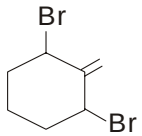
(d) Alkane IIIa is more stable than Ia and IIa

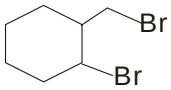
2. NBS is used for brominating allylic carbon atom. Predict the product in the following reaction



(a) 

(b) 

(c) 

(d) 

3. Allylic substituion in $CH_3CH{=}CH_2$ may be carried out by

(a) Sulphuryl chloride, SO_2Cl_2

(b) *tert*-butyl hypochlorite, Me_3COCl

(c) NBS

(d) Chlorine at 350°C

4. Propene (I), 2-methylpropene (II), and ethene (III), each containing one carbon-carbon double bond, is separately treated with HI under the same set of conditions. The order of reactivity for the three alkenes should be

(a) I is more reactive than II as well as III

(b) I is more reactive than III, but less than II

(c) II is more reactive than both I and III

(d) III is more reactive than I which is more reactive than II

5. Arrange the following compounds in decreasing order of reactivity with Br_2

$CH_2 = CH_2$ (I), $CH \equiv CH$ (II), CH_2 $CHCl$ (III)

(a) II > I as well as III

(b) I > II as well as III

(c) II is more reactive than III but less than I

(d) II is less reactive than III but more than I

6. Which of the dihydroxybutane can be converted easily into 1,3-butadiene?

(a) $CH_3CH(OH)CH(OH)CH_3$

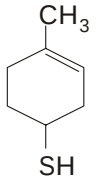
(b) $HOCH_2CH_2CH_2CH_2OH$

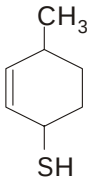
(c) $HOCH_2CH_2CH(OH)CH_3$

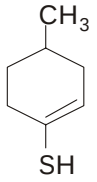
(d) $CH_2OHCHOHCH_2CH_3$

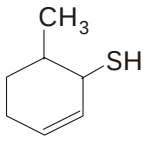
7. 1-Methyl-1,3-cyclohexadiene + H_2S (1 eq.) $\xrightarrow{\text{Peroxide}}$

Product does not have

(a) 

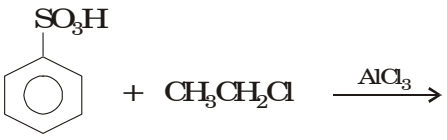
(b) 

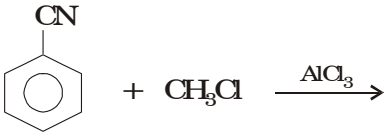
(c) 

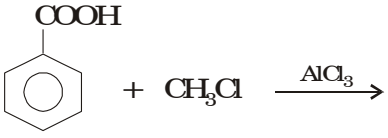
(d) 

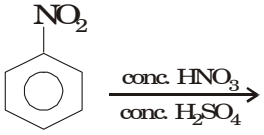
MARK YOUR RESPONSE	1. ⓐⓑⓒⓓ	2. ⓐⓑⓒⓓ	3. ⓐⓑⓒⓓ	4. ⓐⓑⓒⓓ	5. ⓐⓑⓒⓓ
	6. ⓐⓑⓒⓓ	7. ⓐⓑⓒⓓ			

8. Which of the reaction does not give quantitative yield of the expected product?

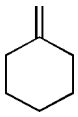
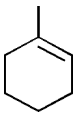
(a) 

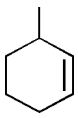
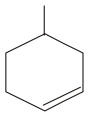
(b) 

(c) 

(d) 

9. A $\xrightarrow{\text{dil. } H_2SO_4 / Hg^{2+}}$ 1-Methylcyclohexanol. Here A is

(*a*)  (*b*) 

(*c*)  (*d*) 

10. 1,3-Butadiene is treated with 1 equivalent of HBr under two different conditions

$$B \xleftarrow{\text{peroxide}} CH_2 = CH - CH = CH_2 + HBr \text{ (1 e.q.)} \xrightarrow{-80^\circ C} A$$

Which of the following statement is true regarding above reactions?

(a) Both give similar products

(b) Both give different products

(c) Products A and B is $CH_3CH{=}CHCH_2Br$

(d) Product A is $CH_3CHBrCH{=}CH_2$, while B is $CH_3CH{=}CHCH_2Br$

11. Which of the following involves the formation of an allylic carbocation?

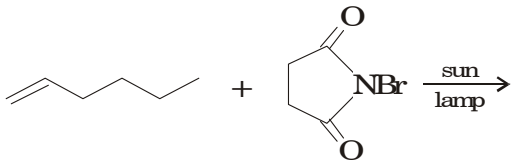
(a) 1,3-Butadiene + Br_2 $\longrightarrow$

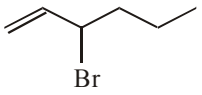
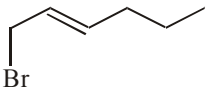
(b) 1-Chloro-2-butene + aq. $AgNO_3$ $\longrightarrow$

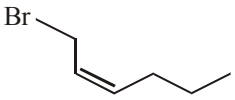
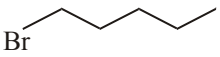
(c) 3-Chloro-1-methylcyclopentene + NBS $\longrightarrow$

(d) $CH_3CH = CH_2$ + NBS $\longrightarrow$

12. The possible compounds formed in the following reaction is



(a)  (b) 

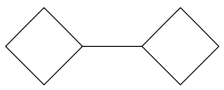
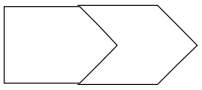
(c)  (d) 

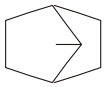
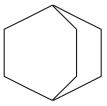
13. C_nH_{2n} is the general formula of

(a) alkenes (b) cycloalkenes

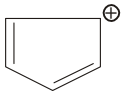
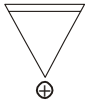
(c) cycloalkanes (d) alicyclic compounds

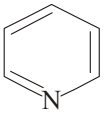
14. Which of the following hydrocarbons contains 12 secondary and 2 tertiary hydrogen atoms ?

(a)  (b) 

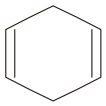
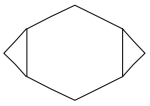
(c)  (d) 

15. Which of the following are antiaromatic ?

(a)  (b) 

(c)  (d) 

MARK YOUR RESPONSE	8. ⓐⓑⓒⓓ	9. ⓐⓑⓒⓓ	10. ⓐⓑⓒⓓ	11. ⓐⓑⓒⓓ	12. ⓐⓑⓒⓓ
	13. ⓐⓑⓒⓓ	14. ⓐⓑⓒⓓ	15. ⓐⓑⓒⓓ		

16.  can be converted into  by

(a) CH_2I_2, Zn (b) $CH_2 = CH_2$, light

(c) CH_2N_2, light (d) $CH_3I + KOH$

17. Which of the following will not give Friedel-Craft alkylation when heated with benzene and $AlCl_3$?

(a) $CH_2 = CHCH_2Cl$ (b) $CH_2 = CHCl$

(c) $C_6H_5CH_2Cl$ (d) C_6H_5Cl

18. Which of the following substituent in benzene is deactivating but *o, p*-directing ?

(a) $-OCH_3$ (b) $-Cl$

(c) $-N = O$ (d) $-NO_2$

19. Select the correct statement regarding 3-methylbutene.

(a) It may be converted into primary alcohol by hydroboration-oxidation reaction

(b) It may be converted into tertiary alcohol by acidic hydration

(c) It may be converted into a racemic mixture of primary alcohol by oxymercuration-demercuration

(d) It may be converted into a racemic mixture of secondary alcohols by oxymercuration-demercuration

20. Which of the following statement is true regarding addition of HBr in absence of peroxide ?

(a) $CH_3CH = CH_2$ adds HBr according to Markownikof's way.

(b) $CN\ CH = CH_2$ adds HBr in Markownikof's way.

(c) $CH_2 = CH\ CN$ adds HBr giving anti-Markownikof's product.

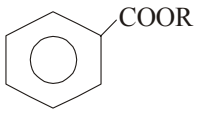
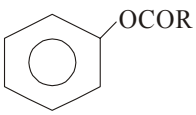
(d) $CH_2 = CH\ CH_2OH$ adds HBr giving anti-Markownikof's product.

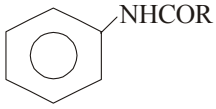
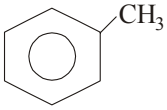
21. Triphenylmethane can be prepared by treating excess of benzene with ..... in presence of anhydrous $AlCl_3$.

(a) C_6H_5Cl (b) $C_6H_5CHCl_2$

(c) CH_2Cl_2 (d) $CHCl_3$

22. Which of the following is more reactive than diphenyl regarding electrophilic aromatic substitution ?

(a)  (b) 

(c)  (d) 

23. Which of the following reagents can be used to distinguish between propene and propyne ?

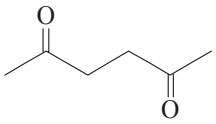
(a) Bromine water (b) Grignard reagent

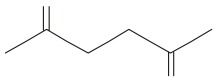
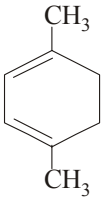
(c) Ammonical $AgNO_3$ (d) Lucas reagent

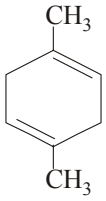
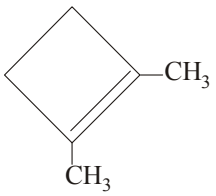
24. Which of the following on reductive ozonolysis give glyoxal as the exclusive product ?

(a) Ethene (b) Ethyne

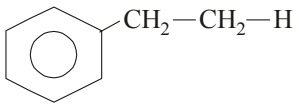
(c) Benzene (d) Toluene

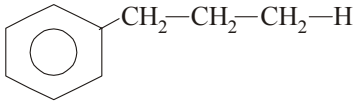
25. An organic compound on reaction with ozone followed by zinc and water gives  as the final product. The compound may be

(a)  (b) 

(c)  (d) 

26. Which of the following order is correct regarding reactivity of the C—H bond ?

(a)  >



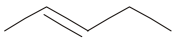
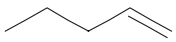
(b) $CH_2 = CH\ CH_2 - H > CH_3CH_2CH_2 - H > CH_3 - H$

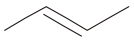
(c) $C_6H_5CH_2C_6H_5 \approx C_6H_5CH_2CH_2C_6H_5$

(d) $CH_3CH_2CH_2CH_2 - H < CH_3CH_2\underset{\displaystyle H}{\underset{|}{C}}H\ CH_3$

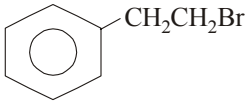
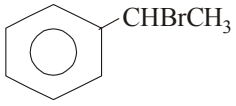
MARK YOUR RESPONSE					
	16. ⓐⓑⓒⓓ	17. ⓐⓑⓒⓓ	18. ⓐⓑⓒⓓ	19. ⓐⓑⓒⓓ	20. ⓐⓑⓒⓓ
	21. ⓐⓑⓒⓓ	22. ⓐⓑⓒⓓ	23. ⓐⓑⓒⓓ	24. ⓐⓑⓒⓓ	25. ⓐⓑⓒⓓ
	26. ⓐⓑⓒⓓ				

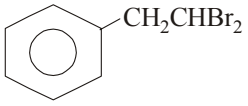
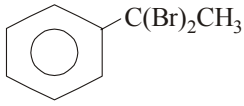
27. Which of the following products are likely to be formed when pentane is heated with CrO_3/Al_2O_3 at 600°C ?

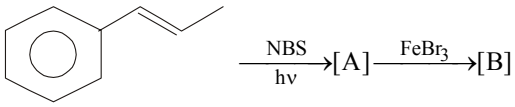
(a)  (b) 

(c)  (d) H_2

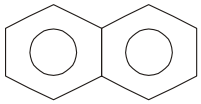
28. Bromination of ethylbenzene gives mainly

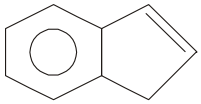
(a)  (b) 

(c)  (d) 

29. 

Which of the following facts are true regarding above reaction sequence ?

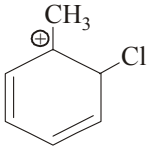
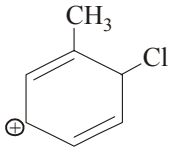
(a) The product [B] is 

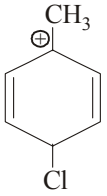
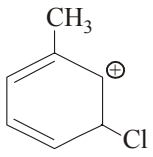
(b) The product [B] is 

(c) The sequence involves electrophilic and free radical substitution reactions

(d) The reaction involves nucleophilic and free radical substitution reactions

30. Which of the following are formed when toluene is chlorinated in presence of $FeCl_3$?

(a)  (b) 

(c)  (d) 

31. Which of the following gives rearrangement of carbocation in the addition of propene in presence of peroxide ?

(a) HCl (b) HBr

(c) NBS/$h\nu$ (d) HF

32. Which of the following may react with sodamide ?

(a) $HC \equiv CH$ (b) $H_2C = CH_2$

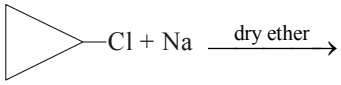
(c) $CH_3CH = CHCH_3$ (d) $CH_3C \equiv CCH_3$

33. Identify the products in the following reaction

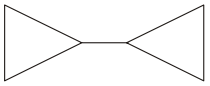
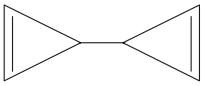
$$CH_3CH_2CH = CH_2 + NBS \longrightarrow$$

(a) $CH_2 = CHCH_2CH_2Br$ (b) $CH_3CHBrCH = CH_2$

(c) $CH_3CH = CHCH_2Br$ (d) $CH_2 = CHCH = CH_2$

34.  Possible products are

(a)  (b) 

(c)  (d) 

35. $CH_3CH_2C \equiv CH \xrightarrow[\text{heat}]{NaNH_2} CH_3C \equiv CCH_3$

(a) It involves repeated deprotonation and protonation

(b) The first deprotonated and protonated species are $CH_3\bar{C}HC \equiv CH$ and $CH_3CH = C = CH_2$ respectively

(c) The second deprotonated species is $CH_3\bar{C} = C = CH_2$ which is resonance stabilised to $CH_3C \equiv C\bar{C}H_2$

(d) The above conversion is not possible

36. Which of the following statement is/are correct ?

(a) During nitration of benzene with conc. H_2SO_4 and conc. HNO_3, temperature should not be more than 50°C

(b) In nitrating mixture ($HNO_3 + H_2SO_4$), HNO_3 acts as a base

(c) Nitration can be done by means of N_2 and H_2SO_4

(d) Nitration can be done by HNO_3 + mercury nitrate

MARK YOUR RESPONSE					
	27. ⓐⓑⓒⓓ	28. ⓐⓑⓒⓓ	29. ⓐⓑⓒⓓ	30. ⓐⓑⓒⓓ	31. ⓐⓑⓒⓓ
	32. ⓐⓑⓒⓓ	33. ⓐⓑⓒⓓ	34. ⓐⓑⓒⓓ	35. ⓐⓑⓒⓓ	36. ⓐⓑⓒⓓ

37. Which of the following follow free radical mechanism ?

(a) Cracking of alkanes

(b) Isomerisation of alkanes

(c) Nitration of alkanes

(d) Sulphonation of alkanes

38. Which of the following are examples of electrophilic addition?

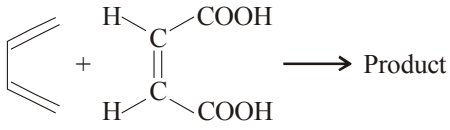
(a) $CH_3CH = CH_2 + HCl \xrightarrow{\text{Peroxide}} CH_3\overset{Cl}{\overset{|}{C}}HCH_3$

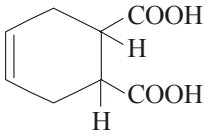
(b) $CH_3CH = CHCH_3 + Cl_2 \longrightarrow CH_3\overset{Cl}{\overset{|}{C}}H - \overset{Cl}{\overset{|}{C}}HCH_3$

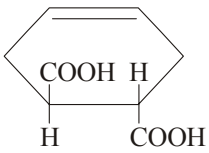
(c) $CH_3CH = CH_2 + HBr \longrightarrow CH_3\overset{Br}{\overset{|}{C}}HCH_3$

(d) $CH_3CH = CH_2 + H_2O \longrightarrow CH_3\overset{OH}{\overset{|}{C}}HCH_3$

39. Which of the following option(s) is/are correct in the following reaction ?



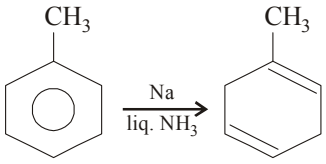
(a) 

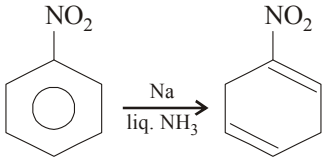
(b) 

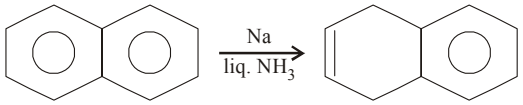
(c) The reaction is an example of Diel's – Alder reaction

(d) It is an electrophilic addition reaction

40. Which of the following are examples of Birch reduction ?

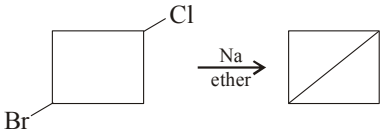
(a) 

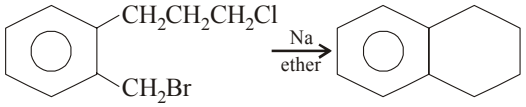
(b) 

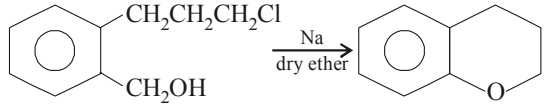
(c) 

(d) $CH_3C \equiv CCH_3 \xrightarrow[\text{liq. } NH_3]{Na} CH_3CH = CHCH_3$

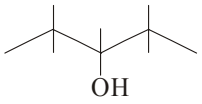
41. Which of the following is/are example of Wurtz reaction ?

(a) 

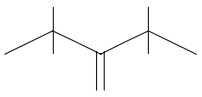
(b) 

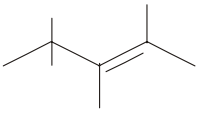
(c) 

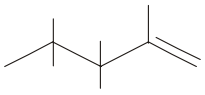
(d) All the three

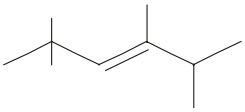
42. 

$\xrightarrow{\text{conc. } H_2SO_4}$ Product(s) is/are

(a) 

(b) 

(c) 

(d) 

43. $CH_2 = CHBr + HBr \longrightarrow [X]$

$CH_2 = CHCOOH + HBr \longrightarrow [Y]$

Pick up the structures of [X] and [Y]

(a) X is CH_2BrCH_2Br

(b) Y is $CH_2Br - CH_2COOH$

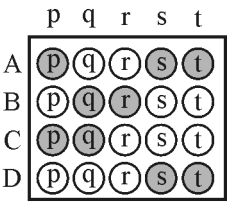
(c) X is CH_3CHBr_2

(d) Y is $CH_3CH(Br)COOH$

MARK YOUR RESPONSE					
	37. ⓐⓑⓒⓓ	38. ⓐⓑⓒⓓ	39. ⓐⓑⓒⓓ	40. ⓐⓑⓒⓓ	41. ⓐⓑⓒⓓ
	42. ⓐⓑⓒⓓ	43. ⓐⓑⓒⓓ			

E MATRIX-MATCH TYPE

Each question contains statements given in two columns, which have to be matched. The statements in Column-I are labeled A, B, C and D, while the statements in Column-II are labelled p, q, r, s and t. Any given statement in Column -I can have correct matching with ONE OR MORE statement(s) in Column-II. The appropriate bubbles corresponding to the answers to these questions have to be darkened as illustrated in the following example:
If the correct matches are A–p, s and t; B–q and r; C–p and q; and D–s then the correct darkening of bubbles will look like the given.



1.

	Column-I **Reaction**		**Column-II** **Factor responsible for the reaction**
(A)	$CH_3CH_2CH = CHCH_3$ on reaction with HCl gives two products	p.	Rearrangement
(B)	$CH_2 = CH–CH = CH_2$ reacts with HCl to form 1, 2- and 1, 4-addition products	q.	Inductive effect
(C)	$C_6H_5CH=CHCH_3+HBr$ gives only one product	r.	Hyperconjugation
(D)	$C_6H_5CH_2CH = CH_2 + HBr$ forms a compound identical to that obtained in (C).	s.	Resonance

2.

	Column-I		**Column-II**
(A)	$CH_2 = CHCN + (CH_3)_2NH \longrightarrow$	p.	Transition state involves pentavalent carbon
(B)	$CH_2 = CHCN \xrightarrow{\text{catalyst}}$	q.	Nucleophilic substitution
(C)	$CH_3-\overset{\overset{O}{\|\|}}{C}-Cl + (CH_3)_2NH \longrightarrow$	r.	Nucleophilic addition
(D)	$ClCH_2CH = CHCN + (CH_3)_2NH \longrightarrow$	s.	Free radical addition

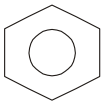
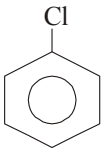
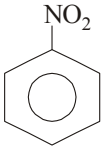
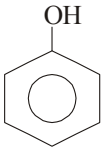
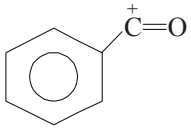
3.

	Column-I		**Column-II**
(A)	Carbocations	p.	Addition to alkenes
(B)	Singlet carbenes	q.	Free electrons are paired
(C)	Free radicals	r.	Disproportionation
(D)	Triplet carbenes	s.	1, 2-Hydride shift

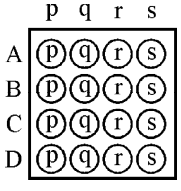
4.

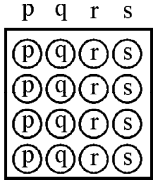
	Column - I		**Column - II**
(A)	Aromatic	p.	Planar
(B)	Antiaromatic	q.	Non-planar
(C)	Huckel rule	r.	$4n\pi$ localised electrons
(D)	Cyclo-octatetraene	s.	$(4n + 2)\pi$ delocalised electrons

5.

	Column I *(Substrate, S)*		**Column II** *(Electrophile for S)*
(A)		p.	Cl^+
(B)		q.	$\overset{+}{C}H_3$
(C)		r.	$CH_3\overset{+}{C}O$
(D)		s.	

MARK YOUR RESPONSE

1.


2.


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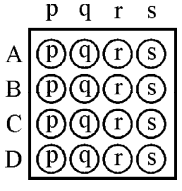

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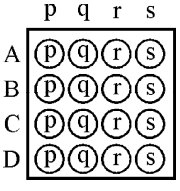

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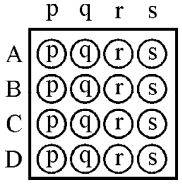
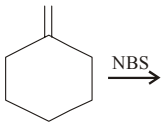
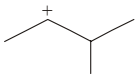
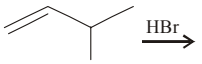
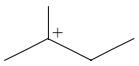
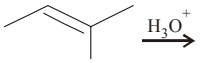
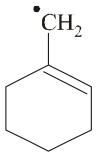
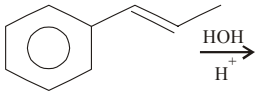
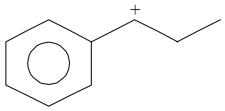


6.

Column I **Reactants**		*Column II* **No. of chlorinated products**
(A) Benzene $\xrightarrow{Cl_2, light}$	p.	Three compounds
(B) Toluene $\xrightarrow{Cl_2, light}$	q.	Four compounds
(C) Methane $\xrightarrow{Cl_2, light}$	r.	Single monochloro derivative
(D) Benzene $\xrightarrow{Cl_2, AlCl_3}$	s.	Six isomeric compounds

7.

Column I		*Column II*
(A) 	p.	
(B) 	q.	
(C) 	r.	
(D) 	s.	

MARK YOUR RESPONSE

6.

	p	q	r	s
A	Ⓟ	Ⓠ	Ⓡ	Ⓢ
B	Ⓟ	Ⓠ	Ⓡ	Ⓢ
C	Ⓟ	Ⓠ	Ⓡ	Ⓢ
D	Ⓟ	Ⓠ	Ⓡ	Ⓢ

7.

	p	q	r	s
A	Ⓟ	Ⓠ	Ⓡ	Ⓢ
B	Ⓟ	Ⓠ	Ⓡ	Ⓢ
C	Ⓟ	Ⓠ	Ⓡ	Ⓢ
D	Ⓟ	Ⓠ	Ⓡ	Ⓢ

Answerkey

A Single Correct Choice Type

1.	(c)	**11.**	(c)	**21.**	(c)	**31.**	(b)	**41.**	(d)	**51.**	(c)	**61.**	(d)
2.	(d)	**12.**	(b)	**22.**	(b)	**32.**	(b)	**42.**	(c)	**52.**	(d)	**62.**	(d)
3.	(d)	**13.**	(b)	**23.**	(c)	**33.**	(c)	**43.**	(c)	**53.**	(c)	**63.**	(c)
4.	(c)	**14.**	(c)	**24.**	(c)	**34.**	(c)	**44.**	(d)	**54.**	(b)	**64.**	(b)
5.	(c)	**15.**	(d)	**25.**	(d)	**35.**	(b)	**45.**	(d)	**55.**	(b)	**65.**	(b)
6.	(b)	**16.**	(c)	**26.**	(d)	**36.**	(d)	**46.**	(b)	**56.**	(b)	**66.**	(c)
7.	(a)	**17.**	(b)	**27.**	(c)	**37.**	(c)	**47.**	(d)	**57.**	(b)	**67.**	(c)
8.	(c)	**18.**	(b)	**28.**	(d)	**38.**	(b)	**48.**	(c)	**58.**	(c)		
9.	(b)	**19.**	(c)	**29.**	(c)	**39.**	(b)	**49.**	(c)	**59.**	(d)		
10.	(c)	**20.**	(b)	**30.**	(c)	**40.**	(c)	**50.**	(c)	**60.**	(d)		

B Comprehension Type

1	(a)	**7**	(a)	**13**	(c)	**19**	(c)	**25**	(d)	**31**	(d)
2	(d)	**8**	(b)	**14**	(d)	**20**	(c)	**26**	(b)	**32**	(c)
3	(c)	**9**	(d)	**15**	(b)	**21**	(b)	**27**	(a)	**33**	(d)
4	(b)	**10**	(b)	**16**	(b)	**22**	(b)	**28**	(d)		
5	(d)	**11**	(b)	**17**	(b)	**23**	(b)	**29**	(a)		
6	(b)	**12**	(d)	**18**	(d)	**24**	(a)	**30**	(c)		

C Reasoning Type

1	(a)	**4**	(a)	**7**	(a)	**10**	(c)	**13**	(d)	**16**	(d)
2	(a)	**5**	(c)	**8**	(c)	**11**	(d)	**14**	(a)	**17**	(d)
3	(a)	**6**	(c)	**9**	(a)	**12**	(b)	**15**	(d)	**18**	(a)

D Multiple Correct Choice Type

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

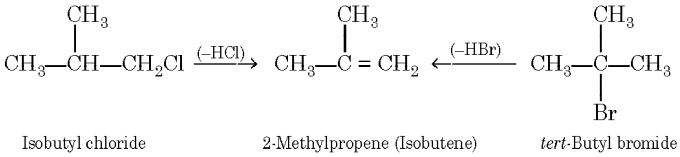
E Matrix-Match Type

1. **A-q, r; B-s; C-s; D-p, s**
2. **A-r; B-s; C-q; D-p, q, r**
3. **A-p, s; B-p, q; C-p, r; D-p**
4. **A-p, s; B-p, r; C-s; D-q, r**
5. **A-p, q, r, s; B-p, q, r, s; C-p; D-p**
6. **A-s; B-p, r; C-q, r; D-r**
7. **A-r; B-p, q; C-p, q; D-s**

Solutions

A SINGLE CORRECT CHOICE TYPE

1. **(c)**



Isobutyl chloride 2-Methylpropene (Isobutene) *tert*-Butyl bromide

2. **(d)** Hydration of alkenes to form alcohols and dehydration of alcohols to form alkenes are reversible.

$$RCH = CH_2 + H_2O \underset{(-H_2O)}{\overset{H^+}{\rightleftharpoons}} RCH_2CH_2OH$$

Low H_2O concentration and high temperature favour alkene formation because the volatile alkene distills out of the reaction mixture and shifts the equilibrium toward alkene. On the other hand, hydration of alkenes occurs at low temperature and with dil. acid which provides a high concentration of H_2O as reactant.

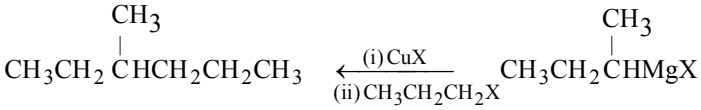
3. **(d)** Symmetrical alkenes give same product whether the addition of HBr takes place in absence or presence of a peroxide. Among the four options, only 2-butene is symmetrical.

4. **(c)** Performic acid causes hydroxylation of the double bond ; the two –OH groups add in *anti*-manner. Hence *cis*-isomer gives racemic mixture while the *trans*-isomer gives meso.

5. **(c)** Tollen's reagent is ammonical silver nitrate which reacts with 1-alkynes to form white percipitate of silver alkynide.

$$CH_3CH_2C \equiv CH + \underbrace{AgNO_3 + NH_4OH}_{} \rightarrow \underset{\text{white ppt.}}{CH_3CH_2C \equiv CAg \downarrow} + NH_4NO_3 + H_2O$$

6. **(b)** For getting good yields in Corey-House synthesis, the alkyl halide should be primary, while the alkyl halide used in the form of organometallic compound may be 1°, 2° or 3°.



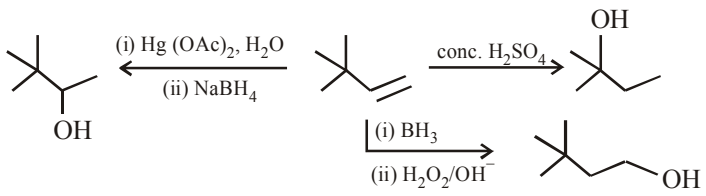
7. **(a)** More is the reactivity of a free radical, lesser is its selectivity for different type of H atoms (1°, 2°, or 3°) and hence the probability factor will be more in such reagent. Since $Cl^{\bullet}$ is more reactive, it is less selective and hence it will be more influenced by the probability factor.

8. **(c)** A conformation is defined as the relative arrangement of atoms or groups around a central atom, obtained by the free rotation of one part of the molecule with respect to rest of the molecule. For a complete rotation of 360°, one part may rotate through any degree say 0.1°, 0.5°, 1° etc. giving rise to infinite number of relative arrangements of group (atom) around a central atom, keeping other part fixed.

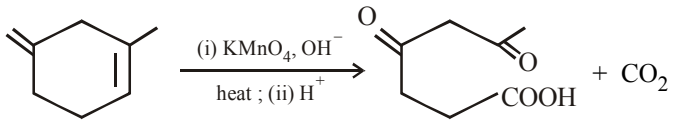
9. **(b)** $CH_3CH_2CH = CH_2$, $(CH_3)_2C = CH_2$, $CH_3CH = CHCH_3$ (*cis*- and *trans*-)

10. **(c)** The two stereoisomers which are not enantiomers are known as diastereomers.

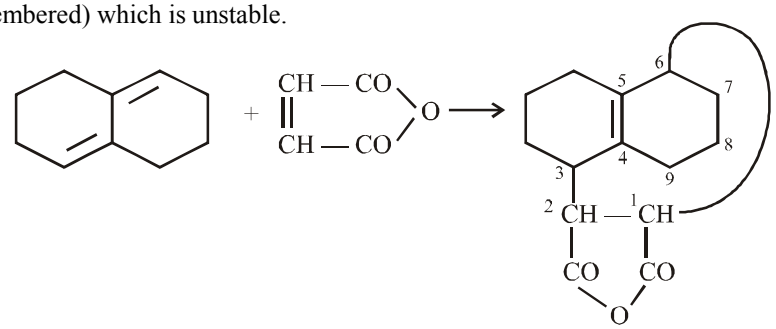
11. **(c)** Acid-catalyzed addition of water to the double bond gives Markovnikov's product with rearrangement. Oxymercuration-demercuration gives Markovnikov's product without rearrangement. Hydroboration-oxidation of an alkene gives *anti*-Markovnikov's product without rearrangement.



12. **(b)** Alkenes are oxidatively cleaved by hot alk. $KMnO_4$ in the following way. The terminal CH_2 group (= CH_2) is completely oxidised to CO_2 and H_2O ; a monosubstituted atom of a double bond is converted to aldehyde which is further oxidised to carboxylic acid, and the disubstituted atom of a double bond is oxidised to ketone.



13. **(b)** It is an example of Diel's-Alder reaction in which a dienophile (maleic anhydride, here) reacts with a conjugated diene to form cyclic adduct. Here although structures (i), (iii) and (iv) have conjugated system of double bonds, hence theoretically all the three can undergo Diel's-Alder reaction, but structure (iii) does not undergo this reaction because this will lead to larger ring (9-membered) which is unstable.



14. **(c)** $CH_3CH_2CH_2CHO \xleftarrow[(ii)\,H_2O_2/OH^-]{(i)\,BH_3} CH_3CH_2C\equiv CH \xrightarrow{H^+/Hg^{2+}} CH_3CH_2COCH_3$

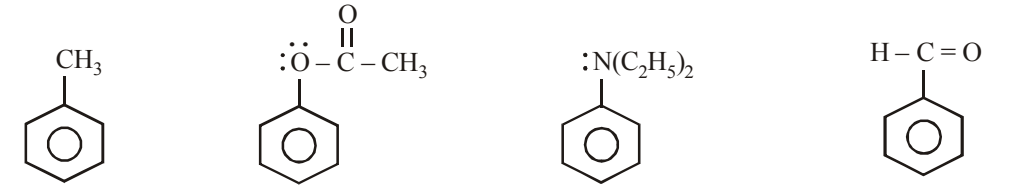
(an aldehyde) (A ketone with $-COCH_3$ group)

15. **(d)** Vinyl and aryl halides can't be used as the halide component because they do not form carbocations readily ; $-NH_2$, $-NHR$ and $-NR_2$ groups react with Lewis acids used in Friedal-Craft reaction to form electron-withdrawing groups, which deactivate the benzene nucleus for electrophilic substitution.

$\overset{+}{-NH_2}AlCl_3^-$ is electron-withdrawing

On the same reason, presence of electron-withdrawing group like $-NO_2$, $-\overset{+}{N}H_3$, $-CF_3$, $-$ COOH, $-$COR, $-SO_3H$ etc. make the benzene ring less prone to Friedel-Craft reaction.

16. **(c)**



Activating due to +I and hyperconjugation (weak effects)

Electron pair on O delocalised to C = O hence moderate activating group

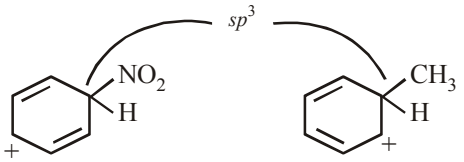
Electron pair on N causes +M effect (a powerful effect) **(Most activating)**

Deactivating group

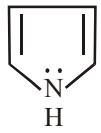
17. **(b)** $-CH_2Cl$ may be weakly activating group due to hyperconjugative effect, but the strong electron-withdrawing nature of $-$Cl makes it weakly deactivating.

18. **(b)** All the three compounds have same electron-releasing groups, but the presence of two such groups in II and III make them more reactive than I. Further note that in *m*-xylene (II), the two methyl groups cooperate each other at two positions, while in III no position is activated by both the groups.

19. **(c)** An aromatic compound have cyclic clouds of delocalised $(4n+2)\ \pi$ electrons above and below the plane of the molecule. Among the given three compounds, only compound (*c*) satisfies these conditions.

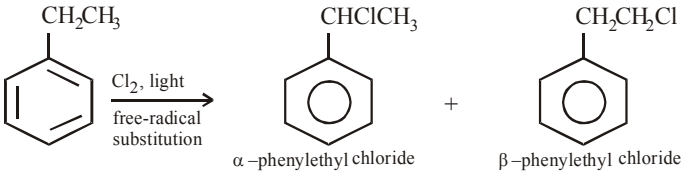


Carbon bearing $-NO_2$ (or $-CH_3$) group is sp^3 hybridised and does not have a *p* orbital with the result delocalisation of π electrons over the complete ring is interrupted.



4π electrons and 2 non-bonding electrons (present in *p* orbital of N) form a cyclic cloud of 6π electrons

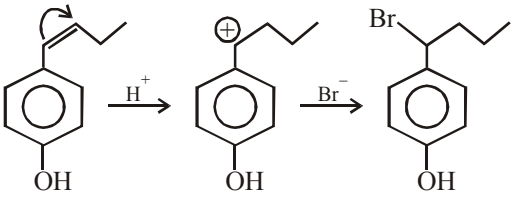
20. **(b)**



α –phenylethyl chloride **(major)** + β –phenylethyl chloride **(minor)**

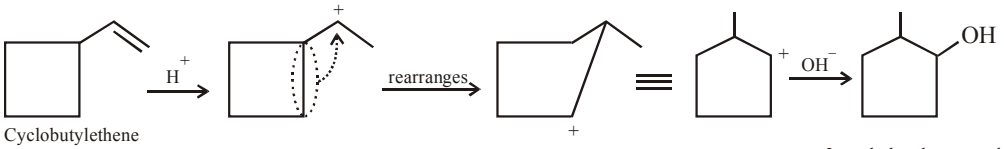
21. **(c)** When non-terminal alkynes are heated with $NaNH_2$ in an inert solvent, the triple bond migrates to the end carbon atom.

22. **(b)**



Benzyl cabocation (more stable)

23. **(c)**



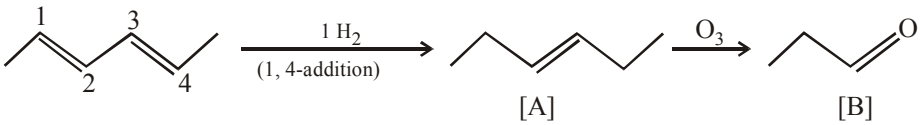
Cyclobutylethene — 5–membered 2° carbocation (more stable) — 2-methylcyclopentanol

24. **(c)** When acid anhydride is used, more amount of $AlCl_3$ is required because one mole of the catalyst ($AlCl_3$) is used up in liberating acyl halide which is the actual acylating reagent.

$$(CH_3CO)_2O + AlCl_3 \rightarrow CH_3COCl + CH_3COOAlCl_2$$

$$C_6H_6 + CH_3COCl \xrightarrow{AlCl_3} C_6H_5\overset{\overset{+}{}}{\underset{\underset{CH_3}{|}}{C}}OAl\bar{C}l_3 \xrightarrow[\text{dil. } H^+]{\text{ice cold}} C_6H_5COCH_3 + AlCl_3$$

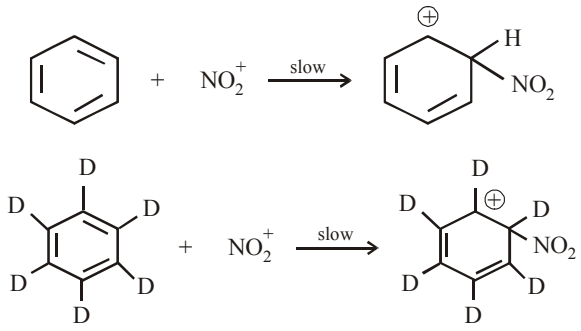
25. **(d)** Conjugated dienes add H_2 in 1, 4 -addition



[A] [B]

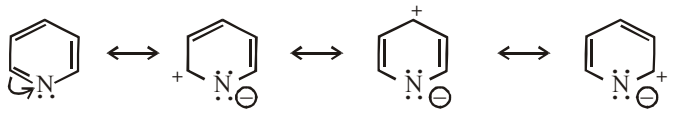
26. **(d)** Presence of electron-withdrawing substituent (e.g. C = O, –COOH, –COOR, –CN, etc.) deactivates the carbon-carbon double bond towards electrophilic addition.

27. **(c)** Electrophilic substitution in benzene is a two step reaction in which slow step (first step) is common in both reactions as it does not involve the breaking of C – H or C – D bond.

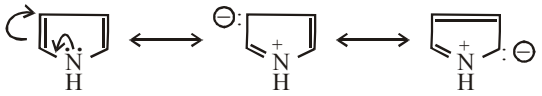


Had the rate determining step (slow step) involved the cleavage of C – H or C – D bond, nitration of benzene would have been faster than that of hexadeuterated benzene.

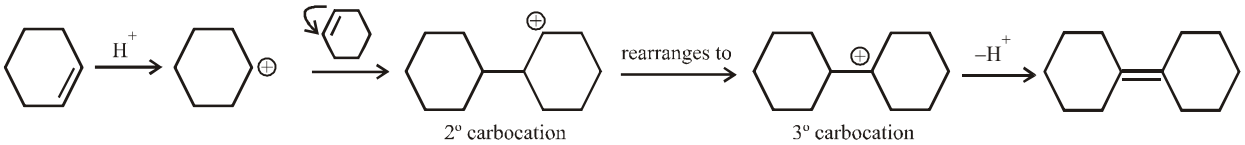
28. **(d)** Pyridine contains a doubly bonded N, so here N attracts electrons from the ring making the ring electron deficient.



On the other hand, in pyrrole N supplies electron to the ring rather than attracting electrons from the ring.



29. **(c)**



30. **(c)** Here hydration occurs in *anti*-Markovnikov's way because of electron-withdrawing nature of –COOH which destabilises carbocation I more than the II.

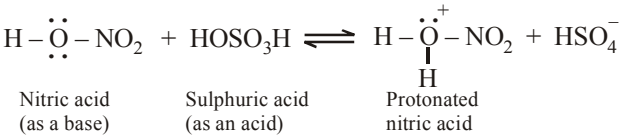
$$HC \equiv C - COOH \xrightarrow{H^+} \underset{\text{I (+ve charge more intensified)}}{H_2C = \overset{+}{C} \rightarrow COOH} \quad \text{or} \quad \underset{\text{II (+ve charge less intensified) More stable}}{\overset{+}{H}C = CH \rightarrow COOH}$$

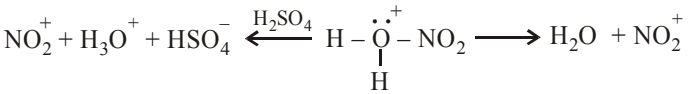
$$\underset{\text{II}}{\overset{+}{H}C = CH - COOH} \xrightarrow{OH^-} \underset{OH}{HC = CH - COOH} \rightleftharpoons OHC - CH_2 - COOH$$

31. **(b)** Attack of electrophile on benzene ring (step 2) is the slow step.

32. **(b)** Step 1 involves the conversion of sp^2 carbon to sp^3 carbon (carbon having electrophile E) while step 2 involves the conversion of sp^3 carbon to sp^2 carbon.

33. **(c)**



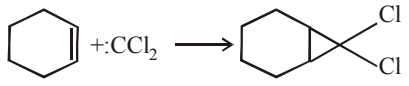


34. **(c)** Since cyclohexene is soluble in chloroform and not in water, while NaOH is soluble in water but not in $CHCl_3$, the three reagents can't interact each other because these are present in different layers (chloroform and aqueous layers). The tetrabutylammonium chloride acts as a phase-transfer catalyst in the following way.

$$\underset{\text{Ion pair}}{Bu_4N^+Cl^-} + NaOH \longrightarrow Bu_4N^+OH^- + Na^+Cl^-$$

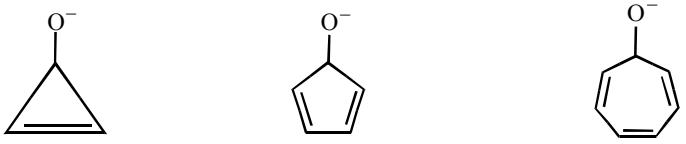
The ion pair has large alkyl groups, so it becomes soluble in organic solvent and hence migrates to chloroform layer where it reacts with $CHCl_3$ and cyclohexene to form the final product.

$$\underset{\text{Ion pair}\ (\text{soluble in } CHCl_3)}{Bu_4N^+OH^-} + CHCl_3 \longrightarrow Bu_4N^+CCl_3 + H_2O$$
$$\hookrightarrow Bu_4N^+\bar{C}l + :CCl_2$$



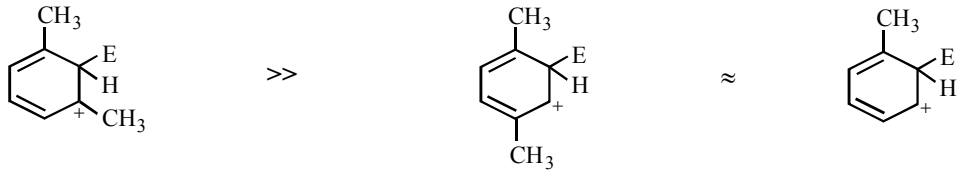
Cyclohexene
(present in $CHCl_3$ layer)

35. (b) Draw the resonating structure due to C = O group only and observe the stability



2π electrons (aromatic) | 4π electrons (antiaromatic) (least stable) | 6π electrons (aromatic)

36. (d) The intermediate σ complex II is much more stable than III which is equally stable to I.



II
Two resonating structures are 3° carbocation (**most stable**)

III
Only one resonating structure is 3° carbocation

I
Only one resonating is 3° carbocation

37. (c) Addition of $\dot{Br}$ is a reversible reaction to give alkene back, while allylic bromination leads to resonance stabilized allylic radical which does not allow the reaction to go backward.

38. (b) Here Cl^+ can not be produced.

39. (b) Four chlorine decreases electron density around C = C double bond which can't polarise Cl_2 to form Cl^+. Addition of $AlCl_3$ produces Cl^+ in the following way.

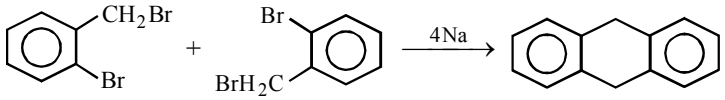
$$AlCl_3 + Cl_2 \longrightarrow AlCl_4^- + Cl^+$$

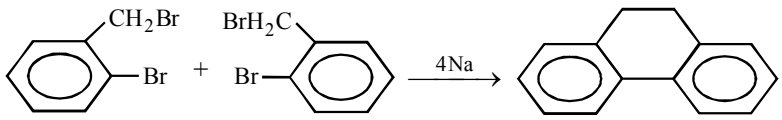
40. (c) It is an example of Diel's-Alder reaction, and the reagent (conjugated diene) should be 1,3-butadiene.

41. (d) Since the starting compound is fumaric acid (a *trans*-isomer), *trans*- product will be formed.

42. (c) Isolated carbon-carbon double bonds are not normally reduced during Birch reduction because formation of the intermediate electron addition products requires more energy.

43. (c)





44. (d) Formation of only CH_3COOH by ozonolysis indicates that the compound Y should be $CH_3CH = CHCH_3$ which can be formed by all of the three given compounds

$$\underset{X}{CH_2 = CH - CH = CH_2} \xrightarrow{1H_2/Pt} \underset{Y}{CH_3CH = CHCH_3} \xleftarrow{1H_2/Pt} \underset{X}{CH_3C \equiv CCH_3}$$

$$\underset{X}{CH_2 = C = CHCH_3} \xrightarrow{1H_2/Pt} \underset{Y}{CH_3CH = CHCH_3} \xrightarrow{O_3} 2CH_3COOH$$

45. **(d)** Compound in which all hydrogen atoms are equivalent will form one monochloro derivative, which is (*d*) here

(a) $CH_3(CH_2)_6CH_3$ (b) $(CH_3)_2CHCH_2(CH_2)_3CH_3$

(c) $CH_3C(CH_3)_2CH_2CH(CH_3)CH_3$ (d) $CH_3-C(CH_3)_2-C(CH_3)_2-CH_3$

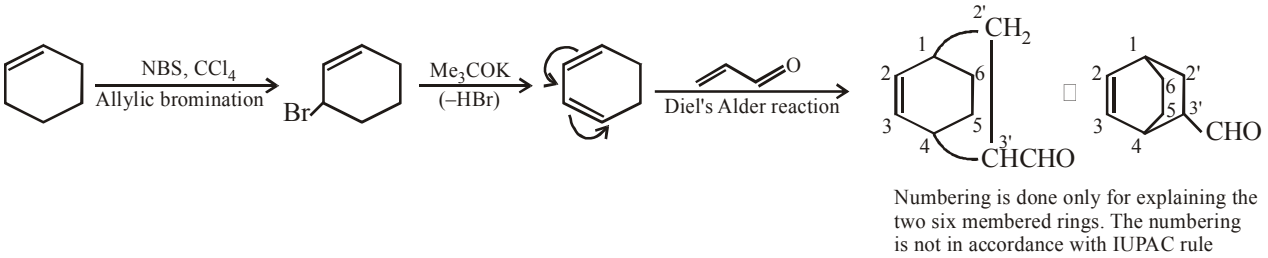
46. **(b)** The reaction may be considered as a modification of Wurtz reaction.

$$(C_6H_5)_2CCl_2 + Cl_2C(C_6H_5)_2 \xrightarrow{Cu} (C_6H_5)_2C=C(C_6H_5)_2$$

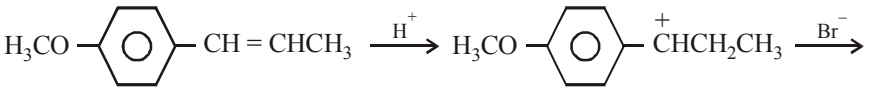
47. **(d)** $C_6H_5CHCl_2 \xrightarrow{Me_3COK} C_6H_5\ddot{C}Cl + HCl$

A carbene

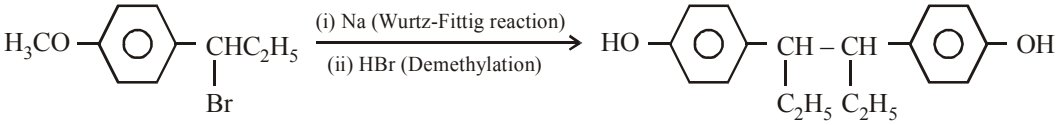
$$C_6H_5C\equiv CC_6H_5 \xrightarrow{C_6H_5\ddot{C}Cl} C_6H_5C=C(C_6H_5)(Cl)$$

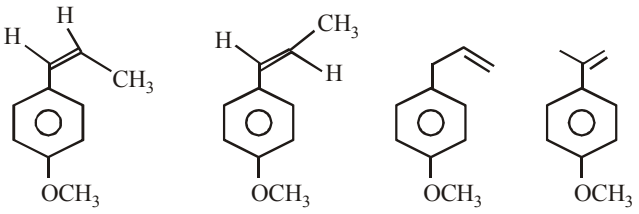
48. **(c)** 

Numbering is done only for explaining the two six membered rings. The numbering is not in accordance with IUPAC rule

49. **(c)** 

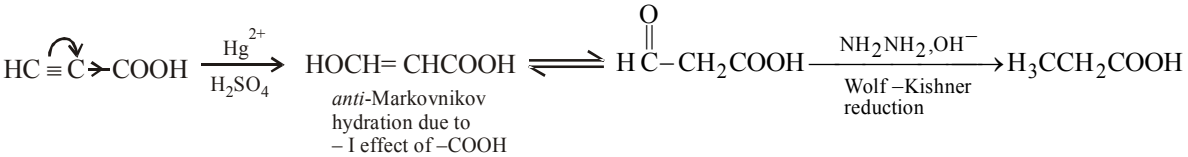
Benzylic carbocation



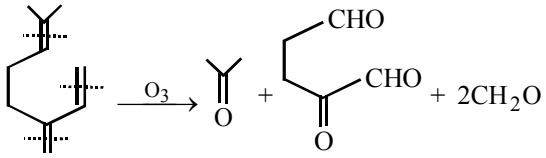
50. **(c)** 

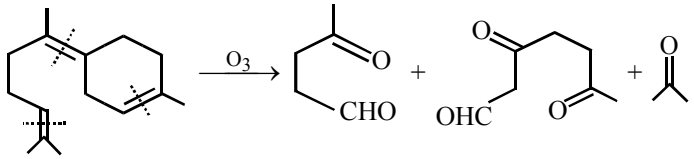
cis - *trans* -

51. **(c)** Recall that in III, key atom is *tert*-carbon, so it can't be oxidised.

52. **(d)** 

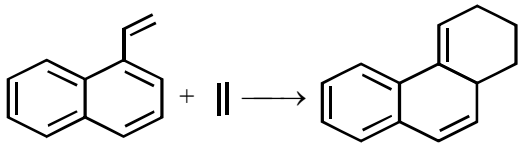
53. **(c)** This is an example of **Ullmann reaction.**

54. **(b)** 

55. **(b)** 

56. **(b)** In presence of $NH_4^+Cl^-$, NBS undergoes addition reaction instead of usual allylic bromination.

57. **(b)** This is an example of Diels – Alder reaction, here ethylene acts as dienophile.



58. **(c)** Here D^+ from D_2SO_4 acts as an electrophile.

B COMPREHENSION TYPE

1. **(a)** In chain-propagating steps, a reactive intermediate is converted into different reactive intermediate.

2. **(d)** $^\bullet Cl + {}^\bullet Cl \longrightarrow Cl_2$ $\qquad$ $^\bullet CH_3 + {}^\bullet Cl \longrightarrow CH_3 - Cl$ $\qquad$ $^\bullet CH_3 + {}^\bullet CH_3 \longrightarrow CH_3 - CH_3$

3. **(c)** The chain-initiating step $(Cl - Cl \longrightarrow 2\,{}^\bullet Cl)$ is highly endothermic (DH = + 58 kcal/mol) and therefore requires high temperatures.

4. **(b)** Oxygen reacts with the methyl radical to form new radical $(CH_3OO^\bullet)$ which is *markedly less reactive*

$$^\bullet CH_3 + O - O \longrightarrow CH_3 - O - O^\bullet$$

than $^\bullet CH_3$ and therefore drastically slows down the chain reaction.

C REASONING TYPE

5. **(c)** Here assertion is correct but reasoning is incorect. In presence of peroxide, addition of HBr on alkenes takes place via free radicals; here two free radical are formed, *2° free radical, being more stable, governs the product.*

$$\underset{\substack{1^\circ \text{ free radical}\\(\text{less stable})}}{CH_3CH_2CHBr\dot{C}H_2} \xleftarrow{Br^\bullet} CH_3CH_2CH = CH_2 \xrightarrow{Br^\bullet} \underset{\substack{2^\circ \text{ free radical}\\(\text{more stable})}}{CH_3CH_2\dot{C}HCH_2Br}$$

6. **(c)** **Correct R :** CH_3CO group in acetophenone being electron-withdrawing reduces the electron density in the benzene ring, thereby preventing further electrophilic substitution.

8. **(c)** Alkyl halides give polyalkylation products.

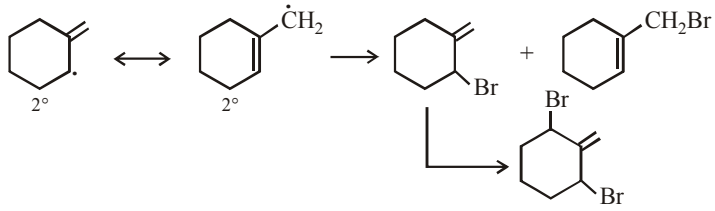
11. **(d)** Assertion is false, explanation is although true but it is not correct explanation of assertion.

12. **(b)** Assertion is true, explanation is true but it is not correct explanation of the assertion.

D MULTIPLE CORRECT CHOICE TYPE

1. **(a,d)** The three alkenes have similar heat of hydrogenation because the alkanes formed have similar energies. The branched alkane is more stable, greater the branching in an alkane, more is its stability.

2. **(a,b,c)**



3. **(a,b,c,d)** All the four reagents can cause allylic substitution.

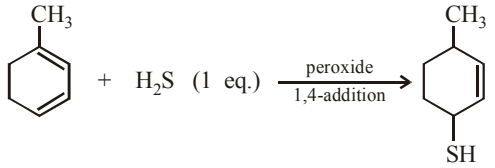
4. **(b,c)** $CH_2 = \underset{|}{\overset{CH_3}{C}} - CH_3 (II) > CH_2 = CH - CH_3 (I) > CH_2 = CH_2 (III)$

Intermediate $\underset{3^\circ \text{ carbocation}}{CH_3 - \overset{CH_3}{\overset{|}{\overset{+}{C}}} - CH_3} > \underset{2^\circ \text{ carbocation}}{CH_3 - \overset{+}{C}H - CH_3} > \underset{1^\circ \text{ carbocation}}{CH_3 - \overset{+}{C}H_2}$

5. **(b,c)** Stability of the carbocation formed follows the order

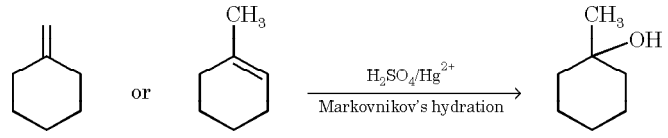
$\underset{\text{from I}}{BrCH_2 - \overset{+}{C}H_2} > \underset{\text{from II}}{BrCH = \overset{+}{C}H} > \underset{\text{from III}}{\overset{+}{C}H_2 - CH(Cl)Br}$

7. **(a,c,d)**



Other products are not formed.

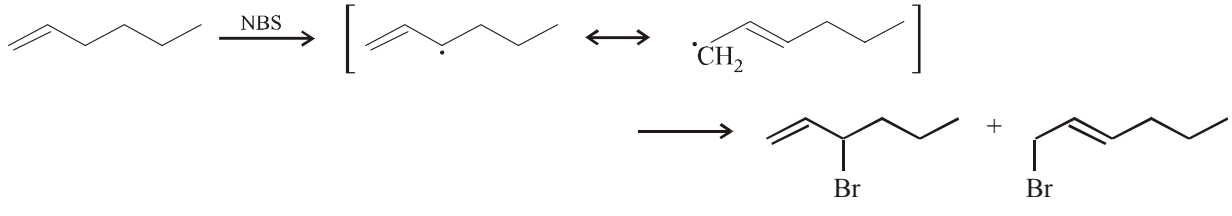
9. **(a,b)**



10. **(b,d)** The more stable product is the thermodynamically controlled product at high temperature, while (A) the more stable carbocation is major intermediate at low temperature (kinetic controlled).

11. **(a,b,c,d)** All of the four involve allylic carbocation.

12. **(a,b,c)**



cis- and *trans*-

E MATRIX-MATCH TYPE

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

(A) $CH_3\overset{+}{C}H_2CH_2CHCH_3 \xleftarrow{H^+} CH_3CH_2CH=CHCH_3 \xrightarrow{H^+} CH_3CH_2\overset{+}{C}HCH_2CH_3$

(Five hyperconjugative structures)

Highly favoured due to inductive of ethyl group (4 hyperconjugative structures)

$\xrightarrow{Cl^-}$ $CH_3CH_2CH_2\underset{Cl}{\underset{|}{C}}HCH_3$

$\xrightarrow{Cl^-}$ $CH_3CH_2\underset{Cl}{\underset{|}{C}}HCH_2CH_3$

(B) $CH_2=CH-CH=CH_2 \xrightarrow{H} \left[CH_3\overset{+}{C}HCH \quad CH_2 \longrightarrow CH_3CH \quad \overset{+}{C}HCH_2\right]$

2 Carbocation, stable due to resonance

$\xrightarrow{Cl^-}$ $CH_3\underset{Cl}{\underset{|}{C}}HCH \quad CH_2$ (1, 2 – addition)

$CH_3CH \quad \underset{Cl}{\underset{|}{C}}HCH_2$ (1, 4 – addition)

(C) $\bigcirc\!\!-CH \quad CHCH_3 \quad H \longrightarrow \bigcirc\!\!-\overset{+}{C}HCH_2CH_3 \xrightarrow{Br^-} \bigcirc\!\!-\underset{Br}{\underset{|}{C}}HCH_2CH_3$

Highly stable benzyl carbocation

(D) $\bigcirc\!\!-CH_2CH=CH_2 + H^+ \longrightarrow \bigcirc\!\!-CH_2\overset{+}{C}HCH_3 \xrightarrow[\text{hydride shift}]{1,2-}$

2° carbocation

$\bigcirc\!\!-CH\overset{+}{C}HCH_2CH_3 \xrightarrow{Br^-} \bigcirc\!\!-\underset{Br}{\underset{|}{C}}HCH_2CH_3$

More stable benzyl carbocation

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

. (A) The electron-withdrawing group (–C ≡ N) is in conjugation with the carbon-carbon double bond, hence the intermediate carbanion, formed by the attack of nucleophile, stabilizes due to resonance. Hence such alkenes undergo nucleophilic addition reactions.

(B) Vinyl monomers when heated in presence of catalyst undergo free radical polymerisation.

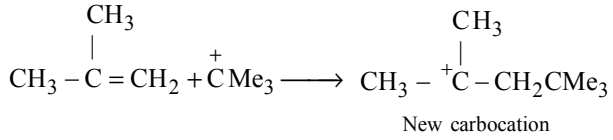
(C) Acyl halides, typically, undergo nucleophilic substitution. This is due to the fact that – Cl is a good leaving group.

(D) The given compound has 1° alkyl halide, hence undergoes S_{N^2} reaction involving transition state with pentavalent carbon.

Further the presence of – $CH_2CH = CN$ grouping causes the compound to undergo nucleophilic addition.

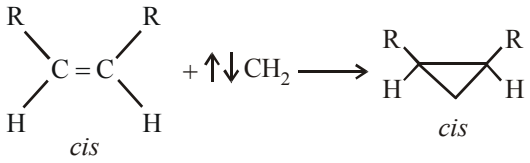
3. A-p, s; B-p, q; C-p, r; D-p

. (A) Carbocations add on alkenes and also undergo rearrangement by 1, 2 -shift



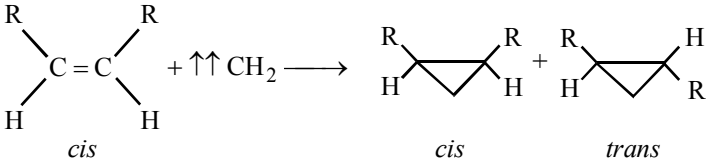
New carbocation

(B,D)Carbenes add on alkenes to form cyclopropane derivatives. Singlet carbenes (both electrons in one orbital) add to alkenes in a stereospecific manner, i.e. stereochemistry of the alkene is retained.



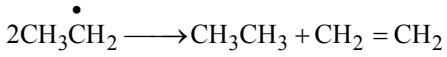
cis *cis*

Conversely, the triplet carbenes (two electrons are present in different orbitals) add on alkenes non-stereospecifically with the result both products are formed.



cis *cis* *trans*

(C) Free radicals add on alkenes to form new free radical e.g. polymerisation of ethylene. Further, disproportionation is one of the characteristic reactions of free radicals



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