Table for Ortho Meta and Para directing group:

Substituent	Character relative to H	Activating / deactivating	Directing
-O^-	Electron donating	Strongly activate	Ortho/para
-NR_2		Strongly activate	Ortho/para
-NH_2		Strongly activate	Ortho/para
-OH		Strongly activate	Ortho/para
-OR		Strongly activate	Ortho/para
-NHC(O)R		Moderately activate	Ortho/para
-OC(O)R		Moderately activate	Ortho/para
-R		Weakly activate	Ortho/para
-Ph		Weakly activate	Ortho/para
-$CH{=}CR_2$		Weakly activate	Ortho/para
-H	Reference	Neutral	Ortho/para
-X(X=halo)	Electron withdrawing	Weakly activate	Ortho/para
-C(O)H		Moderately activate	Meta
-C(O)R		Moderately activate	Meta
-C(O)OR		Moderately activate	Meta
-C(O)OH		Moderately activate	Meta
-CF_3		Strongly deactivate	Meta
-CN		Strongly deactivate	Meta

Solved Examples

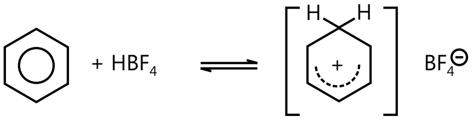
JEE Main/Boards

Example 1: Benzene, toluene, xylene, (o,m,p) and mesitylene dissolve in HBF_4 to from salts. Explain the order of basicity:

Sol: The more stable the σ-complex greater would be the basicity.

Mesitylene>m-Xylene>o-and p-Xylene>

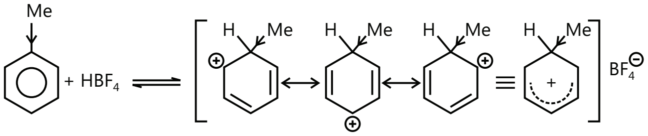
Toluene> Benzene



σ-Complex

Since the reaction is reversible; as more stable the σ-complex more will be the equilibrium on the right, i.e., the more basic is the arene.

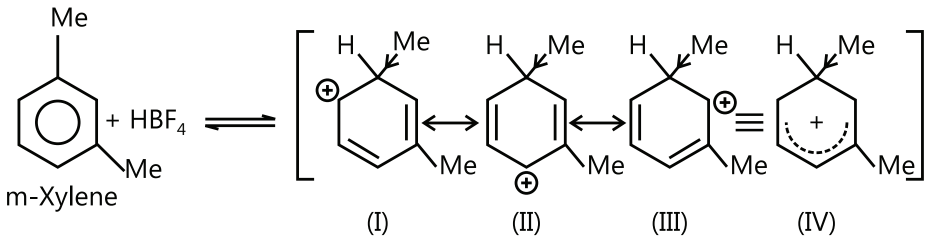
As the number of electron donating group increases more stable is the complex, and more basic is the compound.

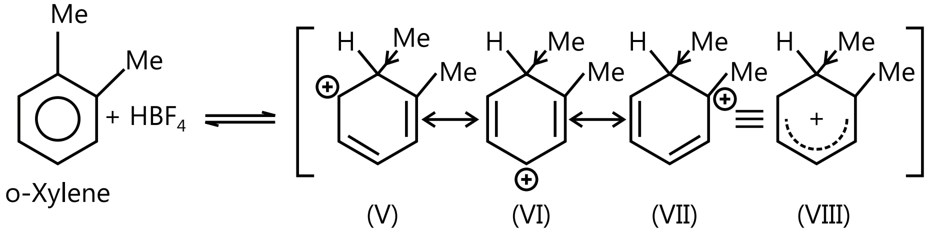


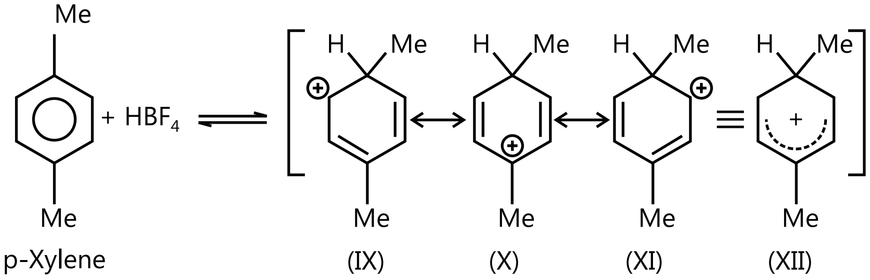
Because of + I effect of (Me), the positive charge is partially neutralized and (Me) group acquires+ δ charge i.e., there is charge spreading which increases the stability of the σ-complex and thus increases the basic character of toluene w.r.t. benzene.

Mesitylene has three (Me) groups. So it must be the strongest base accordingly.

Resonating structures of m-, o-, and p-xylenes are.

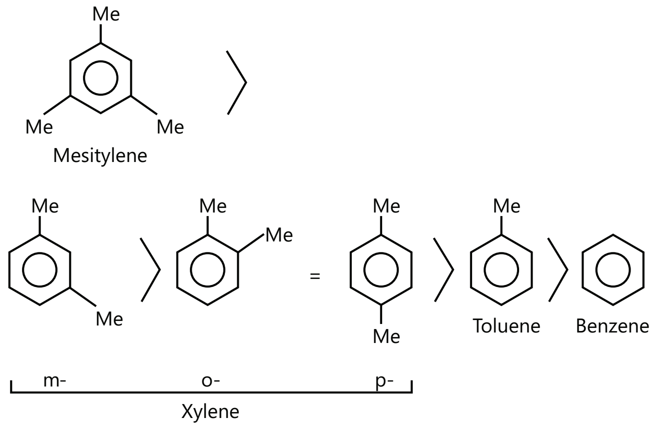






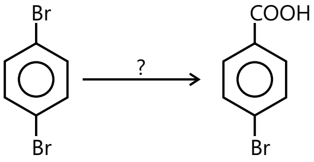
In o-and p-xylenes, the resonance-contributing structures (VII) and (X) are slightly less stable than other resonating structures.

So one can conclude that resonating structures of m-xylene are more stable than o-and p-xylenes, which increases the basic character of m-xylene than o-and p-xylenes. So the order of basic character is:

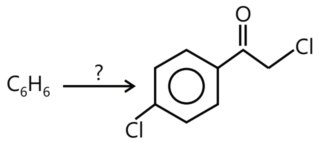


Example 2:

(A)

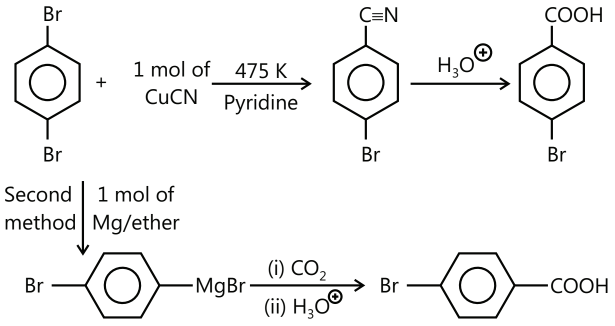


(B)

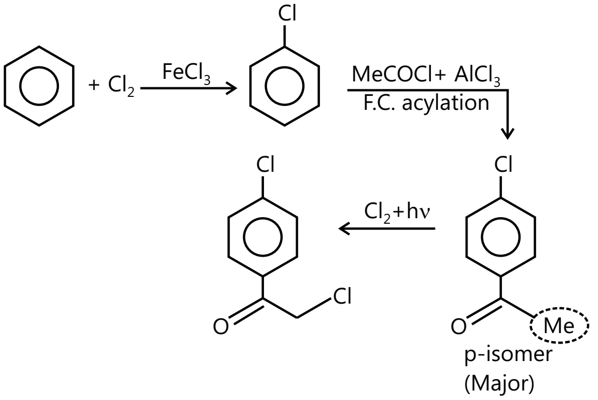


Sol: Generally Aryl halides are less reactive towards Nucleophilic substitution reaction. However when a strong Electron withdrawing group are present in o-or/ and p-positions they undergo such reaction.

(A) (-Br) can be replaced by (-CN) group under high pressure and at high-temperature conditions (Dow's process).



(B) This involves friedal craft acylation of chlorobenzene. Chloro groups directs acyl group at para position which on chlorination in presence of light gives the product.



Example 3: The treatment of RX with aqueous KOH leads to the formation of alcohols but in the presence of alcoholic KOH or NaOH, Alkenes are the major products. Explain why.

Sol: NaOH or KOH is completely ionised in aqueous solution to give OH^- ions, which acts as a strong nucleophile, so SN reaction takes place with RX to give alcohols.

Moreover OH^- ions are hydrated or solvated in aqueous solution which reduces the basic character of OH^- that cannot abstract acidic $\beta-H$ atom of RX to form alkene.

In case of alcoholic solution of NaOH or KOH, OH^- reacts with ROH to form RO^{Θ} (alkoxide ion) which is a stronger base than OH^-, and RO^{Θ} can abstract acidic $\beta-H$ atom of RX easily to form alkanes.

Example 4: CHF_3 is less acidic than $CHCl_3$.Explain.

Sol: By considering the stability of conjugate base, acidity of the two species can be explained.

Negative inductive effect of F> Cl. According to –I effect, CHF_3 should be more acidic than $CHCl_3$. But this is not observed.

The reason is the stability of conjugate base.

The conjugate base $-CCl_3$ is resonance stabilized due to the presence of d-orbital in Cl [2p(C) -3d(Cl)] overlap.

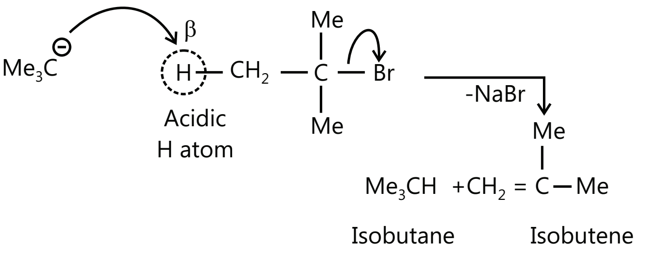
Conjugate base $\overset{\Theta}{C}F_3$ is not resonance stabilized due to the absence of d-orbitals in F.

Example 5: Wurtz reaction in case of tert-alkyl halide fails. Explian.

Sol: $Me_3C-X+2Na \rightarrow \underset{\text{t–Butylsodium}}{Me_3\overset{\Theta}{C}-\overset{\oplus}{Na}}+NaX$

t-Alkyl halides undergo dehydrohalogenation in the presence of strong base such as Na metal rather than Wurtz reaction.

Therefore, 1° and 2° RX undergo Wurtz reaction, while 3° RX undergo dehydrohalogenation to give alkenes.



Example 6: Give the decreasing order of ArSN reaction in:

(A) PhCl

(B) $p-NO_2-C_6H_4-Cl$

(C) 2, 4, 6-Trinitro Chlorobenzene

(D) 2, 4-Dinitro Chlorobenzene

Sol: ArSN reactions are favored by Electron withdrawing group at o-and p-positions; more the EWG presents at these positions, faster is the ArSN reaction.

The decreasing order of ArSN reaction:

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

(C) $\Rightarrow$ Three (N_2) groups at o-and p-,

(D) $\Rightarrow$ Two NO_2, groups at o-and p-,

(B) $\Rightarrow$ One (NO_2) group at p-,

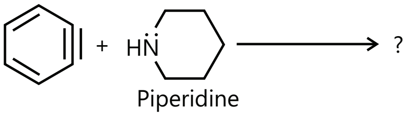
(A) $\Rightarrow$ (Cl) group.

Example 7: Distinguish between the following compounds:

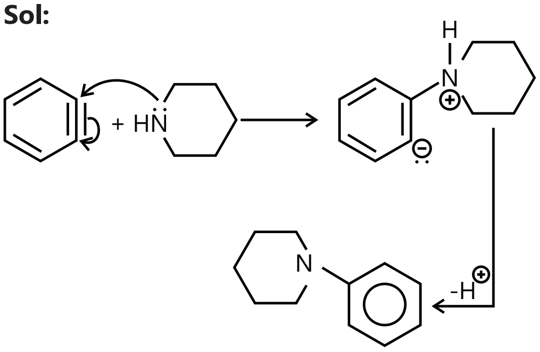
(I) m-Iodotoluene and (II) Benzyl iodide,

Sol: (II) Gives a yellow precipitate of AgI with $AgNO_3$, whereas (I) Does not.

Example 8:

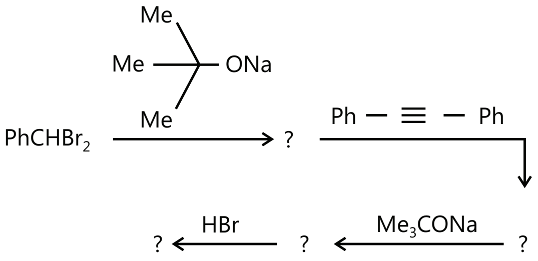


Sol:

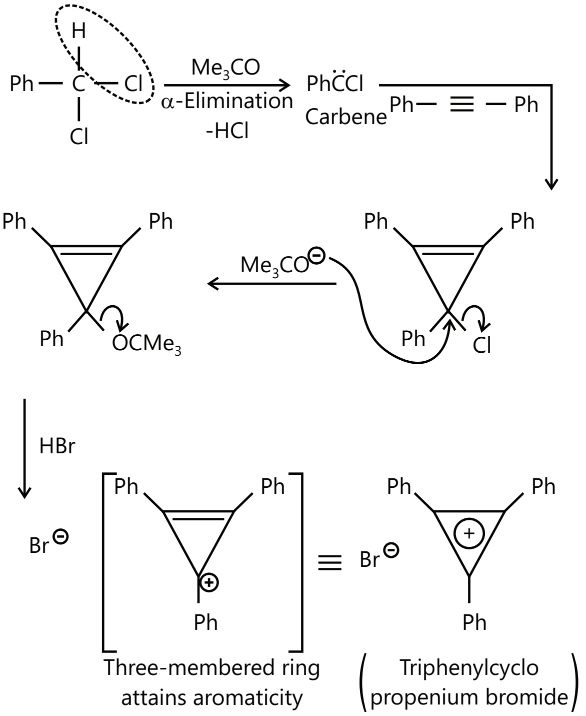


JEE Advanced/Boards

Example 1:

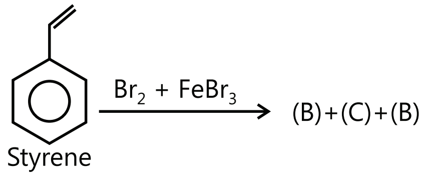


Sol:

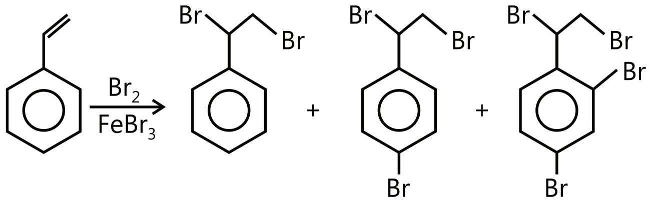


The absence of $\beta - H$ atom suggests α-elimination via the formation of carbine intermediate which forms ring with $(C \equiv C)$

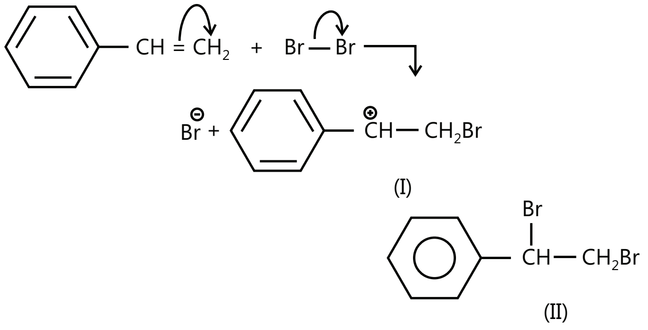
Example 2:



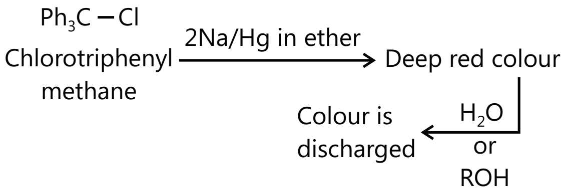
Sol:



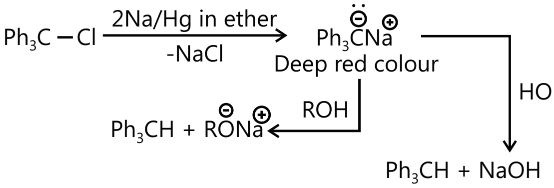
Since the benezene ring does not contain any EDG (activiting group) and vinyl $(-C=CH_2)$ group is a weakly activating (and o, p-directing), SE reaction with Br^- is very slow. Hence, Br_2 first adds to the double bond to form major contributing stable structure (I) (due to the retention of aromaticity), leading to the product (II).



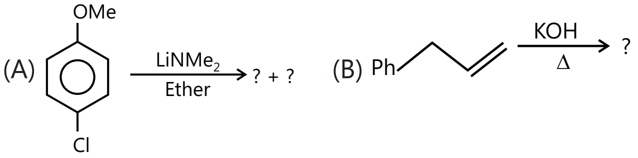
Example 3:



Sol: Strong reducing agent, such as Na/Hg amalgam, converts Ph_3C-Cl to the sodium salt, very stable Ph_3C^{Θ} (triphenyl methyl or trityl anion) because of delocalisation of negative charge to three Ph rings. The strongly basic carbanion accepts H^+ from either weakly acidic H_2O or ROH giving colorless Ph_3CH.



Example 4:



Sol: It is an example of ArSN (elimination-addition) reaction via benzyne intermediate, since strong Electron withdrawing group o or/and p-to the eliminating group is not present. Thus, ArSN (addition-elimination) is not possible.

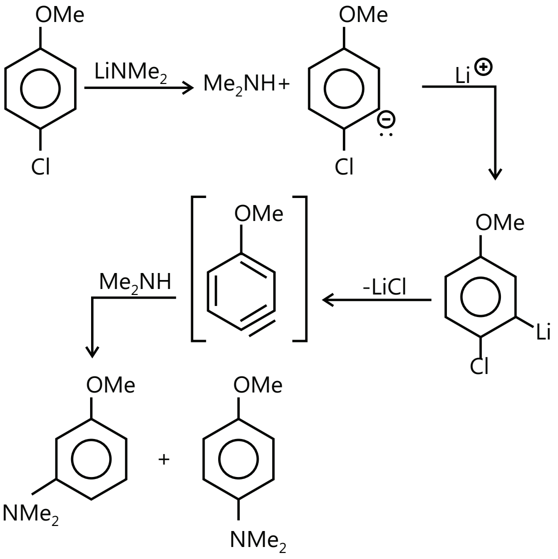
$\left(:\overset{\Theta}{N}Me_2\right)$ Group in ($LiNMe_2$) acts as a base to remove ortho-H atom to the eliminating group.

Since the rearranged product has increased conjugation with the ring, it is a thermodynamically controlled product (T.C.P) and is the result of an equilibrium-controlled Reaction.

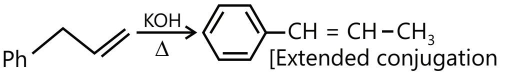
Hence, the starting material is the kinetically controlled product (K.C.P).

The conversion of K.C.P. to T.C.P is due to the removal of α -H atom by base, and α -H atom is acidic due to the -I effect of (Ph-) group.

(A)

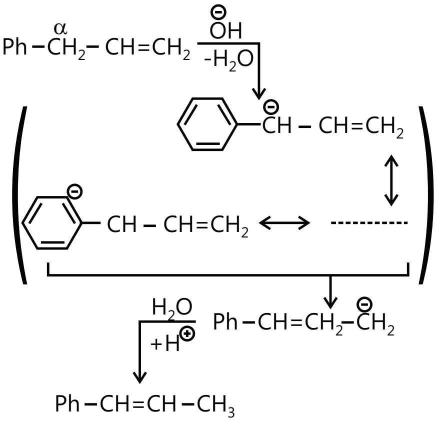


(B)

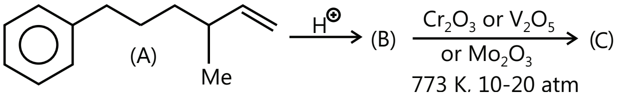


[Extended conjugation with (C=C) of (Ph-) group]

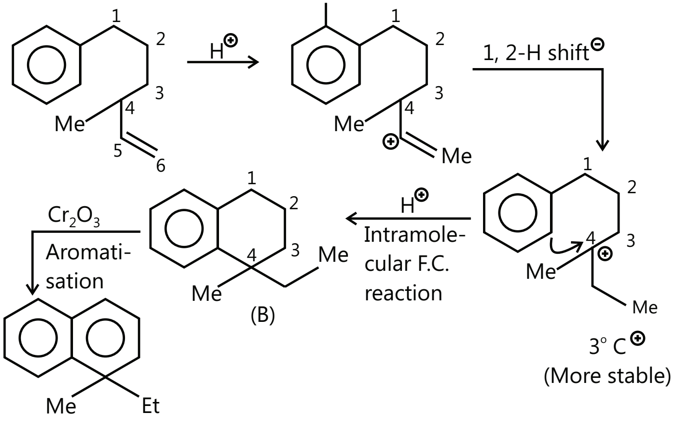
Steps involved are:



Example 5:

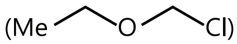


Sol:



1-Ethyl-1-methyl naphthalene (C)

Example 6: (A) Account of the rapid of ethanolysis of

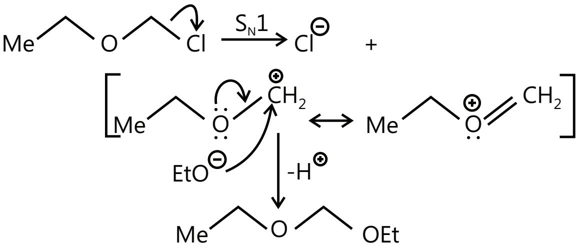


Although is 1° halide.

Sol: (A) This is due to the stability of carbocation bonded to by resonance.

The NO_2 is an ambident nucleophile (two nucleophilic centers N and O).

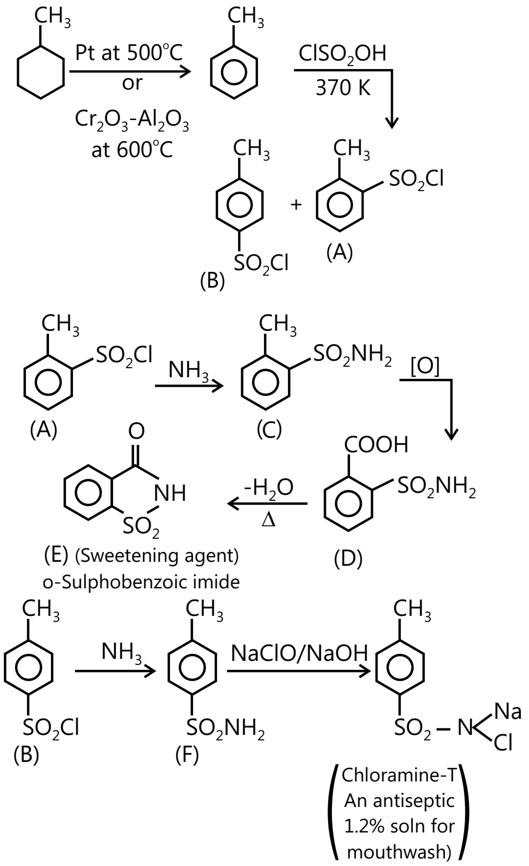
More is the positive charge on the carbocation formed, it will attack at the more electronegative (EN) nucleophilic center and vice versa. (Since EN of O>N)

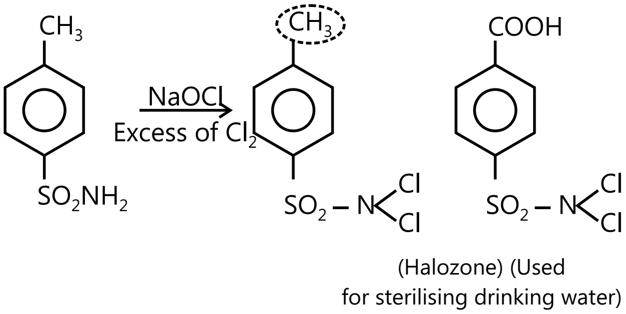


Example 7: Catalytic dehydrogenation of methyl cyclohexane, obtained from petroleum, gives a liquid which on treatment with chlorosulphonic acid at 370 K yields a mixture of two isomers (A) and (B), $C_7H_7SO_2Cl$. The major isomer (A) reacts with ammonia to form (C), which on oxidation with permanganate gives compound (D). On heating, compound (D) gives a well-known sweetening (E). The minor isomer (B) also reacts with ammonia to give

a compound (F) which on treatment with NaClO/NaOH gives an antiseptic (G): Identify (A) to (G).

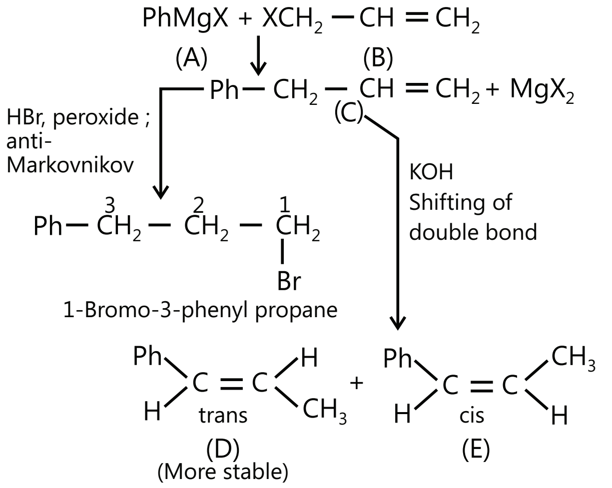
Sol:





Example 8: A Grignard reagent (A) and a halo alkene (B) react together to give (C). compound (C) on heating with KOH yields a mixture of two geometrical isomers. (D) And (E), of which (D) predominates. (C) Gives 1-bromo-3-phenyl propane on reaction with HBr in the presence of a peroxide. Give the structure of (A), (B), and (C) and the configurations of (D) and (E).

Sol:



JEE Main/Boards

Exercise 1

Q.1 Name the following halides according to IUPAC system and classify them as alkyl, allyl, banzyl (primary, secondary, tertiary), vinyl or aryl halides:

(i) $(CH_3)_2\ CHCH(Cl)CH_3$

(ii) $CH_3\ CH_2\ CH(CH_3)CH(C_2H_5)\ Cl$

(iii) $CH_3\ CH_2\ C(CH_3)_2CH_2\ I$

(iv) $(CH_3)_2CCH_2\ CH(Br)C_6H_5$

(v) $CH_3\ CH(CH_3)CH(Br)\ CH_3$

(vi) $CH_3C(C_2H_5)_2\ CH_2\ Br$

(vii) $CH_3C(Cl)\ (C_2H_5)\ CH_2CH_3$

(Viii) $CH_3\ CH{=}C(Cl)CH_2(CH_3)_2$

(ix) $CH_3\ CH{=}CHC(Br)\ (CH_3)_2$

(x) p-$ClC_6H_4CH_2CH(CH_3)_2$

Q.2 Which one of the following has the highest dipole moment why?

(i) CH_2Cl_2 (ii) $CHCl_3$ (iii) CCl_4

Q.3 What are ambident nucleophiles? Explain with an example.

Q.4 Write the equation Wurtz-fittig reaction.

Q.5 p-Dichlorobenzene has higher m.p. and solubility than those of o-and m-isomers. Discuss.

Q.6 An alkyl halide, (X) of formula C_6H_{13} Cl on treatment with potassium tertiary butoxide gives two isomeric alkenes (Y) and (Z). (C_6H_{12}). Both alkenes on hydrogenation give 2, 3-dimethybutane. Predict the structures of (X), (Y) and (Z).

Q.7 What happens when and complete equation?

(i) n-butyl chloride is treated with alcoholic KOH.

(ii) Bromobenzene is treated with Mg in the presence of dry ether.

(iii) Chlorobezene is subjected to hydrolysis.

(iv) Ethyl chloride is treated with aqueous KOH.

(v) Methyl bromide is treated with sodium in the presence of dry ether.

(vi) Methyl chloride is treated with KCN.

Q.8 What is meant by chiral or asymmetric carbon atom?

Q.9 Write the equations for the preparation of 1-iodobutane from

(i) 1-butanol (ii) 1-Chlorobutane (iii) But-1-ene.

Q.10 Which compound in each of the following pairs will react faster in S_N 2 reaction with –OH?

(i) CH_3 Br or CH_3I (ii) $(CH_3)_3$ CCl or CH_3 Cl

Q.11 Predict all the alkenes that would be formed by dehydrohalogenation of the following halides with sodium ethoxide in ethanol and identify the major alkene:

(i) 1-Bromo-1-methylcyclohexane

(ii) 2-chloro-2- methylbutane

(iii) 2,2,3-Trimethyl-3-bromopentane.

Q.12 Gives the uses of Freon 12,DDT, carbon tetrachloride and iodoform.

Q.13 Write the mechanism of the following reaction:

$$\text{nBuBr} + \text{KCN} \xrightarrow{\text{BOH–H}_2\text{O}} \text{nBuCN}$$

Q.14 Out of $C_6H_5CH_2Cl$ and $C_6H_5CHClC_6H_5$, which is more easily hydrolyzed by aqueous KOH?

Q.15 The treatment of alkyl chlorides with aqueous KOH leads to the formation of alcohols but in the presence of alcoholic KOH, alkenes are major products. Explain.

Q.16 Identify and indicate the presence of chirality, if any in the following molecule. How many stereo isomers are possible for those containing chiral center?

Q.17 Give two example of molecules which contain chirality centers but process a chiral structure?

Q.18 Write the equation of elimination with mechanism?

Q.19 (i) Why are haloalkanes more reactive towards nucleophilic substitution reaction than haloarenes?

(ii) Which of the following two substance undergo S_N1 reaction faster and why?

Q.20 Identify and indicate the presence of center of chirality, if any in the following molecules. How many stereoisomers are possible for those containing chiral center?

(i) 1, 2-dichloropropane

(ii) 3-bromo-pent-1-ene

Q.21 Does the presence of two chiral carbon atoms always make the molecule optically active? Explain giving an example.

Q.22 How can iodoform be prepared from ethanol? (Give equation)

Q.23 How can methyl bromide preferentially converted to methyl isocynaide?

Q.24 Write the difference between S_N1 and S_N2 reaction?

Q.25 Explain nucleophilic substitution reaction in aryl halides?

Q.26 How will you bring about the following conversions?

(i) Bromoethane to cis-hex-3-ene

(ii) Benzyl alcohol to phenylethanenitrile

(iii) Cyclopentene to cyclopenta-1, 3-diene

Q.27 Write the equation of Swarts reaction.

Q.28 Although chlorine is an electron withdrawing group, yet it is ortho-para directing in electrophilic acromatic substitution reactions. Why?

Q.29 Explain why (i) The dipole moment of chlorobenzene is lower than that cyclohexyl chloride.

(ii) Alkyl halides, though polar, are immiscible with water.

(iii) Grignard reagents should be prepared under anhydrous conditions.

Q.30 Write the method formation of halo arenes.

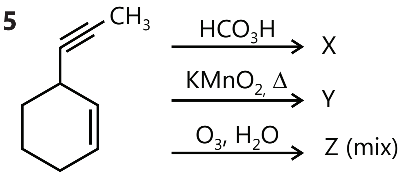
Q.31 Write the chemical properties of halo arenes.

Q.32 Explain S_N1 Mechanism with example.

Q.33 What are arenes? How are they classified? Discuss briefly the isomerism and nomenclature of arenes.

Q.34 Discuss of structure of benzene laying emphasis on resonance and orbital structure.

Q.35



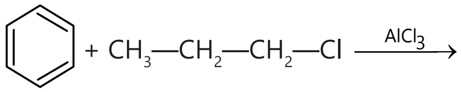
Identify X, Y and Z

Q.36 Justify the Statement: Benzene is highly unsaturated compound but behaves like a saturated compound.

Q.37 Discuss briefly the mechanism of electrophilic substitution reactions in benzene.

Q.38 Explain the directive influence of various substituent and their effect on reactivity of arenes.

Q.39 Complete the following sequences



Exercise 2

Single Correct Choice Type

Q.1 Consider the following halo alkanes:

1. CH_3F 2. CH_3Cl 3. CH_3Br 4. CH_3I

The increasing order of reactivity in nucleophilic substitution reaction is

(A) 1<2<4<3 (B) 1<2<3<4

(C) 1<3<2<4 (D) 4<3<2<1

Q.2 Which of the following haloalkane is hydrolyzed by S_N1 mechanism?

(A) CH_3Br (B) CH_3CH_2Br

(C) $CH_3CH_2CH_2Br$ (D) $(CH_3)_3$ CBr

Q.3 The reaction of t-butyl chloride and sodium exthoxide gives mainly

(A) t-butyl ethyl ether (B) 2, 2-dimethylbutane

(C) 2-methylprop-1-ene (D) Isopropyl n-propyl ether

Q.4 The fire extinguisher 'pyrene' contains.

(A) Carbon dioxide (B) Carbon disulphide

(C) Carbon Tetrachloride (D) Chloroform

Q.5 The final product (Z) is the following sequence of reactions

$$CH_3CH_2NH_2 \xrightarrow{HNO_2} (X) \xrightarrow{SOCl_2} (Y) \xrightarrow{NH_3} (Z) \text{ is}$$

(A) Methanamine (B) Ethanamide

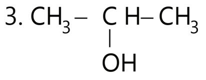
(C) Ethanamine (D) Propan-1-amine

Q.6 Consider the following reactions:

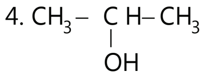
1. $CH_3CH_2CH_2Cl + I^- \rightarrow$
2. $(CH_3)_3$ C-Br+ ethanolic KCN $\rightarrow$
3. $CH_3CHBrCH_3$+aqueous KOH $\rightarrow$
4. $CH_3CHBrCH_3$+alcoholic KOH $\rightarrow$

The most likely products is these reactions would be

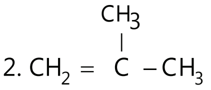
(A) 1. $CH_3CH_2CH_2I$ 2. $(CH_3)_3C-CN$

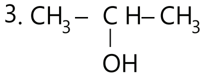


3. $CH_3-\underset{\displaystyle OH}{\underset{|}{C}}H-CH_3$

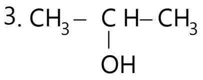


4. $CH_3-\underset{\displaystyle OH}{\underset{|}{C}}H-CH_3$

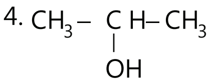
(B) 1. $CH_3CH_2CH_2Cl$ 2. 
$CH_2 = \overset{CH_3}{\overset{|}{C}} - CH_3$

3. 
$CH_3 - \underset{OH}{\underset{|}{C}}H - CH_3$
4. $CH_3 - CH = CH_2$

(C) 1. $CH_3 - CH = CH_2$ 2. $(CH_3)_3C - CN$

3. 
$CH_3 - \underset{OH}{\underset{|}{C}}H - CH_3$
4. $CH_3 - CH = CH_2$

(D) 1. $CH_3 - CHCH_2I$ 2. $(CH_3)_3C - CN$

3. $CH_3 - CH = CH_2$ 4. 
$CH_3 - \underset{OH}{\underset{|}{C}}H - CH_3$

Q.7 Aryl halides are less reactive towards nucleophilic substitution reaction as compared to alkyl halides due to

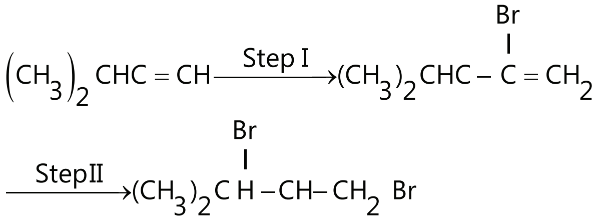
(A) The formation of less stable carbonium ion

(B) Resonance stabilization

(C) Longer carbon-halogen bond

(D) sp^2-hybridized C attached to the H

Q.8 In the following reaction:



$$(CH_3)_2CHC = CH \xrightarrow{\text{Step I}} (CH_3)_2CHC - \overset{Br}{\overset{|}{C}} = CH_2 \xrightarrow{\text{Step II}} (CH_3)_2C\overset{Br}{\overset{|}{H}} - CH - CH_2\,Br$$

Which of the following sets of reagents can be used for step I and step II?

Step I	Step II
1. HBr	HBr and peroxide
2. HBr and peroxide	HBr
3. Br_2	HBr
4. Br_2	HBr and peroxide

Select the correct answer using the codes given below

(A) 1, 2 and 4 (B) 2 and 4

(C) 3 and 4 (D) 1 Alone

Q.9 $Cl-CH_2-O-CH_2CH_3$ will undergo rapid

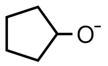
(A) S_N1 substitution

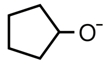
(B) S_N2 substitution

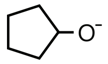
(C) Both equal rates (S_N1 and S_N2)

(D) None of these

Q.10 The correct order of nucleophilicity is

(A) $Me_3CO^- > Me_2CHO^- >$ 

(B)  $> Me_2CHO^- > Me_3CO^-$

(C) $Me_2CHO^- >$  $> Me_3CO^-$

(D) None of these

Q.11 Arrange the following in order of decreasing reactivity towards S_N2 reaction.

(i) $CH_3CH_2CH_2Cl$ (ii) $CH_3CH_2\,CHClCH_3$

(iii) $(CH_3)_2CHCH_2Cl$ (iv) $(CH_3)_3CCl$

(A) (i) > (ii) > (iii) > (iv) (B) (iii) > (iv) > (ii) > (i)

(C) (i) > (iii) > (ii) > (iv) (D) (iv) > (iii) > (ii) > (i)

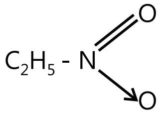
Q.12 In the reaction:

$$A \xrightarrow{KCN} B \xrightarrow{[H]} C_2H_5NH_2$$

(A) A is CH_3I (B) B is $CH_3\,NC$

(C) A is $C_2H_5\,I$ (D) B is C_2H_5NC

Q.13 $C_2H_5I \xrightarrow{AgNO_2} \underset{\text{(Major product)}}{X}$. Here X is

(A) C_2H_5-O-N=O (B) 

(C) C_2H_5-N=O (D) C_2H_5-N=N-C_2H_5

Q.14 $C_6H_5Cl \xrightarrow{Ni-Al/NaOH} X$ The compound X is

(A) Phenol

(B) Benzene

(C) o-and p-Chlorophenol

(D) Benzol

Q.15 Which of the following is least reactive towards nucleophilic displacement reaction when treated with aqueous KOH?

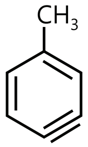
(A) 2, 4, 6-Trinitrochlorobenzene

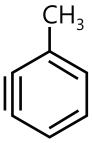
(B) 2, 4-Dinitrochlorobenzene

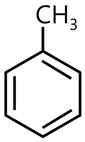
(C) 4-Nitrochlorobenzene

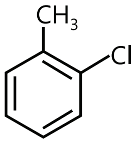
(D) 3- Nitrochlorobenzene

Q.16 o-Chlorotoluene reacts with sodamide in liquid NH_3 to give o-toluidine, and m-toluidine. This proceeds through an Intermediate

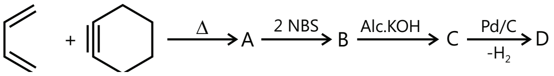
(A)


(B)


(C)


(D)


Q.17 The final product D in the above sequence of reactions is



(A) Benzene (B) Tetralin

(C) Decalin (D) Naphthalene

Q.18 1, 3-Dichloropropane reacts with Zn and NaI and gives (major product)

(A) Propane (B) Propane

(C) Cyclopropane (D) n-Proyl iodine

Q.19 S_N2 reactions are

(A) Stereospecific but not stereo selective

(B) Stereo selective but not Stereospecific

(C) Stereo selective as well as Stereospecific

(D) Neither stereo selective nor Stereospecific

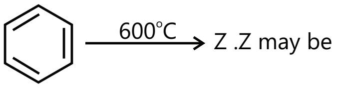
Q.20 Benzyl Chloride ($C_6H_5CH_2Cl$) can be prepared from toluene by chlorination with

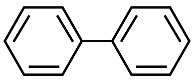
(A) $SO_2\ Cl_2$ (B) $SOCl_2$ (C) HCl (D) NaOCl

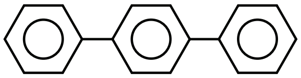
Q.21 Which xylene gives only one monobromo derivative?

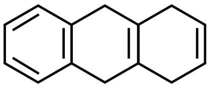
(A) Ortho (B) Para

(C) Meta (D) None of these

Q.22


(A)


(B)


(C)


(D) None of these

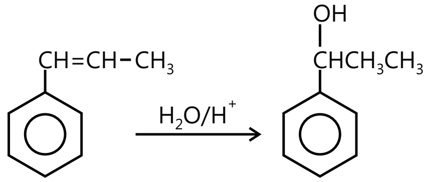
Q.23 Which of the following is used for aromatization of n-hexane?

(A) $AlCl_3$

(B) Na in liquid NH_2

(C) Cr_2O_3/Al_2O_3 with heat

(D) Wilkinson's catalyst

Q.24


The stereochemistry of product is

(A) Dextro (B) Laevo

(C) Meso (D) Racemic

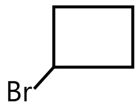
Previous Years' Questions

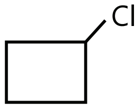
Q.1 Among the following, the molecule with the highest dipole moment is ***(2003)***

(A) CH_3Cl (B) CH_2Cl_2

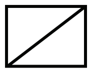
(C) $CHCl_3$ (D) CCl_4

Q.2 What would be the product formed when 1-Bromo-3-chloro cyclobutane reacts with two equivalents of metallic sodium in ether ***(2005)***

(A)


(B)


(C)


(D)


Q.3 Aryl halide are less reactive towards nucleophilic substitution reaction as compared to alkyl halide due to ***(1990)***

(A) The formation of less stable carbonium ion

(B) Resonance stabilization

(C) Longer carbon-halogen bond

(D) The inductive effect

(E) sp^2-hybridized carbon attached to the halogen

Q.4 The compounds used as refrigerant are ***(1990)***

(A) NH_3 (B) CCl_4

(C) CF_4 (D) CF_2Cl_2 (E) CH_2F_2

Q.5 The products of reaction of alcoholic silver nitrite with ethyl bromide are ***(1991)***

(A) Ethane (B) Ethene

(C) Nitro ethane (D) Ethyl alcohol

(E) Ethyl nitrite

Q.6 A new carbon-carbon bond formation is possible in ***(1998)***

(A) Cannizzaro reaction

(B) Friedel-Craft's alkylation

(C) Clemmensen reduction

(D) Riemer- Tiemann reaction

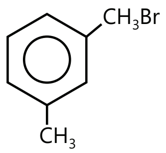
Q.7 Which of the following compounds does not disslove in conc.H_2SO_4 even on warming? ***(1983)***

(A) Ethylene (B) Benzene

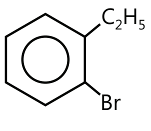
(C) Hexane (D) Aniline

Q.8 Compound (A), C_8H_9Br, gives a white precipitate when warmed with alcoholic $AgNO_3$. Oxidation of (A) gives an acid (B), $C_8H_6O_4$. (B) easily forms anhydride on heating. Identify thecompound (A). ***(2013)***

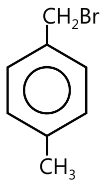
(A)



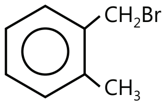
(B)



(C)



(D)

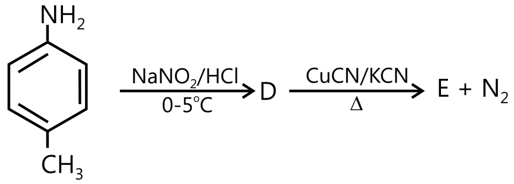


Q.9 The synthesis of alkyl fluorides is best accomplished by: ***(2015)***

(A) Free radical fluorination (B) Sandmeyer's reaction

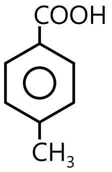
(C) Finkelstein reaction (D) Swarts reaction

Q.10 In the reaction ***(2015)***



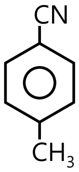
The product E is:

(A)

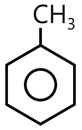


(B)

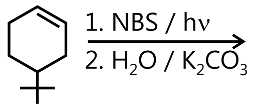
(C)



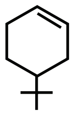
(D)



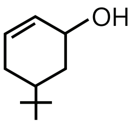
Q. 11 The product of the reaction given below is: ***(2016)***



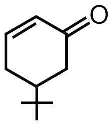
(A)



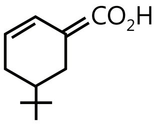
(B)



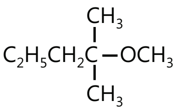
(C)



(D)

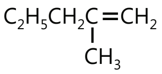


Q.12 2- Chloro -2 – methyl pentane on reaction with sodium methoxide in methanol yields : ***(2016)***



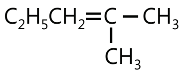
$C_2H_5CH_2\overset{CH_3}{\underset{CH_3}{C}}-OCH_3$

(i)



$C_2H_5CH_2\underset{CH_3}{C}=CH_2$

(ii)



$C_2H_5CH_2=\underset{CH_3}{C}-CH_3$

(iii)

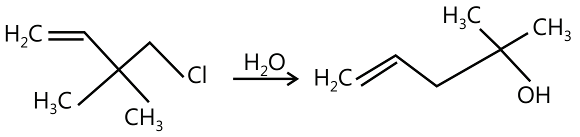
(A) All of these (B) (i) and (iii)

(C) (iii) only (D) (i) and (ii)

JEE Advanced/Boards

Exercise 1

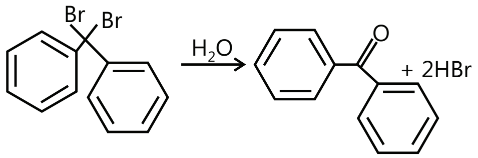
Q.1 Account for the observation that the hydrolysis (solvolysis in water) of (I) occurs much faster than other primary chlorides, and gives mainly (II).

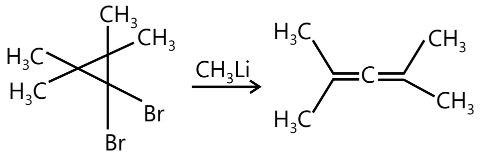


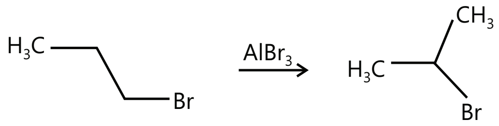
(I) (II)

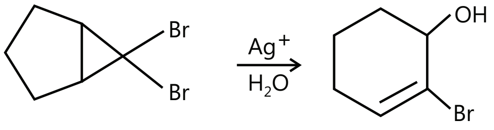
Q.2 Vinyl chloride does not give S_N reaction but allyl chloride gives. Explain.

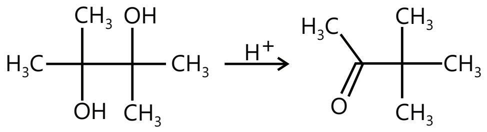
Q.3 Suggest a mechanism for each transformation below. Show all steps in each of your mechanisms.

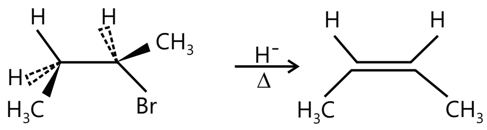
(A)


(B)


(C)


(D)


(E)


(F)


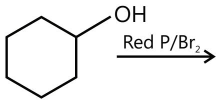
Q.4 Explain electrophilic substitution reactions of aryl halide.

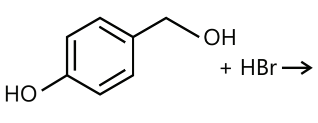
Q.5 Write the structure of the major organic product in each of the following reactions:

(A) $(CH_3)_3\,CBr + KOH \xrightarrow[\text{Heat}]{\text{Ethanol}}$

(B) $CH_3CH(Br)CH_2CH_3 + NaOH \xrightarrow{\text{Water}}$

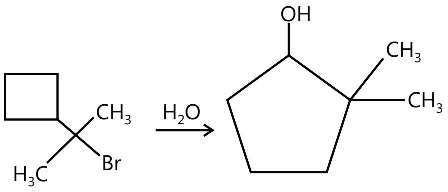
(C) $CH_2{=}CHCH_2Br + CH_3C \equiv CNa^+ \xrightarrow{\text{Liq.}NH_3}$

(D)


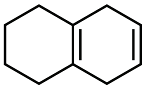
(E)


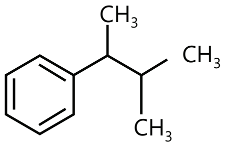
Q.6 Explain miscellaneous reactions of aryl halide.

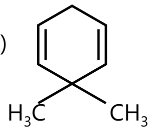
Q.7 Propose a mechanism for the following reaction

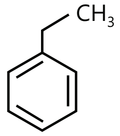


Q.8 What products would be formed when each of the following compounds reacts with N-bromosuccinimide in CCl_4 in the presence of light.

(A)


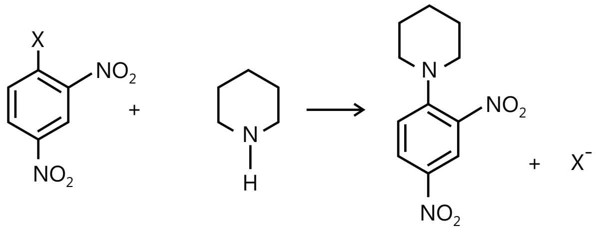
(B)


(C)


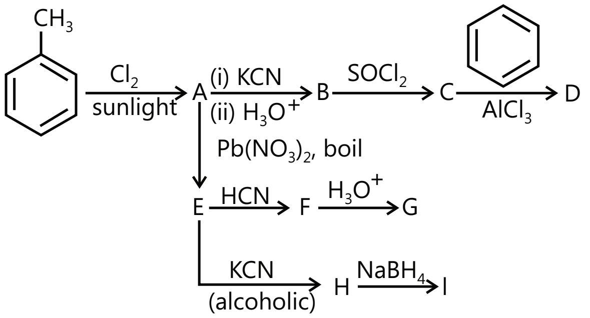
(D)


Q.9 (a) p-Methoxylbenzyl bromide reacts faster than p-nitrobenzyl with ethanol to from an ether product. Explain why.

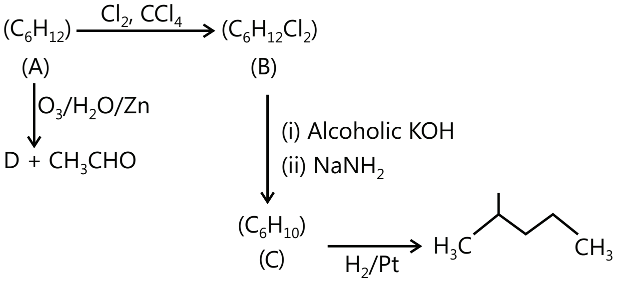
(b) In the following reaction the relative rate is 3,300 faster when X = F than I. explain.



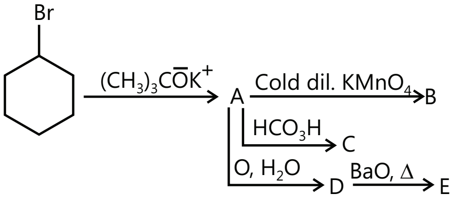
Q.10 (a) Complete the following transformations:



(b) Identify A, B, C, D and E in the following

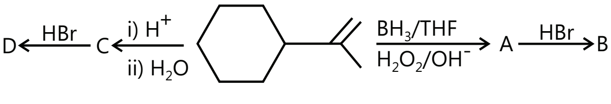


(c) Identify A, B, C, D and E in the following



Q.11 Identify A, B, C and D in the following:

Also select pair of isomers if any



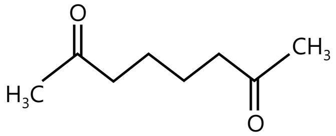
Q.12 Three compounds A, B and C all have the formula C_6H_{10}. All three compounds rapidly decolorise Br_2 in CCl_4; all three are soluble in cold conc. H_2SO_4. Compound a gives a precipitate when treated with $AgNO_3$ in NH_3 (aq), but compound B and C do not. Compound A and B both yield hexane when they are treated with excess H_2 in the presence of platinum catalyst, under these conditions C absorbs only one molar equivalent of H_2 and gives a product with the formula C_6H_{12}. When A is oxidized with basic $KMnO_4$ and the resulting solution acidified, the only organic product that can be isolated is $CH_3(CH_2)_3CO_2H$. Similar oxidation only $CH_3CH_2CO_2H$ and C gives only $HO_2C(CH_2)COH$. What are structures of A, B and C.

Q.13 The alkyl halide C_4H_4Br (A) reacts alcoholic KOH and gives an alkene (B), which reacts with bromine to give dibromide (C). (C) is transformed with sodamide to a gas (D) which forms a precipitate when passed through an ammonical silver nitrate solution. Give the structural formulae of the compounds (A), (B),and (D) and explain reactions involved.

Q.14 An optically active compound A (assume that it is dextrorotatory) has the molecular formula $C_7H_{11}Br$. A reacts with HBr, in the absence of peroxide to yield isomeric products, B and C, with molecular formula $C_7H_{12}Br_2$. Compound B is optically active C is not. Treating B with 1 mol of potassium tert-butoxide yields $(\pm A)$. Treating A with potassium tert-butoxide yields $D(C_7H_{10})$. Subjecting 1 mol of D to ozonolysis followed by treatment with zinc and water yield 2 mol of formaldehyde and 1 mol of 1, 3-cyclopentandione. Propose strereo-chemical formulae for A, B, C and D and outline the reaction involved in these transformations

Q.15 Explain elimination reaction in halo arene.

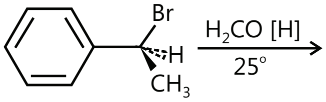
Q.16 Compound A ($C_8H_{12}Cl$) exists as a racemic form. Compound A does not decolorise either Br_2/CCl_4 or dilute aqueous$KMnO_4$. When A is treated with Zn/CH_3COOH, two fractions B and C both with molecular formula C_8H_{16} are obtained fraction B consists of a racemic form and can be resolved. Fraction C can't be resolved. Treating A with sodium ethoxide in ethanol converts A into $D(C_8H_{14})$. Hydrogenation of D using platinum catalyst yields C. Ozonolysis of D, followed by treatment with zinc and water yields.



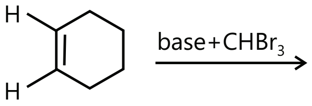
Assign structure to A, B, C and D.

Q.17 For each reaction below, fill in the structure of the expected product, showing stereochemistry where appropriate. Then indicate the type of reaction and/or mechanism involved.

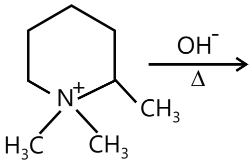
(A)



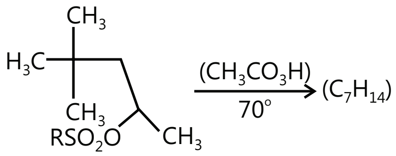
(B)



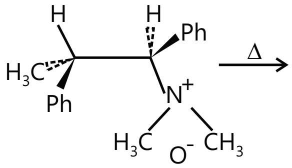
(C)



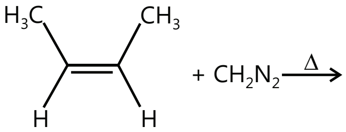
(D)



(E)

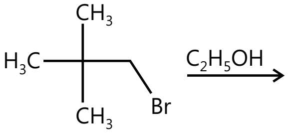


(F)

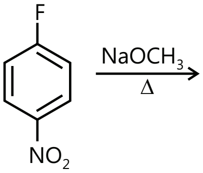


Q.18 What would be the major product in each of the following reactions?

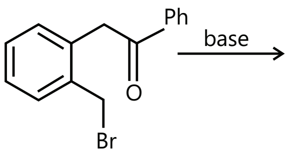
(I)



(II)



(III)



Q.19 Convert with equation.

(i) Benzene to p-nitrochlorobenzene

(ii) Benzene to aniline

(iii) Benzene to m- nitrochlorobenzene

(iv) Benzene to dipehnyl

(v) Benzene to p-chlorotoluene

(vi) chlorobenzene to DDT

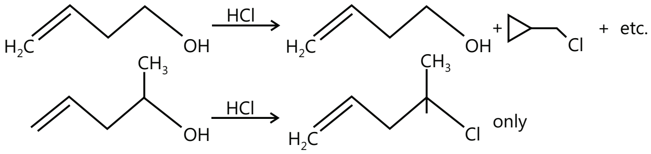
(vii) chlorobenzene to phenyl cyanide

(viii) Benzene diazonium chloride to aniline.

(ix) Aniline to phenyl isocyanide.

Q.20 An organic compound A, $C_6H_{10}O$, on reaction with CH_3Mg Br followed by acid treatment gives compound B. The compound B on ozonolysis gives compound C, which in presence of a base gives 1-acetyl cyclopentene D. The compound B on reaction with HBr gives compound E. Write the structures of A, B, C and E. Show how D is formed from C.

Q.21 Explain briefly the formation of the products giving the structures of the intermediates.



Q.22 Explain why

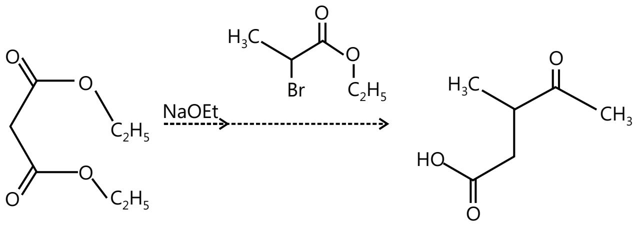
(i) Vinyl chloride is unreactive in nucleophilic substitution reaction?

(ii) Neo-pentyl bromide undergoes nucleophilic substitution reaction very slowly?

(iii) 3- bromocyclohexene is more reactive than 4-bromocyclhexene in hydrolysis with aqueous NaOH ?

(iv) Tert-butyl chloride reacts with aqueous sodium hydroxide by S_N1 mechanism while n-buty chloride reacts with by S_N2 mechanism?

Q.23 Write down the intermediate steps in the followed reaction



Q.24 Optically active 2-iodobutane on treatment with NaI in acetone gives a product which does not show optical activity. Explain why?

Q.25 An organic compound 'A' having molecular formula C_4H_8 on treatment H_2SO_4 gives 'B'. 'B' on treatment with conc. HCl and anhydrous $ZnCl_2$ gives 'C'; and on treatment with sodium ethoxide gives back 'A' identify the compounds 'A', 'B' and 'C' and write the equations involved.

Q.26 (W) and (X) are optically active isomers of C_6H_9Cl. (W) on treatment with one mole of H_2 is converted to an optically inactive compound (Y), but (X) gives an optically active compound (Z) under the same conditions. Give structure of (Y) and configuration of(W), (X) and (Z) in Fischer projections.

Q.27 A white precipitate was formed slowly when $AgNO_3$ was added to a compound (A) with molecular formula $C_6H_{13}Cl$. Compound (A) on treatment with hot alcoholic KOH gave a mixture of two isomeric alkenes (B) and (C) having formula C_6H_{12}. The mixture of (B) and (C) on ozonolysis furnished four compounds.

(i) CH_3CHO; (ii) C_2H_5CHO;

(iii) CH_3COCH_3; (iv) $(CH_3)_2CHCHO$.

What are (A), (B) and C?

Q.28 Primary alkyl halide C_4H_9Br (a) reacted with alcoholic KOH to give compound (b). Compound (b) is reacted with HBr to give (c) which is an isomer of (a). When (a) is reacted with sodium metal it gives compound (d), C_8H_{18} which is different form the compound formed when n-butyl bromide is reacted with sodium. Give the structural formula of (a) and write the equations for all the reactions.

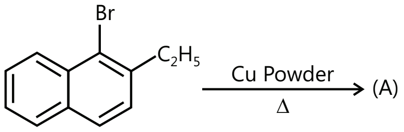
Q.29 Cyclobutyl bromide on treatment with magnesium in dry ether forms an organometallic (A). The organometallic react with ethanol to give an alcohol (B) after mild acidification. Prolonged treatment of alcohol (B) with an equivalent amount of HBr gives 1-bromo-1-methyl-cyclopentane (C). Write the structures of (A), (B) and explain how (C) is obtained from (B).

Q.30 An organic compound (X) on analysis gives 24.24% C, 4.04% H. Further sodium extract of 1.0 g of (X) gives 2.90 g of AgCl with acidified $AgNO_3$ solution. The compound (X) may be represented by two isomeric structures (Y) and (Z). (Y) on treatment with aqueous KOH solution gives a dihydroxy compound, while (Z) on similar treatment gives ethanol. Find out (X), (Y) and (Z).

Q.31 The freezing point constant of C_6H_6 is 4.90 and its melting point 5.51°C. A solution of 0.810 g of a compound (A) when dissolved in 7.5 gms of benzene freezes at 1.59°C. The compound (A) has C = 70.58%. Compound (A) on heating with sodalime gives another compound (B) which on oxidation and subsequent acidifications gives an acid (C) of equivalent weight 122. (C) on heating with sodalime gives benzene. Identify (A), (B) and (C) and explain the reactions involved.

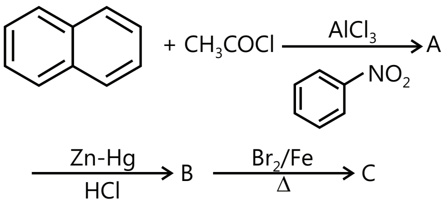
Q.32 When bromo benzene is mono chlorinated, two isomeric compounds (A) and (B) are obtained. Monobromination of (A) gives several isomeric products of formula $C_6H_3ClBr_2$. While monobromination of (B) yields only two isomeric (C) and (D). Compound (C) is identical with one of the compound obtained from the bromination of (A). However (D) is totally different from any of the isomeric compounds obtained from bromination of (A). Give structures of (A), (B) and (D) with explanation.

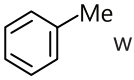
Q.33



Write the structure of A and explain its stereochemistry

Q.34

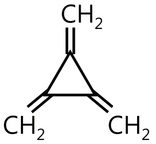


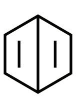
Q.35 Nitration of  with HNO_3 in acetic acid solvent at 45°C occurs 25 times faster than nitration of  under same condition and the percentage are ortho = 56.5 meta = 3.5 and para 40.0. What is the partial rate factor. Can these values be taken for other electrophilic substitution reactions of toluene.

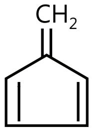
Q.36 An aromatic hydrocarbon (A) (mol. wt.=92) containing C=91.3% and H=8.7% gave on treatment with chlorine three isomeric compounds (B), (C) and (D) each containing 28% chlorine. On oxidation, each of three gave monobasic acids X, Y and Z respectively. The acid (X) can also be obtained by the oxidation of (A) while (Y) and (Z) contained chlorine also. The acid X on reaction with soda lime gave benzene while acids (Y) and (Z) on similar treatment gave chlorobenzene. What are A, B, C, D, X, Y, Z.

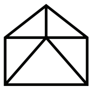
Q.37 The values for nitration of t-butyl benzene are o = 4.5, m= 3.0, p = 75. How much more reactive is t-butyl benzene than benzene.

Q.38 Which of the following C_6H_6 structure gives only one C_6H_5 Br isomer

(A)


(B)


(C)


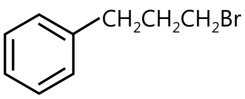
(D)


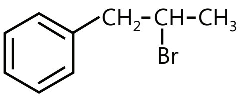
Q.39 Write the Mechanism of nitration of benzene and toluene.

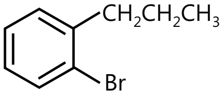
Exercise 2

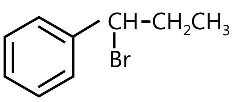
Single Correct Choice Type

Q.1 Propylbenzene reacts with bromine in presence of light or heat to give

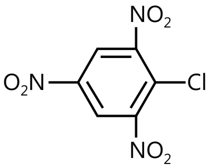
(A)


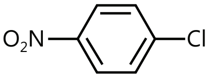
(C)


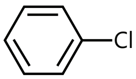
(B)


(D)


Q.2 Which one of the following would undergo hydrolysis most readily with aqueous sodium hydroxide to form the corresponding hydroxide derivative?

(A)


(D)


(B)


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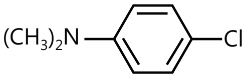
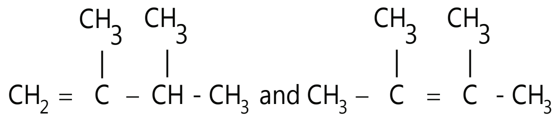
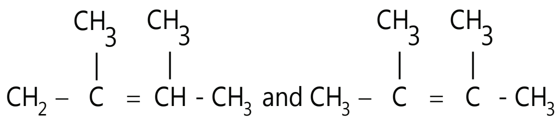


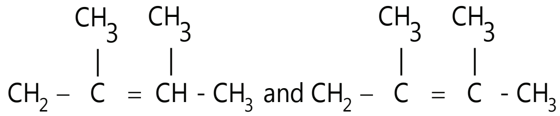
Q.3 An alkyl halide of formula $C_6H_{13}Cl$ on treatment with potassium tertiary butoxide gives two isomeric alkenes (C_6H_{12}). Both alkenes on hydrogenation give 2, 3-dimethybutane. Isomeric alkenes are

(A)


$CH_2=\overset{\overset{CH_3}{|}}{C}-\overset{\overset{CH_3}{|}}{CH}-CH_3$ and $CH_3-\overset{\overset{CH_3}{|}}{C}=\overset{\overset{CH_3}{|}}{C}-CH_3$

(B)


$CH_2-\overset{\overset{CH_3}{|}}{C}=\overset{\overset{CH_3}{|}}{CH}-CH_3$ and $CH_3-\overset{\overset{CH_3}{|}}{C}=\overset{\overset{CH_3}{|}}{C}-CH_3$

(C)


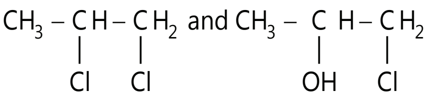
$CH_2-\overset{\overset{CH_3}{|}}{C}=\overset{\overset{CH_3}{|}}{CH}-CH_3$ and $CH_2-\overset{\overset{CH_3}{|}}{C}=\overset{\overset{CH_3}{|}}{C}-CH_3$

(D) None of these

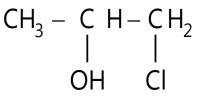
Q.4 $CH_3-CH_2CH_2Br \xrightarrow{Aq.NaOH} X$

$$X \xrightarrow[Heat]{Al_2O_3} Y \xrightarrow{Cl_2/H_2O}$$

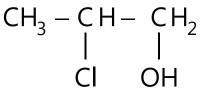
Identify 'z' in

(A) Mixture of


$CH_3-\underset{\underset{Cl}{|}}{C}H-\underset{\underset{Cl}{|}}{C}H_2$ and $CH_3-\underset{\underset{OH}{|}}{C}H-\underset{\underset{Cl}{|}}{C}H_2$

(B)


$CH_3-\underset{\underset{OH}{|}}{C}H-\underset{\underset{Cl}{|}}{C}H_2$

(C)


$CH_3-\underset{\underset{Cl}{|}}{C}H-\underset{\underset{OH}{|}}{C}H_2$

(D) None of these

Q.5 The correct order of leaving tendency of

(i) OH^- (ii) $ArSO_3^-$ (iii) $MeCOO^-$ is

(A) i < ii < iii (B) i < iii < ii (C) iii < i < ii (D) iii < ii < i

Q.6 List the hydrogen halide acids in decreasing order of reactivity in the following reaction: $R\text{-}OH+HX \rightarrow RX+H_2O$

(A) HI>HBr>HCl>HF (B) HBr>HI>HCl>HF

(C) HI>HCl>HBr>HF (D) HI>HF>HBr>HI.

Q.7 In the mechanism for the reaction of HBr with t-butyl alcohol, pick out the incorrect statement.

(A) Formation of protonated alcohol is a slow step

(B) Formation of $(CH_3)_3\ C^+$ is a slow step

(C) Formation of $(CH_3)_3$ CBr from $(CH_3)_3$ C^+ is a slow step

(D) Formation of $(CH_3)_3$ C^+ is a fast step

Q.8 S_N1 reactions occur through the intermediate formation of

(A) Carbocations (B) Carbanions

(C) Free radicals (D) None of these

Q.9 S_N1 reactions are favored by

(A) None polar solvents

(B) Bulky groups on the carbon atom attached to the halogen atom

(C) Small groups on carbon atom attached to the halogen atom

(D) None of these

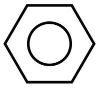
Q.10 The main product formed when ethylbenzene reacts with chlorine in presence of UV light is

(A) 1-Chloro-1-phenylethane

(B) o-Chloroethylbenzene

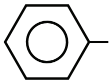
(C) 2-Chloro-1-phenylethane

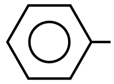
(D) p-Chloroethylbenzene

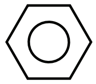
Q.11 

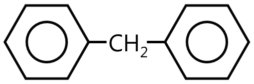
Excess

+ $CH_2Cl_2 \xrightarrow[AlCl_3]{Anhyd.}$ A. A is

(A)  $-CH_2Cl$

(B)  $-CHCl_2$

(C) 

(D) 

Q.12 A sample of chloroform before being used as an anaesthetic agent is tested by

(A) Fehling's solution

(B) Ammoniacal cuprous chloride

(C) Silver nitrate solution in the cold

(D) Silver nitrate solution after boiling with alcoholic KOH

Q.13 One of the important constituents of tear gas is

(A) $COCl_2$ (B) CCl_3 NO_2

(C) $SOCl_2$ (D) CH_3-N=C=O

Q.14 When propane is heated with excess of Cl_2 at 573-673 K under 75-100 atm. Pressure, the products obtained are

(A) $CH_3CH_2CH_2Cl + CH_3CHClCH_3$

(B) $CCl_4+C_2Cl_6$

(C) $CH_3CH_2CHCl + CH_3CHClCH_2Cl$

(D) $CHCl_3 + CH_3CH_2Cl$

Q.15 Which of the following is used as a camphor substitute?

(A) C_2Cl_6 (B) $CHCl_3$ (C) CCl_4 (D) CF_2Cl_2

Q.16 Freon used as a refrigerant is

(A) Acetylene tetrachloride

(B) Trichloroethylene

(C) Dichlorodifluoromethane

(D) Ethylene dichloride

Q.17 n-Propyl bromide on treatment with ethanolic potassium hydroxide produces

(A) Propane (B) Propene

(C) Propyne (D) Propanol

Q.18 Chlorobenzene can be prepared by reacting aniline with

(A) Hydrochloride acid

(B) Cuprous chloride

(C) Chlorine in presence of anhydrous aluminum chloride

(D) Nitrous acid followed by heating with cuprous chloride

Q.19 Carbylamine test is performed in alcoholic KOH by heating a mixture of

(A) Chloroform and silver powder

(B) Trihalogenated methane and a primary amine

(C) An alkyl halide and a primary amine

(D) An alkyl cyanide and a primary amine

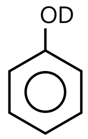
Q.20 Pick out the correct equations:

(A) $CH_3CH=CH_2+HCl \rightarrow CH_3CHClCH_3$

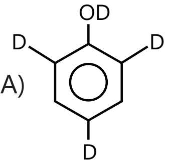
(B) $CH_3CH=CH_2+HBr \rightarrow CH_3CH_2CH_2Br$

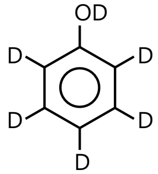
(C) $CH_3CH=CH_2+HBr \xrightarrow{peroxide} CH_3CH_2CH_2Br$

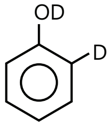
(D) $CH_3CH=CH_2+HI \xrightarrow{\text{peroxide}} CH_3CHICH_3$

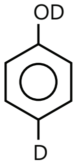
Q.21 

$+D_2SO_4 \xrightarrow[\Delta]{+D_2O}$ Z. Z may be

(A) 

(B) 

(C) 

or 

(D) None of these

Assertion Reasoning Type

Each of other questions given below consists of two statements, an assertion (A) and reason (R). Select the number corresponding to the appropriate alternative as follows

(A) If both assertion and reason are true and R is the correct explanation of assertion, then mark (A)

(B) If both assertion and reason are true but reason is not the correct explanation of assertion, then mark (B)

(C) If assertion is true but reason is false, then mark (C)

(D) If both assertion and reason are false, then mark (D)

Q.22 Assertion: Alkyl halides are not soluble in water.

Reason: Although polar in nature, yet alkyl halides are not able to from H-bonds with water molecules.

Q.23 Assertion: Chloral is not alkyl halide.

Reason: Although molecules contains two OH groups linked to same C atom.

Q.24 Assertion: The reaction of vinyl chloride and hydroiodic acid produces 1-chloro-2-iodoethane.

Reason: HI adds on vinyl chloride against Markovnikov's rule.

Q.25 Assertion: Chloroform is generally stored in brown bottles which are filled up to brim.

Reason: Chloroform reacts with glass in the presence of sunlight.

Q.26 Assertion: Chlorobanzene is easily hydrolysed as compared to chloromethane.

Reason: Carbon chlorine bond in chlorobenzene is relatively shorter than that in chloroethane.

Q.27 Assertion: Carbon tetrachloride is used as fire extinguisher.

Reason: Carbon tetrachloride is a non-polar substance.

Q.28 Assertion: Tertiary haloalkanes are more reactive than 1° alkyl halides towards elimination. Positive

Reason: Inductive effect of alkyl groups weakens carbon halogen in 3° halides.

Q.29 Assertion: In comparison to ethyl chloride, it is difficult to carry out nucleophilic substitution on vinyl chloride.

Reason: Vinyl group is electron donating group.

Q.30 Assertion: Free radical chlorination of n-butane gives 72% 2-chlorobutane and 28% 1-chlorobutane though it has six primary and four secondary hydrogen's.

Reason: A secondary hydrogen is abstracted more easily than the primary hydrogen.

Q.31 Assertion: Benzyl chloride is more reactive than p-chlorotoluene towards aqueous NaOH.

Reason: The C-Cl bond in benzyl chloride is more polar than C-Cl bond in p-chlorotouene.

Q.32 Assertion: Nucleophilic substitution reaction on an optically active alkyl halide gives a mixture of enantiomers

Reason: The reaction occurs by S_Ni mechanism.

Q.33 Assertion: Ethyl bromide reacts with alcoholic silver cyanide solution to give ethyl carbylamine as the major product along with a small amount of ethyl cyanide.

Reason: CN^- is an ambident nucleophile.

Q.34 Assertion: $CH_3-CH=CH_2 \xrightarrow{Cl_2,773K} ClCH_2-CH=CH_2+HCl$

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

Q.35 Assertion: Tertiary haloalkanes are more reactive than primary haloalkanes towards elimination reactions.

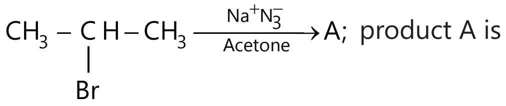
Reason: The +I-effect of the alkyl groups weakens the C-X bond.

Comprehension Type

There are several factors which decide the fate of substrate in presence of nucleophile (or base). One of them is nature of solvent.

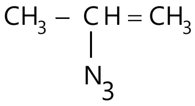
In mildly basic, neutral or acidic solution primarily substitution takes place. This will occur via S_N2 mechanism for 1° alkyl halides and via S_N1 mechanism for 3° alkyl halides. When 2° alkyl halides react with (-) charge nucleophile in polar protic solvents, the S_N2 mechanism is followed when 2° alkyl halides react with H_2O or ROH as solvent S_N1 mechanism is followed.

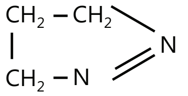
In strongly basic solutions primarily elimination takes place with 2° and 3° alkyl halides moderate or strong basic solutions arise when followed are present NaOH, KOH, NaOEt. When we use strong and sterically hindered base, KOtBu, even 1° alkyl halides given elimination products primarily.

Q.36 
$CH_3-\underset{\underset{Br}{|}}{C}H-CH_3 \xrightarrow[Acetone]{Na^+N_3^-} A$; product A is

(A) $CH_3CH = CH_2$

(B) $CH_3-CH_2-CH_2-N_3$

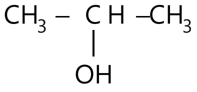
(C) 
$CH_3-\underset{\underset{N_3}{|}}{C}H=CH_3$

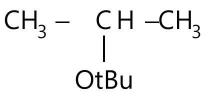
(D) 

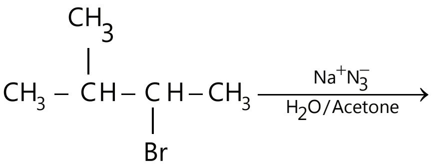
Q.37 $CH_3CH_2CH_2Br \xrightarrow[t\ BuOH]{KOH} B$; product B is

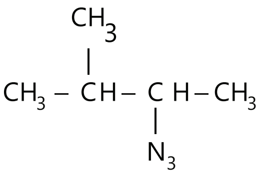
(A) $CH_3CH = CH_2$

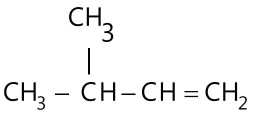
(B) $CH_3CH_2CH_2OH$

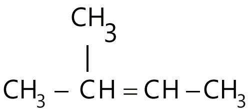
(C) 
$CH_3-\underset{\underset{OH}{|}}{C}H-CH_3$

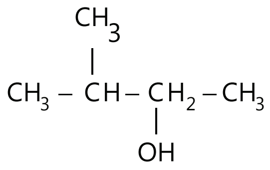
(D) 
$CH_3-\underset{\underset{OtBu}{|}}{C}H-CH_3$

Q.38 
$CH_3-\overset{\overset{CH_3}{|}}{C}H-\underset{\underset{Br}{|}}{C}H-CH_3 \xrightarrow[H_2O/Acetone]{Na^+N_3^-}$

(A) 
$CH_3-\overset{\overset{CH_3}{|}}{C}H-\underset{\underset{N_3}{|}}{C}H-CH_3$

(B) 
$CH_3-\overset{\overset{CH_3}{|}}{C}H-CH=CH_2$

(C) 
$CH_3-\overset{\overset{CH_3}{|}}{C}H=CH-CH_3$

(D) 
$CH_3-\overset{\overset{CH_3}{|}}{C}H-\underset{\underset{OH}{|}}{C}H_2-CH_3$

Multiple Correct Choice Type

Q.39 When nitrobenzene is treated with Br_2 in the presence of $FeBr_3$, the major product formed is m-bromonitrobenzene. Statements which are related to obtain the m-isomer are

(A) The electron density on meta carbon is more than that on ortho and para positions

(B) The intermediate carbonium ion formed after initial attack of Br^+ at the meta position is least destabilished

(C) Loss of aromaticity when Br^+ attacks at the ortho and para positions and not at meta position

(D) Easier loss of H^+ to regain aromaticity from the meta position than from ortho and para positions

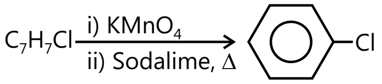
Q.40 Benzene can undergo

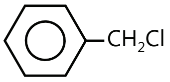
(A) Substitution

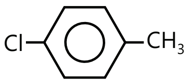
(B) Addition

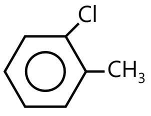
(C) Elimination

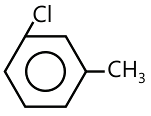
(D) Oxidation

Q.41 

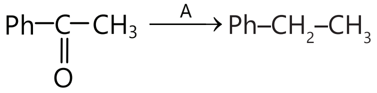
(A) 

(B) 

(C) 

(D) 

In the above reactions, compound (A) is

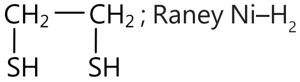
Q.42 
$Ph-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{A} Ph-CH_2-CH_3$

A could be:

(A) NH_2NH_2, glycol/OH^-

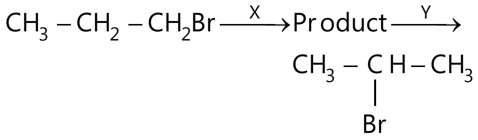
(B) Na(Hg)/conc. HCl

(C) Red P/HI

(D) 
$\underset{\underset{SH}{|}}{CH_2}-\underset{\underset{SH}{|}}{CH_2}$; Raney Ni–$H_2$

Previous Years' Questions

Q.1 Identify the set of reagents/reaction conditions X and Y in the following set of transformations ***(2002)***



$$CH_3-CH_2-CH_2Br \xrightarrow{X} \text{Product} \xrightarrow{Y} CH_3-\underset{\substack{|\\ Br}}{C}H-CH_3$$

(A) X = dilute aqueous NaOH, 20°C,

Y = HBr/acetic acid, 20°C,

(B) X = concentrated alcoholic NaOH, 80°C,

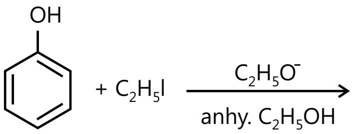
Y = HBr/ acetic acid, 20°C,

(C) X = dilute aqueous NaOH, 20°C, Y = $Br_2/CHCl_3$, 0°C

(D) X = concentrated aqueous NaOH, 80°C,

Y = $Br_2/CHCl_3$, 0°C

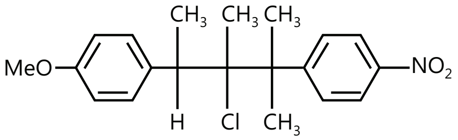
Q.2 The product of following reaction is



(A) $C_6H_5OC_2H_5$ (B) $C_2H_5OC_2H_5$

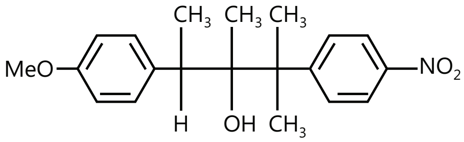
(C) $C_6H_5OC_6H_5$ (D) C_6H_5I

Q.3 The following compound on hydrolysis in aqueous acetone will give: ***(2005)***

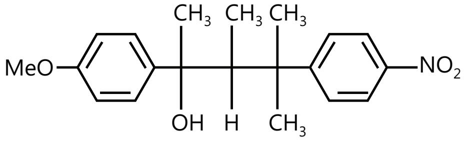


It mainly gives

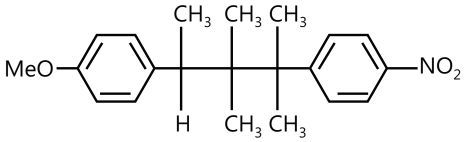
(K)



(L)

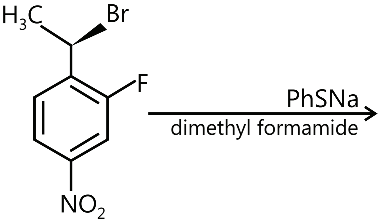


(M)

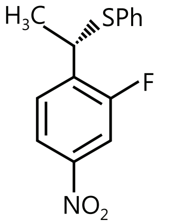


(A) K and L (B) Only K (C) L and M (D) Only M

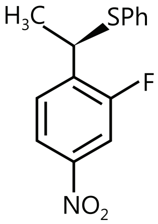
Q.4 The major product of the following reaction is



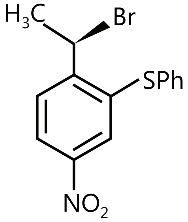
(A)



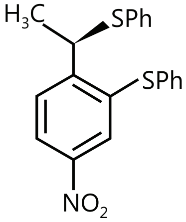
(B)



(C)



(D)



Q.5 The compound used as refrigerant are ***(1990)***

(A) NH_3 (B) CCl_4

(C) CF_4 (D) CF_2Cl_2 (E) CH_2 F_2

Q.6 Match the following

Column I	Column II
(A) CH_3-CHBr-CD_3 on treatment with alc. KOH gives CH_2=CH-CD_3 as a major product.	(p) E1 reaction
(B) Ph-CHBr-CH_3 reacts faster than Ph-CHBr-CD_3	(q) E2 reaction
(C) Ph-CH_2-CH_2Br on treatment with $C_2H_5OD/C_2H_5O^-$ gives Ph-CD=CH_2 as the major product.	(r) E1CB reaction
(D) PhCH_2 CH_3CH_2 Br and PhCD_2 CH_2 Br react with same rate.	(s) First order reaction

Q.7 Which of the following is the correct method for synthesizing methyl-t-butyl ether and why?

$(CH_3)_3CBr+NaOMe\rightarrow$

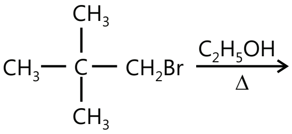
or

$CH_3Br+NaO\text{-}t\text{-}Bu\rightarrow$ ***(1997)***

Q.8 Write the structures of the products: ***(1998)***

$C_6H_5CH_2CHClC_6H_5 \xrightarrow{\text{Alc.KOH}}$

Q.9 What would be the major product in each of the following reactions? ***(2000)***



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2Br \xrightarrow[\Delta]{C_2H_5OH}$$

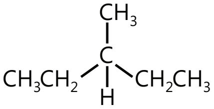
Q.10 Identify X, Y and Z in the following synthetic scheme and write their structures

$$CH_3CH_2C\equiv CH \xrightarrow[\text{(ii)}\,CH_3CH_2Br]{\text{(i) Na NH}_2} X$$

$$X \xrightarrow{H_2/Pd\text{–}BaSO_4} Y \xrightarrow[KMnO_4]{\text{Akaline}} Z$$ ***(2002)***

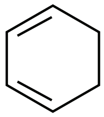
Q.11 The total number of alkenes possible by dehydrobromination of 3-bromo-3-cyclopentylhexane using alcoholic KOH is ***(2011)***

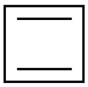
Q.12 The maximum number of isomers (including stereoisomers) that are possible on monochlorination of the following compound, is ***(2011)***

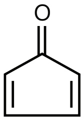


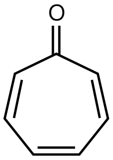
$$CH_3CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}-CH_2CH_3$$

Q.13 Which of the following molecules, in pure form, is (are) **unstable** at room temperature? ***(2012)***

(A) 

(B) 

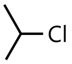
(C) 

(D) 

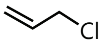
Q.14 KI in acetone, undergoes S_N2 reaction with each of P, Q, R and S. The rates of the reaction vary as ***(2013)***

H_3C-Cl

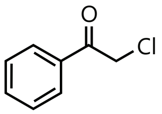
P



Q



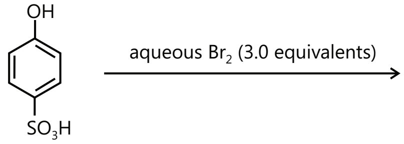
R

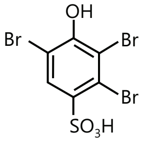


S

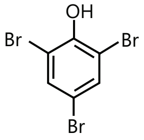
(A) P>Q>R>S
(B) S>P>R>Q
(C) P>R>Q>S
(D) R>P>S>Q

Q.15 The major product(s) of the following reaction is(are) ***(2013)***

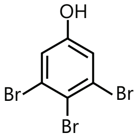




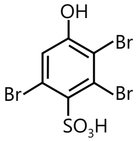
P



Q



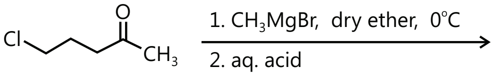
R

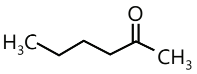


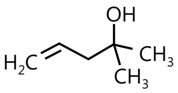
S

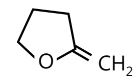
(A) P (B) Q (C) R (D) S

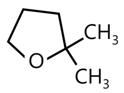
Q.16 The major product in the following reaction is ***(2014)***



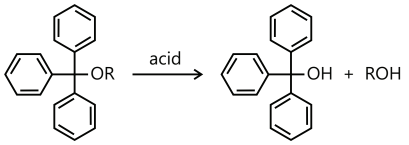
(A) 

(B) 

(C) 

(D) 

Q.17 The acidic hydrolysis of ether(X) shown below is fastest when ***(2014)***



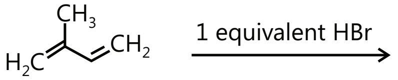
(A) One phenyl group is replaced by a methyl group.

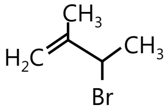
(B) One phenyl group is replaced by a para-mehoxyphenyl group

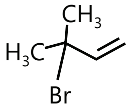
(C) Two phenyl groups are replaced by two para-methoxyphenyl group

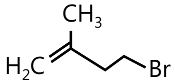
(D) No structural change is made to X.

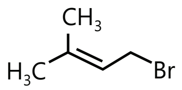
Q.18 In the following reaction, the major product is ***(2015)***



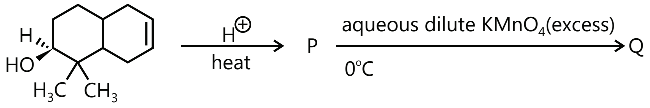
(A) 

(B) 

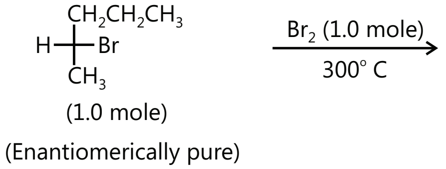
(C) 

(D) 

Q.19 The number of hydroxyl group(s) in **Q** is ***(2015)***

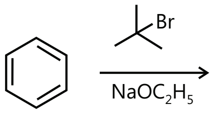


Q.20 In the following monobromination reaction, the number of possible chiral products is ***(2016)***

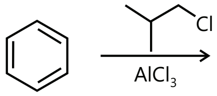


Q.21 Among the following, reaction(s) which gives(give) *tert*-butyl benzene as the major product is(are) ***(2016)***

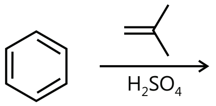
(A)



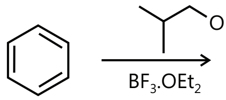
(B)



(C)



(D)



PlancEssential Questions

JEE Main/Boards

Exercise 1

Q.2 Q.4 Q.6 Q.7(iii, v)
Q.9(iii) Q.11 Q.16 Q.18
Q.19 Q.22 Q.24 Q.25
Q.27 Q.32

Exercise 2

Q.4 Q.5 Q.8 Q.10
Q.14 Q.16 Q.17 Q.22
Q.24

Previous Years' Questions

Q.3 Q.6

JEE Advanced/Boards

Exercise 1

Q.3 (B, D, E) Q.5 (E) Q.8 (B, D) Q.10
Q.14 Q.17 (C, E) Q.19 (vi, ix) Q.21
Q.24 Q.27 Q.29

Exercise 2

Q.1 Q.3 Q.11 Q.14
Q.19 Q.25 Q.33 Q.38
Q.40

Previous Years' Questons

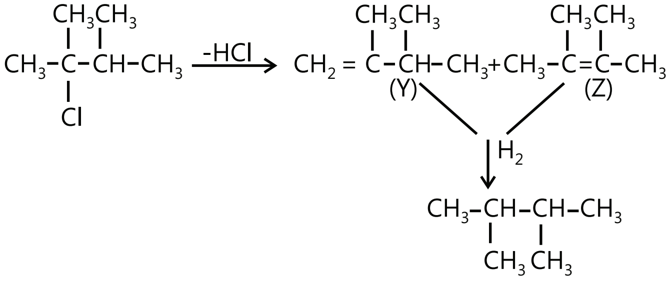
Q.3 Q.4 Q.6 Q.10

Answer Key

JEE Main/Boards

Exercise 1

Q.6



Exercise 2

Single Correct Choice Type

Q.1 B
Q.2 D
Q.3 C
Q.4 C
Q.5 C
Q.6 B
Q.7 B
Q.8 D
Q.9 B
Q.10 A
Q.11 C
Q.12 A
Q.13 B
Q.14 B
Q.15 D
Q.16 B
Q.17 D
Q.18 C
Q.19 C
Q.20 A
Q.21 B
Q.22 A
Q.23 C
Q.24 D

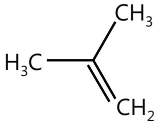
Previous Year's Questions

Q.1 A
Q.2 D
Q.3 B, E
Q.4 A, D
Q.5 C, E
Q.6 B, D
Q.7 C
Q.8 D
Q.9 D
Q.10 C
Q.11 B
Q.12 A

JEE Advanced/Boards

Exercise 1

Q.5

(A)


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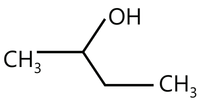

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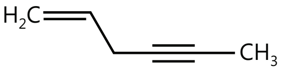

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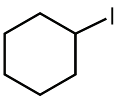

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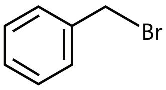
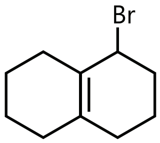


Q.8

(A)


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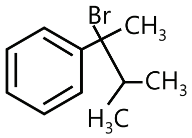

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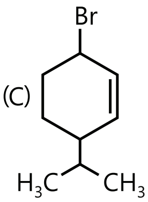

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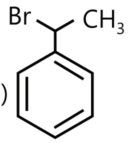
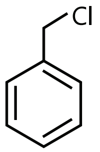


Q.10 (a)

(A)


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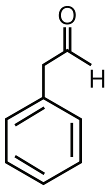

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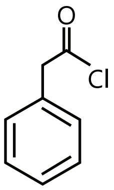

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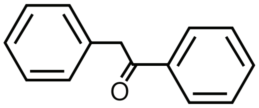

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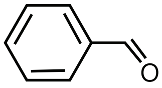

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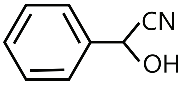

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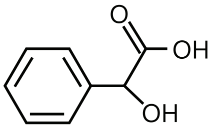

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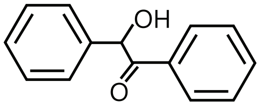

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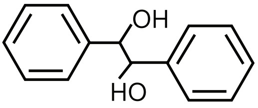
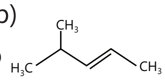


(b)

(A)


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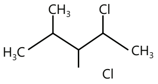

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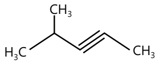

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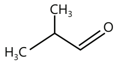
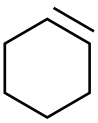
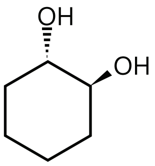


(c)

(A)


(B)


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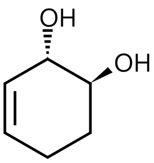

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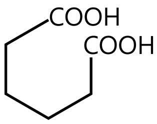

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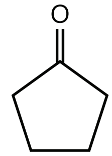
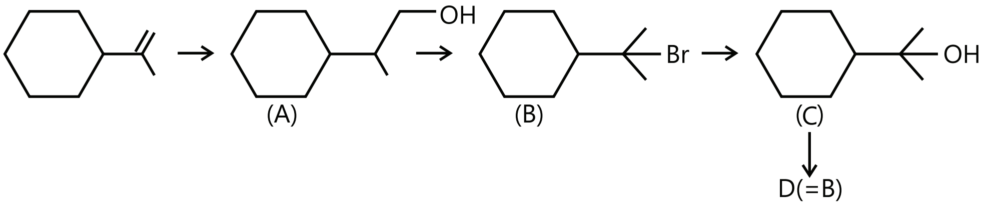
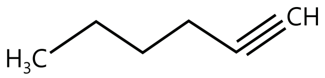


Q.11



Q.12

(A)


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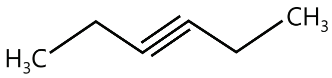

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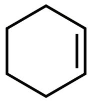
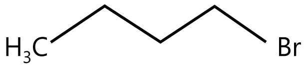


Q.13

(A)


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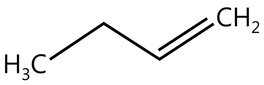

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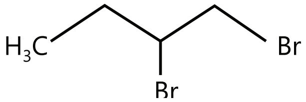

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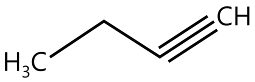
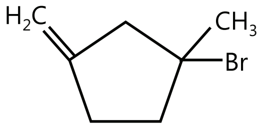
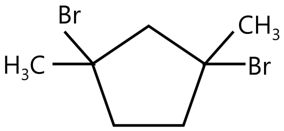
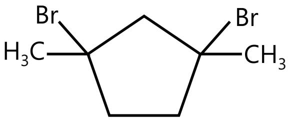
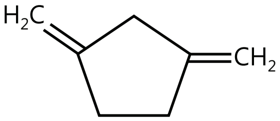


Q.14

(A)


(B)


(C)


(D)


Q.16

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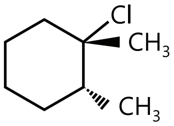

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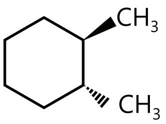

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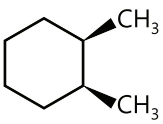

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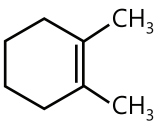
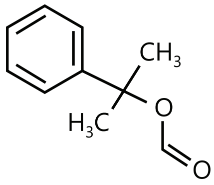
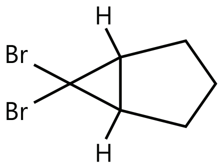
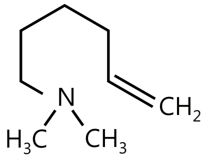
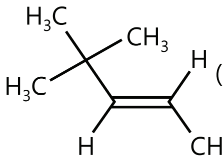


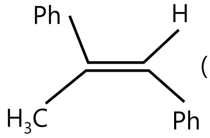
Q.17

(A) Racemic

S_N1

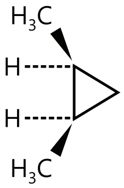
(B)

(Carbenoid cyclopropanation)

(C)

(Hofmann E_2)

(D)

(Saytzeff E_1)

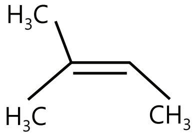
(E) 

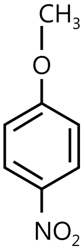
(E2)

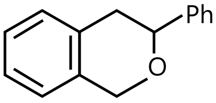
(F) 

(Singlet carbene cycloaddition)

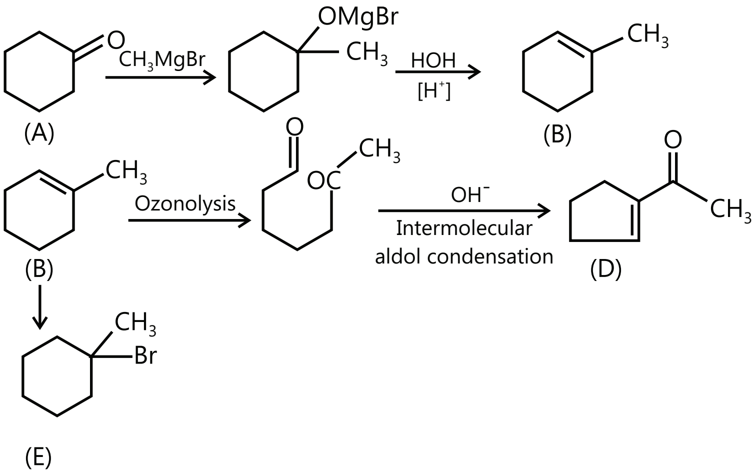
Q.18

(I) 

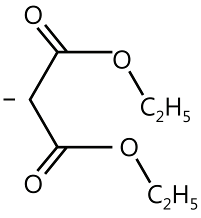
(II) 

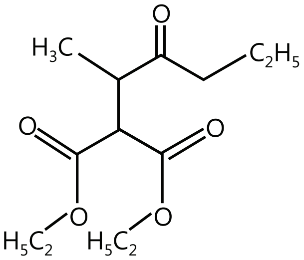
(III) 

Q.20

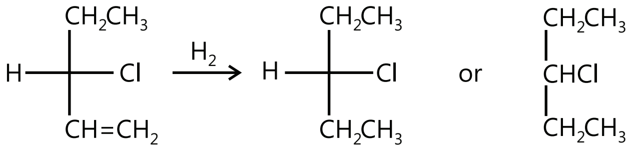


Q.23

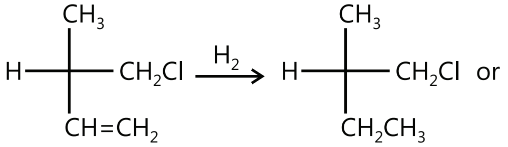




Q.26 The given statements suggest that (W) and (X) are as follows:

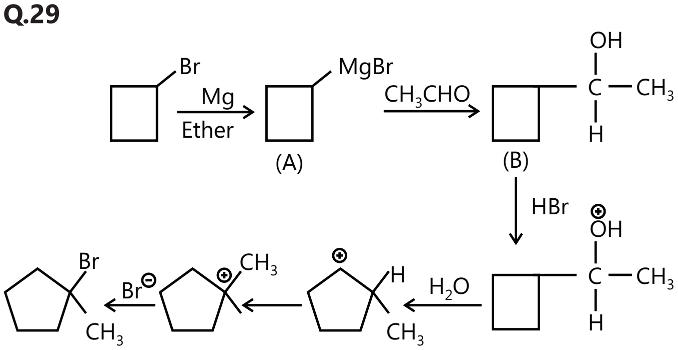


(W) Optically inactive (Y) (Structure of Y)



(X) Optically inactive (Z)

Q.29



Q.30 (1) The compound (X) has two isomers(Y) and (Z).

(2) The compound (X) has C, H and Cl atoms.

(3) % of Cl in (X) =71.72% ∴ Empiricial formula of (X) is CH_2Cl

Exercise 2

Single Correct Choice Type

Q.1 D	**Q.2** A	**Q.3** A	**Q.4** A	**Q.5** B	**Q.6** A
Q.7 B	**Q.8** A	**Q.9** B	**Q.10** A	**Q.11** D	**Q.12** C
Q.13 B	**Q.14** B	**Q.15** A	**Q.16** C	**Q.17** B	**Q.18** D
Q.19 B	**Q.20** B	**Q.21** B			

Assertion Reasoning Type

Q.22 A	**Q.23** B	**Q.24** A	**Q.25** C	**Q.26** D	**Q.27** B
Q.28 A	**Q.29** C	**Q.30** A			

Comprehension Type

Q.31 C	**Q.32** A	**Q.33** D	**Q.34** A	**Q.35** A	**Q.36** A
Q.37 A	**Q.38** B				

Single Correct Choice Type

Q.39 A,B **Q.40** A, D **Q.41** B, C, D **Q.42** A,D

Previous Years' Questions

Q.1 B **Q.2** A **Q.3** A **Q.4** A **Q.5** D, E

Q.6 A → q; B → q; C → r; D → p, s

Q.11 5 **Q.12** 8 **Q.13** B, C **Q.14** B **Q.15** B **Q.16** D

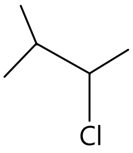
Q.17 C **Q.18** D **Q.19** 4 **Q.20** 5 **Q.21** B, C, D

Solutions

JEE Main/Boards

Exercise 1

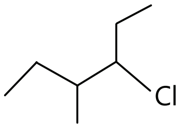
Sol 1: (i)



2-chloro-3-methylbutane

Alkyl 2°

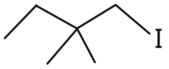
(ii)



3-chloro-4-methylhexane

Alkyl 2°

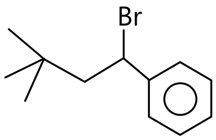
(iii)



1-Iodo-2,3-dimethylbutane

Alkyl 1°

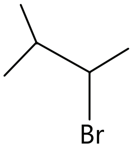
(iv)



3-Bromo-4-benzyl-2,2,-dimethyl butane

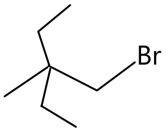
Benzyl 2°

(v)



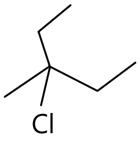
2-Bromo-3-methyl butane

Alkyl 2°

(vi)


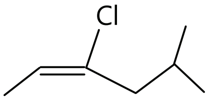
1-Bromo-2-ethyl-3-methylbutane

Alkyl 1°

(vii)


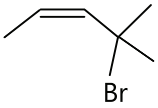
2-Chloro-2-ethyl butane

Alkyl 3°

(viii)


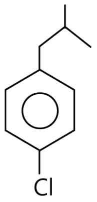
3-Chloro-5-methyl hex-2-ene

Vinyl 2°

(ix)


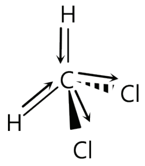
4-Bromo-4-methyl-pent-2-ene

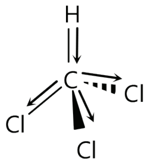
Alkyl 3°

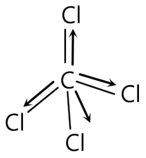
(x)


P-Chloro-sec phenyl butane

Benzyl 2°

Sol 2: (i)


(ii)


(iii)


vector addition in one direction

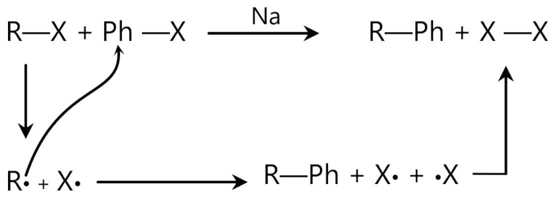
∴ Highest dipole addition

$\mu_2 > \mu_1 > \mu_3$

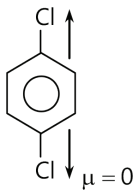
Sol 3: Ambident nucleophile have 2 or more than 2 sites to donate electron to the electrophile

Eg. $\overset{\ominus}{C} \equiv N:$ here C and N both are nucleophiles.

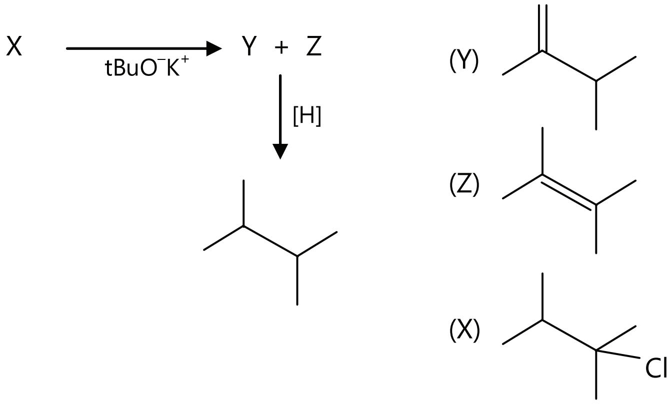
Sol 4: Wurtz-fittig reaction:



Sol 5: P-Dichlorobenzene



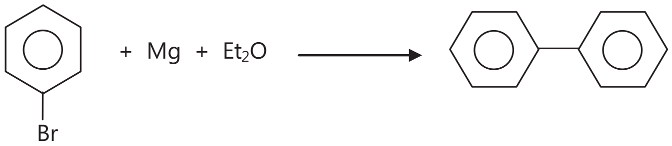
Sol 6:



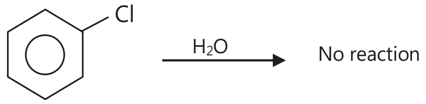
Sol 7:

(i)

(ii)



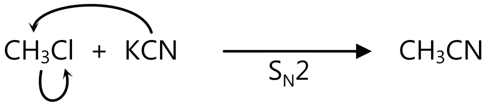
(iii)



(iv) $C_2H_5Cl + \text{Aq.KOH} \xrightarrow{S_N2} C_2H_5OH$

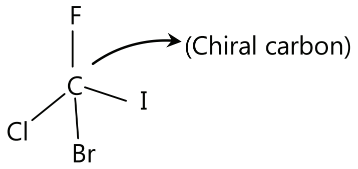
(v) $CH_3Br + Na + Et_2O \longrightarrow CH_3—CH_3$ Free radical substitution

(vi)

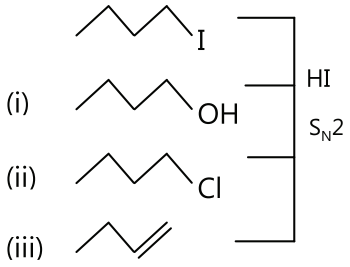


$CH_3Cl + KCN \xrightarrow[S_N2]{} CH_3CN$

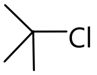
Sol 8: sp^3 hybridized carbon which have u different valency is a chiral or asymmetric carbon atom.



Sol 9:

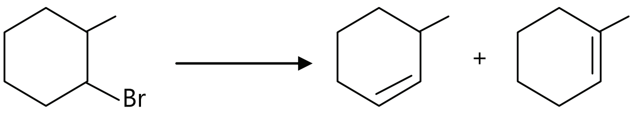


Sol 10: (i) $CH_3Br < CH_3I \longrightarrow$ better leaving group

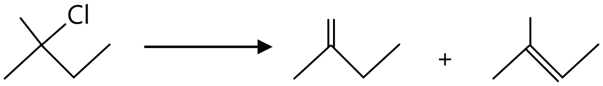
(ii)  $< CH_3Cl \longrightarrow$ sterically less hindered

Sol 11: Reagent: $EtO^- Na + EtOH$

(i)



(ii)



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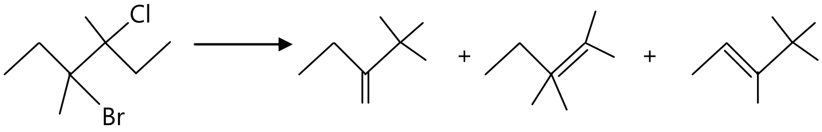


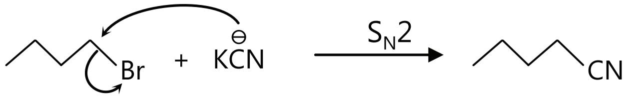
Sol 12: Freon 12 — refrigerant

DDT — insectiside, pesticide

CCl_4 — fire extinguisher

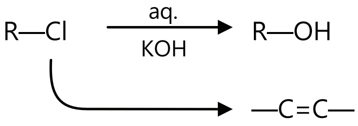
CHI_3 — disinfectant and in iodoform test

Sol 13:

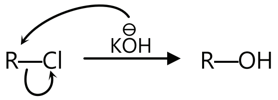


Sol 14: $C_6H_5CHClC_6H_5$ because 2 e^- withdrawing phenyl rings.

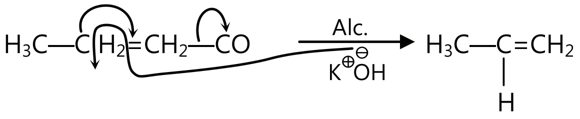
Sol 15:



Gives substitution reaction so, it will give



But Alc. KOH gives elimination reaction because $\overset{\ominus}{O}H$ is not polarized so it can directly attack. H_2O is formed

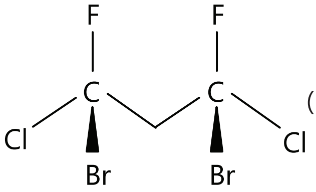


Sol 16: Intermolecular substitution reaction is known as S_N1 mechanism in which both nucleophile is in same molecule.

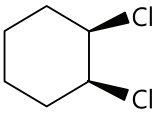
E.g. Darzen Process

$R—OH + SOCl_2 \quad R—Cl + SO_2 + HCl$

Sol 17: (a)



(b)

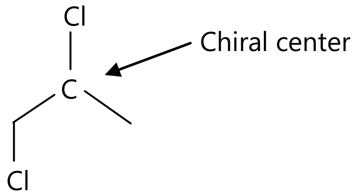


Sol 18: Refer theory.

Sol 19: (i) Halo alkanes have σ-bond so it is easily cleared but in haloarenes π-bond electrons get resonates so there will be π-bond character which requires high energy

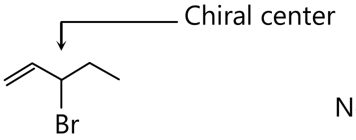
Sol 20:

(i)



No. of stereoisomers = 2

(ii)



No. of stereoisomers = 2

Sol 21: It is not necessary that a compound which have optically active carbon atom is wholely a optically active compound.

Sol 22:

$$\begin{tikzcd}
\text{EtOH} \arrow[r] \arrow[d, "\text{oxidation}"] & \text{CHI}_3 \\
\text{CH}_3\text{—CHO} \arrow[ru, "\text{NaOH} + \text{I}_2\ (\text{Iodoform reaction})"'] &
\end{tikzcd}$$

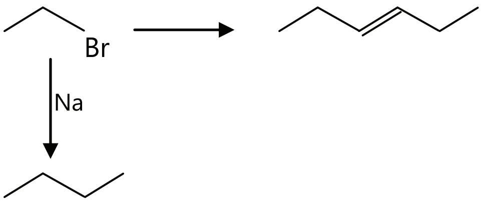
Sol 23: $CH_3Br \xrightarrow{KCN} CH_3CN$ methylcyanide

$\xrightarrow{AgCN} CH_3CN$ methylisocyanide

Sol 24: Refer theory.

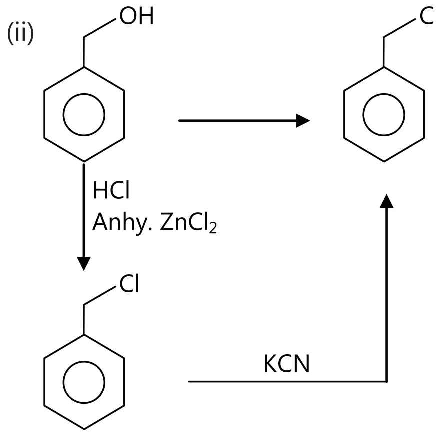
Sol 25: Refer theory.

Sol 26: (i)

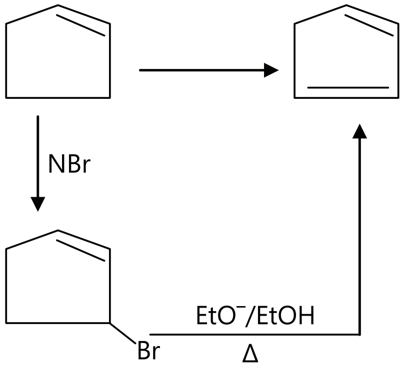


Cl is

(ii)

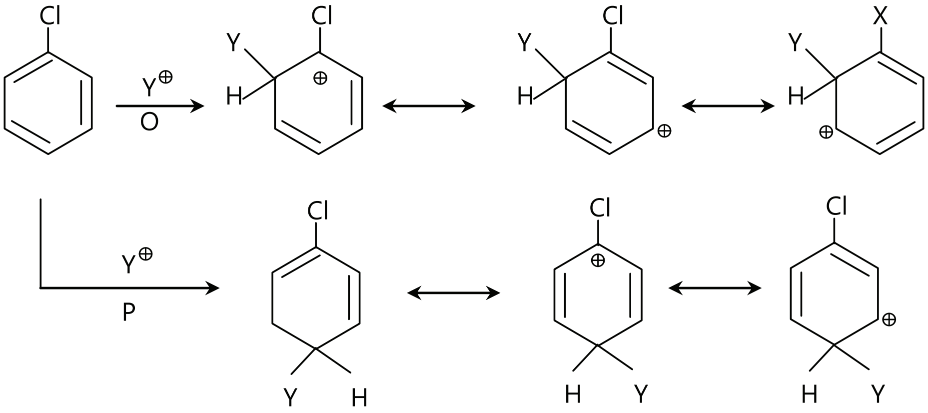


(iii)



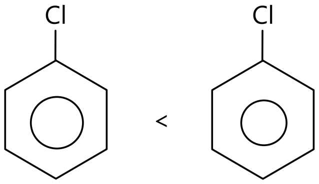
Sol 27: Swarts reactions: $R—Cl / R—Br \xrightarrow[Hg_2F_2]{} R—F$

Sol 28: In chlorobenzene, ortho-para is preferable position because when electrophile attacks on ortho or para position, it forms a stable intermediate.



stable complex formation

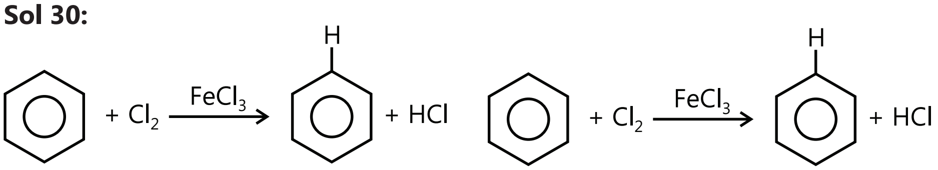
Sol 29: (i)



In chlorobenzene due to resonance of e^- s of Cl the C—Cl bond is getting less polarized while in cyclohexyl chloride there is no such effect seen

(ii) Alkyl halides are not soluble in water because they are unable to form hydrogen bonds with water.

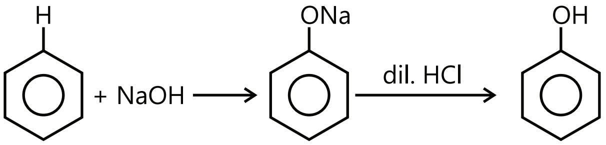
Sol 30:



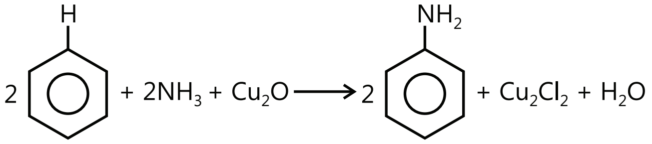
Sol 31: Properties

1. They are less reactive than haloalkanes

2. They can undergo replacement of halogen by hydroxyl group



3. Replacement by group.



Sol 32: Intermolecular substitution reaction is known as $S_N i$ mechanism in which both nucleophile is in same molecule.

Eg. Darzen Process

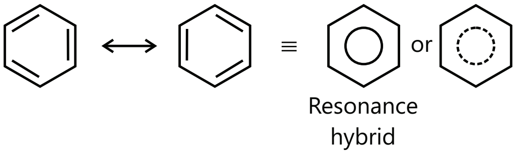
$$R—OH + SOCl_2 \longrightarrow R—Cl + SO_2\uparrow + HCl$$

Sol 33: Arenes: Compounds with pleasant smell and they are called aromatic compounds.

They contain benzene having ring of six carbon atoms. Later on, it was found that many compound having these benzene rings do not have pleasant smell.

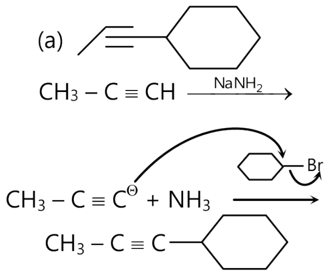
Arenes are benzene substituted compounds. So, the nomenclature is based on the position of group substituted which are named as ortho, meta, para.

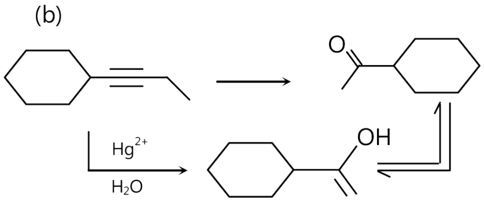
Sol 34:



Each carbon atom is sp^2 hybridised. Each carbon has 3 sp^2 hybrid orbitals lying in 1 plane at angle. There is one unhybridised p-orbital which participates in side ways overlapping to form $p\pi - p\pi$ bond. 2 hybridised orbital do axial overlapping with C atoms to form C – C σ bond and 1 to form C – H σ bond.

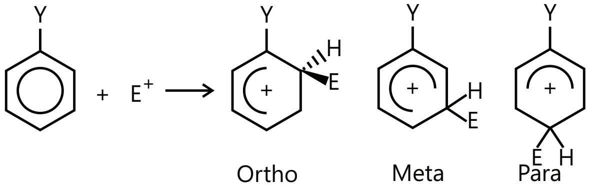
Sol 35:





Sol 36: Benzene is highly unsaturated because it is having 3C = C bond but because of its extra resonance stability, it is inert toward addition reaction & nucleophilic substitution but undergoes electrophilic substitution, like saturated alkanes.

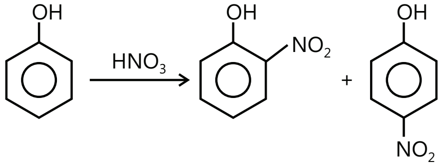
Sol 37:

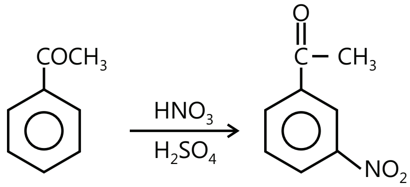


Sol 38: Substitution is influenced by the group already present in benzene ring. There are 2 types of groups

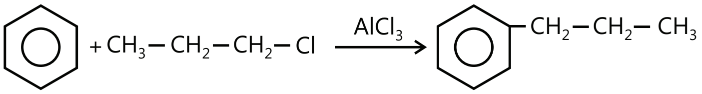
- Activators (O/P) directors

- Deactivators (m-directors)





Sol 39:



Exercise 2

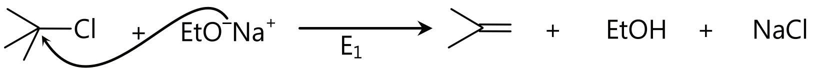
Single Correct Choice Type

Sol 1: (B) Good leaving group tendency is the driving force

$\therefore CH_3I > CH_3Br > CH_3Cl > CH_3F$

Sol 2: (D) Hydrolysis of 3° alkane is preferable by S_N1 mechanism because of the carbocation stability(D)

Sol 3: (C)



(Mechanism)

Sol 4: (C) Pyrene contains CCl_4

Sol 5: (C)

$$CH_3CH_2NH_2 \xrightarrow{HNO_2} \overset{(X)}{CH_3CH_2OH} + H_2O + N_2$$

$$\downarrow SOCl_2$$

$$(Y)\quad CH_3CH_2Cl + SO_2 + HCl$$

$$\downarrow NH_3$$

$$(Z)\quad CH_3CH_2NH_2 + HCl$$

Ethanamine

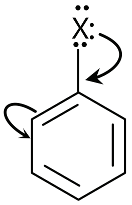
Sol 6: (B) 1. I^- is better leaving group so no reaction

2. E1

3. S_N2

4. E1

Sol 7: (B)

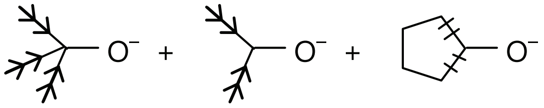


Sol 8: (D) HBr will give step (I) while Br_2 will give 2Br groups in step (I) only.

1° alkyl halide so S_N2 substitution(B) peroxide will cause allyl substitution

Sol 9: (B) More electron density than high nucleophilicity. More electron density than high more +I effect, high e^- density.

Sol 10: (A)



Sol 11: (C) For S_N2 1° > 2° > 3°

Thus order of decreasing reactivity towards S_N2 reaction is

$$\underbrace{CH_3CH_2CH_2Cl > (CH_3)_2CHCH_2Cl}_{1^\circ} > \underbrace{CH_3CH_2CHClCH_3}_{2^\circ} > \underbrace{(CH_3)_3CCl}_{3^\circ}$$

Sol 12: (A) $CH_3I \xrightarrow{KCN} CH_3CN \xrightarrow{[H]} CH_3CH_2NH_2$

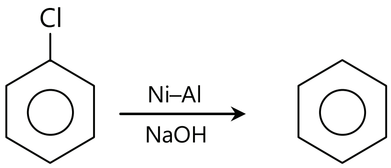
(A) (B)

Sol 13: (B) $AgNO_2$ has a covalent bond

$\hookrightarrow Ag–O–N=O \xrightarrow{RI} R–NO_2$ (B)

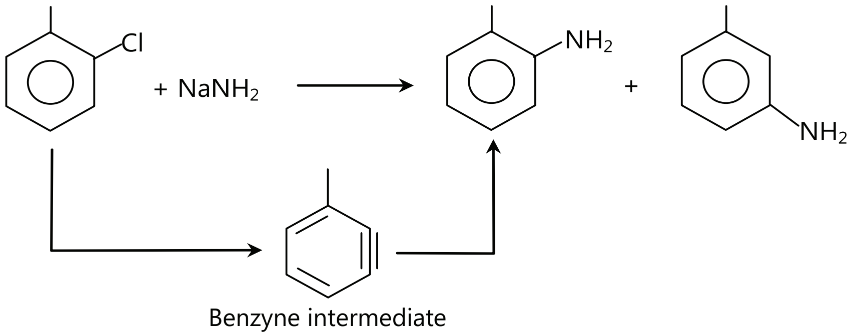
attacking site

Sol 14: (B)

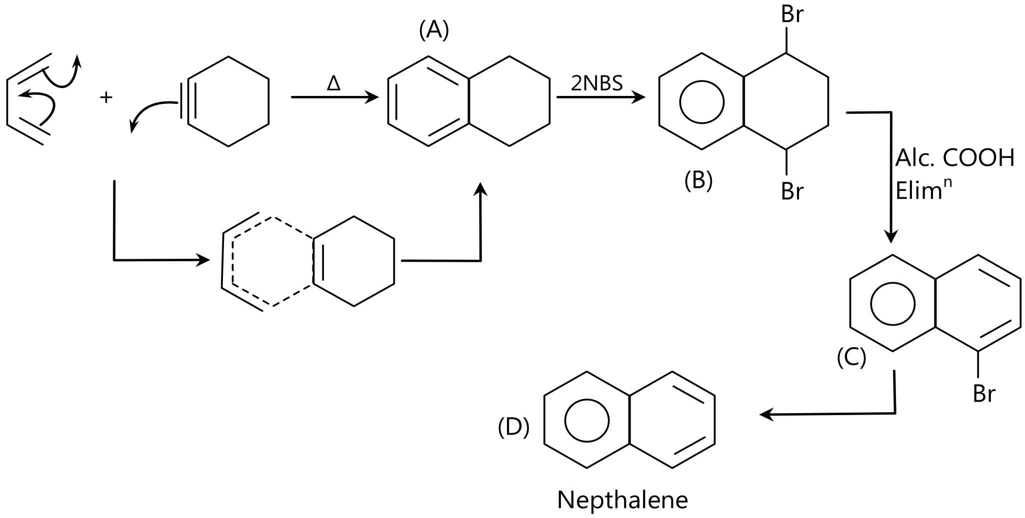


Sol 15: (D) Least electron deficient carbon site

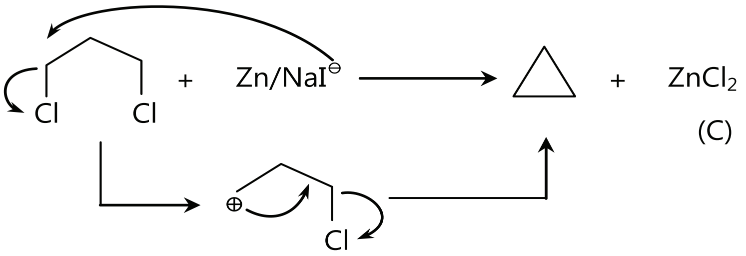
Sol 16: (B)



Sol 17: (D)



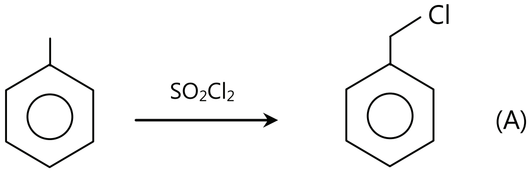
Sol 18: (C)



Sol 19: (C) S_N2 – seteroselective – Attack on specific site

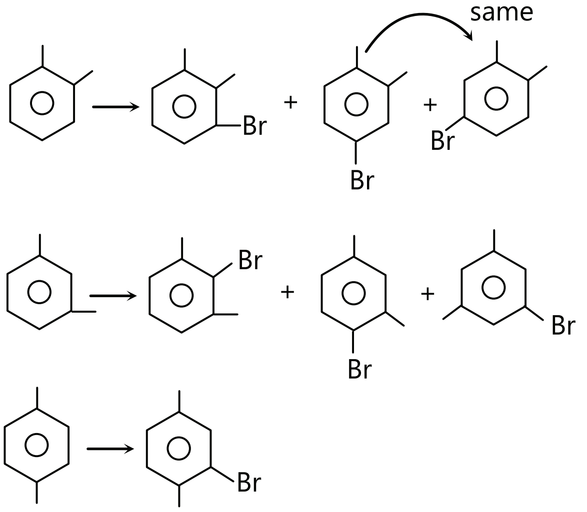
Stereospecific – Only one configuration formed

Sol 20: (A)

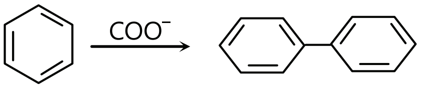


Free radical mechanism

Sol 21: (B)

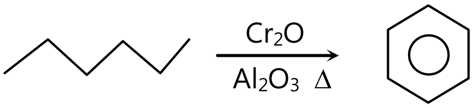


Sol 22: (A)

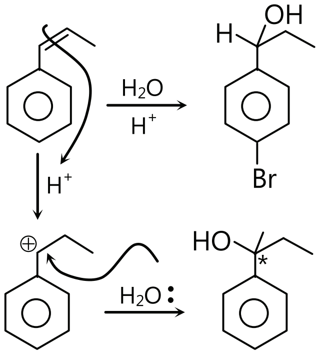


Dimerization of benzene.

Sol 23: (C)



Sol 24: (D)

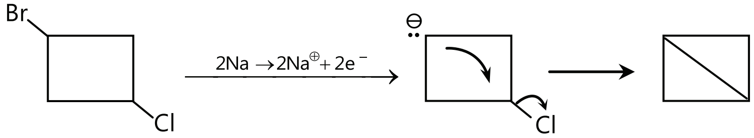


Both optically active isomer so reacemic mixture. Planar carbocation attack can be from both up and down.

Previous Years' Questions

Sol 1: (A) CH_3Cl have one Cl atom which is more electronegative so it will have highest dipole moment.

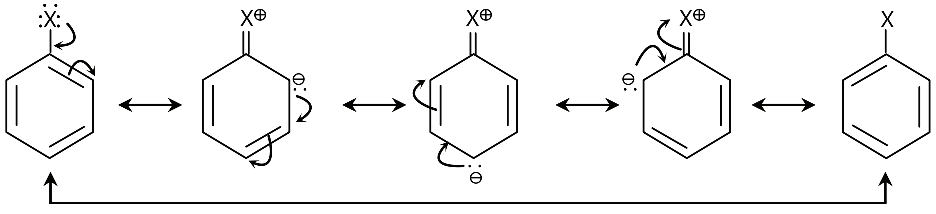
Sol 2: (D) It is the example of Wurtz reaction.



Sol 3: (B, E) Aryl halide are less reactive towards nucleophilic substitution reaction as compared to alkyl halide due to following reasons

(B) Resonance stabilization

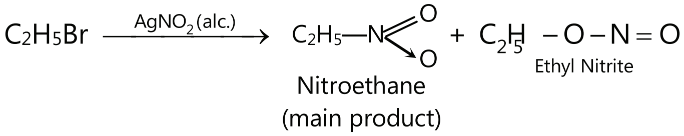
(E) sp^2-hybridized carbon attached to the halogen.



Resonating structures of aryl halide

Sol 4: (A D) NH_3 and dichlorodifluoro methane are used as refrigerant.

Sol 5: (C E)

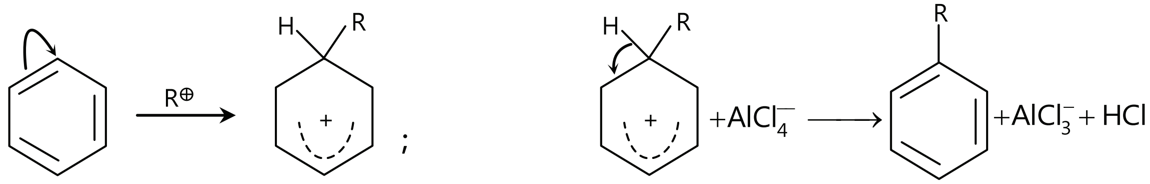


$$C_2H_5Br \xrightarrow{AgNO_2\,(alc.)} \underset{\text{(main product)}}{\underset{\text{Nitroethane}}{C_2H_5-N\overset{O}{\underset{O}{\lessdot}}}} + \underset{\text{Ethyl Nitrite}}{C_2H_5-O-N=O}$$

The main product of this reaction is nitroethane but ethylnitrite is also formed as a side product along with silver bromide.

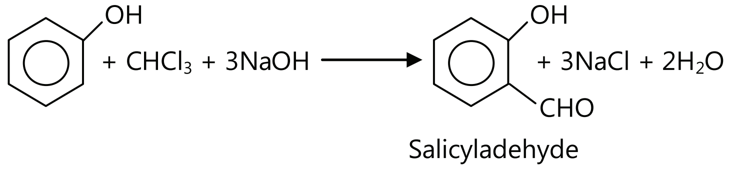
Sol 6: (B, D) New carbon-carbon bond formation take place in Friedel Craft's alkylation following mechanism involve

$R-Cl + AlCl_3 \rightleftharpoons \underset{\text{Alkyl carbonium ion}}{R^{\oplus}} + AlCl_4^{\ominus} + HCl$



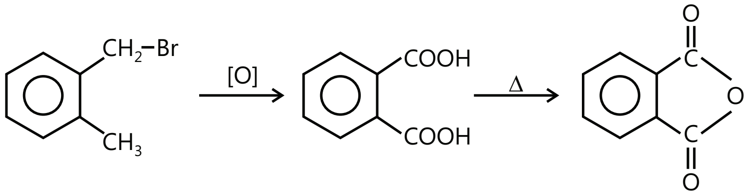
Here new C—C bond formed between carbon of benzene ring and alkyl group.

Similarly, in Reimer-Tiemann reaction.



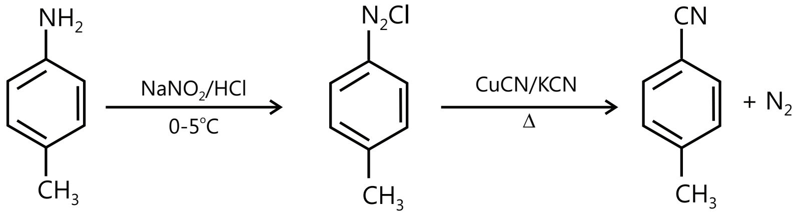
Sol 7: (C) Hexane is very unreactive with no non polar bond.

Sol 8: (D)

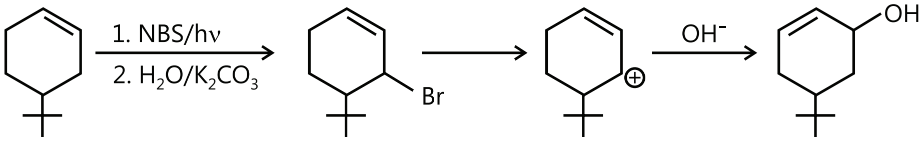


Sol 9: (D) $R-I+agF \rightarrow R-F+AgI$ (Swarts Reaction)

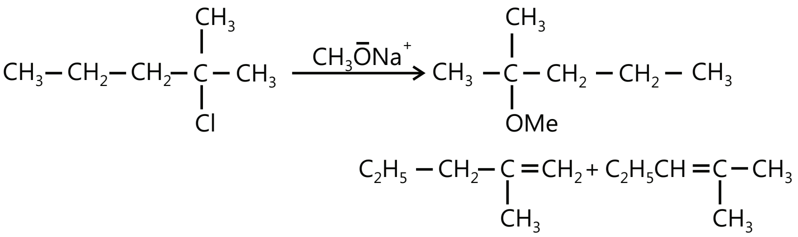
Sol 10: (C)



Sol 11: (B)



Sol 12: (A)



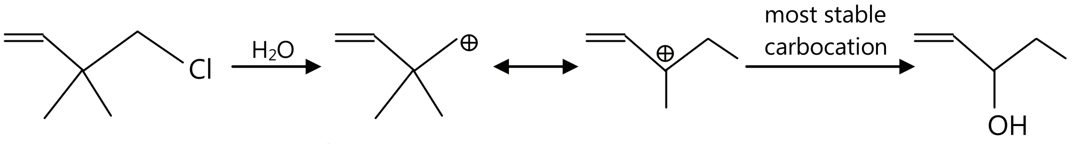
$$CH_3-CH_2-CH_2-\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \xrightarrow{CH_3\bar{O}Na^+} CH_3-\underset{\underset{OMe}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_2-CH_3$$

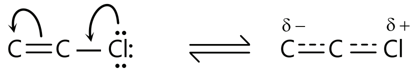
$$C_2H_5-CH_2-\underset{\underset{CH_3}{|}}{C}=CH_2 + C_2H_5CH=\underset{\underset{CH_3}{|}}{C}-CH_3$$

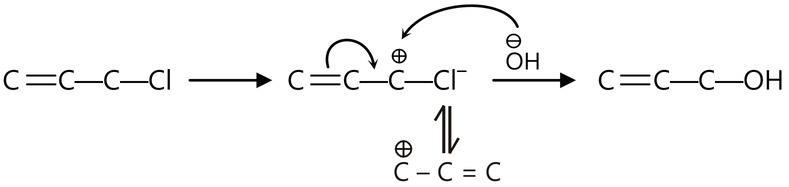
JEE Advanced/Boards

Exercise 1

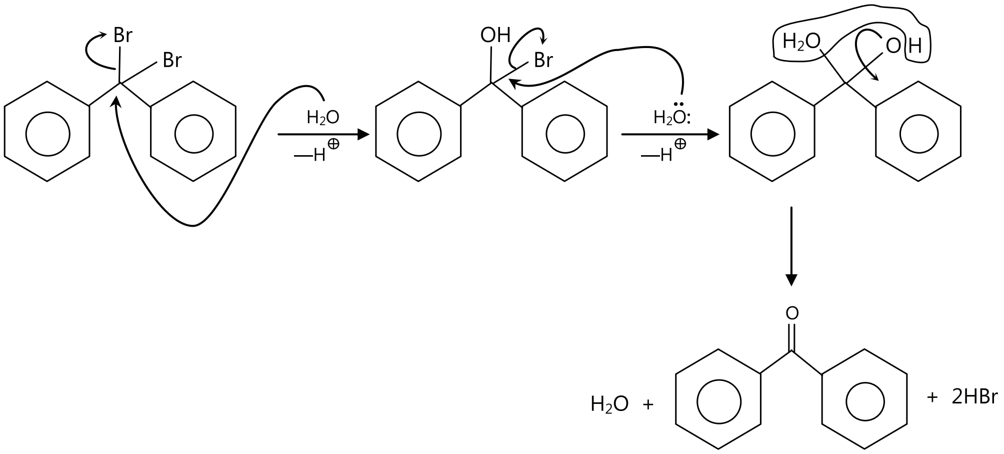
Sol 1:



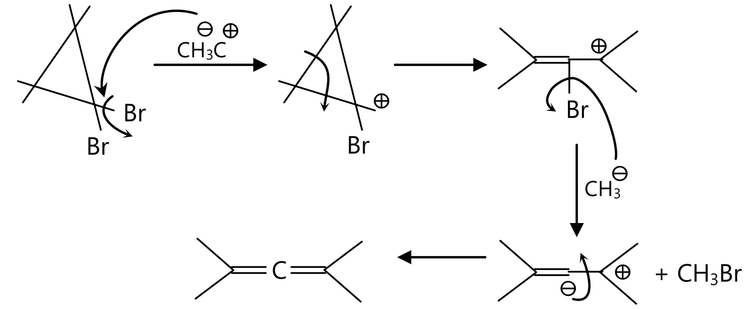
Sol 2: Vinyl chlorides eg.  have double bond character in C—Cl bond because of which it requires high energy to cleave that bond and substitute the reset one but in alkyl chlorides gives S_N AE mechanism or S_N1 because reaction they form stable carbocation.



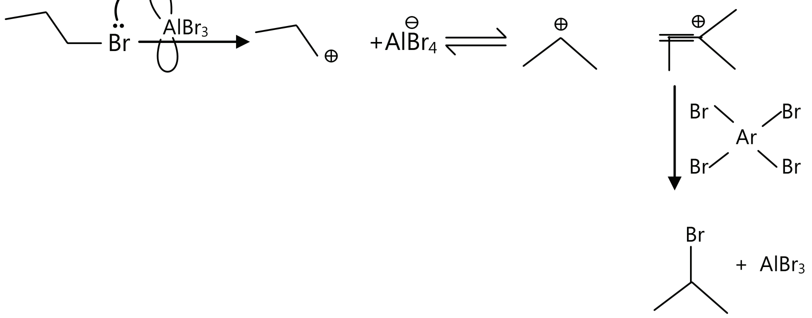
Sol 3: (A)



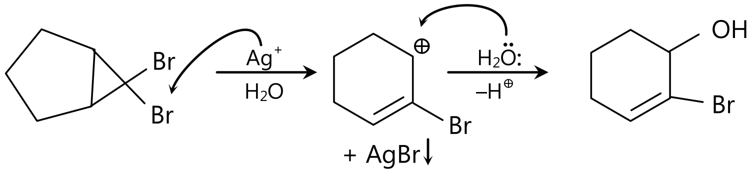
(B)



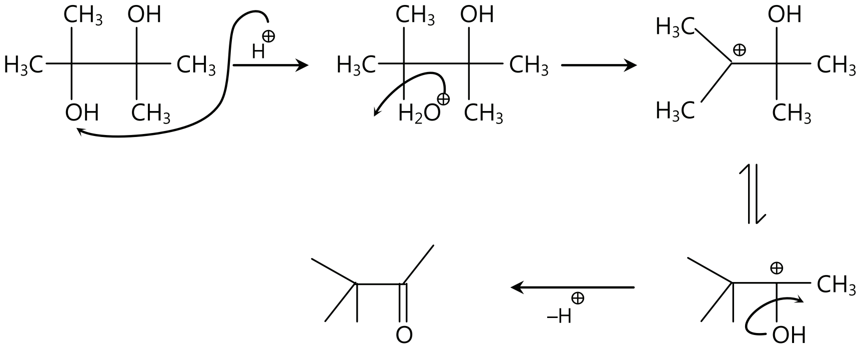
(C)



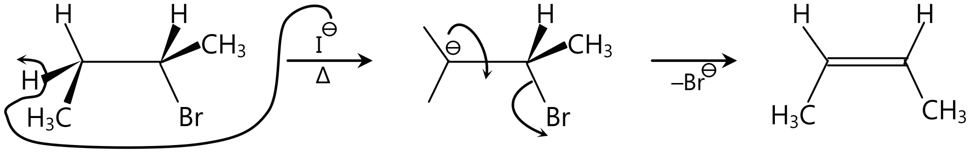
(D)



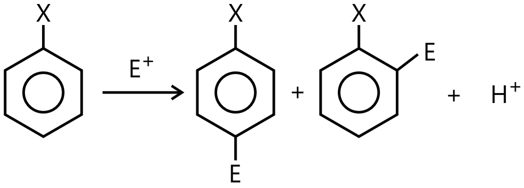
(E)

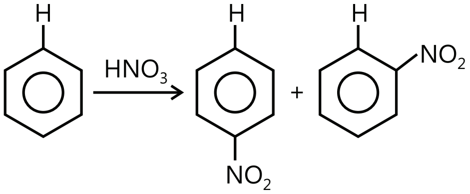


(F)



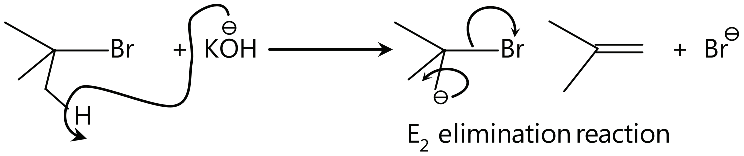
Sol 4:





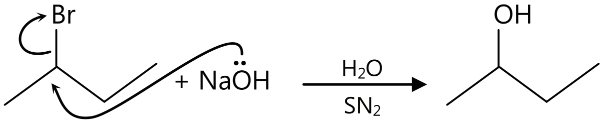
E_2 elimination reaction

Sol 5: (a)

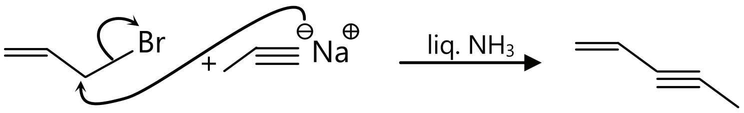


E_2 elimination reaction

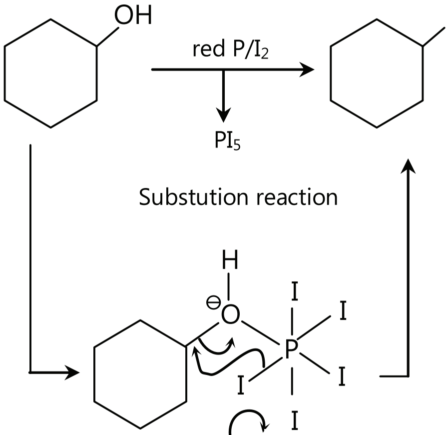
(b)



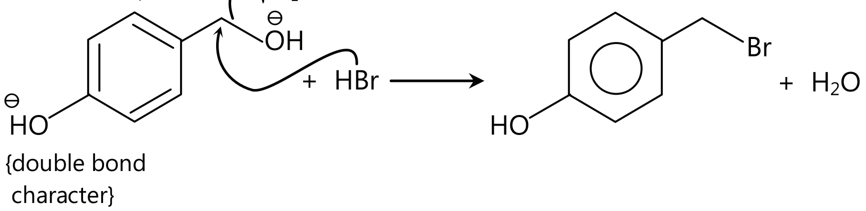
(c)



(d)

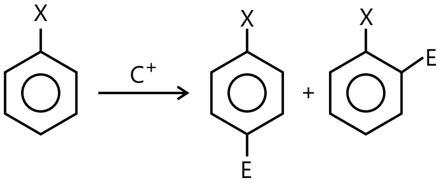


(e)

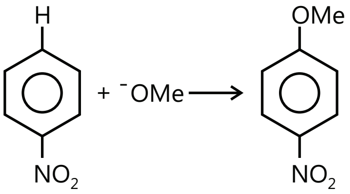


So substitution will be take place at site (1)

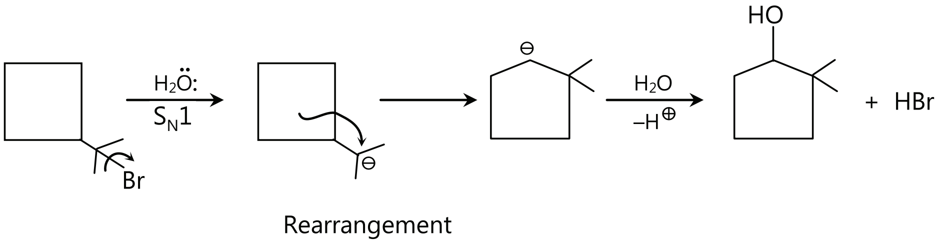
Sol 6: (a) Electrophie Aromatic Substitution



(b) Addition Elimination



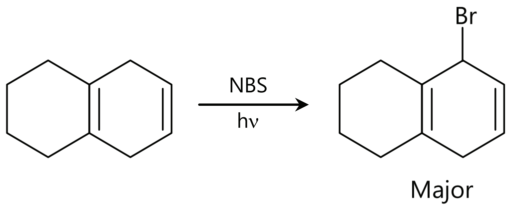
Sol 7:



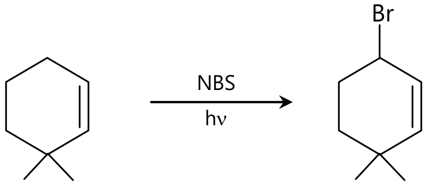
Sol 8: Reagent - NBS

Reaction - Bromination of allylic and benzylic carbon

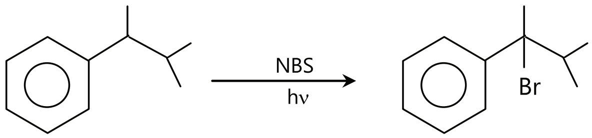
(a)



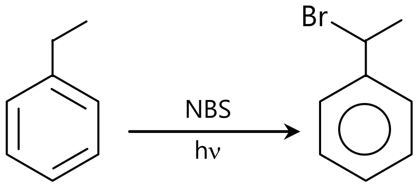
(c)



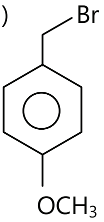
(b)



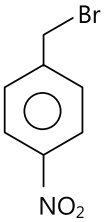
(d)



Sol 9: (a) (1)

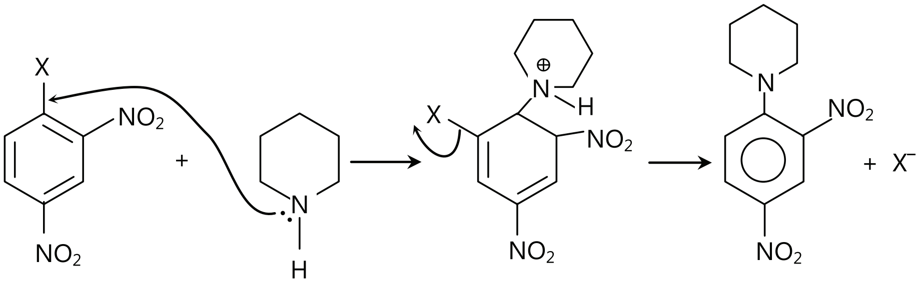


(2)



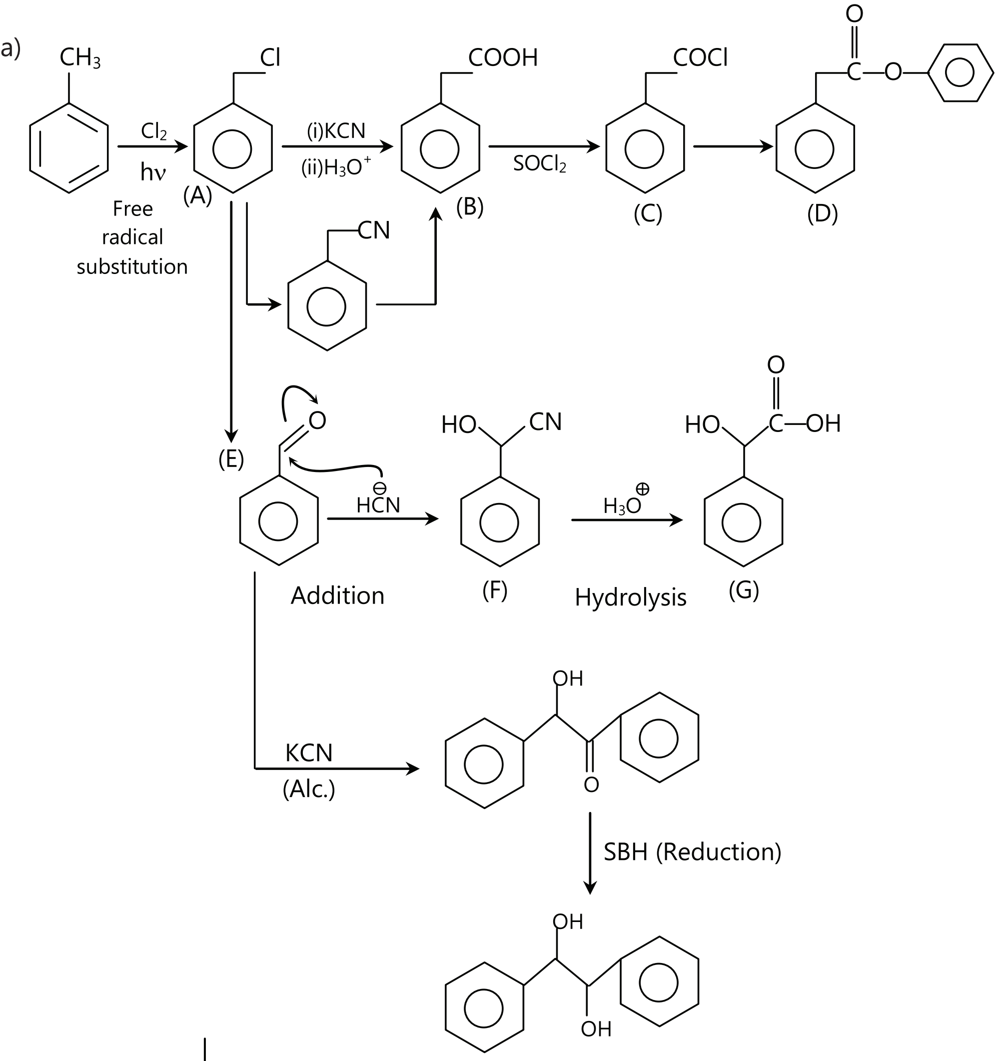
Carbon (1) has more $e^{\ominus}$ density than (2) so bond of C_1—Br is weaker than C_2—Br so it get cleaned easily.

(b)

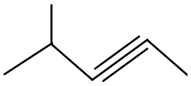


F creates make better nucleophile site due to its light electronegativity than I

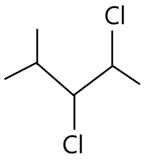
Sol 10: (a)



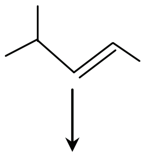
(b) (C) C_6H_{10} (≡ bond)



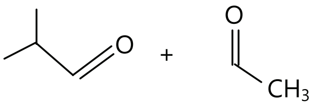
(B)



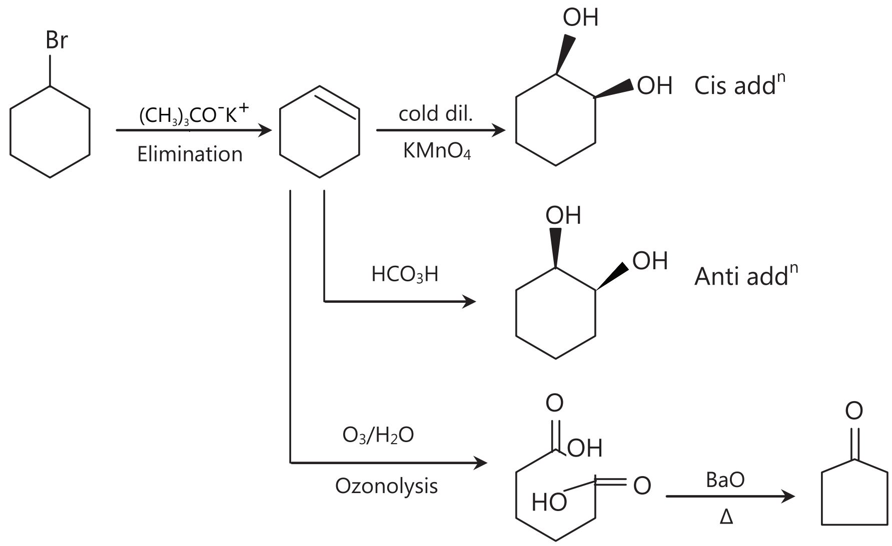
(A)



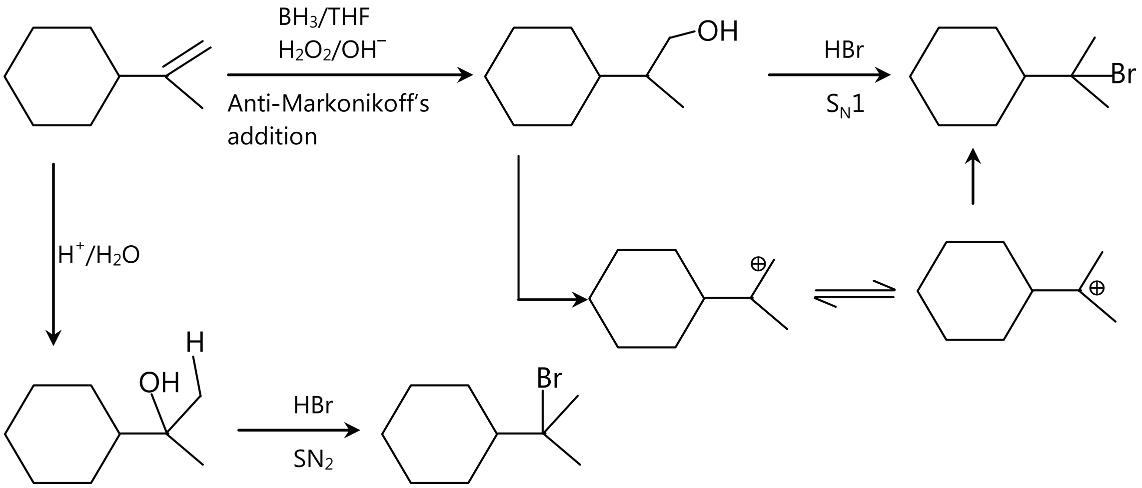
(D)



(C)



Sol 11:



Sol 12: A, B, C ⟶ C_6H_6

Br_2/CCl_4 decolorisation ⟶ –C = C– present

soluble in cold con.H_2SO_4 ⟶ –OH present

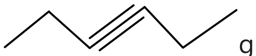
A ⟶ terminal alkyne

A,B simple chain compound

C ⟶ ring with double bond

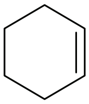
∴ A ⟶

B ⟶

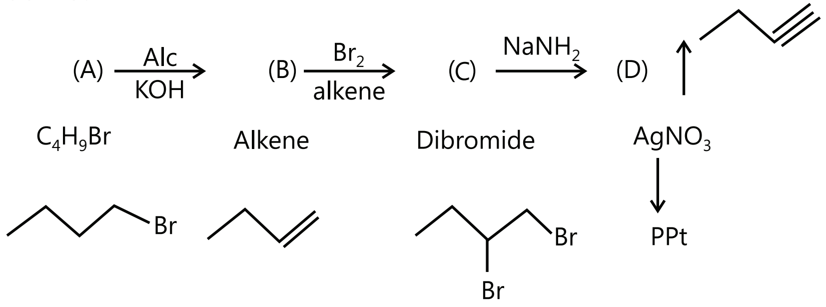


gives symmetry cleavage during ozonolysis

C ⟶

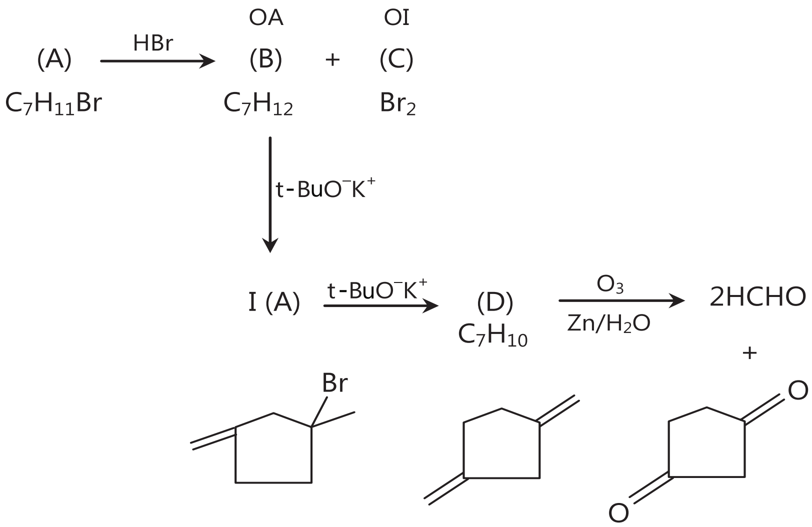


Sol 13:

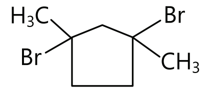


Terminal alkyne gives ppt. with amm. $AgNO_3$

Sol 14:

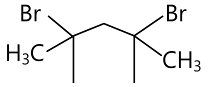


(A) ≡



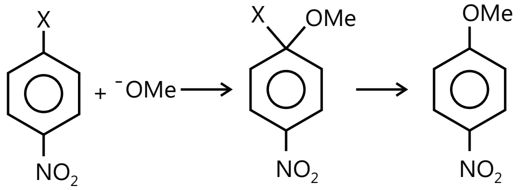
opt. active

(B) ≡

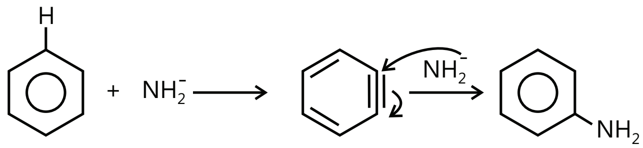


opt. inactive

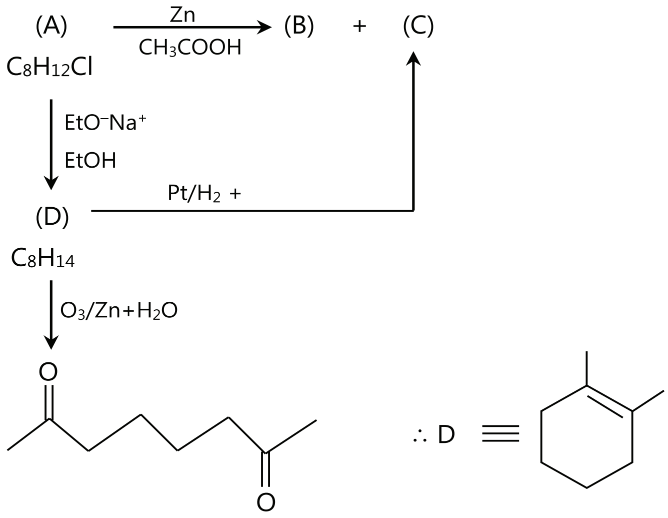
Sol 15: (a) Addition Elimination



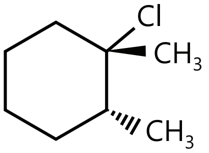
(b) Elimination Addition



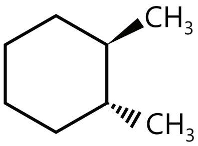
Sol 16:



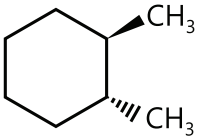
A =



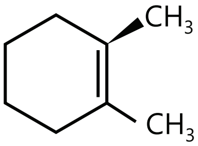
B =



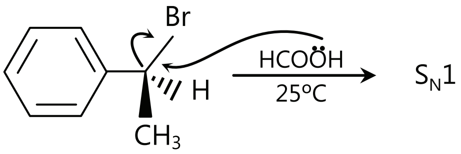
C =



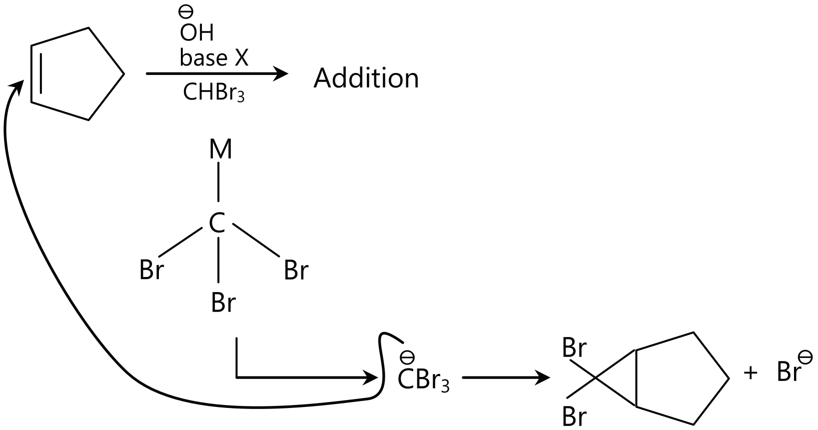
D =



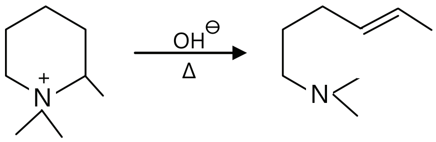
Sol 17: (A)



(B)

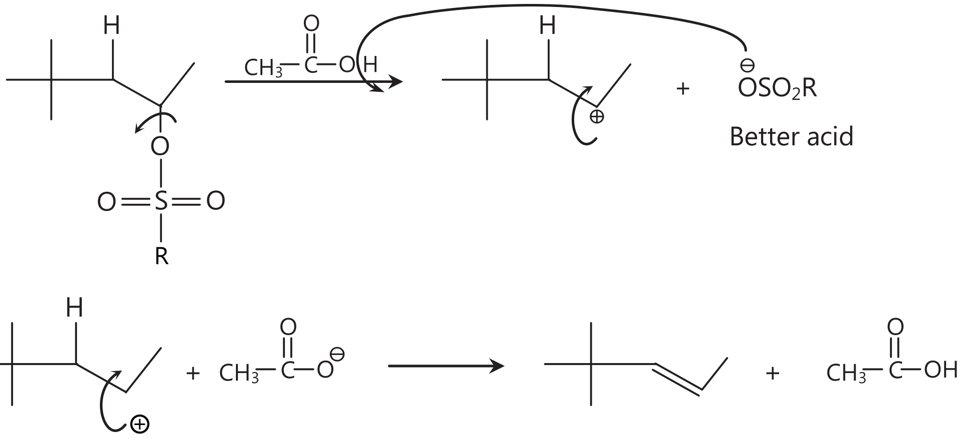


(C)

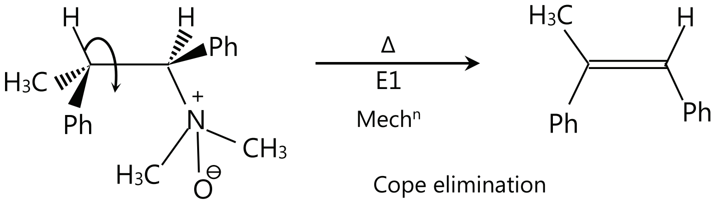


Elimination (E2) Hoffmann

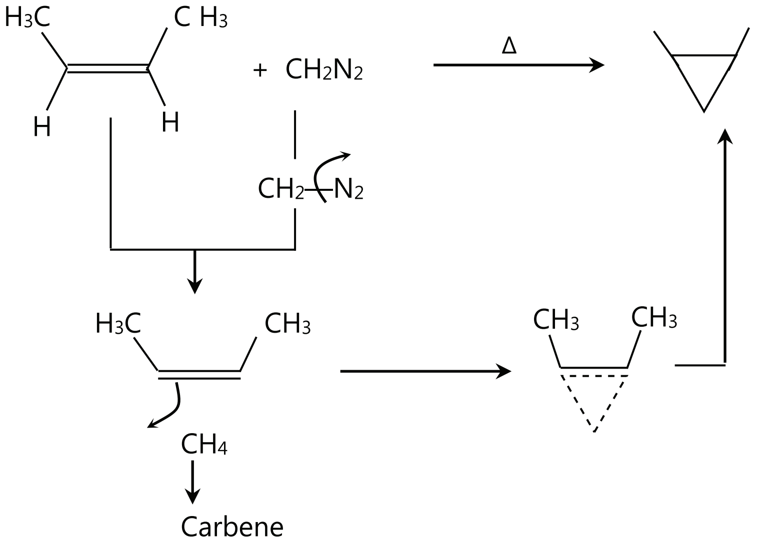
(D)



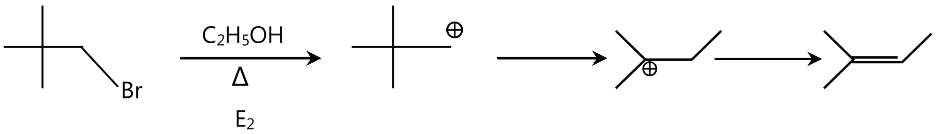
(E)



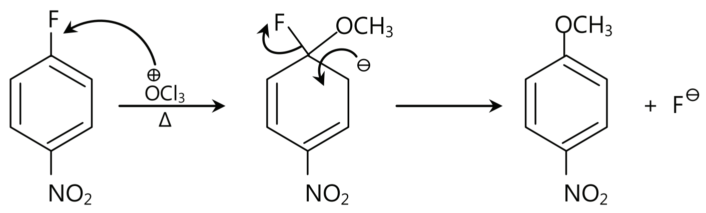
(F)



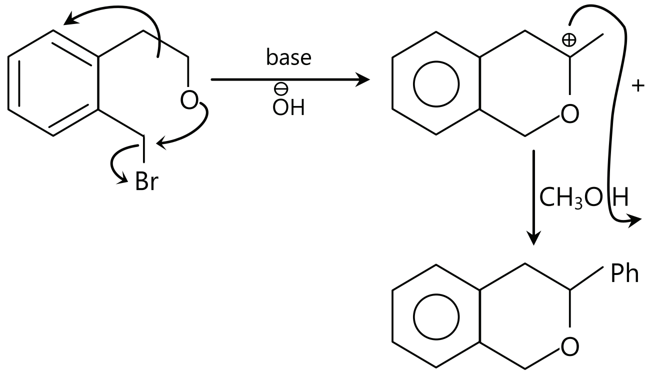
Sol 18: (i)



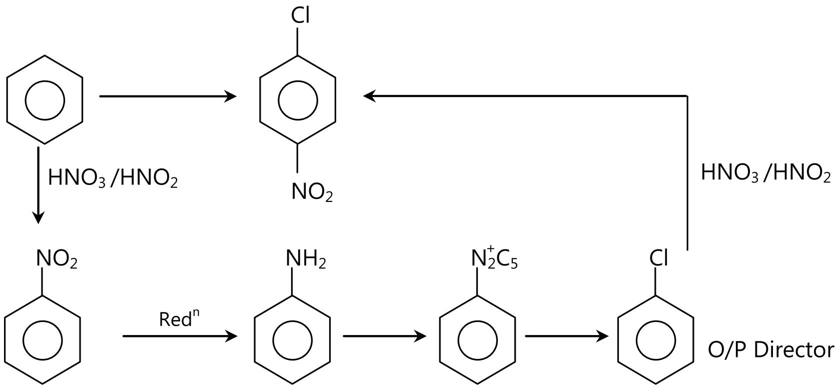
(ii)



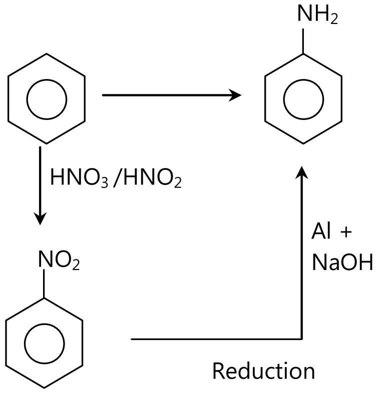
(iii)



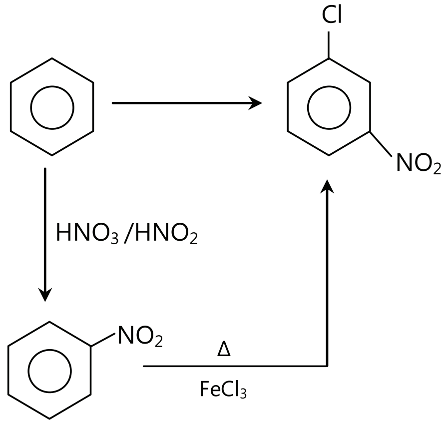
Sol 19: (i)



(ii)

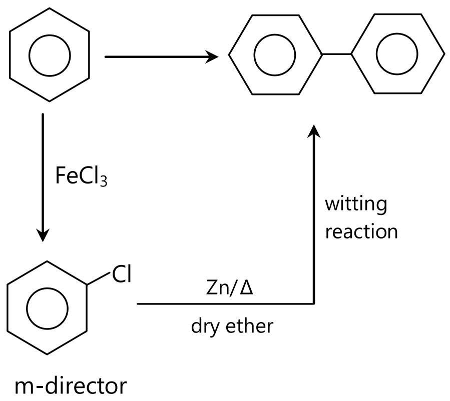


(iii)

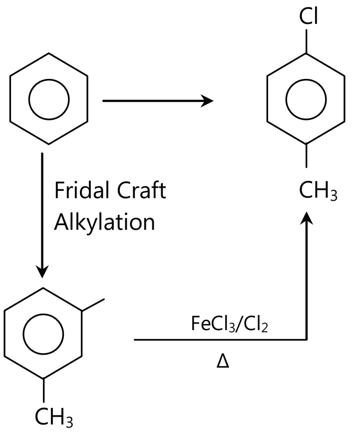


m-director

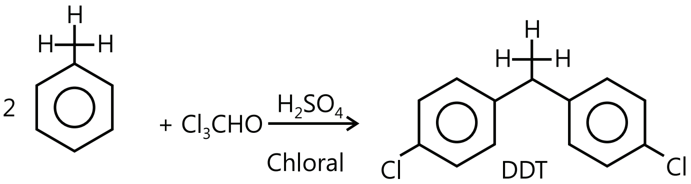
(iv)



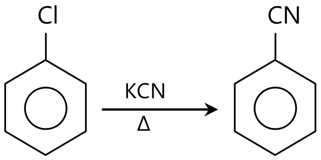
(v)



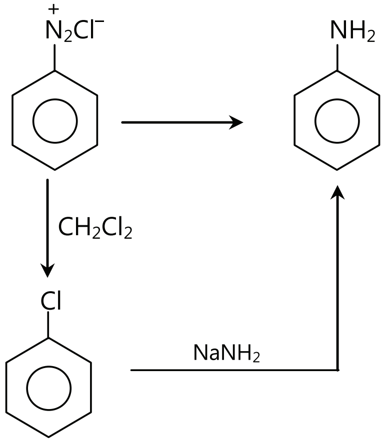
(vi)



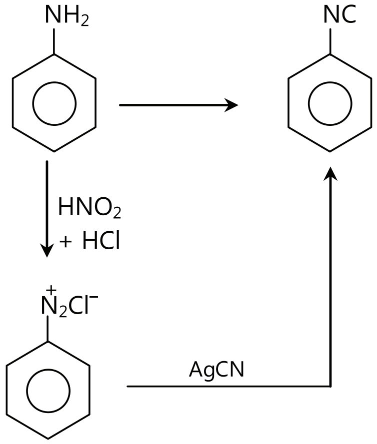
(vii)



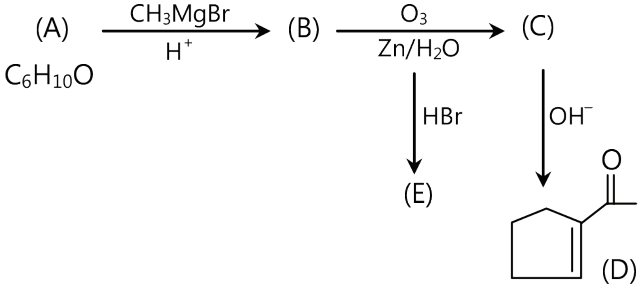
(viii)



(ix)



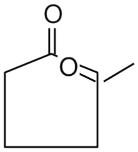
Sol 20:



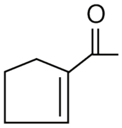
(C) $\longrightarrow$ (D)

Intramolecular Aldol reaction

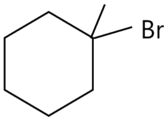
∴ (C) $\longrightarrow$



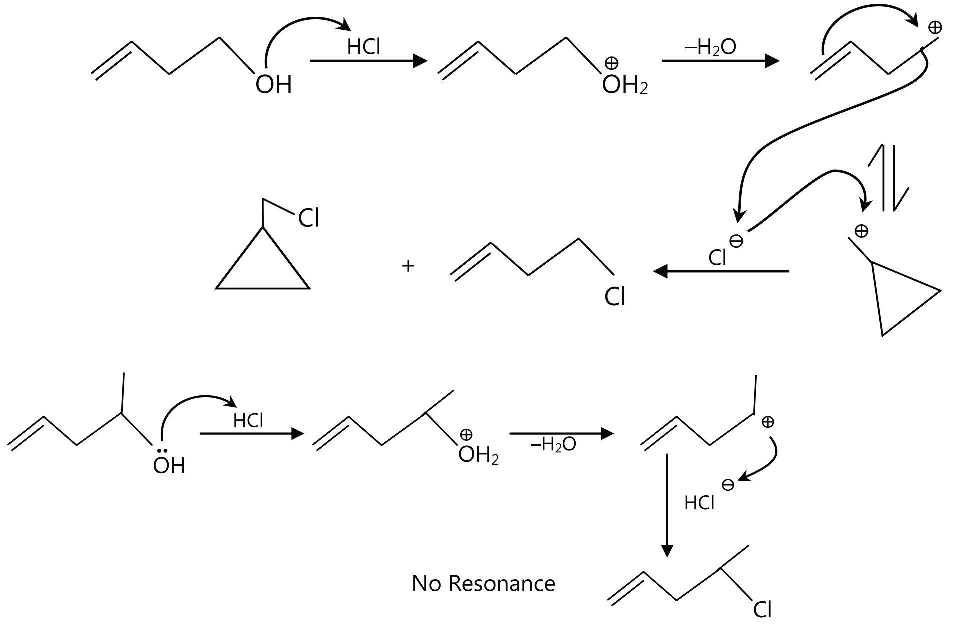
(D)



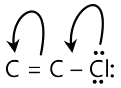
(E)

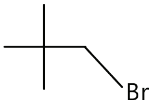


Sol 21:

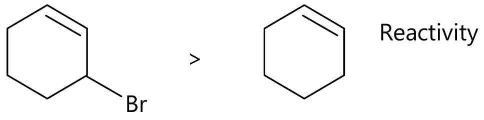


Sol 22: (i) Vinyl chloride do not undergo SN reaction because of double bond character due to resonance.



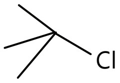
(ii) 

can’t go S_N2 because satirically hindered site and for S_N1 also it is not a stable carbocation initially.

(iii) 

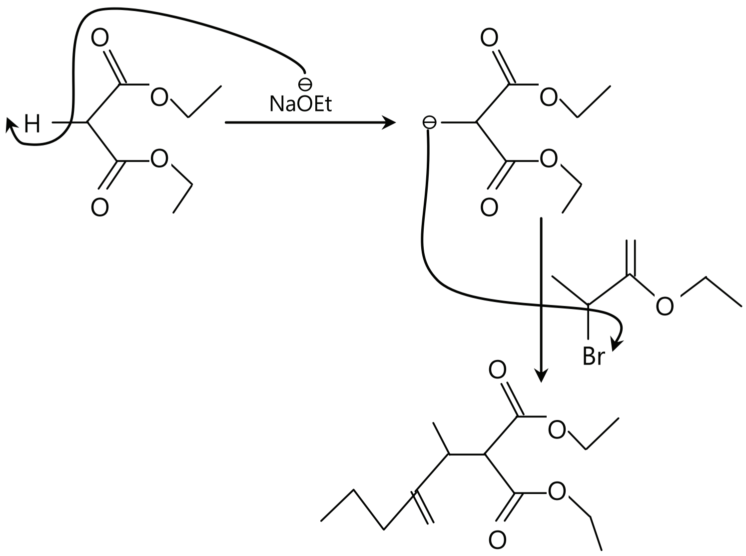
(I) (II)

Because intermediate of (I) is resonance stabilized while (II) there is only +I effect.

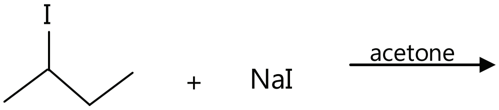
(iv) 

$\xrightarrow[\text{NaOH}]{\text{Ag.}}$ S_N1 3° halides undergo S_N1 mechn became S_N2 is restricted till less satirically hindered site And 3° carbocation is more stable than 1°.

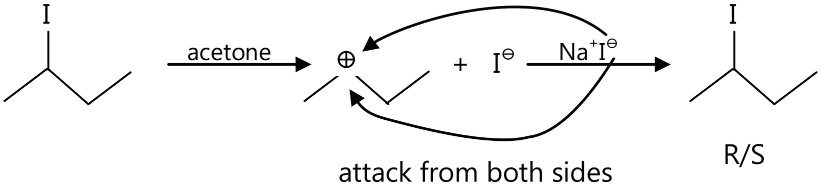
Sol 23:



Sol 24:



It will go via S_N1 mechanism

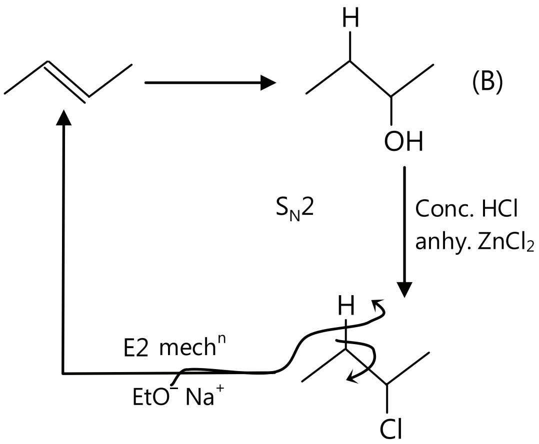


Racemic mixture

Sol 25:

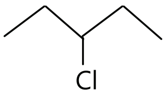
$$\begin{tikzcd} \underset{C_4H_8}{(A)} \arrow[r, "\text{dil. } H_2SO_4"] & (B) \arrow[r, "\text{Conc. HCl}", "ZnCl_2"'] & (C) \arrow[ll, bend left, "EtO^-Na^+"] \end{tikzcd}$$

A should be  treat in with dil. H_2SO_4 via add^n

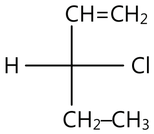


Sol 26:

$$\begin{tikzcd} OA & & OA & \\ W \arrow[d, "H_2"] & + & X \arrow[d, "H_2"] & C_5H_9Cl \\ y & & Z & \\ OI & & OA & \end{tikzcd}$$

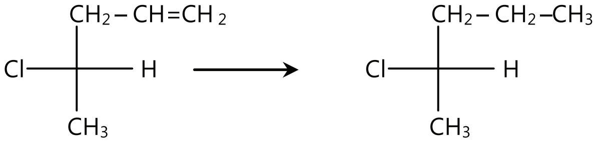
Y 

Optical inactive

W 

$$W: \; H - \overset{CH=CH_2}{\underset{CH_2-CH_3}{C}} - Cl$$

$$X \xrightarrow{H_2} Z$$



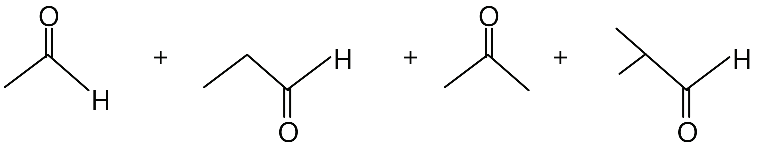
$$Cl - \overset{CH_2-CH=CH_2}{\underset{CH_3}{C}} - H \longrightarrow Cl - \overset{CH_2-CH_2-CH_3}{\underset{CH_3}{C}} - H$$

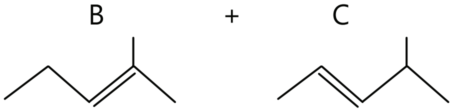
Sol 27:

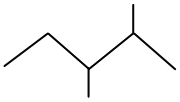
$$\begin{tikzcd} A \arrow[r, "Hot.\ alc."', "KOH"] \arrow[d, "AgNO_3"] & B\ (C_6H_{12}) + C \\ \text{White ppt} & \end{tikzcd}$$

2 isomeric alkenes

$$\xrightarrow{O_3,\ Zn/H_2O}$$



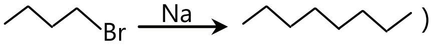


A $\longrightarrow$ 

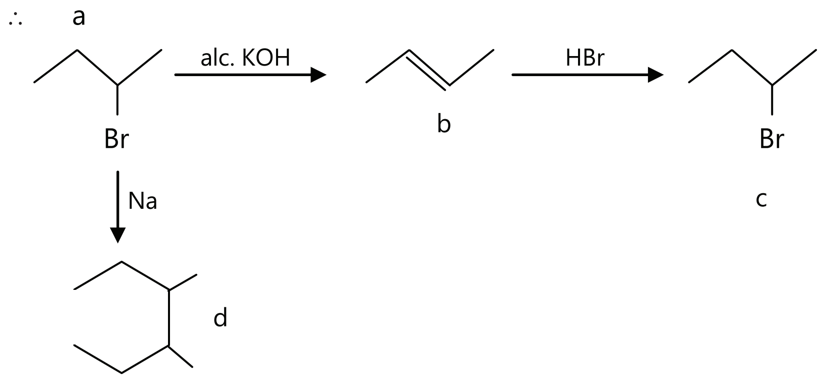
Sol 28:

$$\underset{a}{C_4H_9Br} \xrightarrow{alc.\ KOH} b \xrightarrow{HBr} c \quad \text{(isomer of a)}$$

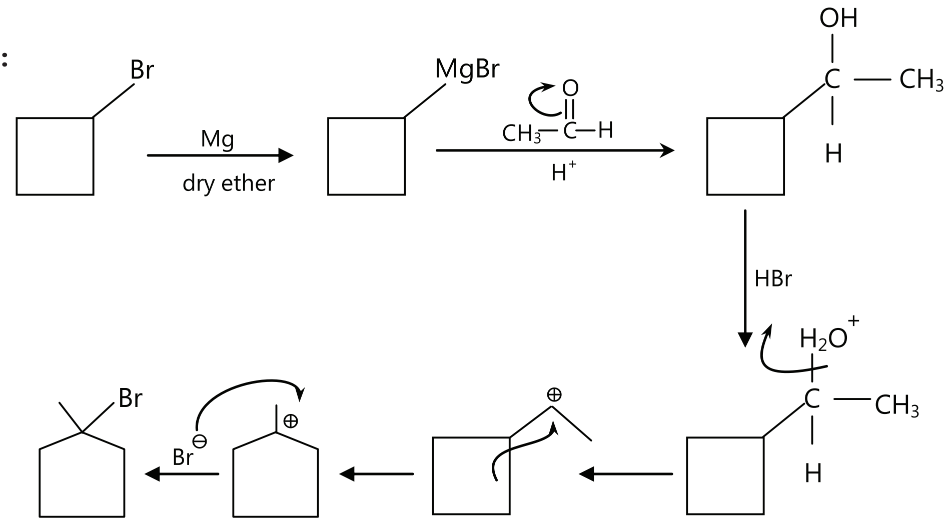
$$a \xrightarrow{Na} d \quad C_8H_{18}$$

d C_8H_{18} (not same as )

∴



Sol 29:



Sol 30: $X \longrightarrow$ 24.24% C

4.04% H

∴ 71.72% Cl

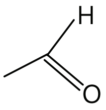
$\downarrow$

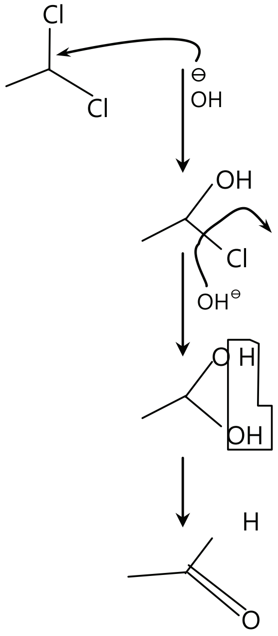
2.9 gmof AgCl (2 moles)

Y + Z

Y $\xrightarrow{\text{aq. KOH}}$ dihydroxy compound

Z $\longrightarrow$ Ethanol

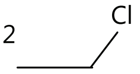




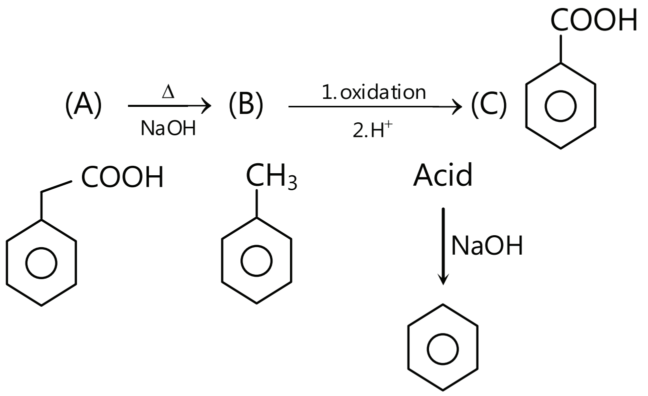
So X $\longrightarrow$ CH_2Cl (Empirical formula)

∴ X $\longrightarrow$ $C_2H_4Cl_2$

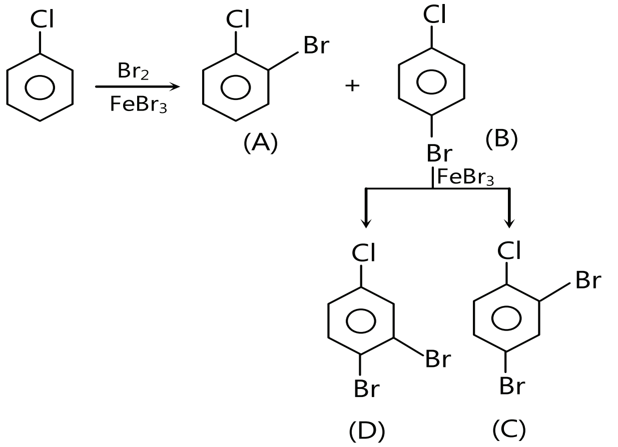
4 2



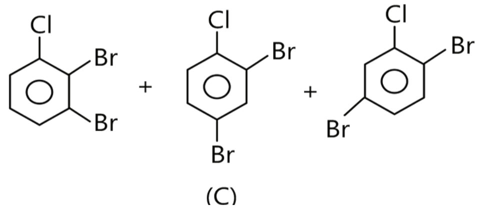
Sol 31:



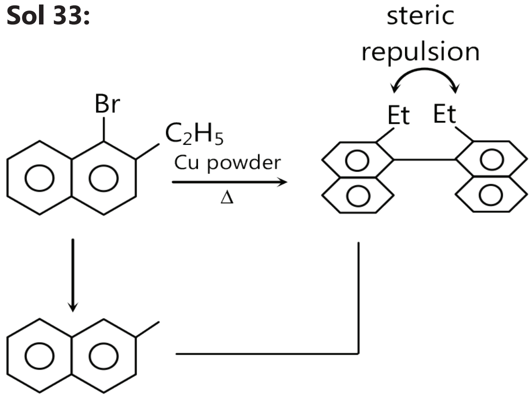
Sol 32:



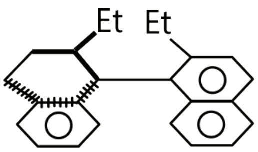
Bromination product of (A) :



Sol 33:

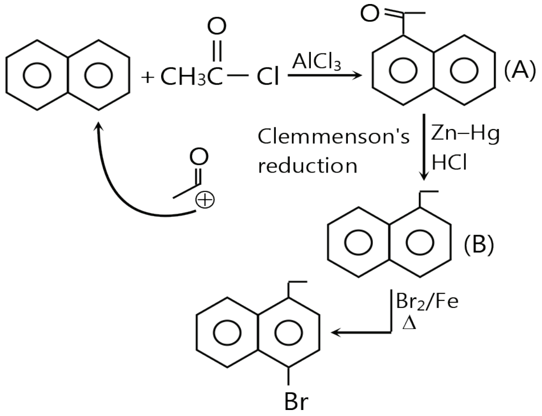


Stereochemistry :

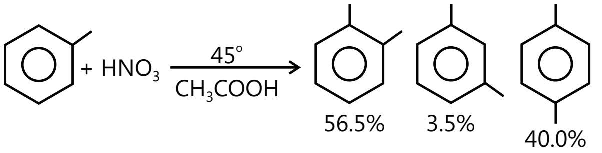


Both rings are in different planes so optically active.

Sol 34:



Sol 35:

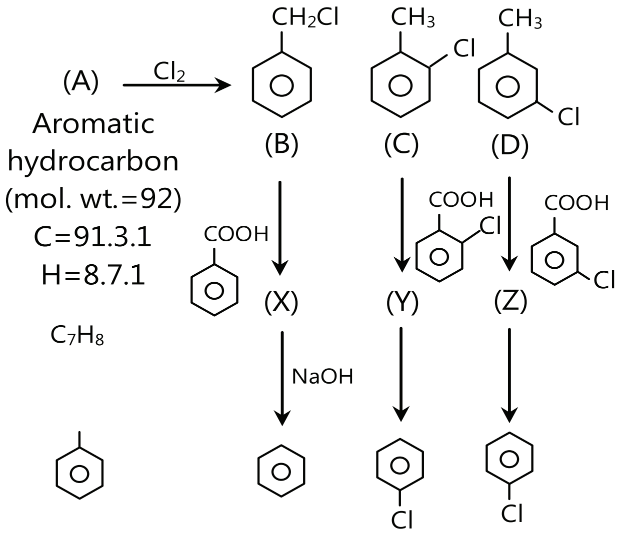


since $-CH_3$ group is electron donating group it will activate the ring and rate of reaction will be more for toluene than benzene $-CH_3$ group show +I effect so it will be distance dependent and it is –o/–p director.

Ortho position will be more activated than para.

% product : (ortho > para) >> meta

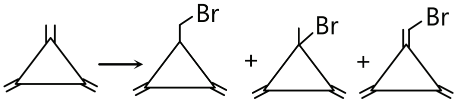
Sol 36:



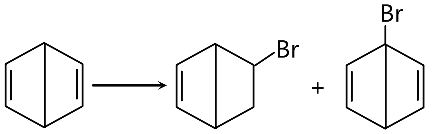
Sol 37: t-butyl benzene is very much reaction than benzene due to strong +I og t-butyl group. Value for nitration at Para position is the withiest due to big size of butyl group which Coues stearic hindrance at or the position

Sol 38:

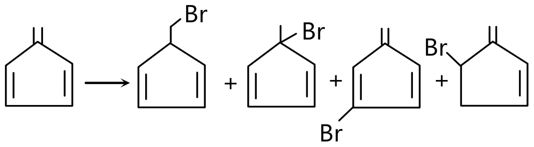
(a)



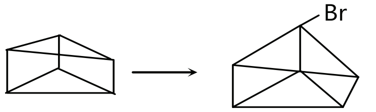
(b)



(c)

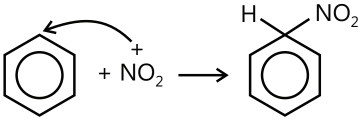


(d)



All positions
are symmetric

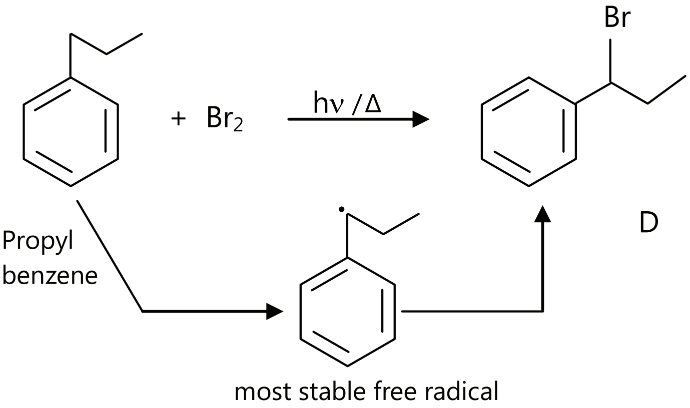
Sol 39: $HNO_3 + 2N_2SO_4 \rightarrow \overset{+}{N}O_2 + 2NSO^{-}{}_4 + H_3O^{+}$



Exercise 2

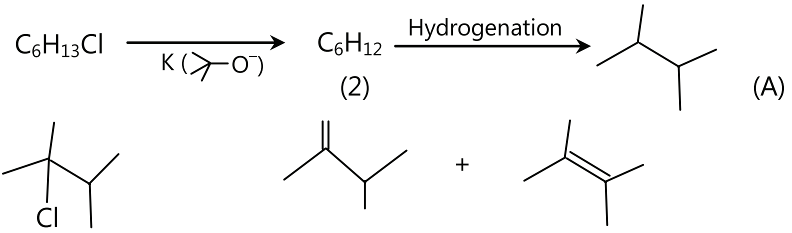
Single Correct Choice Type

Sol 1: (D)

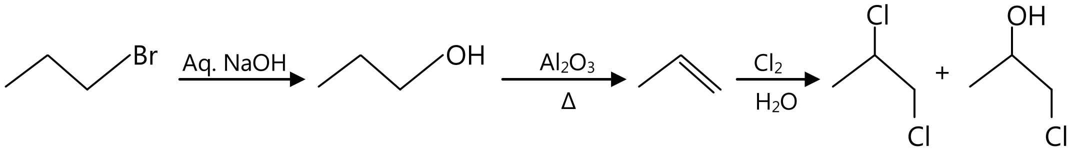


Sol 2: (A) Most electron deficient side will attract OH^- towards it and $–NO_2$ group show –M-effect (A)

Sol 3: (A)



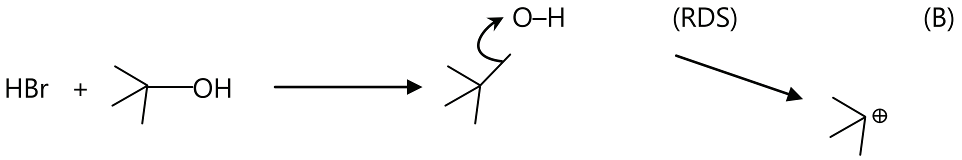
Sol4: (A)



Sol 5: (B) Stable group have high livability tendency A <<< B (Resonance) (B)

Sol 6: (A) High polarizability will attributes to high nucleophilicity (A)

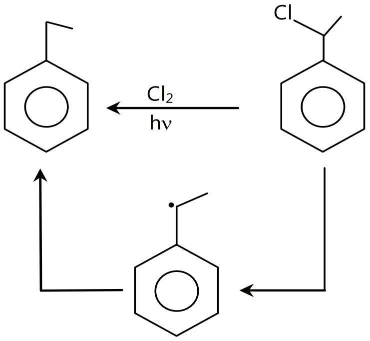
Sol 7: (B)



Sol 8: (A) $R–OH + X^- \longrightarrow R^+ \longrightarrow R–X + OH^-$

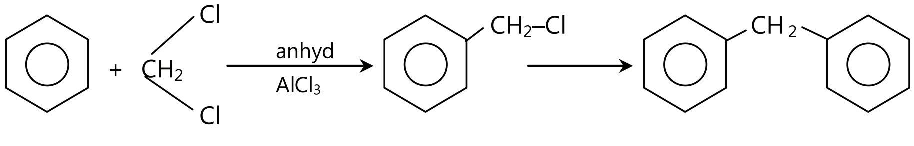
Sol 9: (B) R should be large to avoid S_N2

Sol 10: (A)



most stable free radical

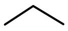
Sol 11: (D)



(Friedel Craft's Reaction)

Sol 12: (C) Other alcohols are poisonous for our body. So, silver nitrate precipitate out them as nitrates.

Sol 13: (B) CCl_3NO_2 (Chloropicrin) because it forms phosgene ($COCl_2$) after reaction phosgene is harmful for our body.

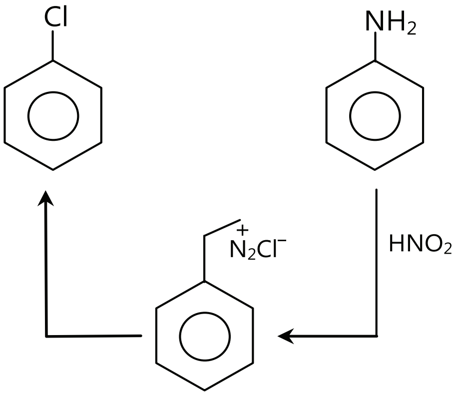
Sol 14: (B)  $+ Cl_2 \xrightarrow[75\text{–}100\text{ atm}]{573\text{–}673\text{ K}} CCl_4 + C_2Cl_6$

At such high p & T , it cleaves the C—C bond and chlorinate all valency of carbon.

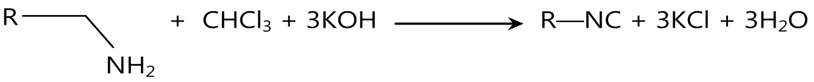
Sol 15: (A) Computer substitute is C_2Cl_6 because it has same odour (A)

Sol 16: (C) CF_2Cl_2(C)

Sol 17: (B) 

Sol 18: (D) 

Sandmayer's Reaction

Sol 19: (B) 

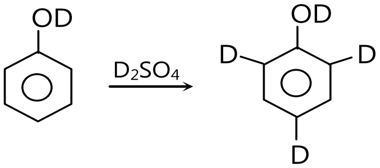
Carbylamine Test

Sol 20: (B) 

$$\underset{\text{more }e^{\ominus}\text{deficient}}{CH_3\text{–}CH{=}CH_2} + HBr \longrightarrow CH_3\text{–}CH_2\text{–}CH_2\text{–}Br$$

(C)/(D) this are the minor products of Kharasch effect

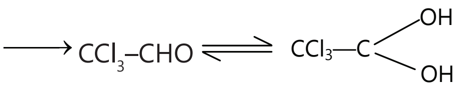
Sol 21: (B)



o/p activator group.

Assertion Reasoning Type

Sol 22: (A) They do not form H-bonds because of electron donating alkyl group. and also because of very bond blooding.

Sol 23: (B) Chloral 

$$\text{Chloral} \longrightarrow CCl_3\text{–}CHO \rightleftharpoons CCl_3\text{—}C(OH)_2$$

It is a alkyl halide according to IUPAC nomenclature.

Sol 24: (A) Because chloride attached carbon has less electron density so it attaches to the other one against markonikoff's rule.

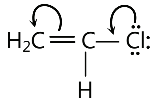
Sol 25: (C) In presence of sunlight chloroform forms phosgene which is harmful for our body. (Poisonous gas).

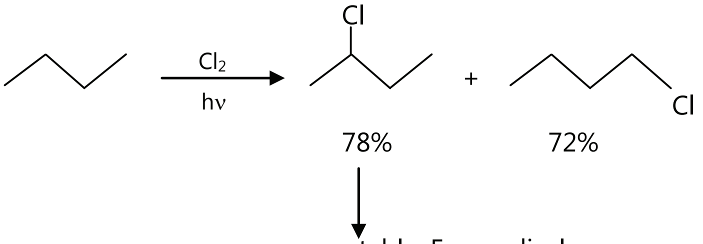
Sol 26: (D) Chlorobenzene undergoes resonance so C–Cl bond have some double-bond character it will get hard to hydrolysis it.

Sol 27: (B) It extinguishes five because it inhibits the chemical reactions not because of its non-polar nature solvent.

Sol 28: (A) Inductive effect increases electron density on carbon so it will be easy for Cl-atom to leave the site so bond will get weakened.

Sol 29: (C) Vinyl group's carbon area sp^2 hybridised and thus are more electronegative than sp^3 so they will not donate electron and more important reason is resonance factor electron and more important reason is resonance factor.



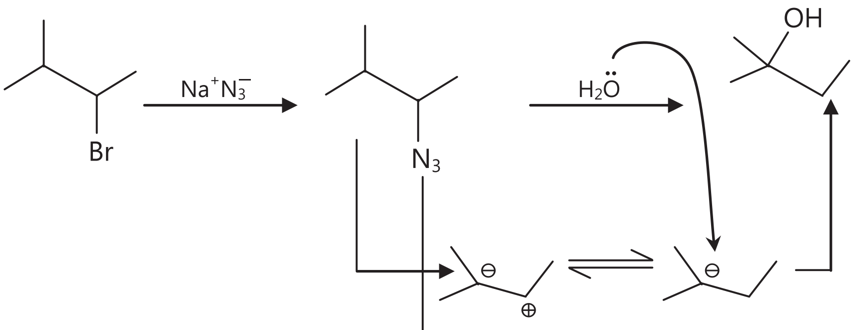
Sol 30: (A) 

more stable, Free radical

intermediate which overcome the number factor.

Comprehension Type

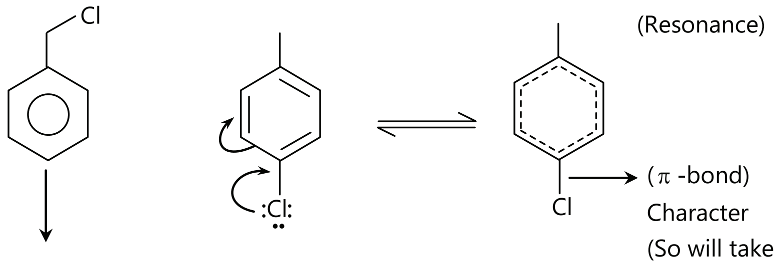
Sol 31: (C) Polar solvent so via S_N2 reaction $-N_3$ will get substitute on 2° alkyl halide**Sol 32: (A)** Strong sterecially hindered base gives elimination products.

Sol 33: (D) 

Better leaving group

so go via S_N1 path

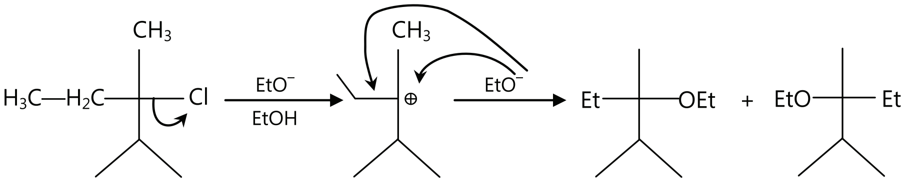
Sol 34: (A)



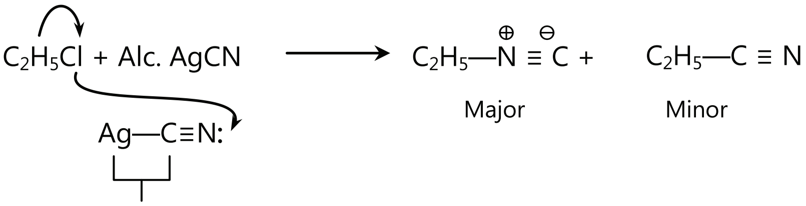
here only
σ -bond
so more polarity while in p-chlorotoluene it gets
distributed so less polar bond

(π -bond)
Character
(So will take more energy
to cleave the bond)

Sol 35: (A) S_N1 mechanism:



Only 1 configuration Carbocation Enantiomers



Sol 36: (A) C_2H_5Cl + Alc. AgCN $\longrightarrow$ $C_2H_5—\overset{\oplus}{N} \equiv \overset{\ominus}{C}$ + $C_2H_5—C \equiv N$

Major Minor

Ag—C≡N:

covalent bond
Character

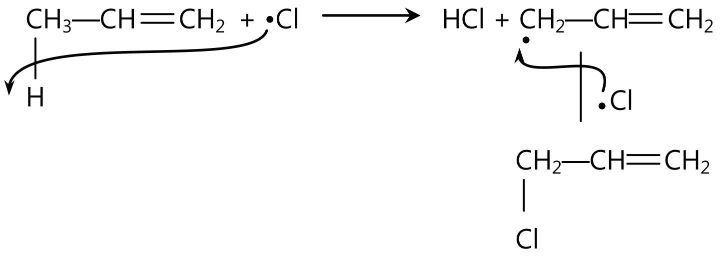
$CN^- \longrightarrow \overset{\ominus}{C} \equiv N:$ two donating site

∴ ambident nucleophile

Sol 37: (A) $CH_3 – CH = CH_2$

Step 1: $Cl_2 \longrightarrow Cl\bullet + \bullet Cl$

Step 2:



$CH_3—CH=CH_2 + \bullet Cl \longrightarrow HCl + \dot{C}H_2—CH=CH_2$

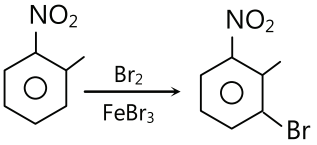
$CH_2—CH=CH_2$ with Cl on the first carbon:

$\underset{\displaystyle Cl}{\underset{|}{C}H_2}—CH=CH_2$

Sol 38: (B) Reason is incorrect.

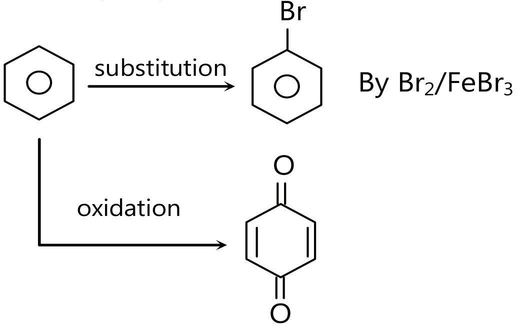
Multiple Correct Choice Type

Sol 39: (A, B)

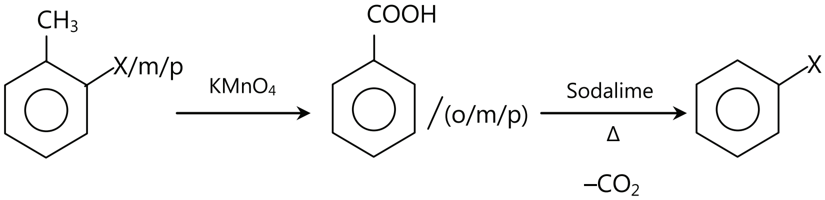


$–NO_2$ is a deactivating group so it is meta director.

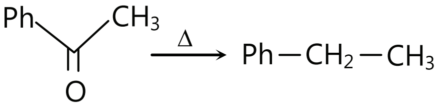
Sol 40: (A, D)



Sol 41: (B, C, D)

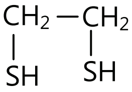


Sol 42: (A, D)

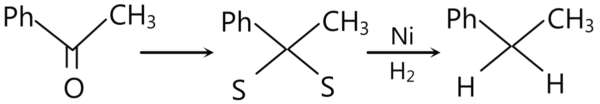


Clemenson reduction Na(Hg) /Con. Na Wolf-kishner $NH_2–NH_2$ glycol/$OH^–$

Red P/HI

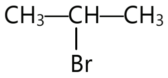


$\underset{SH}{\underset{|}{CH_2}}-\underset{SH}{\underset{|}{CH_2}}$ Raney Ni, H_2



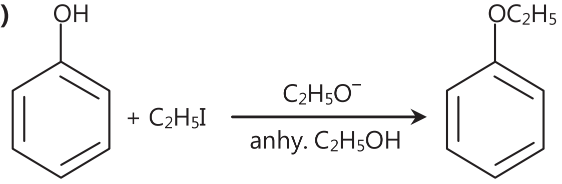
Previous Years' Questions

Sol 1: (B)



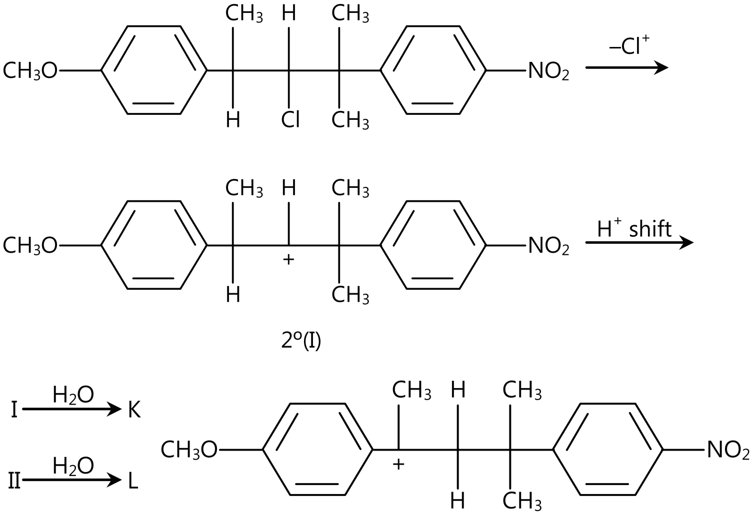
$CH_3–CH_2–CH_2Br \xrightarrow[80°C]{\text{Alcoholic NaOH}} CH_3–CH=CH_2 \xrightarrow{HBr} CH_3—\underset{Br}{\underset{|}{CH}}—CH_3$

Sol 2: (A)



S_N2 reaction

Sol 3: (A) Reaction proceed through carbocation intermediate

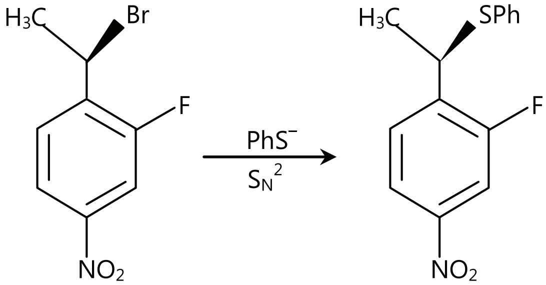


2°(I)

3°(II)

Stabilized by + R effect of –OCH_3

Sol 4: (A) Nucleophile PhS^- substitute the Br^- through S_N2 mechanism with inversion of configuration at $\alpha - C$.



Sol 5: (D, E) The compound used as refrigerant are CF_2Cl_2, $CH_2 F_2$.

Sol 6: A → q; B → q; C → r; D → p, s

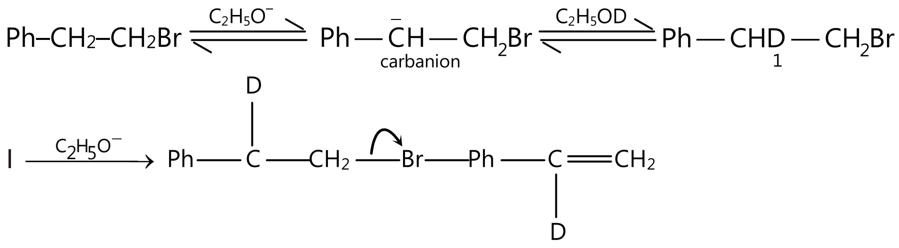
(A) $CH_3–CHBr–CD_3 \xrightarrow[E2]{Alc. KOH} CH_2=CH–CD_3$

E2 reaction is a single-step reaction in which both deprotonation from $\beta - C$ and loss of leaving group from $\alpha - C$ occur simultaneously in the rate-determining step. C–D bond is stronger than C–H bond, C–H is preferably broken in elimination.

(B) $Ph–CHBr–CH_3$ reacts faster than $Ph–CHBr–CD_3$ in E2 reaction because in later case, stronger C–D bond is to be broken in the rate determining step.

(C) $Ph–CH_2–CH_2Br \xrightarrow[C_2H_5O^-]{C_2H_5OD} Ph–CD=CH_2$

Deuterium incorporation in the product indicates E1CB mechanism

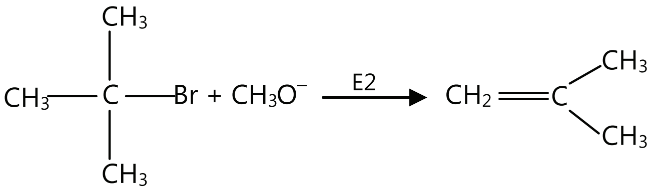


$$Ph{-}CH_2{-}CH_2Br \underset{}{\overset{C_2H_5O^-}{\rightleftharpoons}} \underset{\text{carbanion}}{Ph{-}\overset{-}{C}H{-}CH_2Br} \overset{C_2H_5OD}{\rightleftharpoons} \underset{1}{Ph{-}CHD{-}CH_2Br}$$

$$I \xrightarrow{C_2H_5O^-} Ph{-}\overset{D}{\overset{|}{C}}{-}CH_2{-}Br \longrightarrow Ph{-}\underset{D}{\underset{|}{C}}{=}CH_2$$

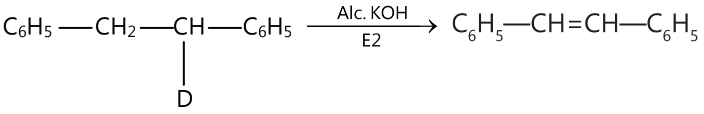
(D) Both $PhCH_2CH_2Br$ and $PhCD_2CH_2Br$ will react at same rate in E1 reaction because C–H bond is broken in fast non rate-determining step. Also E1 reaction follow first order kinetics.

Sol 7:



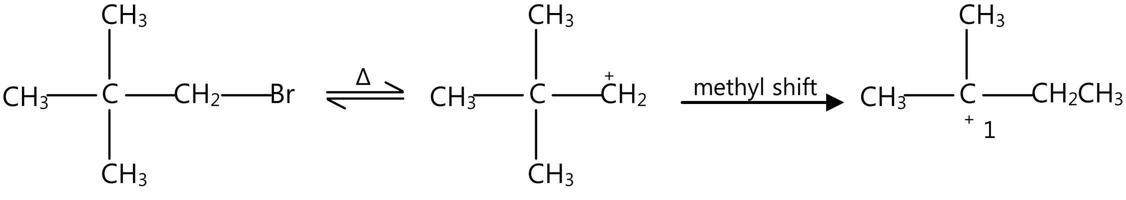
$$CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}Br + CH_3O^- \xrightarrow{E2} CH_2{=}C(CH_3)_2$$

Sol 8:

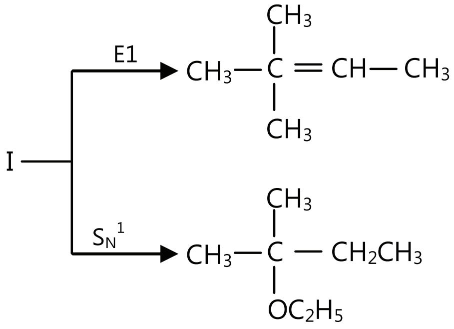


$$C_6H_5{-}CH_2{-}\underset{D}{\underset{|}{C}H}{-}C_6H_5 \xrightarrow[E2]{\text{Alc. KOH}} C_6H_5{-}CH{=}CH{-}C_6H_5$$

Sol 9: Unimolecular reaction occur



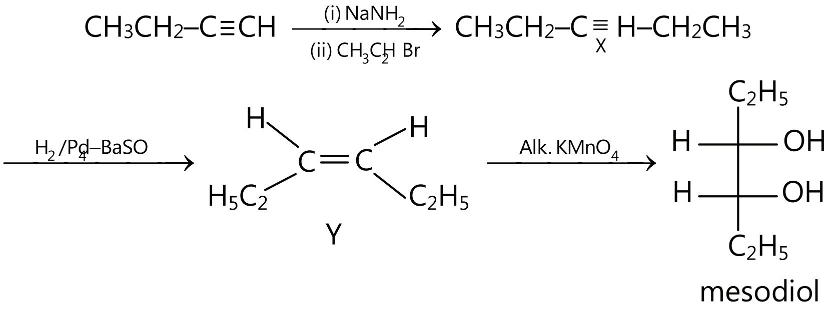
$$CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2{-}Br \overset{\Delta}{\rightleftharpoons} \underset{\text{primary carbocation}}{CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}\overset{+}{C}H_2} \xrightarrow{\text{methyl shift}} CH_3{-}\underset{+\ 1}{\overset{CH_3}{C}}{-}CH_2CH_3$$



$$I \xrightarrow{E1} CH_3{-}\overset{CH_3}{C}{=}CH{-}CH_3$$

$$I \xrightarrow{S_N1} CH_3{-}\underset{OC_2H_5}{\overset{CH_3}{C}}{-}CH_2CH_3$$

Sol 10:

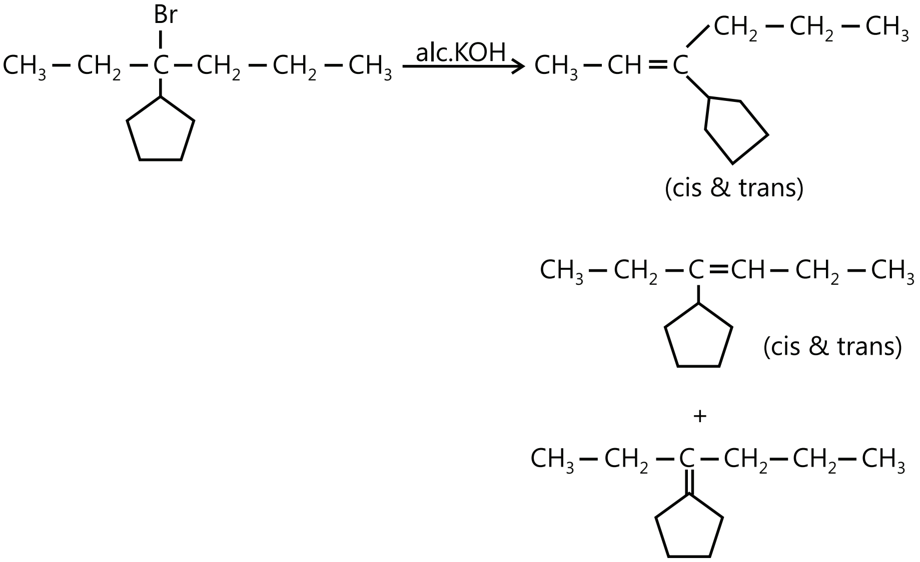


$$CH_3CH_2{-}C{\equiv}CH \xrightarrow[\text{(ii) } CH_3CH_2Br]{\text{(i) } NaNH_2} \underset{X}{CH_3CH_2{-}C{\equiv}H{-}CH_2CH_3}$$

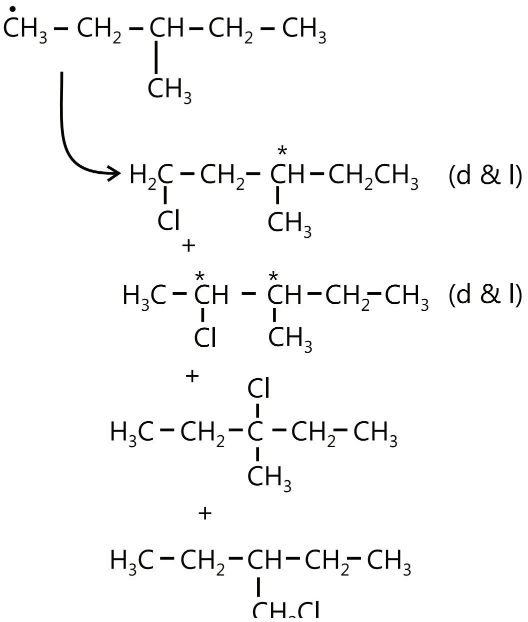
$$\xrightarrow{H_2/Pd{-}BaSO_4} \underset{Y}{(H)(H_5C_2)C{=}C(H)(C_2H_5)} \xrightarrow{\text{Alk. } KMnO_4} \text{mesodiol}$$

mesodiol

Sol 11: (5)



Sol 12: (8)



$$\dot{C}H_3-CH_2-\underset{\displaystyle CH_3}{CH}-CH_2-CH_3$$

$$\longrightarrow H_2\underset{\displaystyle Cl}{C}-CH_2-\underset{\displaystyle CH_3}{\overset{*}{C}H}-CH_2CH_3 \quad (d\ \&\ l)$$

$$+$$

$$H_3C-\underset{\displaystyle Cl}{\overset{*}{C}H}-\underset{\displaystyle CH_3}{\overset{*}{C}H}-CH_2-CH_3 \quad (d\ \&\ l)$$

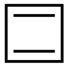
$$+$$

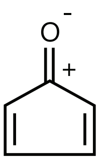
$$H_3C-CH_2-\underset{\displaystyle CH_3}{\overset{\displaystyle Cl}{C}}-CH_2-CH_3$$

$$+$$

$$H_3C-CH_2-\underset{\displaystyle CH_2Cl}{CH}-CH_2-CH_3$$

Sol 13: (B, C)

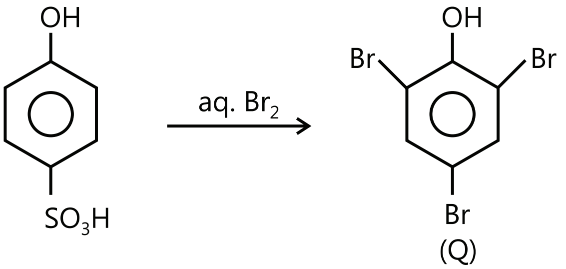
(B)  antiaromatic

(C) 

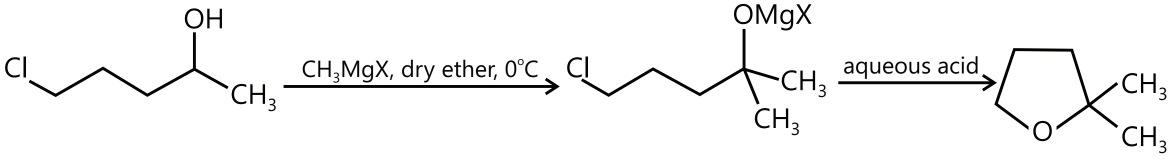
is antiaromatic

Sol 14: (B) S_N2 reaction are through back attack of attacking Nu^- and not on the basic of stability of carbocation.

Sol 15: (B)

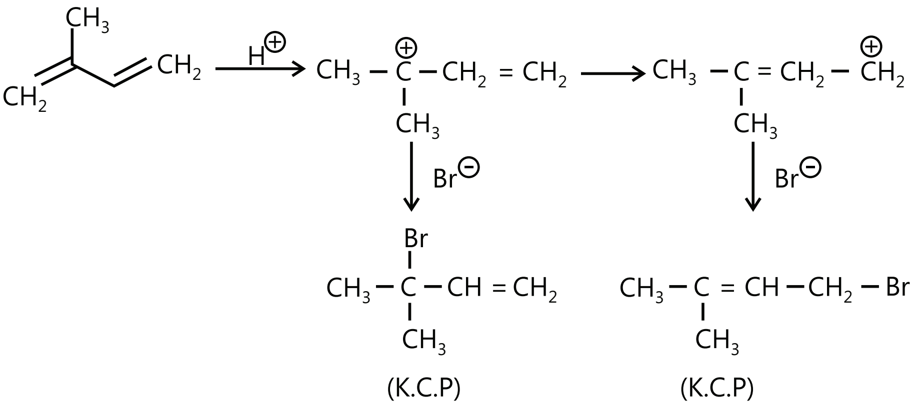


Sol 16: (D)

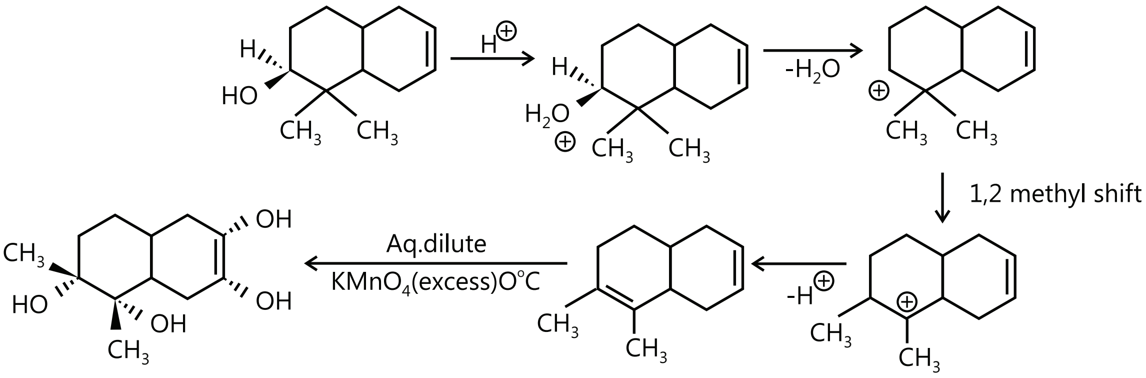


Sol 17: (C) When two phenyl groups are replaced by two para methoxy group, carbocation formed will be more stable.

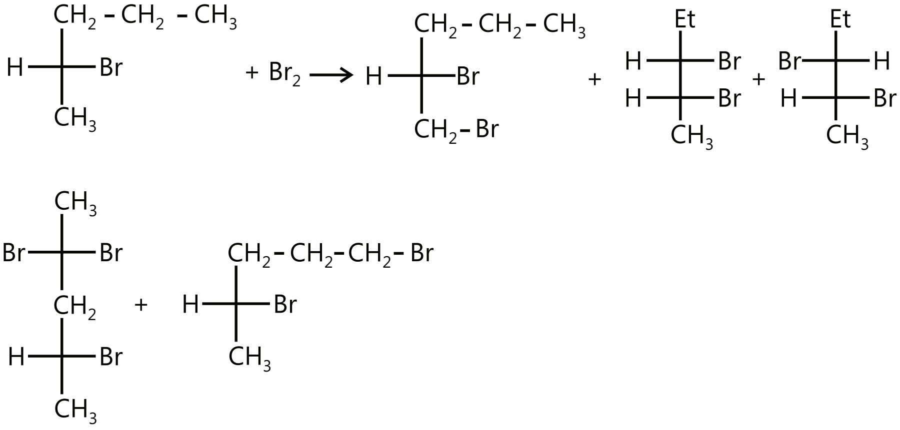
Sol 18: (D)



Sol 19: (4)

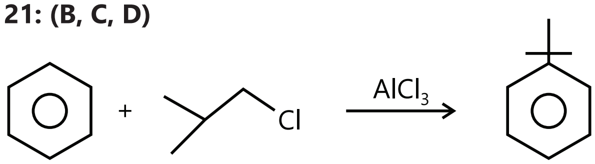


Sol 20: (5)

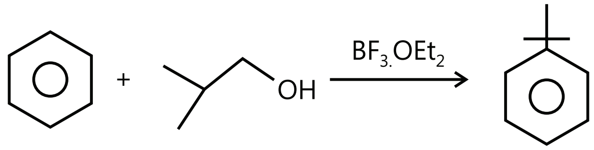


Sol 21: (B, C, D)

(A)



(C)



(B)