Class 12 Chemistry

Haloalkanes And Haloarenes

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Exercise 10.1

Write structures of the following compounds:

(i) 2-Chloro-3-methylpentane

(ii) 1-Chloro-4-ethylcyclohexane

(iii) 4-tert. Butyl-3-iodoheptane

(iv) 1,4-Dibromobut-2-ene

(v) 1-Bromo-4-sec. butyl-2-methylbenzene.

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Exercise 10.2

Why is sulphuric acid not used during the reaction of alcohols with

KI?

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Exercise 10.3

Write structures of different dihalogen derivatives of propane.

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Exercise 10.4

Among the isomeric alkanes of molecular formula C_5H_{12}, identify the one that on photochemical chlorination yields

(i) A single monochloride.

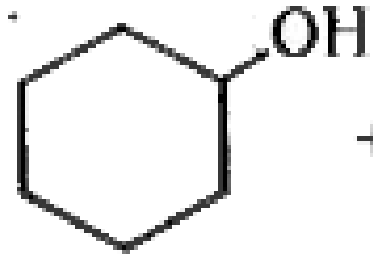
(ii) Three isomeric monochlorides.

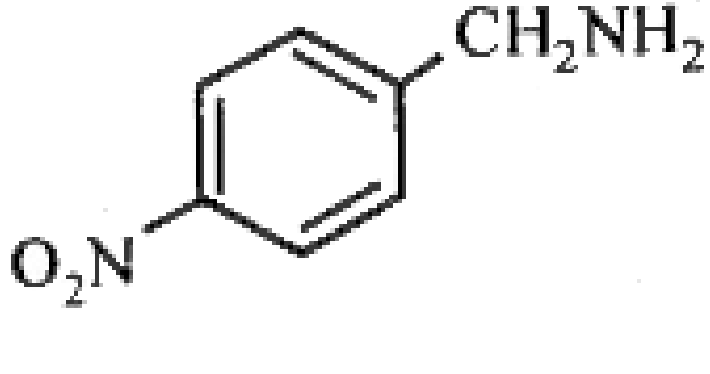
(iii) Four isomeric monochlorides.

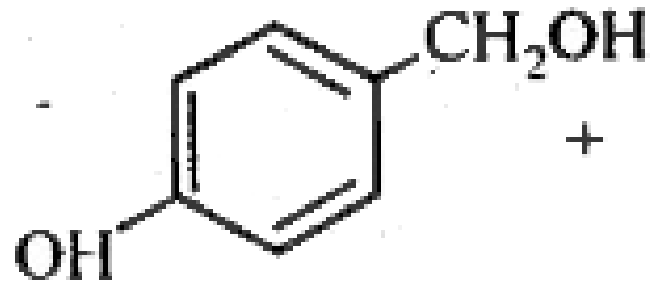
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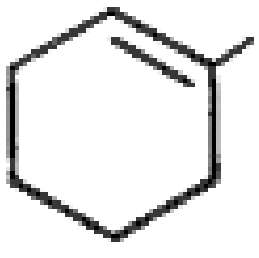
Exercise 10.5

Draw the structures of major monohalo products in each of the following reactions:

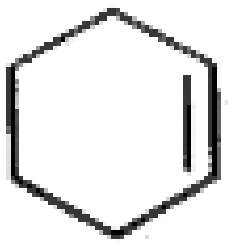
(i)  $+ \quad SOCl_2 \longrightarrow$

(ii)  $\xrightarrow[\text{UV light}]{Br_2, \text{heat or}}$

(iii)  $+ \quad HCl \xrightarrow{\text{heat}}$

(iv)  $+ \quad HI \longrightarrow$

(v) $CH_3CH_2Br + NaI \longrightarrow$

(vi)  $+ \quad Br_2 \xrightarrow[\text{UV light}]{\text{heat or}}$

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Exercise 10.6

Arrange each set of compounds in order of increasing boiling points.

(i) Bromomethane, Bromoform, Chloromethane, Dibromomethane.

(ii) 1-Chloropropane, Isopropyl chloride, 1-Chlorobutane.

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Exercise 10.7

Which alkyl halide from the following pairs would you expect to react more rapidly by an SN2 mechanism? Explain your answer.

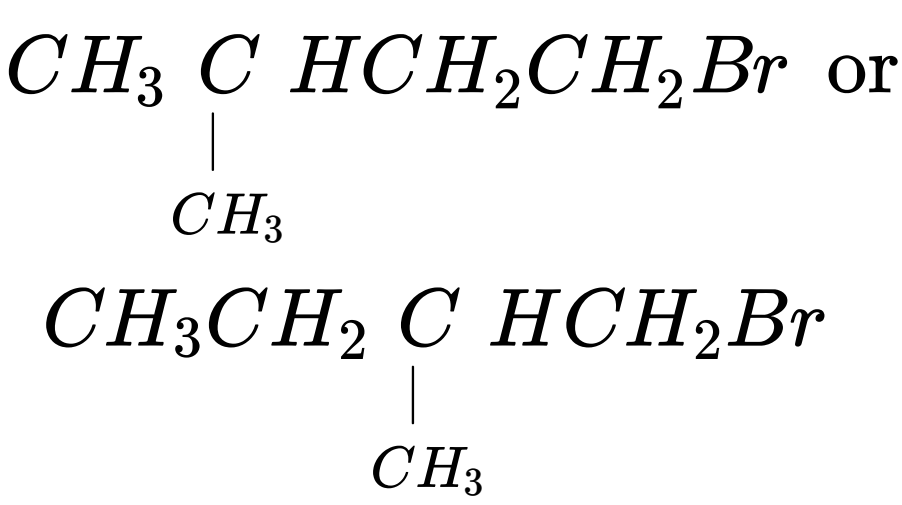
$(i) CH_3CH_2CH_2CH_2Br$ or

$CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3,$

$(ii) CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3$ or

$$H_3C - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}} - Br$$

(iii)



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Exercise 10.8

In the following pairs of halogen compounds, which compound undergoes faster S_N1 reaction?

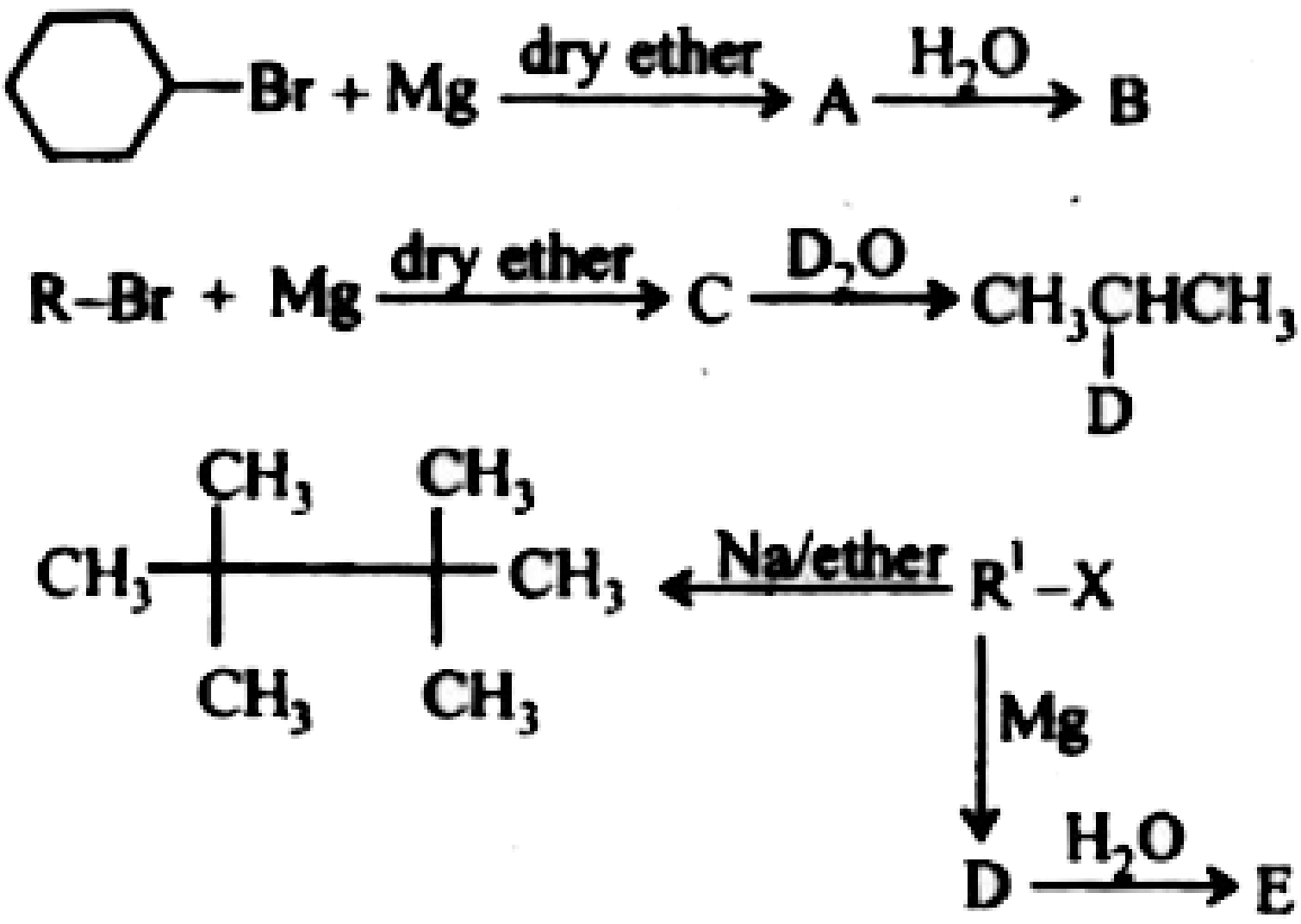
(i) 

(ii) 

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Exercise 10.9

Identify A, B, C, D, E, R and R^1 in the following:



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Exercise 10.10

Name the following halides according to IUPAC system and classify them asalkyl, allyl, benzyl (primary, secondary, tertiary), vinyl or aryl halides:

(i)

$(CH_3)_2CHCH(Cl)CH_3,$

$(ii)CH_3CH_2CH(CH_3)CH$

$(C_2H_5)Cl$

(iii)

$CH_3CH_2C(CH_3)_2CH_2I,$

$(iv)(CH_3)_3CCH_2CH(Br$

$)C_6H_5$

(v)

$CH_3CH(CH_3)CH(Br)CH_3,$

$(vi)CH_3C(C_2H_5)_2CH_2Br$

$(vii)CH_3C(Cl)(C_2H_5$

$)CH_2CH_3, (viii)CH_3CH$

$= C(Cl)CH_2CH(CH_3)_2$

(ix)

CH_3CH

$= CHC(Br)(CH_3)_2(x)p$

$- ClC_6H_4CH_2CH(CH_3)_2$

(xi)

m

$-ClCH_2C_6H_4CH_2C(CH_3$

$)_3$, (xii)$o-Br$

$-C_6H_4CH(CH_3)CH_2CH_3$

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Exercise 10.11

Give the IUPAC names of the following compounds:

(i)

$CH_3CH(Cl)CH(Br)CH_3(ii$

$)CHF_2CBrClF(iii)ClCH_2C$

$\equiv CCH_2Br$

$(iv)(CCl_3)_3CCl(v)CH_3C(p$

$-ClC_6H_4)_2CH(Br)CH_3(vi$

$)(CH_3)_3CCH=CClC_6H_4I$

$-p$

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Exercise 10.12

Write the structures of the following organic halogen compounds.

(i) 2-Chloro-3-methylpentane (ii) p-Bromochlorobenzene ,

(iii) 1-Chloro-4-ethylcyclohexane (iv) 2-(2-Chlorophenyl)-1-

iodooctane ,

(v) 2-Bromobutane (vi) 4-tert-Butyl-3-iodoheptane ,

(vii) 1-Bromo-4-sec-butyl-2-methylbenzene (viii) 1,4-Dibromobut-

2-ene

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Exercise 10.13

Which one of the following has the highest dipole moment?

(i)

CH_2Cl_2, $(ii)CHCl_3$,

$(iii)CCl_4$

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Exercise 10.14

A hydrocarbon C_5H_{10} does not react with chlorine in dark but gives a single monochloro compound C_5H_9Cl in bright sunlight. Identify the hydrocarbon.

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Exercise 10.15

Write the isomers of the compound having formula C_4H_9Br.

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Exercise 10.16

Write the equations for the preparation of 1-iodobutane from

(i) 1-butanol , (ii) 1-chlorobutane , (iii) but-1-ene.

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Exercise 10.17

What are ambident nucleophiles? Explain with an example.

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Exercise 10.18

Which compound in each of the following pairs will react faster in S_N2 reaction with . OH ?

(i)

CH_3Br or CH_3I,

$(ii)(CH_3)_3CCl$ or CH_3Cl

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Exercise 10.19

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

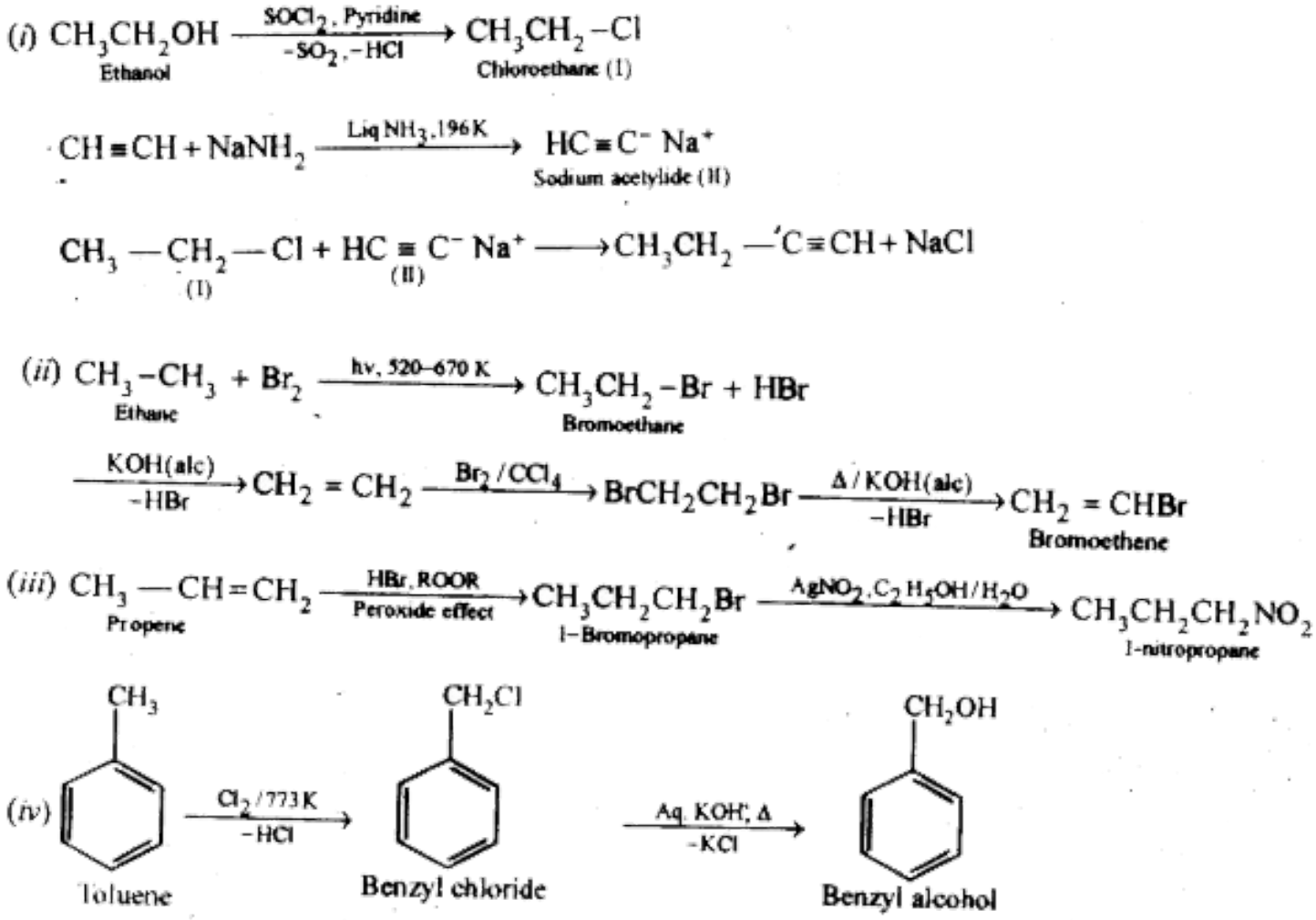
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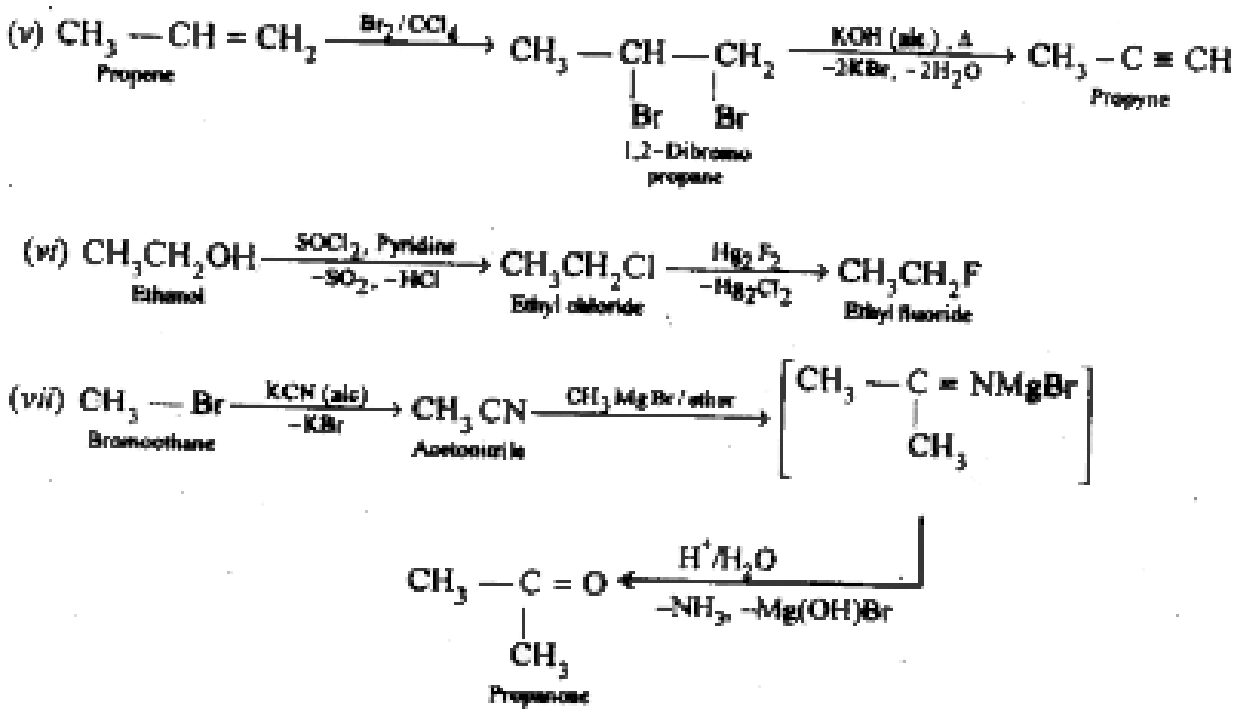
Exercise 10.20

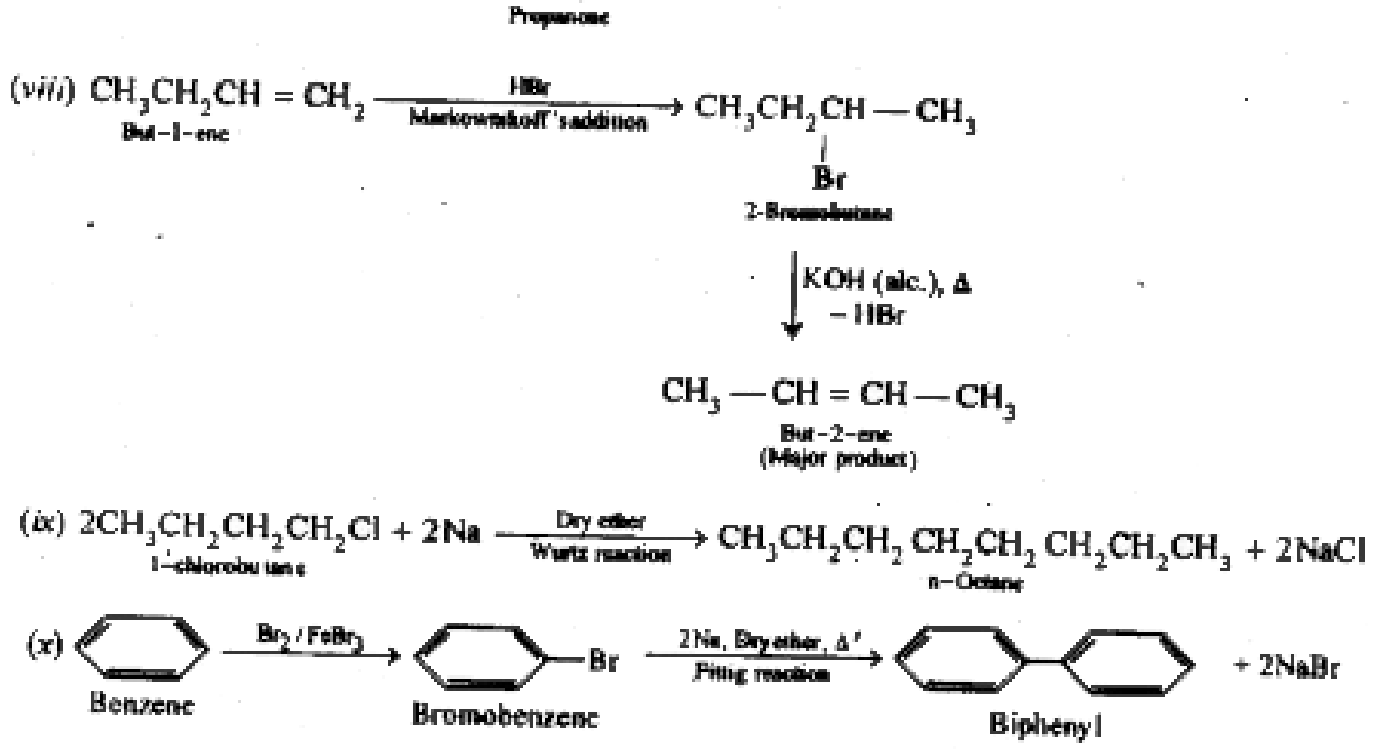
How will you bring about the following conversions?

(i) Ethanol to but-1-yne (ii) Ethane to bromoethene (iii) Propene to 1-nitropropane (iv) Toluene to benzyl alcohol (v) Propene to propyne (vi) Ethanol to ethyl fluoride (vii) Bromomethane to propanone (viii) But-1-ene to but-2-ene (ix) 1-Chlorobutane to n-octane (x) Benzene to biphenyl.

SOLUTION:







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Exercise 10.21

Explain why

(i) the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride?

(ii) alkyl halides, though polar, are immiscible with water?

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

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Exercise 10.22

Give the uses of freon 12, DDT, carbon tetrachloride and iodoform.

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Exercise 10.23

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

(i)

$$CH_3CH_2CH_2Cl + NaI \xrightarrow[\text{heat}]{\text{acetone}}$$

(ii) $(CH_3)_3CBr + KOH \xrightarrow[\text{heat}]{\text{ethanol}}$

(iii)

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

(iv)

$$CH_3CH_2Br + KCN \xrightarrow{\text{aq. ethanol}}$$

(v) $C_6H_5ONa + C_2H_5Cl \rightarrow$

(vi)

$$CH_3CH_2CH_2OH + SOCl_2 \rightarrow$$

(vii)

$$CH_3CH_2CH = CH_2 + HBr \xrightarrow{\text{peroxide}}$$

(viii)

$$CH3CH = C(CH3)2 + HBr \rightarrow$$

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Exercise 10.24

Write the mechanism of the following reaction:

$$\text{nBuBr + KCN} \xrightarrow{EtOH - H_2O} \text{nBuCN}$$

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Exercise 10.25

Arrange the compounds of each set in order of reactivity towards

S_N2 displacement:

(i) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane

(ii) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 2-Bromo-3-methylbutane

(iii) 1-Bromobutane, 1-Bromo-2,2-dimethylpropane, 1-Bromo-2-methylbutane, 1-Bromo-3-methylbutane.

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Exercise 10.26

Out of $C_6H_5CH_2Cl$ and $C_6H_5CHClC_6H_5$, which is more easily hydrolysed by aqueous KOH.

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Exercise 10.27

p-Dichlorobenzene has higher m.p. than those of o- and m-isomers.

Discuss

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Exercise 10.28

How the following conversions can be carried out?

(i) Propene to propan-1-ol

(ii) Ethanol to but-1-yne

(iii) 1-Bromopropane to 2-bromopropane (iv) Toluene to benzyl alcohol

(v) Benzene to 4-bromonitrobenzene

(vi) Benzyl alcohol to 2-phenylethanoic acid

(vii) Ethanol to propanenitrile

(viii) Aniline to chlorobenzene

(ix) 2-Chlorobutane to 3, 4-dimethylhexane

(x) 2-Methyl-1-propene to 2-chloro-2-methylpropane

(xi) Ethyl chloride to propanoic acid

(xii) But-1-ene to n-butyliodide

(xiii) 2-Chloropropane to 1-propanol

(xiv) Isopropyl alcohol to iodoform

(xv) Chlorobenzene to p-nitrophenol (xvi) 2-Bromopropane to 1-bromopropane

(xvii) Chloroethane to butane

(xviii) Benzene to diphenyl

(xix) tert-Butyl bromide to isobutyl bromide

(xx) Aniline to phenylisocyanide

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Exercise 10.29

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.

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Exercise 10.30

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 from 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.

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Exercise 10.31

What happens when

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

(ii) bromobenzene is treated with Mg in the presence of dry ether,

(iii) chlorobenzene 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?

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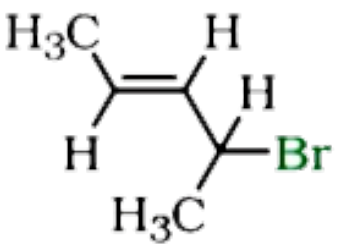
Solved Example 1

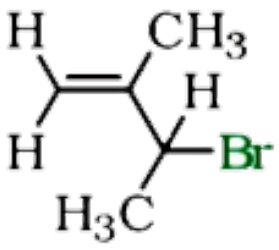
Draw the structures of all the eight structural isomers that have the molecular formula C_5H_{11} Br. Name each isomer according to IUPAC system and classify them as primary, secondary or tertiary bromide.

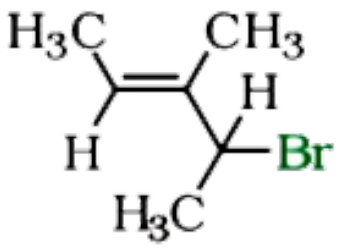
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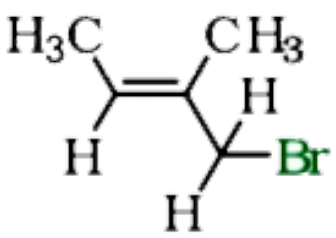
Solved Example 2

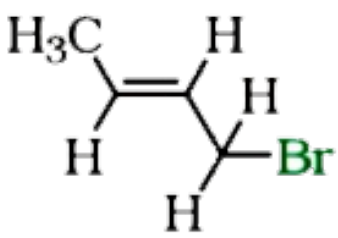
Write IUPAC names of the following:

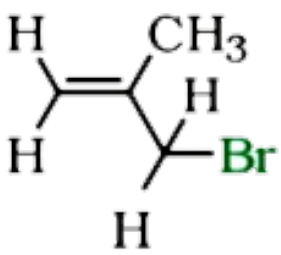
(i) 

(ii) 

(iii) 

(iv) 

(v) 

(vi) 

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Solved Example 3

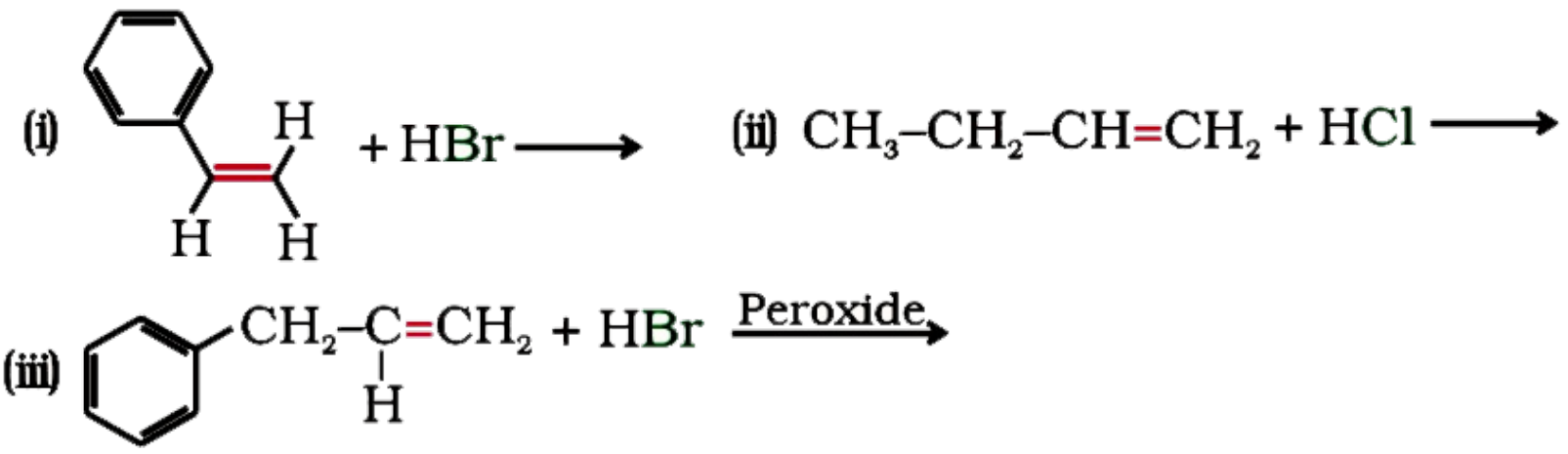
Identify all the possible monochloro structural isomers expected to be formed on free radical monochlorination of $(CH_3)_2CHCH_2CH_3$.

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Solved Example 4

Write the products of the following reactions:

(i)



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Solved Example 5

Haloalkanes react with KCN to form alkyl cyanides as main product while AgCN forms isocyanides as the chief product. Explain.

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Solved Example 6

In the following pairs of halogen compounds, which would undergo S_N2 reaction faster?



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Solved Example 7

Predict the order of reactivity of the following compounds in S_N1 and S_N2 reactions:

(i) The four isomeric bromobutanes

(ii)

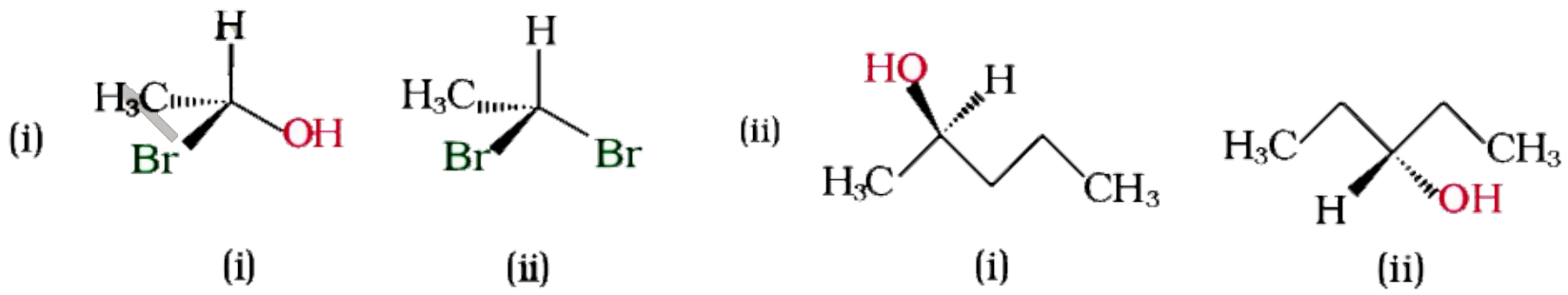
$C_6H_5CH_2Br$,
$C_6H_5CH(C_6H_5)Br$,
$C_6H_5CH(CH_3)Br$,
$C_6H_5C(CH_3)(C_6H_5)Br$

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Solved Example 8

Identify chiral and achiral molecules in each of the following pair of

compounds. (Wedge and Dash representations according to Class XI, Fig. 12.1). ltbgt



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Solved Example 9

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

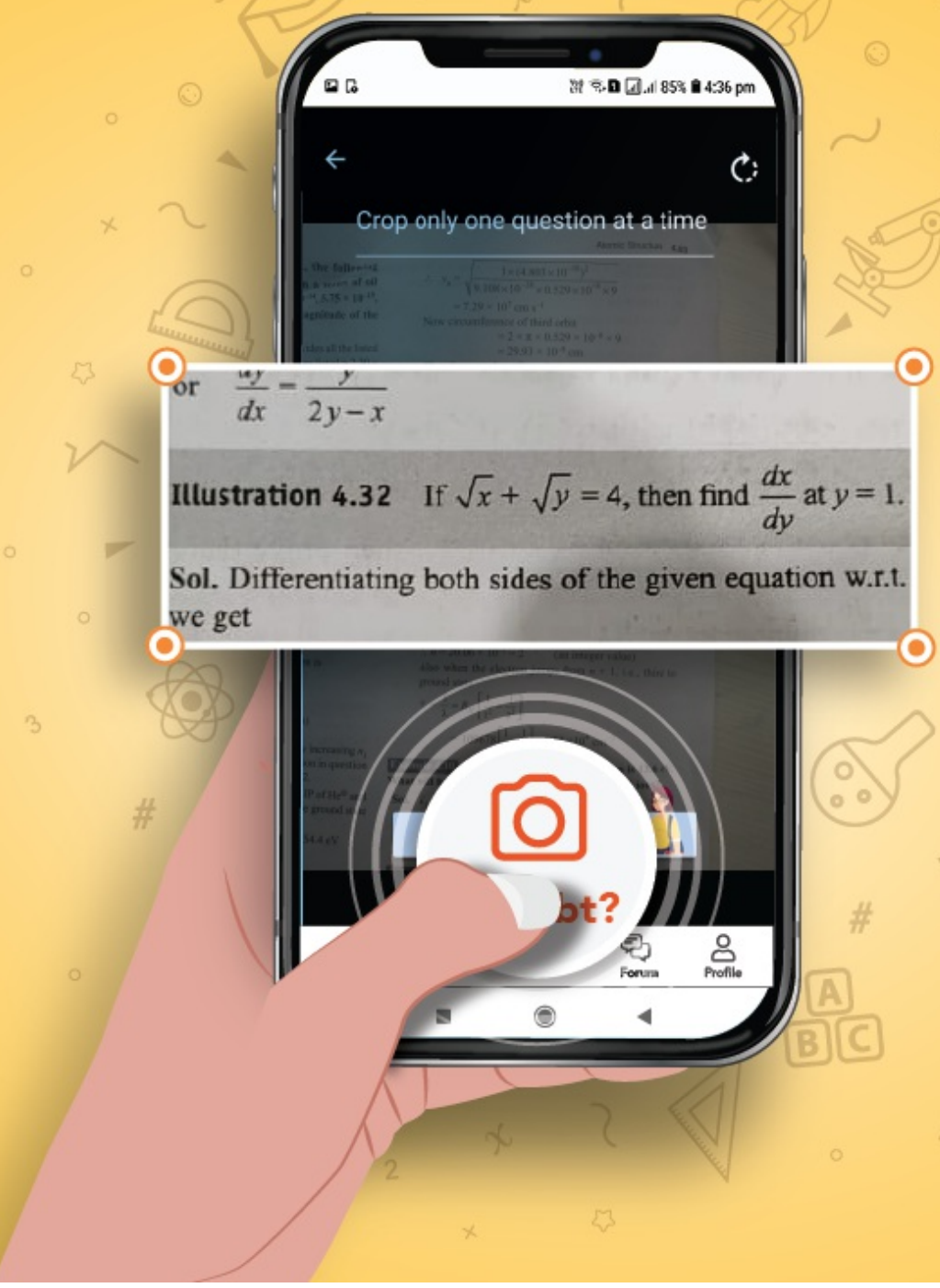
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