#452369

Topic: Nomenclature of halogen compounds

Name the following halides according to IUPAC system and classify them as alkyl, 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) $o-Br-C_6H_4CH(CH_3)CH_2CH_3$

Solution

The IUPAC names of various compounds are given below in order:

(1) 2-Chloro-3-methylbutane (secondary alkyl halide)

(ii) 3-Chloro-4-methylhexane (secondary alkyl halide)

(iii) 1-Iodo-2,2-dimethylbutane (primary alkyl halide)

(iv) 1-Bromo-3,3-dimethyl-1-phenylbutane (secondary benzyl halide)

(v) 2-Bromo-3-methylbutane (secondary alkyl halide)

(vi) 1-Bromo-2-ethyl-2-methylbutane (primary alkyl halide)

(vii) 3-Chloro-3-methylpentane (tertiary alkyl halide)

(viii) 3-Chloro-5-methylhex-2-ene (vinyl halide)

(ix) 4-Bromo-4-methylpent-2-ene (allyl halide)

(x) 1-Chloro-4-(2-methylpropyl) benzene (aryl halide)

(xi) 1-Chloromethyl-3-(2,2-dimethylpropyl) benzene (primary benzyl halide)

(xii) 1-Bromo-2-(1-methylpropyl) benzene (aryl halide)

#452389

Topic: Nomenclature of halogen compounds

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) $(CH_3)_3CCH=CClC_6H_4I-p$

Solution

The IUPAC names of various compounds are given below in order:

(i) 2-Bromo-3-chlorobutane

(ii) 1-Bromo-1-chloro-1,22-trifluoroethane

(iii) 1-Bromo-4-chlorobut-2-yne

(iv) 2-(Trichloromethyl)-1,1,1,2,3,3,3-heptachloropropane

(v) 2-Bromo-3,3-bis (4-chlororphenyl) butane

(vi) 1-Chloro-1-(4-iodophenyl)-3,3-dimethylbut-1-ene

#452395

Topic: Nomenclature of halogen compounds

Write the structures of the following organic halogen compounds.

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

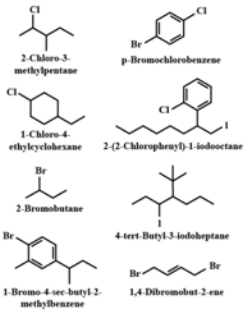
(iii) 1-Chloro-4-ethylcyclohexane (iv) 2-(2-Chlorophenyl)-1-iodooctane

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

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

Solution

The structures of various compounds are given above:



#452403

Topic: Physical properties of haloalkanes and haloarenes

Which one of the following has the highest dipole moment?

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

Solution

Dichloromethane has highest dipole moment among $CH_2Cl_2,\ CHCl_3$ and CCl_4. The decreasing order of dipole moments is $CH_2Cl_2 > CHCl_3 > CCl_4$. These molecule have tetrahedral geometry due to sp^3 hybridization of carbon atom.In CCl_4, the individual $C-Cl$ bond dipoles cancel each other which results in zero dipole moment. Hence, CCl_4 is non polar.

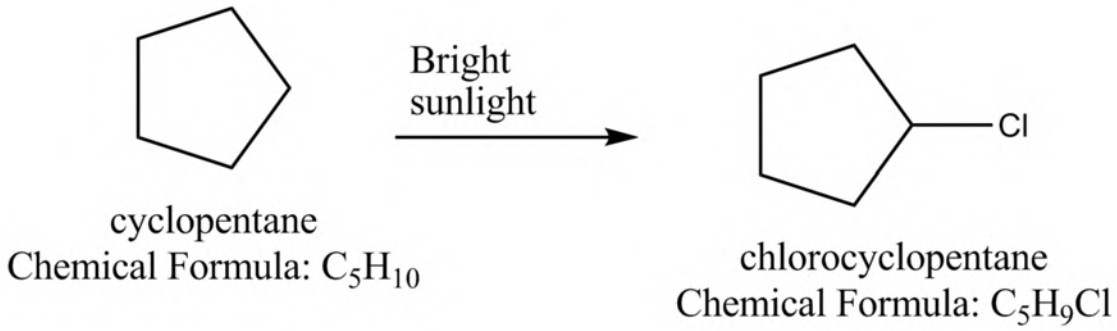
#452404

Topic: Methods of preparation of haloalkanes

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.

Solution

The molecular formula of hydrocarbon is C_5H_{10}. It satisfies the general formula C_nH_{2n} . It suggests that the hydrocarbon is either alkene or cyclloalkane. It does not react wit chlorine in dark. Hence, it cannot be alkene. Hence, it is cycloalkane. It gives a single monochloro compound C_5H_9Cl in bright sunlight. Hence, the hydrocarbon.is cyclopentane.



#452405

Topic: Chemical reactions of haloarenes

Write the number of structural isomersof the compound having formula C_4H_9Br.

A 4

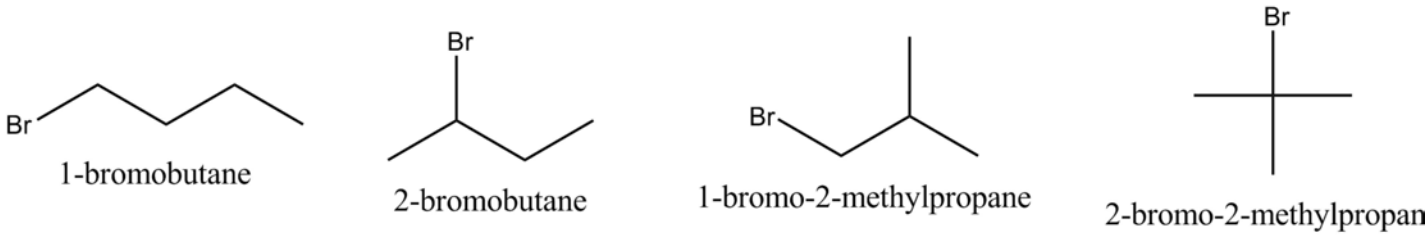
B 5

C 6

D 7

Solution

The isomers of the compound having formula C_4H_9Br are shown above. Among the above compounds, only the second compound shown is chiral. Hence, it has two optical isomers.



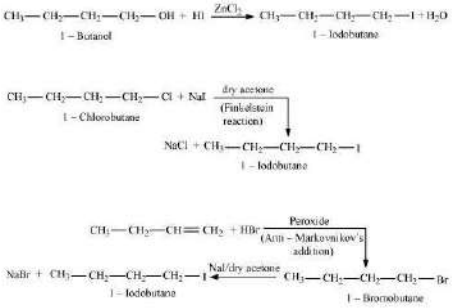
#452406

Topic: Methods of preparation of haloalkanes

Write the equations for the preparation of 1-iodobutane from following.

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

Solution



#452408

Topic: Chemical reactions of haloalkanes - Elimination reactions

Which compound in each of the following pairs will react faster in SN^2 reaction with OH?

(i) CH_3Br or CH_3I

(ii) $(CH_3)_3CCl$ or CH_3Cl

Solution

(i) Since, iodide ion is better leaving group than bromide ion, methyl iodide will react faster than methyl bromide in SN^2 reaction with hydroxide ion.

(ii) Due to steric hindrance in tert butyl chloride, methyl chloride is more reactive than tert butyl chloride towards SN^2 reaction.

#452409

Topic: Chemical reactions of haloalkanes - Elimination reactions

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.

Solution

The reactions are given above:

(i) 1-Bromo-1-methylcyclohexane is the major product.

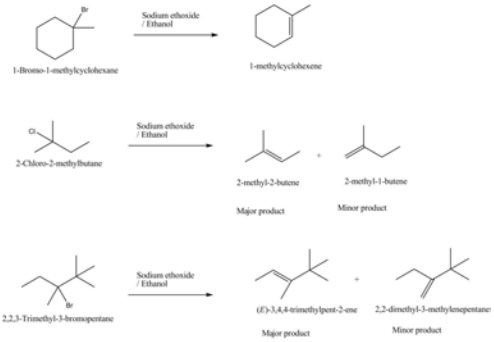
Only one alkene is formed as beta H atoms on either side of Br atoms are equivalent.

(ii) 2-Chloro-2-methylbutane is the major product.

Two different alkenes are formed. More substituted alkene is the major product as it is more stable. This is in accordance with Saytzeff's rule.

(iii) 2,2,3-Trimethyl-3-bromopentane is the major product.

Two different alkenes are formed. More substituted alkene is the major product as it is more stable. This is in accordance with Saytzeff's rule.



#452410

Topic: Chemical reactions of haloalkanes - Elimination reactions

How will you bring about the following conversions?

(i) Ethanol to but-1-yne

(ii) Ethane to bromoethene

(iii) Propene to1-nitropropane

(iv) Toluene to benzyl alcohol

(v) Propene to propyne

(vi) Ethanol to ethyl fluoride

(vii) Bromomethane to propanone

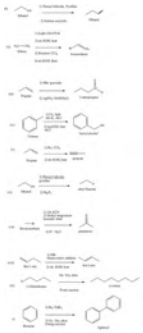
(viii) But-1-eneto but-2-ene

(ix) 1-Chlorobutane to n-octane

(x) Benzene to biphenyl.

Solution

The conversions are shown above:



#452411

Topic: Physical properties of haloalkanes and haloarenes

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?

Solution

(i) In chlorobenzene, the C atom of C-Cl bond is sp^2 hybridized and has more s character and electronegativity. In cyclohexyl chloride, the C atom of C-Cl bond is sp^3 hybridize has less s character and less electronegative. Hence, C-Cl bond in chlorobenzene is less polar than C-Cl bond in cycloheyl chloride.
Also, in chlorobenzene, the lone pair of electron on Cl atom is in resonance with benzene ring. This gives partial double bond character to C-Cl bond and there is decrease in the magnitude of partial negative charge on Cl atom. However, in cyclohexyl chloride, there is C-Cl single bond. Dipole moment is a product of charge and distance. Also C-Cl bond with partial double bond character has lower bond length than with C-Cl single bond. Hence, chlorobenzene has lower dipole moment than cyclohexyl chloride.

(ii) Inter-molecular attractive forces present in alkyl halides are dipole dipole interactions and in case of water molecules, inter-molecular hydrogen bonds are present. When alkyl halides are added to water, the inter-molecular attractive force present between alkyl halide and water molecules are weaker than the forces that are already present between two alkly halide molecules and two water molecules. Hence, alkyl halides are water immiscible.

(iii) Grignards reagents are highly reactive with moisture that is present in apparatus or starting materials. Hence, we should prepare grignard reagents in anhydrous condition.
$RMgX + HOH \rightarrow R_H + MgOHX$

#452414
Topic: Polyhalogen compounds

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

Solution

The uses of various compounds ar given below.

Freon 12

$1)$ It is used as a refrigerant in refrigerators and air conditioners.

$2)$ It is used in aerosol spray propellants such as body sprays, hair sprays etc.

DDT :

$1)$ It is used as an insecticide.

$2)$ It is effective against mosquitoes and lice.

Carbon tetrachloride:

$1)$ It is used in manufacturing refrigerants and propellants for aerosol cans.

$2)$ It is used as feedstock in the synthesis of chlorofluorocarbons and other chemicals.

$3)$ It is used as a solvent in the manufacture of pharmaceutical products.

$4)$ Till 1960's, it was used as a cleaning fluid, a degreasing agent and a fire extinguisher.

Iodoform.:

It was used as an antiseptic as it liberates free iodine when it comes in contact with the skin.

#452415
Topic: Chemical reactions of haloalkanes - Substitution reactions

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

(i) $CH_3CH_2CH_2Cl + NaI \xrightarrow{acetone}$

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

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

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

(v) $C_6H_5ONa + C_2H_5Cl \longrightarrow$

(vi) $CH_3CH_2CH_2OH + SOCl_2 \longrightarrow$

(vii) $CH_3CH_2CH = CH_2 + HBr \xrightarrow{peroxide}$

(viii) $CH_3CH = C(CH_3)_2 + HBr \longrightarrow$

Solution

The major organic products are shown below.

(i) $CH_3CH_2CH_2Cl + NaI \xrightarrow[heat]{acetone} CH_3CH_2CH_2I(1-iodopropane) + NaCl$

(ii) $(CH_3)_3CBr + KOH \xrightarrow[heat]{ethanol} CH_3C(CH_3) = CH_2(2-methylpropene) + KBr + H_2O$

(iii) $CH_3CH(Br)CH_2CH_3 + NaOH \xrightarrow{water} CH_3 - CHOHCH_2CH_3(2-butanol)$

(iv) $(CH_3)_3CBr + KOH \xrightarrow[heat]{ethanol} CH_3CH_2CN(propanenitrlie) + KBr$

(v) $C_6H_5ONa + C_2H_5Cl \longrightarrow C_6H_5OCH_2H_3 + NaCl$

(vi) $CH_3CH_2CH_2OH + SOCl_2 \longrightarrow CH_3CH_2CH_2 - Cl(1-chloropropane) + HCl + SO_2$

(vii) $CH_3CH_2CH = CH_2 + HBr \xrightarrow{peroxide} CH_3CH_2CH_2CH_2 - Br(1-bromobutane)$

(viii) $CH_3CH = C(CH_3)_2 + HBr \longrightarrow CH_3CH_2C(Br)(CH_3)CH_3(2-bromo-2-methylbutane)$

#452423

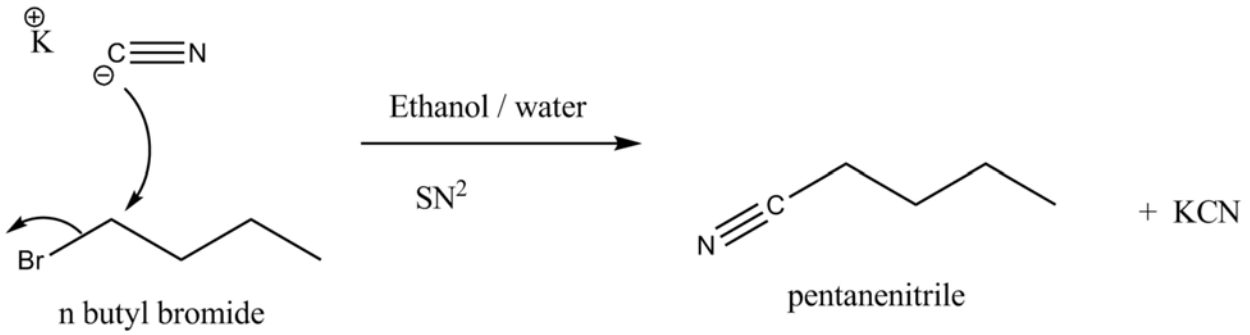
Topic: Chemical reactions of haloalkanes - Elimination reactions

Write the mechanism of the following reaction:

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

Solution

This is an example of bimolecular nucleophilic substitution reaction S_N2. Cyanide ion acts as a nucleophile and bromide ion acts as leaving group. It is one step reaction and the mechanism is as shown above.



#452424

Topic: Chemical reactions of haloalkanes - Elimination reactions

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.

Solution

In SN^2 reaction, steric factors determine the reactivity. more reactive alkyl halides have less steric hindrance. Hence, the decreasing order of the reactivity of alkyl halides is $1^o > 2^o > 3^o$.

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

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

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

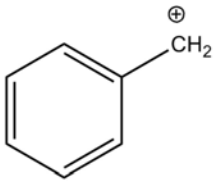
#452427

Topic: Chemical reactions of haloalkanes - Elimination reactions

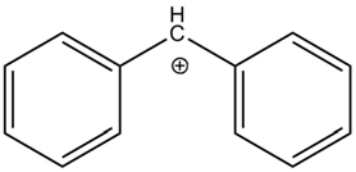
Out of $C_6H_5CH_2Cl$ and $C_6H_5CHClC_6H_5$, which is more easily hydrolysed by aqueous KOH?

Solution

$C_6H_5CHClC_6H_5$ is more easily hydrolysed by aqueous KOH. It involves formation of a secondary carbocation which is stablized by resonance with two phenyl groups. Or the other hand, during hydrolysis of $C_6H_5CH_2Cl$, a primary carbocation is formed which is stablized by resonance with only one phenyl group and is less stable and less readily formed.



Less stable
less readily
formed



More stable
More readily formed

#452428

Topic: Physical properties of haloalkanes and haloarenes

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

Solution

In case of dichlorobenzenes, para isomer is more symmetrical than ortho and meta isomers.

Hence, in the crystal lattice, para isomer fits more closely than ortho and meta isomers.

Due to this, more energy is required to break the crystal lattice of para isomer.

Hence, p-Dichlorobenzene has higher melting point than those of o- and m-isomers.

#452429

Topic: Chemical reactions of haloalkanes - Elimination reactions

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

Solution

The reagents used for the given conversions are as follows:

(i) Propene to propan-1-ol

(a) HBr/ peroxide, (b) aq KOH

(ii) Ethanol to but-1-yne

(a) P, iodine heat (b) alc. KOH, heat (c) bromine, CCl_4 (d) $NaNH_2/liqNH_3$ (2 equiv) (e) excess methyl iodide

(iii) 1-Bromopropane to 2-bromopropane

(a) Alc. KOH heat (b) HBr Markovnikoff's addition

(iv) Toluene to benzyl alcohol

(a) Chlorine, sunlight, (b) aq KOH, heat

(v) Benzene to 4-bromonitrobenzene

(a) Bromine, ferric bromide, (b) Conc. HNO_3+ conc. H_2SO_4

(vi) Benzyl alcohol to 2-phenylethanoic acid

(a) Thionyl chloride (b) alc KCN (c) H^+ / water

(vii) Ethanol to propanenitrile

(a) P, I_2 heat, (b) alc KCN

(viii) Aniline to chlorobenzene

(a) $NaNO_2, HCl$ 273-278 K, (b) $CuCl, HCl$ sandmeyer reaction.

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

Na wurtz reaction

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

HCl markownikoff's addition

(xi) Ethyl chloride to propanoic acid

(a) Alc KCN (b) H^+, H_2O hydrolysis

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

(a) HBr peroxide (b) NaI acetone

(xiii) 2-Chloropropane to 1-propanol

(a) alc. KOH heat, (b) HBr peroxide (c) alc. KOH, heat

(xiv) Isopropyl alcohol to iodoform

$I_2/NaOH$ heat

(xv) Chlorobenzene to p-nitrophenol

(a) Conc. HNO_3 + conc. H_2SO_4 (b) aq NaOH (15%), 433 K (c) dil HCl

(xvi) 2-Bromopropane to 1-bromopropane

(a) alc KOH heat (b) HBr peroxide.

(xvii) Chloroethane to butane

Na wurtz reaction

(xviii) Benzene to diphenyl

(a) Bromine, ferric bromide (b) Na Dry ether fitting reaction

(xix) tert-Butyl bromide to isobutyl bromide

(a) Alc KOH, heat (b) HBr peroxide

(xx) Aniline to phenylisocyanide

$CHCl_3/KOH$ warm

#452449

Topic: Chemical reactions of haloalkanes - Elimination reactions

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.

Solution

$R-Cl+KOH(\text{aq})\rightarrow R-OH+KCl$

$R-CH_2-CH_2-Cl+KOH(\text{alc})\rightarrow R-CH=CH_2+KCl+H_2O$

The ionization of aqueous KOH produces hydroxide ions which are strong nucleophiles. Hence, alkyl chlorides undergo substitution to form alcohol.

Alcoholic KOH solution gives alkoxide ion which is a strong base. It abstracts β hydrogen atom of alkyl chloride. A molecule of HCl is eliminated and an alkene is formed.

Note: The basicity of hydroxide ion is much lower than the basicity of alkoxide ion as hydroxide ion is significantly hydrated in aqueous solution.

Hence, hydroxide ion cannot abstract β hydrogen atom of alkyl chloride.

#452450

Topic: Chemical reactions of haloalkanes - Elimination reactions

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 w 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.

Solution

Two primary alkyl halides with molecular formula C_4H_9Br are possible. They are n-butyl bromide and isobutyl bromide.

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. Hence, compound a is isobutyl bromide and compound d is 2,5-dimethylhexane.

$2CH_3CH_2CH_2CH_2Br + 2Na \xrightarrow{Wurtz\ reaction} CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3(n-octane)$

$2CH_3CH(CH_3)CH_2Br + 2Na \xrightarrow{wurtz\ reaction} CH_3CH(CH_3)CH_2CH_2CH(CH_3)CH_3(2,5-dimethylhexane)$

(a) reacted with alcoholic KOH to give compound (b).

$CH_3CH(CH_3)CH_2Br \xrightarrow{alcKOH} CH_3C(CH_3)=CH_2(2-methyl-1-propene)$

Compound (b) is reacted with HBr to give (c) which is an isomer of (a).

$CH_3-C(CH_3)=CH_2 \xrightarrow[Markownikoff's\ rule]{HBr} CH_3-CBr(CH_3)CH_3(tert-butylbromide)$

#452451

Topic: Chemical reactions of haloalkanes - Elimination reactions

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?

Solution

The products of various reactions are as shown.