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Chapter 4: Alkylhalides (R-X, X = Cl, Br, I)

These are compounds with atleast one halogen aaton attached to the parent chain.

Classification of mono substutued alkylhalide

As seen earlier, they are classified like alcohols.

They are **three** classes of alkylhalide depending on the number of alkyl groups attached to a carbon atom that carry a halide.

(a) Primary alkylhalide have one alkyl group on the carbon atom that carries a halide.

Examples

(b) Secondary alkylhalide have two alkyl groups attached to a carbon atom that carry a halide

Examples

(c) Tertiary alkylhalide

Tertiary alkylhalide have three alkylgroups attached to the carbon atoms that carry OH group Examples

2-bromo-2-methylbutanane

2-iodo-2-phenylpropane

Preparation of alkylhalide

1. By reacting alkenes with halogenhalide

Example

$$CH_3CH \xrightarrow{\qquad CH_2} CH_3CH \xrightarrow{\qquad CH_2} CH_2$$

Mechanism

Remember: the reaction occurs at the double bond and hydrogen atom goes to a carbon that carries highest number of hydrogen atoms.

Exercise

Complete and write a mechanism for the following reactions (mark yourself after)

(a)
$$CH_3CH_2CH \longrightarrow CH_2 \longrightarrow HI$$

(b) $CH \longrightarrow CH_2 \longrightarrow HI$

Mark yourself

In these reactions, the double bond breaks and hydrogen halide adds itself a cross the carbon atoms that were forming the double bond. Hydrogen atom add to a carbon atom the carries the highest number of hydrogen atom of those that form a double bond. Make sure you account for the charges.

(a)
$$CH_3CH_2CH$$
 \longrightarrow CH_2 \longrightarrow CH_3CH_2C \longrightarrow CH_2 \longrightarrow CH_3CH_2C \longrightarrow CH_2

$$CH_{3}CH_{2}C \longrightarrow CH_{2} \longrightarrow CH_{3}CH_{2}C \longrightarrow CH_{2} \longrightarrow CH_{3}CH_{2}C \longrightarrow CH_{2}$$

$$H \longrightarrow CH_{3}CH_{2}C \longrightarrow CH_{2}$$

(b)
$$CH = CH_2$$
 $HI \longrightarrow CH_2$ CH_2

Mechanism

$$\begin{array}{c|c} H \\ \hline \\ C \\ \hline \\ H \\ \hline \end{array} \begin{array}{c} H \\ \hline \\ C \\ \hline \\ I \\ \hline \end{array} \begin{array}{c} H \\ \hline \\ C \\ \hline \\ I \\ \hline \end{array} \begin{array}{c} H \\ \hline \\ C \\ \hline \\ I \\ \hline \end{array} \begin{array}{c} H \\ \hline \\ I \\ \hline \\ H \\ \end{array}$$

2. By reacting chlorine gas or bromine with alkanes. The reaction occurs in the presence of u.v light. This was dealt with when dealing with reactions of alkanes.

Complete the following equation and write a mechanism

(a)
$$CH_4 + Cl_2 \xrightarrow{u.v-light}$$

(b) $CH_3 + Br_2 \xrightarrow{u.v-light}$

Mark yourself

These reactions follow a free radical mechanism, be keen to observe the initiation and formation of free radicals as the reaction proceeds. Every dot (un paired electron) must be accounted for.

(a)
$$CH_4 + Cl_2 \xrightarrow{u.v-light} CH_3Cl$$

Methane chloromethane

Cl₂
$$\xrightarrow{\text{u.v-light}}$$
 $2\dot{\text{Cl}}$ chlorine radical

H₃C—H + $\dot{\text{Cl}}$ \longrightarrow H₃ $\dot{\text{C}}$ + HCl methyl radical

$$H_3\dot{C} + Cl_2 \longrightarrow H_3C \longrightarrow Cl + \dot{C}l$$

Mechanism

- 3. By reacting alcohols with
 - (a) Phosphorus halide

Examples

(i)
$$CH_3CH_2OH$$
 $\xrightarrow{PCl_5}$ CH_3CH_2Cl
(ii) CH_3CHCH_3 $\xrightarrow{PBr_3}$ CH_3CHCH_3 \xrightarrow{OH} OH

(b) With HX (X= Cl, Br, I)

HI and HBr react readily with alcohols but the reaction of HCl is catalyzed with anhydrous zinc chloride. The mechanism of the reaction depends on the class of alcohol. Though secondary alcohols react like either primary or tertiary alcohols.

Examples
$$\begin{array}{cccc} \text{Primary alcohol} \\ \text{CH}_3\text{CH}_2\text{OH} & + \text{HI} & \longrightarrow & \text{CH}_3\text{CH}_2\text{I} + \text{H}_2\text{O} \\ \text{Mechanism} \end{array}$$

$$\begin{array}{c|c} CH_3CH_2OH & H & C & CH_3CH_2I \\ \hline \\ H & H & H \\ \hline \\ H & H \\ \hline \\ H & H \end{array}$$

$$\begin{array}{c} CH_3CH_2I \\ \hline \\ H \\ \hline \\ H \end{array}$$

Tertiary alcohol

Mechanism

Exercise

Complete and write a mechanism, thereafter mark yourself

(i)
$$CH_2OH + HI$$
 $CH_2OH + HI$ $CH_3OH + HBr$ OH

Mark yourself

(i)
$$CH_2OH + HI$$
 $CH_2I + H_2OC$ Phenylmethanol Iodophenylmethane

Mechanism

Note that phenylmethanol is a primary alcohol

$$\begin{array}{c|c} CH_2OH & H \\ \hline \\ CH_2OH & CH_2I \\ \hline \\ H \\ \hline \\ I^- \end{array}$$

(ii)
$$C (CH_3)_2 + HBr$$
 $C (CH_3)_2$ $C (CH_3)_3$ $C (CH_3)_3$ $C (CH_3)_3$ $C (CH_3)_3$ $C (CH_3)_3$ $C (CH_3)_3$ $C (CH$

Please note that 2-phenylpropan-2-ol is a tertiary alcohol

$$\begin{array}{c} CH_3 \\ CH_4 \\ CH_3 \\ CH_4 \\ CH_5 \\ CH$$

(c) Reaction of HCl with alcohols is catalyzed by anhydrous zinc chloride because HCl bond is strong. Primary alcohol does not react, secondary alcohol reacts slowly, and tertiary alcohol reacts faster.

Example

$$(CH_3)_3COH \xrightarrow{HCl/ZnCl_2} (CH_3)_3CCl$$

Mechanism

$$(CH_3)_3C - OH \longrightarrow (CH_3)_3C \xrightarrow{\uparrow} OH_2 \longrightarrow (CH_3)_3C \xrightarrow{\downarrow} (CH_3)_2CC$$

(d) Reaction of alcohol with KX (X= Cl, Br, I)

The mechanisms depend on the class of alcohols. The mechanism of secondary alcohols Primary alcohol

$$CH_3CH_2OH + KCl \longrightarrow CH_3CH_2Cl + \bar{O}H$$

Mechanism

$$\begin{array}{c|c} H & H \\ \hline \\ H & \hline \\ C & \hline \\ C & \hline \\ H & H \end{array} \longrightarrow \begin{array}{c} CH_3CH_2CI + \bar{O}H \\ \hline \\ H & \hline \\ CI^- \end{array}$$

Tertiary alcohol

$$(CH_3)_3COH$$
 \longrightarrow
 $(CH_3)_3CBr$

Mechanism

 $(CH_3)_3C$
 \longrightarrow
 $(CH_3)_3C$
 \longrightarrow
 $(CH_3)_3C$
 \longrightarrow
 $(CH_3)_2CB$

CHEMICAL PROPERTIES

(a) Formation of alkenes

Alkylhalides react with hot alcoholic potassium hydroxide to form alkenes. The mechanism depend on the class of alkylhalide but mechanism of reaction for secondary alkylhalide is similar to that of the primary or tertiary alkylalide. These reactions were also considered when we dealt with preparation of alkene

(i) Example for primary alkylhalides,

$$\begin{array}{cccc} CH_3CH_2Cl & & ethanol/KOH & & CH_2=CH_2 \\ Chloroethane & & Ethene \end{array}$$

Mechanism

$$CH_3CH_2OH + \overline{O}H$$
 \longrightarrow $CH_3CH_2\overline{O} + H_2O$
Ethanol

Then
$$H \longrightarrow C$$
 $CH_2=CH_2$ $CH_3CH_2\bar{O}$:

Example II

$$\begin{array}{ccc} \text{CH}_3\text{CH}_2\text{CH}_2\text{Br} & \xrightarrow{\text{CH}_3\text{CH}_2\text{OH/OH}} & \text{CH}_3\text{CH}=\text{CH}_2 \\ \text{1-Bbromopropane} & & \text{Propene} \end{array}$$

$$CH_3CH_2OH + \overline{O}H \longrightarrow CH_3CH_2\overline{O} + H_2O$$

Ethanol

Then
$$H \to H$$
 $H_3C \to C$
 $C \to Br$
 $CH_2=CH_2$
 $CH_3CH_2O:$

Exercise

Complete and write a mechanism

Solution

Mechanism
$$H$$
 H C $CH=CH_2$ CH

- (ii) Secondary alkyl halides undergo the same mechanism as primary alkyl halides or that of tertiary alkyl halides
- (iii) Tertiary alkyl halides undergo a mechanism called E1 or elimination unimolecular because a water molecule is eliminated and the slowest step involves one molecule only.

Example

$$H_3C$$
 CH_3
 CH_3
 CH_3O/CH_3OH
 CH_3
 CH_3
 CH_3
 CH_3

2-Iodo-2-methylpropane

2-methylpropene

Mechanism

$$H_3C$$
 CH_3
 H_3C
 CH_3
 H_4C
 CH_5
 CH_5
 CH_5

Exercise

Complete and write a mechanism

Solution

$$\begin{array}{c|c} CH_3 & CH_3 \\ \hline C & -CH_3 & EtO/EtOH \\ \hline C & heat \\ \end{array}$$

Mechanism

$$\begin{array}{c} CH_3 \\ CH_3 \\ CH_3 \\ CH_3 \\ CH_3 \\ CH_5 \\ CH_7 \\ CH$$

(b) Reaction of alkyl halide with alkalis (NaOH or KOH)

Alkyl halides react with hot alkalis to form alcohols. The secondary alkyl halides react by either mechanism of primary or tertiary alkyl halides.

Primary alkyl halide

$$CH_3CH_2CI + KOH \longrightarrow CH_3CH_2OH + CI^-$$

Mechanisms

The mechanism is described as SN² (substitution nucleophilic bimolecular)because a nucleophile (-OH) substitutes a halide atom and the slow step in the reaction involved to species i.e. –OH and alkylhalide.

$$(CH_3)_3CBr \longrightarrow (CH_3)_3COH$$

Mechanism

$$(CH_3)_3C$$
 Br $\stackrel{\text{slow}}{\longrightarrow}$ $(CH_3)_3\overset{\text{c}}{\longleftarrow}$ $(CH_3)_2COH$

Exercise

Complete and write a mechanism, thereafter mark yourself

(i)
$$CH_2CI + NaOH$$
 $CH_2CI + NaOH$ (ii) $CH_3CI + KOH$

Mark yourself

(i)
$$CH_2CI + NaOH$$
 warm $CH_2OH + CI$ Chlorophenylmethane Phenylmethanol

Note that chlorophenylmethane is a primary alkyl halide

(ii)
$$C (CH_3)_2 + NaOH$$
 warm $C (CH_3)_2$ OH 2-Iodo-2-phenylpropane 2-phenylpropan-2-ol

Mechanism

Note that 2-iodo-2-phenylpropane is a tertiary alkyl halide

$$CH_3$$
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3

(c) Reaction with potassium cyanide

Alkyl halides react with potassium cyanide to form nitrile. This reaction is important because it increases the carbon chain by one carbon atom. Primary alkyl halide undergo SN² while tertiary alkyl halide undergo SN¹ mechanism whereas secondary alkyl halides undergo either mechanism.

Examples

Mechanism (note that chloroethane is a primary alkyl halide)

$$\begin{array}{c|c} H & \\ \hline \\ CH_3 & \hline \\ C & \\ \hline \\ H & \\ \hline \vdots \\ \hline CN & \\ \end{array} \qquad \begin{array}{c} \text{slow} \\ \text{CH}_3\text{CH}_2\text{CN} \\ \end{array}$$

(ii)
$$(CH_3)_3CBr \longrightarrow (CH_3)_3CCN$$

2-bromo-2-methylpropane

Mechanism (2-bromo-2-methylpropane is tertiary alkyl halide)

$$(CH_3)_3C$$
 Br \xrightarrow{slow} $(CH_3)_3C$ $(CH_3)_2CCN$

(d) Coupling reaction

Two alkyl halides couple in presence of sodium and dry ether or zinc-copper couple to form alkane of twice the number of carbon atoms as the parent alkyl halide.

(e) Formation of Gridnard's reagent

Alkyl halides react with magnesium in presence of dry ether to form compound called Gridnard's reagent.

Example

$$\begin{array}{ccc} CH_3CH_2Cl & + Mg & \xrightarrow{dry \ ether} CH_3CH_2MgCl \\ Generally & & & \\ RX + Mg & \xrightarrow{dry \ ether} & RMgX \end{array}$$

Gridnard's reagents are important synthetic molecules that enable us to increase the parent carbon chain by unlimited number of carbon atoms in synthesis.

(i) Gridnard's reagent reacts with carbon dioxide to produce carboxylic acid. The parent chain increase by one carbon atom.

(ii) Gridnard's reagent reacts with methanal to produce primary alcohols. The parent chain increase by one carbon atom.

$$RMgX + HCHO \xrightarrow{dry \text{ ether}} R \xrightarrow{H} COMgX \xrightarrow{H^+} RC OH$$

Example

$$CH_{3}MgBr + HCHO \xrightarrow{dry \text{ ether}} CH_{3} \xrightarrow{H} COMgBr \xrightarrow{H^{+}} CH_{3}C \longrightarrow OH$$

(iii) Gridnard's reagent reacts with aldehydes to produce secondary alcohols.

RMgBr +R'CHO
$$\xrightarrow{\text{dry ether}}$$
 R $\xrightarrow{\text{COMgBr}}$ $\xrightarrow{\text{H}^+}$ CH₃C $\xrightarrow{\text{CH}}$ OH

Example

$$CH_{3}MgBr + CH_{3}CH_{2}CHO \xrightarrow{dry \text{ ether}} CH_{3} \xrightarrow{CH_{3}CH_{2}} CH_{3} \xrightarrow{H^{+}} CH_{3}C \xrightarrow{H^{-}} CH_{2}CH_{3}$$

(iv) Gridnard's reagent reacts with ketones to produce secondary alcohols.

$$RMgBr + R'CO \xrightarrow{dry \text{ ether}} R \xrightarrow{R'} COMgBr \xrightarrow{H^+} CH_3C \xrightarrow{R'} OH$$

Example

