This page looks at reactions in which the -OH group in an alcohol is replaced by a halogen such as chlorine or bromine. It includes a simple test for an -OH group using phosphorus(V) chloride. The general reaction looks like this:

\[ ROH + HX \rightarrow RX + H_2O \]

**Reaction with hydrogen chloride**

Tertiary alcohols react reasonably rapidly with concentrated hydrochloric acid, but for primary or secondary alcohols the reaction rates are too slow for the reaction to be of much importance. A tertiary alcohol reacts if it is shaken with with concentrated hydrochloric acid at room temperature. A tertiary halogenoalkane (haloalkane or alkyl halide) is formed.

\[
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3
\end{array}
\text{H}_2\text{C}-\text{C}-\text{OH}
\quad +
\quad \text{HCl}
\quad \rightarrow
\quad \begin{array}{c}
\text{CH}_3 \\
\text{CH}_3
\end{array}
\text{H}_2\text{C}-\text{C}-\text{Cl}
\quad +
\quad \text{H}_2\text{O}
\end{array}
\]

**Replacing -OH by bromine**

Rather than using hydrobromic acid, the alcohol is typically treated with a mixture of sodium or potassium bromide and concentrated sulfuric acid. This produces hydrogen bromide, which reacts with the alcohol. The mixture is warmed to distil off the bromoalkane.

\[ \text{CH}_3\text{CH}_2\text{OH} + \text{HBr} \rightarrow \text{CH}_3\text{CH}_2\text{Br} + \text{H}_2\text{O} \]

**Replacing -OH by iodine**

In this case, the alcohol is reacted with a mixture of sodium or potassium iodide and concentrated phosphoric(V) acid, $\text{H}_3\text{PO}_4$, and the iodoalkane is distilled off. The mixture of the iodide and phosphoric(V) acid produces hydrogen iodide, which reacts with the alcohol.

\[ \text{CH}_3\text{CH}_2\text{OH} + \text{HI} \rightarrow \text{CH}_3\text{CH}_2\text{I} + \text{H}_2\text{O} \]

Phosphoric(V) acid is used instead of concentrated sulfuric acid because sulfuric acid oxidizes iodide ions to iodine and produces hardly any hydrogen iodide. A similar phenomenon occurs to some extent with bromide ions in the preparation of bromoalkanes but not enough to interfere with the main reaction. There is no reason why you could not use phosphoric(V) acid in the bromide case instead of sulfuric acid if desired.

**Reacting Alcohols with Phosphorus Halides**

Alcohols react with liquid phosphorus(III) chloride (also called phosphorus trichloride) to yield chloroalkanes.

\[ 3\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{PCl}_3 \rightarrow 3\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} + \text{H}_3\text{PO}_3 \]

Alcohols also violently react with solid phosphorus(V) chloride (phosphorus pentachloride) at room temperature, producing clouds of hydrogen chloride gas. While it is not a good approach to make chloroalkanes, it is a good test for the
presence of -OH groups. To show that a substance was an alcohol, you would first have to eliminate all the other groups that also react with phosphorus(V) chloride. For example, carboxylic acids (containing the -COOH group) also react with it (because of the -OH in -COOH) as does water (H-OH).

If you have a neutral liquid not contaminated with water, and clouds of hydrogen chloride are produced when you add phosphorus(V) chloride, then you have an alcohol group present.

\[ CH_3CH_2CH_2OH + PCl_5 \rightarrow CH_3CH_2CH_2Cl + POCl_3 + HCl \]

There are also side reactions involving the \(POCl_3\) reacting with the alcohol.

Other reactions involving phosphorus halides

Instead of using phosphorus(III) bromide or iodide, the alcohol is usually heated under reflux with a mixture of red phosphorus and either bromine or iodine. The phosphorus first reacts with the bromine or iodine to give the phosphorus(III) halide.

\[ 2P_{(s)} + 3Br_2 \rightarrow 2PBr_3 \]
\[ 2P_{(s)} + 3I_2 \rightarrow 2PI_3 \]

These then react with the alcohol to give the corresponding halogenoalkane, which can be distilled off.

\[ 3CH_3CH_2CH_2OH + PBr_3 \rightarrow 3CH_3CH_2CH_2Br + H_3PO_3 \]
\[ 3CH_3CH_2CH_2OH + PI_3 \rightarrow 3CH_3CH_2CH_2I + H_3PO_3 \]

Reacting alcohols with Thionyl Chloride

Sulfur dichloride oxide (thionyl chloride) has the formula SOCl₂. Traditionally, the formula is written as shown, despite the fact that the modern name writes the chlorine before the oxygen (alphabetical order). The sulfur dichloride oxide reacts with alcohols at room temperature to produce a chloroalkane. Sulfur dioxide and hydrogen chloride are given off. Care would have to be taken because both of these are poisonous.

\[ CH_3CH_2CH_2OH + SOCl_2 \rightarrow CH_3CH_2CH_2Cl + SO_2 + HCl \]

The advantage that this reaction has over the use of either of the phosphorus chlorides is that the two other products of the reaction (sulfur dioxide and HCl) are both gases. That means that they separate themselves from the reaction mixture.

Contributors

- Jim Clark (Chemguide.co.uk)