This page discusses the methods of swapping the -OH group in the -COOH group of a carboxylic acid for a chlorine atom to make acyl chlorides (acid chlorides). This section covers the use of phosphorus(V) chloride, phosphorus(III) chloride and sulfur dichloride oxide (thionyl chloride). In the examples below, consider the conversion of ethanoic acid to ethanoyl chloride to be typical of these types of reactions.

Replacing the -OH group using phosphorus(V) chloride, PCl₅

Phosphorus(V) chloride is a solid that reacts with carboxylic acids under cold conditions to produce hydrogen chloride fumes. The reaction leaves a liquid mixture of acyl chloride and a phosphorus compound, phosphorus trichloride oxide (phosphorus oxychloride, POCl₃). The acyl chloride can be separated by fractional distillation. The equation for this reaction is given below:

\[
3\text{CH}_3\text{COOH} + \text{PCl}_5 \rightarrow 3\text{CH}_3\text{COCl} + \text{POCl}_3 + \text{HCl}
\]

Replacing the -OH group using Phosphorous(III) chloride, PCl₃

Phosphorus(III) chloride is a liquid at room temperature. Its reaction with a carboxylic acid is less dramatic than that of phosphorus(V) chloride because there is no hydrogen chloride produced. A mixture of the acyl chloride and phosphoric(III) acid is produced (old names: phosphorous acid or orthophosphorous acid), (H₃PO₃). For example:

\[
3\text{CH}_3\text{COOH} + \text{PCl}_3 \rightarrow 3\text{CH}_3\text{COCl} + \text{H}_3\text{PO}_3
\]

As before, ethanoyl chloride can be separated by fractional distillation.

Replacing the -OH group using sulfur dichloride oxide (thionyl chloride)

Sulfur dichloride oxide (thionyl chloride) is a liquid at room temperature and has the formula (SOCl₂). Traditionally, the formula is written as shown, although the modern name writes the chlorine before the oxygen. Sulfur dichloride oxide reacts with carboxylic acids to produce an acyl chloride, giving off sulfur dioxide and hydrogen chloride gases. For example:

\[
\text{CH}_3\text{COOH} + \text{SOCl}_2 \rightarrow \text{CH}_3\text{COCl} + \text{SO}_2 + \text{HCl}
\]
The separation is simplified to an extent because the by-products are both gases. Fractional distillation is still required to separate the acyl chloride from any excess acid or sulfur dichloride oxide.

Contributors

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