22.4 ALPHA BROMINATION OF CARBOXYLIC ACIDS

OBJECTIVES

After completing this section, you should be able to

1. write an equation to illustrate the Hell-Volhard-Zelinskii reaction.
2. identify the product formed from the reaction of a given carboxylic acid with bromine and phosphorus tribromide.
3. identify the carboxylic acid, the reagents, or both, needed to synthesize a given α-bromo carboxylic acid.
4. outline the stereochemical implications of the fact that the Hell-Volhard-Zelinskii reaction proceeds through the formation of an acid bromide enol.

KEY TERMS

Make certain that you can define, and use in context, the key term below.

- Hell-Volhard-Zelinskii reaction

STUDY NOTES

The reagents for the Hell-Volhard-Zelinskii reaction are given as bromine and phosphorus tribromide. In some questions, you may observe that only bromine and phosphorus are listed as reagents. Really there is no difference, as phosphorus tribromide would be formed in situ by the combination of bromine and red phosphorus:

\[3\text{Br}_2 + 2\text{P} \rightarrow 2\text{PBr}_3\]

Excess bromine is required to ensure that enough reagent is available for the reaction with the enol.

Although the alpha bromination of some carbonyl compounds, such as aldehydes and ketones, can be accomplished with Br\(_2\) under acidic conditions, the reaction will generally not occur with acids, esters, and amides. This is because only aldehydes and ketones enolize to a sufficient extent to allow the reaction to occur. However, carboxylic acids, can be brominated in the alpha position with a mixture of Br\(_2\) and PBr\(_3\) in a reaction called the Hell-Volhard-Zelinskii reaction.

\[
\begin{align*}
\text{R} & \quad \text{C} & \quad \text{O} & \quad \text{H} & \quad \text{2) H}_2\text{O} \\
& \quad \text{OH} & & & \\
\text{R} & \quad \text{C} & \quad \text{O} & \quad \text{H} & \quad \text{Br}
\end{align*}
\]

1) Br\(_2\), PBr\(_3\)

The mechanism of this reaction involves an acid bromide enol instead of the expected carboxylic acid enol. The reaction starts with the reaction of the carboxylic acid with PBr\(_3\) to form the acid bromide and HBr. The HBr then catalyzes the formation of the acid bromide enol which subsequently reacts with Br\(_2\) to give alpha bromination. Lastly, the acid bromide reacts with water to reform the carboxylic acid.
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