

Alpha Carbon Chemistry: Enols and Enolates

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INTRODUCTION

When an acid or a basic catalyst is utilised, ketones and aldehydes react with halogens at the alpha position. The acid's job is to help the carbonyl tautomerize into the appropriate enol, which is nucleophilic enough to react with the halogen.

Enols are alkenes that have a strong electron donating substituent. Enolates are the conjugate bases or anions of enols, similar to how alkoxides are the anions of alcohols, and they can be made with a base.

Let's begin by going through the mechanism of acid-catalyzed halogenation. The reaction takes place in either acetic acid or another solvent with an acid catalyst added. The acid's job is to help the carbonyl tautomerize into the appropriate enol, which is nucleophilic enough to react with the halogen. The reaction is essentially a substitution of H for a halogen on the carbon.

Because halogen is an excellent leaving group, this halogenated carbon close to the carbonyl (position) represents a new reaction site for substitution and elimination processes.

In the base, there is an alpha halogenation

Under basic conditions, halogenation happens through the creation of enolates, which, despite being similar, is less helpful because it is difficult to stop the process at mono-halogenation.

The increased acidity of the alpha proton coupled to the carbon with an electronegative halogen atom is the cause of this increased reactivity. As a result, all of the protons in methyl ketones are replaced by halogens, resulting in di-halogenation and tri-halo carbonyl compounds.

To help visualize this, let's look at the mechanism of base-catalyzed halogenation. The reaction begins with the loss of a proton, resulting in the formation of an enolate that can attack the halogen.

The trisubstituted ketones are now particularly reactive towards a nucleophilic acyl substitution and react with the hydroxide to form a carboxylate salt.

The reaction is possible because the tri halogens stabilise the carbon's negative charge, giving it an excellent leaving group.

The haloform (CHX_3) reaction is the reaction of methyl ketones with an excess of halogen, which we will cover in a different essay. In the presence of catalytic amounts of phosphorus (or a phosphorus tri-bromide), carboxylic acids with hydrogen atoms can be brominated to generate α -bromo carboxylic acids. The Hell-Volhard-Zelinski (or HVZ) response is the name for this reaction.

We observed that the alpha halogenation of ketones and aldehydes occurs through the synthesis of enols or enolates, therefore carboxylic acids, despite having hydrogens, cannot be halogenated by this mechanism. The problem is that carboxylic acids are deprotonated before protons are removed, hence enols are difficult to produce.

Instead, the carboxylic acid interacts first with PBr_3 to generate an acid bromide, which then forms an equilibrium with an enol. After then, it works in the same way as halogenation of ketones and aldehydes does. Finally, the acid bromide is hydrolyzed to produce the carboxylic acid.

Carboxylic acid iodination with alpha chlorination

The three of them invented the Hell-Volhard-Zelinski reaction in 1881, but it took nearly a century for David N. Harpp of McGill University to establish an efficient method for chlorination and iodination of carboxylic acids.

It's a similar technique that uses N-chlorosuccinimide (NCS) and thionyl chloride for in-situ carboxylic acid conversion into acid chlorides. It's good for unwinding and getting a good night's sleep.

When you work out, your body expends a lot of energy that it must restore later. This usually occurs when you are sleeping. You fall asleep quickly to allow your body to begin the healing processes that will recover the energy you expended while exercising.

Enhances your mood

Physical activity improves your mood and alleviates stress, depression, and anxiety. Fitness training enhances stress and anxiety-controlling brain processes.

Increases the amount of energy you have regular exercise will boost your energy levels regardless of whether you are healthy or have a medical problem.

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