

19.3: OXIDATION OF ALDEHYDES AND KETONES

OBJECTIVES

After completing this section, you should be able to

- write an equation for the oxidation of an aldehyde using
 - CrO_3 /sulphuric acid.
 - Tollens reagent.
- explain the difference in structure which makes aldehydes susceptible to oxidation and ketones difficult to oxidize.
- identify the carboxylic acid produced when a given aldehyde is oxidized.
- identify the aldehyde, the oxidizing agent, or both, needed to prepare a given carboxylic acid.

KEY TERMS

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

- Tollens reagent

STUDY NOTES

An important difference between aldehydes and ketones is the ease with which the latter can be oxidized. Tollen's reagent is a classical organic laboratory technique to test for the presence of an aldehyde. The reagent consists of silver(I) ions dissolved in dilute ammonia. When the aldehyde is oxidized, the silver(I) ions are reduced to silver metal. When the reaction is carried out in a test-tube, the metallic silver is deposited on the walls of the tube, giving it a mirrorlike appearance. This characteristic accounts for the term "silver mirror test" which is applied when this reaction is used to distinguish between aldehydes and ketones—the latter, of course, do not react.

WHY DO ALDEHYDES AND KETONES BEHAVE DIFFERENTLY?

Aldehydes have a proton attached to the carbonyl carbon which can be abstracted, allowing them to be easily oxidized to form carboxylic acids. The lack of this hydrogen, makes ketones generally inert to these oxidation conditions. Nevertheless, ketones can be oxidized but only under extreme conditions.

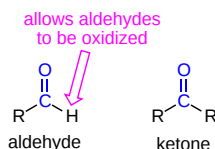
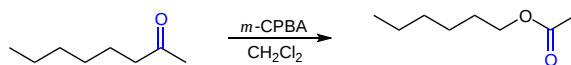
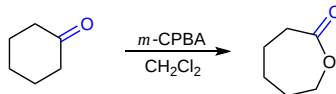


Figure 19.3.1: This characteristic accounts for the term "silver mirror test" which is applied when this reaction is used to distinguish between aldehydes and ketones—the latter, of course, do not react.

A significant distinction between aldehydes and ketones lies in their susceptibility to oxidation, with aldehydes being more easily oxidized than ketones. One of the classic methods for identifying aldehydes in the laboratory is through the use of **Tollen's reagent** which consists of silver(I) ions dissolved in dilute ammonia. When an aldehyde is present, it undergoes oxidation, causing the silver(I) ions to be reduced to metallic silver. This reduction results in the deposition of silver on the surface of the test tube, forming a reflective, mirror-like coating. This reaction is commonly referred to as the "silver mirror test," and it serves as a reliable way to distinguish aldehydes from ketones. Ketones, in contrast, do not react with Tollen's reagent, making this test specific for aldehydes.



Baeyer-Villiger Oxidation of 2-octanone to form hexyl ethanoate

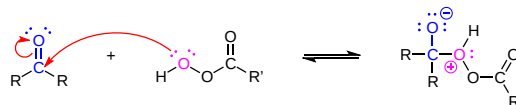


Baeyer-Villiger Oxidation of cyclohexanone to 6-hexanolactone

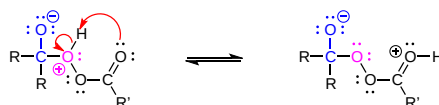
MECHANISM

The mechanism of the Baeyer-Villiger oxidation has been studied extensively and is of interest because it involves a rearrangement step in which a substituent group (R) moves from a carbon to an oxygen. In the first step, one oxygen from the peroxy carboxylic acid adds to the carbonyl group of the ketone. The adduct has multiple oxygen atoms on which protons can reside. An intramolecular proton transfer followed by protonation allows for generation of the Criegee intermediate. Migration of an alkyl group and elimination of a carboxylic acid, R^1CO_2H , then occur in the fourth step. This generates a protonated form of the ester product, which is deprotonated in the final step of the mechanism.

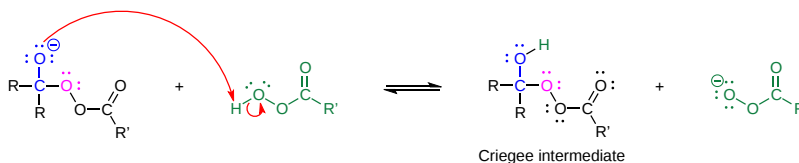
STEP 1: NUCLEOPHILIC ATTACK ON THE CARBONYL



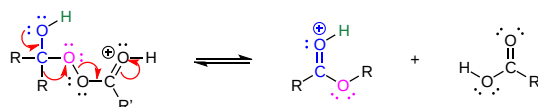
STEP 2: INTRAMOLECULAR PROTON TRANSFER



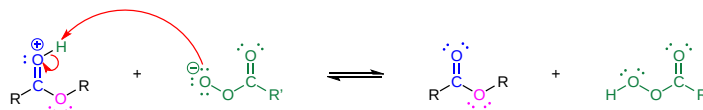
STEP 3: PROTONATION OF THE ALKOXIDE



STEP 4: MIGRATION OF AN ALKYL GROUP



STEP 5: DEPROTONATION



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