

## 5.4: 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
  - $\text{CrO}_3$ /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.

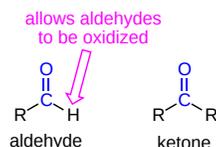
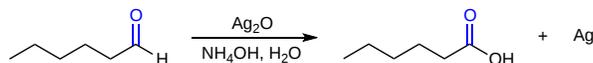


Figure 1). This characteristic accounts for the term "silver mirror test" which is applied when this reaction is used to distinguish between aldehydes and ketones—the latter, of course, do not react.



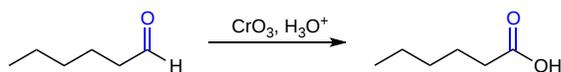
Figure 5.4.1: Tollens test for Aldehyde: Left Side Positive (silver mirror), Right Side Negative



Oxidation of hexanal to form hexanoic acid using Tollens Reagent

## OXIDATION OF ALDEHYDES

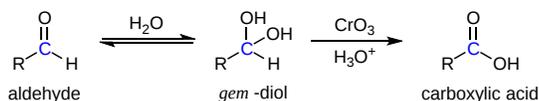
There are a wide variety of reagents which can cause the oxidation of aldehydes to carboxylic acids. The most common reagent for this conversion is  $\text{CrO}_3$  in aqueous acid also called **Jones Reagent**. This reaction generally gives good yields at room temperature.



Oxidation of hexanal to form hexanoic acid using Jones Reagent

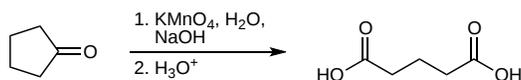
### MECHANISM

The oxidation of aldehydes occur through the reversible nucleophilic addition of water to the carbonyl to form a *gem*-diol functional group. This addition reaction is discussed in greater detail in [Section 19.5](#). One of the OH groups of the *gem*-diol is oxidized to create a carbonyl ( $\text{C}=\text{O}$ ) thereby forming a carboxylic acid.



## OXIDATION OF KETONES

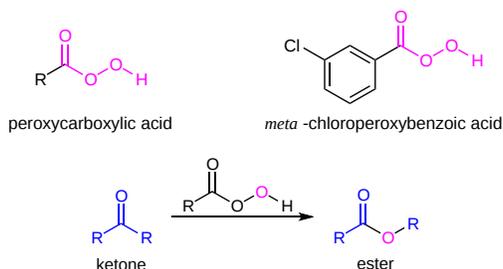
Because ketones do not have hydrogen atom attached to their carbonyl, they are resistant to oxidation. Only very strong oxidizing agents such as potassium manganate(VII) (potassium permanganate) solution oxidize ketones. However, this type of powerful oxidation occurs with cleavage, breaking carbon-carbon bonds and forming two carboxylic acids. Because of this destructive nature this reaction is rarely used.



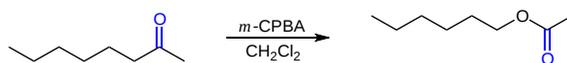
Oxidation of cyclopentanone to form pentanedioic acid

## BAEYER-VILLIGER OXIDATION

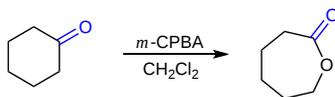
**Peroxyacetic acids**, such as **meta-chloroperoxybenzoic acid (mCPBA)**, are capable of oxidizing ketones to esters in a reaction known as the **Baeyer-Villiger oxidation**. Baeyer-Villiger oxidation has considerable synthetic utility because ketones normally are difficult to oxidize without degrading the structure to smaller fragments.



Baeyer-Villiger oxidations can be used with both straight chain ketones and cyclic ketones as shown in the following examples.



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



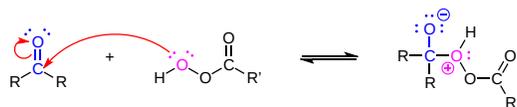
Baeyer-Villiger Oxidation of cyclohexanone to 6-hexanolactone

### 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.

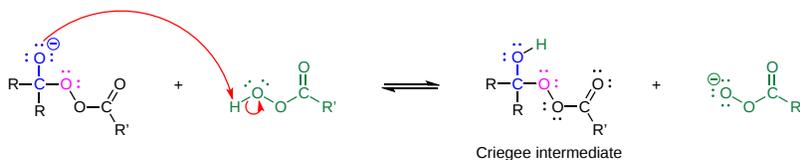
**Step 1) Nucleophilic attack on the carbonyl**



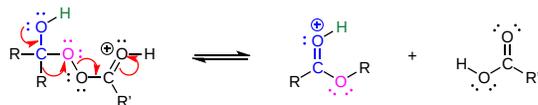
**Step 2) Intramolecular Proton Transfer**



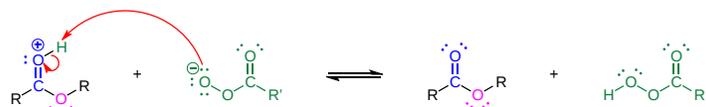
**Step 3) Protonation of the alkoxide**



**Step 4) Migration of an Alkyl Group**



**Step 5) Deprotonation**



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