

B.Sc Semester – IV MJC – 6(T) Organic Chemistry

Unit – I Alcohols, Phenols, Esters and Epoxides

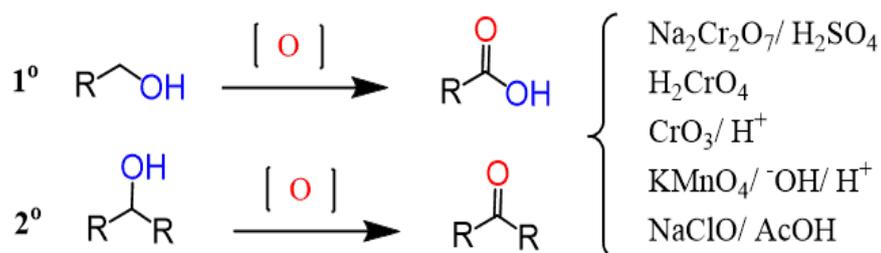
Pyridinium Chlorochromate (PCC) Oxidation and Oppenauer Oxidation

Pyridinium Chlorochromate (PCC) Oxidation

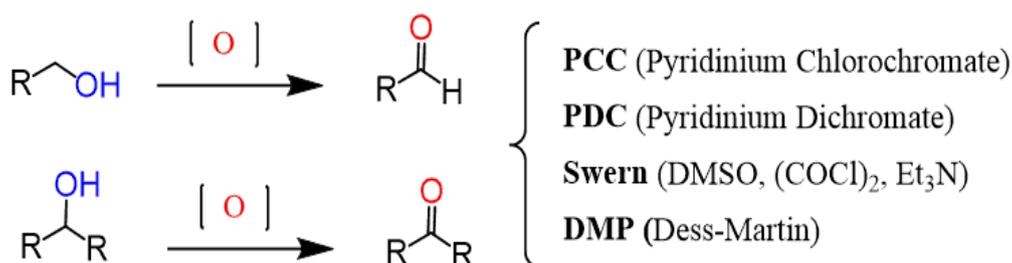
PCC oxidation is one of the selective methods for oxidizing primary alcohols to aldehydes. Although very often the outcome of the oxidation will depend on the presence or absence of water, traditionally, the most common mild oxidizing agents are considered pyridinium chlorochromate (PCC), pyridinium dichromate (PDC), [Swern oxidation](#) using DMSO, (COCl)₂ and Et₃N, and the Dess-Martin (DMP) oxidation:

Oxidation of Alcohols using Strong and Mild Oxidizing Agents

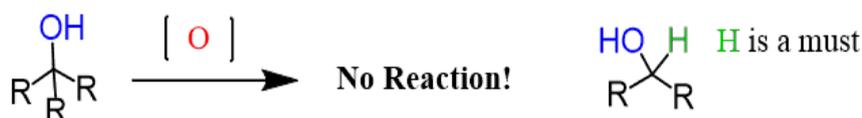
Strong Oxidizing Agents oxidize **Primary Alcohols** to **Carboxylic Acids** and **Secondary Alcohols** to **Ketones**



Some oxidizing agents can selectively oxidize primary alcohols to aldehyde:

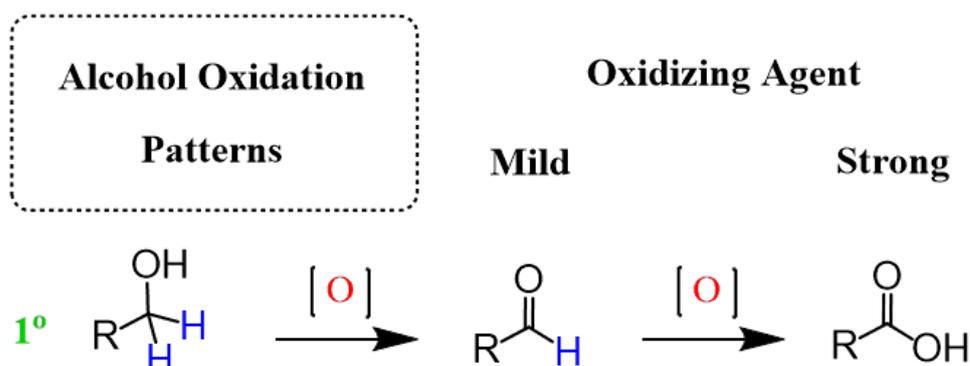


Tertiary alcohols cannot be oxidized! (well, except for burning them to CO₂)

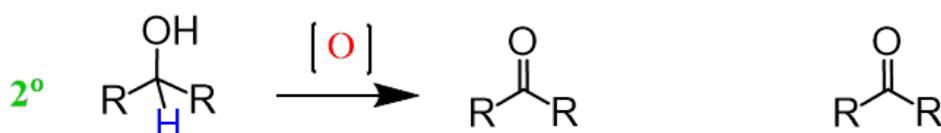


This is the advantage of mild oxidizing agents since, remember, strong oxidizing agents, such as [Jones'](#), oxidize primary alcohols all the way to carboxylic acids.

Below is a **general scheme of the alcohol oxidation** patterns depending on the nature of the oxidizing agent, and this is covered in a lot more detail in this post: [Oxidation of Alcohols](#).



For 1° alcohols, an aldehyde is formed first which is then oxidized further to a carboxylic acid.



For 2° alcohols, a ketone is formed which can no longer be oxidized regardless of the oxidizing agent.



3° alcohols cannot be oxidized regardless of the oxidizing agent.

As shown above, **mild reagents** stop the oxidation once the carbonyl group is formed. And if it is a **primary alcohol, the product is an aldehyde**, while the oxidation of a **secondary alcohol results in a ketone**.

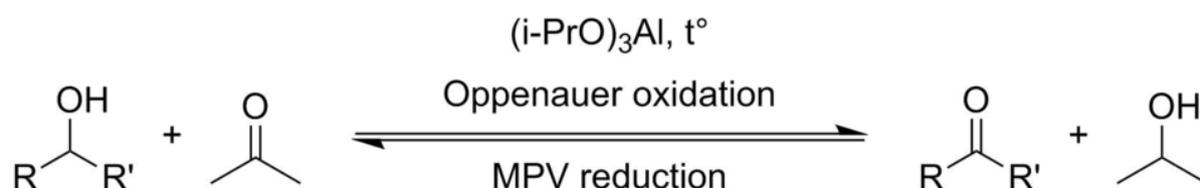
For now, let's focus on the **PCC oxidation**. Like other mild oxidizing agents, such as the **Swern** and **Dess-Martin** (DMP) oxidation, it stops the oxidation of the alcohol once a carbonyl group is formed. If it is a **primary alcohol, the product is an aldehyde**, while the oxidation of **secondary alcohols results in a ketone**:

PCC belongs to the family of chromium-based oxidizing agents, most of which are CrO_3 , $\text{Na}_2\text{Cr}_2\text{O}_7$, and chromic acid, collectively known as Jones oxidation, but unlike those, it is a mild oxidizing agent.

Oppenauer Oxidation

Oppenauer Oxidation is the process of conversion of secondary alcohols to ketones by selective oxidation. This reaction is named after Rupert Viktor Oppenauer. Oxidation reaction takes place in the presence of $[\text{Al}(\text{i-Pro})_3]$ in excess of acetone.

It is an aluminium alkoxide catalysed oxidation of a secondary alcohol to the corresponding ketone. This is the reverse of the Meerwein Ponndorf Verley reduction. It is a very good method to oxidise allylic alcohols to α, β -unsaturated ketones.



Mechanism

1. In the first step, alcohol coordinates with aluminium isopropoxide to form a complex
2. This complex reacts with a ketone to form a six-membered transition complex
3. The alpha-carbon of the alcohol is converted to the carbonyl carbon from the aluminium-catalysed hydride shift.
4. The acetone proceeds over a six-membered transition state.
5. The desired ketone is formed after the hydride transfer

