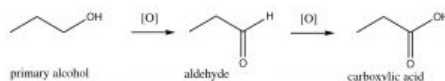


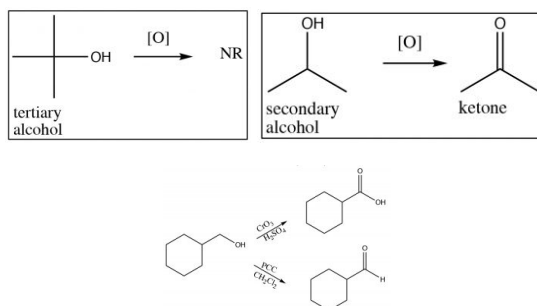
6.4: Oxidation of Alcohols

Before we discuss oxidation of alcohols, it should be clear what we mean by the “oxidation” and “reduction” of carbon compounds. Recall that in earlier discussions we used the term reduction to mean the addition of hydrogen and oxidation to mean the addition of oxygen, rather than calculating changes in oxidation numbers (decrease for reduction, increase for oxidation). The reason is because oxidation numbers in organic compounds can be hard to calculate and apply^[3]. In this section, we consider how alcohols can be oxidized to give aldehydes, ketones, or carboxylic acids. In general, we consider a carbon compound to be oxidized when the number of bonds between the C and electronegative atoms (often, but not always, O) is increased.

For example, a primary alcohol can be oxidized (which we will denote by O for the time being) to an aldehyde; depending upon the reagent used, the reaction can proceed through a second step to produce the corresponding carboxylic acid. At each step, the oxidation level of the carbon is increasing.



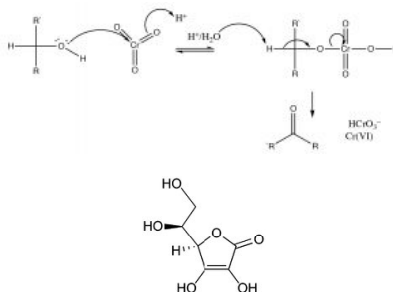
Starting with a secondary alcohol, the product of an oxidation reaction is the corresponding ketone, but tertiary alcohols do not give useful products and may simply lead to degradation (C – C bond breaking). Generally, it is not possible to oxidize a secondary carbon beyond the ketone level without breaking carbon-carbon bonds, and similarly, tertiary alcohols cannot be oxidized under normal circumstances.



Typical oxidizing reagents include transition metals in high-oxidation states (that is able to accept [bond to] O atom). For example, chromium (VI) in the form of chromium trioxide (CrO_3) or sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$), when in concentrated H_2SO_4 , are both powerful oxidizing agents and both will oxidize a primary alcohol through both steps, that is, all the way to the carboxylic acid form. Pyridinium chlorochromate (PCC \rightarrow) is a milder oxidizing agent that will oxidize primary alcohols, only through the first step, to produce an aldehyde.

The general mechanism of oxidation is shown below, note electrons leave the alcohol and end up on the Cr, reducing its oxidation state from 6 to 4, and the alcohol carbon ends up oxidized.

Primary alcohols can be selectively oxidized to aldehydes with PCC



One problematic aspect of such oxidizing reagents is that they contain highly toxic and carcinogenic Cr (VI) in one form or another. Such materials oxidize a range of biomolecules such as vitamin C (ascorbic acid) and some thiols (such as the amino acid cysteine). Reduced chromium also reacts with nucleic acids and can lead to mutations, which can lead to cell death and/or cancer. To avoid using such toxic chemicals, there has been increasing in what has come to be known as **green chemistry**^[4]. One of the tenets of green chemistry is to minimize the use of toxic reagents (such as chromium compounds).^[5]

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