

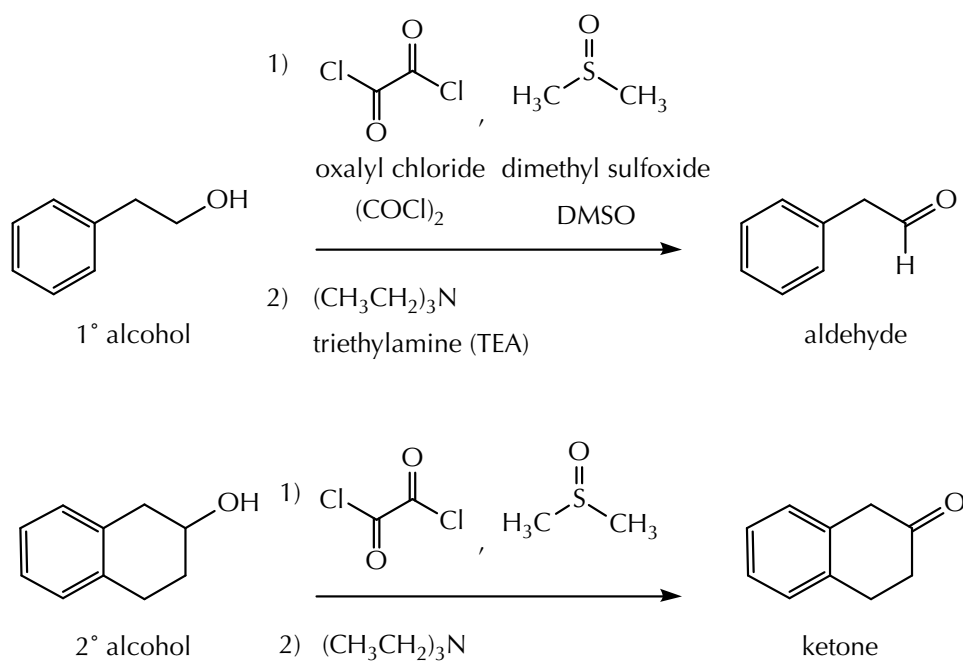
D. Swern Oxidation

Although there are many other options for carrying out oxidation reactions, the chromium (VI) reagents are easy to perform and quite general in their applicability—they work predictably well on more or less all of the primary and secondary alcohols they are combined with. Unfortunately, chromium salts are toxic environmental pollutants, and so finding more environmentally friendly and sustainable options for chemical reactions, and oxidation reactions, in particular, is of great interest.

An early entry in the list of non-chromium oxidation reactions was the Swern oxidation, which was developed in 1978, about the same time as the PCC and PDC reagents appeared (Figure 1120).

Figure 1120

The Swern oxidation: 1° alcohols to aldehydes; 2° alcohols to ketones.



The reaction is anhydrous, so the functional group relationships are exactly the same as with the anhydrous chromium reagents: Primary alcohols are oxidized to their corresponding aldehydes and **secondary** alcohols, as they do under all conditions, are oxidized to their corresponding ketones.

Although the reaction conditions are completely unlike the chromium reagents, these are still oxidation reactions and they still follow the general mechanistic picture: (a) the oxygen atom of the organic alcohol reacts with the oxidant to pick up a potential leaving group, (b) the original OH group is then deprotonated, and (c) an elimination reaction takes place to form the new CO pi bond.

The oxidizing agent in the Swern reaction is the chloro(dimethyl)sulfonium ion $[(\text{CH}_3)_2\text{S}^+\text{Cl}]$, which was originally prepared, as reported by Daniel Swern, using oxalyl chloride and dimethyl sulfoxide (DMSO). Variations that give the same ion are dimethyl sulfide in combination with either molecular chlorine or *N*-chlorosuccinimide (NCS). These three methods for generating the oxidizing agent, including their mechanisms of formation, are given in Figure 1121.