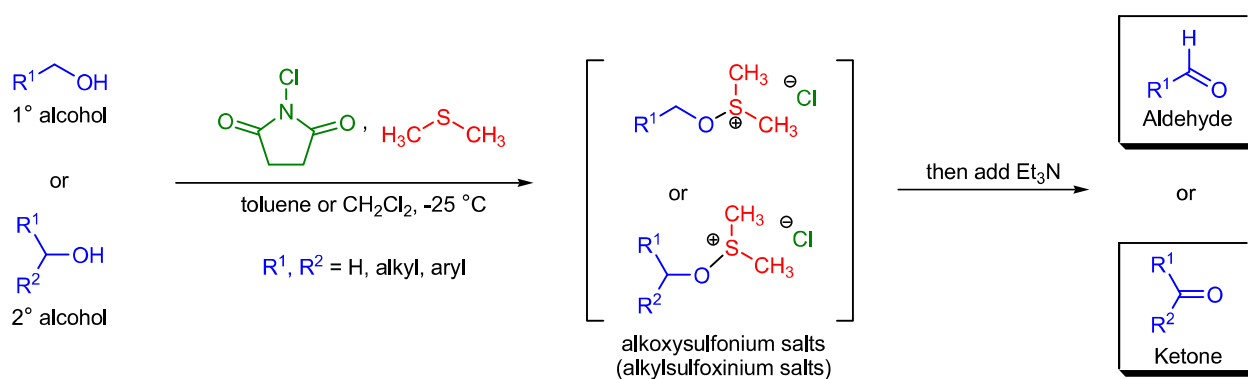


COREY-KIM OXIDATION

(References are on page 566)

Importance:[Seminal Publications¹⁻³; Modifications & Improvements^{4,5}]

In 1972, E.J. Corey and C.U. Kim developed a new process for the efficient conversion of alcohols to aldehydes and ketones using *N*-chlorosuccinimide (NCS), dimethylsulfide (DMS) and triethylamine (TEA).² The oxidation of primary and secondary alcohols with NCS/DMS is known as the *Corey-Kim oxidation*. The active reagent, *S,S*-dimethylsuccinimidium sulfonium chloride, is formed *in situ* when NCS and DMS are reacted and is called the *Corey-Kim reagent*.¹ This protocol can be used for the oxidation of a wide variety of primary and secondary alcohols except for allylic and benzylic alcohols, where the substrates are predominantly converted to the allylic and benzylic halides. In polar solvents, a side-reaction may occur in which the alcohol forms the corresponding methylthiomethyl ether (ROCH₂SCH₃). The reaction conditions for the *Corey-Kim oxidation* are mild and tolerate most functional and protecting groups. Therefore, the protocol can be applied to the oxidation of polyfunctionalized molecules. Recent modifications of the original procedure led to the development of the fluororous⁴ and odorless⁵ *Corey-Kim oxidations*. In addition to being an effective oxidant for alcohols, the *Corey-Kim reagent* has also been used to dehydrate aldoximes to nitriles,⁶ convert 3-hydroxycarbonyl compounds to 1,3-dicarbonyls,⁷ synthesize stable sulfur ylides from active methylene compounds⁸ and to prepare 3(*H*)-indoles from 1(*H*)-indoles.⁹

**Mechanism:**^{2,4}

The first step of the mechanism of the *Corey-Kim oxidation* is the reaction of dimethylsulfide with *N*-chlorosuccinimide to generate the electrophilic active species, *S,S*-dimethylsuccinimidium sulfonium chloride (*Corey-Kim reagent*) via dimethylsulfonium chloride. The sulfonium salt is then attacked by the nucleophilic alcohol to afford an alkoxysulfonium salt. This alkoxysulfonium salt is deprotonated by triethylamine and the desired carbonyl compound is formed. The dimethylsulfide is regenerated, and it is easily removed from the reaction mixture *in vacuo*. In the *odorless Corey-Kim oxidation*⁵ instead of dimethylsulfide, dodecylmethylsulfide is used. This sulfide lacks the unpleasant odor of DMS due to its low volatility.

