PROBLEM 18

[SUPPL Problem 18 # 2]

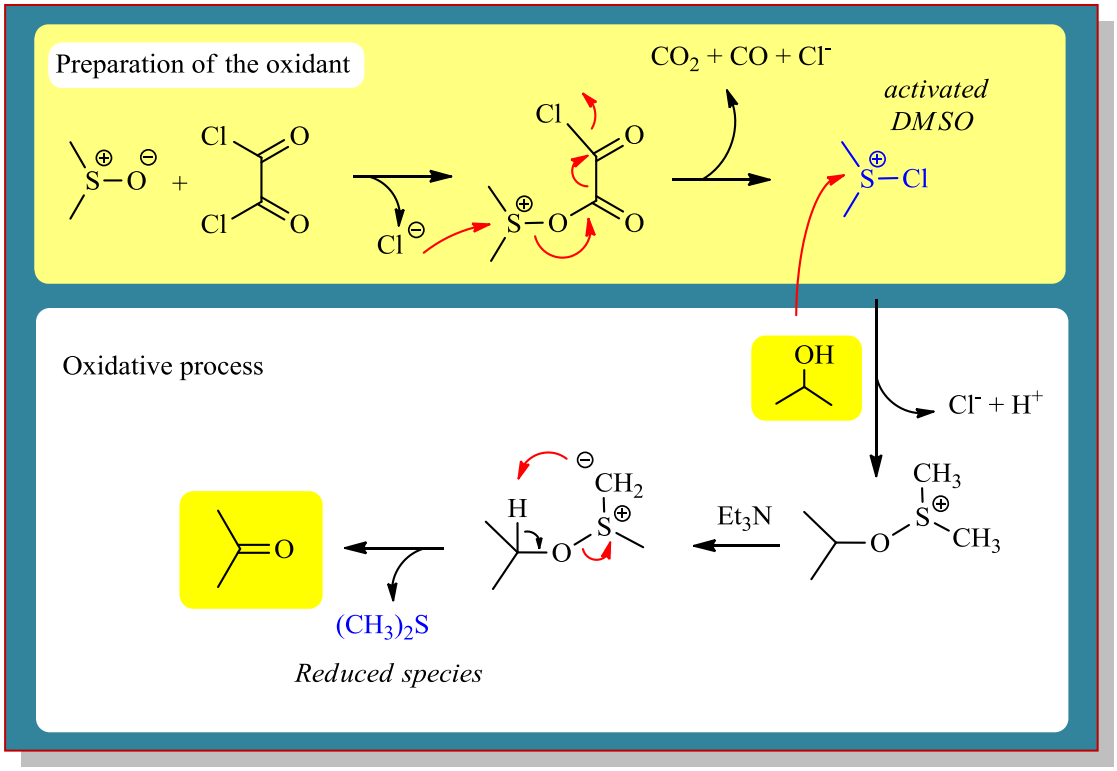
Arabic compound numbers in TAPSOC,
Roman numerals in Supplementary material

The Swern oxidation: mechanism.

Everyone in the trade knows that the majority of the oxidation reagents of general use in organic reactions include a metal ion. There is no scarcity of classical Cr, Mn, Ag and other transition metal compounds most synthesis labs cannot do without. Over the years, however, demand for increasing regioselectivity, mild conditions and product sophistication has brought about a refreshing wave of oxidants without the metal core [1]. Ozone, elementary sulfur, perchlorates, hydrogen peroxide and peroxyacids are ancient additions. But others are designed on an organic framework.

Among a variety of concept chemicals, combinations of dimethyl sulfoxide (DMSO) and a number of electrophiles are capable of taking electrons away from organic substrates. These compounds are reactive enough to operate at low to very low temperatures, providing a valuable handle on reaction control. Successful electrophiles were as varied as dicyclohexyl carbodiimide, acetic anhydride, phosphorous pentoxide, SO_3-pyridine complex, and DMSO-halogen combinations.

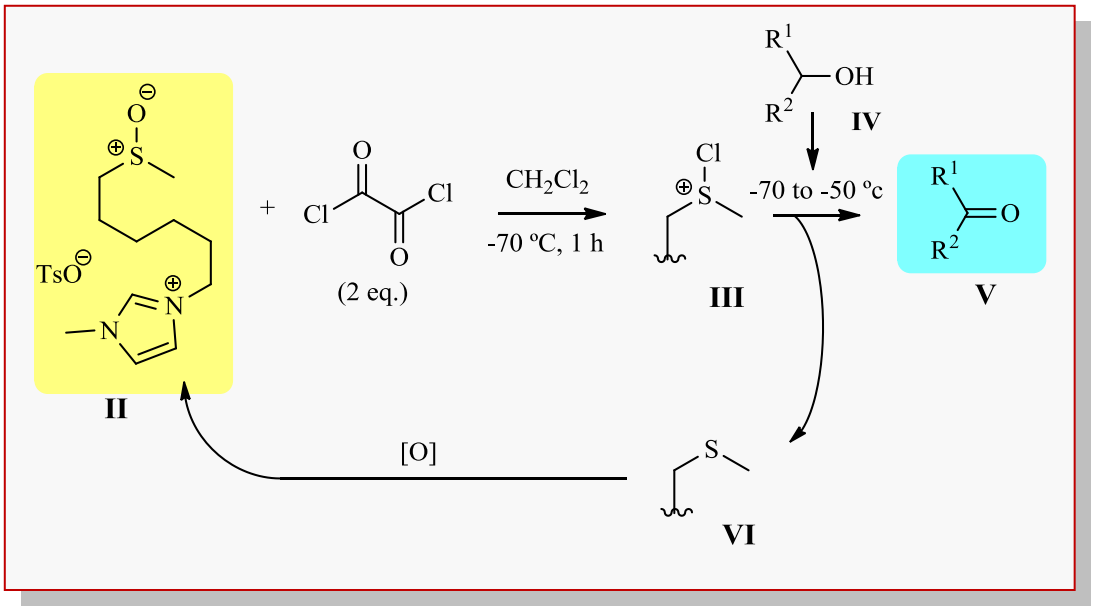
The Swern oxidation [2] is one such DMSO – halogen combination with assistance from oxallyl chloride to enhance the reactivity of DMSO towards chloride anion to form the actual oxidizing reagent. Mechanism particulars are shown in Scheme SP 18.2.1.



SCHEME SP18.2.1

The reduced species, dimethyl sulfide, has a very pungent, odor. Experimentally, it is convenient to set a nitrogen flow over the reaction mixture to drive away this gas and bubble it through a NaOCl solution or other oxidant to scrub this compound [3].

But organic chemists' ingenuity seems to know no limits. If the methyl sulfide section is bonded to a larger, solvent soluble and non volatile molecule, it not only won't pollute the air around the experiment but the reduced sulfide can be recovered and re-oxidized to be used again (Scheme SP18.2.2) [4].



SCHEME SP18.2.2

REFERENCES:

[1] For a review, see: Adam W, Saha-Möller CR, Ganeshpure PA. Chem. Rev. 2001;101:3499-3548.

[2] Omura K, Swern D. Tetrahedron 1978;34:1651-1660.

[3] These procedures are used industrially to control malodorous sulfur emissions from sewage sludge and chemical plants. See: Devai I, Delaune RD. Environ. Technol. 2002;23:319-329.

[4] Tsuchiya D, Moriyama K, Togo H. Synlett 2011:2701-2704.