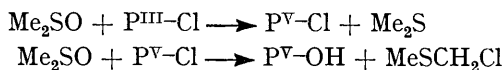


1163. Sulphoxides. Part II.¹ Reactions of Dimethyl Sulphoxide with Inorganic and Organic Acid Halides *

By E. H. AMONOO-NEIZER, S. K. RAY, R. A. SHAW, and B. C. SMITH

Dimethyl sulphoxide reacts with acid chlorides to give acids and chloromethyl methyl sulphide. Oxidation precedes hydroxylation in reactions with phosphorus(III) chlorides, which give dimethyl sulphide, chloromethyl methyl sulphide, and phosphorus(V) acids. Mechanisms for the hydroxylation reactions are proposed.

DIMETHYL SULPHOXIDE is an oxidising agent which reacts with trivalent phosphorus compounds to give phosphoryl compounds and dimethyl sulphide.^{1,2} A further reaction takes place in the presence of phosphorus-halogen bonds, and a preliminary account of our observations of the hydroxylating properties of dimethyl sulphoxide has appeared.² Chlorine is replaced by hydroxyl to give the corresponding phosphorus(V) acid, and chloromethyl methyl sulphide is formed.



Stoichiometric quantities of dimethyl sulphoxide react readily with acid halides in boiling methylene chloride or ether, or in the absence of a solvent at room temperature. The method is particularly suitable for the preparation of compounds which are unstable in the presence of moisture. The reactions of dimethyl sulphoxide with diphenylchlorophosphine or diphenylchlorophosphine oxide, phenyldichlorophosphine, phosphorus trichloride, cyanuric chloride, benzoyl chloride, and benzene sulphonyl chloride give diphenylphosphinic acid, phenylphosphonic acid, orthophosphoric acid, cyanuric acid, benzoic acid, and benzene sulphonic acid, respectively. The oxidation of trivalent phosphorus compounds, which precedes hydroxylation, is accompanied by the evolution of dimethyl sulphide.

Reactions of sulphoxides with acid chlorides, including thionyl chloride, *p*-nitrobenzoyl chloride, and benzoyl chloride were first investigated by Bordwell and Pitt,³ and vigorous reactions with other acid halides have been reported.⁴ Issleib and Tzschach⁵ investigated the reactions of diphenyl sulphoxide with silicon halides which give silica or silicon oxychlorides together with, depending on the halide, varying proportions of diphenyl sulphide, *p*-halogenophenyl phenyl sulphide, and di-*p*-halogenophenyl sulphide. Reactions of sulphoxides with silicon tetrachloride and boron trichloride have been studied in some detail by Lappert and Smith.⁶ Dimethyl sulphoxide gives silica and chloromethyl methyl sulphide, and a boron oxychloride-chloromethyl methyl sulphide addition compound, respectively. Reactions of dimethyl sulphoxide with some cyclic phosphorus chlorides have also been investigated by Rätz and Sweeting.⁷

The mechanism of the hydroxylation reaction presumably involves initial nucleophilic attack by sulphoxide oxygen on the atom M to which the halogen atom X is attached, the remaining portion of the molecule being represented by Z. The initial stage may lead to a transition state (I) or an intermediate (II), formed either by addition to the double bond when M is carbonyl carbon, or by the use of vacant orbitals when M is boron, silicon,

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¹ Part I, E. H. Amonoo-Neizer, S. K. Ray, R. A. Shaw, and B. C. Smith, *J.*, 1965, 2997.

² S. K. Ray, R. A. Shaw, and B. C. Smith, *Nature*, 1962, **196**, 372.

³ F. G. Bordwell and B. M. Pitt, *J. Amer. Chem. Soc.*, 1955, **77**, 572.

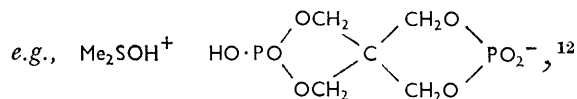
⁴ S. A. Heininger and J. Dazzi, *Chem. Eng. News*, 1957, **35**, [9], 87.

⁵ K. Issleib and M. Tzschach, *Z. anorg. Chem.*, 1960, **305**, 198.

⁶ M. F. Lappert and J. K. Smith, *J.*, 1961, 3224.

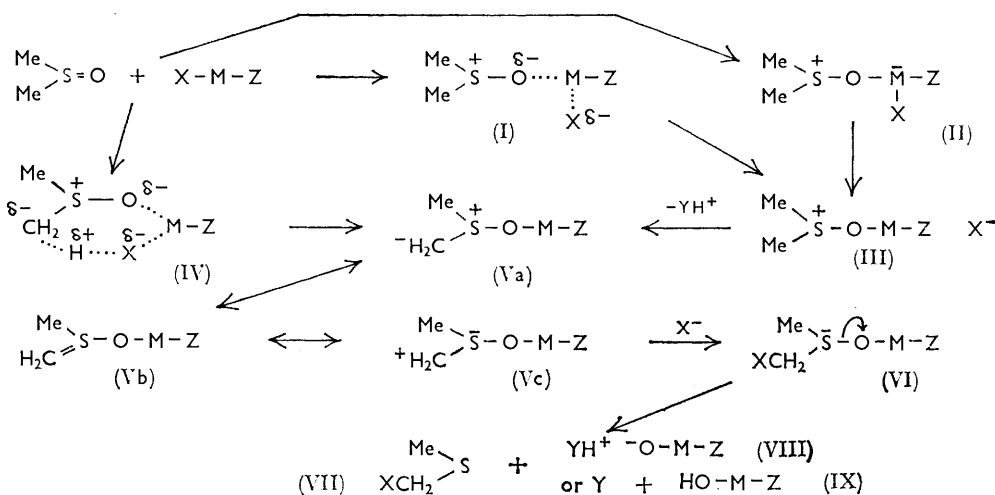
⁷ R. Rätz and O. J. Sweeting, *Tetrahedron Letters*, 1963, **8**, 529; *J. Org. Chem.*, 1963, **28**, 1612.

phosphorus, or sulphur, which can be isolated in some cases, *e.g.*, $\text{Me}_2\text{SO}\cdot\text{BF}_3$ ^{6,8} and $(\text{Me}_2\text{SO})_2\cdot\text{SiF}_4$ ^{6,9}. Elimination of the halide ion X^- can give a salt (III), *e.g.*, $[(\text{Me}_2\text{SO})_6\text{Al}]\text{Cl}_3$ ⁸. Structures analogous to (III) have been postulated for the very reactive adducts formed between dimethylformamide and certain phosphorus(v) derivatives which can be isolated as deliquescent solids at low temperatures.¹⁰ The presence of positively charged sulphur facilitates the subsequent abstraction of a proton by a nucleophile Y, which may be the displaced halide ion, a second sulphoxide molecule, or another proton acceptor. An alternative mechanism involving a six-membered transition state (IV) would lead directly from the reactants by HX elimination to the ylid (V).¹¹ The oxygen atom attached to sulphur favours the resonance form (Vc) which combines readily with nucleophilic reagents, *e.g.*, X^- . The phosphazene "adducts" with chloromethyl methyl sulphide² may well contain the anions (VI). Simultaneous or subsequent heterolysis of the S-O bond gives chloromethyl methyl sulphide (VII), and depending on the nature and concentration of Y the salt (VIII),



or the acid (IX) can be isolated.

This differs in some respects from other proposed mechanisms^{5,6} involving halogeno-sulphonium halides, where it is stated or implied that each sulphoxide molecule displaces two halogen atoms. Similar products are obtained, but the stoichiometries of the reactions are different. Diphenylchlorophosphine oxide, benzene sulphonyl chloride, and



benzoyl chloride provide a convenient comparison for the two mechanisms. The corresponding acids are stable, with little tendency to condense under the experimental conditions. In all three cases reaction of dimethyl sulphoxide (1 mole) with acid halide (2 moles) gives chloromethyl methyl sulphide (1 mole), acid (1 mole), and unreacted acid halide (1 mole). The products of some other systems investigated, including thionyl chloride and

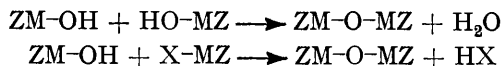
⁸ F. A. Cotton and R. Francis, *J. Amer. Chem. Soc.*, 1960, **82**, 2986.

⁹ V. Gutmann and K. Utvary, *Monatsh.*, 1959, **90**, 706.

¹⁰ H. Bredereck, R. Gompper, K. Klemm, and H. Rempfer, *Chem. Ber.*, 1959, **92**, 837; F. Cramer and M. Winter, *ibid.*, 1961, **94**, 989.

¹¹ S. Trippett, *Quart. Rev.*, 1963, **17**, 436.

boron and halides, silicon are acids which are capable of further reaction by condensation.



The water produced reacts with a further quantity of acid halide to give acid and hydrogen halide. Hydrogen halides react with dimethyl sulphoxide to give water and halogenosulphonium halides, which break down into halogenomethyl methyl sulphide and hydrogen halide.¹² The halogenosulphonium halide mechanism occurring additionally in reactions involving unstable acid products would account for the second halogen atom consumed by each sulphoxide molecule.

The mechanism proposed here, with which Lappert finds himself in agreement,¹³ accounts satisfactorily for all the reported observations, and a modified version may apply to reactions of other sulphoxides. Diphenyl sulphoxide reacts less readily than dimethyl sulphoxide, and in reactions of methyl phenyl sulphoxide substitution by chlorine occurs in the methyl rather than in the phenyl group.³ The mechanism is capable of wider extension, and reactions of sulphoxides with acid anhydrides¹⁴ may also proceed by this type of scheme.

EXPERIMENTAL

Reactions were carried out in an atmosphere of dry nitrogen. Dimethyl sulphoxide was added slowly to the acid halide or to its solution in methylene chloride or ether. Dimethyl sulphide, b. p. 34–36°, was evolved from reactions with trivalent phosphorus compounds and was collected at –80°. Solid products were removed by filtration and the acids were characterised by m. p.s and mixed m. p.s with authentic samples. Fractional distillation of the filtrate gave chloromethyl methyl sulphide, b. p. 107–110° (Found: C, 24.8; H, 5.1; S, 34.4%; *M*, 95. Calc. for C₂H₅ClS: C, 24.85; H, 5.2; S, 33.4%; *M*, 96.5). Filtrates from the reactions with diphenylchlorophosphine oxide, benzene sulphonyl chloride, and cyanuric chloride were distilled on a spinning band column and starting material was recovered in each case. Yields are recorded in the Table.

Reactions of dimethyl sulphoxide					
Me ₂ SO (mole)	Acid chloride	(mole)	MeSCH ₂ Cl (%)	Product	(%)
0.2	Ph ₂ PCl	0.1	83	Ph ₂ PO ₂ H	94
0.3	PhPCl ₂	0.1	96	PhPO(OH) ₂	75
0.4	PCl ₃	0.1	90	H ₃ PO ₄	96
0.3	N ₃ C ₃ Cl ₃	0.1	73	N ₃ C ₃ O ₃ H ₃	84
0.1	Ph ₂ POCl	0.2	95	Ph ₂ POCl	50
				Ph ₂ PO ₂ H	48
0.1	PhSO ₂ Cl	0.2	97	PhSO ₂ Cl	49
				PhSO ₃ H	48
0.1	PhCOCl	0.2	98	PhCOCl	49
				PhCO ₂ H	49

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¹² H. H. Szmant, "Organic Sulphur Compounds," ed. N. Kharasch, Pergamon Press, London, 1961, ch. 16; W. O. Ranky and D. C. Nelson, *ibid.*, ch. 17.

¹³ M. F. Lappert, personal communication.

¹⁴ L. Horner and P. Kaiser, *Annalen*, 1959, **626**, 19; *ibid.*, 1960, **631**, 198.