Preparation of Alkoxy and Other Sulphonium Salts *via* an Intermediate Adduct Between Methyl Chlorosulphinate and Dimethyl Sulphoxide

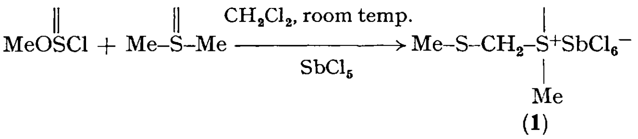
By Yoshinori Hara and Minoru Matsuda*

(*Chemical Research Institute of Non-aqueous Solutions, Tohoku University, Sendai,* 980 *Japan*)

Summary A simple and efficient synthetic approach to alkoxy- and other sulphonium salts is described.

Relatively few studies have been performed on syntheses of alkoxysulphonium salts.[1] In general, they are prepared by alkylation of the corresponding sulphoxides with trialkyloxonium salts,[2] or by routes involving oxonium ions or positive halogen compounds.[1b,3] We now report a simple and widely applicable method for the preparation of alkoxy and other sulphonium salts *via* an intermediate adduct between methyl chlorosulphinate and dimethyl sulphoxide.

Me_2SO (1 mol. equiv.) was added to a solution of the alkyl chlorosulphinate in CH_2Cl_2 at $-78°$. After 1 h, addition of $SbCl_5$ produced immediately the corresponding alkoxydimethylsulphonium hexachloroantimonate in good yield (see Table 1).† These reactions seem to be essentially identical with the decarboxylation of alkyl chloroformates in Me_2SO yielding the alkoxysulphonium salts.[4,5] However, it is interesting that at room temperature the reaction of MeOS(:O)Cl with Me_2SO gave compound (**1**) as the main product (Table 1).



$$\mathrm{MeO}\overset{\displaystyle \mathrm{O}}{\overset{\|}{\mathrm{S}}}\mathrm{Cl} + \mathrm{Me{-}}\overset{\displaystyle \mathrm{O}}{\overset{\|}{\mathrm{S}}}\mathrm{{-}Me} \xrightarrow[\mathrm{SbCl_5}]{\mathrm{CH_2Cl_2,\ room\ temp.}} \mathrm{Me{-}S{-}CH_2{-}}\overset{\displaystyle \mathrm{Me}}{\underset{\displaystyle \mathrm{Me}}{\mathrm{S^+}}}\mathrm{SbCl_6^-}$$

(**1**)

† Satisfactory elemental analyses have been obtained for all compounds.

TABLE 1. Products from the reaction of alkyl chlorosulphinates with sulphoxides at −78° and at room temperature.

Chlorosulphinate $R^1OS(:O)Cl$ R^1	Sulphoxide $R^2{}_2SO$ R^2	Product $R^2{}_2(R^3)S^+SbCl_6{}^-$ R^2	R^3	M.p./°C	Yield (%)
Me[a]	Me	Me	MeO	174	86
Et[a]	"	"	EtO	108[3b]	84
Pr^i[a]	"	"	Pr^{i}O	132—133[3b]	86
Me[a]	Ph	Ph	MeO	165—166	58
Me[b]	Me	Me	$MeSCH_2$	133—135[3b]	27—28
Et[b]	"	"	"	"	22—26

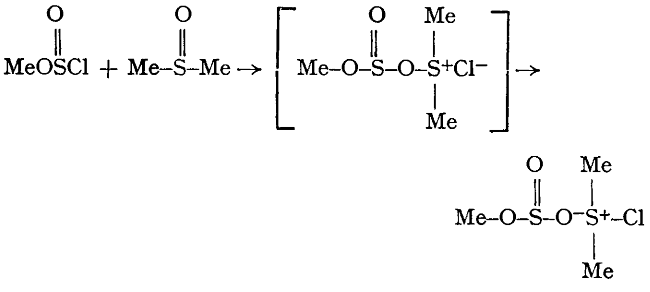
[a] At −78° for 1 h. [b] At room temp. for 5 h.

EtOS(:O)Cl also gave compound (**1**) at room temperature. Moreover, the n.m.r. spectrum of the product prepared from the reaction of MeOS(:O)Cl with $(CD_3)_2SO$ showed no protons which could be ascribed to MeOS(:O)Cl indicating that compound (**1**) is formed from 2 Me_2SO units. The reaction of a mixture of MeOS(:O)Cl and Me_2SO in liquid SO_2 at room temperature gave equimolar amounts of HCHO and $Me_2(MeSCH_2)S^+Cl^-$ (detected by n.m.r. spectroscopy) An intermediate adduct formed between MeOS(:O)Cl and Me_2SO must react further with the Me_2S which is produced from the decomposition of adduct, presumably analogous to Kornblum oxidation.[4] The adduct obtained by the addition of alkyl chlorosulphinate to Me_2SO at −78° was a colourless viscous oil which dissolved only in polar solvents such as SO_2 and CH_2Cl_2. We investigated the reaction of the adduct prepared at −78° with various substrates (Table 2); the substrate (1 mol. equiv.) was added to the adduct at −78°, the mixture was stirred at the temperature in Table 2 for 1 h, the mixture was cooled to −78°, and $SbCl_5$ (1 mol. equiv.) was added. Compound (**1**) was obtained in high yield using Me_2S as substrate, alcohols gave the corresponding alkoxy sulphonium salts instead of the methoxysulphonium salts described above, disulphides and thiols produced mercapto-sulphonium salts, and secondary amines produced amino-sulphonium salt. This method is thus of wide applicability for the preparation of sulphonium salts. The adduct between MeOS(:O)Cl and Me_2SO is presumed to be dimethylchlorosulphonium methylsulphinate (A) from the similarity in reactivity to the stable chlorosulphonium salt prepared by Meerwein *et al.*[3b]

TABLE 2. Products from the reaction (1 h) of various substrates and the adduct prepared at −78° from MeOS(:O)Cl and Me_2SO.

Substrate	T/°C	Products $Me_2(R)S^+SbCl_6{}^-$ R	M.p./°C	Yield (%)
Me_2S	−20—0	$MeSCH_2$	—	83
EtOH	−78	EtO	—	72
Bu^{t}OH	0	Bu^{t}O	156—158	46
Me_2CO	0	$MeC(:O)CH_2$[b]	118	40
PhSSPh	0	PhS	145	80
EtSH	0	EtS	141—142	77
Et_2NH[a]	−70 to −50	MeO	—	15
		Et_2N	93—95	35

[a] 0·5 h reaction. [b] ν_{C-O} 1720 cm^{-1}.



$$MeOS(=O)Cl + Me\text{-}S(=O)\text{-}Me \rightarrow \left[Me\text{-}O\text{-}S(=O)\text{-}O\text{-}S^+(Me)_2Cl^- \right] \rightarrow Me\text{-}O\text{-}S(=O)\text{-}O^-S^+(Me)_2\text{-}Cl$$

(A)

(*Received*, 3*rd September* 1974; *Com.* 1121.)

---

[1] (a) C. R. Johnson and W. G. Phillips, *J. Org. Chem.*, 1967, **32**, 1926; (b) M. A. Khuddus and D. Swern, *J. Amer. Chem. Soc.*, 1973, **95**, 8393; (c) C. R. Johnson and W. G. Phillips, *ibid.*, 1969, **91**, 682.

[2] H. Meerwein, E. Battenburg, H. Gold, E. Pfeil, and G. Willfang, *J. prakt. Chem.*, 1939, **154**, 83.

[3] (a) K. Tossell, *Acta Chem. Scand.*, 1967, **21**, 1; (b) H. Meerwein, K. F. Zenner, and R. Gipp, *Annalen*, 1965, **688**, 67; (c) C. R. Bacon and W. D. Kingsbury, *Tetrahedron Letters*, 1972, 501.

[4] D. H. R. Barton, J. B. Ganner, and R. H. Wightman, *J. Chem. Soc.*, 1964, 1855.

[5] K. Tossell, *Tetrahedron Letters*, 1966, 4445.