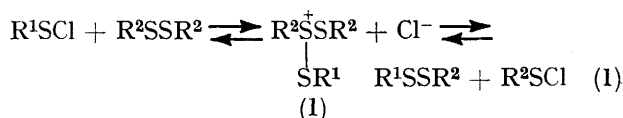# Reactions of Sulphenyl Chlorides and Disulphides in Acidic Media. Trapping of Alkyl(bisalkylthio)sulphonium Ion Intermediates

By **Giuseppe Capozzi, Vittorio Lucchini, Giorgio Modena,** and **Franco Rivetti,** Centro ' Meccanismi di Reazioni Organiche ' del C.N.R. Istituto di Chimica Organica, Universita' di Padova, 35100 Padova, Italy

A ^{1}H n.m.r. study of the reaction between alkanesulphenyl chlorides and dialkyl disulphides in sulphur dioxide in the presence of Lewis acids and in strong acids (FSO_3H or 98% of H_2SO_4) led to the characterization of alkyl-(bisalkylthio)sulphonium ions $R\overset{+}{S}(SR)_2$ (1). Results of conductimetric and ^{1}H n.m.r. experiments at low temperatures suggest that the formation of (1) also occurs to a large extent in the absence of Lewis acids. It was observed that ions (1) are also formed from disulphides by the action of strong acids.

THE intervention of intermediates, or transition states, (1) has been proposed in the exchange reaction of sulphenyl chlorides with disulphides [1,2] [equation (1)] as

$$R^1SCl + R^2SSR^2 \rightleftharpoons R^2\overset{+}{\underset{\underset{(1)}{SR^1}}{S}}SR^2 + Cl^- \rightleftharpoons R^1SSR^2 + R^2SCl \quad (1)$$

well as in other reactions involving sulphur–sulphur bond fission with electrophilic catalysis.[3,4] In particular, kinetic and spectroscopic results suggested that (1) may be a key intermediate in the reaction of dimethyl disulphide with dimethyl methylthiosulphonium tetrafluoroborate.[5] Direct proof of the existence of (1) has never been offered although the tendency of sulphenyl compounds to give ions similar to (1) has been recently reported [6,7] in the reaction of alkanesulphenyl chlorides with Lewis acids which gives alkyl(alkylthio)chlorosulphonium ions (2) [equation (2)].

$$2RSCl \overset{i}{\rightleftharpoons} R\overset{+}{\underset{\underset{(2)}{Cl}}{S}}SR + Cl^- \quad (2)$$
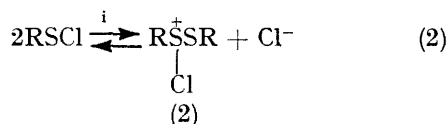
Reagents: i, SO_2 or SO_2–Lewis acid.

† We preferred the use of the collapse temperature to compare the rates of this process since the presence of excess of methanesulphenyl chloride over dimethyl disulphide presents difficulties in making a full line shape analysis [7] (see Discussion section).

[1] C. G. Moore and M. Porter, *J. Chem. Soc.,* 1958, 2890.
[2] F. Pietra and D. Vitali, *J. Chem. Soc. (B),* 1970, 623.

We report here an n.m.r. study of reaction (1) leading to the characterization of ions (1) and of the conductimetric behaviour of dimethyl disulphide in the presence of methanesulphenyl chloride in liquid sulphur dioxide.

RESULTS

Reaction of Methanesulphenyl Chloride and Dimethyl Disulphide in Sulphur Dioxide.—The n.m.r. spectrum, at -70 to $+37°$, of a mixture of methanesulphenyl chloride (0·4M) and dimethyl disulphide (0·3M) in sulphur dioxide containing antimony pentafluoride (0·6M) shows two main signals at δ 3·45 and 2·88 with an intensity ratio of 1 : 2. The spectrum also shows two minor bands at δ 4·07 and 3·25 with an intensity ratio of 1 : 1 which are due to the methyl(methylthio)chlorosulphonium ion (2; R = Me) formed from the excess of methanesulphenyl chloride [6,7] [see equation (2)].

Methanesulphenyl chloride (0·4M) and dimethyl disulphide (0·3M) in the presence of boron trifluoride (1·2M), displays an n.m.r. spectrum at $-70°$ identical with that observed in the presence of SbF_5. With increasing temperature the signals broaden and then collapse into a single line at δ 3·10 (Figure 1). Increasing the boron trifluoride concentration increases the temperature of collapse. Table 1 reports data † on how changes in BF_3 concentration affect the dynamic n.m.r. spectra.

[3] J. L. Kice, *Progr. Inorg. Chem.,* 1972, **17**, 147.
[4] B. Miller and C. H. Han, *J. Org. Chem.,* 1971, **36**, 1513.
[5] S. H. Smallcombe and M. C. Caserio, *J. Amer. Chem. Soc.,* 1971, **93**, 5826.
[6] G. Capozzi, V. Lucchini, and G. Modena, *Chim. e Ind. (Italy),* 1972, **54**, 41.
[7] G. Capozzi, V. Lucchini, G. Modena, and F. Rivetti, *J.C.S. Perkin II,* 1975, 361.

The n.m.r. behaviour of mixtures of methanesulphenyl chloride (0·4M) and dimethyl disulphide (0·3M) in sulphur dioxide alone is similar with that in the presence of Lewis
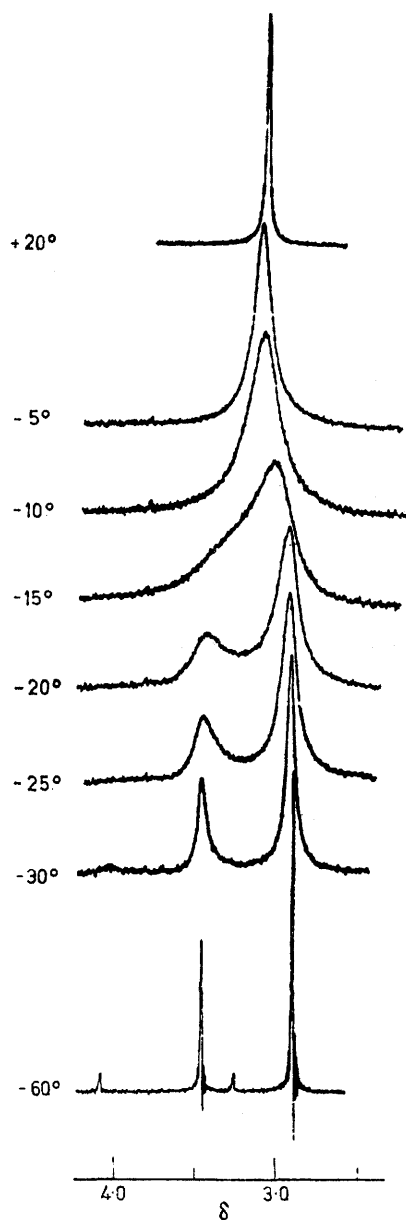

FIGURE 1 N.m.r. spectra of a mixture of methanesulphenyl chloride (0·4M) and dimethyl disulphide (0·3M) in sulphur dioxide in the presence of boron trifluoride (1·2M) at different temperatures

acids. Indeed at relatively high temperatures (−30 to −60°) the n.m.r. spectrum shows only a singlet whose chemical shift depends on the temperature (δ 2·88 at −30; 3·09 at −50°). Further cooling first causes broadening of the signal and then splitting into two absorptions, which at −78° are centred at δ 3·43 and 2·89 with an intensity ratio of ca. 1 : 2. The signals are still broad at −78° but we could not obtain lower temperatures because of freezing of the solution. The collapse temperature is ca. −73°.

The splitting process was no longer observed when dimethyl disulphide was in even small excess over methane-

sulphenyl chloride which indicates that disulphide accelerates the dynamic process. The results are consistent with

TABLE 1

Coalescence temperatures (T_c) of the 90 MHz n.m.r. spectra of solutions of methanesulphenyl chloride (0·4M) and dimethyl disulphide (0·3M) in sulphur dioxide at different boron trifluoride concentrations

[BF₃]/M	T_c(°C) [a]
1·00	−17·5
1·20	−15·0
1·45	−12·0
1·80	−7·0

[a] ±0·5°.

the formation of methyl(bismethylthio)sulphonium ion according to equation (3).

$$CH_3SCl + CH_3SSCH_3 \underset{\overset{}{\longleftarrow}}{\overset{i}{\longrightarrow}} CH_3\overset{+}{S}SCH_3 + Cl^- \quad (3)$$
$$| \\ SCH_3$$
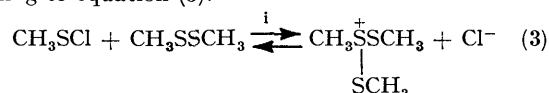
(3)   (4)

Reagents: i, SO₂, SO₂-BF₃, or SO₂-SbF₅.

Further information on reaction (3) was obtained from conductimetric experiments. To a solution of dimethyl disulphide (0·097M) in sulphur dioxide (7·0 ml) at −63°, methanesulphenyl chloride was added dropwise and the values of the conductance plotted against the amounts of CH₃SCl added (Figure 2). The conductivity increased linearly up to an inflection point which occurred at 0·09M-CH₃SCl, i.e. at a molar ratio not far from one. Further addition of methanesulphenyl chloride caused an increase in conductivity but with different slope. The lower part of the curve is consistent with the formation of the sulphonium ion, the upper part can be attributed to the formation of (2) from the excess of sulphenyl chloride.[7]
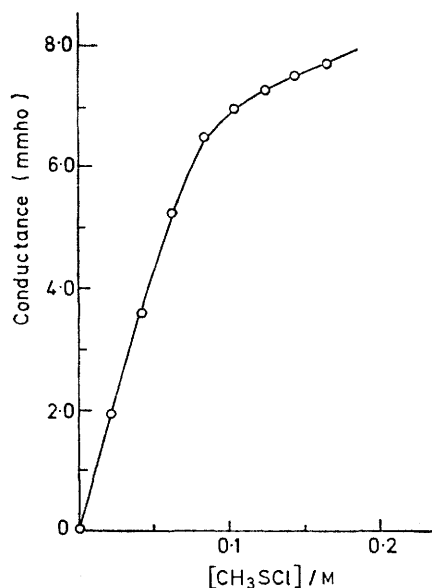

FIGURE 2 Conductance of dimethyl disulphide (0·097M) in sulphur dioxide at −63° as a function of added methanesulphenyl chloride. Inflection point at 0·09M-CH₃SCl

The equivalent conductance of 0·04M-methyl(bismethylthio)sulphonium ion was evaluated with and without addition of SbCl₅ (Table 2). Addition of the Lewis acid caused a

decrease in conductivity. This may be due to the decreased mobility of the larger $SbCl_6^-$ anion with respect to Cl^- and implies that the number of ions is not significantly increased by the addition of the Lewis acid.
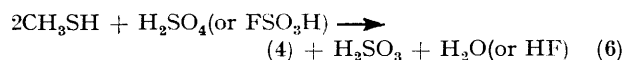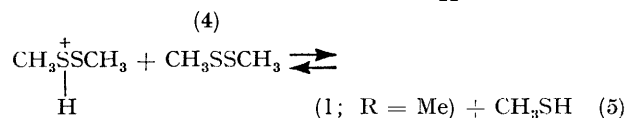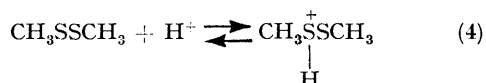
<div align="center">TABLE 2</div>

Equivalent conductance (ohm^{-1} cm^2 mol^{-1}) of 0·04N-methyl(bismethylthio)sulphonium (1; R = Me) and -methyl(methylthio)chlorosulphonium ions (2) in sulphur dioxide at $-63°$

	Cl^-	$SbCl_6^-$ [a]
(1; R = Me)	43	36
(2) [b]	11	39

[a] In the presence of excess of antimony pentachloride.
[b] Ref. 7.

Dialkyl Disulphides and Alkanesulphenyl Chlorides in Fluorosulphonic Acid and 98% Sulphuric Acid.[*]—When a mixture of methanesulphenyl chloride (0·4M) and dimethyl disulphide (0·3M) was dissolved in fluorosulphonic acid, or in 98% sulphuric acid, the n.m.r. spectrum of the solution at $+27°$ shows two major peaks at δ 3·57 and 3·05 with an intensity ratio of 1 : 2 (δ 3·84 and 3·31 in 98% H_2SO_4) and two signals at δ 4·16 and 3·37 with an intensity ratio of 1 : 1 (δ 4·44 and 3·63 in 98% H_2SO_4). The latter pair coincides with that attributed to the sulphonium ion (2) [7] and the former corresponds to that expected for methyl(bismethylthio)sulphonium ion.

The n.m.r. spectrum of a solution of dimethyl disulphide in FSO_3H (or in 98% H_2SO_4) at $+27°$ shows two singlets at δ 3·57 and 3·04 (δ 3·85 and 3·31 in 98% H_2SO_4) with intensity ratio 1 : 2. This indicates that methyl(bismethylthio)sulphonium ion is the sole reaction product, *i.e.* protonation of the disulphide [equation (4)] is followed by nucleophilic substitution which gives rise to the sulphonium ion and methanethiol [equation (5)]. This, in turn, is oxidized to disulphide [equation (6)]. When methanethiol

$$CH_3SSCH_3 + H^+ \rightleftharpoons CH_3\overset{+}{\underset{|}{S}}SCH_3 \quad (4)$$
$$_H$$

(4)

$$CH_3\overset{+}{\underset{|}{S}}SCH_3 + CH_3SSCH_3 \rightleftharpoons$$
$$_H \qquad (1; R = Me) + CH_3SH \quad (5)$$

$$2CH_3SH + H_2SO_4(\text{or } FSO_3H) \longrightarrow$$
$$(4) + H_2SO_3 + H_2O(\text{or } HF) \quad (6)$$

is dissolved at room temperature in fluorosulphonic acid or 98% sulphuric acid, oxidation occurs readily (n.m.r.). Only the two signals due to methyl(bismethylthio)sulphonium ion were observed.

The n.m.r. spectrum of a solution of diethyl disulphide in FSO_3H at $+27°$ shows two quartets at δ 3·95 (J 7·3 Hz) and 3·57 (J 7·3 Hz) with an intensity ratio of 1 : 2 and two partially overlapping triplets at δ 1·86 and 1·77 (J 7·3 Hz). This spectrum is consistent with the presence in solution of the ethyl(bisethylthio)sulphonium ion; in fact the lower field quartet can be attributed to the methylene protons of the alkyl group linked to the sulphonium sulphur atom and the higher field quartet to the magnetically equivalent methylene protons linked to the dico-ordinate sulphur

* Chemical shifts reported in this section refer to external tetramethylsilane (capillary tube).

[8] E. Ciuffarin and A. Fava, *Progr. Inorg. Chem.*, 1968, **6**, 81.
[9] A. J. Parker and N. Kharasch, *Chem. Rev.*, 1959, **59**, 583.

atoms. In 98% sulphuric acid the same spectrum but with slight differences in chemical shifts was observed.

Dimethyl Disulphide and Boron Trifluoride in Sulphur Dioxide.—The addition of boron trifluoride to a solution of dimethyl disulphide in sulphur dioxide gives rise to an n.m.r. spectrum which at $-50°$ consists of two main bands at δ 3·43 and 2·88 with an intensity ratio of 1 : 2 and three minor signals at δ 3·26, 2·92, and 2·82 with an intensity ratio of *ca.* 1 : 1 : 1. Exchange takes place on increasing the temperature and the signals collapse into a band at δ 3·10. The bands at δ 3·43 and 2·88 are consistent with the formation of methyl(bismethylthio)sulphonium ion. The other three signals correspond to different boron trifluoride complexes of methanethiolate ion formed according to equation (7). Possibly some oxidation of methanethiolate also occurs in this system as observed in fluorosulphonic acid or 98% sulphuric acid. In fact when sodium methanethiolate is dissolved in sulphur dioxide in the presence of boron trifluoride, sulphur precipitates and the same dynamic spectrum, but with lines of different intensity ratio is observed.

$$2CH_3SSCH_3 \xrightarrow[SO_2-BF_3]{} CH_3\overset{+}{\underset{|}{S}}SCH_3 + CH_3S^- \quad (7)$$
$$_{SCH_3}$$
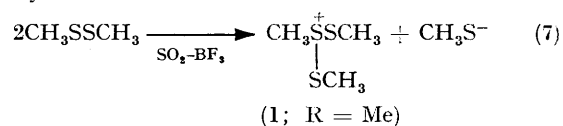
(1; R = Me)

DISCUSSION

In the light [6,7] of the results on the formation of ions (2) in the reaction of alkanesulphenyl halides with Lewis acids in liquid SO_2 [equation (2)], it is quite safe to assume that process (1) describes the reaction between dimethyl disulphide and methanesulphenyl chloride. This hypothesis is also consistent with several results for acid catalysed exchange of asymmetric disulphides.[3,8,9]

Our results suggest that ions (1) are formed more easily and are more stable than (2). This is as expected since disulphides are stronger bases than sulphenyl halides. However it is remarkable that the formation of (2) appears to be complete, or almost so, in pure liquid sulphur dioxide, although its ability to solvate chloride ions is well known.[10,11]

The dynamic process observed for ions (1) shows the same features observed for sulphenyl chloride–Lewis acid systems [6,7] and may be rationalised in a similar manner, *i.e.* by attack on (1) of an external nucleophile which may be either chloride ion or disulphide when the latter is in excess.

It is worth pointing out that we have not found any evidence for unimolecular exchange of the two sets of protons in methyl(bismethylthio)sulphonium ion. This makes it unlikely that under our conditions a 1,2 sulphur shift occurs *via* a cyclic intermediate, or transition state, (5) which in principle could be postulated.

$$RS\underset{\overset{+}{\diagdown}\overset{}{\underset{R}{S}}\diagup}{\overline{}}SR$$

(5)
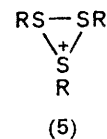
[10] F. J. Woodhouse and J. H. Norris, *Inorg. Chem.*, 1971, **10**, 14.
[11] T. C. Waddington, ' Non-aqueous Solvent Systems,' Academic Press, New York, 1965.

Our results indicate that (1) is a relatively stable species. However attempts to isolate it in pure form have failed so far, possibly because of the highly hygroscopic nature of the salts. We obtained a salt-like compound by reaction of methanesulphenyl chloride and dimethyl disulphide in the presence of antimony pentachloride. The isolated compound, dissolved in sulphur dioxide, gave a single line spectrum at the frequency expected for the collapsed spectrum of the sulphonium ion, but on cooling at $-78°$ we were not able to resolve the spectrum to the characteristic two line system. This was obtained, however, by addition of a small amount of SbCl$_5$ or BF$_3$. This, together with the fast exchange observed in the presence of excess of disulphide, suggests that minute amounts of disulphide are formed from the sulphonium salt, probably because of adventitious traces of water, in the isolation process.

Finally, we point out that the formation of (1) directly from the disulphide in sulphuric or fluorosulphonic acid also offers a simple explanation for alkane thiolations *via* disulphide in the presence of Lewis acids without invoking the intervention of sulphenyl cations or other unlikely species.

[12] H. Britzinger, H. Koddesbuch, K. H. Kling, and G. Jung, *Ber.*, 1952, **85**, 455.
[13] H. Britzinger and H. Langheck, *Ber.*, 1953, **86**, 557.
[14] J. B. Douglas, R. V. Norton, R. L. Weichman, and R. B. Clarkson, *J. Org. Chem.*, 1969, **34**, 1803.

EXPERIMENTAL

Materials.—Methane-[12] and ethane-sulphenyl chloride [13] were prepared by published methods. In all experiments freshly prepared sulphenyl chlorides were used.[14] High purity commercial gases and solvents were used without further purification.

N.m.r. and Conductimetric Experiments.—N.m.r. spectra were recorded on a Bruker HFX-10 90 MHz spectrometer. Conductimetric measurements were performed with a Radiometer CDM-3 bridge. The cell constant was found to be 0·565 cm^{-1} from measurements of a 0·01M aqueous solution of KCl at 25°. Detailed experimental procedures have been described previously.[7]

Methyl(bismethylthio)sulphonium Hexachloroantimonate.—To an ice cooled solution of SbCl$_5$ (7·85 mmol) in anhydrous dichloromethane (5 ml) a solution of methanesulphenyl chloride (7·85 mmol) and dimethyl disulphide (7·85 mmol) in the dichloromethane (10 ml) was added dropwise. The product partially precipitated from the solution; addition of pentane (15 ml) caused complete precipitation of the *hexachloroantimonate*. The product (95% yield) was isolated by filtration in a dry-box. The crude material was crystallized from dichloromethane–pentane, m.p. 123—125° (decomp.) (Found: C, 7·5; H, 1·85; Cl, 51·4; S, 19·25. C$_3$H$_9$Cl$_6$S$_3$Sb requires C, 7·6; H, 1·9; Cl, 44·7; S, 20·2%).