The Generation and Electrophilic Reactions of Dimethyl Sulphide Cation Radicals

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In anhydrous methylene chloride, nitrosomium tetrafluoroborate and dimethyl sulphide reacted to give a fairly stable red-brown solution at −70° which slowly decomposed at *ca.* −20° to afford trimethylsulphonium tetrafluoroborate. The red-brown solution reacted with olefins to afford 2-nitrosoalkyldimethylsulphonium salts and/or 1,2-bis-sulphonium salts, and with anisole to give *p*-methoxyphenyldimethylsulphonium salt. The reactions were interpreted as involving the electrophilic dimethyl sulphide cation radical as a reactive intermediate leading the attack on the π-bond systems. This is followed by radical combination or electron transfer–elimination to complete the addition and substitution pathways.

It has been known for some time that stable heteroaromatic sulphide cation radicals can be generated from the oxidation of the parent sulphides with perchloric acid [1] or iodine–silver perchlorate [2,3] or by anode oxidation;[4,5] for example, the perchlorate of the thianthrene cation radical, prepared by chemical oxidation, can be isolated and stored under ordinary conditions.[6] By analogy with aminium radicals [7,8] sulphide cation radicals are expected to be electrophilic and, thus, are expected to attack carbon–carbon double bonds to form sulphonium salts. Indeed, reactions of the stable aromatic sulphide cation radicals with various nucleophiles have been reported, including recent reports of reactions with olefins.[9] We describe here a new type of electrophilic addition of a dimethyl sulphide species to π-bond systems which we believe involves the dimethyl sulphide cation radical as the reactive intermediate.

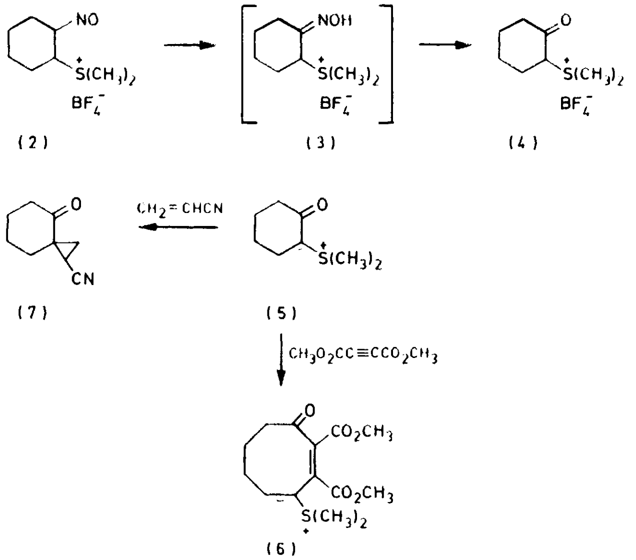
RESULTS

Under anhydrous conditions, nitrosonium tetrafluoroborate ($NOBF_4$) reacted rapidly with an excess (five-fold or more) of dimethyl sulphide (DMS) in methylene chloride at −70° to give an orange precipitate which dissolved to form a red-brown solution. If only one mol. equiv. of DMS was used, a green oil separated from the red-brown solution and gave a complex mixture in the subsequent reaction with olefins. The red-brown colour persisted for more than 24 h under anhydrous conditions at −70° and the solution exhibited a u.v. absorption at $\lambda_{max.}$ 305 nm. The colour as well as the absorption faded slowly at −20° or higher and quickly on exposure to moisture to give a pale yellow solution. The solution obtained from slow decomposition under anhydrous conditions was worked up to give trimethylsulphonium tetrafluoroborate (1) which was also prepared by the interaction of DMS with trimethyloxonium tetrafluoroborate.

$$NOBF_4 + (CH_3)_2S \longrightarrow \underset{(1)}{(CH_3)_3\overset{+}{S}\ BF_4^-}$$

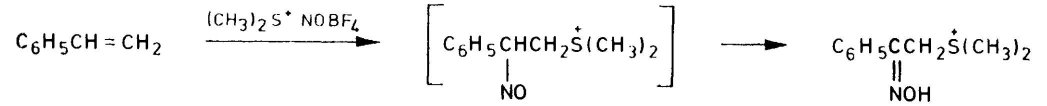
The red-brown solution reacted slowly with cyclohexene at −70° under anhydrous conditions but more quickly at *ca.* −10°; generally this mixture was allowed to warm to room temperature overnight to give the dimer of the nitrososulphonium tetrafluoroborate (2) as a precipitate in 50—60% yields. The liquid recovered from the filtrate comprised a mixture of several compounds arising from the decomposition of (2) as shown by successive t.l.c. analyses. Acetonitrile was also used to give comparable results but generally methylene chloride was used as the solvent.

When dissolved in deuteriated dimethyl sulphoxide or acetonitrile, the dimer of (2) decomposed extensively giving coloured solutions and complex n.m.r. spectra. But the thoroughly washed sample gave a good analysis for (2) and the presence of the *anti*-azodioxy-linkage was clearly indicated by i.r. absorptions at 1 290, 1 260, and 1 215 cm^{-1} and a u.v. absorption at 298 nm. The dimerization of *C*-nitroso-compounds generally gives the more stable *anti*-azodioxy-compound without contamination by the *syn*-isomer.[10-13] The sample was probably a mixture of ± and *meso*-azodioxy-compounds arising from dimerization of the enantiomers [10-13] of (2). Furthermore, the addition of the nitroso and sulphonium group could result in the *cis*- or *trans*-isomer or both. The instability of the dimer in solution prevented purification and the aquisition of other spectral data to solve these stereochemical questions.



Many attempts to isomerize the dimer of the *C*-nitroso-compound (2) under a variety of acidic or basic conditions were not successful. However, in dilute aqueous tetrafluoroboric acid, this dimer can be depolymerized, tautomerized, and hydrolysed to give the oxosulphonium salt (4) though in low yield (*ca.* 30%) due to the difficulty in recovering it from the aqueous hydrolysate. The oxosulphonium salt showed the expected i.r. absorption at 1 715 cm^{-1} for the carbonyl group and two n.m.r. singlets due to the diastereoisotopic methyl groups. Treatment of (4) with sodium hydroxide generated the hygroscopic ylide (5) which showed an i.r. absorption at 1 530 cm^{-1} for the carbonyl group as reported previously.[14] The conversion of (2) into (5) could be carried out in one operation to give a better yield of (5) without the isolation of (4). In view of the scarcity of physical data for (4) and (5) for comparison,[15] ylide (5) was treated with dimethyl acetylenedicarboxylate to give a well characterized ylide (6), according to the reported procedure.[14] The ylide (5) also reacted with acrylonitrile to give a mixture of diastereoisomeric spirocyclopropyl ketones (7).

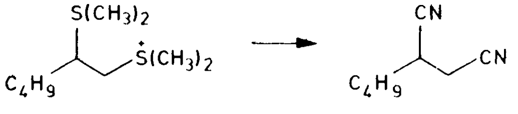
The reaction of the red-brown solution with styrene apparently gave good yields of the *C*-nitrososulphonium tetrafluoroborate (8) as shown by the copious precipitate. The solid gradually turned to a viscous oil from which a moderate yield of oxime (9) was obtained on treatment with methanol. The oxime (9) isolated in this manner gave a sharp m.p. and good elemental analyses and is stable in the solid state. A solution of (9), either in deuteriated acetonitrile or dimethyl sulphoxide, gave n.m.r. signals compatible with the structure when taken immediately; these solutions developed a colour rapidly and showed other complex n.m.r. signals at the expense of the originals. Since only one oxime of (9) was isolated, as shown by the n.m.r. spectrum, the configuration of the hydroxyimino group in (9) could not be assigned.[16] The structure of (9) indicated that the dimethylsulphonium moiety attached itself to the least substituted carbon of the styrene double bond during the addition.



$$C_6H_5CH{=}CH_2 \xrightarrow{(CH_3)_2S^{+}\ NOBF_4} \left[C_6H_5\underset{\underset{NO}{|}}{C}HCH_2\overset{+}{S}(CH_3)_2\right] \longrightarrow C_6H_5\underset{\underset{NOH}{\|}}{C}CH_2\overset{+}{S}(CH_3)_2$$

(8) (9)

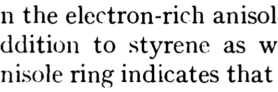
The treatment of the red-brown solution with 3,3-dimethylbut-1-ene or hex-1-ene afforded large amounts of liquids which showed i.r. absorptions corresponding to a *C*-nitroso dimer (1 290 cm^{-1}), an oxime (1 000—900 cm^{-1}), and others. Attempts to separate products from the liquids were largely unsuccessful but, in the latter case, bis-sulphonium bistetrafluoroborate (10) was also obtained in a low yield by crystallization. Considerable effort was spent to purify the liquids or to modify them with various reagents (*e.g.*, base, nucleophiles, reduction, *etc.*) without success. The bis-sulphonium salt (10) was easily characterized by showing four signals for the two pairs of the diastereotopic S–CH$_3$ groups in the ^{1}H and ^{13}C n.m.r. spectra. Species (10) reacted with sodium cyanide to give 1,2-dicyanohexane which showed a strong mass peak at 57 corresponding to the $C_4H_9^+$ moiety.



(10) (11)

Under oxygen, the red-brown solution reacted with hex-1-ene to give bis-sulphonium salt (10), in an amount similar to that obtained under nitrogen, and an oil exhibiting absorptions at 1 640, 1 280, and 860 cm^{-1} typical of a nitrate group and 1 545 and 700 cm^{-1} for an aliphatic nitro group. While these nitrate and nitro derivatives could not be isolated, it was very likely that oxygen was incorporated into the products in a similar manner to that observed in oxidative photoaddition of nitrosamines.[8]

While the red solution failed to react with benzene and toluene, it reacted with anisole to give good yields of *p*-methoxyphenyldimethylsulphonium tetrafluoroborate (12) together with sulphonium salt (1) (22%): in the former reaction sulphonium salt (1) was the only product isolated. Careful monitoring by n.m.r. spectroscopy of various fractions from crystallization showed no isomer other than *p*-methoxyphenylsulphonium salt (12). The structure of (12) was indicated by the pertinent n.m.r. signals of the AA′BB′ type aromatic protons in the δ 7.7 region and two singlets at δ 3.23 for the S(CH$_3$)$_2$ group and at 3.88 for the OCH$_3$ group. From the mother-liquor, a small amount of *p*-methylmercaptoanisole (13) was also isolated by chromatography. The structure was assigned on the basis of spectral data.



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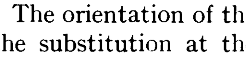
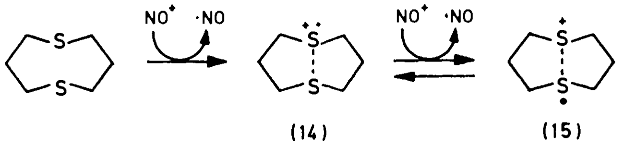


(13)

DISCUSSION

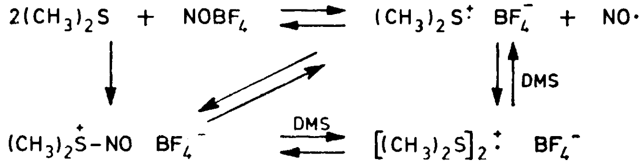
The overall reaction pattern of the red-brown solution, obtained from NOBF$_4$ and DMS under anhydrous conditions, may be interpreted as the addition of the reagent to olefinic π-bonds and electrophilic substitution on the electron-rich anisole ring. The orientation of the addition to styrene as well as the substitution at the anisole ring indicates that an electrophilic DMS species is generated and initiates the attack on π-bond systems. We propose that the reactive intermediate is the dimethyl sulphide cation radical $(CH_3)_2S^{+\cdot}$ on the basis of the following discussion.

While this research was in progress, two reports describing the reaction of NOBF$_4$ with sulphides appeared. One describes the preparation of the stable heteroaromatic sulphide cation radicals, *e.g.*, thianthrene cation radical, by NOBF$_4$ oxidation.[17] The other elegantly demonstrates the generation of the stable sulphide cation radical (14) by interaction of one mol. equiv. of NOBF$_4$ with 1,5-dithiacyclo-octane under vacuum and further shows that the second equivalent of NOBF$_4$ oxidizes (14) to dication (15): in both cases, the yields of nitric oxide, the reduction product, have been determined as quantitative.[18] The stability of these species is believed to arise from the S–S bridge as demonstrated by e.s.r. and n.m.r. spectroscopy.[18] By analogy with these reports, the interaction of $NOBF_4$ is expected to generate the dimethyl sulphide cation radical in a similar manner to the one electron oxidation process.



(14) (15)

Transient dialkyl sulphide cation radicals have been obtained by oxidation of sulphides with the ·OH radical generated in the Ti^{III}–hydrogen peroxide reaction and γ-radiolysis in aqueous solution. They are characterized by e.s.r. spectroscopy[19] and by kinetic studies.[20,21] Significantly, these studies have convincingly demonstrated that the reactive dimethyl sulphide cation radical, $(CH_3)_2S^{+\cdot}$, is stabilized by reversibly complexing with another DMS molecule through a three electron S–S bond giving $[(CH_3)_2S]_2^{+\cdot}$; it decays solely by the reaction of $(CH_3)_2S^{+\cdot}$, in which the bimolecular rate constant is 0.5×10^9 l mol^{-1} and the unimolecular one is 2.5×10^3 s^{-1}. The latter must include pseudo-first-order components of the reactions with various nucleophiles, *e.g.* water and OH^-. In the anhydrous system, in the absence of nucleophiles other than excess of DMS, such as the system used here, the possible pathways of the reaction between DMS and $NOBF_4$ may be represented as in the Scheme. The formation of $(CH_3)_2S^{+\cdot}$ is formally a one-electron oxidation and may occur by a direct electron transfer or by the formation of nitrosodimethylsulphonium ion, $(CH_3)_2S–NO^+$, followed by homolysis. In view of the fact that most nitrosyl derivatives are deeply coloured, the red-brown colour and the orange solid may be assigned to $(CH_3)_2S–NO^+$. Thus, we favour the latter process.



SCHEME

In principle, the electrophilic species initiating the addition can be $(CH_3)_2S^{+\cdot}$, $[(CH_3)_2S]_2^{+\cdot}$, $(CH_3)_2SNO^+$, or $(CH_3)_2S^{2+}$ in the Scheme; the latter two should attack a π-bond by ionic processes and the former two by a radical mechanism. The dication $(CH_3)_2S^{2+}$ can arise from disproportionation[6] of $(CH_3)_2S^{+\cdot}$, as in reaction (1). But this species cannot be the major reactive intermediate since it is difficult to write a pathway to arrive at the observed addition products (2) and (8). It has also been shown that the disproportionation of a sulphide cation radical as in (1) is slow and that, in the presence of a sulphide, the reaction is reversed quantitatively.[18] The addition initiated by nitrosonium ion [or analogously by $(CH_3)_2S–NO^+$] must be considered in view of the reactivity of nitrosyl chloride[10,13] and $NOBF_4$[22] towards olefins. This ionic pathway can be ruled out from the orientation of (12) in the substitution on anisole and from that of (8) in the addition to styrene. Addition of $NOBF_4$ to olefins in acetonitrile also involves the solvent as nucleophile.[22] In the reaction of $NOBF_4$ and DMS in acetonitrile, no product incorporating the acetonitrile moiety has been detected; this also indirectly contradicts the ionic mechanism. Further, it is very unlikely that $(CH_3)_2S–NO^+$ can react with olefins or anisole by an electrophilic attack with a significant rate, on steric grounds.

$$2(CH_3)_2S^{+\cdot} \rightleftharpoons (CH_3)_2S^{2+} + (CH_3)_2S \qquad (1)$$

Alternatively, the reaction pattern strongly indicates that $(CH_3)_2S^{+\cdot}$ and/or $[(CH_3)_2S]_2^{+\cdot}$ are the electrophilic species involved in addition and substitution. Since $[(CH_3)_2S]_2^{+\cdot}$ has been shown to be practically unreactive by comparison with $(CH_3)_2S^{+\cdot}$ in aqueous solution,[20,21] we assume that the reactive intermediate in the present system is also $(CH_3)_2S^{+\cdot}$. In the absence of suitable substrates (nucleophiles), $(CH_3)_2S^{+\cdot}$ may exist at a low concentration in equilibria with $(CH_3)_2S–NO^+$ and $[(CH_3)_2S]_2^{+\cdot}$ in the presence of a large excess of DMS. As dialkyl sulphide cation radicals are reported to show u.v. absorption at *ca.* 310 nm,[21] the observed absorption at 305 nm may be due to the $(CH_3)_2S^{+\cdot}$ radical. However, the reported absorption of $[(CH_3)_2S]_2^{+\cdot}$ at *ca.* 480 nm (in water)[20] has not been detected in our system. The slow formation of sulphonium salt (1) may be interpreted by reaction (2) and/or by the disproportionation reaction (3). In γ-radiolysis, trialkylsulphonium ions R_3S^+ were also obtained as a product, but no reaction was proposed to account for their formation.[20] For steric reasons, among others, these reactions should be slow.

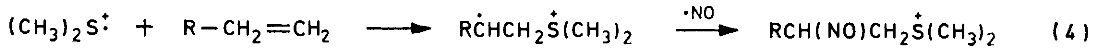
The incorporation of oxygen as nitrate and nitro groups also supports the radical mechanism since such a phenomenon has been observed in the photoaddition of nitrosamines to olefins[23] and the photorearrangement of nitrities[24] under oxygen where radical mechanisms have been well proven. In analogy to these reactions[7,8] the $(CH_3)_2S^{+\cdot}$ addition to olefins can be formally represented as in equation (4). Also in analogy to the thianthrene cation radical reaction,[4] the aromatic substitution can be written as shown in equation (5). The substitution reactions of heteroaromatic sulphide cation radicals with reactive aromatic substrates have been well established[4,25] and require a second mole of the cation radical as an electron acceptor. In the present case, since the combined yield of (1) and (12) is much higher than 50%, it is reasonable to assume that nitric oxide acts as the electron acceptor. The identical *para*-substitution

$$(CH_3)_2S + (CH_3)_2S^{+\cdot} \longrightarrow (CH_3)_3S^+ + CH_3S\cdot \qquad (2)$$

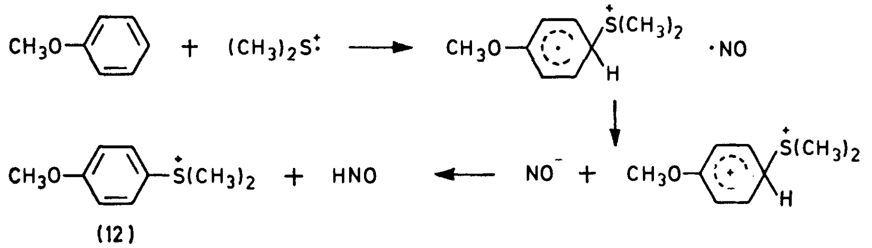
$$2(CH_3)_2S^{+\cdot} \longrightarrow (CH_3)_3S^+ + CH_2{=}S + H^+ \qquad (3)$$

pattern of anisole with the thianthrene cation radical addition[4] may be taken as strong support for the sulphide cation radical intermediate.

Since sulphonium salt (12) can be recrystallized without obvious sign of decomposition, the formation of sulphide (13) must arise from other pathways; one possibility is from attack of the $CH_3S\cdot$ radical generated in reaction (2) on anisole. A simple interpretation of the formation of the bis-sulphonium salt (10) is to propose a pathway similar to reaction (4). The addition of thianthrene cation radical to olefins is shown to give the same type of bis-sulphonium salt,[9] it is unlikely that (10) is formed from the unisolated $(CH_3)_2S$-NO^+ ion by nucleophilic substitution since a 20-fold increase in DMS concentration does not substantially change the yield of (10).



$$(CH_3)_2\dot{S}^{+} + R-CH_2{=}CH_2 \longrightarrow R\dot{C}HCH_2\overset{+}{S}(CH_3)_2 \xrightarrow{\cdot NO} RCH(NO)CH_2\overset{+}{S}(CH_3)_2 \quad (4)$$



(5)

While the reaction pattern described above appears to be best accommodated by radical pathways initiated by dimethyl sulphide cation radical, it is interesting that products expected from abstraction of a benzylic or allylic hydrogen have not been observed. The e.s.r. studies of DMS and $NOBF_4$ in methylene chloride at low temperatures showed a broad irregular signal at *g ca.* 2.01 and provided very little information. It should be added that diphenyl sulphide and di-t-butyl sulphide were also used in the addition but gave only low yields of the corresponding sulphoxide without the expected addition products.

EXPERIMENTAL

General.—Unless specified otherwise the following conditions were used. I.r. spectra were recorded with a Perkin-Elmer 547 spectrophotometer using liquid films or Nujol mulls. U.v. spectra were taken with either a Cary 14 or a Unicam SP 8000 spectrophotometer. N.m.r. spectra were recorded in $CDCl_3$ with Me_4Si as internal standard with a Varian A56/60 or a XL-100 instrument equipped with a Nicolet 1080 computer. Mass spectra were recorded with a Hitachi-Perkin-Elmer RMU-6E mass spectrometer. Elemental analyses were carried out by Mr. M. K. Yang using a Perkin-Elmer 240 microanalyser.

Materials.—Commercial solvents, dimethyl sulphide (DMS), and olefins were dried and distilled. Nitrosonium tetrafluoroborate ($NOBF_4$) (95%) was supplied by Ventron Corporation, Danvers, Massachusetts.

Reaction of $NOBF_4$ *and* DMS.—To a suspension of $NOBF_4$ (1.23 g, 10.5 mmol) in dry methylene chloride (60 ml) cooled at −70°, a solution of DMS (4 g, 60 mmol) in dry methylene chloride (20 ml) under dry nitrogen was added. The mixture was stirred at −70° to give an orange precipitate and a red-brown solution. The solution showed a u.v. absorption at $\lambda_{max.}$ 305 nm but it immediately turned light yellow on exposure to moist air. The red-brown colour persisted for 12 h if kept at −70° but slowly turned to a pale yellow solution at −10°. The solution was evaporated to give a crude semi-solid (1.5 g). Crystallization of the oil from methanol gave crystals of *trimethylsulphonium tetrafluoroborate* (1) (560 mg), m.p. 194—207 °C; $\nu_{max.}$ 3 040, 1 290, 1 150—1 000br, s, 940, and 655 cm^{-1}; δ ([$^2H_6$]DMSO$_6$) 2.85 (s); *m/e* (%) 96 (4), 95 (4), 94 (5), 85 (30), 79 (14), 78 (7), 77 (7), 62 (100), 61 (40), 49 (51), and 47 (75) (Found: C, 22.15; H, 5.45. $C_3H_9BF_4S$ requires C, 21.95; H, 5.5%).

Reaction of $NOBF_4$, DMS *and Cyclohexane*.—The same red-brown solution as above was prepared. A solution of cyclohexene (5.01 g, 61 mmol) in methylene chloride was added at −78° and the mixture was slowly warmed to room temperature overnight to give a precipitate. Filtration and washing with cold methylene chloride gave solid 2-nitrosocyclohexyldimethylsulphonium tetrafluoroborate (2) (1.72 g); m.p. 165—173° (decomp.); $\lambda_{max.}(CH_3CN)$ 298 nm (ε 7 700); $\nu_{max.}$ 3 030w, 1 290s, 1 260s, 1 215m, 1 205m, and 1 050br, s cm^{-1} (Found: C, 37.15; H, 6.2; N, 5.35. $C_8H_{16}BF_4NOS$ requires C, 36.8; H, 6.2; N, 5.35%).

The methylene chloride solution was evaporated to give an oil (750 mg) which was a mixture of unidentified compounds, $\nu_{max.}$ 3 030, 1 430s, 1 280, 1 050s, 950, and 880 cm^{-1}.

Hydrolysis of the Dimer of (2).—A solution of the dimer of (2) (261 mg) in 2N-tetrafluoroboric acid solution (10 ml) was stirred for 24 h and was extracted with methylene chloride. The methylene chloride solution was evaporated to afford oily 2-oxocyclohexyldimethylsulphonium tetrafluoroborate (4) (80 mg); $\nu_{max.}$ 3 030m, 1 715s, 1 450, 1 530s, 1 305m, 1 190, and 1 040br, s cm^{-1}; δ(CD_2Cl_2) 1.35—2.95 (8 H, m), 2.85 (3 H, s), 2.94 (3 H, s), and 4.60 (1 H, m).

Ylide (5).—To a solution of (4) (240 mg) in methylene chloride, a saturated potassium carbonate solution containing sodium hydroxide was added. The heterogeneous mixture was stirred for 10 h at room temperature. The methylene chloride layer was worked up in the usual manner to give a hygroscopic oil, ylide (5) (160 mg) (lit., m.p. 107°); $\nu_{max.}$ 3 300br, 1 530s, 1 450, 1 420, 1 380, 1 305, 1 260, 1 130, 1 140, and 990 cm^{-1}; δ($CHCl_3$) 1.70 (4 H, m), 2.20 (4 H, m), and 2.68 (6 H, s); $\lambda_{max.}$(EtOH) 270 nm (ε ~7 000); *m/e* 158 (M^+, 64%), 143 (23), 115 (49), 68 (23), 67 (100), 62 (36), 61 (48), 55 (29), 47 (31), and 41 (35).

Ylide (5) (80 mg) and dimethyl acetylenedicarboxylate (75 mg) in dry dimethyl sulphoxide (4 ml) was stirred at room temperature overnight. Ether (150 ml) was stirred in to give a brown semi-solid. The semi-solid was treated with hot methylene chloride to give yellow precipitate. This precipitate was recrystallized from methanol–methylene chloride to give ylide (6) (28 mg), m.p. 167—168° (lit.,[14] 166.5—167.5°); $\nu_{\text{max.}}$ 1 725s, 1 625s, 1 575, and 1 525 cm^{-1}; δ([$^2H_6$]DMSO) 1.2—2.8 (8 H, m), 2.94 (6 H, s), 3.32 (3 H, s), and 3.64 (3 H, s); *m/e* 300 (M^+, 57%), 286 (41), 254 (100), 221 (73), 193 (75), 91 (70), 79 (43), 78 (26), 77 (34), 63 (41), 62 (63), 61 (50), 59 (66), 55 (36), and 47 (57); $\lambda_{\text{max.}}$(EtOH) 278 (ε 12 000) and 358 nm (7 100).

Reaction of the Dimer of (2).—A suspension of the dimer of (2) (260 mg) in aqueous 0.2N-tetrafluoroboric acid was heated at 60° for 6 h to form a solution. To this solution potassium carbonate (600 mg) and sodium hydroxide (80 mg) were added at 0 °C. After 1 h, a solution of acrylonitrile (500 mg) in acetonitrile (5 ml) was added. After 3 h the solution was extracted with methylene chloride, the extracts of which were worked up to give an oil (118 mg). This oil was distilled to give nitrile (7), $\nu_{\text{max.}}$ 2 250m, 1 710s, 1 050s, 990m, 940m, and 915m cm^{-1} (Found: C, 72.6; H, 7.2; N, 9.15. $C_9H_{11}NO$ requires C, 72.45; H, 7.45; N, 9.4%).

Reaction of NOBF$_4$ *and* DMS *with Olefins*.—(1) *With styrene*. To the red-brown solution, prepared from NOBF$_4$ (1.56 g, 13.3 mmol) and DMS (4.1 g, 66 mmol) in methylene chloride at −70°, was added styrene (1.46 g, 14 mmol) while the solution was blanketed under dry nitrogen. The mixture was kept at −50° for 10 h and gradually warmed to room temperature overnight to give a large amount of viscous oil on the bottom of the flask. The mixture was evaporated. The residue was treated with warm methanol (30 ml) to give a solid which was repeatedly washed with methanol to afford the *oxime of phenacyldimethylsulphonium tetrafluoroborate* (9) (1.12 g), m.p. 103—104° (decomp.); $\nu_{\text{max.}}$ 3 100w, 3 020w, 1 580, 1 500, 1 380, 1 265, 1 230, 1 210, 1 050s, 770, and 710 cm^{-1}; $\delta(CD_3CN)$ 2.53 (3 H, s), 2.88 (3 H, s), 5.10 (2 H, s), and 7.50 (5 H) (Found: C, 42.55; H, 4.95; H, 5.0. $C_{10}H_{14}BF_4NOS$ requires C, 42.45; H, 5.0; N, 4.95%).

Oxime (9) was stable as a solid stored in a freezer but decomposed quickly in acetonitrile or dimethyl sulphoxide solution as shown by disappearance of the n.m.r. signals and the appearance of other complex signals.

(2) *With hex*-1-*ene*. To the red-brown solution obtained from NOBF$_4$ (1.76 g, 15 mmol) and DMS (6.65 g, 107 mmol) in dry methylene chloride (160 ml) under dry nitrogen at −70° was added hex-1-ene (7.16 g, 97 mmol) in methylene chloride (50 ml). The mixture was warmed slowly to −20° over 20 h when it turned to a pale yellow suspension. The solvent was removed and the residue was treated with methanol (20 ml). Cooling of the solution afforded crystals (350 mg). Recrystallization from methanol gave 1,2-bisdimethylsulphonium salt (10), m.p. 154—157.5°; $\nu_{\text{max.}}$ 3 040, 1 290, 1 275, and 1 050br, s cm^{-1}; δ([$^2H_6$]DMSO) 2.92 (3 H, s), 2.97 (6 H, s), 3.00 (3 H, s), 0.6—2.7 (9 H, m), and 3.90br (3 H, m); δ_C([$^2H_6$]DMSO) 47.6 (d), 41.8 (t), 27.6 (t), 26.6 (t), 25.7 (q), 25.1 (q), 22.1 (q), 21.8 (t), 20.2 (q), and 13.8 (q) (Found: C, 31.3; H, 6.25. $C_{10}H_{24}S_2B_2F_8$ requires C, 31.4; H, 6.3%).

The filtrate from the recrystallization was evaporated to give an oil (3.05 g) which showed a complex t.l.c. pattern, $\nu_{\text{max.}}$ 3 040, 1 440br, 1 290w, 1 050br, s, 950, and 870 cm^{-1}.

Bis-sulphonium salt (10) (30 mg) and sodium cyanide (102 mg) in dimethyl sulphoxide (2 ml) was stirred at room temperature for two days. The mixture was poured into methylene chloride which was washed thoroughly with water. The usual work up gave an oil (14 mg). This oil was distilled to afford 1,2-dicyanohexane (11); $\nu_{\text{max.}}$ 2 250m, 1 055, 1 035, 1 010, 820, and 740 cm^{-1}; δ 0.7—2.5 (9 H, m) and 2.6—3.1 (3 H, m); *m/e* 136 (M^+, 4%), 135 (9), 122 (12), 121 (23), 109 (25), 108 (52), 107 (24), 86 (48), 84 (70), 81 (36), 80 (59), 69 (56), 68 (100), 66 (43), 57 (70), 55 (63), and 54 (58); g.l.c. on 10% SE 30 at 200 °C, R_t 1.8 min, single peak.

A similar reaction of NOBF$_4$ (1.4 g), DMS (3.5 g), and hex-1-ene (5 ml) was run in methylene chloride (75 ml) under oxygen. The crude product (4.25 g) afforded (10) (240 mg) by crystallization; the remaining oil showed i.r. absorptions at 3 350, 3 010, 1 640, 1 555, 1 440, 1 280, 1 050 (s), 950, 860, and 700 cm^{-1}. Attempted separation of the oil by crystallization was not successful. The reduction of the oil with LAH gave only a small amount of oil (*ca.* 20 mg) extracted by ether.

(3) *With* 3,3-*dimethylbut*-1-*ene*. To the red-brown solution obtained from NOBF$_4$ (1.17 g, 10 mmol) and DMS (3.1 g, 50 mmol) in dry methylene chloride (80 mol), 3,3-dimethylbut-1-ene (5 g, 60 mmol) in methylene chloride (20 ml) was added at −70°. This was worked up in the usual manner to afford an oil (1.78 g), $\nu_{\text{max.}}$ 3 550br, 3 030w, 1 630, 1 430, 1 050br, s, and 890 cm^{-1}. Crystallization from various solvents was not successful.

Reaction of NOBF$_4$ *and* DMS *with Aromatic Compounds*.—(1) *With benzene or toluene*. To a red-brown solution prepared from NOBF$_4$ (780 mg) and DMS (2.5 g) in dry methylene chloride (45 ml) at −70°, benzene (20 ml) was added at −40°. The solution was kept at −20° for 5 h and then slowly warmed to room temperature. The solvent was evaporated and the residue (940 mg) was crystallized from methanol to give sulphonium salt (1) (203 mg), m.p. 194—207°. Evaporation of the mother-liquor gave an oil which showed singlets at δ 2.70, 3.34, and 2.88 [for (1)] but no aromatic protons.

When toluene (10 ml) was used instead of benzene, a similar result was obtained and sulphonium salt (1) was obtained in 26% isolated yield.

(2) *With anisole*. Anisole (2 g, 10 mmol) in dry methylene chloride (10 ml) was added to a red-brown solution obtained from NOBF$_4$ (1.18 g, 9.6 mmol) and DMS (3 g, 48 mmol) in dry methylene chloride (50 ml) at −40°. The solution was slowly warmed to room temperature overnight. Evaporation of the solvent gave an oil which was washed with ether. The ether insoluble solid (1.6 g) showed n.m.r. singlets at δ 2.88 for (1) and δ 3.23 and 3.88 (2.1 ratio) for (12). The ratio of (1) to (12) calculated from the singlets was 1 : 3.5. The solid was recrystallized from propan-2-ol–benzene to give a solid, *p*-methoxyphenyldimethylsulphonium tetrafluoroborate (12) contaminated with (1); $\nu_{\text{max.}}$ 3 040, 1 595, 1 505s, 1 435, 1 270s, 1 185s, 1 050br, s, 835, 800, and 770 cm^{-1}; δ([$^2H_6$]DMSO) 3.23 (s, 6 H), 3.88 (s, 3 H), and 7.25 and 800 (4 H, AA′BB′ pattern).

The ether solution was evaporated to give an oil (450 mg). A portion of this oil (200 mg) was separated by preparative t.l.c. to give an oil (12 mg) of *p*-methylthioanisole (13); $\nu_{\text{max.}}$ 1 580, 1 495, 1 245, 1 180, 1 030, 955, and 830 cm^{-1}; $\delta(CDCl_3)$ 2.45s, 3.80s, and 6.84 and 7.00 (m, AA′BB′ pattern); *m/e* 154 (M^+, 100%), 139 (93), 124 (6), 111 (12), 96 (10), 95 (8), 77 (8), 70 (6), and 69 (7).

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REFERENCES

[1] S. R. Mani and H. J. Shine, *J. Org. Chem.*, 1975, **40**, 2756.

[2] H. J. Shine, J. J. Silber, R. J. Bussey, and T. Okuyama, *J. Org. Chem.*, 1972, **37**, 2691.

[3] B. K. Bandlish, A. C. Padilla, and H. J. Shine, *J. Org. Chem.*, 1975, **40**, 2590.

[4] O. Hammerich and V. D. Parker, *Electrochim. Acta*, 1973, **18**, 537.

[5] U. Svanholm, O. Hammerich, and V. D. Parker, *J. Amer. Chem. Soc.*, 1975, **97**, 101; U. Svanholm and V. D. Parker, *ibid.*, 1976, **98**, 997.

[6] Y. Murata and H. J. Shine, *J. Org. Chem.*, 1969, **34**, 3368.

[7] Y. L. Chow, W. C. Danen, S. F. Nelsen, and D. H. Rosenblatt, *Chem. Rev.*, 1978, **78**, 243.

[8] Y. L. Chow, *Accounts Chem. Res.*, 1973, **6**, 354.

[9] (*a*) H. J. Shine in ' Organic Free Radical,' ACS Symposium Series, ed. W. A. Pryor, American Chemical Society, Washington, 1978, p. 359; (*b*) H. J. Shine, B. K. Bandlish, S. R. Mani, and A. G. Padilla, *J. Org. Chem.*, 1979, **44**, 915. We are grateful to Dr. H. J. Shine for the preprint.

[10] M. M. Rogic, T. R. Demmin, R. Fuhrmann, and F. W. Koff, *J. Amer. Chem. Soc.*, 1975, **97**, 3241.

[11] M. M. Rogic, J. Vitron, and M. D. Swerdloff, *J. Amer. Chem. Soc.*, 1977, **99**, 1156.

[12] K. P. Klein, T. R. Demmin, B. C. Oxenrider, M. M. Rogic, and M. T. Tetenbaum, *J. Org. Chem.*, 1979, **44**, 275.

[13] H. Richard, K. S. Pillay, and Y. L. Chow, *Canad. J. Chem.*, 1979, **57**, 2923.

[14] M. Higo, T. Sakashita, M. Toyoda, and T. Mukaiyama, *Bull. Chem. Soc. Japan*, 1972, **45**, 250.

[15] B. M. Trost and L. S. Melvin, jun., ' Sulfur Ylides,' Academic Press, New York, 1975, p. 13

[16] Y. L. Chow and C. J. Colon, *J. Org. Chem.*, 1968, **33**, 2598.

[17] B. K. Bandlish and H. J. Shine, *J. Org. Chem.*, 1977, **42**, 561.

[18] W. K. Musker and T. L. Wolford, *J. Amer. Chem. Soc.*, 1976, **98**, 3055; W. K. Musker and P. D. Roush, *ibid.*, p. 6745; W. K. Musker, T. L. Wolford, and P. B. Roush, *ibid.*, 1978, **100**, 6417.

[19] B. G. Gilbert, D. K. C. Hodgeman, and R. O. C. Norman, *J.C.S. Perkin II*, 1973, 1748.

[20] M. Bonifačić, H. Möckel, D. Bahnmann, and K. D. Asmus, *J.C S. Perkin II*, 1975, 675.

[21] K. D. Asmus, D. Bahnmann, M. Bonifačić, and H. A. Gillis, *J.C.S. Faraday Discuss.*, 1978, 217.

[22] M. L. Sheinbaum and M. B. Dines, *Tetrahedron Letters*, 1971, 2205.

[23] R. A. Perry, R. W. Lockhart, M. Kitadami, and Y. L. Chow, *Canad. J. Chem.*, 1978, **56**, 2906.

[24] Y. L. Chow, T. Hayasaka, and J. N. S. Tam, *Canad. J. Chem.*, 1970, **48**, 508.

[25] J. J. Silber and H. J. Shins, *J. Org. Chem.*, 1971, **36**, 2923.