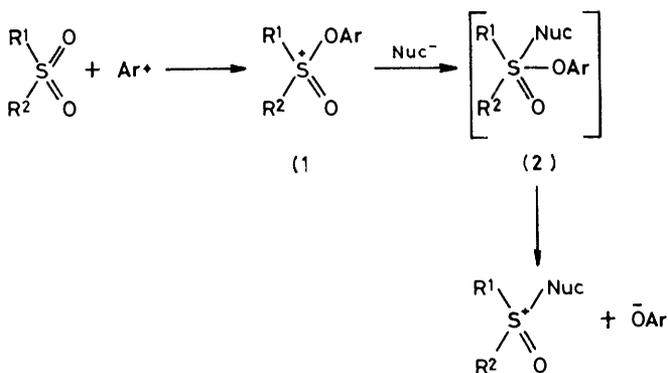


The Reactions of Aryloxysulphoxonium Salts with Amines and Other Nucleophiles

By G. Roger Chalkley, David J. Snodin, Graham Stevens, and Mark C. Whiting,* School of Chemistry, The University, Bristol BS8 1TS

Aryloxysulphoxonium salts, easily accessible from diazonium salts and sulphonyl compounds, are effective electrophiles. With aliphatic primary and secondary amines they react by attack on sulphur, to give a range of sulphur-nitrogen compounds, including derivatives of quinquevalent cationic sulphur; oxygen nucleophiles usually react similarly. Otherwise unreactive bases, e.g. tertiary amines, give ylides, which may rearrange to give hydroxy-sulphoxides. Attack may also occur at aliphatic carbon. Qualitative or semiquantitative conclusions are reached on the mechanisms of the reactions reported.

WE have described¹ the arylation of a number of sulphonyl compounds, $R^1R^2SO_2$, by decomposing aryl-diazonium salts in them and trapping the reactive intermediate, presumably² the aryl cation itself:



R^1, R^2 may be alkyl, aryl, dialkylamino, or aryloxy-groups (but not alkoxy)

The resultant aryloxysulphoxonium cations (1) might be expected to show reactivity toward nucleophiles at

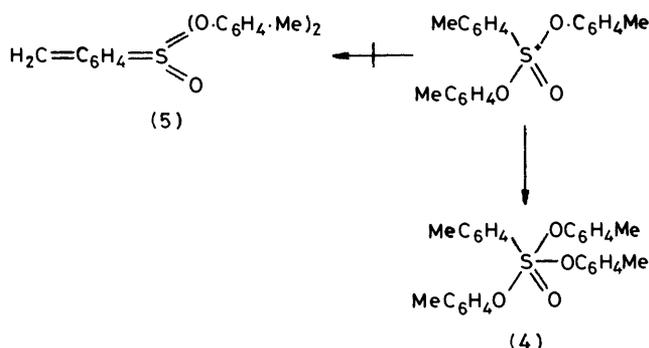
various centres, but especially at the cationic sulphur atom, as indicated above. We now report that they are highly reactive, and that this is indeed the commonest mode of reaction. When tetrafluoroborates derived from sulphones (1; $Ar = Ph, R^1R^2 = [CH_2]_4$ or Me_2) were dissolved in aqueous phosphate buffer solutions at pH 7.0 or 5.8, hydrolysis occurred, as shown by an increase in light-absorption attributable to the liberation of phenol. The pH 7 solutions showed much the faster rates, and multiplication of first-order rate constants by calculated hydroxide ion concentrations in the two solutions gave concordant values for $10^4 k_2$ of 23 and 24 ($R^1, R^2 = [CH_2]_4$), and of 9.6 and 9.7 $l\ mol^{-1}\ s^{-1}$ ($R^1 = R^2 = Me$) respectively, at 20 °C. Evidently the reaction involves attack by HO^- at sulphur, the corresponding reaction by neutral solvent being unimportant under these conditions. The hexafluorophosphate of cation (1; $R^1 = Ar = p$ -tolyl; $R^2 = p$ -tolylxy) was hydro-

¹ G. R. Chalkley, D. J. Snodin, G. Stevens, and M. C. Whiting, *J. Chem. Soc. (C)*, 1970, 682.

² A. N. Nesmayanov, L. G. Makarova, and T. P. Tolstaya, *Tetrahedron*, 1957, 1, 145.

lysed by the same buffer solutions at 27 °C, giving $10^4 k_2 = 0.15$ and $0.20 \text{ l mol}^{-1} \text{ s}^{-1}$, and thus has a half-life of the order of hours at physiological pH values.

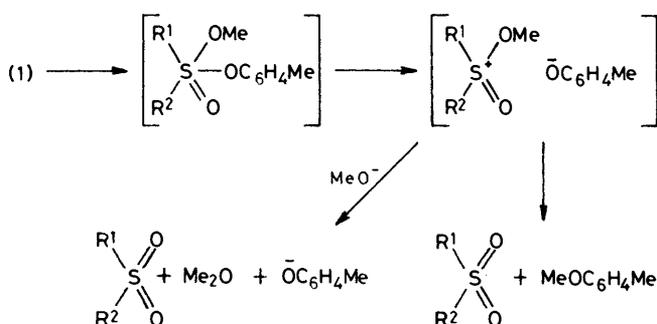
Postulated intermediates (2) having 5-co-ordinate sulphur atoms³ are species of obvious interest, and



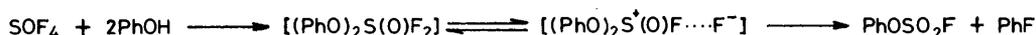
attempts were made to observe (4) directly. When solutions of cation (1; $R^1 = \text{Ar} = p\text{-tolyl}$; $R^2 = p\text{-tolylloxy}$) were treated with sodium *p*-methylphenoxide in diglyme, much trouble was caused by adventitious water, so that the only products isolated were *p*-methylphenol and the obvious hydrolysis product, *p*-tolyl toluene-*p*-sulphonate. However, the n.m.r. spectra of the mixture showed, on one occasion, three AB quartets with the usual 8 Hz coupling constants, and having an intensity ratio of 1:1:2. This is the result expected for compound (4) assuming slow interconversion of apical and equatorial ligands and a preference for the form with one aryloxy-group and the oxygen atom apical. The formation of compound (5), or the occurrence of no reaction, or of mere hydrolysis, were ruled out.

The reactions of cations (1) with sodium methoxide in methanol present some problems, but probably involve initial attack by methoxide ion on sulphur. The four salts (1; $\text{Ar} = \text{Ph}$ or *p*-tolyl; $R^1R^2 = [\text{CH}_2]_4$ or Me_2) were investigated first; in every case the products were methoxybenzene or *p*-methoxytoluene, plus dimethyl

aryl oxide exchange in basic media. In an attempt to deduce the mechanism of the reaction with methoxide, cation (1; $\text{Ar} = R^1 = p\text{-tolyl}$, $R^2 = p\text{-tolylloxy}$) as its hexafluorophosphate was treated with increasing concentrations of sodium methoxide in methanol. The ratio, *p*-methoxytoluene : *p*-methylphenoxide was found to increase somewhat (1.1, 1.8, and 2.6 for methoxide/cation ratios of 4, 9, and 19, respectively). An acceptable mechanism is as follows. Addition of methoxide ion gives an intermediate analogous to (4), which rapidly loses aryl oxide ion, forming an ion-pair of which the cation is an aliphatic analogue of (1). Such a species must be a potent methylating agent, known^{1,2} to react even with tetrafluoroborate anion, and its ion-pair may collapse before dissociation to give a methyl aryl ether, or after dissociation with any base, but especially with methoxide ion to give dimethyl ether. Most alternative schemes would imply a decrease in the ratio of *p*-methoxytoluene to (*p*-methylphenoxide + dimethyl ether) as the



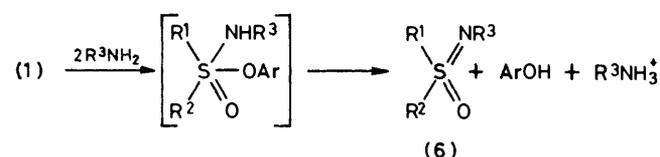
methoxide ion/cation ratio is increased; even the above mechanism does not account for the apparent increase, verification and interpretation of which would require more work. This explanation avoids the need to postulate nucleophilic attack on unactivated phenyl groups, although a good analogy for such attack in fact exists, in the reported⁴ formation of fluorobenzene from thionyl tetrafluoride and phenol:



ether and phenol or *p*-methylphenol; dimethyl sulphone or tetramethylene sulphone was presumably formed also. The *p*-methoxytoluene was free from *m*-methoxytoluene, so benzyne intermediates are ruled out. When the two salts with $\text{Ar} = \text{Ph}$ were treated with *p*-methylphenol (1 mol) in methanol for 20 s, then excess of sodium methoxide solution, methoxybenzene and *p*-methoxytoluene were formed in about equal yield; when the two salts were treated with a methanol solution containing both sodium methoxide (1 mol) and sodium *p*-methylphenoxide (1 mol), however, the two aromatic ethers were formed in a ratio of 93 : 7. Thus, (a) rapid interchange of aryloxy-groups takes place in near-neutral conditions; (b) the reaction of methoxide ion is more rapid than this

A similar explanation for methyl aryl ether formation in our reactions cannot be ruled out.

The reactions of aryloxysulphoxonium salts with amines are of greater synthetic interest than those with oxygen bases, and again may involve attack on sulphur:



Primary aliphatic amines attack cations (1) where R^1, R^2 are aryl, or aryloxy, giving the *N*-alkylsulphoximide (6; $R^1 = R^2 = \text{Ph}$, $R^3 = \text{Me}$) (case not studied in detail) or the aryloxysulphoximides (6; $R^1, R^2 = \text{aryloxy}$ or dialkylamino). When $R^1 = \text{Me}_2\text{N}$ and $R^2 = \text{aryl}$, the

³ B. M. Trost, R. LaRochelle, and R. C. Atkins, *J. Amer. Chem. Soc.*, 1969, **91**, 2175.

⁴ R. Cramer and D. D. Coffman, *J. Org. Chem.*, 1961, **26**, 4164.

product was analogous to an amidine; when $R^1 = \text{Me}_2\text{N}$ and $R^2 = \text{aryloxy}$, an analogue of a urea derivative was formed. All these products, listed in the Table, were formed in good yield in every case investigated, except

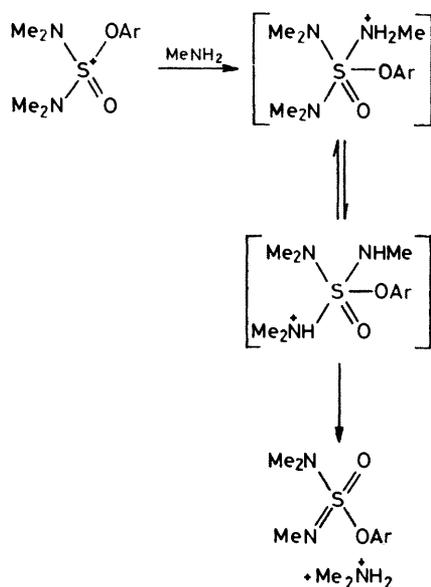
The compounds tabulated were identified by analysis and/or n.m.r. spectra, which included diastereotopic hydrogen atoms in compounds obtained from benzylamine and ethylamine when $R^1 \neq R^2$. The urethane

Properties of sulphoximides (6)

R^1	R^2	R^3	M.p. or (b.p.) ^b [$\theta_c/^\circ\text{C}$]	Yield	Found (%)			Required (%)			N.m.r.			$\nu_{\text{max.}}(\text{CCl}_4)/\text{cm}^{-1}$			
					C	H	N	C	H	N	$R^1(\tau)$	$R^2(\tau)$	$R^3\tau$				
Ph	Ph	Me		74										1 150	1 251		
C_7H_7^a	Me_2N	Me	(115—125) ^c	78	56.65	7.7	13.35	56.65	7.55	13.2	2.24, 2.70	7.59	2.0—2.7	7.37	7.15	1 163	1 267, 1 300
$\text{C}_7\text{H}_7\text{O}$	Me_2N	Me	(90—100) ^d	76	52.9	6.9		52.7	7.0		2.86	7.67		7.07	7.15	1 150, 1 175	1 259, (1 296), 1 305
PhO	C_7H_7	Me	62—63	81	64.25	5.6		64.4	5.75		2.7—3.35 (m)		2.28, 2.68	7.64	7.05	1 157, 1 182	1 305
$\text{C}_7\text{H}_7\text{O}$	C_7H_7	Me	62—63	95	65.55	6.05	4.9	65.5	6.2	5.1	3.01, 3.29	7.74	2.23, 2.79	7.62	6.94	1 157, 1 180, (1 186)	1 305
$\text{C}_7\text{H}_7\text{O}$	$\text{C}_7\text{H}_7\text{O}$	Me		76							2.85	7.67	2.85	7.67	7.08	1 150, 1 181	(1 245) (1 353)
PhO	C_7H_7	CH_2Me	(130—140)	86	65.15	6.15	5.4	65.5	6.2	5.1	2.7—3.3 (m)		2.17, 2.75	7.60	8.71;	1 154, 1 174	1 275, 1 302
$\text{C}_7\text{H}_7\text{O}$	C_7H_7	CH_2Me	(140—150) ^e	83	65.9	6.75		66.45	6.6		3.10, 3.36	7.82	2.28, 2.88	7.70	6.2—6.8 (m) 8.75;	1 155, 1 174	1 274, 1 299
$\text{C}_7\text{H}_7\text{O}$	C_7H_7	CMe_3	(135—145)	3.7	68.75	7.8		68.15	7.05		3.10, 3.35	7.79	2.32, 2.86	7.65	6.66, 6.51 ^h	1 175, (1 181)	1 301
$\text{C}_7\text{H}_7\text{O}$	C_7H_7	C_6H_{11} ^g	(170—180)	89	68.95	7.5	4.6	69.95	7.3	4.1	3.09, 3.35	7.79	2.28, 2.86	7.66	8—8.9 (m); 6.36 (m)	1 155, 1 166, 1 182	1 300
$\text{C}_7\text{H}_7\text{O}$	C_7H_7	CH_2Ph	(200—210)	82	71.0	6.1		71.8	6.0		3.09, 3.37	7.79	2.21, 2.80	7.65	2.6—3.0 (m); 5.36, 5.50 ^j	1 153, 1 161	1 298
$\text{C}_7\text{H}_7\text{O}$	$\text{C}_7\text{H}_7\text{O}$	CH_2Ph	(180—190) ^f	66	68.35	5.55		68.65	5.7		2.95	7.73	2.95	7.73	2.82; 5.59	1 149, 1 180	(1 344)

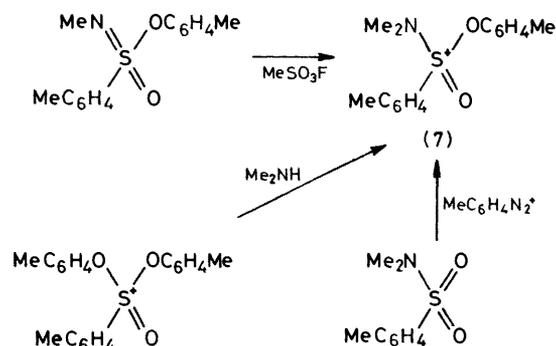
^a C_7H_7 is *p*-tolyl. ^b Bath temperature, at 10^{-4} mmHg. ^c n_D^{21} 1.5486. ^d n_D^{24} 1.5218. ^e n_D^{25} 1.5660. ^f n_D^{25} 1.5741. ^g Cyclohexyl. ^h $J_{\text{AB}} = 13.3$ Hz. ⁱ $J_{\text{AB}} = 14.5$ Hz.

for $R^3 = \text{Bu}^t$, when steric hindrance is probably to blame, as even here the product was tractable. Only when both R^1 and R^2 were Me_2N did the reaction take a different course, dimethylamine being eliminated instead of a phenol from the assumed intermediate:



An alternative view of this process is that the methylamine attacked one of the four methyl groups of the original cation, giving the dimethylammonium ion without fission of the S—N bond; this process would be analogous to methylation by the $\ddot{\text{S}}\text{—OMe}$ cation, as described above. The use of ethylamine here would decide between the two mechanisms.

analogue (6; $R^1 = p$ -tolyl, $R^2 = \text{PhO}$, $R^3 = \text{Me}$) was hydrolysed, rapidly by dilute mineral acid at 20°C , or slowly by sodium hydroxide at 75°C , to *N*-methyl-toluene-*p*-sulphonamide and phenol. The S=NMe groups in these compounds showed marked nucleophilicity; thus in trifluoroacetic acid the compounds (6; $R^1 = p$ -toloxy, $R^3 = \text{Me}$, and $R^2 = \text{either } p\text{-tolyl or } \text{Me}_2\text{N}$) showed a strong displacement of the methyl signal, consistent with *N*-protonation, although no sign of coupling to $\dot{\text{N}}\text{—H}$ could be discerned, nor could any salt be isolated. The former compound underwent *N*-methylation, using methyl fluorosulphonate,⁵ to a cation (7) which had already been prepared by arylation.¹ A third synthesis of cation (7) involved treating cation (1; $R^1 = \text{Ar} =$



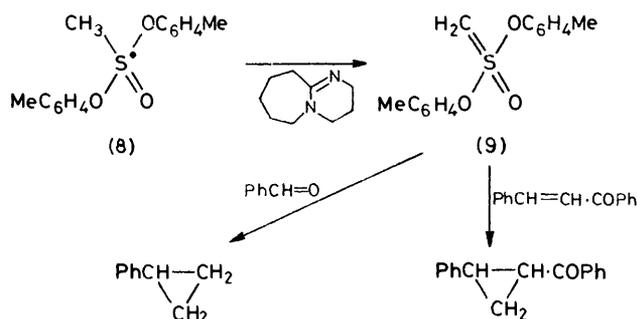
p-toloxy, $R^2 = p$ -tolyl) with dimethylamine. Such reactions of secondary aliphatic amines are probably general, although no other was attempted. Indeed, an extensive chemistry of quinquivalent cationic

⁵ M. G. Ahmed, R. W. Alder, G. H. James, M. L. Sinnott, and M. C. Whiting, *Chem. Comm.*, 1968, 1533.

hexavalent neutral sulphur compounds like (7) and (6) must exist, corresponding to neutral and anionic phosphorus analogues. The arylation reaction¹ provides a convenient entrance to it; other methods, however, have been reported.⁶ Cations such as (7) with one or two nitrogen atoms attached to sulphur are stable in aqueous solution, and their biological behaviour could well be interesting.

The smooth reactions of aliphatic amines do not extend to arylamines, or to ammonia itself, although these reactions were not investigated in detail. In none of the compounds prepared was there n.m.r. evidence for restricted rotation about the -N=S bond.

Trialkylsulphoxonium salts readily give ylides on treatment with base; in the same way cation (8) reacted



with strong bases, most conveniently with diazabicycloundecene,⁷ to give a crystalline ylide (9), which was sufficiently stable to be characterised by its n.m.r. spectrum (although not obtained sharply melting or analytically pure). When cations analogous to (8), but having two different aryl groups, were used, the resultant ylides, although crystalline, showed irregular multiplets in place of the sharp singlet signal for CH_2 at $\tau = 8.04$ in the ylide (9). Probably some aryloxy-interchange had occurred, and the ylides obtained were mixtures of symmetrical and unsymmetrical compounds. The reactions of ylide (9) were briefly investigated; water gave *p*-tolyl methanesulphonate and *p*-methylphenol; benzaldehyde was converted into styrene oxide (10%), and benzylideneacetophenone into 2-benzoyl-1-phenylcyclopropane (27%). The yields were inferior to those obtained with the ylide from trimethylsulphoxonium salts,⁸ probably because species like (9) are capable of rearrangement by a route to be described below, and not available to the aliphatic ylides.

When cations, e.g. (1; $\text{R}^1 = \text{R}^2 = \text{Me}$, $\text{Ar} = \text{Ph}$), derived from dimethyl sulphone, were dissolved in deuterium oxide, the n.m.r. signal for methyl gradually disappeared, at a rate about ten times faster than that of hydrolysis (which itself could be followed by the replace-

ment of one aromatic multiplet by another at higher τ value). In the cation (1; $\text{R}^1\text{R}^2 = [\text{CH}_2]_4$, $\text{Ar} = \text{Ph}$) the two processes took place at about the same rate. These cations therefore exchange their protons around 150 and 30 times as fast as the trimethylsulphoxonium cation,⁹ respectively, presumably *via* the ylide. The cation (1; $\text{R}^1 = \text{Me}$, $\text{R}^2 = p$ -tolyl, $\text{Ar} = p$ -tolyl) reacted more rapidly still, too fast to be followed by n.m.r. measurements; its trideuterio-derivative was readily obtained as the hexafluorophosphate, 93% labelled and in 60% yield, by recrystallisation from acetonitrile and deuterium oxide.

In isotopic exchange an ylide may have only transient existence, but treatment of the cation (1, $\text{R}^1 = \text{R}^2 = \text{Me}$, $\text{Ar} = \text{Ph}$) with sodium phenoxide gave, presumably after a rearrangement of the ylide, the isomeric *o*-hydroxy-sulphoxide (10), the structure of which follows straight-



forwardly from its spectra. This reaction is formally analogous to rearrangements of cationic trivalent sulphur compounds, which have been discussed.¹⁰ Higher yields and more information were obtained in the corresponding reaction of the cation (1; $\text{R}^1\text{R}^2 = [\text{CH}_2]_4$, $\text{Ar} = \text{Ph}$) with sodium phenoxide or, preferably, trimethylamine. The main products, separable by chromatography on silica with gradient elution, were two crystalline monosulphoxides (11) and (12), and a disulphoxide fraction which was obtained crystalline only when the separation was carried out at 0 °C. Of the two monosulphoxides, the first eluted (11) [ν_{max} (S=O str) 990 cm^{-1}] constituted 7%, the second (12) (ν_{max} 1008 cm^{-1}) 93% of the fraction. By a process discovered accidentally and not seriously investigated mechanistically, either sulphoxide could be converted by purified bromoform at 150 °C in 7 min, or by purified chloroform at 65 °C in 32 h, into an equilibrium mixture of the two sulphoxides, ratio 78:22. We assign the more easily eluted isomer having the lower S=O stretching frequency the configuration with *o*-hydroxyphenyl *cis* to the oxygen atom (11), on the basis that this should have the S=O bond order reduced by hydrogen bonding, while in the *trans*-form (12) weaker hydrogen bonding to the sulphur lone-pair should increase the bond order and the frequency of the stretching vibration.

The crystalline disulphoxide showed a simple n.m.r. spectrum in the aromatic region, easily interpreted as an AB_2 system, and was therefore taken to be a single isomer having either C_s or C_2 symmetry; presumably it had the same *trans*-relationship between the aryl group

⁷ H. Oeidger and Fr. Möller, *Angew. Chem. Internat. Edn.*, 1967, **6**, 76.

⁸ E. J. Corey and M. Chaykowsky, *J. Amer. Chem. Soc.*, 1965, **87**, 1353.

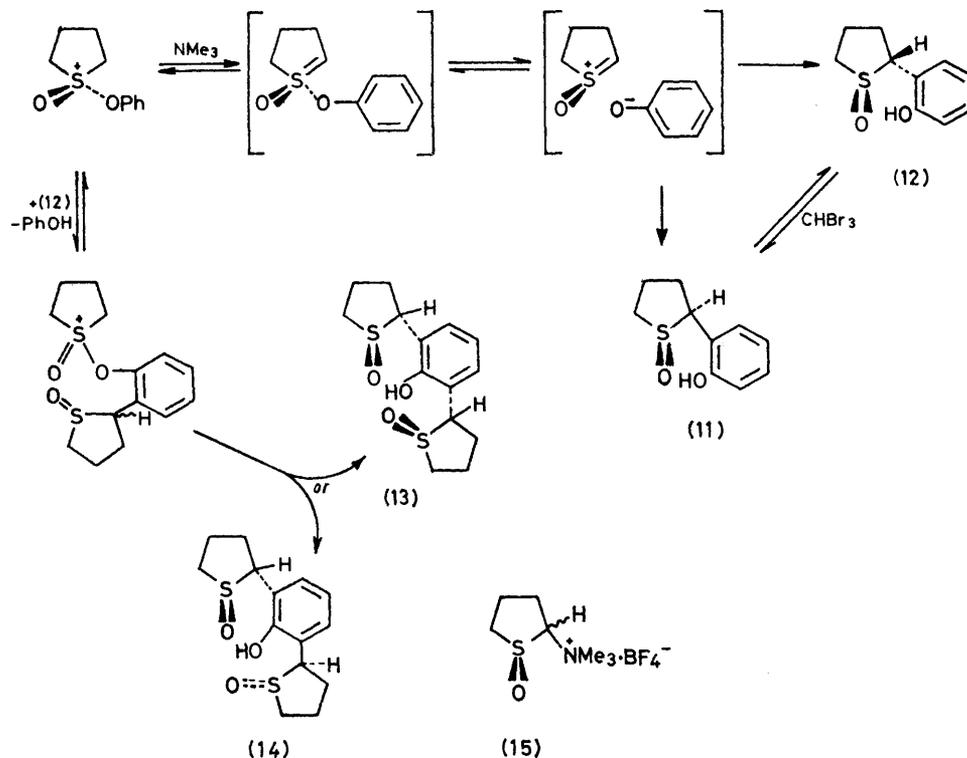
⁹ S. G. Smith and S. Winstein, *Tetrahedron*, 1958, **3**, 317.

⁶ H. Takei, I. Watanabe, and T. Mukaiyama, *Bull. Chem. Soc. Japan*, 1965, **38**, 1989; R. G. Laughlin, *J. Amer. Chem. Soc.*, 1968, **90**, 2651; E. S. Levchenko, E. S. Kozlov, and A. V. Kirsanov, *Zhur. obschei. Khim.*, 1961, **31**, 2381 (*Chem. Abs.*, 1962, **56**, 4653h); *J. Gen. Chem. (U.S.S.R.)*, 1962, **32**, 873, 2548; 1963, **33**, 559; E. S. Levchenko, L. N. Markovskii, and A. V. Kirsanov, *J. Org. Chem. (U.S.S.R.)*, 1967, **3**, 1234, 1439; L. N. Markovskii, E. S. Levchenko, A. A. Kisilenko, and A. V. Kirsanov, *ibid.*, p. 2169.

¹⁰ T. Thompson and T. S. Stevens, *J. Chem. Soc.*, 1932, 69; L. A. Pinck and G. E. Hilbert, *J. Amer. Chem. Soc.*, 1946, **68**, 751; C. R. Hauser, S. W. Kantor, and W. R. Brasen, *ibid.*, 1953, **75**, 2660; M. G. Burdon and J. G. Moffat, *ibid.*, 1965, **87**, 4656.

and the sulphoxide oxygen atoms as did the major monosulphoxide (12), and so was either (13) or (14). It constituted 70% of the disulphoxide fraction, and the residual 30% may well have been mainly the same isomer; thus in the process of aryloxy-exchange which must be assumed to account for the disulphoxide, the cation derived from monosulphoxide (12) must have been formed with high stereoselectivity, although it is hard to guess why, or in what sense. (Just possibly the crystalline product was a mixture, the sharp n.m.r. spectrum being the result of coincidence.) The disulphoxide system was notably more labile stereochemically than

to regard it as involving an intimate ion-pair which usually reacts to give isomer (12) (the least-motion product) but after some relative movement may yield isomer (11), in analogy with the racemisation of various ion-pairs during internal return, or the intramolecular inversion process¹² in aliphatic deamination. After dissociation, partial, to a solvent-separated ion-pair, or complete, the cation may be intercepted by an external nucleophile, *e.g.* trimethylamine. However, we have no evidence that would exclude a concerted 3,2-sigmatropic shift giving isomer (12) and a dissociation process taking place simultaneously.



that of the two monosulphoxides, easily giving an inseparable syrupy mixture of isomers. The disulphoxide fraction was formed in larger yield than the monosulphoxides, and the ratio, albeit imperfectly measured, was not reduced by increasing the dilution.

These rearrangements require explanation; formally similar processes in compounds containing sulphur in a lower valency state have been regarded¹¹ as concerted sigmatropic rearrangements, for good reasons. Here, however, stereoselectivity is incomplete; furthermore, a search in the mother liquors and in the most-polar fraction for the *para*-substituted phenols corresponding to (11) and (12) (which were not found) brought to light the presence of the tetrafluoroborate (15), of which the gross structure, but not the configuration, followed from analysis and spectra. We therefore doubt the concerted character of the rearrangement of the ylide, and prefer

A number of other bases gave a similar mixture of phenolic sulphoxides; triethylamine did so in superior yield, presumably having less tendency to divert the reaction to a quaternary salt. Methylamine reacted in acetonitrile at 0 °C with cation (1; R¹R² = [CH₂]₄, Ar = *p*-tolyl) to give the mono- and di-sulphoxides, no sulphoximide being isolable.

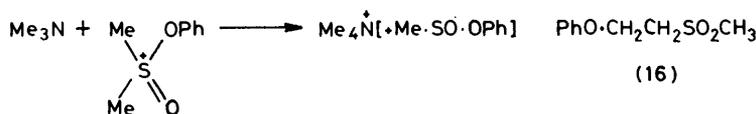
The by-products of the reaction between the tetrafluoroborate of cation (1; R¹ = R² = Me, Ar = Ph) and trimethylamine were also examined. Tetramethylammonium tetrafluoroborate was one, presumably formed by nucleophilic attack on aliphatic carbon, see over. The fate of phenyl methanesulphonate is unknown. A second was the sulphone (16) (6% yield), for which any proposed mechanism must be speculative.

The attack on aliphatic carbon by a nucleophile, displacing a sulphur compound of lower valency, constitutes

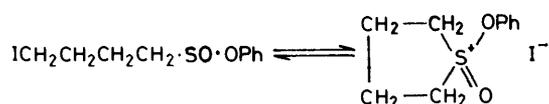
¹¹ R. W. C. Cose, A. M. Davies, W. D. Ollis, C. Smith, and I. O. Sutherland, *Chem. Comm.*, 1969, 263; S. Mageswaran, W. D. Ollis, and I. O. Sutherland, *ibid.*, 1973, 656.

¹² E. H. White and C. A. Aufdermarsh, *J. Amer. Chem. Soc.*, 1961, **83**, 1179.

a third fundamental mechanism for the reaction of nucleophiles with aryloxy-sulphonium salts. Two



additional examples were encountered; the hexafluorophosphate of cation (1; $\text{R}^1 = \text{Me}$, $\text{R}^2 = p$ -tolyl) reacted with pyridine to give the *N*-methylpyridinium salt and di-*p*-tolyl sulphite (identified by their i.r. spectra), and the tetrafluoroborate of the cation (1; $\text{R}^1\text{R}^2 = [\text{CH}_2]_4$, $\text{Ar} = \text{Ph}$) gave with sodium iodide or bromide in acetonitrile unstable petroleum-soluble compounds which must be formulated as phenyl esters of 4-halogenobutanesulphonic acid; the latter had n.m.r. spectra at room temperature consisting, in the aliphatic region, of symmetrical multiplets. Probably these are undergoing rapid scrambling in deuteriochloroform, *via* the original cation:



Finally, it may be useful to turn from exploratory mechanistic work to the synthetic aspects of a reaction which converts aniline and a sulphone into an *o*-hydroxy-sulphoxide in two stages:



This process may be useful in cases where its brevity or stereospecificity compensates for moderate yield, but the reaction first described by Burdon and Moffat,¹⁰ in which phenol and a sulphoxide are condensed with a carbodi-imide or with acetic anhydride to a dialkylphenoxysulphonium salt, is directly competitive.

EXPERIMENTAL

Reactions between Cations (1) and Sodium Methoxide.—To a solution prepared from sodium (0.3 g) in dry methanol (3 cm³), a solution of cation (1; $\text{R}^1\text{R}^2 = [\text{CH}_2]_4$, $\text{Ar} = \text{Ph}$) tetrafluoroborate (60 mg) in dry methanol (2 cm³) was added. The reaction mixture became warm and effervesced. A stream of dry nitrogen swept volatile products through a tube containing sodium hydride (50% in oil) into an n.m.r. tube cooled in acetone-carbon dioxide. To the condensate, fluorotrichloromethane and a little chloroform were added, and the tube was sealed. The spectrum observed included singlets for dimethyl ether ($\tau = 6.8$) and, in a ratio 3 : 1, at τ 6.65 and 8, for methanol. A very similar spectrum was obtained when dimethyl sulphate was substituted for the salt, and also when the tetrafluoroborate of cation (1; $\text{R}^1 = \text{R}^2 = \text{Me}$, $\text{Ar} = \text{Ph}$) was used.

In similar experiments a solution of sodium methoxide (6 mol) was added to the solid tetrafluoroborates of cations (1) having $\text{R}^1\text{R}^2 = [\text{CH}_2]_4$ and Me_2 (*a*) with $\text{Ar} = \text{Ph}$ and (*b*) with $\text{Ar} = p$ -tolyl. In cases (*a*) the reaction mixture was added to an excess of ether, in cases (*b*) to iso-octane; the solutions were washed with 2M-sodium hydroxide, dried,

and made up to a standard volume. Analysis by u.v. spectrometry gave yields of aryl methyl ether as 54 and 55%,

respectively [case (*a*)]; 46% and 55% [case (*a*), repeated]; and 55 and 63% [case (*b*)]. The experiments (*a*) were then repeated with a 20-s contact between the salt and a solution of *p*-methylphenol (1 mol) in methanol preceding the addition of an excess of methoxide; the yields of the two ethers formed were measured using two wavelengths (total yield 50 and 62%), and the ratio more accurately obtained by a g.l.c. analysis (58 : 42 and 62 : 38). When instead the solid salts [case (*a*)] were treated with a solution of sodium *p*-methylphenoxide (1 mol) and sodium methoxide (10 mol) the yields of methyl aryl ether were 61% and 64% and the ration, $\text{C}_6\text{H}_5\text{OMe}/\text{C}_7\text{H}_7\text{OMe}$, was 93 : 7 for both salts.

Reactions with Amines.—These involved treating the crystalline salts with the anhydrous methylamine at -78°C , or with ethylamine at 0°C , or with benzylamine at room temperature. After being set aside at room temperature for 30 min the mixture was extracted with ether, and the extract was washed with 2M-sodium hydroxide solution and water, and then dried, evaporated, and warmed *in vacuo* to remove amine. The residue was either crystallised from light petroleum or distilled at 10^{-4} mmHg. Under these conditions *t*-butylamine did not react, so the mixture of an amine and the hexafluorophosphate were heated to 115°C in a Carius tube for 36 h. The product was chromato-

graphed on grade 1 alumina, using a solvent varied continuously from light petroleum to ether using a mechanical gradient-elution device. The aryloxy-sulphoximide (70 mg) had λ_{max} 226 nm and an inflexion at 275 nm; *p*-tolyl toluene-*p*-sulphonate, *N*-*t*-butyl toluene-*p*-sulphonamide, and *p*-methylphenol were isolated from more polar fractions.

Bisdimethylamino-*p*-methylphenoxysulphoxonium (1; $\text{R}^1 = \text{R}^2 = \text{Me}_2\text{N}$, $\text{Ar} = p$ -tolyl) hexafluorophosphate was insoluble in methylamine at -78°C , and the mixture was therefore heated to 100°C for 3.5 h in a Carius tube to effect reaction. The product was identical with that obtained from cation (1; $\text{R}^1 = \text{Me}_2\text{N}$, $\text{R}^2 = p$ -tolyl, $\text{Ar} = p$ -tolyl).

Dimethylamino-*p*-tolyl-*p*-methylphenoxysulphoxonium (1; $\text{R}^1 = \text{Me}_2\text{N}$, $\text{R}^2 = \text{Ar} = p$ -tolyl) hexafluorophosphate was prepared from dimethylamine (10 ml), and the hexafluorophosphate of cation (1; $\text{R}^1 = \text{Ar} = p$ -tolyl, $\text{R}^2 = p$ -tolyl) (763 mg) at room temperature. Removal of excess of amine by evaporation and of *p*-methylphenol by extraction with hot light petroleum gave a solid (653 mg, 98%), m.p. $137\text{--}139^\circ\text{C}$ (lit.¹ m.p. $140.5\text{--}141.5^\circ\text{C}$), with the expected i.r. and n.m.r. spectra.

Dimethylamino-*p*-tolyl-*p*-methylphenoxysulphoxonium (1; $\text{R}^1 = \text{Me}_2\text{N}$, $\text{R}^2 = \text{Ar} = p$ -tolyl) fluorosulphate was obtained as a precipitate when *p*-methylphenoxy-*p*-tolyl-*N*-methylsulphoximide (130 mg) was dissolved in methyl fluoro-sulphate⁵ (excess) and the solution was added to dry ether (10 cm³). Recrystallisation from methylene chloride-ether gave the salt (100 mg, 54%), m.p. $122\text{--}123^\circ\text{C}$ (Found: C, 49.9; H, 5.2; N, 3.45. $\text{C}_{16}\text{H}_{20}\text{FNO}_5\text{S}_2$ requires C, 49.35;

H, 5.15; N, 3.6%), ν_{\max} (Nujol) 1 503, 1 295, 1 276, 1 093, 1 070, 970, 870, and 719 cm^{-1} .

Observation of tri-p-tolyl toluene-p-orthosulphonate (4). A methanolic solution of sodium *p*-methylphenoxide was evaporated to dryness and the residue extracted with dry acetonitrile in a Soxhlet apparatus; the product was then cooled, collected, and washed with dry ether under nitrogen to give anhydrous sodium *p*-methylphenoxide. When this salt (3 mmol) was dissolved in the minimum quantity of dry diethylene glycol dimethyl ether and a solution of the hexafluorophosphate (3 mmol) of the cation (1; $R^1 = \text{Ar} = p\text{-tolyl}$, $R^2 = p\text{-tolylxy}$) in the same solvent was added, the n.m.r. spectrum in the aromatic region consisted of three AB quartets, having $\tau = 2.40$ and 2.82 (MeC_6H_4); 3.08 and 3.32 ($\text{MeC}_6\text{H}_4\text{O}$); and 3.17 and 3.42 ($2 \times \text{MeC}_6\text{H}_4\text{O}$) (all coupling constants *ca.* 8.5 Hz). Unfortunately the methyl region was obscured by solvent bands. On other occasions the spectra were less clear-cut, quartets attributable to *p*-tolyl toluene-*p*-sulphonate and *p*-methylphenol being superimposed on the foregoing signals.

Trideuteriomethylbis-p-methylphenoxysulphoxonium (1; $R^1 = \text{Me}$, $R^2 = p\text{-toloxy}$, $\text{Ar} = p\text{-tolyl}$) hexafluorophosphate was prepared from the unlabelled salt (1.51 g), dry acetonitrile (3 cm^3) and deuterium oxide (1 cm^3) at room temperature for 1 h. Addition of dry ether (40 cm^3) gave a white precipitate, which was subjected to a second similar treatment, giving material (0.90 g), m.p. 89–90.5 °C (lit.,¹ 88–89 °C) for which the n.m.r. spectrum in dry acetonitrile showed that at least 93% of the $\text{CH}_3\text{-S}^+$ group had been deuteriated. The i.r. spectrum resembled that of the unlabelled salt, but showed weak extra bands at 2 370, 2 265, and 2 237 cm^{-1} (CH_2Cl_2).

Methylenebis-p-methylphenoxysulphur oxide (9) was best purified in a Y tube having a sintered glass plate in one arm and a bulb in a second. The hexafluorophosphate (0.5 mmol) of the cation (1, $R^1 = \text{Me}$, $R^2 = p\text{-toloxy}$, $\text{Ar} = p\text{-tolyl}$) was dissolved in dry methylene chloride, and diazabicycloundecene⁷ was added; after 5 min solvent was removed under reduced pressure, nitrogen was admitted, and the ylide was extracted with fluorotrichloromethane ($3 \times 5 \text{ cm}^3$). Removal of solvent under reduced pressure and admission of nitrogen left a solid, which was dissolved in fluorotrichloromethane, transferred to the bulb of the Y tube, and cooled, in a nitrogen atmosphere, to -78 °C, until crystallisation was complete. After inversion of the apparatus, the solid was collected on the sinter under nitrogen pressure, then recrystallised the same way, solvent being finally evaporated in a stream of dry nitrogen. If exposed to air, the ylide reacted with water, being completely converted into *p*-tolyl methanesulphonate and *p*-methylphenol in 3 h, and on heating it decomposed before melting; n.m.r. (CFCl_3) at -40 °C comprised signals at τ 8.12 (2 H), 7.69 (6 H), and 2.94 (8 H, completely collapsed AA'BB' system), ν_{\max} (CCl_4) *inter alia* 3 165w, 1 282m, 1 183m, and 1 115m cm^{-1} , the first being a C-H stretching frequency associated with the methylene group.

Methyl o-Hydroxybenzyl Sulphoxide.—A solution of sodium phenoxide (1.16 g, 1 mol) in dry acetonitrile (100 cm^3) was mixed with dimethylphenoxysulphoxonium (1; $R^1 = R^2 = \text{Me}$, $\text{Ar} = \text{Ph}$) tetrafluoroborate (2.58 g, 1 mol) at room temperature. After 12 h, removal of solvent *in vacuo* left a residue which was extracted with benzene ($3 \times 10 \text{ cm}^3$, at 70 °C). The insoluble residue appeared to be sodium tetrafluoroborate. Chromatography of the soluble fraction (1.89 g) on silica gel (370 g) using benzene

changed continuously to ethyl acetate, over 3 l, then to methanol over a further 3 l, gave phenol (83%), dimethyl sulphone (35%), and the *sulphoxide* (16%), m.p. 108–110 °C (Found, C, 56.4; H, 5.55; S, 18.0. $\text{C}_8\text{H}_{10}\text{SO}_2$ requires C, 56.45; H, 5.9; S, 18.8%), λ_{\max} 279 nm, $\epsilon = 3 400$, ν_{\max} 1 025 cm^{-1} (S=O stretch), 760 cm^{-1} (*o*-disubstituted benzene), n.m.r. signals at τ 7.5 (3 H), 6.13, 5.57 (2 H; AB quartet, $J = 13.7$ Hz), and *ca.* 3 (4 H, multiplet, also a broad signal at τ *ca.* 1.0, removed on treatment with D_2O).

In a similar experiment *methyl 2-phenoxyethyl sulphone*, m.p. 115 °C, was isolated in 6% yield (Found: M^+ 200.0497; $\text{C}_9\text{H}_{12}\text{O}_2\text{S}$ requires M , 200.0507); λ_{\max} 270 and 277 nm ($\epsilon = 2 225$ and 1 960, respectively); n.m.r. (CDCl_3) τ 7.02(s), 3 H), 6.64 (t) and 5.64 (t, forming an A_2X_2 system, $J = 5$ Hz), 2.6–3.3 (m, 5 H); ν_{\max} 1 138 and 1 325 cm^{-1} (S=O stretch).

Potassium *t*-butoxide in diethylene glycol dimethyl ether gave the *o*-hydroxybenzyl methyl sulphoxide (3%), phenol, and dimethyl sulphone. With trimethylamine as base (*cf.* reaction described below) little sulphoxide was formed, but tetramethylammonium tetrafluoroborate (34.5%) was obtained. In this case methoxybenzene was shown to be absent (yield < 0.01%); much of the product appeared to be polymeric and very polar.

Reactions between the Tetrafluoroborate of Cation (1; $R^1R^2 = [\text{CH}_2]_4$; $\text{Ar} = \text{Ph}$) and Bases.—These reactions were studied extensively, especially when the base was trimethylamine. Typically, the salt (22.72 g, 0.08 mol) was dissolved in acetonitrile (80 cm^3 , dried by distillation over phosphorus pentaoxide) and a solution (10%) of trimethylamine (dried over sodium hydride) in acetonitrile (as above) (120 cm^3 , 0.2 mol) was added, with cooling to 0 °C. After 1.5 h at this temperature, amine and solvent were removed under reduced pressure with gentle warming, and the residue (29.6 g) was extracted with benzene ($4 \times 32 \text{ cm}^3$). Evaporation gave a residue which was chromatographed on silica gel (1 072 g; Whatman Chromedia SG 31), using ethyl acetate. Phenol and sulpholan were eluted; the solvent was then changed to a mixture of methanol and ethyl acetate, the percentage of the former being steadily increased using a gradient-elution apparatus. A mono-sulphoxide fraction came off with 5–10% of methanol, and a disulphoxide fraction with 18–30%. The former (2 g) was dissolved in 5% methanol–95% ethyl acetate and rechromatographed more carefully on 405 g of silica gel, some sixty 50- cm^3 fractions being collected and analysed by u.v. spectrometry. A good, but not complete, separation was achieved between a *cis*-isomer (11) (6.6%) and a *trans*-isomer (12) (93.4%), the first (600–1 250 cm^3 eluant, 7.5–8.5% methanol) separating from acetonitrile or methylene chloride–ether (50 : 50), m.p. 168 °C (Found: C, 61.2; H, 6.1%), the second (1 250–2 900 cm^3 eluant, 8.5–10.5% methanol) crystallising from methylene chloride, m.p. 163 °C (Found: C, 60.8; H, 6.15; S, 16.4. $\text{C}_{10}\text{H}_{12}\text{O}_2\text{S}$ requires C, 61.2; H, 6.15; S, 16.3%). In methanol–ethyl acetate mixtures, both isomers had λ_{\max} 280 nm (ϵ 3 300 and 2 850). The 6.6 : 93.4 ratio was deduced from spectrophotometric results, involving graphical resolution of the two peaks in the plot of optical density *versus* fraction number, and should be accurate to $\pm 0.5\%$ at worst. Yields of crystalline material were slightly lower than calculated.

Epimerisation. Attempts to use bromoform as an i.r. solvent revealed the conversion of either isomer into an equilibrium mixture, reaction being essentially complete at

150 °C in 7 min; in chloroform it required 32 h at reflux temperature. Both halogenoforms were purified by washing with sulphuric acid, water, and sodium carbonate solution and dried before use. No evidence could be found for epimerisation in refluxing ethanol (in 6.5 h) or in acetonitrile at 80 °C (1 h). The equilibrated mixture from the *trans*-isomer (730 mg) in bromoform (25 cm³) after 10 min was chromatographed, after removal of solvent at 0.5 mmHg, giving, by spectrophotometric assay, the *cis*-isomer (318 mg) and the *trans*-isomer (92 mg); a liquid mixture (231 mg) of dehydration products, eluted early, was also obtained.

After the elution of the monosulphoxide fraction, a second set of fractions showing u.v. absorption was eluted when the methanol percentage reached 20–30%, but this obstinately resisted crystallisation. A similar experiment was therefore carried out, in which the temperature never exceeded 0 °C, except briefly during benzene extraction of the crude product at 20 °C. The preliminary and final chromatogram were carried out in a cold-room. In the latter, on 440 g of silica gel, elution began with 22 : 78 methanol–ethyl acetate, the methanol proportion being increased to 28% over 3.5 l, then to 40% over a further 3.5 l. Chromophoric material began after 1.2 l; a plot of optical density against fraction number showed a single broad peak. Three groups of 50-cm³ fractions (29–34, 51–54, and 70–75, inclusive) were evaporated at 0.1 mmHg, and found to show similar n.m.r. spectra, and three others (35–50, 55–69, and 76–90) were similarly evaporated, and on dissolution in acetonitrile and cooling gave crystals, with the same m.p. and mixed m.p.s. Some 70% of the total weight was obtained crystalline; no difference could be observed between the n.m.r. spectra of crystalline and non-crystalline materials. The isomer of the *disulphoxide* (13) or (14) so obtained had m.p. 168 °C (Found: C, 56.0; H, 6.2; S, 21.65. C₁₄H₁₈O₃S₂ requires C, 56.35; H, 6.1; S, 21.5%). The n.m.r. spectrum ([²H₆]dimethyl sulphoxide) consisted of a multiplet analysed as an AB₂ system ($\tau = 3.15, 2.96$; $J = 8$ Hz), a double doublet (apparent triplet) assigned to 2C-H adjacent to S=O at $\tau = 5.69$, and a complex multiplet (12 H) at 6.5–8.2.

The benzene-insoluble residue originally obtained was extracted with methylene chloride (100 cm³), evaporation of which left a viscous residue from which one isomer of *trimethyl-2-tetrahydrothiophenylammonium tetrafluoroborate S-oxide* (15) separated, m.p. 121 °C (Found: C, 33.9; H, 6.6; N, 5.75; S, 12.9. C₇H₁₆BF₄NOS requires C, 33.8; H, 6.5; N, 5.6; S, 12.85%). The final residue appeared from its i.r. spectrum to be trimethylammonium tetrafluoroborate, but contained 2.9% of sulphur; the total yield of both isomers of the above salt could be as high as 13.6%.

When triethylamine was substituted for trimethylamine, the yields of mono- and di-sulphoxides (19.5 and 37.5%, respectively) were significantly higher, and no sign was observed of a salt analogous to (15). Sodium phenoxide was not extensively investigated, but appeared to give the monosulphoxide in 16% yield.

Phenyl 4-iodobutanesulphinat. The tetrafluoroborate of the cation (1; R¹R² = [CH₂]₄, Ar = Ph) (1.24 g) was added to a solution of sodium iodide (1.5 g) in acetonitrile (20 cm³) in the dark at 17 °C. After 30 min an excess of dry ether was added and the precipitated inorganic salts were removed. Distillation of solvent left a dark residue (1.22 g) which was extracted with warm, light petroleum, leaving a residue (0.20 g); the solution was washed with 2M-sodium hydroxide, dried, and evaporated under reduced pressure to give the *ester* (0.87 g, 70%), λ_{max} 211 and 272 nm (ϵ 5 400 and 1 490); ν_{max} 3 000, 1 600, 1 490, 1 460, 1 200, 1 130, 835, and 690 cm⁻¹ (Found: C, 37.45; H, 4.4; S, 9.05. C₁₀H₁₃IO₂S requires C, 37.15; H, 4.2; S, 9.9%).

Phenyl 4-bromobutanesulphinat was prepared in exactly the same way, though in only 23% yield (Found: C, 43.0; H, 4.9; S, 10.55. C₁₀H₁₃BrO₂S requires C, 43.35; H, 4.7; S, 11.55%), and had an almost identical i.r. spectrum; like the iodo-compound, it decomposed on distillation.

Reaction of the Hexafluorophosphate of the Cation (1; R¹ = Me, R² = *p*-tolyl, Ar = *p*-tolyl) with Pyridine.—The salt (211 mg) and dry pyridine (2 cm³) were warmed to 90 °C for 1 h and cooled. Addition of ether (30 cm³) precipitated *N*-methylpyridinium hexafluorophosphate, m.p. 191–197 °C, recognised by its i.r. and n.m.r. spectra which were similar to those of other methylpyridinium salts; washing of the ethereal solution with hydrochloric acid (3 × 20 cm³), sodium hydroxide (3 × 15 cm³), and water, drying, and evaporation left an oil (100 mg, 75%) which was recognised as di-*p*-tolyl sulphite by i.r. and n.m.r. comparison with an authentic specimen.

Measurements of Rates of Hydrolysis.—Tetrafluoroborates of the cations (1; R¹R² = [CH₂]₄, Ar = Ph) and (1; R¹ = R² = Me, Ar = Ph) (6 mg each) were added to phosphate buffer solutions (25 cm³) of pH 7 and 5.8 at 22 °C, and the spectra were repeatedly scanned over the range 230–290 nm until constant. Using the final spectrum as an experimental infinity value, first-order plots were made and slopes estimated graphically, giving rates of 2.3 × 10⁻² s⁻¹ and 9.6 × 10⁻³ s⁻¹ (pH 7) and 2.1 × 10⁻³ and 8.4 × 10⁻⁴ s⁻¹ (pH 5.8). Multiplication by assumed hydroxide-ion concentrations converts these values to 2.3 × 10⁵ and 9.6 × 10⁴ l mol⁻¹ s⁻¹ (pH 7 experiments) and 2.4 × 10⁵ and 9.7 × 10⁴ l mol⁻¹ s⁻¹ (pH 5.8 experiments), respectively. In the same way, the hexafluorophosphate of the cation (1; R¹ = *p*-tolyl, R² = Ar = *p*-tolyl) was examined at 27 °C, using filtered saturated solutions, a range of 230–260 nm, and following optical densities at 245 nm, where the salt has ϵ ca. 20 000, whereas *p*-methylphenol and *p*-tolyl toluene-*p*-sulphonate have $\epsilon = 60$ and 1 200, respectively. In this case, first-order rates were 1.5 × 10⁻⁴ s⁻¹ (pH 7) and 3.2 × 10⁻⁵ s⁻¹ (pH 5.8), giving bimolecular rates of 1.5 × 10³ and 2 × 10³ l mol⁻¹ s⁻¹, respectively.

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