Cytotoxic Compounds. Part XIV.[1] Reactions of the Bismethanesulphonates of 3-Arylthiopropane-1,2-diols and of 2-Arylthiopropane-1,3-diols with Nucleophiles

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The products formed in the title reactions have been examined by ^{1}H n.m.r. spectroscopy. The aryl group was *p*-methoxy-, *p*-methylthio-, *p*-chloro-, or 2,4-dinitro-phenyl, and the ease of cyclisation to an episulphonium ion, as judged by the formation of rearranged products, decreases in that order. Solvolysis in acetic acid gives mainly the 1,2-diacetate in all cases, the result of thermodynamic control (except with the 2,4-dinitro-compounds, where kinetic control obtains). With potassium acetate in acetic anhydride, mixtures of isomeric diacetates are formed in which the proportion of 1,3-compound decreases with increasing electron-withdrawing character of the aryl group, and a similar trend occurs with tetramethylammonium acetate in acetone, though elimination then competes to an increasing extent, becoming the exclusive mode of reaction of the 2,4-dinitro-compounds. With sodium methoxide, elimination is dominant and sometimes is accompanied by allylic rearrangement. All the elimination reactions occur without the intervention of an episulphonium ion. Solvolysis in methanol proceeds under kinetic control and gives mixtures of the 1,2- and 1,3-dimethyl ethers. Sodium phenyl sulphide effects substitution at least very largely by direct S_N2 attack, and this occurs also in the reactions of the two 2,4-dinitro-compounds with lithium bromide, but the other bismethanesulphonates give mixtures of dibromides, formed under thermodynamic control. With sodium azide, substitution occurs both directly and through intermediate episulphonium ions.

The ^{1}H n.m.r. spectra of twenty allyl and vinyl sulphides are reported.

In Part IX,[2] the reactions of various nucleophiles with the alkylating agents 3-phenylthiopropane-1,2-diol bismethanesulphonate (11) and 2-phenylthiopropane-1,3-diol bismethanesulphonate (36) were described. Powerful nucleophiles, such as sodium phenyl sulphide, effected substitution without rearrangement, whereas solvolysis in acetic acid gave only the 1,2-diacetate (1) from both bismethanesulphonates, as a result of thermodynamic control involving an intermediate episulphonium ion (56). With potassium acetate each gave a mixture of diacetates (1) and (26), and with methanol, a mixture of dimethyl ethers (6) and (31), these reactions giving kinetically controlled products. With tetraethylammonium acetate or sodium methoxide, elimination reactions became dominant.

These investigations on the mode of action of alkylating agents related to the 'mustards' have now been extended to a series of bismethanesulphonates in which the phenyl ring contains *p*-methoxy-, *p*-methylthio-, *p*-chloro-, or 2,4-dinitro-substituents. The parent alcohols, their diacetates (2)—(5), (27)—(30), bismethyl ethers (7)—(10), (32)—(35), and the bismethanesulphonates (12)—(15), (38)—(40), have already been described;[3] the bismethanesulphonate (37) of 2-(*p*-methoxyphenylthio)propane-1,3-diol could not be isolated because it readily isomerised to the 1,2-isomer (12). As in the earlier work,[2] ^{1}H n.m.r. spectroscopy was extensively used for the qualitative and quantitative evaluation of products, data for many of the authentic compounds being already available.[3]

Solvolysis of each of the seven bismethanesulphonates in dry acetic acid gave the 1,2-diacetate (2)—(5); from the *p*-methylthio-derivatives (13) and (38) the 1,2-diacetate (3) was in both cases accompanied by *ca.* 20% of the 1,3-isomer (28), but in all the other experiments no 1,3-diacetate could be detected. Identification was based on the characteristic resonances for S·CH_2 (τ *ca.* 6·9) and CH·OAc (τ *ca.* 4·9) in the 1,2-diacetates, and for S·CH (τ *ca.* 6·5) in the 1,3-isomers. Control experiments were carried out in which each of the 1,3-diacetates

ArS·CH_2·CHR(·CH_2R)	ArS·$CH(CH_2R)_2$	Ar	R
(1)	(26)	Ph	OAc
(2)	(27)	*p*-MeO·C_6H_4	OAc
(3)	(28)	*p*-MeS·C_6H_4	OAc
(4)	(29)	*p*-ClC_6H_4	OAc
(5)	(30)	2,4-$(NO_2)_2C_6H_3$	OAc
(6)	(31)	Ph	OMe
(7)	(32)	*p*-MeO·C_6H_4	OMe
(8)	(33)	*p*-MeS·C_6H_4	OMe
(9)	(34)	*p*-ClC_6H_4	OMe
(10)	(35)	2,4-$(NO_2)_2C_6H_3$	OMe
(11)	(36)	Ph	O·SO_2Me
(12)	(37)	*p*-MeO·C_6H_4	O·SO_2Me
(13)	(38)	*p*-MeS·C_6H_4	O·SO_2Me
(14)	(39)	*p*-ClC_6H_4	O·SO_2Me
(15)	(40)	2,4-$(NO_2)_2C_6H_3$	O·SO_2Me
(16)	(41)	*p*-MeO·C_6H_4	SPh
(17)	(42)	*p*-MeS·C_6H_4	SPh
(18)	(43)	*p*-ClC_6H_4	SPh
(19)	(44)	*p*-MeO·C_6H_4	Br
(20)	(45)	*p*-MeS·C_6H_4	Br
(21)	(46)	*p*-ClC_6H_4	Br
(22)	(47)	2,4-$(NO_2)_2C_6H_3$	Br
(23)	(48)	*p*-MeO·C_6H_4	N_3
(24)	(49)	*p*-MeS·C_6H_4	N_3
(25)	(50)	*p*-ClC_6H_4	N_3

(27)—(30) was heated in acetic acid, in the presence of 2 equiv. of methanesulphonic acid, under the conditions used for solvolysis of the bismethanesulphonates. By such treatment the *p*-methoxy- and the *p*-chloro-compounds were completely converted into the 1,2-diacetates, whereas the *p*-methylthio-compound gave a product with a composition similar to that of two mixtures obtained from the bismethanesulphonates (13) and (38); thermodynamic control is evidently operative, therefore, in the solvolysis of the bismethanesulphonates

[1] Part XIII, M. S. Khan and L. N. Owen, *J. Chem. Soc.* (*C*), 1971, 1448.

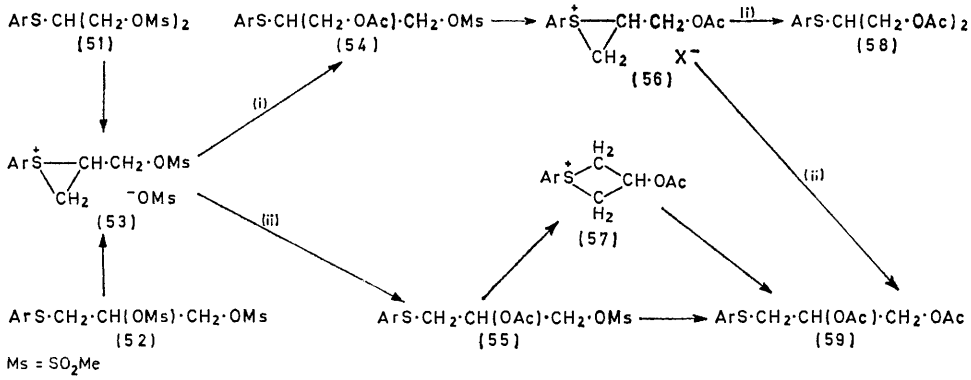
[2] M. V. A. Baig and L. N. Owen, *J. Chem. Soc.* (*C*), 1967, 1400.

[3] M. S. Khan and L. N. Owen, *J. Chem. Soc.* (*C*), 1971, 1442.

(12)—(14), (38), and (39). The 2,4-dinitro-compound (30), however, was unchanged, and it follows that the formation of diacetate (5) from both bismethanesulphonates (15) and (40) must be kinetically controlled. Furthermore, there is obviously no direct displacement involved in the reaction of the 1,3-bismethanesulphonate (40) (otherwise the resulting 1,3-diacetate would be detected), so that it is improbable that there is any in the reaction of the 1,2-isomer (15). Consequently it can be assumed that episulphonium ions are involved, not only with the 2,4-dinitro-compounds but with the other bismethanesulphonates also, since they are even more likely to react through such intermediates.

In general terms, where thermodynamic control exists, the formation of products consisting largely or entirely of the 1,2-diacetate (59) could be due to equilibration of this compound and the 1,3-isomer (58) could well yield the 1,2-diacetate (59) by direct displacement not involving the ion (57), but this does not affect the main point of interest, which concerns the position of attack on the three-membered episulphonium ions. The fact [3] that the 1,3-bismethanesulphonates (51), with the exception of the 2,4-dinitrophenyl compound, readily isomerise to the 1,2-bismethanesulphonates (52) by collapse of the ion pair (53) is also irrelevant to any discussion of the reactions of the ion pair with external nucleophiles; furthermore, the observation [3] that the 1,3-compounds are much more rapidly solvolysed than their 1,2-counterparts shows that such collapse can play no more than a minor part in the overall reactions of the 1,3-bismethanesulphonates.

With potassium acetate in acetic anhydride the *p*-methoxy-derivative (12) gave a mixture of diacetates (2) and (27) containing *ca.* 70% of the latter. Mixtures



(i) Attack at primary position. (ii) Attack at secondary position.

through the common episulphonium ion (56; X = OAc), and distinction between the two pathways from the ion pair (53) cannot be made. With the 2,4-dinitro-compounds, however, the electron-withdrawing character of the aryl group weakens the tendency of the sulphur atom to participate in the expulsion of acetate (a much poorer leaving group than methanesulphonate) to such an extent that the two diacetates are not interconvertible; but although kinetic control is therefore in force the exclusive formation of the 1,2-diacetate could still be possible by either route. If it were formed only *via* monoacetate (54) this would require specific attack at the primary position in the ion (53) and at the secondary position in the ion (56; X = O·SO_2Me), but such a fundamental difference in the behaviour of these two ions is hardly likely. Consequently, the route *via* monoacetate (55), involving attack at the secondary position of ion (53), plays the dominant role in the reactions of the 2,4-dinitro-compounds with acetic acid. This conclusion is in accord with further evidence, presented in the following paper. The tendency to form a four-membered ring (57) by participation of a sulphur atom is much less than that to form a three-membered ring,[4] and the monomethanesulphonate (55) of diacetates were also obtained from the *p*-methylthio-compounds (13) and (38), each of which gave a slight preponderance of the 1,3-isomer (28), and from the *p*-chloro-compounds (14) and (39), which gave equal proportions of the diacetates (4) and (29). These results again show that the reactions proceed through episulphonium intermediates, and since the products under these conditions are kinetically controlled [2] the variation in proportions of the 1,2- and 1,3-diacetates must be a consequence of the electronic effect of the substituents in the aromatic ring. From the episulphonium ion (53) the 1,3-diacetate (58) can only be formed by the upper pathway, and consequently requires attack by the nucleophile at the primary position in both the ions (53) and (56) (to an average extent of over 80% if 70% of that diacetate is formed). The direction of opening is dependent both on steric and polar factors,[5] and the former directs attack to the primary position (reaction of the S_N2 type); but dispersal of charge in an episulphonium ion can confer some degree of carbonium ion character on either of the two carbon atoms in the ring, and if CH_2R is electron-donating by virtue of inductive or hyperconjugative effects the form (76) is

[4] F. G. Bordwell and W. T. Brannen, *J. Amer. Chem. Soc.*, 1964, **86**, 4645.

[5] K. D. Gundermann, *Angew. Chem. Internat. Edn.*, 1963, **2**, 674; N. V. Schwartz, *J. Org. Chem.*, 1968, **33**, 2895; W. H. Mueller, *Angew. Chem. Internat. Edn.*, 1969, **8**, 482.

favoured, resulting in S_N1-type attack by the nucleophile at the secondary position. If the aryl group, attached to the sulphur atom, carries an electron-donating substituent, the dispersal of positive charge towards the ring carbon atoms will be diminished, so that the sterically preferred attack on the primary position becomes more effective, as observed with the *p*-methoxy-compound (12). Conversely, electron-attracting substituents in the aryl group should diminish the proportion of 1,3-product and it would be expected that with potassium acetate the two 2,4-dinitro-compounds (15) and (40) would give mainly the 1,2-diacetate (5); this was true so far as the composition of the saturated acetates was concerned, because no 1,3-compound could be detected, but from each of these bismethanesulphonates the major product (*ca.* 85%) was unsaturated. That from the 1,2-compound (15) was 3-(2,4-dinitrophenylthio)prop-2-enyl acetate (62), whilst the 1,3-compound (40) gave 2-(2,4-dinitrophenylthio)prop-2-enyl acetate (69); these products were identical with those described later.

The reaction of the *p*-methoxy-derivative (12) with tetramethylammonium acetate in acetone gave a mixture of diacetates (2) and (27) (*ca.* 1 : 3), whereas the *p*-methylthio-derivatives (13) and (38) each gave a mixture of diacetates (3 and (28 (*ca.* 1 : 2), the change in proportions showing the same trend as that observed in the reactions with potassium acetate, though the n.m.r. spectra of the products from the *p*-methylthio-compounds showed that small amounts of unsaturated acetates were present, that from the 1,3-bismethanesulphonate being identified from the spectrum as 2-(*p*-methylthiophenylthio)prop-2-enyl acetate (67). The *p*-chloro-compounds gave very little diacetate; the 1,2-bismethanesulphonate (14) afforded 3-(*p*-chlorophenylthio)prop-2-enyl acetate (61), the ^{1}H n.m.r. spectrum of which was similar to that recorded and discussed [2] for the parent compound (60) and showed the presence of both the *cis*- and the *trans*-isomer, whereas the 1,3-bismethanesulphonate (39) gave 2-(*p*-chlorophenylthio)prop-2-enyl acetate (68), the structure of which, evident from the ^{1}H n.m.r. spectrum (see Table), was confirmed by the reaction of the product with 2,4-dinitrophenylhydrazine and sulphuric acid in ethanol to give the 2,4-dinitrophenylosazone of methylglyoxal (*cf.* ref. 2). The 2,4-dinitro-derivatives (15) and (40) with tetramethylammonium acetate gave exclusively the unsaturated compounds (62) and (69), identified by their ^{1}H n.m.r. spectra.

$ArS{\cdot}CH{:}CH{\cdot}CH_2R$

	Ar	R
(60)	Ph	OAc
(61)	*p*-ClC_6H_4	OAc
(62)	2,4-$(NO_2)_2C_6H_3$	OAc
(63)	Ph	OMe
(64)	*p*-$MeS{\cdot}C_6H_4$	OMe
(65)	*p*-ClC_6H_4	OMe
(66)	2,4-$(NO_2)_2C_6H_3$	OMe

$ArS{\cdot}C(:CH_2){\cdot}CH_2R$

	Ar	R
(67)	*p*-$MeS{\cdot}C_6H_4$	OAc
(68)	*p*-ClC_6H_4	OAc
(69)	2,4-$(NO_2)_2C_6H_3$	OAc
(70)	*p*-$MeS{\cdot}C_6H_4$	OMe
(71)	*p*-ClC_6H_4	OMe
(72)	2,4-$(NO_2)_2C_6H_3$	OMe

$ArS{\cdot}CH(OMe){\cdot}CH{:}CH_2$

	Ar
(73)	Ph
(74)	*p*-$MeS{\cdot}C_6H_4$
(75)	*p*-ClC_6H_4

Solvolysis of the *p*-methoxy-derivative (12) in methanol gave a mixture of the bismethyl ethers (7) and (32) (*ca.* 4 : 1; estimated from the signal for $S{\cdot}CH_2$ at τ 7·0), but the ^{1}H n.m.r. spectra of the mixtures obtained from the bismethanesulphonates (13), (38), (14), and (39), although indicating that both isomeric bismethyl ethers were formed in each case, were insufficiently resolved for quantitative estimations to be made. It was established that the various bismethyl ethers were not isomerised under the reaction conditions, so that the solvolytic products from the five bismethanesulphonates were the result of kinetic control. In the 2,4-dinitro-series the 1,2-compound (15) showed low reactivity: even after prolonged treatment it was largely unchanged. The 1,3-compound (40) reacted slowly to give mainly the 1,3-bismethyl ether (35) (*ca.* 70%), in marked contrast to the solvolysis in acetic acid, which had given solely the 1,2-diacetate. It seems that in methanol the tendency for the dinitro-compound to form the episulphonium ion is so low that solvolysis occurs largely without such intervention, though participation by the sulphur atom may still play a limited role in assisting the first step of the S_N1 process.

The reaction of the *p*-methoxy-derivative (12) with sodium methoxide in methanol gave a mixture of the bismethyl ethers (7) and (32) (*ca.* 1 : 2), a striking difference from the result of solvolysis in methanol, and attributable to the more strongly nucleophilic methoxide anion, which favours the S_N2 type of attack on the primary position of the episulphonium ions. With this reagent, however, the other six bismethanesulphonates were converted mainly or entirely into unsaturated products. The 1,3-compounds behaved in a manner similar to that in their reactions with tetramethylammonium acetate and gave the 2-arylthio-3-methoxypropenes (70)—(72), as shown by their ^{1}H n.m.r. spectra (see Table), though the 2,4-dinitro-compound (40) also underwent some nucleophilic attack on the ring to give 2,4-dinitroanisole, a type of displacement not without precedent.[6] The constitution of the *p*-chloro-compound (71) was confirmed also by the formation of methylglyoxal 2,4-dinitrophenylosazone on treatment with 2,4-dinitrophenylhydrazine reagent. Of the 1,2-bismethanesulphonates, the 2,4-dinitro-compound (15) likewise behaved as it had done towards tetramethylammonium acetate and gave 1-(2,4-dinitrophenylthio)-3-methoxypropene (66) (some 2,4-dinitroanisole was also formed), but the ^{1}H n.m.r. spectra of the products obtained from the bismethanesulphonates (13) and (14) were not consistent with structures analogous to (66) and resembled the spectrum of the unsaturated product obtained earlier [2] from the reaction of the unsubstituted bismethanesulphonate (11) with sodium methoxide, and not hitherto identified. These products, though showing weak resonances in the n.m.r. spectra corresponding to the normal compounds (63)—(65), consist mainly of the allylically rearranged materials (73)—(75).

[6] N. Kharasch and R. Swidler, *J. Org. Chem.*, 1954, **19**, 1704.

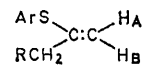
The resonances (see Table), if the effect of the methoxy-group is taken into account, were generally similar to those of some allyl aryl sulphides which were synthesised by reaction of allyl bromide with several arenethiols. The signals for H_A and H_B overlapped, but decoupling experiments at 100 Hz on allyl phenyl sulphide and allyl *p*-methoxyphenyl sulphide revealed the coupling constants J_{AC} and J_{BC} and readily allowed the identification of the individual resonances due to H_A and H_B. Since couplings of similar magnitudes could be detected in the spectra of the other sulphides in sections (iii) and (iv) of the Table (with the exception of the 2,4-dinitrophenyl compounds), the individual chemical shifts for H_A and H_B were thereby determined.

Several important features are revealed in the formation of the unsaturated acetates and unsaturated methyl ethers. The fact that constitutionally different products were obtained from the 1,2- and the 1,3-bismethanesulphonates demonstrates that the elimination reactions do not proceed through an episulphonium intermediate, and are therefore likely to be of the *E*2 rather than the *E*1 type; this is supported by the occurrence of elimination with sodium methoxide and not with methanol. The striking differences between the behaviour towards potassium acetate in acetic anhydride and that towards tetramethylammonium acetate in acetone requires further investigation, but is probably a solvent effect, whereby the formation of the episulphonium ion (leading to substitution) is more favoured in acetic anhydride. The increasing tendency for elimination to occur as the substituents in the aryl ring become more electron-attracting is an evident consequence of the resulting increase in the acidity of the methine or methylene protons next to the sulphur atom. A strong base (methoxide) favours *E*2 elimination, leading to the allylic methanesulphonates (77) and (79), and the rearranged methyl ethers (73)—(75) thus arise through the mesomeric allylic carbonium ion (78) (there being no obvious factor likely to promote the S_N2' mechanism);

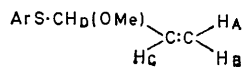
N.m.r. data (τ values; solutions in $CDCl_3$; J in Hz)

(i) $ArS{\cdot}CH_A{:}CH_B{\cdot}CH_2R$

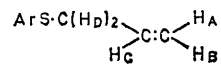
Ar	R	H_A	H_B	CH_2 (*cis*)	CH_2 (*trans*)
Ph (ref. 2)	OAc	3·63 (m)	4·18 (m)	5·32 (d)	5·50 (d)
p-ClC_6H_4	OAc	3·62 (m)	4·13 (m)	5·25 (d)	5·42 (d)
2,4-$(NO_2)_2C_6H_3$	OAc	3·54 (m)		5·20 (m)	
2,4-$(NO_2)_2C_6H_3$	OMe	3·40br (s)		5·80 (d)	

(ii) 

Ar	R	H_A	H_B	CH_2	OMe
Ph (ref. 2)	OAc	4·56 (t)	4·81 (s)	5·48 (d)	
p-$MeS{\cdot}C_6H_4$	OAc	4·50 (t)	4·75 (s)	5·38 (d)	
p-ClC_6H_4	OAc	4·48 (t)	4·72 (s)	5·40 (s)	
2,4-$(NO_2)_2C_6H_3$	OAc	3·70 (t)	3·85 (t)	5·28 (t)	
Ph (ref. 2)	OMe	4·55 (m)	4·88 (s)	6·15 (t)	6·75 (s)
p-$MeS{\cdot}C_6H_4$	OMe	4·53 (t)	4·89 (s)	6·00 (d)	6·65 (s)
p-ClC_6H_4	OMe	4·52 (t)	4·86br (s)	6·06 (d)	6·67 (s)
2,4-$(NO_2)_2C_6H_3$	OMe	3·65 (t)	3·91 (t)	5·97 (t)	6·57 (s)

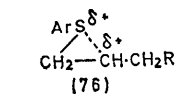
(iii) 

Ar	H_A	H_B	H_C	H_D	OMe	J_{AC}	J_{BC}	J_{CD}
Ph	4·88 (m)	5·01 (m)	4·20 (m)	6·14 (m)	6·52 (s)	16	10	6
p-$MeS{\cdot}C_6H_4$	4·81 (m)	4·93 (m)	4·25 (m)	6·05 (m)	6·50 (s)	16	11	6
p-ClC_6H_4	4·84 (m)	4·95 (m)	4·22 (m)	6·05 (m)	6·51 (s)	16	10	5·5

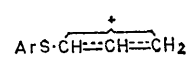
(iv) 

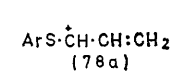
Ar	H_A	H_B	H_C	CH_2	J_{AC}	J_{BC}	J_{CD}
Ph	4·87 (m)	4·95 (m)	4·22 (m)	6·54 (d) *	17	10	7
p-$MeO{\cdot}C_6H_4$	5·08 (m)	5·05 (m)	4·20 (m)	6·66 (d) *	17	9	7
p-$MeS{\cdot}C_6H_4$	4·90 (m)	4·94 (m)	4·10 (m)	6·50 (d) *	17	9·5	6·5
p-ClC_6H_4	4·96 (m)	4·99 (m)	4·16 (m)	6·52 (d) *	17	10	6·5
2,4-$(NO_2)_2C_6H_3$	4·3—4·8 (m)		*ca.* 4 (m)	6·25 (d)			

* With additional fine structure due to long-range coupling (J_{AD} and J_{BD} 0·5—1·0 Hz).


(76)

$ArS{\cdot}CH{:}CH{\cdot}CH_2{\cdot}O{\cdot}SO_2Me$
(77)


(78)


(78a)

$ArS{\cdot}C(:CH_2){\cdot}CH_2{\cdot}O{\cdot}SO_2Me$
(79)

this preferential nucleophilic attack at the secondary position suggests a major contribution from the canonical form (78a), which is possibly favoured by electron donation from sulphur.* The absence of rearrangement in the formation of the 2,4-dinitro-compound (66) could be explained by reversal of this effect by the electron attraction of the aryl function or by the incursion of direct S_N2 displacement on the intermediate (77). Further reactions of the intermediate (79) with methoxide could also occur with allylic rearrangement, but in this system it cannot be recognised.

The unrearranged acetates (60)—(62) could also be derived through the allylic intermediate (77), but although the course of substitution reactions on allylic halides depends to some extent on the solvent and on the nature of the nucleophile [8] it seems unlikely that this can be the explanation for the difference between the acetates and the methyl ethers. More probably, with the weaker base (acetate ion), substitution of the primary group in the 1,2-bismethanesulphonates occurs first, and is followed by elimination.

With sodium phenyl sulphide in methanol the *p*-methoxy-compound (12) gave a solid, the ^{1}H n.m.r. spectrum of which showed only a sharp singlet for the five aliphatic protons, a feature previously noted [2] with the unsubstituted analogue, 1,2,3-trisphenylthiopropane. Oxidation of the trisulphide gave a trisulphone, but the n.m.r. spectrum of this, although showing some resolution of the aliphatic protons, was still of no diagnostic value, and the constitution of the product is therefore uncertain, though it is very probably the 1,2-bisphenylthio-compound (16). Sharp five-proton singlets were also present in the spectra of the four sulphides similarly obtained from the bismethanesulphonates (13), (14), (38), and (39); again the spectra of the corresponding sulphones were uninformative, but the m.p.s were all different and it can be concluded that the displacement reactions occurred at least very largely by direct S_N2 attack, as previously established [2] for the reactions of the bismethanesulphonates (11) and (36) with sodium benzyl sulphide. The products can therefore be allocated the structures (17), (18), (42), and (43). The reactions of the 2,4-dinitro-derivatives (15) and (40) towards benzenethiolate were not examined because of the probable occurrence of side reactions involving reduction of the nitro-group.

Lithium bromide in acetone reacted with the *p*-methoxy-compound (12) to give a mixture of the dibromides (19) and (44) (*ca.* 9 : 1; estimated from the SCH_2 quartet at τ 6·62). A mixture of bromides (20) and (45), of similar composition, was obtained both from the 1,2- (13) and from the 1,3-bismethanesulphonate (38) in the *p*-methylthio-series; the two *p*-chloro-compounds (14) and (39) likewise gave identical products in which the two dibromides (21) and (46) were present in a ratio of *ca.* 6 : 1. Although authentic compounds were not available for comparison, the 1,2-dibromide in these mixtures was readily detected and estimated from the characteristic $S{\cdot}CH_2$ quartet at *ca.* τ 6·6. Thermodynamic control is clearly involved in these reactions, and is promoted by the good leaving group character of bromide ion. In contrast, but in conformity with their reluctance to form episulphonium intermediates, the two dinitro-compounds (15) and (40) gave individual dibromides, which therefore must be (22) and (47) respectively, though because of overlapping resonances the $S{\cdot}CH_2$ quartet could not be identified in the spectrum of (22).

The *p*-methoxy-compound (12) reacted with sodium azide in dimethylformamide to give a mixture (*ca.* 1 : 1) of diazides (23) and (48). The *p*-methylthio-compound (13) gave a mixture (*ca.* 2 : 1) of diazides (24) and (49), whereas from the 1,3-isomer (38) the proportions were *ca.* 1 : 1. The *p*-chloro-compound (14) gave almost entirely the 1,2-diazide (25) whereas the 1,3-isomer (39) gave both azides (25) and (50) in about equal amounts. These estimates were again based on the $S{\cdot}CH_2$ signal, at *ca.* τ 7·0. The proportions of the various azides formed demonstrate that even with the strongly nucleophilic azide ion an episulphonium intermediate is involved, but this cannot be the only pathway; the different compositions of the products obtained from an isomeric pair of bismethanesulphonates (where both were available) indicates that the nucleophile is able to some extent to effect direct S_N2 substitution. The possibility cannot be excluded that the presence of a 1,2-compound in the product from the reaction of a 1,3-bismethanesulphonate might be due to S_N2 substitution on the rearranged methanesulphonate, but the formation of a 1,3-diazide from a 1,2-bismethanesulphonate certainly involves attack by azide on an episulphonium ion, since the 1,2 $\rightleftharpoons$ 1,3 equilibrium for the bismethanesulphonates is essentially entirely in favour of the 1,2-isomer.[3]

When the 2,4-dinitro-compounds (15) and (40) were treated with sodium azide the only recognisable product in both cases was 2,4-dinitroaniline. This is probably formed by nucleophilic attack on the aromatic ring to give 2,4-dinitrophenyl azide, which is then reduced by the liberated thiol.

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded for solutions in deuteriochloroform on a Varian A-60 (Mrs. A. I. Boston) or HA-100 instrument (Mr. P. Jenkins). The methanesulphonates were freshly prepared by the methods previously described.[3] For each nucleophile, one experiment is described in detail;

* There is evidence that electron release can occur from a divalent sulphur atom, though there is disagreement about both its extent and the theoretical justification for invoking such a donation.[7]

[7] F. A. Carey and J. R. Neergard, *J. Org. Chem.*, 1971, **36**, 2731; *cf.* C. C. Price and S. Oae, 'Sulfur Bonding,' Ronald Press, New York, 1964; R. L. Autrey and P. W. Scullard, *J. Amer. Chem. Soc.*, 1968, **90**, 4924.

[8] P. B. D. de la Mare, in 'Molecular Rearrangements,' ed. P. de Mayo, Interscience, New York, 1963, Part 1, p. 27ff.; R. H. DeWolfe and W. G. Young, in 'The Chemistry of Alkenes,' ed. S. Patai, Interscience, New York, 1964, p. 681ff.; P. B. D. de la Mare and C. A. Vernon, in 'Studies on Chemical Structure and Reactivity,' ed. J. H. Ridd, Methuen, London, 1966, p. 11ff.

unless otherwise stated, the same conditions were used for the reactions of the other methanesulphonates with the same nucleophile, and in such cases the experiments are not recorded, unless there is a special reason for so doing. Products were identified mainly from their n.m.r. spectra, but these are recorded only if not already discussed here or previously tabulated for authentic compounds.[3] Petroleum refers to the fraction b.p. 40—60°. Organic extracts were dried over magnesium sulphate. I.r. spectra were measured for solutions in carbon tetrachloride.

Tetramethylammonium Acetate.—By a procedure similar to that described for the tetraethyl compound,[9] an aqueous 25% solution (25 ml) of tetramethylammonium hydroxide was exactly neutralised with acetic acid and evaporated to dryness under reduced pressure. A solution of the residue in dry acetone was cooled (acetone–carbon dioxide), and when no further crystallisation occurred the mother liquor was decanted. The crystals were quickly washed with dry ether and immediately transferred to a vacuum desiccator, where they were dried (P_2O_5) to give the acetate (8·4 g). The compound is very hygroscopic but is stable in a dry atmosphere.

Reactions of 3-Arylthiopropane-1,2-diyl Bismethanesulphonates.—(a) *With acetic acid.* (i) A solution of 3-(*p*-methoxyphenylthio)propane-1,2-diyl bismethanesulphonate (12) (0·5 g) in acetic acid (40 ml) and acetic anhydride (1·5 ml) was boiled gently under reflux for 7 h, then cooled, diluted with water (125 ml), and extracted with benzene. The extract was washed thrice with 2N-sodium hydroxide, then with water, dried, and evaporated to an oil. Distillation afforded 3-(*p*-methoxyphenylthio)propane-1,2-diyl diacetate (2) (0·3 g), b.p. 130° at 10^{-5} mmHg, n_D^{24} 1·5258.

(ii) The 2,4-dinitro-compound (15) (0·6 g) gave the 1,2-diacetate (5) (0·4 g), m.p. 114° (from benzene–petroleum) (lit.,[3] 115°).

(b) *With potassium acetate.* The *p*-methoxy-compound (12) (0·5 g) and anhydrous potassium acetate (3·0 g) in acetic anhydride (25 ml) were heated together at 100° for 5 h. The cooled mixture was stirred with water until the anhydride was destroyed and then extracted with benzene. The extract was washed and dried as before and evaporated to an oil, which on distillation gave a mixture (0·3 g) of 1,2- and 1,3-diacetates (2) and (27) (3 : 7), b.p. 160° at 10^{-4} mmHg, n_D^{26} 1·5256.

(c) *With tetramethylammonium acetate.* (i) A mixture of the *p*-methoxy-compound (12) (0·7 g) and tetramethylammonium acetate (2·0 g) in dry acetone (40 ml) was boiled under reflux for 6 h and then concentrated. The residue was extracted with benzene, and the extract was washed with water, then dried and evaporated to afford a mixture (0·4 g) of the 1,2- and 1,3-diacetates (2) and (27) (1 : 3).

(ii) The 2,4-dinitro-compound (15) (0·6 g) gave a solid, which on recrystallisation from benzene–petroleum afforded 3-(2,4-*dinitrophenylthio*)*prop*-2-*enyl acetate* (62) (0·25 g), m.p. 72° (Found: C, 44·6; H, 3·6; N, 9·5; S, 11·2. $C_{11}H_{10}N_2O_6S_2$ requires C, 44·3; H, 3·4; N, 9·4; S, 10·75%).

(d) *With methanol.* (i) A solution of the *p*-methoxy-compound (12) (0·5 g) in methanol (40 ml) was boiled under reflux for 12 h, then concentrated, diluted with water, and extracted with benzene. The extract was washed twice with aqueous sodium hydrogen carbonate and with water, and then dried and evaporated. Distillation afforded a mixture (0·2 g) of the 1,2- and 1,3-bismethyl ethers (7) and (32) (4 : 1), b.p. 108° at 10^{-5} mmHg, n_D^{20} 1·5430.

(ii) The 2,4-dinitro-compound (15) (0·5 g) was dissolved in pure chloroform (30 ml). Methanol (40 ml) was added, and the solution was boiled under reflux for 60 h. The solution was then concentrated, diluted with water, and extracted with chloroform. The extract was washed with water, then dried and evaporated. The residue (0·3 g) was mainly the bismethanesulphonate (15), with *ca.* 20% of methyl ethers.

(e) *With sodium methoxide.* (i) When the reaction of sodium (0·1 g) with dry methanol (25 ml) was complete, the *p*-methoxy-compound (12) (0·7 g) was added, and the solution was boiled under reflux for 5 h, then concentrated, diluted with water, and extracted with benzene. The extract was washed with water, then dried and evaporated to yield a mixture (0·3 g) of the 1,2- and 1,3-bismethyl ethers (7) and (32) (1 : 2), b.p. 108° at 10^{-5} mmHg, n_D^{20} 1·5430.

(ii) The 2,4-dinitro-compound (15) (0·5 g), at ambient temperature for 15 h, gave a mixture (0·22 g) of 2,4-dinitroanisole, the 1,2-bismethyl ether (10), and 1-(2,4-*dinitrophenylthio*)-3-*methoxypropene* (66). The unsaturated compound was separated by preparative plate chromatography on silica (development with dichloromethane) and when recrystallised from benzene–petroleum had m.p. 70—72° (Found: C, 44·3; H, 4·0; N, 10·1; S, 11·8. $C_{10}H_{10}N_2O_5S$ requires C, 44·4; H, 3·7; N, 10·4; S, 11·9%).

(f) *With sodium phenyl sulphide.* (i) Benzenethiol (4·0 g) was added to a solution prepared from sodium (0·6 g) and methanol (30 ml), followed by the *p*-methoxy-compound (12) (1·4 g). The mixture was boiled under reflux, in an atmosphere of nitrogen, for 4 h, then concentrated and extracted with benzene. The extract was washed twice with 2N-sodium hydroxide, then with water, and dried. Evaporation gave 1-(p-*methoxyphenylthio*)-2,3-*bisphenylthiopropane* (16) (0·8 g), m.p. 80° (from methanol), τ 6·82 (s, 5H), and 6·26 (s, 3H, OMe) (Found: C, 66·5; H, 5·6; S, 24·1. $C_{22}H_{22}OS_3$ requires C, 66·3; H, 5·6; S, 24·1%).

30% Hydrogen peroxide (3·5 ml) was added to a solution of this trisulphide (0·2 g) in acetic acid (3 ml), and the mixture was heated on a steam-bath for 1 h, then cooled. The solid was collected and afforded the *trisulphone* (0·2 g), m.p. 177° (from acetone–petroleum) (Found: C, 53·2; H, 4·7; S, 19·2. $C_{22}H_{22}O_7S_3$ requires C, 53·4; H, 4·5; S, 19·45%).

(ii) The *p*-methylthio-compound (13) (1·0 g) gave 1-(p-*methylthiophenylthio*)-2,3-*bisphenylthiopropane* (17) (0·7 g) as an oil, τ 6·75 (s, 5H) and 7·55 (s, 3H, SMe) (Found: C, 63·45; H, 5·6; S, 31·4. $C_{22}H_{22}S_4$ requires C, 63·7; H, 5·35; S, 30·9%). The *tetrasulphone* had m.p. 212° (from acetone–petroleum) (Found: C, 48·9; H, 4·2; S, 23·3. $C_{22}H_{22}O_8S_4$ requires C, 48·7; H, 4·1; S, 23·6%).

(iii) The *p*-chloro-compound (14) (1·2 g) gave 1-(p-*chlorophenylthio*)-2,3-*bisphenylthiopropane* (18) (0·7 g), b.p. 180° at 10^{-5} mmHg, n_D^{25} 1·6546, τ 6·79 (s, 5H) (Found: C, 62·7; H, 4·9; S, 23·9. $C_{21}H_{19}ClS_3$ requires C, 62·6; H, 4·75; S, 23·9%). The oil solidified after several weeks, and had m.p. *ca.* 45°. The *trisulphone* had m.p. 196—197° (from acetone–petroleum) (Found: C, 50·4; H, 4·0; S, 19·1. $C_{21}H_{19}ClO_6S_3$ requires C, 50·5; H, 3·8; S, 19·3%).

A similar reaction of the *p*-chloro-compound (14) (0·8 g) with a reagent prepared from 2,4-dinitrobenzenethiol (1·2 g) gave 1-(p-*chlorophenylthio*)-2,3-*bis*-2,4-*dinitrophenylthiopropane* (0·9 g), m.p. 75—76° (from chloroform–petroleum),

[9] J. Steigmann and L. P. Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 2536.

τ 6·37br (s, 5H) (Found: C, 43·5; H, 2·8; N, 9·75; S, 16·6. $C_{21}H_{15}ClN_4O_8S_3$ requires C, 43·25; H, 2·6; N, 9·6; S, 16·5%).

(g) *With lithium bromide.* (i) A solution of the *p*-methoxy-compound (12) (0·6 g) and lithium bromide (4·0 g) in acetone (30 ml) was boiled under reflux for 6 h, then concentrated, diluted with water, and extracted with benzene. The extract was washed with water, dried, and evaporated to give a mixture (0·4 g) of the dibromides (19) and (44) (9 : 1), b.p. 132° at 10^{-5} mmHg, n_D^{24} 1·6050, τ 6·62 (q, 1·8H, SCH_2), 5·6—6·4 (m, 3·2H), and 6·22 (s, 3H, OMe) (Found: C, 36·9; H, 3·9; Br, 46·1. Calc. for $C_{10}H_{12}Br_2OS$: C, 35·3; H, 3·6; Br, 47·0%).

(ii) The *p*-methylthio-compound (13) (1·0 g) gave a mixture (0·7 g) of the dibromides (20) and (45) (9 : 1), τ 6·51 (q, 1·8H, SCH_2), 5·6—6·3 (m, 3·2H), and 7·55 (s, 3H, SMe) (Found: C, 34·7; H, 3·6; Br, 42·25. Calc. for $C_{10}H_{12}Br_2S_2$: C, 33·7; H, 3·4; Br, 44·9%). Purification by distillation could not be effected because of decomposition.

(iii) The *p*-chloro-compound (14) (1·0 g) gave a mixture (0·8 g) of the dibromides (21) and (46) (6 : 1), b.p. 124° at 10^{-5} mmHg, n_D^{23} 1·6279, τ 6·54 (q, 1·7H, SCH_2) and 5·7—6·4 (m, 3·3H) (Found: C, 32·1; H, 2·7; S, 9·3. Calc. for $C_9H_9Br_2ClS$: C, 31·4; H, 2·6; S, 9·3%).

(iv) The 2,4-dinitro-compound (15) (1·0 g), after reaction for 24 h, gave 1,2-*dibromo*-3-(2,4-*dinitrophenylthio*)*propane* (22) (0·8 g), m.p. 62° [from petroleum (b.p. 100—120°)], τ 5·6 (m, 1H, CHBr) and 5·8—6·5 m (4H, CH_2Br and SCH_2) (Found: C, 27·8; H, 2·5; Br, 38·2; N, 7·3. $C_9H_8Br_2N_2O_4S$ requires C, 27·0; H, 2·0; Br, 39·9; N, 7·0%).

(h) *With sodium azide.* (i) A solution of the *p*-methoxy-compound (12) (0·7 g) and sodium azide (3·0 g) in dimethylformamide (30 ml) was maintained at 60° for 6 h, then concentrated under reduced pressure and diluted with benzene. After being washed five times with water, the dried solution was evaporated to give a mixture (0·4 g) of the diazides (23) and (48) (1 : 1), b.p. 140° at 10^{-3} mmHg, n_D^{21} 1·5796, $\nu_{max.}$ 2140 cm^{-1} (azide), τ 7·05 (m, 1H, SCH_2), 6·4—6·9 (m, 4H), and 6·22 (s, 3H, OMe) (Found: C, 45·5; H, 4·7; N, 31·9; S, 12·4. Calc. for $C_{10}H_{12}N_6OS$: C, 45·4; H, 4·6; N, 31·8; S, 12·1%).

(ii) The *p*-methylthio-compound (13) (0·8 g) gave a mixture (0·4 g) of the diazides (24) and (49) (2 : 1), b.p. 180° at 10^{-5} mmHg, $\nu_{max.}$ 2150 cm^{-1}, τ 6·93 (m, 1·3H, SCH_2), 6·3—6·7 (m, 3·7H), and 7·55 (s, 3H, SMe) (Found: C, 43·0; H, 4·4; N, 29·8; S, 23·2. Calc. for $C_{10}H_{12}N_6S_2$: C, 42·8; H, 4·3; N, 30·0; S, 22·9%).

(iii) The *p*-chloro-compound (14) (1·1 g) gave a product (0·4 g) which consisted almost entirely of 1,2-*diazido*-3-(*p*-*chlorophenylthio*)*propane* (25), which could be distilled with slight decomposition and had b.p. 126° at 10^{-4} mmHg, n_D^{21} 1·5949, $\nu_{max.}$ 2140 cm^{-1}, τ 6·95 (m, 2H, SCH_2) and 6·4—6·7 (m, 3H) (Found: C, 41·0; H, 3·6; N, 30·2; S, 11·75. $C_9H_9ClN_6S$ requires C, 40·2; H, 3·4; N, 31·3; S, 11·9%). The aromatic region of the n.m.r. spectrum indicated [3] the presence of a very small amount of the 1,3-isomer.

(iv) The 2,4-dinitro-compound (15), after reaction for 12 h, gave a brown mass which contained no azide (i.r. spectrum). Preparative-plate chromatography (silica; chloroform) furnished 2,4-dinitroaniline, m.p. 176° (Found: C, 39·4; H, 2·6; N, 23·0. Calc. for $C_6H_5N_3O_4$: C, 39·4; H, 2·75; N, 22·95%).

Reactions of 2-*Arylthiopropane*-1,3-*diyl Bismethanesulphonates.*—(a) *With acetic acid.* The 2,4-dinitro-compound (40) (0·8 g) gave the 1,2-diacetate (5) (0·6 g), m.p. 115° (from benzene–petroleum).

(b) *With potassium acetate.* The 2,4-dinitro-compound (40) (0·8 g) gave a mixture (0·4 g) containing the 1,2-diacetate (5) (20%) and 2-(2,4-*dinitrophenylthio*)*prop*-2-*enyl acetate* (69) (70%). The unsaturated acetate was separated by preparative-plate chromatography (silica; dichloromethane) and the solid (0·23 g), after recrystallisation from methanol, had m.p. 73° (Found: C, 44·65; H, 3·65; N, 9·6; S, 10·9. $C_{11}H_{10}N_2O_6S_2$ requires C, 44·3; H, 3·4; N, 9·4; S, 10·75%).

(c) *With tetramethylammonium acetate.* (i) The *p*-chloro-compound (39) (1·0 g) gave an oil (0·7 g) which was mainly 2-(*p*-chlorophenylthio)prop-2-enyl acetate (68). A portion (0·2 g) was boiled under reflux for 4 h with 2,4-dinitrophenylhydrazine (0·5 g), sulphuric acid (1·5 g), and ethanol (7 ml), to give a red solid, which was collected and washed with boiling ethanol. Crystallisation from acetic acid gave methylglyoxal bis-2,4-dinitrophenylhydrazone, m.p. 299° (*cf.* ref. 2).

(ii) The 2,4-dinitro-compound (40) (0·8 g) gave 2-(2,4-dinitrophenylthio)prop-2-enyl acetate (69) (0·35 g), m.p. 73° (from methanol).

(d) *With methanol.* The 2,4-dinitro-compound (40) (0·4 g), after reaction for 60 h, gave a product (0·2 g) which contained the 1,2- and 1,3-bismethyl ethers (10) and (35) (20 and 70%, respectively) and a small amount of unchanged or partly reacted methanesulphonate.

(e) *With sodium methoxide.* (i) The *p*-chloro-compound (39) (0·6 g) gave a mixture (0·3 g) of 3-methoxy-2-(*p*-chlorophenylthio)propene (71) (*ca.* 80%) and the 1,2- and 1,3-bismethyl ethers (9) and (34). Treatment of a portion (0·12 g) with 2,4-dinitrophenylhydrazine (0·4 g) and sulphuric acid (1·0 g) in boiling ethanol (6 ml) for 4 h gave methylglyoxal bis-2,4-dinitrophenylhydrazone, m.p. 301° (from acetic acid).

(ii) The 2,4-dinitro-compound (40) (0·6 g) at ambient temperature for 15 h gave a mixture (0·3 g) of 2,4-dinitroanisole and 3-*methoxy*-2-(2,4-*dinitrophenylthio*)*propene* (72). The unsaturated compound was isolated by chromatography (silica; dichloromethane) and recrystallised from petroleum (b.p. 80—100°); it had m.p. 92° (Found: C, 44·4; H, 3·9; N, 10·4; S, 11·8; $C_{10}H_{10}N_2O_5S$ requires C, 44·4; H, 3·7; N, 10·4; S, 11·9%).

(f) *With sodium phenyl sulphide.* (i) The *p*-methylthio-compound (38) (0·9 g) gave 2-(p-*methylthiophenylthio*)-1,3-*bisphenylthiopropane* (42) (0·7 g) as an oil, τ 6·75 (s, 5H) and 7·55 (s, 3H, SMe) (Found: C, 63·9; H, 5·25; S, 31·0. $C_{22}H_{22}S_4$ requires C, 63·7; H, 5·35; S, 30·9%). The *tetrasulphone*, crystallised from acetone–petroleum (b.p. 60—80°), had m.p. 230° (Found: C, 48·55; H, 4·2; S, 23·6. $C_{22}H_{22}O_8S_4$ requires C, 48·7; H, 4·1; S, 23·6%).

(ii) The *p*-chloro-compound (39) (0·5 g) afforded 2-(*p*-*chlorophenylthio*)-1,3-*bisphenylthiopropane* (43) (0·4 g), b.p. 190° at 10^{-5} mmHg, n_D^{23} 1·6494, τ 6·79 (s, 5H) (Found: C, 62·4; H, 4·8; S, 23·3. $C_{21}H_{19}ClS_3$ requires C, 62·6; H, 4·75; S, 23·9%). The oil slowly solidified and had m.p. *ca.* 43°. The *trisulphone*, crystallised from methanol, had m.p. 183° (Found: C, 50·4; H, 3·7; S, 19·05. $C_{21}H_{19}ClO_6S_3$ requires C, 50·5; H, 3·8; S, 19·3%).

(g) *With lithium bromide.* (i) The *p*-methylthio-compound (38) (0·6 g) gave a mixture (0·5 g) of the dibromides (20) and (45) (9 : 1), τ 6·52 (q, 1·8H, SCH_2), 5·6—6·3 (3·2H), and 7·55 (s, 3H, SMe).

(ii) The *p*-chloro-compound (39) (0·6 g) gave a mixture

(0·4 g) of the dibromides (21) and (46) (6 : 1), b.p. 122° at 10^{-5} mmHg, τ 6·55 (q, 1·7H, SCH_2), and 5·7—6·3 (m, 3·3H).

(iii) The 2,4-dinitro-compound (40) (1·0 g), after reaction for 16 h, afforded *1,3-dibromo-2-(2,4-dinitrophenylthio)propane* (47) (0·8 g), m.p. 107—108° (from benzene–petroleum), τ 6·08 (d, 4H, CH_2) and 6·67 (m, 1H, SCH) (Found: C, 27·6; H, 2·2; Br, 39·6; N, 7·15. $C_9H_8Br_2N_2O_4S$ requires C, 27·0; H, 2·0; Br, 39·9; N, 7·0%).

(h) *With sodium azide.* (i) The *p*-methylthio-compound (38) (0·6 g) gave a mixture (0·3 g) of the diazides (24) and (49) (1 : 1), $\nu_{max.}$ 2150 cm^{-1}, τ 6·93 (d, 1H, SCH_2), 6·25—6·75 (m, 4H), and 7·55 (s, 3H, SMe) (Found: C, 42·9; H, 4·6; N, 29·9; S, 22·8. Calc. for $C_{10}H_{12}N_6S_2$: C, 42·8; H, 4·3; N, 30·0; S, 22·9%).

(ii) The *p*-chloro-compound (39) (0·6 g) gave a mixture (0·3 g) of the diazides (25) and (50) (1 : 1), b.p. 130° at 10^{-4} mmHg, n_D^{22} 1·5913, $\nu_{max.}$ ($CHCl_3$) 2130 cm^{-1}, τ 6·95 (d, 1H, SCH_2) and 6·4—6·65 (m, 4H) (Found: C, 40·3; H, 3·55; N, 31·0; S, 12·3. Calc. for $C_9H_9ClN_6S$: C, 40·2; H, 3·4; N, 31·3; S, 11·9%).

(iii) The 2,4-dinitro-compound (40) (0·8 g) gave 2,4-dinitroaniline (0·23 g), m.p. 176°, as the only recognised product.

Control Experiments.—(a) *On acetates.* Typically a mixture of 2-(*p*-methoxyphenylthio)propane-1,3-diyl diacetate (27) (110 mg), methanesulphonic acid (70 mg), acetic anhydride (0·5 ml), and acetic acid (15 ml) was boiled gently under reflux for 7 h, and then worked up as described for the solvolysis of the bismethanesulphonate (12) to give the 1,2-diacetate (2) (98 mg).

[10] C. M. Suter and H. L. Hansen, *J. Amer. Chem. Soc.*, 1932, **54**, 4100; *cf.* G. W. Perold and P. F. A. van Lingen, *Chem. Ber.*, 1959, **92**, 293.

(b) *On methyl ethers.* Typically, 1,2-dimethoxy-3-(*p*-methoxyphenylthio)propane (7) (560 mg), methanesulphonic acid (190 mg), and methanol (40 ml) were boiled together under reflux for 12 h. The solution was worked up as described for the solvolysis of the bismethanesulphonate (12) to give unchanged 1,2-bismethyl ether (480 mg), b.p. 112° at 10^{-3} mmHg, n_D^{22} 1·5348.

Allyl Aryl Sulphides.—(i) *p*-Methoxybenzenethiol [10] (3·4 g) and allyl bromide (3·0 g) were added to a solution prepared from sodium (0·7 g) and ethanol (30 ml), and the mixture was set aside overnight and then concentrated. Benzene and water were added to the residue, and the organic layer was washed with 2N-sodium hydroxide, then dried and distilled to give *allyl* p-*anisyl sulphide* (3·8 g), b.p. 85—86° at 0·7 mmHg, n_D^{21} 1·5706 (Found: C, 66·4; H, 6·7; S, 17·9. $C_{10}H_{14}OS$ requires C, 66·6; H, 6·7; S, 17·8%).

(ii) A similar reaction with *p*-(methylthio)benzenethiol [11] (1·0 g), allyl bromide (1·2 g), sodium (0·2 g), and ethanol (30 ml) gave *allyl* p-(*methylthio*)*phenyl sulphide* (1·2 g), b.p. 98° at 10^{-4} mmHg, n_D^{24} 1·6240 (Found: C, 61·4; H, 6·0; S, 32·75. $C_{10}H_{12}S_2$ requires C, 61·2; H, 6·2; S, 32·7%).

(iii) *p*-Chlorobenzenethiol (2·0 g), allyl bromide (1·8 g), sodium (0·3 g), and ethanol (30 ml) gave *allyl* p-*chlorophenyl sulphide* (2·4 g), b.p. 70° at 0·4 mmHg, n_D^{21} 1·5860 (Found: C, 58·5; H, 5·0; S, 17·4. C_9H_9ClS requires C, 58·5; H, 4·9; S, 17·4%).

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[11] M. Protiva, M. Rajšner, E. Alderová, V. Seidlová, and J. Vejdělek, *Coll. Czech. Chem. Comm.*, 1964, **29**, 2161; *cf.* A. Burawoy, J. P. Critchley, and A. R. Thompson, *Tetrahedron*, 1958, **4**, 403.