Cytotoxic Compounds. Part XV.[1] Reactions of the Methanesulphonates of 1-Arylthiopropan-2-ols and of 2-(2,4-Dinitrophenylthio)propan-1-ol with Nucleophiles

By **M. S. Khan** and **L. N. Owen,*** Department of Chemistry, Imperial College, London S.W.7

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, or phenyl, and the formation of an episulphonium intermediate is favoured by electron-donation from the aromatic ring. Solvolysis in acetic acid gives mainly the secondary acetates, the products (except those from the 2,4-dinitro-compounds) being thermodynamically controlled. With potassium acetate in acetic anhydride, approximately equal proportions of primary and secondary acetates are formed, except from the secondary 2,4-dinitro-compound, which gives 50% of 1-(2,4-dinitrophenylthio)propene. With tetramethylammonium acetate and with sodium methoxide, both 2,4-dinitro-compounds give vinyl sulphides, the other methanesulphonates yielding only mixtures of acetates or methyl ethers; the elimination reactions do not involve an intermediate episulphonium ion. Solvolysis in methanol gives mainly or entirely the secondary methyl ether, under kinetic control from the 2,4-dinitro-compounds but under varying degrees of thermodynamic control from the other methanesulphonates. An episulphonium intermediate is involved in the reactions of all the methanesulphonates with lithium bromide and with sodium azide, and in the reaction of the *p*-methoxy-compound with sodium phenyl sulphide, mixtures of bromides, azides, or sulphides being obtained; but the *p*-methylthio- and the *p*-chloro-compounds react with sodium phenyl sulphide by direct substitution, to give single products.

An earlier Paper[2] described syntheses of 2-phenylthiopropan-1-ol and 1-phenylthiopropan-2-ol, and of other pairs of isomers in which the phenyl ring carried *p*-methoxy-, *p*-methylthio-, *p*-chloro-, or 2,4-dinitro-substituents. Each alcohol gave the corresponding acetate and methyl ether, but 2-(2,4-dinitrophenylthio)-propan-1-ol was the only primary alcohol in the series to give an unrearranged methanesulphonate (18); the

---

[1] Part XIV, M. S. Khan and L. N. Owen, preceding paper.

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

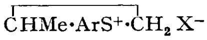
other four all gave methanesulphonates identical with the derivatives of the corresponding secondary alcohols. In spite of this limitation it was nevertheless of interest to examine the behaviour of the six methanesulphonates (6)—(10) and (18) towards a variety of nucleophiles, by the methods previously used[1,3] for bismethanesulphonates of types (1) and (3). The situation is simplified with the monomethanesulphonates because there is only one intermediate episulphonium cation [*cf.* (5)] to consider.

$\mathrm{ArS{\cdot}CH_2{\cdot}CHR{\cdot}CH_2R}$

(1) $\mathrm{R = O{\cdot}SO_2Me}$
(2) $\mathrm{R = OMe}$

$\mathrm{ArS{\cdot}CH(CH_2R)_2}$

(3) $\mathrm{R = O{\cdot}SO_2Me}$
(4) $\mathrm{R = OMe}$

(5) 
$\mathrm{\overline{CHMe{\cdot}ArS^{+}{\cdot}CH_2}\ X^-}$

$\mathrm{ArS{\cdot}CH_2{\cdot}CHRMe}$

	Ar	R
(6)	Ph	$\mathrm{O{\cdot}SO_2Me}$
(7)	*p*-$\mathrm{MeO{\cdot}C_6H_4}$	$\mathrm{O{\cdot}SO_2Me}$
(8)	*p*-$\mathrm{MeS{\cdot}C_6H_4}$	$\mathrm{O{\cdot}SO_2Me}$
(9)	*p*-$\mathrm{ClC_6H_4}$	$\mathrm{O{\cdot}SO_2Me}$
(10)	2,4-$\mathrm{(NO_2)_2C_6H_3}$	$\mathrm{O{\cdot}SO_2Me}$
(11)	2,4-$\mathrm{(NO_2)_2C_6H_3}$	OAc
(12)	2,4-$\mathrm{(NO_2)_2C_6H_3}$	OMe
(13)	2,4-$\mathrm{(NO_2)_2C_6H_3}$	Br
(14)	2,4-$\mathrm{(NO_2)_2C_6H_3}$	$\mathrm{N_3}$
(15)	*p*-$\mathrm{MeO{\cdot}C_6H_4}$	SPh
(16)	*p*-$\mathrm{MeS{\cdot}C_6H_4}$	SPh
(17)	*p*-$\mathrm{ClC_6H_4}$	SPh

$\mathrm{ArS{\cdot}CHMe{\cdot}CH_2R}$

	Ar	R
(18)	2,4-$\mathrm{(NO_2)_2C_6H_3}$	$\mathrm{O{\cdot}SO_2Me}$
(19)	2,4-$\mathrm{(NO_2)_2C_6H_3}$	OAc
(20)	2,4-$\mathrm{(NO_2)_2C_6H_3}$	OMe
(21)	2,4-$\mathrm{(NO_2)_2C_6H_3}$	Br
(22)	2,4-$\mathrm{(NO_2)_2C_6H_3}$	$\mathrm{N_3}$
(23)	Ph	OMe
(24)	*p*-$\mathrm{MeO{\cdot}C_6H_4}$	OMe
(25)	*p*-$\mathrm{MeS{\cdot}C_6H_4}$	OMe
(26)	*p*-$\mathrm{ClC_6H_4}$	OMe
(27)	Ph	SPh
(28)	*p*-$\mathrm{MeO{\cdot}C_6H_4}$	SPh

2,4-$\mathrm{(NO_2)_2C_6H_3{\cdot}S{\cdot}CMe{:}CH_2}$
(29)

2,4-$\mathrm{(NO_2)_2C_6H_3{\cdot}S{\cdot}CH{:}CHMe}$
(30)

Solvolysis of each of the six compounds in acetic acid gave a mixture of primary and secondary acetates, *ca.* 1 : 9 in each instance, assessed from the ^{1}H n.m.r. spectra. Control experiments, in which the individual synthetic acetates[2] were treated with acetic acid containing 1 equiv. of methanesulphonic acid, established that thermodynamic control was operative in all cases except for those of the two dinitro-compounds; during the standard time of heating, 2-(2,4-dinitrophenylthio)propyl acetate was isomerised only to the extent of about 10%, a further illustration of the effect of electron withdrawal in retarding formation of the necessary episulphonium ion.[1] The production of 90% of secondary acetate by solvolysis of the primary methanesulphonate (18) must therefore be the result of kinetic control and indicative of preferential attack by the nucleophile at the secondary position of the cyclic ion (5), which is formed much more readily from the methanesulphonate than from the acetate. The position of attack can be rationalised on the basis of delocalisation of positive charge from the sulphur atom on to the secondary ring-carbon atom, as discussed previously.[1]

Mixtures of acetates were also formed when the six methanesulphonates were treated with potassium acetate in acetic anhydride, but with one exception the amount of primary ester in the products was now 40—50%; an increased proportion of the sterically controlled attack at the primary position under these experimental conditions had also been observed with the bismethanesulphonates.[1] The dinitro-compound (10), however, gave 40% of secondary acetate (11), 10% of primary acetate (19), and 50% of 1-(2,4-dinitrophenylthio)propene (30), identified from the n.m.r. spectrum. This olefinic product (probably a *cis–trans* mixture; see later) must be formed by direct elimination, not involving the episulphonium ion, otherwise it should also have been formed from the isomeric methanesulphonate (18); the latter, however, formed no unsaturated product, and gave only a mixture of the two acetates (11) and (19).

Very similar behaviour was shown by the four methanesulphonates (6)—(9) towards tetramethylammonium acetate in acetone, the products consisting of approximately equal proportions of primary and secondary acetates. The primary 2,4-dinitro-compound (18), however, gave about 40% of an unsaturated product which was separated by chromatography and identified as 2-(2,4-dinitrophenylthio)propene (29) from its n.m.r. spectrum, which showed a 3-proton singlet at τ 7·95 (Me) and two 1-proton singlets at τ 4·20 and 4·26 ($\mathrm{{:}CH_2}$). The remaining 60% of the product was a mixture of the acetates (11) and (19) (*ca.* 1 : 3). The secondary 2,4-dinitro-compound (10) gave only unsaturated material, the n.m.r. spectrum showing it to consist of a mixture of *cis*- and *trans*-1-(2,4-dinitrophenylthio)propene (30) (methyl doublets at τ 7·96 and τ 8·02). One stereoisomer was separated by fractional crystallisation and showed one methyl doublet at τ 7·96; the m.p. indicated that it was identical with the compound described by Mannich and Fresenius.[4] The formation of constitutionally different unsaturated products from the two methanesulphonates (10) and (18) again shows that an episulphonium ion is not involved in the elimination reactions. As noted with the reactions of the bismethanesulphonates,[1] elimination occurs to a greater extent with tetramethylammonium acetate in acetone than with potassium acetate in acetic anhydride.

Solvolysis of the two 2,4-dinitro-compounds (10) and (18) in dry methanol gave exclusively the secondary methyl ether (12) in each case. A control experiment established that the primary methyl ether (20) was not isomerised under these conditions; consequently, selective nucleophilic attack on the secondary position in the episulphonium ion is again operative. Solvolysis of the other four methanesulphonates (6)—(9) gave products containing 85—90% of the appropriate secondary methyl ether, but in these cases thermodynamic control may have played some part, though a variable one, since under the same experimental conditions the primary methyl ethers (23)—(26) were isomerised to the secondary compounds to the extent of 70, 25, 20, and 15%, respectively. These observations illustrate the progressive decrease in electron donation by sulphur, to form the episulphonium ring, as the nature of the aromatic substituent is changed, but they also reveal an interesting difference from the behaviour of the 1,3-bismethyl ethers (4), none of which underwent isomerisation in acidic methanol.[1] The lability of the

---

[3] M. V. A. Baig and L. N. Owen, *J. Chem. Soc.* (*C*), 1967, 1400.
[4] C. Mannich and P. Fresenius, *Arch. Pharm.*, 1936, **274**, 461.

monomethyl ethers can be attributed to the relatively good electron-donating property of the methyl group (in comparison with the methoxymethyl group), which facilitates electron release by the sulphur atom, as suggested [2] in explanation of the high reactivity of the monomethanesulphonates themselves.

With sodium methoxide in methanol the four methanesulphonates (6)—(9) all gave mixtures of primary and secondary methyl ethers in a ratio of *ca.* 1 : 3. Under similar conditions the secondary 2,4-dinitro-compound (10) underwent attack on the aromatic ring, to give 2,4-dinitroanisole, as observed with the dinitro-compounds of types (1) and (3). Under milder conditions the products formed, identified from the n.m.r. spectrum, were 2,4-dinitroanisole (45%), the secondary methyl ether (12) (10%) and 1-(2,4-dinitrophenylthio)propene (30) (45%). The primary 2,4-dinitro-compound (18), also under the milder conditions, gave 2,4-dinitroanisole (60%), 2-(2,4-dinitrophenylthio)propene (29) (20%), and unchanged methanesulphonate (20%).

With sodium phenyl sulphide the unsubstituted compound (6) afforded the product (27), which in this particular case could be formed either with or without rearrangement. The *p*-methylthio- and the *p*-chloro-compounds (8) and (9) gave single products, each showing a clean methyl doublet in the n.m.r. spectrum; from analogy with the earlier work [1,3] these sulphides are (16) and (17), formed by direct S_N2 substitution. The *p*-methoxy-compound (7), however, gave a mixture which showed two methyl doublets, at τ 8·62 (weak) and 8·65 (strong); the main product is no doubt the secondary sulphide (15), but the electron-donating *p*-methoxy-group allows a small degree of cyclic ion formation, which permits the production of some primary sulphide (28) as a result of sterically controlled attack by the powerful nucleophile. Some of the secondary sulphide may also of course be derived through the episulphonium ion. The 2,4-dinitro-compounds (10) and (18) both gave complex mixtures, probably because of partial reduction by the reagent.

Lithium bromide in acetone reacted with the primary 2,4-dinitro-compound (18) to give a mixture of bromides (13) and (21); the n.m.r. spectrum showed doublets for the methyl group at τ 8·10 (weak) and 8·36 (strong). The secondary isomer (10) also gave a mixture, but the intensities of the methyl doublets were now reversed, showing that the resonance at higher field is due to the primary bromide. The proportions of primary and secondary bromides were 5 : 1 from the primary methanesulphonate and 1 : 5 from the secondary isomer, showing that the reactions had proceeded mainly by direct S_N2 displacement, but to a small extent through the episulphonium ion; thermodynamic control is evidently not significantly involved. The other four methanesulphonates (6)—(9) all gave mixtures of primary and secondary bromides in the ratio of *ca.* 1 : 3 (on the assumption that the methyl doublet at higher field can always be assigned to primary bromide), but, in the absence of the primary methanesulphonates for comparison, no indication can be obtained as to whether any direct displacement occurred; in any event, thermodynamic control was probably dominant.

The behaviour of the methanesulphonates towards sodium azide showed a similar pattern to that observed with lithium bromide. The primary dinitro-compound (18) gave a mixture in which the ratio of primary (22) to secondary azide (14) was 6 : 1, whilst the secondary isomer (10) gave a ratio of 1 : 9, showing that direct substitution was again occurring to a considerable extent. In these products there was no distinction between the methyl resonances, but the S·CH_2 doublet at τ 6·78, weak in the n.m.r. spectrum of the first mixture, strong in that of the second, was used for the assessment. The other four methanesulphonates (6)—(9) gave mixtures all containing *ca.* 70% of secondary azide.

A striking difference between the behaviour of the monomethanesulphonates and the bismethanesulphonates is that all the latter (except the *p*-methoxy-compound) gave unsaturated acetates and methyl ethers in amounts increasing with the electron-attractive character of the aromatic substituent, whereas of the monomethanesulphonates only the 2,4-dinitro-compounds underwent elimination. As shown above, episulphonium ions are formed more readily by the mono- than by the corresponding bis-methanesulphonates; the elimination reactions do not proceed through such intermediates and therefore, being in competition with the cyclisation, occur less readily with the monomethanesulphonates.

EXPERIMENTAL

The methanesulphonates were freshly prepared by the methods previously described.[2] For general experimental notes, see the preceding paper.[1] Where no details are given, conditions were the same as those used previously [1] for reactions with the same nucleophile. The results of many experiments not recorded here are discussed in the text.

Reactions of 1-*Arylthio*-2-*methylsulphonyloxypropanes*.—(a) *With acetic acid*. The 2,4-dinitro-compound (10) (1·0 g) gave a crude product which contained *ca.* 10% of primary acetate, but crystallisation from benzene–petroleum furnished 2-acetoxy-1-(2,4-dinitrophenylthio)propane (0·6 g), m.p. and mixed m.p. 56°.

(b) *With potassium acetate*. See above.

(c) *With tetramethylammonium acetate*. The 2,4-dinitro-compound (10) (1·3 g), after reaction for 2·5 h, gave *cis*- and *trans*-1-(2,4-dinitrophenylthio)propene (30) (0·6 g), m.p. 96°, τ 3·2—4·0 (m, 2H), and 7·96 (d) and 8·02 (d) (3H) (Found: C, 45·3; H, 3·55; N, 11·8; S, 13·6. Calc. for $C_9H_8N_2O_4S$: C, 45·0; H, 3·4; N, 11·7; S, 13·35%). Fractional crystallisation from methanol gave one stereoisomer, m.p. 119° (lit.,[4] 118°), τ 3·2—4·0 (m, 2H) and 7·96 (d, 3H).

(d) *With methanol*. The 2,4-dinitro-compound (10) (1·0 g) gave 2-methoxy-1-(2,4-dinitrophenylthio)propane (12) (0·7 g), m.p. and mixed m.p. 51°.

(e) *With sodium methoxide*. The 2,4-dinitro-compound (10) (0·3 g), treated at ambient temperature for 15 h, gave a mixture (0·2 g) of secondary methyl ether (12) (10%), 1-(2,4-dinitrophenylthio)propene (30) (45%), and 2,4-dinitroanisole (45%), τ 5·88 (s, ArOMe).

(f) *With sodium phenyl sulphide.* (i) Benzenethiol (3·0 g) and 2-methylsulphonyloxy-1-phenylthiopropane (6) (1·0 g) were added to a solution prepared from sodium (0·5 g) and methanol (30 ml). After being kept at 55° under nitrogen for 4 h the mixture was concentrated and extracted with benzene. The extract was washed twice with 2N-sodium hydroxide, then with water, and dried. Evaporation gave a brown oil which was purified by column chromatography on silica, with petroleum as eluant. The first fraction was diphenyl disulphide (1·2 g), m.p. 60°. Distillation of the second fraction gave 1,2-*bisphenylthiopropane* (27) (0·6 g), b.p. 124° at 10^{-4} mmHg, n_D^{19} 1·6210, τ 6·5—7·5 (m, 3H) and 8·58 (d, 3H) (Found: C, 69·3; H, 6·5; S, 24·6. $C_{15}H_{16}S_2$ requires C, 69·2; H, 6·2; S, 24·6%).

(ii) The *p*-methoxy-compound (7) (1·3 g) gave a mixture (0·8 g) of 1-(*p*-methoxyphenylthio)-2-phenylthiopropane (15) and 2-(*p*-methoxyphenylthio)-1-phenylthiopropane (28), b.p. 146° at 10^{-4} mmHg, n_D^{23} 1·6140, τ 6·5—7·5 (m, 3H), 8·62 (d) and 8·65 (d) (3H, CMe), and 6·25 (s, 3H, OMe), b.p. 146° at 10^{-4} mmHg, n_D^{23} 1·6140 (Found: C, 66·15; H, 6·2; S, 22·4. Calc. for $C_{16}H_{18}OS_2$: C, 66·2; H, 6·2; S, 22·1%).

(iii) The *p*-methylthio-compound (8) (0·7 g) gave 2-(p-*methylthiophenylthio*)-1-*phenylthiopropane* (16) (0·5 g), b.p. 166° at 10^{-5} mmHg, n_D^{19} 1·6496, τ 6·5—7·4 (m, 3H), 8·60 (d, 3H, CMe), and 7·54 (s, SMe) (Found: C, 63·3; H, 5·9; S, 31·4. $C_{16}H_{18}S_3$ requires C, 62·7; H, 5·9; S, 31·4%).

(iv) The *p*-chloro-compound (9) (0·9 g) gave 1-(p-*chlorophenylthio*)-2-*phenylthiopropane* (17) (0·8 g), b.p. 143° at 10^{-3} mmHg, n_D^{21} 1·6240, τ 6·5—7·5 (m, 3H) and 8·60 (d, 3H, CMe) (Found: C, 61·45; H, 5·3; S, 22·1. $C_{15}H_{15}ClS_2$ requires C, 61·1; H, 5·1; S, 21·75%).

(g) *With lithium bromide.* (i) 2-Methylsulphonyloxy-1-phenylthiopropane (6) (1·3 g) and lithium bromide (4·0 g) in dry acetone (30 ml) were boiled under reflux for 6 h. The solvent was then evaporated and the residue was extracted with benzene. The extract was washed with water, then dried and distilled to give a mixture (0·9 g) of 2-bromo-1-phenylthiopropane and 1-bromo-2-phenylthiopropane (3 : 1), b.p. 76° at 10^{-2} mmHg, n_D^{20} 1·5883, τ 5·9 (m, 0·8H), 6·7 (m, 2·2H), 8·22 (d, 2·2H), and 8·57 (d, 0·8H) (Found: C, 46·5; H, 5·0; Br, 34·1. Calc. for $C_9H_{11}BrS$: C, 46·8; H, 4·8; Br, 34·6%).

(ii) The *p*-methoxy-compound (7) (0·8 g) gave a mixture (0·6 g) of 2-bromo-1-(*p*-methoxyphenylthio)propane and 1-bromo-2-(*p*-methoxyphenylthio)propane (2 : 1), b.p. 106° at 10^{-5} mmHg, n_D^{22} 1·5821, τ 6·0 (m, 0·5H), 6·7 (m, 2·5H), 8·21 (d, 2H), and 8·62 (d, 1H) (Found: C, 45·9; H, 4·9; Br, 29·1; S, 12·8. Calc. for $C_{10}H_{13}BrOS$: C, 46·0; H, 5·0; Br, 30·0; S, 12·3%).

(iii) The *p*-methylthio-compound (8) (1·0 g) gave a mixture (0·8 g) of 2-bromo-1-(*p*-methylthiophenylthio)propane and 1-bromo-2-(*p*-methylthiophenylthio)propane (3 : 1), b.p. 132° at 10^{-5} mmHg, n_D^{24} 1·6315, τ 5·8 (m, 1H), 6·7 (m, 2H), 8·23 (d, 2·2H), and 8·56 (d, 0·8H) (Found: C, 43·1; H, 4·9; Br, 29·0. $C_{10}H_{13}BrS_2$ requires C, 43·3; H, 4·7; Br, 28·8%).

(iv) The *p*-chloro-compound (9) (0·8 g) gave a mixture (0·6 g) of 2-bromo-1-(*p*-chlorophenylthio)propane and 1-bromo-2-(*p*-chlorophenylthio)propane (3 : 1), b.p. 91° at 10^{-2} mmHg, n_D^{22} 1·5959, τ 6·2 (m, 1H), 6·7 (m, 2H), 8·22 (d, 2·2H), and 8·73 (d, 0·8H) (Found: C, 41·3; H, 4·5; S, 12·7. Calc. for $C_9H_{10}BrClS$: C, 40·7; H, 3·8; S, 12·7%).

(v) The 2,4-dinitro-compound (10) (0·6 g) gave a mixture (0·4 g) of 2-bromo-1-(2,4-dinitrophenylthio)propane (13) and 1-bromo-2-(2,4-dinitrophenylthio)propane (21) (5 : 1), m.p. 83—85° (from benzene–petroleum), τ 5·7 (m, 1H), 6·5 (m, 2H), 8·10 (d, 2·5H), and 8·36 (d, 0·5H) (Found: C, 34·4; H, 3·2; Br, 24·0; N, 8·8. Calc. for $C_9H_9BrN_2O_4S$: C, 33·7; H, 2·8; Br, 24·9; N, 8·7%).

(h) *With sodium azide.* (i) A mixture of 2-methylsulphonyloxy-1-phenylthiopropane (6) (0·9 g), sodium azide (2·5 g), and dimethylformamide (30 ml) was kept at 60° for 6 h, then diluted with water (300 ml) and extracted with benzene. The extract was washed repeatedly with water, then dried and evaporated to give a mixture (0·4 g) of 2-azido-1-phenylthiopropane and 1-azido-2-phenylthiopropane (7 : 3), b.p. 72° at 10^{-4} mmHg, n_D^{19} 1·5672, $\nu_{max.}$ 2140 cm^{-1}, τ 6·2—6·7 (m, 1·6H), 7·02 (dd, 1·4H), and 8·65 (d, 3H) (Found: C, 55·8; H, 5·7; N, 22·0; S, 16·5. Calc. for $C_9H_{11}N_3S$: C, 55·9; H, 5·7; N, 21·7; S, 16·6%).

(ii) The *p*-methoxy-compound (7) (0·8 g) gave a mixture (0·5 g) of 2-azido-1-(*p*-methoxyphenylthio)propane and 1-azido-2-(*p*-methoxyphenylthio)propane (7 : 3), b.p. 96° at 10^{-2} mmHg, n_D^{23} 1·5630, $\nu_{max.}$ 2150 cm^{-1}, τ 6·3—6·9 (m, 1·6H), 7·10 (dd, 1·4H), 8·70 (d, 3H), and 6·23 (s, 3H, OMe) (Found: C, 53·8; H, 5·8; N, 18·9; S, 14·6. Calc. for $C_{10}H_{13}N_3OS$: C, 53·8; H, 5·9; N, 18·8; S, 14·35%).

(iii) The *p*-methylthio-compound (8) (0·7 g) gave a mixture (0·4 g) of 2-azido-1-(*p*-methylthiophenylthio)propane and 1-azido-2-(*p*-methylthiophenylthio)propane (7 : 3), b.p. 119° at 10^{-4} mmHg, n_D^{20} 1·6112, $\nu_{max.}$ 2140 cm^{-1}, τ 6·2—6·8 (m, 1·6H), 7·02 (dd, 1·4H), 8·68 (d, 3H), and 7·52 (s, 3H, SMe) (Found: C, 50·1; H, 5·4; N, 17·7; S, 27·0. Calc. for $C_{10}H_{13}N_3S_3$: C, 50·2; H, 5·5; N, 17·6; S, 26·8%).

(iv) The *p*-chloro-compound (9) (1·0 g) gave a mixture (0·5 g) of 2-azido-1-(*p*-chlorophenylthio)propane and 1-azido-2-(*p*-chlorophenylthio)propane (3 : 2), b.p. 92° at 10^{-3} mmHg, n_D^{20} 1·5795, $\nu_{max.}$ 2150 cm^{-1}, τ 6·2—6·8 (1·8H), 7·03 (dd, 1·2H), and 8·67 (d, 3H) (Found: C, 47·4; H, 4·5; N, 18·6; S, 14·1. Calc. for $C_9H_{10}ClN_3S$: C, 47·5; H, 4·4; N, 18·45; S, 14·1%).

(v) The 2,4-dinitro-compound (10) (0·7 g) gave a mixture (0·4 g) of 2-azido-1-(2,4-dinitrophenylthio)propane (14) and 1-azido-2-(2,4-dinitrophenylthio)propane (22) (9 : 1), m.p. 83° (from benzene–petroleum), $\nu_{max.}$ ($CHCl_3$) 2150 cm^{-1}, τ 5·9—6·3 (m, 1·2H), 6·80 (d, 1·8H), and 8·50 (d, 3H) (Found: C, 38·4; H, 3·5; N, 24·8; S, 11·4. Calc. for $C_9H_9N_5O_4S$: C, 38·1; H, 3·2; N, 24·7; S, 11·3%). A small amount of 2,4-dinitroaniline was isolated from the mother liquors.

Reactions of 2-(2,4-*Dinitrophenylthio*)*propyl Methanesulphonate* (18).—(a) *With acetic acid.* The methanesulphonate (0·9 g) gave a crude product which contained 10% of the primary acetate (19). Recrystallisation from benzene–petroleum gave the pure secondary acetate (11), m.p. and mixed m.p. 57·5°.

(b) *With potassium acetate.* See general notes.

(c) *With tetramethylammonium acetate.* The methanesulphonate (0·45 g) gave a mixture (0·35 g) of secondary acetate (11) (15%), primary acetate (19) (45%), and 2-(2,4-*dinitrophenylthio*)*propene* (29) (40%). The unsaturated compound was separated by preparative-plate chromatography (silica; dichloromethane) and after recrystallisation from methanol had m.p. 80° (Found: C, 45·2; H, 3·4; N, 11·7. $C_9H_8N_2O_4S$ requires C, 45·0; H, 3·4; N, 11·7%); for n.m.r. spectrum, see text.

(d) *With methanol.* The methanesulphonate (0·8 g) gave only the secondary methyl ether (12) (0·5 g), m.p. and mixed m.p. 52°.

(e) *With sodium methoxide.* The reaction of the methanesulphonate (0·35 g) for 15 h at ambient temperature gave a mixture (0·23 g) of 2-(2,4-dinitrophenylthio)propene (29) (20%), 2,4-dinitroanisole (60%), and unchanged methanesulphonate (20%).

(f) *With lithium bromide.* The methanesulphonate (0·5 g) gave a mixture (0·4 g) of 2-bromo-1-(2,4-dinitrophenylthio)-propane (13) and 1-bromo-2-(2,4-dinitrophenylthio)propane (21) (1 : 5), m.p. 105° (from benzene–petroleum), τ 5·8—6·8 (m, 3H), 8·10 (d, 0·5H), and 8·36 (d, 2·5H) (Found: C, 33·9; H, 2·8; Br, 25·3; N, 8·5. Calc. for $C_9H_9BrN_2O_4S$: C, 33·7; H, 2·8; Br, 24·9; N, 8·7%).

(g) *With sodium azide.* The methanesulphonate (0·8 g) gave a mixture (0·5 g) of 2-azido-1-(2,4-dinitrophenylthio)-propane (14) and 1-azido-2-(2,4-dinitrophenylthio)propane (22) (1 : 6), m.p. 53° (from benzene–petroleum), $\nu_{max.}$ 2130 cm^{-1}, τ 6·0—6·6 (m, 2·7H), 6·79 (d, 0·3H), and 8·50 (d, 3H) (Found: C, 38·2; H, 3·5; N, 24·6; S, 11·3. Calc. for $C_9H_9N_5O_4S$: C, 38·1; H, 3·2; N, 24·7; S, 11·3%).

Control Experiments.—These were performed as previously described.[1] For results, see text.

[2/311 *Received*, 11*th February*, 1972]