

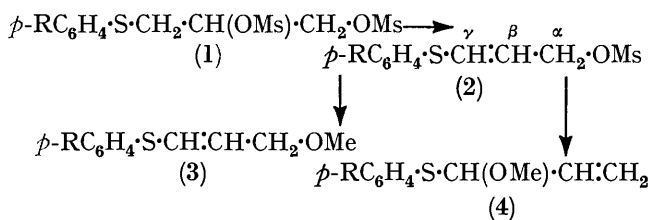
Cytotoxic Compounds. Part XIX.¹ Allylic Rearrangements in the Reactions of 3-(Phenylthio)prop-2-enyl Chloride, 3-(*p*-Nitrophenylthio)prop-2-enyl Methanesulphonate, and 3-(*p*-Nitrophenylthio)prop-2-enyl Chloride with Nucleophiles

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Addition of arenethiols to prop-2-yn-1-ol proceeds in both directions, to give 2- and 3-(arylthio)prop-2-en-1-ols. From the latter, the title compounds were prepared; in their reactions with sodium methoxide, potassium acetate, and tetramethylammonium acetate, mixtures of normal and allylically rearranged products were obtained, the proportions depending on the nature of the reagent and of the leaving group. With sodium azide, only the normal (primary) azide was formed. Solvolysis of the two nitro-compounds in methanol gave a mixture of normal and rearranged ethers, but under the same conditions 3-(phenylthio)prop-2-enyl chloride gave the dimethyl acetal of 3-(phenylthio)propanal.

The ¹H n.m.r. spectra of all the allylic compounds (both *cis*- and *trans*-isomers in most applicable cases) are tabulated.

DURING a study of the reactivities of certain bismethanesulphonates with nucleophiles^{2,3} it was found that the arylthio-compounds (1; R = H, Cl, or MeS), on treatment with sodium methoxide in methanol, gave mainly the 3-arylthio-3-methoxypropenes (4),† with small amounts of the isomers (3). It was assumed that elimination preceded substitution and that these reactions occurred through intermediate allylic methanesulphonates (2), which are also vinyl sulphides, though compounds of this particular type, or the analogous halides, have never been described. This deficiency has now been remedied, and the properties of these compounds have been studied.



The addition of benzenethiol to prop-2-yn-1-ol in the presence of potassium hydroxide has been reported⁴ to give *trans*-3-(phenylthio)allyl alcohol (6), but although quoted analytical figures are acceptable the

† In the Table of n.m.r. data for the olefins (4) in ref. 3 the figures under the headings H_D and J_{CD} were included in error; they refer to resonances due to the CH_2 function in the accompanying isomers (3).

¹ Part XVIII, A. Behzadi and L. N. Owen, *J.C.S. Perkin I*, 1973, 2733.

assignment of configuration was based only on the i.r. spectrum, and there was no proof of homogeneity. We find that, under the conditions described, the product is a 2 : 1 : 1 mixture of the *trans*-alcohol (6), the *cis*-isomer (5), and 2-(phenylthio)allyl alcohol (28). Furthermore, the composition depends upon the amount of base used, and with a much smaller quantity the product, obtained in much better yield, contains no *trans*-alcohol and is a 3 : 2 mixture of the *cis*-alcohol (5) (the expected product of *trans*-addition) and the positional isomer (28), which are readily separable by t.l.c. Partial isomerisation of the *cis*-alcohol into the *trans*-isomer under basic conditions was confirmed by heating it with sodium 2-hydroxyethoxide in ethane-1,2-diol. The pure *trans*-alcohol could not be separated from its stereoisomer, but its characteristic resonances were readily identifiable in the ¹H n.m.r. spectrum of this mixture. The constitution of the 2-phenylthio-compound (28) was confirmed by conversion into its acetate, the n.m.r. spectrum of which was identical with that reported for material obtained in a different way.²

To serve as reference compounds for identification of subsequent reaction products, the *cis*-acetate (7) and the *cis*-methyl ether (9) were prepared from the *cis*-alcohol (5). The mixture of stereoisomeric alcohols

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

³ M. S. Khan and L. N. Owen, *J.C.S. Perkin I*, 1972, 2060.

⁴ A. M. Kuliev, A. A. Dzhafarov, and F. N. Mamedov, *Azerb. khim. Zhur.*, 1967(2), 25 (*Chem. Abs.*, 1968, 68, 29,373).

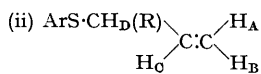
(5) and (6) was also acetylated and methylated, and the chemical shifts for the *trans*-acetate (8) and the *trans*-methyl ether (10) were deduced from the n.m.r. spectra of the mixed acetates and mixed ethers. Compounds in the *cis*- and in the *trans*-series can be clearly differentiated by the mutual coupling constant of the olefinic protons (see Table).

without isolation of the methanesulphonate. The n.m.r. spectrum, recorded for a deuteriochloroform extract, showed the derivative to be essentially pure in dilute solution. Under less mild conditions, reaction of the *cis*-alcohol with methanesulphonyl chloride gave a mixture of the *cis*- (21) and the *trans*-chloride (22). In the preparation of the *cis*-alcohol the

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

(i) $\text{ArS}\cdot\text{CH}_A\cdot\text{CH}_B\cdot\text{CH}_2\text{R}$

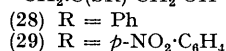
Formula no.	Ar	R	Config.	H_A	H_B	CH_2	CH_3 in R	J_{AB}	J_{BC}
(5)	Ph	OH	<i>cis</i>	3.63d	4.05sx	5.64d		10	6
(6)	Ph	OH	<i>trans</i>	3.51d	4.08sx	5.85d		15	5
(7)	Ph	OAc	<i>cis</i>	3.51d	4.11sx	5.21d	7.92s	9.5	6.5
(8)	Ph	OAc	<i>trans</i>	3.47d	4.17sx	5.40d	7.95s	15	6
(9)	Ph	OMe	<i>cis</i>	3.56d	4.09sx	5.86d	6.63s	10	6
(10)	Ph	OMe	<i>trans</i>	3.48d	4.13sx	6.03d	6.66s	15	6
(11)	Ph	Cl	<i>cis</i>	3.53d	4.1m	5.75d		10	7.5
(12)	Ph	Cl	<i>trans</i>	3.44d	4.18sx	5.92d		15	7
(13)	Ph	N_3	<i>cis</i>	3.49d	4.2m	6.00d		10	7
(14)	Ph	N_3	<i>trans</i>	3.47d	4.26sx	6.20d		15	6
(15)	<i>p</i> - $\text{NO}_2\cdot\text{C}_6\text{H}_4$	OH	<i>cis</i>		3.7m	5.62d			4.5
(16)	<i>p</i> - $\text{NO}_2\cdot\text{C}_6\text{H}_4$	OAc	<i>cis</i>	3.46d	3.85sx	5.20d	7.90s	9.5	6
(17)	<i>p</i> - $\text{NO}_2\cdot\text{C}_6\text{H}_4$	OAc	<i>trans</i>	3.41d	3.84sx	5.30d	7.88s	15	5
(18)	<i>p</i> - $\text{NO}_2\cdot\text{C}_6\text{H}_4$	OMe	<i>cis</i>	3.53d	3.85sx	5.85d	6.62s	9.5	5.5
(19)	<i>p</i> - $\text{NO}_2\cdot\text{C}_6\text{H}_4$	OMe	<i>trans</i>	3.47d	3.9m	5.94d	6.57s	15	4.5
(20)	<i>p</i> - $\text{NO}_2\cdot\text{C}_6\text{H}_4$	$\text{O}\cdot\text{SO}_2\text{Me}$	<i>cis</i>	3.36d	3.82sx	5.07d	6.91s	9.5	5.5
(21)	<i>p</i> - $\text{NO}_2\cdot\text{C}_6\text{H}_4$	Cl	<i>cis</i>	3.45d	3.9m	5.69d		9.5	5.5
(22)	<i>p</i> - $\text{NO}_2\cdot\text{C}_6\text{H}_4$	Cl	<i>trans</i>	3.33d	3.9m	5.80d		15	4.5
(23)	<i>p</i> - $\text{NO}_2\cdot\text{C}_6\text{H}_4$	N_3	<i>cis</i>	3.39d	3.86sx	5.93d		9	6.5



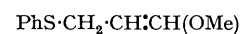
(Resonances for H_D were obscured by those of H_A and H_B ; $J_{AB} < 1$)

Formula no.	Ar	R	H_A	H_B	H_D	CH_3 in R	J_{AC}	J_{BC}	J_{CD}
(24)	Ph	OAc	4.73d*	4.86d*	4.1m	7.93s	17	11	4
(25)	Ph	OMe	4.78dd	4.91dd	4.06oct	6.48s	17	10	4
(26)	<i>p</i> - $\text{NO}_2\cdot\text{C}_6\text{H}_4$	OAc	4.6m		3.98oct	7.85s	21	10	4
(27)	<i>p</i> - $\text{NO}_2\cdot\text{C}_6\text{H}_4$	OMe	4.7m		4.04oct	6.45s	17	10	4

* With additional fine structure.



(30)



(31)



(32)

Allylic methanesulphonates are predictably highly reactive compounds, and attempts to prepare the proposed intermediate (2; R = H) from the alcohol (5) were unsuccessful. However, reaction of the alcohol with methanesulphonyl chloride, in the presence of triethylamine gave a good yield of *trans*-3-(phenylthio)-prop-2-enyl chloride (12).

2,4-Dinitrobenzenethiol gave no recognisable product when heated with prop-2-yn-1-ol and potassium hydroxide, but *p*-nitrobenzenethiol gave a separable mixture (3 : 1) of the *cis*-alcohol (15) and the positional isomer (29). Reference samples of the *cis*-acetate (16) and *cis*-methyl ether (18) were prepared from the *cis*-alcohol, which, unlike the unsubstituted analogue, also gave the *cis*-methanesulphonate (20) as a fairly stable dichloromethane extract. Evaporation of this extract gave an oil which rapidly decomposed, and the substitution reactions described later were performed

trans-isomer was not encountered, though no doubt it could be obtained by base-catalysed isomerisation; consequently, authentic *trans*-acetate (17) and *trans*-methyl ether (19) were not made, and the n.m.r. parameters for these compounds were obtained from the spectra of the products of substitution reactions.

When treated with sodium methoxide in methanol, the *trans*-chloride (12) gave a mixture of the *trans*-methyl ether (10) and, as major product, the rearranged ether (25), which were separated by t.l.c. Comparison of the n.m.r. spectra of these two compounds with the original spectrum of the reaction product obtained² from the bismethanesulphonate (1; R = H) confirmed that the earlier material was a similar mixture, and the proposed intermediacy of the allylic methanesulphonate is substantiated.

From this result it would be expected that solvolysis of the same chloride (12) in methanol would also lead

mainly to the allylically rearranged ether, but the product was saturated and contained two methoxy-groups, which appeared as a sharp six-proton singlet in the n.m.r. spectrum. It was identified as 1,1-dimethoxy-3-(phenylthio)propane (30), and on treatment with 2,4-dinitrophenylhydrazine in acid solution it gave the known⁵ derivative of 3-(phenylthio)propanal. A possible explanation of this result is that the chloride does indeed give a mixture of normal and rearranged ethers, but the former, under the acidic conditions, undergoes prototropy to form the vinyl ether (31) from which the acetal (30) would be readily formed. Equilibration of normal and rearranged ethers would account for the eventual formation of only the acetal. The occurrence of prototropy in certain allylic systems is known⁶ and it appears to be a feature of the present system, because the same 2,4-dinitrophenylhydrazone was formed, though in lower yield, when either of the methyl ethers (10) and (25), or the chloride (12), was treated with acidic 2,4-dinitrophenylhydrazine.

Although rearranged acetates were not encountered in the reaction of the bismethanesulphonates (1) with potassium acetate or tetramethylammonium acetate (presumably because these reagents are less basic than sodium methoxide, and therefore elimination does not precede substitution), it was nevertheless of interest to investigate the reactions of the chloride (12) with these nucleophiles. With potassium acetate in acetic anhydride the product was a mixture (1:2) of the *trans*-acetate (8) and the rearranged acetate (24), whilst with tetramethylammonium acetate in acetone a mixture (5:2) of the same compounds was obtained. This remarkable difference in proportions is in accord with an earlier observation⁷ that, in reaction with 3,5-dibromocyclopentene, tetraethylammonium acetate gives much less allylically rearranged product than potassium acetate; the effect may, at least in part, be attributed to the difference in solvents. The mixtures of acetates (8) and (24), and also the *cis*-acetate (7), on treatment with acidic 2,4-dinitrophenylhydrazine also gave the 2,4-dinitrophenylhydrazone of 3-(phenylthio)propanal, again illustrating the ready occurrence of prototropy.

The allylic chloride (12) reacted with sodium azide to give the *trans*-azide (14), indicating that this powerful nucleophile attacks by a normal S_N2 mechanism. With lithium chloride in acetone, the chloride underwent stereomutation to give a 1:1 mixture of the *cis*- (11) and the *trans*-chloride (12), which with sodium azide gave a similarly composed mixture of the *cis*- (13) and the *trans*-azide (14), confirming that this substitution is purely of the S_N2 type.

cis-3-(*p*-Nitrophenylthio)prop-2-enyl methanesulphon-

ate (20) reacted with sodium methoxide to give a mixture of the *cis*- (18) and the *trans*-methyl ether (19), and the rearranged product (27), separable by t.l.c., in the ratio 1:4 (normal:abnormal). In contrast to the methanolysis of the unsubstituted chloride (12), a similar mixture of methyl ethers (though containing slightly less rearranged compound) was obtained when this methanesulphonate was solvolysed in methanol. No dimethyl acetal was detected, and this absence of prototropy can be explained by the greater electron-withdrawing character of the *p*-nitrophenylthio-group, which would favour regeneration of the βγ-unsaturated structure [cf. (2)] (rather than the prototropically rearranged αβ-unsaturated isomer) from the protonated form (32). This is supported by the result of a control experiment in which the pure *cis*-methyl ether (18) was treated with methanol and methanesulphonic acid, under the conditions of the solvolysis. Partial stereomutation to the *trans*-ether (19) occurred, but the n.m.r. spectrum of the product showed no trace of rearranged ether or of the dimethyl acetal.

With potassium acetate in acetic anhydride the methanesulphonate gave a 1:2 mixture of *trans*-acetate (17) and rearranged acetate (26), whilst with tetramethylammonium acetate in acetone the product was a 3:1 mixture of *cis*-acetate (16) and rearranged acetate (26). The latter reagent again results in strikingly less rearrangement, and the retention of configuration suggests that it is engaged in direct S_N2 attack. Solvolysis of the methanesulphonate in acetic acid gave entirely the *trans*-acetate (17), evidently the consequence of thermodynamic control, because treatment of the mixture obtained in the potassium acetate reaction with acetic acid and methanesulphonic acid resulted in essentially complete isomerisation to the *trans*-acetate (17).

In conformity with the results obtained with the *trans*-chloride (12), the *cis*-methanesulphonate (20) reacted with sodium azide by direct S_N2 displacement to give unrearranged *cis*-azide (23) as the sole product, the configuration being evident from the olefinic coupling constant.

The mixture of *cis*- (21) and *trans*-chloride (22) on reaction with sodium methoxide gave a 1:2 mixture of normal (*cis*- and *trans*-) and rearranged methyl ethers, whilst solvolysis in methanol gave a 1:1 mixture. In both cases, therefore, the proportion of rearranged product is significantly less than was formed in similar reactions on the methanesulphonate, a result which illustrates the importance of the nature of the leaving group on product composition (a factor which has received scant attention in studies on allylic rearrangements). The formation of what is nevertheless a major amount of rearranged ether (in contrast to the usual behaviour of primary allylic chlorides, which react with alkoxides by the S_N2 mechanism to give the

⁵ K. Sirotanovic, M. Bajlon-Rocen, and D. Galovic, *Glasnik Hem. Društva, Beograd*, 1960—1961, **25/26**, 509 (*Chem. Abs.*, 1963, **59**, 8635).

⁶ I. M. Heilbron, E. R. H. Jones, P. Smith, and B. C. L. Weedon, *J. Chem. Soc.*, 1946, 54; P. B. D. de la Mare, in 'Molecular Rearrangements,' ed. P. de Mayo, Interscience, New York, 1963, Part 1, p. 108.

⁷ L. N. Owen and P. N. Smith, *J. Chem. Soc.*, 1952, 4035; cf. J. D. Roberts, W. G. Young, and S. Winstein, *J. Amer. Chem. Soc.*, 1942, **64**, 2157.

normal ethers⁸) suggests that an S_N2' process is operative; this could also provide an explanation for the production of the abnormal product in those other reactions carried out under S_N2 conditions, such as with tetramethylammonium acetate, though in the absence of kinetic evidence the validity of an S_N2' mechanism (the actual existence of which is now the subject of renewed controversy⁹) can only be speculative. It is, however, clear that the greatly varying degrees of rearrangement produced by the different reagents cannot be reconciled with the intervention only of a conventional mesomeric carbonium ion.

In comparable reactions the *p*-nitro-compounds produce a higher proportion of rearranged product than is obtained from the unsubstituted chloride, yet the 2,4-dinitrophenylthio-analogue of the bismethanesulphonate (1), on reaction with sodium methoxide,³ gave only the normal methyl ether corresponding to (3). Possibly, in the intermediate allylic system the 2-nitro-group shields the γ -carbon atom from anionic attack; alternatively the more powerful electron-attracting character of the dinitrophenyl group may polarise the allylic double bond sufficiently to induce a partial negative charge on the γ -carbon atom and render it immune to such attack, a suggestion similar to that put forward¹⁰ to explain the production only of normal products from displacement reactions on 3-trifluoromethylprop-2-enyl *p*-bromobenzenesulphonate.

EXPERIMENTAL

¹H N.m.r. spectra were recorded for solutions in deuteriochloroform on a Varian A-60 or HA-100 instrument, and reaction products were mainly identified, qualitatively and quantitatively, from these spectra. Routine recordings of i.r. spectra were made, but the absorptions, which were unexceptional, are not cited. Petroleum refers to the fraction of b.p. 40–60°. Kieselgel GF₂₅₄ (Merck) was used for t.l.c. The allylic compounds were unstable at ambient temperature and were stored at 0°.

2- and 3-(Phenylthio)prop-2-en-1-ol.—Benzenethiol (20 g) was added dropwise to a stirred mixture of prop-2-yn-1-ol (12 g) and powdered potassium hydroxide (0.4 g) at 125°. After 2 h, the mixture was cooled and extracted with ethyl acetate, and the extract was washed with 2N-sodium hydroxide and with water, then dried and distilled to give an oil (26 g), b.p. 90–110° at 0.2 mmHg, which was a 2:3 mixture of the 2- and the 3-(phenylthio)-compound. Preparative t.l.c. (ether–petroleum, 1:1) gave, as the faster-running fraction, 2-(phenylthio)prop-2-en-1-ol, n_D^{18} 1.5940, τ 2.4–2.8 (5H, m, aromatic), 4.38 (1H, t, J 1.2 Hz), 4.76 (1H, t, J 1.0 Hz), 5.78br (2H, s), and 7.38br (1H, s, OH) (Found: C, 64.8; H, 6.0; S, 19.1. $C_9H_{10}OS$ requires C, 65.0; H, 6.1; S, 19.3%). The acetate (acetic anhydride–pyridine), purified by preparative t.l.c. (benzene), had n_D^{19} 1.5517, τ 2.4–2.8 (5H, m, aromatic), 4.47 (1H, t, J 1.2 Hz), 4.69 (1H, s), 5.36 (2H, s), and 7.94 (3H, s) (Found: C, 63.2; H, 5.9; S, 15.2. $C_{11}H_{12}O_2S$ requires C, 63.4; H, 5.8; S, 15.4%).

⁸ R. H. DeWolfe and W. G. Young, in 'The Chemistry of Alkenes,' ed. S. Patai, Interscience, New York, 1964, p. 691.

⁹ F. G. Bordwell and T. G. Mecca, *J. Amer. Chem. Soc.*, 1972, **94**, 5829.

The second fraction from the mixture of alcohols was *cis*-3-(phenylthio)prop-2-en-1-ol, n_D^{17} 1.6058 (Found: C, 64.7; H, 6.0; S, 19.1%). It gave the acetate, n_D^{19} 1.5664 (Found: C, 63.3; H, 5.85; S, 15.5%), and the methyl ether (dimethyl sulphate–potassium hydroxide¹) (Found: C, 66.8; H, 6.8; S, 17.7. $C_{10}H_{12}OS$ requires C, 66.6; H, 6.7; S, 17.8%), both of which were purified by t.l.c. (benzene).

When the reaction with prop-2-yn-1-ol was done with a larger amount of potassium hydroxide (2 g), a considerable proportion of *trans*-alcohol was formed (see text).

Isomerisation of *cis*-3-(Phenylthio)prop-2-en-1-ol.—The *cis*-alcohol (0.20 g) was added to ethylene glycol (20 ml) with which sodium (0.20 g) had reacted, and the mixture was heated at 125° for 2 h, then cooled, diluted with water, and extracted with ethyl acetate to give a mixture (0.18 g) of the *cis*- and the *trans*-alcohol (3:2).

trans-3-(Phenylthio)prop-2-enyl Chloride.—A solution of the *cis*-alcohol (0.15 g) and triethylamine (0.14 g) in dichloromethane (20 ml) was added dropwise to a stirred solution of methanesulphonyl chloride (0.12 g) in dichloromethane (10 ml) at 7–8°. After a further 3 h at this temperature the mixture was quickly washed with cold solutions of 2N-hydrochloric acid and sodium hydrogen carbonate, then with water, and was dried and evaporated to give the *trans*-chloride (0.15 g), n_D^{15} 1.6085 (Found: C, 58.55; H, 5.1. C_9H_9ClS requires C, 58.5; H, 4.9%).

2- and 3-(*p*-Nitrophenylthio)prop-2-en-1-ol.—Reaction of *p*-nitrobenzenethiol¹¹ (15.5 g) with prop-2-yn-1-ol (7.5 g) and powdered potassium hydroxide (0.25 g) at 130° for 4 h, as described for benzenethiol, gave a black oil (14 g) which was separated by t.l.c. (benzene–ethyl acetate, 1:3) into 2-(*p*-nitrophenylthio)prop-2-en-1-ol (first fraction, 2.4 g), m.p. 39–42° (from ether–petroleum), τ 1.89 (2H, d, aromatic), 2.57 (2H, d, aromatic), 4.20 (1H, t, J 1.5 Hz), 4.29 (1H, t, J 1.2 Hz), 5.81br (2H, s), and 7.10br (1H, s, OH) (Found: C, 51.0; H, 4.3; N, 6.6; S, 15.0. $C_8H_9NO_3S$ requires C, 51.2; H, 4.3; N, 6.6; S, 15.2%). and *cis*-3-(*p*-nitrophenylthio)prop-2-en-1-ol (second fraction, 7.0 g), m.p. 60–67° (from ether–petroleum) (Found: C, 51.05; H, 4.4; N, 6.5; S, 15.4%).

The latter alcohol gave the *cis*-acetate, m.p. 59–60° (Found: C, 52.0; H, 4.3; N, 5.5; S, 12.6. $C_{11}H_{11}NO_4S$ requires C, 52.2; H, 4.4; N, 5.5; S, 12.7%), and the *cis*-methyl ether, an oil (Found: C, 53.1; H, 4.9; N, 6.3; S, 14.2. $C_{10}H_{11}NO_3S$ requires C, 53.3; H, 4.9; N, 6.2; S, 14.2%).

cis-3-(*p*-Nitrophenylthio)prop-2-enyl Methanesulphonate.—A solution of methanesulphonyl chloride (0.25 g) in dichloromethane (10 ml) was added dropwise to a stirred solution of the *cis*-alcohol (0.42 g) and triethylamine (0.3 g) in dichloromethane (25 ml) at 0°. After a further 1 h at 0°, the mixture was quickly washed with cooled 2N-hydrochloric acid, and with water, and dried. Evaporation at 0° gave a yellow oil which became black within 2 min, and in subsequent preparations the solution was concentrated at 0° to ca. 4 ml, and used immediately for substitution reactions.

3-(*p*-Nitrophenylthio)prop-2-enyl Chloride.—The *cis*-alcohol (0.42 g) was treated as in the preceding experiment, but the mixture was left at ambient temperature for 20 h.

¹⁰ J. A. Pegolotti and W. G. Young, *J. Amer. Chem. Soc.*, 1961, **83**, 3258.

¹¹ C. C. Price and G. W. Stacy, *J. Amer. Chem. Soc.*, 1946, **68**, 498.

Evaporation of the washed and dried solution gave a 1 : 1 mixture (0.40 g) of the *cis*- and the *trans*-chloride, m.p. 85—94° (Found: C, 47.3; H, 3.6; N, 6.1; Cl, 15.1. $C_9H_8ClNO_2S$ requires C, 47.1; H, 3.5; N, 6.1; Cl, 15.4%).

Reactions of trans-3-(Phenylthio)prop-2-enyl Chloride.—The freshly prepared chloride was allowed to react for 2 days at ambient temperature. The mixture was then diluted with water and extracted with ethyl acetate. The extract was washed with aqueous sodium hydrogen carbonate (if acidic) and with water, and was then dried and evaporated.

(i) The chloride (0.7 g) was added to a solution prepared from sodium (0.15 g) and methanol (30 ml). The product was separated by t.l.c. (benzene) into 3-phenylthio-3-methoxypropene (25) (first fraction, 0.32 g) (Found: C, 66.4; H, 6.7; S, 17.9. $C_{10}H_{12}OS$ requires C, 66.6; H, 6.7; S, 17.8%) and *trans*-1-phenylthio-3-methoxypropene (10) (second fraction, 0.12 g) (Found: C, 66.9; H, 6.7; S, 17.7%).

(ii) The chloride (0.4 g) in methanol (20 ml) gave 1,1-dimethoxy-3-(phenylthio)propane (30) (0.28 g), purified by t.l.c. (benzene), τ 2.5—2.8 (5H, m, aromatic), 5.48 (1H, t, H-1), 6.66 (6H, s, OMe), 7.02 (2H, t, H-3), and 7.9—8.3 (2H, m, H-2) (Found: C, 62.2; H, 7.4; S, 15.3. $C_{11}H_{16}O_2S$ requires C, 62.2; H, 7.6; S, 15.1%).

(iii) The chloride (0.4 g) with potassium acetate (0.3 g) in acetic anhydride (25 ml) gave a 1 : 2 mixture (0.3 g) of *trans*-3-(phenylthio)prop-2-enyl acetate (8) (Found: C, 63.15; H, 5.8; S, 16.0. $C_{11}H_{12}O_2S$ requires C, 63.4; H, 5.8; S, 15.4%) and 1-(phenylthio)prop-2-enyl acetate (24). The former was isolated by t.l.c. (benzene), but the latter decomposed.

(iv) The chloride (0.4 g) and tetramethylammonium acetate (0.4 g) in acetone (30 ml) gave a 5 : 2 mixture (0.3 g) of the same acetates (8) and (24).

(v) The chloride (0.45 g) and sodium azide (0.4 g) in dimethylformamide (30 ml) gave *trans*-3-azido-1-phenylthiopropene (14) (0.38 g), n_D^{17} 1.6008, purified by t.l.c. (benzene) (Found: C, 56.6; H, 4.7; N, 21.6; S, 17.0. $C_9H_9N_3S$ requires C, 56.5; H, 4.7; N, 22.0; S, 16.8%).

(vi) The chloride (0.4 g) and lithium chloride (0.3 g) in acetone (25 ml), but at 0°, gave a 1 : 1 mixture (0.3 g) of the *cis*- and the *trans*-chloride, which with sodium azide (0.3 g) under standard conditions gave a 1 : 1 mixture (0.27 g) of the *cis*- and the *trans*-azide.

(vii) The chloride (0.1 g) was added to a saturated solution of hydrogen chloride in dichloromethane (10 ml) to give (probably) 1,3-dichloro-1-(phenylthio)propane (80 mg), τ 2.2—2.8 (5H, m, aromatic), 4.52 (1H, t), 6.23 (2H, t), and 7.54 (2H, q).

3-(Phenylthio)propanal 2,4-Dinitrophenylhydrazone.—(i) 1,1-Dimethoxy-3-(phenylthio)propane (0.13 g) was added to a solution of 2,4-dinitrophenylhydrazine (0.3 g) and sulphuric acid (1.8 g) in ethanol (7 ml). The mixture was stirred at 40° for 5 h, and the yellow solid was collected, washed with ethanol, and recrystallised from chloroform-petroleum to give the dinitrophenylhydrazone (0.15 g), m.p. 126—127° (lit.,⁵ m.p. 126°).

(ii) *cis*-3-(Phenylthio)prop-2-enyl acetate (0.15 g), similarly gave the same derivative (0.14 g), m.p. 122—126°.

(iii) The mixture of acetates (0.4 g) obtained from the potassium acetate reaction gave the derivative (0.11 g), m.p. 125—127°, after purification by t.l.c. (chloroform).

(iv) *trans*-3-Methoxy-1-phenylthiopropene (0.1 g), 3-methoxy-3-phenylthiopropene (0.36 g), and *trans*-3-(phenylthio)prop-2-enyl chloride (0.2 g), individually gave, after purification by t.l.c., the derivative (55 mg, 0.22 g, 0.1 g), m.p.s 126—128, 126—128, and 124—128°, respectively.

Reactions of trans-3-(p-Nitrophenylthio)prop-2-enyl Methanesulphonate.—Procedures were the same as described for *trans*-3-(phenylthio)prop-2-enyl chloride, except that the time of reaction was 1 day. Freshly prepared solutions of the methanesulphonate in dichloromethane (*ca.* 4 ml) were used.

(i) The methanesulphonate (*ca.* 0.65 g) was added to a solution prepared from sodium (0.15 g) and methanol (30 ml), to give a mixture of 3-methoxy-3-(p-nitrophenylthio)propene (27) (0.4 g) (Found: C, 53.2; H, 4.7; N, 6.1; S, 14.7. $C_{10}H_{11}NO_3S$ requires C, 53.3; H, 4.9; N, 6.2; S, 14.2%), and 3-methoxy-1-(p-nitrophenylthio)propene (mixture of *cis*- and *trans*-) (0.1 g) (Found: C, 53.1; H, 4.9; N, 6.1; S, 14.45%). The former compound, on storage for a week, solidified; repeated crystallisation from ether-petroleum gave a product, m.p. 56—60°, ν_{max} (CHCl₃) 1640, 1110, and 960 cm⁻¹, τ 1.87 (4H, d, aromatic), 2.65 (4H, d, aromatic), 3.42 (2H, d, *J* 12 Hz), 5.17 (2H, dt, *J* 12 and 7.5 Hz), 6.2—6.5 (4H, m), and 6.45 (6H, s, OMe) (Found: C, 53.1; H, 4.8; N, 6.2; S, 14.6%), possibly a dimer.

(ii) A solution of the methanesulphonate (*ca.* 0.15 g) in methanol (20 ml) gave a 3 : 1 mixture (0.12 g) of 3-methoxy-3-(p-nitrophenylthio)propene and (*cis* + *trans*)-3-methoxy-1-(p-nitrophenylthio)propene.

(iii) The same quantity, in acetic acid (20 ml) and acetic anhydride (1 ml) gave *trans*-3-(p-nitrophenylthio)prop-2-enyl acetate (17) (0.14 g), which after t.l.c. (benzene) and recrystallisation from ether-petroleum had m.p. 60—62° (Found: C, 52.1; H, 4.5; N, 5.5; S, 12.4. $C_{11}H_{11}NO_4S$ requires C, 52.2; H, 4.4; N, 5.5; S, 12.7%).

(iv) The methanesulphonate (*ca.* 0.2 g), with potassium acetate (0.3 g) in acetic anhydride (25 ml) gave a 2 : 1 mixture (0.19 g) of 1-(p-nitrophenylthio)prop-2-enyl acetate (26) and *trans*-3-(p-nitrophenylthio)prop-2-enyl acetate (17). A portion of this mixture (100 mg) in acetic acid (10 ml), containing methanesulphonic acid (20 mg) was set aside for 20 h; the product was essentially the *trans*-acetate (17) with *ca.* 5% of the isomer (26).

(v) The same quantity, with tetramethylammonium acetate (0.3 g) in acetone (25 ml) gave a 1 : 3 mixture (0.2 g) of 1-(p-nitrophenylthio)prop-2-enyl acetate and *cis*-3-(p-nitrophenylthio)prop-2-enyl acetate (16).

(vi) The methanesulphonate (*ca.* 0.3 g) and sodium azide (0.3 g) in dimethylformamide (20 ml) gave *cis*-3-azido-1-(p-nitrophenylthio)propene (23) (0.2 g), purified by t.l.c. (benzene) (Found: C, 45.7; H, 3.45; N, 23.95; S, 13.7. $C_9H_8N_4O_2S$ requires C, 45.75; H, 3.4; N, 23.7; S, 13.6%).

Reactions of 3-(p-Nitrophenylthio)prop-2-enyl Chloride.—Conditions were as described for the corresponding reactions of *trans*-3-(phenylthio)prop-2-enyl chloride; for results, see text.

Isomerisation of cis-3-Methoxy-1-(p-nitrophenylthio)propene.—A solution of the methyl ether (80 mg) and methanesulphonic acid (30 mg) in methanol (20 ml) was kept at ambient temperature for 48 h; the product (70 mg) was a 3 : 2 mixture of the *cis*- and the *trans*-methyl ether.