Elimination–Addition. Part XXI.[1] Addition–Dealkylation Reactions of Acetylenic Sulphonium Salts with Oxygen, Sulphur, and Nitrogen Nucleophiles †

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Reactions of nucleophiles with dimethylprop-2-ynylsulphonium and *S*-prop-2-ynyltetrahydrothiophenium bromides have been investigated. These salts readily isomerise to the allenic isomers (>S⁺·C:C:C), which are susceptible to nucleophilic addition. The initially formed adducts, according to their structure, undergo several types of subsequent reaction. Most commonly, isomerisation of the initial non-conjugated adduct to the conjugated isomer is either followed by addition of a second nucleophile or the nucleophile dealkylates the sulphonium group by attack at carbon adjacent to sulphur. In the case of the cyclic sulphonium salt, dealkylation results in ring cleavage and formation of open-chain sulphides.

Nucleophilic reactions with alcohols, phenols, and thiols have been studied. The formation of the products obtained is interpreted in terms of the basicity of the nucleophile and its nucleophility for sp^3 and sp^2 carbon centres. Double addition to the allene system is restricted to small nucleophiles irrespective of the nucleophilic atom.

Comparisons are drawn with earlier work on allenic sulphones and, where appropriate, the stereochemistry of the products is discussed.

REACTIONS of several types of nucleophile with allenic sulphones have been studied previously.[2-4] In later work, reactions of propargylic sulphonium salts with nucleophiles were investigated [5] and it was established that the system S⁺·C·C:C readily isomerised to the conjugated allenic system S⁺·C:C:C, which is susceptible, unlike its acetylenic precursor, to nucleophilic addition. Allenic sulphonium salts have not so far been isolated in a pure state but throughout this paper our interpretations of the reaction pathways depend upon the presumption that initial isomerisation to the allene is followed by nucleophilic addition to give non-conjugated adducts (2) as *kinetic* products.

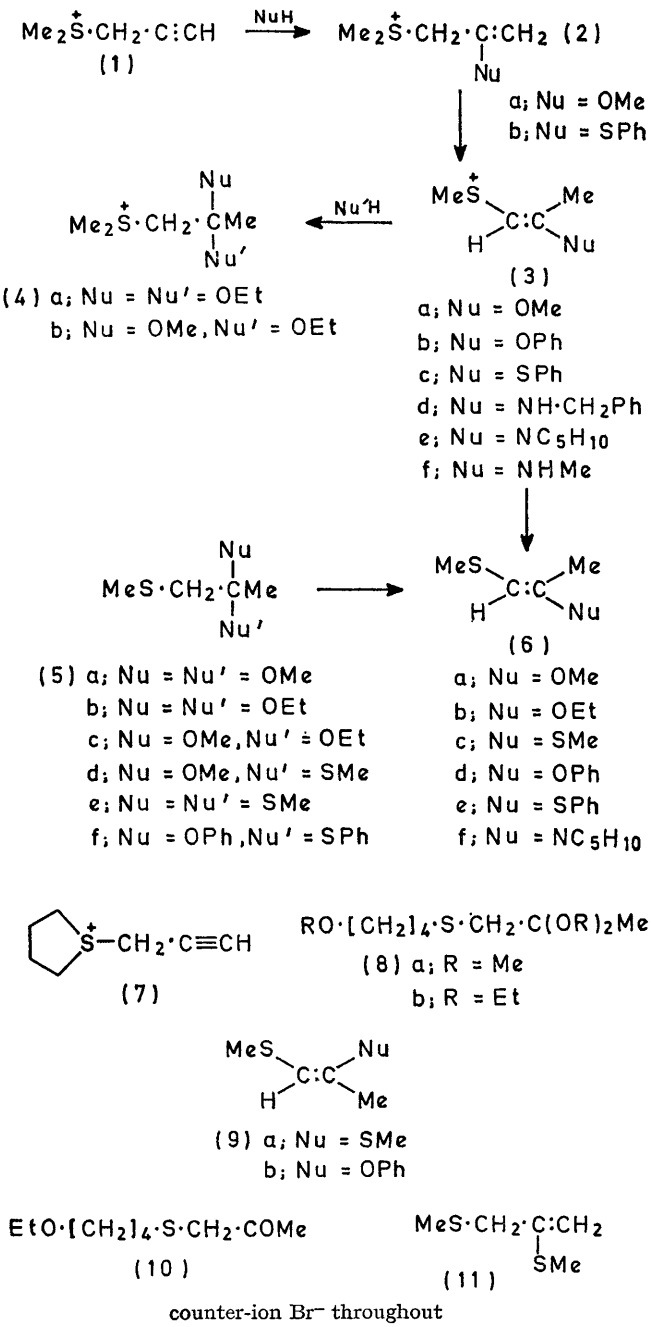
Sulphonium salts differ from sulphones in the important respect that the sulphonium group, while resembling the sulphonyl group in its ability to activate an adjacent carbon–carbon double bond towards nucleophilic addition, is much more powerful in this respect.[6] Another difference in reactivity is that a sulphonium group, unlike a sulphonyl group, is subject

† Part of this work was presented at the IVth International Symposium on Organic Sulphur Chemistry, Venice, 1970.

[1] Part XX, J. Crosby and C. J. M. Stirling, *J. Chem. Soc.* (*B*), 1970, 679.
[2] C. J. M. Stirling, *J. Chem. Soc.*, 1964, 5856.
[3] C. J. M. Stirling, *J. Chem. Soc.*, 1964, 5863.
[4] S. T. McDowell and C. J. M. Stirling, *J. Chem. Soc.* (*B*), 1967, 351.
[5] G. D. Appleyard and C. J. M. Stirling, *J. Chem. Soc.* (*C*), 1969, 1904.
[6] C. J. M. Stirling in 'Organic Chemistry of Sulphur,' ed. S. Oae, Plenum Press, London, in the press.

to nucleophilic attack at carbon adjacent to sulphur with expulsion of sulphide as leaving group. The possibility of displacement of the sulphonium group thus renders an allenic sulphonium salt potentially trifunctional; two successive nucleophilic additions to the carbon–carbon double bond may be followed by subsequent reaction at the sulphonium group under appropriate reaction conditions.

SCHEME



counter-ion Br^- throughout

Bis-addition may be succeeded by dealkylation of the sulphonium group. If this occurs at the α-carbon atom of the original allenic system, sulphide is displaced from the adduct. On the other hand, if attack occurs at any other group attached to sulphur, sulphur is retained in the adduct and the product is a substituted sulphide. Possible reaction pathways are outlined in the Scheme. Examples of all have been found.

This paper deals with simple addition–dealkylation reactions. The following paper reports application of addition–dealkylation reactions to the synthesis of furans.

Reactions with Alkoxide Ions.—When the salt (1) is treated with methanolic 0·005M-sodium methoxide, ^1H n.m.r. spectroscopy clearly shows the formation of the *non-conjugated* [2] adduct (2a). This initial adduct is replaced successively by the conjugated adduct (3a) and then by the bis-adduct (4a), isolated in 86% yield when stronger sodium methoxide (0·05M) is used. Further addition in this system occurs much more readily than in the corresponding sulphone,[3] which forms an equilibrium mixture containing conjugated adduct and the bis-adduct even with high concentrations of alkoxide. In other work with allenic ketones, esters, and nitriles, conjugated adducts [7] of type (3) and in certain cases [8] acetals are eventually produced.

Although it was possible to isolate the initial non-conjugated adduct and the bis-adduct in high yield, pure monomethoxy-adduct (3a) was not obtainable from the direct reaction although it is a product of an indirect reaction of the non-conjugated adduct with phenol (see later).

When the bis-adduct was subjected to even more severe conditions (hot methanolic sodium methoxide) dialkylation of the sulphonium group occurred and the acetal (5a) was obtained. Similarly, in reactions with ethanolic sodium ethoxide, the main product was the acetal (5b), formed together with a small amount of the vinylic sulphide (6b). The acetal was authenticated by comparison with a specimen obtained by reaction of (methylthio)acetone with triethyl orthoformate.[9] Thermal decomposition of the acetal gave the mono-alkoxy-sulphide (6b) (83%); the diethyl acetal (5b) was much more labile than the dimethyl acetal in this respect.

With the cyclic sulphonium salt (7), a similar pattern of double addition and dealkylation was followed, and in this case dealkylation resulted in fission of the five-membered ring and formation of the alkoxy-sulphide (8). No product consistent with displacement of the sulphonium group as tetrahydrothiophen was found.

An authentic specimen of the trialkoxy-sulphide (8b) was obtained by treating 1-bromo-4-ethoxybutane with thiourea. Hydrolysis of the thiouronium salt gave 4-ethoxybutanethiol, which with chloroacetone gave the ketone (10), converted into the acetal by treatment with triethyl orthoformate. The high yield obtained suggests that this type of reaction which produces a butyl group, with differing functionality at α- and ω-positions, is of synthetic value and we are investigating this possibility.

[7] D. R. Taylor, *Chem. Rev.*, 1967, **67**, 317.
[8] M. Verny and R. Vessière, *Bull. Soc. chim. France*, 1967, 2508, and references cited therein.
[9] C. L. Stevens and A. E. Sherr, *J. Org. Chem.*, 1952, **17**, 1228.

Addition of two molecules of an alcohol to the activated allenic system suggested the possibility of addition of a different nucleophile in the second stage so as to give an unsymmetrical adduct of type (4; Nu ≠ Nu'). This sequence was attempted with the non-conjugated monomethoxy-adduct (2a) with ethanol as addend. The mixed acetal (4b) (71%) was obtained under conditions not sufficiently severe to cause dealkylation. This reaction is clearly not an equilibration, in contrast to another procedure [10] which involves equilibration of acetal with a different alcohol in the presence of sulphuric acid.

Under conditions sufficiently severe to cause dealkylation, a mixture of products was formed. The symmetrical diethyl acetal (5b) clearly results from elimination of the methoxy-group from the initial unsymmetrical adduct. The enol ether (6b) results from decomposition of an acetal as before. Together with these products, g.l.c. showed the presence of a third compound of intermediate retention time, probably the unsymmetrical acetal (5c). In accordance with this view, the retention time of this compound was identical with that of one of the three products resulting from the equilibration of (methylthio)acetone with a mixture of trimethyl and triethyl orthoformates in the presence of sulphuric acid. The other two compounds had the same retention times as the dimethyl (5a) and diethyl (5b) acetals, respectively.

The elimination–addition sequence which gives the diethyl acetal (5b) occurs in the *sulphonium* salt before dealkylation. This is confirmed by the inertness of the dimethyl acetal (5a).

When the methoxy-sulphonium salt (2a) was treated with methanethiolate in methanol, the products were (methylthio)acetone (resulting from hydrolysis of a vinyl ether intermediate) and a mixture of (*Z*)- [11] and (*E*)-methylthiopropenes (9a) and (6c), respectively. These last two products probably result from decomposition of the acetal (5d) on distillation, as the crude product before distillation showed no vinylic protons in the ^{1}H n.m.r. spectrum. It is interesting that this process is non-stereospecific. A trace of 1,2,2-trismethylthiopropane (5e) was also detected by g.l.c.

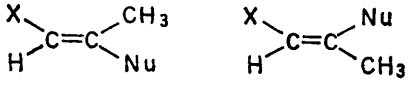
Formation of oxothio-acetals by alcoholysis of α-chloro-sulphides is known [12] but this is believed to be the first example of such a structure arising from a nucleophilic addition process.

An attempt to add phenoxide ion to the monomethoxysulphonium salt (2a) failed; instead, isomerisation to the conjugated salt (3a) occurred. This salt, by analogy with earlier work,[3] is assigned the thermodynamically preferred *E*-configuration, and n.m.r. data, which indicate the stereochemistry by the chemical shift of the *C*-methyl group, are in accordance with this assignment (Table).

Reactions with Phenoxide Ion.—On treatment with sodium phenoxide, the salt (1) gave the conjugated thermodynamic adduct (3b), again with *E*-configuration. Further reaction to give bis-addition under mild conditions could not be achieved with phenoxide in phenol, nor with methoxide or thiophenoxide in methanol. It appears that steric factors in the second stage of the addition are paramount in controlling whether or not bis-addition can occur. A large group already in place in the substrate or a large nucleophilic addend, or both, inhibit further addition. Nucleophilic addition to electrophilic olefins is known from previous work [13] to be extremely sensitive to substitution β to the activating group.

Treatment of the phenoxy-salt (3b) with hot methanolic sodium methoxide caused elimination of phenol and formation of the methoxy-sulphides (5a) and (6a). When forcing conditions, with thiophenoxide in methanol, were used, dealkylation of the salt (3b) occurred, and, unexpectedly, a mixture of *E*- and *Z*-adducts (6d) and (9b) was obtained. It is improbable that these are formed by equilibration induced by addition of thiophenoxide, known to be a poorer leaving group than phenoxide under similar conditions [14] and no bis-adduct was isolated. Even if bis-adduct had been formed and demethylation produced the sulphide (5f), non-stereospecific elimination of thiophenoxide in total preference to phenoxide would have to be proposed. The pathway followed is thus still in doubt. It is notable that thiophenoxide does not become incorporated in the product. Thiophenoxide is generally an

^{1}H N.m.r. chemical shifts of *C*-methyl protons in adducts from sulphones and sulphonium salts



E *Z*

Assignment	X	Nu	τ(CH$_3$)
E	Me_2S^+O	HN·CH$_2$Ph	7·80
E	Me_2S^+O	HNMe	7·75
E	Me_2S^+O	NC_5H_{10}	7·85
E	Me_2S^+O	OMe	7·80
E	Me_2S^+O	OPh	7·40
E	Me_2S^+O	SPh	7·75
Z	MeS	OPh	8·10
E	MeS	OPh	7·80
E	$MeSO_2$	SO_2Ph	7·70
E	MeS	OEt	8·15
E	MeS	NC_5H_{10}	8·15
E	PhS	SPh	7·90
E	$PhSO_2$	SPh	7·56
Z	$PhSO_2$	SPh	8·25
E	$PhSO_2$	HN·CH$_2$Ph	7·84
Z	$PhSO_2$	HN·CH$_2$Ph	8·14

[10] M. F. Shostakovskii, N. V. Kuznetsov, and Ya. B. Zaretskaya, *Izvest. Akad. Nauk, S.S.S.R., Otdel, khim. Nauk*, 1963, 922 (*Chem. Abs.*, 1963, **59**, 7364).

[11] J. E. Blackwood, C. L. Gladys, K. L. Loening, A. E. Petrarca, and J. E. Rush, *J. Amer. Chem. Soc.*, 1968, **90**, 509.

[12] H. Böhme and H. Bentler, *Chem. Ber.*, 1956, **89**, 1470.

[13] S. T. McDowell and C. J. M. Stirling, *J. Chem. Soc.* (*B*), 1967, 343.

[14] R. P. Redman and C. J. M. Stirling, *Chem. Comm.*, 1970, 633.

excellent nucleophile in additions to electrophilic olefins.[15]

Reactions with Thiols.—Thiophenoxide reacts with the sulphonium salt (1) to give an only moderate yield of the conjugated monoadduct (3c) in contrast to reaction with the corresponding sulphone in which the non-conjugated adduct (2b; $PhSO_2$ for $Me_2\overset{+}{S}$) is obtained in high yield. The sulphonium group, however, is much better than the sulphonyl group in carbanion stabilisation, and prototropic reactions are undoubtedly much more favourable in the sulphonium salt. When an excess of thiophenoxide was used in reactions with the sulphonium salt, demethylation occurred with formation of the bis-sulphide (6c). The *E*-configuration is tentatively assigned; the assumption is made that demethylation occurs without change in configuration at the carbon–carbon double bond. Demethylation occurs readily in comparison with reactions of other nucleophiles, in accordance with the high nucleophilicity of thiophenoxide for sp^3 carbon.[16]

With methanethiol in excess, the salt (1) gave the non-conjugated sulphide (11) together with a small amount of the tris-sulphide (5e). Dealkylation for this nucleophile evidently competes effectively with isomerisation. Formation of the tris-sulphide again suggests that bis-addition can be accomplished only with ' small ' nucleophiles, in contrast to the situation found with thiophenoxide. Equilibrium formation of thioacetals by nucleophilic addition of ethanethiol to β-alkylthioacrylic esters has recently been reported.[17] Further, formation of the non-conjugated adduct indicates that in the isomerisation–second addition sequence, the latter step is much more rapid than the former.

Thiophenoxide reacted with the tetrahydrothiophenium salt (7) causing displacement of tetrahydrothiophen (in contrast to the alkoxide reactions) and giving the conjugated bis-sulphide (6e PhS for MeS), characterised as the *E*-bis-sulphone, identical with a specimen obtained earlier. This product evidently arises by vinylic displacement, a reaction familiar in halide–thiolate systems. Although these reactions are slow, the alternative routes, which involve direct or S_N' displacement in the initial non-conjugated adduct (2b), appear less likely because the reaction occurs under conditions too mild to cause subsequent isomerisation to the bis-sulphide.

Evidently, in this reaction, nucleophilic ring scission, the analogue of demethylation in salt (1) is disfavoured. Displacement at methyl groups is always preferred over displacement at higher alkyl groups or cycloalkyl groups.

Reactions with Amines.—Addition of amines to electrophilic allenes and acetylenes has received much recent attention, particularly, with regard to the stereochemistry of the adducts formed.[18] Two generalisations have emerged from previous work: conjugated adducts are always formed, and for secondary amines these have *E*-configurations. With primary amines, mixtures of geometric isomers are obtained whose composition is determined by hydrogen bonding between the activating group and the amino-group. This factor is dependent on the structure of the activating group and the conditions under which the isomer proportions are determined.

Benzylamine reacts with sulphonium salt (1) to give the conjugated monoadduct (3d); the same type of adduct (3e) was obtained in reaction with piperidine. The piperidino-adduct is assigned the *E*-configuration as in earlier work with sulphones. Comparison of the chemical shift of the *C*-methyl protons of this adduct with those of the benzylamine adduct shows that these have essentially the same environment, and this also applies to the methylamine adduct (3f). The exclusive formation of single adducts from these amines was easily established by n.m.r. spectroscopy. Assignment of the *E*-structure to all is consistent with the lack of opportunity for intramolecular hydrogen bonding in the primary amino-adduct and consequent disfavourment of the *Z*-adduct in what is undoubtedly an equilibrium mixture.[18]

The enamino-sulphonium salts, *e.g.* (3e), were, like other acyclic enamines,[19] unstable in the presence of water and decomposed to amine and keto-sulphonium salt ($Me_2\overset{+}{S}\cdot CH_2\cdot COMe\,B\bar{r}$) on exposure to moist air.

In reactions with excess of amine, bis-addition did not occur, even with an excess of the ' small ' nucleophile, dimethylamine. This is not surprising; the amino-group adjacent to the double bond effectively reduces polarisation and discourages subsequent nucleophilic addition. Under severe conditions, slow demethylation occurred, and with piperidine the piperidino-sulphide (6f) was formed. This was unstable under the reaction conditions and was isolated only in moderate yield. It was identical (g.l.c.) with an authentic specimen obtained from (methylthio)acetone and tripiperidinoboron.[20] The other products were the complementary dealkylation products *N*-methylpiperidine and (methylthio)acetone. The last product probably arises from hydrolysis of the enamino-sulphide.

EXPERIMENTAL

Dimethylprop-2-ynylsulphonium bromide was prepared as previously.[5] 1-(Prop-2-ynyl)tetrahydrothiophenium bromide was obtained by addition of tetrahydrothiophen to 3-bromopropyne (1 mol. equiv.) is dichloromethane at 25°. After 16 h crystals of the salt (89%), m.p. 81—83° (lit.,[21] 82—84°) were filtered off.

Reactions of Dimethylprop-2-ynylsulphonium Bromide.—(a) *With methanol.* (i) The salt (1·81 g) in methanol (25 ml)

[15] S. Patai and Z. Rappoport, 'The Chemistry of the Alkenes,' ed. S. Patai, Interscience, London, 1964, ch. 8.
[16] R. G. Pearson, H. Sobel, and J. Songstad, *J. Amer. Chem. Soc.*, 1968, **90**, 319.
[17] M. Verny and R. Vessière, *Bull. Soc. chim. France*, 1970, 746.
[18] E. Winterfeldt, ' Chemistry of Acetylenes,' ed. H. G. Viehe, Dekker, New York, 1969, ch. 4.
[19] A. G. Cook, ' Enamines—Synthesis, Structure, and Reactions,' Dekker, London, 1969.
[20] W. D. English, A. L. McCloskey, and H. Steinberg, *J. Amer. Chem. Soc.*, 1961, **83**, 2122.
[21] H. Johnston, U.S.P. 2,965,649 (*Chem. Abs.*, 1961, **55**, 10480).

was treated with methanolic M-sodium methoxide (0·15 ml). After 30 min the mixture was evaporated and the residue, on treatment with ether, gave *2-methoxyprop-1-enyldimethylsulphonium bromide* (2a) (80%), m.p. 92—93° [raised to 96—98° (from methanol–ether)] (Found: C, 33·5; H, 6·1. $C_6H_{13}BrOS$ requires C, 33·8; H, 6·1%), $\nu_{max.}$ 1630 cm^{-1} (C=C str.), τ (D_2O) 5·4br (2H), 5·9 (2H), 6·3 (3H, s), and 7·1 (6H, s).

Reaction between the salt and methanol at 31° was followed by ^1H n.m.r. spectroscopy for 90 min. Bands at τ 5·9, 7·8, and 8·4 were observed as characteristic of the non-conjugated adduct (2a), the conjugated adduct (3a), and the acetal (4a), respectively. Both monoadducts were present after 12 min and the acetal was first detected after 17 min. No conjugated adduct was present after 30 min.

(ii) Repetition of the experiment with methanolic M-sodium methoxide (1 ml) gave, after 19 h, the bis-adduct, *2,2-dimethoxypropyldimethylsulphonium bromide* (4a) (86%), m.p. 150—153° [raised to 157—158° (from methanol–ether)] (Found: C, 34·7; H, 6·6. $C_7H_{17}BrO_2S$ requires C, 34·3; H, 7·0%), τ (D_2O) 6·3 (2H, s), 6·7 (6H, s), 7·05 (6H, s), and 8·4 (3H, s).

(iii) Treatment of the sulphonium salt (10 mmol) in methanol (25 ml) with methanolic 0·25M-sodium methoxide at 60° for 4 h yielded, after removal of the solvent, *2,2-dimethoxy-1-methylthiopropane* (5a) (69%), b.p. 65—67° at 11 Torr, n_D^{25} 1·4563 (Found: C, 48·1; H, 9·4. $C_6H_{14}O_2S$ requires C, 48·0; H, 9·4%), τ ($CDCl_3$) 6·8 (6H, s), 7·3 (2H, s), 7·9 (3H, s), and 8·6 (3H, s).

(b) *With ethanol.* Repetition of the previous experiment but with ethanol in place of methanol gave a residue which on g.l.c. showed three components in the ratio 91 : 6 : 3. Comparison of retention times with those of authentic specimens (see later) showed that the main product was 2,2-diethoxy-1-methylthiopropane (5b) and the smallest peak was 2-ethoxy-1-methylthioprop-1-ene (6b). The third component was not identified. Distillation of the residue gave the diethoxy-compound (5b) (70%), b.p. 76—79° at 15 Torr.

(c) *With phenol.* (i) The salt (0·9 g) and phenol (0·47 g, 5 mmol) in ethanol (25 ml) were treated with ethanolic M-sodium ethoxide (0·2 mmol). After 30 min at 25°, concentration of the mixture and treatment of the residue with ether gave *dimethyl-2-phenoxyprop-1-enylsulphonium bromide* (3b) (84%), m.p. 113—114° [raised to 119—120° (from ethanol–ether)] (Found: C, 48·3; H, 4·9. $C_{11}H_{15}BrOS$ requires C, 48·0; H, 5·4%), $\nu_{max.}$ 1610 cm^{-1} (C=C str.), τ (D_2O) 2·3—2·8 (5H, m), 4·75br (1H), 6·95 (6H, s), and 7·4br (3H, s).

(ii) The salt (20 mmol) in phenol (100 ml) was treated with a solution of sodium phenoxide (20 mmol) in phenol (100 ml) at 75° and the mixture was kept at 100° for 4 h. Phenol and other low-boiling components were distilled off at 13 Torr. Fractional distillation of the residue at 0·08 torr gave an initial fraction of b.p. up to 82° (1·01 g) shown by g.l.c. (SE30 at 195°) to contain anisole (0·49 g), which was also present (0·98 g) in the solvent distilled from the reaction mixtures (total yield 68%).

The remainder of this fraction combined with the following fraction, b.p. 82—85° (1·56 g) was separated by g.l.c. (SE30 at 194°) into approximately equal amounts of: (Z)-*1-methylthio-2-phenoxyprop-1-ene* (9b), n_D^{18} 1·5151 (Found: C, 66·2; H, 7·0. $C_{10}H_{12}OS$ requires C, 66·6; H, 6·7%), $\nu_{max.}$ 1645 cm^{-1} (C=C str.), τ (CCl_4) 2·4—3·0 (5H, m), 4·5 (1H, q, J 1·0 Hz), 7·75 (3H, s), and 8·1 (3H, d, J 1·0 Hz), and (E)-*1-methylthio-2-phenoxyprop-1-ene* (6d), n_D^{18} 1·5608 (Found: C, 66·6; H, 6·9%), $\nu_{max.}$ 1635 cm^{-1} (C=C str.), τ (CCl_4) 2·4—2·9 (5H, m), 4·6 (1H, q, J, 0·5 Hz), 7·7 (3H, s), and 7·8 (3H, d, J 0·5 Hz).

(d) *With benzenethiol.* (i) The salt (2·7 mmol) and benzenethiol (2·7 mmol) in ethanol (20 ml) were treated with ethanolic M-sodium ethoxide (0·054 mmol). After 19 h at 25°, evaporation of the solvent and addition of ether gave *dimethyl-2-(phenylthio)prop-1-enylsulphonium bromide* (53·5%), m.p. 102—103° (from methanol–ether) (Found: C, 45·2; H, 4·75. $C_{11}H_{15}BrS_2$ requires C, 45·4; H, 5·2%), $\nu_{max.}$ 1605 cm^{-1} (C=C str.), τ (D_2O) 2·55 (5H, m), 4·9br (1H), 7·3 (6H, s), and 7·75br (3H, s).

(ii) The salt (28 mmol) in ethanol (70 ml) was treated with benzenethiol (56 mmol) and sodium ethoxide (28 mmol) in ethanol (70 ml). After 2 h, the mixture was poured into saturated brine (100 ml) and extraction with dichloromethane gave a residue which, on fractional distillation, gave fractions (i) b.p. 70—80° at 12 Torr (2·44 g) shown by g.l.c. (Carbowax 1540 at 120°) to comprise thioanisole (1·56 g, 45%) and (methylthio)acetone (0·88 g, 33%), and (ii) b.p. 86—96° at 10·05 Torr (3·65 g). T.l.c. showed that the main component of fraction (ii) was contaminated by a number of minor components. A portion (2·65 g) was oxidised by Rydon's [22] method with hydrogen peroxide (100 vol.; 25 ml) and ammonium molybdate (1·5 g) in water (4 ml) and methanol (35 ml) for 2 h at 25°. The mixture was poured into water and extraction with dichloromethane gave *1-methylsulphonyl-2-phenylsulphonylprop-1-ene* (6e; SO_2 for S) (2·59 g, 73%) (Found: C, 46·5; H, 4·8. $C_{10}H_{12}O_4S_2$ requires C, 46·2; H, 4·6%), $\nu_{max.}$ 1130 and 1295 (SO_2) and 1625 cm^{-1} (C=C str.), τ ($CDCl_3$) 2·0—2·7 (6H, m), 6·9 (3H, s), and 7·7 (3H, d, J 1·5 Hz).

(e) *With methanethiol.* The salt (1) (10 mmol) in ethanol (50 ml) was treated with methanethiol (30 mmol) and sodium ethoxide (10 mmol) in ethanol (100 ml). After 19 h, the mixture was boiled under reflux for 30 min. Ethanol was removed through a helix-packed column and the residue, on fractional distillation, gave fractions (i), b.p. 78—82° at 12 Torr (0·47 g), shown to be *2,3-bismethylthioprop-1-ene* (11) (Found: C, 44·4; H, 7·1. $C_5H_{10}S_2$ requires C, 44·8; H, 7·5%), τ (CCl_4) 4·6br (1H, s), 5·15 (1H, s), 6·7br (2H, s), 7·7 (3H, s), and 7·95 (3H, s), and (ii), b.p. 110—115° at 12 torr (0·28 g), shown by n.m.r. spectroscopy to contain approximately 75% of 1,2,2-trismethylthiopropane. The presence of this compound was confirmed by oxidation of the sulphide (0·25 g) with *m*-chloroperbenzoic acid (2·00 g, 8 mol. equiv.) in chloroform (27 ml). After 7 days at 25°, filtration and evaporation yielded the *trisulphone* (100 mg, 27%), m.p. 137° (from $CHCl_3$) (Found: C, 25·6; H, 5·1. $C_6H_{14}O_6S_3$ requires C, 25·9; H, 5·1%), $\nu_{max.}$ 1135 and 1300 cm^{-1} (SO_2). The other components of this fraction were not identified.

(f) *With amines.* (i) *Benzylamine.* Benzylamine (10 mmol) was added dropwise to the salt (10 mmol) in ethanol (25 ml). Reaction was exothermic and after 30 min, ethanol was evaporated off and the residue, on treatment with ether, gave *2-benzylaminoprop-1-enyldimethylsulphonium bromide* (3d) (89%), m.p. 106—107° [raised to 110—112° (from ethanol–ether)] (Found: C, 50·3; H, 6·4. $C_{12}H_{18}BrNS$ requires C, 50·0; H, 6·3%), $\nu_{max.}$ 1590 (C=C str.) and 3250 cm^{-1} (NH str.), τ (D_2O) 2·55 (5H, m), 5·65 (2H, s), 7·3 (6H, s), and 7·8 (3H, s).

[22] P. M. Hardy, H. N. Rydon, and R. C. Thompson, *Tetrahedron Letters*, 1968, 2525.

(ii) *Piperidine*. The salt was treated with piperidine, as for benzylamine, to give *dimethyl-2-piperidinoprop-1-enyl-sulphonium bromide* (3e) (96%), melting indefinitely with decomposition (Found: C, 45·0; H, 7·3. $C_{10}H_{20}BrNS$ requires C, 45·1; H, 7·6%), $\nu_{max.}$ 1605 cm^{-1} (C=C str.), τ ($CDCl_3$) 4·9 (1H, s), 6·9 (10H, m), 7·85 (3H, s), and 8·55 (6H, m).

The adduct darkened and liquefied in moist air and acquired a strong smell of piperidine. The i.r. spectrum showed strong absorption at 1710 cm^{-1} consistent with hydrolysis of the enamine to ketone and amine.

The salt (1) (10 mmol) was treated with piperidine (40 mmol) in methanol (25 ml) at 60° for 6 h. Solvent was removed by distillation and the residue was triturated with ether and filtered. The residue was piperidine hydrobromide (1·58 g), m.p. and mixed m.p. 234—236°. G.l.c. analysis (15% SE 301 and 15% PPE—5% KOH at 100°) of the filtrate with anisole as internal standard and authentic sample comparisons, showed that the components of the mixture were *N*-methylpiperidine (52%), (piperidinomethylthio)acetone (15%), and 1-methylthio-2-piperidinopropene (6f) (36%).

(iii) *Methylamine*. The salt (1) (5 mmol) in ethanol (26·4 ml) was treated with methylamine (15 mmol). After 20 h solvent was removed, leaving *dimethyl-2-methylaminoprop-1-enylsulphonium bromide* (96%), m.p. 114° [raised to 118° (from ethanol–ether)] (Found: C, 33·5; H, 6·6. $C_6H_{14}BrNS$ requires C, 34·0; H, 6·6%), $\nu_{max.}$ 1590 (C=C) and 3280 cm^{-1} (NH), τ (D_2O) 5·2 (1H, s), 7·0 (6H, s), 7·1 (3H, s), and 7·75 (3H, s).

Reactions with the Tetrahydrothiophenium Salt (7).—(a) *With methoxide*. The salt (20 mmol), in methanol (200 ml) was treated with sodium methoxide (20 mmol). After being boiled under reflux for 4 h, the mixture was evaporated and the residue was treated with ether. Filtration and evaporation of the filtrates gave 2,2-*dimethoxy*-1-(4-*methoxybutylthio*)*propane* (8e) (81%), n_D^{20} 1·4643 (Found: C, 53·9; H, 9·8. $C_{10}H_{22}O_3S$ requires C, 54·0; H, 10·0%), τ (CCl_4) 6·7 (11H, m), 7·3 (4H, m), 8·3 (4H, m), and 8·6 (3H, s).

(b) *With ethanol*. The experiment was repeated with ethanol as solvent, sodium ethoxide as base, and a heating period of 3 h. The product was 2,2-*diethoxy*-1-(4-*ethoxybutylthio*)*propane* (8b) (90%), n_D^{20} 1·4600 (Found: C, 59·2; H, 10·7. $C_{13}H_{28}O_3S$ requires C, 59·0; H, 10·7%), τ (CCl_4) 6·6 (8H, m), 7·4 (4H, m), 8·35 (4H, m), 8·6 (3H, s), and 8·8 (9H, m), identical (n.m.r. and i.r.) with a specimen obtained by a different route (see later).

(c) *With benzenethiol*. The salt (20 mmol) in ethanol (100 ml) was added to benzenethiol (40 mmol) and sodium ethoxide (20 mmol) in ethanol (100 ml). After 30 min the mixture was treated as before to give 1,2-bisphenylthioprop-1-ene (6e; PhS for MeS) (67%), b.p. 153° at 0·1 Torr (Found: C, 69·5; H, 5·4; S, 24·6. $C_{15}H_{14}S_2$ requires C, 69·7; H, 5·5; S, 24·8%), τ ($CDCl_3$) 2·6 (10H, m), 3·5br (1H, s), and 7·9br (3H, s).

Oxidation of the product (1·7 g) with ammonium molybdate–hydrogen peroxide, as before, gave (*E*)-1,2-bisphenylsulphonylprop-1-ene (86%), m.p. 143—144° (from ethanol) (lit.,[2] 144—145°) (Found: C, 55·5; H, 4·3. Calc. for $C_{15}H_{14}O_4S_2$: C, 55·9; H, 4·4%), identical (mixed m.p.) with an authentic specimen.

Consecutive Reactions with Dissimilar Nucleophiles.—*Attempted Reaction of Methoxide Ion with the Monophenoxy-adduct* (3b).—The adduct (5 mmol) in methanol (25 ml) was treated with methanolic 0·5M-sodium methoxide (1 ml). After 3 days, neutralisation with acetic acid and removal of solvent gave unchanged adduct (89%), m.p. and mixed m.p. 118°.

Attempted Addition of Benzenethiol to the Phenoxy-adduct (3b).—(i) The adduct (5 mmol), in methanol (25 ml), was treated with benzenethiol (5 mmol) in methanolic 0·33M-sodium methoxide. After 3 days at 25°, neutralisation and removal of the solvent gave unchanged adduct (90%), m.p. and mixed m.p. 118°.

(ii) The adduct (16 mmol) in ethanol (50 ml) was treated with benzenethiol (20 mmol) and sodium ethoxide (16 mmol) in ethanol (100 ml). The mixture was kept at 20° for 19 h and then boiled under reflux in nitrogen for 4 h. The usual work-up gave a residue which was distilled into fractions (i), b.p. 88—91° at 13 mmHg (1·78 g), which was shown by g.l.c. and ^1H n.m.r. to be thioanisole (71%), and (ii), b.p. 78—82° at 0·15 mmHg (2·03 g). Fraction (ii) was separated into two components, present in roughly equal proportions, by g.l.c. (SE 30) at 194°. These components were identical with (*E*)- and (*Z*)-1-methylthio-2-phenoxyprop-1-enes obtained from treatment of the phenoxy-adduct (3b) with sodium phenoxide under forcing conditions.

Attempted Addition of Phenoxide to the Methoxy-adduct (2a).—The adduct (10 mmol), in ethanol (30 ml), was treated with phenol (10 mmol) and ethanolic 0·5M-sodium ethoxide (1 mmol). After 24 h at 25°, neutralization and removal of solvent gave *dimethyl*-(2-*methoxyprop*-1-*enyl*)-*sulphonium bromide* (3a) (98%), m.p. 161—162° (from ethanol–ether) (Found: C, 33·3; H, 6·0. $C_6H_{13}BrOS$ requires C, 33·8; H, 6·1%), τ (D_2O) 4·65 (1H, s), 6·15 (3H, s), 7·05 (6H, s), and 7·8 (3H, s).

Addition of Ethanol to the Methoxy-adduct (2a).—The adduct (6·5 mmol), in ethanol (50 ml), was treated with ethanolic 0·65M-sodium methoxide. After 24 h, the usual work-up gave 2-*ethoxy*-2-*methoxypropyldimethylsulphonium bromide* (5c) (71%), m.p. 119—120° [raised to 120—121° (from ethanol–ether)] (Found: C, 36·7; H, 7·0. $C_8H_{19}BrO_2S$ requires C, 37·1; H, 7·4%), τ (D_2O) 6·2—6·7 (7H, m), 7·05 (6H, s), 8·45 (3H, s), and 8·8 (3H, t, *J* 7·5 Hz).

This adduct (20 mmol), in ethanol (100 ml), was treated with ethanolic 0·4M-sodium methoxide at 78° for 3 h. Solvent was removed by distillation and the residue was treated with ether. Filtration and evaporation of the filtrate gave a residue, b.p. 80—90° at 13 Torr, g.l.c. (SE30; 120°) of which showed three major components identified by comparison with authentic specimens (see later) as 2,2-diethoxy-1-(methylthio)propane (5b) (37%), 2-ethoxy-1-(methylthio)propene (6b) (15%), and (putatively) 2-ethoxy-2-methoxy-1-(methylthio)propane (5c) (48%).

Reaction of Methanethiolate with the Monomethoxy-adduct (2a).—The adduct was treated with methanethiol (30 mmol) and sodium methoxide (10 mmol) in methanol (20 ml). After 17 h solvent was removed by distillation through a helix-packed column and ether (200 ml) was added to the residue. Filtration and evaporation of the filtrates gave a residue which g.l.c. showed to contain, as main components, (methylthio)acetone and a compound with longer retention time. Distillation gave (methylthio)acetone (27%), b.p. 38—39° at 12 Torr, n_D^{20} 1·4687 (lit.,[23] b.p. 152·5—153° at 760 Torr; n_D^{20} 1·4713) and a mixture, b.p. 80—82° at 12 Torr (0·3 g). ^1H N.m.r. spectroscopy showed a number of methylthio-groups (τ 7·5—8·0) and a methoxy-group

[23] C. K. Bradsher, S. C. Brown, and R. J. Grantham, *J. Amer. Chem. Soc.*, 1954, **76**, 114.

(τ 6·8). G.l.c. of this mixture showed that the proportions of two of the minor components in the crude residue had increased after distillation.

The higher boiling distillate was heated in toluene solution and analysed at intervals over 3 h. The longest retention component, comprising 90% of the residue before distillation, decreased to 0%, while two shorter retention peaks comprising 10% of the original residue, and present to the extent of 30 and 34% of the second fraction of the distillate, increased to 60 and 40%, respectively. The n.m.r. spectrum of the final mixture was consistent with that of a mixture of (*Z*)- and (*E*)-1,2-bismethylthiopropenes containing 60% of the *E*-isomer,[24] τ (CCl_4) 4·0 (1H, q, *J* 1·4 Hz), 7·7 (3H, s), and 8·0 (3H, d, *J* 1·4 Hz) (*Z*-isomer); and 4·2 (1H, q, *J* 1 Hz), 7·7 (3H, s), and 8·1 (3H, d, *J* 1 Hz) (*E*-isomer).

2,2-*Diethoxy*-1-(*methylthio*)*propane*. — (Methylthio)-acetone[23] (1·6 g), ethanol (0·3 ml), and triethyl orthoformate (2·4 g) were treated with conc. sulphuric acid (0·05 ml). After 19 h at 25°, neutralisation with ethanolic sodium ethoxide and subsequent distillation gave the *acetal* (41%), b.p. 33—36° at 0·1 Torr, n_D^{21} 1·4484 (Found: C, 54·5; H, 10·1. $C_8H_{18}O_2S$ requires C, 54·0; H, 10·1%), τ ($CDCl_3$) 6·5 (4H, q, *J* 7 Hz), 7·3 (2H, s), 7·9 (3H, s), 8·6 (3H, s), and 8·85 (6H, t, *J* 7 Hz).

2-*Ethoxy*-1-(*methylthio*)*propene*.—The foregoing compound (0·8 g) was kept at 130° for 1 h. Distillation gave ethanol (82%) (i.r. spectrum) and 2-*ethoxy*-1-(*methylthio*)*propene* (0·49 g, 83%), b.p. 156—160°, n_D^{22} 1·4715 (Found: C, 54·1; H, 9·2. $C_6H_{12}OS$ requires C, 54·5; H, 9·1%), τ ($CDCl_3$) 5·1br (1H, s), 6·35 (2H, q, *J* 7 Hz), 8·0 (3H, s), 8·15br (3H, s), and 8·8 (3H, t, *J* 7 Hz).

1-*Methylthio*-2-*piperidinopropene* (cf. *ref.* 25).—Tripiperidinoboron[20] (11 mmol), (methylthio)acetone (10 mmol), and piperidine (13 mmol) in benzene (125 ml) were treated with toluene-*p*-sulphonic acid (0·03 mmol) and the mixture was kept at 80° until (48 h) i.r. spectroscopy showed the absence of carbonyl absorption. Solvent was evaporated off and distillation gave the *enamine* (73%), b.p. 67—68° at 0·1 Torr, n_D^{21} 1·5283 (Found: C, 62·5; H, 10·1. $C_9H_{17}NS$ requires C, 63·1; H, 10·0%), τ ($CDCl_3$) 5·25br (1H, s), 7·2 (4H, m), 8·0 (3H, s), 8·15br (3H, s), and 8·6 (6H, m).

1-*Bromo*-4-*ethoxybutane*. Sodium ethoxide (0·29 mol), in ethanol (100 ml), was added dropwise to 1,4-dibromobutane (0·29 mol) in ethanol (70 ml). The mixture was boiled for 4 h, cooled, and evaporated. The residue was washed with water, and dried, and the product was separated by g.l.c. (SE30; 100°) from 1,4-diethoxybutane and unchanged 1,4-dibromobutane. The ethoxy-bromide had n_D^{17} 1·4519 (lit.,[26] n_D^{30} 1·4490), τ (CCl_4) 6·5 (6H, m), 8·1 (4H, m), and 8·8 (3H, t, *J* 7 Hz).

(4-*Ethoxybutylthio*)*acetone*.—The preceding ethoxy-bromide (50 mmol) and thiourea (15 mmol) were kept at 78° in ethanol (55 ml) for 2 h. Sodium hydroxide (30 mmol), in water (50 ml), was added, followed by chloroacetone (50 mmol). The mixture was kept at 100° for 7 h, ethanol was removed by distillation, and the residue was extracted with ether. Distillation of the extract gave the *ketone* (54%), b.p. 119—123° at 11 Torr, n_D^{15} 1·4732 (Found: C, 56·8; H, 9·7. $C_9H_{18}O_2S$ requires C, 56·8; H, 9·5%), τ (CCl_4) 6·5 (4H, m), 6·8 (2H, s), 7·45 (2H, m), 7·7 (3H, s), 8·3 (4H, m), and 8·8 (3H, t, *J* 7 Hz).

2,2-*Diethoxy*-1-(4-*ethoxybutylthio*)*propane* (8b).—The foregoing ketone (5 mmol), triethyl orthoformate (5 mmol), and ethanol (0·3 ml) were treated with conc. sulphuric acid (0·05 ml) and after 19 h the mixture was neutralised with ethanolic sodium ethoxide. Removal of ethanol gave the *acetal* (59%), b.p. 142—144° at 12 Torr, n_D^{20} 1·4600 (Found: C, 59·2; H, 10·7. $C_{13}H_{28}O_3S$ requires C, 59·0; H, 10·7%), τ (CCl_4) 6·6 (8H, m), 7·4 (4H, m), 8·35 (4H, m), 8·6 (3H, s), and 8·8 (9H, m).

We thank the S.R.C. for a C.A.P.S. grant (to P. D. H.) and Mr. W. Bevan for technical assistance.

[2/1263 *Received*, 5*th June*, 1972]

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