Elimination and Addition Reactions. Part 28.[1] Nucleophilic Addition–Displacement Reactions with Allenic Sulphonium Salts

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Addition of enolate ions stabilised by conjugative groups to allenic sulphonium salts has been investigated. Addition of a cyano-stabilised enolate leads to a cyano-furan but heterocyclic products are not obtained when the stabilising group is dimethylsulphonio or nitro. In each case, alternative reactions which do not involve the allenic sulphonium salt are preferred. ^{13}C Labelling studies show that in the formation of furans where the cyclisation step can involve direct substitution (S_N) or addition–elimination (S_N'). the former is exclusively preferred.

Addition of bidentate sulphur nucleophiles in the presence of proton donors gives mixtures of cyclic and acyclic products which result from bis-addition or addition–displacement sequences.

Addition of cyanide and arenesulphinate ions to allenic sulphonium salts gives initial adducts which are activated towards further addition. and eventual displacement of the sulphonium group yields products derived from incorporation of three of the nucleophilic species into the original allene chain. ^{13}C Labelling and structural studies of the arenesulphinate reactions show that S_N' reactions occur very rapidly and lead to equilibration of the α and γ termini of the allene systems.

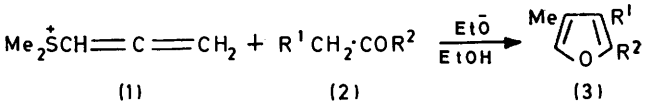
THE sulphonium group is among the most versatile of functional groups.[2] It behaves as a leaving group in displacement reactions, renders adjacent carbon–carbon multiple bonds susceptible to nucleophilic addition, and

[1] Part 27. J. W. Batty, P. D. Howes, and C. J. M. Stirling, *J.C.S. Perkin I*, 1976, 1543.

[2] C. J. M. Stirling in ' Organo-sulphur Chemistry,' ed. S. Oae, Plenum Press, New York, 1976.

confers appreciable acidity on adjacent carbon–hydrogen bonds. It is not surprising, therefore, that the sulphonium group has found wide use in mechanistic studies and in synthesis.[3,4]

In three previous papers of this series, addition reactions of allenic sulphonium salts with carboxylate[5]



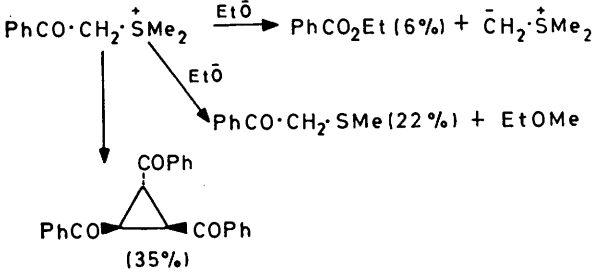
(1) (2) (3)

SCHEME 1

ions and other simple monodentate nucleophiles[6] were reported, together with applications of reactions with carbonyl-stabilised carbanions to furan synthesis.[4] We now report on additions of nucleophiles to allenic sulphonium salts in which initial addition is followed by intramolecular substitution or by addition–elimination.

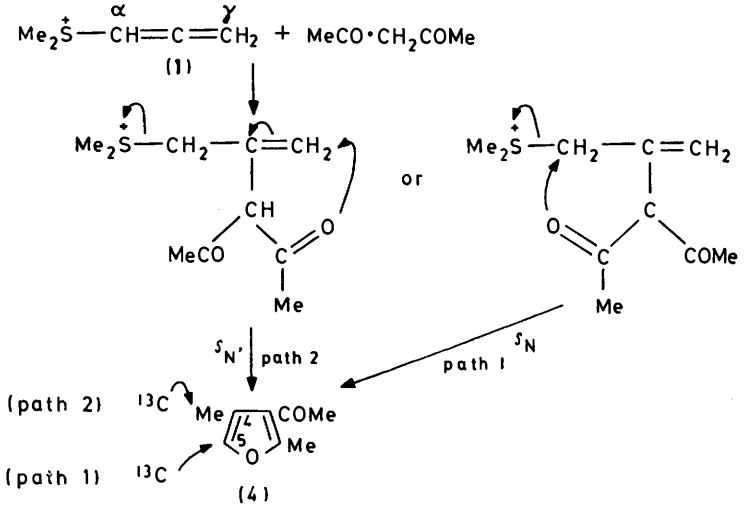
Addition–Intramolecular Substitution.—Reactions with enolate ions. We described earlier[4] the reactions of enolate ions to give trisubstituted furans by addition–cyclisation (Scheme 1). The reaction was shown to be applicable with R^1 = Ac, $ArSO_2$, or CO_2R. We have explored the extension of the scope of the synthesis to systems in which R^1 = CN, NO_2, or $\overset{+}{S}Me_2$.

Formation of the cyanofuran (3; R^1 = CN, R^2 = Ph) occurs in moderate yield and the structure was confirmed by hydrolysis to the known carboxylic acid (3; $R^1 = CO_2H$, R^2 = Ph). Attempted syntheses with ω-nitroacetophenone (2; $R^1 = NO_2$, R^2 = Ph) and with the sulphonium salt (2; $R^1 = Me_2\overset{+}{S}$, R^2 = Ph) were unsuccessful. The nitro-ketone was recovered under conditions in which the cyano-ketone gave cyanofuran; presumably the nitro-group renders the enolate anion so feebly nucleophilic that addition to the sulphonium salt is unacceptably slow. Reaction of ethoxide ion with the nitro-ketone was also a serious competing reaction, yielding considerable amounts of ethyl benzoate. In the case of the oxo-sulphonium salt (2; $R^1 = \overset{+}{S}Me_2$, R^2 = Ph), reaction in ethanolic sodium ethoxide at 80 °C gave degradation products of the oxo-sulphonium salt (Scheme 2), some of which had been obtained in an earlier study.[7]



SCHEME 2

An unresolved problem remaining from the previous study of furan syntheses[4] was the question of whether the α- or γ-carbon atom of the allenic sulphonium salt was attacked in the cyclisation step, *i.e.* whether this step was an S_N or S_N' (≡ addition–elimination) process.

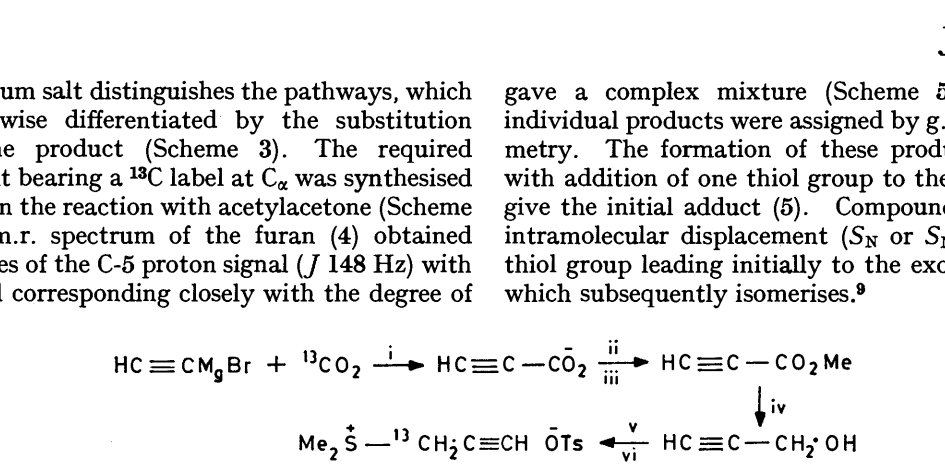


SCHEME 3

It had been shown earlier that when the α-carbon atom of the allenic group bore a methyl group, the exclusive path, presumably chosen for steric reasons, was S_N' (path 2), and that with a γ-phenyl group, cyclisation was exclusively S_N (path 1). For the unsubstituted allene system, a simple isotopic labelling experiment with

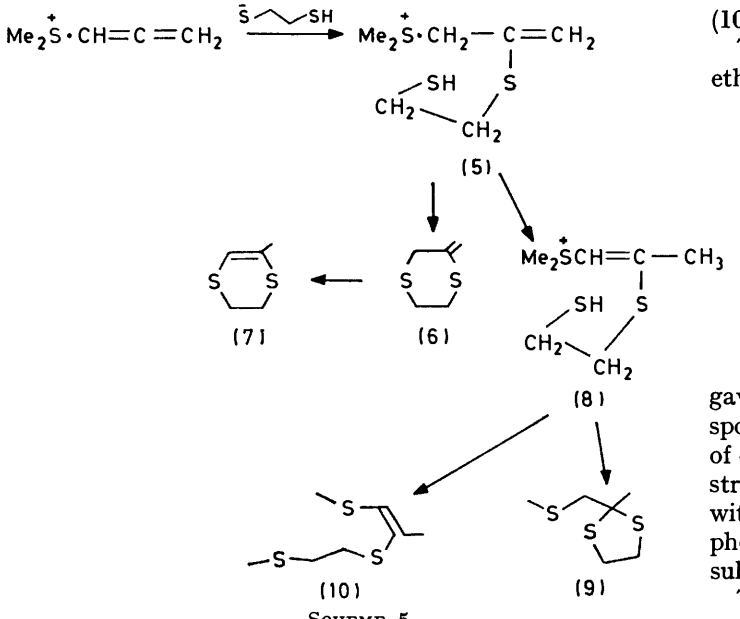
[3] B. M. Trost and L. S. Melvin, 'Sulphur Ylids,' Academic Press, New York, 1975.
[4] J. W. Batty, P. D. Howes, and C. J. M. Stirling, *J.C.S. Perkin I*, 1973, 65.
[5] G. D. Appleyard and C. J. M. Stirling, *J. Chem. Soc.* (*C*), 1969, 1904.
[6] J. W. Batty, P. D. Howes, and C. J. M. Stirling, *J.C.S. Perkin I*, 1973, 59.
[7] A. W. Johnson and R. T. Amel, *Tetrahedron Letters*, 1966, 819.

[α-^{13}C]sulphonium salt distinguishes the pathways, which are not otherwise differentiated by the substitution pattern of the product (Scheme 3). The required sulphonium salt bearing a ^{13}C label at C_α was synthesised (Scheme 4). In the reaction with acetylacetone (Scheme 3), the ^{1}H n.m.r. spectrum of the furan (4) obtained showed satellites of the C-5 proton signal (J 148 Hz) with a total integral corresponding closely with the degree of isotopic enrichment of the barium carbonate source. No satellite signals of the C-4 methyl group were observed. The ^{13}C n.m.r. spectrum showed powerful intensification of the signal 138.0 p.p.m. downfield from Me_4Si assigned to C-5. All other signals were comparable in intensity with those of the isotopically normal furan. It is concluded, therefore, that cyclisation occurs exclusively by S_N displacement (path 1) and that the rival S_N' (path 2) is adopted only when an α-substituent is present. We ascribe the change of mechanism to the steric effect of the α-substituent. In α-methylallyl halides, S_N reactions [8] of neutral and basic nucleophiles are retarded by factors of *ca.* 20—50 in comparison with the parent systems.



SCHEME 4 Reagents: i, tetrahydrofuran at −20 °C; ii, $KHSO_4$; iii, CH_2N_2; iv, $LiAlH_4$; v, TsCl–KOH–Et_2O; vi, MeS–MeCN

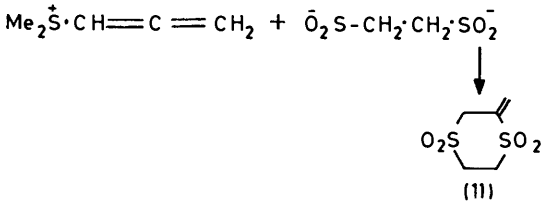
Reactions with bidentate sulphur nucleophiles. The reaction of the sulphonium salt (1) with ethanedithiol gave a complex mixture (Scheme 5); structures of individual products were assigned by g.l.c.–mass spectrometry. The formation of these products is consistent with addition of one thiol group to the allene system to give the initial adduct (5). Compound (7) results from intramolecular displacement (S_N or S_N') by the second thiol group leading initially to the exocyclic isomer (6), which subsequently isomerises.[9]



SCHEME 5

Isomerisation of the adduct (5) to the conjugated isomer (8) and intramolecular addition of the second thiol group at C_β leads to the dithiolan (9). Methylation of the thiol group of (8) by a sulphonium group (probably not intermolecularly [10]) leads to the acyclic tris-sulphide (10).

The reaction of the sulphonium salt (1) with disodium ethane-1,2-disulphinate and acetic acid as proton donor [11]



SCHEME 6

gave the cyclic bis-sulphone (11). This product corresponds to the presumed intermediate (6) in the addition of ethane-1,2-dithiol, but isomerisation to the endocyclic structure analogous to (7) does not occur, in conformity with previous observations that βγ-unsaturated sulphones are of lower free energy [9] than αβ-unsaturated sulphones.

The scope of the reaction between bidentate nucleophiles and allenic sulphonium salts is clearly wide, but the synthetic applicability is likely to be limited by the variety of competing reaction pathways.

Addition–Elimination Reactions with Monodentate Nucleophiles.—In this section we report on addition of cyanide and arenesulphinate ions to the allenic sulphonium salt (1). These nucleophiles have the common characteristic that when nucleophilic addition to the electrophilic allene has occurred, the remaining carbon–carbon double bond in the adduct (12) (Scheme 7) becomes electrophilic under the influence of the group Z. Further reaction of Z with (13) then occurs in which displacement of the sulphonium group, presumably by an S_N' pathway, leads to bis-adducts of type (13). Thus the sulphonium salt (1) with aqueous potassium cyanide

[8] E. L. Eliel, ' Steric Effects in Organic Chemistry,' ed. M. S. Newman, Wiley, New York, 1956, ch. 2.

[9] J. Hine and N. W. Fachskam, *J. Amer. Chem. Soc.*, 1973, **95**, 1179.

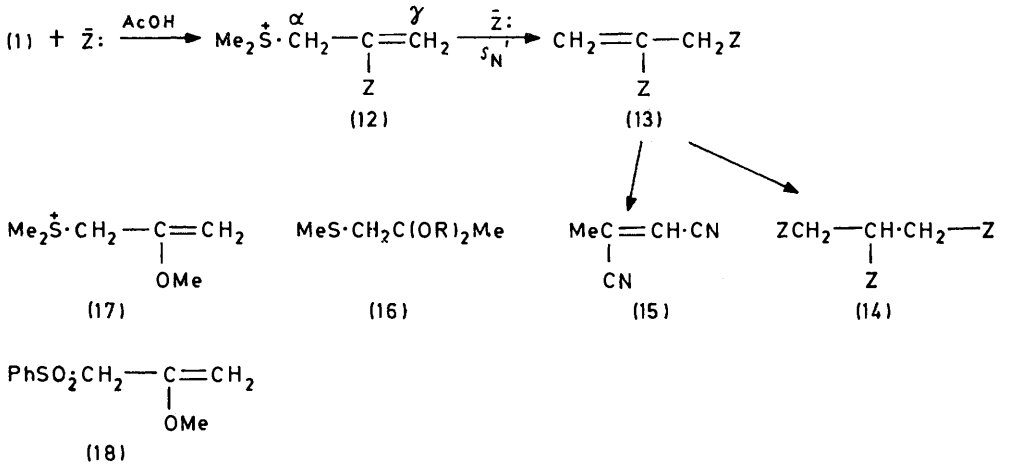
[10] L. Tenud, S. Farooq, J. Seibl, and A. Eschenmoser, *Helv. Chim. Acta*, 1970, **53**, 2059.

gave mixtures of the dinitriles (13; Z = CN) and (15) together with the trinitrile (14; Z = CN). The proportions varied with the reactant ratio and maximum yields obtained were 33% of (13) and (15) together with 42% of (14). A proton donor such as acetic acid was essential to obtain cyano-adducts. In alcohols, in the absence of proton donors other than the solvent, or even with phenol present, the major product was the acetal sulphide (16) resulting from addition–dealkylation reactions of alkoxide ion [6] generated by protonation of the ylide produced by nucleophilic addition.

With benzenesulphinate ion as nucleophile and acetic acid as proton donor, the products again varied with the reactant ratio. When this was 1 : 1, the principal product was the bis-sulphone (13; Z = $PhSO_2$) and the tris-sulphone (14; Z = $PhSO_2$) was obtained in yields up to 72% as the ratio of sulphinate to sulphonium salt was increased. No conjugated bis-sulphone of type (15) was obtained although it has been obtained by another route.[11] This again is consistent with the instability of αβ-unsaturated sulphones. Attempts were made to isolate the initial adduct (12; Z = SO_2Ph), but even when very small sulphinate–sulphonium salt ratios were used, low yields of disulphone (13) were obtained together with unchanged sulphonium salt. The initial adduct (12) must be more rapidly attacked by sulphinate ion than the starting sulphonium salt (1).

Formation of adducts of type (13) is consistent with direct displacement of sulphide by allylic substitution in (12) or with an S_N' process occurring by addition at C_γ and subsequent βα-elimination. Elimination of sulphonium groups from carbanions is extremely rapid,[12] whereas leaving group ability of sulphonium groups in S_N processes is rather poor. On the basis of this experience, we assign the S_N' mechanism to the conversion of (12) into (13) but we have strengthened this conclusion in two ways: first, the methoxy-sulphonium salt (17) as a model for the sulphone-sulphonium salt (12; Z = SO_2Ph) was treated with sodium benzenesulphinate under the conditions of the conversion of (1) into (13; Z = SO_2Ph). Conversion into the methoxy-sulphone (18) was much slower than for (1) into (13; Z = $PhSO_2$). In the sulphonium salt (17), nucleophilic addition to the carbon–carbon double bond is precluded by the absence of an activating group, and only the direct S_N pathway is available.

Secondly, the sulphonium salt (1) enriched at C_α with ^{13}C was treated with benzenesulphinate ion under the usual conditions. The ^1H n.m.r. spectrum of the product (13) clearly showed satellite absorptions, due to ^{13}C–H coupling, of the signals for the protons at *both* C_α and C_γ. Integrals showed that the proportion of ^{13}C at each site was the same within 5%. In ^{13}C n.m.r. spectra, intensification of signals for *both* C_α and C_γ in (13; Z = $PhSO_2$) to comparable extents was apparent. The results suggest that C_α and C_γ become equivalent, and we suggest that this equilibration occurs by rapid elimination–addition *via* the S_N' pathway. In this connection, β-disulphones have been shown to exchange rapidly with sulphinates in what is evidently an elimination–addition process.[13]



SCHEME 7

EXPERIMENTAL

Extractions, unless otherwise stated, were carried out with dichloromethane, and extracts were dried over Na_2SO_4. Light petroleum refers to the fraction of b.p. 40—60°. $Ba^{13}CO_3$ was supplied by Prochem Ltd. Dimethylprop-2-ynylsulphonium bromide was prepared as previously described.[5] ^{13}C N.m.r. spectra were obtained with a JEOL FX60 instrument.

*Dimethylprop-2-ynylsulphonium Toluene-*p*-sulphonate.*—Prop-2-yn-1-ol in tetrahydrofuran was treated with toluene-*p*-sulphonyl chloride (1.25 equiv.) and to the solution at

[11] C. J. M. Stirling, *J. Chem. Soc.*, 1964, 5856.
[12] D. R. Marshall, P. J. Thomas, and C. J. M. Stirling, *J.C.S. Chem. Comm.*, 1975, 940.
[13] W. E. Truce and E. Wellisch, *J. Amer. Chem. Soc.*, 1952, **74**, 5177.

−10 °C was added powdered potassium hydroxide (2 equiv.) with stirring. After 1 h, saturated brine was added; extraction with dichloromethane gave crude prop-2-ynyl toluene-*p*-sulphonate, which was treated with dimethyl sulphide (2 molar proportions) in acetonitrile. The mixture was stirred for 16 h in a darkened flask; addition of ether gave the *salt* (80%), m.p. 135° (from ethanol–ether) (Found: C, 53.1; H, 6.2. $C_{12}H_{16}O_3S_2$ requires C, 53.0; H, 6.5%).

Dimethyl[1-^{13}C]*prop-2-ynylsulphonium Toluene*-p-*sulphonate.*—(a) [1-^{13}C]*Prop-2-yn-1-ol.* The literature directions [14] for the preparation of ethynylmagnesium bromide were followed except that ethylmagnesium bromide was added to the solution of acetylene in tetrahydrofuran at −10 °C. [^{13}C]Carbon dioxide was liberated by warming an intimate mixture of $Ba^{13}CO_3$ (10% enriched) and potassium hydrogen sulphate at *ca.* 200 °C on a vacuum line, and the liberated gas was drawn through three bubblers containing a two-molar excess of ethynylmagnesium bromide. The ethereal suspensions were combined and an excess of saturated aqueous potassium hydrogen sulphate was cautiously added with stirring. The ethereal solution was titrated against standard aqueous sodium hydroxide and then treated with ethereal diazomethane standardised by titration against benzoic acid. The resulting solution of methyl propiolate was reduced with standardised (I_2) ethereal 0.3M-lithium aluminium hydride (0.5 mol per mol) in the usual manner. G.l.c. analysis of the ethereal extracts of the reaction mixture showed that prop-2-yn-1-ol was obtained in *ca.* 80% yield, and the extracts were concentrated by fractional distillation. The residue in tetrahydrofuran was treated as for the isotopically normal alcohol to give dimethyl[1-^{13}C]prop-2-ynylsulphonium toluene-*p*-sulphonate (60%), m.p. 135° (from ethanol–ether) alone or mixed with an isotopically normal specimen, τ (D_2O) 2.3—2.8 (4 H, m), 5.85 (2 H, d, J_{HH} 3, J_{CH} 144 Hz), 6.85 (1 H, t, *J* 3 Hz), 7.20 (6 H, s), and 7.70 (3 H, s).

Reactions of Sulphonium Salts with Enolate Ions.—(a) *From ω-cyanoacetophenone.* Dimethylprop-2-ynylsulphonium toluene-*p*-sulphonate (2.7 g, 0.01 mol) and ω-cyanoacetophenone [15] (1.45 g, 0.01 mol) in ethanol (50 ml) were treated with ethanolic sodium ethoxide (0.03M; 0.01 mol). The mixture was stirred (under N_2) for 7 days and evaporated. Extraction of the residue with dichloromethane and distillation gave *4-methyl-2-phenylfuran-3-carbonitrile* (1.15 g, 60%), b.p. 165° at 18 mmHg, m.p. 64° (from cyclohexane) (Found: C, 78.6; H, 4.8; N, 7.4. $C_{12}H_9NO$ requires C, 78.7; H, 4.9; N, 7.6%), τ ($CDCl_3$) 1.8—2.7 (5 H, m), 2.8 (1 H, s), and 7.9 (3 H, s), $\nu_{C\equiv N}$ str. 2 230 cm^{-1}.

Hydrolysis of the nitrile with boiling aqueous ethanolic sodium hydroxide gave 4-methyl-2-phenyl-3-furoic acid (41%), m.p. 159° (from EtOH–H_2O) (Found: C, 71.5; H, 4.8. Calc. for $C_{12}H_{10}O_3$: C, 71.3; H, 4.9%) (lit.,[16] m.p. 161°), τ ($CDCl_3$) −2.3 (1 H, s), 1.7—2.6 (5 H, m), 2.75 (1 H, s), and 7.85 (3 H, s).

(b) *From dimethylphenacylsulphonium bromide.* The sulphonium toluene-*p*-sulphonate (1) (0.01 mol), and dimethylphenacylsulphonium bromide [17] (0.01 mol) were heated under reflux with ethanolic 0.3M-sodium ethoxide (0.02 mol) until the solution was neutral (24 h). Evaporation and extraction of the residue with dichloromethane gave a residue (1.505 g) which, on g.l.c., gave ethyl benzoate (6%), acetophenone (11%), ethyl phenylacetate (4%), and methyl phenacyl sulphide [18] (22%). Each component was identified by g.l.c., i.r., and n.m.r. comparison with an authentic specimen.

The residue (0.637 g), on crystallisation from ethanol, gave *trans*-1,2,3-tribenzoylcyclopropane (0.411 g, 35%), m.p. 220° alone or mixed with authentic *trans*-1,2,3-tribenzoylcyclopropane prepared [19] (97%) by treatment of dimethylphenacylsulphonium bromide with triethylamine and of the resulting ylide with phenacyl bromide (Found: C, 80.2; H, 5.15. $C_{24}H_{18}O_3$ requires C, 81.5; H, 5.1%).

(c) *From ω-nitroacetophenone.* Ethanolic sodium ethoxide [from sodium (0.14 g) and ethanol (25 ml)] was added to ω-nitroacetophenone [20] (1 g) in ethanol (25 ml) and the suspension was added to the sulphonium bromide (1) in ethanol (25 ml). The mixture was boiled under reflux for 3 h and evaporated. Extraction of the residue with cold methanol left material (0.12 g) which was soluble in water, and the aqueous solution on acidification gave ω-nitroacetophenone, m.p. and mixed m.p. 104—105°. The methanolic extract was evaporated and ethyl benzoate (0.281 g) was isolated by preparative t.l.c. and distillation (b.p. 95° at 45 mmHg; i.r. and n.m.r. data identical with those of an authentic specimen). No other component of the mixture was mobile under the conditions used for t.l.c.

(d) *With acetylacetone and dimethyl*[1-^{13}C]*prop-2-ynylsulphonium toluene*-p-*sulphonate.* The ^{13}C-labelled sulphonium salt (5.6 mmol) in ethanol (15 ml) was added to acetylacetone (5.6 mmol) and sodium ethoxide (5.6 mmol) in ethanol (11 ml). The mixture was boiled under reflux for 6 h and ethanol was removed through a helix-packed column. Ether (20 ml) was added to the residue and after filtration, distillation of the filtrate gave 3-acetyl-2,4-dimethylfuran (0.50 g, 66%), b.p. 86° at 11 mmHg, n_D^{18} 1.4940 (lit.,[4] b.p. 83° at 11 mmHg; n_D^{20} 1.4935), τ ($CDCl_3$) 3.0 (1 H, q, J_{HH} 1.1, J_{CH} 199 Hz), 7.6 (3 H, s), 7.73 (3 H, q, *J* 1 Hz), and 7.91 (3 H, q, *J* 1 Hz), δ_C ($CDCl_3$) 10.78, 15.33, 30.93, 120.72, 122.54, 138.0, 159.32, and 194.92. The ^{13}C signal at 138.0 assigned [21] to C-5 was considerably enhanced relative to isotopically normal material. All other signals, including that at 15.33 assigned to the 4-Me, were of the same relative intensity.

Reactions of Dimethylprop-2-ynylsulphonium Bromide with Bidentate Sulphur Nucleophiles.—(a) *Ethane-1,2-dithiol.* The dithiol (50 mmol) was added to sodium ethoxide (50 mmol) in ethanol (100 ml). The solution was purged with N_2 and the sulphonium salt (50 mmol) in ethanol (100 ml) was added. The mixture was boiled under reflux for 8 h and ethanol was distilled off through a helix-packed column. Ether was added to the residue and sodium bromide was filtered off. The filtrate on distillation gave two fractions: (*a*) b.p. 70—160° at 12 mmHg, and (*b*) b.p. 120—126° at 0.2 mmHg (total 5.18 g).

[14] L. Skattebøl, E. R. H. Jones, and M. C. Whiting, *Org. Synth.*, 1959, **39**, 56.
[15] S. Gabriel and G. Eschenbach, *Ber.*, 1897, **30**, 1126.
[16] J. C. Hanson, J. H. C. Nayler, T. Taylor, and P. H. Gore, *J. Chem. Soc.*, 1965, 5984.
[17] K. W. Ratts and A. N. Yao, *J. Org. Chem.*, 1966, **31**, 1185.
[18] V. Prelog, V. Hahn, H. Brauchli, and H. C. Beyerman, *Helv. Chim. Acta*, 1944, **27**, 1209.
[19] A. W. Johnson and R. T. Amel, *J. Org. Chem.*, 1969, **34**, 1240.
[20] L. Long and H. D. Troutman, *J. Amer. Chem. Soc.*, 1949, **71**, 2469.
[21] G. C. Levy and G. L. Nelson, ' Carbon-13 Nuclear Magnetic Resonance for Chemists,' Wiley, New York, 1972.

The two fractions showed a total of seven components on g.l.c. analysis (Apiezon L; 180 °C), and the structural assignments made below in decreasing order of concentration in the mixture are based on mass spectra (A.E.I. MS20 coupled to the Pye 104 chromatograph) and/or comparisons of retention times with those of authentic specimens. Yields are calculated on the basis of assigned structures.

The most abundant component, sixth in order of retention, showed *m/e* 180 (parent) and a high intensity peak at *m/e* 119, consistent with the ethylene dithioacetal (9) of (methylthio)acetone (23%). Fragmentation producing the ion $MeC^+(S_2[CH_2]_2)$ is of the type extensively studied by Breslow [22] and his collaborators.

Component 2 (22%) was tentatively identified as 1,2-bismethylthioethane from the identity of its retention time with that of an authentic specimen prepared by methylation of ethane-1,2-dithiol with methyl iodide and sodium methoxide in methanol (79% yield); b.p. 67° at 12 mmHg, n_D^{20} 1.5232 (lit.,[23] b.p. 182°, n_D^{25} 1.5260), τ (CCl_4) 7.2 (2 H, s) and 8.0 (3 H, s).

Component 3, *m/e* 132 (parent) and a prominent fragment at *m/e* 59; τ (CCl_4) 3.95 (1 H, s), 6.7 (4 H, broad s), and 7.8 (3 H, s), was identified as 2,3-dihydro-5-methyl-1,4-dithiin (7) (16%).

Component 7 showed *m/e* 194 (parent), 75 (base), 147, 119, and 61, consistent with 1-methylthio-2-[(2-methylthio)ethylthio]propene (10) (7%).

When the reaction was repeated at one fifth of the concentration to encourage intra- *versus* inter-molecular reaction, the amount of component 3 was increased relative to that of component 7.

(b) *Ethane-1,2-disulphinic acid.* Ethane-1,2-dithiol (7.0 g, 74 mmol) in dichloromethane (12.5 ml) was treated with chlorine (5.3 g, 74 mmol). A white polymeric material (4.5 g) was formed and a portion (3.4 g) in dichloromethane (22.5 ml) was treated with acetic acid (4.4 g, 73 mmol) and chlorine (7.9 g, 111 mmol). After 2 h, evaporation gave ethane-1,2-disulphinyl chloride (3.94 g, 65%), m.p. 61° (lit.,[24] 62.5—63.5°). The sulphinyl chloride (3.9 g, 20 mmol) was hydrolysed with aqueous 7% sodium hydrogen carbonate (80 mmol) and to the solution were successively added acetic acid (1.2 g, 20 mmol) and dimethylprop-2-ynylsulphonium bromide (3.62 g, 20 mmol) in water (40 ml). After 19 h, the mixture was continuously extracted with dichloromethane to give 2-methylenedithian 1,1,4,4-tetraoxide (11) (1.96 g, 50%), m.p. 248° (lit.,[25] 250—251°) (Found: C, 30.6; H, 4.1. Calc. for $C_5H_8O_4S_2$: C, 30.6; H, 4.3%), τ [$(CD_3)_2SO$] 3.78 (2 H, broad s), 5.30 (2 H, s), and 6.30 (4 H, m).

Reaction of Cyanide Ion with Dimethylprop-2-ynylsulphonium Bromide.—(a) *Without proton donor.* The dimethylsulphonium salt (10 mmol) in methanol (50 ml) was treated with sodium cyanide (30 mmol) and the mixture was refluxed for 3 h. Methanol was distilled off and the black residue was extracted to give material of b.p. 71° at 14 mmHg (0.61 g), shown by ^1H n.m.r. spectroscopy and g.l.c. (Carbowax 20M; 125 °C) to be mainly 2,2-dimethoxy-1-methylthiopropane.[6] I.r. spectroscopy showed that a minor component contained a nitrile group.

(b) *With proton donor.* (i) The previous experiment was repeated with ethanol instead of methanol as solvent and with phenol (10 mmol) as proton donor. The major product (^1H n.m.r. and g.l.c.) was 2,2-diethoxy-1-methylthiopropane.[6]

(ii) The experiment was repeated with the sulphonium salt (20 mmol) in water (25 ml) containing acetic acid (20 mmol). Sodium cyanide (40 mmol) in water (25 ml) was added and the mixture became hot with separation of tar. After 30 min, extraction and distillation of the residue from evaporation of the extracts yielded first material (0.09 g, 5%) of b.p. 42 at 0.1 mmHg whose ^1H n.m.r. spectrum suggested that it was a mixture of (*Z*)- and (*E*)-propene-1,2-dicarbonitrile and propene-2,3-dicarbonitrile. The second fraction (0.65 g, 42%), b.p. 158° at 0.1 mmHg, m.p. 51—52° (from ethanol–water) was *propane-1,2,3-tricarbonitrile* (Found: C, 60.2; H, 4.25. $C_6H_5N_3$ requires C, 60.5; H, 4.2%), $\nu_{C\equiv N\ str.}$ 2 260 cm^{-1}, τ [$(CD_3)_2SO$] 6.2 (1 H, q, *J* 7 Hz) and 6.9 (4 H, d, *J* 7 Hz).

When the reaction was repeated below 20 °C the first fraction (33%) was mainly propene-2,3-dicarbonitrile, $\nu_{C\equiv N}$ 2 240 and 2 260 cm^{-1}, τ ($CDCl_3$) 3.7 (2 H, t, *J* 1 Hz), 6.5 (2 H, t, *J* 1 Hz); propane-1,2,3-tricarbonitrile (15%), m.p. 52°, was also isolated.

Reactions of Sodium Benzenesulphinate.—(a) *With dimethylprop-2-ynylsulphonium bromide.* The sulphonium salt (10 mmol) in methanol (15 ml) containing acetic acid (10 mmol) was treated with sodium benzenesulphinate (30 mmol). After 30 min, filtration gave 1,2,3-trisphenylsulphonylpropane (72%), m.p. and mixed m.p. 239° (lit.,[11] 242°) (Found: C, 54.5; H, 4.7; S, 20.8. Calc. for $C_{21}H_{20}O_6S_3$: C, 54.3; H, 4.3; S, 20.7%), $\nu_{SO_2\ str.}$ 1 310 and 1 150 cm^{-1}; τ ($CF_3{\cdot}CO_2H$) 2.0—2.5 (15 H, m), 5.6 (1 H, m), and 6.05 (4 H, d, *J* 6 Hz). Addition of water to the filtrate, extraction, and addition of light petroleum to the residue from evaporation, gave 2,3-bisphenylsulphonylpropene (15%), m.p. and mixed m.p. 127° (lit.,[11] 126—128°).

When the reaction was repeated with 11 mmol of sodium benzenesulphinate, the products were 2,3-bisphenylsulphonylpropene (76%) and the tris-sulphone (9%).

(b) *With (2-methoxyprop-2-enyl)dimethylsulphonium bromide.* The sulphonium salt [6] (10 mmol) in methanol (10 ml) containing acetic acid (10 mmol) was treated with sodium benzenesulphinate (11 mmol). After 3 h, addition of water and extraction gave 2-methoxy-1-phenylsulphonylpropene (31%), m.p. and mixed m.p. 64° (from di-isopropyl ether) (lit.,[26] 65—66°). The yield of sulphone after 16 h was 72%.

(c) *With dimethyl[1-^{13}C]prop-2-ynylsulphonium toluene-p-sulphonate.* The sulphonium salt (3.7 mmol) in methanol (10 ml) was treated with acetic acid (4 mmol) and then sodium benzenesulphinate (4 mmol). After 3 h, the mixture was filtered. The residue (0.046 g) was 1,2,3-trisphenylsulphonylpropane, m.p. and mixed m.p. 234°. Water was added to the filtrate and extraction with dichloromethane gave 2,3-bisphenylsulphonylpropene (100 mg), m.p. and mixed m.p. 125°, τ (CCl_4) 2.2—2.6 (10 H, m), 3.45 (1 H, d, J_{HH} 0.4, J_{CH} 167 Hz), 3.60 (1 H, d, J_{HH} 0.4, J_{CH} 166 Hz), and 6.1 (2 H, d, *J* 0.4, J_{CH} 140 Hz), δ_C 54.19, 128.52, 129.43, 131.25, 134.20, 137.87, and 139.56. The signals at 54.19 and at 131.25 assigned to the α- and γ-carbon atoms were considerably more intense than in the

[22] R. Breslow and P. C. Scholl, *J. Amer. Chem. Soc.*, 1971, **93**, 2331.
[23] D. M. Burness, *J. Org. Chem.*, 1959, **24**, 849.
[24] I. B. Douglass, B. S. Farah, and E. G. Thomas, *J. Org. Chem.*, 1961, **26**, 1996.
[25] R. C. Fuson and A. J. Speziale, *J. Amer. Chem. Soc.*, 1949, **71**, 1582.
[26] C. J. M. Stirling, *J. Chem. Soc.*, 1964, 5863.

isotopically normal compound. Other signals were of the same relative intensities.

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