Elimination and Addition Reactions. Part 29.[1,2] Ylide Rearrangement in Adducts from Allenic Sulphonium Salts and Malonic Esters

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Addition of malonic esters to allenic sulphonium salts gives isolable allylic adducts. When the adducts are treated with ethanolic sodium ethoxide they undergo 2,3-sigmatropic rearrangement of the derived ylide. When the central malonyl carbon atom bears an alkyl group, rearrangement occurs directly, but when this atom bears a hydrogen atom, ylide rearrangement is preceded by a 1,3-prototropic shift and occurs exclusively by way of the conjugated tautomer.

Rearrangement in the conjugated tautomer is regiospecific and occurs entirely through an *S*-methyl rather than an *S*-ethyl group. A by-product of the addition–rearrangement sequence appears to be derived from the competitive addition of alkoxide ion followed by displacement of the sulphonium group by malonate ion

When reactions were carried out in the probe of an n.m.r. spectrometer no emission signals were detected, showing that the alternative (Stevens) rearrangement pathway is probably unimportant.

NUCLEOPHILIC addition to allenic sulphonium salts has been shown to occur readily with a variety of oxygen,[3,4] sulphur,[4] nitrogen,[4] and carbon nucleophiles.[1,5,6] Sulphonium is a versatile functional group:[7] not only does it render an adjacent carbon–carbon double bond susceptible to nucleophilic addition, but it also acts as a leaving group, so that addition may be followed by inter-[1,4] or intra-molecular substitution. The latter leads to ring formation.[5,6] In this paper we report on the addition of malonate esters to allenic sulphonium salts and the rearrangements which occur in reactions of the adducts with bases.

Treatment of the sulphonium salt (1a) with diethyl malonate and an equimolecular proportion of ethanolic sodium ethoxide gave the ester sulphide (6a). The pathway to this product is not immediately obvious and in particular it was important to rule out the alternative structure (10). This latter structure would be the result of formation of an initial adduct (4a) of the type characterised[3,4] in earlier studies of additions to allenic sulphonium salts. Subsequent deprotonation of this adduct could generate the anion (4b), and the deceptively simple transfer of a methyl group from the sulphonium group to the carbanion centre either inter- or intra-molecularly would lead to (10). Because we initially believed the product to have structure (10) we carried out crossover experiments to determine whether the apparent alkyl transfer was inter- or intra-molecular. A mixture of salts (1a and b) was treated similarly and g.l.c. analysis of the products showed conclusively that there was no scrambling of ethyl and methyl groups. This suggested that the reaction was entirely intra-molecular. In that case, however, conversion of the anion of (4a) to (10) would require interpretation as an example of endocyclic nucleophilic substitution *via* a non-linear transition state. Eschenmoser and his collaborators[8] have shown that this type of transition state is disfavoured.

The n.m.r. spectrum did not provide an unequivocal distinction between structures (6a) and (10); it consisted of a series of singlets (apart from the ethoxy-multiplets) with a slight broadening of the *C*-methyl signal, a feature which, however, rendered structure (10) questionable. We then resorted to a chemical method of structure assignment. Oxidation of the product from the salt (1a) gave the sulphone corresponding to (6a) or (10) (SO_2 for S), which on catalytic hydrogenation gave the saturated sulphone ester (9). This was conclusively shown by n.m.r. spectroscopy to possess an isopropyl group and hence to be derived from (6a) and not (10).

In a similar way, the diethyl salt (1b) and the tetra-

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[3] G. D. Appleyard and C. J. M. Stirling, *J. Chem. Soc.* (*C*), 1969, 1904.
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[6] P. D. Howes and C. J. M. Stirling, *Org. Synth.*, 1973, **53**, 1.
[7] C. J. M. Stirling, in ' Organo-sulphur Chemistry,' ed. S. Oae, Plenum Press, New York, 1976.
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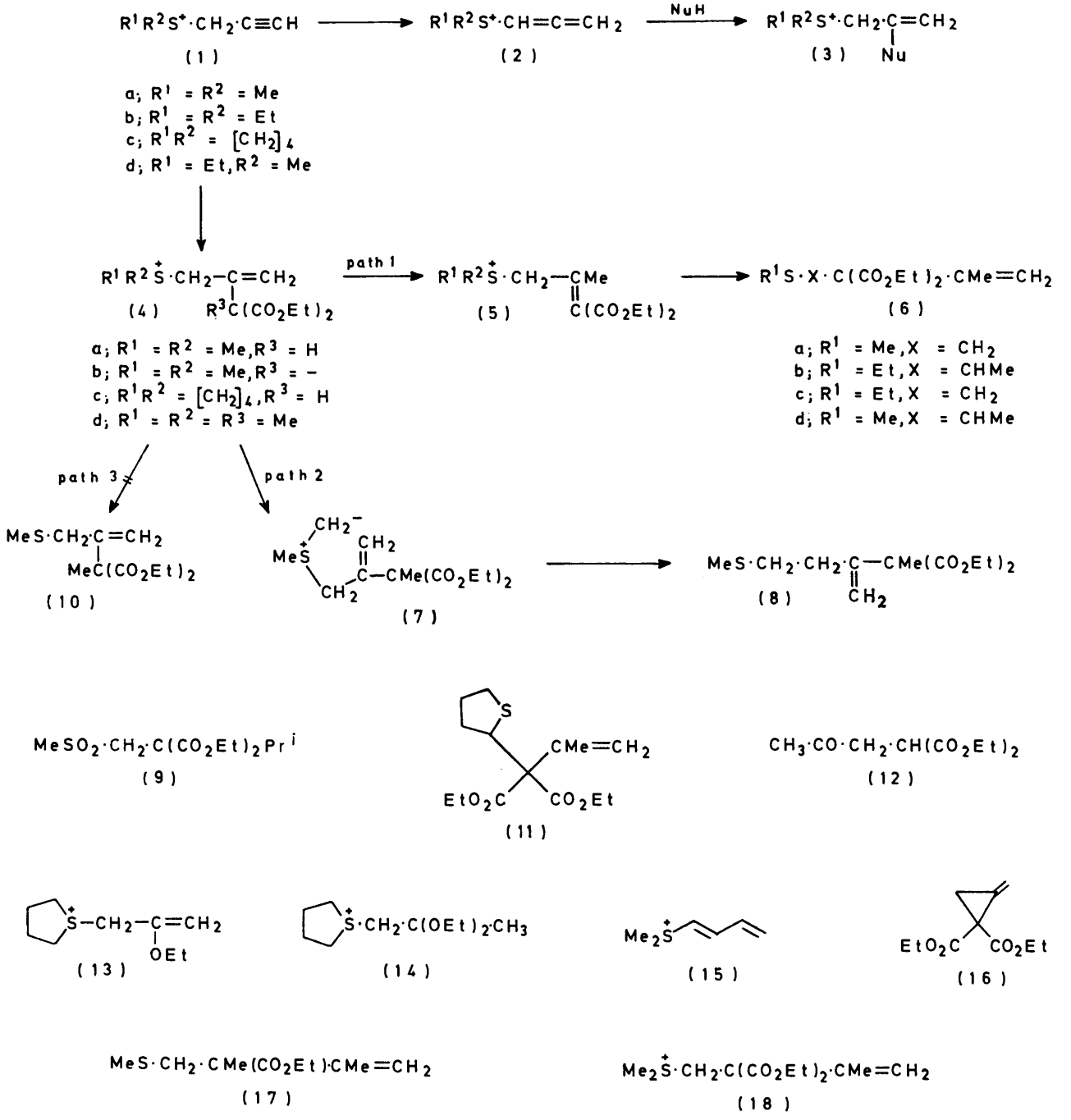
hydrothiophenium salt (1c) gave the corresponding products (6b) and (11).

In the case of the salt (1c), the sulphide ester (11) was a minor (17%) product when treatment of the adduct with base was carried out *in situ*. The main product



was diethyl acetonylmalonate (12) (49%). This ester appears to result from preferential addition of ethoxide ion to the allenic sulphonium salt derived from the salt (1c), with formation of an equilibrium mixture of the vinyl ether (13) and the acetal (14). Displacement of the sulphonium group in either of these compounds by nucleophilic attack of malonate ion and subsequent hydrolysis of the acetal or vinyl ether function yields the oxo-ester (12). Two observations are consistent with this postulate: (i) tetrahydrothiophen (59%) is formed concurrently in the reaction and (ii) when the *pre-formed* adduct (4c) is treated with ethanolic sodium ethoxide, the yield of the sulphide ester (11) rises to 30%.

The sequence of reactions leading from the acetylenic salts (1) can be interpreted as involving initial prototropy to form the allenes (2), a process directly observable

spectroscopically.[3] This is followed by formation of the adducts (4) with malonic ester. The adducts (4a, c, and d) may be isolated crystalline from additions catalysed by sodium hydride in the malonic ester as solvent. In solutions of ethanolic sodium ethoxide, deprotonation at the central malonyl carbon atom subsequently occurs in the adducts (4a—c), as these are fairly strong acids; the pK_a (10.5) of the adduct (4a) was determined by titration. Re-protonation at the methylene group gives the isomer (5) in which the carbon–carbon double bond is now conjugated with the alkoxycarbonyl groups. This product (5), like (4), is an allylic sulphonium salt and undergoes 2,3-sigmatropic rearrangement (path 1) to give the sulphide (6). Such 2,3-sigmatropic rearrangement of sulphonium ylides is well established,[9] and is a further manifestation of the versatility of the sulphonium group. The ready deprotonation of the sulphonium group [10] is the necessary prelude to the rearrangement.

Sigmatropic rearrangements of allenic sulphonium salts giving $\gamma\delta$-acetylenic sulphides have been described.[11] In the present systems, addition to the allenic group is much more rapid than sigmatropic rearrangement. Further, in relation to the present work, Kresze and his collaborators have shown [12] that addition of simple nucleophiles such as methoxide ion to butadienylsulphonium salts (15) initially gives $\beta\gamma$-unsaturated sulphonium salts, which undergo 2,3-sigmatropic rearrangement. In these cases, sigmatropic rearrangement prior to addition is not a potentially competing reaction. When the nucleophile is malonate ion, addition is followed by an S_N' process leading to vinylcyclopropane derivatives [13] in a manner mechanistically similar to reactions described in an earlier paper.[1] Addition of malonate ion to alkenylsulphonium salts yields cyclopropane derivatives by subsequent intramolecular nucleophilic displacement of the sulphonium group.[14] Formation of cyclopropanes by intramolecular displacement in malonyl derivatives occurs extremely rapidly,[15] but no cyclisation of the ion (4b) to the ester (16) was observed in the present work. Such cyclisation is presumably disfavoured by the additional ring strain [16] of *ca.* 13 kcal mol^{-1} involved in the formation of a methylenecyclopropane.

It was of interest to examine the regiospecificity of the 2,3-sigmatropic rearrangement, and to this end the sulphonium salt (1d) was treated with diethyl malonate and ethanolic sodium ethoxide. The product was the sulphide ester (6c) resulting from deprotonation of the *S*-methyl group in preference to the *S*-ethyl group. This is to be expected for formation of a carbanion in which negative charge is localised on carbon [17] in contrast to the anions derived from carbon acids such as nitroalkanes where the negative charge is extensively delocalised.

We have suggested that a 1,3-prototropic shift in the adduct precedes 2,3-sigmatropic rearrangement, and in this connection we examined the addition of diethyl methylmalonate to the sulphonium salt (1a). In this case a prototropic shift in the adduct (4d) is blocked by the *C*-methyl group, and the product (8) is formed by 2,3-sigmatropic shift in the initial adduct (path 2). In reactions with pre-formed adduct, a minor (*ca.* 15%) product is tentatively assigned structure (17), which is believed to arise from a retro-Claisen reaction of the adduct with subsequent prototropic and ylide rearrangements *via* path 1.

These results show that in these sulphonium salts, 2,3-sigmatropic rearrangements may have different termini, and that path 1 is preferred except when blocked by a substituent on the central malonyl carbon atom. The results also further support the disfavourment of endocyclic substitution. None of the product of this path (3) is found in any of these reactions.

The Stevens 1,2-rearrangement *via* radical intermediates is an alternative pathway sometimes observed [18] to occur in parallel with 2,3-sigmatropic rearrangement. Reactions of the salt (1a) with diethyl malonate and with diethyl methylmalonate have been run in the probe of an n.m.r. spectrometer. Neither emission nor intensification of absorption spectra were observed as a result of CIDNP effects in products derived from radical intermediates.[19] We tentatively conclude that the Stevens rearrangement is not a favoured pathway to the observed products of these reactions.

EXPERIMENTAL

Extractions, unless otherwise stated, were performed with dichloromethane, and extracts were dried over Na_2SO_4. Light petroleum refers to the fraction of b.p. 40—60 °C.

Dimethyl-[3] and diethyl-[3]prop-2-ynylsulphonium and 1-(prop-2-ynyl)tetrahydrothiophenium [4] bromide were prepared as previously described.

Sulphonium Salt–Malonate Adducts.—In a typical procedure, a 50% suspension of sodium hydride in oil suspension (0.2 g) was washed successively with light petroleum and anhydrous ether. The oil-free hydride was treated with diethyl malonate (4 ml) and the resulting suspension was added with stirring and cooling to a suspension of the sulphonium salt (5 g) in diethyl malonate (6 ml) and ethanol (1 ml). After 1 h the mixture had set solid, and the product

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[10] Ref. 9, pp. 24—29.
[11] G. Pourcelot, L. Veniard, and P. Cadiot, *Bull. Soc. chim. France*, 1975, 1275.
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[18] Ref. 10, p. 111.
[19] D. Bethell and M. R. Brinkmann, *Adv. Phys. Org. Chem.*, 1973, **10**, 53.

was washed with anhydrous ether and then suspended in chloroform. Filtration removed sodium bromide, and the filtrate was evaporated below 40 °C. The residue was triturated with ethyl acetate and recrystallised from ethanol–ether.

2-(*Bisethoxycarbonylmethyl*)*allyl*(*dimethyl*)*sulphonium bromide* (4a) (59%) from dimethylprop-2-ynylsulphonium bromide had m.p. 83° (Found: C, 42.2; H, 6.15. $C_{12}H_{21}BrO_4S$ requires C, 42.2; H, 6.15%), τ(D_2O) 4.20 (1 H, s), 4.35 (1 H, s), 5.7 (6 H, q + s), 7.05 (6 H, s), and 8.7 (6 H, t); δ_C (D_2O) 14.32, 25.91, 49.87, 57.94, 64.97, 78.12, 130.20, and 170.31.

The *salt* (4c) (43%) from prop-2-ynyltetrahydrothiophenium bromide had m.p. 109° (Found: C, 45.6; H, 6.1. $C_{14}H_{23}BrO_4S$ requires C, 45.8; H, 6.3%), τ(D_2O) 4.25 (1 H, s), 4.4 (1 H, s), 5.75 (6 H, q + s), 6.5 (4 H, m), 7.6 (4 H, m), and 8.7 (6 H, t).

The *salt* (4d) (37%) from dimethylprop-2-ynylsulphonium bromide and diethyl methylmalonate had m.p. 101° (Found: C, 43.8; H, 6.3. $C_{13}H_{23}BrO_4S$ requires C, 44.0; H, 6.45%); τ(D_2O) 5.2 (2 H, s), 5.75 (4 H, q), 6.6 (6 H, s), 8.4 (3 H, s), and 8.7 (6 H, t).

The pK_a value of the adduct (4a) was determined by titration of an aqueous solution with aqueous sodium hydroxide, the value being read from the titration curve in the pH range 8—12.

Reactions with Diethyl Malonate.—(a) *With dimethylprop-2-ynylsulphonium bromide.* The sulphonium salt (10 mmol) in ethanol (75 ml) was added to a mixture of diethyl malonate (20 mmol) and sodium ethoxide (10 mmol) in ethanol (65 ml). The mixture was boiled under N_2 for 6 h and most of the ethanol was distilled off. Addition of water to the residue and extraction gave diethyl malonate (43%), b.p. 91° at 10 mmHg, and *diethyl isopropenyl*(*methylthiomethyl*)*malonate* (6a) (74%), b.p. 157° at 15 mmHg, n_D^{20} 1.474 0 (Found: C, 55.8; H, 7.7. $C_{12}H_{20}O_4S$ requires C, 55.4; H, 7.7%); τ($CDCl_3$) 4.82 (2 H, s with slight broadening), 5.70 (4 H, q, *J* 7 Hz), 6.76 (2 H, s), 7.79 (3 H, s), 8.07 (3 H, s), and 8.65 (6 H, t, *J* 7 Hz), δ_C 14.06, 18.23, 21.35, 39.32, 61.85, 65.23, 116.41, 140.89, and 169.66.

Treatment of the sulphide ester (6a) (1 g) with methyl iodide (1.5 g) in acetonitrile (2 ml) at 20 °C for 24 h, gave the *methiodide* (18) (1.05 g), m.p. 96.6° (from ethanol–ether) (Found: C, 38.6; H, 5.6. $C_{13}H_{23}IO_4S$ requires C, 38.8; H, 5.7%); τ($CDCl_3$) 4.9 (1 H, s), 5.15 (1 H, s), 5.7 (4 H, q), 6.0 (2 H, s), 8.2 (3 H, s), and 8.75 (6 H, t).

The product (6a) (5 mmol) was stirred with aqueous hydrogen peroxide (100 vol.; 60 mmol), ammonium molybdate (0.75 g), and water (2 ml) in methanol (25 ml) for 2 h. Addition of water (200 ml) and extraction gave the *sulphone* (73%), b.p. 147° at 0.1 mmHg, n_D^{20} 1.477 0 (Found: C, 49.5; H, 6.9. $C_{12}H_{20}O_6S$ requires C, 49.3; H, 6.9%); τ($CDCl_3$) 4.95 (2 H, s), 5.8 (4 H, q, *J* 7 Hz), 6.3 (2 H, s), 7.1 (3 H, s), 8.2 (3 H, s), and 8.7 (6 H, t, *J* 7 Hz).

The sulphone (0.68 g) was hydrogenated over 10% palladised charcoal (0.25 g) in ethyl acetate (10 ml). When uptake was complete, removal of the catalyst and distillation gave *diethyl isopropyl*(*methylsulphonylmethyl*)*malonate* (9) (0.49 g), m.p. 28°, b.p. 110° at 0.1 mmHg, n_D^{15} 1.466 6 (Found: C, 49.0; H, 7.1. $C_{12}H_{22}O_6S$ requires C, 49.0; H, 7.45%); τ($CDCl_3$) 5.75 (4 H, q, *J* 6 Hz), 6.35 (2 H, s), 7.0 (3 H, s), 7.6 (1 H, 6 lines of a septet?, *J* 7 Hz), 8.72 (6 H, t, *J* 6 Hz), and 9.0 (6 H, d, *J* 7 Hz).

When the reaction was repeated with pre-formed adduct (700 mg), the sulphide ester (6a) was obtained in 67% yield.

(b) *With diethylprop-2-ynylsulphonium bromide.* Reaction as for the dimethyl salt yielded diethyl malonate (43%) and the *sulphide ester* (6b) (72%), b.p. 152° at 15 mmHg, n_D^{20} 1.466 2 (Found: C, 58.1; H, 8.5. $C_{14}H_{24}O_4S$ requires C, 58.3; H, 8.4%); τ(CCl_4) 4.84 (1 H, s), 5.02 (1 H, s), 5.75 (4 H, q), 6.56 (1 H, q), 7.35 (2 H, q), 8.1 (3 H, s), and 8.5—8.9 (12 H, m).

Oxidation of the sulphide as before gave the *sulphone* (75%), b.p. 135° at 0.1 mmHg, m.p. 62—63° [raised to 66° (from benzene–light petroleum)] (Found: C, 52.4; H, 7.5. $C_{14}H_{24}O_6S$ requires C, 52.5: H, 7.55%); τ($CDCl_3$) 4.85 (1 H, q, *J* 1 Hz), 5.08 (1 H, s), 5.8 (4 H, m), 5.95 (1 H, q, *J* 5 Hz), 6.85 (2 H, q, *J* 6 Hz), 8.2 (3 H, s), 8.4—8.8 (12 H, m); δ_C ($CDCl_3$) 6.23, 12.99, 13.77, and 21.18, 29.75, 43.38, 61.33, 61.99, 62.63, 66.14, 118.25, 138.78, 167.76, and 169.58; *m/e* 320 (M^+), 227 (M − $EtSO_2$), 93 ($EtSO_2$), and 64 (SO_2).

When the reaction was repeated with an equimolecular mixture of the ethyl and methyl salts and two molar proportions of diethyl malonate, g.l.c. analysis of the mixed product (25% Apiezon L at 197 °C) showed compounds with the retention times of the sulphides obtained from the single-salt experiments, but no others.

(c) *With 1-*(*prop-2-ynyl*)*tetrahydrothiophenium bromide.* Reaction on the same scale as before gave a mixture, distillation of which gave first diethyl malonate (37%), and then a mixture (3.8 g), b.p. 100—145° at 0.15 mmHg. The mixture was separated by preparative-scale g.l.c. (25% Apiezon L at 197 °C) and the component with the shorter retention time was identified as diethyl acetonylmalonate (12) (2.13 g, 49%); τ 5.79 (4 H, q), 6.19 (1 H, t, *J* 7 Hz), 6.9 (2 H, d, *J* 7 Hz), 7.79 (3 H, s), and 8.73 (6 H, t); δ_C ($CDCl_3$) 14.06, 29.82, 42.19, 47.14, 61.85, 169.27, and 205.47; identical (spectra) with an authentic specimen prepared from chloroacetone and diethyl malonate.[20] The longer-retained component was the *sulphide ester* (11) (0.95 g, 17%), n_D^{18} 1.494 1 (Found: C, 58.8; H, 7.7. $C_{14}H_{22}O_4S$ requires C, 58.7; H, 7.7%); *m/e* 286, 213, 87, and 44; $\nu_{max.}$ 1 725 (C:O str.) and 1 640 cm^{-1} (C:C str.); τ(CCl_4) 4.8 (2 H, q, *J* 0.8 Hz), 5.7 (5 H, 2 superimposed q), 7.25 (2 H, m), 7.85 (2 H, m), 8.15 (3 H, q?), and 8.7 (6 H, t, *J* 8 Hz); δ_C ($CDCl_3$) 14.06, 31.38, 32.16, 33.07, 51.04, 61.46, 116.41, 140.89, 169.4, and 170.44.

When the reaction was repeated with pre-formed adduct under the same conditions, the yield of sulphide ester (11) was 30%.

(d) *With ethylmethylprop-2-ynylsulphonium bromide.* The sulphonium salt was obtained as an oil from treatment of ethyl methyl sulphide with 3-bromopropyne in acetonitrile; τ(D_2O) 5.25 (2 H, d), 6.14 (2 H, q), 6.36 (1 H, d), 6.62 (3 H, s), and 8.10 (3 H, t). Treatment of the salt as before with diethyl malonate and sodium ethoxide in ethanol gave the *sulphide ester* (6c) (66%), b.p. 150° at 10 mmHg, n_D^{20} 1.470 5 (Found: C, 57.5; H, 7.7. $C_{12}H_{20}O_4S$ requires C, 56.9, H, 8.0%); τ($CDCl_3$) 4.87 (2 H, s), 5.77 (4 H, q, *J* 7 Hz), 6.81 (2 H, s), 7.43 (2 H, q, *J* 7 Hz), 8.12 (3 H, s), and 8.71 (12 H, m); δ_C ($CDCl_3$) 14.06, 14.84, 21.35, 28.51, 36.59, 61.72, 65.10, 116.41, 140.89, and 169.66. G.l.c. analysis (Apiezon L at 200 °C or Carbowax 20 M at 200 °C) showed a single component.

Reaction of Dimethylprop-2-ynylsulphonium Bromide with Diethyl Methylmalonate.—The reaction was carried out with the salt (40 mmol) as for the reaction with diethyl

[20] C. D. Hurd and M. L. McAuley, *J. Amer. Chem. Soc.*, 1948, **70**, 1650.

malonate. After 3 h the mixture was neutral; the usual work-up gave a residue which on distillation gave diethyl methylmalonate (49%), b.p. 86—88° at 14 mmHg, and then the *sulphide ester* (8) (32%), b.p. 171° at 14 mmHg, n_D^{25} 1.475 8 (Found: C. 56.9; H, 7.75. $C_{13}H_{22}O_4S$ requires C, 56.9; H, 8.0%); τ($CDCl_3$) 4.89 (2 H, s), 5.78 (4 H, q, *J* 7 Hz), 7.43 (4 H, m), 7.88 (3 H, s), 8.39 (3 H, s), and 8.73 (6 H, t, *J* 7 Hz); δ_C 14.06, 15.62, 20.83, 33.07, 33.46, 60.55, 61.72, 113.80, 145.96, and 171.35.

G.l.c. analysis of the entire residue showed two components with shorter retention times than the sulphide ester to be present in small (*ca.* 5%) amounts. These have not been identified.

When the reaction was repeated with pre-formed adduct, the yield of sulphide ester (8) was 85%. The minor, shorter-retained, component (*ca.* 15%) was separated by preparative g.l.c.; it showed τ($CDCl_3$) 5.15br (2 H, s), 5.90 (2 H, q), 7.15 (2 H, s), 7.95 (3 H, s), 7.30 (3 H, s), 8.62 (3 H, s), and 8.80 (3 H, t); δ_C ($CDCl_3$) 15.49, 19.14, 21.48, 22.66, 43.62, 54.17, 62.37, 114.06, 147.14, and 176.3 (Found: C, 59.3; H, 8.6. $C_{10}H_{18}O_2S$ requires C, 59.4; H, 8.9%). This compound was *not* obtained when the main product was treated with ethanolic sodium ethoxide under the conditions used for reaction with the sulphonium salt (4).

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