Formation of Vinyl Sulphides *via* Successive Sigmatropic Rearrangements of an Allylic Sulphonium Ylide

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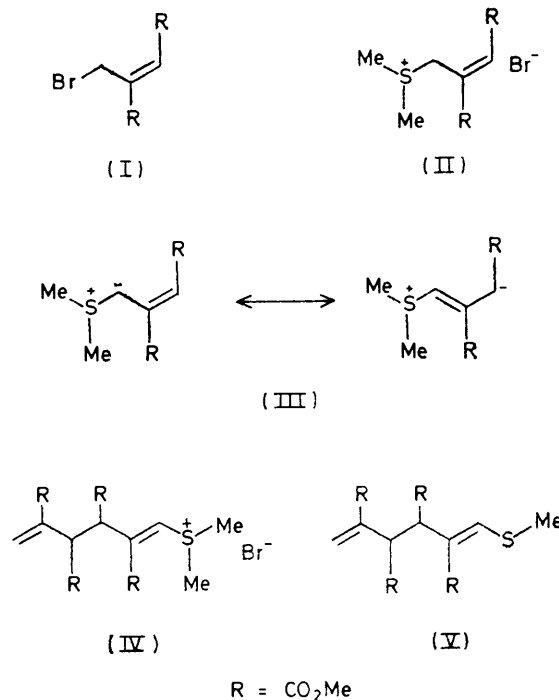Chemistry Department, University of Stellenbosch, Republic of South Africa

It is shown that the sulphonium ylide (VIII) derived from the bisallylic sulphonium salt bis-(2,3-dimethoxy-carbonylprop-2-enyl)methylsulphonium tetrafluoroborate (VII) undergoes a [2,3] sigmatropic rearrangement to produce the diastereoisomers (IX) and (X) of tetramethyl 3-(methylthio)hexa-1,5-diene-1,2,4,5-tetracarboxylate. The stereochemical outcome of the Cope rearrangements of the sulphides (IX) and (X) to (E,E)- and (Z,E)-tetramethyl 6-(methylthio)hexa-1,5-diene-1,2,4,5-tetracarboxylate (XI) and (XII), respectively, is invoked to determine the relative configurations at the chiral centres of (IX) and (X).

WE have recently [1,2] described the novel and highly stereospecific formation of the vinyl sulphide (V) during attempted oxidation of dimethyl α-(bromomethyl)fumarate (I) by dimethyl sulphoxide in the presence of a weak base. We demonstrated that the production of the vinyl sulphide (V) under these conditions took place *via* the intermediate sulphonium bromide (II).

Although formation of the vinyl sulphide (V) was rationalized as being the result of a stereospecific Michael addition of the ylide (III) to the sulphonium bromide (II), followed by elimination of dimethyl sulphide and de-methylation of the resulting salt (IV) by bromide ion, we were aware of an alternative reaction path *via* the intermediate sulphonium ylide (VIII) (Scheme 1).[2] In order to evaluate the importance of the latter pathway, we have investigated the base-induced reactions of the sulphonium salt (VII).

Treatment of a mixture of the sulphide (VI) [2] and silver tetrafluoroborate with dimethyl α-(bromomethyl)fumarate (I) in nitromethane [3] produced the sulphonium tetrafluoroborate (VII) in high yield. When a solution of the salt (VII) in dimethyl sulphoxide was heated (60 °C; 4 h) in the presence of sodium hydrogen carbonate, a mixture of products was formed from which the sulphide (IX) (14.7%) and the vinyl sulphide (XII) (43%) were sep-arated by chromatography on activated silica gel, along with the sulphides (X) and (XI) as minor components. No trace of the isomeric vinyl sulphide (V) was, however, detected.

Formation of the diastereoisomerically related sulph-ides (IX) and (X) most likely resulted from a non-stereospecific [2,3] sigmatropic rearrangement [4] of the

(I)   (II)

(III)

(IV)   (X)

R = CO$_2$Me

intermediate sulphonium ylide (VIII). Subsequent Cope rearrangement of the sulphide (X) (at 60 °C) pro-duced the vinyl sulphide (XII), and the isomeric vinyl

[1] J. E. Baldwin, J. A. Walker, A. J. H. Labuschagne, and D. F. Schneider, *Chem. Comm.*, 1971, 1382.

[2] C. F. Garbers, A. J. H. Labuschagne, C. J. Meyer, and D. F. Schneider, *J.C.S. Perkin I*, 1973, 2016.

[3] B. M. Trost and M. J. Bogdanowicz, *J. Amer. Chem. Soc.*, 1973, **95**, 5298.

[4] (a) J. E. Baldwin, R. E. Hackler, and D. P. Kelly, *Chem. Comm.*, 1968, 538; (b) J. E. Baldwin and W. E. Erickson, *ibid.*, 1971, 359.

sulphide (XI) likewise resulted from the sulphide (IX). Both the isomeric sulphides (IX) and (X) could indeed be smoothly rearranged, after isolation, to the corresponding

went a dramatic paramagnetic shift as well as a change to an ABX system upon treatment of a solution in [²H]-chloroform with the shift reagent Eu(fod)₃.[5] Desulphur-

R = CO₂Me

Scheme 1
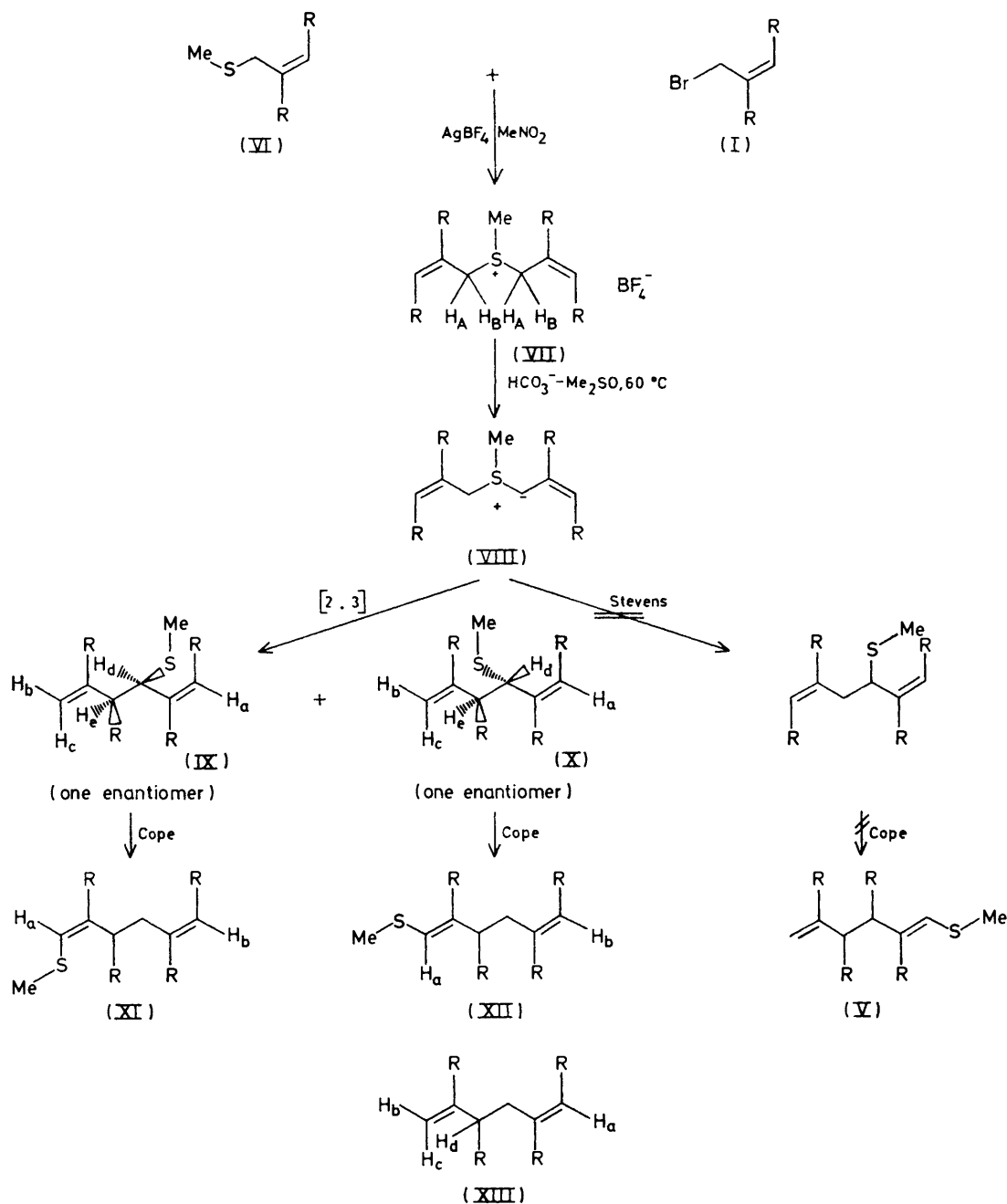
vinyl sulphides (XI) and (XII) at 150 and 100 °C, respectively. The complex ABC multiplet at δ 3.76—3.25, partially obscured by the methoxycarbonyl resonances in the ¹H n.m.r. spectrum of the vinyl sulphide (XII), under-

ization [2,6] of the vinyl sulphide (XII) with Raney nickel produced the tetraester (XIII), the formation of which established the carbon skeleton of (XII).

⁵ R. E. Rondeau and R. E. Sievers, J. Amer. Chem. Soc., 1971, 93. 1522.

⁶ (a) G. R. Pettit and E. E. van Tamelen, Org. Reactions, 1962, 12, 356; (b) L. F. Fieser and M. Fieser, 'Reagents for Organic Synthesis,' Wiley, New York, p. 729.

The indicated relative configurations at the chiral centres of the sulphides (IX) and (X) are in accord with the expected stereochemical outcome of their Cope rearrangements *via* generally accepted four-centred, chair-like transition states [7] to produce the corresponding (*E,E*)- and (*Z,E*)-vinyl sulphides (XI) and (XII).

Although chemical proof of the structure of the vinyl sulphide (V) was provided [2] by mild desulphurization with Raney nickel, which produced the crystalline tetra-ester (XIV) as the major cleavage product together with a smaller quantity of the isomeric (*E,E*)-tetraester (XV),

(XIV)

(XIV)

(XV) (*E,E*)

(XVI) (*E,Z*)

(XIV) (*meso*)

(XVI) (*E,Z*)

(XVII)

R = CO₂Me

SCHEME 2
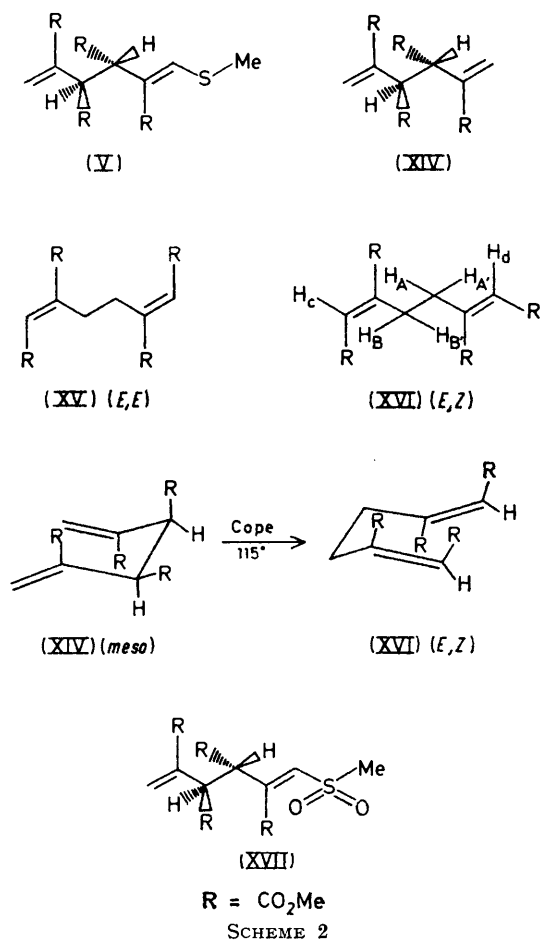
the relative configuration at the chiral centres of the sulphide (V) remained unresolved. In order to solve this problem, the tetraester (XIV) was smoothly rearranged at 115 °C to produce the (*E,Z*)-tetraester (XVI) as the only rearrangement product. The indicated relative configurations at the chiral centres of the tetraester (XIV) and vinyl sulphide (V) are again in full agreement with the stereochemical outcome of the Cope rearrangement [7] of the *meso*-tetraester (XIV) to the (*E,Z*)-tetraester (XVI).

Formation of the (*E,E*)-tetraester (XV) most likely resulted from partial epimerization of the vinyl sulphide

(V) in the presence of residual alkali on the Raney nickel catalyst, prior to desulphurization and subsequent Cope rearrangement of the resulting (±)-tetraester (XIV). Cope rearrangement of the *meso*-tetraester (XIV) *via* the 'second-best' boat-like transition state [8] may also produce the (*E,E*)-tetraester (XV), but this is regarded as a remote possibility. Treatment of pure samples of both the tetraesters (XIV) and (XVI) with Raney nickel at room temperature did not give the tetraester (XV) in detectable quantity.

X-Ray crystal structure analyses * of the sulphone (XVII) produced by oxidation of the vinyl sulphide (V) with *m*-chloroperbenzoic acid [9] and of the sulphide (IX) have demonstrated unequivocally the validity of the proposed relative configurations at the chiral centres of (V) and (IX) and, therefore, also of the diastereoisomer (X).

Heating the sulphonium salt (VII) for 3 h at 60 °C in dimethyl sulphoxide in the presence of sodium hydrogen carbonate and bromide ions led to the sulphides (IX) (4%), (X) (3%), and (XII) (12.4%), as well as the vinyl sulphide (V) (6%) and dimethyl α-(methylthiomethyl)-fumarate (VI) (22%). Formation of the sulphide (VI) under these conditions most likely resulted from dissociation of the sulphonium salt (VII) in the presence of bromide ions, with concomitant production of dimethyl α-(bromomethyl)fumarate (I). Since the vinyl sulphide (V) was produced in low yield (*ca.* 6%) during attempted oxidation of the bromo-ester (I) with dimethyl sulphoxide in the presence of sodium hydrogen carbonate,[2] we do not regard the sulphonium ylide (VIII) as an intermediate in the formation of the vinyl sulphide (V) under these circumstances.

A direct coupling between the bromo-ester (I) and the sulphide (VI) was also attempted in the presence of sodium hydrogen carbonate in methanol. Under these conditions the sulphonium ylide (III)–salt (II) pathway was completely eliminated and the coupling reaction consequently proceeded *via* the labile sulphonium bromide (XVIII). Products under these conditions were the vinyl sulphides (XII), (XIX), and (XXI), but no vinyl sulphide (V) was detected. The ether (XXII), which was the major product, most likely resulted from solvolysis of the bromo-ester (I) followed by addition of methanol to the unsaturated system.

The vinyl sulphides (XIX) and (XXI) resulted from base-catalysed isomerization of the sulphide (VI). Production of the vinyl sulphide (XII) strongly supports the initial formation of the sulphonium bromide (XVIII) as an intermediate under these circumstances.

Repetition of the latter condensation in the absence of sodium hydrogen carbonate led, as expected, to the symmetrical sulphide (XX) and trimethylsulphonium bromide. Even under these non-basic conditions, the intermediate sulphonium bromide (XVIII) underwent deprotonation to the ylide (VIII) followed by rearrangement to

[7] W. von E. Doering and W. R. Roth, *Tetrahedron*, 1962, **18**, 67.

[8] J. A. Berson and P. B. Dervan, *J. Amer. Chem. Soc.*, 1972, **94**, 7597.

[9] (*a*) D. J. Brown and P. W. Ford, *J. Chem. Soc.* (*C*), 1969, 2720; (*b*) G. A. Russel and L. A. Ochrymowycz, *J. Org. Chem.*, 1970, **35**, 2106.

the vinyl sulphide (XII), a minor product. The major product under these circumstances, however, was the ether (XXIII), a solvolysis product of the bromo-ester (I).

Thus, although the foregoing results disprove the intermediacy of the sulphonium ylide (VIII) in the formation of the vinyl sulphide (V), the ylide (VIII) is indeed an intermediate in a related coupling reaction.

EXPERIMENTAL

U.v. spectra were recorded for solutions in 96% ethanol with a Unicam SP 1800 spectrophotometer. I.r. and mass

40—60°. All operations were, as far as possible, carried out in a nitrogen atmosphere. Silica gel (0.05—0.2 mm; Merck) was used for column chromatography. Dimethyl sulphoxide was purified by distillation from calcium hydride.

Di-(2,3-bismethoxycarbonylprop-2-enyl)methylsulphonium Tetrafluoroborate (VII).—A mixture of dimethyl α-(methylthiomethyl)fumarate (VI) [2] (10 g, 50 mmol) and silver tetrafluoroborate (9.5 g, 50 mmol) in dry nitromethane (distilled and stored over 3 Å molecular sieves) (60 ml) was stirred for 30 min at room temperature. The resulting suspension was treated dropwise with a solution of dimethyl α-(bromomethyl)fumarate (I) (23.2 g, 100 mmol) in nitromethane

R = CO$_2$Me
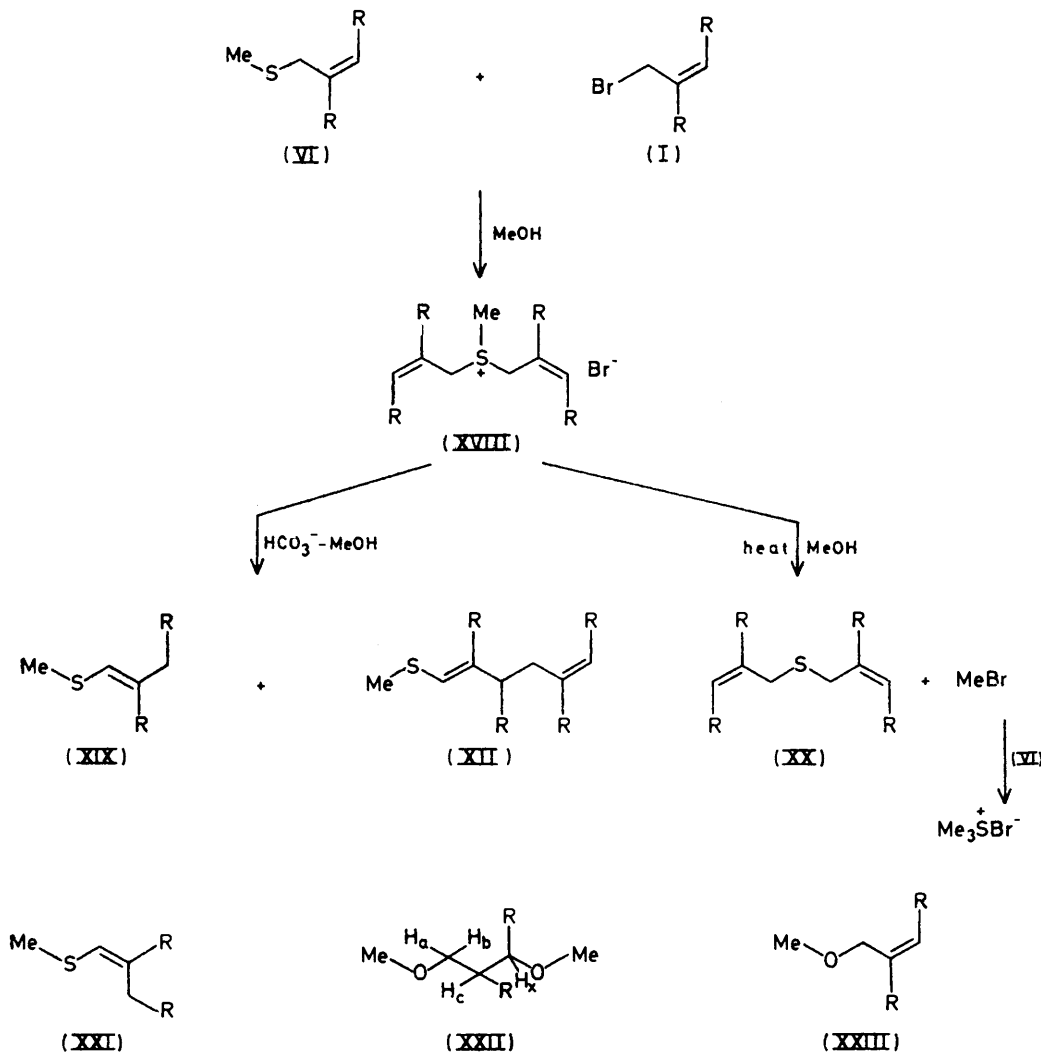
SCHEME 3

spectra were determined with a Unicam SP 200 spectrophotometer and an A.E.I. MS 902 spectrometer, respectively. [1]H N.m.r. spectra were, unless otherwise indicated, recorded for solutions in [^{2}H]chloroform with a Varian HA-60IL spectrometer and tetramethylsilane as internal standard.

Combustion analyses were performed by Dr. F. Pascher, Bonn, Germany; petroleum refers to the fraction of b.p.

(25 ml) and stirred at room temperature. After 13 h the resulting suspension was filtered and the residue from the filtrate recrystallized from methyl acetate to yield the *sulphonium salt* (VII) (18 g, 82%), m.p. 91.5°, δ 7.16 (2 H, s), 4.82 [4 H, ABq, J_{AB} 13.3 Hz; $δ_A$ 4.99, $δ_B$ 4.62 (calc.[10])],

[10] R. H. Bible, ' Interpretation of N.M.R. Spectra,' Plenum Press, New York, 1965, p. 83.

3.88 (6 H, s), 3.82 (6 H, s), and 3.26 (3 H, s) (Found: C, 39.8; H, 4.65. $C_{15}H_{21}BF_4O_8S$ requires C, 40.2; H, 4.7%).

Base-induced Rearrangement of the Sulphonium Tetrafluoroborate (VII).—Anhydrous sodium hydrogen carbonate (4.2 g) was added to a solution of the sulphonium salt (VII) (11.0 g) in dimethyl sulphoxide (40 ml) and the stirred suspension was heated for 4 h at 60 °C. Ether (200 ml) was added to the cooled (room temperature) mixture and the ethereal solution was extracted with water. Chromatographic separation of the residue from the dried (Na_2SO_4) ether layer gave, on elution with ether–petroleum (3:2), racemic *tetramethyl 3-(methylthio)hexa-1,5-diene-1,2,4,5-tetracarboxylate* (IX) (1.30 g, 14.7%), m.p. 80° (from ether), λ_{max} 209 nm (ε 14 630), δ 6.70 (1 H, s, H_a), 6.31 (1 H, s, H_b), 5.94 (1 H, s, H_c), 5.40 (1 H, d, H_d, J 11.8 Hz), 4.39 (1 H, d, H_e, J 11.8 Hz), 3.77 (6 H, s), 3.74 (3 H, s), 3.69 (3 H, s), and 2.21 (3 H, s, SMe) (Found: C, 50.0; H, 5.8%; M^+, 360.0902. $C_{15}H_{20}O_8S$ requires C, 50.0; H, 5.6%; M, 360.0879), the racemic sulphide (X)* (0.30 g, 3.4%), b.p. 110° (air-bath temperature) at 10^{-5} mmHg, λ_{max} 205 nm, δ 6.75 (1 H, s, H_a), 6.47 (1 H, s, H_b), 5.96 (1 H, s, H_c), 5.33 (1 H, d, H_d, J 11.8 Hz), 4.53 (1 H, d, H_e, J 11.8 Hz), 3.84—3.77 (9 H, m), 3.58 (3 H, s), and 2.01 (3H, s, SMe), M^+ 360, and (Z,E)-*tetramethyl 6-(methylthio)hexa-1,5-diene-1,2,4,5-tetracarboxylate* (XII) (3.80 g, 43%), b.p. 110° (air-bath temperature) at 10^{-5} mmHg, λ_{max} 215 and 294 nm (ε 12 690 and 10 820) δ 6.95 (1 H, s, H_a), 6.80 (1 H, s, H_b), 3.87—3.25 (3 H, ABCm), 3,78 (3 H, s), 3.73 (6 H, s), 3.64 (3 H, s), and 2.35 (3 H, s, SMe), (Found: C, 50.06; H, 5.55%; M^+, 360.0863). Elution with ether–petroleum (7:3) gave (E,E)-*tetramethyl 6-(methylthio)hexa-1,5-diene-1,2,4,5-tetracarboxylate* (XI) (20 mg, 0.2%), b.p. 100° (air-bath temperature) at 10^{-5} mmHg, λ_{max} 221 and 283 nm (ε 11 146 and 13 528), δ 7.57 (1 H, s, H_a), 6.83 (1 H, s, H_b), 3.90—3.31 (3 H, ABCm), 3.79 (3 H, s), 3.75 (6 H, s), 3.68 (3 H, s), and 2.39 (3 H, s, SMe) (Found: C, 49.9; H, 5.5%; M^+, 360.0885).

Desulphurization of (Z,E)-Tetramethyl 6-(Methylthio)hexa-1,5-diene-1,2,4,5-tetracarboxylate (XII).—The vinyl sulphide (XII) (1.30 g, 3.6 mmol) was added at room temperature to a stirred suspension of Raney nickel (*ca.* 2 g) in methanol (10 ml).[6] After 20 min at room temperature the initial u.v. maximum at 294 nm had completely disappeared. The mixture was filtered and the oily residue from the filtrate separated by chromatography with ether–petroleum (9:11) as eluant to yield *tetramethyl hexa-1,5-diene-1,2,4,5-tetracarboxylate* (XIII) (0.29 g, 25%), b.p. 80° (air-bath temperature) at 10^{-5} mmHg, λ_{max} 212 nm (ε 12 800), δ 6.82 (1 H, s, H_a), 6.28 (1 H, d, H_b, J 1 Hz), 5.65 (1 H, overlapping dd, H_c, J_{cb} 1, J_{cd} 1 Hz), 3.85—3.21 (3 H, ABCm), 3.79 (3 H, s), 3.75 (6 H, s), and 3.65 (3 H, s) (Found: C, 53.6; H, 6.0%; M^+, 314.1014. $C_{14}H_{18}O_8$ requires C, 53.5; H, 5.75%; M, 314.1002).

Cope Rearrangement of the Sulphide (IX).—The sulphide (IX) was heated for 3 h at 150 °C to produce the (E,E)-vinyl sulphide (XI) in quantitative yield. Distillation of the sulphide (IX), b.p. 115° (air-bath temperature) at 10^{-5} mmHg, proceeded smoothly without rearrangement.

(Z)-Tetramethyl 1-(Methylsulphonyl)hexa-1,5-diene-2,3,4,5-tetracarboxylate (XVII).—m-Chloroperbenzoic acid (1.14 g, 6.6 mmol) in chloroform (20 ml) was added dropwise to a stirred solution of (Z)-tetramethyl 1-(methylthio)hexa-1,5-

diene-2,3,4,5-tetracarboxylate (V) (1.2 g, 3.3 mmol) in chloroform (20 ml) at —10 °C.[9] The mixture was stirred for a further 24 h at room temperature, cooled in a refrigerator for 3 days, and successively extracted with aqueous sodium hydrogen carbonate and water. The residue from the dried ($MgSO_4$) chloroform solution was recrystallized from chloroform to yield the (Z)-sulphone (XVII) (0.79 g, 61%), m.p. 96° (lit.,[1] 98—100°), δ 6.74 (1 H, s), 6.41 (1 H, s), 5.86 (1 H, s), 4.17 [2 H, ABq, J_{AB} 10.9 Hz; δ_A 4.24, δ_B 4.11 (calc.[10])], 3.87 (3 H, s), 3.80 (3 H, s), 3.69 (3 H, s), 3.66 (3 H, s), and 3.07 (3 H, s), M^+ 392 (Found: C, 45.85; H, 5.15. $C_{15}H_{20}O_{10}S$ requires C, 45.9; H, 5.15%).

Cope Rearrangement of Tetramethyl Hexa-1,5-diene-2,3,4,5-tetracarboxylate (XIV).—The tetraester (XIV) (60 mg, 0.2 mmol) was heated for 24 h at 115 °C to produce (E,Z)-*tetramethyl hexa-1,5-diene-1,2,5,6-tetracarboxylate* (XVI) (60 mg, 100%), b.p. 100° (air-bath temperature) at 10^{-5} mmHg, λ_{max} 213 nm (ε 13 920), δ 6.83 (1 H, s, H_c), 5.92 (1 H, overlapping dd, H_d, J_{dA} 1, $J_{dA'}$ 1 Hz), 3.84 (3 H, s), 3.81 (3 H, s), 3.77 (3 H, s), 3.73 (3 H, s), and 3.18—2.33 (4 H, AA'BB'm) (Found: C, 53.3; H, 5.7%; M^+, 314.1001. $C_{14}H_{18}O_8$ requires C, 53.5; H, 5.75%; M, 314.1002).

A similar Cope rearrangement could be effected in 95% yield by heating a methanolic solution of the tetraester (XIV) for 96 h at reflux temperature.

Coupling of Dimethyl α-(Methylthiomethyl)fumarate (VI) *and Dimethyl α-(Bromomethyl)fumarate* (I).—(a) *In the presence of sodium hydrogen carbonate.* A stirred suspension of sodium hydrogen carbonate (2 g) in a solution of the sulphide (VI)[2] (2.5 g, 12 mmol) and the bromo-ester (I) (3 g, 12 mmol) in methanol (15 ml) was refluxed for 30 h. Ether (100 ml) was added to the cooled (room temperature) mixture and the ethereal solution was extracted with water. Chromatographic separation of the residue from the dried (Na_2SO_4) organic phase gave, on elution with ether–petroleum (3:2), unchanged sulphide (VI) (0.39 g, 15.6%), (E)-*dimethyl 3-(methylthio)prop-2-ene-1,2-dicarboxylate* (XXI) (85.3 mg, 3.4%), b.p. 85° (air-bath temperature) at 0.1 mmHg, λ_{max} 203 and 283 nm (ε 3 225 and 12 270), δ 7.68 (1 H, s), 3.73 (3 H, s), 3.68 (3 H, s), 3.36 (2 H, s), and 2.45 (3 H, s) (Found: C, 47.1; H, 5.85%; M^+, 204.0486. $C_8H_{12}O_4S$ requires C, 47.05; H, 5.9%; M, 204.0456), (Z)-*dimethyl 3-(methylthio)prop-2-ene-1,2-dicarboxylate* (XIX) (0.17 g, 6.9%), b.p. 100° (air-bath temperature) at 0.1 mmHg, λ_{max} 203 and 293 nm (ε 2 232 and 9 806), δ 6.95 (1 H, t, J 1 Hz), 3.74 (3 H, s), 3.67 (3 H, s), 3.28 (2 H, d, J 1 Hz), and 2.37 (3 H, s) (Found: C, 47.15; H, 6.0%; M^+, 204.0476), and the sulphide (IX) (0.19 g, 4.4%). Elution with ether–petroleum (7:3) produced *dimethyl 1,3-dimethoxypropane-1,2-dicarboxylate* (XXII) (0.5 g, 20%), b.p. 65° (air-bath temperature) at 0.1 mmHg, δ 4.09 (1 H, d, H_x, J_{xc} 5.5 Hz), 3.78 (3 H, s), 3.70 (3 H, s), 3.43 (3 H, s), 3.34 (3 H, s), and 3.75—2.92 (3 H, ABC portion of ABCXm, J_{ab} 10.5, J_{ac} 6.5, J_{bc} 6.25 Hz),† M^+ 220 (Found: C, 49.15; H, 7.25. $C_9H_{16}O_6$ requires C, 49.1; H, 7.3%), and the (Z,E)-vinyl sulphide (XII) (0.56 g, 12.7%). A small quantity of the (E,E)-vinyl sulphide (XI) (12 mg, 0.27%) was also eluted with ether–petroleum (4:1).

(b) *In the absence of sodium hydrogen carbonate.* A solution of dimethyl α-(bromomethyl)fumarate (I) (3.6 g, 15

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* Despite several chromatographic separations, the sulphide (X) could not be freed from a small quantity of the vinyl sulphide (XII) owing to its very ready Cope rearrangement. Distillation of the partially purified sulphide (X) produced the spectroscopically and analytically pure vinyl sulphide (XII) as the sole product.

† The complex ABCX multiplet (H_a, H_b, H_c, and H_x), which partially overlaps with the four methoxy-resonances in the ^{1}H n.m.r. spectrum of the ether (XXII), was reduced to a first-order splitting pattern upon treatment of a solution in [^{2}H]chloroform with Eu(fod)₃.[5]

mmol) and dimethyl α-(methylthiomethyl)fumarate (VI) [2] (3.0 g, 15 mmol) in methanol (30 ml) was refluxed for 12 days. Acetone (50 ml) was added to the cooled (room temperature) mixture and the resultant trimethylsulphonium bromide (0.34 g, 14%), m.p. 198° (from acetone–methanol) (lit.,[11] 195°), δ (D₂O) 2.97 (9 H, s), was collected. The residue from the combined filtrates was chromatographed as before with ether–petroleum mixtures as eluants to yield *dimethyl* α-*(methoxymethyl)fumarate* (XXIII) (1.2 g, 43%), b.p. 55° (air-bath temperature) at 0.25 mmHg, $\lambda_{max.}$ 212 nm (ε 10 270), δ 6.81 (1 H, t, *J* 0.8 Hz), 4.55 (2 H, d, *J* 0.8 Hz), 3.81 (3 H, s), 3.77 (3 H, s), and 3.33 (3 H, s) (Found: C, 50.75; H, 6.55%; M^+, 188.0698. $C_8H_{12}O_5$ requires C, 51.05; H, 6.4%; *M*, 188.0685), *di-(2,3-bismethoxycarbonylprop-2-enyl) sulphide* (XX) (0.28 g, 5.6%), b.p. 120° (air-bath temperature) at 10^{-5} mmHg, $\lambda_{max.}$ 222 nm (ε 15 460), δ 6.71 (2 H, s), 3.99 (4 H, s), 3.82 (6 H, s), and 3.76 (6 H, s) (Found: C, 48.6; H, 5.25%; M^+, 346.0715. $C_{14}H_{18}O_8S$ requires C, 48.55; H, 5.25%; *M*, 346.0722), the (*E*)-vinyl sulphide (XXI) (28 mg, 1%), the (*Z*)-vinyl sulphide (XIX) (82 mg,

2.7%), the racemic sulphide (IX) (49 mg, 0.93%), the (*Z*,*E*)-vinyl sulphide (XII) (0.30 g, 5.6%), and the (*E*,*E*)-vinyl sulphide (XI) (46 mg).

Base-induced Reaction of the Sulphonium Tetrafluoroborate (VII) *in the Presence of Sodium Bromide.*—A stirred suspension of sodium hydrogen carbonate (1.88 g) and sodium bromide (3 g, 22.3 mmol) in a solution of the sulphonium salt (VII) (5 g, 11.2 mmol) in dimethyl sulphoxide (35 ml), was heated for 3 h at 60 °C. The cooled (room temperature) mixture was worked up and chromatographed as in the previous experiment to yield dimethyl α-(methylthiomethyl)-fumarate (VI) [2] (0.50 g, 22%), the racemic sulphide (IX) (0.16 g, 4%), the racemic sulphide (X) (0.11 g, 3%), the (*E*)-vinyl sulphide (XXI) (15 mg), the (*Z*)-vinyl sulphide (XIX) (27 mg), the (*Z*,*E*)-vinyl sulphide (XII) (0.50 g, 12.4%), and (*Z*)-tetramethyl 1-(methylthio)hexa-1,5-diene-2,3,4,5-tetracarboxylate (V) (0.24 g, 6%).[2]

[11] P. Mamalis, *J. Chem. Soc.*, 1960, 4747.