Functionalisation of Alkenes by a Cycloaddition–Cycloreversion Sequence. Part 2.† Anionic Cycloreversion Reactions of 2,5-Dihydrothiophene Derivatives

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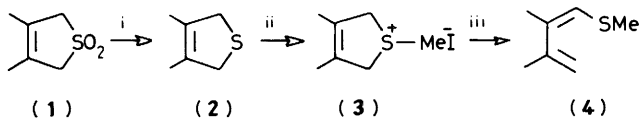
The anionic cycloreversions of the 2,5-dihydrothiophene sulphonium salts (**3**), (**7**), (**12**), and (**16**) gave the thiodienes (**4**), (**8**), (**13**), and (**17**) respectively. The 2,5-dihydrothiophenes were prepared by reduction of the corresponding sulphones (which were obtained by SO_2 addition to appropriate dienes) or by the cycloaddition of thiocarbonyl ylides to electron-deficient dipolarophiles.

In a previous paper we showed that the anionic cycloreversion of octahydrobenzo[*c*]thiophene *S*-methyl sulphonium salt gave in good yield 1-methylthio-octa-1,7-diene.[1] In this paper, the scope of the cycloreversion reaction is extended to sulphonium salts of 2,5-dihydrothiophene derivatives.

Anionic cycloreversion reactions of 2,5-dihydrofuran have previously been studied by Kloosterziel[2] and Rautenstrauch.[3] Mention has also been made of the analogous reaction in unspecified yield for 2,5-dihydrothiophene,[2] and Trost[4] has encountered cycloreversion of dihydrothiophene derivatives as a side reaction in the treatment of *cis*- or *trans*-2,5-dihydro-2,5-dimethylthiophenium hexafluorophosphates with n-butyllithium, but no serious investigation of the synthetic utility of such reactions has appeared. Kellogg[5] has observed the formation of dienes and unsaturated thiiranes on photochemical or thermal treatment of some 2,5-dihydrothiophene-3,4-dicarboxylate derivatives.

The first sulphonium salt (**3**) to be studied was obtained by methyl iodide methylation of 3,4-dimethyl-2,5-dihydrothiophene (**2**) which is, in turn, obtained by Bu^i_2AlH reduction[6a] of the sulphone (**1**).[7] Cycloreversion of (**3**) in the presence of sodium hydride in *N*,*N*-dimethylformamide (DMF) gave the diene (**4**), indicating that such a cycloreversion sequence was feasible (Scheme 1). On the basis of the principle of least



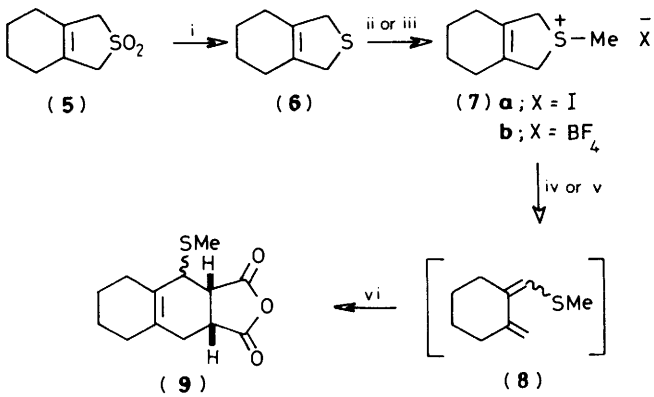
(**1**) (**2**) (**3**) (**4**)

Scheme 1. *Reagents*: i, Bu^i_2AlH, hexane–toluene, reflux, 24 h (47%); ii, MeI, EtOH, room temp., 64.5 h (87%); iii, NaH (4 equiv.), DMF, 0—1.5 °C, 3 h (19%).

motion,[8] the thio-enol ether configuration of (**4**) is likely to be *Z*, but this has not been rigorously established.

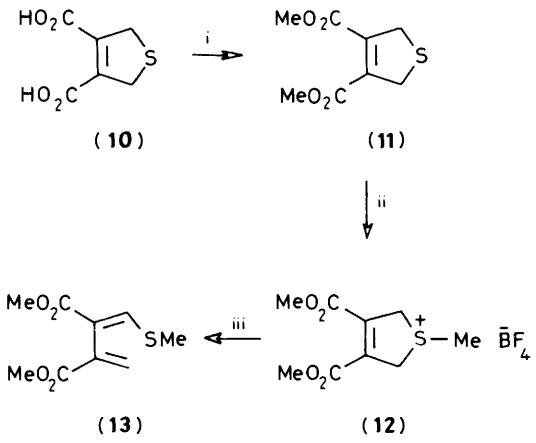
Attention was then directed to the bicyclic series, as represented by the benzo[*c*]thiophenium salts (**7**). These were most conveniently prepared from the key dihydrothiophene (**6**).[9] This was prepared by Bu^i_2AlH reduction[6a] of the sulphone (**5**), despite the fact that earlier workers had reported this to be impossible,[9] or at least to be complicated by side reactions;[6b–d] it therefore represents a superior method of preparation to that previously described. Cycloreversion of either the iodide (**7a**) or tetrafluoroborate salts (**7b**) with either n-butyl-lithium in hexane or lithium di-isopropylamide (LDA) in tetrahydrofuran (THF) gave the diene (**8**) which was difficult to purify, but which could be readily trapped as its maleic anhydride Diels-Alder adduct (**9**) (mixture of stereoisomers) (Scheme 2).

† Part 1, ref. 1.



Scheme 2. *Reagents*: i, Bu^i_2AlH; ii, MeI; iii, $Me_3\overset{+}{O}\overset{-}{B}F_4$; iv, Bu^nLi, hexane; v, LDA–THF (82%); vi, maleic anhydride (41%).

Substrates with electron-withdrawing substituents were next examined in anticipation of those most likely to be easily accessible by a dipolar cycloaddition of a thiocarbonyl ylide[10] to electron-deficient alkynes. Esterification of the di-acid (**10**)[11] gave the diester (**11**) which was converted into the corresponding sulphonium salt (**12**). Cycloreversion of (**12**) gave the thiodiene (**13**) in good yield (Scheme 3). The *E*-configuration

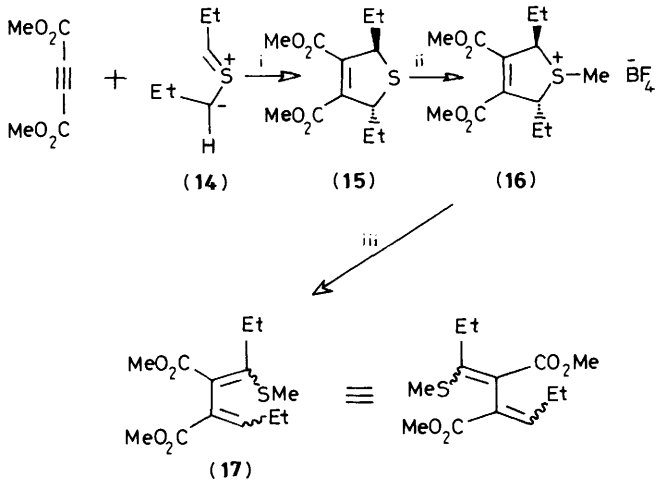


Scheme 3. *Reagents*: i, BF_3·MeOH; ii, $Me_3\overset{+}{O}\overset{-}{B}F_4$ (89%); iii, LDA, THF (71%).

for the trisubstituted double bond of (**13**) can reasonably be assigned both on mechanistic grounds[8] and on the basis of ^1H n.m.r. chemical-shift data. The isolated vinyl proton of (**13**)

resonates at δ 7.67, a value which is more consistent with that (δ 7.32) expected for the *E*-configuration of closely related model compounds, and significantly different from the calculated value (δ 6.84) for the *Z*-configuration.[12]

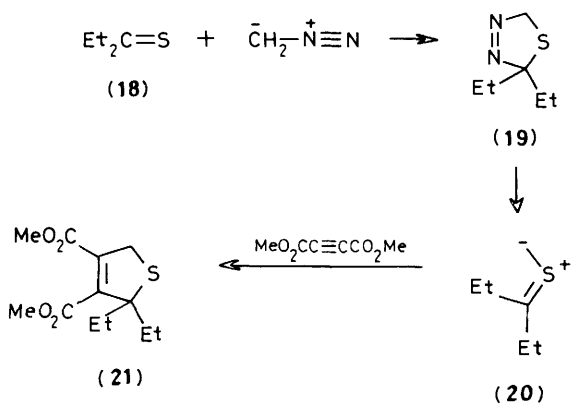
The full sequence for cycloaddition–cycloreversion was carried out using the diethyl thiocarbonyl ylide (**14**) and dimethyl acetylenedicarboxylate (Scheme 4). The resulting dipolar adduct (**15**)[13] was methylated to give (**16**) which underwent cycloreversion in good yield to give the thiodiene (**17**). The configuration of both double bonds in (**17**) cannot be established with certainty. On mechanistic grounds[8] the thioenol would again be expected to have the *E*-configuration. The observed chemical shift of the vinyl proton (δ 6.83) in the ^{1}H n.m.r. spectrum of (**17**) is consistent with the calculated value for the *E*-(δ 6.66) rather than the *Z*-(δ 6.18) configuration.



Scheme 4. *Reagents*: i, Benzene, reflux, 1 h; ii, $Me_3\overset{+}{O}\overset{-}{B}F_4$ (77%); iii, LDA, THF, room temp., 3.75 h (84%).

The reactions in Schemes 1—4 illustrate the use of the cycloreversion of sulphonium salts of 2,5-dihydrothiophenes (which themselves are accessible by the dipolar cycloaddition of thiocarbonyl ylides to electron-deficient acetylenes) in preparing potentially interesting thiodienes. These are masked β,γ-unsaturated aldehydes, as well as being interesting dienes, and can be elaborated in further synthetically interesting transformations.[14]

In a search for alternative routes to 2,5-dihydrothiophene derivatives we examined the Schönberg reaction[15] of diazomethane with diethyl thioketone (**18**). On carrying out the reaction in the presence of dimethyl acetylenedicarboxylate at 0—5 °C a low yield of the dihydrothiophene (**21**) was obtained. This was clearly being produced by dipolar cycloaddition of the presumed thiocarbonyl ylide (**20**) to dimethyl acetylenedicarboxylate. The ylide (**20**) was produced by cycloreversion (N_2 extrusion) of the thiadiazoline (**19**) which was the primary product of the Schönberg reaction (Scheme 5).

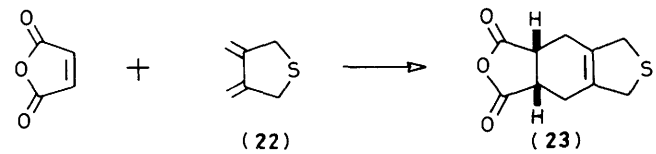


Scheme 5.

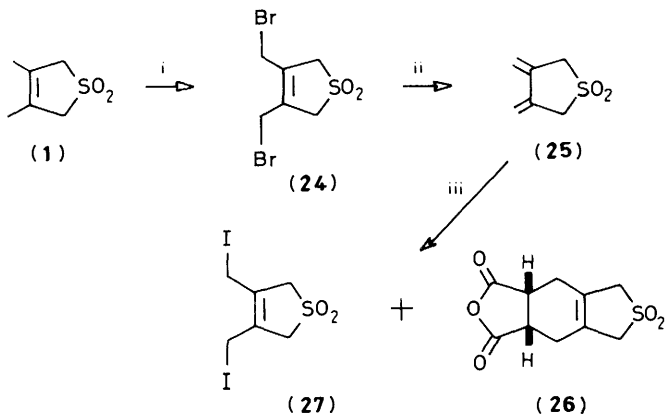
After we had completed our own studies, Huisgen and co-workers published a definitive study of the Schönberg reaction using thiobenzophenone.[16] These workers showed in an elegant series of experiments that a thiadiazoline could be formed in high yield from the low-temperature addition of diazomethane to thiobenzophenone, and that this decomposed above −30 °C with nitrogen evolution to give the corresponding thiocarbonyl ylide. The best dipolarophiles for the thiocarbonyl ylide are thiones themselves, and good yields of dihydrothiophene adducts can only be obtained by dipolar cycloaddition reactions using the preformed thiadazoline. These observations nicely explain the poor yield of (**21**) obtained in the present work, since a competing side reaction would have been further dipolar addition of (**18**) to (**20**), as well as dimerisation of the thione to tetraethyldithietane.

It is interesting to note in passing that simple frontier orbital analysis of the HOMO of diazomethane (−9.0 eV)[17] and the LUMO of dimethyl thioketone (0.99 eV; the u.v. absorption bands of various thiones are unaffected by alkyl substituents[18]) would predict the opposite regiochemistry of the dipolar product (**19**), but the evidence for this and related adducts[16] is unambiguous.

Two alternative [2 + 4] cycloaddition routes to 3,4-fused 2,5-dihydrothiophene derivatives were briefly investigated, but not pursued. These are summarised in Schemes 6 [maleic anhydride addition to 3,4-dimethyleneperhydrothiophene (**22**)[19]], and 7 [maleic anhydride addition to 3,4-dimethyleneperhydrothiophene *S*,*S*-dioxide (**25**) generated *in situ* from the corresponding 3,4-bisbromomethyl compound (**24**)[7]]. Both methods suffered from low yields. In addition the latter required selective reduction of the sulphone (**26**) which was not further investigated.



Scheme 6.



Scheme 7. *Reagents*: i, NBS (ref. 19); ii, NaI, room temp. 19.5 h; iii, maleic anhydride (30%).

Experimental

Apparatus, techniques, and instruments were reported in a previous paper.[1]

2,5-*Dihydro*-3,4-*dimethylthiophenium Iodide* (**3**).—A solution of di-isobutylaluminium hydride (25% in toluene; 24 ml) was added slowly under dry argon to an ice-cooled mixture of 2,5-dihydro-3,4-dimethylthiophene 1,1-dioxide (**1**)[7] (2 g, 5 mmol) in 1,2-dimethoxyethane (20 ml, dried by distillation from sodium benzophenone ketyl) in a 100 ml flask equipped with condenser and magnetic stirrer. The mixture was warmed carefully to 60 °C (the resulting vigorous reaction had to be moderated by interrupting the heating), and then heated under reflux (24 h). The reaction mixture was cooled (ice-bath), and treated carefully with dry ethanol (6 ml), water (11 ml), and concentrated HCl (6 ml) in succession. The resulting mixture was poured into water (100 ml), shaken, and the organic layer was separated and washed with water (40 ml). The combined aqueous layers were extracted with pentane (20 ml), and the organic layers were combined and dried (Na_2SO_4). The solvent was evaporated, and the residue was chromatographed on Merck silica (85 g), the column being eluted with hexane (to remove toluene), and hexane–ethyl acetate (90:10) to give 2,5-dihydro-3,4-dimethylthiophene (**2**) as a colourless oil (0.74 g, 47%); δ (CCl_4; 60 MHz) 1.67 (6 H, s) and 3.57 (4 H, s). The sulphone (**1**) (0.23 g, 10%) was recovered by eluting the column with ethyl acetate. The dihydrothiophene (**2**) (1.69 g, 14.8 mmol) was dissolved in dry ethanol (2.6 ml) and stirred at room temperature with methyl iodide (4.21 g, 29.6 mmol). The mixture was then diluted with ether (9.5 ml), and the white precipitate was separated by decantation; it was then washed with pentane (7 ml) and dried under a stream of dry nitrogen (3.09 g, 81%). After four recrystallisations from methanol the *sulphonium salt* (**3**) was obtained as a colourless solid, δ [$(CD_3)_2CO$—$(CD_3)_2SO$] 1.77 (6 H, s), 2.87 (3 H, s), 4.00 (2 H, d, *J* 16 Hz), and 4.34 (2 H, d, *J* 16 Hz); δ ($CDCl_3$) 1.77 (6 H, s) 3.33 (3 H, s), 4.16 (2 H, d), and 4.72 (2 H, d) (Found: C, 33.1; H, 5.2; I, 49.8; S, 12.2. $C_7H_{13}IS$ requires C, 32.8; H, 5.1; I, 49.5; S, 12.5%).

1-*Methylthio*-2,3-*dimethylbuta*-1,3-*diene* (**4**).—Sodium hydride (50% dispersion in oil; 2.17 g, 45 mmol), freed from the dispersion oil by washing with dry ether (3 × 15 ml), was mixed with dry dimethylformamide (DMF) (105 ml). The mixture was cooled to 5—10 °C under dry N_2, and a solution of the sulphonium salt (**3**) (2.69 g, 10.5 mmol) in DMF (105 ml) was added slowly with stirring such that the reaction temperature remained at 0 °C. After being stirred for 3 h at 0—1.5 °C the reaction mixture was poured into water (1.8 l), and the whole extracted with pentane (2 × 125 ml). The organic layers were combined, washed with water (2 × 50 ml), dried (Na_2SO_4), and evaporated (temperature of bath < 5 °C). Kugelrohr distillation room temp., 20 mmHg, then room temp., 0.5 mmHg) of the residual oil gave the *diene* (**4**) as a colourless oil (260 mg, 19%); δ ($CDCl_3$, 60 MHz) 1.85 (6 H, m) 2.22 (3 H, s), 4.85 (1 H, m), 5.03 (1 H, m), and 5.68 (1 H, m); $\nu_{max.}$ (CCl_4) 3 080s, 1 620m, 1 610m, 960s, and 835s cm^{-1}; *m/z* 128 (M^+ − 15, 21%), 115 (97), and 113 (100) (Found: C, 65.8; H, 9.4; $M^+ - CH_3$, *m/z* 113.0432. $C_7H_{12}S$ requires C, 65.6; H, 9.4%; C_9H_9S requires *m/z* 113.0425).

1,3,4,5,6,7-*Hexahydrobenzo*[c]*thiophene* (**6**).—To the sulphone (**5**)[9] (100 mg; 0.58 mmol) and 1,2-dimethoxyethane (0.85 ml) was added carefully with stirring a hexane solution (1M) of di-isobutylaluminium hydride (1.75 ml, 1.75 mmol) under an argon atmosphere. When the slightly exothermic reaction had moderated (5 min), the mixture was stirred and boiled under reflux for 18.5 h. It was then cooled in ice and diluted with ethanol (0.25 ml), and then with water (1 ml) and concentrated HCl (0.75 ml). The mixture was separated and the organic layer was washed with water (2 × 1 ml). The combined aqueous washings were re-extracted with pentane (2 × 2 ml), and the organic layers were combined, dried, and evaporated. The residue was triturated with pentane to remove starting material (**5**) [50.2 mg, m.p. 93—94 °C (lit.,[9] 94 °C)] and the supernatant solution yielded *crude* (**6**) (27.6 mg, 34%) as an oil: δ ($CDCl_3$, 60 MHz) 1.3—3.0 (8 H, m) and 3.58 (4 H, br s). When the reaction was repeated using (**5**) (6 g) over 15.75 h (**6**) (1.6 g, 33%), b.p. (Kugelrohr bath) 75—80 °C/2.5 mmHg was obtained.

1,3,4,5,6,7-*Hexahydro*-2-*methylbenzo*[c]*thiophenium Iodide* (**7a**).—To the crude hexahydrothiophene (**6**) (0.276 g, 1.9 mmol) was added methyl iodide (1.95 g, 1.373 mmol) and ethanol (1 ml). The mixture was boiled under reflux (48 °C) for 1 h, and then cooled and diluted with pentane (8 ml). The product was precipitated as a green gum and crystallised from ethanol to give the *sulphonium iodide* (**7a**) (0.227 g, 36%) as a yellow solid, δ ($CDCl_3$, 60 MHz) 1.75 (4 H, m), 2.15 (4 H, m), 3.35 (3 H, s), 4.27 (2 H, d, *J* 16 Hz), and 4.70 (2 H, d, *J* 16 Hz).

1,3,4,5,6,7-*Hexahydro*-2-*methylbenzo*[c]*thiophenium Tetrafluoroborate* (**7b**).—A mixture of the hexahydrothiophene (**6**) (1.514 g, 10.81 mmol) trimethyloxonium tetrafluoroborate (1.92 g, 12.97 mmol) and chloroform (15 ml) was stirred at room temperature under argon for 19.5 h. The resulting deep violet suspension was evaporated to dryness and the residue was triturated with acetone–pentane (1:1). The suspension was filtered and the filtrate was evaporated to give the *sulphonium tetrafluoroborate* (**7b**) (1.54 g, 58%) as colourless crystals.

Cycloreversion of (**7a**) *with n-Butyl-lithium*.—n-Butyl-lithium in hexane (1.62M) solution (0.38 ml, 0.62 mmol) was added under argon with stirring to a mixture of the sulphonium iodide (**7a**) (85 mg, 0.30 mmol) in hexane (1 ml). After being stirred (47 h) at room temperature, the mixture was carefully treated with water (3 ml) and pentane (3 ml). The mixture was shaken and then the organic layer was separated and the aqueous layer was extracted with ether (2 ml). The combined organic layers were dried and evaporated to yield the *thiodiene* (**8**) as an oil; δ (CCl_4, 60 MHz) 0.7—2.2 (8 H, m), 2.22 (3 H, s), 4.78 (1 H, m), 5.02 (1 H, m), and 5.60 (1 H, m).

3*a*,4,5,6,7,8,9,9*a*-*Octahydro*-9-*methylthio*-1H,3H-*naphtho*-[3,4-b]*furan*-1,3-*dione* (**9**).—To a suspension of the sulphonium tetrafluoroborate (**7b**) (266 mg, 1.1 mmol) in THF (1 ml) at room temperature under dry argon was added with stirring lithium di-isopropylamide [prepared from di-isopropylamine (156.7 mg, 1.5 mmol) and n-butyl-lithium in hexane (1.44M) (0.7 ml, 1.1 mmol)] in THF (2 ml). A yellow solution formed immediately with a slight increase in temperature. The reaction mixture was stirred at room temperature (1.5 h), and then diluted with water (10 ml) and extracted with pentane (2 × 10 ml). The combined organic layers were washed with water (3 × 10 ml), aqueous NH_4Cl (10%; 10 ml), and water (2 × 10 ml). They were then dried (Na_2SO_4) and evaporated to give the *diene* (**8**) (138.1 mg, 82%) as an oil, b.p. 115—120 °C (Kugelrohr bath temp.)/20 mmHg (Found: C, 67.8; H, 8.6. $C_9H_{14}S$ requires C, 70.1; H, 8.6%). A mixture of the oil (**8**) (137 mg, 0.89 mmol), maleic anhydride (87.1 mg, 0.89 mmol), and toluene (0.5 ml) was heated under reflux (0.75 h). The colour of the reaction mixture changed from yellow to orange. The mixture was then evaporated to dryness and chromatographed on a preparative t.l.c. plate which was eluted with ethyl acetate–hexane (1:3) as eluant. The band at R_F 0.32 was extracted with methanol–dichloromethane (10:90; 2 × 25 ml) to yield after evaporation of solvent the *adduct* (**9**) (91.2 mg, 41%) as an oil, δ ($CDCl_3$, 60 MHz) 1.4—2.7 (13 H, m), 2.15 (s), and 2.19 (s) (total 3 H); $\nu_{max.}$

(CCl_4) 1 867 s and 1 790 s cm^{-1}; *m/z* 252 (M^+, 21%), 236 (3), 222 (8), 205 (7), 204 (22), 178 (20), 177 (81), 176 (7), 133 (53), 132 (34), 131 (38), 104 (23), and 91 (100); (Found: M^+, *m/z* 252.0808. $C_{13}H_{16}O_3S$ requires M^+, *m/z* 252.0820).

Dimethyl 2,5-*Dihydrothiophene*-3,4-*dicarboxylate* (**11**).—2,5-Dihydrothiophene-3,4-dicarboxylic acid (**10**)[11] (2.53 g, 14.5 mmol) was boiled under reflux with BF_3·MeOH complex (51% BF_3; 6.38 ml, 37.8 mmol) and dry methanol (32 ml) for 2.75 h. After cooling the mixture was poured into saturated aqueous $NaHCO_3$ (120 ml). The product was extracted with CH_2Cl_2 (3 × 80 ml), and the organic layers were combined, washed (water), dried, and evaporated. This gave the diester (**11**) (2.93 g, 100%) as an oil, b.p. 102—107 °C (Kugelrohr bath)/0.75 mmHg (lit.,[20] b.p. 130—131 °C/3 mmHg), δ ($CDCl_3$, 60 MHz) 3.8 (6 H, s) and 4.03 (4 H, s).

3,4-*Bismethoxycarbonyl*-2,5-*dihydro*-1-*methylthiophenium Tetrafluoroborate* (**12**).—A solution of the diester (**11**) (0.5 g, 2.48 mmol) in dry chloroform (3 ml) was stirred under nitrogen at room temperature with trimethyloxonium tetrafluoroborate (445 mg, 3 mmol) for 6 h after which acetone (13 ml) was added. The mixture was then boiled, and subsequently cooled in a solid CO_2–acetone bath to give a precipitate which was filtered off. This was washed with cold acetone (4 ml) and dried *in vacuo* over P_2O_5 to give the *sulphonium tetrafluoroborate salt* (**12**) (0.56 g, 89%) as a colourless solid, m.p. 187—188.5 °C; δ [$(CD_3)_2SO$, 60 MHz] 2.85 (3 H, s), 3.72 (6 H, s), 4.28 (2 H, d, *J* 17 Hz), and 4.58 (2 H, d, *J* 17 Hz).

1-*Methylthio*-2,3-*bismethoxycarbonylbuta*-1,3-*diene* (**13**).—A solution of lithium di-isopropylamide [prepared from di-isopropylamine (252 μl, 164 mg, 1.62 mmol) and n-butyl-lithium (0.79 ml, 1.14 mmol, 1.44M in hexane)] free from n-butyl-lithium (Michler's ketone test[21])* was added slowly to a stirred suspension of the salt (**12**) (347 mg, 1.14 mmol) in THF (2 ml) at room temperature (water-bath cooling). The resulting brown solution was stirred at room temperature (2.5 h) and then was partitioned between saturated aqueous NaCl solution (25 ml) and pentane (20 ml). The aqueous layer was separated and re-extracted with pentane (2 × 10 ml). The organic layers were combined, washed with saturated aqueous NaCl (10 ml), dried, and evaporated. Chromatography of the residual oil on preparative t.l.c. plates, and two elutions with methyl acetate–hexane (1:3) gave a band at R_F 0.23—0.37. Upon extraction with MeOH–CH_2Cl_2 (20 : 80) there was obtained the *diene* (**13**) (174.5 mg, 71%) as a yellow oil, δ ($CDCl_3$, 60 MHz) 2.42 (3 H, s), 3.63 (3 H, s), 3.68 (3 H, s), 5.67 (1 H, d, *J* 1.5 Hz), 6.42 (1 H, d, *J* 1.5 Hz), and 7.67 (1 H, s); $\nu_{max.}$ (CCl_4) 1 717s, 1 630m, and 1 580m cm^{-1}; *m/z* (M^+, 30%), 201 (21), 185 (16), 169 (43), 157 (100), 14 (9), 139 (10), 125 (28), 111 (44), 97 (38), and 59 (92) (Found: C, 50.5; H, 5.9; M^+, 216.0450. $C_9H_{12}SO_4$ requires C, 50.0; H, 5.6%; M^+, 216.0456).

trans-2,5-*Diethyl*-2,5-*dihydro*-3,4-*bismethoxycarbonyl*-1-*methylthiophenium Tetrafluoroborate* (**16**).—A mixture of the dihydrothiophene (**15**)[13] (4.3 g, 16.7 mmol), chloroform (37 ml), and trimethyloxonium tetrafluoroborate (2.97 g, 20.1 mmol) was stirred at room temperature under argon for 22.5 h. After evaporating the reaction mixture to dryness the residue was treated with acetone (30 ml) and pentane (75 ml) and cooled in a dry ice–ethanol bath. This gave the *sulphonium tetrafluoroborate* (**16**) (4.61 g, 77%) as colourless crystals, [$(CO_3)_2SO$, 60 MHz] [$(CD_3)_2CO$, 60 MHz] 1.18 (6H, t, *J* 7 Hz), 1.9—2.5 (4H, m), 3.13 (3H, s), 3.80 (3H, s), 3.85 (3H, s), 5.02 (1H, m), and 5.58 (1H, m).

* An excess of (12.5%) of di-isopropylamine was required to remove all the BuLi.

3-*Methylthio*-4,5-*bismethoxycarbonylocta*-3,5-*diene* (**17**).—A solution of lithium di-isopropylamide [prepared from di-isopropylamine (1.768 g, 17.5 mmol) and n-butyl-lithium (1.44M in hexane; 8.68 ml, 12.5 mmol)] in THF (20 ml) was added in portions during 3 min to an ice–water cooled suspension of the salt (**16**) (4.496 g, 12.49 mmol) in THF (20 ml) under argon. The resulting deep brown solution was stirred at room temperature for 2.5 h, and was then poured into water (250 ml) and extracted with pentane (3 × 100 ml). The organic layers were combined and washed with water (100 ml), 10% aqueous NH_4Cl (100 ml), and finally with water again (2 × 100 ml). The extract was dried and evaporated to give the *diene* (**17**) (2.843 g, 84%) as a yellow oil, b.p. 135—140 °C (Kugelrohr bath temperature)/3 mmHg; δ ($CDCl_3$, 60 MHz) 1.05 (3 H, t, *J* 7 Hz), 1.22 (3 H, t, *J* 7 Hz), 1.7—2.5 (2 H, m), 2.26 (3 H, s), 3.02 (2 H, q, *J* 7 Hz), 3.59 (3 H, s), 3.68 (3 H, s), and 6.83 (1 H, t, *J* 7.5 Hz); $\nu_{max.}$ (CCl_4) 1 715s and 1 680m cm^{-1}; *m/z* 272 (M^+, 28%), 257 (32), 241 (11), 240 (10), 226 (6), 225 (100), 213 (26), 197 (79), 181 (20), 153 (22), 133 (28), 113 (45), 105 (67), 91 (76), and 59 (88) (Found: C, 57.65; H, 7.6; M^+, 272.1066. $C_{13}H_{20}SO_4$ requires C, 57.33; H, 7.4%; M^+, 272.1082).

Dimethyl 2,2-*Diethyl*-2,5-*dihydrothiophene*-3,4-*dicarboxylate* (**21**).—Into a solution of pentane-3-thione (**18**)[22] [prepared from 3,3-diethoxypentane (1.96 g, 19.2 mmol)] and hydroquinone (13.5 mg) in light petroleum (b.p. 40—60 °C; 50 ml) cooled to 0—5 °C in an ice-bath was distilled gaseous diazomethane in ether [prepared from *N*-methyl-*N*-nitroso-toluene-*p*-sulphonamide (9.3 mmol)] over 25 min until the pink solution had turned completely yellow. Dimethyl acetylenedicarboxylate (2.64 g, 18.6 mmol) was added at 0—5 °C to this solution which was then allowed to warm slowly to room temperature when it was boiled under reflux (30—40 °C) until the evolution of N_2 gas had ceased. Benzene (100 ml) was added and the mixture was distilled until the temperature of the vapour reached 75 °C. The remaining solution was boiled for 35 min and then left overnight at room temperature. The solvent was evaporated and the resultant yellow unpleasant smelling oil was distilled, first at atmospheric pressure to remove residual solvent and then under reduced pressure. The forerun (8.33 g, b.p. 88—98 °C/23 mmHg) was discarded. The remaining distillate (0.68 g), b.p. 98—170 °C/23 mmHg was further chromatographed on a silica column which was eluted with methyl acetate–hexane and then by preparative h.p.l.c. [Lichrosorb Si 60 (10), 45 cm × $\frac{3}{8}$ in (diam.)]. Elution with methyl acetate–hexane (3.7:96.3; 156 ml) gave the *dihydrothiophene* (**21**) (47.2 mg) as an oil, b.p. 85—95 °C (Kugelrohr bath)/0.3 mmHg; δ ($CDCl_3$, 90 MHz) 1.02 (6 H, t, *J* 7 Hz), 1.6—2.0 (4 H, m), 3.72 (3 H, s), 3.77 (3 H, s), and 3.84 (2 H, s); $\nu_{max.}$ (CCl_4) 1 735s and 1 660m cm^{-1}; *m/z* 258 (M^+, 24%), 231 (6), 230 (12), 229 (100), 228 (6), 227 (17), 199 (8), 198 (11), 197 (68), 186 (8), 185 (76), 167 (9), 139 (24), 113 (26), 111 (19), and 59 (60) (Found: C, 55.5; H, 7.00; M^+, 258.0939. $C_{12}H_{18}SO_4$ requires C, 55.8, H, 7.0%; M^+, 258.0926).

3*a*,4,5,7,8,8*a*-*Hexahydro*-1H,3H-*thieno*[3,4-e]*isobenzofuran*-1,3-*dione* (**23**).—A mixture of 3,4-bismethylenetetrahydrothiophene (**22**)[19] (112 mg, 1 mmol), maleic anhydride (100 mg, 1.02 mmol), and anhydrous toluene (5 ml) was boiled under reflux in the dark for 2.5 h. Evaporation of the mixture to dryness and fractional distillation at 125—127 °C (Kugelrohr bath temperature)/1.5 mmHg of the residue gave a sample which was recrystallised from carbon tetrachloride to yield the *adduct* (**23**) (73 mg, 35%) as colourless crystals, m.p. 134—135 °C; δ ($CDCl_3$, 60 MHz) 2.2—2.8 (4 H, m), 3.46 (2 H, m), and 3.73 (4 H, s); $\nu_{max.}$ ($CHCl_3$) 1 850s and 1 780s cm^{-1}; *m/z* 210 (M^+ 25%), 183 (8), 182 (100), 138 (10), 137 (68), 136 (13), 135 (91), 134 (7), 123 (15), 111 (10), 110 (50), and 105 (22) (Found: C, 56.9; H, 4.9; S, 14.7%; M^+, 210.0337. $C_{10}H_{10}SO_3$ requires C, 57.1; H, 4.8; S, 15.3%; M^+, 210.0350).

*3a,4,5,7,8,8a-Hexahydro-*1H,3H-*thieno*[3,4-e]*isobenzofuran-*1,3-*dione* S,S-*Dioxide* (**26**).—The bisbromomethyl sulphone (**24**)[7] (5.02 g, 16.5 mmol) and maleic anhydride (1.62 g, 16.5 mmol) were dissolved in dry acetone (84 ml), and the solution was added with stirring at room temperature during 5 min to sodium iodide (4.95 g, 33 mmol) in acetone (300 ml). The mixture became brown and a precipitate formed. After further stirring for 20.5 h at room temperature the reaction mixture was evaporated to dryness and the residue was diluted with a mixture of chloroform (200 ml) and aqueous 16% sodium thiosulphate (250 ml). An insoluble precipitate which formed was filtered off, washed with water, and dried (1.2 g, 30%). Recrystallisation from acetone gave the *adduct* (**26**) as colourless crystals, m.p. 183—184 °C (decomp.); δ [$(CD_3)_2SO_3$–$CDCl_3$, 60 MHz] 2.52 (4 H, m), 3.25 (2 H, s), and 3.4—3.9 (4 H, m); $\nu_{max.}$ ($CHCl_3$) 1 845s, 1 780s, and 1 305s cm^{-1} (Found: C, 49.7; H, 4.4%; M^+, 242.0249. $C_{10}H_{10}SO_5$ requires C, 49.6; H, 4.2%; M^+, 242.0249). The above chloroform solution contained *3,4-bisiodomethylsulpholene* (**27**) (0.73 g) which recrystallised from methanol as a colourless solid, m.p. 110—111 °C; δ ($CDCl_3$, 60 MHz) 4.03 (8 H, m); $\nu_{max.}$ (KBr) 1 310 cm^{-1}; *m/z* 398, (M^+, 0.1%), 271 (5), 254 (20), 225 (22), 223 (20), 161 (42), 159 (41), 80 (45), and 79 (10) (Found: M^+, 397.8335. $C_6H_8I_2SO_2$ requires M^+, 397.8335).

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