One-pot Multialkylation Reactions of Sulphol-3-enes

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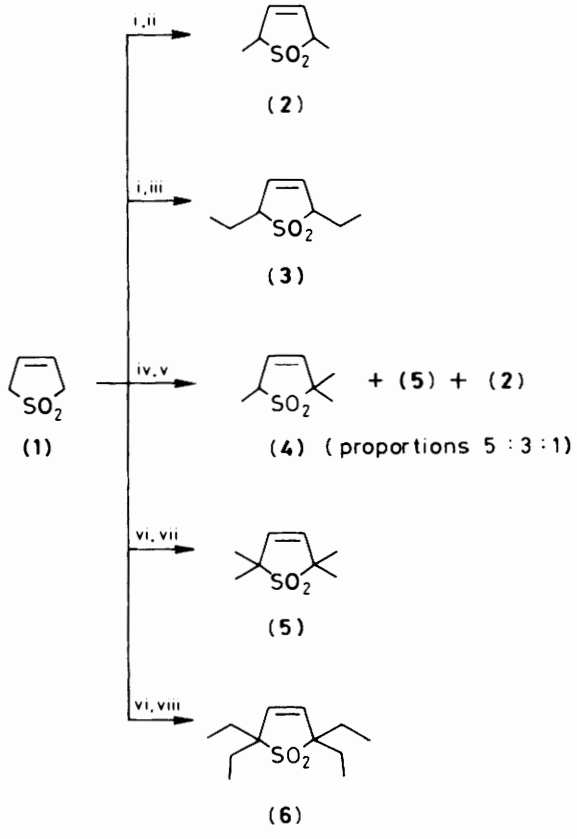
The one-pot multialkylation reactions of sulphol-3-enes have been studied. By varying the ratio of the reagents, the degree of alkylation could be controlled. In most cases, the multiple deprotonation/alkylation took place sequentially at the C-2, C-5, C-2, and C-5 positions. The regiochemistry of the third alkylation of an unsymmetrically disubstituted sulpholene was determined by the pre-existing substituents. The multialkylated 3-sulpholenes should be easily transformed into the 1,4-multialkylated buta-1,3-dienes by cheletropic extrusion of sulphur dioxide. Dicyclohexylidene–ethane was easily prepared by this way.

In continuation of our exploration of the synthetic applications of the direct deprotonation/alkylation reactions of sulphol-3-ene (**1**)[1] we were interested in the nature of multialkylation reactions and their possible applications. The direct monoalkylation reactions of sulphol-3-enes were known to take place selectively at the 2-position.[1,2] A systematic reaction sequence was carried out to study the regiochemistry of the second, the third, and the fourth alkylation reactions.

When compound (**1**) was treated with lithium hexamethyldisilazide (LiHMDS) (2 equiv.) and MeI (2 equiv.) in tetrahydrofuran (THF), the 2,5-dimethylsulpholene (**2**) was produced cleanly in good yield. Similarly, the 2,5-diethylsulpholene (**3**) was produced by reaction with EtI. These results showed that the second alkylation would occur at the 5-position. When compound (**1**) was treated with LiHMDS (3 equiv.) and MeI (3 equiv.) the trisubstituted sulpholene (**4**) was produced as the major product, and was accompanied by compounds (**2**) and (**5**). Although the trimethylsulpholene (**4**) could not be prepared cleanly by this route, the result revealed that the multialkylation was highly regioselective, following the order C-2, C-5, C-2, C-5 (Scheme 1). Actually, if a large excess of LiHMDS and MeI (4.2 equiv.) was treated with compound (**1**), the tetramethyl derivative (**5**) could be obtained almost quantitatively. Similarly, treatment of compound (**1**) with a large excess of LiHMDS and EtI gave the tetraethyl product (**6**) quantitatively. It was interesting to note that the 2,2-disubstituted or 3- or 4-substituted sulpholenes were not observed. The one-pot multialkylation reactions of sulpholene (**1**) were quite different from the alkylations of ketones in terms of regioselectivity.[3] The fact that no alkylation occurred at the 3- or 4-position was in agreement with the report of the charge density at the α-position being higher than that at the γ-position in an allylic sulphone system.[4]

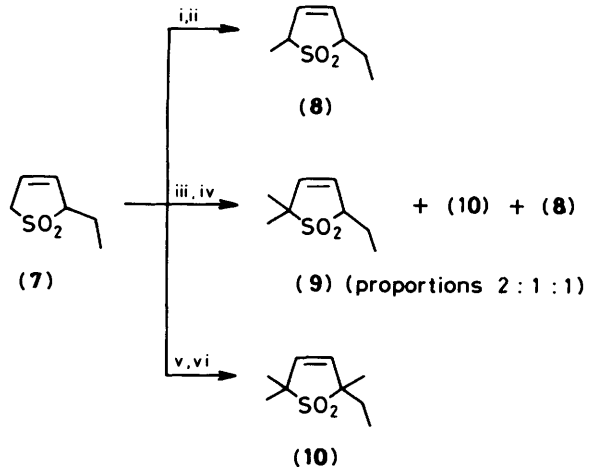
The regioselectivity for the introduction of the third alkyl group onto an unsymmetrical 2,5-disubstituted sulphol-3-ene was studied. When 2-ethylsulphol-3-ene (**7**)[1a] was treated with LiHMDS (2 equiv.) and MeI (2 equiv.), compound (**9**) was obtained as the major product, and was accompanied by products (**8**) and (**10**) (Scheme 2). No other products were formed in any significant quantity. Product (**8**) could be prepared from compound (**7**) by reaction with LiHMDS (1 equiv.) and MeI (1 equiv.). Compound (**9**) must have resulted from the further methylation of compound (**8**), and so compound (**10**) in turn must have resulted from compound (**9**). The preference of the deprotonation/methylation of the unsymmetrical sulpholene (**8**) for the carbon bearing the smaller and the less electron-donating methyl group over that bearing the larger and the more electron-donating ethyl group was predictable. Nevertheless, such high selectivity demonstrated



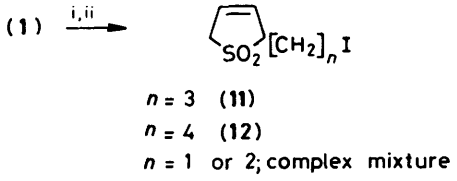
Scheme 1. *Reagents:* i, LiHMDS (2 equiv.); ii, MeI (2 equiv); iii, EtI (2 equiv.); iv, LiHMDS (3 equiv.); v, MeI (3 equiv.); vi, LiHMDS (4 equiv.); vii, MeI (4 equiv.); viii, EtI (4 equiv.)

that the regiochemistry of the third alkyl group introduced onto sulpholenes was extremely sensitive to the pre-existing substituents. Compound (**10**) could also be prepared quantitatively from the monoalkylated sulpholene (**7**) by reaction with LiHMDS (3 equiv.) and MeI (3 equiv.).

When sulpholene (**1**) was treated with LiHMDS (0.5 equiv.) and 1,3-di-iodopropane or 1,4-di-iodobutane (0.5 equiv.), the monoalkylated products (**11**) and (**12**) could be obtained, respectively. However, similar treatment of compound (**1**) with di-iodomethane or 1,2-di-iodoethane, regardless of the ratios of the reagents, resulted in complex mixtures with no indication of the formation of the desired alkylated products (Scheme 3).

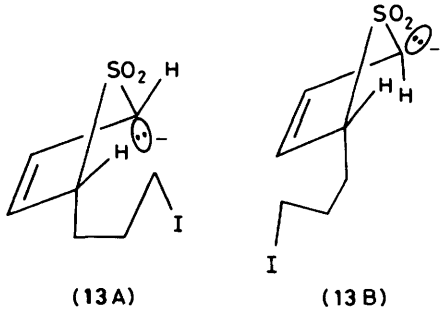


Scheme 2. *Reagents:* i, LiHMDS (1 equiv.); ii, MeI (1 equiv.); iii, LiHMDS (2 equiv.); iv, MeI (2 equiv.); v, LiHMDS (3 equiv.); vi, MeI (3 equiv.)



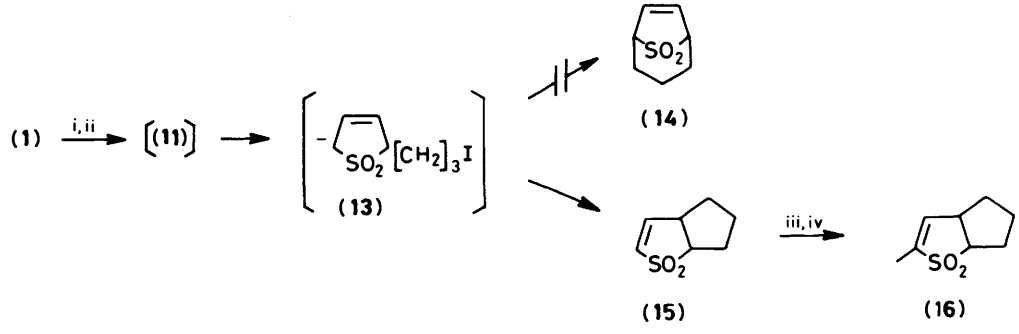
Scheme 3. *Reagents:* i, LiHMDS (0.5 equiv.); ii, $I[CH_2]_nI$ (n = 1—4) (0.5 equiv.)

Products (**11**) and (**12**), containing a terminally iodinated carbon chain at the 2-position, were ideal precursors for the intramolecular alkylations. Since it was established in Schemes 1 and 2 that the dialkylation of sulpholene (**1**) took place at C-2 and C-5, the product from the intramolecular alkylation of (**11**) was expected to be the bridged bicyclic sulphone (**14**). However, when (**1**) was treated with LiHMDS (2 equiv.) and 1,3-di-iodopropane (1 equiv.), the only product obtained was the fused bicyclic sulphone (**15**) (Scheme 4). Compound (**15**) must have been formed in a stepwise manner by way of intermediates (**11**) and (**13**). Examination of a molecular model of the intermediate (**13**) revealed that if the 5-carbanion lone pair were oriented *cis* to the iodopropyl group (**13A**), the cyclization reaction should proceed fairly easily to give compound (**15**) because of its nicely aligned conformation. Our inability to form compound (**14**) suggested that the 5-carbanion was *trans* to the iodopropyl group, as in (**13B**). This was in agreement with Takayama's report that the dialkylation of sulpholenes (**1**) resulted in *trans* products.[2] If anion (**13B**) were to undertake an intramolecular alkylation reaction, it could happen only at the 3-position to give compound (**15**). Moreover, one can consider another possible factor in favour of the observed product (**15**) over (**14**) to be that the olefinic double bond is conjugated to the sulphonyl group in product (**15**), thus giving additional stability to this compound. However, the conjugation factor should not play a significant role in this case because it had been found that sulphol-3-ene and sulphol-2-ene were in a *ca.* 1:1 ratio under equilibrium conditions.[1a] It was noted that compound (**15**) was the first and so far the only example of a γ-alkylation product in a sulpholene system. Compound (**15**) could be further deprotonated and methylated to give compound (**16**). Deprotonation at the vinyl carbon of a sulphol-2-ene system has already been reported.[5]

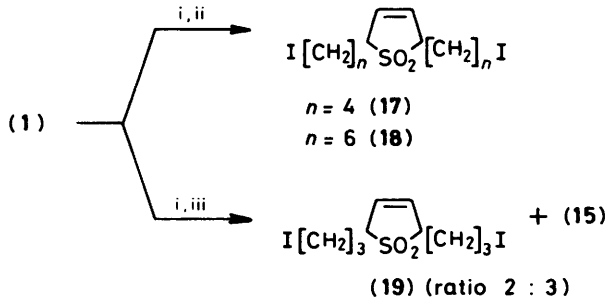


Attempted syntheses of any bicyclic sulphone systems by treatment of sulpholene (**1**) with LiHMDS (2 equiv.) and other α,ω-di-iodoalkanes (1 equiv.) were all unsuccessful. However, the dialkylation reactions of compound (**1**) with LiHMDS (2 equiv.) and of some di-iodoalkanes (2 equiv.) proceeded smoothly to give di-iodides (**17**) and (**18**) as the major products (Scheme 5). Interestingly, reaction of sulpholene (**1**) with di-iodopropane under these conditions gave the bis-(3-iodopropyl)sulphol-3-ene (**19**) and the bicycle (**15**) in a *ca.* 2:3 ratio. Apparently, the competition between inter- and intra-molecular alkylation in this system was in favour of the latter.

Compounds such as (**17**), (**18**), and (**19**) were expected to be susceptible to further intramolecular alkylation if the proper conditions were used. In fact, their isolations were thought to be unnecessary because the multialkylation could be achieved in one pot. Thus, sulpholene (**1**) was treated with LiHMDS (4 equiv.) and a di-iodoalkane (2 equiv.). The intramolecular cyclization reactions indeed took place very easily for di-iodobutane and di-iodopentane as the electrophiles to give the dispirocyclic sulphones (**20**) and (**21**), respectively (Scheme 6). However, the similar reaction with di-iodohexane did not give



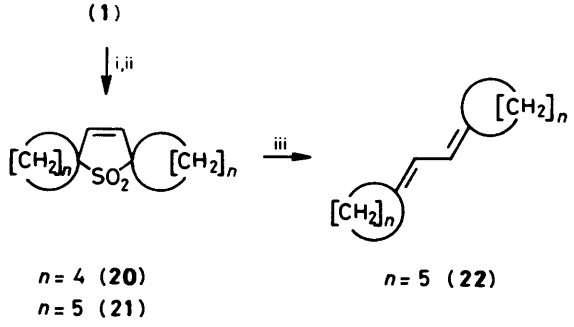
Scheme 4. *Reagents:* i, LiHMDS (2 equiv.); ii, $I[CH_2]_3I$ (1 equiv.); iii, LiHMDS (1 equiv.); iv, MeI (1 equiv.)



Scheme 5. *Reagents:* i, LiHMDS (2 equiv.); ii, $I[CH_2]_nI$ (2 equiv., n = 4 or 6); iii, $I[CH_2]_3I$ (2 equiv.)

the dispirocyclic sulphone but resulted in a complex mixture of products. Attempted intramolecular alkylation of compound (**19**) by treatment with LiHMDS (2 equiv.) also failed to give the dispirocyclic sulphone. These failures of the dispirocyclization should be attributed to the difficulty in the formation of seven- and four-membered rings.*

The multialkylated sulpholenes should be converted into the corresponding buta-1,3-dienes simply by the well established cheletropic extrusion of sulphur dioxide.[6] For example, when compound (**21**) was thermolysed by passage through a hot tube at 350 °C, the buta-1,3-diene (**22**) was produced in quantitative yield. Although compound (**22**)[7] could be obtained by other reactions, our one-pot multialkylation method doubtless serves as the most efficient and suitable for large-scale preparations.



Scheme 6. *Reagents:* i, LiHMDS (4 equiv.); ii, $I[CH_2]_nI$ (2 equiv., n = 4 or 5); iii, thermolysis at 350 °C

In summary, the regiochemistry and the degree of alkylation are easily controlled in the one-pot multialkylation reactions of sulpholene (**1**). This selectivity, coupled with the subsequent extrusion of SO_2, makes sulpholene (**1**) the butadiene 1-anion equivalent upon monoalkylation; the butadiene 1,4-dianion equivalent upon dialkylation; and the 1,1,4,4-tetra-anion equivalent upon tetra-alkylation. Therefore, this approach provides an extremely short and convenient route toward the syntheses of multialkylated buta-1,3-dienes.

Experimental

General.—^1H N.m.r. spectra were determined on a Varian EM390 n.m.r. spectrometer for solutions in $CDCl_3$. ^{13}C N.m.r. spectra were determined on a Jeol FX-100 n.m.r. spectrometer. I.r. spectra were determined on a Perkin-Elmer 297 i.r. spectrophotometer and u.v. spectra were obtained on a Shimadzu UV-210 u.v.–vis. spectrophotometer. Mass spectra were recorded on a Hitachi EMS-4 mass spectrometer or a Jeol JMS-D-100 mass spectrometer. Elemental analyses were performed at the National Taiwan University, Taipei. All reactions were carried out under an atmosphere of dry nitrogen. All anhydrous solvents were freshly distilled before use.

Multialkylation Reactions of Sulpholenes with Iodoalkanes.—To a mixture of a sulpholene (2 mmol), an iodoalkane (quantity used is indicated below), and hexamethylphosphoramide (HMPA) (8 mmol) in anhydrous THF (15 ml) cooled to −78 °C was added dropwise a solution of LiHMDS [generated in THF from hexamethyldisilazane (HMDS) (1.6 equiv.) and n-butyl-lithium (1.0 equiv.) by mixing at 0 °C and stirring at room temperature for 30 min; quantity used is indicated below] during *ca.* 30 min. The reaction mixture was then stirred at −78 °C for another 2 h, after which time EtOAc–n-hexane (1:1; 20 ml) was added in one portion. The cooling bath was then removed and the reaction mixture was stirred at room temperature for 5 min. After removal of the solvent under reduced pressure, the crude reaction mixture was eluted through a silica gel column with EtOAc–n-hexane (1:2) to remove HMPA, HMDS, and inorganic salts, and was then purified by high-pressure liquid chromatography (h.p.l.c.) (LiChrosorb column, Merck) with EtOAc–n-hexane (1:2) as eluant to give the pure alkylated products.

2,5-*Dimethyl*-2,5-*dihydrothiophene* 1,1-*dioxide* (**2**). This was obtained from the reaction of (**1**), MeI (2 equiv.), and LiHMDS (2 equiv.) in 83% yield: *oil*; $\nu_{max.}$(liquid) 1 620, 1 450, 1 300, 1 120, and 1 075 cm^{-1}; δ_H 1.41 (6 H, d, *J* 6.0 Hz), 3.70 (2 H, q, *J* 6.0 Hz), and 5.92 (2 H, s); *m/z* 146 (M^+), 82, and 67 (100%) (Found: C, 49.5; H, 6.8. $C_6H_{10}O_2S$ requires C, 49.3; H, 6.9%).

2,5-*Diethyl*-2,5-*dihydrothiophene* 1,1-*dioxide* (**3**). This was obtained from the reaction of (**1**), EtI (2 equiv.), and LiHMDS (2 equiv.) in 62% yield. The spectral data were identical with those reported earlier.[1a]

2,2,5-*Trimethyl*-2,5-*dihydrothiophene* 1,1-*dioxide* (**4**). This was obtained from the reaction of (**1**), MeI (3 equiv.), and LiHMDS (3 equiv.) in 50% yield, and was accompanied by formation of compounds (**2**) (10% yield) and (**5**) (30% yield). *Compound* (**4**) was produced as white crystal, m.p. 54.0—55.0 °C; $\nu_{max.}$(CCl_4) 1 300, 1 130, and 1 075 cm^{-1}; δ_H 1.30—1.40 (9 H, m), 3.31 (1 H, q, *J* 6.0 Hz), and 5.87 (2 H, s); *m/z* 160 (M^+), 96 (100%), 81, and 67 (Found: C, 52.15; H, 7.55. $C_7H_{12}O_2S$ requires C, 52.5; H, 7.55%).

2,2,5,5-*Tetramethyl*-2,5-*dihydrothiophene* 1,1-*dioxide* (**5**). This was obtained from the reaction of (**1**), MeI (4.2 equiv.), and LiHMDS (4.2 equiv.) in quantitative yield as a white *solid*, m.p. 84.0—86.0 °C; $\nu_{max.}$(KBr) 1 460, 1 290, 1 120, and 1 080 cm^{-1}; δ_H 1.37 (12 H, s) and 5.77 (2 H, s); *m/z* 174 (M^+), 110 (100%), 95, and 81 (Found: C, 55.1; H, 8.0. $C_8H_{14}O_2S$ requires C, 55.1; H, 8.1%).

2,2,5,5-*Tetraethyl*-2,5-*dihydrothiophene* 1,1-*dioxide* (**6**). This was obtained from the reaction of (**1**), EtI (4.2 equiv.), and LiHMDS (4.2 equiv.) in quantitative yield as a white solid, m.p. 47.0—48.5 °C; $\nu_{max.}$(KBr) 1 520, 1 450, 1 300, 1 220, 1 130, and 1 100 cm^{-1}; δ_H 0.98 (12 H, t, *J* 7.0 Hz), 1.79 (8 H, q, *J* 7.0 Hz), and 5.80 (2 H, s); *m/z* 166 ($M^+ - SO_2$), 137, 117, and 81 (100%) (Found: C, 62.5; H, 9.6. $C_{12}H_{22}O_2S$ requires C, 62.6; H, 9.6%).

2-*Ethyl*-5-*methyl*-2,5-*dihydrothiophene* 1,1-*dioxide* (**8**). This was obtained from the reaction of (**7**), MeI (1 equiv.), and LiHMDS (1 equiv.) in 81% yield as an oil, $\nu_{max.}$(liquid) 1 450, 1 300, 1 230, and 1 120 cm^{-1}; δ_H 1.10 (3 H, t, *J* 7.0 Hz), 1.40 (3 H, d, *J* 7.0 Hz), 1.50—2.24 (2 H, m), 3.41—3.80 (2 H, m), and 5.95 (2 H, s); *m/z* 160 (M^+), 96 (100%), 81, and 67 (Found: C, 52.3; H, 7.55. $C_7H_{12}O_2S$ requires C, 52.5; H, 7.55%).

* Recently, a successful dispirocyclization of a 3-aminosulpholane was reported: T. Tsuji, R. Kikichi, and S. Nishida, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 1603.

5-*Ethyl*-2,2-*dimethyl*-2,5-*dihydrothiophene* 1,1-*dioxide* (**9**). This was obtained from the reaction of (**7**), MeI (2 equiv.), and LiHMDS (2 equiv.) in 40% yield. The product was accompanied by formation of compounds (**8**) in 20% yield, and (**10**) in 20% yield. *Compound* (**9**) was an oil, $\nu_{max.}$(liquid) 1 460, 1 290, 1 200, and 1 110 cm^{-1}; δ_H 1.10 (3 H, t, *J* 7.0 Hz), 1.40 (3 H, s), 1.47 (3 H, s), 1.50—2.24 (2 H, m), 3.59 (1 H, t, *J* 7.0 Hz), and 5.87 (2 H, s); *m/z* 174 (M^+), 110 (100%), 95, and 81 (Found: C, 54.7; H, 7.9. $C_8H_{14}O_2S$ requires C, 55.1; H, 8.1%).

2-*Ethyl*-2,5,5-*trimethyl*-2,5-*dihydrothiophene* 1,1-*dioxide* (**10**). This was obtained from the reaction of (**7**), MeI (3.2 equiv.), and LiHMDS (3.2 equiv.) in quantitative yield as an *oil*, $\nu_{max.}$(liquid) 1 470, 1 300, 1 200, 1 135, and 1 100 cm^{-1}; δ_H 1.03 (3 H, t, *J* 7.0 Hz), 1.43 (9 H, s), 1.60—2.03 (2 H, m), and 5.80 (2 H, s); *m/z* 188 (M^+), 124 (100%), 109, 95, and 81 (Found: C, 57.4; H, 8.5. $C_9H_{16}O_2S$ requires C, 57.4; H, 8.6%).

2-(3-*Iodopropyl*)-2,5-*dihydrothiophene* 1,1-*dioxide* (**11**). This was obtained from the reaction of (**1**), 1,3-di-iodopropane (0.5 equiv.), and LiHMDS (0.5 equiv.) in 56% yield as a pale yellow oil, $\nu_{max.}$(liquid) 1 620, 1 440, 1 410, 1 300, 1 240, 1 205, and 1 130 cm^{-1}; δ_H 1.67—2.20 (6 H, m), 3.23 (2 H, t, *J* 6.0 Hz), 3.73 (2 H, s), 3.50—3.80 (1 H, m), and 6.00 (2 H, s); *m/z* 286 (M^+), 222, 159 (100%), 95, and 67 (Found: C, 29.9; H, 3.6. $C_7H_{11}IO_2S$ requires C, 29.5; H, 3.9%).

2-(4-*Iodobutyl*)-2,5-*dihydrothiophene* 1,1-*dioxide* (**12**). Similarly, reaction of (**1**), 1,4-di-iodobutane (0.5 equiv.), and LiHMDS (0.5 equiv.) gave the *title compound* as a pale yellow oil in 53% yield, $\nu_{max.}$(liquid) 1 620, 1 450, 1 425, 1 405, 1 300, 1 240, and 1 130 cm^{-1}; δ_H 1.40—2.15 (6 H, m), 3.18 (2 H, t, *J* 6 Hz), 3.63 (1 H, t, *J* 6.0 Hz), 3.72 (2 H, s), and 6.01 (2 H, s); *m/z* 300 (M^+), 326, 173 (100%), 109, 107, and 67 (Found: C, 32.25; H, 4.4. $C_8H_{13}IO_2S$ requires C, 32.0; H, 4.4%).

2-*Thiabicyclo*[3.3.0]*oct*-3-*ene* 2,2-*dioxide* (**15**). This was obtained from the reaction of (**1**), 1,3-di-iodopropane (1 equiv.), and LiHMDS (2 equiv.) in 68% yield as a white solid, m.p. 42.0—43.0 °C; $\nu_{max.}$(KBr) 1 610, 1 450, 1 390, 1 230, 1 140, and 1 100 cm^{-1}; δ_H 1.30—2.16 (5 H, m), 2.27—2.60 (1 H, m), 3.33—3.83 (2 H, m), and 6.57 (2 H, s); δ_C 141.3, 131.9, 61.5, 46.9, 31.9, 28.4, and 24.8; *m/z* 158 (M^+, 100%), 143, 125, 91, 79, and 67 (Found: C, 52.9; H, 6.3. $C_7H_{10}O_2S$ requires C, 53.1; H, 6.3%).

3-*Methyl*-2-*thiabicyclo*[3.3.0]*oct*-3-*ene* 2,2-*dioxide* (**16**). Reaction of compound (**15**), MeI (1 equiv), and LiHMDS (1 equiv.) gave, in 83% yield, the *methylated product* (**16**) as a white solid, m.p. 53.0—54.0 °C; $\nu_{max.}$(KBr) 1 660, 1 440, 1 280, 1 220, 1 150, and 1 100 cm^{-1}; δ_H 1.25—2.10 (5 H, m). 2.00 (3 H, s), 2.27—2.62 (1 H, m), 3.27—3.58 (2 H, m), and 6.03 (1 H, s); *m/z* 172 (M^+), 155, 93 (100%), 79, and 67 (Found: C, 55.8; H, 7.0. $C_8H_{12}O_2S$ requires C, 55.8; H, 7.0%).

2,5-*Bis*(4-*iodobutyl*)-2,5-*dihydrothiophene* 1,1-*dioxide* (**17**). This was obtained from the reaction of (**1**), 1,4-di-iodobutane (2 equiv.), and LiHMDS (2 equiv.) in 57% yield as a pale yellow oil, $\nu_{max.}$(liquid) 1 450, 1 430, 1 300, 1 205, and 1 125 cm^{-1}; δ_H 1.31—2.22 (12 H, m), 3.20 (4 H, t, *J* 6.0 Hz), 3.60 (2 H, t, *J* 6.0 Hz), and 6.01 (2 H, s); *m/z* 482 (M^+), 418 (100%), 249, 235, 209, 121, and 109 (Found: C, 29.75; H, 4.2. $C_{12}H_{20}I_2O_2S$ requires C, 29.9; H, 4.2%).

2,5-*Bis*-(6-*iodohexyl*)-2,5-*dihydrothiophene* 1,1-*dioxide* (**18**). Similarly, reaction of (**1**), 1,6-di-iodohexane (2 equiv.), and LiHMDS (2 equiv.) gave the title compound as a pale yellow oil in 53% yield, $\nu_{max.}$(liquid) 1 460, 1 300, 1 230, and 1 120 cm^{-1}; δ_H 1.11—2.30 (20 H, m), 3.17 (4 H, t, *J* 6.0 Hz), 3.58 (2 H, t, *J* 6.0 Hz), and 5.96 (2 H, s); *m/z* 538 (M^+), 474 (100%), 411, 344, 346, 345, 344, 155, 109, and 95 (Found: C, 36.0; H, 5.5. $C_{18}H_{28}I_2O_2S$ requires C, 35.7; H, 5.25%).

2,5-*Bis*-(3-*iodopropyl*)-2,5-*dihydrothiophene* 1,1-*dioxide* (**19**). In a similar manner, reaction of (**1**), 1,3-di-iodopropane (2 equiv.), and LiHMDS (2 equiv.) gave the *title compound* as a pale yellow oil in 32% yield. The product was accompanied by the formation of (**15**) (48% yield). Compound (**19**) had $\nu_{max.}$(liquid) 1 620, 1 440, 1 300, 1 215, and 1 120 cm^{-1}; δ_H 1.67—2.30 (8 H, m), 3.22 (4 H, t, *J* 6.0 Hz), 3.60 (2 H, t, *J* 6.0 Hz), and 6.00 (2 H, s); *m/z* 454 (M^+), 390 (100%), 327, 263, 235, 155, and 95 (Found: C, 26.4; H, 3.6. $C_{10}H_{16}I_2O_2S$ requires C, 26.45; H, 3.55%).

Dispirocyclization Reactions of Sulphol-3-*ene*.—To a mixture of compound (**1**) (4 mmol), a di-iodoalkane (8 mmol), and HMPA (16 mmol) in anhydrous THF (50 ml) cooled at −78 °C was added dropwise a solution of LiHMDS (16 mmol) in THF (15 ml). The reaction mixture was stirred at −78 °C for 2.5 h, after which time EtOAc–n-hexane (1:1; 20 ml) was added in one portion. The cooling bath was removed and the reaction mixture was stirred at room temperature for 10 min. After the removal of the solvent under reduced pressure, the crude product was eluted through a silica gel column with EtOAc–n-hexane (1:2) to remove HMPA, HMDS, and inorganic salts, and was then purified by h.p.l.c. (LiChrosorb column, Merck) with EtOAc–n-hexane (1:2) to give the pure products.

6-*Thiadispiro*[4.1.4.2]*tridec*-12-*ene* 6,6-*dioxide* (**20**). This was obtained from the reaction of (**1**), 1,4-di-iodobutane (2 equiv.), and LiHMDS (4 equiv.) in 46% yield as a white solid, m.p. 68.5—69.0 °C; $\nu_{max.}$(CCl_4) 1 450, 1 300, 1 130, and 950 cm^{-1}; δ_H 1.40—2.10 (12 H, m), 2.16—2.70 (4 H, m), and 5.80 (2 H, s); *m/z* 226 (M^+), 185 (100%), and 93 (Found: C, 63.5; H, 8.0. $C_{12}H_{18}O_2S$ requires C, 63.65; H, 8.0%).

7-*Thiadispiro*[5.1.5.2]*pentadec*-14-*ene* 7,7-*dioxide* (**21**). Similarly, reaction of (**1**), 1,5-di-iodopentane (2 equiv.), and LiHMDS (4 equiv.) gave, in 51% yield, the *title spiro compound* as a white solid, m.p. 108—109 °C; $\nu_{max.}$(KBr) 1 615, 1 460, 1 320, 1 290, 1 185, and 1 130 cm^{-1}; δ_H 1.10—2.20 (20 H, m) and 6.03 (2 H, s); *m/z* 254 (M^+), 185 (100%), 106, and 75 (Found: C, 66.0; H, 8.8. $C_{14}H_{22}O_2S$ requires C, 66.1; H, 8.7%).

Thermolysis of Dispirocyclic Sulphone (**21**).—A solution of the dispirocyclic sulphone (**21**) (0.5 mmol) in n-hexane (10 ml) was passed through a vertical hot tube at 350 °C containing Pyrex glass beads (1 mm diameter) at a rate of 20 ml h^{-1} with nitrogen as the carrier gas. The condensate was collected and the solvent was removed under reduced pressure to give the essentially pure product dicyclohexylidene-ethane (**22**) in quantitative yield. An analytical sample was obtained by h.p.l.c. (LiChrosorb, Merck) with n-hexane as eluant. The u.v. and n.m.r. spectral data were identical with those reported.[7]

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