Dialkylative Cyclization Reactions of 3-Sulfolenes with 1,3-Diiodopropane and 1,2-Bis(bromomethyl)benzene

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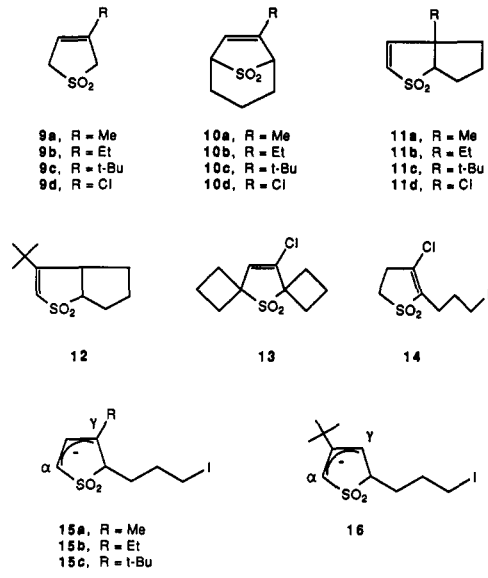
Previously, we had found a method to overcome the entropic problem in the preparation of seven-membered carbocycles via the dialkylative cyclization of a rigid functionalized ring system.[1] For example, the reaction of 3-sulfolene (1) with 2-methylene-1,3-diiodopropane (2) in the presence of 2 equiv of a strong base gave 4 in good yield (Scheme I).[2] However, the dialkylative cyclization reaction of 1 with 1,3-diiodopropane (6) produced only the linearly fused bicyclic 2-sulfolene 8.[3]

The formation of bridged bicyclic compounds and linearly fused bicyclic compounds may be envisioned as a competition between α- and γ-alkylation of the monoalkylated intermediates (cf. 3 and 7). In the reaction of an allylic sulfone anion[4] or a 3-sulfolenyl anion[5] with an electrophile, the α-substitution reaction generally predominates. In other words, in the dialkylative cyclization reactions of 3-sulfolenes, electronic effects should favor the α-alkylative cyclization giving bridged bicyclic sulfones. The preferential formation of 8 indicates that the electronic effects are outweighed by other factors. Since electronic effects, geometric factors, π-π interactions, and steric effects may all influence the mode of dialkylative cyclization, additional experiments were carried out in an effort to understand the steric effects that influence the outcome of these dialkylative cyclizations.

When 3-methyl-3-sulfolene (**9a**) was treated with **6** in the presence of 2 equiv of base, both bridged and fused dialkylative cyclization products **10a** (58%) and **11a** (32%) were observed (Table I). A similar result was obtained when 3-ethyl-3-sulfolene (**9b**) was reacted with **6** where **10b** (57%) and **11b** (28%) were produced. Comparing these results with that of the reaction of 1 with **6** in Scheme I, the steric effects evidently are the reason for the difference in the mode of reactions. The first stage alkylation reaction of **6** with **9a** or **9b** may take place regioselectively at the 2-position[6] to give, after the second deprotonation, the intermediate anion **15a** or **15b**. The steric hindrance of the alkyl group of **15a** and **15b** disfavors γ-alkylation at the 3-position; hence, some of the cyclization proceeded via α-alkylation and a mixture of products was obtained.

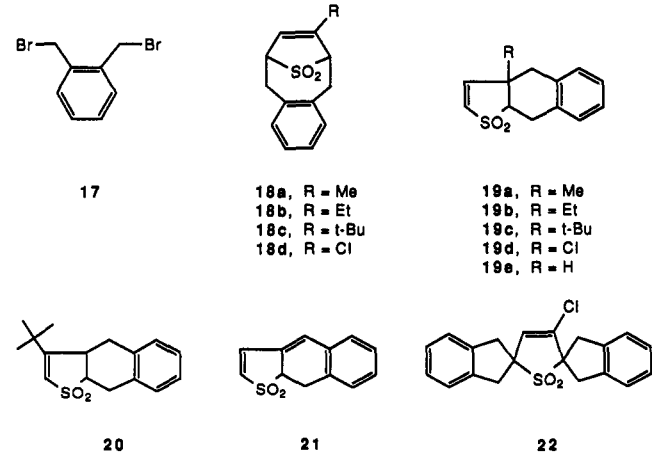
The reaction of 3-*tert*-butyl-3-sulfolene (**9c**) with **6** gave a mixture of three products **10c**, **11c**, and **12**. In addition to the main product **10c** (59%) from bridged cyclization, two kinds of linearly fused bicyclic sulfones were obtained. The fused bicyclic sulfones **11c** and **12** must be produced via the anionic intermediates **15c** and **16**, respectively, whereas the bridged bicyclic product **10c** may be formed via both intermediates.

The reaction of chloroprene sulfone **9d** with **6** gave a mixture of products **11d**, **13**, and **14** in an overall 48% yield. Low yields have routinely been observed in the alkylation reactions of 3-halogenated 3-sulfolenes.[7] These halogenated 3-sulfolenes give intractable, tarry materials under the reaction conditions. We were unable to detect the existence of the bridged bicyclic product **10d**. Obviously, the electron-withdrawing nature of chlorine offsets the steric hindrance it exerts at the 3-position during the cyclization process so that γ-cyclization prevails.



As we started to examine the dialkylative bridged bicyclization of 3-sulfolenes with dihaloalkanes with different carbon chain length, we found that the reactions of **9a** and **9b** with diiodobutane or diiodopentane did not give bridged bicyclic products. Therefore, dihaloalkanes of longer carbon chains were not studied further. On the other hand, 1,2-bis(bromomethyl)benzene **17** was chosen to study the possibility of four-carbon bicyclization of 3-sulfolenes.

When **9a** and **9b** were treated with **17** in the presence of 2 equiv of base, mixtures of bridged and fused bicyclic products were obtained in low yields. It is noteworthy that the ratios of bridged bicyclization to fused bicyclization (1.8:1 for **10a**/**11a**, 2:1 for **10b**/**11b**, 2.5:1 for **18a**/**19a**, and 2.7:1 for **18b**/**19b**) are relatively higher for the reactions with **17** than with **6**.



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0022-3263/91/1956-4560$02.50/0

Scheme I

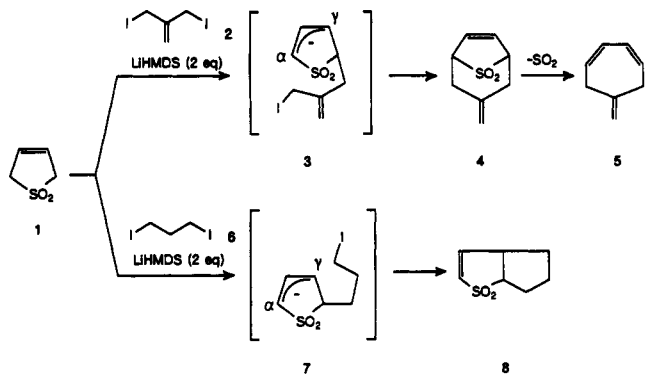

Table I. Dialkylative Cyclization Reactions of 3-Sulfolenes

reactants[a]	products and yields[b]
9a + **6**	**10a** (58)[c] + **11a** (32)[c]
9b + **6**	**10b** (57) + **11b** (28)
9c + **6**	**10c** (59) + **11c** (4) + **12** (13)
9d + **6**	**11d** (30) + **13** (7) + **14** (11)
9a + **17**	**18a** (18) + **19a** (7)
9b + **17**	**18b** (30) + **19b** (11)
9c + **17**	**18c** (21) + **20** (39)
9d + **17**	**18d** (5) + **19d** (15) + **21** (8) + **22** (5)
1 + **17**	**19e** (47)

[a] The reactions were carried out at −78 °C in the presence of 2 equiv of lithium hexamethyldisilazide. [b] The numbers in parentheses are isolated yields unless otherwise noted. [c] Compounds **10a** and **11a** were obtained as an unseparable mixture. Thermolysis of the mixture removes **10a** as volatiles, giving **11a** in pure form.

The reaction of 3-*tert*-butyl-3-sulfolene (**9c**) with **17** yielded a mixture of **18c** (27%) and **20** (39%) without giving **19c**, the fused bicyclic product expected from the reaction sequence of α-alkylation and γ-alkylative cyclization. This is different from the result of the reaction of **9c** with **6** where both kinds of linearly fused bicyclization products **11c** and **12** are obtainable. It was also noted that the reaction of **9c** with **6** gave predominantly bridged bicyclic product **10c** (59%) while that with **17** gave predominantly fused bicyclic product **20** (39%).

The dialkylative cyclization of **9d** with **17** gave a mixture of four products **18d**, **19d**, **21**, and **22** in an overall 33% yield. The presence of the bridged bicyclic product **18d**, albeit formed in low yield, in this reaction as compared with the absence of **10d** in the product mixture with **6** indicates again the higher tendency of **17** than **6** to afford bridged bicyclization. However, the electron-withdrawing effect of the chlorine atom may partially offset the steric hindrance effect, since the ratio of the bridged bicyclic (**18d**) to fused bicyclics (**19d** and **21**) is only 1:4.6, smaller than those ratios observed for **18a**/**19a** and **18b**/**19b**. When the parent 3-sulfolene **1** was reacted with **17**, only the linearly fused product **19e** was produced (47%). Apparently, without a bulky group at the 3-positions, the intermediate of the first-stage alkylation tends to undergo γ-alkylative cyclization.

In order to confirm the structures of the bridged bicyclic sulfones and to demonstrate that they are precursors to seven- and eight-membered carbocycles, we studied the SO_2 extrusion reaction[8] of these compounds (Table II). Treatment of **10c** and **18a–c** with $LiAlH_4$/THF for 12 h at room temperature gave **23c** and **24a–c**, respectively, in satisfactory yields. However, such reaction conditions failed for compounds **10a** and **10b** because of the difficulty encountered in the separation of the low-boiling carbocyclic products. Alternatively, **10a** and **11a** were conveniently pyrolyzed under vacuum to yield the corresponding dienes. When the unseparable mixture of **10a** and **11a** was subjected to bulb-to-bulb pyrolysis at 180 °C, **11a** remained unchanged while **10a** lost SO_2 to give **23a**. An analytically pure sample of **11a** was thus obtained.

In summary, we have shown that dialkylative cyclization reactions of 3-sulfolenes with dihalo substrates provide bridged bicyclic [3.2.1] and [4.2.1] systems. The competitive bicyclization reactions giving linearly fused [3.3.0] and [4.3.0] products can be reduced by placing a bulky substituent on 3-sulfolene. The bridged bicyclic sulfolenes thus prepared are easily converted to the corresponding 1,3-dienyl carbocycles by direct thermolysis or by treatment with $LiAlH_4$ at room temperature.

Experimental Section

General Methods. ^1H NMR spectra were determined on a Bruker ACF-200 NMR spectrometer as solutions in $CDCl_3$. IR spectra were determined on a Perkin-Elmer 290 IR spectrophotometer. Mass spectra were determined on a VG 70-250S mass spectrometer. Elemental analyses were performed on a Perkin-Elmer 240C analyzer. THF was freshly distilled from potassium before use. All reactions were performed under an inert atmosphere of nitrogen. Dihalides **6** and **17** were puchased from Aldrich Chemical Co. Sulfolenes **1**, **9a**, and **9b** were purchased from Fluka Chemical Co., while **9c** and **9d** were prepared from the corresponding butadienes.[9]

Dialkylative Cyclization Reactions of 3-Sulfolenes 1 and 9a–d with 1,3-Diiodopropane (6) and 1,2-Bis(bromomethyl)benzene (17). To a solution of sulfolene (1 mmol), hexamethylphosphoramide (HMPA, 4 mmol), and a dihalide (**6** or **17**, 1 mmol) in THF (10 mL) cooled at −78 °C was added dropwise a solution of lithium hexamethyldisilazide (LiHMDS, 2 mmol, freshly prepared from HMDS (3 mmol) and *n*-BuLi (2 M in hexane, 2 mmol) at room temperature). The reaction was monitored by TLC until the complete disappearance of the reacting sulfolene. Ethyl acetate (10 mL) was added when the reaction was judged complete, and the reaction mixture was allowed to warm to room temperature. The volatiles were removed under reduced pressure, and the crude oil was eluted through a silica gel (Merck No. 7734, 10 g; hexane/EtOAc (4:1)) to give the pure products. Analytically pure samples of the products were obtained by HPLC (LiChrosorb column).

6-Methyl-8-thiabicyclo[3.2.1]-6-octene 8,8-Dioxide (10a). Obtained from the reaction of **9a** with **6** as a mixture unseparable from **11a**. The yield of **10a** was estimated to be 58% by the analysis of the ^1H NMR spectrum of the mixture of **10a** and **11a**: δ 5.97–5.90 (m, 1 H), 3.56–3.45 (m, 1 H), 3.28–3.20 (m, 1 H), 2.50–1.15 (m, 9 H).

6-Ethyl-8-thiabicyclo[3.2.1]-6-octene 8,8-Dioxide (10b). A colorless oil: IR (neat) 2939, 1628, 1447, 1293, 1110 cm^{-1}; ^1H NMR δ 5.97–5.90 (m, 1 H), 3.60–3.50 (m, 1 H), 3.37–3.30 (m, 1 H), 2.35–2.15 (m, 4 H), 1.87–1.65 (m, 2 H), 1.54–1.20 (m, 2 H), 1.10 (t, 3 H, J = 7.4 Hz); MS m/z 186 (M^+), 122, 107, 93 (100), 79; exact mass calcd for $C_9H_{14}O_2S$ 186.0174, found 186.0171. Anal. Calcd for $C_9H_{14}O_2S$: C, 58.03; H, 7.58. Found: C, 58.10; H, 7.55.

6-*tert*-Butyl-8-thiabicyclo[3.2.1]-6-octene 8,8-Dioxide (10c). A white solid: mp 127–127.5 °C; IR (KBr) 2962, 1606, 1286, 1192, 1111 cm^{-1}; ^1H NMR δ 6.00–5.97 (m, 1 H), 3.63–3.55 (m, 2 H), 2.46–2.21 (m, 2 H), 1.91–1.72 (m, 2 H), 1.56–1.28 (m, 2 H), 1.16 (s, 9 H); MS m/z 150 (M^+ − 64) 135, 107, 57 (100). Anal. Calcd for $C_{11}H_{18}O_2S$: C, 61.64; H, 8.47. Found: C, 61.75; H, 8.42.

5-Methyl-2-thiabicyclo[3.3.0]-3-octene 2,2-Dioxide (11a). Obtained from the reaction of **9a** with **6** as a mixture unseparable from **10a**. After thermolytical removal of **10a** (see procedure for thermolysis) and column chromatography, **11a** was obtained in

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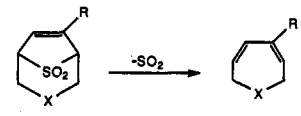
Table II. Extrusion Reactions of SO_2 from Bridged Bicyclic Sulfones



entry	starting material	condition[a]	product	yield (%)
1, R = Me, X = $-CH_2-$	**10a + 11a**	B	**23a**	93
2, R = Et, X = $-CH_2-$	**10b**	B	**23b**	90
3, R = *t*-Bu, X = $-CH_2-$	**10c**	A	**23c**	93
4, R = Me, X = 	**18a**	A	**24a**	85
5, R = Et, X = 	**18b**	A	**24b**	84
6, R = *t*-Bu, X = 	**18c**	A	**24c**	90

[a] Key: Condition A, $LiAlH_4$/THF at room temperature for 8 h; condition B, bulb-to-bulb pyrolysis at 180 °C.

32% yield as a colorless oil: IR (neat) 3074, 2961, 1628, 1289, 1111 cm^{-1}; ^1H NMR δ 6.51 (d, 1 H, J = 6.6 Hz), 6.40 (d, 1 H, J = 6.6 Hz), 3.12–3.03 (m, 1 H), 2.48–2.35 (m, 1 H), 2.06–1.40 (m, 8 H); MS m/z 172 (M^+), 155, 108, 93 (100), 79; exact mass calcd for $C_8H_{12}O_2S$ 172.0558, found 172.0562. Anal. Calcd for $C_8H_{12}O_2S$: C, 55.79; H, 7.02. Found: C, 55.81; H, 6.98.

5-Ethyl-2-thiabicyclo[3.3.0]-3-octene 2,2-Dioxide (11b). A white solid: mp 69.5–70.5 °C; IR (KBr) 2963, 1601, 1443, 1275, 1108 cm^{-1}; ^1H NMR δ 6.56 (d, 1 H, J = 6.6 Hz), 6.40 (d, 1 H, J = 6.6 Hz), 3.13–3.04 (m, 1 H), 2.50–2.35 (m, 1 H), 1.98–1.35 (m, 7 H), 0.94 (t, 3 H, J = 7.4 Hz); MS m/z 186 (M^+), 169 (100), 151, 93, 85. Anal. Calcd for $C_9H_{14}O_2S$: C, 58.03; H, 7.58. Found: C, 58.06; H, 7.54.

5-*tert*-Butyl-2-thiabicyclo[3.3.0]-3-octene 2,2-Dioxide (11c). A colorless oil: IR (neat) 2963, 1606, 1290, 1139 cm^{-1}; ^1H NMR δ 6.59 (s, 2 H), 3.27–3.18 (m, 1 H), 2.55–2.43 (m, 1 H), 1.90–1.10 (m, 5 H), 0.98 (s, 9 H); MS m/z 214 (M^+), 158 (100), 141, 100, 91, 79; exact mass calcd for $C_{11}H_{18}O_2S$ 214.1027, found 214.1030. Anal. Calcd for $C_{11}H_{18}O_2S$: C, 61.64; H, 8.47. Found: C, 61.69; H, 8.46.

5-Chloro-2-thiabicyclo[3.3.0]-3-octene 2,2-Dioxide (11d). The purity of compound **11d** was judged to be >95% by ^1H NMR spectral determination (see supplementary material): colorless oil; IR (neat) 3078, 2973, 1605, 1372, 1298, 1144 cm^{-1}; ^1H NMR δ 6.71–6.58 (m, 2 H), 3.73 (dd, 1 H, J = 9.3, 2.7 Hz), 2.55–2.15 (m, 3 H), 2.04–1.90 (m, 1 H), 1.76–1.50 (m, 2 H); MS m/z 192 (M^+), 175, 157, 139, 108, 91 (100), 77; exact mass calcd for $C_7H_9ClO_2S$ 192.0012, found 192.0011.

4-*tert*-Butyl-2-thiabicyclo[3.3.0]-3-octene 2,2-Dioxide (12). A white solid: mp 88.5–89 °C; IR (KBr) 3022, 2971, 1605, 1287, 1123 cm^{-1}; ^1H NMR δ 6.25 (s, 1 H), 3.76–3.44 (m, 2 H), 2.48–2.28 (m, 1 H), 2.15–1.94 (m, 3 H), 1.19 (s, 9 H); MS m/z 214 (M^+), 197, 151, 135 (100), 93, 79, 57. Anal. Calcd for $C_{11}H_{18}O_2S$: C, 61.64; H, 8.47. Found: C, 61.75; H, 8.42.

10-Chloro-5-thiadispiro[3.1.3.2]-10-undecene 5,5-Dioxide (13). The purity of compound **13** was judged to be >95% by ^1H NMR spectral determination (see supplementary material): colorless oil; IR (neat) 3057, 2991, 1608, 1304, 1142 cm^{-1}; ^1H NMR δ 6.14 (s, 1 H), 2.96–2.85 (m, 4 H), 2.51–2.34 (m, 2 H), 2.24–1.90 (m, 6 H); MS m/z 232 (M^+), 204, 176, 168, 112, 105 (100), 91; exact mass calcd for $C_{10}H_{13}ClO_2S$ 232.0325, found 232.0317.

3-Chloro-2-(3-iodopropyl)-2-sulfolene (14). The purity of compound **14** was judged to be >95% by ^1H NMR spectral determination (see supplementary material): colorless oil; IR (neat) 2985, 1650, 1299, 1128 cm^{-1}; ^1H NMR δ 3.45–3.38 (m, 2 H), 3.24 (t, 2 H, J = 6.8 Hz), 3.12–3.00 (m, 2 H), 2.70–2.60 (m, 2 H), 2.30–2.12 (m, 2 H); MS m/z 320 (M^+), 279, 241, 193 (100), 155, 91, 77; exact mass calcd for $C_7H_{10}ClIO_2S$ 319.9135, found 319.9132.

3,4-Benzo-7-methyl-9-thiabicyclo[4.2.1]-3,7-nonadiene 9,9-Dioxide (18a). A white solid: mp 137–137.5 °C; IR (KBr) 3015, 2975, 1625, 1475, 1280, 1105 cm^{-1}; ^1H NMR δ 7.22–6.98 (m, 4 H), 5.76–5.68 (m, 1 H), 3.84–3.50 (m, 4 H), 3.24–3.08 (m, 2 H), 1.69 (s, 3 H); MS m/z 236 (M^+ + 2), 169 (100), 155, 115, 81. Anal. Calcd for $C_{13}H_{14}O_2S$: C, 66.64; H, 6.02. Found: C, 66.64; H, 6.03.

3,4-Benzo-7-ethyl-9-thiabicyclo[4.2.1]-3,7-nonadiene 9,9-Dioxide (18b). A white solid: mp 96.5–97 °C; IR (KBr) 3026, 2970, 1626, 1490, 1299, 1111, 763 cm^{-1}; ^1H NMR δ 7.20–6.97 (m, 4 H), 5.76–5.68 (m, 1 H), 3.86–3.56 (m, 4 H), 3.15 (ddd, 2 H, J = 15.9, 8.9, 5.1 Hz), 2.18–1.90 (m, 2 H), 0.87 (t, 3 H, J = 8.9 Hz); MS m/z 248 (M^+), 219, 183 (100), 155, 91, 77. Anal. Calcd for $C_{14}H_{16}O_2S$: C, 67.71; H, 6.49. Found: C, 67.60; H, 6.50.

3,4-Benzo-7-*tert*-butyl-9-thiabicyclo[4.2.1]-3,7-nonadiene 9,9-Dioxide (18c). A white solid: mp 116.5–117.5 °C; IR (KBr) 3073, 2963, 1602, 1447, 1269, 1121 cm^{-1}; ^1H NMR δ 7.17–6.97 (m, 4 H), 5.75 (d, 1 H, J = 4.9 Hz), 3.85–3.66 (m, 4 H), 3.14 (ddd, J = 16.7, 8.7, 1.8 Hz), 0.96 (s, 9 H); MS m/z 277 (M^+ + 1), 211 (100), 197, 155, 115, 91; exact mass calcd for $C_{16}H_{20}O_2S$ 276.1184, found 276.1191. Anal. Calcd for $C_{16}H_{20}O_2S$: C, 69.53; H, 7.29. Found: C, 69.33, H, 7.18.

3,4-Benzo-7-chloro-9-thiabicyclo[4.2.1]-7-nonene 9,9-Dioxide (18d). The purity of compound **18d** was judged to be >95% by ^1H NMR spectral determination (see supplementary material): white solid; mp 148–149 °C; IR (KBr) 3095, 2922, 1606, 1442, 1301, 1113 cm^{-1}; ^1H NMR δ 7.26–7.03 (m, 4 H), 6.07 (d, 1 H, J = 6.4 Hz), 4.0–3.92 (m, 1 H), 3.85–3.65 (m, 3 H), 3.38–3.16 (m, 2 H); MS m/z 254 (M^+), 236, 219, 189 (100), 153, 115, 91, 77; exact mass calcd for $C_{12}H_{11}ClO_2S$ 254.0168, found 254.0173.

3a-Methyl-3a,4,9,9a-tetrahydronaphtho[2,3-*b*]thiophene 1,1-Dioxide (19a). A white solid: mp 142.5–143.5 °C; IR (KBr) 3081, 2942, 1605, 1448, 1285, 1128 cm^{-1}; ^1H NMR δ 7.30–7.07 (m, 4 H), 6.48 (d, 1 H, J = 7.0 Hz), 6.41 (d, 1 H, J = 7.0 Hz), 3.26–3.00 (m, 3 H), 2.71 (s, 2 H), 1.34 (s, 3 H); MS m/z 234 (M^+, 100), 216, 199, 167, 128, 115, 91, 77. Anal. Calcd for $C_{13}H_{14}O_2S$: C, 66.64; H, 6.02. Found: C, 66.32; H, 6.07.

3a-Ethyl-3a,4,9,9a-tetrahydronaphtho[2,3-*b*]thiophene 1,1-Dioxide (19b). A colorles oil: IR (neat) 3081, 3033, 2977, 1608, 1459, 1306, 1125 cm^{-1}; ^1H NMR δ 7.32–7.04 (m, 4 H), 6.50 (d, 1 H, J = 7.2 Hz), 6.39 (d, 1 H, J = 7.2 Hz), 3.30–2.96 (m, 3 H), 2.80 (d, 1 H, J = 14.3 Hz), 2.66 (d, 1 H, J = 14.3 Hz), 1.74–1.55 (m, 3 H), 0.96 (t, 3 H, J = 8.6 Hz); MS m/z 248 (M^+), 219 (100), 181, 168, 128, 91, 77; exact mass calcd for $C_{14}H_{16}O_2S$ 248.0871, found 248.0877. Anal. Calcd for $C_{14}H_{16}O_2S$: C, 67.71; H, 6.49. Found: C, 67.71; H, 6.45.

3a-Chloro-3a,4,9,9a-tetrahydronaphtho[2,3-*b*]thiophene 1,1-Dioxide (19d). The purity of compound **19d** was judged to be >95% by ^1H NMR spectral determination (see supplementary material): white solid; mp 123–124 °C; IR (KBr) 3084, 3074, 1608, 1296, 1114 cm^{-1}; ^1H NMR δ 7.34–7.14 (m, 4 H), 6.66 (d, 1 H, J = 6.3 Hz), 6.62 (d, 1 H, J = 6.3 Hz), 3.91 (t, 1 H, J = 7.6 Hz), 3.38–3.09 (m, 4 H); MS m/z 254 (M^+), 219, 168, 152, 128 (100), 115, 77; exact mass calcd for $C_{12}H_{11}ClO_2S$ 254.0168, found 254.0168.

3a,4,9,9a-Tetrahydronaphtho[2,3-*b*]thiophene 1,1-Dioxide (19e). A white solid: mp 146–146.5 °C; IR (KBr) 3083, 2934, 1604, 1480, 1287, 1132, 1092 cm^{-1}; ^1H NMR δ 7.25–7.05 (m, 4 H), 6.65–6.55 (m, 2 H), 3.62–3.45 (m, 2 H), 3.24–2.93 (m, 3 H), 2.61

(dd, 1 H, J = 14, 8.3 Hz); MS m/z 220 (M^+), 185, 81, 69 (100), 57. Anal. Calcd for $C_{12}H_{12}O_2S$: C, 65.43; H, 5.49. Found: C, 65.16; H, 5.51.

3-*tert*-Butyl-3a,4,9,9a-tetrahydronaphtho[2,3-*b*]thiophene 1,1-Dioxide (20). A white solid: mp 155.5–156.5 °C; IR (KBr) 3074, 2970, 1603, 1457, 1272, 1127 cm^{-1}; ^1H NMR δ 7.30–7.12 (m, 4 H), 6.55 (s, 1 H), 3.64 (dd, 1 H, J = 18.1, 9.5 Hz); MS m/z 276 (M^+), 211, 185, 115, 57 (100). Anal. Calcd for $C_{16}H_{20}O_2S$: C, 69.53; H, 7.29. Found: C, 69.37; H, 7.29.

9,9a-Dihydronaphtho[2,3-*b*]thiophene 1,1-Dioxide (21). A white solid: mp 141–142 °C; IR (KBr) 3071, 2928, 1620, 1283, 1127 cm^{-1}; ^1H NMR δ 7.36–7.10 (m, 5 H), 6.90–6.76 (m, 2 H), 4.08 (ddd, 1 H, J = 12.7, 7.6, 2.5 Hz), 3.38–3.10 (m, 2 H); MS m/z 218 (M^+), 153 (100), 128, 115, 76; exact mass calcd for $C_{12}H_{10}O_2S$ 218.0402, found 218.0400. Anal. Calcd for $C_{12}H_{12}O_2S$: C, 66.03; H, 4.61. Found: C, 65.81; H, 4.60.

3,4:9,10-Dibenzo-12-chloro-6-thiadispiro[4.1.4.2]-3,9,12-tridecatriene 6,6-Dioxide (22). The purity of compound **22** was judged to be >95% by ^1H NMR spectral determination (see supplementary material): white solid; mp 172–173 °C; IR (KBr) 3058, 2950, 1609, 1422, 1302, 1140 cm^{-1}; ^1H NMR δ 7.35–7.15 (m, 8 H), 6.15 (s, 1 H), 3.99 (d, 2 H, J = 16.8 Hz), 3.95 (d, 2 H, J = 16.8 Hz), 3.44 (d, 2 H, J = 17.3 Hz), 3.12 (d, 2 H, J = 17.3 Hz); MS m/z 356 (M^+), 255 (100), 171, 131, 62; exact mass calcd for $C_{20}H_{17}ClO_2S$ 356.0638, found 356.0637.

Extrusion of Sulfur Dioxide from 3-Sulfolenes. Procedure A. To a suspension of $LiAlH_4$ (weight equal to weight of the sulfolene used) in anhydrous THF (10 mL/100 mg of $LiAlH_4$) was added a solution of 3-sulfolene **10c** or **18a–c** in THF (1 mL/100 mg of sulfolene). The mixture was stirred at room temperature for 12 h, and the excess of $LiAlH_4$ was destroyed by adding aqueous ether. The resulting solution was dried (Na_2SO_4), filtered, and evaporated under reduced pressure to give essentially pure dienyl product.

Procedure B. Sulfolene **10a** or **10b** (1 mmol) was thermolyzed at 180 °C in Kugehlrohr under vacuum (0.1 Torr) to give the analytically pure dienyl product.

2-Methyl-1,3-cycloheptadiene (23a). Obtained in 93% yield by procedure B from an unseparable mixture of **10a** and **11a** as a colorless oil: IR (neat) 2918, 1663, 1294, 1050 cm^{-1}; ^1H NMR δ 5.84–5.57 (m, 3 H), 2.35–2.14 (m, 4 H), 1.88–1.77 (m, 5 H); MS m/z 108 (M^+, 100), 93, 80; exact mass calcd for C_8H_{12} 108.0940 found 108.0935. Anal. Calcd for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.51; H, 11.24.

2-Ethyl-1,3-cycloheptadiene (23b). A colorless oil: IR (neat) 2964, 1629, 1214, 1048 cm^{-1}; ^1H NMR δ 5.88–5.56 (m, 3 H), 2.33–2.15 (m, 4 H), 2.08–1.96 (m, 2 H), 1.87–1.75 (m, 2 H), 0.99 (t, 3 H, J = 7.5 Hz); MS m/z 122 (M^+, 100), 107, 93, 79; exact mass calcd for C_9H_{14} 122.1095, found 122.1083. Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.24; H, 11.70.

2-*tert*-Butyl-1,3-cycloheptadiene (23c). A colorless oil: IR (neat) 2924, 1628, 1455 cm^{-1}; ^1H NMR δ 6.05–5.78 (m, 3 H), 2.10–1.85 (m, 6 H), 1.03 (s, 9 H); MS m/z 150 (M^+), 135, 107, 57 (100); exact mass calcd for $C_{11}H_{18}$ 150.1408, found 150.1391. Anal. Calcd for $C_{11}H_{18}$: C, 87.93; H, 12.07. Found: C, 87.50; H, 12.31.

6,7-Benzo-2-methyl-1,3,6-cyclooctatriene (24a). A colorless oil: IR (neat) 3012, 2931, 1637, 1428, 745 cm^{-1}; ^1H NMR δ 7.21–7.05 (m, 4 H), 6.15 (d, 1 H, J = 10 Hz), 5.77–5.62 (m, 1 H), 5.53–5.40 (m, 1 H), 3.38 (t, 4 H, J = 7.5 Hz), 1.81 (s, 3 H); MS m/z 170 (M^+), 155 (100), 142, 128, 115, 97; exact mass calcd for $C_{13}H_{14}$ 170.1096, found 170.1096. Anal. Calcd for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.57; H, 8.35.

6,7-Benzo-2-ethyl-1,3,6-cyclooctatriene (24b). A colorless oil: IR (neat) 3012, 2964, 1651, 1426, 746 cm^{-1}; ^1H NMR δ 7.20–7.04 (m, 4 H), 6.19 (d, 1 H, J = 10 Hz), 5.82–5.67 (m, 1 H), 5.46 (t, 1 H, J = 7.7 Hz), 3.46–3.30 (m, 4 H), 2.16 (q, 2 H, J = 7.4 Hz), 1.06 (t, 3 H, J = 7.4 Hz); MS m/z 184 (M^+), 169, 155 (100), 128, 115, 91; exact mass calcd for $C_{14}H_{16}$ 184.1252, found 184.1242. Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 90.98; H, 8.83.

6,7-Benzo-2-*tert*-butyl-1,3,6-cyclooctatriene (24c). A colorless oil: IR (neat) 3016, 2960, 1631, 1453, 1262 cm^{-1}; ^1H NMR δ 7.17–7.05 (m, 4 H), 6.37 (d, 1 H, J = 10 Hz), 5.81–5.68 (m, 1 H), 5.48 (t, 1 H, J = 7.7 Hz), 3.35 (d, 4 H, J = 7.7 Hz), 1.08 (s, 9 H); MS m/z 212 (M^+), 197, 169, 155 (100), 129, 115, 91; exact mass calcd for $C_{16}H_{20}$ 212.1565, found 212.1565. Anal. Calcd for $C_{16}H_{20}$: C, 90.51; H, 9.49. Found: C, 90.39; H, 9.62.

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Registry No. **1**, 77-79-2; **6**, 627-31-6; **9a**, 1193-10-8; **9b**, 62157-91-9; **9c**, 62157-93-1; **9d**, 7311-87-7; **10a**, 133753-91-0; **10b**, 133753-92-1; **10c**, 133753-93-2; **11a**, 133753-94-3; **11b**, 133753-95-4; **11c**, 133753-96-5; **11d**, 133753-97-6; **12**, 133753-98-7; **13**, 133753-99-8; **14**, 133754-00-4; **17**, 91-13-4; **18a**, 133754-01-5; **18b**, 133754-02-6; **18c**, 133754-03-7; **18d**, 133754-04-8; **19a**, 133754-05-9; **19b**, 133754-06-0; **19d**, 133754-07-1; **19e**, 133754-08-2; **20**, 133754-09-3; **21**, 133754-10-6; **22**, 133754-11-7; **23a**, 14947-21-8; **23b**, 133754-12-8; **23c**, 51284-27-6; **24a**, 133754-13-9; **24b**, 133754-14-0; **24c**, 133754-15-1.

Supplementary Material Available: ^1H NMR spectra for compounds **11d**, **13**, **14**, **18d**, **19d**, and **22** (6 pages). Ordering information is given on any current masthead page.

Model Studies toward the Synthesis of Leukotrienes: Hetero-Diels–Alder Reactivity of Tricarbonyl(diene)iron Complexes

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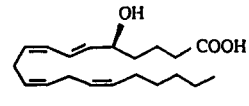
The application of (η^4-diene)$Fe(CO)_3$ complexes to organic synthesis has recently shown great promise due to their ease of preparation, resolution, and diastereoselective reactivity.[2] The possibility of utilizing these complexes for the synthesis of biologically interesting linear polyenes, such as the leukotrienes, has been reported.[3] In addition, we have found that (η^5-pentadienyl)$Fe(CO)_3$ cations may also prove useful for the preparation of the (*E,Z,Z*)-1,3,6-triene portion of the leukotrienes.[4] In order to develop routes for the further elaboration of these triene complexes into the HETEs,[5] we have investigated the hetero-Diels–Alder reaction[6] of (sorbaldehyde)$Fe(CO)_3$ (**1**) as a model system.[7,8]



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