

**Registry No.** 2-Methylbenzophenone, 131-58-8; anthracene, 120-12-7; fluorene, 86-73-7; 2-methyldiphenyl ketimine, 22627-00-5; 2-benzylbenzoxazole, 56153-61-8; benzonitrile, 100-47-0; *o*-tolunitrile, 529-19-1; 2,4,6-trimethylbenzophenone, 954-16-5; bromomesitylene, 576-83-0; methyl benzoate, 93-58-3; bromobenzene, 108-86-1; (2,4,6-trimethylphenyl)phenyl ketimine, 65232-41-9; 2-chlorobenzophenone, 5162-03-8; (2-chlorophenyl)phenylmethane, 29921-41-3; 2,4-dimethylfluorene, 2928-44-1; 2-methylfluorene, 1430-97-3; 4-methylfluorene, 1556-99-6; 1,3-dimethylantracene, 610-46-8; 1-methylantracene, 610-48-0; 2-methylantracene, 613-12-7; 2,4,6-trimethylbenzoxazole, 2571-52-0; 2-benzyl-4,6-dimethylbenzoxazole, 73466-76-9.

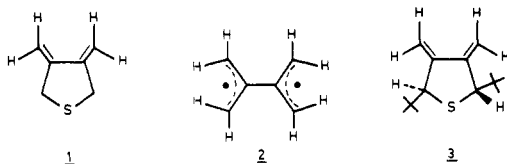
### Synthesis and Reactions of a 3,4-Dimethylenethiolane Derivative

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A structurally interesting but little known compound type is represented by 3,4-dialkylidenethiolanes. The parent compound, 3,4-dimethylenethiolane (1), is, for in-



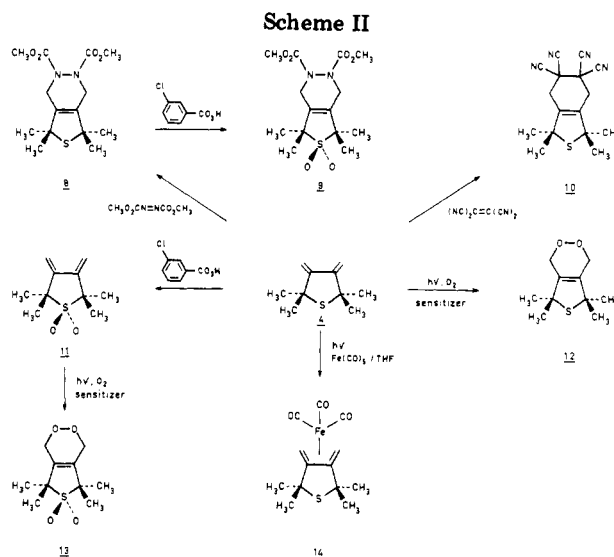
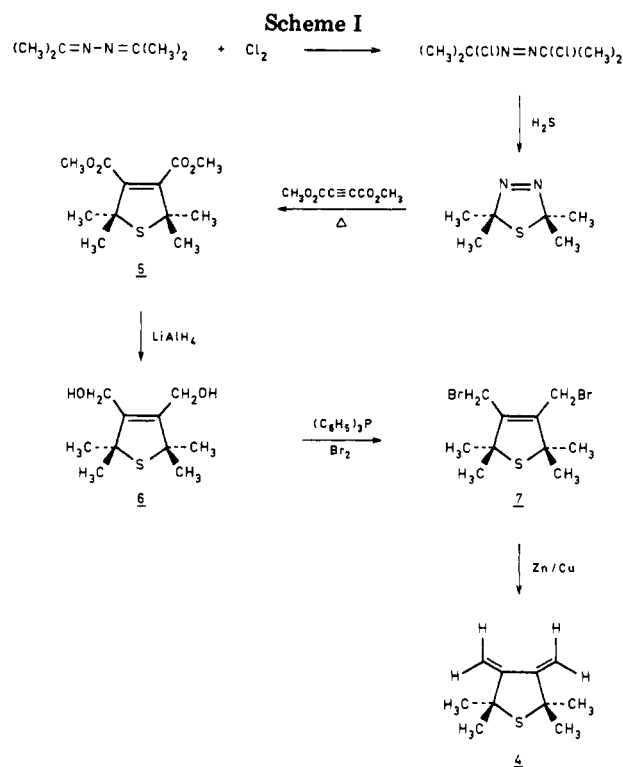
stance, an unusual (double) exocyclic isomer of 3,4-dimethylthiophene. One notes also that the carbon framework of 1 corresponds to that of tetramethyleneethane (2); for the case of 3, for which we developed a synthesis, the sulfur bridge separating the 3,4-dimethylenethiolane from a tetramethyleneethane was removed by means of an indirect route.<sup>1</sup>

Syntheses of 3,4-dialkylidenethiolanes have been restricted to 1,<sup>2</sup> which polymerizes readily, and 3.<sup>1</sup> We report here a synthesis of 2,2,5,5-tetramethyl-3,4-dimethylenethiolane (4) following the path used for the synthesis of 3.

Appropriate manipulation of the cycloadducts (5) obtained from 1,3-dipolar cycloaddition of a thiocarbonyl ylide<sup>3</sup> to dimethyl acetylenedicarboxylate forms the basis of the synthesis (Scheme I). All the reactions proceeded without notable complications once optimum conditions were found (see Experimental Section). The thiolane 4 is somewhat unstable toward polymerization, at least directly after its preparation from zinc/copper couple, perhaps owing to trace amounts of metal in the diene. It was usually prepared directly before use from dibromide 7. The debromination proceeds quantitatively, and removal of metal by filtration leaves virtually pure 4 in solution. Well-purified samples of 4 are entirely stable.

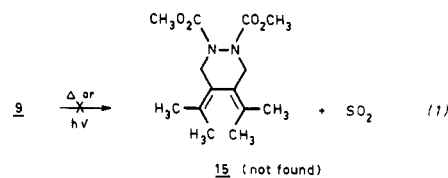
Some of the reactions carried out on 4 are shown in Scheme II.

Oxidation of 4 to sulfone 11 proceeded smoothly without detectable amounts of reaction at the double bonds. 11 is extremely stable, not undergoing decomposition or polymerization even on vigorous heating; 11 is also very insoluble and dissolves poorly only in chlorinated solvents.



Cycloadditions with dimethyl azodicarboxylate or tetracyanoethylene failed with 11.

These dienophiles reacted smoothly, however, with 4 to give cycloadducts 8 and 10, respectively. The former was oxidized readily to sulfone 9; all attempts, either thermal or photochemical, to remove SO<sub>2</sub> from 9 (eq 1) failed.



The failure to obtain 15 prevented us from going any further in a tetramethyleneethane synthesis along the lines described earlier.<sup>1</sup> Difficulty in removing SO<sub>2</sub> from 2,2,5,5-tetramethylbutadiene sulfones has been encountered before;<sup>4</sup> apparently steric crowding of opposing

(1) Beetz, T.; Kellogg, R. M. *J. Am. Chem. Soc.* 1973, 95, 7925.

(2) (a) Sadeh, S.; Gaoni, Y. *Tetrahedron Lett.* 1973, 2365. (b) Gaoni, Y. *Ibid.* 1973, 2361. See also: (c) Marvel, C. S.; Ryder, E. E., Jr. *J. Am. Chem. Soc.* 1955, 77, 66. (d) Marvel, C. S.; Nowak, R. M.; Economy, J. *Ibid.* 1956, 78, 6171.

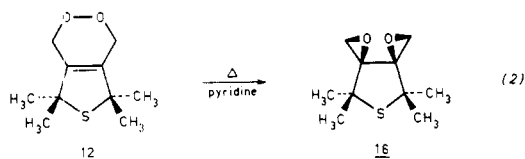
(3) (a) Buter, J.; Wassenaar, S.; Kellogg, R. M. *J. Org. Chem.* 1972, 37, 4045. (b) Kellogg, R. M. *Tetrahedron* 1976, 32, 2165.

(4) Kellogg, R. M.; Prins, W. L. *J. Org. Chem.* 1974, 39, 2366.

methyl groups during disrotatory ring opening is the cause of the failure of the reaction.

The cycloaddition product **8** as well as its sulfone **9** exhibited at 25 °C two sets of absorptions for the 2,5-methyl groups in the <sup>1</sup>H NMR spectrum. This is consistent with slow inversion rates of the pyramidal nitrogen atoms relative to the <sup>1</sup>H NMR time scale and overall C<sub>2</sub> symmetry of **8** and **9**. Coalescence occurred for **8** at 96 °C (ΔG<sup>‡</sup> = 19.9 kcal/mol) and for **9** at 86 °C (ΔG<sup>‡</sup> = 19.4 kcal/mol).

The smooth cycloadditions of **4** and **11** with singlet oxygen were somewhat surprising. No spectroscopic evidence of sulfur oxidation products from **4** was obtained despite the known high reactivity of aliphatic sulfides towards singlet oxygen.<sup>5</sup> The structures of the cyclic peroxides **12** and **13** were established by analysis of <sup>1</sup>H NMR, IR, and analytical data (see Experimental Section). The thermally induced rearrangements of Diels–Alder adducts with singlet oxygen to diepoxides is well-known.<sup>6</sup> In pyridine, **12** rearranged on warming, as judged by the <sup>1</sup>H NMR spectra, to a product that was likely **16** (eq 2). We were unable



to isolate this compound, however. Thermal reactions of **13** led only to uncharacterized material. Details of these experiments are given in the Experimental Section.

Repeated attempts to add dichlorocarbene under phase-transfer conditions<sup>7</sup> to **4** to give bis(1,1-dichlorocyclopropane) derivatives, which are excellent precursors of diallenic compounds,<sup>8</sup> resulted only in polymerization of **4**.

Preparation of the iron tricarbonyl complex **14** was eventually accomplished after several unsuccessful approaches via the route shown in Scheme III. The complex **14** is a potential precursor of a metal-complexed tetramethyleneethane,<sup>9</sup> although we have not carried out any experiments designed toward this transformation. The dark red complex of Fe(CO)<sub>4</sub> and tetrahydrofuran (THF)<sup>10</sup> reacts with **4** to generate complex **14**. Careful monitoring of the course of the reaction by <sup>1</sup>H NMR spectroscopy allowed the detection of two intermediates tentatively assigned structures **17** [<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 1.45 (s, 12, CH<sub>3</sub>), 5.15 (s, 2, vinyl H), 4.60 (s, 2, vinyl H)] and **18** [<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 1.40 (s, 6, CH<sub>3</sub>), 1.20 (s, 6, CH<sub>3</sub>), 1.10 (d, 2, J = 3 Hz, vinyl H), -0.40 (d, 2, J = 3 Hz, vinyl H)] on the basis of the chemical shifts and observed chemistry. (Complex **14** has vinyl absorptions at δ 1.30 (d, 2, J = 3 Hz) and δ -0.35 (d, 2, J = 3 Hz.) Initial attack of iron carbonyl at sulfur in an unsaturated sulfide has good chemical precedent.<sup>11</sup>

Consideration of the above results leads to the conclusion that either the diene system of **4** or the sulfur atom is susceptible to appreciable and selective manipulation. The derived products offer numerous potential openings for the synthesis of carbon skeletons of structural interest.

### Experimental Section

**3,4-Bis(methoxycarbonyl)-2,2,5,5-tetramethyl-2,5-dihydrothiophene (5).** The following procedure is an improved version of literature procedures.<sup>3a,4</sup> Addition of chlorine in the usual way<sup>3a</sup> to acetone azine gave the dichloro azo compound which was used directly. In a heavy-walled glass tube was put 20 g (0.11 mol) of dichloro azo compound dissolved in 30 mL of CHCl<sub>3</sub> (it is essential that the concentration be very high). The contents were cooled to -180 °C and a large excess of H<sub>2</sub>S was condensed in the tube, which was then melted shut. The tube was shaken for 3 days at room temperature and opened, and the contents of the tube were taken up in CH<sub>3</sub>OH. The insoluble salt was filtered off. The organic material was carefully recrystallized from a little CH<sub>3</sub>OH to give 8 g (55.6 mmol, 51% yield) of 2,2,5,5-tetramethyl-1,3,4-thiadiazoline, mp 92.7–93.5 °C. The thiadiazoline (4.5 g, 31 mmol) was dissolved in 50 mL of a 10:1 methylcyclohexane/benzene mixture and was added, at a rate of 1–2 drops/min, to dimethyl acetylenedicarboxylate (17 g, 119 mmol) in 25 mL of refluxing methylcyclohexane. The total addition time was 8–10 h. After addition was complete, reflux was continued for 24 h. (Slow addition is essential for a good yield of cycloadduct; otherwise tetramethylthiirane is formed.) Distillation of the crude product gave **5**, bp 85–90 °C (0.05 mm), which was recrystallized from pentane to give 4.3 g (17 mmol, 53% yield) of product, mp 80–82.5 °C.<sup>3a</sup>

**2,4-Bis(hydroxymethyl)-2,2,5,5-tetramethyl-2,5-dihydrothiophene (6)** was prepared by reducing **5** (1 g, 3.9 mmol) dissolved in 15 mL of diethyl ether in a slurry of LiAlH<sub>4</sub> (300 mg, 7.9 mmol) in 15 mL of diethyl ether to which AlCl<sub>3</sub> (400 mg, 3 mmol) had been added. Workup with 10% HCl solution and extraction with ether followed by drying over MgSO<sub>4</sub> gave a heavy oil that slowly became crystalline. Recrystallization from petroleum ether (bp 40–60 °C) gave **6** (700 mg, 3.46 mmol, 89% yield): mp 90–91.5 °C; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 1.45 (s, 12, CH<sub>3</sub>), 3.35 (s, 2, OH), 4.0 (s, 4, CH<sub>2</sub>); IR (neat) 3100–3500 cm<sup>-1</sup> (br, OH). Anal. Calcd for C<sub>10</sub>H<sub>18</sub>O<sub>2</sub>S: C, 59.41; H, 8.91; S, 15.84. Found: C, 59.24; H, 8.94; S, 15.66.

**2,2,5,5-Tetramethyl-3,4-dimethylenethiolane (4).** A stirred solution of triphenylphosphine (1.57 g, 6 mmol) in 10 mL of CH<sub>3</sub>CN was cooled in an ice bath. Br<sub>2</sub> was added to this solution until the bromine color just remained (ca. 1 g). The diol **6** (600 mg, 2.9 mmol) dissolved in 10 mL of CH<sub>3</sub>CN was added quickly; the reaction mixture was warmed until homogeneous and thereafter stirred at room temperature for 1 h. Removal of the solvent left a yellow-white solid and an oil which were taken up in a mixture of petroleum ether (bp 40–60 °C)/acetone (4/1). Elution over a silica gel column gave 0.9 g (2.75 mmol, 95% yield) of **7**, <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 1.40 (s, 12, CH<sub>3</sub>) and 3.75 (s, 4, CH<sub>2</sub>), which was usually pure enough for further use. Careful recrystallization from C<sub>2</sub>H<sub>5</sub>OH gave material, mp 60–61 °C. Additional purification can, if necessary, be achieved by a second passage over an alumina column. The dibromide is somewhat unstable and was used immediately; further characterization was omitted.

Cu(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub> (400 mg, 2.2 mmol) was warmed and stirred in 15 mL of acetic acid until the solution became homogeneous. To the hot and well-stirred solution was added Zn powder (7 g, 107 mmol). Stirring was continued for 1 min, the solution was allowed to stand for 1 min, and the solid was isolated by filtration (P-4 glass filter). The solid was washed with 10 mL of CH<sub>3</sub>CO<sub>2</sub>H and thereafter 4 times with 20-mL portions of dry ether. The zinc-copper couple (1 g) was suspended in 15 mL of dry ether and dibromide **7** (1 g, 3 mmol) dissolved in 10 mL of dry ether was added. Stirring was continued for 2 h and the precipitate was removed by filtration. The crude reaction product in ether was washed with 10% NaHCO<sub>3</sub> solution (to prevent dibromide **7** from being re-formed by Br<sub>2</sub> addition). A white precipitate of ZnBr<sub>2</sub> formed. Removal of the ether layer followed by drying over MgSO<sub>4</sub> and removal of the solvent left 500 mg (3.84 mmol, 100% yield) of **4**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 1.6 (s, 12, CH<sub>3</sub>), 4.7 (s, 2, HCH=),

(5) For example: (a) Foote, C. S.; Peters, J. W. *J. Am. Chem. Soc.* **1971**, *93*, 3795. (b) Foote, C. S. *Pure Appl. Chem.* **1971**, *27*, 635. (c) Corey, E. J., Ouannès, C. *Tetrahedron Lett.* **1976**, 4263.

(6) For a summary of the literature, see: Denney, R. W.; Nickon, A. *Org. React.* **1973**, *20*, 133.

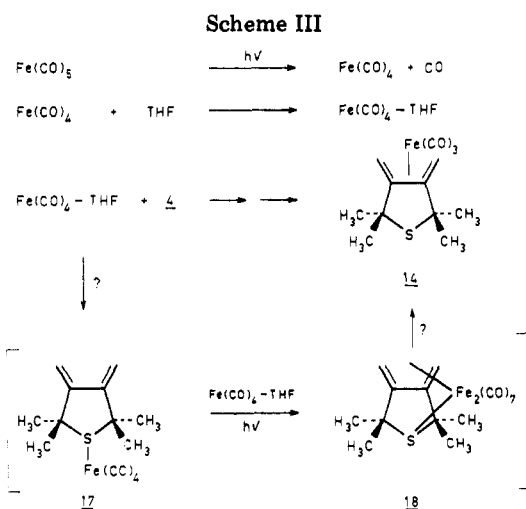
(7) (a) Skattebøl, L. *Acta Chem. Scand.* **1963**, *17*, 1683. (b) Makosza, M.; Wawrzyniewicz, W. *Tetrahedron Lett.* **1969**, 4659.

(8) For example: Heldeweg, R. F.; Hogeveen, H. *J. Org. Chem.* **1978**, *43*, 1916.

(9) For example: (a) Nakamura, A. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 543. (b) Ben-Shoshan, R.; Pettit, R. *Chem. Commun.* **1968**, 247. (c) Davis, R. E. *Ibid.* **1968**, 248.

(10) Cotton, F. A.; Troup, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 3438.

(11) (a) Eekhof, J. H.; Hogeveen, H.; Kellogg, R. M.; Schudde, E. P. *J. Organomet. Chem.* **1976**, *105*, C35. (b) "The Organic Chemistry of Iron"; Koerner von Gustorf, E. A.; Grevels, F. W.; Fischler, I., Eds.; Academic Press: New York, 1978; Vol. 1.



5.3 (s, 2, HCH=); UV ( $\text{C}_2\text{H}_5\text{OH}$ )  $\lambda_{\text{max}}$  230 nm ( $\epsilon$  not known because of unknown amount of impurities in 4).

No attempt was made to obtain an elemental analysis owing to the instability of the diene. It was normally prepared immediately before use in a reaction since polymerization can occur on storage.

**2,2,5,5-Tetramethyl-3,4-dimethylenethiolane 1,1-dioxide (11)** was prepared by oxidation at 0 °C of 4 (200 mg, 1.19 mmol) with 85% *m*-chloroperbenzoic acid (500 mg, 2.5 mmol) in  $\text{CHCl}_3$ . The reaction mixture was worked up after 12 h ( $\text{NaHSO}_3$  solution,  $\text{H}_2\text{O}$ , drying over  $\text{MgSO}_4$ ). There was obtained 11 (200 mg, 1.11 mol, 93% yield): mp 118–120 °C (from  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H NMR}$  ( $\text{CCl}_4$ )  $\delta$  1.40 (s, 12,  $\text{CH}_3$ ), 5.00 (s, 2, HCH=), 5.50 (s, 2, HCH=); IR (KBr) 1100 and 1300  $\text{cm}^{-1}$  ( $\text{SO}_2$ ). Anal. Calcd for  $\text{C}_{10}\text{H}_{16}\text{O}_2\text{S}$ : C, 59.95; H, 8.07; S, 16.00. Found: C, 59.90; H, 8.04; S, 16.04.

**Cycloaddition of 4 with dimethyl azodicarboxylate** was carried with thiolane 4 (200 mg, 1.19 mmol) and dimethyl azodicarboxylate (300 mg, 2 mmol) in 40 mL of dry  $\text{C}_6\text{H}_6$ . The solution was refluxed overnight. After workup (washing with  $\text{NaHSO}_3$  until colorless, thereafter with  $\text{H}_2\text{O}$ , drying over  $\text{MgSO}_4$ ) there was obtained pyridazine 8 (300 mg, 0.96 mmol, 80% yield) as spectrally pure material; short-path distillation (0.01 mm, free flame, boiling point not measurable) led to further purification. At room temperature 8 has  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  1.30 (s, 6,  $\text{CH}_3$ ), 1.45 (s, 6,  $\text{CH}_3$ ), 3.60–3.90 (complex, 4,  $\text{CH}_2$ ), and 3.50 (s, 6,  $\text{OCH}_3$ ). Coalescence of the 2,5- $\text{CH}_3$  signals occurred at 96 °C.

The pyridazine 8 (200 mg, 0.64 mmol) was oxidized with *m*-chloroperbenzoic acid (400 mg, 2 mmol) at 0 °C. After standing overnight the reaction mixture was worked up to give after recrystallization from  $(\text{C}_2\text{H}_5)_2\text{O}/\text{CHCl}_3$  (10/1) the sulfone 9 (180 mg, 0.52 mmol, 81% yield): mp 146–147.5 °C;  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  1.20 (s, 6,  $\text{CH}_3$ ), 1.35 (s, 6,  $\text{CH}_3$ ), 3.75–4.0 (complex, 4,  $\text{CH}_2$ ), 3.70 (s, 6,  $\text{OCH}_3$ ). Coalescence of the 2,5-methyl groups occurred at 86 °C. Anal. Calcd for  $\text{C}_{14}\text{H}_{22}\text{N}_2\text{O}_6\text{S}$ : C, 47.6; H, 5.41; N, 7.1; S, 8.3. Found: C, 48.2; H, 6.4; N, 8.1; S, 9.1.

Attempts to improve the elemental analysis failed.

Neither on heating to 250 °C (above that temperature charring occurs) nor on irradiation was any trace of  $\text{SO}_2$  elimination from 9 found.

**Cycloaddition of 4 with tetracyanoethylene** was carried out with thiolane 4 (200 mg, 1.19 mmol) and tetracyanoethylene (200 mg, 1.5 mmol) in tetrahydrofuran. The solution was refluxed overnight. Removal of solvent and three crystallizations from petroleum ether (bp 40–60 °C)/ $\text{C}_6\text{H}_6$  (10/1) gave 10 (220 mg, 0.74 mmol, 63% yield): mp 202–204 °C;  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  1.15 (s, 12,  $\text{CH}_3$ ), 2.35 (s, 4,  $\text{CH}_2$ ). Anal. Calcd for  $\text{C}_{16}\text{H}_{16}\text{N}_4\text{S}$ : C, 64.83;

H, 5.41; N, 18.90; S, 10.82. Found: C, 64.80; H, 5.42; N, 18.75; S, 10.54.

**Reaction of 4 with singlet oxygen** was carried out at 15 °C in a double-walled vessel cooled with  $\text{K}_2\text{Cr}_2\text{O}_7$  solution and irradiated externally with a Philips F/28 UV lamp. Oxygen was bubbled through the solution. A solution of 4 (100 mg, 0.6 mmol) in 60 mL of dry benzene was irradiated for 10 h in the presence of 10 mg of tetraphenylporphine. The solvent was removed, a small amount of  $\text{CH}_3\text{OH}$  was added, the insoluble tetraphenylporphine was removed, and the remaining material was recrystallized from a minimum amount of *n*-hexane to give 12 (110 mg, 0.55 mmol, 92% yield): mp 105–107 °C;  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  1.35 (s, 12,  $\text{CH}_3$ ), 4.40 (s, 4,  $\text{CH}_2$ ).

Heating of 12 in an NMR tube (pyridine solvent) at 70 °C for 3 h gave rise to an unstable compound,  $^1\text{H NMR}$   $\delta$  1.50 (s, 6,  $\text{CH}_3$ ), 1.60 (s, 6,  $\text{CH}_3$ ), 1.40 (d,  $J = 9$  Hz, 2, HCH), and 1.65 (d,  $J = 9$  Hz, 2, HCH), which may have been the diepoxide 16. Attempts to isolate this compound failed and further heating led to decomposition.

**Reaction of 11 with Singlet Oxygen.** In the apparatus described above, sulfone 11 (70 mg, 0.35 mmol) was dissolved in 50 mL of  $\text{CH}_2\text{Cl}_2$  to which 10 mg of Methylene Blue was added. All the material had been consumed after 15 h of irradiation. The Methylene Blue was removed from the reaction mixture by treatment with charcoal followed by addition of a small amount of silica gel. The residue was recrystallized from *n*-hexane to give 13 (60 mg, 0.26 mmol, 74% yield): mp 166–170 °C;  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  1.15 (s, 12,  $\text{CH}_3$ ), 4.20 (s, 4,  $\text{CH}_2$ ).

An acceptable elemental analysis could not be obtained.

**Preparation of iron tricarbonyl complex 14** proceeded in a reproducible fashion by using the following procedure. A solution of thiolane 4 (150 mg, 0.89 mmol) and  $\text{Fe}(\text{CO})_5$  (1.4 g, 7.12 mmol) in 60 mL of dry tetrahydrofuran under a  $\text{N}_2$  atmosphere was irradiated for 3 days with a quartz-jacketed Hanovia TQ 81 lamp. The crude reaction product was chromatographed over neutral alumina with petroleum ether (bp 40–60 °C)/ether (1/1) as eluant. The yellow oil obtained was sublimed at 40 °C (0.05 mm). There was obtained complex 14 (70 mg, 0.228 mmol, 20% yield), mp 65–70 °C. The melting point remained broad despite further attempts at purification:  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  0.35 (d,  $J = 3$  Hz, 2, HCH=), 1.30 (d,  $J = 3$  Hz, 2, HCH=), 1.40 (s, 6,  $\text{CH}_3$ ), 1.63 (s, 6,  $\text{CH}_3$ ); IR (KBr) 1990, 2040, and 2100 (CO), 1650  $\text{cm}^{-1}$  (C=C); mass spectrum,  $m/e$  308 (parent), 280 (–CO), 252 (–CO), 224 (–CO); UV (hexane)  $\lambda_{\text{max}}$  208 and 215 nm; noise-decoupled  $^{13}\text{C NMR}$  ( $\text{CS}_2/\text{C}_6\text{D}_6$ )  $\delta$  29.296, and 29.463 ( $\text{H}_2\text{C}=\text{C}$ ), 30.159 ( $\text{CH}_3$ ), 36.474 ( $\text{CH}_3$ ), 54.246 ( $(\text{CH}_3)_2\text{C}$ ), 118.243 ( $=\text{CC}=\text{C}$ ), 211.242 (CO). At –50 °C, the lowest temperature obtainable before the complex crystallized from solution, no indication of line broadening of the CO signal (freezing out of pseudorotation) was obtained. Anal. Calcd for  $\text{C}_{13}\text{H}_{16}\text{FeO}_3\text{S}$ : C, 50.67; H, 5.23; S, 10.40; Fe, 18.12. Found: C, 51.12; H, 5.42; S, 10.25; Fe, 17.73.

Considerable material was lost during workup; reactions proceeded, moreover, to only about 50% completion despite repeated cleaning of the lamp surface during irradiation.

Reaction of 4 with  $\text{Fe}_2(\text{CO})_9$  in tetrahydrofuran at 66 °C gave also complex 14.

Details of the  $^1\text{H NMR}$  spectra of reaction intermediates are given in the text.

**Registry No.** 4, 73368-55-5; 5, 36614-53-6; 6, 73368-56-6; 7, 73368-57-7; 8, 73368-58-8; 9, 73368-59-9; 10, 73368-60-2; 11, 73368-61-3; 12, 73368-62-4; 13, 73368-63-5; 14, 73378-33-3; 16, 73368-64-6; 17, 73378-34-4; 18, 73384-22-2; 2,2,5,5-tetramethyl-1,3,4-thiadiazoline, 36635-89-9; dimethyl acetylenedicarboxylate, 762-42-5; dimethyl azodicarboxylate, 2446-84-6; tetracyanoethylene, 670-54-2;  $\text{Fe}(\text{CO})_5$ , 13463-40-6;  $\text{Fe}_2(\text{CO})_9$ , 15321-51-4;  $\text{Fe}(\text{CO})_4(\text{THF})$ , 52268-67-4.