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- (21) **Note Added in Proof.** While this paper was processed, the full paper by Black and Davis appeared: D. St. C. Black and V. C. Davis, *Aust. J. Chem.*, **29**, 1735 (1976). In this paper full experimental data are given for reactions of Δ^1 -pyrroline *N*-oxides **1a**, **1d**, and **1e** with **3** using sodium hydride in DME. The physical data given for the products of the reactions of **1a** and **1e** agree with those obtained in our work for **6a**, **6e**, and **7a** (R = C₂H₅). However, Black and Davis assigned structure **6d** (R = C₂H₅) for the product of the reaction of **1d** with **3**. In this reaction we obtained a mixture of products **6g** and **6h**.

Cycloaddition Reactions of Vinyl Sulfene Generated from Thiete 1,1-Dioxide¹

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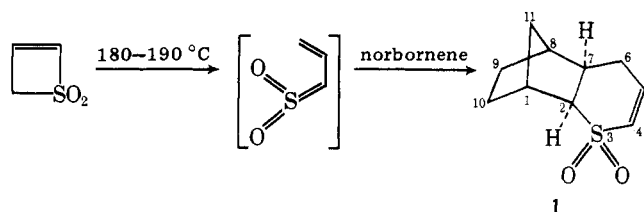
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Thermolysis of thiete 1,1-dioxides in the presence of norbornenes gives cycloadducts of the Diels-Alder type resulting from the trapping of vinyl sulfene formed by ring opening of the thiete 1,1-dioxides. Other cyclic or acyclic alkenes gave little or no reaction.

Sulfenes (R₂C=SO₂) undergo [2 + 2] cycloadditions to activated olefins (e.g., enamines) to yield thietane 1,1-dioxides,² and sulfene itself (CH₂=SO₂) may serve as a dienophile in a [4 + 2] cycloaddition to enamino ketones.³ Vinyl sulfenes (e.g., R₂C=CHCH=SO₂) have the capability of undergoing both [2 + 2] and [4 + 2] cycloadditions in which the vinyl sulfene may serve as either the two- or the four-electron reactant. These conjugated sulfenes have been proposed as intermediates in reactions of 1- or 2-propenesulfonyl chloride,⁴ in the photolysis of cyclic unsaturated sultones and sulfones,⁵ and in the thermal decomposition of thiete 1,1-dioxides.⁶ The presence of vinyl sulfene intermediates has been supported by trapping experiments with phenol^{6b,d} and by the formation of sultines^{6a-d,g} and α,β -unsaturated carbonyl compounds.^{6c,e,f} This report is about the trapping of vinyl sulfene intermediates acting as dienes in Diels-Alder or [4 + 2] cycloaddition reactions. Previously, Truce and Norell reported that vinyl sulfene obtained from 1- or 2-propenesulfonyl chloride gave a low yield (6.5-7.6%) of a [4 + 2] adduct with ketene diethyl acetal.^{4a}

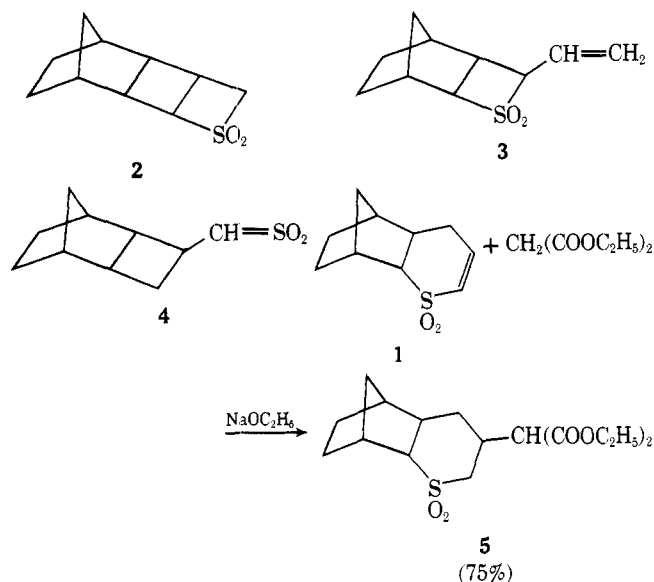
Results and Discussion

When thiete 1,1-dioxide is thermolyzed at 180-190 °C in the presence of norbornene in a sealed, degassed flask for 5 days, a 63-79% yield of an adduct, **1**, was obtained. The solvent was either *m*-xylene or benzene, the latter being preferred because of higher yields and the ease of workup of the reaction mixture. The thermolysis is quite clean, no tar being formed. At the end of the reaction period, a pale yellow solution remains which yields a crystalline adduct on removal of solvent.



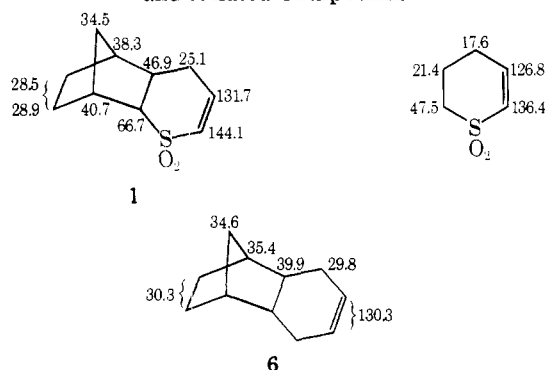
The elemental analysis and mass spectrum are in agreement with the proposed structure, **1**, 3-thiatricyclo[6.2.1.0^{2,7}] undec-4-ene 3,3-dioxide. In addition to providing the molecular weight, the mass spectrum shows evidence for the retro-Diels-Alder reaction: intense ions at *m/e* 94 for norbornene and at *m/e* 104 for vinyl sulfene are observed. The presence of the sulfone group is indicated by strong absorption in the infrared at 1298 and 1120 cm⁻¹. A carbon-carbon double bond is indicated by the infrared spectrum (1620 cm⁻¹)⁷ and by the ¹H and ¹³C NMR spectra.⁸ The presence of the double bond excludes structure **2** and the ¹H NMR spectrum excludes structures **3** and **4**; the latter, a sulfene, would not be expected to be particularly stable. The double bond in **1** is conjugated with the sulfone group and undergoes, as expected, a Michael reaction with the anion of diethyl malonate to yield **5**.

The carbon chemical shifts of **1** are compared in Chart I with those of dihydrothiapyran 1,1-dioxide and with those calculated⁹ for the strictly carbocyclic analogue (**6**) of **1**. The chemical shifts of the alkene carbons in **1** are assigned on the basis of the shifts observed in thiete 1,1-dioxide.¹⁰ A partially proton-decoupled ¹³C NMR spectrum of **1** shows a doublet for each alkene carbon atom which is caused by a one-bond coupling (*J*_{αCH} = 165; *J*_{βCH} = 184 Hz). Each component of the



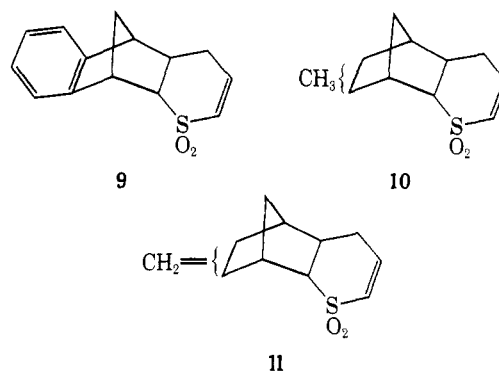
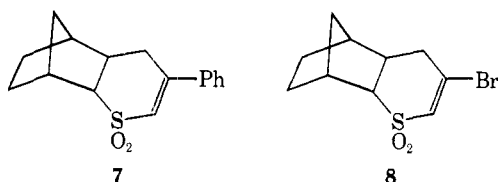
two doublets is split further into an apparent triplet (probably consisting of overlapping doublets) by long-range couplings involving the alkene protons and the methylene protons α to the double bond ($J \sim 6$ Hz). The spectrum was obtained on a Varian CFT-20 spectrometer with the decoupler on during pulse delay and off during acquisition: 4K data points, 20 000 transients, 3- μ s pulse width, 0 pulse delay, 0.5-s acquisition time. The partial proton decoupling also aided in distinguishing methine and methylene carbons in 1. The near identity of the chemical shifts for C-9 and C-10 (δ 28.5, 28.9) in adduct 1 and the similarity of the shifts to those for C-2 and C-3 in norbornane (δ 30.1)¹¹ support a cis-exo configuration for 1. Endo-2-substituted norbornanes show significant shifts to higher field for C-6 (δ C-6, exo 2-CH₃, 29.0; endo 2-CH₃, 22.4; exo 2-COOCH₃, 28.7; endo 2-COOCH₃, 25.1).¹¹ A trans configuration of the fused six-membered sulfone ring obviously would require one endo and one exo linkage and C-9 and C-10 should differ considerably in their chemical shifts.

Chart I. Carbon Chemical Shifts (δ) Relative to Me₄Si for 1 and Related Compounds^a



^a The shifts for 6 are calculated ones.⁹

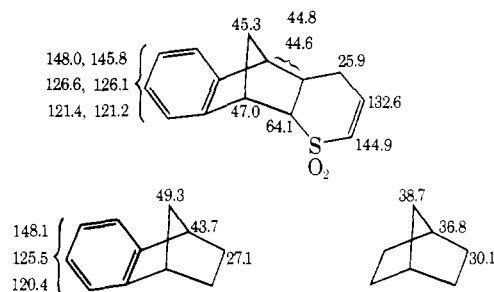
Adducts 7-11 also were obtained from 3-phenylthiethene 1,1-dioxide (60-71%) or 3-bromothiethene 1,1-dioxide (52%) and norbornene and from thiethene 1,1-dioxide and benzonorbornene (48-60%), 2-methylnorbornene (55-73%), and 2-methylene-



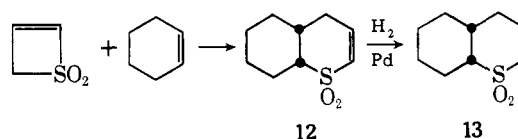
norbornene (50%). The regioselectivity of addition to the latter two norbornenes is not known.

The carbon chemical shifts of the benzonorbornene adduct are compared with those of benzonorbornene¹² itself, and with norbornane,¹¹ in Chart II. The assignment of the shift of δ 25.1 to the allylic carbon (C-6) in 1 is supported by the spectrum of 9 in which absorption for the allylic carbon is at δ 25.9.

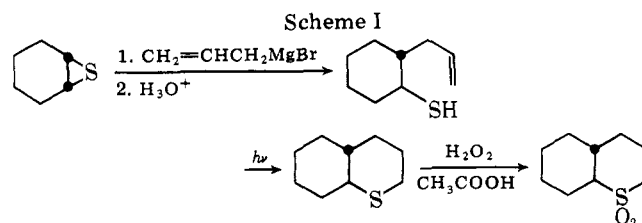
Chart II. Carbon Chemical Shifts (δ) Relative to Me₄Si



Thermolysis of thiethene 1,1-dioxide in cyclohexene for 5 days at 170 °C gave mainly tar and a very low yield (0.6%) of an adduct, formulated as 12. Attempts to improve the yield of adduct failed and in most cases no adduct at all was obtained. Only the elemental analysis, infrared, and mass spectra could be obtained on the small quantity of 12 available; these data,



however, were in agreement with the proposed structure. Both cyclohexene (m/e 82) and vinyl sulfene (m/e 104) fragments are observed in the mass spectrum. The cis thiadecalin structure is suggested by analogy with other cis Diels-Alder adducts. Hydrogenation of the double bond in 12 yields a saturated sulfone, 13, mp 75-77 °C, whose infrared spectrum and mass spectrum are similar to those obtained for the saturated sulfone (mp 109-110 °C) obtained from 1-thiadecalin¹³ as outlined in Scheme I. The thiadecalin synthesis ought to



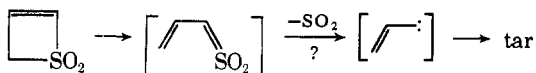
result in a trans ring fusion. Unfortunately, not enough of 13 could be obtained for a thorough investigation of its stereochemistry.

The failure of cyclohexene to give an appreciable yield of adduct points to the strain energy associated with the double

bond in the norbornenes as the origin of the facile reaction with vinyl sulfene. The difference in strain energy between norbornane and norbornene is calculated to be about 9 times greater than the difference between cyclohexane and cyclohexene.¹⁴ Norbornene functions as a dienophile in Diels–Alder cycloadditions and reacts about 24 times faster with hexachlorocyclopentadiene than cyclohexene does.^{15a} If vinyl sulfene were a highly reactive diene component in a Diels–Alder reaction, it should be less discriminating toward various alkenes than hexachlorocyclopentadiene and considerable addition of vinyl sulfene to cyclohexene would be expected.^{15b} Therefore, the data available suggest that vinyl sulfene is not necessarily a particularly reactive dienelike species.

Thermolysis of thiete 1,1-dioxide with camphene, bicyclo[2.2.2]octene, *cis*-2-butene, cyclopentene, dicyclopentadiene, and diphenylacetylene yielded only tar.

After the first synthesis of thiete 1,1-dioxide,¹⁶ we observed that it decomposed considerably above its melting point to a black tar with the evolution of what appeared to be sulfur dioxide as indicated by its odor and acidic properties (pH paper). The possible dissociation of vinyl sulfene to vinyl carbene and sulfur dioxide was considered, and it was an attempt to trap the vinyl carbene that led us to do the thermolysis reaction in cyclohexene. Although the dissociation of sulfene ($\text{CH}_2=\text{SO}_2$), itself to methylene and sulfur dioxide is believed to be highly endothermic,¹⁷ the loss of sulfur dioxide from vinyl sulfene may be more favorable because of the possibilities for conjugative stabilization in vinyl carbene as compared to methylene. The tar, in part, may be derived from products arising via vinyl carbene whose reactions and electronic structures may be diverse.¹⁸ Tar formation occurs in 36–48 h on heating thiete 1,1-dioxide alone in benzene at 170 °C. The decomposition occurs within 10 min at 260 °C in benzene; at this temperature in the presence of norbornene only a 20% yield of 1 is obtained along with tar. This suggests that at lower temperatures in solution the decomposition of vinyl sulfene is slow relative to its addition to norbornene; at higher temperatures the decomposition competes more favorably with the cycloaddition. The lack of any observed addition products of vinyl carbene with the alkenes may be caused by instability of the adducts, e.g., vinylcyclopropanes. However, one mode of decomposition of the latter is to cyclopentene derivatives,¹⁹ none of which were observed. Neither were any adducts of vinyl sulfene and cyclopropene found.



Experimental Section

Infrared spectra were taken on a Perkin-Elmer Model 137 infrared spectrophotometer. The proton magnetic resonance spectra were taken on either Varian A-60, T-60, or XL-100 spectrometers. The carbon-13 nuclear magnetic resonance spectra were obtained on Varian XL-100, CFT-20, and JEOL FX-60 spectrometers. The ¹³C NMR absorptions were referenced to tetramethylsilane. Microanalyses were performed at Micro-Analysis Inc., Wilmington, Del. Mass spectra were obtained on a Perkin-Elmer Hitachi Model RMU-6E single focusing spectrometer. Melting points were obtained on a Mel-Temp melting point apparatus and are uncorrected.

The thermolysis reactions of thiete 1,1-dioxides were run in round-bottomed flasks with a break seal and a side arm. The flasks and their contents were degassed under vacuum by cooling in liquid nitrogen followed by gradual warming to room temperature. This was repeated until gases were no longer seen to issue from the flask. The flasks with their contents were sealed under vacuum and heated in an oil bath.

Thermolysis of Thiete 1,1-Dioxide. A. With Norbornene. Thiete 1,1-dioxide¹⁶ (1.04 g, 10 mmol), norbornene (1.41 g, 15 mmol), and dry benzene (15 mL, distilled and stored over Linde 4A molecular sieves) were placed in the thermolysis flask. The flask and its contents were

degassed four times and heated at 180–190 °C for 5 days. The flask was cooled and opened, and the solvent was removed from the pale yellow solution at reduced pressure, leaving an oil which rapidly crystallized. Recrystallization from ether containing a few drops of ethanol gave adduct 1 (3-thiatricyclo[6.2.1.0^{2,7}]undec-4-ene 3,3-dioxide) as colorless needles (1.5 g, 7.6 mmol, 79%): mp 109–110 °C; IR (KBr) 1620 (m), 1298 (s), 1120 (s), 870 (s), 790 (s), and 680 cm⁻¹ (s); ¹H NMR (60 MHz, CDCl₃) δ 6.8 (triplet of doublets, 1 H), 6.5 (doublet of doublets, 1 H), 2.9 (m, 2 H), 2.3 (m, 5 H), 1.7 (m, 2 H), 1.2 (m, 3 H); ¹³C NMR δ 25.1 (t), 28.5 (t), 28.9 (t), 34.5 (t), 38.3 (d), 40.7 (d), 46.9 (d), 66.7 (d), 131.7 (d), 144.1 (d); mass spectrum (70 eV) *m/e* 198 (M), 150 (M – SO), 134 (M – SO₂), 133 (M – SO₂H), 104, 94. Anal. Calcd for C₁₀H₁₄O₂S: C, 60.61; H, 7.07; S, 16.16. Found: C, 60.42; H, 6.99; S, 16.10.

Diethyl malonate (1.6 g, 10 mmol) was added to a stirred solution of sodium ethoxide [prepared by adding sodium (0.23 g, 10 mmol) to absolute ethanol (25 mL)]. The resulting solution was stirred for 5 min, and then adduct 1 (1.98 g, 10 mmol) was added in portions during 5 min. The solution was stirred at reflux for 3 h, cooled, and acidified with acetic acid (10%, 15 mL). The aqueous solution was extracted continuously with methylene chloride (100 mL) for 12 h. The methylene chloride was washed with sodium bicarbonate (10 mL, 10% solution), dried (MgSO₄), and filtered, and the solvent removed to give a brown oil that slowly crystallized at 0 °C. Recrystallization from ether gave the Michael adduct, 5, as colorless crystals (2.7 g, 7.5 mmol, 75%): mp 78–80 °C; IR (KBr) 2950 (m), 1740 (s), 1298 (s), 1120 (s), 1020 (m), and 860 cm⁻¹ (m); ¹H NMR (CDCl₃) δ 4.2 (q, 4 H, *J* = 6 Hz), 2.6–3.6 (m, 6 H), 2.0 (m, 10 H), 1.2 (t, 6 H, *J* = 6 Hz); ¹³C NMR (CDCl₃) δ 13.5, 25.4, 28.1, 28.9, 31.4, 33.8, 36.5, 41.2, 43.9, 49.3, 56.6, 61.1, 61.2, 63.3, 166.9, 167.5. Anal. Calcd for C₁₇H₂₆O₆S: C, 56.98; H, 7.26; S, 8.94. Found: C, 56.74; H, 7.15; S, 9.02.

B. With Benzonorbornadiene. Thiete 1,1-dioxide (250 mg, 2.4 mmol), benzonorbornadiene²⁰ (430 mg, 3.0 mmol), and benzene (10 mL) were treated as described for the reaction of thiete 1,1-dioxide and norbornene. The flask and its contents were heated at 160–170 °C for 5 days. A light yellow solid was obtained which was recrystallized from benzene containing a few milliliters of ether to give colorless crystals of 9 (340 mg, 1.37 mmol, 60%): mp 186–187 °C; IR (KBr) 3050 (w), 1620 (m), 1300 (s), 1100 (s), 890 (m), 850 (m), 790 (m), 760 (s), and 750 cm⁻¹ (s); ¹H NMR (Me₂SO-*d*₆) δ 6.6 (m, 5 H), 6.2 (doublet of doublet, 1 H), 3.6 (m, 1 H), 1.6–3.2 (m, 7 H); ¹³C NMR (Me₂SO-*d*₆) δ 25.9, 44.6, 44.8, 45.3, 47.0, 64.1, 121.2, 121.4, 126.1, 126.6, 132.6, 144.9, 145.8, 148.0; mass spectrum (70 eV) *m/e* 246 (M), 198 (M – SO), 182 (M – SO₂), 181 (M – SO₂H), 142, 104. Anal. Calcd for C₁₄H₁₄O₂S: C, 68.2; H, 5.69; S, 13.0. Found: C, 68.4; H, 5.53; S, 13.04.

C. With 5-Methylene-2-norbornene. Thiete 1,1-dioxide (1.04 g, 10 mmol) and 5-methylene-2-norbornene (Aldrich Chemical Co.) (1.1 g, 11 mmol) in *m*-xylene (10 mL) were heated at 180–190 °C for 5 days to give an oil that was chromatographed on Florisil (elution with ether) to give a white, fluffy solid, 11 (1.05 g, 5 mmol, 50%): mp 75–77 °C; IR (thin film) 3000 (m), 1670 (m), 1620 (m), 1300 (s), 1120 (s), 880 (m), and 805 cm⁻¹ (m); NMR (CDCl₃) δ 6.8 (triplet of doublets, 1 H), 6.4 (doublet of doublets, 1 H), 4.9 (d, 2 H), 3.2 (m, 2 H), 1.0–2.8 (m, 8 H); mass spectrum (70 eV) *m/e* 210 (M), 162 (M – SO), 146 (M – SO₂), 145 (M – SO₂H), 106, 104. Anal. Calcd for C₁₁H₁₄O₂S: C, 62.86; H, 6.67; S, 15.24. Found: C, 62.78; H, 6.76; S, 14.92.

D. With 5-Methyl-2-norbornene. Thiete 1,1-dioxide (2.00 g, 19.2 mmol), 5-methyl-2-norbornene (Aldrich Chemical Co.) (4.54 g, 38.4 mmol), and benzene (20 mL) were heated at 140–145 °C for 4 days to give an oil which crystallized rapidly. The product was recrystallized from acetone–heptane (20 mL, 90:10, 0–5 °C) to give white crystals of 10 (2.97 g, 14.0 mmol, 73%): mp 83–84 °C; IR (KBr) 1640 (m), 1298 (s), 1260 (s), 1120 (s), 870 (m), and 805 cm⁻¹ (m); NMR (100 MHz, CDCl₃) δ 6.8 (triplet of doublets, 1 H), 6.5 (doublet of triplets, 1 H), 2.8 (m, 2 H), 1.2–2.5 (m, 9 H), 1.0 (d, 3 H); mass spectrum (70 eV) *m/e* 212 (M), 165 (M – SO), 149 (M – SO₂), 148 (M – SO₂H), 109, 104. Anal. Calcd for C₁₁H₁₆O₂S: C, 62.22; H, 7.60; S, 15.10. Found: C, 62.15; H, 7.19; S, 14.83.

E. With Cyclohexene. Thiete 1,1-dioxide (1.04 g, 10 mmol) and cyclohexene (10 mL) were heated at 160–170 °C for 5 days to give a black, tarry mixture. After the excess cyclohexene was removed the residue was extracted with methylene chloride (3 × 5 mL) and subjected to column chromatography (silica gel, elution by 1:1 ether–ethanol). A white, crystalline material tentatively identified as 12 was obtained (11 mg, 0.060 mmol, 0.6%): mp 102–103 °C; IR (KBr) 2950 (m), 1640 (m), 1460 (m), 1298 (s), 1120 (s), and 870 cm⁻¹ (m); mass spectrum (70 eV) *m/e* 186 (M), 122 (M – SO₂), 121 (M – SO₂H), 104, 82. Anal. Calcd for C₉H₁₄O₂S: C, 58.11; H, 7.52. Found: C, 57.92; H, 7.43.

Compound 12 (15.8 mg, 0.085 mmol) in ethanol was reduced in a

Brown microhydrogenator with a palladium/carbon catalyst to yield a white, crystalline material tentatively identified as the saturated sulfone **13** (15 mg, 0.080 mmol, 94%): mp 75–77 °C; IR (KBr) 2950 (m), 1450 (m), 1298 (s), 1120 (s), and 870 cm⁻¹ (m); mass spectrum (70 eV) *m/e* 188 (M), 124 (M - SO₂), 123 (M - SO₂H).

1-Thiadecalin 1,1-Dioxide. 1-Thiadecalin¹³ (1.0 g, 0.64 mmol) was dissolved in glacial acetic acid (2 mL). Excess hydrogen peroxide (30%) was added and the mixture was allowed to stand overnight. Dilution with water (10 mL) gave a precipitate which was removed by filtration, dried, and sublimed to give a white, crystalline material (654 mg, 0.34 mmol, 55%): mp 109–111 °C (lit.¹³ mp 114–114.9 °C); IR (KBr) 2950 (m), 1450 (m), 1298 (s), 1120 (s), 875 (m), and 720 cm⁻¹ (m); NMR (CDCl₃) δ 2.8–3.2 (m, 2 H), 2.4–2.75 (m, 1 H), 0.8–2.3 (m, 13 H); mass spectrum (70 eV) *m/e* 188 (M), 124 (M - SO₂), 123 (M - SO₂H). Anal. Calcd for C₉H₁₆O₂S: C, 57.41; H, 8.56; S, 17.0. Found: C, 57.34; H, 8.51; S, 16.78.

Thermolysis of 3-Phenylthiethene 1,1-Dioxide with Norbornene. 3-Phenylthiethene 1,1-dioxide²¹ (450 mg, 2.5 mmol), norbornene (350 mg, 3.1 mmol), and *m*-xylene (10 mL, distilled and stored over Linde 4A molecular sieves) were heated at 190–200 °C for 5 days. A light tan solid was obtained which was recrystallized from benzene containing a few drops of ether to give adduct **7** as colorless crystals (412 mg, 1.5 mmol, 60%): mp 89–91 °C; IR (KBr) 3050 (m), 1610 (m), 1298 (s), 1120 (s), 875 (s), 840 (s), and 745 cm⁻¹ (s); NMR (60 MHz, CDCl₃) δ 7.35 (broad singlet, 5 H), 6.5 (s, 1 H), 1.8–3.2 (complex multiplet, 7 H), 1.4 (m, 5 H); mass spectrum (70 eV) *m/e* 274 (M), 226 (M - SO), 210 (M - SO₂), 209 (M - SO₂H), 172, 104. Anal. Calcd for C₁₆H₁₈O₂S: C, 70.4; H, 6.56, 11.68. Found: C, 69.96; H, 6.45; S, 11.91.

Thermolysis of 3-Bromothiethene 1,1-Dioxide with Norbornene. 3-Bromothiethene 1,1-dioxide²¹ (250 mg, 1.4 mmol), norbornene (188 mg, 3 mmol), and *m*-xylene (10 mL) were heated at 160–170 °C for 7 days, giving an oil that crystallized upon the addition of pentane (10 mL) and cooling to -20 °C. The crude product was purified by chromatography on a short column of Florisil (ether) to give a white, granular solid, **8** (200 mg, 0.73 mmol, 52%): mp 106–107 °C; IR (KBr) 1600 (m), 1300 (s), 1120 (s), 1000 (m), 865 (m), and 800 cm⁻¹ (m); NMR (60 MHz, CDCl₃) δ 6.8 (s, 1 H), 2.8 (m, 5 H), 1.0–2.3 (m, 7 H); mass spectrum (70 eV) *m/e* 277 (M), 229 (M - SO), 213 (M - SO₂), 212 (M - SO₂H), 175, 104. Anal. Calcd for C₁₀H₁₃BrO₂S: C, 43.33; H, 4.72; Br, 28.83. Found: C, 43.51; H, 4.80; Br, 28.67.

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Registry No.—1, 61770-37-4; 5, 61770-38-5; 7, 61770-39-6; 8, 61770-40-9; 9, 61770-41-0; 10, 61787-31-3; 11, 61787-32-4; 12, 61770-42-1; 13, 61770-43-2; thiethene 1,1-dioxide, 7285-32-7; norbornene, 498-66-8; diethyl malonate, 105-53-3; benzonorbornadiene, 4453-90-1; 5-methylene-2-norbornene, 694-91-7; 5-methyl-2-norbornene, 882-96-8; cyclohexene, 110-83-8; 1-thiadecalin 1,1-dioxide, 29108-28-9; 1-thiadecalin, 29100-30-9; hydrogen peroxide, 7722-84-1; 3-phenylthiethene 1,1-dioxide, 25903-17-7; 3-bromothiethene 1,1-dioxide, 59463-74-0.

References and Notes

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