succinimide, and a trace of benzoyl peroxide in 50 ml of carbon tetrachloride was refluxed under nitrogen for 3 hr. The reaction mixture was cooled to room temperature, and the succinimide was removed by filtration. The carbon tetrachloride was evaporated and the residual oil was dissolved in 50 ml of anhydrous tetrahydrofuran and cooled to 0°. To this magnetically stirred solution was added in one portion under nitrogen 1.2 g (11.25 mmol) of powdered potassium *tert*-butoxide. The mixture was stirred at room temperature for 20 hr, water and ether were added, and the organic layer was processed as before. Preparative scale vpc separation of the resulting two-component oil afforded 180 mg (30%) of recovered **16** and 68 mg (16%) of **17**, a colorless liquid, $\nu_{max}^{neat}$ 2995, 2890, 2825, 765, and 695 cm$^{-1}$.

*Anal.* Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 91.20; H, 8.85.

Hydrogenation of 37 mg of this triene also led to [4.4.2]propellane (26 mg, 68%).

**[5.4.2]Propella-9,12-diene (23).** To an ice cold magnetically stirred solution of 17.83 g (0.065 mol) of **22**[1] in 250 ml of anhydrous tetrahydrofuran was added 30.0 g (0.268 mol) of potassium *tert*-butoxide in one portion and the mixture was stirred at room temperature for 2.5 hr. With ice cooling, enough water was added to destroy the excess base; more water was added and the entire solution was extracted with pentane. The combined pentane extracts were washed with water and saturated sodium chloride solution and dried. The solvent was carefully removed by distillation at atmospheric pressure through a 6-in. metal helix packed Vigreux column and the product was distilled to give 7.46 g (66%) of **23**: bp 85° (0.5 mm); $\nu_{max}^{neat}$ 2940, 2850, 2790, 1445, 755, and 750 cm$^{-1}$; $\delta_{TMS}^{CDCl_3}$ 5.75 (s, 2, cyclobutene protons), 5.70 (m, 2, vinyl), 1.95 (m, 4, allyl), and 1.60 (br s, 10, methylene).

*Anal.* Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.64; H, 10.34.

**Bicyclo[5.4.2]trideca-7,9,11,13-tetraene (25).** A magnetically stirred mixture of 199 mg (1.14 mmol) of **23**, 232 mg (1.30 mmol) of *N*-bromosuccinimide, and a trace of benzoyl peroxide in 5 ml of carbon tetrachloride was immersed in an oil bath preheated to 120° and allowed to reflux for 15 min. After cooling, the succinimide was filtered and the filtrate was evaporated at 25°. The resulting pale red crystalline solid was dissolved in 25 ml of dry tetrahydrofuran and this solution was cooled to 0° prior to the addition of 843 mg (7.51 mmol) of potassium *tert*-butoxide. After stirring for 18 hr at ambient temperature, the mixture was treated with sufficient water to destroy the excess base. Subsequently, the solution was diluted with water and extracted three times with pentane. The combined pentane extracts were washed with water and saturated sodium chloride solution and dried. Most of the solvent was removed by distillation through a metal helix packed column. The concentrate was subjected to preparative scale vpc (10 ft × 0.25 in. column packed with 10% SF-96 on Chromosorb G at 130°). There was obtained 67.7 mg (34.5%) of **25** as a pale yellow oil and 11.6 mg (5.8%) of recovered **23**. For **25**, $\nu_{max}^{neat}$ 2920, 2860, 1650, 1455, 1435, 1055, 865, 835, and 785 cm$^{-1}$; $\delta_{TMS}^{CDCl_3}$ 5.90, 5.74, and 5.52 (s, 2 H each, vinyl), *ca.* 2.0 (m, 4, allyl), and 1.20 (br m, 6, methylene); *m/e* 172.1253 (calcd 172.1252).

*Anal.* Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.71; H, 9.33.

**[4.4.2]Propella-2,4,7,9,11-pentaene (28).** To a magnetically stirred ice cold solution of **31** (1.09 g, 4.30 mmol) in 125 ml of ether was added 2.5 g (22 mmol) of powdered potassium *tert*-butoxide in one portion. The mixture was stirred for 4 hr at ambient temperature under nitrogen. Water (40 ml) was added and the organic layer separated and washed with water (two 40-ml portions) and saturated sodium chloride solution (20 ml). The ether layer was dried and evaporated to give a dark oil, purification of which by preparative scale vpc (5 ft × 0.25 in. column packed with 10% SE-30 and 60–80 mesh Chromosorb G) gave 91 mg (14%) of **28** as a colorless oil: $\nu_{max}^{neat}$ 2890, 1217, 954, 762, and 720 cm$^{-1}$; *m/e* 154.0776 (calcd 154.0782).

*Anal.* Calcd for $C_{12}H_{10}$: C, 93.46; H, 6.54. Found: C, 93.56; H, 6.71.

Hydrogenation of **28** (23.8 mg) in methanol over 10% palladium on charcoal catalyst at atmospheric pressure gave 18 mg (71%) of **8**.

**Acknowledgment.** Financial support of this research through grants from the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society, is acknowledged with gratitude.

# [4.2.2]Propella-3,7-diene[1]

**Leo A. Paquette* and Robert W. Houser**[2]

*Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.* *Received October 16, 1970*

**Abstract:** [4.2.2]Propella-3,7-diene (**1**), the most highly strained unsaturated propellane known to date, has been synthesized. Treatment of *cis*-1,6-bis(methanesulfonyloxymethyl)bicyclo[4.2.0]oct-3-ene with sodium sulfide in anhydrous hexamethylphosphoramide gave 8-thia[4.3.2]propell-3-ene (**5**), chlorination–oxidation of which afforded a mixture of α-chloro sulfones **6** (68%) and **7** (32%). The relative configurations of the chlorine atoms in these molecules and the probable cause of the directive effect noted during the functionalization of **5** were determined in a series of additional experiments and are discussed. The action of potassium *tert*-butoxide in tetrahydrofuran on **6** led only to *tert*-butyl ether **15**; somewhat analogously, **7** gave sulfone **11** (60%) together with **15** (11%). The likely causative factors for the nonproduction of **1** under these conditions are presented. In contrast, exposure of **6** or **7** to *n*-butyllithium in ether did give rise to **1**, albeit in low yields. Chloride **24** was the only other volatile product formed. The spectral properties of **1** are cited.

The α-halo sulfone rearrangement has been shown to be an efficient method for the synthesis of propellenes containing a cyclobutene ring.[1,3] Although alternative synthetic entries to such molecules are available, the aforementioned route proceeds in good overall yield from readily available starting materials in a relatively small number of steps. For this reason, it became of interest to determine if the Ramberg–Bäcklund reaction[4] could be extended to the synthesis

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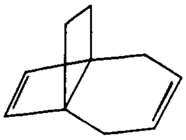
(1) α-Halo Sulfones. XIX. For previous paper in this series, see L. A. Paquette, J. C. Philips, and R. E. Wingard, Jr., *J. Amer. Chem. Soc.*, **93**, 4516 (1971).

(2) NDEA Fellow, 1967–1970.

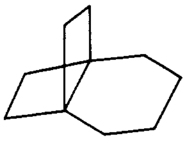
(3) (a) L. A. Paquette and J. C. Philips, *Tetrahedron Lett.*, 4645 (1967); (b) L. A. Paquette and J. C. Philips, *Chem. Commun.*, 680 (1969); (c) L. A. Paquette and J. C. Philips, *J. Amer. Chem. Soc.*, **91**, 3973 (1969).

(4) Reviews: (a) L. A. Paquette, "Mechanisms of Molecular Migrations," Vol. I, B. S. Thyagarajan, Ed., Interscience, New York, N. Y., 1968, pp 121–156; (b) L. A. Paquette, *Accounts Chem. Res.*, **1**, 209 (1968).

of unsaturated propellanes in which the central bond is substantially strained. [4.2.2]Propella-3,6-diene (**1**) was selected for study, since the chemical and physical properties of this diene could be compared with the reactivity of **2** prepared earlier by Eaton.[5]



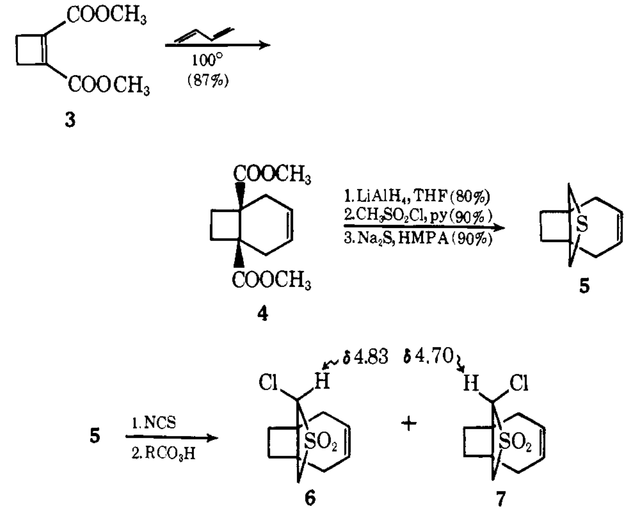
**1**



**2**

Our initial aim was the synthesis of sulfide **5** (Scheme I). Chlorination of **5** with *N*-chlorosuccinimide, followed by oxidation and exposure to strongly basic conditions, was expected to lead to **1**. The starting material was *cis*-bicyclo[4.2.0]oct-3-ene-1,6-dicarboxylic acid dimethyl ester (**4**), which could be prepared readily in 87% yield by cycloaddition of dimethyl cyclobutene-1,2-dicarboxylate (**3**) to butadiene at 100°. Reduction of **4** with lithium aluminum hydride afforded the related diol which was transformed into **5** by reaction with methanesulfonyl chloride in pyridine followed by sodium sulfide in anhydrous hexamethylphosphoramide (HMPA).[6] The nmr spectrum of **5** ($CCl_4$) showed a two-proton multiplet (vinyl) at δ 5.79–5.99, a singlet of area 4 at 2.56 ($-CH_2S-$), a broad four-proton multiplet (allyl) at 1.82–2.12, and a methylene envelope (4 H) at 1.47–1.69.

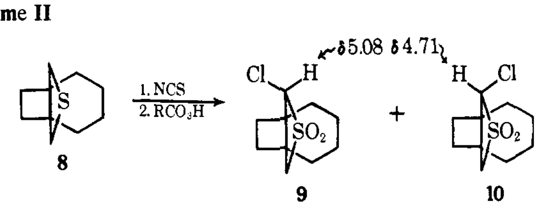
**Scheme I**



Interestingly, chlorination–oxidation of **5** gave the two isomeric α-chloro sulfones **6** and **7** in a ratio of 68:32, respectively. This product distribution was derived from integration of the >C*H*Cl protons (singlets at δ 4.83 and 4.70, respectively) in the nmr spectra of unpurified mixtures. The individual pure isomers were obtained by column chromatography on silica gel.

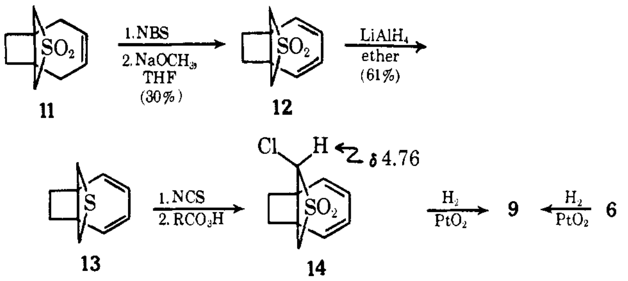
In order to deduce the relative configurations of the chlorine substituents in **6** and **7** and also to shed light on directive effects of NCS chlorination in the [4.3.2]propellane series, it became necessary to prepare their saturated and diene analogs. To this end, chlorination–oxdiation of sulfide **8** yielded a mixture of **9** and **10** in a ratio of 37.5:62.5 (Scheme II). The C*H*Cl protons in these sulfones were seen at δ 5.08 and 4.71, respectively.

**Scheme II**



Treatment of sulfone **11** with *N*-bromosuccinimide followed by dehydrobromination with sodium methoxide in anhydrous tetrahydrofuran afforded **12** (Scheme III). Reduction of **12** with lithium aluminum hydride in ether led to diene sulfide **13**, chlorination–oxidation of which yielded a lone α-chloro sulfone (**14**, >C*H*Cl absorption at δ 4.76).

**Scheme III**



Catalytic hydrogenation of **6** and **14** at atmospheric pressure afforded exclusively saturated α-chloro sulfone **9**. Thus, these three substances were of the same configurational series. Evidence that the relative configuration of the chlorine substituent in these isomers was *R**[7] (as drawn) was available from two sources. (a) The chemical shift of the proton geminal to chlorine in **7** and **10** is constant within experimental error (δ 4.70), whereas the chemical shifts of the same protons in **6**, **9**, and **14** are related directly to the extent of shielding produced by the varying degrees of unsaturation present in the six-membered ring (δ 4.76–5.08). This phenomenon has been observed earlier in 12-thia[4.4.3]propellanes whose structures have been verified by X-ray analysis.[6] (b) Base-catalyzed equilibration of **6** and **7** gave identical mixtures of **6** (16%) and **7** (84%). Clearly, α-chloro sulfone **7** is favored in the thermodynamic sense, as expected from that isomer in which the relatively large chlorine atom is positioned syn to the less sterically congested cyclohexene ring.

It will be noted that chlorination–oxidation of the unsaturated 8-thia[4.3.2]propellanes **5** and **13** parallels closely in directive effects the behavior of 12-thia[4.4.3]-propellanes,[6] in the sense that entry of chlorine from the more hindered direction is again preferred. This directional selectivity is particularly evident with **13** where the *R** chloro sulfone is the exclusive product. In contrast, the predominant product in the case of **8** is the *S** isomer (**10**). These observations are readily accommodated by the mechanistic treatment advanced in our earlier paper.[6]

Treatment of **6** with excess potassium *tert*-butoxide in anhydrous tetrahydrofuran at 0° did not afford

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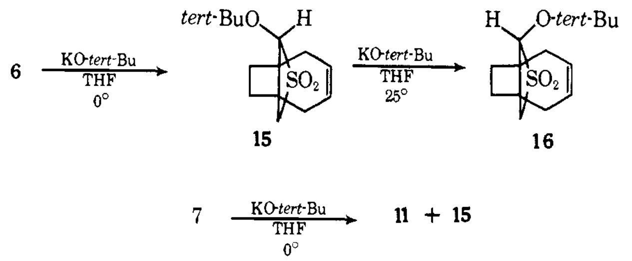
(5) P. E. Eaton, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Abstract P1; P. E. Eaton and K. Nyi, *J. Amer. Chem. Soc.*, **93**, 2786 (1971).

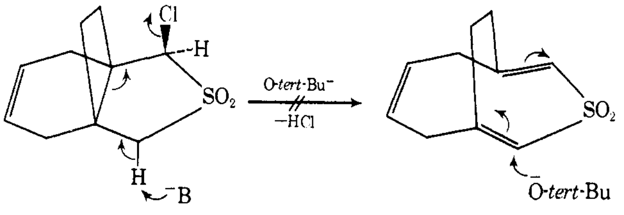
(6) L. A. Paquette, R. E. Wingard, Jr., C., J Philips, G. L. Thompson, L. K. Read, and J. Clardy, *ibid.*, **93**, 4508 (1971).

(7) For an explanation of this usage, consult ref 6, footnote 14.

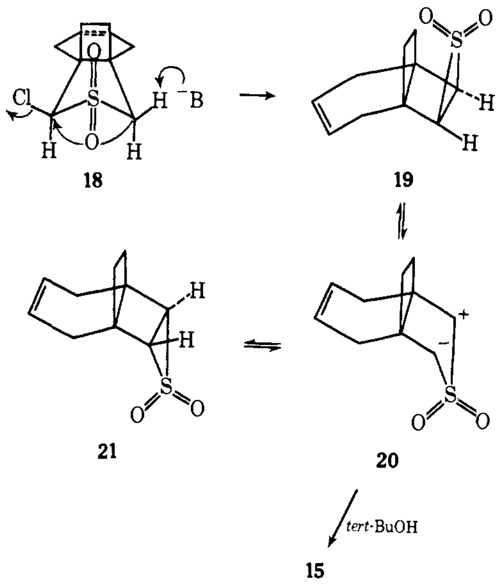
the desired diene (**1**), but rather the *tert*-butyl ether **15** in 40% yield. With **7**, however, the major product was **11** (60%), together with a lesser amount of **15** (11%). Exposure of **15** to potassium *tert*-butoxide at room temperature for 24 hr led to a mixture of two isomers in which epimer **16** predominated by a factor of 4. The nmr absorption of the $-CH_2SO_2-$ protons in **15** is seen as a sharp singlet at δ 2.97; in contrast, the same protons in **16** appear as an AB quartet (δ 3.34 and 2.91, $J_{AB} = 14$ Hz). These data may be compared with the $-CH_2SO_2-$ peaks in **6** (s, δ 3.18) and **7** (AB quartet, $J_{AB} = 14$ Hz, δ 3.29 and 3.09). Such considerations in conjunction with the ready equilibration of **15** to **16** serve as the basis for the stereochemical assignments.



The conversion of **6** to **15** poses an interesting mechanistic problem. Direct SN2 displacement α to the sulfonyl group[8] cannot be considered operative since overall retention of configuration is involved. Alternatively, it could perhaps be argued that epimerization precedes displacement; however, this argument would require that **7** be converted to **15** with still greater facility, but this is not seen. Likewise, an elimination-readdition mechanism involving intermediate **17** can be disregarded, since the Michael addition of *tert*-butoxide to this substrate would be expected to occur from the less hindered side.[9] However, the product of such a reaction (*i.e.*, **16**) is clearly not the product of kinetic control. The simplest mechanistically plausible pathway requires that **6** give rise initially to episulfone **19**. The topology of **6** is such that intramolecular nucleophilic displacement of chloride ion can proceed readily by way of the preferred W-plan geometry[10] involving inversion of configuration at the two reacting centers (*cf.* **18**). In episulfone **19**, one of the sulfonyl oxygen atoms is necessarily tightly compressed against the cyclobutane ring. In order to alleviate this interaction, it is proposed that ring inversion occurs *via* **20**. Facile carbon–carbon bond cleavage in the episulfone ring of **19** (and **21**) would not be unexpected. Many examples of such processes are known in closely related three-membered heterocyclic molecules.[11] Additionally, the C–C bond length in *cis*-2-butene episulfone (1.60 Å) far exceeds the theoretical value of 1.47–1.49 Å,[12] thereby giving rise to speculation that dipolar contributions such as are thought to be present in cyclopropanones[13] are of importance in such strained sulfones. Furthermore, recent investigations have shown that the C–C bonds of certain episulfones undergo rupture under very mild conditions.[14] Breaking of this bond as indicated in **20** would then permit the protic solvent to react with this species in its preferred conformation under kinetically controlled conditions.

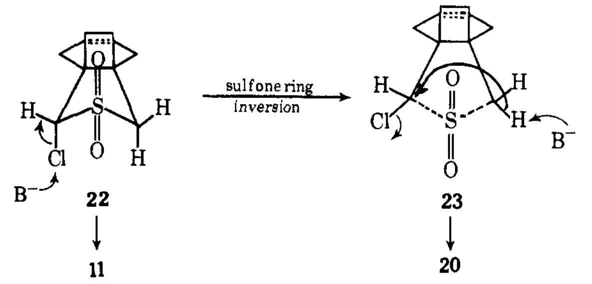


**6** **17**



It is recognized that the severe nonbonded interactions in **19** could perhaps also be alleviated by the expulsion of sulfur dioxide in the normal way. However, the formation of diene **1** is not realized under these conditions, perhaps due to the magnitude of the energy barrier encountered in the generation of the new highly strained π bond.

The differing behavior of **7** in the presence of potassium *tert*-butoxide can be attributed in large measure to the geometry of this α-chloro sulfone. Evaluation of molecular models suggests that the overwhelmingly preferred conformation of **7** is that in which the chlorine atom occupies an axial position (*cf.* **22**). As a result, the halogen atom is not properly disposed for facile 1,3 elimination of hydrogen chloride; ring inversion



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[8] F. G. Bordwell and B. B. Jarvis, *J. Org. Chem.*, **33**, 1182 (1968).

[9] E. D. Bergmann, D. Ginsburg, and R. Pappo, *Org. React.* **10**, 179 (1959).

[10] (a) F. G. Bordwell, B. B. Jarvis, and P. W. R. Corfield, *J. Amer. Chem. Soc.*, **90**, 5298 (1968); (b) L. A. Paquette and R. W. Houser, *ibid.*, **91**, 3870 (1969); (c) F. G. Bordwell, E. Doomes, and P. W. R. Corfield, *ibid.*, **92**, 2581 (1970).

[11] For summaries of references, see (a) W. C. Agosta and A. B. Smith, III, *Chem. Commun.*, 685 (1970); (b) J. W. Lown and K. Matsumoto, *ibid.*, 692 (1970).

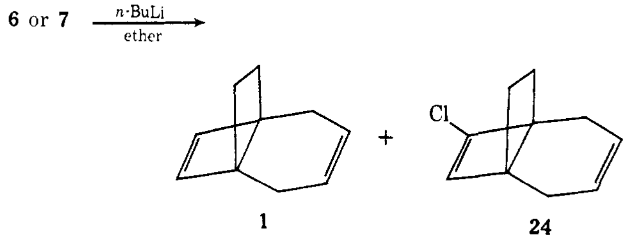
[12] R. Desiderato and R. L. Sass, *Acta Crystallogr.*, **23**, 430 (1967).

[13] N. J. Turro, *Accounts Chem. Res.*, **2**, 25 (1969).

[14] (a) W. L. Mock, *Chem. Commun.*, 1254 (1970); (b) L. A. Paquette and S. Maiorana, *ibid.*, 313 (1971).

to energetically unfavored conformer **23** appears necessary for episulfone (**21**) formation. Under such circumstances, the competing reduction to form **11** predominates.

These mechanistic assumptions suggested that, in the absence of a protic solvent such as *tert*-butyl alcohol, intermediates **19**–**21** would not be diverted to the formation of *tert*-butyl ethers, and therefore perhaps could be channeled into olefin production. In actuality, when **7** was treated with *n*-butyllithium in ether at −78°, diene **1** was indeed produced, albeit in low yield (2.6%), together with lesser amounts of **24**. The major product was a water-soluble polymer which could not satisfactorily be characterized. Similar results were obtained with **6** which afforded **1** in 1.4% yield and only a trace of **24**; no other volatile components were seen.



Pure samples of **1** and **24** were obtained by preparative scale vpc. The nmr spectrum of **1** ($CDCl_3$) showed a two-proton singlet at $\delta$ 6.22 assignable to the cyclobutene hydrogens and multiplets at 5.77, 2.14, and 1.86 due to the two vinyl, four allylic, and four cyclobutyl protons, respectively. By comparison, **24** exhibited a spectrum characterized by a one-proton singlet at $\delta$ 6.00 and multiplets at 5.76 (2 H, vinyl), 2.16 (4 H, allyl), and 1.94 (4 H, cyclobutyl). Both the diene and its chloro derivative displayed appropriate mass spectral molecular ion peaks at *m/e* 132 and 166, respectively. The structure of **1** was confirmed by catalytic hydrogenation at atmospheric pressure in ethyl acetate solution using platinum oxide as catalyst. The ir and nmr spectra of the tetrahydro product were identical with those of an authentic sample.[5,15]

As the yields attest, the $\alpha$-halo sulfone rearrangement does not provide an *efficient* synthetic entry to molecules endowed with appreciable ring strain. Notwithstanding, the successful application of this reaction to the preparation of **1** has given rise to the smallest and most highly strained unsaturated propellane reported to date.

## Experimental Section[16]

*cis*-**Bicyclo[4.2.0]oct-3-ene-1,6-dicarboxylic Acid Dimethyl Ester (4).** A mixture of 9.4 g (0.055 mol) of **3**[17] and 100 g (1.85 mol) of butadiene was heated in a glass pressure vessel at 100° for 48 hr. The solution was then cooled in a Dry Ice–acetone bath and poured into a 250-ml round-bottomed flask. After the excess butadiene had evaporated, the residual oil was distilled under reduced pressure to afford 10.8 g (87%) of **4**, bp 81–87° (0.1 mm) [lit.[17b] bp 113–114° (0.4 mm)].

*cis*-**Bicyclo[4.2.0]oct-3-ene-1,6-dimethanol.** To a slurry of 8.2 g (0.2 mol) of lithium aluminum hydride in 300 ml of anhydrous tetrahydrofuran cooled to 0° under a nitrogen atmosphere was added dropwise a solution containing 8.02 g (0.036 mol) of **4** in 50 ml of the same solvent. After being stirred at room temperature for 18 hr, the reaction mixture was cooled in ice and treated cautiously with 8.2 g of water, 8.2 ml of 30% sodium hydroxide solution, 24.6 ml of water, and 10 g of anhydrous magnesium sulfate, in that order. The inorganic salts were removed by filtration and the solvent was evaporated to afford 4.8 g (79.5%) of diol: mp 114–116° (from ether–petroleum ether); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.97 (m, 2, vinyl), 4.54 (br s, 2, -O*H*), 4.04 and 3.24 (AB quartet, $J_{AB}$ = 12 Hz, 4, -C*H*$_2$O-), 2.44 and 1.73 (complex AB pattern, $J_{AB}$ = 15 Hz, 4, allyl), and 1.48 (s, 4, methylene).

*Anal.* Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.30; H, 9.59.

*cis*-**1,6-Bis(methanesulfonyloxymethyl)bicyclo[4.2.0]oct-3-ene.** To a solution of 5.05 g (0.03 mol) of diol in 200 ml of cold pyridine under a nitrogen atmosphere was added dropwise 10.3 g (0.09 mol) of methanesulfonyl chloride. The reaction mixture was stirred at 0° for 1 hr, stored at −10° for 2 days, and then poured into 1200 ml of ice water. This mixture was placed in a refrigerator for 3 hr and filtered. There was obtained 9.2 g (94.6%) of dimesylate: mp 72–73° (from benzene–hexane); $\nu_{\max}^{\mathrm{CHCl_3}}$ 1355 and 1175 cm$^{-1}$ (-SO$_2$-); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.86 (m, 2, vinyl), 4.24 and 4.08 (AB quartet, $J_{AB}$ = 10 Hz, 4, -C*H*$_2$O-), 2.98 (s, 6, methyl), 2.00 (m, 4, allyl), and 1.70 (m, 4, methylene).

*Anal.* Calcd for $C_{12}H_{20}O_6S_2$: C, 44.46; H, 6.17; S, 19.48. Found: C, 44.43; H, 6.21; S, 19.77.

**8-Thia[4.3.2]propell-3-ene (5).** To a 500-ml, three-necked flask fitted with a mechanical stirrer, distillation head, and glass stopper was added 7.2 g (0.03 mol) of sodium sulfide nonahydrate and 30 ml of redistilled hexamethylphosphoramide. The reaction mixture was dehydrated by distilling the HMPA at 25 mm until the temperature of the distillate reached 115°. The blue solution was cooled and 2.0 g (6.1 mmol) of dimesylate was added. The temperature was maintained at 45–55° for 24 hr. The reaction mixture was cooled in ice and water (30 ml) together with ether (100 ml) were added. The water layer was extracted with ether (3 × 50 ml) and discarded. The combined ether solutions were washed with water (3 × 100 ml), dried, and evaporated. There was obtained 0.91 g (90%) of **5** as a pale yellow oil, bp 63–64° (0.25 mm).

**8-Thia[4.3.2]propell-3-ene 8,8-Dioxide (11).** To a solution of 410 mg (2.46 mmol) of **5** in 30 ml of ether cooled to 0° was added dropwise a solution of 840 mg (4.92 mmol) of 85% *m*-chloroperbenzoic acid in 30 ml of ether. After stirring overnight at room temperature, the solution was washed with saturated potassium carbonate (3 × 25 ml) and sodium sulfite (1 × 25 ml) solutions and dried. The ether was evaporated to give 440 mg (90%) of **11**: mp 137.5–139° (from ether–hexane); $\nu_{\max}^{\mathrm{CHCl_3}}$ 1300, 1115, and 1100 cm$^{-1}$ (-SO$_2$-); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.97–6.15 (m, 2, vinyl), 3.19 and 3.02 (AB quartet, $J_{AB}$ = 14 Hz, 4, -CH$_2$SO$_2$-), and 1.70–2.25 (m, 8, allyl and methylene).

*Anal.* Calcd for $C_{10}H_{14}O_2S$: C, 60.57; H, 7.12; S, 16.17. Found: C, 60.70; H, 7.22; S, 16.07.

**7(*R**)- and 7(*S**)-Chloro-8-thia-1(*R**),6(*S**)-[4.3.2]propell-3-ene 8,8-Dioxide (6 and 7).** A mixture of 6.0 g (0.032 mol) of **5**, 4.2 g (0.032 mol) of *N*-chlorosuccinimide, and 200 ml of carbon tetrachloride was heated at reflux for 1 hr, cooled, and filtered. The solvent was removed *in vacuo* and the resulting oil was dissolved in 50 ml of dry ether. To this cooled (0°) solution was added dropwise 14.0 g (0.065 mol) of 85% *m*-chloroperbenzoic acid in 200 ml of ether. The reaction mixture was stirred overnight at room temperature and worked up as above to give a yellowish oil. A typical nmr analysis of such a crude product mixture indicated a product ratio of 68% of **6** and 32% of **7**. Chromatography of the oil on silica gel and elution with hexane containing increasing amounts of ether afforded 3.12 g (38.4%) of **6**: mp 92–93° (from ethyl acetate–hexane); $\nu_{\max}^{\mathrm{CHCl_3}}$ 1330 and 116 cm$^{-1}$ (-SO$_2$-); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 6.08 (m, 2, vinyl), 4.83 (s, 1, >C*H*Cl), 3.18 (s, 2, -C*H*$_2$SO$_2$-), and 2.16 (m, 8, allyl and methylene).

*Anal.* Calcd for $C_{10}H_{13}ClO_2S$: C, 51.61; H, 5.63; S, 13.78. Found: C, 51.95; H, 5.42; S, 13.71.

Second to be eluted was **7** (1.90 g, 25.5%): mp 119–120.5° (from ethyl acetate–hexane); $\nu_{\max}^{\mathrm{CHCl_3}}$ 1335 and 1192 cm$^{-1}$ (-SO$_2$-); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 6.15 (m, 2, vinyl), 4.70 (s, 1, >C*H*Cl), 3.29 and 3.09 (AB quartet, $J_{AB}$ = 14 Hz, 2, -C*H*$_2$SO$_2$-) and 2.08 (m, 8, allyl and methylene).

*Anal.* Calcd for $C_{10}H_{13}ClO_2S$: C, 51.61; H, 5.63; S, 13.78. Found: C, 52.08; H, 5.68; S, 13.65.

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(15) We thank Professor Eaton for making these spectra available to us.

(16) The sulfides **5**, **8**, and **13** were not submitted directly for elemental analysis but rather were characterized as their crystalline sulfones. Notwithstanding, the infrared and nmr spectra of these substances indicated them to be of high purity.

(17) (a) W. H. Perkin, Jr., *J. Chem. Soc.*, **65**, 950 (1894); (b) E. Vogel, O. Roos, and K.-H. Disch, *Justus Liebigs Ann. Chem.*, **653**, 55 (1962).

***cis*-1,6-Bis(methanesulfonyloxymethyl)bicylco[4.2.0]octane.** A mixture of 1.0 g (3.10 mmol) of unsaturated dimesylate, 100 ml of methanol, and 50 mg of 10% palladium on charcoal was placed in a Paar hydrogenator at 50 psig for 1 hr, filtered, and concentrated *in vacuo.* There was obtained 1.1 g (100%) of product, an oil which was not further purified; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 4.27 and 4.12 (AB quartet, $J_{\mathrm{AB}}$ = 10 Hz, 4, $-CH_2O-$), 3.06 (s, 6, methyls), 1.84 (s, 4, cyclobutyl), and 1.58 (s, 8, methylene).

**8-Thia[4.3.2]propellane (8).** A 3.62-g (0.011 mol) sample of dimesylate was treated as above with 14.2 g (0.058 mol) of sodium sulfide nonahydrate in 150 ml of HMPA (dried carefully by azeotropic distillation) and heated overnight at 50°. This solution was cooled to 0° and treated with water (150 ml) and ether (150 ml). Processing in the predescribed manner gave 1.35 g (72.5%) of **8**, a yellowish oil which was not further purified; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 2.83 and 2.73 (AB quartet, $J_{\mathrm{AB}}$ = 11 Hz, $-CH_2S-$), 1.81 (s, 4, cyclobutyl), and 1.58 (s, 8, methylene).

**7(*R**)- and 7(*S**)-Chloro-8-thia-1(*S**),6(*R**)-[4.3.2]propellane 8,8-Dioxide (9 and 10).** A mixture of 1.29 g (7.8 mol) of **8**, 1.05 g (7.9 mmol) of *N*-chlorosuccinimide, and 100 ml of carbon tetrachloride was heated at reflux for 1.5 hr and processed as above. Oxidation of the α-chloro sulfide with *m*-chloroperbenzoic acid in ether gave a crude product which by nmr analysis contained 37.5% **9** and 62.5% **10**. Chromatography on silica gel caused **10** to be eluted first: white crystals, 540 mg (28.4%); mp 81–82° (from ethyl acetate–hexane); $\nu_{\max}^{\mathrm{CHCl_3}}$ 1330 and 1117 cm$^{-1}$ ($-SO_2-$); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 4.71 (s, 1, >C*H*Cl), 3.37 and 3.13 (AB quartet, $J_{\mathrm{AB}}$ = 14 Hz, 2, $-CH_2SO_2-$), and 1.30–2.65 (m, 12, methylene).

*Anal.* Calcd for $C_{10}H_{15}ClO_2S$: C, 51.16; H, 6.44; S, 13.66. Found: C, 51.13; H, 6.58; S, 13.66.

Second to be eluted was **9**: 360 mg (19.7%); mp 133–134° (from ethyl acetate–hexane); $\nu_{\max}^{\mathrm{CHCl_3}}$ 1325 and 1135 cm$^{-1}$ ($-SO_2-$); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.08 (s, 1, >C*H*Cl), 3.35 and 3.13 (AB quartet, $J_{\mathrm{AB}}$ = 14 Hz, 2, $-CH_2SO_2-$), 2.16 (m, 4, cyclobutyl), and 1.65 (m, 8, methylene).

*Anal.* Calcd for $C_{10}H_{15}ClO_2S$: C, 51.16; H, 6.44; S, 13.66. Found: C, 51.45; H, 6.54; S, 14.01.

**8-Thia[4.3.2]propella-2,4-diene 8,8-Dioxide (12).** A mixture of 2.0 g (0.010 mol) of **11**, 2.0 g (0.011 mol) of *N*-bromosuccinimide, 120 ml of carbon tetrachloride, and a trace of benzoyl peroxide was heated at reflux for 30 min, cooled, and filtered. The solvent was removed *in vacuo* and the resulting oil was admixed with a slurry of 5.4 g (0.10 mol) of sodium methoxide in 150 ml of dry tetrahydrofuran. After being heated overnight at reflux, the mixture was evaporated *in vacuo* and the resulting semisolid was treated with 50 ml of water and 50 ml of methylene chloride. The water layer was extracted with 25 ml of methylene chloride and the combined organic layers were dried and evaporated. The yellowish semisolid was triturated with carbon tetrachloride and stored overnight at −10°. Filtration afforded 580 mg (29.8%) of colorless crystals: mp 115–116° (from ethyl acetate); $\nu_{\max}^{\mathrm{CHCl_3}}$ 1310 and 1120 cm$^{-1}$ ($-SO_2-$); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.72 (m, 4, vinyl), 3.25 (m, 4, $-CH_2SO_2-$), and 2.53 (s, 4, cyclobutyl).

*Anal.* Calcd for $C_{10}H_{12}O_2S$: C, 61.19; H, 6.16; S, 16.34. Found: C, 61.06; H, 6.13; S, 16.07.

**8-Thia[4.3.2]propella-2,4-diene (13).** To a slurry of 1.5 g (0.04 mol) of lithium aluminum hydride in 200 ml of ether under nitrogen was added dropwise a solution of 1.95 g (0.01 mol) of **12** in 100 ml of ether. The mixture was heated at reflux for 48 hr, cooled, and quenched in the usual alkaline fashion. The resulting yellowish oil was dissolved in pentane and quickly filtered through 10 g of neutral alumina. The pentane was removed *in vacuo* to yield 1.0 g (67%) of **13**: $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.72 (m, 4, vinyl), 2.84 and 2.68 (AB quartet, $J_{\mathrm{AB}}$ = 10 Hz, 4, $-CH_2S-$), and 2.07 (m, 4, cyclobutyl).

**7(*R**)-Chloro-8-thia-1(*R**),6(*S**)-[4.3.2]propella-2,4-diene 8,8-Dioxide (14).** A 920-mg (5.60 mmol) sample of **13** was chlorinated and oxidized in the predescribed manner using 750 mg (5.60 mmol) of *N*-chlorosuccinimide and 2.50 g (0.015 mol) of 85% *m*-chloroperbenzoic acid. There was obtained an oil, the nmr spectrum of which showed the presence of only one isomer. Chromatography afforded 510 mg (38.6%) of **14**: mp 66–68° (from ethyl acetate–hexane); $\nu_{\max}^{\mathrm{CHCl_3}}$ 1328 and 1117 cm$^{-1}$ ($-SO_2-$); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.83 (m, 4, vinyl), 4.76 (s, 1, >C*H*Cl), 3.34 (s, 2, $-CH_2SO_2-$), and 2.57 (m, 4, cyclobutyl).

*Anal.* Calcd for $C_{10}H_{11}ClO_2S$: C, 52.05; H, 4.81; S, 13.90. Found: C, 52.31; H, 4.83; S, 13.71.

**7(*S**)- and 7(*R**)-(*tert*-Butoxy)-8-thia-1(*R**),6(*S**)-[4.3.2]propell-3-ene 8,8-Dioxide (15 and 16).** To a solution of 1.0 g (4.40 mmol) of **6** in 20 ml of tetrahydrofuran cooled to 0° under a nitrogen atmosphere was added 2.5 g (0.02 mol) of potassium *tert*-butoxide in small portions. The reaction mixture was stirred for 4 hr at 0° and then quenched with 20 ml of water. The water layer was extracted with ether (3 × 20 ml) and discarded. The combined ether layers were dried, filtered, and concentrated to afford 0.50 g (40%) of **15**: mp 143–144° (from cyclohexane–ethyl acetate); $\nu_{\max}^{\mathrm{CHCl_3}}$ 1310, 1135, and 1115 cm$^{-1}$ ($-SO_2-$); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 6.08 (m, 2, vinyl), 4.37 (s, 1, C*H*O–), 2.97 (s, 2, $-CH_2SO_2-$), 1.58–2.67 (m, 8, allyl and cyclobutyl), and 1.30 (s, 9, *tert*-butyl).

*Anal.* Calcd for $C_{14}H_{22}O_3S$: C, 62.19; H, 8.20; S, 11.86. Found: C, 62.19; H, 8.14; S, 11.79.

Treatment of **15** with excess potassium *tert*-butoxide in tetrahydrofuran for 24 hr at room temperature afforded a 4:1 mixture of **16** and **15**. Pure **16**, mp 107–109° (from ether–petroleum ether), was obtained by chromatography on silica gel; $\nu_{\max}^{\mathrm{CHCl_3}}$ 1312, 1140, and 1113 cm$^{-1}$ ($-SO_2-$); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 6.03 (m, 2, vinyl), 4.33 (br s, 1, >C*H*O–), 3.34 and 2.91 (AB quartet, $J_{\mathrm{AB}}$ = 14 Hz, 2, $-CH_2SO_2-$), 2.06 (m, 8, allyl and cyclobutyl), and 1.24 (s, 9, *tert*-butyl).

*Anal.* Calcd for $C_{14}H_{22}O_3S$: C, 62.19; H, 8.20, S, 11.86. Found: C, 62.05; H, 8.16; S, 11.84.

When **7** (1.0 g, 4.40 mmol) was treated in the same manner as **6** with potassium *tert*-butoxide, a mixture of **11** and **15** was obtained. Chromatography of this mixture on silica gel yielded 520 mg (60%) of **11**, mp 135–137°, and 140 mg (11%) of **15**, mp 142–144°.

**[4.2.2]Propella-3,7-diene (1).** To a slurry of 560 mg (2.40 mmol) of **7** in 15 ml of ether cooled to −78° under nitrogen was added 2.70 ml (5.27 mmol) of 1.95 *M n*-butyllithium in pentane. The mixture was stored at −10° overnight. Water (20 ml) was added and the ether layer was separated and dried. The ether solution was concentrated to 5 ml by distillation at atmospheric pressure through a 33-cm glass helix-packed column. Pentane (15 ml) was added and unreacted **7** was removed by filtration through silica gel. The solution was again carefully concentrated to 5 ml and subjected to preparative scale vpc (5.5 ft × 0.25 in. Al column packed with 5% Carbowax 6000 on 60–80 mesh Chromosorb G) at 125°. There was isolated 8.3 mg (2.6%) of **1** with a retention time of 5 min: $\nu_{\max}^{\mathrm{neat}}$ 2950, 2874, 1460, 1433, and 769 cm$^{-1}$; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 6.22 (s, 2, cyclobutene), 5.77 (m, 2, vinyl), 2.14 (m, 4, allyl), and 1.86 (m, 4, cyclobutyl); *m/e* 132.

*Anal.* Calcd for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.57; H, 9.35.

Also collected was **24** with a retention time of 12 min: $\nu_{\max}^{\mathrm{neat}}$ 2932, 2865, 1562, 1424, 1155, 1030, 934, and 825 cm$^{-1}$; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 6.00 (s, 1, cyclobutene), 5.76 (m, 2, vinyl), 2.16 (m, 4, allyl), and 1.94 (m, 4, cyclobutyl); *m/e* 166.

*Anal.* Calcd for $C_{10}H_{11}Cl$: C, 72.07; H, 6.65. Found: C, 72.11; H, 7.04.

Treatment of **6** (1.0 g) with *n*-butyllithium afforded 7.8 mg (1.4%) of **1** and only a trace of **24**.

**Hydrogenation of 1.** A solution of 12 mg of **1** in ethyl acetate solution was hydrogenated at atmospheric pressure using platinum oxide as catalyst. The product (6 mg) was purified by vpc on a 5.5 ft × 0.25 in. Al column packed with 10% SE-30 on 60–80 mesh Chromosorb W at 95°: $\nu_{\max}^{\mathrm{neat}}$ 2950, 2880, and 1415 cm$^{-1}$; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 2.04 (m, 8, cyclobutyl) and 1.41 (s, 8, cyclohexyl). These spectra were identical with those of **2** prepared independently by Eaton.[5]

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