and 2 *N* sulfuric acid. Evaporation of the dried ether phase gave 16 mg (4% recovery) of **10**.

The acidic solution was rendered alkaline and extracted with ether. Evaporation of the dried ether solution afforded 339 mg (94%) of **13** (88% pure by vpc analysis). Preparative scale vpc purification on a 12 ft × 0.25 in. column packed with 20% Apiezon L/KOH (4:1) on 60–80 mesh Chromosorb W gave **13** as a colorless liquid: $\nu_{\max}^{\text{neat}}$ 3210 cm^{-1}; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 2.98 (d of d, J = 11.0 and 3.0 Hz, 1, endo methylene), 2.62 (d, J = 11.0 Hz, 1, exo methylene), 1.80 (s, 1, >NH), 1.11 (s, 3, methyl), 1.07 (s, 6, methyls), 0.90–1.20 (m, 1, cyclopropyl), and 0.0–0.50 (m, 2, cyclopropyl).

Anal. Calcd for $C_8H_{15}N$: C, 76.74; H, 12.08. Found: C, C, 76.39; H, 12.00.

1,4,4,5-Tetramethyl-3-azabicyclo[3.1.0]hexan-2-one (15). A solution of 835 mg (7.5 mmol) of 1,2,2,3-tetramethylbicyclobutane (**14**)[28] in 30 ml of dry methylene chloride cooled to −78° was treated dropwise with a solution of 1.06 g (7.5 mmol) of CSI in methylene chloride (30 ml). After 4.5 hr, the solvent was evaporated under reduced pressure and the resulting pale yellow oil was triturated with ether to give 1.8 g of almost colorless crystals. This product was dissolved in acetone (5 ml) and the solution cooled to 0°. Thiophenol (1.8 g) in acetone (5 ml) was added, followed by the dropwise addition of pyridine (0.8 g) in acetone (10 ml). This mixture was stirred at 0° for 15 min and then water (50 ml) added. The pale yellow solid obtained from the organic phase was chromatographed on Florisil. Pentane–benzene (1:1) elution removed the diphenyl disulfide, whereas chloroform elution furnished 585 mg (51%) of **15** as colorless prisms, mp 137–137.5°, from methylene chloride–hexane: $\nu_{\max}^{\text{CHCl}_3}$ 3390, 3190, and 1685 cm^{-1}; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 1.27 (s, 6, methyls), 1.23 and 1.19 (s, 3 H each, methyls), 0.91 and 0.49 (d, J = 4 Hz, 1H each, cyclopropyls).

Anal. Calcd for $C_9H_{15}NO$: C, 70.55; H, 9.87; N, 9.14. Found: C, 70.53; H, 9.84; N, 9.14.

1,4-Dimethyl-2-azabicyclo[2.1.1]hexan-3-one (17). 1,3-Dimethylbicyclo[1.1.0]butane[31] (1.57 g, 0.019 mol) was dissolved in 25 ml of dry methylene chloride (previously treated with basic alumina) and the solution was cooled to −78°. CSI (2.82 g, 0.02 mol) in the same solvent (30 ml) was added dropwise with stirring during 0.5 hr under nitrogen. The solution was stirred at −78° for 4 hr and at 0° for an additional 2 hr. The solvent was evaporated under reduced pressure at 25°, the pale brown oily residue was dissolved in acetone (15 ml), and this solution was treated with thiophenol (0.04 mol) and pyridine (0.025 mol) in the usual way. The resulting pale yellow oil was chromatographed on Florisil and elution with ether afforded 370 mg (15.5%) of **17** which was molecularly distilled and recrystallized from methylene chloride–pentane at 0° to give colorless prisms: mp 74.5–75°; $\nu_{\max}^{\text{CHCl}_3}$ 1745 cm^{-1}; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 6.70 (br s, 1, >NH), 1.75–2.47 (m, 4, methylenes), 1.31 and 1.20 (s, 3 each, methyls).

Anal. Calcd for $C_7H_{11}NO$: C, 67.16; H, 8.86; N, 11.19. Found: C, 67.33; H, 8.89; N, 11.24.

Reaction of Bicyclo[2.1.0]pentane with CSI. A solution of 953 mg (14 mmol) of **18**[32] in 10 ml of dry methylene chloride cooled to −78° was treated dropwise with a solution of 1.99 g (1.17 ml, 14 mmol) of CSI in 2 ml of the same solvent. After 1 hr at −78°, the solution was stirred at room temperature for 5 hr, evaporated, and hydrolyzed with 4 *N* sodium hydroxide in aqueous acetone as before. Processing of the methylene chloride extracts and chromatography on silica gel afforded 480 mg (31%) of 2-azabicyclo[2.2.1]heptan-3-one (**19**) as a colorless liquid which crystallized on cooling: mp 32–33° (lit.[18] mp 32–34°); $\nu_{\max}^{\text{neat}}$ 3225 and 1745 cm^{-1}; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 7.00 (br s, 1, >NH), 4.09 (m, 1, >C*H*–N<), 3.51 (m, 1, >C*H*CO–), and 1.10–2.20 (m, 6, methylene).

Continuous extraction of the aqueous phase with methylene chloride for 3 days yielded 80 mg (7%) of cyclopentene-3-carboxamide, mp 136°, from methylene chloride (lit.[18] mp 135–137°): $\delta_{\text{TMS}}^{\text{CDCl}_3}$ *ca.* 5.8 (br m, 2, –NH_2), 5.62–5.90 (m, 2, vinyl), 3.38 (1, >C*H*CO–), and 1.73–2.61 (m, 4, methylene).

Acknowledgment. This study was aided by a grant from the National Science Foundation for which we are most grateful. The cooperation of Dr. John R. Malpass in the early phases of this work was most welcomed.

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(31) (a) W. von E. Doering and J. F. Coburn, Jr., *Tetrahedron Lett.*, 991 (1965); (b) K. Griesbaum and P. E. Butler, *Angew. Chem., Int. Ed. Engl.*, **6**, 444 (1967).

(32) R. Criegee and A. Rimmelin, *Chem. Ber.*, **90**, 414 (1957).

α-Halo Sulfones. XVII. Directive Effects in the Chlorination of Thiapropellanes[1]

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Gerald L. Thompson,[2,3c] Leonard K. Read,[4] and Jon Clardy[4]

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Received October 16, 1970

Abstract: To probe the role of steric effects operative in the α-chlorination of sulfides, six thiapropellanes were exposed to the action of *N*-chlorosuccinimide and subsequently oxidized. Where applicable, the isomeric α-chloro sulfones were separated and their ratio in the product mixtures was determined. The configurations of the chlorine substituents, assigned initially on the basis of nmr correlations, were confirmed by X-ray structure analysis of two representative examples. The observed product distributions appear not to be due exclusively to steric factors, although such considerations are of considerable importance. Rather, the data suggest that electronic effects gain significance in those examples which have sites of unsaturation in close proximity to the developing sulfonium ion.

The synthetic scheme developed in this laboratory for the preparation of unsaturated propellanes endowed with at least one cyclobutene ring[5–7] depends upon the base-induced rearrangement of appropriate

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(1) For paper XVI, see L. A. Paquette and R. W. Houser, *J. Org. Chem.*, **36**, 1015 (1971).

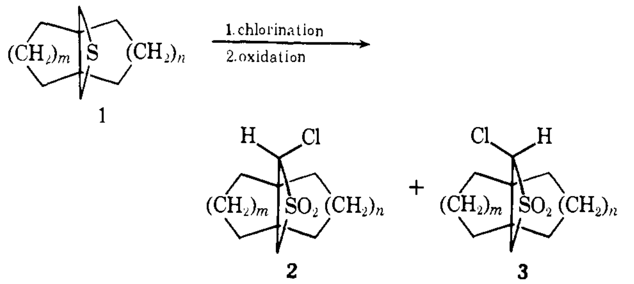
(2) The Ohio State University.

(3) (a) University Fellow, 1968–1969; National Institutes of Health Predoctoral Fellow, 1969–1971; (b) National Institutes of Health Predoctoral Fellow, 1966–1968; (c) Phillips Petroleum Fellow, 1970–1971.

(4) Iowa State University.

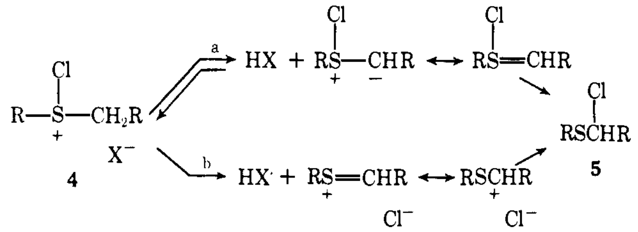
(5) For preliminary reports of this work, see: (a) L. A. Paquette and J. C. Philips, *Tetrahedron Lett.*, 4645 (1967); (b) L. A. Paquette and J. C. Philips, *J. Amer. Chem. Soc.*, **91**, 3973 (1969); (c) L. A. Paquette and J. C. Philips, *Chem. Commun.*, 680 (1969).

α-chloro sulfones.[8] Such α-halo sulfones (*e.g.*, **2** and **3**) are most conveniently prepared by chlorination and subsequent oxidation of the parent sulfides (**1**). For the present purposes, these sulfides are necessarily tricyclic systems conjoined by a single carbon–carbon bond. Two questions which arise when dealing with nonsymmetrical derivatives of **1** ($m \neq n$) concern the stereochemistry of the chlorination step and, subsequently, the dependence of chlorine configuration on the ease of the cyclobutene-forming reaction. The first of these points forms the subject of this paper, whereas the latter consideration is dealt with in the ensuing publication.



Sulfides which possess at least one α-hydrogen atom are recognized to react readily with chlorine,[9] sulfuryl chloride,[10] or *N*-chlorosuccinimide (NCS)[11] in an inert solvent and afford α-chloro sulfides. These transformations proceed by a polar mechanism involving chlorosulfonium salts (**4**) as initial intermediates. The passage of **4** to **5** may occur *via* an Elcb type mechanism (path a) when X⁻ is the weakly basic chloride ion, or an E2 related process (path b) when the more basic succinimidyl anion is involved (Scheme I).[11a] In actuality, it is entirely plausible that a continuum exists between these two extremes. Although the physical organic aspects of this chlorination reaction have recently received considerable attention,[11b,c] the role of steric influences remained to be explored.

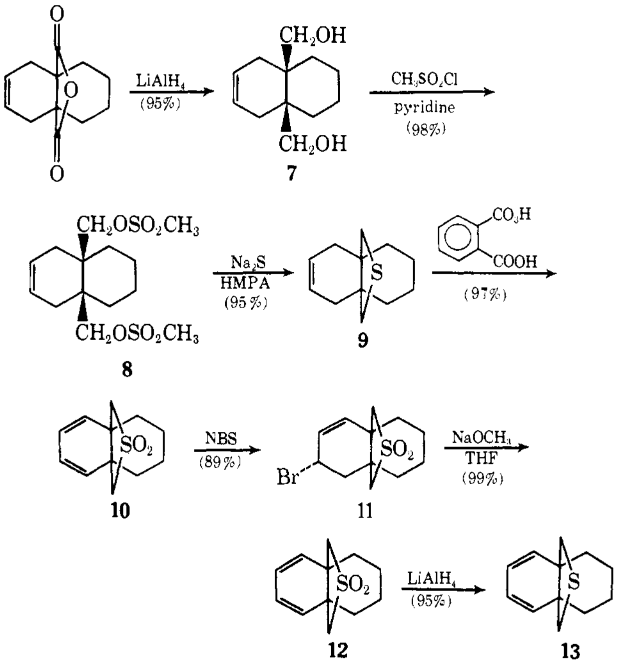
Scheme I



The unique structural features inherent in thiapropellanes such as **1** cause these molecules to be ideal substrates with which to investigate the steric question. Specifically, the fixed three-dimensional nature of **1** brings into play a capability for nonbonded interaction not available to other molecular types. NCS was utilized exclusively in this study. This reagent has the advantage that hydrogen chloride is not generated as a by-product; also, no detectable sulfoxide formation, allylic chlorination, or chlorinolysis is seen to result.

Synthetic Considerations. Our attention was directed initially toward the synthesis of sulfides **9** and **13**. This was accomplished by the reaction sequence shown in Scheme II. The starting material was Δ^2-octalin-9,10-dicarboxylic anhydride which by reduction with lithium aluminum hydride and treatment with methanesulfonyl chloride in pyridine gave the dimesylate **8** in high yield. Heating **8** in dry hexamethylphosphoramide (HMPA) with anhydrous sodium sulfide led to sulfide **9** in 95% yield. The use of dry HMPA is essential to the success of this twofold SN2 displacement–cyclization. In its absence, the capability of sulfide ion to attack at the neopentyl centers is greatly diminished and little or no **9** is produced. Clearly, the high cation-solvating capacity of HMPA, which greatly reduces the effective size of the nucleophile relative to its bulk in other (especially protic) media, causes a marked acceleration of the desired chemical change. Allylic bromination of the sulfone **10** derived from **9**, followed by dehydrobromination with excess powdered sodium methoxide in tetrahydrofuran, led readily to diene sulfone **12** in high yield. It is to be noted that the position of the bromine substituent in **11** results from an allylic shift during the bromination step. The structural assignment is based upon double resonance nmr experiments (see Experimental Section) and is reasonable when one considers the alternative possibility which would require the bromine substituent to become bonded to a neopentyl site. The endo configuration

Scheme II



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(6) L. A. Paquette, J. C. Philips, and R. E. Wingard, Jr., *J. Amer. Chem. Soc.*, **93**, 4516 (1971).

(7) L. A. Paquette and R. W. Houser, *ibid.*, **93**, 4522 (1971).

(8) For reviews of the α-halo sulfone rearrangement, consult: (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).

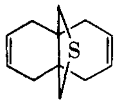
(9) H. Böhme, H. Fischer, and R. Frank, *Justus Liebigs Ann. Chem.*, **563**, 54 (1949), and pertinent references cited therein.

(10) (a) L. A. Paquette, L. S. Wittenbrook, and K. Schreiber, *J. Org. Chem.*, **33**, 1080 (1968); (b) L. A. Paquette and L. S. Wittenbrook, *J. Amer. Chem. Soc.*, **90**, 6783, 6790 (1969); (c) L. A. Paquette, L. S. Wittenbrook, and V. V. Kane, *ibid.*, **89**, 4487 (1967); (d) L. A. Paquette and L. S. Wittenbrook, *ibid.*, **89**, 4483 (1967); (e) L. A. Paquette, *ibid.*, **86**, 4085, 4089 (1964); (f) F. G. Bordwell, G. D. Cooper, and H. Morita, *ibid.*, **79**, 376 (1957); (g) F. G. Bordwell and B. M. Pitt, *ibid.*, **77**, 572 (1955); (h) W. E. Truce, G. H. Birum, and E. T. McBee, *ibid.*, **74**, 3594 (1952).

(11) (a) D. L. Tuleen and T. B. Stephens, *J. Org. Chem.*, **34**, 31 (1969); (b) D. L. Tuleen, *ibid.*, **32**, 4006 (1967); (c) D. L. Tuleen and V. C. Marcum, *ibid.*, **32**, 304 (1967); (d) D. L. Tuleen and T. B. Stephens, *Chem. Ind. (London)*, 1555 (1966).

of the halogen atom follows from the high degree of stereoselectivity observed in reactions of closely related propellanes.[12] When **12** was reduced with lithium aluminum hydride in refluxing ether, the desired sulfide **13** was produced in 95% yield.

Preparation of the requisite symmetrical model compounds **15** and **18** was carried out following essentially the same route as outlined above (see Experimental Section). For the synthesis of 13-thia[5.4.3]propell-9-ene and its diene counterpart **18**, it was necessary to develop a ready and efficient synthesis of cycloheptene-1,2-dicarboxylic anhydride (**17**). To this end, 2-carbethoxycyclooctanone (**16**) was dibrominated and subjected to quasi-Favorskii rearrangement.[13] This anhydride was converted to **18** according to the pathway employed earlier.



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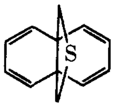

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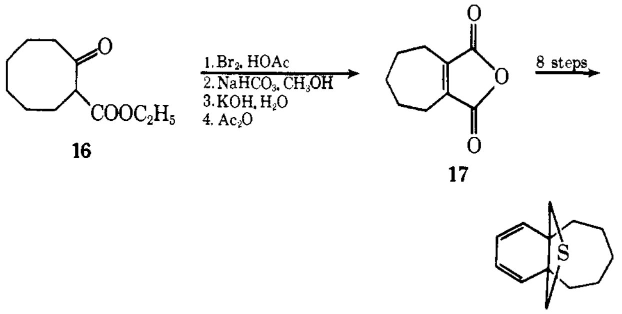
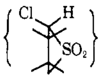
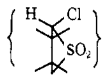
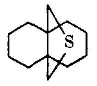
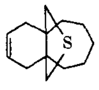


16 **17** **18**

Chlorination Studies. Each of the six sulfides was exposed to an equimolar amount of NCS in refluxing carbon tetrachloride solution, followed by direct oxidation of the resulting α-chloro sulfide with 2 equiv of monoperphthalic acid in ether. In the case of **9**, the nmr spectrum of the α-chloro sulfone mixture so obtained (97% yield) displayed, *inter alia*, two >C*H*Cl singlets at δ 5.41 and 5.00. Careful integration of these absorptions indicated the ratio of the two components to be 44:56 respectively (Table I). Column chromatography on silica gel readily separated the more rapidly eluted minor isomer (**19**) from the major product (**20**). The configurational assignments of the chlorine substituents, while founded chiefly on comparative nmr chemical shift data for the >C*H*Cl proton, have received appropriate verification from the X-ray analysis of **21** (see below).

12-Thia[4.4.3]propella-2,4-diene (**13**) was considered next. The chlorination–oxidation sequence again afforded a mixture of two α-chloro sulfones in excellent (97%) yield. Whereas *a priori* considerations would perhaps predict that the added unsaturation present in the cyclohexadiene portion of **13** should lead to an increased proportion of chlorination from the direction syn to this grouping, the ratio of products was found to be 35:65 in favor of **22**. Chloro sulfone **21** exhibited a δ 5.37 singlet for the >C*H*Cl proton which compares well with the chemical shift of the related hydrogen in **19**, and especially in **24**. Likewise, **21** was eluted more rapidly than **22** from a silica gel column. Not unexpectedly, the >C*H*Cl proton in **22** is downfield shifted by δ 0.17 relative to that in **20** as a result of increased deshielding introduced by the proximate diene functionality. This shift difference is in good agreement with the $\Delta\delta$ value of 0.24 observed for **25** and **26** (Table I). Conclusive proof that **21** was indeed 11(*R**)-chloro-12-thia-1(*R**),6(*S**)[4.4.3]propella-2,4-diene 12,12-dioxide[14] was gained from a three-dimensional X-ray crystal-structure analysis.[15a]

Table I. Product Distribution and Nmr Spectral Data of α-Chloro Sulfones Resulting from NCS Chlorination of Various Thiapropellanes

						
Sulfide	No.	%	δ (>CHCl)	No.	%	δ (>C*H*Cl
9	**19**	44	5.41	**20**	56	5.00
13	**21**	35	5.37	**22**	65	5.17
 **23**	**24**		5.38			
14				**25**		5.08
15				**26**		5.29
 **27**	**28**	72	5.22	**29**	28	5.00
18	**30**	65	5.22	**31**	35	5.22

Sulfide **27** was analogously chlorinated and oxidized. Nmr spectra of the epimeric mixtures so produced revealed that the major product showed a >C*H*Cl absorption at δ 5.22, while the comparable singlet for the minor isomer was seen at 5.00. In view of the spectral correspondence with the previous α-chloro sulfones, it seemed likely that the predominant isomer in this instance was **28**. The correctness of this conclusion was attested to by an X-ray analysis of **28**, a structural view of which is given in Figure 1.[15b] The Cl atom is attached to C(12) such that it is on the same side of the five-membered ring [S(1), C(12), C(1), C(7) and C(13)] as the cyclohexene ring. The cycloheptane ring [C(1)–C(7)] is in a chair conformation and

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(12) G. L. Thompson, results as yet unpublished.

(13) This sequence represents a modification of an earlier procedure described in Netherlands Patent Application No. 6,513,202 (1966); *Chem. Abstr.*, **65**, 20032*h* (1966).

(14) In order to assign unequivocally the spatial configuration of a substituent on a propellane ring system endowed with three dissimilar component rings, it becomes necessary to employ three stereochemical descriptors. For convenience, we have utilized the prefixes *R** and *S** where the capitalized letters have their accepted configurational meaning according to the sequence rules. However, to denote that relative rather than absolute stereochemistry is involved (at least insofar as the optically inactive substances dealt with herein are concerned), asterisks are added to the designation. The composite stereochemical descriptors must then specify not only the configuration of the ring atom bearing the substituent in question, but also the configuration of the two carbon atoms which are common to the three rings. If the arrangement of the three rings is not specified in this manner, it may be easily shown that the relative configuration of the substituent cannot be adequately defined. We wish to acknowledge a helpful discussion of this subject with Dr. Michael O'Hara of Chemical Abstracts Service.

(15) (a) Details of this analysis, performed by Dr. Jack Blount of Hofmann-LaRoche, Nutley, N. J., will be published separately. (b) A listing of structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.

cis fused to the five-membered ring. The cyclohexene ring [C(1) and (C(7)–C(11)] is also in the chair conformation and cis fused. In the five-membered ring C(7), C(12), C(13), and S(1) are essentially planar and C(1) is out of the plane. As a result, C(12) is displaced toward the cycloheptane ring and C(13) toward the cyclohexene ring. The resultant molecular geometry has a staggered conformation for all atom pairs with the exceptions of the eclipsed hydrogens on C(3) and C(4) and the eclipsed hydrogens and oxygens on C(13) and S(1). There are no abnormally short intramolecular contacts. In particular, the Cl atom does not approach any other atom within a sum of van der Waals radii. All bond distances and angles (esd's 0.02 Å and 1.5°, respectively) agree well with generally accepted values.

The remaining sulfide, namely **18**, led under analogous conditions to a mixture of **30** (65%) and **31** (35%). Because the >C*H*Cl proton in both α-chloro sulfones appeared at δ 5.22, hydrogenation of the original mixture was necessary to resolve the question of isomer distribution. As expected, the >C*H*Cl absorption of tetrahydro-**30** (δ 5.23) remained essentially unchanged relative to its diene counterpart while the >C*H*Cl absorption of tetrahydro-**31** was downfield shifted to δ 5.45. Further support for the assignment of structure **30** to the major product came from additional nmr comparisons (especially **28**, Table I) and the more rapid elution of this isomer on silica gel chromatography.

These data reveal that chlorination of 11-thia[4.4.3]-propellanes (**9** and **13**) results in preferential entry of the halogen atom from what may be formally considered to be the more hindered side. This trend is reversed in the two 12-thia[5.4.3]propellanes (**27** and **18**) examined. Because the relative effective steric bulk of the various bridges in these sulfides could only be inferred from studies of molecular models, a means of evaluating such nonbonded interactions was sought. The simplest method of gaining such insight involved equilibration of the α-chloro sulfone products. It was recognized that such information would provide suggestive evidence of the prevailing steric effects, since sulfones were to be used rather than sulfides. However, the almost equivalent stereochemical disposition of the two sulfone oxygen atoms toward the other two bridges (*cf.* Figure 1 for example) was not expected to produce a significant imbalance of spatial factors operative in the molecules under consideration.

The various α-chloro sulfones were readily equilibrated by heating in aqueous dioxane containing sodium hydroxide. The results, which have been summarized in Table II, are based upon ultimate quantitative nmr analyses of the >C*H*Cl absorptions as above. Most enlightening were the observations that the equilibrated product distributions from the α-chloro sulfone pairs **19** and **20** and **21** and **22** approached 1:1, while those in the [5.4.3]propellane series (**28** and **29**) favored somewhat the epimers with the halogen syn to the six-membered ring. Hitherto, discussion of the directive effects noted upon chlorination of these thiapropellanes would likely have been based almost entirely upon steric considerations. However, it would appear that steric factors alone do not necessarily govern the stereochemistry of the final product. There exists little doubt that nonbonded interactions represent the major controlling influence in the rate-determining transition state. However, interaction of the positive charge developing on sulfonium sulfur with the π system present in the molecule would appear to be another controlling factor which gains increased importance as the level of unsaturation is enhanced.

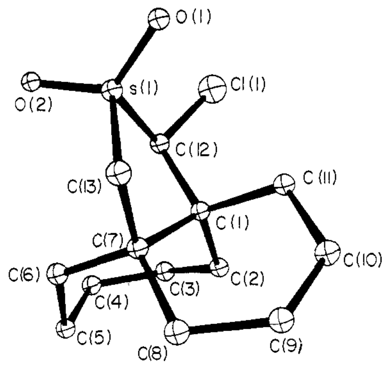


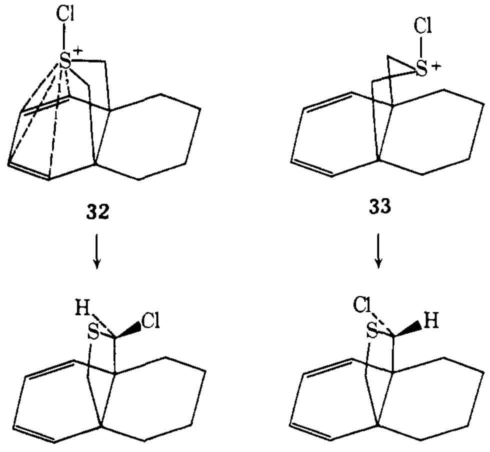
Figure 1. A structural view of **28** as determined by X-ray analysis showing the conformation of the molecule.

Table II. Comparison of Equilibrium Data with Percentage Compositions from Chlorination–Oxidation Sequence for Various α-Chloro Sulfones

α-Chloro sulfone	% of mixture[a]: From chlor-oxid seq	At equil
19	44	51.5
20	56	48.5
21	35	50
22	65	50
28	72	66
29	28	34
30	65	
31	35	

[a] Based on expanded-scale integrations of the nmr absorptions (singlets) due to the >C*H*Cl absorption of each isomer.

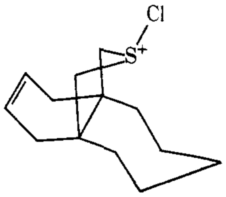
To illustrate, the case of **13** is considered in some detail. Chlorination of this sulfide can be expected to be controlled stereochemically by the initial configurations of the first-formed *S*-chlorosulfonium salts. Consideration of the steric and electronic influences present in **32** and **33** includes an awareness that sulfonium



32 **33** **34** **35**

ion **32** can experience added stabilization of both a steric and electronic nature which is not available to **33**. As a result, subsequent intramolecular migration of chlorine from sulfur to carbon (see Scheme I) would result in the formation of **34** and **35**, with the former predominating.[16] In actuality, subsequent oxidation of such a reaction mixture has shown that **34** exceeds **35** by a factor of approximately 2.

The more remote nature of the double bond in **9** would result in a diminution of effective π overlap with sulfonium sulfur and the establishment of a more equitable reactivity balance. As expected from such considerations, **20** should be marginally favored over **19** and this is observed. Interestingly, the decrease in the amount of anti chloro isomer is 10%. In the chlorination of **27**, it appears that the enhanced conformational flexibility of the cycloheptane ring assumes the dominating role. In **36**, for example, the interaction potential between the chlorine atom and the polymethylene chain is likely to be minimized appreciably relative to that existing in the [4.4.3]propellane analog. Because **28** predominates over **29** in the distribution of α-chloro sulfone epimers, steric factors seemingly emerge as the more important influence with increasing size of one bridge. Electronic influences are not totally absent, however, since chlorination–oxidation of diene counterpart **18** results in an entirely comparable 7% increase of the anti chloro isomer **31**, an effect which is unreasonable on steric grounds alone.



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Clearly, the magnitude of the effect under discussion is small. The product distributions require differences in activation energies for the two transition states of approximately 0.5 kcal/mol. The mechanistic suggestions advanced above are understandably speculative at the present time; in an optimistic sense, however, these considerations may provide a general mechanistic basis for explaining a variety of stereochemical observations which will be encountered subsequently in the functionalization of propellane molecules.

Experimental Section[17,18]

Δ^2-Octalin-9,10-dicarboxylic Anhydride (6). The anhydride was prepared by initial rearrangement of 4-cyclohexene-*cis*-1,2-dicarboxylic anhydride to the conjugated isomer with phosphorus pentoxide at 195°,[19] followed by condensation with butadiene in benzene solution at 160–170° under atuoclave conditions.[20]

***cis*-9, 10-Bis(hydroxymethyl)-Δ^2-octalin (7).** A solution of 123.6 g (0.60 mol) of **6** in 500 ml of anhydrous tetrahydrofuran was added dropwise to a stirred suspension of 27.8 g (0.73 mol) of lithium aluminum hydride in 1 l. of the same solvent. After being heated at reflux for 40 hr, the mixture was cooled and treated carefully with approximately 300 ml of water until a milky white suspension was produced. The reaction mixture was divided into two equal portions, each of which was placed in a 6-l. Erlenmeyer flask and cooled in ice during the addition of 1 l. of ice-cold 5% sulfuric acid. Each solution was diluted to a total volume of 6 l. with ice water and allowed to stand in an ice bath for 1 hr. The product was filtered, washed with water, and dried to give 111.5 g (95%) of diol: mp 147–149° (from benzene); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.61 (m, 2, vinyl), 3.45, 3.64, 3.68, and 3.87 (AB quartet, J = 12 Hz, $-\mathrm{C}H_2\mathrm{OH}$), 2.91 (s, 2, $-\mathrm{O}H$), 2.08 (2 lines, 4 H, allyl), and 1.53 (br s, 8, methylene).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.62; H, 10.10.

***cis*-9,10-Bis(methanesulfonyloxymethyl)-Δ^2-octalin (8).** To an ice-cold mechanically stirred solution of 370 g (3.21 mol) of methanesulfonyl chloride in 700 ml of pyridine was added dropwise during 2 hr a solution of 209 g (1.07 mol) of **7** in 800 ml of pyridine. The temperature was maintained at 0–5° during the addition and the mixture was allowed to stir in the cold for an additional 2 hr. Cold 10% hydrochloric acid (9 l.) was added and the resulting precipitate was filtered, washed well with water, and dried. There was obtained 368 g (98%) of **8**: mp 124.5–125.5 (from methanol); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.52 (br s, 2, vinyl), 3.97, 4.12, 4.18, 4.33 (AB quartet, J = 9 Hz, 4, $-\mathrm{C}H_2\mathrm{O}-$), 2.99 (s, 6, methyl), 2.11 (br s, 4, allyl), and 1.56 (s, 8, methylene).

Anal. Calcd for $C_{14}H_{24}O_6S_2$: C, 47.70; H, 6.86. Found: C, 48.08; H, 6.96.

12-Thia[4.4.3]propell-3-ene (9). A mechanically stirred slurry of 410 g (1.71 mol) of sodium sulfide nonahydrate in 1.5 l. of HMPA (distilled from calcium hydride and stored over molecular sieves) was heated to 97° (~20 mm) and the aqueous distillate (max bp 83°) was collected and discarded. The slurry was cooled to ambient temperature, 216.4 g (0.614 mol) of **8** was added in one portion, and the dark green reaction mixture was stirred at 120° for 24 hr. The brownish-colored contents were cooled, treated with 1.5 l. of water, and extracted with three 1-l. portions of ether. The combined organic extracts were washed with water (three 1-l. portions) and saturated salt solution (250 ml) and evaporated. There was obtained 117.7 g (98%) of sulfide: mp 85–87° (from methanol); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.52 (m, 2, vinyl), 2.96, 2.78, 2.72, and 2.54 (AB quartet, J = 10 Hz, 4, $-\mathrm{C}H_2\mathrm{S}-$), 2.05 (br s, 4, allyl), and 1.52 (br s, 8, methylene).

Anal. Calcd for $C_{12}H_{18}S$: C, 74.16; H, 9.33. Found: C, 74.12; H, 9.28.

12-Thia[4.4.3]propell-3-ene 12,12-Dioxide (10). To an ice-cold, magnetically stirred solution of 2.32 g (11.9 mmol) of **9** in 20 ml of ether was added dropwise a standardized ethereal solution containing 24 mmol of monoperphthalic acid.[21] The mixture was stirred at ambient temperature for 2 hr, filtered to remove phthalic acid, and washed with 0.5 *N* sodium hydroxide solution, water, and saturated sodium chloride solution. The ether was removed to give 2.6 g (97%) of sulfone: mp 138–140° (from hexane); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.65 (t, J = ~1 Hz, Z, vinyl), 3.41, 3.19, 3.10, and 2.88 (AB quartet, J = 13 Hz, 4, $-\mathrm{C}H_2\mathrm{SO_2}-$), 2.24 (d, J = 1 Hz, 4, allyl), and 1.62 (s, 8, methylene).

Anal. Calcd for $C_{12}H_{18}O_2S$: C, 63.68; H, 8.01; S, 14.17. Found: C, 63.70; H, 8.03; S, 14.05.

4-Bromo-12-thia[4.4.3]propell-2-ene 12,12-Dioxide (11). A magnetically stirred mixture of 40.0 g (0.176 mol) of **10**, 34.5 g (0.194 mol) of recrystallized *N*-bromosuccinimide, a catalytic amount of benzoyl peroxide, and 1 l. of carbon tetrachloride was refluxed for 5 hr. The solution was cooled, filtered to remove succinimide, and evaporated to give sticky crystals which were recrystallized with some difficulty from acetone–ether: 48.0 g (89%): mp 141.5–142°; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 6.12, 5.95, 5.69, 5.52 (AB quartet, J = 10 Hz, 2, vinyl), 4.85 (m, 1, $>\mathrm{C}H\mathrm{Br}-$), 3.61, 3.38, 3.11, 2.88 (AB quartet, J = 18 Hz, 2, $-\mathrm{C}H_2\mathrm{SO_2}-$), 3.11 (s, 2, $-\mathrm{C}H_2\mathrm{SO_2}-$), 2.45 (dd, J = 15 and 7.0 Hz, one H-5), 2.37 (dd, J = 15 and 7.0 Hz, other H-5), and 1.4–2.0 (br m, 8, methylene). Double irradiation at δ 4.85 caused simplification of the two low-field AB quartets to doublets (the reverse spin decouplings were also performed) and of the 2.45 and 2.37 absorptions to doublets (J = 15 Hz).

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(16) The possibility exists, of course, that the migration of chlorine does not proceed stereospecifically. Despite this possibility, the present outline is adequate for our purposes, since it is likely that similar steric and electronic forces would operate on the ylide or sulfonium ion intermediates, albeit perhaps to a lesser extent.

(17) All melting points were taken in open capillaries and are corrected, while boiling points are uncorrected.

(18) The sulfides prepared herein were not submitted directly for 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.

(19) M. E. Bailey and E. D. Amstutz, *J. Amer. Chem. Soc.*, **78**, 3828 (1956).

(20) K. Alder and K. H. Backendorf, *Chem. Ber.*, **71**, 2199 (1938).

(21) E. E. Royals and L. L. Harrell, *J. Amer. Chem. Soc.*, **77**, 3405 (1955).

Anal. Calcd for $C_{12}H_{17}BrO_2S$: C, 47.21; H, 5.62; S, 10.50. Found: C, 47.11; H, 5.60; S, 10.55.

12-Thia[4.4.3]propella-2,4-diene 12,12-Dioxide (12). A magnetically stirred mixture of 50.0 g (0.163 ml) of **11** and 100 g of powdered sodium methoxide in 1 l. of dry tetrahydrofuran was refluxed under nitrogen for 24 hr, cooled to 0°, and treated with 250 ml of water (slow addition). The aqueous layer was separated and washed three times with ether. The combined organic layers were washed with saturated sodium chloride solution, dried, and evaporated. Crystallization of the resulting pale yellow oil from ethyl acetate–cyclohexane gave 36.9 g (99%) of **12**: mp 94.5–95°; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.57–6.20 (A_2B_2. 4, vinyl), 3.20 (s, 4, $-CH_2SO_2-$), and 1.33–1.83 (br m, 8, methylene).

Anal. Calcd for $C_{12}H_{16}O_2S$: C, 64.27; H, 7.19; S, 14.27. Found: C, 63.88; H, 7.05; S, 14.11.

12-Thia[4.4.3]propella-2,4-diene (13). To a magnetically stirred mixture of 9.1 g (0.24 mol) of lithium aluminum hydride in 50 ml of ether was added 18.4 g (0.0814 mol) of **12**. After being refluxed for 24 hr, the mixture was processed in the customary alkaline fashion to give 15.0 g (95%) of **13** as a viscous oil. Repeated sublimation of this material afforded a waxy solid, mp 51.0–52.5°, which was employed for the chlorination studies: $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.50–6.06 (A_2B_2, 4, vinyl), 2.91 (s, 4, $-CH_2S-$), and 1.33–1.66 (br m, 8, methylene).

cis-**9,10-Bis(methanesulfonyloxymethyl)-$\Delta^{2,6}$-hexalin.** This dimesylate was obtained in 99.3% yield by treatment of the diol[22] with methanesulfonyl chloride as above. The white crystalline solid melted at 115–116° (lit.[22] mp 115–116°); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.52 (br s, 4, vinyl), 4.20 (s, 4, $-CH_2O-$), 2.98 (s, 6, methyl), and 2.07 (br s, 8, allyl).

12-Thia[4.4.3]propella-3,8-diene (14). Reaction of 225 g (0.644 mol) of dimesylate with 400 g (1.67 mol) of sodium sulfide nonahydrate in 1.2 l. of anhydrous HMPA strictly in accordance with the predescribed conditions (18 hr at 120°) gave a tan semisolid. This material was subjected to 0.1 mm vacuum until complete crystallization occurred. The solid was dissolved in pentane and passed through an alumina (neutral, activity I) column. Removal of the pentane afforded 121 g (98.8%) of **14** as a waxy white solid: $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.45 (m, 4, vinyl), 2.76 (s, 4, $-CH_2S-$), and 2.08 (m, 8, allyl).

12-Thia[4.4.3]propella-3,8-diene 12,12-Dioxide. Oxidation of 225 g (1.17 mol) of **14** in anhydrous ether with 2.34 mol of monoperphthalic acid (25°, 12 hr) in the above fashion led to the isolation of 226 g (86.5%) of crystalline sulfone: mp 115–116.5° (from ligroin): $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.60 (m, 4, vinyl), 3.15 (s, 4, $-CH_2SO_2-$), and 2.33 (m, 8, allyl).

Anal. Calcd for $C_{12}H_{16}O_2S$: C, 64.25; H, 7.19; S, 14.29. Found: C, 64.49; H, 7.25; S, 14.20.

12-Thia[4.4.3]propella-2,4,7,9-tetraene 12,12-Dioxide. A solution of 10.0 g (0.0624 mol) of bromine in 10 ml of methylene chloride was added dropwise to an ice-cold magnetically stirred solution of 6.99 g (0.0312 mol) of sulfone in 50 ml of methylene chloride. The reaction mixture was allowed to warm to room temperature with continued stirring during 4 hr. The solvent was removed and the crude tetrabromo sulfone was added to a mixture of 13.5 g (0.25 mol) of sodium methoxide in 200 ml of dry tetrahydrofuran. The mixture was refluxed for 6 hr under nitrogen and cooled. Most of the tetrahydrofuran was evaporated *in vacuo*, and 50 ml of ether was added. The ethereal slurry was washed with water (three 100-ml portions), dried, and concentrated. The resulting oily crystals were recrystallized from benzene to give 1.3 g (45%) of white solid: mp 160–162° (from benzene); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.82 (A_2B_2, 8, vinyl) and 3.36 (s, 4, $-CH_2SO_2-$).

Anal. Calcd for $C_{12}H_{12}O_2S$: C, 65.42; H, 5.49; S, 14.56. Found: C, 65.53; H, 5.34; S, 14.27.

12-Thia[4.4.3]propella-2,4,7,9-tetraene (15). To a magnetically stirred slurry of 2.0 g (0.053 mol) of lithium aluminum hydride in 150 ml of ether was added in one portion 5.84 g (0.0265 mol) of tetraene sulfone. The reaction mixture was refluxed for 6 hr, cooled, and subjected to alkaline hydrolysis as above. Evaporation of the solvent afforded 5.0 g (100%) of **15** which was used without further purification in the chlorination studes: $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.31–6.14 (A_2B_2, 8, vinyl) and 3.08 (s, 4, $-CH_2S-$).

Cycloheptene-1,2-dicarboxylic Anhydride (17). To a magnetically stirred solution of 29.7 g (0.15 mol) of **16**[23] in 150 ml of glacial acetic acid was added dropwise over a 1-hr period 24 g (0.15 mol) of bromine in 75 ml of glacial acetic acid. After stirring for 4 days, an additional 24 g of bromine was added dropwise and stirring was continued for 2 days. The solvent was removed on a rotary evaporator and the residue was dissolved in 150 ml of ether and washed with 100 ml of 10% sodium bicarbonate solution and 100 ml of water. The solution was dried and evaporated, and the residual oil was stirred with 50 g of sodium bicarbonate in 450 ml of anhydrous methanol for 24 hr. Following this, the undissolved sodium bicarbonate was removed by filtration and the methanol was evaporated. Ether (200 ml) and water (100 ml) were next added and the organic layer was separated and washed again with 100 ml of water. The ethereal layer was evaporated to an oil and 500 ml of water was added along with 56.1 g (1.0 mol) of potassium hydroxide. After being stirred overnight, the solution was filtered through diatomaceous earth and acidified with concentrated hydrochloric acid. The dark precipitated solid (13.0 g) was thoroughly dried and dissolved in 120 ml of acetic anhydride. The solution was refluxed for 1 hr, cooled, and evaporated. Trituration of the residual black oil with ether (0°, overnight) afforded dark brown crystals which were dissolved in ether and heated in the presence of charcoal for 30 min. From the resulting clear solution there could be isolated 7.82 g (31.5%) of **17** as white crystals, mp 56.5–58.5° (lit.[13] mp 57°).

12,14-Dioxo-13-oxa[5.4.3]propell-9-ene. A 2-l. thick-walled glass tube charged with 30.0 g (0.818 mol) of **17**, 140 g (2.6 mol) of butadiene, and 50 ml of benzene was heated for 72 hr in an oil bath maintained at 150°. The solvent was removed on a rotary evaporator. At a pressure of 0.5 mm, all volatile materials were distilled away from the butadiene polymers (bulb to bulb); oil bath temperatures in the vicinity of 220° were required to complete the distillation. The white crystalline distillate was dissolved in ether and this solution was washed with 10% potassium carbonate solution until the evolution of carbon dioxide ceased. A final wash with saturated sodium chloride solution was followed by drying and evaporation of the solvent. There resulted 20.4 g (51.5%) of anhydride: mp 98.5–100° (from ligroin); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.93–6.15 (m, 2, vinyl) and 1.59–2.71 (broad envelope, 14, allyl and methylene).

Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.85; H, 7.25.

Unreacted starting material may be recovered by careful acidification of the carbonate washes with concentrated hydrochloric acid and extraction with ether. The diacid so obtained is converted to **17** by heating overnight with twice its weight of acetic anhydride. Removal of the acetic anhydride and acetic acid *in vacuo*, followed by treatment with decolorizing charcoal in refluxing ether and recrystallization from ligroin, gives 89% of **17** based upon the theoretical amount of unreacted anhydride.

cis-**1,7-Bis(hydroxymethyl)bicyclo[5.4.0]undec-9-ene.** Reduction of 20.4 g (0.073 mol) of anhydride with 9.5 g (0.25 mol) of lithium aluminum hydride in 250 ml of refluxing dry tetrahydrofuran for 60 hr yielded 14.6 g (75%) of diol: mp 139–140° (from ligroin); $\delta_{\mathrm{TMS}}^{\mathrm{acetone}\text{-}d_6}$ 5.80–5.90 (m, 2, vinyl), 3.37–3.51 (m, 4, $-CH_2OH$), 2.60–2.70 (m, 2, $-OH$), 1.90–2.10 (m, 4, allyl), and 1.56 (br s, 10, methylene).

Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.24; H, 10.52.

cis-**1,7-Bis(methanesulfonyloxymethyl)bicyclo[5.4.0]undec-9-ene.** Reaction of 14.6 g (0.069 mol) of diol with 57.3 g (0.50 mol) of methanesulfonyl chloride in 500 ml of pyridine at −5° for 2.5 hr afforded a quantitative yield of dimesylate: mp 160–161° (from chloroform–ethanol); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.62–5.73 (m, 2, vinyl), 4.46, 4.30, 4.25, 4.09 (AB, $J = 9.5$ Hz, 4, $-CH_2O-$), 3.03 (s, 6, methyl), 2.20 (br s, 4, allyl), and 1.70 (br s, 10, methylene).

Anal. Calcd for $C_{15}H_{26}O_6S_2$: C, 49.17; H, 7.15; S, 17.47. Found: C, 48.92; H, 7.12; S, 17.39.

13-Thia[5.4.3]propell-9-ene. From 27.5 g (0.075 mol) of dimesylate and 193 g (1.24 mol) of sodium sulfide nonahydrate in 500 ml of dry HMPA at 120° for 18 hr there was obtained a pale yellow oil. Dissolution of this material in pentane and passage through a column of alumina (neutral, activity I) gave 13.0 g (83.5%) of sulfide as a colorless viscous oil: $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.50–5.61 (m, 2, vinyl), 2.71 (br s, 4, $-CH_2S-$), 2.02–2.20 (m, 4, allyl), and 1.63 (br s, 10, methylene).

The sulfone, prepared by monoperphthalic acid oxidation in ether, was obtained in 91.2% yield as white needles, mp 98–99°, from ether–ligroin: $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.60–5.73 (m, 2, vinyl), 3.1 (s, 4, $-CH_2SO_2-$), 2.26 (s, 4, allyl), and 1.50–1.91 (br m, 10, methylene).

Anal. Calcd for $C_{13}H_{20}O_2S$: C, 64.68; H, 8.39; S, 13.31. Found: C, 64.90; H, 8.39; S, 13.16.

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[22] G. Snatzke and G. Zanati, *Justus Liebigs Ann. Chem.*, **684**, 62 (1965).

[23] P. Krapcho, J. Diamonti, C. Cayen, and R. Bingham, *Org. Syn.*, 47, 20 (1967).

13-Thia[5.4.3]propella-8,10-diene 13,13-Dioxide. Treatment of 8.77 g (0.037 mol) of sulfone with 7.10 g (0.040 mol) of *N*-bromosuccinimide and a catalytic amount of benzoyl peroxide in 50 ml of carbon tetrachloride as before (reflux for 15 min) afforded a pale yellow oil which was treated directly with 25 g of sodium methoxide in 125 ml of dry tetrahydrofuran (reflux for 15 hr). There was obtained 2.41 g (27.7%) of diene sulfone as white needles: mp 107–108°, from ether–petroleum ether (65–110°); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.79 (A_2B_2, 4, vinyl), 3.23 (s, 4, $-CH_2SO_2-$), and 1.40–2.14 (br m, 10, methylene).

Anal. Calcd for $C_{13}H_{18}O_2S$: C, 65.53; H, 7.61; S, 13.43. Found: C, 65.40; H, 7.61; S, 13.37.

13-Thia[5.4.3]propella-8,10-diene (18). Reduction of 2.41 g (0.01 mol) of diene sulfone with 3.80 g (0.10 mol) of lithium aluminum hydride in 75 ml of ether (reflux for 36 hr) as described above furnished 1.86 g (89.5%) of **18** after chromatography of the crude product on neutral alumina (activity I): $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.68 (A_2B_2, 4, vinyl), 2.86 (s, 4, $-CH_2S-$), and 1.4–1.8 (br m, 10, methylene).

Generalized Chlorination–Oxidation Procedure. The following procedure exemplifies the general method employed in this study.

A mixture of 11.6 g (0.060 mol) of **9**, 8.0 g (0.06 mol) of NCS, and 150 ml of carbon tetrachloride was refluxed under nitrogen for 1.5 hr. The reaction mixture was cooled and the succinimide was removed by filtration. The carbon tetrachloride was evaporated and the residual oil was dissolved in 50 ml of ether and cooled to 0°. To this magnetically stirred solution was added dropwise a standardized ethereal solution containing 0.12 mol of monoperphthalic acid. The reaction mixture was allowed to stir at ambient temperature for 6 hr. The phthalic acid was removed by filtration and the filtrate was washed with 1 *N* sodium hydroxide solution (two 100-ml portions), water (two 100-ml portions), and saturated sodium chloride solution (one 30-ml portion). The ethereal solution was dried and the solvent was evaporated to give 15 g (97%) of crystalline α-chloro sulfone mixture, mp 105–120°. Integration of the nmr singlets ($CDCl_3$) evident at δ 5.41 and 5.00 (>*CH*Cl proton of the two components) indicated a ratio of 44:56 for the two isomers. Three recrystallizations of the mixture from ligroin increased the melting point to 127–134°.

Anal. Calcd for $C_{12}H_{17}ClO_2S$: C, 55.26; H, 6.57; S, 12.30. Found: C, 55.50; H, 6.60; S, 12.18.

Separation of the mixture into its components was achieved by column chromatography on silica gel and elution with gradually increasing percentages of ether in petroleum ether. The minor isomer **19**, mp 129–131°, was the first substance to be eluted: $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.57–5.78 (m, 2, vinyl), 5.41 (s, 1, >*CH*Cl), 3.40, 3.20, 3.05, 2.83 (AB, J = 13.1 Hz, 2, $-CH_2SO_2-$), 1.3–2.8 (br m, 12, allyl and methylene).

The major isomer **20** was subsequently obtained as white crystals: mp 136–137.5°; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.62–5.75 (m, 2, vinyl), 5.00 (s, 1, >CHCl), 3.72, 3.50, 2.98, 2.77 (AB, J = 13.2 Hz, 2, $-CH_2SO_2-$), and 1.2–2.7 (br m, 12, allyl and methylene).

Chlorination–Oxidation of 13. Reaction of 12.4 g (0.063 mol) of **13** with 8.55 g (0.064 mol) of NCS and subsequent peracid oxidation afforded 15.8 g (97%) of α-chloro sulfone mixture. Integration of the nmr singlets ($CDCl_3$) evident at δ 5.37 and 5.17 (>*CH*Cl proton of the two components) indicated a ratio of 35:65 for the two isomers. Column chromatography on silica gel (30:1 by weight) and elution with 5–10% ether in hexane caused the minor isomer **21** to be eluted first. Recrystallization from ethyl acetate–cyclohexane gave pure **21**: mp 161.5–163°; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.50–6.45 (m, 4, vinyl), 5.37 (s, 1, >*CH*Cl), 3.23 and 3.05 (AB quartet, J_{AB} = 13.5 Hz, 2, $-CH_2SO_2-$), and 1.0–2.1 (m, 8, methylene).

Anal. Calcd for $C_{12}H_{15}ClO_2S$: C, 55.69; H, 5.84; S, 12.39. Found: C, 55.60; H, 5.86; S, 12.30.

The major isomer **22** was obtained as white crystals: mp 115–118° (from ethyl acetate–cyclohexane); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.46–6.37 (m, 4, vinyl), 5.17 (s, 1, >*CH*Cl), 3.20 and 3.53 (AB quartet, J_{AB} = 13.5 Hz, 2, $-CH_2SO_2-$), and 0.8–2.2 (m, 8, methylene).

Anal. Calcd for $C_{12}H_{15}ClO_2S$: C, 55.69; H, 5.84; S, 12.39. Found: C, 55.69; H, 5.86; S, 12.29.

11-Chloro-12-thia[4.4.3]propellane 12,12-Dioxide (23). A solution of α-chloro sulfones **21** and **22** (260 mg, 1 mmol) in 10 ml of ethyl acetate was hydrogenated at atmospheric pressure using three 40-mg portions of Adams' catalyst. The product was chromatographed on silica gel and recrystallized twice from ethyl acetate–cyclohexane to yield an analytical sample: mp 177–178°; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.38 (s, 1, >*CH*Cl), 3.57 and 2.87 (AB quartet, J_{AB} = 13.5 Hz, 2, $-CH_2SO_2-$), and 0.9–2.4 (m, 16, methylene).

Anal. Calcd for $C_{14}H_{19}ClO_2S$: C, 54.84; H, 7.29; S, 12.20. Found: C, 54.92; H, 7.28; S, 12.16.

11-Chloro-12-thia[4.4.3]propella-3,8-diene 12,12-Dioxide (25). From 14.1 g (0.0733 mol) of **14**, 9.8 g (0.0733 mol) of NCS, and 0.147 mol of monoperphthalic acid, there was obtained 15.0 g (79%) of **25**: mp 111–113° (from ether at −20°); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.59 (m, 4, vinyl), 5.05 (s, 1, >*CH*Cl), 3.42, 3.21, 3.11, and 2.89 (AB quartet, J_{AB} = 13 Hz, 2, $-CH_2SO_2-$), and 1.59–2.82 (m, 8, allyl).

Anal. Calcd for $C_{12}H_{15}ClO_2S$: C, 55.70; H, 5.84; Cl, 13.70. Found: C, 55.70; H, 5.72; Cl, 13.90.

11-Chloro-12-thia[4.4.3]propella-2,4,7,9-tetraene 12,12-Dioxide (26). From 5.0 g (0.0265 mol) of **15**, 3.55 g (0.0265 mol) of NCS, and 0.053 mol of monoperphthalic acid, there was obtained 2.9 g (42%) of **26**: mp 151–153° (from benzene); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.14–6.47 (m, 8, vinyl), 5.29 (s, 1, >*CH*Cl), 3.67, 3.45, 3.42, and 3.19 (AB quartet, J_{AB} = 13 Hz, 2, $-CH_2SO_2-$).

Anal. Calcd for $C_{12}H_{11}ClO_2S$: C, 56.58; H, 4.35; Cl, 13.92. Found: C, 56.45; H, 4.33; Cl, 14.14.

Chlorination–Oxidation of 27. Reaction of 1.159 g (5.58 mmol) of **27** with 748 mg (5.58 mmol) of NCS and subsequent peracid (11.16 mmol) oxidation afforded 1.447 g (94%) of α-chloro sulfone mixture as a clear viscous oil. Integration of the nmr singlets ($CDCl_3$) at δ 5.22 and 5.00 (>*CH*Cl proton of the two components) indicated a ratio of 72:28 for the two isomers. Column chromatography on silica gel (30:1 by weight) and elution with hexane–ether (incremental from 0 to 10%) caused the major isomer **28** to be eluted first, mp 94.5–95.5° (from ether); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.57–5.72 (m, 2, vinyl), 5.22 (s, 1, >*CH*Cl), 3.37, 3.15, 2.99, 2.77 (AB quartet, J_{AB} = 13 Hz, 2, $-CH_2SO_2-$), 1.9–2.7 (m, 4, allyl), and 1.70 (br s, 10, methylene).

Anal. Calcd for $C_{13}H_{19}ClO_2S$: C, 56.80; H, 6.97. Found: C, 56.97; H, 6.98.

The less rapidly eluted minor isomer **29** was obtained as white crystals: mp 139.5–140.5° (from ether–chloroform); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.60–5.75 (m, 2, vinyl), 5.00 (s, 1, >*CH*Cl), 3.62, 3.40, 3.02, 2.80 (AB quartet, J_{AB} = 13 Hz, 2, $-CH_2SO_2-$), 2.0–2.7 (m, 4, allyl), and 1.66 (br s, 10, methylene).

Anal. Calcd for $C_{13}H_{19}ClO_2S$: C, 56.80; H, 6.97; S, 11.69. Found: C, 56.78; H, 6.97; S, 12.03.

Chlorination–Oxidation of 18. Reaction of 3.56 g (17.3 mmol) of **18** with 2.32 g (17.3 mmol) of NCS and subsequent *m*-chloroperbenzoic acid oxidation (34.6 mmol) afforded 4.21 g (89.3%) of α-chloro sulfone mixture as a clear viscous oil. Column chromatography on silica gel (30:1 by weight) and elution with hexane–ether (incremental from 0 to 10%) caused the major isomer **30** to be eluted first: mp 97–98° (from ether–petroleum ether); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.48–6.23 (m, 4, vinyl), 5.22 (s, 1, >*CH*Cl), 3.46, 3.24, 3.17, 2.95 (AB quartet, J_{AB} = 13 Hz, 2, $-CH_2SO_2-$), and 1.4–2.2 (br m, 10, methylene).

Anal. Calcd for $C_{13}H_{17}ClO_2S$: C, 57.24; H, 6.28; Cl, 13.00. Found: C, 57.20; H, 6.25; Cl, 13.04.

The minor isomer **31** which was subsequently eluted failed to crystallize and was not examined further.

A 300-mg sample of the crude α-chloro sulfone mixture was catalytically hydrogenated over Adams' catalyst in ethyl acetate solution at atmospheric pressure. Quantitative nmr analysis of the resulting product mixture (304 mg, 96%) revealed the presence of two α-chloro sulfones in the ratio of 65 (δ 5.23) to 35 (δ 5.45). Recrystallization of the solid from ether gave white crystals, mp 124–142°.

Anal. Calcd for $C_{13}H_{21}ClO_2S$: C, 56.40; H, 7.65; Cl, 12.81. Found: C, 56.57; H, 7.53; Cl, 12.59.

Equilibration Procedure. A solution of 100–170 mg of pure α-chloro sulfone isomer, 7.5 ml of 20–25% sodium hydroxide solution, and 20–25 ml of dioxane was heated at reflux for 24 hr. After cooling, water and ether were added, and the organic layer was washed three times with water, dried, and evaporated. A quantitative yield of α-chloro sulfone mixture resulted. Deuteriochloroform solutions of this material were analyzed quantitatively by nmr spectroscopy. The results are summarized in Table II.

Preliminary Crystallographic Examination of 28. Microscopic investigation revealed clear, colorless needles with sharply defined faces. Preliminary Weissenberg and precession photographs exhibited the $2/m$ Laue symmetry appropriate for the monoclinic crystal class. The systematic absences on $0k0$ (for $k = 2n + 1$) and $h0l$ (for $l = 2n + 1$) uniquely determine the space group as $P2_1/c$ (C_{2h}^5). A crystal of approximate dimensions 0.15 × 0.10 × 0.10 mm mounted along b was then transferred to a fully automated Hilger–Watts four-circle diffractometer.

Data Collection. Accurate values were obtained for 12 reflections on the diffractometer. A least-squares fit of cell constants of these θ values gave $a = 7.785 \pm 0.005$, $b = 13.518 \pm 0.003$, $c =$

Table III. Final Fractional Coordinates for Nonhydrogen Atoms of **28**[a]

Atom	x/a	y/b	z/c
S(1)	0.1279 (4)	0.1140 (4)	0.1727 (2)
Cl(1)	0.1469 (4)	0.1829 (3)	0.4035 (2)
O(1)	0.2387 (9)	0.1969 (6)	0.1725 (7)
O(2)	0.1494 (9)	0.0173 (5)	0.1549 (6)
C(7)	−0.2139 (10)	0.1068 (9)	0.1346 (7)
C(6)	−0.2296 (13)	−0.0079 (7)	0.1372 (8)
C(5)	−0.3518 (14)	−0.0554 (9)	0.2092 (9)
C(4)	−0.2679 (16)	−0.0553 (8)	0.3304 (10)
C(3)	−0.2694 (15)	0.0402 (9)	0.3924 (9)
C(2)	−0.2878 (12)	0.1386 (8)	0.3270 (8)
C(1)	−0.1562 (11)	0.1578 (8)	0.2509 (7)
C(11)	−0.1445 (13)	0.2722 (8)	0.2328 (8)
C(10)	−0.2971 (16)	0.3121 (9)	0.1531 (9)
C(9)	−0.3980 (13)	0.2607 (9)	0.0795 (9)
C(8)	−0.3843 (12)	0.1486 (8)	0.0685 (8)
C(13)	−0.0665 (11)	0.1299 (8)	0.0737 (7)
C(12)	0.0227 (11)	0.1170 (8)	0.2942 (7)

[a] Estimated standard deviations, shown in parentheses, are right adjusted to the least significant digit of the preceding number.

Table IV. Final Anisotropic Thermal Parameters for Nonhydrogen Atoms of **28**[a,b]

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^3\beta_{23}$
S(1)	107 (4)	81 (2)	65 (2)	5 (2)	38 (2)	7 (2)
Cl(1)	206 (6)	136 (3)	61 (2)	−12 (3)	−29 (3)	−14 (2)
O(1)	169 (14)	110 (6)	110 (7)	−25 (8)	53 (9)	12 (6)
O(2)	212 (15)	79 (5)	81 (6)	18 (7)	43 (8)	−5 (4)
C(7)	87 (14)	89 (8)	40 (6)	7 (9)	31 (7)	−8 (6)
C(6)	187 (20)	68 (7)	58 (8)	−15 (10)	35 (11)	−8 (6)
C(5)	195 (21)	110 (10)	67 (9)	−42 (12)	46 (11)	−3 (8)
C(4)	308 (28)	63 (7)	77 (9)	−8 (12)	37 (13)	16 (8)
C(3)	264 (26)	86 (9)	66 (9)	2 (13)	67 (12)	9 (7)
C(2)	152 (18)	87 (8)	57 (7)	0 (10)	54 (9)	−1 (7)
C(1)	116 (16)	92 (8)	32 (6)	2 (9)	25 (8)	10 (6)
C(11)	182 (19)	65 (7)	60 (8)	−9 (10)	23 (11)	−4 (6)
C(10)	256 (27)	92 (9)	80 (10)	44 (14)	83 (15)	17 (8)
C(9)	176 (20)	98 (10)	51 (8)	19 (12)	21 (10)	−3 (8)
C(8)	134 (18)	95 (9)	59 (8)	8 (10)	13 (9)	5 (7)
C(13)	89 (14)	106 (9)	48 (7)	−8 (10)	29 (8)	0 (6)
C(12)	151 (18)	109 (9)	42 (6)	0 (11)	27 (9)	−7 (7)

[a] Estimated standard deviations are shown in parentheses. [b] The form of the anisotropic temperature factor expression is $[-(\beta_{11}h^2 + \beta_{22}k + \beta_{33}l + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table V. Selected Bond Distances in **28**[a]

Atoms	Distance, Å	Atoms	Distance, Å
S(1)-O(1)	1.42	C(2)-C(3)	1.54
S(1)-O(2)	1.43	C(3)-C(4)	1.51
S(1)-C(12)	1.82	C(4)-C(5)	1.50
S(1)-C(13)	1.75	C(5)-C(6)	1.55
Cl(1)-C(12)	1.73	C(6)-C(7)	1.55
C(1)-C(2)	1.53	C(7)-C(8)	1.52
C(1)-C(7)	1.56	C(7)-C(13)	1.51
C(1)-C(11)	1.57	C(8)-C(9)	1.52
C(1)-C(12)	1.50	C(9)-C(10)	1.33
		C(10)-C(11)	1.50

[a] The average estimated standard deviation calculated from the inverse matrix of least-squares refinement is 0.02 Å.

12.151 ± 0.003 Å, and β = 101.15 ± 0.05°. The calculated density is 1.45 g/cm^3 for $Z = 4$, indicating one molecule per asymmetric unit.

Data were collected at room temperature with Nb-filtered Mo Kα (0.7107 Å) radiation. Within a θ sphere of 25°, all data in the hkl and $\bar{h}kl$ octants were collected using a stationary crystal-stationary counter technique. Intensities were measured by counting at the peak center (θ_{hkl}) for 10 sec and subtracting two 5-sec backgrounds measured at $\theta_{hkl} \pm [(0.25 + 0.01)\theta_{hkl}]$. As a general check on crystal and electronic stability the intensities of three judiciously chosen reflections were periodically monitored. No appreciable instability could be detected in this manner. The intensity data were corrected for Lorentz and polarization factors and converted to scan data by the method of Alexander and Smith.[24]

Since the absorption coefficient is only 4.49 cm^{-1} for Mo Kα radiation no correction for this effect was deemed necessary. The intensities were submitted to a 3σ test and symmetry equivalent reflections were averaged to yield the 1381 independent F_o^2 used in refinement.

Solution and Refinement. A sharpened three-dimensional Patterson synthesis computed from the 1381 F_o^2 revealed the Cl and S positions. A three-dimensional electron density synthesis using the S and Cl phases readily revealed the 15 remaining nonhydrogen atoms. Full-matrix least-squares refinements with anisotropic temperature factors for all atoms and the scattering factor tables of Hanson, *et al.*,[25] (154 parameters) converged rapidly to a conventional discrepancy index, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, of 0.094 and a weighted discrepancy index, $wR = \Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2$, of 0.115. A final electron density difference map revealed no peaks larger than 0.5 e Å^{-3}. At this stage the structural analysis was judged correct and complete. Final atomic positional parameters are given in Table III. Final thermal parameters are given in Table IV. Selected bond distances and angles are given in Tables V and VI.

Table VI. Selected Bond Angles in **28**[a]

Atoms	Angle, deg	Atoms	Angle, deg
O(1)-S(1)-O(2)	133	C(2)-C(3)-C(4)	120
C(12)-S(1)-C(13)	95	C(3)-C(4)-C(5)	117
O(1)-S(1)-C(12)	111	C(4)-C(5)-C(6)	111
O(1)-S(1)-C(13)	110	C(5)-C(6)-C(7)	119
O(2)-S(1)-C(12)	105	C(1)-C(7)-C(6)	116
O(2)-S(1)-C(13)	97	C(1)-C(7)-C(8)	112
C(2)-C(1)-C(7)	111	C(1)-C(7)-C(13)	104
C(2)-C(1)-C(11)	108	C(6)-C(7)-C(8)	108
C(2)-C(1)-C(12)	114	C(6)-C(7)-C(13)	106
C(7)-C(1)-C(11)	109	C(8)-C(7)-C(13)	109
C(7)-C(1)-C(12)	104	C(7)-C(8)-C(9)	113
C(11)-C(1)-C(12)	110	C(8)-C(9)-C(10)	124
C(1)-C(2)-C(3)	117	C(9)-C(10)-C(11)	124
		C(10)-C(11)-C(1)	111

[a] The average estimated standard deviation calculated from the inverse matrix of least-squares refinement is 1.5°.

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α-Halo Sulfones. XVIII. The Ramberg–Bäcklund Rearrangement as a Synthetic Entry to Unsaturated Propellanes[1]

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Abstract: Several polyunsaturated propellanes have been synthesized. Ramberg–Bäcklund rearrangement of α-chloro sulfone **1** with potassium *tert*-butoxide in dry tetrahydrofuran affords [4.4.2]propella-3,8,11-triene (**3**) in good yield. The advantages of this approach to **3** relative to an alternative route involving at the key stage the trimethyl phosphite induced decomposition of a *cis*-thiocarbonate ester are discussed. The route to [4.4.2]propella-2,4,11-triene (**17**) consists in initial rearrangement of **14** to diene **16**, followed by allylic bromination and dehydrobromination. This triene is shown to be thermally stable and not to exhibit valence isomerism to the disubstituted cyclooctatetraene **18**. In contrast, triene **24** prepared by similar treatment of **23** displays properties uniquely consistent with tetraene formulation **25**. Lengthening of the polymethylene bridge to five units clearly results in the capability to arrive at a relatively strain-free bridged cyclooctatetraene derivative. Last, the synthesis and properties of [4.4.2]propella-2,4,7,9-11-pentaene (**28**) are discussed. It is concluded from the spectral parameters exhibited by **28** that the molecule is decidedly polyolefinic. That is to say, orbital overlap of the ten π electrons in the unusual fashion demanded by the geometry of **28** results in little or no enhancement of thermodynamic stabilization.

In the preceding paper, we have described the preparation of a number of α-chloro sulfones of the propellane type, *i.e.*, tricyclic structures in which the three rings are conjoined in a carbon–carbon single bond. We now report the utilization of such molecules in the synthesis of unsaturated propellanes containing one cyclobutene ring.

This study began several years ago with the intention of probing more deeply into the relationships which exist between π-electronic interaction and the presence or absence of thermodynamic stabilization. During the past decade, an awareness has developed that stabilization is a function not only of the geometry of orbital overlap, but also of the sum and distribution of π electrons. For example, whereas alignment of the terminal p orbitals of hexatriene within orbital overlap as in benzene produces aromatic stabilization, similar arrangement of the p orbitals of butadiene as in cyclobutadiene results in loss of delocalization energy.[4] Placement of three ethylenic moieties in a cylindrical array as in barrelene results in no obvious delocalization;[5] in contrast, the bicycloheptadien-7-yl cation is decidedly stabilized and bicycloaromatic.[6]

Consequently, there was considerable interest in achieving syntheses of a variety of unsaturated propellanes. Specifically, the fixed three-dimensional nature of such polyenes readily allows for unique orthogonal (or nearly orthogonal) p orbital interactions along the top surface of the hydrocarbons. In addition to the question of electronic interaction, we were also interested in the possible valence isomerization of **17**, **24**, and **28**. This aspect of the study is discussed in the individual sections which follow.

[4.4.2]Propella-3,8,11-triene.[7] For reasons of readier accessibility and the inherent symmetry of **3**, the behavior of α-chloro sulfone **1** was studied first. When **1** was subjected to the customary conditions of the Ramberg–Bäcklund rearrangement,[8] *i.e.*, *ca.* 2 *N* sodium hydroxide in refluxing aqueous dioxane, and heated for extended periods of time (up to 4 days), the α-chloro sulfone was recovered quantitatively. The generation of α-sulfonyl carbanions under these conditions was established unequivocally by conducting the reaction in deuterium oxide (with NaOD) for 40 hr; trideuterated chloro sulfone **2** was obtained in high yield. In contrast, treatment of **1** with powdered potassium *tert*-butoxide in anhydrous tetrahydrofuran at 0° resulted in ready conversion to **3** in 53% yield (Scheme I). It was now apparent that both base and solvent play central roles in the practical aspects of the α-halo sulfone rearrangement. The inertness of **1** to the aque-

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