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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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(1) For paper XVII, see L. A. Paquette, R. E. Wingard, Jr., J. C. Philips, G. L. Thompson, L. K. Read, and J. Clardy, *J. Amer. Chem. Soc.*, **93**, 4508 (1971).

(2) National Institutes of Health Predoctoral Fellow, 1966–1968.

(3) University Fellow, 1968–1969; National Institutes of Health Predoctoral Fellow, 1969–1971.

(4) M. J. S. Dewar and G. J. Gleicher, *J. Amer. Chem. Soc.*, 87, 3255 (1965).

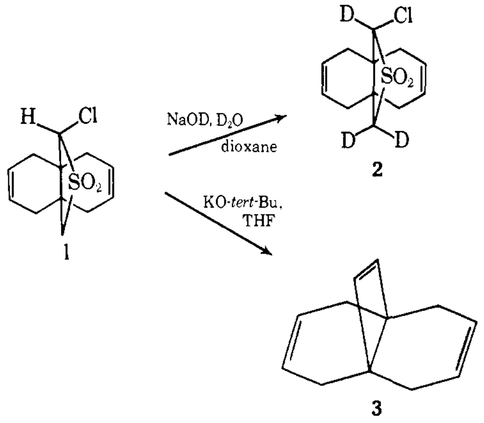
(5) H. E. Zimmerman, G. L. Grunewald, R. M. Paufler, and M. A. Sherwin, *ibid.*, **91**, 2330 (1969); H. E. Zimmerman and R. M. Paufler, *ibid.*, 82, 1514 (1960).

(6) M. J. Goldstein, *ibid.*, 89, 6357 (1967).

(7) For a preliminary report, see L. A. Paquette and J. C. Philips, *Tetrahedron Lett.*, 4645 (1967).

(8) (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).

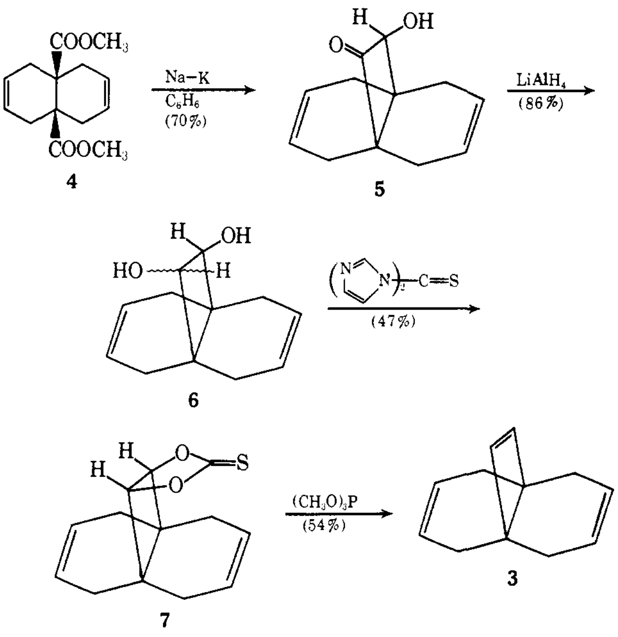
Scheme I



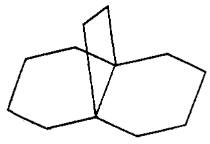
ous dioxane conditions may be attributed to the fact that strong aqueous solvation of the carbanionic centers prevents the attainment of a geometry favorable to the requisite intramolecular SN2 process.[8] As shown in the preceding paper, the aqueous hydroxide–dioxane medium is effective in equilibrating the α-chloro substituent in unsymmetrical analogs of **1**. However, for the purpose of synthesizing cyclobutene rings, the increased basicity and anhydrous solvent system were shown to be mandatory and were employed in the subsequent work.[9]

The overall yield of **3** from readily available starting materials was 41%. At this point, it was deemed of interest to compare the efficiency of the α-chloro sulfone approach with a reasonable alternative route. To this end, triene **3** was also prepared by means of the sequence shown in Scheme II. Acyloin **5** was available from the reaction of diester **4** with 1:1 sodium–potassium alloy according to the procedure of Bloomfield and Irelan.[10] Lithium aluminum hydride reduction of **5** afforded a mixture of cis and trans 1,2-diols which without purification was treated with *N*,*N*-thiocarbonyldiimidazole.[11] The cis diol was thereby readily transformed (47% yield) to *cis*-thiocarbonate ester **7**. When a solution of **7** in trimethyl phosphite was refluxed for 96 hr,[12] the desired hydrocarbon (**3**) was obtained in 54% yield and a high state of purity after one distillation. Nevertheless, the tedious nature of the conversion of **4** to **5**, together with the overall low yield (15%), augured well for the more convenient α-chloro sulfone route.

Scheme II



The mass spectrum of **3** exhibits a molecular ion peak (*m/e* 158) and a base peak (*m/e* 104) corresponding to loss of a neutral butadiene fragment. The structural assignment follows also from its nmr spectrum which displays multiplets at δ 5.75 (6 H) and 2.02 (8 H) for the vinyl and allylic protons, respectively, and catalytic hydrogenation at atmospheric pressure to the known saturated propellane **8**.



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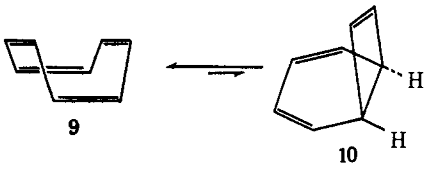
[4.4.2]Propella-2,4,11-triene.[13] Previous studies of the valence tautomerization of cyclooctatetraene (**9**) have revealed that, although it is not possible to detect the presence of bicyclo[4.2.0]octatriene **10** by spectroscopic techniques, (4 + 2)π cycloaddition reactions of **9** proceed by kinetic control and involve exclusively **10**.[14] Extrapolation from dilatometric rate data for such cycloadditions indicates that cyclooctatetraene exists in equilibrium with 0.01% of **10** at 100°.[15]



Several attempts to prepare **10** have been reported. Three groups have noted that unsensitized irradiation of **9** results in formation of an unstable photoproduct with ultraviolet absorption in the 281–282-nm region.[16] This photoproduct was assumed to be **10**, since hydrogenation of solutions containing this substance resulted in formation of cyclooctane and bicyclo[4.2.0]octane.[17] The most successful route to **10** has been that based

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[9] Take note, however, of later difficulties encountered with this base–solvent system as the overall size of the thiapropellane is decreased: L. A. Paquette and R. W. Houser, *J. Amer. Chem. Soc.*, **93**, 4522 (1971).

[10] J. J. Bloomfield and J. R. S. Irelan, *J. Org. Chem.*, 31, 2017 (1966).

[11] H. A. Staab and J. Walther, *Justus Liebigs Ann. Chem.*, **657**, 98 (1962).

[12] E. J. Corey and R. A. E. Winter, *J. Amer. Chem. Soc.*, **85**, 2677 (1963); E. J. Corey, F. A. Carey, and R. A. E. Winter, *ibid.*, **87**, 934 (1965).

[13] A preliminary communication of these results has appeared: L. A. Paquette and J. C. Philips, *Chem. Commun.*, 680 (1969).

[14] For a review of cyclooctatetraene chemistry, consult G. Schröder, "Cyclooctatetraen," Verlag Chemie, Weinheim/Bergstr., Germany, 1965.

[15] R. Huisgen and F. Mietzsch, *Angew. Chem.*, **76**, 36 (1964); *Angew. Chem., Int. Ed. Engl.*, **3**, 83 (1964).

[16] (a) E. Migirdicyan and S. Leach, *Bull. Soc. Chim. Belges*, **71**, 845 (1962); (b) G. J. Fonken, *Chem. Ind. (London)*, 1625 (1963); (c) E. H. White, E. W. Friend, Jr., R. L. Stern, and H. Maskill, *J. Amer. Chem. Soc.*, **91**, 523 (1969).

[17] More recently, low-temperature, acetone-sensitized irradiation of cyclooctatetraene has been observed to result in the reversible formation of semibullvalene: H. E. Zimmerman and H. Iwamura, *ibid.*, **92**, 2015 (1970).

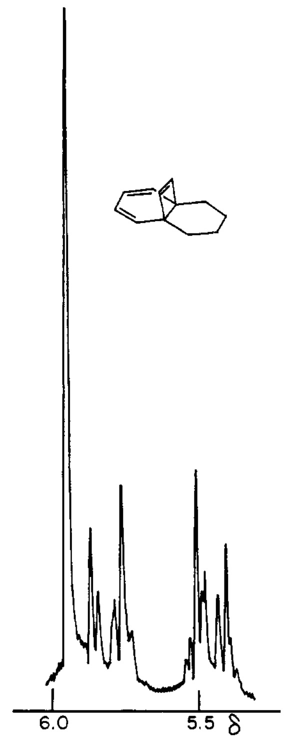
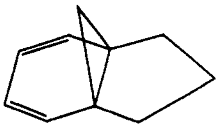


Figure 1. The partial 100-MHz nmr spectrum of [4.4.2]propella-2,4,11-triene.

on the debromination of cyclooctatetraene dibromide.[18] However, only impure samples of **10** [uv maxima at 273 (ϵ 3100) and 277 nm (ϵ 3000)] were obtained because of the extreme thermal instability of the triene relative to **9**.

The intriguing possibility presented itself of utilizing a tetramethylene bridge in **10** (*cf.* **17**) to guarantee the absence of valence tautomerism to a cyclooctatetraene derivative for reasons of steric strain. Vogel has demonstrated that the result of bridging a cycloheptatriene ring by a trimethylene chain at the 1 and 6 positions was to impose sufficient strain to restrict the molecule to its valence tautomeric norcaradiene form (**11**).[19] Complete reversal in favor of the triene **12** was noted when the chain was lengthened to four methylene groups.[20] Annelation by a four-carbon bridge in the present instance was deemed adequate since models indicated that the unsaturated diatomic bridge represented by the cyclobutene ring causes a "pinching effect" on C-1 and C-6 greatly exceeding that produced by a methylene group. Furthermore, azapropellene **13** had already been shown to exist exclusively as the azabicyclooctatriene.[21]



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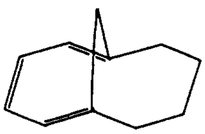

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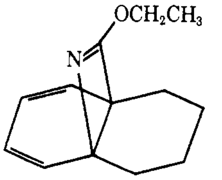
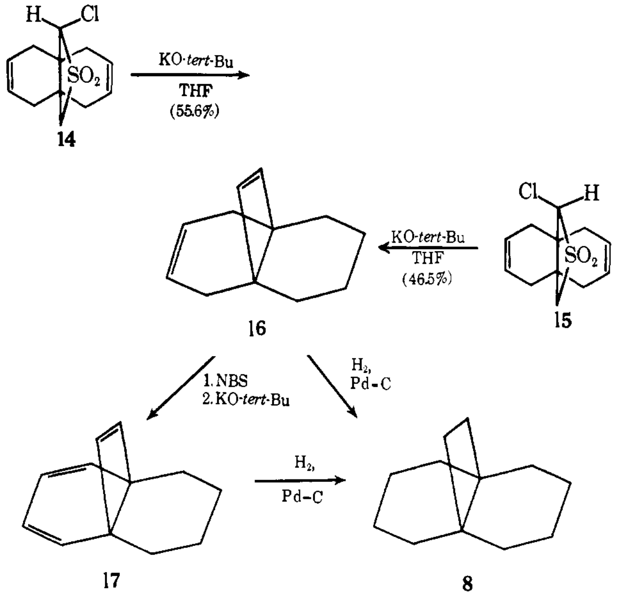


13

For reasons discussed elsewhere,[22] the sequence in which the cyclobutene and cyclohexadiene units were to be introduced necessitated the synthesis of diene **16** and subsequent allylic bromination–dehydrobromination to give **17**. Ramberg-Bäcklund rearrangement of **14** and **15** with powdered potassium *tert*-butoxide in tetrahydrofuran at ambient temperatures led to the formation of [4.4.2]propella-3,11,diene (**16**, 55.6 and 46.5%, respectively, Scheme III). Clearly, the success of the cyclobutene-forming step is independent of the configuration of the α-chloro sulfone. The yields in each case are easily duplicated, but it is not clear if the 9% discrepancy which is consistently observed is directly related to the initial chlorine stereochemistry. The nmr spectrum of **16** ($CDCl_3$) displays the expected signals for the cyclobutene and vinyl protons at δ 5.90 (s, 2 H) and 5.75 (m, 2 H), respectively, in addition to the broad multiplets attributable to the allylic (δ 1.87, 4 H) and saturated methylene protons (δ 1.57, 8 H). The hydrocarbon was found to give a parent ion of *m/e* 160 in the mass spectrum and to undergo facile reduction to **8**.

Scheme III



When a purified sample of **16** was treated with slightly more than 1 equiv of *N*-bromosuccinimide in refluxing carbon tetrachloride solution, followed by direct dehydrobromination of the crude allylic bromide with potassium *tert*-butoxide in anhydrous tetrahydrofuran at 25°, the desired triene (**17**) was readily obtained after preparative scale vpc separation from unchanged **16**. The mass spectrum of the product gave ready evidence that the molecular ion was at *m/e* 158. The 100-MHz nmr spectrum (Figure 1) showed the expected A_2B_2 pattern for the cyclohexadiene protons with an overlapping singlet for the two cyclobutene protons. The ring methylene protons appear as a broadened singlet at high field (δ 1.54). Triene **17** exhibited an ultraviolet maximum (in isooctane) at 268 nm (ϵ 2400) and a slight inflection at 276 nm (ϵ 2100). Again

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(18) E. Vogel, H. Kiefer, and W. R. Roth, *Angew. Chem.*, **76**, 432 (1964); *Angew. Chem., Int. Ed. Engl.*, **3**, 442 (1964).

(19) E. Vogel, W. Wiedemann, H. Kiefer, and W. F. Harrison, *Tetrahedron Lett.*, 673 (1963).

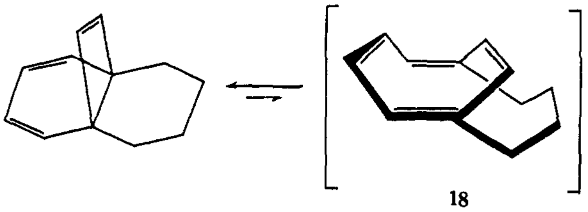
(20) E. Vogel, W. Maier, and J. Eimer, *ibid.*, 655 (1966).

(21) (a) L. A. Paquette and J. C. Philips, *J. Amer.. Chem. Soc.*, **90**, 3898 (1968); (b) L. A. Paquette, T. Kakihana, J. F. Hansen, and J. C. Philips, *ibid.*, **93**, 152 (1971).

(22) L. A. Paquette, R. E. Wingard, Jr., and R. H. Meisinger, *ibid.*, **93**, 1047 (1971).

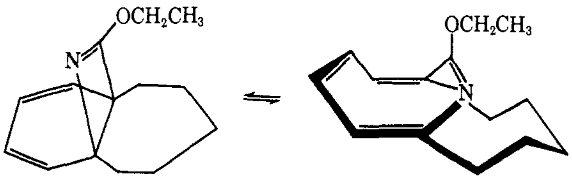
in this instance, the structural assignment was confirmed by catalytic hydrogenation to **8**.

The nmr spectrum of annellated bicyclooctatriene **17** is temperature independent from +40 to +165°. The triene was heated at 165° for 30 min, and its nmr spectrum at this temperature gave no indication of thermal decomposition or valence bond tautomerization to the disubstituted cyclooctatetraene **18**. Consequently, **17** represents the first thermally stable bicyclo[4.2.0]octatriene system. Orbital symmetry considerations are in complete agreement with the observed reluctance of **17** to undergo thermal fragmentation. Thus, if valence isomerization of the triene is precluded as it evidently is in **17**, the concerted thermal fragmentation reaction with loss of acetylene is required to be a $[_{\sigma}2_s + {}_{\sigma}2_a]$ process. However, not one of the four carbon atoms which must rehybridize if cyclobutene ring rupture were to commence can adopt an antarafacial mode. In the potential acetylene fragment, inversion is inhibited because of the existing double bond, while a trans double bond in the tetralin moiety can obviously not be tolerated. By way of contrast, the concerted photochemical decomposition of **17** necessitates a $[_{\sigma}2_s + {}_{\sigma}2_s]$ fragmentation pathway, a symmetry requirement easily accommodated by this structure. Not unexpectedly, therefore, irradiation of ether solutions of **17** at 25° with 2537-Å light results in the rapid formation of tetralin and acetylene.[13,23]

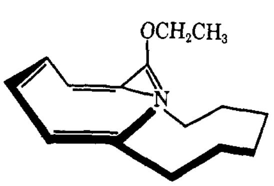


18

Bicyclo[5.4.2]trideca-7,9,11,12-tetraene. The demonstrated inability of **17** to isomerize to **18** prompted an examination of the valence tautomeric properties of the homologous triene **24**. At issue was the matter of the relationship of I strain engendered by the methylene bridge to the valence tautomeric capabilities of the polyene. In the azapropellatriene series recently studied in this laboratory, it was found that lengthening of the bridge to five methylene units as in **19** resulted in maintenance of essentially complete bias in favor of the 1-azetine structure at ambient temperatures.[21] However, contrary to the behavior of **13**, **19** exhibits a temperature-dependent nmr spectrum, particularly evident in the 100–150° region. Such changes have been shown to denote displacement of the azabicyclooctatriene–azocine equilibrium in favor of **20** at the elevated temperatures.[21] An additional experimental finding was that extension of the annellating chain to six carbon atoms in the aza series gave rise to an essentially strain-free molecule characterized as tetraene **21**.



19 **20**



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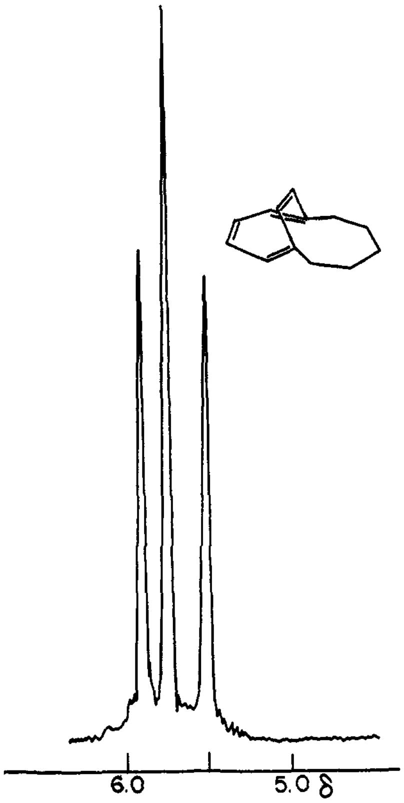
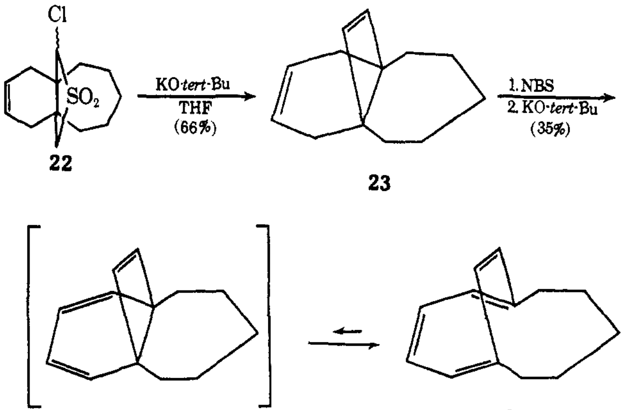


Figure 2. The partial 100-MHz nmr spectrum of bicyclo[5.4.2]trideca-7,9,11,13-tetracene (**25**).

The synthesis of **25** was conveniently achieved by the Ramberg–Bäcklund rearrangement of **22** (as a mixture of the two isomers) and subsequent allylic bromination–dehydrobromination of diene **23** (Scheme IV). The resulting hydrocarbon differed substantially from **17** in its spectral properties. For example, its ultraviolet spectrum in isooctane solution displayed a shoulder at 250 nm (ε 865) on the fringe of intense end absorption. In particular, the nmr spectrum in

Scheme IV



22 **23** **24** **25**

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(23) Full details of the chemical reactions of 17 will be reported separately.

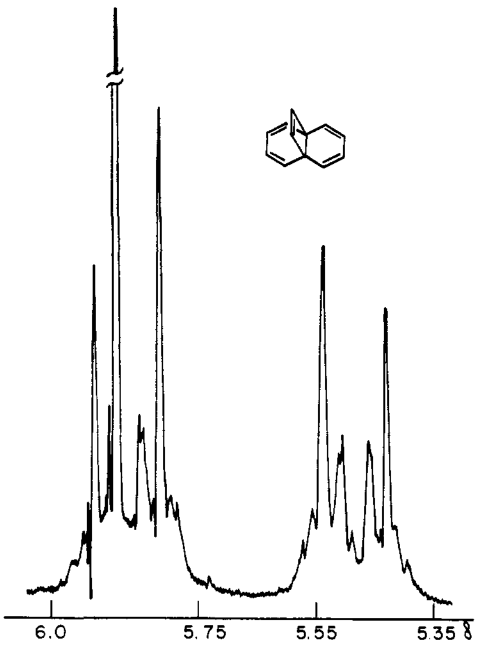
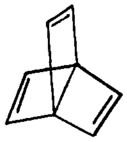


Figure 3. The 100-MHz nmr spectrum of [4.4.2]propella-2,4,7,9,11-pentaene (**28**).

$CDCl_3$ (Figure 2) proved conclusive for tetraene formulation **25**. At 100 MHz, the six vinyl protons appear as three singlets each of area 2 at δ 5.90, 5.74, and 5.52. Assignment of the δ 5.74 peak to H-12 and H-13 is founded principally on the fact that it is the sharpest peak in the spectrum. A four-proton multiplet centered at δ 2.0 indicates the presence of allylic hydrogens; a similar absorption is not seen in the spectrum of **17**. Last, the remaining six methylene protons are seen as a broad envelope at δ 1.2. The nmr spectrum of **25** was temperature invariant from −80 to +40°.

Thus, the reaction course followed in the allylic bromination–dehydrobromination of **23** was initial formation of triene **24**, followed by essentially irreversible valence bond isomerization to tetraene **25**. The differing effects produced by the diatomic bridges in **19** and **24** are not clearly understood at this time. Possibly, the internal bond angles in a 1-azetine are somewhat less than those in cyclobutenes as a result of the hybridization state of the nitrogen atom. Implicit in this reasoning is the assumption that angle strain is the major contributing influence to the position of equilibrium. This need not necessarily be the case; however, definitive data on such possible alternative contributing influences as inductive and resonance effects in the isomeric possibilities still have not been evaluated for their importance. Whatever the underlying causative factors, a chain of five methylene units is seen to permit the attainment of a uniform bridged cyclooctatetraene tautomer. A comparative study of the chemical properties of **17** and **25** is presently being actively pursued.

[4.4.2]Propella-2,4,7,9,11-pentaene.[24] Among the various possible fully unsaturated propellanes, polyenes **26–29** certainly occupy a particularly intriguing position. In the case of **28**, a major portion of the interest derives from the inherent geometry of the system which makes possible a novel type of 10-electron π–π interaction involving the upper lobes of the cyclohexadiene π orbitals and both lobes of the cyclobutene double bond and the possibility of valence isomerization to cyclodecapentaene **30**.



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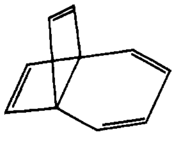

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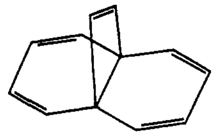

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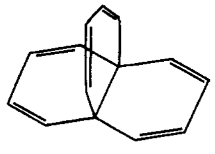

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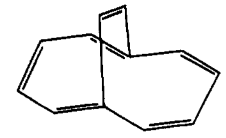

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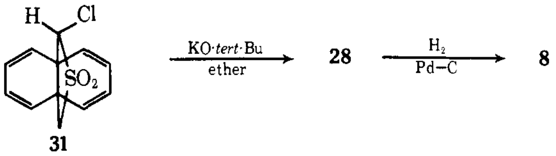
Initially, the action of 2 equiv of *N*-bromosuccinimide on triene **3**, followed by potassium *tert*-butoxide promoted dehydrobromination, was examined as a synthetic approach to **28.** However, complex mixtures of products were invariably generated. Consequently, an alternative route, involving introduction of the cyclobutene ring in the final step, was attempted. To this end, treatment of α-chloro sulfone **31** with potassium *tert*-butoxide in ether resulted in the formation of a new hydrocarbon which was purified by preparative scale vpc (120°) and isolated in 14% yield. Assignment of structure **28** to this substance was based on its nmr spectrum (Figure 3) which exhibits only vinyl absorption including the expected cyclobutene singlet at δ 5.90. The mass spectrum showed a molecular ion peak at *m/e* 154.0776 (calcd *m/e* 154.0782). Hydrogenation of **28** proceeded with the constant uptake of 5 equiv of hydrogen and formation of [4.4.2]propellane **8**.



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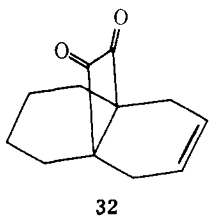
The ultraviolet spectrum of **28** in isooctane displayed two maxima at 247 (ε 2500) and 290 nm (ε 2100). These spectral properties compare favorably with those of related cyclohexadienes and support the conclusion that **28** is polyolefinic in nature. It is interesting to note, however, that the 290-nm band of **28** represents the longest wavelength absorption yet reported for a cyclohexadiene system. Since the 1,2-cyclobutanediones **32** and **33** exhibit more dramatic shifts to longer



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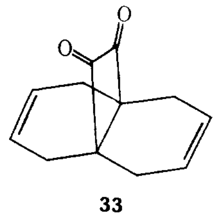

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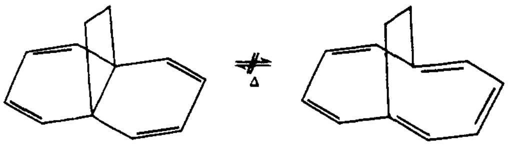
[24] These data were originally communicated in L. A. Paquette and J. C. Philips, *J. Amer. Chem. Soc.*, 91, 3973 (1969).

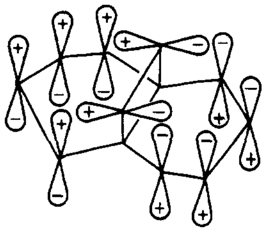
wavelengths because of enhanced stabilization of the excited state by interaction of the dione system with the double bond(s),[25] it is quite possible that the structural elements in **28** are not sufficiently sensitive probes for orthogonal overlap. This point remains to be resolved.

Pentaene **28** exhibits appreciable thermal stability, but no tendency for valence isomerization to **30**. These observations are in agreement with the properties of **34** studied independently by Vogel[20] and Bloomfield.[26] Evidently, a two-carbon bridge spanning the 1,6 positions of a cyclodecapentaene system results in torsional strain sufficient to preclude planarity and thereby cause the molecule to exist exclusively as the propellane tautomer.



34 **35**

In light of the properties of **28**, it would appear that orbital overlap of ten π electrons in the unusual fashion demanded by the geometry of this hydrocarbon results in little or no enhancement of thermodynamic stabilization. It is quite possible that **28** is subject to some electron delocalization, but without the usually attendant delocalization energy, because of the sign discontinuity encountered by the p orbitals on the underside of the polyene (*cf.* **36**).



36

The relatively ready availability of **28** now makes possible the opportunity to examine its chemical reactivity in detail, a study which we hope to report on at a later date.

Experimental Section

Deuterium Exchange of 11-Chloro-12-thia[4.4.3]propella-3,8-diene 12,12-Dioxide (1). To a magnetically stirred solution of 1.0 g (3.86 mmol) of **1**[1] in 30 ml of dioxane was added 10 ml of 10% sodium deuterioxide in D_2O. The reaction mixture was refluxed for 20 hr, cooled to room temperature, and treated with 50 ml of benzene. The organic layer was separated and washed with deuterium oxide (4 × 2 ml). The solvent was evaporated and the crystalline residue was recycled in the above fashion. The latter benzene solution was dried and evaporated to give 790 mg (78%) of **2**, mp 106–108° (from benzene). The nmr spectrum of this material lacked the singlet peak at δ 5.05 and the AB quartet in the δ 3.15 region due to the α-sulfonyl protons in **1**.

Anal. Calcd for $C_{12}H_{12}D_3ClO_2S$: D (atom % excess), 20.0. Found: D, 19.45.[27]

[4.4.2]Propella-3,8,11-triene (3). To an ice cold, magnetically stirred solution of 4.64 g (0.0179 mol) of **1**[1] in 50 ml of anhydrous tetrahydrofuran was added 6.0 g (0.0537 mol) of powdered potassium *tert*-butoxide in one portion. The reaction mixture was stirred magnetically for 5 hr at 0° under a nitrogen atmosphere. A mixture of 40 ml of water and 30 ml of ether was added to the reaction mixture. The organic layer was separated, washed with water (two 20-ml portions), and dried. Concentration of the filtrate and short-path distillation of the residue afforded 1.51 g (53%) of **3** as a colorless oil: bp 75° (5 mm); $\nu_{\max}^{\text{neat}}$ 3003, 2875, 2793, and 1645 cm^{-1}.

Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 90.76; H, 8.93.

[4.4.2]Propella-3,8-diene-10,11-diol (6) and Thionocarbonate Ester 7. To a stirred mixture of 760 mg (0.02 mol) of lithium aluminum hydride in 50 ml of anhydrous ether was added dropwise a solution of 2.13 g (0.011 mol) of **5**[10] in 50 ml of the same solvent. The reaction mixture was refluxed for 1 hr and allowed to stir overnight at room temperature. After an alkaline work-up,[1] the resulting ethereal solution was decanted from the magnesium salts and filtered through anhydrous magnesium sulfate. Concentration of the filtrate gave 1.8 g (86%) of **6** as a white solid, mp 66–70°, which was converted directly to thionocarbonate ester.

A magnetically stirred solution containing 6.0 g (0.031 mol) of **6**, 6.1 g (0.034 mol) of *N*,*N*-thiocarbonyldiimidazole,[11] and 150 ml of toluene was refluxed under nitrogen for 40 min. The solvent was evaporated and the residue was triturated with methanol. Filtration gave 3.45 g (48%) of tan crystals. Three recrystallizations from methanol afforded analytically pure **7**: mp 122.5–123.5°; $\nu_{\max}^{CHCl_3}$ 1302, 1290, and 1000 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 5.97 (m, 4, vinyl), 4.62 (s, 2, >C*H*–O–), and 1.38–2.65 (m, 8, allyl).

Anal. Calcd for $C_{13}H_{14}O_2S$: C, 66.64; H, 6.02; S, 13.69. Found: C, 66.24; H, 6.03; S, 13.53.

[4.4.2]Propella-3,8,11-triene (3) from 7. A magnetically stirred solution of 6.0 g (0.026 mol) of **7** in 45 ml of trimethyl phosphite was refluxed for 96 hr under nitrogen. After cooling in an ice bath, the reaction mixture was diluted with ether (500 ml) and 2 *N* sodium hydroxide (200 ml) was added dropwise. The mixture was allowed to warm to room temperature with continued stirring during 6 hr. The organic layer was separated, and the aqueous layer was extracted twice with ether. The combined extracts were washed with water, dried, and evaporated. Distillation of the residual oil in a short-path apparatus afforded 2.2 g (54%) of **3** as a colorless oil, bp 70° (5 mm), identical in all respects with the triene prepared from α-chloro sulfone **1**.

Hydrogenation of 3. A solution of 131 mg (0.83 mmol) of **3** in 15 ml of methanol was hydrogenated at atmospheric pressure over 10% palladium on carbon until the uptake of hydrogen ceased (3 equiv was consumed). The catalyst was removed by filtration and the solvent was evaporated. Final purification by preparative scale vpc (5 ft × 0.25 in. column packed with 10% SF 96 on 60–80 Chromosorb G) yielded 90 mg (66%) of propellane **8** which was identified by its characteristic ir and nmr spectra.[20,26,28]

[4.4.2]Propella-3,11-diene (16). A. From α-Chloro Sulfone 14. The following procedure was utilized for both **14** and **15**. Potassium *tert*-butoxide (5 equiv) was added slowly under nitrogen to an ice cold, magnetically stirred solution of α-chloro sulfone in dry tetrahydrofuran. The mixture was allowed to stir at ambient temperature for 4 hr, at which point water and ether (1:1) were added and the organic layer was washed with water, dried, and evaporated at atmospheric pressure (distillation through a 6-in. packed Vigreux column). The product was adsorbed on a short, dry-packed silica gel column and eluted with hexane. A known weight of cyclodecane was added and the amount of **16** present was determined from corrected vpc response times.

From 250 mg of **14**, there was obtained 85 mg of **16** as a colorless oil: bp 100–102° (30 mm);[29] $\nu_{\max}^{\text{neat}}$ 3003, 2890, 766, and 677 cm^{-1}.

Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 90.01; H, 10.07.

B. From α-Chloro Sulfone 15. From 99 mg of **15** under totally analogous conditions, there was produced 28.3 mg (46.5%) of **16**.

Hydrogenation of 16. Hydrogenation of a solution of 276 mg (1.72 mol) of **16** in 15 ml of methanol at atmospheric pressure in the predescribed fashion yielded 180 mg (64%) of **8** after preparative scale vpc.

[4.4.2]Propella-2,4,11-triene (17). A magnetically stirred mixture of 600 mg (3.74 mmol) of **16**, 0.8 g (4.50 mmol) of *N*-bromo-

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[25] J. J. Bloomfield and R. E. Moser, *J. Amer. Chem. Soc.*, **90**, 5625 (1968).

[26] J. J. Bloomfield and J. R. S. Irelan, *Tetrahedron Lett.*, 2971 (1966).

[27] The combustion deuterium analysis (falling drop method) was performed by Josef Nemeth, Urbana, Ill.

[28] J. Altman, E. Babad, J. Itzchaki, and D. Ginsburg, *Tetrahedron, Suppl.*, No. 8, 279 (1967).

[29] This boiling point was obtained by distillation of a 2.4-g sample of **16** in a different experiment.

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, ν_{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); ν_{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**, ν_{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: ν_{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**.

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

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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).