Functionalized Polyunsaturated [4.4.4]Propellanes. Synthesis, Intraring Chemistry, and Backbone Rearrangements. [4.4.4]Propella-2,4,7,9,12-pentaene and Its Thermal Frangibility

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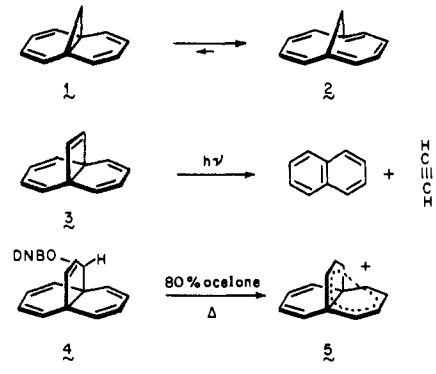
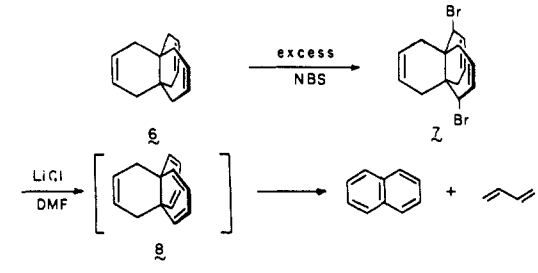
Abstract: The feasibility of preparing [4.4.4]propella-1,3,6,10-tetraene (**37**) and -1,3,5,7,10-pentaene (**8**) from a common ketonic precursor has been examined. [4.4.4]Propella-3,6,10-trien-2-one (**13**) was prepared as shown in Scheme I. The relative reactivity of its double bonds toward electrophiles was studied. Exposure of the tetrabromide of **13** (**19**) to strongly basic conditions furnished tetracyclo[4.4.4.$0^{1,6}$.$0^{5,8}$]tetradeca-2,9,11,13-tetraen-4-one (Scheme II), a substance observed to undergo fascinating thermal rearrangement (Scheme IV). Through prior ketalization of **19**, it proved possible to obtain [4.4.4]propella-3,5,7,10-tetraen-2-one (**28**) (Scheme III), whose susceptibility to intramolecular Diels–Alder cycloaddition was noted. Controlled reduction of **13** followed by dehydration led to **37**, the chemistry of which was briefly scrutinized (Scheme VI). Comparable handling of **28** gave **8** and set the stage for direct comparison of the lability of these hydrocarbons to retrograde [4 + 2] fragmentation.

Nearly two decades ago, several reports describing the first deliberate synthetic approaches to alicyclic propellanes made their appearance almost simultaneously.[2] The informative conformational, reactivity, and electronic properties of this class of compounds have intrigued chemists ever since.[3] Particularly significant information has emerged from studies involving substrates that are either highly strained[4] or extensively unsaturated. The latter category comprises the focus of the present discussion. Thus, Vogel et al.[5] have evaluated in inspiring depth the proclivity of **1** and its homologues to undergo electrocyclic ring opening and conversion to aromatic structural types, e.g., **2**, and pioneered the investigation of bridged annulene chemistry. A contrasting example is the [4.4.2]propellapentaene **3** prepared by Paquette and Philips.[6] The hydrocarbon experiences homoconjugative interaction comparable in magnitude to that of the π-orbitals in norbornadiene[7] and shows good thermal stability but exhibits *no* tendency for valence isomerization.[6,8] Additionally, **3** is very susceptible to retrograde [2 + 2] fragmentation from its excited state and is readily transformed when irradiated into naphthalene and acetylene.[6] The [4.4.3]propellanyl 3,5-dinitrobenzoate **4** has been found to ionize with anchimeric assistance and generation of the bishomotropylium ion **5**.[9] Noteworthy here is the fact that



this carbocation is geometrically incapable of availing itself of more extensive longicyclic delocalization.[10]

Our knowledge of the properties of olefinic [4.4.4]propellanes has progressed to a substantially lesser degree. Ginsburg and co-workers were successful in gaining access to triene **6**.[11] Attempts on their part to effect the complete bromination of **6** with *N*-bromosuccinimide produced only a dibromide assumed to be **7**. Since the action of lithium chloride in dimethylformamide on **7** gave rise to naphthalene, the inference was drawn that the presumed intermediate **8** was especially prone to retrograde Diels–Alder fragmentation.[12,13]



(1) Postdoctoral Fellow of the Deutscher Akademischer Austauschdienst (NATO), 1981-1982.

(2) (a) Vogel, E.; Meckel, W.; Grimme, W. *Angew. Chem.* **1964**, *76*, 786. Vogel, E.; Maier, W.; Eimer, J. *Tetrahedron Lett.* **1976**, 655. (b) Nerdel, F.; Janowsky, K.; Frank, D. *Ibid.* **1965**, 2979. (c) Snatzke, G.; Zanati, G. *Justus Liebigs Ann. Chem.* **1965**, *684*, 62. (d) Cargill, R. L.; Damewood, J. R. Cooper, M. M. *J. Am. Chem. Soc.* **1966**, *88*, 1330. Cargill, R. L.; Beckham, M. E.; Siebert, A. E.; Dorn, J. *J. Org. Chem.* **1965**, *30*, 3647. (e) Bloomfield, J. J.; Mitra, A. *Chem. Ind. (London)* **1966**, 2012. Bloomfield, J. J.; Irelan, J. R. S. *Tetrahedron Lett.* **1966**, 2971. Bloomfield, J. J.; Irelan, J. R. S. *J. Org. Chem.* **1966**, *31*, 2017. (f) Altman, J.; Babad, E.; Itzchaki, J.; Ginsburg, D. *Tetrahedron* **1966**, Suppl. 8, Part 1, 279.

(3) (a) Ginsburg, D. *Propellanes*; Verlag Chemie: Weinheim, West Germany, 1975. (b) Ginsburg, D. *Propellanes*, Sequel I; Department of Chemistry: Technion, Haifa, Israel, 1981. (c) Ginsburg, D. *Propellanes*, Sequel II; Department of Chemistry: Technion, Haifa, Israel, 1985.

(4) Wiberg, K. B.; Walker, F. H.; Pratt, W. E.; Michel, J. *J. Am. Chem. Soc.* **1983**, *105*, 3638. Wiberg, K. B. *Ibid.* **1983**, *105*, 1227. Wiberg, K. B.; Walker, F. J. *Ibid.* **1982**, *104*, 2056 and pertinent references cited therein.

(5) (a) Vogel, D. *Pure Appl. Chem.* **1971**, *28*, 355. (b) Vogel, E. *Chimia* **1968**, *22*, 21. (c) Vogel, E. In *Aromaticity*; Special Publication No. 21; Chemical Society: London, 1967; p 113. (d) Vogel, E. Proceedings of the R. A. Welch Foundation, Conference on Synthesis, Houston, Texas, 1969; p 215.

(6) Paquette, L. A.; Philips, J. C. *J. Am. Chem. Soc.* **1969**, *91*, 3973.

(7) Gleiter, R.; Heilbronner, E.; Paquette, L. A.; Thompson, G. L.; Wingard, R. E., Jr. *Tetrahedron* **1973**, *29*, 565.

(8) Paquette, L. A.; Philips, J. C.; Wingard, R. E., Jr. *J. Am. Chem. Soc.* **1971**, *93*, 4516.

(9) Paquette, L. A.; Jelich, K.; Ohkata, K. *Tetrahedron Lett.* **1982**, 2749. Paquette, L. A.; Ohkata, K.; Jelich, K.; Kitching, W. *J. Am. Chem. Soc.* **1983**, *105*, 2800.

(10) Goldstein, M. J. *J. Am. Chem. Soc.* **1967**, *89*, 6357. Goldstein, M. J.; Hoffmann, R. *Ibid.* **1971**, *93*, 6193.

(11) Altman, J.; Babad, E.; Pucknat, J.; Reshef, N.; Ginsburg, D. *Tetrahedron* **1968**, *24*, 975.

(12) Reference 3a, p 15.

(13) For another prima facie unlikely claim regarding the transient formation and Diels–Alder fragmentation of an unsaturated [4.4.4]propellane, see: Gilbert, A.; Walsh, R. *J. Am. Chem. Soc.* **1976**, *98*, 1606.

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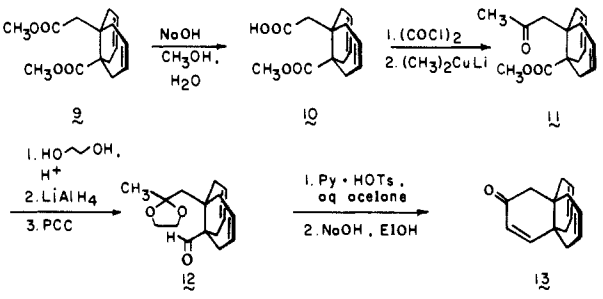
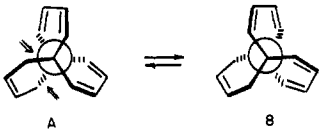
Scheme I



To our mind, this interpretation was less than satisfactory. Dreiding models of **8** clearly indicate the molecule to exist in one or the other enantiomerically related conformation A or B. This conclusion is supported by X-ray crystal structure data for lesser



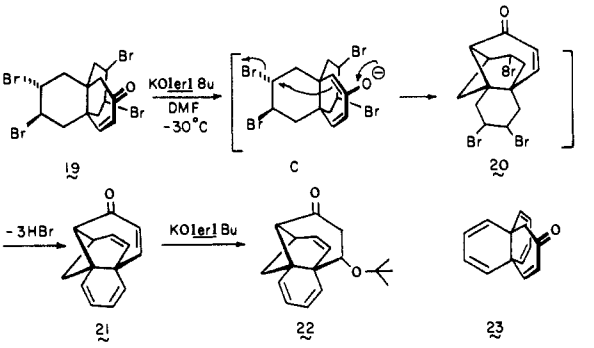
unsaturated analogues.[14] Consequently, the double bonds in the cyclohexadiene rings of **8** are not coplanar, and the allylically disposed single bonds of the cyclohexene subunit are pronouncedly tilted in opposite directions (note arrows in A). Substantial topological realignment must precede fragmentation, and the energy costs this feature introduces are likely to be approximately 12 kcal/mol.[15,16] Since concerted bond cleavage is unlikely to occur until the conformational distortion is first redressed,[17] we thought it unlikely that **8** is as frangible as originally claimed.

For these reasons, we have undertaken to prepare **8** and the related tetraene **37** and to compare their thermal stability.[18] Our synthetic strategy was designed to bypass as long as possible intermediates whose structural features cause them to be candidates for retrograde [4 + 2] fragmentation. This effort has led to the discovery of several interesting transformations involving bonding between the constituent rings as well as skeletal rearrangements.[19] This paper also provides a full account of these coincident developments, which arise because of the unique architecture of this family of molecules.

Results and Discussion

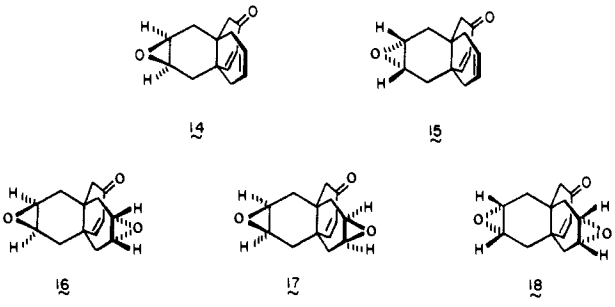
[4.4.4]Propella-3,6,10-trien-2-one (13). Ketone **13** was an obvious choice as precursor. The location of its carbonyl group necessitates that enolization precede retrodienic loss of the oxygenated ring, a less than likely prospect under ordinary laboratory conditions. Beyond that, we hoped that the relatively stable enone assembly, or a blocked form thereof, would withstand those subsequent operations needed for elaboration of the cyclohexadiene rings. Diester **9**, expediently prepared from readily available $\Delta^{2,6}$-hexalin-9,10-dicarboxylic anhydride,[9] seemed uniquely qualified to serve as starting material. The task, therefore, reduced

Scheme II



itself to setting the stage for an intramolecular aldol condensation. In the event, **9** was selectively hydrolyzed,[20] its less sterically encumbered carbomethoxy group responding more readily to nucleophilic attack by hydroxide ion in aqueous methanol. The acid chloride of **10** reacted with lithium dimethylcuprate[21] to provide keto ester **11**. Following ketalization and alteration of the ester oxidation level to give aldehyde **12**, the [4.4.4]propellatrienone **13** was obtained conventionally. Although the final cyclization proceeded only with an efficiency of 57%, the overall yield for the entire eight-step synthesis of **13** from **9** was a satisfactory 31%.

Chemospecific Electrophilic Additions to 13. Complications from Intraring Reactions. In order to set the stage for later operations, two simple electrophilic additions to **13** were now effected. First, the enone was treated with 2.2 equiv of *m*-chloroperoxybenzoic acid in dichloromethane. The five products that resulted could be readily separated by medium-pressure liquid chromatography (MPLC). The unsymmetrical diepoxide **16** was easily distinguished on the basis of its spectral properties. The assignment of stereochemistry to the oxirane rings in the pairs **14**/**15** and **17**/**18** was arrived at chiefly according to their R_f values on silica



gel. The expectation that syn orientation of the epoxide and enone functionalities lends itself to increased polarity was the basis for formulating the less rapidly eluted compounds as **15** and **18**. In any event, the point is not one of importance, since the central issue is the lack of enone reactivity under these conditions.

Next, **13** was exposed to the action of excess bromine in dichloromethane at low temperature. A very insoluble tetrabromide product (**19**) was isolated in essentially quantitative yield. Its 200-MHz ^{1}H NMR spectrum (long accumulation times necessary in FT) clearly revealed that the enone moiety had again remained intact. Somewhat unexpectedly, the appearance of a single set of doublets for the pair of olefinic protons suggested that **19** is a single homogeneous stereoisomer.[22] This same phenomenon was witnessed upon bromination of the ethylene ketal of **13**.

To achieve the exhaustive dehydrobromination of **19**, the tetrabromide was treated with excess potassium *tert*-butoxide in dimethylformamide at −30 °C for 3 h (Scheme II). Although a beautifully crystalline $C_{14}H_{12}O$ ketone was isolated in 55% yield,

(14) Ermer, O.; Gerdil, R.; Dunitz, J. D. *Helv. Chim. Acta* **1971**, *54*, 2476.
(15) The single reasonable mechanism for dynamic enantiomer interconversion of two [4.4.4]propellatrienetriones, i.e., the operation of synchronous three-ring flipping, occurs with E_A = 12.0–12.8 kcal/mol [Jendralla, H.; Doecke, C. W.; Paquette, L. A. *J. Chem. Soc., Chem. Commun.* **1984**, 942]. The levels of stress necessarily placed on the central bond at the transition state, i.e., at that point when all rings are planar, may well be closely comparable to that attending the retrodienic fragmentation.
(16) The dynamic behavior of **6** and 3,3-difluoro[4.4.4]propellane has also been examined [Gilboa, H.; Altman, J.; Loewenstein, A. *J. Am. Chem. Soc.* **1969**, *91*, 6062]. Sequential ring inversions are probably involved here.
(17) The converse of this conclusion is also thought to be true. Thus, for certain symmetry-allowed cycloaddition reactions that pass through an aromatic transition state yet have large activation barriers, considerable energy is required to distort the reactants away from their closed-shell geometries in order to facilitate stabilizing HOMO–LUMO interaction [Houk, K. N.; Gandour, R. W.; Strozier, R. W.; Rondan, N. G.; Paquette, L. A. *J. Am. Chem. Soc.* **1979**, *101*, 6797].
(18) Preliminary communication: Paquette, L. A.; Jendralla, H.; DeLucca, G. *J. Am. Chem. Soc.* **1984**, *106*, 1518.
(19) Preliminary communication: Paquette, L. A.; Jendralla, H.; Jelich, K.; Korp, J. D.; Bernal, I. *J. Am. Chem. Soc.* **1984**, *106*, 433.
(20) Paquette, L. A.; Nelson, N. A. *J. Org. Chem.* **1962**, *27*, 2272.
(21) Paquette, L. A.; Snow R. A.; Muthard, J. L.; Cynkowski, T. *J. Am. Chem. Soc.* **1979**, *101*, 6991 and references cited therein.
(22) Confirmation of this fact by ^{13}C NMR spectroscopy was not feasible due to the solubility properties of the substance.

it became immediately obvious that the anticipated tricyclic pentaenone **23** was not in hand. Instead, the presence of only 8 olefinic protons (^{1}H NMR) and the lack of planar symmetry (fourteen ^{13}C signals) indicated the compound to be necessarily tetracyclic.

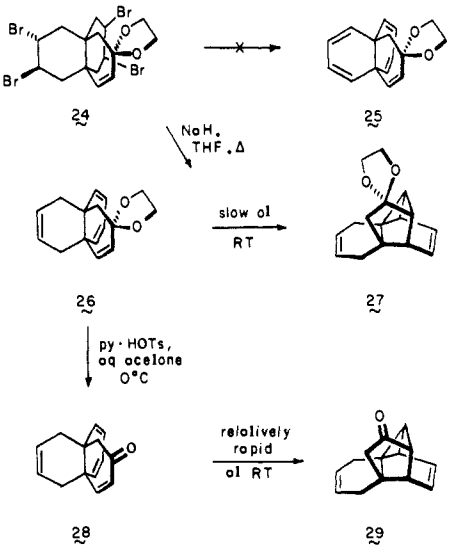
That the α,β-unsaturated carbonyl moiety had remained intact was denoted by a pair of doublets with J = 9.7 Hz at δ 6.98 and 5.60. However, the $\Delta\delta$ of this pair of signals (1.38 ppm) is significantly larger than that observed for **13** (0.93 ppm), indicating that the chromophoric unit was now more planar.[9] The combination of UV and ^{1}H NMR spectroscopy provided evidence that one cyclohexadiene ring was present. However, it was not possible to discern unequivocally whether intramolecular cyclization had proceeded via a four- or five-membered transition state. In the end, the structure was rigorously established to be **21** by X-ray crystallographic analysis.[23] The formation of **21**, outlined in Scheme II, may be explained in terms of intramolecular displacement by the enolate anion of a properly stereodisposed δ-bromine substituent (see C). If this event were to trigger the ensuing sequence of dehydrobrominations, tribromo ketone **20** would necessarily be a pivotal intermediate. On the other hand, the closure depicted in C could operate only after partial dehydrobromination had taken place in the third ring. Whatever the actual mechanitic scenario, it is clear that the bromination of **13** has resulted in the installation of at least one pair of bromine atoms (and possibly both) as depicted in C. This leaves open the likelihood that the conversion of **19** to **21** is stereochemically and not thermodynamically controlled. No five-ring product resulting from 1,5-elimination was detected.

In several runs, small and variable quantities of **22** also were isolated. Although its genesis from Michael addition of *tert*-butoxide ion to **21** was confirmed by independent experiment, no attempt was made to elucidate the relative configuration of the new stereogenic center in the resulting single isomer.

Although the enone double bond of **13** displays suitably low reactivity toward electrophilic reagents, the proclivity of **19** for cyclization to **21** necessitated prior ketalization. To this end, heating **19** with ethylene glycol and *p*-toluenesulfonic acid in benzene was effected and **24** was obtained in quantitative yield. The next maneuver, exhaustive dehydrobromination of **24**, proved to be unusually troublesome. Numerous attempts to achieve conversion to **25** met with failure. During studies designed to define the source of the complication, it became apparent that **24** is particularly prone to monodebromination (see Experimental Section).[24] With this information in hand, we set out to maximize the conversion to **26**. The best conditions uncovered involved exposure of **24** to excess sodium hydride in refluxing tetrahydrofuran (Scheme III).[25] Subsequent to silica gel chromatography, there was isolated the desired tetraene ketal (45%) along with **27** (8%). The latter product is recognized to be the result of intramolecular Diels–Alder cycloaddition involving the cyclohexadiene and ketal cyclohexene subunits within **26**, a conversion that can be duly accelerated on heating. Subsequent independent thermal activation of **27** left the substance unaltered, thereby denoting that this process may be irreversible. This cyclization, occurring readily as it does without activation of the dienophilic double bond, signals favorable entropy control of the electronic reorganization.

Despite the obvious concerns that this thermal sensitivity brought to the fore, the exceptional reactivity of **26** to hydrolysis permitted efficient conversion to **28**. Simply by stirring **26** with pyridinium tosylate in wet acetone at 0 °C for 15 h could unmasking of the ketone be achieved quantitatively. Since **28** was expectedly more prone than **26** to intramolecular cyclization, it

Scheme III



was mandatory that the tetraenone not be stored prior to use (see below).

Rearrangement Reactions of 21 and the Derived Alcohol. During preliminary attempts to purify **21** by vapor-phase chromatography, its lability to heat was noted. Further experimentation revealed that the thermolysis of **21** could be conveniently carried out on a variety of packed columns (Carbowax 20M, SE-30, QF-1) in the 130–175 °C range. Under these conditions, **31** and **32** were efficiently produced in the approximate ratio of 1.0:1.1. Following VPC separation, both compounds were obtained as crystalline solids. It was clear from the IR and ^{13}C NMR spectra of the major product (**32**) that the oxygen atom no longer was in the form of a carbonyl group. Analysis of its 300-MHz ^{1}H NMR spectrum also revealed the presence of 4 aromatic protons, 5 olefinic hydrogens, a unique downfield-shifted proton (δ 5.27) having high spin interaction (dt, J = 12.5 and 4.3 Hz), and an AB-related pair of hydrogens at δ 3.28 and 2.61. That **32** was an interesting benzo-fused oxa[10]annulene derivative was ultimately established by X-ray crystal-structure analysis.[23]

The structural assignment to **31** was inferred from its 300-MHz ^{1}H NMR spectrum. The ortho-disubstituted benzene ring resonances occur at similar chemical shifts to those in **32**. The α,β-unsaturated carbonyl moiety appears as two well-separated doublet of doublets (δ 7.48 and 5.51). The large $\Delta\delta$ (1.97 ppm) of these signals is due to structurally enforced coplanarity of the neighboring carbonyl and olefinic centers. This information, in conjunction with evidence for the presence of a terminal vinyl group and spin-decoupling studies involving the bridgehead protons located at δ 3.78 and 3.60, proved fully consistent with the assigned formula. The stereodisposition of the vinyl group is based on the mechanistic considerations that follow.

The proportion of **31** to **32** remained constant over a wide range of conditions and was invariant to the percent conversion of **21**. A common intermediate is therefore assumed in their formation. While a thermodynamically driven propensity for aromatization of the cyclohexadiene ring was anticipated, covalent incorporation of the carbonyl group with loss of the stability normally associated with a C–O double bond was not. In actual fact, two quaternary carbons in **21** must be disrupted to permit arrival at a benzenoid ring. This chemical feat can be most cogently accomplished by transient intervention of pentaenone **30** (Scheme IV). The conversion of **21** to **30** can be economically achieved by three simple antiperiplanar carbon shifts as in D. However, the process need not be concerted, the stepwise options depicted in E being available as well.

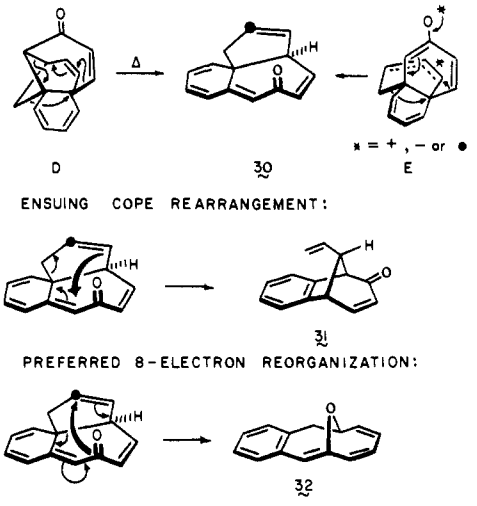
Dreiding models of **30** shows that the carbonyl oxygen is positioned at a distance only 3.3 Å away from the dotted olefinic carbon atom in a geometric relationship particularly conducive to pπ–pπ overlap and that aromatization can be achieved by Cope rearrangement involving unsaturated centers initially 3.7 Å distant.

(23) We thank Professor Ivan Bernal and Dr. James D. Korp (University of Houston) for this analysis. The details of their investigation may be found in the supplementary material of ref 19.

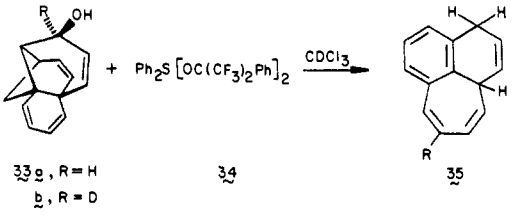
(24) Compound **19** also appears to be subject to debromination, although to a much lesser extent (consult Experimental Section).

(25) For an excellent review of complex reducing agents that includes novel ways in which sodium hydride has been utilized in synthesis, see: Caubere, P. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 599.

Scheme IV



Scheme V



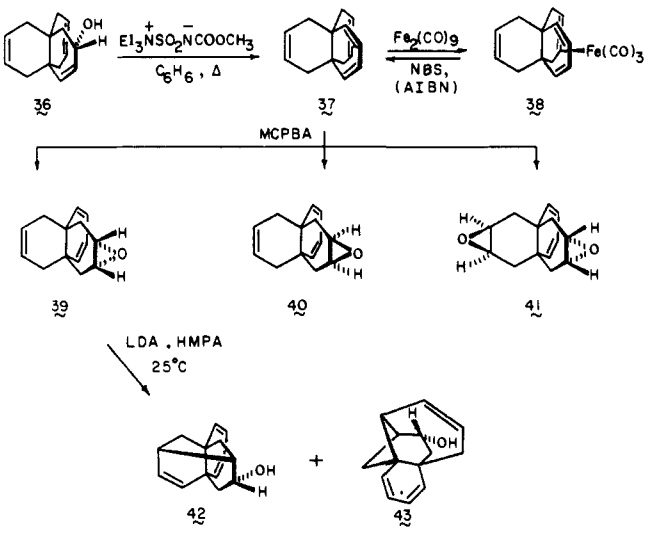
While the latter process likely proceeds concertedly according to the dictates of orbital symmetry (six-electron sigmatropy),[26] the requisite reorganization of eight electrons to arrive at **32** is not comparably favored (Scheme IV). Nevertheless, the dominant formation of **32**, also with concurrent aromatization, belies the preferred operation of this hypothetical pathway. For the present, the proximity and relative orientation of the carbonyl group in **30** is deemed responsible for this phenomenon.

A comparably deep-seated rearrangement occurred when structurally related alcohol **33a** was treated with the powerful dehydrating agent diphenylbis(1,1,1,3,3,3-hexafluoro-2-phenyl-2-propoxy)sulfurane (**34**)[27] in $CDCl_3$ at room temperature (Scheme V). Hydrocarbon product **35a** has been obtained with comparably high efficiency in another context.[28] As a result, considerations pertinent to the proof of structure and to the mechanistic facets of this chemistry are deferred to the following paper.[28] Nonetheless, it is appropriate to note here that incorporation of a deuterium label as in **33b** leads specifically to **35b** (^{1}H NMR analysis).

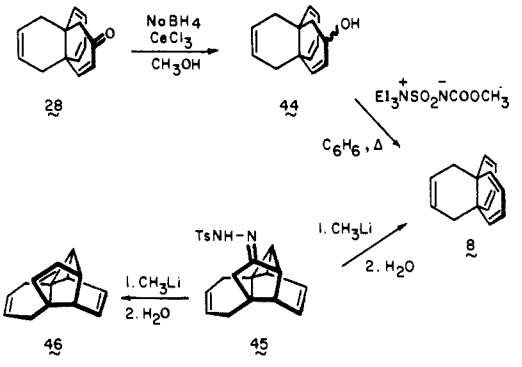
Preparation of [4.4.4]Propella-1,3,6,10-tetraene (37). Selected Reactions. Reduction of **13** with cerium(III) chloride doped sodium borohydride[29] provided alcohol **36** whose dehydration was most successfully achieved (92% yield) by heating with a slight excess of the Burgess reagent[30] in benzene solution for 1 h. That no skeletal rearrangement had materialized in this instance was attested to by the five-line ^{13}C NMR spectrum. In addition, the 300-MHz ^{1}H NMR spectrum clearly displayed the AA'BB' resonances of the two identical (time-average basis) cyclohexene units. The electronic spectrum of **37** in cyclohexane solution consisted of a single maximum at 267 nm (ϵ 2640).

As shown in Scheme VI, **37** entered into reaction with excess iron nonacarbonyl in benzene at room temperature to deliver the

Scheme VI



Scheme VII



complex **38**. Unfortunately, this bright yellow crystalline solid proved not to be a serviceable intermediate. For example, oxidative loss of the $Fe(CO)_3$ group occurred immediately upon titration with bromine in carbon tetrachloride and more slowly with *N*-bromosuccinimide at more elevated temperatures. Less expectedly, treatment of **37** with 2.2 equiv of *m*-chloroperoxybenzoic acid furnished monoepoxide **39**. Unusual chemical behavior has been noted with other reagents.[31]

As a consequence, it became necessary to determine if the isolated double bond in **37** could be functionalized without protection of the conjugated diene. It will be recalled that the 1,3-diene fragment should be appreciably twisted in its ground-state conformation (A or B). The component π-linkages are not capable of maximally extended delocalization and should consequently be inductively deactivated relative to planar butadienes. This expectation was borne out during epoxidation (2 equiv of MCPBA), as monoepoxides **39** and **40** together with diepoxide **41** were obtained in a ratio approximating 4:2:1. The stereochemistry of **41** was easily deduced from the nonequivalence of the two epoxide rings in the ^{1}H NMR spectrum. Distinction between **39** and **40** was made on the basis of chemical reactivity. In an attempt to transform **39** directly into a tetraenic allylic alcohol by means of lithium diisopropylamide at room temperature,[32] it was discovered that intraring cyclization was kinetically favored. None of the desired product was formed. Instead, a chromatographically separable mixture of **42** (62%) and **43** (13%) was obtained. Structural assignments to the two alcohols were deduced from 300-MHz ^{1}H NMR data and facilitated in the case of **43** by spectral comparison with the other compounds of identical carbon skeleton obtained earlier in this study. Evidently, proton abstraction from one of the methylene groups α to the oxirane ring in **39** cannot compete with the production of an allylic anion

(26) Woodward, R. B.; Hoffmann, R. *Conservation of Orbital Symmetry*; Verlag Chemie, Academic Press: Weinheim/Bergstr., New York, 1970.
(27) Martin, J. C.; Arhart, R. J. *J. Am. Chem. Soc.* **1971**, *93*, 2341, 4327. We thank Professor Martin for making a generous supply of the sulfurane available to us.
(28) Paquette, L. A.; Waykole, L.; Jendralla, H.; Cottrell, C. E. *J. Am. Chem. Soc.*, following paper in this issue.
(29) Luche, J.-L. *J. Am. Chem. Soc.* **1978**, *100*, 2226.
(30) Burgess, E. M.; Penton, H. R., Jr.; Taylor, E. A. *J. Org. Chem.* **1973**, *38*, 26.
(31) Jendralla, H., unpublished results.
(32) Crandall, J. K.; Apparu, M. *Org. React.* **1983**, *29*, 345.

in the cyclohexene subunit of the molecule. Subsequent transannular closure, made feasible by the relative stereochemistry of the oxirane ring, favors the five-ring transition state leading to **42** by a factor approaching 5 relative to that associated with cyclobutane ring formation and generation of **43**.

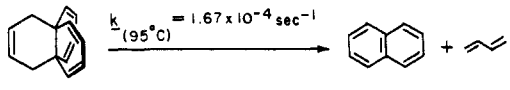
To overcome these complications and achieve synthetic access to the title pentaene, thermally labile ketone **28** was reduced and dehydrated in a fashion parallel to **13**.

Synthesis of [4.4.4]Propella-2,4,7,9,12-pentaene (8) and Its Thermal Stability. Freshly prepared **28** was immediately treated with $NaBH_4/CeCl_3$ in methanol. A 3:1 ratio of diastereomeric tetraenols **44** was recovered in **93%** yield. Their separation could be achieved chromatographically, but this proved not be necessary as both diastereomers underwent dehydration to **8** in the presence of Burgess reagent (Scheme VII). The colorless oil exhibited a five-line ^{13}C NMR spectrum, a ^1H NMR spectrum fully consistent with its symmetrical nature (see Experimental Section), and a UV maximum in cyclohexane at 250 nm (ϵ 10010). As we had anticipated, **8** proved to be indefinitely stable at room temperature.

An alternative though less efficient route to **8** consisted of converting ketone **29** to its tosylhydrazone (**45**) followed by Shapiro degradation with methyllithium.[33] The consequence of this sequence was to deliver **46** as the major product, alongside **8** and a lesser quantity of an unidentified hydrocarbon.

At this point, it becomes important to indicate that the structural features embodied in **8** and **37** make these molecules ideally suited to an investigation of retrograde Diels–Alder behavior. The simplest *cis*-[34] and *trans*-1,4,4a,8a-tetrahydronaphthalenes[35] are known. However, heating of these hydrocarbons can be expected to induce kinetically preferred electrocyclization rather than [4 + 2] fragmentation.[36] The presence of a third six-membered ring safeguards against disrotatory ring opening and introduces well-defined ground-state conformational characteristics.

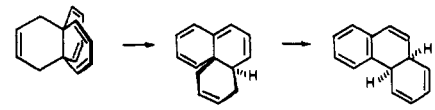
The task of determining the thermal stabilities of **8** and **37** was addressed by sealing dilute degassed chlorobenzene-d_5 solutions of the hydrocarbons into evacuated NMR tubes. Following heating of **37** at 160 °C for 90 h, there was no spectral evidence for Diels–Alder fragmentation.[36] Since as little as 3% reaction could have been detected, the rate constant for this unobserved reaction must be less than 1×10^{-7} s^{-1}. In contrast, **8** was found to undergo smooth conversion to naphthalene and 1,3-butadiene at 95 °C with good first-order kinetics.



8

If the cleavage of both C–C σ bonds in **8** is indeed a concerted process, the kinetic inequality that is observed would quite possibly be a reflection of the widely divergent $C_{10}H_8/C_6H_6$ resonance energies (61 vs. 36 kcal/mol) manifested in the respective transition states. A stepwise pathway would be more concerned with the relative stabilities of the intermediate biradicals. In either event, **8** is predicted to be more thermally labile. Comparisons with other systems are not particularly informative because the transient species (if involved) and end products are necessarily different. Thus, shock tube conditions at 900–1150 K have been found necessary to achieve the conversion of cyclohexene to butadiene and ethylene.[37] In another context, 9,10-dihydro-9,10-ethanoanthracene, a molecule in which relevant torsion angles approach zero, reverts to anthracene with a rate constant of 7.11×10^{-5} s^{-1} at 278 °C.[38] Pentaene **8** is unquestionably more frangible than either of these substrates. However, it can hardly be viewed as a highly fragile molecule.

We have uncovered no spectral evidence that [1,5]-sigmatropic carbon shift within **8** to deliver F and/or its further transformation products such as G precedes the loss of butadiene. The obvious



8 **F** **G**

driving force for **8** (but not for 37) would be the development of a more highly conjugated π network. These putative structures would be readily susceptible to retrograde [4 + 2] fragmentation in their own right. Accordingly, it is not possible at this time to rule out this less direct mechanistic option. The following paper[28] examines a closely related rearrangement protocol.

Experimental Section

Methyl *cis*-9-(Carboxymethyl)-$\Delta^{2,6}$-hexalin-10-carboxylate (10). Solutions of diester **9** (16.7 g, 6.33 mmol) in methanol (200 mL) and of sodium hydroxide (2.92 g, 1.15 equiv) in water (100 mL) were mixed and heated at reflux for 6 h. Most of the solvent was evaporated, water (100 mL) was added, and extraction with ether (100 mL) was carried out to remove unreacted starting material. The aqueous phase was acidified with concentrated hydrochloric acid and extracted with ether (4 × 100 mL). The combined organic phases were washed with water, dried, and evaporated to give 13.87 g (87.7%) of **10** as a viscous, pale yellow oil that slowly solidified on standing: ^1H NMR (200 MHz, $CDCl_3$) δ 11.1 (br s, 1 H), 5.62–5.5 (m, 4 H), 3.60 (s, 3 H), 2.75 (s, 2 H), 2.4–2.2 (m, 8 H); *m/z* calcd (M^+) 250.1205, obsd 250.1211.

Methyl *cis*-9-(Acetonyl)-$\Delta^{2,6}$-hexalin-10-carboxylate (11). To a solution of **10** (13.87 g, 55.5 mmol) in dry benzene (200 mL) was slowly added 23 g (0.181 mol) of freshly distilled oxalyl chloride and the mixture was stirred at room temperature for 3 h. Solvent evaporation left 14.9 g (100%) of the acid chloride as a yellow oil: IR ($CDCl_3$, cm^{-1}) 3030, 2910, 1800, 1720, 1430; ^1H NMR (200 MHz, $CDCl_3$) δ 5.6–5.45 (m, 4 H), 3.62 (s, 3 H), 3.47 (s, 2 H), 2.4–2.2 (m, 8 H); *m/z* calcd (M^+) 268.0866, obsd 268.0876.

Methyllithium (210 mL of 1.25 M in ether) was added to 27 g (0.142 mol) of cuprous iodide at −20 °C under nitrogen. When a clear yellowish solution resulted, the preparation was cooled to −70 °C and the acid chloride (14.9 g, 55.5 mmol) was introduced via syringe under nitrogen. Following 30 min of mechanical stirring at −70 °C, dry methanol (distilled from magnesium methoxide, 30 mL) was added dropwise at −70 °C. The reaction mixture was allowed to reach room temperature, poured into saturated ammonium chloride solution (200 mL), and extracted with ether (4 × 80 mL). The combined ether phases were washed with saturated ammonium chloride solution (3×) and brine (1×), dried, and evaporated. There was isolated 12.68 g (92%) of **11** as a colorless oil that crystallized: mp 49–50 °C (from methanol); IR (CCl_4, cm^{-1}) 3025, 2900, 1738, 1727, 1425; ^1H NMR (200 MHz, $CDCl_3$) δ 5.6–5.4 (m, 4 H), 3.65 (s, 3 H), 2.83 (s, 2 H), 2.45–2.2 (m, 8 H), 2.15 (s, 3 H).

Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.53; H, 8.12. Found: C, 72.56; H, 8.05.

Ketalization of 11. A solution of **11** (12.68 g, 51.1 mmol), ethylene glycol (100 mL), and *p*-toluenesulfonic acid (2.7 g, 17.3 mmol) in dry benzene (200 mL) was heated at reflux for 20 h under a Dean-Stark trap. The cooled reaction mixture was diluted with ether (200 mL) and poured into saturated sodium bicarbonate solution (100 mL). The aqueous phase was extracted with ether (3 × 50 mL) and the combined organic layers were washed with saturated sodium bicarbonate solution (2×) and brine prior to drying and evaporation. The ketal ester was obtained as a colorless oil (14.92 g, 100%): IR ($CDCl_3$, cm^{-1}) 3025, 2950, 2880, 1720, 1425; ^1H NMR (200 MHz, $CDCl_3$) δ 5.6–5.4 (m, 4 H), 3.90 (s, 4 H), 3.63 (s, 3 H), 2.6–1.8 (series of m, 8 H), 2.0 (s, 2 H), 1.4 (s, 3 H); *m/z* calcd (M^+) 292.1674, obsd 292.1664.

Reduction of the Ketal Ester. To a mechanically stirred suspension of lithium aluminum hydride (3.5 g, 92.1 mmol) in dry ether (200 mL) was added dropwise a solution of the ketal ester (14.92 g, 51.1 mmol) in the same solvent (50 mL) at room temperature under nitrogen. The mixture was stirred for 30 min, treated dropwise with saturated sodium sulfate solution, and separated into two layers. The aqueous layer was extracted with ether (3 × 50 mL) and the combined ethereal solutions were washed with brine (2×), dried, and evaporated. There was isolated 13.37 g (99%) of ketal alcohol as a colorless oil: IR ($CDCl_3$, cm^{-1}) 3640, 3600–3200, 3010, 2870, 1425; ^1H NMR (200 MHz, $CDCl_3$) δ 5.6–5.4 (m, 4 H), 3.86 (s, 4 H), 3.60 (s, 2 H), 2.25–1.85 (series of m, 11 H), 1.35

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(38) Taagepera, M.; Thornton, E. R. *J. Am. Chem. Soc.* **1968**, *91*, 6062.

(s, 3 H); m/z calcd (M^+ - CH_3) 249.1490, obsd 249.1498.

Oxidation of the Ketal Alcohol. To a solution of pyridinium chlorochromate (22 g, 0.102 mol) in dry dichloromethane (distilled from phosphorus pentoxide) was added a solution of ketal alcohol (13.37 g, 50.6 mmol) in the same solvent (50 mL) under nitrogen at room temperature. The reaction mixture was stirred for 25 min, ether (200 mL) was added, and the solution was decanted from the tar. The viscous residue was triturated several times with ether (total volume ca 100 mL) and the combined organic solutions were washed with saturated sodium bicarbonate solution, 10% hydrochloric acid (3×), saturated sodium bicarbonate solution (3×), and brine. Drying and solvent evaporation afforded 11.83 g (89%) of ketal aldehyde as a dark yellow oil which was directly utilized without further purification: IR ($CDCl_3$, cm^{-1}) 3020, 25880, 1715, 1440; ^1H NMR (200 MHz, $CDCl_3$) δ 9.9 (s, 1 H), 5.6–5.4 (m, 4 H), 3.9 (s, 4 H), 2.5–1.8 (m, 10 H), 1.35 (s, 3 H).

[4.4.4]Propella-3,6,10-trien-2-one (13). A solution of the ketal aldehyde (11.83 g, 45.1 mmol) and pyridinium tosylate (3.2 g, 12.8 mmol) in acetone–water (9:1, 250 mL) was heated at reflux for 2.5 h. After the solution was cooled to room temperature, most of the acetone was removed by evaporation and ether (150 mL) was added. This solution was washed with saturated sodium bicarbonate solution (2×), 10% hydrochloric acid (2×), saturated sodium bicarbonate solution, and brine. Following drying and solvent evaporation, there was isolated 7.79 g (79.1%) of keto aldehyde as a yellow oil: IR ($CDCl_3$, cm^{-1}) 3020, 2880, 1710, 1425, 1355; ^1H NMR (200 MHz, $CDCl_3$) δ 9.83 (s, 1 H), 5.6–5.4 (m, 4 H), 3.53 (s, 2 H), 2.4–2.1 (m, 8 H), 2.1 (s, 3 H); m/z calcd (M^+) 218.1307, obsd 218.1313.

The unpurified keto aldehyde (7.79 g, 35.7 mmol) was dissolved in a solution containing 12 g of sodium hydroxide in 350 mL of absolute ethanol. The dark yellow solution was stirred at room temperature for 15 h, poured into 2.5 L of ether, and washed with water until the washings were colorless. The organic phase was dried and evaporated to leave a residual oil that was purified by HPLC on silica gel (elution with petroleum ether–ethyl acetate, 85:15). Ketone **13** (4.07 g, 57%) was obtained as a colorless crystalline sample: mp 55–56 °C (from ethyl acetate); IR (KBr, cm^{-1}) 3030, 2980, 2840, 1670, 1445, 1425, 1412, 1380, 1268, 1233, 1155, 1080, 996, 862, 756, 660; ^1H NMR (300 MHz, $CDCl_3$) δ 6.80 (d, J = 9.9 Hz, 1 H), 5.87 d, J = 9.9 Hz, 1 H), 5.62 (dt, J = 10.1 and 1.7 Hz, 2 H), 5.53 (d, J = 10.1 Hz, 2 H), 2.6–1.8 (series of m, 10 H); ^{13}C NMR ($CDCl_3$) ppm 199.82 (s), 160.34 (d), 127.89 (d), 127.40 (d, 4 C), 45.87 (t), 37.31 (s), 35.33 (t, 2 C), 35.07 (s), 34.37 (t, 2 C); m/z calcd (M^+) 200.1201, obsd 200.1213.

Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.70; H, 8.06.

Epoxidation of 13. To an ice-cooled stirred slurry of sodium bicarbonate (555 mg, 6.6 mmol) and **13** (300 mg, 1.5 mmol) in dry chloromethane (15 mL) was added dropwise a solution of *m*-chloroperoxybenzoic acid (670 mg of 85%, 3.3 mmol) in the same solvent (10 mL). The reaction mixture was stirred for 1 h at 0 °C and 12 h at room temperature, washed with water (15 mL), saturated sodium sulfite solution (2 × 15 mL), saturated sodium bicarbonate solution (2 × 15 mL), and brine (15 mL), dried, and evaporated. The colorless crystalline residue (290 mg) was separated into its components by MPLC on silica gel (elution with ethyl acetate–petroleum ether, 51:49). The melting points reported were determined without further recrystallization.

For **14**: 110 mg (34%); white solid, mp 74 °C; IR (KBr, cm^{-1}) 3020, 2980, 2900, 2830, 1670, 1440, 1420, 1230, 800, 655; ^1H NMR (300 MHz, $CDCl_3$) δ 6.78 (d, J = 10.0 Hz, 1 H), 5.83 (d, J = 10.0 Hz, 1 H), 5.68 (AB system with fine coupling, 2 H), 3.23 (br s, 1 H), 3.16 (br s, 1 H), 2.6–1.5 (series of m, 10 H); m/z calcd (M^+) 216.1151, obsd 216.1192.

For **15**: 26 mg (8%); white solid, mp 90–92 °C; IR (KBr, cm^{-1}) 3020, 2960, 2915, 2895 (sh), 2875 (sh), 2845, 1670, 1425, 1260, 1155, 1090, 1015 (br), 800, 665; ^1H NMR (300 MHz, $CDCl_3$) δ 6.75 (d, J = 10.0 Hz, 1 H), 5.92 (d, J = 10.0 Hz, 1 H), 5.64 (AB system with fine coupling, 2H), 3.29 (t, $J \sim 4$ Hz, 1 H), 3.18 (t, $J \sim 4.4$ Hz, 1 H), 1.8–2.4 (series of m, 10 H); m/z calcd (M^+) 216.1151, obsd 216.1192.

For **16**: 55 mg (16%); white solid, mp 138–140 °C; IR (KBr, cm^{-1}) 3010, 2915, 1670, 1445, 1430, 1415, 1270, 1240, 820, 800, 790, 720; ^1H NMR (300 MHz, $CDCl_3$) δ 6.66 (d, J = 10.0 Hz, 1 H), 5.82 (d, J = 10.0 Hz, 1 H), 3.28 (t, J = 3.6 Hz, 1 H), 3.16 (t, J = 4.3 Hz, 2 H), 3.09 (t, J = 4.3 Hz, 1 H), 2.70–2.2 (m, 3 H), 2.11 (d, J = 16.0 Hz, 1 H), 1.86 (d, J = 16.0 Hz, 1 H), 1.82 (dd, J = 16.0 and 3.7 Hz, 1 H), 1.64 (dd, J = 16.0 and 5.2 Hz, 1 H), 2.00–1.70 (m, 3 H); m/z calcd (M^+) 232.1099, obsd 232.1079.

For **17**: 12 mg (4%); white solid, 179–182 °C; IR (KBr, cm^{-1}) 3050, 3020, 2995, 2920, 1665, 1450, 1425, 1325, 1065, 810, 760, 730, 690; ^1H NMR (300 MHz, $CDCl_3$) δ 6.68 (d, J = 10.0 Hz, 1 H), 5.93 (d, J = 10.0 Hz, 1 H), 3.22 (t, J = 4.2 Hz, 2 H), 3.12 (t, J = 4.2 Hz, 2 H), 2.45 (d, J = 16.0 Hz, 2 H), 2.32 (s, 2 H), 2.18 (d, J = 16.1 Hz, 2 H), 1.81 (dd, J = 16.0 and 4.4 Hz, 2 H), 1.67 (dd, J = 16.0 and 4.4 Hz, 2 H); m/z calcd (M^+ - H_2O) 214.0993, obsd 214.0965.

For **18**: 35 mg (10%); white solid, mp 189–193 °C; IR (KBr, cm^{-1}) 3000, 2920, 1660, 1250, 1240, 970, 830, 820, 800, 770; ^1H NMR (300 MHz, $CDCl_3$) δ 6.65 (d, J = 10.0 Hz, 1 H), 5.81 (d, J = 10.0 Hz, 1 H), 3.22 (br s, 4 H), 2.20–1.50 (series of m, 10 H); m/z calcd (M^+) 232.1099, obsd 232.1064.

6,7,10,11-Tetrabromo[4.4.4]propell-3-en-2-one (19). A cold (−78 °C), magnetically stirred solution of **13** (500 mg, 2.5 mmol) in dry dichloromethane (80 mL, distilled from phosphorus pentoxide) was treated dropwise under a nitrogen atmosphere with bromine (840 mg, 5.25 mmol) dissolved in the same solvent (5 mL). The reaction mixture was stirred for 5 h at −78 °C and poured into a solution of sodium sulfite (200 mg) in water (20 mL). The layers were separated and the aqueous phase was extracted with dichloromethane (2 × 10 mL). The combined organic layers were washed with saturated sodium bicarbonate solution, dried, and freed of solvent. There was obtained 1.28 g (98%) of **19** as a highly insoluble white powder. Washing of this solid with chloroform (3×) gave material melting at 217–218 °C: IR (KBr, cm^{-1}) 2938, 1670, 1453, 1113, 1064, 765, 695, 618, 550; ^1H NMR (200 MHz, $CD_2Cl_2/CDCl_3$, 3:1) δ 6.88 (d, J = 10.2 Hz, 1 H), 5.91 (d, J = 10.2 Hz, 1 H), 5.0–4.0 (br m, 4 H), 3.7 (m, 1 H), 3.2–1.3 (series of m, 9 H); m/z (M^+) 522.8017, 520.8047, 518.8017.

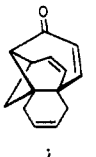
Dehydrobromination of 19. Tetracyclo[4.4.4.0^{1,6}.0^{5,8}]tetradeca-2,9,11,13-tetraen-4-one (21). To a cold (−30 °C), magnetically stirred solution of **19** (2.6 g, 5.0 mmol) in freshly distilled (from CaH_2) dimethylformamide (90 mL) was added dropwise under nitrogen during 10 min a solution of freshly sublimed potassium *tert*-butoxide (4.90 g, 44.7 mmol) in the same solvent 90 mL). The deep orange reaction mixture was stirred at −25 to −30 °C for 3 h, poured into a rapidly stirred 1 M sodium hydroxide solution, and extracted with ether (3 × 75 mL). The combined organic layers were washed with water (4×), dried, and evaporated. The resulting brown-yellow semisolid was purified by HPLC on silica gel (elution with petroleum ether–ethyl acetate, 80:20). The most rapidly eluted substance proved to be **22** (51 mg): colorless needles; mp 69–70 °C (from *n*-pentane at −78 °C); IR (KBr, cm^{-1}) 3030, 3020, 2975, 1700, 1388, 1360, 1207, 1057, 923, 730; ^1H NMR (300 MHz, $CDCl_3$) δ 6.39 (dd, J = 8.5 and 6.3 Hz, 1 H), 5.94–5.77 (m, 4 H), 5.55 (d, J = 9.2 Hz, 1 H), 4.26 (dd, J = 9.6 and 6.3 Hz, 1 H), 2.79 (m, 1 H), 2.66 (d, J = 6.2 Hz, 1 H), 2.59 (dd, J = 6.3 and 1.1 Hz, 1 H), 2.31 (ddd, J = 18.5, 8.8, and 1.1 Hz, 1 H), 1.77 (d, J = 8.2 Hz, 1 H), 1.61 (dd, J = 8.2 and 5.3 Hz, 1 H), 1.00 (s, 9 H); ^{13}C NMR ($CDCl_3$) 210.62 (s), 135.37 (d), 132.37 (d), 131.86 (d), 127.51 (d), 122.98 (d), 122.72 (d), 73.92 (s), 67.98 (d), 54.50 (d), 49.07 (t), 46.96 (s), 45.17 (s), 37.63 (d), 35.84 (t), 28.88 ppm (q, 3 C).

Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 79.71; H, 8.11.

Next to be eluted was **21** (556 mg, 55%): colorless crystals; mp 140 °C (from *n*-pentane); IR (KBr, cm^{-1}) 3040, 3020, 2980, 2940, 1665, 1372, 1240, 1215, 1140, 1094, 845, 802, 763, 728, 705; UV (cyclohexane, λ_{max}) 358 nm (ϵ 57), 260 (4160), 221 (sh, 6265); ^1H NMR (300 MHz, $CDCl_3$) δ 6.98 (d, J = 9.7 Hz, 1 H), 6.29–6.22 (m, 2 H), 6.07 (dd, J = 9.5 and 5.1 Hz, 1 H), 5.88–5.82 (m, 2 H), 5.76 (d, J = 8.4 Hz, 1 H), 5.60 (d, J = 9.5 Hz, 1 H), 3.13 (m, 1 H), 2.95 (d, J = 6.3 Hz, 1 H), 1.83 (dd, J = 8.4 and 5.2 Hz, 1 H), 1.74 (d, J = 8.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) 196.18 (s), 158.65 (d), 133.26 (d), 132.94 (d), 132.43 (d), 130.73 (d), 128.53 (d), 124.66 (d), 122.97 (d), 54.20 (d), 46.89 (s), 44.08 (s), 37.79 (d), 37.28 ppm (t); m/z calcd (M^+) 196.0888, obsd 196.0881.

Anal. Calcd for $C_{14}H_{12}O$: C, 85.68; H, 6.16. Found: C, 85.20; H, 6.26.

On occasion, small quantities of i could also be found.[24] Structural assignment is based upon spectral comparison with **21**: IR ($CDCl_3$, cm^{-1}) 3025, 2930, 1664, 1220, 1135; ^1H NMR (300 MHz, $CDCl_3$) δ 7.13 (d,



i

J = 9.6 Hz, 1 H), 6.14 (dd, J = 9.6 and 0.9 Hz, 1 H), 6.07 (dd, J = 8.4 and 6.5 Hz, 1 H), 5.71 (m, 1 H), 5.61 (m, 1 H), 5.49 (d, J = 8.5 Hz, 1 H), 3.09 (m, 1 H), 2.63 (d, J = 6.6 Hz, 1 H), 2.40–2.14 (m, 3 H), 1.93 (m, 1 H), 1.91 (dd, J = 8.4 and 5.35 Hz, 1 H), 1.67 (d, J = 8.4 Hz, 1 H); m/z calcd (M^+) 198.1045, obsd 198.0999.

Ketalization of 19. A solution of **19** (2.0 g, 0.01 mmol), ethylene glycol (8 mL), and *p*-toluenesulfonic acid monohydrate (400 mg) in benzene (250 mL) was heated at reflux for 20 h under a Dean-Stark trap. The cooled reaction mixture was diluted with ether (250 mL) and poured

into saturated sodium bicarbonate solution. The aqueous phase was extracted with ether (3 × 40 mL) and the combined organic layers were washed with saturated sodium bicarbonate solution (2×) and brine (2×) prior to drying. There was isolated 2.17 g (100%) of **24** as a colorless solid, mp 183–185 °C, which exhibited an unusual sensitivity to traces of acid or water: IR ($CDCl_3$ cm^{-1}) 2950, 2890, 1450, 1420, 1320, 1260, 1205, 1185, 1170, 1135, 1120, 1060, 1020, 940, 765; ^1H NMR (300 MHz, $CDCl_3$) δ 5.86 (d, J = 10.2 Hz, 1 H), 5.48 (d, J = 10.2 Hz, 1 H), 4.7–4.4 (br m, 2 H), 4.4–4.0 (br m, 2 H), 3.95 (br s, 4 H), 3.6–1.3 (series of m, 10 H); m/z calcd (M^+) 561.7999, obsd 561.7924. The above spectra were obtained by rapid scanning since deketalization is complete in ca. 1 h at −20 °C even after filtration of the $CDCl_3$ through basic alumina.

Anal. Calcd for $C_{16}H_{18}Br_4O_2$: C, 34.08; H, 3.57. Found: C, 34.49; H, 3.90.

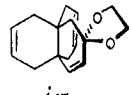
Partial or Complete Debromination of 24. (A) Reduction with LiF and Li_2CO_3 in HMPA. A mixture of **24** (564 mg, 1.0 mmol), lithium fluoride (260 mg, 10.0 mmol), lithium carbonate (739 mg, 10.0 mmol), and powdered soft glass (100 mg) was allowed to stand in a desiccator over silica gel at high vacuum for 12 h. Hexamethylphosphoramide (15 mL) was directly distilled from calcium hydride into the flask under a dry nitrogen atmosphere. The magnetically stirred suspension was heated at 60–65 °C for 20 h, cooled, poured into water (50 mL), and extracted with ether (6 × 50 mL). The combined organic layers were washed with water (4 × 20 mL) and brine (20 mL), dried, and evaporated. MPLC of the residual pale yellow solid (495 mg) on silica gel (elution with 8% ethyl acetate in petroleum ether) afforded 290 mg (72%) of ii as a colorless solid: mp 150–151 °C; IR ($CDCl_3$, cm^{-1}) 3030, 2960, 2895, 1145, 1120, 1102, 1070, 950; ^1H NMR (90 MHz, $CDCl_3$) δ 5.50 (m, 4 H), 4.4–4.2 (m, 2 H), 3.90 (m, 4 H), 3.0–1.2 (series of m, 10 H); ^{13}C NMR ($CDCl_3$) 140.36, 126.96, 125.76, 122.37, 101.52, 64.86, 63.93, 54.58, 53.81, 45.94, 45.67, 45.06, 40.53, 37.46, 33.36, 33.25 ppm; m/z calcd (M^+) 403.9809, obsd 403.9784.

ii

iii

Deketalization of ii to ketone iii takes place slowly in $CDCl_3$ if it is not rigorously dried: IR ($CDCl_3$, cm^{-1}) 3030, 2905, 1670, 1165; ^1H NMR (300 MHz, $CDCl_3$) δ 6.55 (d, J = 10.5 Hz, 1 H), 5.95 (d, J = 10.5 Hz, 1 H), 5.70 (m, $J_{AB} \sim 9$ Hz, 1 H), 5.57 (m, $J_{AB} \sim 9$ Hz, 1 H), 4.40–4.25 (m, 2 H), 2.90 (d, J = 16.5 Hz, 1 H), 2.58 (d of extet, J = 18 and 1.5 Hz, 1 H), 2.4–1.9 (m, 7 H), 1.72 (br d, J = 18 Hz, 1 H); ^{13}C NMR ($CDCl_3$) 197.76, 157.52, 129.20, 125.71, 123.46, 53.43, 52.44, 45.01, 44.68, 44.52, 40.53, 38.94, 35.06, 32.65 ppm.

(B) Reaction with Lithium 2,2,6,6-Tetramethylpiperidide. A magnetically stirred solution of 2,2,6,6-tetramethylpiperidine (2.82 g, 20 mmol) in cold (0 °C) anhydrous tetrahydrofuran was treated under nitrogen with 12 mL of 1.6 M n-butyllithium in ether via syringe. The clear pale yellow solution was stirred at 0 °C for 1 h before cooling to −70 °C. A solution of **24** (564 mg, 1.0 mmol) in dry tetrahydrofuran (10 mL) was syringed into the reaction mixture, which was then allowed to warm slowly to −20 °C. After 1 h at −20 °C and 1 h at room temperature, the solution was poured into 2 M sodium hydroxide solution (100 mL). The aqueous phase was extracted with ether (2 × 30 mL) and the combined organic layers were washed with ice-cold 10% hydrochloric acid (2 × 50 mL) and saturated sodium bicarbonate solution before drying. Solvent evaporation yielded a yellow oil that slowly crystallized. ^1H NMR analysis showed this material to be nearly pure **13** with a trace of its ketal iv (200 mg, 83%). The latter was prepared conventionally from **13** and exhibited the following spectral properties: IR ($CDCl_3$, cm^{-1}) 3020, 2970, 2955, 2895, 2840, 1425, 1130, 1110, 1075,



iv

1060, 1010, 1000; ^1H NMR (90 MHz, $CDCl_3$) δ 5.70 (d, J = 10 Hz, 1 H), 5.46 (s, 4 H), 5.40 (d, J = 10 Hz, 1 H), 3.90 (s, 4 H), 2.6–1.8 (series of m, 10 H); ^{13}C NMR ($CDCl_3$) 142.93 (d), 125.76 (d, 2 C), 125.05 (d), 124.28 (d, 2 C), 106.24 (t), 64.14 (t, 2 C), 42.33 (t), 35.88 (s), 34.51 (t, 2 C), 33.80 ppm (s); m/z calcd (M^+) 244.1463, obsd 244.1465.

[4.4.4]Propella-3,5,7,10-tetraen-2-one Ethylene Ketal (26). A 25.6-g sample of sodium hydride (50% oil dispersion) was placed in a flask and washed 5× with anhydrous tetrahydrofuran. A stirring bar was introduced, followed by a solution of **24** (18.03 g, 32 mmol) in anhydrous tetrahydrofuran (500 mL). The mixture was heated at reflux under argon for 24 h, cooled in a dry ice–isopropyl alcohol bath, and treated dropwise with water (20 mL) while being stirred. The cooling bath was removed, and the mixture was allowed to warm to room temperature. Additional water (30 mL) and pentane (300 mL) were added and the organic phase was separated after a 10-min delay. The aqueous phase was extracted once with ether and the combined organic layers were washed with water (2×), dried, and evaporated. The residual yellow oil (10.1 g) was subjected to MPLC on silica gel (elution with 7% ethyl acetate in petroleum ether) to give 3.49 g (45%) of **26** and 619 mg (8%) of **27**.

For **26**: colorless oil; IR (CCl_4, cm^{-1}) 3025, 2970, 2805, 1655, 1425, 1385, 1315, 1205, 1135, 1115, 1070, 975, 940, 690, 655; UV (cyclohexane, λ_{max}) 262 nm (ϵ 2548); ^1H NMR (300 MHz, C_6D_6) δ 6.02 (d, J = 8 Hz, 1 H), 5.90–5.79 (m, 3 H), 5.74–5.67 (m, 2 H), 5.58 (d, J = 10.0 Hz, 1 H), 5.49 (d, J = 9.1 Hz, 1 H), 3.66–3.61 (m, 4 H), 2.24–2.11 (m, 6 H); ^{13}C NMR (C_6D_6) 139.15, 135.27, 135.11, 126.52, 125.32, 123.90, 121.77, 105.91, 64.20, 40.80, 38.34, 37.19, 36.32, 35.39 ppm; m/z calcd (M^+) 242.1307, obsd 242.1331.

For **27**: colorless solid; mp 63–64 °C (after VPC on 0.25 in × 12 ft 15% SE-30 on Chromosorb G at 175 °C); IR (KBr, cm^{-1}) 3020, 3015, 2950, 2900, 2870, 2810, 1300, 1110, 1055, 715; ^1H NMR (300 MHz, $CDCl_3$) δ 6.23 (ddd, J = 8.0, 5.8, and 1.0 Hz, 1 H), 5.64 (narrow AB, J = 13.5 Hz, 2 H), 5.58 (ddd, J = 8.0, 7.0, and 1.5 Hz, 1 H), 3.99–3.87 (m, 4 H), 2.58 (d, J = 19 Hz, 1 H), 2.47 (d, J = 7.0 Hz, 1 H), 2.05 (d, J = 13.0 Hz, 1 H), 1.91 (br d, J = 19 Hz, 1 H), 1.84 (br d, J = 19 Hz, 1 H), 1.66 (br d, J = 19 Hz, 1 H), 1.62 (d, J = 13.0 Hz, 1 H), 1.62 (dd, J = 6.7 and 5.8 Hz, 1 H), 1.49 (narrow t, J = 1.5 Hz, 1 H), 1.38 (d, J = 6.7 Hz, 1 H); ^{13}C NMR (C_6D_6) 125.76, 120.35, (two trigonal carbons are hidden under the C_6D_6 triplet), 117.01, 64.47, 64.05, 45.94, 45.83, 44.63, 41.18, 28.50, 27.79, 26.65, 25.22, 21.72 ppm; m/z calcd (M^+) 242.1307, obsd 242.1307.

Also isolated was a small amount of an unidentified ketal.

[4.4.4]Propella-3,5,7,10-tetraen-2-one (28). A sample of the ketal mixture from above (4.09 g, 16.9 mmol) was dissolved in acetone (76 mL) and water (8.5 mL). Following the addition of pyridinium tosylate (1.6 g), the flask was flushed with argon, tightly stoppered, and stored at 0 °C for 15 h. The solvent was removed in vacuo (no heat) and the residual was twice triturated with petroleum ether (2 × 10 mL). Filtration and evaporation was followed by MPLC on silica gel (elution with 7% ethyl acetate in petroleum ether). There was isolated 550 mg of **26**, 2.38 g of **28**, and 280 mg of the ketone related to the unknown ketal.

For **28**: colorless oil; IR ($CDCl_3$, cm^{-1}) 3020, 2890, 1670, 1425, 1380, 1260, 1245, 1175, 1155; ^1H NMR (200 MHz, $CDCl_3$) δ 6.47 (d, J = 10.0 Hz, 1 H), 5.95 (d, J = 10.0 Hz, 1 H), 6.06–5.82 (m, 2 H), 5.75 (very narrow AB system, J_{AB} = 12 Hz, 2 H), 5.59 (t, J = 8.3 Hz, 2 H), 2.43 (narrow AB system, J = 16.6 Hz, 2 H), 2.28 (d, J = 16 Hz, 1 H), 2.08 (m, 2 H), 1.85 (d, J = 16 Hz, 1 H); ^{13}C NMR ($CDCl_3$) 199.73, 151.89, 137.68, 132.70, 128.60, 127.95, 125.76, 125.10, 123.35, 45.01, 38.83, 34.95, 34.84 ppm (one C not observed); m/z calcd (M^+) 198.1045, obsd 198.1061.

For the unknown ketone: colorless oil that crystallized on prolonged standing at 0 °C; IR ($CDCl_3$, cm^{-1}) 3025, 2895, 2830, 1670, 1445, 1425, 1410, 1380, 1332, 1262, 1155; ^1H NMR (200 MHz, $CDCl_3$) δ 6.62 (d, J = 10 Hz, 1 H), 5.83 (d, J = 10 Hz, 1 H), 5.81 (m, 1 H), 5.52 (AB, J_{AB} = 12 Hz, 2 H), 2.80–1.40 (series of m, 9 H); ^{13}C NMR ($CDCl_3$) 199.46, 158.73, 128.82, 126.63, 124.99, 124.61, 119.09, 45.83, 44.57, 40.25, 37.03, 35.71, 38.84, 34.35 ppm; m/z calcd (M^+) 198.1045, obsd 198.1079.

Intramolecular Diels–Alder Cyclization of 28. A 25-mg sample of **28** in $CDCl_3$ (0.2 mL) was stored at room temperature for 12 h. Conversion to **29** occurred during this time (56% complete after 5 days): colorless solid; mp 106–107 °C; IR (CCl_4, cm^{-1}) 3020, 2900, 2825, 1750, 1440, 1430, 1410, 1300, 1210, 1200, 1180, 1170, 1150, 1130, 1060, 715, 655; ^1H NMR (300 MHz, C_6D_6) δ 6.32 (ddd, J = 8.0, 6.0, and 1.1 Hz, 1 H), 5.51 (narrow AB with fine triplet coupling, J = 13.5 and 2.1 Hz, 2 H), 5.40 (ddd, J = 8.0, 7.0, and 1.1 Hz), 2.28 (d, J = 17.3 Hz, 1 H), 2.15 (br d, J = 18.8 Hz, 1 H), 2.06 (d, J = 7.0 Hz, 1 H), 1.84 (s, 1 H), 1.81 (dd, J = 18 and 1.5 Hz, 1 H), 1.63 (dd, J = 17.3 and 1.0 Hz, 1 H), 1.55 (br d, J = 18.8 Hz, 1 H), 1.42 (br d, J = 18 Hz, 1 H), 1.38 (dd, J = 6.6 and 6.0 Hz, 1 H), 1.05 (d, J = 6.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) 219.52, 126.49 (2 C), 125.34, 119.08, 50.03, 46.19, 45.04, 40.38, 27.86, 27.16, 26.71, 26.33, 21.66 ppm; m/z (M^+) 198.1045, obsd 198.1092.

Thermal Rearrangement of 21. The thermolysis of **21** was carried out in packed (Carbowax 20M, SE-30, or QF-1) VPC columns in the 130–175 °C range. Under these conditions, **31** and **32** were efficiently produced and separated by preparative VPC at 130 °C (8 ft × 0.25 in. 7% SE-30 on Chromosorb W).

For **31**: colorless crystals; mp 82–83 °C (from ether–pentane at −78 °C); IR (KBr, cm^{-1}) 3080, 2960, 1677, 1465, 1367, 1230, 1000, 932, 890, 880, 795, 780, 760, 735; ^1H NMR (300 MHz, $CDCl_3$) δ 7.48 (dd, J =

9.6 and 6.9 Hz, 1 H), 7.38 (dd, J = 5.1 and 3.3 Hz, 1 H), 7.25 (d, 1 H), 7.15–7.11 (m, 2 H), 5.66 (ddd, J = 17.2, 10.2, and 7.2 Hz, 1 H), 5.51 (dd, J = 9.6 and 1.6 Hz, 1 H), 5.13 (dt, J = 17.2 and 1.2 Hz, 1 H), 5.02 (dd, J = 10.3 and 1.0 Hz, 1 H), 3.78 (br s, 1 H), 3.60 (d, J = 7.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$) 197.75 (s), 154.54 (d), 146.78 (s), 137.74 (s), 137.55 (d), 127.42 (d), 127.17 (d), 126.51 (d), 124.00 (d), 123.50 (d), 117.28 (t), 64.85 (d), 63.64 (d), 48.95 ppm (d); m/z calcd (M^+) 196.0888, obsd 196.0937.

For **32**: colorless crystals; mp 96 °C (from methanol–ether); IR (KBr, cm^{-1}) 3025, 1480, 1430, 1420, 1385, 1235, 1145, 1077, 885, 740, 690; UV (cyclohexane, λ_{max}) 329 nm (ϵ 6240), 241.5 (18 600), 206 sh (14 465); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24–7.07 (m, 4 H), 6.46 (br d, J = 8.6 Hz, 1 H), 6.03 (s, 1 H), 5.95 (m, 1 H), 5.81 (m, 1 H), 5.27 (dt, J = 12.5 and 4.3 Hz, 1 H), 3.28 (t, J = 13.2 Hz, 1 H), 2.61 (dd, J = 13.8 and 4.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$) 152.82 (s), 138.12 (s), 136.91 (d), 134.89 (s), 131.50 (d), 129.20 (d), 128.93 (d), 127.18 (d, 2C), 126.14 (d), 124.39 (d), 115.65 (d), 91.86 (d), 40.91 ppm (t).

Anal. Calcd for $C_{14}H_{12}O$: C, 85.68; H, 6.16. Found: C, 85.54; H, 6.12.

[4.4.4]Propella-3,6,10-trien-2-ol (36). Reduction of **13** (600 mg, 3.0 mmol) with $NaBH_4$ and $CeCl_3$ in the manner described above afforded 580 mg (96%) of **36** as a colorless solid: mp 69–70 °C; IR (KBr, cm^{-1}) 3300 (br), 3020, 2900, 2840, 1427, 1385, 1013, 650; ^{1}H NMR (90 MHz, CCl_4) δ 5.7–5.35 (m, 6 H), 4.5 (br t, 7.5 Hz, 1 H), 2.6–1.3 (series of m, 11 H); m/z calcd (M^+) 184.1252, obsd 184.1218.

[4.4.4]Propella-1,3,6,10-tetraene (37). A solution of **36** (50 mg, 0.25 mmol) in benzene (50 mL) was added dropwise to a solution of freshly prepared Burgess reagent (71.4 mg, 0.3 mmol) in the same solvent (5 mL) at room temperature under a nitrogen atmosphere. The reaction mixture was stirred at 50 °C for 1 h and treated with water (5 mL). The benzene layer was dried and carefully evaporated to provide a colorless oil. Preparative VPC purification (12 ft × 0.25 in. 15% SE-30 on Chromosorb W, 150 °C) of this material gave 42 mg (92%) of pure **37**: IR ($CDCl_3$, cm^{-1}) 3025, 2900, 2840, 1425, 985; UV (cyclohexane, λ_{max}) 267 nm (ϵ 2640); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.81 (AA′ part of AA′BB′ system treated as dd, J = 7.5 and 2.8 Hz, 2 H), 5.61 (s, 4 H, superimposed on BB′ part of AA′BB′ system, 2 H), 1.94 (center of AB′ system, J = 16.5 Hz, 4 H); ^{13}C NMR ($CDCl_3$) 140.77 (2 C), 127.29 (4 C), 123.74 (2 C), 35.82 (2 C), 35.11 ppm (4 C); m/z calcd (M^+) 184.1252, obsd 184.1222.

Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.27; H, 8.90.

[4.4.4]Propella-1,3,6,10-tetraeneiron Tricarbonyl (38). A solution of **37** (1.84 g, 10 mmol) in dry benzene (distilled from CaH_2, 60 mL) was cooled to approximately 0 °C and treated with diiron nonacarbonyl (8.0 g, 22 mmol) in one portion. The suspension was stirred at room temperature under argon for 6 h, treated with an additional quantity of $Fe_2(CO)_9$ (4.0 g, 11 mmol, and stirred for 6 h more. The reaction mixture was filtered through Celite to remove unreacted $Fe_2(CO)_9$ (4.3 g was recovered). The filtrate was evaporated to leave 2.52 g of a deep green-brown solid. Chromatography of this material on silica gel (cyclohexane elution) separated unreacted **37** and product **38** from the more polar $Fe_3(CO)_{12}$. The **37**/**38** mixture was dissolved in n-pentane, filtered to remove small amounts of a brown residue, and cooled at −35 °C for 1 day to give 920 mg of **38**. The mother liquor was concentrated to 10 mL and cooled as before to furnish an additional 230 mg of complex. The free tetraene (760 mg, 42%) was recovered from the mother liquor.

The total amount of **38** (1.15 g) obtained represents a 36% conversion: bright yellow crystals; mp 163–164 °C; IR (CCl_4, cm^{-1}) 3040, 2920, 2030, 1955, 695, 620, 605, 570; UV (cyclohexane, λ_{max}) 280 sh nm (ϵ 3460); ^{1}H NMR (300 MHz, C_6D_6) δ 5.84 (t, J = 3.5 Hz, 2 H), 5.54 (t, J = 3.5 Hz, 2 H), 4.54 (dd, J = 4.7 and 3.1 Hz, 2 H), 2.42 (d, J = 14.2 Hz, 2 H), 2.36 (dd, J = 7.8 and 3.5 Hz, 2 H), 1.94 (d, J = 14.0 Hz, 2 H), 1.60 (d, J = 14.2 Hz, with additional coupling $J \sim 3$ Hz, 2 H), 1.46 (d, J = 14.0 Hz, broadened by fine coupling $J \sim 3$ Hz, 2 H); m/z calcd (M^+ - CO) 296.0499, obsd 296.0507.

Epoxidation of 37. To an ice-cold stirred slurry of **37** (276 mg, 1.5 mmol) and sodium bicarbonate (833 mg, 9.9 mmol) in dry dichloromethane (20 mL) was added dropwise a solution of m-chloroperoxybenzoic acid (672 mg of 85%, 2.2 equiv) in the same solvent (15 mL). The suspension was stirred at 0 °C until **37** had just disappeared (30 min, TLC analysis), at which point it was washed with water (15 mL), saturated sodium sulfite solution (2 × 15 mL), saturated sodium bicarbonate solution (2 × 15 mL), and brine (15 mL). The organic phase was dried and evaporated to leave a residue that was subjected to MPLC on silica gel (elution with 5% ethyl acetate in petroleum ether). The order of elution follows:

40: 26 mg (8.7%); colorless oil that crystallized very slowly after 5 days in vacuo; IR (CCl_4, cm^{-1}) 3025, 2905, 1445, 985, 910, 840, 690, 650; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.85 (dd, J = 7.5 and 2.9 Hz, 2 H), 5.68 (t, J = 1.4 Hz, 2 H), 5.58 (dd, J = 7.5 and 2.9 Hz, 2 H), 3.22 (t, J = 1.2 Hz, 2 H), 2.12 (d, J = 16.4 Hz, 2 H), 1.92 (d, J = 16.4 Hz, 2 H), 1.91 (t, J = 1.3 Hz, 4 H); m/z calcd (M^+) 200.1201, obsd 200.1206.

39: 67 mg (22.3%); colorless solid; mp 84–85 °C; IR (KBr, cm^{-1}) 3025, 3010, 2995, 2940, 2905, 1420, 1000, 990, 800, 690, 660; UV (ethanol, λ_{max}) 263 nm (ϵ 2800); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.82 (dd, J = 7.5 and 2.9 Hz, 2 H), 5.70 (s, 2 H), 5.66 (dd, J = 7.5 and 2.9 Hz, 2 H), 3.13 (s, 2 H), 1.95 (s, J = 16.3 Hz, 2 H), 1.89 (s, 4 H), 1.81 (d, J = 16.3 Hz, 2 H); m/z calcd (M^+) 200.1201, obsd 200.1203.

41: 20 mg (5%); low-melting colorless solid; IR (KBr, cm^{-1}) 3020, 2980, 2910, 2850, 1425, 1000, 985, 880, 825, 812, 790, 740, 680; UV (cyclohexane, λ_{max}) 264.5 nm (ϵ 3480); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.81 (dd, J = 7.5 and 2.9 Hz, 2 H), 5.59 (dd, J = 7.5 and 2.9 Hz, 2 H), 3.18 (s with fine coupling, $J \sim 1.3$ Hz, 2 H), 3.08 (dd, J = 2.8 and 0.7 Hz, 2 H), 2.08 (dd, J = 15.6 and 2.8 Hz, 2 H), 1.83 (d, J = 1.2 Hz, 4 H), 1.73 (d, J = 15.6 Hz, 2 H); m/z calcd (M^+) 216.1150, obsd 216.1106.

Intramolecular Base-Promoted Ring Opening of 39. To a cold (0 °C) solution of lithium diisopropylamide [from 0.7 mL of 1.6 M n-butyllithium in hexane and 101 mg (1.0 mmol) of diisopropylamine in 1.5 mL of anhydrous ether] was added 358 mg (2 mmol) of hexamethylphosphoramide (freshly distilled from CaH_2) via syringe. The previously colorless solution immediately became yellow. The reaction mixture was heated at 100 °C for 5 min and the volatile solvents were removed in a stream of argon. A solution of **39** (67 mg, 0.3 mmol) in HMPA (4 mL) was added at room temperature. After 1 h of stirring at 20 °C, hydrolysis was achieved by the addition of saturated ammonium chloride solution (15 mL). The resulting solution was extracted with ether (5 × 10 mL) and the combined organic layers were washed with ice-cold 1 N hydrochloric acid solution (2×), saturated sodium bicarbonate solution, and brine. Drying and solvent evaporation gave 63.1 mg, (94%) of a mixture of **42** and **43** as a colorless semisolid. Their separation was achieved by MPLC on silica gel (elution with 20% ethyl acetate in petroleum ether). There was isolated 41.3 mg (61.7%) of **42** and 8.7 mg (13%) of **43**.

For **42**: colorless solid, mp 65–66 °C; IR (KBr, cm^{-1}) 3300, 3020, 2945, 2925, 2900, 1135, 1045, 675; UV (cyclohexane, λ_{max}) 270 nm (ϵ 2710); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.98–5.93 (m, 2 H), 5.84–5.75 (m, 4 H), 4.19–4.15 (m, 1 H), 2.43–2.40 (m, 2 H), 2.12–2.00 (m, 3 H), 1.74–1.40 (m, 4 H); ^{13}C NMR ($CDCl_3$) 136.31, 132.70, 130.24, 127.18, 125.32, 124.01, 72.02, 54.74, 49.44, 45.34, 43.59, 40.96, 34.46, 26.42 ppm; m/z calcd (M^+) 200.1201, obsd 200.1212.

For **43**: colorless solid; mp 67–68 °C; IR (KBr, cm^{-1}) 3320, 3020, 2935, 2900, 1020, 695; UV (cyclohexane, λ_{max}) 271 nm (ϵ 2425); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.95 (dd, J = 10.2 and 4.5 Hz, 1 H), 5.70 (superimposed dd, J = 7.8 and 3.0 Hz, and J = 7.3 and 2.6 Hz, total 2 H), 5.61 (dt, J = 10.2 and 5.0 Hz, 1 H), 5.54 (dd, J = 7.8 and 2.6 Hz, 1 H), 5.44 (dd, J = 7.3 and 3.0 Hz, 1 H), 4.29 (t, J = 5.6 Hz, 1 H), 2.61 (t, J = 4.5 Hz, 1 H), 2.30 (d, J = 10.2 Hz, 1 H), 2.27–2.22 (m, 2 H), 2.00 (dd, J = 13.9 and 7.6 Hz, 1 H), 1.84 (ddd, J = 13.9, 7.9, and 1.7 Hz, 1 H), 1.65 (dd, J = 17.5 and 5.9 Hz, 1 H), 1.58 (s, 1 H), 1.35 (dd, J = 10.2 and 5.6 Hz, 1 H); m/z calcd (M^+) 182.1095, obsd 182.1109.

[4.4.4]Propella-1,3,5,10-tetraen-7-ol (44). Freshly purified **28** (2.38 g, 12.0 mmol) was immediately dissolved in anhydrous methanol (200 mL), cooled to −5 °C, and treated with 3.33 g of cerium trichloride. This mixture was stirred under argon for 20 min and sodium borohydride (1.0 g) was added in small portions over 10 min. Stirring was continued for 15 min, at which point the reaction mixture was poured in cold (0 °C) 1 N sodium hydroxide solution (200 mL) and agitated for a final 15 min. The solution was filtered through Celite, and the filter cake was rinsed with ether (200 mL). The aqueous phase was extracted with ether (3 × 100 mL), and the combined organic layers were washed with water and brine, dried, and evaporated. There was obtained 2.23 g (92.8%) of a 3:1 mixture of the two epimers of **44** as a colorless solid: mp 91–93 °C; IR (KBr, cm^{-1}) 3280, 3015, 2955, 2935, 2905, 2885, 1425, 1257, 1055, 1012, 980, 795, 740, 690, 655; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.96–5.40 (m, 8 H), 4.51 (t, J = 3 Hz, carbinol proton of major epimer), 4.23 (br s, carbinol proton of minor isomer, intensity ratio = 1.1:0.4), 2.8 (very narrow AB system), 2.03–1.70 (m, 4 H), 1.45 (br s, 1 H); m/z calcd (M^+) 200.1201, obsd 200.1220.

The epimers were shown to be separable by MPLC on silica gel (elution with 15% ethyl acetate in petroleum ether), but was not carried out on a preparative scale.

[4.4.4]Propella-1,3,5,7,10-pentaene (8). The epimeric mixture of tetraenols **44** (2.23 g, 11.1 mmol) was dissolved in dry benzene (150 mL) and added dropwise at room temperature under argon to a stirred solution of Burgess reagent (3.20 g) in the same solvent (200 mL). The reaction mixture was heated at 50 °C for 16 h, the solvent was removed in vacuo, and the residue was partitioned between water and petroleum ether. The dried organic phase was concentrated and subjected to MPLC

on silica gel (elution with petroleum ether). There was isolated 110 mg (4.6%) of tetraene **37** and 546 mg of pentaene **8**: colorless oil; IR (CCl_4, cm^{-1}) 3025, 2895, 1428, 1175, 975, 910, 712, 688, 675, 648; UV (cyclohexane, λ_{max}) 250 nm (ϵ 10010); ^1H NMR (200 MHz, $CDCl_3$) δ 5.91 (dd, J = 7.5 and 2.9 Hz, 4 H), 5.84 (t, J = 1.4 Hz, 2 H), 5.48 (dd, J = 7.5 and 2.9 Hz, 4 H), 2.09 (d, J = 1.4 Hz, 4 H); ^{13}C NMR ($CDCl_3$) 134.56 (4 C), 128.66 (2 C), 123.96 (4 C), 38.07 (2 C), 35.61 ppm (2 C); m/z calcd (M^+) 182.1096, obsd 182.1093.

Shapiro Degradation of 45. A solution of **29** (780 mg, 3.94 mmol) and *p*-toluenesulfonylhydrazide (790 mg, 4.2 mmol) in methanol (50 mL) containing 2 drops of concentrated hydrochloric acid was stirred at room temperature for 24 h. The solvent was removed in vacuo at 20 °C to deliver **45** as a pale yellow solid. A suspension of the unpurified tosylhydrazone in ether (100 mL) was cooled to −60 °C under nitrogen and treated with methyllithium (13 mL of 1.6 M in ether, 20.8 mmol). The reaction mixture was stirred at −60 °C for 30 min, allowed to warm to room temperature, and stirred for an additional 7 h. Water (40 mL) was added and the products were extracted into ether (3×). The combined organic layers were dried and carefully evaporated to leave an oily residue that was subjected to MPLC on silica gel (petroleum ether elution). There was isolated 350 mg of **46**, 25 mg of **8**, and 15 mg of an unidentified hydrocarbon.

For **46**: ^1H NMR (300 MHz, $CDCl_3$) δ 6.63 (dd, J = 5.4 and 3.1 Hz, 1 H), 6.49 (d, J = 5.4 Hz, 1 H), 6.48 (m, 1 H), 5.76 (dt, J = 7.2 and 2.0 Hz, 1 H), 5.71 (d, J = 2.4 Hz, 2 H), 2.46–2.32 (m, 3 H), 2.03 (dt, J = 18.1 and 2.4 Hz, 1 H), 1.94–1.86 (m, 2 H), 1.74 (d, J = 18.9 Hz, 1 H), 1.48 (d, J = 6.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) 147.08, 140.74, 127.73, 126.85 (2 C), 124.99, 59.77, 49.16, 41.62, 40.20, 36.59, 33.97, 29.54, 25.11 ppm; m/z calcd (M^+) 182.1084, obsd 182.1094.

Kinetic Measurements. In each case, the compound was dissolved in chlorobenzene-d_5 and sealed under vacuum in an NMR tube after several freeze–thaw cycles. The tubes were heated at 160 °C for **37** and at 95 °C for **8**. The rate of reaction was determined with a Bruker WP-300 instrument. The tetraene did not react measurably after being heated for 90 h. Assuming first-order decomposition and a detection limit of much less than 5% reaction, the actual rate constant must be less than the value shown below:

$$\ln (100/95) = kt;\ k < 1.58 \times 10^{-7}\ s$$

The pentaene underwent smooth retro-Diels–Alder reaction at 95 °C. No internal standard was used and the assumption was made that only the relative proportions of pentaene and naphthalene (+ butadiene) changed with time. The data adhere well to first-order kinetics with k = 1.67×10^{-4} s (r = 0.997).

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Dual Generation of the [4.4.4]Propella-2,4,7,9,11-pentaenyl Cation. Its Threefold Wagner–Meerwein Rearrangement Cascade Leading to 4a,7-Dihydropleiadiene

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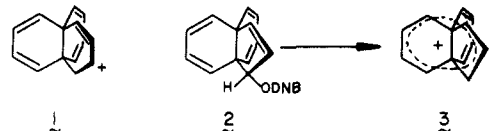
Abstract: On treatment with diphenylbis(1,1,1,3,3,3-hexafluoro-2-phenyl-2-propoxy)sulfurane, tetracyclo[4.4.4.$0^{1,6}$,$0^{5,8}$]tetradeca-2,9,11,13-tetraen-4-ol (**5a**) is transformed via a deep-seated carbocation rearrangement cascade into 4a,7-dihydropleiadiene (**6a**). The structure of the hydrocarbon product was unraveled by a series of 2-D NMR experiments including the INADEQUATE technique. When the *4-d* derivative of **5a** was comparably dehydrated, the isotopic label was found uniquely at position 2. Because of the suspected intermediacy of the [4.4.4]propella-2,4,7,9,11-pentaenyl cation (**1**), [4.4.4]propella-2,4,7,9,11-pentaen-13-ol (**10**) was also prepared. When heated with the Burgess reagent, **10** also furnished **6a**. The relationship of these observations to the topography of polyunsaturated propellanes of this type is discussed. Most relevantly, the barrier to ring flipping within **1** is sufficiently high that enantiomerism cannot occur by this mechanism. As a result, **1** maintains its dissymmetry, only one of the flanking cyclohexadiene rings finds it stereoelectronically feasible to undertake Wagner–Meerwein migration, and the deuterium label is not dissipated to more than one site. These results provide unusual insight into a chemical phenomenon that has appealing future prospects.

As part of a study of cationic delocalization within polyunsaturated propellanes, we have presently examined two methods for generation of the [4.4.4]propella-2,4,7,9,11-pentaenyl cation (**1**), the largest such system currently known. The chemical properties of **1** have been found to contrast remarkably with those of its lower homologue **3**, which we have recently shown to arise from **2** with anchimeric assistance and to possess bishomotropylium ion character.[2] Relevantly, **3** is resistant to structural isomeri-



1 **2** **3**

zation and gives rise only to unrearranged solvolysis products. This striking kinetic stability is quite uncharacteristic of longicyclic carbocations to which **1** is apparently more closely related.[3] Of complementary mechanistic significance is the cascade of migratory rearrangements to which **1** is subject that eventuates in formation of 4a,7-dihydropleiadiene (**6**). Most significantly, the propeller-shaped **1** has been found capable of maintaining its dissymmetry during the course of chemical events that lead to **6**.

Results

The Cyclobuta[*d*]naphthalenol Approach. The preparation of ketone **4** has been previously described.[4] When this substance

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