On the Electronic Character of Progressively Unsaturated [4.4.3]Propellanyl Cations under Long- and Short-Life Conditions

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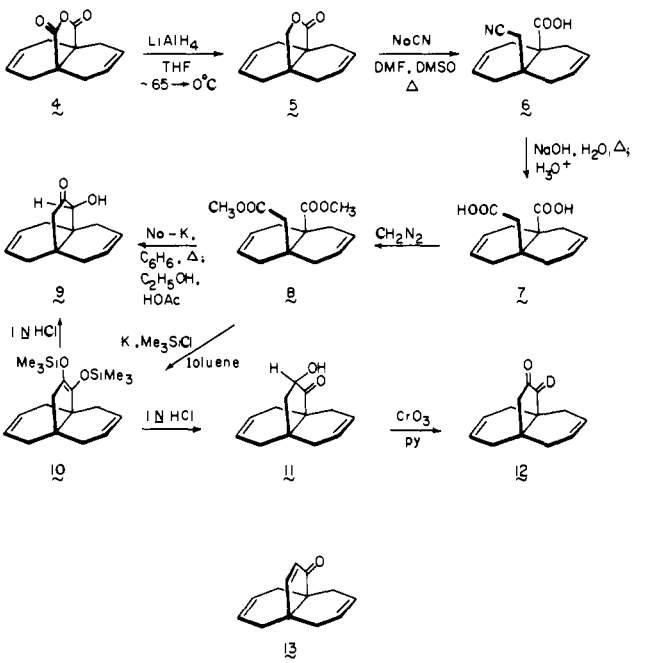
Abstract: Preparation of the four progressively unsaturated [4.4.3]propellanyl 3,5-dinitrobenzoates **36c–38c** and **46c** is described. Their solvolysis in 80% aqueous acetone proceeds with clean first-order kinetics and with a relative rate spread of 39:0.4:1:7.8, respectively, at 75 °C. Methanolysis experiments showed alkyl–oxygen cleavage to be occurring in each of the examples. Product studies revealed that all systems retain their tricyclic structural features during the conversion to their carbocations. Consequently, it follows that both **36c** and **46c** ionize with anchimeric assistance in the form of bishomotropylium ion formation. The reduced rate for **46c**, which is attributed to adverse inductive effects, rules out the possibility of longicyclic stabilization, at least under short-life conditions. Our findings show that **52**-H^+ also does not profit from longicyclic charge delocalization under long-life conditions.

Early research in organic chemistry identified a phenomenon termed "aromatic character" which in the late 1930's was fashioned by Hückel into a nicely comprehensive MO model.[2] During the years following upon this classic development, observations made in conjunction with certain cationic systems[3] suggested to Winstein[4] that interruption of otherwise continuous $(4n + 2)\pi$ cyclic conjugation need not be destructive of delocalization. Such *two-dimensional* charge stabilization, termed homoaromaticity, initially elicited a great deal of interest.[5] Our scrutiny of all aspects of this phenomenon in 1978 resulted in an urging of restraint with regard to possible overinterpretation of existing data.[6] As matters have turned out, more recent opinion has become unsupportive of the existence of homoaromaticity in neutral molecules[7] and carbanions.[8]

Scheme I



During the same period, Goldstein and Hoffmann proposed for consideration the ingenious possibility that ribbons of π orbitals arranged in proper *three-dimensional* array might also be capable of (longicyclic) stabilization.[9] These authors distinguished four types of longicyclic systems, categorized on the basis of the number to π electrons in each ribbon ($4n + 2 = 2$; $4n = 0$): (0,0,0), (2,0,0), (2,2,0), and (2,2,2). Of these, (2,0,0) was viewed as stabilized but not bicycloaromatic, while only (2,2,0) was considered bicycloaromatic. The remaining two types were assumed to have no stabilization. These designations were made in comparison with a corresponding two-ribbon longicyclic system having an equal number of π electrons, with all other factors being somehow kept constant. The (2,2,0) system, with $4n\pi$ electrons, benefitted by its comparison to a bishomoantiaromatic model.

As access has been gained to certain of the more fundamental variants of these orbital topologies, a less than clear-cut picutre has evolved. Certainly, the propensity of the 2-bicyclo[3.2.2]-

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(7) Houk, K. N.; Gandour, R. W.; Strozier, R. W.; Rondan, N. G.; Paquette, L. A. *J. Am. Chem. Soc.* **1979**, *101*, 6797.

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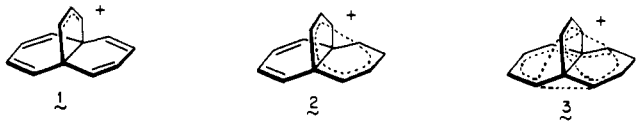
nonatrienylium cation, the only known (2,2,2), for structural rearrangement[10] and the failure to observe longicyclic stabilization in several (2,2,0) examples [the bicyclo[4.3.2]undecatetraenylium cation,[11] 9-bicyclo[4.2.1]nona-2,4,7-trienly anion,[12] and 2-bicyclo[3.3.2]nonatrienyl anion[10c,13]] might be viewed as encouraging. However, the properties of the three known (2,0,0) species [the 9-bicyclo[4.2.1]nona-2,4,7-trienyl anion,[14] bicyclo[4.3.2]undecatetraenyl anion,[15] and bicyclo[3.3.2]decatrienyl dianion[16]] have caused us to question the validity of the longicyclic stabilization rule.

For these reasons, additional studies of select (2,0,0) carbocationic systems appeared warranted. A particularly attractive candidate was the $4^0 4^0 3^+$ cation which fulfills the requirement that the ribbon containing the empty p orbital lie proximate and central to the pair of high-lying occupied π ribbons. Particularly, noteworthy is the fact that this species may adopt ordinary allylic character as in **1**, take on a bishomoaromatic nature as in **2**, or command interaction among all three bridges as in **3** and truly avail itself of longicyclic stabilization. Herein we detail our efforts

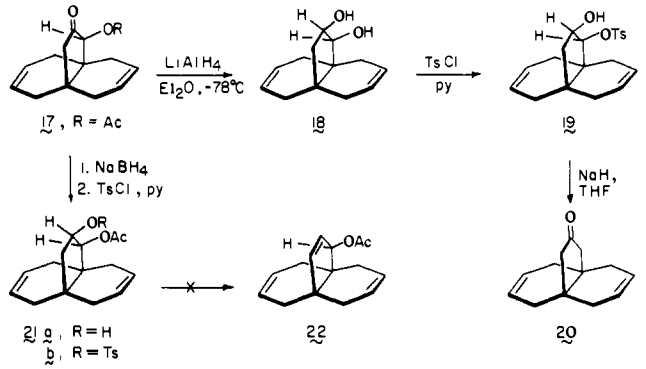


to elucidate the behavior of tricyclo[4.4.3.0^{1,6}]tridecapentaenyl and related tricyclo[4.4.3.0^{1,6}]trideca-2,4,11-trienyl cations in order to provide insight into the relative merits of 2π3C (allylic), 6π9C (bishomoaromatic), and 10π13C (longicyclic) stabilization within this propellane derivative.[17] To our knowledge, **46** and **52** represent the largest fully unsaturated propellanes yet reported.

Synthesis

Early Probes of Methods for Installing the Unsaturated Five-Membered Ring. From the outset, we considered it necessary to take into account the possibility that functional group manipulation within the five-membered ring of a [4.4.3]propellapentaene might result in ready loss of the three-carbon fragment and formation of naphthalene.[18] Consequently, incorporation of a high level of useful functionality into the cyclopentane subunit as early as possible and prior to elaboration of the flanking cyclohexadiene rings was considered desirable. To this end, anhydride **4**[19] was first converted to lactone **5** by controlled lithium aluminum hydride reduction[20,21] (Scheme I). Homologation to diester **8** was predicated chiefly upon the efficient ring opening of **5** with sodium cyanide in a hot dimethylformamide–dimethyl sulfoxide solvent system.[22] Initial acyloin cyclization studies on **8** were conducted in refluxing benzene solution with 1:1 sodium–potassium alloy.[23] It was hoped that a reasonable proportion of the product would be the 12-hydroxy 11-ketone **11** which was to serve as precursor to target trienone **13**. However, the single pure compound that was isolated (89% yield) proved instead to be **9**. Its structural identity, suggested initially by appearance of the carbinol proton as a singlet, was confirmed by reduction to the known[4.4.3]-propella-3,8-dien-12-one (**20**)[24] and several other chemical transformations that are described below. The *apparently exclusive* formation of **9** is considered to be an artifact of the workup procedure, the relatively long time required for decomposition of the excess Na–K with ethanol fostering base-catalyzed equilibration.[25] The reasons underlying the thermodynamic preference of **9** are unclear but may have their origin in steric and angle strain effects.

Scheme II



When the acyloin cyclization of **8** was modified so as to involve potassium metal in hot toluene containing chlorotrimethylsilane,[26] bis((trimethylsilyl)oxy) derivative **10** was readily formed. Upon acidic hydrolysis, an 80:20 distribution of **9** and **11** (^{1}H NMR analysis) was realized. In view of this development, the mixture of acyloins was oxidized[27] to α-diketone **12** in anticipation of subsequently achieving selective reduction of its less hindered carbonyl group. Suitable conditions for returning to **11** were never found. The ultraviolet spectrum of **12** [$\lambda_{max}^{isooctane}$ 465 nm (ϵ 20)] suggests that little, if any, σ/π interaction is operative within this system. This finding stands in marked contrast to the electronic properties of the structurally related cyclobutanedione.[28,29]

An examination of molecular models of [4.4.3]propella-3,8-diene **14** suggested that its hydroxyl and tosylate groups might well be properly aligned for cyclization to epoxide **15**. Were **15** to become available, several methods for its subsequent conversion

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(21) On one occasion after HCl quench of the reaction mixture and workup, a highly crystalline material of generally low solubility was obtained in very high yield and identified as the hydroxy acid: mp 118–119 °C (from chloroform); IR (Nujol, cm^{-1}) 3400, 3000 (very br), 1700; ^{1}H NMR ($CDCl_3$) δ 5.6 (br s, 4 H), 3.43 (s, 2 H), 2.4 (br, 2 OH), 2.0 (m, 8 H); *m/e* ($M^+ - H_2O$) 190. Treatment of this substance with acid afforded **5** quantitatively.

(22) Nerdel, F.; Janowsky, K.; Frank, D. *Tetrahedron Lett.* **1965**, 2979.

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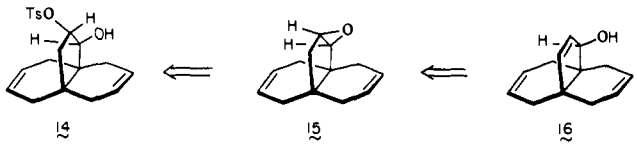
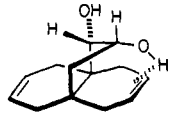


14 15 16

to **16** were to be implemented. In pursuit of this objective, **9** was carefully reduced with lithium aluminum hydride in ether at −70 °C. A single diol was obtained (93%), the ^{1}H NMR spectrum of which showed (following D_2O exchange) the carbinol protons to comprise the AB segment of an ABXY spin system with J_{AB} = 7.5 Hz. It is not possible to decide stereochemistry on this basis since vicinal ^{1}H–^{1}H coupling in five-membered rings is rarely diagnostic. For example, in the indane-1,2-diols, $^{vic}J_{trans}$ and $^{vic}J_{cis}$ differ by only 0.3 Hz.[30] Generally, $^{vic}J_{cis} > {}^{vic}J_{trans}$ in cyclopentane systems, but the enhanced conformational rigidity in **18** and the presence of electronegative functional groups render interpretation hazardous.

Although attempts to form an acetonide proved unsuccessful (likely for steric reasons), **18** was eventually shown to be the cis stereoisomer. Confirmatory evidence was obtained following monotosylation (100% regiospecific) and treatment of **19** with sodium hydride in tetrahydrofuran (Scheme II). Under these conditions, none of the epoxide was formed; instead a substantial amount of ketone **20** was generated. Evidently, **19** first experiences E_2 elimination to the enol, a process which requires a cis relationship between the –OH and –OTs groups. Additionally, the position of the carbonyl group in **20** indicates that the monotosylation of **18** has taken place at the seemingly more hindered neopentyl carbinol site (C_{11}). This result may be dictated by the fact that intramolecular hydrogen bonding of C_{12}–OH within **18** as in **23** flexes the five-membered ring enough to splay the C_{11}–OH



23

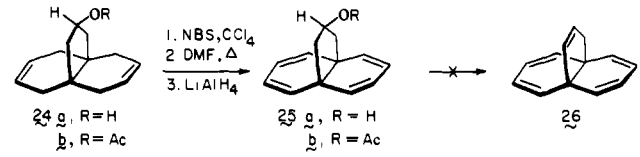
outward to a site where it becomes reasonably accessible. This line of reasoning is highly speculative, however, since the extent of intramolecular hydrogen bonding within **18** in pyridine solution is unknown.

A complementary line of reasoning led to the preparation of acetoxy tosylate **21b**. Unfortunately, a satisfactory means of transforming **21b** to **22** by elimination chemistry was not uncovered.

Consequently, our attention was next turned to pentaene **26**, the intent being to assess the level of fragmentation to naphthalene that might materialize during the requisite allylic functionalization procedure. The secondary carbinol **24a** and acetate **24b** were formed without event, and conversion to tetraenic alcohol **25a** proved unusually efficient (Scheme III). In contrast, the dehydration of **25a** could not be accomplished under a variety of conditions (occasional naphthalene formation), and we therefore returned to our original plan that called for elaboration of an oxygenated five-menbered ring in the earliest possible stages of the synthesis.

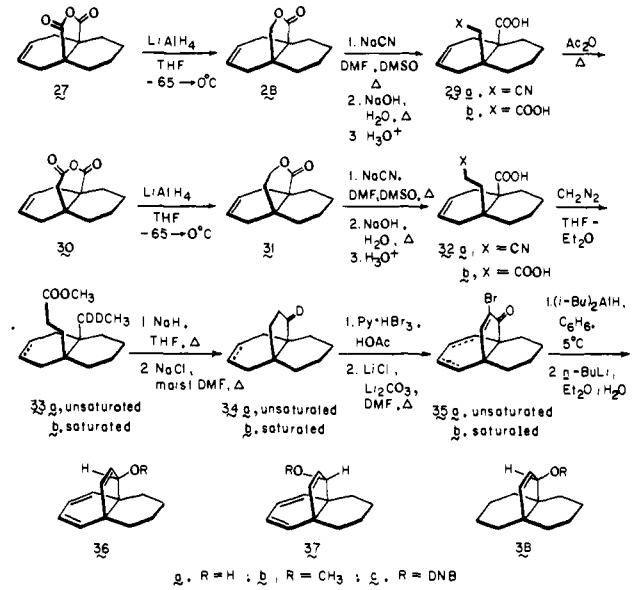
As a final point, the ^{1}H NMR spectrum of **25b** provides an opportunity for deducing the values of $^{vic}J_{cis}$ and $^{vic}J_{trans}$ in the five-membered rings of these polyunsaturated propellanes. While the acetate substituent shields vicinal cis hydrogens, vicinal trans hydrogens are deshielded.[31] Analysis of the resulting AA′BB′X system in **25b** leads to $J_{BX} = J_{B'X}$(trans) = 5.5 Hz and $J_{AX} = J_{A'X}$(cis) = 7.5 Hz. These values are in agreement with existing generalizations and lend additional confirmatory support to the cis stereochemistry of diol **18**.

Scheme III



24 a, R=H; b, R=Ac 25 a, R=H; b, R=Ac 26

Scheme IV



27 28 29 a, X=CN; b, X=COOH 30 31 32 a, X=CN; b, X=COOH 33 a, unsaturated; b, saturated 34 a, unsaturated; b, saturated 35 a, unsaturated; b, saturated 36 37 38

a, R=H; b, R=CH$_3$; c, R=DNB

The Successful Approach to Dienol 38a and the Epimeric Trienols 36a and 37a. Comparable controlled reduction and homologation of anhydride **27**[19] afforded diacid **29b** which was cyclized to **30** with acetic anhydride (Scheme IV). When **30** was treated with lithium aluminum hydride in tetrahydrofuran at −65 → 0 °C, we were pleased to discover that the *less hindered* carbonyl group had been reduced almost exclusively to afford γ-lactone **31** in 97% yield. This regioselectivity runs contrary to existing precedent[20,32] that has recently been carefully scrutinized by Dunitz and co-workers using their elegant comparative X-ray crystal structure analysis approach on crystalline succinimide isosteres.[33] Although the factor(s) responsible for this seemingly anomalous behavior has (have) not been elucidated, the availability of **31** allowed for repetition of the homologation procedure and arrival at diacid **32b**. Dieckmann cyclization of its dimethyl ester (**33a**) afforded the tricyclic ketone **34a**. Crossover to saturated [4.4.3]propellanone **34b** could be achieved by catalytic hydrogenation of any of the intermediates leading to and including **34a**.

All of the available reactive sites in **34a** were now brominated with an excess of pyridinium hydrobromide perbromide. Subsequent treatment with lithium chloride and lithium carbonate in refluxing dimethylformamide resulted not only in elaboration of the cyclohexadiene ring but also in conversion of the α,α-dibromo ketone moiety into a more highly unsaturated α-bromo enone. Thus, by means of this two-step procedure, the carbonyl group and requisite double bonds were efficiently set into place. The remaining task associated with removal of the final bromine atom was accomplished by diisobutylaluminum hydride reduction and halogen–metal exchange in the resulting epimeric allylic alcohols.[34]

Separation of **36a** from **37a** was easily accomplished by medium-pressure liquid chromatography on silica gel. Individual configurational assignments were initially advanced tenuously on

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Table I. Chemical Shift Data for Alcohols 36a–38a, 46a, and Their Derivatives (δ, $CDCl_3$)

series	>C*H*OH	multiplicity[a]	>C*H*OCH$_3$	multiplicity	aryl proton multiplicity in c
36a	4.72	sharp	4.27	triplet (J = 1.5 Hz)	9.36–9.06 (m)
37a	4.04	broad	4.15	singlet	9.43–8.90 (series of m)
38a	4.83	sharp	4.37	singlet	9.30–9.03 (m)
46a	4.61	broad	4.45	triplet (J = 1.5 Hz)	9.46–8.93 (series of m)

[a] The extent of multiplicity is dependent upon the acidity of the medium and varies somewhat from spectrum to spectrum. These factors persist in the bromo alcohols.

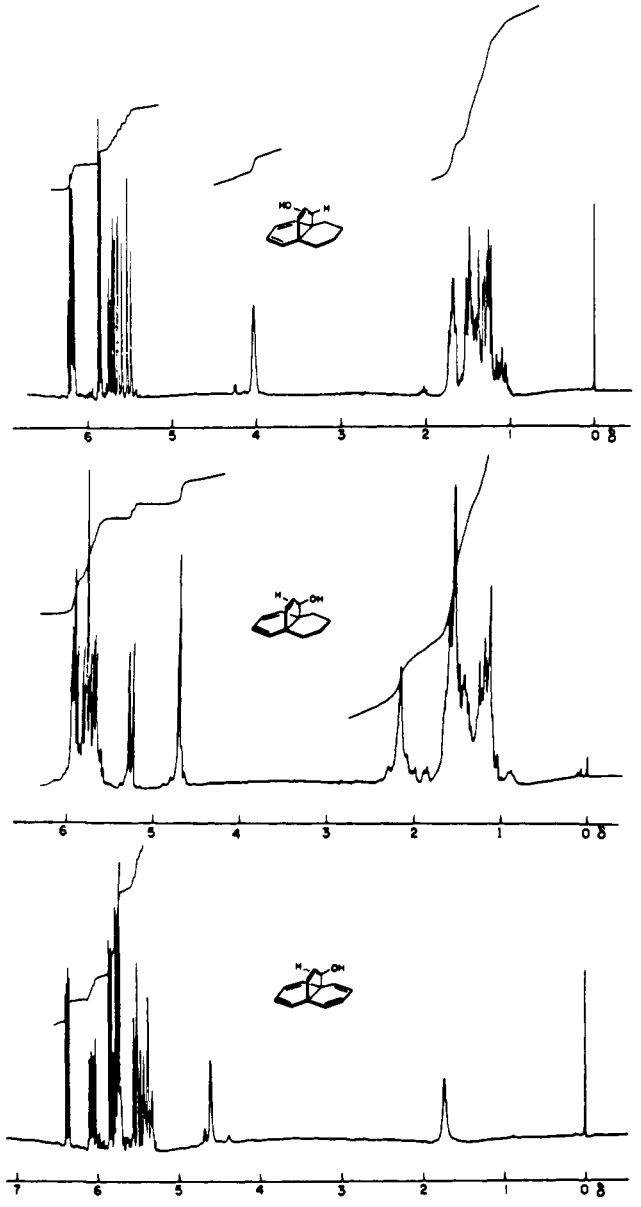


Figure 1. 200-MHz ^{1}H NMR spectra of **36a**, **37a**, and **46a** ($CDCl_3$ solution).

the basis of very distinctive chemical shifts and multiplicity patterns shown by the carbinol protons in the alcohols (Figure 1) and the aryl hydrogens in their 3,5-dinitrobenzoates (Table I). Additional suggestive evidence was derived from sodium borohydride/cerium chloride reduction[35] of ketone **51** (**36a**/**37a** = 3:2 as anticipated from steric approach control), the relative solvolytic behavior of **36c** and **37c**, and product distribution (see below). The ^{1}H NMR spectra displayed in Figure 1 suggest that intramolecular hydrogen bonding to the conjugated diene functionality exists when the –OH group in the alcohols has syn stereochemistry. This property, a consequence of which is enhanced structural rigidity and heightened shielding of the α-

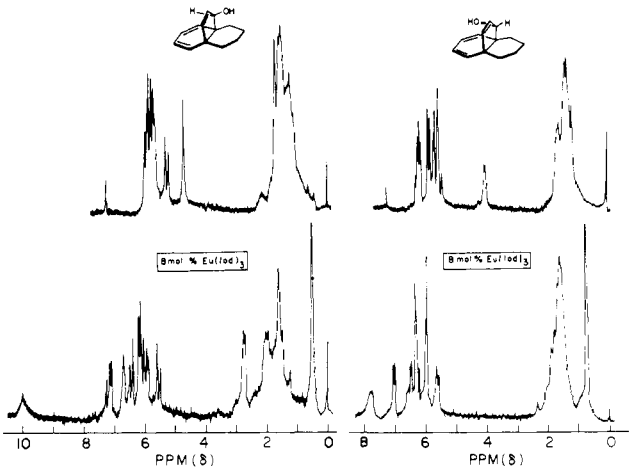
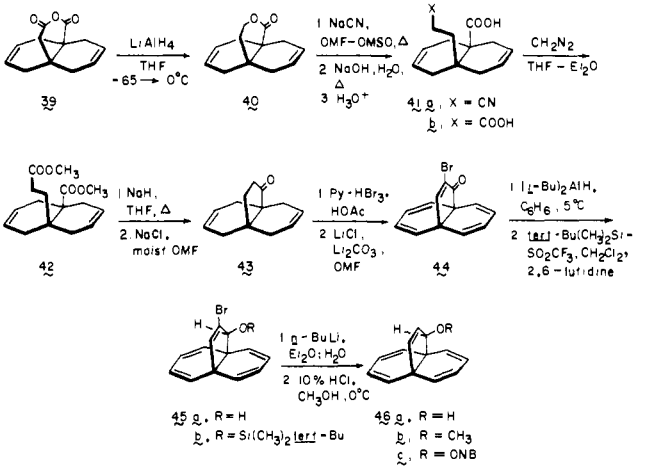


Figure 2. 90-MHz ^{1}H NMR spectra of **36a** and **37a** free of Eu(fod)$_3$ and containing 8 mol % of the shift reagent. The extent to which the aliphatic protons in **36a** are deshielded by the lanthanide already becomes quite apparent at this concentration level.

Scheme V



carbinol proton, has been fully corrobotated by appropriate infrared dilution and lanthanide shift studies (Figure 2). For comparison, the epimeric methyl ethers **36b** and **37b** are seen to exhibit greatly reduced chemical shift differences (Table I).

Entry to the Pentaene System. With the demonstrated feasibility of Scheme IV in hand, we proceeded to convert diacid **7** to its anhydride and to explore the controlled reduction of **39**. As with **30**, the less hindered carbonyl group was the seat of reaction and **40** was produced efficiently (Scheme V). The ensuing multistep conversion of this lactone to bromo pentaenone **44** proved quite satisfactory. However, when the pentaenic bromo alcohol was treated with *n*-butyllithium at 0 °C, naphthalene proved to be the major product. Although the mechanism of this degradation was not investigated, it was found that preliminary blocking of the hydroxyl function with *tert*-butyldimethylsilyl trifluoroacetate[36] effectively minimized fragmentative aromatization during the **45b** → **46a** transformation.

(35) Luche, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 2226.

(36) Corey, E. J.; Cho, H.; Rucker, C.; Hua, D. H. *Tetrahedron Lett.* **1981**, 3455.

Table II. Kinetic Data for 3,5-Dinitrobenzoate Solvolysis in 80% Acetone-Water

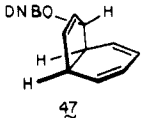
compd	T, °C	k, s⁻¹	corr coeff
36c	40.9	5.24 × 10⁻⁶	0.9991
	41.6	7.32 × 10⁻⁶	0.9923
	50.0	2.15 × 10⁻⁵	0.9937
	50.2	1.71 × 10⁻⁵	0.9983
	60.1	7.93 × 10⁻⁵	0.9987
	60.4	8.67 × 10⁻⁵	0.9975
	84.5	8.69 × 10⁻⁴	0.9888
	75[a]	3.74 × 10⁻⁴	
37c	75[a]	3.89 × 10⁻⁶	
	80.7	8.62 × 10⁻⁶	0.9948
	90.6	2.43 × 10⁻⁵	0.9981
	90.6	2.22 × 10⁻⁵	0.9981
	99.5	8.58 × 10⁻⁵	0.9977
	99.5	7.54 × 10⁻⁵	0.9994
	114.5	4.43 × 10⁻⁴	0.9985
	114.6	3.07 × 10⁻⁴	0.9895
38c	68.7	4.13 × 10⁻⁶	0.9949
	75.0	1.01 × 10⁻⁵	0.9878
	75.1	8.77 × 10⁻⁶	0.9991
	88.1	4.57 × 10⁻⁵	0.9998
	88.2	4.81 × 10⁻⁵	0.9986
	99.3	1.36 × 10⁻⁴	0.9975
	99.5	1.50 × 10⁻⁴	0.9956
	110.0	3.96 × 10⁻⁴	0.9981
46c	42.9	1.51 × 10⁻⁶	0.9987
	61.4	1.94 × 10⁻⁵	0.9990
	61.7	1.51 × 10⁻⁵	0.9988
	75.2	7.43 × 10⁻⁵	0.9997
	75.4	7.27 × 10⁻⁵	0.9961
	85.2	1.62 × 10⁻⁴	0.9985
	85.5	2.01 × 10⁻⁴	0.9977

[a] Extrapolated values based upon the activation parameters.

Solvolysis Studies. The rates of solvolysis of the four 3,5-dinitrobenzoates, determined at four or more temperatures in 80% acetone–water, were followed by titration of the liberated acid. Good first-order kinetics was observed in all cases (Tables II and III), with the infinity titers invariably agreeing well with the calculated values. Consequently, internal return to less reactive 3,5-dinitrobenzoates did not surface as a complication.

Only unrearranged products were formed upon ionization. In the case of **38c** and **46c**, conversion uniquely to **38a** and **46a**, respectively, was observed under these conditions. Where **36c** and **37c** are concerned, an essentially identical 10:1 mixture of **36a** and **37a** was recovered. Another result common to all four systems was found when the solvolyses were conducted in methanol containing 2,6-lutidine, ionization proceeding to give the methyl ethers cleanly (**36b**/**37b** = 85:15). The absence of alcohols signals the exclusive operation of alkyl oxygen cleavage.

The solvolysis results obtained for the epimeric pair **36c**/**37c** are particularly informative with regard to the development of long-range charge delocalization. The anti/syn rate ratio of ca. 100 is suggestive of substantial participation during the rate-determining ionization of **36c**. When this value is compared to that previously determined for **47** and **48** (exo/endo = 12),[10h] it



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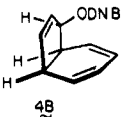

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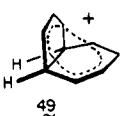


49

becomes clear that the presence of an additional fused cyclohexane ring is either more conductive to the development of bishomoaromatic character as in **49** or less favorable to the ionization of **37c**. The k_{rel} (75 °C) for **47** (3.6)[37] is taken as an indication that

Table III. Activation Parameter and Relative Rate Data for the 3,5-Dinitrobenzoates

	36c	37c	38c	46c
$\Delta H^{\ddagger}_{22}$°C, kcal/mol	25.4	30.5	27.8	24.6
$\Delta S^{\ddagger}_{25}$°C, eu	−1.5	+4.0	+0.1	−5.3
$\Delta G^{\ddagger}_{25}$°C, kcal/mol	25.9	29.3	27.8	26.2
$\Delta E^{\ddagger}$, kcal/mol	26.0	31.1	28.4	25.2
A, s⁻¹	7.95 × 10¹²	1.28 × 10¹⁴	6.58 × 10¹²	4.37 × 10¹¹
corr coeff	0.9958	0.9946	0.9984	0.9970
k_{rel} (75 °C)	39	0.4	1	7.8

Table IV. Spectral Data for Ketones 50-52

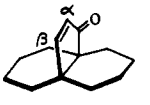
	δ ($CDCl_3$)		λmax (CH_3CN), nm (ε)	νmax (C=O) (CCl_4), cm⁻¹	δ (FSO_3H–SO_2ClF–CD_2Cl_2, −80 °C	
compd	H_α	H_β			H_α	H_β
50	6.05	7.38	231 (6460)	1715	6.72	9.02
51	6.37	7.33	222 (10 910) 268 (2265)	1715	7.20	8.63
52	6.65	7.48	216 (15 800) 270 (2105)	1720	7.43	8.76

the first conclusion is probably more nearly correct.

The kinetic response of **46c** is 5 times slower than that of **36c**. These results suggest that bishomotropylium ion **2** and not the fully delocalized species **3** is being generated under short-lived conditions. Indeed, the relative rate of **46c** correlates well with that of **36c** after proper allowance is made for the rate-retarding inductive effect of the second 1,3-cyclohexadiene moiety. Nevertheless, a caveat remains. One could argue that the leaving group stereochemically prevents effective participation by the third π ribbon in the ionization transition state. The molecular topology of **46** also probably prevents interaction of the third ribbon from the underside, i.e., interaction of the diene–diene–allyl type. Moreover, the entropy contribution is seen to be the factor that slows down **46c** relative to **36c**.

Finally, allowance must be made for the fact that **36c** and **37c** give rise to identical product distributions within experimental error. Thus, the syn isomer must undergo an allyl → bishomotropylium electronic reorganization subsequent to the ionization event. It remained to observe comparable phenomena under long-life conditions where NMR spectroscopy functions as the primary research tool.

Experiments under Conditions of Long Life. All attempts to generate cations from **36a**, **37a**, and **46a** under superacid conditions led to rapid polymerization.[39] For this reason, ketones **50–52**



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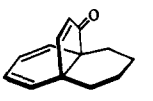
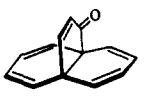
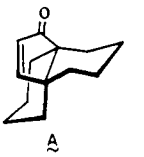


51



52



A

were prepared with a view to obtaining their conjugate acids for spectroscopic examination. While **50** and **51** proved readily accessible by means of manganese dioxide oxidation of the respective alcohols in refluxing cyclohexane, **46a** was converted chiefly into

(37) The kinetic measurements were actually conducted on *p*-nitrobenzoates.[10h] These data have been adjusted on the basis of the relationship $k_{ODNB}/k_{OPNB} = 6$.[38]

(38) Schleyer, R. von R.; van Dine, G. W. *J. Am. Chem. Soc.* **1966**, *88*, 2321, footnote *i* of Table I.

(39) The ^{13}C NMR spectrum of **38a** in CD_2Cl_2–SO_2ClF–FSO_3H at −60 °C exhibits allyl cation signals at 213 and 157 ppm.

naphthalene when comparably handled. With the substitution of pyridinium dichromate in methanol at room temperature, a 58% isolated yield of **52** was achieved.

As can be seen in Table IV, the infrared carbonyl absorptions of the three unsaturated [4.4.3]propellanones are essentially constant and normal. However, the ultraviolet spectra are characterized by a progressive bathochromic shift and increase in ϵ as unsaturation is heightened. This phenomenon, which has been observed in other contexts,[40] appears to be due to the differing degrees to which the cyclopentenone rings attain planarity. While the cis-decalin backbone in **50** (see A) forces distortion upon the α,β-unsaturated carbonyl unit, this conformationally enforced flexing becomes gradually reduced as the level of unsaturation is increased in the flanking six-membered rings. The ^{1}H NMR spectra are consistent with this analysis (Figure 3). When planarity reaches a maximum in **52**, H_α experiences the greatest deshielding due to its fully eclipsed relationship with the carbonyl oxygen. Concomitantly, H_β is subject to maximum electron withdrawal. Were bishomotropone character to develop in **52**, leakage of the electron density into the enone segment would have attenuated the deshielding of H_β. Since this is not seen, longicyclic stabilization in neutral **52** is considered to be inoperative.

Solutions of the triad of ketones in FSO_3H–SO_2ClF–CD_2Cl_2 were recorded at 300 MHz and −80 °C. The protonation of **50**, which strictly restricts positive charge to the enone segment of the molecule, is accompanied by pronounced downfield shifting of H_α and H_β as well as a substantial increase in their chemical shift separation (1.33 → 2.30 ppm) (Figure 4). Were **51**-H^+ bishomoaromatic and **52**-H^+ bicycloaromatic, a *progressive* attenuation of these intense deshielding effects should be observed. Comparison of the ^{1}H NMR data for the conjugate acid of **51** reveals that a significant alteration in electronic character has taken place. The $\Delta\delta$ gap is now only 1.43 ppm, primarily as a result of the appreciably less deshielded nature of H_β (Table IV), in complete agreement with the development of 6π9C charge delocalization. On the other hand, there exists little distinction between **51**-H^+ and **52**-H^+ ($\Delta\delta$ = 1.33 ppm). Although the deshielding of H_α and H_β has increased somewhat, these changes are cogently interpretable in terms of the higher electron-withdrawing inductive influence of the second cyclohexadiene ring. Accordingly, **52**-H^+ gives no indication of longicyclic stabilization. The development of extended delocalization should have been signaled by added charge dispersal away from the protonated enone moiety, with resultant appearance of H_α and H_β at more shielded chemical shift positions than those exhibited by **51**-H^+. The *total deshielding* of $H_\alpha + H_\beta$ in **52**-H^+ relative to **52** (2.06 ppm) is only slightly less than the comparable *total deshielding* in **51**-H^+ relative to **51**. We believe this difference to be too low to signal the onset of longicyclic stabilization.

Summary and Conclusions. The principal objectives of this research were to generate tricyclo[4.4.3.$0^{1,6}$]tridecapentaenyl cations via solvolysis and under superacid conditions, to obtain information about the electronic character of these structurally interesting intermediates, and to correlate our findings with the general behavior of purported longicyclic systems. The first striking property of $4^04^03^+$ cations is the existence of a deterrent against structural isomerization, a feature quite uncharacteristic of other longicyclic candidates. Through examination of the kinetic behavior of triene derivatives **36c** and **37c**, the consequences of leaving group stereochemistry on rate have been made quite clear. Under comparable short-life conditions, **46c** undergoes alkyl–oxygen cleavage with a driving force comparable to that of **36c**, once the adverse inductive effect of the second cyclohexadiene ring is given consideration.

The prevalence of bishomoaromatic, but not longicyclic, character is further revealed in the conjugate acids of ketones **50–52**. Our failure to detect charge delocalization simultaneously to all three bridges as in **3** may well result because of geometric distortion within [4.4.3]propellanyl cations away from a C_{2v} symmetric nature. The development of bishomotropylium character in this system is almost certain to be a result of disrotatory folding of a three- and four-carbon bridge for the purpose of achieving through-space interaction and maximizing orbital overlap. The end result is isolation of the second set of diene fragment orbitals. Similar tilting has been invoked in the 7-norbornadienyl cation.[41] As in this well studied system, the three-carbon bridge in **3** may experience rapid flipping from one side to the other, although this issue remains to be examined.[42]

The remaining point to be addressed is the apparent inability of **2** to transform itself into **3**, especially during long-life conditions. Our conclusion is that total charge delocalization within this propellanyl system does not offer enough in the way of stabilization energy to be able to redress the framework to a C_{2v} geometry. We hasten to add that this need not be a shortcoming inherent to the longicyclic stabilization rule. Rather, it is entirely possible that the lobes of the $p\pi$ orbitals in the three-carbon bridge of the hypothetical C_{2v} symmetric cation **3** reside at distances from the diene termini orbitals that are simply too great to permit adequate levels of interaction. Geometric factors may also intervene, since in **3** the key $p\pi$ orbital overlappings required to achieve bicycloaromatic delocalization approach a perpendicular relationship.

In the end, therefore, the concept of longicyclic stabilization may be misleading because of the unlikelihood that three-dimensional molecules having ribbon topologies capable of *effective overlap* can ever be designed. The requirement that the three constituent π-orbital segments be interconnected by at least two anchoring atoms appears to be adequate to position them too far apart and at dihedral angles that are inadequate to achieve realization of suitable overlap between all three bridges.

Experimental Section

Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded at 60 (Varian T-60), 90 (Varian EM-390), 200 (Bruker WP-200), and 300 MHz (Bruker WM-300). ^{13}C NMR spectra were obtained with a Bruker WP-80 instrument. Infrared spectra were determined on a Perkin-Elmer Model 467 instrument. Mass spectra were recorded on an AEI-MS9 spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

11-Oxo-12-oxa[4.4.3]propella-3,8-diene (5). To a cold (−65 °C), mechanically stirred slurry of lithium aluminum hydride (6.84 g, 0.18 mol) in dry tetrahydrofuran (200 mL) was added a solution of **4** (61.2 g, 0.3 mol) in the same solvent (200 mL) at such a rate as to maintain the temperature below −55 °C (ca. 2 h). Upon completion of the addition, the reaction mixture was stirred for an additional hour at −65 °C, allowed to warm to 0 °C during 90 min, and recooled to −15 °C prior to treatment with ether (200 mL) and 6 N hydrochloric acid (200 mL). Hydrolysis was allowed to proceed for 1 h before the organic layer was separated and the aqueous phase was further extracted with ether (3 × 175 mL). The combined organic layers were dried and concentrated to leave 55.1 g (97%) of **5** as a pale yellow solid. Recrystallization from petroleum ether afforded colorless crystals: mp 78–80 °C (lit.[20] mp 80.6–81.8 °C); IR (cm^{-1}, KBr) 1770; ^{1}H NMR ($CDCl_3$) δ 5.60 (br s, 4 H), 3.97 (s, 2 H), 2.8–1.7 (series of m, 8 H); *m/e* (M^+) calcd 190.0994, obsd 190.0997.

***cis*-9-(Cyanomethyl)-$\Delta^{2,6}$-hexalin-10-carboxylic Acid (6).** A mixture of **5** (107 g, 0.56 mol) and sodium cyanide (100 g, 2 mol) in dimethylformamide (500 mL) and dimethyl sulfoxide (150 mL) was heated at the reflux temperature with stirring for 6 days. After being cooled, the reaction mixture was poured into water (500 mL) and acidified with 6 N hydrochloric acid. The resulting precipitate was collected and dried to give 98 g (80%) of **6** as a tan solid. A pure sample was obtained by recrystallization from aqueous ethanol or petroleum ether–ether: colorless crystals; mp 126–127 °C; IR (cm^{-1}, Nujol) 3000, 2280, 1700, 1200; ^{1}H NMR ($CDCl_3$) δ 5.57 (br s, 4 H), 2.93 (s, 2 H), 2.33 (br s, 8 H); *m/e* (M^+) calcd 217.1103, obsd 217.1106.

Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.88; H, 6.91. Found: C, 71.64; H, 6.92.

***cis*-9-(Carboxymethyl)-$\Delta^{2,6}$-hexalin-10-carboxylic Acid (7).** A mixture of **6** (93 g, 0.43 mol) and sodium hydroxide (180 g) in water (1200

(40) Jaffé, H. H.; Orchin, M. "Theory and Applications of Ultraviolet Spectroscopy"; Wiley: New York, 1964; Chapter 15.

(41) Brookhart, M.; Lustgarten, R. K.; Winstein, S. *J. Am. Chem. Soc.* **1967**, *89*, 6352.

(42) The ^{1}H NMR spectrum of **52**-H^+ showed no temperature dependency between −80 °C and 0 °C.

mL) was heated at the reflux temperature for 48 h, cooled, and acidified to furnish 96 g of crude diacid. Recrystallization from acetone–water afforded **7** as a pure colorless solid (88 g, 87%): mp 198–199 °C; IR (cm^{-1}, Nujol) 3000, 1710, 1295, 1205, 910; ^1H NMR (CD_3COCD_3) δ 7.83 (br s, 2 H), 5.53 (m, 4 H), 2.70 (s, 2 H), 2.5–2.2 (m, 8 H); *m/e* (M^+) calcd 236.1048, obsd 236.1052.

Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83. Found: C, 65.92; H, 6.81.

Treatment of tetrahydrofuran solutions of **7** with a slight excess of diazomethane (2+ equiv) afforded dimethyl ester **8** as a colorless liquid: IR (cm^{-1}, film) 1720; ^1H NMR ($CDCl_3$) δ 5.51 (br m, 4 H), 3.61 (s, 3 H), 3.59 (s, 3 H), 2.61 (s, 2 H), 2.25 (br m, 8 H); *m/e* (M^+) calcd 264.1361, obsd 264.1368.

Anal. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.16; H, 7.67.

11-Hydroxy-12-oxo[4.4.3]propella-3,8-diene (9). Potassium (19.5 g, 0.48 mg-atom) was added under a nitrogen atmosphere to anhydrous benzene (1050 mL), and the mixture was heated to reflux with rapid stirring to produce a dispersion. Sodium metal (18.6 g, 0.81 mmol) was introduced in small pieces, and heating was continued for 30 min. Diester **8** (19.0 g, 72 mmol) in benzene (75 mL) was then added over a 2-h period. Following 16 h of heating, the reaction mixture was cooled in ice and carefully treated dropwise with absolute ethanol (30 mL). Subsequently, acetic acid (75 mL) and water were also added. The organic layer was separated from the aqueous phase, which was further extracted with benzene. The combined benzene layers were washed with brine, dried, and evaporated to leave a pale yellow oil, which crystallized on standing (13 g, 89%). Recrystallization from pentane–ether gave **9** as colorless crystals: mp 77.5–78.5 °C; IR (cm^{-1}, Nujol) 3050, 1745; ^1H NMR ($CDCl_3$) δ 5.63 (br s, 4 H), 4.26 (s, 1 H), 2.98 (br, 1 H), 2.4–1.75 (series of m, 10 H); *m/e* (M^+) calcd 204.1150, obsd 204.1148.

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.22; H, 7.90.

Alternative Acyloin Cyclization of 8. Sodium (1.0 g, 45 mg-atom) in dry toluene (35 mL) was heated and stirred until the metal was finely divided. Chlorotrimethylsilane (10 mL) was slowly introduced via syringe followed by dropwise addition of **8** (4.7 g, 18 mmol), and the reaction mixture was heated overnight at reflux. The insoluble solids were filtered off, and the filtrate was concentrated. The resulting disiloxy compound **10** (4.7 g, quant) exhibited (in $CDCl_3$) a broad singlet at δ 5.75 (4 H), singlet at 2.07 (2 H), and multiplet at 2.05 (8 H) in addition to two sharp singlets at δ 0.16 (9 H) and 0.14 (9 H); *m/e* (M^+) calcd 348.1941, obsd 348.1945.

This material was dissolved in tetrahydrofuran (25 mL), and 1 N hydrochloric acid (1.2 mL) was added, and the solution was heated at reflux for 3 h. After the solution was cooled, solid calcium carbonate was added until neutral, the precipitated solid was separated by filtration, and the filtrate was evaporated. Examination of the ^1H NMR spectrum of this material revealed that **9** was again formed, but in addition a doublet of doublets (J = 8.5 and 5.5 Hz) centered at δ 4.4 was apparent and indicated that 15–20% of **11** was present.

Reduction of 9 to 12-Oxo[4.4.3]propella-3,8-diene. Granular zinc (10 g, 0.15 g-atom) was quickly (ca. 30 s) washed with 5 N hydrochloric acid and rinsed with water. Subsequently, water (10 mL), mercuric chloride (0.8 g), and concentrated hydrochloric acid (1 mL) were added, and the lot was vigorously shaken to achieve amalgamation. The metal was washed and placed into a three-necked 100-mL flask containing 6 N hydrochloric acid (20 mL) and pentane (30 mL). Following addition of **9** (2.15 g, 0.01 mol), the reaction mixture was stirred at the reflux temperature for 9.75 h and at 20 °C for 12 h. The solution was decanted from residual zinc, which was rinsed with ether. The combined organic layers were washed with saturated sodium bicarbonate solution, dried, and evaporated. There was obtained 1.6 g (90%) of **20** as a colorless solid, mp 38–40 °C, with a camphoraceous odor (>95% purity by VPC) having spectral properties identical with those earlier reported;[24] *m/e* (M^+) calcd 188.1201, obsd 188.1204.

11,12-Dioxo[4.4.3]propella-3,8-diene (12). Chromium trioxide (3.00 g, 30 mmol) was added to a magnetically stirred solution of pyridine (4.75 g, 60 mmol) in dichloromethane (75 mL). The flask was stoppered and stirred at room temperature for 15 min. Acyloins **9/11** (1.02 g, 5.0 mmol) were added in one portion, the mixture was stirred for 15 min, and the solution was decanted from the solids, which were rinsed with ether (100 mL). The combined organic layers were washed with 5% sodium hydroxide solution (3 × 100 mL), 5% hydrochloric acid (100 mL), 5% sodium bicarbonate solution (100 mL), and brine (100 mL) prior to drying and solvent evaporation. The resulting golden yellow oil was crystallized from pentane–ether (5:1) to give 830 mg (85%) of **12** as a yellow solid: mp 79–79.5 °C; IR (cm^{-1}, CCl_4) 3019, 1755; UV (nm, isooctane) 465 (ϵ 20); ^1H NMR ($CDCl_3$) δ 5.64 (br s, 4 H), 2.40 (s, 2 H), 2.52–1.70 (series of m, 8 H); ^{13}C NMR ($CDCl_3$, ppm) 205.48, 201.51, 124.23, 122.70, 48.86, 45.21, 33.16, 31.94, 27.78; *m/e* (M^+) calcd 202.0994, obsd 202.0996.

Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 76.85; H, 7.06.

A 2,4-dinitrophenylhydrazone of this α-diketone exhibited a melting point of 199–200 °C.

11-Acetoxy-12-oxo[4.4.31propella-3,8-diene (17). A magnetically stirred solution of **9** (2.04 g, 0.01 mol) in dry pyridine (15 mL) and ether (35 mL) was cooled (0 °C) and treated dropwise over 15 min with acetyl chloride (2.0 mL) in ether (25 mL). The reaction mixture was stirred for 1 h at 0 °C and 4 h at room temperature and poured into water (100 mL) and ether (50 mL). The organic phase was washed with 10% hydrochloric acid (100 mL) and water (2 × 100 mL) prior to drying and solvent evaporation. The acetate was obtained as a clear, sweet-smelling oil: IR (cm^{-1}, CCl_4) 1750; ^1H NMR ($CDCl_3$) δ 5.64 (br s, 4 H), 5.52 (s, 1 H), 2.16 (s, 3 H), 2.3–1.8 (m, 10 H); *m/e* (M^+) calcd 246.1256, obsd 246.1260.

***cis*-11,12-Dihydroxy[4.4.3]propella-3,8-diene (18).** A solution of **17** (750 mg, 3.75 mmol) in ether (5 mL) was added dropwise to a cold (−70 °C) stirred slurry of lithium aluminum hydride (0.30 g, 7.5 mmol) in the same solvent (25 mL). After 2 h, saturated sodium sulfate solution was added until the precipitated salts turned white. The insolubles were filtered and rinsed well with ether. The filtrates were dried and evaporated to leave 700 mg (93%) of **18** as a colorless solid: mp 111.5–112 °C (from ether–pentane); IR (cm^{-1}, Nujol) 3500; ^1H NMR ($CDCl_3$) δ 5.56 (m, 4 H), 4.36 (m, 1 H), 4.02 (d, J = 7.5 Hz, 1 H), 3.0 (br, 2 H), 2.4–1.6 (series of m, 10 H); *m/e* (M^+) calcd 206.1307, obsd 206.1310.

Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.70; H, 8.83.

***cis*-11-(Tosyloxy)-12-hydroxy[4.4.3]propella-3,8-diene (19).** *p*-Toluenesulfonyl chloride (763 mg, 4.0 mmol) was added to a cold (0 °C), magnetically stirred solution of **18** (824 mg, 4.0 mmol) in pyridine (12 mL). This solution was stored at 5 °C for 60 h and then poured onto ice and 5% hydrochloric acid. The semisolid product was extracted into ether (2 × 100 mL), dried, and evaporated. One and two-tenths grams (84%) of **19** was obtained as a clear oil, which slowly crystallized: IR (cm^{-1}, CCl_4) 3400–3300, 1240, 1210; ^1H NMR ($CDCl_3$) δ 7.5 and 7.1 (AA′BB′, 4 H), 5.56 (m, 4 H), 4.4 (m, 1 H), 3.8 (d, J = 8 Hz, 1 H), 2.4 (s, 3 H), 2.2–1.7 (series of m, 10 H); *m/e* (M^+) 360.

Base-Promoted Isomerization of 19. Sodium hydride (135 mg of 50% in oil, 10% excess) was washed free of oil with dry tetrahydrofuran and treated with a solution of **19** (1.0 g) in tetrahydrofuran (25 mL) under nitrogen. The reaction mixture was stirred at room temperature for 18 h, evaporated, and partitioned between water and ether. The organic phase was dried and evaporated to give **20** whose spectral properties were identical with those of the ketone earlier isolated.

11-Acetoxy-12-hydroxy[4.4.3]propella-3,8-diene (21a). A magnetically stirred solution of **17** (2.2 g, 9.0 mmol) in methanol (25 mL) was cooled to 0 °C, treated portionwise with sodium borohydride (200 mg, 5.0 mmol), and kept at room temperature for 2 h, prior to being poured into water (150 mL) and extracted with ether (2 × 100 mL). The combined organic layers were dried and evaporated to give **21a** as an oil (2.0 g, 91%): IR (cm^{-1}, CCl_4) 3500, 1745, 1250; ^1H NMR ($CDCl_3$) δ 5.6 (br s, 4 H), 5.6–5.2 (m, 2 H), 2.12 (s, 3 H), 2.4–1.7 (series of m, 10 H); *m/e* (M^+) calcd 248.1412, obsd 248.1416.

11-Acetoxy-12-(tosyloxy)[4.4.3]propella-3,8-diene (21b). Acetoxy alcohol **21a** was converted to its tosylate in the previously described manner (93% yield): IR (cm^{-1}, CCl_4) 1735, 1240, 1210; ^1H NMR ($CDCl_3$) δ 7.6–7.2 (AA′BB′, 4 H), 5.6–5.0 (m, 2 H), 2.4 (s, 3 H), 2.17–1.67 (series of m, 10 H), 1.90 (s, 3 H).

11-Hydroxy[4.4.3]propella-3,8-diene (24a). Ketone **20** was reduced with excess sodium borohydride in methanol at 0 °C as predescribed. The resulting alcohol (96% yield) was obtained as a colorless crystalline solid: mp 69–70 °C (from pentane–ether); IR (cm^{-1}, Nujol) 3400; ^1H NMR ($CDCl_3$) δ 5.4 (br s, 4 H), 4.53 (tt, J = 7.5 and 3.5 Hz, 1 H), 2.36–1.36 (series of m, 12 H), 1.61 (br, 1 H); *m/e* (M^+) calcd 190.1358, obsd 190.1361.

11-Acetoxy[4.4.3]propella-3,8-diene (24b). Alcohol **24a** was converted to its acetate in 93% yield as previously described: IR (cm^{-1}, CCl_4) 3022, 1745, 1250; ^1H NMR ($CDCl_3$) δ 5.56 (m, 4 H), 5.4 (m, 1 H), 2.04 (s, 3 H), 2.2–1.56 (series of m, 12 H).

Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.48; H, 8.91.

12-Acetoxy[4.4.3]propella-2,4,7,9-tetraene (25b). A mixture of **24b** (580 mg, 2.5 mmol), recrystallized dry *N*-bromosuccinimide (900 mg, 5.0 mmol), and a spatulaful of azobis(isobutyronitrile) was gently refluxed for 30 min. After the solution was cooled, the insolubles were separated by filtration and the filtrate was evaporated to yield an oil that was not characterized and was dissolved directly in dry dimethylformamide (25 mL). This solution was heated at 90 °C for 15 h, cooled,

poured into water (100 mL), and extracted with ether (2 × 100 mL). The combined organic layers were dried and evaporated. There was obtained 558 mg (93%) of the tetraenyl acetate, which was purified for analysis by preparative VPC (2 ft × 0.25 in. 10% SE-30) at 140 °C: IR (cm^{-1}, CCl_4) 1740, 1240; ^1H NMR ($CDCl_3$) δ 6.08–5.25 (m, 8 H), 5.00 (tt, J = 7.5 and 5.5 Hz, 1 H), 2.63–1.9 (AB part of ABX, 4 H), 1.98 (s, 3 H); m/e (M^+) 228 ($M^+ - CH_3COOH$) 169 (parent ion).

Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 79.21; H, 7.34.

11-Hydroxy[4.4.3]propella-2,4,7,9-tetraene (25a). Acetate **25b** (1.30 g, 5.7 mmol) in ether (20 mL) was added dropwise to a stirred slurry of lithium aluminum hydride (190 mg, 5 mmol) in ether (25 mL). The reaction mixture was gently heated at reflux for 4 h and processed in the predescribed manner. Nine-hundred and ten milligrams (90%) of **25a** was isolated: IR (cm^{-1}, CCl_4) 3330; ^1H NMR ($CDCl_3$) δ 6.16–5.16 (m, 8 H), 4.2 (tt, J = 7.0 and 4.5 Hz, 1 H), 2.6–1.83 (AA'BB' part of AA'BB'X, 4 H), 1.90 (br, 1 H); m/e (M^+) calcd 186.1045, obsd 186.1049.

11-Oxo-12-oxa[4.4.3]propell-3-ene (28). Reduction of anhydride **27** (61.8 g, 0.3 mol) with lithium aluminum hydride (6.84 g, 0.18 mol) in tetrahydrofuran (400 mL) at −65 °C as described above afforded 56.6 g (98%) of **28** as a colorless oil: IR (cm^{-1}, neat) 1770, 1290, 1000; ^1H NMR ($CDCl_3$) δ 5.63 (br s, 2 H), 3.97 and 3.80 (AB_q, J = 9 Hz, 2 H), 2.4–1.3 (series of m, 12 H); m/e (M^+) calcd 192.1150, obsd 192.1153.

***cis*-9-(Cyanomethyl)-Δ²-octalin-10-carboxylic Acid (29a).** Heating of **28** (80 g, 0.42 mol) with sodium cyanide (100 g, 2 mol) in dimethylformamide (500 mL) and dimethyl sulfoxide (150 mL) for 6 days gave 66.9 g (72%) of **29a** as a colorless solid: mp 137–138 °C (from ether–petroleum ether); IR (cm^{-1}, Nujol) 2220, 1685, 945; ^1H NMR ($CDCl_3$) δ 8.19 (br s, 1 H), 5.57 (br s, 2 H), 3.10 and 2.53 (ABq, J = 16 Hz, 2 H), 2.30 (br s, 4 H), 2.1–1.4 (series of m, 8 H).

Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81. Found: C, 71.23; H, 7.82.

***cis*-9-(Carboxymethyl)-Δ²-octalin-10-carboxylic Acid (29b).** Heating of **29a** (65.6 g, 0.30 mol) with sodium hydroxide (120 g, 3 mol) in water (800 mL) for 48 h gave 68 g (95%) of **29b** as a colorless solid: mp 195–196 °C (from acetone–water); IR (cm^{-1}, Nujol) 1715, 1230, 925; ^1H NMR (CD_3COCD_3) δ 5.54 (br s, 2 H), 2.93 and 2.34 (ABq, J = 14 Hz, 2 H), 2.31 (br s, 4 H), 2.0–1.4 (m, 8 H); m/e (M^+) calcd 238.1205, obsd 238.1208.

Anal. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.55 H, 7.61.

7,9-Dioxo-8-oxa[4.4.4]propell-3-ene (30). A solution of **29b** (97.5 g, 0.41 mol) in acetic anhydride (600 mL) was heated in the reflux temperature for 12 h, and the solvent was evaporated. Recrystallization of the residue from hexane–benzene furnished 87.2 g (97%) of **30**: mp 88.0–88.5 °C; IR (cm^{-1}, Nujol) 1800, 1760, 1160, 1125, 1030; ^1H NMR ($CDCl_3$) δ 5.57 (br, s, 2 H), 2.93 and 2.33 (ABq, J = 16 Hz, 2 H), 2.8–2.1 (m, 4 H), 2.1–1.3 (m, 8 H).

Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.82; H, 7.40.

7-Oxo-8-oxa[4.4.4]propell-3-ene (31). Reduction of **30** (78.7 g, 0.36 mol) with lithium aluminum hydride (8.21 g, 0.216 mol) in tetrahydrofuran (500 mL) at −65 °C as before provided 72.0 g (97%) of **31**: mp 73–75 °C (from ether–petroleum ether); IR (cm^{-1}, Nujol) 1810, 1745, 1195, 1150, 1070; ^1H NMR ($CDCl_3$) δ 5.57 (br s, 2 H), 4.6–4.2 (m, 2 H), 2.8–1.0 (series of m, 14 H); m/e (M^+) calcd 206.1307, obsd 206.1310.

***cis*-9-(2-Cyanoethyl)-Δ²-octalin-10-carboxylic Acid (32a).** When 81.4 g (0.395 mol) of **31** was heated with sodium cyanide (100 g, 2 mol) in dimethylformamide (500 mL) and dimethyl sulfoxide (150 mL) for 6 days, 77.0 g (84%) of **32a** was obtained: mp 139–140 °C (from ether–petroleum ether); IR (cm^{-1}, Nujol) 2240, 1695, 1295; ^1H NMR ($CDCl_3$) δ 6.8 (br s, 1 H), 5.4 (br s, 2 H), 2.4–1.3 (series of m, 16 H).

Anal. Calcd for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21. Found: C, 71.98; H, 8.13.

***cis*-9-(2-Carboxyethyl)-Δ²-octalin-10-carboxylic Acid (32b).** When 74.0 g (0.32 mol) of **32a** was heated with sodium hydroxide (150 g) in water (1 L) for 48 h, 70 g (87%) of **32b** was isolated: mp 200–202 °C, after recrystallization from acetone–water; IR (cm^{-1}, Nujol) 1710, 1300, 940; ^1H NMR ($CDCl_3$) δ 10.2 (br s, 2 H), 5.57 (br s, 2 H), 2.5–1.3 (series of m, 16 H).

Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.65; H, 7.97. Found: C, 66.49; H, 7.93.

Treatment of a tetrahydrofuran solution (100 mL) of **32b** (31.8 g, 0.126 mol) with excess ethereal diazomethane followed by silica gel chromatography (elution with petroleum ether) afforded 35.0 g (99%) of diester **33a** as a colorless oil: IR (cm^{-1}, film) 2960, 1730, 1430, 1190; ^1H NMR ($CDCl_3$) δ 5.33 (br s, 2 H), 3.63 (s, 6 H), 2.4–1.4 (series of m, 16 H); m/e (M^+) calcd 280.1674, obsd 280.1682.

11-Oxo[4.4.3]propell-3-ene (34a). A solution of **33a** (35.0 g, 0.125 mol) in tetrahydrofuran (200 mL) was added dropwise over 1 h to a rapidly stirred, cold (0 °C) suspension of sodium hydride [24 g of 50% oil dispersion (washed with ether), 0.5 mol] in the same solvent (300 mL). Upon completion of the addition, the reaction mixture was stirred at room temperature for 1 h, heated at reflux for 22 h, cooled, and poured into ice-cold 3 N hydrochloric acid. The product was extracted into petroleum ether, and the combined organic phases were washed with saturated sodium bicarbonate solution and water, dried, and concentrated. The keto ester was obtained as a colorless oil (24.5 g, 79%) after silica gel chromatography (elution with petroleum ether–ether, 9:1): IR (cm^{-1}, film) 2930, 1725, 1150; ^1H NMR ($CDCl_3$) δ 5.60 (br s, 2 H), 3.73 (s, 1.5 H), 3.70 (s, 1.5 H), 3.7–3.2 (m, 1 H), 2.6–1.1 (series of m, 14 H); m/e calcd 248.1412, obsd 248.1416.

A solution of the keto ester (41.5 g, 0.167 mol) and sodium chloride (20 g, 0.34 mol) in water (6 mL) and dimethylformamide (500 mL) was heated at the reflux temperature for 5.5 h, cooled, and poured into a mixture of ice and water. The product was extracted into petroleum ether, and the combined organic layers were washed with water before drying. Removal of solvent followed by silica gel chromatography afforded 31.0 g (98%) of **34a** as a colorless, waxy semisolid. An analytical sample was obtained by preparative VPC (2 ft × 0.25 in. 10% SE-30, 170 °C): IR (cm^{-1}, Nujol) 1735, 1180, 1090, 845; ^1H NMR ($CDCl_3$) δ 5.53 (br s, 2 H), 2.5–1.0 (series of m, 16 H).

Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.96; H, 9.32.

12-Bromo[4.4.3]propella-2,4,12-trien-11-one (35a). A solution of **34a** (1.12 g, 5.9 mmol) and pyridinium hydrobromide perbromide (7.6 g, 24 mmol) in acetic acid (20 mL) was stirred at room temperature for 15 h and at 40–50 °C for 2 h. The reaction mixture was poured into ice and water, and the product was extracted into dichloromethane. The combined organic layers were washed with sodium bisulfite solution, dried, and evaporated to leave a colorless solid (2.95 g). Without purification, this material was added to a mixture of lithium chloride (8.0 g, 186 mmol) and lithium carbonate (8.0 g, 109 mmol) in dimethylformamide (30 mL). Following 12 h of stirring at room temperature and 16 h at 115–120 °C, water and ice were added and the product was isolated by continuous extraction with petroleum ether. The organic solution was washed with water, dried, and concentrated to provide 1.36 g (86%) of **35a**. Final purification to a colorless oil was achieved by preparative TLC on silica gel (elution with petroleum ether–ether, 4:1): IR (cm^{-1}, film) 1705; ^1H NMR ($CDCl_3$) δ 7.33 (s, 1 H), 6.0–5.6 (m, 2 H), 5.6–5.1 (m, 2 H), 2.2–1.2 (series of m, 8 H).

***anti*- and *syn*-[4.4.3]Propella-2,4,12-trien-11-ols (36a and 37a).** Bromo ketone **35a** (1.36 g, 5.1 mmol) dissolved in 40 mL of dry benzene was treated with diisobutylaluminum hydride (12 mL of 25% hexane solution) at 5 °C. The reaction mixture was stirred at this temperature for 2.5 h before decomposition with 10% sodium hydroxide solution (12 mL) was begun. The product was extracted into petroleum ether, and the combined organic layers were dried and evaporated. A 1:1 mixture (1.35 g, 99%) of bromo alcohols was obtained: ^1H NMR ($CDCl_3$) δ 6.4–5.0 (m, 5 H), 4.57 (br s, 1 H), 3.90 (br d, 1 H), 2.2–1.2 (series of m, 9 H).

This bromo alcohol (660 mg, 2.5 mmol) dissolved in cold (0 °C), dry ether (20 mL) was treated under nitrogen with 5 mL of 1.6 M *n*-butyllithium in hexane. The resultant solution was stirred for 1 h at 0 °C and for 4.5 h at room temperature. Water (5 mL) was carefully introduced at 0 °C, the product was extracted into petroleum ether, and the combined organic layers were washed with water prior to drying and evaporation. Isomer separation was achieved by MPLC chromatography on silica gel (elution with dichloromethane–ether, 50:3). Both alcohols were obtained as low melting colorless solids.

For **36a**: mp 65–66 °C; IR (cm^{-1}, CCl_4) 3620, 3540–3080, 3025, 2920, 2845, 1445, 1382; ^1H NMR ($CDCl_3$) δ 6.0–5.6 (m, 5 H), 5.3–5.2 (m, 1 H), 4.75 (t, J = 2 Hz, 1 H), 2.6 (br s, 1 H), 1.7–1.2 (m, 8 H); m/e (M^+) calcd 188.1021, obsd 188.1204.

Reaction of **36a** (400 mg, 2.13 mmol) with 3,5-dinitrobenzoyl chloride (1.0 g, 4.34 mmol) in dry pyridine for 2 days at room temperature, followed by MPLC purification on silica gel (elution with petroleum ether–ethyl acetate, 5:1) afforded **36c** (350 mg, 43%) as a pale yellow solid: mp 60 °C; IR (cm^{-1}, $CHCl_3$) 1728; ^1H NMR ($CDCl_3$) δ 9.36–9.06 (m, 3 H), 6.1–5.5 (m, 7 H), 1.8–1.2 (m, 8 H); m/e (M^+) calcd 382.1165, obsd 382.1174.

For **37a**: mp 48–49 °C; IR (cm^{-1}, CCl_4) 3580, 3025, 2920, 2845, 1445, 1390; ^1H NMR ($CDCl_3$) δ 6.25–6.1 (m, 2 H), 5.8–5.5 (m, 4 H), 4.1 (d, J = 3 Hz, 1 H), 2.0 (br s, 1 H), 1.4–1.2 (m, 8 H); m/e (M^+) calcd 188.1201, obsd 188.1195.

The 3,5-dinitrobenzoate (**37c**) was prepared as above (74%) and obtained as a pale yellow solid: mp 134.5–135.5 °C; IR (cm^{-1}, $CHCl_3$) 1725; ^1H NMR ($CDCl_3$) δ 9.43–8.90 (m, 3 H), 6.2–5.4 (m, 7 H), 2.0–1.0

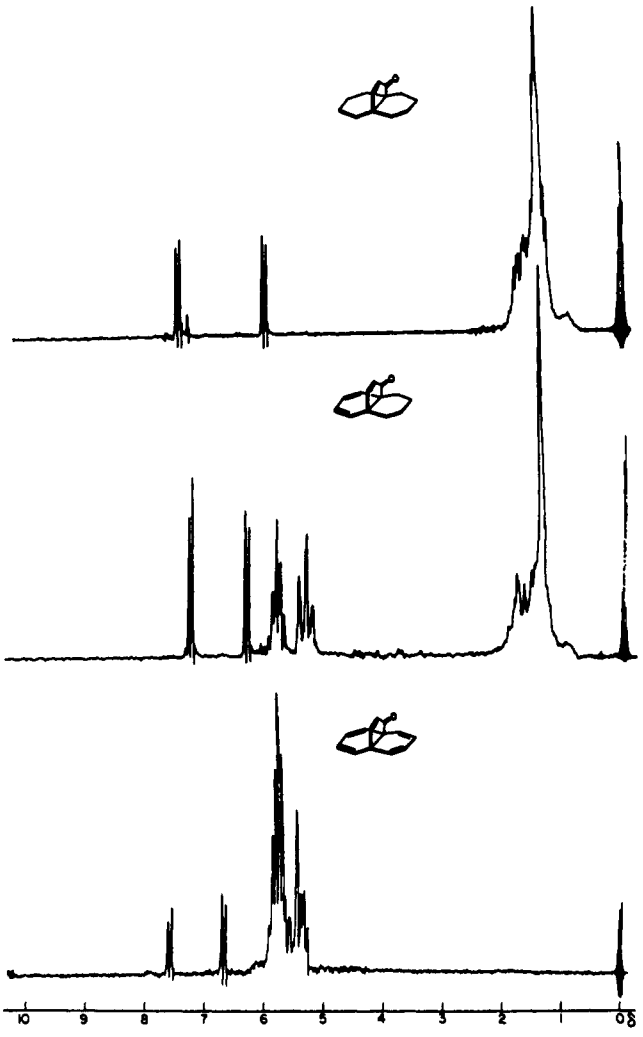


Figure 3. 90-MHz ^1H NMR spectra of **50–52** ($CDCl_3$ solution).

(series of m, 8 H); *m/e* (M^+) calcd 382.1165, obsd 382.1174.

Anal. Calcd for $C_{20}H_{18}N_2O_6$: C, 62.82; H, 4.74. Found: C, 62.86; H, 5.04.

Additional ^1H NMR Characteristics and Infrared Dilution Studies. Repeated ^1H NMR spectral determinations of $CDCl_3$ solutions of *syn*-trienol **37a** revealed observable coupling of the –OH proton with the α proton. This phenomenon was also observed in pentaenol **46a** but not in *anti*-trienol **36a**. To confirm the assumption that this difference arose because of intramolecular hydrogen bridging in **37a** and **46a** (not possible in **36a**), the infrared spectra of these compounds were determined in CCl_4 at various concentrations. At high dilution, syn isomer **37a** showed a band at ~3400 cm^{-1} that was very weak compared to the intramolecular hydrogen bonded OH absorption at 3600 cm^{-1}. Pentaenol **46a** at the same concentration level exhibited both bands in approximately equal intensity. For anti isomer **36a**, the band at 3500–3200 cm^{-1} due to intermolecular hydrogen bonding was vastly more intensive than the band at 3600 cm^{-1}, a feature shared in common with **38a**.

***cis*-9-(2-Carboxyethyl)decalin-10-carboxylic Acid Dimethyl Ester (33b).** A mixture of **32b** (10.0 g, 40 mmol) and 5% palladium on charcoal (1 g) in 200 mL of absolute ethanol was hydrogenated at 50 psi for 15 h. After filtration and solvent evaporation, the fully saturated diacid was obtained quantitatively as a colorless solid: mp 217–218 °C (from ethanol); IR (cm^{-1}, Njuol) 1705, 1300, 1255, 840; ^1H NMR (CD_3COCD_3) δ 7.0 (br, 2 H), 1.9–1.2 (series of m, 20 H).

Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.12; H, 8.70. Found: C, 66.06; H, 8.74.

Reaction of this diacid (9.5 g, 37 mmol) with excess ethereal diazomethane in dioxane (50 mL) followed by silica gel chroamtography (elution with petroleum ether) afforded **33b** in 96% yield: IR (cm^{-1}, film) 1740, 1430, 1220, 1145; ^1H NMR ($CDCl_3$) δ 3.60 (s, 6 H), 2.3–1.2 (series of m, 20 H); *m/e* (M^+) calcd 282.1831, obsd 282.1837.

[4.4.3]Propellan-11-one (34b). Reaction of **33b** (9.8 g, 35 mmol) dissolved in tetrahydrofuran (50 mL) with sodium hydride (6.7 g of 50% oil dispersion, 140 mmol) in the same solvent (80 mL) in the predescribed manner afforded 7.8 g (89%) of keto ester after silica gel chromatography: IR (cm^{-1}, film) 1755, 1730, 1450, 1330, 1155; ^1H NMR ($CDCl_3$) δ 3.73 (s, 3 H), 3.40 (d, J = 10 Hz, 1 H), 2.47 (dd, J = 12 and 10 Hz, 1 H), 2.0–1.0 (series of m, 17 H); *m/e* calcd 250.1569, obsd 250.1573.

Heating this keto ester (7.8 g, 31 mmol) with sodium chloride (3.6 g, 62 mmol) and water (1.4 g, 0.08 mol) in dimethylformamide (250 mL) gave 5.7 g (96%) of **34b** as a colorless oil: IR (cm^{-1}, Nujol) 1735, 1085; ^1H NMR ($CDCl_3$) δ 2.30 (q, J = 8 Hz, 2 H), 2.0–1.0 (series of m, 18 H).

Anal. Calcd for $C_{12}H_{20}O$: C, 81.20; H, 10.48. Found: C, 80.97; H, 10.32.

[4.4.3]Propell-12-en-11-one (50). A solution of **34b** (1.375 g, 7.15 mmol) and pyridinium hydrobromide perbromide (2.27 g, 7.15 mmol) in 30 mL of acetic acid was stirred at 10 °C for 3 h and at room temperature for 13 h. The reaction mixture was poured into iced water, the product was extracted into dichloromethane, and the combined organic layers were washed with saturated sodium bicarbonate solution and water prior to drying and solvent evaporation. A mixture of monobromide, dibromide, and unreacted **34b** (ca. 33% of the latter) remained. After TLC on silica gel, 440 mg of monobromide was isolated: ^1H NMR ($CDCl_3$) δ 4.30 (t, J = 8 Hz, 1 H), 2.20 (d, J = 8 Hz, 2 H), 2.0–1.0 (series of m, 16 H).

A mixture of the monobromide (440 mg, 1.6 mmol), lithium chloride (1.0 g, 24 mmol), and lithium carbonate (2.0 g, 27 mmol) in dimethylformamide (20 mL) was heated at reflux for 5 days. Workup in the predescribed manner, followed by preparative TLC on silica gel (elution with petroleum ether–ether, 4:1) afforded pure **50** (190 mg, 63%) as a colorless solid: mp 66–68 °C; IR (cm^{-1}, CCl_4) 2930, 2850, 1715, 1450; UV (nm, CH_3CN) 231 (ϵ 6460); ^1H NMR ($CDCl_3$) δ 7.38 (d, J = 6 Hz, 1 H), 6.05 (d, J = 6 Hz, 1 H), 2.0–1.0 (series of m, 16 H); ^{13}C NMR ($CDCl_3$, ppm) 214.59, 171.92, 129.44, 51.95, 48.12, 35.80, 30.95, 22.09, 21.66; *m/e* (M^+) calcd 190.1358, obsd 190.1364.

Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.81; H, 9.40.

[4.4.3]Propell-12-en-11-ol (38a). To a solution of **50** (150 mg, 0.79 mmol) in benzene (10 mL) was added diisobutylaluminum hydride (3 mL of a 25% hexane solution) at 5 °C, and stirring was maintained for 2.5 h at this temperature before 10% sodium hydroxide solution (3 mL) was added. The usual workup gave 130 mg (89%) of **38a** as colorless crystals: mp 93–94 °C (from petroleum ether); IR (cm^{-1}, Nujol) 3350, 1070, 1015; ^1H NMR ($CDCl_3$) δ 5.8–5.4 (m, 2 H), 4.77 (br s, 1 H), 2.3–2.0 (br s, 1 H), 2.0–1.0 (series of m, 16 H); *m/e* calcd 192.1514, obsd 192.1519.

Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 80.97; H, 10.52.

The 3,5-dinitrobenzoate (**38c**) was obtained in 51% yield as a pale yellow solid, mp 90–92 °C (from ether–petroleum ether); IR (cm^{-1}, Nujol) 1720, 1545, 1345, 1170; ^1H NMR ($CDCl_3$) δ 9.30–9.03 (m, 3 H), 6.07 (br s, 1 H), 5.90 and 5.60 (br ABq, J = 6 Hz, 2 H), 1.8–1.1 (series of m, 16 H); *m/e* (M^+) calcd 386.1478, obsd 386.1482.

7-Oxo-8-oxa[4.4.4]propella-3,12-diene (40). Reduction of **39** (73 g, 0.357 mmol) with lithium aluminum hydride (8.15 g, 0.214 mol) in tetrahydrofuran (500 mL) at –65 °C as before provided 68 g (93%) of **40**, which was used without further purification: IR (cm^{-1}, Nujol) 1725, 1275, 1175, 1115; ^1H NMR ($CDCl_3$) δ 5.53 (br s, 4 H), 4.47 (t, J = 8 Hz, 2 H), 3.0–1.7 (series of m, 10 H); *m/e* (M^+) calcd 204.1150, obsd 204.1153.

***cis*-9-(2-Cyanoethyl)-$\Delta^{2,6}$-hexalin-10-carboxylic Acid (41a).** Heating of **40** (67 g, 0.33 mol) with sodium cyanide (75 g, 1.5 mol) in dry dimethylformamide (400 mL) and dry dimethyl sulfoxide (120 mL) for 3 days as before afforded 54 g (71%) of **41a**: mp 114–115 °C (from ether–petroleum ether); IR (cm^{-1}, Nujol) 2225, 1685, 1285, 1225; ^1H NMR ($CDCl_3$) δ 10.80 (br s, 1 H), 5.53 (br s, 4 H), 2.5–1.0 (series of m, 12 H).

Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41. Found: C, 72.66; H, 7.45.

***cis*-9-(2-Carboxyethyl)-$\Delta^{2,6}$-hexalin-10-carboxylic Acid (41b).** Hydrolysis of **41a** (52 g, 0.23 mol) with sodium hydroxide (110 g) in water (750 mL) at the reflux temperature for 2 days afforded **41a** in 87% yield: mp 182–183 °C; IR (cm^{-1}, Nujol) 1705, 1680, 1295; ^1H NMR (CD_3COCD_3) δ 6.5–5.8 (m, 2 H), 5.50 (br s, 4 H), 2.5–1.9 (series of m, 12 H).

Anal. Calcd for $C_{14}H_{18}O_4$: C, 67.19; H, 7.25. Found: C, 67.17; H, 7.17.

Esterification of **41a** (47.9 g, 0.19 mol) in tetrahydrofuran (50 mL) with excess ethereal diazomethane afforded **42** (52 g, 98%) as a colorless solid: mp 64–65 °C (from petroleum ether; IR (cm^{-1}, Nujol) 1640, 1165; ^1H NMR ($CDCl_3$) δ 5.50 (br s, 4 H), 3.63 (s, 6 H), 2.4–1.8 (series of m, 12 H).

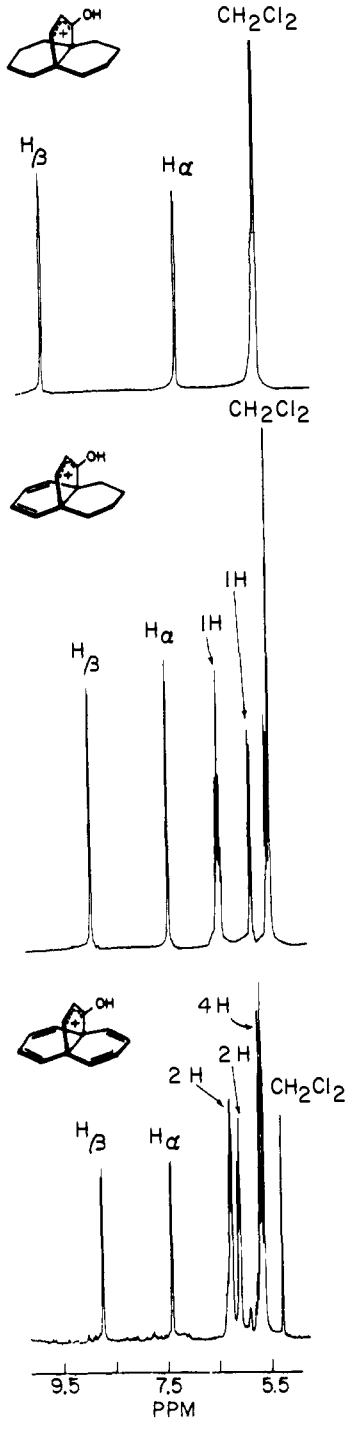


Figure 4. 200-MHz ^1H NMR spectra of the olefinic proton regions for **50**-H^+, **51**-H^+, and **52**-H^+ (SO_2ClF–FSO_3H–CD_2Cl_2 solutions at −80 °C).

Anal. Calcd for $C_{16}H_{22}O_4$: C, 69.05; H, 7.97. Found: C, 69.09; H, 7.99.

11-Oxo[4.4.3]propella-3,8-diene (43). Cyclization of **42** (38.3 g, 0.14 mol) with sodium hydride in the manner outlined above and subsequent decarbomethoxylation with sodium chloride in moist dimethylformamide furnished **43** in 89% overall yield. Analytically pure **43** was obtained by preparative VPC (2 ft × 0.25 in. 10% SE-30) at 140 °C: IR (cm^{-1}, Nujol) 1745, 1650, 1155, 1085, 995; ^1H NMR ($CDCl_3$) δ 5.50 (br s, 4 H), 2.7–1.5 (series of m, 12 H); ^{13}C NMR ($CDCl_3$, ppm) 218.47, 124.47, 123.44, 49.22, 37.35, 33.13, 32.68, 29.58, 28.98.

Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.55. Found: C, 83.09; H, 8.43.

12-Bromo[4.4.3]propella-2,4,7,9,12-pentaen-11-one (44). A solution of **43** (1.7 g, 9.0 mmol) and pyridinium hydrobromide perbromide (14.3 g, 45 mmol) in glacial acetic acid (100 mL) was stirred at room temperature for 15 h and at 40–50 °C for 2 h. The reaction mixture was poured into ice water (300 mL) and filtered to give 5.5 g of white solid after drying. This material was added along with lithium chloride (16 g, 0.38 mol) and lithium carbonate (16 g, 0.22 mol) to 150 mL of dimethylformamide and stirred at room temperature for 7 h and at 100–120 °C for 15 h. After cooling and dilution with water, the product was continuously extracted with petroleum ether. The organic phase was washed with water, dried, and evaporated to leave 2.2 g of yellowish oil. Crystallization and recrystallization from ether–petroleum ether furnished **44** as a colorless crystalline product: mp 90–92 °C (1.6 g, 66%); IR (cm^{-1}, Nujol) 1705, 1575, 810; ^1H NMR ($CDCl_3$) δ 7.50 (s, 1 H), 6.0–5.1 (m, 8 H).

12-Bromo[4.4.3]propella-2,4,7,9,12-pentaen-11-ol (45a). A solution of **44** (850 mg, 3.3 mmol) in dry benzene (30 mL) was treated with diisobutylaluminum hydride (6 mL of 25% hexane solution) at 5 °C. After 3 h, the usual workup was applied to give 770 mg (89%) of **45a** as a colorless solid: mp 79–80 °C (from petroleum ether); ^1H NMR ($CDCl_3$) δ 6.2–5.0 (m, 9 H), 4.43 (d, J = 9 Hz, 1 H), 2.03 (d, J = 9 Hz, 1 H).

The *tert*-butyldimethylsilyl ether **45b** was prepared by dissolving **45a** (5.5 g, 20.9 mmol) and freshly distilled 2,6-lutidine (4 g, 48.2 mmol) in dry dichloromethane (150 mL) and adding dropwise to this solution *tert*-butyldimethylsilyl triflate[36] (9.2 g, 37.1 mmol) with stirring under nitrogen. The reaction mixture was stirred at room temperature for 90 min and poured into ice water. The layers were separated, and the aqueous phase was extracted with dichloromethane (2 × 50 mL). The combined organic layers were washed with ice-cold 5% hydrochloric acid (2×) and water (1×). After the mixture was dried, the solvent was evaporated to give **45b** (9.5 g) as a yellow oil, which was used without further purification: ^1H NMR ($CDCl_3$) δ 5.9–5.7 (m, 5 H), 5.6–5.2 (m, 4 H), 4.8 (d, J = 1.7 Hz, 1 H), 1.0 (s, 9 H), 0.2 (s, 3 H), 0.1 (s, 3 H); m/e (M^+) calcd 376.0858, obsd 376.0866.

[4.4.3]Propella-2,4,7,9,12-pentaen-11-ol (46a). The above material (9.5 g) was dissolved in dry ether (200 mL) and added dropwise to 70 mL of *n*-butyllithium solution (1.6 M in hexane) at 0 °C under nitrogen during 45 min. After an additional hour, water (50 mL) was added slowly, the layers were separated, and the aqueous phase was extracted with petroleum ether (3 × 50 mL). The combined extracts were washed with water, dried, and evaporated, and the residue was quickly chromatographed on silica gel (elution with petroleum ether) to remove the silanol. The colorless oil so obtained (4.21 g) consisted of the debrominated silyl ether admixed with ca. 25% naphthalene: ^1H NMR ($CDCl_3$) δ 6.15 (dd, J = 8 and 2 Hz, 1 H), 5.8–5.2 (m, 9 H), 4.95 (t, J = 2 Hz, 1 H), 1.0 (s, 9 H), 0.1 (s, 6 H); m/e (M^+) calcd 298.1753, obsd 298.1761.

This mixture was dissolved in methanol (200 mL), treated with 5% hydrochloric acid (1 mL), and stirred at room temperature for 5 h. Following concentration, the residue was taken up in ether (100 mL), washed with brine, dried, and concentrated to leave 2.85 g of a light yellow oil. MPLC purification on silica gel (elution with petroleum ether-ethyl acetate, 4:1) gave **46a** as a colorless waxy solid (1.4 g, 36% for last three steps): IR (cm^{-1}, CCl_4) 3580, 3520–3160, 3060, 3035, 1390; ^1H NMR ($CDCl_3$) δ 6.25 (dd, J = 8 and 2 Hz, 1 H), 6.2–5.3 (m, 9 H), 4.61 (m, 1 H); m/e (M^+) calcd 184.0888, obsd 184.0895.

The 3,5-dinitrobenzoate (**46c**) was obtained in 88% yield as a yellow crystalline solid: mp 148 °C (from carbon tetrachloride); IR (cm^{-1}, $CHCl_3$) 3095, 3030, 1725, 1625, 1545, 1340, 1270, 1160; ^1H NMR ($CDCl_3$) δ 9.46–8.93 (m, 3 H), 6.4–5.2 (m, 11 H); m/e (M^+) calcd 378.0852, obsd 378.0860.

Anal. Calcd for $C_{20}H_{14}N_2O_6$: C, 63.49; H, 3.73. Found: C, 63.53; H, 3.75.

***syn*-11-Methoxy[4.4.3]propella-2,4,12-triene (37b).** Sodium hydride (80 mg of 50% oil dispersion, 1.67 mmol) was washed with hexane and dried under a stream of nitrogen. A solution of **37a** (32.6 mg, 0.17 mmol) in dry tetrahydrofuran (5 mL) was added, and the mixture was stirred at room temperature for 4 h prior to the addition of methyl iodide (300 mg, 2.1 mmol, freshly passed through alumina). After an additional 20 h, ice water (10 mL) was slowly added and the product was taken up in dichloromethane. The organic phase was washed with water, dried, and evaporated. The residual oil was purified by preparative VPC (12 ft × 0.25 in. 5% SE-30) at 175 °C; ^1H NMR ($CDCl_3$) δ 6.1–5.2 (m, 6 H), 4.15 (s, 1 H), 3.35 (s, 3 H), 1.65–1.2 (m, 8 H).

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.13; H, 8.98.

***anti*-11-Methoxy[4.4.3]propella-2,4,12-triene (36b). A. Methanolysis of *syn*-3,5-Dinitrobenzoate 37c.** A solution of **37c** (157 mg, 0.41 mmol) and 2,6-lutidine (0.3 mL) in absolute methanol (25 mL) was heated in a sealed ampule at 125 °C for 2 days. After the solution was cooled, methanol was evaporated, the residue was dissolved in dichloromethane, and this solution was washed with saturated sodium bicarbonate solution and water prior to drying. Following solvent removal, there was obtained

113.1 mg of a yellowish solid, ^{1}H NMR analysis of which showed ethers **36b** (δ 3.4) and **37b** (δ 3.35) as well as methyl 3,5-dinitrobenzoate (δ 4.0) to be present in a 62:9:29 ratio. The combined yield of **36b/37b** was therefore 97%. A separate control experiment showed methanol to react with 3,5-dinitrobenzoic acid to form ester under the conditions employed. Ester formation was not encountered with **37a** under comparable conditions.

B. Methanolysis of *anti*-3,5-Dinitrobenzoate 36c. A solution of **36c** (202 mg, 0.53 mmol) and 2,6-lutidine (0.4 mL) in absolute methanol (25 mL) was heated in a sealed ampule under nitrogen at 96 °C for 24 h. The predescribed workup afforded 115 mg of a yellow crystalline solid with a composition very similar to that in A. The calculated yield of methyl ethers was 89%. An analytical sample of **36b** was prepared by preparative VPC as before: ^{1}H NMR ($CDCl_3$) δ 6.1–5.2 (m, 6 H), 4.27 (t, J = 1.7 Hz, 1 H), 3.40 (s, 3 H), 1.8–1.0 (m, 8 H).

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.17; H, 8.93.

11-Methoxy[4.4.3]propell-12-ene (38b). Methanolysis of 38c. A solution of **38c** (145 mg, 0.375 mmol) and 2,6-lutidine (0.5 mL) in absolute methanol (25 mL) was heated in an ampule under nitrogen at 125 °C for 4 days. The usual workup afforded a semicrystalline mixture of **38b** and methyl 3,5-dinitrobenzoate (128 mg) in a ratio of 59:41 (96% of **38b**). The mixture was separated by TLC on silica gel (elution with dichloromethane–petroleum ether, 2:1) to give **38b** as a clear colorless oil: ^{1}H NMR ($CDCl_3$) δ 5.6 (s, 2 H), 4.35 (s, 1 H), 3.40 (s, 3 H), 1.7–1.2 (m, 16 H).

Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.80; H, 10.49.

11-Methoxy[4.4.3]propella-2,4,7,9,12-pentaene (46b). A solution of **46c** (202 mg, 0.53 mmol) and 2,6-lutidine (0.5 mL) in absolute methanol (20 mL) was heated in a sealed ampule under nitrogen at 80 °C for 48 h. The usual workup gave a yellow oil (123 mg) containing 80% of **46b** and 20% of methyl 3,5-dinitrobenzoate (^{1}H NMR analysis). An analytical sample of **46b** was obtained by preparative VPC (170 °C) as before: ^{1}H NMR ($CDCl_3$) δ 6.17 (dd, J = 8 and 2 Hz, 1 H), 5.8–5.2 (m, 9 H), 4.45 (t, J = 1.7 Hz, 1 H), 3.4 (s, 3 H); m/e (M^+) calcd 198.1045, obsd 198.1049.

Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.72; H, 7.17.

Preparative Scale Solvolysis of 38c. A solution of **38c** (200 mg, 0.52 mmol) and 2,6-lutidine (0.6 mL) in 80% aqueous acetone (50 mL) was divided among several Pyrex test tubes, blanketed with nitrogen, sealed at 0 °C, and heated at 100 °C for 3 days. The acetone was evaporated, and the product was extracted into dichloromethane. The organic phase was washed with saturated sodium bicarbonate solution, 3 N hydrochloric acid, saturated sodium bicarbonate solution, and water prior to drying and solvent evaporation. One-hundred and fifteen milligrams of a yellowish solid remained, consisting of >90% **38a** and <10% unreacted **38c**. Preparative TLC separation (silica gel, elution with dichloromethane) gave 90 mg (90%) of **38a**.

Preparative Scale Solvolysis of 36c. Heating a solution of **36c** (45 mg, 0.12 mmol) and 2,6-lutidine (0.2 mL) in 80% aqueous acetone (15 mL) at 100 °C for 20 h afforded 19 mg (86%) of the anti/syn alcohol mixture (10:1, ^{1}H NMR analysis).

Preparative Scale Solvolysis of 37c. Heating a solution of **37c** (73 mg, 0.19 mmol) and 2,6-lutidine (0.3 mL) in 80% aqueous acetone (25 mL) at 95 °C for 20 h afforded 32 mg (90%) of the anti/syn alcohol mixture (10:1, ^{1}H NMR analysis).

Preparative Scale Solvolysis of 46c. From 70 mg (0.18 mmol) of **46c** and 0.2 mL of 2,6-lutidine in 20 mL of 80% aqueous acetone (90 °C, 8 h), 29 mg (85%) of **46a** was obtained as the only detectable product.

Kinetic Studies. A. Preparation of Reagents. Acetone was prepared by distillation from potassium permanganate. Triply distilled water was employed. Methanol was prepared by distillation from magnesium methoxide. The aqueous acetone was prepared on a volume to volume basis. Standard 0.005 N sodium hydroxide was obtained from The Ohio State University Reagents Laboratory. The ampules were cleaned with chromic acid, water, and dilute ammonium hydroxide and thoroughly flushed with water. After being dried, they were narrowed at the neck to facilitate sealing.

B. Determination of Data. Solutions of the 3,5-dinitrobenzoates in 80% aqueous acetone were prepared by weighing the appropriate ester into a 10.0-mL volumetric flask and filling to the mark with 80% aqueous acetone. The concentration of 3,5-dinitrobenzoate varied from 0.0100 to 0.0200 M over all runs. The resulting solution was divided into eight glass ampules (1-mL aliquots), which were sealed under partial vacuum. All ampules were simultaneously immersed into a constant temperature bath. After 5–10 min, one ampule was removed from the rate bath and placed in an ice-water mixture. A timer was started upon removal of the first ampule. The remaining ampules were removed and cooled at appropriate intervals covering 2 half-lives. The final ampule was removed after at least 10 half-lives to provide the infinity point. The individual ampules were allowed to warm to room temperature, at which point a standard aliquot was removed, diluted with 2 mL of acetone, and titrated against 0.0050 N sodium hydroxide using bromothymol blue as indicator. First-order rate data were determined by measuring the amount of 3,5-dinitrobenzoic acid generated by solvolysis relative to the experimental infinity point. Duplicate runs agreeing within 5% were made at all temperatures.

[4.4.3]Propella-2,4,12-trien-11-one (51). A solution of **37a** (130 mg, 0.69 mmol) in cyclohexane (15 mL) was stirred at room temperature with 650 mg (7.47 mmol) of activated manganese dioxide for 12 h and at the reflux point for 60 min. Filtration of the cooled reaction mixture through Celite and filtrate evaporation furnished 90 mg of **51** as a colorless oil, which slowly crystallized: IR (cm^{-1}, CCl_4) 3025, 2930, 2850, 1715, 1445; UV (nm, CH_3CN) 222 (ε 10912), 268 (ε 2265); ^{1}H NMR ($CDCl_3$) δ 7.33 (d, J = 6 Hz, 1 H), 6.37 (d, J = 6 Hz, 1 H), 6.1–5.6 (m, 2 H), 2.0–1.2 (m, 8 H); ^{13}C NMR ($CDCl_3$, ppm) 211.79, 166.64, 132.24, 130.96, 130.23, 123.01, 121.43, 53.95, 49.46, 33.68, 28.83, 18.45 (2 C); m/e (M^+) calcd 186.1045, obsd 186.1049.

Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.68; H, 7.70.

[4.4.3]Propella-2,4,7,9,12-pentaen-11-one (52). A solution of **46a** (43mg, 0.23 mmol) in dry dichloromethane (10 mL) was treated with pyridinium dichromate (120 mg, 0.32 mmol). After 12 h of stirring at room temperature, the mixture was diluted with ether (15 mL), filtered through Celite, and evaporated. The resulting yellow oil was purified by preparative TLC on silica gel (elution with dichloromethane) to give 25 mg (58%) of **52** as a colorless solid: mp 79–80 °C; IR (cm^{-1}, CCl_4) 3030, 1720, 1650, 1580, 1440; UV (nm, CH_3CN) 216 (ε 15800), 270 (ε 2100); ^{1}H NMR ($CDCl_3$) δ 7.48 (d, J = 6 Hz, 1 H), 6.65 (d, J = 6 Hz, 1 H), 5.9–5.1 (m, 8 H); ^{13}C NMR ($CDCl_3$, ppm) 209.37, 167.04, 133.08, 128.50, 127.20, 120.77, 120.58, 55.62, 51.92; m/e (M^+) calcd 182.0732, obsd 182.0740.

Anal. Calcd for $C_{13}H_{10}O$: C, 85.69; H, 5.53. Found: C, 85.43; H, 5.50.

General Procedure for Sample Preparation in Superacid Media. A thin-walled 5-mm NMR tube was immersed in an isopentane–liquid nitrogen slush bath (–140 °C) while being flushed with a stream of dry nitrogen. A 0.10-mL sample of spectrograde fluorosulfuric acid was introduced via pipet into the bottom of the tube where it quickly solidified. Sulfuryl chloride fluoride (0.30 mL) was next added. The organic compound was dissolved in 0.10 mL of dichloromethane-d_2 and placed on top of the sulfuryl chloride fluoride. A thin glass stirring rod was introduced. The NMR tube was allowed to warm until the methylene chloride layer dissolved with stirring. The tube was then stored at −140 °C prior to spectral measurement.

Sodium Borohydride Reduction of 51. A solution of **51** (43 mg, 0.23 mmol) and cerous chloride (63 mg, 0.26 mmol) in methanol (10 mL) was stirred for 15 min at room temperature before sodium borohydride (20 mg, 0.53 mmol) was introduced. Following 3 h of stirring, the reaction mixture was poured into 1 N sodium hydroxide solution (25 mL), stirred for 15 min, and filtered through Celite. The filter cake was rinsed with ether (50 mL), the filtrate layers were separated, and the aqueous phase was extracted with ether (2 × 10 mL). The combined organic layers were washed with water, dried, and evaporated. ^{1}H NMR analysis of the residue showed **36a** and **37a** to be present in a 6:4 ratio by integration of the >C*H*OH signals at δ 4.72 and 4.04, respectively. Approximately 50% of unreacted **51** also remained.

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Registry No. 4, 3642-06-6; **5**, 14679-43-7; **6**, 85067-30-7; **7**, 85067-31-8; **8**, 85067-32-9; **9**, 85067-33-0; **10**, 85082-19-5; **11**, 85067-34-1; **12**, 85067-35-2; **12** 2,4-DNP derivative, 85082-18-4; **17**, 85067-36-3; **18**, 85067-37-4; **19**, 85067-38-5; **20**, 15405-74-0; **21a**, 85067-39-6; **21b**, 85082-20-8; **24a**, 85067-40-9; **24b**, 85067-41-0; **25a**, 85067-42-1; **25b**, 85067-43-2; **27**, 53295-66-2; **28**, 78677-78-8; **29a**, 85067-44-3; **29b**, 85067-45-4; **30**, 85067-46-5; **31**, 85067-47-6; **32a**, 85067-48-7; **32b**, 85067-49-8; **32b** dihydro derivative, 3642-28-2; **33a**, 85082-21-9; **33b**,

3642-51-1; **34a**, 85067-50-1; **34b**, 3642-25-9; **35a**, 85067-51-2; **35b**, 85067-52-3; **36a**, 83187-03-5; **36b**, 83187-08-0; **36c**, 83187-06-8; **37a**, 83213-89-2; **37b**, 83214-18-0; **37c**, 83213-90-5; **38a**, 83187-02-4; **38b**, 85067-53-4; **38c**, 83187-05-7; **39**, 85067-54-5; **40**, 85067-55-6; **41a**, 85067-56-7; **41b**, 85067-57-8; **42**, 85067-58-9; **43**, 85067-59-0; **44**, 85067-60-3; **45a**, 85067-61-4; **45b**, 85067-62-5; **45b** debromo derivative, 85067-63-6; **46a**, 83187-04-6; **46b**, 85067-64-7; **46c**, 83187-07-9; **50**, 83187-09-1; **51**, 83187-10-4; **52**, 83187-11-5.

Chemoselective Behavior of Enolate Carbenes Derived from Dianions of Enol Thioacetals

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Abstract: Evidence is provided for the generality of the newly enunciated concept that the normally stable lithio derivatives of diphenyl thioacetals decompose cleanly to carbenes when another negative charge is present nearby in the same molecule; furthermore, in contrast to conventional carbenes, these carbenes can be highly selective in their reactions which are shown to be determined by the nature of the second anionic site and its juxtaposition with respect to the carbenic carbon atom. When the lithium enolate produced by β-addition of tris(phenylthio)methyllithium to 2-cyclohexenone is treated with *sec*-butyllithium at −50 °C, sulfur–lithium exchange occurs and the resulting double conjugate base of an enol thioacetal, upon being warmed to 0 °C, decomposes to a lithium dienolate which is believed to arise by a 1,2-hydrogen transfer in the intermediate enolate carbene. A similar sequence starting with (−)-carvone results in the production of a bicyclo[4.1.0] system formally resulting from the addition of PhSCH across the enone double bond. The difference in behavior in the two systems is rationalized on the basis of conformational differences. Cyclopentenone gives both types of products.

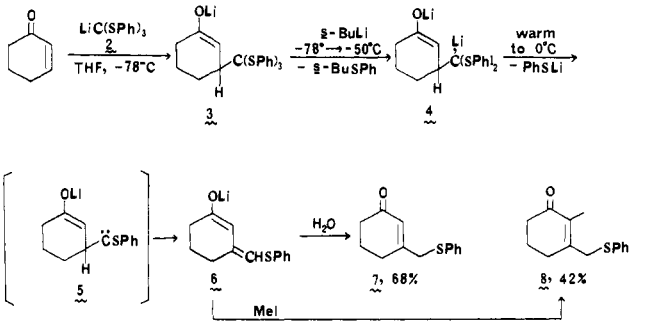
The following previously unrecognized principle, which can be of considerable mechanistic and synthetic significance, has recently been enunciated: Normally stable lithio salts of diphenyl thioacetals decompose to carbenes when they are generated in a molecule with a second anionic site nearby and the anionic moiety of the resulting carbene anion may be influential in determining the reaction course of the carbene.[1] The significance of the concept is that it may allow the ready generation of a usefully substituted and selectively reactive carbene in a variety of types of molecules. One example of the unconventional chemistry engendered by this new concept is the ring closure shown in eq 1 in which the carbene formed by loss of thiophenoxide ion from **1** apparently inserts into the weak alkoxide CH bond.[1]

$$(PhS)_2CH(CH_2)_3CH_2OH \longrightarrow \underset{\mathbf{1}}{(PhS)_2\overset{Li}{C}(CH_2)_3CH_2OLi} \xrightarrow{-PhSLi} \underset{\text{cis + trans}}{\text{OLi, SPh}} \quad (1)$$

We now demonstrate the validity of this principle of carbene generation in the case of a new type of conveniently prepared dianion, formally the double conjugate base of a molecule containing both diphenyl thioacetal and ketone functions, and we provide striking illustrations that, in sharp contradistinction to conventional carbenes, the carbenoid carbon atoms of the enolate carbenes produced from these dianions can be remarkably selective in their intramolecular reactions while maintaining high reactivity; *their reactions appear to be totally determined by the disposition of the anionic site with respect to the carbene.*

When the lithium enolate **3** (Scheme I), produced by the addition of tris(phenylthio)methyllithium (**2**) to 2-cyclohexenone at −78 °C,[2,3] is treated with *sec*-butyllithium and the solution is warmed to −50 °C, clean sulfur–lithium exchange[1] occurs to produce the dianion **4**, which can be detected by protonation and by reaction with other electrophiles as will be detailed in a separate report. When the solution of **4** is warmed to 0 °C, the dianion is smoothly converted to the lithium dienolate **6**. The latter, upon

Scheme I



protonation, provides a good yield of 3-((phenylthio)methyl)-2-cyclohexenone (**7**) and, upon treatment with methyl iodide, yields mainly **8**, the monomethyl derivative of **7**, along with some dimethylation product.[4] The formation of **8** constitutes a one-pot α,β-disubstitution of cyclohexenone.

The dienolate **6** is the product expected from the insertion of the carbenoid carbon atom of **5** into the adjacent CH bond. Although, such 1,2-hydrogen transfers are the most common mode of reaction of carbenes which are uncomplexed to transition metals,[5,6] they were not noted in the carbene anions which were generated previously[1] presumably because other reactions, in which the anionic center plays a dominating role, are far faster than the 1,2-transfer. In the case of **5**, the 1,2-transfer *is* dictated by the negative charge; in fact this transfer should be recognized as a

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(2) Manas, A. R.-B.; Smith, R. A. J. *J. Chem. Soc., Chem. Commun.* **1975**, 216. Smith, R. A. J.; Lal, A. R. *Aust. J. Chem.* **1979**, *32*, 353.
(3) Cohen, T.; Nolan, S. M. *Tetrahedron Lett.* **1978**, 3533.

(4) (a) The dimethylation appeared to occur largely at the 2-position, but the product was obtained impure and was not completely characterized. (b) Remarkably, the lithium dienolate **6** is inert toward reaction with the carbonyl reagents, carbon dioxide, propanal, and benzaldehyde; the products of these reactions are presumably thermodynamically unstable with respect to the reactants.
(5) Reviews of carbenes: (a) Wulfman, D. S.; Poling, B. In "Reactive Intermediates"; Abramovitch, R. A., Ed.; Plenum Press: New York, 1980; Vol. 1. (b) Kirmese, W. "Carbene Chemistry", 2nd ed.; Academic Press: New York, 1971. (c) Moss, R.; Jones, M. "Carbenes"; Wiley: New York, 1973; Vol. 1.
(6) Jones, W. M. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1. Schaefer, H. F., III. *Acc. Chem. Res.* **1979**, *12*, 288.

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