The rapid increase in mobility observed when a functionalized polyethylene sample is placed in ethanol suggests, however, that the surface layer is probably completely swollen in the time (~ 1 h) required to complete the reaction, and that prior immersion in ethanol would not greatly change the behavior of the final samples.
(26) Migration of polar molecules into polyethylene has been observed. For example, copper carboxylate species formed at a polyethylene–copper interface can penetrate deep into the bulk polymer: D. L. Allara, C. W. White, R. L. Meek, and T. H. Briggs, *J. Polym. Sci., Part A-1*, **14**, 93 (1976).
(27) Rotational correlation times are estimates based on studies correlating signal line shape with τ_R.[24,28]
(28) Similar observations have been made for spin labels in solvent-swollen polymers: S. L. Regen, *J. Am. Chem. Soc.*, **97**, 3108 (1975).
(29) H. V. Boenig, "Polyolefins", Elsevier, New York, N.Y., 1966, Chapter 5.
(30) G. P. Rabold, *J. Polym. Sci., Part A-1*, **7**, 1203 (1969).
(31) L. Mandelkern, *Acc. Chem. Res.*, **9**, 81 (1976).
(32) A. Baszkin, N. Nishino, and L. Ter-Minassian-Saraga, *J. Colloid Interfac. Sci.*, **54**, 317 (1976).
(33) Although it might appear that polypropylene or high-density polyethylene are as suitable as low-density polyethylene for these surface studies, it has been reported that of these three polyolefins, only low-density polyethylene film yields a detectable carbonyl signal following oxidation by chromic acid.[34] Analysis of the oxidized films by electron microscopy and contact angle measurements suggested that polypropylene oxidizes rapidly due to the large number of tertiary sites to produce small acid fragments which are soluble in the aqueous reaction medium, and yields a surface relatively free of oxidation products; high-density polyethylene oxidizes slowly but unevenly because of the lack of tertiary sites and the high degree of crystallinity to produce a surface layer with very deep pitting and a low absolute number of oxidation products; and low-density polyethylene oxidizes with extensive pitting due to preferential oxidation deep into the amorphous regions of the polymer film with a concomitant buildup of carbonyl groups.[34]
(34) P. Blais, D. J. Carlsson, G. W. Csullog, and D. M. Wiles, *J. Colloid Interfac. Sci.*, **47**, 636 (1974).
(35) B. J. Gaffney in "Spin Labeling: Theory and Applications", L. J. Berliner, Ed., Academic Press, New York, N.Y., 1975, Chapter 5.

The Question of Delocalization in "Anchored" Ions with Potential Trishomoaromatic Character. 1. Reduction of Tricyclo[5.4.1.$0^{4,12}$]dodeca-2,5,8,10-tetraene as a Route to the 10π11C Dianion

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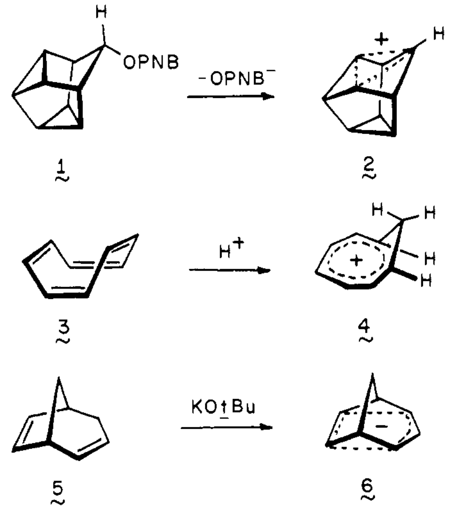
Abstract: The title compound (**13**), although not available from the pyrolysis of **11** (Scheme I), can be obtained in two steps from Schröder's hydrocarbon (**14**, Scheme II). The unprecedented $(CH)_{12}$ interconversions which result during these rearrangements show the richness of the interconnective energy surface. Dissolving metal reduction of **13** does not give rise to a spectroscopically characterizable dianion species, but methanol quenching provides two dihydro ($C_{12}H_{14}$) products and two isomeric $C_{12}H_{12}$ hydrocarbons. These transformations are discussed in terms of a highly basic dianion by virtue of its ensuing reactions. For comparison purposes, the reducibility of bicyclo[6.2.1]undeca-2,4,6,9-tetraene (**31**) has also been examined in the context of generating a bishomocyclooctatetraenyl dianion. The relationship of these observations to the general homoaromaticity phenomenon, particularly as regards the question of multiple interruption of the cyclic π-electron network, is discussed.

These exist two possible ways of attaining that level of electronic interaction which gives rise to homoaromatic delocalization.[2] In the first of these, a strained σ bond (preferably cyclopropyl) is positioned in the structural framework such that moderate rehybridization[3] can provide the necessary contiguous overlap (on one surface only!) of orbitals containing ($4n + 2$) electrons. The solvolysis of **1** is exemplary. Its 10^{12}-fold solvolytic rate acceleration over 7-norbornyl,[5] which cannot be attributed to strain relief because the ensuing rearrangement is degenerate, is best understood in terms of charge development as in **2**. In fact, this trishomocyclopropenyl cation intermediate has been directly observed.[6] The other alternative is to make available an appropriate number of p-π orbitals such that electrophilic attack at one of these sites, ionization at an adjoining sp^3-hybridized center, or introduction of electrons by one of several reductive methods generates a similar type of cyclic conjugation. In larger molecules such as **3** which have adequate conformational flexibility, built-in structural constraints are unnecessary because those three-dimensional features necessary for overlap in the vicinity of the tetrahedral carbon (cf. **4**) can be realized without severe distortion.[7] In other cases typified by **5**, the absence of a rigid structural framework would be inimical to the operation of homoaromatic delocalization.[8]



Although the first of these phenomena has received considerable attention,[2,9] the second aspect has been less systematically investigated. This is perhaps because a series of polyunsaturated molecules having rigid geometry and properly canted π orbitals has not been generally available. In an attempt to develop our understanding of the homoaromaticity phenomenon, we have now conducted a detailed reactivity study of substrates which can serve as precursors to the "anchored" trishomoaromatic ions **7–9**.[10,11] Attention remains

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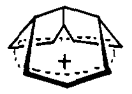

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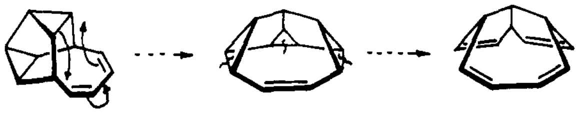
to be directed to **10**, the smallest member of this series. All four species are characterized by the presence of three π-interruptive tetrahedral carbons which are maintained in crucial cisoid juxtaposition[12] by an apical carbon (the so-called "anchor"). On this basis, they are closely related to triquinacene. Although this hydrocarbon is recognized to be weakly homoaromatic,[13-15] the presence in **7–10** of a driving force for change delocalization could very well work in favor of a homoaromatic ring current.

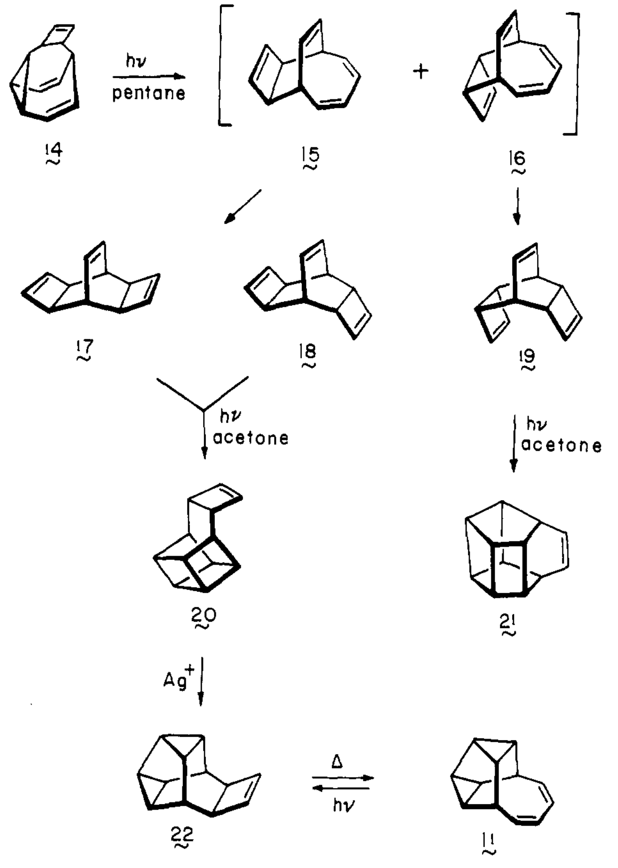
The present paper not only examines our efforts in gaining access to **7** and a related bishomocyclooctatetraenyl dianion, but also describes a number of unusual interconversions on the (CH)$_{12}$ energy surface.

Synthetic Considerations. The generality of bishomoconjugative rearrangements[16] and the recognized ability of snoutene for degenerate thermal rearrangement[17] combined to prompt consideration of the interesting possibility that diene **11** might serve as an immediate precursor to the desired tetraene **13**. Thus, thermally activated **11** could experience symmetry-allowed intramolecular [$_\pi 4_s + _\pi 2_s$] cycloaddition with utilization of one internal cyclopropane bond to provide **12**.[18] The strained nature of this polycyclic hydrocarbon was viewed as adequate to allow subsequent homolysis of the indicated triad of cyclopropyl bonds, perhaps via free-radical intermediates, to deliver **13**.



The successful preparation of **11** is outlined in Scheme I.[19] When irradiated (450-W Hanovia lamp) in dilute pentane solution through quartz for 2 h, tetracyclo[5.3.2.0^{2,5}.0^{6,8}]dodeca-3,9,11-triene (**14**)[20] underwent ready isomerization according to the Katz–Cheung mechanism[21] to furnish **15** and **16** which were not detected because of rapid disrotatory cyclization. The feasibility of the transitory intervention of **15** under the reaction conditions had been previously demonstrated.[22] The comparable behavior of **16** was established later in this work. Vapor phase chromatographic (VPC) analysis indicated **17** and **18** to be the major components of the resulting mixture and this point was verified by its triplet-sensitized (acetone) photocyclization to **20** and **21**[23] (ratio ca. 10:1). Structural assignment to **20** follows from its ^{1}H nuclear magnetic resonance (NMR) spectrum, its vapor phase fragmentation at 450 °C and 2 mm to a mixture of **15** (28%) and **16** (72%), and its rapid quantitative isomerization to **22** upon treatment with silver nitrate in aqueous methanol at 25 °C.[24] Pyrolysis of **22** resulted in partial conversion to **11**, but increases in temperature beyond the necessary 580 °C (1.5 mm, contact time $\sim$2 s) did not eventuate in recognizable isomerization to **13** as desired. The identity of **11** is based upon its electronic and ^{1}H NMR spectra (see Experimental Section) and its rapid and efficient reconversion to **22** upon direct irradiation. The remarkable thermal stability of **11** provides no information on its possible interconversion with **12**. Orbital symmetry considerations suggest that if **12** does exist in equilibrium with **11** at elevated temperatures symmetry-allowed six-electron bond reorganization returning **11** is substantially favored over the forbidden (eight electron) process which would rise to **13**.

Scheme I

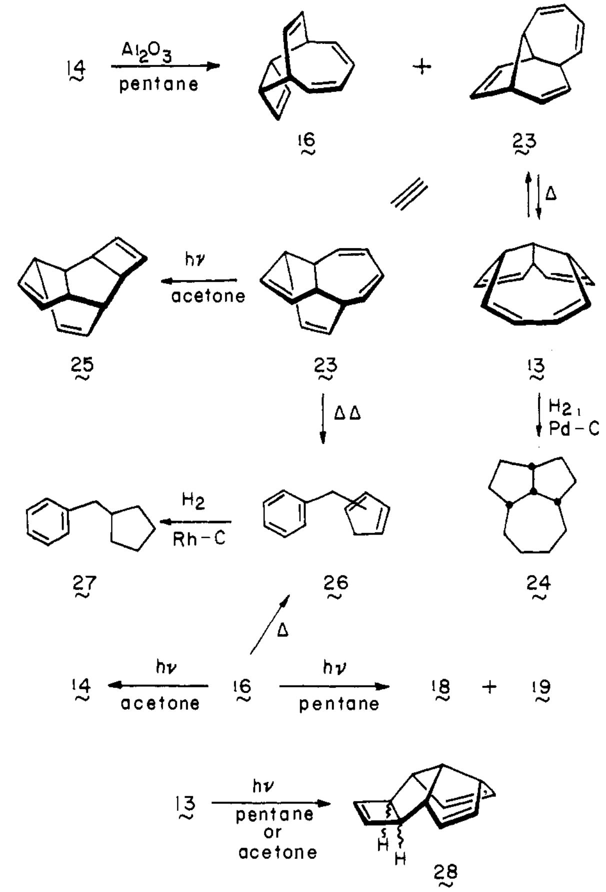


Although desired tetraene **13** was not accessible via the above (CH)$_{12}$ interconversions, the chance discovery that Woelm activity I neutral alumina promoted the deep-seated rearrangement of **14** to **16** and **23** became the basis of its direct two-step synthesis. In a typical experiment, adsorption of a pentane solution of **14** onto this solid phase for several hours resulted in efficient conversion to **16** and **23** in the relative ratio of 3:1 (Scheme II). The ^{1}H NMR spectrum of **16**, which is very similar to that of the exo isomer,[22] is characterized by aliphatic and olefinic multiplets at δ 2.85 (4 H) and 5.65 (6 H), respectively, in addition to a sharp cyclobutene singlet of area 2 at 6.05. The electronic spectrum (ethanol) consists of a series of maxima at 257 sh (ε 1760), 263 (2100), 273 (2070), and 282 rh nm (1290). The ^{1}H NMR spectrum of **23** reveals its structural similarity to lumibullvalene,[21,25] especially with respect to the high-field olefinic multiplet (δ 4.95, 1 H) and the characteristic doublet of doublets at 6.4. The ultraviolet datum [$\lambda_{max}^{C_2H_5OH}$ 235 sh nm (3390)] indicates the twisted nature of the diene moiety.

The structural assignment to **16** was substantiated by its conversion upon direct irradiation (200-W Hanovia lamp) to **18** and **19** which were separable by VPC on QF-1.[26] Use of a more intense (450 W) lamp source did not allow for the isolation of **19** as this triene is now subject to rapid photocyclization to give **21**. Under triplet conditions (acetone), **16** underwent the di-π-methane photorearrangement to return **14**.

Comparable irradiation of **23** in acetone solution prompted conventional diene cyclization with formation of **25**. Although the stereochemistry of the cyclobutene ring in **25** has not been

Scheme II



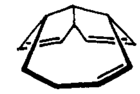
rigorously determined, we favor the exo form since continued exposure to light did not result in (2 + 2) cycloaddition as anticipated for the endo isomer. When pyrolyzed above 575 °C, both **16** and **23** were converted to a mixture of benzylcyclopentadiene isomers (**26**).[27]

Importantly, the desired tetraene (**13**) was obtained upon thermolysis of **23** at 380 °C in a flow system (gas phase, N_2 as carrier gas). Although a single product was formed under these conditions, the conversion realized was only 66%. When the temperature of the chamber was raised to 430 °C, this ratio was unaffected and an equilibrium situation was indicated. This point was subsequently established by comparable treatment of **13** which gave rise to **23** (33%). That **13** possesses the indicated tricyclic framework was indicated by its symmetrical ^1H NMR spectrum (see Experimental Section), its UV absorption maximum (C_2H_5OH, 252 nm, ε 3470) which is characteristic of a conjugated diene moiety, and its catalytic reduction to saturated hydrocarbon **24** of well-established structure.[28] Although the reversible interconversion of **13** with **23** is most simply rationalizable in terms of [1,5]-sigmatropic migration of the appropriate vinyl bridges, this mechanistic hypothesis has not been confirmed and the question remains open.

Key $(CH)_{12}$ hydrocarbon **13** underwent the identical photochemical ring closure to **28** under either singlet or triplet conditions. Stereochemical assignment to **28** has not been made, but this photoproduct points up the close structural similarities between **13** and triquinacene.

Reduction Studies of Tricyclo[5.4.1.0^{4,12}]dodeca-2,5,8,10-triene (13). From our observation that polarographic reduction of **13** in anhydrous tetrahydrofuran at a dropping mercury electrode occurs only at the decomposition limit of the solvent ($E_{1/2} \simeq -3.2$ V vs. SCE), a moderate reluctance on the part of this tetraene to accept electrons can be inferred. As concerns the chemical reduction of **13**, two systems were examined in detail: potassium metal in NH_3 or ND_3 and a potassium mirror with tetrahydrofuran-d_8 as solvent. At −65 °C with strict exclusion of oxygen (vacuum-line techniques), both methods generated a bright red solution almost immediately. Examination of these homogeneous solutions by electron spin resonance (ESR) spectroscopy gave no evidence for the presence of radical anions. The ^1H NMR spectra of these solutions (recorded at −65 °C for ND_3 and between −100 and −65 °C for K/THF within 5-30 min of generation) were extremely complex, although the loss of starting material was clearly indicated. However, it was not possible to discern whether the same species was (were) produced under the different conditions. Subsequent to methanol quenching of the tetrahydrofuran reaction mixture, four products were shown by VPC analysis to be present in meaningful quantities. Gas chromatography-mass spectral examination of this mixture indicated two to be of *m/e* 158 (i.e., $C_{12}H_{14}$) and the remaining pair (no **13**) to be of *m/e* 156. Methanol treatment at −65 °C of the liquid ammonia solution also gave four hydrocarbons as above. Each of the products from the two reactions was separately subjected to catalytic hydrogenation and shown to provide **24** as the sole reduction product. The identities of the basic structural frameworks were thereby established.

On the basis of its mass spectral, UV (no absorption), and ^1H NMR parameters (olefinic/aliphatic = 6:8; no symmetry), the major product is considered to be **29**. The lesser three components contain ultraviolet-responsive chromophores. The isolation of two compounds with the molecular composition $C_{12}H_{12}$ was unexpected. Apparently, these arise from prototropic shifts in **13**, although its exposure to *tert*-butyllithium at room temperature for 48 h induced no comparable rearrangement.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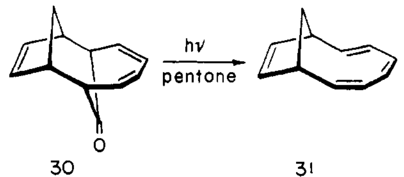
These observations may be rationalized either in terms of direct two-electron reduction of **13** to dianion **7** and ultimate protonation of the latter, or a stepwise reduction sequence mediated by a radical anion which suffers protonation or hydrogen atom abstraction. A distinction between these mechanisms has not been possible because of the high reactivity of these intermediates.

In an effort to bridge the gap between the simple monohomocyclooctatetraenyl dianion[29-31] and **7**, we have also examined the behavior of bicyclo[6.2.1]undeca-2,4,6,9-tetraene (**31**), a possible precursor to bishomoaromatic dianion **32**.

Reduction Studies of Bicyclo[6.2.1]undeca-2,4,6,9-tetraene (31). Photodecarbonylation of the (6 + 4)π tropone-cyclopentadiene adduct (**30**) according to Mukai[32] provides a convenient synthetic entry to **31**. Polarographic and cyclic voltammetric studies on **31** were conducted in anhydrous tetrahydrofuran (THF) and hexamethylphosphoramide (HMPA) solutions. The more extended conjugation in **31** permits reduction to occur at a more accessible potential than **13**. Notwithstanding, the $E_{1/2}$ values remain very negative and appear in the region characteristic of medium-ring conjugated trienes[33] (Table I). The presence of the fourth ($C_{9,10}$) double bond in **31** does not appear to promote more facile reduction



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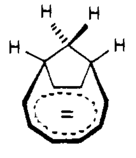

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Table I. Polarographic Half-Wave Potentials, Diffusion Current Constants, and Peak Current Constants from Cyclic Voltammetry

Polyolefin	Sovent	$E_{1/2}$, V vs. SCE	Concn, mM	Slope,[a] V	I_D	n_{app}	I_p[b]	n_{app} (overall)
31	HMPA	−2.44	3.65	0.055	0.77	1	0.296	1
	THF	−2.86	1.66	0.055	4.67	1–1.5	1.24	1
1,3,5-Cyclooctatriene[c]	THF	−2.77		0.029	4.26	1		
Cyclooctatetraene	HMPA	−1.606 −1.981	0.5–1.5		2.52	2	0.42	2
	THF[d]	−1.98	0.218	0.033	4.06	2	0.95	2
		−2.145		0.019	2.24		2.70	

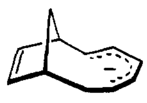
[a] Reciprocal plot of E vs. ln $[i/(i_d - i)]$. [b] Expressed in A/cm^2 V$^{1/2}$ M. [c] Taken from ref 33. [d] Taken from L. A. Paquette, S. V. Ley, R. H. Meisinger, R. K. Russell, and M. Oku, *J. Am. Chem. Soc.*, **96**, 5806 (1974).

compared to 1,3,5-cyclooctatriene. The differing features of the electrochemical behavior of **31** and cyclooctatetraene are particularly noteworthy.

The slopes of the single wave exhibited by **31** indicate the electron transfer process to be non-Nernstian and cyclic voltammetry shows no reoxidizable product except at extremely fast scan rates (10 V/s). The diffusion current (I_D) and peak current constants (I_p) calculated from these data indicate one-electron transfer to be operating. In THF solution, the I_D value was invariably somewhat larger than 1 for unknown reasons. Notwithstanding, this electrochemical evidence does not constitute a satisfactory criterion of homoaromaticity, in keeping with earlier findings.[33]

Treatment of **31** with a potassium mirror in THF-d_8 under dilute conditions (3 mg per 350 μL of solvent) at −100 °C showed no evidence of reaction (Fourier transform ^{1}H NMR). Gradual increases in temperature to 0 °C led to development of yellow color, but no new species could be observed spectroscopically. During 6 h at 0 °C, polymerization occurred.

With potassium in anhydrous liquid ammonia at −78 °C, a dark red solution formed rapidly. After quenching with methanol at this temperature, there was formed a major product identified as **34**. In the ^{13}C NMR spectrum, all 11 carbons including 6 sp^2-hybridized centers were distinctly observed. The $C_{11}H_{14}$ hydrocarbon was therefore not a symmetrical molecule. Because its electronic spectrum lacked absorption above 220 nm, the presence of a conjugated diene unit could be ruled out. The integrity of the bicyclo[6.2.1]undecane framework was established by catalytic reduction to **35** which was independently prepared by analogous hydrogenation of **31**.



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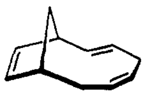

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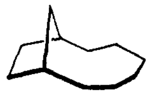

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When consideration is given to the likely electron densities prevailing in dianion **32** or its radical anion counterpart (**36**), C_2 is the anticipated site of initial protonation by solvent.[30,34] This event leads directly, or by subsequent electron transfer, to monoanion **33** whose pentadienylic nature promotes capture by methanol at the central carbon (here C_4) of the delocalized species.[35] Accordingly, the isolation of **34** is fully comprehensible in terms of the intervention of **32** or **36**.

When the reduction with potassium was studied in ND_3 solvent, a spectrum was recorded which was compatible with, but not unequivocally conclusive for, the presence of **33**-d_1. Unfortunately, our inability to observe **32** directly leaves open for the present the question concerning its direct intervention in these reductions. If the behavior of monohomocyclooctatetraenyl dianions serve as useful analogy (the parent species is too rapidly monodeuterated by ND_3 to permit direct observation),[30] then suitable placement of alkyl groups at the tetrahedral sites in **31** might provide adequate resistance against kinetic protonation to permit NMR scrutiny of such derivatives of **32**. Attempted deprotonation of **34** using n-butyllithium and TMEDA at room temperature (below 25 °C no reaction occurred) was, however, unsuccessful.

Concluding Discussion. A most interesting feature of ions **7–10** aside from their potential trishomoaromatic character is the locus of the "anchor" carbon atom almost directly in the axis of the would-be ring current. Because this is the region of maximum shielding, significant upfield shifts of the apical proton can be anticipated. The attainment of such extended electronic delocalization does, of course, depend heavily on the molecular geometry and the extent of atomic orbital overlap at several key sites. Simple HMO calculations[36] predict any interaction between the 1,3-butadienyl dianion and the pair of olefinic moieties in **7** to be favorable (Table II). Thus, we see that such interactions (assuming planarity) give evidence of being appreciable even for the case when (β/β_0) at the three sites of π-interrupted conjugation is as low as 0.3. More specifically, the trishomoaromatic model (case A, Table II) gives evidence of being somewhat more stabilized than its counterpart where *cyclic* delocalization is inhibited by disallowing overlap between C_3 and C_5 (case B). Also, kinetic protonation is predicted to occur predominantly at $C_{8,11}$ in agreement with the isolation of **29** as the major product of methanol quenching.

However, our inability to realize the experimental observation of **7** by the available spectroscopic tools suggests that this species is incapable of delocalizing charge efficiently and consequently may be especially reactive as the result of untoward electron-electron repulsion which can introduce substantial destabilization.[37] Additionally, orbital electronegativity effects arising from the two etheno bridges can exert a small,[38] but possibly important, detrimental effect to multiple electron uptake by the diene unit. Dianion **32** evidently suffers from similar electronic difficulties, this problem having been recognized still earlier at the monohomocyclooctatetraenyl level.[30] The implication here is that perhomoaromatic character might be better served by singly charged entities. This aspect is taken up in two related papers.[10,11]

The thermodynamic and kinetic instabilities of **7** and **32**, if formed, may also result because of less than ideal topological features. In this regard, a study of molecular models suggests that *total* orbital overlap should improve substantially as one progresses from **7** toward **10**. Incremental contraction of the constituent carbocyclic rings does serve to contract the gaps introduced by the three homo bridges. As a consequence, attempts to determine how far perhomoaromaticity can be pushed might also be better served by the smallest possible molecular structure.

The present findings provide an appreciation of the fact that bis- and trishomoaromatic dianions of reasonable geometry are not capable of stabilizing themselves as efficiently as their

Table II. HMO Calculations for **7**[a]

Case A: $\beta_{2,11} = \beta_{3,5} = \beta_{6,8}$		Negative charges				Case B: $\beta_{2,11} = \beta_{6,8}$; $\beta_{3,5} = 0$		Negative charges			
$\beta_{2,11}/\beta_0$	$E\pi - 10\alpha$ (β_0)	$C_{2,6}$	$C_{3,5}$	$C_{8,11}$	$C_{9,10}$	$\beta_{2,11}/\beta_0$	$E\pi - 10\alpha$ (β_0)	$C_{2,6}$	$C_{3,5}$	$C_{8,11}$	$C_{9,10}$
0.0	7.236	0.000	0.000	0.724	0.276						
0.3	7.552	0.100	0.147	0.526	0.226	0.3	7.442	0.037	0.117	0.601	0.246
0.5	8.040	0.177	0.226	0.392	0.204	0.5	7.744	0.056	0.222	0.500	0.222
0.75	8.794	0.226	0.255	0.304	0.214	0.75	8.238	0.059	0.335	0.405	0.201

Case C: $\beta_{2,11} = \beta_{3,5}$; $\beta_{6,8} = 0$		Negative charges							
$\beta_{2,11}/\beta_0$	$E\pi - 10\alpha$ (β_0)	C_2	C_3	C_5	C_6	C_8	C_9	C_{10}	C_{11}
0.3	7.400	0.064	0.145	0.010	0.030	0.645	0.220	0.281	0.605
0.5	7.688	0.138	0.278	0.036	0.132	0.541	0.148	0.285	0.442
0.75	8.199	0.183	0.341	0.054	0.290	0.549	0.086	0.303	0.283

[a] Numbering is based upon the nomenclature of **13**: tricyclo[5.4.1.$0^{4,12}$]dodeca-2,5,8,10-tetraene.

planar p-π or monohomoaromatic congeners which can be evaluated spectroscopically. In the current context then, stabilization mechanisms having their foundation in homoconjugation do not find it possible to overcome those other factors which gain importance when dicarbanions are involved.

Finally, the ready synthesis of **13**[39] should now make available a number of interesting higher vinylogs of triquinacene. Its exploitation as a template for the elaboration of yet other novel structures is under investigation.

Experimental Section

Melting points and boiling points are uncorrected. Proton magnetic resonance spectra were obtained with Varian A-60A, Varian HA-100, and Bruker HX-90 spectrometers; apparent splittings are given in all cases. Infrared spectra were determined on Perkin-Elmer Model 137 and 467 instruments. 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. Preparative VPC work was done on a Varian-Aerograph A90-P3 instrument equipped with a thermal conductivity detector. The ^1H NMR spectra of all the $(CH)_{12}$ isomers have been reproduced in the Ph.D. thesis of M.J.K.[27]

Direct Irradiation of Tetracyclo[5.3.2.$0^{2,5}$.$0^{6,8}$]dodeca-3,9,11-triene (14). The tetracyclic hydrocarbon was obtained by the method of Schröder[20] except that it was separated from the dimethyl phthalate by elution down a short alumina column with pentane. The desired hydrocarbon was generally eluted in the first few fractions and the diester followed in later fractions.

Approximately 700 mg of **14** was dissolved in 130 mL of pentane and irradiated through quartz with a 450-W Hanovia lamp. The progress of the photoconversion was followed by VPC and determined to be complete after 2 h, with greater than 90% conversion to a mixture of three stereoisomers. The solvent was removed by distillation through a 6-in. Vigreux column to yield 600 mg of crude oil. After elution of this material through a short alumina column with pentane, a sample was further purified by preparative VPC (6 ft × 0.25 in. 5% SE-30 on Chromosorb G; 130 °C) and shown by ^1H NMR analysis to be composed of an equimolar mixture of *exo,exo*- (**17**) and *exo,endo*-tetracyclo[4.4.2.$0^{2,5}$.$0^{7,10}$]dodeca-3,8,11-trienes (**18**)[22] plus a small amount of the endo,endo isomer (**19**).

Triplet-Sensitized Photocyclization of Tetracyclo[4.4.2.$0^{2,5}$.$0^{7,10}$]dodeca-3,8,11-trienes 17–19. The crude mixture (600 mg) of stereoisomers from the previous photoisomerization was dissolved in 130 mL of acetone and irradiated with a 200-W Hanovia lamp through a Pyrex filter for 7 h. The solvent was removed by distillation through a 6-in. Vigreux column. A VPC trace of the residue indicated four peaks which were separated by preparative VPC on the SE-30 column (130 °C) to yield 56, 8, 95, and 10 mg, respectively. ^1H NMR analysis indicated the first peak to be unreacted starting materials and the fourth to be the known hydrocarbon **21**.[23] The second component remains unidentified. The major product was **20**: $\delta_{Me_4Si}^{CDCl_3}$ 2.4–2.6 (m, 2 H), 2.6–2.85 (m, 2 H), 2.85–3.3 (m, 6 H), and 6.05 (s, 2 H, cyclobutene); *m/e* calcd 156.0939, found 156.0940.

Anal. Calcd for $C_{12}H_{12}$: C, 92.25; H, 7.75. Found: C, 91.97; H, 7.93.

Silver-Catalyzed Rearrangement of Hexacyclo[6.4.0.$0^{2,11}$.$0^{3,10}$.$0^{4,7}$.$0^{9,12}$]dodec-5-ene (20). An 87-mg sample of **20** was added to a stirred solution of silver nitrate (0.5 g) in 6 mL of 4:1 methanol–water. The flask was covered with aluminum foil and the solution was stirred under nitrogen for 3 h, at which time the rearrangement was deemed complete by VPC analysis. The solution was diluted with water and extracted three times with pentane. The combined organic layers were washed twice with water and once with brine. Removal of the solvent was accomplished by distillation through a 6-in. Vigreux column to give **22** in quantitative yield: $\delta_{Me_4Si}^{CDCl_3}$ 1.12–2.0 (m, 6 H, cyclopropyl), 2.3–2.65 (m, 2 H, bridgehead), 2.65–2.9 (m, 2 H, cyclobutyl), and 6.15 (s, 2 H, cyclobutene).

Anal. Calcd for $C_{12}H_{12}$: C, 92.25; H, 7.75. Found: C, 91.91; H, 7.81.

Pyrolysis of 2,2a,2b,3,3a,5a,5b,5c-Octahydro-1,2,3-metheno-1*H*-cyclobuta[*g*]cycloprop[*cd*]indene (22). With a slow stream of nitrogen, hydrocarbon **22** (35 mg) was volatilized into a 1.5 × 32 cm tube packed with quartz chips and heated to 580 °C at 1.5 mm. A yellow semisolid amounting to 34 mg was collected in a trap cooled with a dry ice–isopropyl alcohol slush bath. VPC analysis revealed this material to be a three-component mixture (ratio of 1.0:0.35:2.2). Preparative VPC (SE-30; 130 °C) allowed isolation of 3, 1, and 5 mg of these components, respectively. Although the second component remains unidentified, the first proved to be recovered starting material (^1H NMR analysis) and the major product was shown by NMR, UV, and rephotolysis to be **11**: $\delta_{Me_4Si}^{CDCl_3}$ 1.25–1.6 (m, 2 H, cyclopropyl), 1.85–2.15 (m, 4 H, cyclopropyl), 2.45–2.8 (m, 2 H, bridgehead), and 5.35–5.6 (m, 4 H, diene); λ_{max}^{EtOH} 285 (ε 2568) and 295 sh nm (2254); *m/e* calcd 156.0939, found 156.0940.

Irradiation of 1,1a,1b,2,2a,2b,2c,2d-Octahydro-1,2-[1,3]butadienodicyclopropa[*cd,gh*]pentalene (11). Diene **11** (3 mg) was dissolved in 1 mL of chloroform and irradiated with a 200-W Hanovia lamp through quartz optics. There was complete conversion to a single product (VPC) in 30 min. The solvent was evaporated in a stream of nitrogen and the resulting oil taken up in a small amount of chloroform and purified by preparative VPC (SE-30; 130 °C). An IR spectrum ($CHCl_3$) of the collected colorless oil proved to be identical with that of an authentic sample of **22**.

Thermolysis of 20. Hydrocarbon **20** (27 mg) was sublimed through the pyrolysis tube heated to 450 °C at 2 mm pressure. Analysis by VPC showed a single product in addition to unreacted starting material. These were separated by preparative VPC (SE-30; 130 °C) to yield 9 and 4 mg, respectively. ^1H NMR analysis showed the product to be a mixture of **17** (72%) and **18** (28%).

Alumina-Catalyzed Rearrangement of Tetracyclo[5.3.2.$0^{2,5}$.$0^{6,8}$]dodeca-3,9,11-triene (14). The dimethyl acetylenedicarboxylate adduct of the cyclooctatetraene dimer (9.5 g) was pyrolyzed as previously described by Schröder.[20] The crude oil so obtained was dissolved in pentane and placed on a 3.5 × 19 cm neutral, activity I Woelm alumina column where it was allowed to remain for 12 h. Elution from the column and VPC analysis showed the hydrocarbon to be substantially rearranged. The oil was resubmitted onto a fresh alumina column. After an additional 9 h, the mixture was again eluted and 2.4 g of the colorless oil was obtained following removal of the solvent. VPC analysis showed little remaining starting material and hydrocarbons **16** and **23** to be present in a ratio of 3:1. The mixture was placed atop a 16 × 2 cm slurry packed 30% $AgNO_3$-silica gel chromatography column. Elution with petroleum ether (30–60 °C) and petroleum ether–ether mixtures furnished 1.6 g of pure **16**. Elution with increasing amounts of methanol in ethyl ether yielded 450 mg of **23** contaminated with small amounts of **14**.

For **23**: $\delta_{Me_4Si}^{CDCl_3}$ 2.3–2.6 (m, 1 H), 2.6–3.1 (m, 3 H), 4.75–5.1 (m, 1 H), 5.6–6.1 (m, 6 H), and 6.3–6.45 (d of d, J = 5.5 and 2.5 Hz, 1 H); λ_{max}^{EtOH} 235 sh nm (ϵ 3390); *m/e* calcd 156.0939, found 156.0941.

Anal. Calcd for $C_{12}H_{12}$: C, 92.25; H, 7.75. Found: C, 91.88; H, 7.79.

For **16**: $\delta_{Me_4Si}^{CDCl_3}$ 2.7–3.0 (m, 4 H), 5.4–5.9 (m, 6 H), and 6.05 (s, 2 H, cyclobutene); λ_{max}^{EtOH} 257 sh nm (ϵ 1760), 263 (2100), 273 (2070), and 282 (1290); *m/e* calcd 156.0939, found 156.0941.

Anal. Calcd for $C_{12}H_{12}$: C, 92.25; H, 7.75. Found: C, 92.01; H, 7.94.

Thermal Rearrangement of Tricyclo[5.5.0.0^{4,8}]dodeca-2,5,9,11-tetraene (23). Tetraene **23** (45 mg) was pyrolyzed as before at 430 °C and 1 mm in a slow stream of nitrogen over a 60-min period. In a dry ice–isopropyl alcohol cooled trap was collected 40 mg of yellowish oil which consisted mainly of one major product and unreacted starting material (ratio of 2:1). The isomers were separated by preparative VPC (6 ft × 0.25 in. 5% XF-1150 on Chromosorb G; 135 °C) and furnished 12 mg of **13**: $\delta_{Me_4Si}^{CDCl_3}$ (60 MHz) 3.2–3.6 (m, 3 H), 3.6–3.9 (m, 1 H), 5.35–5.65 (m, 2 H), and 5.65–6.2 (m, 6 H); λ_{max}^{EtOH} 252 nm (ϵ 3470).

Anal. Calcd for $C_{12}H_{12}$: C, 92.25; H, 7.75. Found: C, 91.92; H, 7.71.

There was also recovered 8 mg of starting tetraene **23**.

Pyrolysis of Tricyclo[5.4.1.0^{4,12}]dodeca-2,5,8,10-tetraene (13). A 5-mg sample of **13** was pyrolyzed at 430 °C and 2 mm under nitrogen in the usual manner. The clear oil collected in a cooled (−78 °C) trap was analyzed on two different VPC columns (5% SE-30; 135 °C and 5% XF-1150; 135 °C). A mixture of recovered starting material and tetraene **23** in a relative ratio of 1.9:1 was indicated.

Catalytic Hydrogenation of Tricyclo[5.4.1.0^{4,12}]dodeca-2,5,8,10-tetraene (13). The 5% palladium on carbon catalyst (10 mg) was suspended in 10 mL of pentane and stirred under a hydrogen atmosphere for 30 min before **13** (12 mg) dissolved in 1.7 mL of pentane was added via syringe to the stirred suspension. After 1.5 h, another batch of catalyst was introduced and stirring under hydrogen continued for another 7.5 h. VPC analysis indicated two peaks of equal intensity and a third minor peak, none of which was **13**. A small amount (20 mg) of 5% Rh/C and 8 drops of glacial acetic acid were added. After 21 h another 12 drops of acetic acid were added and reduction continued for a total of 57 h when analysis showed a single major and two minor components. Preparative VPC (5% SE-30; 135 °C) allowed isolation of 5.5 mg of the former and 2.0 mg of the combined minor peaks. The spectral properties of the major constituent were identical with those of authentic **24**.

Acetone-Sensitized Photoisomerization of Tricyclo[5.5.0.0^{4,8}] dodeca-2,5,9,11-tetraene (23). Hydrocarbon **23** (26 mg) was dissolved in 4 mL of acetone, placed in a Pyrex test tube, and stoppered with a serum cap. The solution was irradiated with a 200-W Hanovia lamp for a total of 4.5 h at which time VPC analysis showed ca. 80% conversion to a single product. After concentration on a rotary evaporator, product **25** (11 mg) and recovered starting material (4 mg) were collected by preparative VPC (6 ft × 0.25 in. 10% XF-1150 on Chromosorb G; 140 °C): $\delta_{Me_4Si}^{CDCl_3}$ 2.2–2.5 (m, 3 H), 2.9–3.2 (m, 2 H), 3.4–3.6 (apparent doublet, J = 3 Hz, 1 H), 5.1–5.5 (m, 1 H), 5.5–6.15 (m, 4 H), and 6.4–6.65 (m, 1 H); *m/e* calcd 156.0941, found 156.0939.

Anal. Calcd for $C_{12}H_{12}$: C, 92.25; H, 7.75. Found: C, 92.21; H, 7.80.

Thermolysis of *endo*-Tricyclo[4.2.2.0^{2,5}]dodeca-3,7,9,11-tetraene (16). Hydrocarbon **16** (30 mg) was sublimed into the same hot tube apparatus at 560 °C and 1 mm with a slow stream of nitrogen. A yellow oil was collected in a trap cooled in a dry ice–isopropyl alcohol slush bath. ^{1}H NMR analysis of the crude product showed a large amount of benzene as well as hydrocarbon product. Analysis by VPC showed a single major $C_{12}H_{12}$ product which was isolated (4 mg) by preparative VPC (5% SE-30; 140 °C) and later shown to be benzylcyclopentadiene **26**: $\delta_{Me_4Si}^{CDCl_3}$ 2.75–3.05 (m, 2 H, benzylic), 3.6–3.8 (br s, aliphatic), 5.8–6.6 (m, olefinic), and 7.15 (s, 5 H, aromatic); λ_{max}^{EtOH} 257 nm (ϵ 5580); *m/e* calcd 156.0939, found 156.0941.

High-Temperature Pyrolysis of Tricyclo[5.5.0.0^{4,8}]dodeca-2,5,9,11-tetraene (26). Tetraene **26** (12 mg) was pyrolyzed in the gas phase through a hot tube packed with quartz chips at 587 °C and 4 mm with a slow stream of nitrogen. The resulting yellow oil was collected in a cooled (−78 °C) trap. A single product (3 mg) was isolated by preparative VPC (5% XF-1150; 135 °C). ^{1}H NMR analysis of the oil showed it to be benzylcyclopentadiene (**26**).

Benzylcyclopentadiene (26). Sodium cyclopentadienide [from 6.8 g (0.1 mol) of cyclopentadiene and 3.3 g (0.143 g-atom) of sodium ribbon] in tetrahydrofuran (100 mL) was added dropwise under nitrogen during 1 h to a stirred solution of benzyl chloride in ether (100 mL) cooled to −20 °C. The resulting reaction mixture was diluted with 200 mL of ice water and 200 mL of pentane. The layers were separated and the organic layer was washed an additional five times with water before drying over anhydrous magnesium sulfate. The solution was filtered and concentrated to yield 13.2 g of yellow oil. Preparative VPC isolation (SE-30; 150 °C) gave a pure sample of thermally equilibrated **26**, the ^{1}H NMR spectrum of which was identical with that of the isomer mixture obtained for the pyrolysis products of **16** and **23**.

Benzylcyclopentane (27). Benzylcyclopentadiene (20 mg) was dissolved in 2 mL of pentane and added by syringe to a stirred suspension of 20 mg of 5% rhodium on carbon in 10 mL of pentane under hydrogen. After 40 h, the mixture was filtered through glass wool and Celite before evaporation and purification by preparative VPC (10% XF-1150; 140 °C). There was obtained 10 mg of colorless oil which was identical by NMR and IR with the material isolated from catalytic reductions of the pyrolysis products from **16** and **23**.

Catalytic Reduction of the Pyrolysis Product of 16. The aromatic hydrocarbon isolated from the pyrolysis of **16** (11 mg) was dissolved in 1 mL of pentane and added by syringe to a stirred suspension of 5% rhodium on carbon in 10 mL of pentane. After 1 h, a VPC aliquot showed complete conversion to a single product. The product (8 mg) was isolated as a colorless oil by preparative GLC (10% XF-1150; 150 °C) and its spectral properties were identical with those of authentic benzylcyclopentane.

Acetone-Sensitized Photoisomerization of *endo*-Tricyclo[4.4.2.0^{2,5}]dodeca-3,7,9,11-tetraene (16). A sample of **16** (10 mg) was dissolved in 4 mL of acetone and placed in a Pyrex test tube. After being sealed with a serum cap, the solution was irradiated with a 450-W Hanovia lamp for a total of 4.5 h. Analysis showed complete loss of starting material and the appearance of a single product which was collected by preparative VPC (5% XF-1150; 130 °C). There was isolated 3–4 mg of **14**.

Irradiation of *endo*-Tricyclo[4.4.2.0^{2,5}]dodeca-3,7,9,11-tetraene (16). Hydrocarbon **16** (25 mg) was dissolved in 2 mL of pentane and placed in a quartz test tube sealed with a serum cap. This solution was irradiated through quartz optics with a 200-W Hanovia lamp for a total of 4.3 h. The single peak (6 mg) isolated by preparative VPC on 5% SE-30 (135 °C) was shown (NMR analysis) to be a 1:1 mixture of *endo,endo*- (**19**) and *endo,exo*-tetracyclo[4.4.2.0^{2,5}.0^{7,10}]dodeca-3,8,11-trienes (**18**) which could be readily separated on a 12 ft × 0.25 in. QF-1 on Chromosorb P (130 °C) preparative VPC column. The spectra of **18** were identical with those previously reported. For **19**: $\delta_{Me_4Si}^{CDCl_3}$ 2.4–2.8 (m, 6 H), 5.95 (s, 4 H, cyclobutenes), and 6.3–6.5 (m, 2 H); *m/e* calcd 156.0939, found 156.0940.

Direct Irradiation of Tricyclo[5.4.1.0^{4,12}]dodeca-2,5,8,10-tetraene (13). Hydrocarbon **13** (20 mg) was dissolved in 1 mL of pentane and placed in a quartz test tube before sealing with a serum cap. The solution was irradiated with a 200-W Hanovia lamp through quartz optics for a period of 6 h. Polymer formed during the reaction was removed by filtration through glass wool and Celite. The single product (**28**) was isolated as a colorless oil (4 mg) by preparative VPC (5% SE-30; 120 °C): $\delta_{Me_4Si}^{CDCl_3}$ 2.9–3.35 (m, 4 H), 3.65–3.85 (m, 2 H), 5.25–5.75 (broadened d of d, J = 12 Hz, 4 H), and 6.1 (s, 2 H, cyclobutenes); *m/e* calcd 156.0939, found 156.0941.

Acetone-Sensitized Photoisomerization of Tricyclo[5.4.1.0^{4,12}] dodeca-2,4,7,10-tetraene (13). A 5–10-mg sample of **13** was dissolved in 1 mL of acetone and placed in a Pyrex test tube, which was stoppered with a serum cap. Irradiation with a 450-W Hanovia lamp for

1 h accomplished complete conversion to a single product (VPC analysis) which proved to be identical with **28** as isolated from irradiation in pentane solution.

Preparative Scale Treatment of Tetraene 13 with Potassium in Liquid Ammonia. Potassium (36 mg, 0.92 g-atom) was added in one portion to 5 mL of dry ammonia (distilled from sodium) in a 15-mL, three-necked flask equipped with a dry ice condenser, nitrogen inlet, and a glass-covered stirring bar. Hydrocarbon **13** (56 mg) was dissolved in 0.5 mL of dry tetrahydrofuran before being added at −78 °C under nitrogen. Because a red oil separated from the dark solution, an additional 0.5 mL of tetrahydrofuran was added. The very dark red mixture was stirred at −78 °C for an additional 45 min before addition of 300 μL of methanol. The color was immediately discharged to a pale yellow. The solution was diluted with 5 mL of pentane and allowed to warm to room temperature with stirring. After the ammonia had evaporated, the remaining pentane was washed twice with water before evaporation. VPC analysis indicated the presence of four major components which were separated by preparative VPC (5% XF-1150; 150 °C) to yield 13, 4, 9, and 5 mg, respectively. The spectral properties of these products (in the same order as isolated) are as follows.

$\delta_{\mathrm{Me_4Si}}^{\mathrm{CDCl_3}}$ 1.4–2.05 (m, 2 H), 2.05–2.5 (m, 2 H), 2.7–3.9 (m, 4 H), and 5.3–6.0 (m, 6 H, olefinic); $\lambda_{\max}^{\mathrm{EtOH}}$ 252 nm (ϵ 615); obsd *m/e* 158.1100 ($C_{12}H_{14}$).

$\delta_{\mathrm{Me_4Si}}^{\mathrm{CDCl_3}}$ 1.5–2.8 (m, 4 H), 2.8–4.2 (m, 4 H), and 5.3–6.3 (m, 6 H, olefinic); $\lambda_{\max}^{\mathrm{EtOH}}$ 237 (ϵ 7740) and 283 nm (2530).

$\delta_{\mathrm{Me_4Si}}^{\mathrm{CDCl_3}}$ 2.1–2.7 (m, 1 H), 2.7–3.3 (m, 1 H), 5.3–5.8 (s, 4 H), and 5.8–6.2 (s, 3 H); $\lambda_{\max}^{\mathrm{EtOH}}$ 251 nm (ϵ 7830).

$\delta_{\mathrm{Me_4Si}}^{\mathrm{CDCl_3}}$ 1.6–3.1 (m, 4 H), 3.1–3.9 (m, 2 H), and 5.2–6.6 (m, 6 H, olefinic); $\lambda_{\max}^{\mathrm{EtOH}}$ 230 (ϵ 18 230) and 291 nm (5080); observed *m/e* 156.0930 ($C_{12}H_{12}$).

Treatment of Tetraene 13 with Potassium Mirror in Tetrahydrofuran. A potassium mirror was formed on the walls of a 15-mL three-necked flask by fusion of a few small pieces of metal under an oxygen-free nitrogen atmosphere with vigorous stirring by a glass-covered magnetic bar. After cooling, 5 mL of dry tetrahydrofuran was added. The reaction vessel was cooled to −78 °C before the hydrocarbon (75 mg) dissolved in a small amount of tetrahydrofuran was introduced by syringe through a serum cap. The solution began to turn red after a short induction period and eventually became very deep red in color. After 30 min at −78 °C, quenching was effected by syringing the red solution into 2 mL of methanol cooled to −78 °C under a nitrogen atmosphere. After 10 min the resultant brown solution was diluted with pentane and washed three times with water. After drying and concentration of the organic phase, VPC analysis indicated the residue to be comprised of four major products. VPC-mass spectral analysis indicated *m/e* values of 158, 156, 158, and 156, respectively. The components were separated by preparative VPC (5% SF-96; 140 °C) to yield 8 (combination of first two peaks), 1, and 4 mg. NMR spectra of the first and fourth products indicated them to be identical with the first and fourth products from the ammonia reaction.

Vacuum Line Experiments with 13. (a) Potassium in ND_3 Reduction. Approximately 0.5 mL of ND_3 was vacuum transferred to a small reaction vessel equipped with a miniaturized glass-encased magnetic bar. Freshly cut potassium metal (ca. 2.5 g-atom equiv) was introduced into the reaction vessel after removal of the serum cap under a positive pressure of dry nitrogen. In practice, nitrogen was simply allowed to flow over the surface of the solid ND_3 during this operation. The cap was replaced and the ND_3 was slowly allowed to thaw by gradual removal of the liquid nitrogen cooling bath and replacement with a dry ice-isopropyl alcohol bath. The hydrocarbon was injected by syringe into the resulting dark blue solution with simultaneous frequent agitation of the reaction mixture by means of an external magnet. When the reduction was complete, the mixture was frozen in the liquid nitrogen bath and the serum cap removed under nitrogen and replaced with an NMR tube side arm containing a plug of glass wool in the upper portion. After regaining partial vacuum (40 mm), the reaction vessel was inverted by rotation about the standard taper $^{10}/_{30}$ joint and the tube rapidly cooled to −78 °C. Upon thawing, the contents of the reaction vessel collected above the glass wool plug. Filtration through the plug was achieved by rapidly removing the dry ice-isopropyl alcohol bath and replacing it with the liquid nitrogen bath. The tube was sealed in vacuo in the customary fashion after degassing the sample and the solid in the tube was carefully thawed by swabbing with cold dry ice-isopropyl alcohol solution. The spectrum was then recorded in a precalibrated cold probe. After this exercise, the tube was opened and the red solution treated with 1 drop of methanol. After evaporation of the ammonia, the residue was analyzed by VPC (5% XF-1150). The same four components as present in the preparative scale run had been formed.

(b) Potassium Mirror in THF-d_8. For the potassium mirror experiments, a 3-mg sample of the tetraene was placed in the NMR tube of an apparatus similar to the above but modified somewhat is design. Dry THF-d_8 (ca. 350 μL) was vacuum transferred from Na-K alloy into this tube and the resulting solution was degassed and then frozen in a liquid nitrogen bath. Small pieces of freshly cut, clean potassium metal (ca. 200 mg) were placed in the adjacent reactor vessel by temporary transfer through an opening previously closed by a rubber septum but now permanently sealed. The total system was pumped down to 10^{-6} Torr and the potassium metal just melted to remove trapped gases and finally vaporized into the NMR tube in small amounts. The metal condensate was carefully moved downward into the tube by continued heating at the top leading edge of the mirror with the Bunsen flame (overheating should be avoided as the glass will tarnish). The entire process generally required 20–30 min. The tube is then sealed off under argon and inverted to permit chemical reaction. The spectrum was quickly recorded at −65 °C and found to be exceedingly complex.

Catalytic Hydrogenation of the Quenching Products. Each of the hydrocarbons isolated from the last two reactions were subjected to catalytic reduction. In a typical procedure the hydrocarbon was dissolved in a small amount of pentane and syringed into a suspension of 5% rhodium on carbon in pentane which had previously been equilibrated under a hydrogen atmosphere for 30 min. This mixture was stirred for 12 h before gravity filtration through glass wool and Celite. After concentration of the solvent, the single product was purified by VPC. The colorless oil isolated in each case proved identical with **24**.

Attempted *tert*-Butyllithium-Promoted Isomerization of 13. A solution of **13** (30 mg, 0.19 mmol) in 5 mL of dry, purified pentane cooled to −78 °C under nitrogen was treated via syringe with 0.22 mL of 1.8 M *tert*-butyllithium in pentane (0.385 mmol). After being stirred at this temperature for 2.5 h, a portion of the light yellow solution (ca. 0.5 mL) was removed and added to 1 mL of methanol-pentane (1:1) cooled to −78 °C. Water (1 mL) was added with shaking, the pentane layer separated and dried, and its contents analyzed by VPC on four different columns. In each instance, a single peak was observed which was superimposable upon that of **13**.

Cycloaddition of Tropone to Cyclopentadiene. The following is an adaptation of earlier procedures[40] as suggested to us by Haywood-Farmer.[41] Tropone (11.5 g) and cyclopentadiene (50 g) were mixed at room temperature under nitogen and stirred for 90 h. A further quantity of cyclopentadiene (25 g) was introduced and stirring continued for an additional 6 days (reaction monitored by ^{1}H NMR analysis of residual tropone). The volatile components were removed at 1 mm and temperatures below 60 °C. The residue was chromatographed on grade I alumina (elution with pentane-ether, 5:1) to give 11.49 g (62%) of white crystals, mp 71–72 °C (from hexane).

Bicyclo[6.2.1]undeca-2,4,6,9-tetraene (31). Ketone **30** (2.0 g) was dissolved in 2 L of pentane and irradiated for 5 h within a Rayonet reactor fitted with 3000-Å lamps. Solvent was removed under reduced pressure and the residue was chromatographed on silica gel (pentane elution) to furnish 528 mg (32%) of **31**: $\delta_{\mathrm{Me_4Si}}^{\mathrm{CCl_4}}$ 5.3–6.05 (m, 8), 3.0–3.38 (m, 2), and 2.05–2.45 (m, 2).

Electrochemical Measurements. The electrochemical apparatus employed in these experiments has been described previously.[42,43] Techniques for purifying solvents and background electrolytes and experimental procedures were identical with those utilized in the earlier work.[33,43,44]

Perparative Scale Reduction of 31 with Potassium in Liquid Ammonia. Potassium (90 mg, 2.3 mg-atom) was added to dry ammonia (25 mL freshly distilled from sodium) at −70 °C under nitrogen. A solution of **31** (130 mg, 0.9 mmol) in dry ether (1 mL) was introduced via syringe during 2 min. The reaction mixture turned dark red within 5 min at −70 °C. Following an additional 25 min, methanol (250 μL) was added (immediate change to colorless) and the ammonia was allowed to evaporate. Water (10 mL) and pentane (15 mL) were added and the aqueous phase was extracted with pentane (3 × 10 mL). The combined organic layers were washed with brine, dried, and evaporated to leave 116 mg of colorless oil. Preparative VPC isolation (XF-1150, 120 °C) gave 62 mg of **34**: $\nu_{\max}^{\mathrm{neat}}$ 3000, 2910, 1465, and 1450 cm^{-1}; $\delta_{\mathrm{Me_4Si}}^{\mathrm{CCl_4}}$ 5.0–5.7 (m, 6), 2.5–3.5 (m, 4), and 2.0–2.45

(m, 4); ^{13}C (CDCl$_3$, ppm) 133.48, 132.56, 129.92, 129.43, 127.14, 123.93, 45.73, 43.03, 32.78, 30.83, and 27.06; *m/e* calcd 146.1095, found 146.1098.

Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.10; H, 9.74.

Bicyclo[6.2.1]undecane (35). (a) **Reduction of 31.** A solution of **31** (45 mg) in pentane (10 mL) was exhaustively hydrogenated in the presence of 10% palladium on charcoal (10 mg) at atmospheric pressure. Filtration and solvent evaporation afforded a colorless liquid (38 mg) which was purified by preparative VPC (12% Carbowax 20M, 130 °C): $\nu_{max}{}^{neat}$ 2968, 2925, 2864, 1477, 1444, 1410, 1262, 1090, 1012, 860, 800, 705, and 660 cm^{-1}; $\delta_{Me_4Si}{}^{CCl_4}$ 1.8–2.4 (br m), 1.6 (br m), and 1.2 (br m); *m/e* calcd 152.1568, found 152.1565.

Anal. Calcd for $C_{11}H_{20}$: C, 86.84; H, 13.16. Found: C, 86.47; H, 13.43.

(b) **Reduction of 34.** Purified triene **34** (24 mg) was exhaustively hydrogenated as described above. The isolated product (15 mg, Carbowax 20M, 130 °C) was identical in all respects with the sample of **35** obtained in Part A.

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