Binding of Unsaturated Propellanes to Transition Metal Centers. $Mo(CO)_6$-Promoted Skeletal Isomerization of [4.4.2]Propella-2,4,11-trienes

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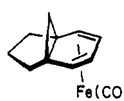
Abstract: The ability of variously unsaturated [4.4.2]propellanes to coordinate with transition metal carbonyl fragments has been assessed experimentally. As expected, $Fe(CO)_3$ is most prone to complex with planar conjugated diene segments. In the reactions with $Mo(CO)_6$, the utilization of nonconjugated double bonds is seen to be favored and $Mo(CO)_4$ complexes result. In the specific case of [4.4.2]propella-2,4,11-trienes, these complexes undergo further [1,5]sigmatropic shifting of the four-membered ring to deliver 1,2-annulated cyclooctatetraenes. This rearrangement can become regiospecific upon appropriate methyl substitution and remains operational upon saturation of the cyclobutane ring. The $Cr(CO)_4$ and $W(CO)_4$ complexes show much greater stability and no tendency to isomerize. The $Mo(CO)_6$-promoted isomerizations proceed at much lower temperatures and by an entirely different mechanism than the thermally induced isomerization of [4.4.2]propella-2,4,11-trienes to annulated cyclooctatetraenes. The transition metal therefore serves not only to blockade the thermal reaction but to redirect the rebonding as well. When both C_{11} and C_{12} carry methyl substituents, more extended circumambulation is seen. The synthetic utility of this rearrangement is exemplified by its application to the synthesis of a pair of stable cyclooctatetraene bond shift isomers.

Some years ago, we developed synthetic methodology designed to permit ready access to a variety of olefinic propellanes.[1,2] By conjoining three rings with a common carbon-carbon σ bond, the multiple sites of unsaturation can be brought into close proximity and in specific instances made to adopt a perpendicular or nearly perpendicular mutual orientation.[3] Since such $p\pi$ orbital arrangements deviate significantly from the 180° in-plane alignment generally preferred for overlap, the intrinsic reactivity patterns of these molecules were examined. Previously documented experimental findings have shown that orbital constructs of this type do not preclude thermally promoted rearrangements, many of which eventuate as deep-seated structural changes.[3-5] Photoelectron spectroscopic analysis has also been made of the prevailing interactions.[6] Likewise, the photofragmentation of certain select propellanes has been given attention.[3,7]

We have more recently been drawn to examine their capability to interact with transition metal carbonyls. In particular, the widely differing electronic requirements, geometric preferences, symmetry demands, and complexation strengths of typical fragments such as $Fe(CO)_3$, $Cr(CO)_3$, and $Mo(CO)_4$ promised to be a powerful tool in analyzing the ligand properties of the unsaturated propellanes. Vogel and Mills have shown that the $Fe(CO)_3$ complex **1** retains its tricyclic character, while **2** is devoid of a central bond to provide the chromium atom with that added pair of electrons necessary to acquire the stable 18-electron configuration.[8] However, the second and third rings in [4.3.1]propella-2,4-diene offer no additional π bonds to provide in principle for alternative modes of bonding. In a different series, the $Mo(CO)_3$ complex of cyclooctatetraene (**3**) is known to possess three contiguous coplanar double bonds,[9] quite unlike the free hydrocarbon which is tub shaped.[10] When exposed to carbon monoxide at atmospheric pressure, **3** is converted to the less stable tetracarbonyl complex **4** where the molybdenum is π bonded to 1,5 olefinic groups and the ligand has returned to a less constrained geometry.[11] This is quite unlike the structure established for **5**[12] despite the identical η^4 electronic requirements of $Mo(CO)_4$ and $Fe(CO)_3$. In generalized terms, $Fe(CO)_3$ and $Cr(CO)_3$ appear most prone to provide stable complexes with planar conjugated dienes[13] and trienes,[14] respectively, while $M(CO)_4$ fragments (M = Cr, Mo, W) prefer bonding to nonconjugated double bonds.[15]



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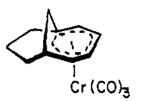

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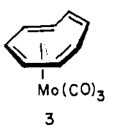

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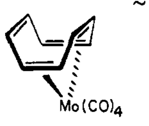

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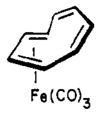

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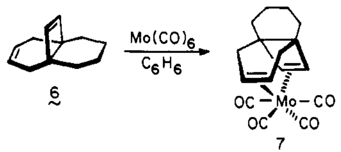
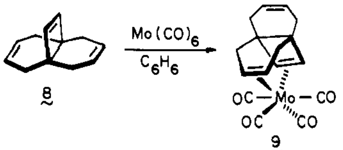
Of additional immediate interest to us was the possibility that at least one of the metal carbonyls might promote a previously unobserved structural reorganization. The basic concept was founded on the expectation that suitable coordination would blockade the utilization of $p\pi$ bonds in otherwise kinetically favored transformations and lead to alternative modes of rearrangement.[16] As will be demonstrated below, $Mo(CO)_6$ is indeed capable of transforming suitably strained propellanes into isomeric hydrocarbons under relatively mild conditions.[17] The synthetic potential of this novel reaction, the mechanistic details of which are explored in a companion paper,[18] is exemplified by its application to the synthesis of stable cyclooctatetraene bond shift isomers.

Results and Discussion

Formation of $M(CO)_4$ Complexes. First we assessed the feasibility of complexation of group 6B metal carbonyl fragments to simple propellanes carrying isolated double bonds in two or more rings. Although previous examples of simultaneous coordination by these transition metal atoms to polycyclic molecules having double bonds in different rings do exist,[15c,19,20] they are relatively few in number. In any event, heating of [4.4.2]propella-3,11-diene (**6**) with $Mo(CO)_6$ in



6 **7**



8 **9**

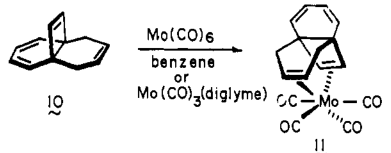
Table I. Carbon Chemical Shifts for Compounds **16–19**

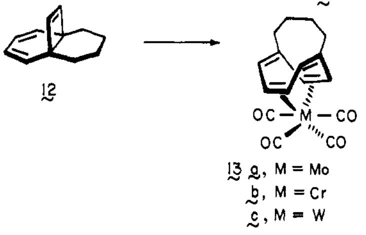
Compd	^{13}C shifts and assignments[a]
16	212.3 (CO's), 146.1 (C_{11}, C_{12}), 85.9 (C_3, C_4), 69.5 (C_2, C_5), 54.3 (C_1, C_6), 27.6 (C_7, C_{10}), and 17.1 (C_8, C_9)
17	212.5 (CO's), 143.7 (C_{11}, C_{12}), 85.6 (C_3, C_4), 73.3 (C_2, C_5), 51.1 (C_1, C_6), 34.2 (C_7, C_{10}), and 18.2 (C_8, C_9)
18	141.5 (C_{11}, C_{12}), 133.1 (C_3, C_4), 120.9 (C_2, C_5), 47.4 (C_1, C_6), 28.7 (C_7, C_{10}), 18.2 (C_8, C_9), and 8.4 (CH_3's)
19	145.4 (C_{11}, C_{12}), 85.3 (C_3, C_4), 69.5 (C_2, C_5), 53.0 (C_1, C_6), 25.1 (C_7, C_{10}), 17.3 (C_8, C_9), and 9.1 (CH_3's)

[a] $CDCl_3$ solutions; shifts in parts per million relative to Me_4Si = 0.

benzene at the reflux temperature for 48 h led to isolation of complex **7** in 43.5% yield. The ^1H NMR spectrum of **7** (in $CDCl_3$) revealed the cyclobutene (δ 4.89, s) and cyclohexene olefinic protons (4.36, t, J = 2.0 Hz) to be upfield shifted relative to their counterparts in **6** (δ 5.90 and 5.75, respectively)[1] as would be expected only if the ligand was coordinated through both of its π bonds. Completely analogous chemical reactivity was exhibited by **8**. The obvious preference for involvement of the cyclobutene π bonds is a reflection of the bonding capabilities of molybdenum[21] which, in this situation, are better served by the smaller of the two rings.

Attention was next turned to [4.4.2]propella-2,4,8,11-tetraene (**10**). Although this polyolefin exhibits no spectroscopically detectable tendency for tautomerization to a 1,4-annulated cyclooctatetraene,[22] it can in theory lead to a variety of mononuclear $M(CO)_4$ complexes.[23-25] In actuality, treatment of **10** with $Mo(CO)_6$ in the predescribed manner gave only **11** having π-coordination features identical with those found in **7** and **9**. As before, the complexed olefinic protons experience appreciable upfield shifting, with the cyclobutene hydrogens (δ 4.85, s) appearing downfield of the cyclohexene pair (4.51, t, J = 2.5 Hz). The presence of a free conjugated diene moiety was clearly indicated by the presence of an AA′BB′ pattern at δ 6.0–5.4.

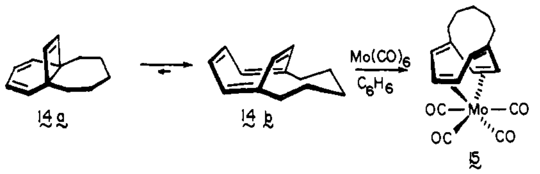




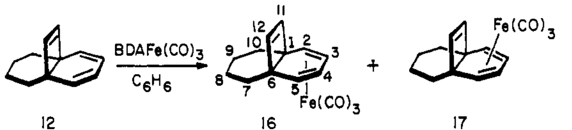
When triene **12**, which lacks the key isolated cyclohexene double bond, was treated with $Mo(CO)_6$, structural rearrangement occurred (vide infra). However, exposure to the more reactive $Mo(CO)_3$(diglyme) reagent[26] in diglyme-benzene (10:3) at 25 °C for 18 h led to the formation of complex **13a** (37%), an air-stable, pale yellow crystalline substance. The ^1H NMR spectrum of **13a** (in $CDCl_3$) consists of three singlets each of relative intensity 2 at δ 5.57, 4.69, and 4.60, and a pair of four-proton multiplets at δ 2.4–2.0 and 1.75–1.1. These features suggested that complexation by molybdenum had occurred to 1,5-olefinic groups in the heretofore unobserved bicyclic valence isomeric form of **12**. This conclusion was confirmed and the complete stereochemistry of the complex elucidated by three-dimensional x-ray crystal structure analysis.[17a,27] Unlike **4**, which tends to disproportionate readily with loss of CO,[11] **13a** exhibits good shelf-life stability. We attribute this reluctance to disproportionate to the inability of the unsaturated ligand (because of annulation) to provide a nearly planar conjugated 1,3,5-triene segment required for hexahapto bonding to $Mo(CO)_3$.

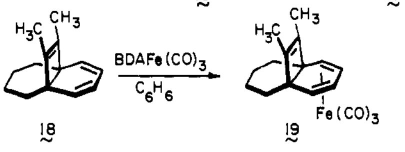
$Cr(CO)_6$ and $W(CO)_6$ also coordinated exclusively with the bridged cyclooctatetraene tautomer of **12** to give **13b** and **13c**, respectively. However, formation of these complexes required refluxing toluene and xylene temperatures, respectively. Heating benzene solutions of **13b** and **13c** up to 200 °C (sealed tube experiments) gave uncharacterizable decomposition products (chiefly tar), but no recognizable rearranged structure as does **13a** (vide infra).

When exposed to $Mo(CO)_6$ in benzene for 17 h at 80 °C, the pentamethylene bridged congener **14a** ⇌ **14b** (the bicyclic tetraene form now heavily predominates[1]) was converted to **15** in 87.5% yield. Unlike **13a**, continued heating of benzene solutions of **15** for more extended periods of time led to recovery of unchanged complex. Thus, it appears that specific structural characteristics of the propellane system are required for the rearrangement process to occur efficiently.



Complexation to $Fe(CO)_3$ Centers. When **12** was stirred with a twofold excess of benzylideneacetoneiron tricarbonyl ($BDAFe(CO)_3$)[24,28] in benzene at 45–55 °C for 2 days, the propellane was converted into a 2:1 mixture of the isomeric complexes **16** and **17**. These were separated through combined use of column chromatography and fractional recrystallization. Since the ^1H and ^{13}C NMR spectra of these compounds clearly denote them to be tricyclic triene complexes, an immediate question becomes the stereochemical relationship of the $Fe(CO)_3$ unit relative to the cyclobutene ring. Although several pieces of spectral data provide the requisite key to ultimate resolution of this issue, chemical corroboration of our assignments was realized by making recourse to **18**.[3] Through methyl substitution of C_{11} and C_{12}, the upper surface of the propellatriene (as drawn) becomes more sterically encumbered than in **12**. And the degree to which this occurs is adequate to direct complexation exclusively to that face of the molecule anti to the unsaturated ring as in **19**.

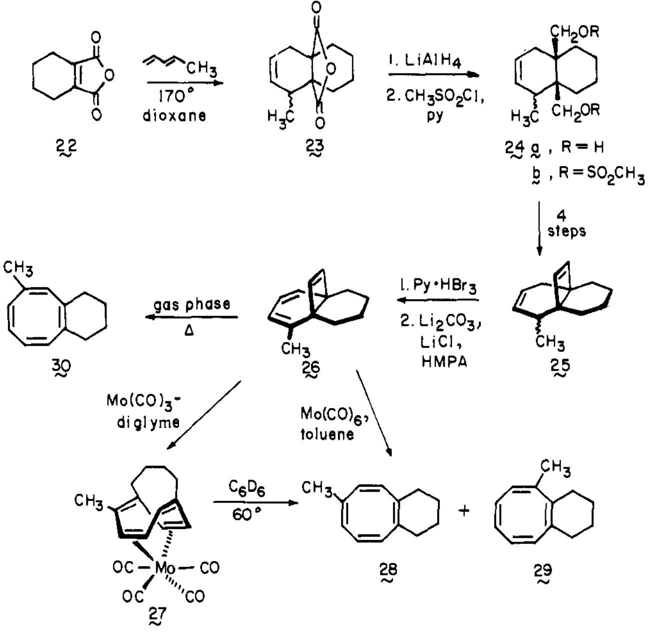




The olefinic protons of **16** comprise an expected[29] AA′XX′ pattern centered at δ 5.47 and 2.84 ($J_{2,3}$ = 6.77, $J_{2,4}$ = 1.48, and $J_{3,4}$ = 4.50 Hz). In contrast, those in **17** appear at δ 5.26 and 3.28 ($J_{2,3}$ = 6.25, $J_{2,4}$ = 1.05, $J_{3,4}$ = 4.10 Hz). Thus, these absorptions are characterized by rather widely differing magnitudes of $\Delta\delta$ (2.63 and 1.98, respectively) in the two isomers. For **19**, the experimentally determined values are δ 5.33 and 2.90, or $\Delta\delta$ = 2.43.

^{13}C NMR spectroscopy also permits ready distinction to be made between the two isomers. In all three complexes, the outside and inside diene carbons are both shifted to lower

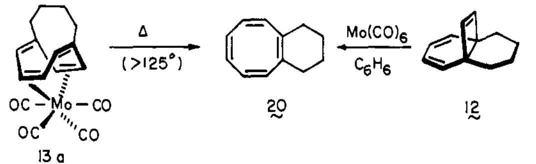
Scheme I



frequencies (Table I). However, C_2 and C_5 in **16** and **19** appear at 69.5 ppm, whereas in **17** they resonate at 73.3 ppm. The saturated methylene carbons C_7 and C_{10} are also diagnostic of stereochemistry. In the related structures **16** and **19,** their chemical shifts are 27.6 and 25.1 ppm, appreciably upfield of their position in **17** (34.2 ppm).

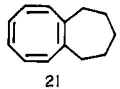
Both **16** and **17** proved to be thermostable and totally inert to reagents which otherwise would attack the cyclobutene double bond. Although these trigonal carbons are little shifted upon coordination of the diene moiety to $Fe(CO)_3$ (see Table I), no reaction was observed with dibromocarbene, the Simmons-Smith reagent, and *m*-chloroperbenzoic acid, evidently owing to high steric congestion.

$Mo(CO)_6$-Promoted Isomerizations. When **13a** dissolved in benzene was heated briefly in a sealed tube at 200 °C, the complex was entirely consumed and a hydrocarbon identified as 1,2-tetramethylenecyclooctatetraene (**20**) was isolated in 72% yield. The pure propellatriene (**12**) was also found to be capable of direct transformation to **20** (77.8% yield) upon heating with 0.5 molar equiv of $Mo(CO)_6$ at the reflux temperature of benzene for 36 h. Aliquots withdrawn at various times from a rearrangement conducted in C_6D_6 clearly revealed the intermediacy of **13a**. Interestingly, there are no indications that **20** is coordinated to a molybdenum carbonyl fragment after it is formed.



Under conditions where **12** experienced rearrangement (C_6H_6, 80 °C), **13a** underwent partial degradation (35%) to give **20** in low yield. With added $Mo(CO)_6$, however, the conversion to **20** proceeded much more efficiently (82% isolated). The propellatriene was recovered quantitatively after heating in the absence of $Mo(CO)_6$ for 2 days.

We have already noted that **14** is less prone than **12** to rearrangement. Conversion to **21** could be accomplished, however, with $Mo(CO)_6$ in refluxing toluene solution, but only in 17.5% yield.



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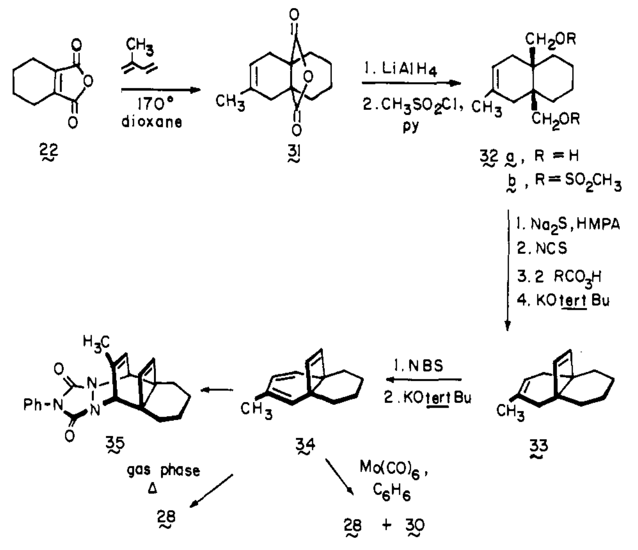
Scheme II

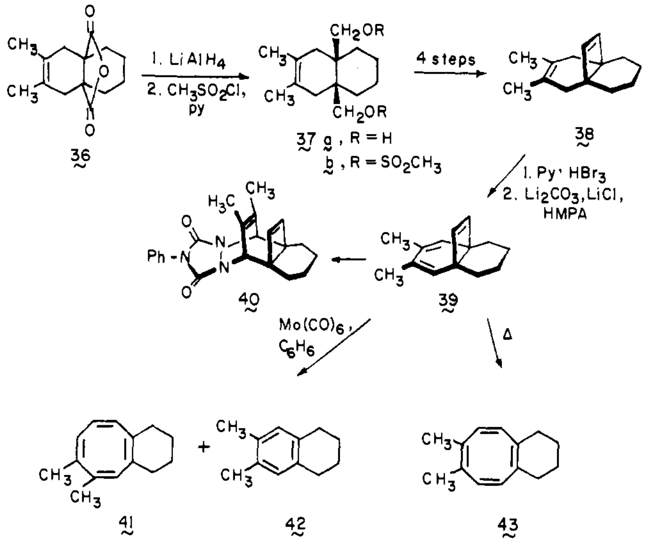


Cyclooctatetraenes **20** and **21** have been isolated earlier from thermal isomerization of the respective propellatrienes in the gas phase at 430-485 °C.[3,5] The purely thermal process proceeds by an intramolecular Diels-Alder reaction, cleavage of two strained cyclopropane bonds in the resulting bishomobenzene intermediate, and ultimate valence tautomerism to deliver product. Incursion of a second symmetry-allowed process, the [1,5] sigmatropic carbon shift, is not observed. Consequently, C_{11} and C_{12} in the propellatriene become C_3 and C_8 in the 1,2-annulated cyclooctatetraene. Analogously, C_2 and C_4 transform to C_4 and C_7.

In principle, a distinction between these and yet other pathways in the $Mo(CO)_6$-promoted rearrangements is realizable by suitable alkyl and deuterium substitution. The effect of alkyl groups in considered here. Attention was directed first to 2-methyl[4.4.2]propella-2,4,11-triene (**26**), prepared as outlined in Scheme I. Reaction of **26** with $Mo(CO)_3$(diglyme) led to the isolation of complex **27**, the unsymmetrical nature of which is clearly apparent in its ^1H NMR spectrum. The protons on the two-carbon bridge give rise to an AB pattern with a separation of 11.5 Hz and J_{AB} = 3.5 Hz. The single proton on the noncoordinated double bonds emerges as a singlet at δ 4.9 while the two remaining olefinic protons appear as a complex multiplet at δ 4.8-4.3. Complex **27** undergoes conversion to a mixture of **28** and **29** (2.7:1) when heated in C_6D_6 at 60 °C for 20 h. The extent of hydrocarbons produced was 30%. This can be compared with the greater efficiency (87%) achieved upon direct exposure of **26** to $Mo(CO)_6$ in benzene solution at 125 °C for 45 min. The identities of **28** and **29** were established by direct spectral comparison of VPC purified samples with authentic specimens prepared as described subsequently. The absence of **30,** independently available from the gas-phase pyrolysis of **26,** was clearly indicated. Therefore, the transition metal catalyzed isomerization proceeds regioselectively (but not regiospecifically as originally believed[17c]) to translocate C_2 of the propellatriene predominantly to C_5, and to a lesser degree to C_3 in the cyclooctatetraene isomer.

3-Methyl[4.4.2]propella-2,4,11-triene (**34**) was synthesized beginning again with anhydride **22** (Scheme II). Sequential treatment of propelladiene **33** with *N*-bromosuccinimide and potassium *tert*-butoxide produced on this occasion a mixture of products containing the desired triene **34** which could not be separated efficiently by chromatographic techniques. Bromination with pyridinium hydrobromide perbromide and

Scheme III



subsequent dehalogenation with lithium carbonate and lithium chloride in anhydrous hexamethylphosphoramide likewise gave an impure product and in lower yield. However, the pure triene could be isolated from this mixture by initial conversion to adduct **35** followed by hydrolysis and oxidation[30] of the latter.

In the case of **34**, treatment with $Mo(CO)_6$ in refluxing benzene led readily (62.5% yield) to a mixture of **28** and **30**, favoring the former to the extent of 60-70%. Thermolysis of **34** provided the authentic sample of **28**.

Since the preceding experiment established that C_3 of the propellatriene becomes either C_4 or C_5 of the cyclooctatetraene product mixture when $Mo(CO)_6$ is involved, we were led to examine the fate of 3,4-dimethyl[4.4.2]propella-2,4,11-triene (**39**) under comparable conditions. The preparation of **39** followed the established sequence (Scheme III). As with **33**, bromination-debromination reactions on **38** gave low yields of product containing only 60-70% of **39**. Again it proved necessary for purification purposes to resort to formation of an N-phenyltriazolinedione adduct (i.e., **40**). Hydrolysis-oxidation of **40** gave pure **39** which when treated with 0.2 molar equiv of $Mo(CO)_6$ in refluxing benzene was transformed to **41** and a minor amount (~5%) of an aromatic by-product believed to be **42**. The thermal rearrangement of **39** furnished **43** (one bond shift isomer illustrated)[31] exclusively.

The structural features of **43** have previously been discussed.[31] The identity of **41**, which expectedly does not undergo cycloaddition with N-phenyltriazolinedione in refluxing ethyl acetate solution, was established on the basis of the identity of its ^1H NMR spectrum and VPC retention times with those of the identical compound obtained in a manner to be discussed subsequently.

The above data reveal that the thermal and metal-catalyzed rearrangement of the [4.4.2]propella-2,4,11-trienes proceed along entirely different mechanistic channels. Further, some mode of [1,5] sigmatropic shifting of a trigonal cyclobutene carbon appears to be implicated when the molybdenum catalyst is present. If this is so, then monoalkyl substitution of the cyclobutene ring should lead to large differences in the migratory aptitudes of C_{11} and C_{12}. Additionally, disubstitution could provide insight into the level of metal coordination which becomes available at the time of, or immediately subsequent to, bond relocation. Working toward clarification of these issues, we next synthesized the tricyclic hydrocarbons **51** and **63**.

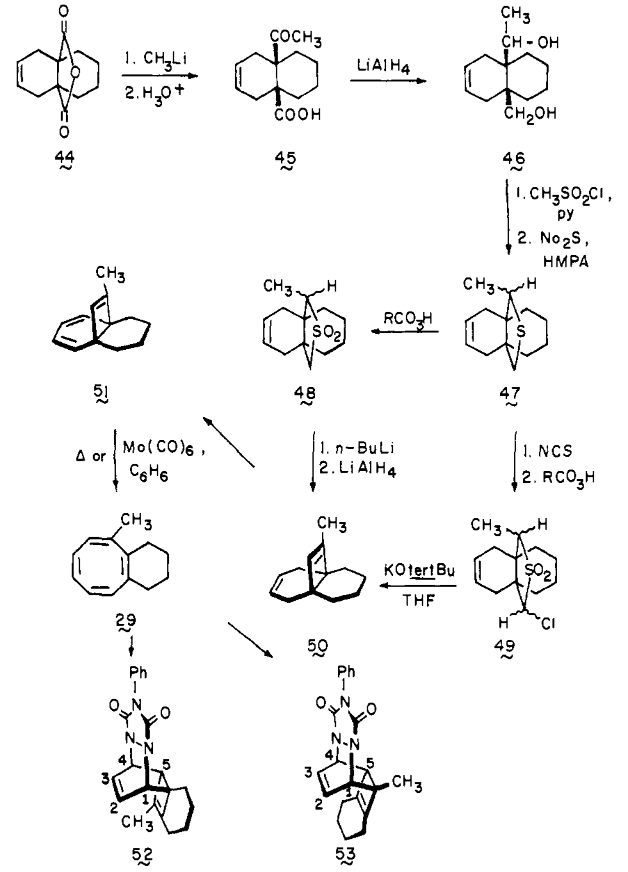
The preparation of **51** began with conversion of readily available anhydride **44** to keto acid **45** by reaction with ethereal methyllithium (Scheme IV). This intermediate was subsequently transformed by well-established procedures to sulfide **47**. Through consecutive oxidation of **47** to its sulfone (**48**) and reductive elimination of the corresponding α-sulfonyl carbanion with lithium aluminum hydride in refluxing dioxane,[32] there was realized a convenient but rather inefficient (10% overall) synthetic entry to diene **50**. Alternate recourse to a Ramberg-Bäcklund rearrangement sequence[33] afforded **50** in superior yield (51% overall). The formal oxidation of **50** to **51** was accomplished efficiently. From treatment of **51** with $Mo(CO)_6$ in refluxing benzene, there was isolated the single rearrangement product **29** in 50% yield. Gas-phase pyrolyses of **51** also led exclusively to **29**, the structural assignment to which was substantiated by conversion to the two isomeric N-phenyltriazolinedione adducts **52** and **53** which were separable by fractional crystallization. As seen from Table II and the Experimental Section, both of these molecules display inter alia an olefinic proton absorption of area 2, a pair of signals due to the dissimilar bridgehead hydrogens, and a broadened doublet arising from the sp^3-bound cyclobutenyl proton. A distinction between these isomers is made possible on the basis of the differing chemical shifts of the methyl singlets (δ 1.53

Table II. ^1H NMR Data for **53**, **54**, and **60-63** (100 MHz, $CDCl_3$, δ)[a,b]

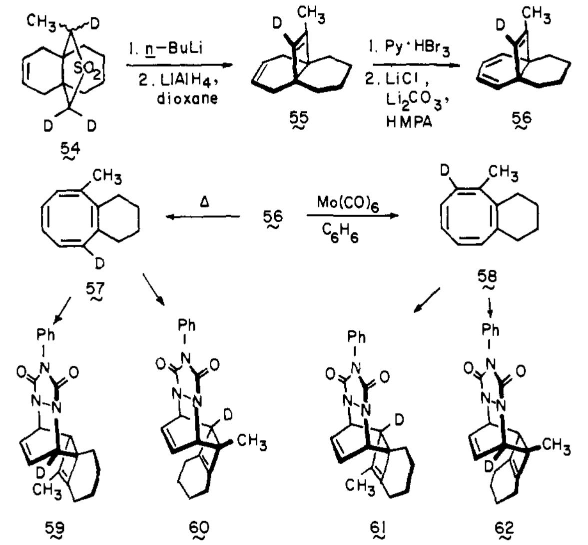
Adduct	H_1	H_4	H_5
52	4.72 (dd)	5.00 (dt)	2.64 (br d)
59		5.00 (dt)	2.64 (br d)
61	4.72 (dd)	5.00 (dd)	
53	4.63 (dd)	5.00 (dt)	2.78 (br d)
60	4.63 (dd)	5.00 (dd)	
62		5.00 (dt)	2.78 (br d)

[a] See formulas **52** and **53** for numbering schemes. [b] Multiplicities are given in parentheses; for coupling constants in the case of **52** and **53**, consult Experimental Section.

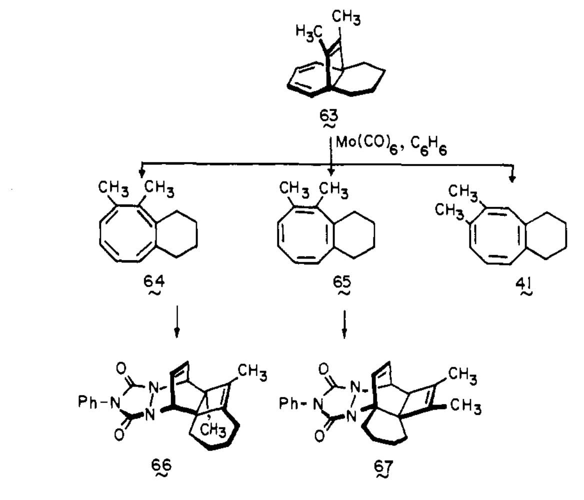
Scheme IV



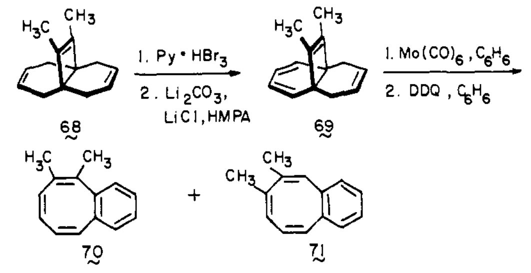
Scheme V



Scheme VI



Scheme VII



and 1.44, respectively). Individual hydrolysis–oxidation of **52** and **53** returned **29.**

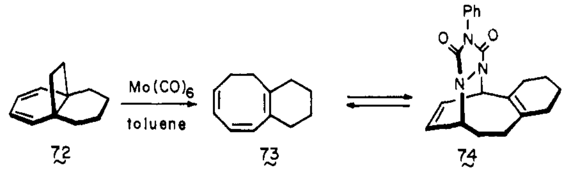
Because of the identity of the metal-catalyzed and pyrolysis products in this instance, it was unclear that the two processes remained mechanistically distinctive upon substitution of C_{11}. To resolve this question the three α-sulfonyl protons in **48** were exchanged to provide the trideuterated sulfone **54** (Scheme V). Reductive ring contraction[32] gave **55** with >95% deuterium at C_{12}. Like its unlabeled counterpart, **56** was converted to 3-methyl-1,2-tetramethylenecyclooctatetraene on pyrolysis and Mo(CO)$_6$-promoted rearrangement. These hydrocarbons were separately treated with *N*-phenyltriazolinedione, the resulting pairs of adducts were separated by fractional crystallization, and the position of the deuterium label in the four compounds was determined by ^{1}H NMR spectroscopy. The relevant data are summarized in Table II. In light of this evidence, the isotopic label in **57** is necessarily at C_8 as expected,[3,5] while that in **58** is positioned at C_4. It is thereby seen that metal-catalyzed rearrangement of **51** (and **56**) may proceed by way of a 1,5-sigmatropic shift of the unsubstituted trigonal C_{12} carbon. That migration of this carbon should occur to the exclusion of C_{11} is considered to be due in large part to steric repulsion by the methyl group. However, as we shall now see, this steric effect is not overriding when both C_{11} and C_{12} are disubstituted.

In preliminary experiments, reaction of **63** with Mo(CO)$_3$(diglyme) at room temperature was seen not to lead to complex formation. At the reflux temperature of the benzene solvent, **63** was no longer recovered but converted instead to a mixture of annulated cyclooctatetraenes. For preparative purposes, **63** was heated with 0.1 molar equiv of Mo(CO)$_6$ in benzene at 80 °C for 36 h. Under these conditions, there was isolated in quantitative yield a mixture composed of ca. 40% of **64,** 36% of **65,** and 24% of **41** (Scheme VI). Direct treatment of these hydrocarbons with *N*-phenyltriazolinedione in refluxing ethyl acetate resulted in the formation of two adducts, annulated cyclooctatetraene **41** not being subject to cycloaddition under these conditions as previously established. Fractional recrystallization from ethyl acetate–hexane permitted separation of the less soluble **67** from **66.** The patterns which emerged from the ^{1}H NMR spectrum of **66** indicated the molecule to possess two bridgehead protons adjoining nitrogen and a pair of olefinic protons. For **67,** the most revealing features were the signals due to the lone bridgehead proton and the allylic hydrogen; additionally, one methylene proton was appreciably downfield shifted from the customary broad envelope of overlapping high-field absorptions. Three-dimensional x-ray crystal structure analysis of both adducts[17b,24] established the presence of an unusual laterally fused cyclohexane ring in both molecules. The hydrolysis-oxidation of **66** led uniquely to **64,** while comparable treatment of **67** afforded isomerically pure **65.** The ^{1}H NMR spectra of these bond shift isomers, while not sufficiently revealing to establish the precise position of π bond fixation, are nevertheless mutually distinctive and quite different from those of **41** and the 3,8-dimethyl derivative.[3]

Resubmission of **64** and **65** to the original rearrangement conditions did not appear to cause their interconversion; neither did they experience further rearrangement to **41.** Rather, the gradual production of several new uncharacterized compounds was seen. Therefore, the two stable bond shift isomers appear to be produced in comparable quantities under kinetically controlled conditions. Furthermore, the isolation of **41** provided the first clue that twofold cyclobutene circumambulation can operate along the periphery of the 1,3-cyclohexadiene unit. Seemingly, the metal–ligand coordination present in the metalloorganic intermediate derived from **63** which causes this reaction channel to be accessible is not attainable when approached from the direction of **64** or **65.**

In an effort to uncover another example of more extended circumambulation, propellatetraene **69** was prepared from the known triene **68**[3] (Scheme VII). This hydrocarbon was treated with Mo(CO)$_6$ in refluxing benzene for 2 days and the resulting isomeric products were treated directly with DDQ under the same conditions (but for only 3 h). The ^{1}H NMR spectrum indicated the isolated colorless oil to be a mixture of the benzocyclooctatetraenes **70** and **71,** but this conclusion is not supported by independent synthesis. In addition to two multiplets each of area 4 due to the aromatic (δ 7.20–6.83) and olefinic protons (δ 6.73–5.50), there was present three closely spaced upfield singlets (total 6 H) at δ 1.95, 1.90, and 1.85 attributable to the various methyl groups. These isomers proved inseparable in our hands and they were also unreactive toward *N*-phenyltriazolinedione. Combustion analysis of the

Scheme VIII



mixture was entirely consistent with a molecular formula of $C_{14}H_{14}$.

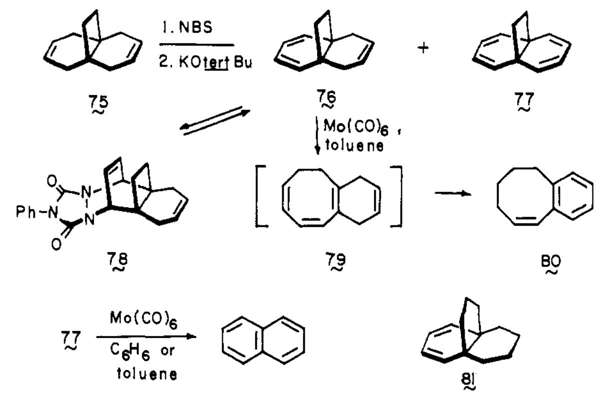
Of particular interest is the susceptibility of **69** to rearrangement. It will be recalled that the structurally related demethyltetraene **10** merely gave a stable π complex under identical conditions. This may be a direct consequence of the fact that the cyclobutene double bond in **69** (and also **63**) is too sterically congested to enter readily into π coordination. When the progress of rearrangement of both **63** and **69** was followed by ^1H NMR as previously described for **12** ($Mo(CO)_6$, C_6D_6, 80 °C), no evidence was obtained for the transient generation of spectroscopically detectable levels of an unstable molybdenum carbonyl complex. The appearance of the uncomplexed cyclooctatetraene isomers was, in contrast, clearly visible.

Rearrangement of Cyclobutane Systems. If coordination of molybdenum to the cyclobutene double bond is a necessary prelude to [1,5] sigmatropic shifting, then removal of this site of unsaturation should disfavor rearrangement. On the other hand, the observed reaction could be dependent only on the availability of a 1,3-cyclohexadiene moiety. In this case, the presence or absence of a double bond in the four-membered ring should not exert major impact on the overall process. An initial experimental test of this question is provided by propelladiene **72**.[35] This unsaturated tricyclic hydrocarbon proved inert to the action of $Mo(CO)_3$(diglyme) at room temperature and to $Mo(CO)_6$ at 80 °C in benzene solution. However, heating of **72** with $Mo(CO)_6$ in refluxing toluene for 48 h led in quantitative yield to an isomeric substance identified as **73** (Scheme VIII). This 1,3,5-cyclooctatriene derivative exhibits an ultraviolet maximum (in hexane) at 267.5 nm (ϵ 3500) and two broad ^1H NMR absorptions (in CCl_4) at δ 5.75–5.33 (4 H) and 2.50–1.35 (12 H). Upon exposure to *N*-phenyltriazolinedione in ethyl acetate solution at room temperature, **73** enters in Diels-Alder cycloaddition with formation of **74**. This unsymmetrical adduct is characterized by a series of four multiplets at δ 7.60–7.20 (4 H, aromatic), 6.53–5.95 (2 H, olefinic), 5.10–4.70 (2 H, bridgehead), and 2.70–1.20 (12 H, methylenes). The chemical shifts of the bridgehead protons clearly identify them as allylic and doubly allylic in nature. In addition, the broad upfield multiplet consists of two slightly overlapping envelopes of equal intensity. This is as expected for **74**. Hydrolysis-oxidation of **74** returned **73** whose spectral properties were identical with those originally recorded.

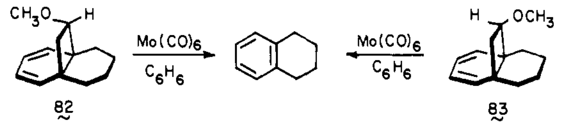
The behavior of **76**, available together with **77** from the bromination-dehydrobromination of **75**[36] (Scheme IX), was also evaluated. To facilitate purification of this triene, the mixture of **76** and **77** was treated with *N*-phenyltriazolinedione and the insoluble bis adduct arising from **77** was separated by filtration. After purification by chromatography on Florisil, **78** (stereochemistry assigned by analogy[37]) was reconverted to **76** by the conventional procedure. When allowed to react with $Mo(CO)_6$ in refluxing toluene, **76** was smoothly converted to benzocycloocta-1,3-diene (**80**, 82.3% isolated) which was identified on the basis of its ^1H NMR spectrum. The formation of **80** can be rationalized as the result of [1,5] sigmatropic shifting of the cyclobutane ring to deliver **79** which subsequently experiences aromatization through hydrogen migrations promoted by the transition metal. The latter transformations are well precedented.[38]

Propellatetraene **77** reacted with $Mo(CO)_6$ slowly in refluxing benzene, and more rapidly in toluene, to give naphthalene and presumably ethylene. The hydrocarbon was observed to be stable to prolonged heating in refluxing toluene in the absence of catalyst. Consequently, the customary rearrangement process is interrupted by a fragmentation in this example.

Scheme IX



Several attempts have been made to study the stereochemical aspects of the sigmatropic migration of a tetrahedral carbon atom under conditions of transition metal catalysis. However, this experimentation has not yet been successful. The two isomeric 11-methoxy[4.4.2]propella-2,4-dienes **82** and **83**,[35] for example, are partially degraded to tetralin when treated with $Mo(CO)_6$ inrefluxing benzene. No sigmatropic shifting could be observed. Also, synthetic entries to 11-alkyl and 11,12-dialkyl derivatives of **72** have yet to be successfully devised. Such studies are continuing.



The feasibility of ethano-bridged propellane rearrangements now having been successfully demonstrated, attention was turned to the higher homologue **81**. This hydrocarbon was found to be totally inert to the action of $Mo(CO)_6$ in refluxing toluene. The requirement of a reasonable level of ring strain in the propellane substrate was again clearly evident.

Summary

Although mechanistic analysis of the above rearrangements will be made only after detailed consideration of deuterium isotope effects,[18] it is of value to summarize the relevant experimental findings at this time. The obvious key structural requirement is a 1,3-cyclohexadiene unit laterally fused to a strained four-membered ring. Since the latter may be saturated or unsaturated, it would appear that prior coordination of this segment to molybdenum is not required. The observed conversions consist operationally of a formal [1,5] shift, but do not distinguish whether the four-membered ring migrates in a rather direct way or the larger third ring shifts in somewhat more circuitous fashion. The latter alternative can be confidently eliminated on the basis of suitable deuterium labeling studies to be discussed.[18] The behavior of **26** reveals therefore a 2.7-fold greater preference for migration of C_{12} away from C_6 than of C_{11} away from C_1. This proclivity for migration toward the more highly substituted cyclohexadiene carbon is also seen in the case of **34** although to a reduced level, presumably as the result of the more distal nature of the methyl substituent. In **51**, where the alkyl side chain is attached directly to the cyclobutene ring, the rearrangement is seen to be highly regiospecific with the less substituted carbon migrating solely. These directive influences are probably of steric origin.

Not only is $Mo(CO)_6$ uniquely capable of promoting this structural isomerization of [4.4.2]propella-2,4,11-trienes, but it is also capable of catalyzing more extended circumambulation when C_{11} and C_{12} are both substituted as in **63** and **69.** Although the specific catalytic effectiveness of $Mo(CO)_6$ among the group 6 metal carbonyls correlates directly with metal-carbon bond strengths (Cr > W > Mo) and the generally accepted order of π back-donation (W-C > Cr-C > Mo-C),[39] its coordinative powers need not be the only factor underlying its ability to promote sigmatropic shifting. Whatever the case, the influential role capable of being exerted by $Mo(CO)_6$ on those orbital symmetry controlled processes in which π-bond interactions gain importance is clearly revealed.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 467 spectrophotometer. The ^1H NMR spectra were determined with Varian A-60A and Bruker HX-90 instruments, and apparent splittings are given in all cases except the AA′XX′ patterns of the 1,3-diene complexes. The ^{13}C spectra were also run on the Bruker spectrometer. Mass spectra were measured on an AEI-MS9 spectrometer at an ionizing energy of 70 eV. Preparative scale VPC separations were performed on a Varian Aerograph Model A-90-P3 instrument equipped with thermal conductivity detectors. Microanalytical determinations were performed at the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

[4.4.2]Propella-3,11-dienemolybdenum Tetracarbonyl (7). A magnetically stirred mixture of freshly sublimed molybdenum hexacarbonyl (2.0 g, 7.6 mmol) and [4.4.2]propella-3,11-diene[1] (**6,** 4.0 g, 25 mmol) in anhydrous benzene (25 mL) was heated at reflux under a dry nitrogen atmosphere for 48 h. The flask was shaken occasionally to return the sublimed $Mo(CO)_6$ to the solution. After cooling, the solution was concentrated under reduced pressure and chromatographed on Florisil. Elution with hexane returned 2.70 g of **6.** Increase in solvent polarity to hexane-benzene (1:1) afforded 1.3 g (43.5%) of **7:** mp 98-100 °C (from pentane); δ_{Me_4Si} ($CDCl_3$) 4.89 (s, 2 H), 4.36 (t, J = 2.0 Hz, 2 H), 2.45-1.70 (m, 4 H), and 1.55 (s, 8 H).

Anal. Calcd for $C_{16}H_{16}MoO_4$: C, 52.16; H, 4.38. Found: C, 52.36; H, 4.48.

[4.4.2]Propella-3,8,11-trienemolybdenum Tetracarbonyl (9). Reaction of 4.0 g (25.3 mmol) of **8**[1] with 2.0 g (7.6 mmol) of $Mo(CO)_6$ in refluxing benzene (20 mL) for 48 h in the predescribed manner gave after Florisil chromatography 2.2 g of unreacted **8** and 1.9 g (45.6%) of **9:** mp 95-97 °C (from pentane); δ_{Me_4Si} ($CDCl_3$) 5.68 (pseudo t, J = 3.9 Hz, 2 H), 4.76 (s, 2 H), 4.48 (t, J = 1.3 Hz, 2 H), and 2.65-1.77 (m, 8 H).

Anal. Calcd for $C_{16}H_{14}MoO_4$: C, 52.48; H, 3.85. Found: C, 52.33; H, 4.01.

[4.4.2]Propella-2,4,8,11-tetraenemolybdenum Tetracarbonyl (11). A. A magnetically stirred mixture of freshly sublimed $Mo(CO)_6$ (3.0 g, 11.4 mmol), dry diglyme (10 mL), and anhydrous benzene (3 mL) was heated at reflux under a dry nitrogen atmosphere for 6 h. The flask was shaken occasionally to return sublimed $Mo(CO)_6$ from the condenser to the solution. This mixture was allowed to cool, 5.0 g (32 mmol) of **10**[22] dissolved in a little benzene was added, and stirring at room temperature was continued for 18 h. Chromatography on Florisil (pentane elution) returned 4.1 g of unreacted **10.** Elution with pentane-benzene (1:1) afforded 1.3 g (62.0%) of **11,** mp 163-164 °C dec. The analytical sample was obtained by sublimation: δ_{Me_4Si} ($CDCl_3$) 6.00-5.40 (m, 4 H), 4.85 (s, 2 H), 4.51 (t, J = 2.5 Hz, 2 H), and 2.60-1.89 (n, 4 H).

Anal. Calcd for $C_{16}H_{12}MoO_4$: C, 52.77; H, 3.32. Found: C, 52.70; H, 3.48.

B. Tetraene **10** (4.0 g, 25.6 mmol) and molybdenum hexacarbonyl (2.0 g, 7.6 mmol) were heated in 30 mL of benzene at the reflux temperature for 48 h. There was isolated after chromatography 2.0 g of recovered **10** and 1.05 g (22.5%) of complex **11.**

1,4-Tetramethylenecyclooctatetraenemolybdenum Tetracarbonyl (13a). To a stirred solution of the $Mo(CO)_3$ diglyme reagent prepared as above was added 5.0 g (31.6 mmol) of **12**[1] contained in a little benzene. After 18 h at room temperature, pentane was added and the diglyme was removed by repeated extraction with water. Concentration of the dried organic layer at room temperature left an oil admixed with unreacted $Mo(CO)_6$. The oil was separated by filtration through cotton and subjected to chromatography on Florisil. Hexane removed 2.9 g of unreacted **12.** Hexane-benzene (1:1) eluted 1.8 g (37.0%) of complex **13a** as a yellow oil that crystallized from pentane as small, yellow plates: mp 90-92 °C; λ_{max} (cyclohexane) 288 nm (ϵ 132 000) and 237 (320 000); δ_{Me_4Si} ($CDCl_3$) 5.57, 4.69, and 4.60 (s, 2 H each), 2.40-2.00 (m, 4 H), and 1.74-1.10 (m, 4 H).

Anal. Calcd for $C_{16}H_{14}MoO_4$: C, 52.48; N, 3.85. Found: C, 52.37; H, 3.92.

1,4-Tetramethylenecyclooctatetraenechromium Tetracarbonyl (13b). A mixture of 2.0 g (12.7 mmol) of **12,** 1.3 g (5.9 mmol) of $Cr(CO)_6$, and 20 mL of toluene (distilled from $LiAlH_4$) was stirred at the reflux temperature under nitrogen for 1.5 days. The chromium hexacarbonyl readily sublimed into the condenser which was scraped frequently with a glass rod to avoid clogging. Vacuum distillation at ambient temperature removed the solvent and unreacted $Cr(CO)_6$. The residue was chromatographed on Florisil; elution was effected with pentane and pentane-benzene (1:1). There were recovered in turn 1.55 g of **12** and 0.26 g (28.5%) of complex **13b,** the latter as an orange solid: mp 93-95 °C (from pentane); δ_{Me_4Si} ($CDCl_3$) 5.51 (br s, 2 H), 4.29 (s, 2 H), 4.20 (s, 2 H), 2.40-2.05 (m, 4 H), and 1.70-1.20 (m, 4 H).

Anal. Calcd for $C_{16}H_{14}CrO_4$: C, 59.63; H, 4.38. Found: C, 59.46; H, 4.48.

1,4-Tetramethylenecyclooctatetraenetungsten Tetracarbonyl (13c). A 1.0-g (6.34 mmol) sample of **12,** 1.0 g (2.84 mmol) of $W(CO)_6$, and 15 mL of xylene (distilled from $LiAlH_4$) were refluxed and magnetically stirred under nitrogen for 14 h. Upon cooling, unreacted $W(CO)_6$ precipitated and was removed by gravity filtration. The solvent was removed by vacuum distillation and the residue was chromatographed on Florisil. Pentane eluted 0.30 g of unreacted **12** followed by 0.90 g (44.7%) of **13c:** mp 103-105 °C (from pentane); δ_{Me_4Si} ($CDCl_3$) 5.81 (br s, 2 H), 4.55 (s, 2 H), 4.47 (br s, 2 H), 2.40-2.05 (m, 4 H), and 1.65-1.20 (m, 4 H).

Anal. Calcd for $C_{16}H_{14}WO_4$: C, 42.32; H, 3.11. Found: C, 42.49; H, 3.40.

1,5-Pentamethylenecyclooctatraenemolybdenum Tetracarbonyl (15). To a solution of 3.0 g (17.5 mmol) of **14**[1] in 40 mL of dry benzene was added 2.0 g (7.6 mmol) of $Mo(CO)_6$ and the mixture was refluxed under nitrogen and magnetically stirred for 17 h. The residue upon concentration was chromatographed on Florisil. Pentane eluted 1.55 g of unreacted **14.** Pentane-benzene (1:1) eluted 2.8 g (87.5%) of complex **15** as an oil which crystallized from pentane-benzene: mp 123-125 °C dec; δ_{Me_4Si} ($CDCl_3$) 5.74 (m, 2 H), 4.68 (s, 4 H), 2.45-2.10 (m, 4 H), and 2.00-0.85 (m, 6 H).

Anal. Calcd for $C_{17}H_{16}MoO_4$: C, 53.70; H, 4.24. Found: C, 54.05; H, 4.28.

***anti*- and *syn*-[4.4.2]Propella-2,4,11-trieneiron Tricarbonyls (16 and 17).** A mixture of **12** (2.0 g, 12.7 mmol) and benzylideneacetoneiron tricarbonyl (7.0 g, 24.3 mmol)[28] in 100 mL of dry benzene was stirred for 48 h while being heated at 55-60 °C under a nitrogen atmosphere. The resulting mixture was concentrated under reduced pressure and the residue was chromatographed on silica gel. Pentane elution furnished 2.5 g (66%) of a yellow oil which proved to be a 2:1 mixture of **16** and **17** (^1H NMR analysis). Dissolution of this material in 3 mL of hexane and cooling gave large yellow crystals of **17.** Further recrystallization from pentane yielded bright yellow crystals: mp 85-86.5 °C; ν_{max} (KBr) 2040, 1985, and 1975 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 6.05 (s, 2 H), 5.26 and 3.28 (AA′XX′, $J_{2,3}$ = 6.25, $J_{2,4}$ = 1.05, $J_{3,4}$ = 4.10 Hz, 4 H), and 1.8-1.3 (m, 8 H); m/e 298.0295 (calcd 298.0292).

Anal. Calcd for $C_{15}H_{14}FeO_3$: C, 60.43; H, 4.73. Found: C, 60.38; H, 4.69.

Chromatography of the residual oil on alumina (pentane elution) afforded crystalline **16** as pale yellow crystals: mp 69-70.5 °C (from pentane); ν_{max} (KBr) 2040, 1980, and 1970 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 6.13 (s, 2 H), 5.47 and 2.84 (AA′XX′, $J_{2,3}$ = 6.77, $J_{2,4}$ = 1.48, and $J_{3,4}$ = 4.50 Hz, 4 H), and 1.7-1.3 (m, 8 H); m/e 298.0295 (calcd 298.0292).

Anal. Calcd for $C_{15}H_{14}FeO_3$: C, 60.43; H, 4.73. Found: C, 60.62; H, 4.77.

***anti*-11,12-Dimethyl[4.4.2]propella-2,4,11-trieneiron Tricarbonyl (19).** A mixture of **18** (1.0 g, 5.9 mmol) and benzylideneacetoneiron tricarbonyl (2.6 g, 9.0 mmol) in 20 mL of dry benzene was heated under nitrogen at 60 °C for 2 days. Chromatography of the crude reaction mixture on silica gel (pentane elution) afforded 1.8 g of reddish oil, ^{1}H NMR analysis of which indicated it to be a mixture of **18** and **19.** Distillation in vacuo returned 540 mg of **18.** Trituration of the residue with methanol gave 350 mg (43.5%) of **19** as yellow-orange plates, mp 88–90 °C. Sublimation at 80 °C and 0.2 Torr afforded bright yellow crystals: mp 90–92 °C; $\delta_{\mathrm{Me_4Si}}$ ($CDCl_3$) 5.33 and 2.90 (AA′XX′, $J_{2,3} = 6.35$, $J_{2,4} = 1.55$, $J_{3,4} = 4.20$ Hz, 4 H), 1.9–1.15 (m, 8 H), and 1.38 (s, 6 H).

Anal. Calcd for $C_{17}H_{18}FeO_3$: C, 63.00; H, 5.56. Found: C, 62.92; H, 5.63.

1,2-Tetramethylenecyclooctatetraene (20). A. Thermal Rearrangement of 13a. A thick-walled Carius tube was charged with a solution of 250 mg (0.68 mmol) of **13a** in 15 mL of benzene. The atmosphere above the solution was flushed with nitrogen and the tube was sealed at −78 °C. The tube was heated to 200 °C in a copper tube furnace and allowed to cool (total time of heating above 100 °C was ca. 7 min). The resulting solution was passed through Florisil (pentane elution) to give 77.6 mg (72.0%) of **20,** the ^{1}H NMR spectrum of which was identical with that previously reported.[3,5]

B. Mo(CO)$_6$-Promoted Rearrangement of 12. To a solution of 486 mg (3.08 mmol) of **12** in 4.5 mL of benzene was added 406 mg (1.54 mmol) of $Mo(CO)_6$ and the mixture was refluxed while magnetically stirred for 36 h. Passage of the reaction mixture through Florisil (pentane elution) afforded 350 mg (72%) of **20.**

C. Mo(CO)$_6$-Assisted Isomerization of 13a. A solution of **13a** (100 mg, 0.27 mmol) and $Mo(CO)_6$ (20 mg, 0.75 mmol) in benzene (10 mL, freshly distilled from $LiAlH_4$) was heated at the reflux temperature while being stirred magnetically for 24 h. The solvent was carefully removed under reduced pressure (30 mm). Chromatography of the residue on Florisil (hexane elution) gave 45 mg (82%) of **20** and a crystalline fraction (110 mg) believed to be C_6H_6–$Mo(CO)_3$ ($\delta_{\mathrm{Me_4Si}}$ ($CDCl_3$) 6.50). There was also recovered 15 mg of unreacted **13a.**

1,2-Pentamethylenecyclooctatetraene (21). A mixture of 2.0 g (11.6 mmol) of **14,** 2.0 g (7.6 mmol) of $Mo(CO)_6$, and 20 mL of toluene was refluxed under nitrogen for 24 h. The reaction mixture was diluted with pentane, filtered, and concentrated in vacuo. The residual oil was passed through Florisil (pentane elution) to give 350 mg (17.5%) of **21**, identified by comparison of the ^{1}H NMR spectrum with that of an authentic sample[3,5] and formation of a TCNE adduct.

Tetracyanoethylene Adduct of 1,2-Pentamethylenecyclooctatetraene. A mixture of 350 mg (2.04 mmol) of **21** and 260 mg (2.04 mmol) of tetracyanoethylene in 5 mL of ethyl acetate was refluxed for 15 h. The solvent was evaporated and the residual oil was chromatographed on Florisil (ether elution) to give 80 mg (13.1%) of adduct: mp 254–255 °C (from hexane–ethyl acetate); $\delta_{\mathrm{Me_4Si}}$ (CD_3COCD_3) 5.42 (dd, $J = 2.8$ and 4.5 Hz, 2 H), 3.90 (m, 2 H), 3.10 (m, 2 H), 2.15–1.90 (m, 4 H), and 1.80–1.40 (br s, 6 H).

Anal. Calcd for $C_{19}H_{16}N_4$: C, 75.97; H, 5.37. Found: C, 75.82; H, 5.51.

1-Methyl-*cis*-9,10-bis(methanesulfonyloxymethyl)-Δ^2-octalin (24b). From a 48-h high-temperature (170 °C) autoclave reaction involving 100 g (0.66 mol) of cyclohexene-*cis*-1,2-dicarboxylic anhydride (**22**) and 250 mL (170 g, 2.5 mol) of 1,2-pentadiene in 500 mL of dioxane, there was obtained 127 g (87.5%) of colorless, oily adduct **23** after bulb-to-bulb vacuum distillation: $\delta_{\mathrm{Me_4Si}}$ (CCl_4) 5.70 (m, 2 H), 2.80–1.80 (m, 3 H), 2.80–1.30 (m, 8 H), and 1.10 (d, $J = 7.0$ Hz, 3 H).

Conversion of 66.0 g (0.30 mol) of this anhydride to the corresponding diol **24a** was effected with 22.8 g (0.60 mol) of lithium aluminum hydride in 1.5 L of tetrahydrofuran at the reflux temperature for 16 h.

The diol was transformed directly to the dimesylate by reaction with 114.5 g (1.0 mol) of methanesulfonyl chloride in 1.5 L of pyridine at 0 °C during 2 h. There was isolated 85.0 g (77.2% from **23**) of **24b:** mp 99–101 °C (from methanol); $\delta_{\mathrm{Me_4Si}}$ ($CDCl_3$) 5.47 (m, 2 H), 4.58–3.97 (m, 4 H), 3.00 (s, 3 H), 2.99 (s, 3 H), 2.85–2.40 and 2.15–2.00 (br m, 3 H), 1.55 (s, 8 H), and 1.05 (d, $J = 7.5$ Hz, 3 H).

Anal. Calcd for $C_{15}H_{26}O_2S_6$: C, 49.16; H, 7.15; S, 17.50. Found: C, 48.98; H, 7.21; S, 17.34.

2-Methyl[4.4.2]propella-3,11-diene (25). A mechanically stirred mixture of 150 g (0.625 mol) of $Na_2S{\cdot}9H_2O$ and 1.2 L of hexamethylphosphoramide was made anhydrous in the manner described subsequently for **33.** From 80.0 g (0.218 mol) of dimesylate **24b**, there was obtained 40.3 g (88.5%) of colorless, semisolid cyclic sulfide after bulb-to-bulb vacuum distillation. Treatment of 20.8 g (0.100 mol) of this sulfide with 13.4 g (0.100 mol) of *N*-chlorosuccinimide in 500 mL of refluxing carbon tetrachloride for 90 min, followed by oxidation with 300 mL of a 0.70 N (0.210 mol) solution of monoperphthalic acid in ether, afforded 27.5 g (100%) of crude α-chloro sulfone as an oil. Treatment of this oil with 45.0 g (0.40 mol) of potassium *tert*-butoxide in 1.2 L of tetrahydrofuran at the reflux temperature for 5 h afforded 8.3 g (47.6%) of **25** after vacuum distillation (bp 0.30 mm, 120 °C): $\delta_{\mathrm{Me_4Si}}$ (CCl_4) 5.84 (dd, $J = 3.2$ and 4.8 Hz, 2 H), 5.75–5.15 (m, 2 H), 2.15–1.65 (m, 3 H), 1.43 (br s, 8 H), and 0.94 (d, $J = 6.6$ Hz, 3 H).

Anal. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.51. Found: C, 89.18; H, 10.55.

2-Methyl[4.4.2]propella-2,4,11-triene (26). To a magnetically stirred solution of 7.6 g (43.6 mmol) of **25** in 200 mL each of carbon tetrachloride and glacial acetic acid was added 15.0 g (47.0 mmol) of pyridinium hydrobromide perbromide. After 2 h at room temperature, water was added and the organic layer was separated, washed three times with saturated aqueous sodium bicarbonate solution, and dried. Filtration and evaporation left a nearly colorless, oily dibromide which was taken up in anhydrous hexamethylphosphoramide (520 mL), treated with 18.25 g (0.436 mol) of lithium chloride and 32.3 g (0.436 mol) of lithium carbonate, and heated with stirring at 90–95 °C for 20 h under a dry nitrogen atmosphere. Water and petroleum ether (bp 30–60 °C) were added, the organic layer was separated, and the aqueous layer was reextracted twice with petroleum ether. The combined organic layers were washed three times with water, dried, and concentrated to leave a yellow oil which was vacuum distilled through a 6-in. Vigreux column (oil bath 100 °C, bp 42 °C at 0.3 mm) to give 3.20 g (42.5%) of triene **26** as a colorless oil: $\delta_{\mathrm{Me_4Si}}$ (CCl_4) 5.90 (AB q, $J_{AB} = 1.5$ Hz, 2 H), 5.75–5.06 (m, 3 H), 1.74 (d, $J = 1.8$ Hz, 3 H), and 1.70–1.30 (m, 8 H).

Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.64; H, 9.33.

2-Methyl-1,4-tetramethylcyclooctatetraenemolybdenum Tetracarbonyl (27). Molybdenum hexacarbonyl (940 mg, 3.5 mmol), 3.1 mL of freshly distilled diglyme, and 1.5 mL of dry benzene were heated with stirring at reflux under nitrogen for 6 h. After cooling to room temperature, this mixture was treated with 1.94 g (10.8 mmol) of **26** and stirred at room temperature for 18 h. Pentane was added and the diglyme was removed by repeated extraction with water. The dried organic layer was concentrated and chromatographed on Florisil. With hexane elution, there was isolated 1.5 g of recovered **26,** while benzene–hexane (1:1) eluted 740 mg (79%) of **27**, pale yellow crystals: mp 92.5–93.5 °C dec (from pentane); $\nu_{\max}$ (Nujol) 2015, 1970, 1960, and 1910 cm^{-1}; $\delta_{\mathrm{Me_4Si}}$ ($CDCl_3$) 5.30 (d, $J = 3.0$ Hz, 1 H), 5.07 (d, $J = 3.0$ Hz, 1 H), 4.93 (s, 1 H), 4.83–4.25 (m, 2 H), 2.30–2.05 (m, 2 H), and 1.95–1.45 (br m, 9 H); *m/e* 382.0110 (calcd 382.0103).

Anal. Calcd for $C_{17}H_{16}MoO_4$: C, 53.70; H, 4.24. Found: C, 53.79; H, 4.42.

Thermal Rearrangement of 27. A 152-mg (0.04 mmol) sample of **27** was dissolved in 1 mL of C_6D_6 and this solution was sealed into a Pyrex NMR tube at 20 Torr. After the tube had been heated at 60 °C in an oil bath for 20 h, a 30% conversion to **28** and **29** (ratio 2.7:1) was evident by ^{1}H NMR analysis.

For preparative purposes, a solution of **27** (0.30 g, 0.08 mmol) in 0.5 mL of benzene contained in an evacuated, sealed Pyrex tube was heated in an oil bath at 100 °C for 24 h. The solution was concentrated and the residue chromatographed on Florisil. Hexane elution furnished 40 mg of a colorless oil, VPC analysis of which on several columns showed it to be a 2.8:1 mixture of **28** and **29.** The isolated hydrocarbons exhibited spectra identical with those of authentic samples.

Mo(CO)$_6$-Promoted Rearrangement of 26. A magnetically stirred mixture of 0.50 g (2.91 mmol) of **26** and 0.768 g (2.91 mmol) of molybdenum hexacarbonyl was heated in 5 mL of refluxing toluene for 24 h. Removal of the solvent produced a dark oil which was chromatographed on Florisil (pentane elution) and further purified by preparative VPC (6 ft × ¼ in. 5% Carbowax 20M on Chromosorb G, 140 °C) to yield 435 mg (87%) of the **28/29** mixture.

4-Methyl-1,2-tetramethylenecyclooctatetraene (30). Pyrolysis of Propellatriene 26. A 200-mg (1.16 mmol) sample of **26** was pyrolyzed by passage in a slow stream of nitrogen through a quartz chip packed quartz tube heated to 480 °C at 2.5 mm. There was obtained 193 mg (91.5%) of a 5:1 mixture of **30** and a second product believed to be the result of 1,5 hydrogen shifting. A pure sample of **50** could be obtained by preparative scale VPC (6 ft × 0.25 in. 5% Carbowax 20M on Chromosorb G, 150 °C) or by selective destruction of the by-product by treatment of the original reaction mixture with *N*-phenyltriazolinedione in refluxing ethyl acetate (**30** reacts only slowly): δ_{Me_4Si} (CCl_4) 5.69, 5.61, and 5.41 (br m, 5 H), 2.40–1.10 (m, 8 H), and 1.71 (d, J = 1.4 Hz, 3 H).

Anal. Calcd for $C_{13}H_{18}$: C, 90.64; H, 9.36. Found: C, 90.88; H, 9.38.

2-Methyl-*cis*-9,10-bis(methanesulfonyloxymethyl)-Δ^2-octalin (32b). A mixture of 152 g (1.00 mol) of cyclohexene-*cis*-1,2-dicarboxylic acid anhydride (**22**), 250 mL (170.5 g, 2.51 mol) of isoprene, and 500 mL of dioxane was heated in a rocking autoclave at 170 °C for 48 h and distilled to afford 142 g (64.5%) of adduct **31** as a colorless oil: δ_{Me_4Si} ($CDCl_3$) 5.40 (m, 1 H), 2.50–2.00 (m, 4 H), and 2.00–1.20 (m, 11 H).

The anhydride (110 g, 0.50 mol) with 38.0 g (1.00 mol) of lithium aluminum hydride in 3 L of tetrahydrofuran when heated at the reflux temperature for 17 h afforded 105 g (100%) of the corresponding diol **32a.**

From 105 g (0.50 mol) of this diol and 120 mL (178 g, 1.55 mol) of methanesulfonyl chloride in 2 L of pyridine at −5 to 0 °C, there was isolated 118 g (64.0%) of dimesylate **32b:** mp 113–114 °C (from methanol); δ_{Me_4Si} ($CDCl_3$) 5.30 (br s, 1 H), 2.21 (AB q, J_{AB} = 9.4, $\Delta\nu_{AB}$ = 10.4 Hz, 4 H), 3.00 (s, 6 H), 2.07, 1.68, and 1.55 (br m, 15 H).

Anal. Calcd for $C_{15}H_{26}O_2S_6$: C, 49.16; H, 7.15; S, 17.50. Found: C, 49.00; H, 7.06; S, 17.50.

3-Methyl[4.4.2]propella-3,11-diene (33). An anhydrous slurry of sodium sulfide in hexamethylphosphoramide [prepared from 120 g (0.50 mol) of $Na_2S{\cdot}9H_2O$ and 1 L of HMPA by vacuum distillation of an aqueous distillate of maximum bp 110 °C (15 mm)] was cooled, treated with 114 g (0.312 mol) of dimesylate **32b,** and heated at 120 °C for 24 h with mechanical stirring. Cold water and petroleum ether (bp 30–60 °C) were added, the organic layer was separated, and the aqueous layer was extracted twice more with petroleum ether. The combined organic layers were washed four times with water, dried, and concentrated. Bulb-to-bulb vacuum distillation afforded 61.0 g (94.0%) of cyclic sulfide.

To a solution of this sulfide (61.0 g, 0.293 mol) in 1 L of carbon tetrachloride was added 39.2 g (0.293 mol) of *N*-chlorosuccinimide and the mixture was maintained at the reflux temperature for 90 min. After chilling, the precipitated succinimide was removed by filtration and the solvent was evaporated. Ether (1 L) was added to dissolve the α-chloro sulfide. This solution was cooled to 0 °C and treated dropwise with slightly greater than 2 equiv of ethereal monoperphthalic acid. After being stirred at room temperature overnight, the reaction mixture was transferred to a separatory funnel and extracted repeatedly with 0.5 N aqueous sodium hydroxide solution until the washings remained basic to litmus and then washed twice with water. Concentration of the dried ethereal solution gave 79.5 g (98.4%) of a white solid mixture of epimeric α-chloro sulfones, mp 139–145 °C.

This mixture was dissolved in 1.5 L of tetrahydrofuran, cooled to −10 °C, and treated slowly with 148 g (1.32 mol) of potassium *tert*-butoxide while mechanically stirred. The contents were allowed to warm to room temperature and heated at reflux for 4.5 h. The crude product was vacuum distilled (bp 42 °C, 0.30 mm) through a 6-in. Vigreux column to yield 23.2 g (46.5%) of colorless **33:** δ_{Me_4Si} (CCl_4) 5.79 (s, 2 H), 5.32 (br m, 1 H), and 1.90–1.45 (m, 15 H).

Anal. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.51. Found: C, 89.61; H, 10.48.

3-Methyl[4.4.2]propella-2,4,11-triene (34). A magnetically stirred mixture of 7.0 g (0.040 mol) of propelladiene **33,** 7.5 g (0.042 mol) of recrystallized *N*-bromosuccinimide, 350 mL of carbon tetrachloride, and a pinch of benzoyl peroxide was heated at the reflux temperature for 4 h. The precipitated succinimide was separated by filtration and the filtrate freed of solvent. The crude product was dissolved in 600 mL of tetrahydrofuran and heated with 20.0 g (0.178 mol) of potassium *tert*-butoxide at the reflux temperature for 3 h. Chromatography on Florisil produced 5.5 g of a pale yellow oil composed of 40–50% of **34.** Reaction with excess *N*-phenyltriazolinedione in ethyl acetate at room temperature followed by chromatography on Florisil gave 3.8 g (37.4% from **33**) of adduct **35:** mp 162–163.5 °C (from ether–ethyl acetate); δ_{Me_4Si} ($CDCl_3$) 7.65–7.25 (m, 5 H), 6.14–5.70 (m, 3 H), 4.64–4.40 (m, 2 H), 1.85 (d, J = 1.5 Hz, 3 H), and 2.4–1.4 (m, 8 H).

Anal. Calcd for $C_{21}H_{21}N_3O_2$: C, 72.60; H, 6.09; N, 11.10. Found: C, 72.08; H, 6.13; N, 11.90.

Hydrolysis-oxidation of 1.15 g (3.32 mol) of **35** was effected by sequential treatment with 1.33 g (33.2 mmol) of sodium hydroxide in 65 mL of 2-propanol at the reflux temperature for 3 h and 2.90 g (33.2 mmol) of manganese dioxide at ambient temperature for 3 h. There was obtained 0.57 g (100%) of **34:** δ_{Me_4Si} (CCl_4) 5.85 (s, 2 H), 5.50 (pseudo q, J = 10.0 Hz, 2 H), 4.05 (m, 1 H), 1.72 (d, J = 1.5 Hz, 3 H), and 1.47 (br s, 8 H).

Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.79; H, 9.39.

$Mo(CO)_6$-Promoted Rearrangement of 34. A mixture of **34** (200 mg, 1.16 mmol), $Mo(CO)_6$ (250 mg, 0.95 mmol), and dry benzene (2.5 mL) was heated at the reflux temperature under nitrogen for 30 h. The cooled reaction mixture was directly chromatographed on Florisil (pentane elution) and gave 125 mg (63.5%) of a mixture of **28** and **30.** ^1H NMR analysis indicated **28** to predominate by 60–70%, a conclusion supported further by VPC analysis on several columns.

5-Methyl-1,2-tetramethylenecyclooctatetraene (28). Pyrolysis of Propellatriene 34. Passage of 160 mg (0.93 mmol) of **34** through the quartz chip packed quartz tube at 470 °C with a slow stream of nitrogen at 2.5 mm gave 159 mg (99.5%) of **28:** δ_{Me_4Si} (CCl_4) 5.80–5.30 (m, 5 H), 2.50–1.40 (m, 8 H), and 1.72 (d, J = 1.2 Hz, 3 H).

Anal. Calcd for $C_{13}H_{18}$: C, 90.64; H, 9.32. Found: C, 90.36; H, 9.36.

2,3-Dimethyl-*cis*-9,10-bis(methanesulfonyloxymethyl)-Δ^2-octalin (37b). A rocking autoclave was charged with 152 g (1.0 mol) of cyclohexene-*cis*-1,2-dicarboxylic anhydride (**22**), 130 g (1.58 mol) of unpurified 2,3-dimethylbutadiene,[40] and 400 mL of dioxane and heated at 170 °C for 24 h. The solvent and low-boiling contaminants were removed on a rotary evaporator. The residual oil was subjected to vacuum distillation (0.10 mm). After a forerun, there was isolated 207 g (88.5%) of solid adduct **36:** mp 56–57 °C (from ether–petroleum ether); δ_{Me_4Si} (CCl_4) 2.30 (m, 4 H), and 1.6–1.8 (m, 14 H).

This crude anhydride (117 g, 0.50 mol) was reduced with lithium aluminum hydride (25.0 g, 0.66 mol) in 2.5 L of tetrahydrofuran as described above to give 110 g (98.1%) of diol **37a.** The diol (110 g, 0.49 mol) in 400 mL of pyridine was converted with 197.5 g (1.68 mol) of methanesulfonyl chloride in 2 L of pyridine at −5 to 0 °C to the dimesylate **57b** (180 g, 96.0%): mp 136–138 °C (from methanol); δ_{Me_4Si} ($CDCl_3$) 4.18 (AB q, J_{AB} = 9.3, $\Delta\nu_{AB}$ = 12.3 Hz, 4 H), 2.99 (s, 6 H), 2.02 (br m, 4 H), 1.60 and 1.53 (br m, total of 14 H).

Anal. Calcd for $C_{16}H_{28}O_6S_2$: C, 50.50; H, 7.42; S, 16.85. Found: C, 50.30; H, 7.45; S, 16.83.

3,4-Dimethyl[4.4.2]propella-3,11-diene (38). A solution of anhydrous sodium sulfide in hexamethylphosphoramide was prepared as described previously from 136 g (0.566 mol) of $Na_2S{\cdot}9H_2O$ and 1.2 L of HMPA. To this mechanically stirred slurry at room temperature was added 108.0 g (0.283 mol) of **37b.** Heating and stirring were maintained for 24 h and the sulfide product was isolated as described earlier. There was obtained 47.5 g (75.5%) of colorless plates from absolute methanol: mp 40–42 °C; δ_{Me_4Si} (CCl_4) 2.70 (AB q, J_{AB} = 10.2, $\Delta\nu_{AB}$ = 9.2 Hz), 2.00 (br s, 4 H), 1.64 and 1.51 (br m, total of 14 H).

The sulfide (45.0 g, 0.202 mol) was treated with *N*-chlorosuccinimide (27.1 g, 0.202 mol) in 1.2 L of refluxing carbon tetrachloride for 2.5 h. The resulting crude α-chloro sulfide in 1 L of ether at 0 °C was oxidized with 700 mL of a 0.65 N (0.455 mol) solution of monoperphthalic acid in ether. Subsequent workup gave 58.5 g (100%) of α-chloro sulfone.

A mechanically stirred solution of the α-chloro sulfone (58.5 g, 0.202 mol) in 2 L of tetrahydrofuran was chilled to −10 °C and treated slowly with 100.0 g (0.893 mol) of potassium *tert*-butoxide. After 5 h at the reflux temperature, there was isolated 15.0 g (39.4%) of **38** as a colorless oil after chromatography on neutral alumina (activity I, pentane elution): δ_{Me_4Si} (CCl_4) 5.86 (s, 2 H), 1.78, 1.65, and 1.51 (narrow m's, total of 18 H).

Anal. Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.34; H, 10.77.

3,4-Dimethyl[4.4.2]propella-2,4,11-triene (39). To a magnetically stirred solution of 15.0 g (0.080 mol) of **38** in 300 mL each of carbon tetrachloride and glacial acetic acid was added in one portion 28.2 g (0.088 mol) of pyridinium hydrobromide perbromide. After 2 h of stirring at ambient temperature, workup in the predescribed manner gave a crude oily dibromide. To a mechanically stirred solution of the dibromide in 1 L of hexamethylphosphoramide were added 55.5 g (0.80 mol) of LiCl and 59.0 g (0.80 mol) of Li_2CO_3. Reaction was allowed to proceed for 22 h at 90–95 °C under a dry nitrogen atmosphere. Subsequent to the usual workup, the product was purified by passage through Florisil (elution with petroleum ether, bp 30-60 °C). There was isolated 8.0 g of a mixture of hydrocarbons. To a solution of this product in 200 mL of ethyl acetate was added a solution of *N*-phenyltriazolinedione in the same solvent until the red color persisted. Upon evaporation of the solvent, the residue was chromatographed on Florisil (ether elution) to afford 2.60 g (9.1% from **38**) of adduct **40:** mp 179-180.5 °C (from ether-petroleum ether); δ_{Me_4Si} ($CDCl_3$) 7.70-7.30 (m, 5 H), 5.98 (s, 2 H), 4.35 (s, 2 H), 2.10-1.40 (m, 8 H), and 1.62 (s, 6 H).

Anal. Calcd for $C_{22}H_{23}N_3O_2$: C, 73.10; H, 6.41; N, 11.63. Found: C, 72.89; H, 6.49; N, 11.38.

Hydrolysis of 2.4 g (6.65 mol) of **40** with 2.66 g (66.5 mol) of sodium hydroxide in 80 mL of boiling 2-propanol for 3 h, acidification, basification, and oxidation with 5.8 g (66.5 mol) of manganese dioxide afforded 1.15 g (92.1%) of triene **39** as a colorless oil after passage through Florisil (pentane elution): δ_{Me_4Si} (CCl_4) 5.82 (s, 2 H), 5.15 (narrow m, 2 H) 1.78 (d, J = 1.6 Hz, 6 H), and 1.45 (s, 8 H).

Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 89.97; H, 9.98.

Thermal Rearrangement of 39. A 100-mg (0.538 mmol) sample of **39** was passed through a hot quartz tube packed with quartz chips heated to 470 °C to give 74 mg (74%) of **43** as a 1:1 mixture of bond shift isomers: δ_{Me_4Si} (CCl_4) 5.50 (s, 2 H), 5.41 (s, 2 H), 2.35-1.30 (br m, 8 H), 1.74 (s, 3 H), and 1.63 (s, 3 H).

Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.35; H, 9.83.

4,5-Dimethyl-1,2-tetramethylenecyclooctatetraene (41). Mo(CO)$_6$-Promoted Rearrangement of Propellatriene 39. A magnetically stirred mixture of 500 mg (2.69 mmol) of **39,** 150 mg (0.57 mmol) of molybdenum hexacarbonyl, and 10 mL of benzene was refluxed under nitrogen for 24 h. The reaction mixture was passed through Florisil (pentane elution) to provide 320 mg (64.0%) of **41,** VPC analysis of which indicated it to be 95% pure. The ^{1}H NMR spectrum of the purified sample was superimposable upon that of the hydrocarbon isolated from the Mo(CO)$_6$-catalyzed rearrangement of **63.** The ^{1}H NMR spectrum of the minor component [δ ($CDCl_3$) 6.75, br s; 2.80-2.55, br m; and 2.18, s] indicated it to be 6,7-dimethyl-1,2,3,4-tetrahydronaphthalene (**42**). Further characterization of **42** was not performed.

***cis*-9-Acetyl-Δ^2-octalin-10-carboxylic Acid (45).** A solution of 136 g (0.66 mol) of Δ^2-octalin 9,10-dicarboxylic anhydride in 2 L of tetrahydrofuran at −78 °C under nitrogen was treated with 1 mol of ethereal methyllithium. After being stirred for 15 min, the reaction mixture was treated with 200 mL of absolute methanol and allowed to warm to room temperature. Water and ether were added. The ether layer was separated and discarded. The aqueous layer was acidified with concentrated hydrochloric acid to precipitate 131 g (89.4%) of **45:** mp 180-181 ° C (from ether); ν_{max} (Nujol) 3400 and 1750 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 5.80 (m, 2 H), 2.30-1.00 (m, 12 H), and 1.56 (s, 3 H).

Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.23; H, 8.11.

***cis*-9-(1-Hydroxyethyl)-10-(hydroxymethyl)-Δ^2-octalin (46).** To a mechanically stirred slurry of 48.0 g (1.26 mol) of lithium aluminum hydride in 3 L of tetrahydrofuran was added dropwise at the reflux temperature a solution of 131 g (0.591 mol) of **45** in 1 L of the same solvent. After 18 h a freshly prepared saturated aqueous sodium sulfate solution was added dropwise until the hydride salts were hydrolyzed. The solids were removed by filtration and washed with ether. The combined filtrates were evaporated to give 117 g (94.4%) of diol **46:** mp 135-137 °C (from hexane-ethyl acetate); ν_{max} (Nujol) 3550-3000 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 5.60 (m, 2 H), 4.4-3.2 (m, 5 H), 2.7-2.3 (m, 2 H), 2.1-1.3 (m, 10 H), and 1.15 (d, J = 7.0 Hz, 3 H).

Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.00; H, 10.48.

11-Methyl-12-thia[4.4.3]propell-3-ene 12,12-Dioxide (48). To 1.5 L of pyridine chilled to 0 °C was slowly added 550 g (4.80 mol) of methanesulfonyl chloride with mechanical stirring. Diethyl ether (100 mL) was added followed by a dropwise addition of 117 g (0.557 mol) of diol **46** dissolved in 750 mL of pyridine. Stirring at ca. 0 °C was continued for 2 h after completion of the addition. The temperature was lowered to −25 °C and cold 10% hydrochloric acid (3 L) was added, very slowly at first. (A vigorous eruption resulted when the acid was poured in quickly.) Addition of ca. 3 mL caused a temperature rise to 46 °C. After the addition was complete, methylene chloride (ca. 1.5 L) was added, and the organic layer was separated, extracted repeatedly with cold 10% HCl until the washing remained acidic, and finally washed with water. The solvent was removed on a rotary evaporator at 25 °C. To the residual oil was added 750 mL of absolute methanol. The dimesylate which crystallized in the cold amounted to 104 g (51.0%), mp 83-85 °C. The solid was unstable and underwent decomposition to a black oil upon standing at room temperature: δ_{Me_4Si} ($CDCl_3$) 5.65 (br s, 2 H), 5.33 (q, J = 7.0 Hz, 1 H), 4.30 (AB q, J_{AB} = 10.0, $\Delta\nu_{AB}$ = 4.80 Hz, 2 H), 3.09 and 3.00 (pair of s, total of 3 H), 2.40-1.90 (m, 4 H), 1.60 (br s, 8 H), and 1.50 (d, J = 6.5 Hz, 3 H).

Anhydrous sodium sulfide in hexamethylphosphoramide was prepared as described above from 130 g (0.541 mol) of $Na_2S{\cdot}9H_2O$ and 1 L of HMPA. To the cooled slurry was added 104 g (0.284 mol) of this dimesylate and the reaction mixture was heated with mechanical stirring at 120 °C for 20 h. Workup as before afforded an orange oil which was vacuum transferred at 0.1 mm to give 42.4 g (72.0%) of sulfide **47** as a semicrystalline, colorless solid.

To a mechanically stirred solution of 26.0 g (0.125 mol) of **47** in 500 mL of ether chilled in an ice bath was added 460 mL of a 0.60 N (0.276 mol) solution of monoperphthalic acid in ether. Stirring at room temperature was maintained for 4 h. Workup in the predescribed manner gave 24.0 g (80.0%) of sulfone **48:** mp 124-132 °C (from ether); δ_{Me_4Si} ($CDCl_3$) 5.62 (m, 2 H), 3.80-1.80 (m, 7 H), 1.60 (m, 8 H), and 1.20 (dd, J = 7.0 and 1.3 Hz, 3 H).

Anal. Calcd for $C_{13}H_{20}O_2S$: C, 64.96; H, 8.39; S, 13.34. Found: C, 64.76; H, 8.24; S, 13.53.

11-Methyl[4.4.2]propella-3,11-diene (50). A. Reductive Desulfonylation of 48. A magnetically stirred solution of 5.5 g (0.0229 mol) of sulfone **48** in 60 mL of dioxane was chilled in a cold water bath and treated with 10.5 mL (0.0229 mol) of a 2.2 M hexane solution of *n*-butyllithium under nitrogen. The resulting reaction mixture was transferred via syringe to a refluxing, mechanically stirred slurry of 4.35 g (0.115 mol) of lithium aluminum hydride in 300 mL of dioxane. After 24 h at this temperature, the mixture was cooled and treated dropwise with a freshly prepared, saturated aqueous sodium sulfate solution until the mixture turned from gray to white. The solids were removed by suction filtration and washed with petroleum ether (bp 30-60 °C). The combined filtrates were diluted with additional petroleum ether and the dioxane was removed by repeated (four to five times) extractions with water. The organic layer was dried and concentrated to give an oil which was distilled through a 6-in. Vigreux column at 0.10 mm from an oil bath heated to 95 °C. There was isolated 465 mg (11.8%) of **50:** δ_{Me_4Si} (CCl_4) 5.62 (m, 2 H), 5.45 (q, J = 1.4 Hz, 1 H), 1.94-1.73 (m, 4 H), and 1.55-1.40 (m, 11 H).

Anal. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.51. Found: C, 89.62; H, 10.54.

B. Ramberg-Bäcklund Sequence. To a stirred solution of **47** (28.7 g, 0.14 mol) in carbon tetrachloride (900 mL) was added 25.8 g (0.14 mol) of *N*-chlorosuccinimide and the mixture was heated at the reflux temperature for 90 min. After cooling, the precipitated succinimide was filtered and the solution was concentrated to yield an oily mixture of epimeric α-chloro sulfides which were directly dissolved in 200 mL of anhydrous ether. This solution was cooled to 0 °C with stirring under nitrogen while 748 mL of 0.64 M ethereal monoperphthalic acid was added dropwise. The customary workup gave **49** as a semisolid which was employed directly in the next step.

The epimeric α-chloro sulfones were dissolved in dry tetrahydrofuran (900 mL), cooled to 0 °C, and treated slowly with 63.0 g (0.55 mol) of potassium *tert*-butoxide. The brown colored mixture was allowed to warm to room temperature for 1 h and then heated to reflux overnight. With ice cooling, water and hexane were introduced, the hexane layer was separated and washed repeatedly with water before drying and evaporation of solvent, and the resulting red oil was eluted (hexane solvent) through alumina. There was isolated 11.5 g (51%) of **50** as a colorless oil.

11-Methyl[4.4.2]propella-2,4,11-triene (51). Treatment of 1.21 g (6.95 mmol) of **50** with 2.40 g (7.50 mmol) of pyridinium hydrobromide perbromide in 30 mL each of carbon tetrachloride and glacial acetic acid, followed by reaction of the resulting dibromide with 5.46 g (0.075 mol) of Li_2CO_3 and 3.15 g (0.075 mol) of LiCl in 150 mL of hexamethylphosphoramide at 90-95 °C for 20 h, afforded after distillation 1.12 g (93.8%) of **51:** δ_{Me_4Si} (CCl_4) 5.85-5.20 (m, 5 H), 1.64 (d, J = 1.9 Hz, 3 H), and 1.51 (br s, 8 H).

Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.32; H, 9.60.

3-Methyl-1,2-tetramethylenecyclooctatetraene (29). A. Pyrolysis of 51. A 40-mg (0.233 mmol) sample of propellatriene **51** was passed in a slow stream of nitrogen through a quartz chip packed quartz tube heated to 480 °C at 2.5 mm. There was obtained 30 mg (75%) of **29** after preparative VPC purification (6 ft × 0.25 in. 5% Carbowax 20M on Chromosorb G, 140 °C): $\delta_{\mathrm{Me_4Si}}$ (CCl_4) 6.69–6.36 (series of m, 5 H), 2.10–1.40 (m, 8 H), and 1.79 (br s, 3 H).

Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.70; H, 9.59.

B. $Mo(CO)_6$-Promoted Rearrangement of 51. A mixture of 1.0 g (5.82 mmol) of **51**, 1.53 g (5.82 mmol) of molybdenum hexacarbonyl, and 10 mL of benzene was refluxed under a nitrogen atmosphere with magnetic stirring for 38 h. Chromatography of the reaction mixture directly on Florisil (pentane elution) gave 0.50 g (50%) of **29**, identical in all respects with the sample isolated above.

***N*-Phenyltriazolinedione Adducts of 3-Methyl-1,2-tetramethylenecyclooctatetraene (52 and 53).** A magnetically stirred solution of 0.50 g (2.91 mmol) of **29** in 20 mL of ethyl acetate was treated dropwise with a solution of 0.51 g (2.91 mmol) of *N*-phenyltriazolinedione in a few milliliters of the same solvent at room temperature. After the solution has been heated at the reflux temperature for 1 h, a few milliliters of absolute methanol were added and heating was continued for an additional 10 min. The solvent was evaporated and the residue was chromatographed on Florisil. Ether elution afforded a single oily fraction which was fractionally crystallized from ether–hexane in the acid. The first isomer to crystallize (**52**) amounted to 91 mg (9%): mp 214–214.5 °C; $\delta_{\mathrm{Me_4Si}}$ ($CDCl_3$) 7.55–7.25 (m, 5 H), 6.45–5.96 (m, 2 H), 5.00 (d of t, J = 4.8 and 2.0 Hz, 1 H), 4.72 (dd, J = 5.0 and 2.1 Hz, 1 H), 2.64 (br d, J = 4.5 Hz, 1 H), 2.40–1.30 (m, 8 H), and 1.53 (s, 3 H).

Anal. Calcd for $C_{21}H_{21}N_3O_2$: C, 72.60; H, 6.09; N, 12.10. Found: C, 72.71; H, 6.07; N, 12.18.

The second isomer to crystallize (**53**) amounted to 222 mg (22%): mp 164–165 °C; $\delta_{\mathrm{Me_4Si}}$ ($CDCl_3$) 7.60–7.25 (m, 5 H), 6.45–5.93 (m, 2 H), 5.00 (dt, J = 4.8 and 2.0 Hz, 1 H), 4.63 (dd, J = 5.0 and 2.0 Hz, 1 H), 2.78 (br d, J = 4.0 Hz, 1 H), 1.95–1.40 (br m, 8 H), and 1.44 (s, 3 H).

Anal. Calcd for $C_{21}H_{21}N_3O_2$: C, 72.60; H, 6.09; N, 12.10. Found: C, 72.39; H, 6.04; N, 11.65.

11-Methyl[4.4.2]propella-3,11-diene-*12-d* (55). A chilled (−78 °C) magnetically stirred solution containing 24.0 g (0.100 mol) of sulfone **48** in 300 mL of ether under a dry nitrogen atmosphere was treated with 100 mL of a 2.0 M (0.200 mol) hexane solution of *n*-butyllithium. After this solution was allowed to warm to about 0 °C, 10 mL of deuterium oxide was slowly added. The sulfone was isolated by ether extraction and the process was repeated a second time. The ^{1}H NMR spectrum of the resulting d_3-sulfone (**54**) revealed the virtually complete absence of the multiplets between δ 3.8 and 2.7 and the broadened appearance of the methyl singlet at δ 1.18.

Following the procedure described for **48**, 22.0 g (0.0905 mol) of **54** in 100 mL of dioxane was treated in turn with 36 mL of a 2.5 M (0.0905 mol) hexane solution of *n*-butyllithium and 18.0 g (0.50 mol) of lithium aluminum hydride in 1.2 L of dioxane at the reflux temperature for 20 h. There was obtained 1.00 g (6.3%) of **55**: $\delta_{\mathrm{Me_4Si}}$ (CCl_4) 5.62 (m, 2 H), 1.93–1.73 (m, 4 H), and 1.47 (br m, 11 H).

11-Methyl[4.4.2]propella-2,4,11-triene-*12-d* (56). Propelladiene **55** (1.00 g, 5.72 mmol) was brominated with pyridinium hydrobromide perbromide (2.0 g, 6.25 mmol) and subsequently dehydrobrominated with $LiCl/Li_2CO_3$/HMPA [3.2 g (76.2 mmol)/5.6 g (75.6 mmol)/150 mL] at 90–95 °C for 17 h as described above to afford after bulb-to-bulb distillation 0.99 g (99.0%) of **56**: $\delta_{\mathrm{Me_4Si}}$ (CCl_4) 5.90–5.20 (m, 4), 1.65 (s, 3 H), and 1.51 (br s, 8 H).

***N*-Phenyltriazolinedione Adducts of 3-Methyl-1,2-tetramethylenecyclooctatetraene-*8-d* (57) (59 and 60).** A 90-mg (0.52 mmol) sample of **56** was pyrolyzed in the predescribed manner to give 85 mg (94.5%) of **57**. This hydrocarbon, when treated with 86 mg (0.59 mmol) of *N*-phenyltriazolinedione in ethyl acetate, afforded 45 mg (46.4%) of a mixture of **59** and **60** which were separated by fractional recrystallization from hexane–ethyl acetate. See Table II for ^{1}H NMR data.

***N*-Phenyltriazolinedione Adducts of 3-Methyl-1,2-tetramethylenecyclooctatetraene-*4-d* (58) (61 and 62).** A 230-mg (1.33 mmol) sample of **56** was treated with 300 mg (1.13 mmol) of molybdenum hexacarbonyl in 5 mL of benzene for 30 h at 80 °C to give 125 mg (54.5%) of **58**. Reaction in ethyl acetate solution with 126 mg (0.72 mmol) of *N*-phenyltriazolinedione afforded 66 mg (26.4%) of a mixture of **61** and **62**. These isomers were separated by fractional recrystallization from hexane–ethyl acetate. See Table II for ^{1}H NMR data.

$Mo(CO)_6$-Promoted Rearrangement of 11,12-Dimethyl[4.4.2]propella-2,4,11-triene (63). To a solution of 5.0 g (26.8 mmol) of **63** in 30 mL of benzene was added 0.71 g (2.68 mmol) of molybdenum hexacarbonyl and the mixture was refluxed under nitrogen while magnetically stirred for 26 h. The solvent was removed on a rotary evaporator and the residual oil was purified by passage through Florisil (pentane elution). There was obtained 5.0 g (100%) of the rearrangement product mixture as a pale yellow oil consisting of ca. 40% of **64**, 36% of **65**, and 24% of **41**.

Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.38; H, 9.65.

A solution of 1.0 g (5.30 mmol) of the purified mixture in 30 mL of ethyl acetate was treated as described earlier with a solution of 0.93 g (5.30 mmol) of *N*-phenyltriazolinedione in 20 mL of ethyl acetate. Chromatography on Florisil (ether elution) produced an oil which was fractionally crystallized from hexane–ethyl acetate. The first crop amounted to 290 mg (15.1%) of pure **69**: mp 195–196 °C; $\delta_{\mathrm{Me_4Si}}$ ($CDCl_3$) 7.60–7.25 (m, 5 H), 6.05 (d, J = 4.2 Hz, 2 H), 4.98 (q, J = 4.2 Hz, 1 H), 3.10 (br d, J = 12.0 Hz, 1 H), 2.63–1.75 (m, 8 H), 1.67 (s with fine coupling, 3 H), and 1.46 (s with fine coupling, 3 H).

Anal. Calcd for $C_{22}H_{23}N_3O_2$: C, 75.10; H, 6.41; N, 11.63. Found: C, 72.79; H, 6.41; N, 11.56.

The second crop amounted to 310 mg (16.2%) of a mixture of **66** and **67**. A pure sample of **66** was obtained by further fractional recrystallization: mp 207–207.5 °C; $\delta_{\mathrm{Me_4Si}}$ ($CDCl_3$) 7.60–7.25 (m, 5 H), 6.26 (pseudo t, J = 4.5 Hz, 2 H), 4.70 (5-line m, 2 H), 2.35–1.20 (br m, 8 H), 1.42 (s, 3 H), and 1.27 (s, 3 H).

Anal. Calcd for $C_{22}H_{23}N_3O_2$: C, 73.10; H, 6.41; N, 11.63. Found: C, 72.91; H, 6.41; N, 11.63.

In another experiment, treatment of 4.0 g (21.5 mmol) of the rearrangement product mixture with *N*-phenyltriazolinedione (2.82 g, 16.1 mmol) afforded 2.5 g (32.3%) of a mixture of adducts **66** and **67**. From the mother liquors there was recovered 0.70 g (17.5%) of unreacted hydrocarbon which was retreated with 0.875 g (5.0 mmol) of *N*-phenyltriazolinedione in ethyl acetate (30 mL) at the reflux temperature for 1 h to afford an additional undetermined quantity of adduct mixture and 65 mg (9.3%) of unreacted **41** after preparative VPC (6 ft × 0.25 in. Carbowax on Chromosorb G, 150 °C); $\delta_{\mathrm{Me_4Si}}$ (CCl_4) 5.75–5.35 (m, 4 H) and 2.10–1.40 (m, 14 H).

Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.22; H, 9.91.

3,4-Dimethyl-1,2-tetramethylenecyclooctatetraene (65). Hydrolysis–Oxidation of Adduct 67. A magnetically stirred solution of 1.0 g (2.77 mmol) of **67** in 65 mL of 2-propanol was treated in turn with 1.11 g (27.7 mmol) of sodium hydroxide at reflux under nitrogen for 1.5 h, 3 N hydrochloric acid, 3 N aqueous ammonia, 100 mL of pentane, and 2.41 g (27.7 mmol) of manganese dioxide as described earlier. Workup afforded 500 mg (97.0%) of **65**: $\delta_{\mathrm{Me_4Si}}$ (CCl_4) 6.00–5.45 (m, 4 H), 2.50–1.55 (br m, 8 H), 1.79 (s, 3 H), and 1.69 (s, 3 H).

Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.40; H, 9.85.

1,8-Dimethyl-2,3-tetramethylenecyclooctatetraene (64). Hydrolysis–Oxidation of Adduct 66. In a manner analogous to that employed for **67**, there was obtained 51 mg (76.2% after preparative VPC; 5.5 ft × 0.25 in. 5% Carbowax on Chromosorb G, 130 °C) of **64** from 130 mg (0.360 mmol) of **66**, 200 mg (5.0 mmol) of sodium hydroxide, and 500 mg (5.75 mmol) of manganese dioxide: $\delta_{\mathrm{Me_4Si}}$ (CCl_4) 5.70 and 5.38 (sharp m, 4 H), 2.85–1.15 (m, 8 H), 1.80 (s, 3 H), and 1.73 (s, 3 H).

Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.30; H, 9.80.

11,12-Dimethyl[4.4.2]propella-2,4,8,11-tetraene (69). A 5.4-g (0.029 mol) sample of **68**[3] was brominated with 10.0 g (0.031 mol) of pyridinium hydrobromide perbromide in 120 mL each of carbon tetrachloride and glacial acetic acid for 1 h as described above. This was followed by dehydrobromination of the crude dibromide with 10.0 g (0.24 mol) of LiCl and 17.0 g (0.23 mol) of Li_2CO_3 in 175 mL of hexamethylphosphoramide at 90–95 °C for 22 h. Purification of the resulting hydrocarbon by chromatography on neutral alumina (hexane elution) gave 2.3 g (42.6%) of **69** as a colorless oil: $\delta_{\mathrm{Me_4Si}}$ (CCl_4)

5.75–5.32 (m, 6 H), 2.10–1.85 (m, 4 H), and 1.48 (s, 6 H).

Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 90.98; H, 8.82.

2,3- and 3,4-Dimethylbenzocyclooctatetraenes (70 and 71). Heating 1.0 g (5.45 mmol) of propellatetraene **69** and 1.43 g (5.45 mmol) of molybdenum hexacarbonyl in 30 mL of benzene at the reflux temperature under nitrogen with magnetic stirring for 50 h and chromatography as above gave 0.50 g (50%) of a colorless oil. The oil was treated with 1.0 g of dichlorodicyano-*p*-benzoquinone in 25 mL of benzene at the reflux temperature for 3 h. Passage of the reaction mixture through Florisil gave 0.31 g (62.0%) of a mixture of **70** and **71:** δ_{Me_4Si} (CCl_4) 7.20–6.83 (m, 4 H), 6.73–5.50 (m, 4 H), 1.95, 1.90, and 1.85 (three s, total of 6 H).

Anal. Calcd for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 92.15; H, 7.69.

1,2-Tetramethylene-1,3,5-cyclooctatriene (73). Mo(CO)$_6$-Catalyzed Rearrangement of [4.4.2]Propella-2,4-diene. A mixture of 0.90 g (5.62 mmol) of propelladiene **72**[35] and 1.54 g (5.62 mmol) of molybdenum hexacarbonyl in 6.0 mL of dry toluene was heated at the reflux temperature with magnetic stirring under nitrogen for 48 h. The reaction mixture was passed through Florisil (hexane elution) to give 0.90 g (100%) of **73:** λ_{max} (hexane) 267.5 nm (ϵ 3500); δ_{Me_4Si} (CCl_4) 5.75–5.33 (m, 4 H) and 2.50–1.35 (m, 12 H).

Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.93; H, 10.15.

***N*-Phenyltriazolinedione Adduct of 1,2-Tetramethylenecycloocta-1,3,5-triene (74).** Treatment of 1.3 g (8.13 mmol) of **73** with 1.3 g (7.44 mmol) of *N*-phenyltriazolinedione in ethyl acetate solution at ambient temperature for 3 h afforded after chromatography on Florisil (ether elution) 1.50 g (60.3%) of **74:** mp 137–138.5 °C (from ether–ethyl acetate); δ_{Me_4Si} ($CDCl_3$) 7.60–7.20 (m, 5 H), 6.53–5.95 (m, 2 H), 5.10–4.70 (m, 2 H), and 2.70–1.20 (m, 12 H).

Anal. Calcd for $C_{20}H_{21}N_3O_2$: C, 71.62; H, 6.31; N, 12.53. Found: C, 71.24; H, 6.26; N, 12.48.

***N*-Phenyltriazolinedione Adduct of [4.4.2]Propella-2,4,8-triene (78).** A magnetically stirred mixture of 8.0 g (0.050 mol) of propelladiene **75**,[36] 11.0 g (0.0618 mol) of recrystallized *N*-bromosuccinimide, and a pinch of benzoyl peroxide in 700 mL of carbon tetrachloride was refluxed for 90 min. The precipitated succinimide was removed by gravity filtration and the solvent was evaporated. To the residual oil was added 1 L of tetrahydrofuran. The solution was chilled below 0 °C, treated slowly with 50.0 g (0.445 mol) of potassium *tert*-butoxide, and then heated under reflux for 3 h. The usual workup gave after distillation (oil bath 90 °C, 0.10 mm) 5.0 g of a colorless, oily mixture of propellanes **75, 76,** and **77.** To a magnetically stirred solution of the product mixture in 125 mL of ethyl acetate was added dropwise a saturated solution of *N*-phenyltriazolinedione in the same solvent. The addition was made at room temperature and continued until the red coloration persisted. The bis adduct of **77** which precipitated was removed by suction filtration. Concentration of the filtrate produced an oil which was chromatographed on Florisil (ether elution). A semisolid was obtained which was triturated with ether–pentane to give 4.40 g (26.4% from **75**) of **78:** mp 210–212 °C; δ_{Me_4Si} ($CDCl_3$) 7.55–7.25 (m, 5 H), 6.63 (t, J = 4.9 Hz, 2 H), 6.08 (m, 2 H), 4.55 (t, J = 3.8 Hz, 2 H), 2.50–1.80 (m, 4 H), and 1.52 (s, 4 H).

Anal. Calcd for $C_{20}H_{19}N_3O_2$: C, 72.05; H, 5.74; N, 12.61. Found: C, 71.86; H, 5.74; N, 12.79.

[4.4.2]Propella-2,4,8-triene (76). Hydrolysis–Oxidation of 78. Treatment of 4.0 g (0.0119 mol) of adduct **78** with 4.8 g (0.110 mol) of sodium hydroxide in 250 mL of refluxing 2-propanol for 3.5 h, followed by acidification, basification, and oxidation with 10.5 g (0.121 mol) of manganese dioxide in 250 mL of pentane, afforded 1.1 g (58.5%) of triene **76** after bulb-to-bulb distillation: δ_{Me_4Si} (CCl_4) 5.91 and 5.75–5.10 (series of m, 6 H) and 2.35–1.50 (m, 8 H).

Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 91.23; H, 9.06.

Benzocycloocta-1,3-diene (80). Mo(CO)$_6$-Promoted Rearrangement of [4.4.2]Propella-2,4,8-triene (76). A magnetically stirred mixture of 0.90 g (5.70 mmol) of **76**, 1.50 g (5.70 mmol) of molybdenum hexacarbonyl, and 10 mL of toluene was heated at the reflux temperature under dry nitrogen for 36 h. The reaction mixture was diluted with pentane (250 mL) and allowed to stand in the cold. An undetermined quantity of toluenemolybdenum tricarbonyl separated. The pentane solution was decanted and concentrated. Passage of the residual oil through Florisil (pentane elution) yielded 0.74 g (81.2%) of **80:** ν_{max} (neat) 3030, 3010, 2910, 1500, 770, 750, 720 cm^{-1}; δ_{Me_4Si} (CCl_4) 7.00 (s, 4 H), 6.12 (d of t, J = 12.0 and 1.8 Hz, 1 H), 5.92–5.54 (d of t, J = 12.0 and 6.0 Hz, 1 H), 2.88–2.60 (m, 2 H), 2.30–1.90 (m, 2 H), and 1.90–1.20 (m, 4 H).

Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 90.87; H, 9.18.

Mo(CO)$_6$-Promoted Fragmentation of 77. A mixture of 2.66 g (17 mmol) of **77** and 3.0 g (11.3 mmol) of Mo(CO)$_6$ in 30 mL of dry toluene was heated at the reflux temperature with stirring under a nitrogen atmosphere for 15 h. VPC analysis indicated complete disappearance of **77** and formation of a single product. The solvent was removed by careful evaporation at 0.1 mm and 40 °C through a Vigreux column. The dark residue was chromatographed on Florisil (hexane elution). There was isolated 2.0 g (92%) of a colorless solid identified as naphthalene on the basis of ^1H NMR and melting point.

Mo(CO)$_6$-Promoted Fragmentation of 82 and 83. A 500-mg (2.63 mmol) sample of methoxypropelladienes **82** and **83**[35] and 695 mg (2.63 mmol) of Mo(CO)$_6$ in 5 mL of anhydrous benzene was heated at the reflux temperature under nitrogen for 2 days. Direct chromatography of the reaction mixture on Florisil (hexane elution) furnished 390 mg of tetralin, identical in all respects with an authentic sample.

Acknowledgment. This investigation was financed by the National Cancer Institute (Grant CA-12115) and Chevron Research Co.

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Molybdenum(0) Catalysis of [1,5]Sigmatropic Carbon Migration in Unsaturated [4.4.2]Propellanes. Deuterium Isotope Effects, Kinetics, and Mechanism

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Received April 28, 1977

Abstract: Through assessment of the $Mo(CO)_6$-promoted isomerizations of the *2,5-* and *11,12-*d_2 [4.4.2]propella-2,4,11-trienes, it could be unequivocally established that C_{11} of the cyclobutene ring and not C_7 of the cyclohexane moiety is directly involved in formal [1,5]sigmatropic migration. The kinetic behavior of the tetrahapto complexes **17–19** revealed several additional mechanistic features: (a) the presence of deuterium atoms at C_2 and C_5 has little impact on the rate-determining step; (b) the 11,12-dideuterio derivative exhibits, in contrast, an appreciable *intermolecular* isotope effect (k_H/k_D = 0.92 at 80.6 °C); and (c) a 2-methyl substituent accelerates rearrangement by a factor of 2. The level of isotopic discrimination realizable during *intramolecular* competition was shown to be entirely comparable (k_H/k_D = 0.93 at 80 °C) by making recourse to the monodeuterated propellatriene **30.** The magnitude and inverse nature of these secondary isotope effects has been interpreted to be incompatible with two mechanistic alternatives involving "top-side" complexation of the propellatriene (i.e., syn to the cyclobutene bridge). Rather, a transition state model involving modified [1,5]sigmatropic migration on that molecular face opposite to the site of molybdenum coordination is shown to account best for the experimentally determined Arrhenius parameters, deuterium fractionation factors, regioselectivity, and circumambulation (the latter operative only when both C_{11} and C_{12} carry methyl groups).

The ability of transition metal carbonyl complexes to promote olefin isomerization has constituted an important and extensively studied area of organometallic chemistry.[1] Most commonly, 1,3- and 1,5-*hydrogen* shifts have been observed. Depending upon the substrate and catalyst system employed, concerted migrations or processes involving transient formation of metal hydride intermediates are seen to operate. In either event, the different types of isomerization have provided evidence of complete intramolecularity when this level of mechanistic detail has been sought.[2]

During a study of the reaction of unsaturated [4.4.2]propellanes with molybdenum hexacarbonyl,[3,4] we observed that skeletal rearrangement occurs in those systems which possess a 1,3-cyclohexadiene part structure. Because these reactions proceed much more readily than purely thermochemical rearrangements and involve [1,5]sigmatropic *carbon* migration rather than an intramolecular cycloaddition scheme,[5] we were interested in eludicating the mechanistic details of this little-precedented phenomenon.[6] Here we present the results of kinetic and deuterium labeling studies which, when taken with earlier findings,[3] provide experimental evidence implicating suprafacial [1,5] carbon migration within the coordination sphere of the metal.

Results

Synthesis and Rearrangement of the *2,5-* and *11,12-*d_2 [4.4.2.]Propella-2,4,11-trienes. Although our earlier results are rationalizable in terms of a [1,5]sigmatropic shift pathway, no insight has been gained into the timing of this migration. Nor has it been unequivocally established that C_{11} of the cyclobutene ring and not C_7 of the tetramethylene bracket is involved in the translocation. Scheme I illustrates these alternatives for the *2,5-*d_2 derivative (**1**) without specifying the relative stereochemistry of the complexing molybdenum or allowing for the possibility that other intermediates are involved. Tetrahapto coordination is also assumed at this time but will receive later substantiation. We see that path a is quite direct, requiring valence isomerization and decomplexation of **2** (not necessarily in that order) to provide the annulated cyclooctatetraene (viz., **3**). Reaction coordinate b requires additional 1,5 deuterium migration in **4** prior to delivering the isomerized product, in this case **6.**

The specifically deuterated propellane **1** was synthesized according to the established sequence (Scheme II). Deuterium incorporation into this hydrocarbon was established to be >90% d_2 by ^1H NMR analysis of its *N*-phenyltriazolinedione