Thermal Valence Isomerization of Cis-Fused Bicyclic Cyclobutenes. A Study of Orbital Symmetry Control[1]

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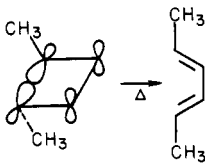
Abstract: This study shows that thermally promoted valence isomerizations of cis-fused bicyclic cyclobutenes, when free of steric constraint, yield products arising from both orbital symmetry allowed conrotatory openings of the labile σ bond in the cyclobutene ring. In the case of the related vinylcyclobutenes, one conrotatory mode produces a stable cis,trans,cis monocyclic triene whereas fission in the other allowed sense affords a thermally labile trans,cis,cis monocyclic triene which, in turn, cyclizes to yield a cyclohexadiene derivative. The product distributions are evaluated in terms of secondary orbital interactions.

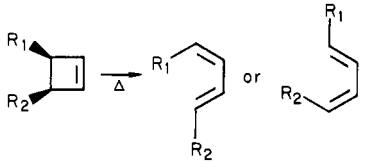
Introduction

The stereospecific, thermally promoted interconversion of cyclobutenes to 1,3-butadienes has been shown to proceed in a concerted fashion, adhering to the rules governing orbital symmetry.[2] Since the orbital systems involved in such a transformation is four electron in nature, a conrotatory fission of the labile α bond is predicted and is, commonly, observed. For example, *trans*-1,4-dimethyl-2-cyclobutene (eq 1) has been shown to yield,



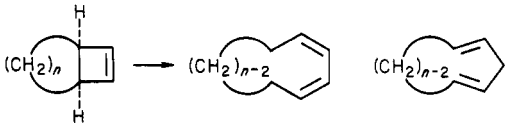
(1)

exclusively, 1,4-dimethyl-*trans,trans*-1,3-butadiene.[3] The equally allowed, conrotatory pathway to yield the related cis,cis isomer has a higher energy of activation due to developing steric interactions in the transition state. In the case of cis-substituted cyclobutenes, conrotatory rupture of the α system has been shown to yield either a *cis,trans*- or a *trans,cis*-1,4-disubstituted-1,3-butadiene or a mixture of the two isomers[2] (eq 2).



(2)

More diverse results are obtained when the cis substituents of a cyclobutene are replaced with a cis-fused methylene chain, and the results obtained upon thermally induced valence isomerization are dependent upon the size of the methylene ring. Thermally induced isomerization of the cyclobutene portion of *cis*-bicyclo[2.2.0]hex-2-ene (**1a**, eq 3) leads to the "unallowed" cis,cis isomer



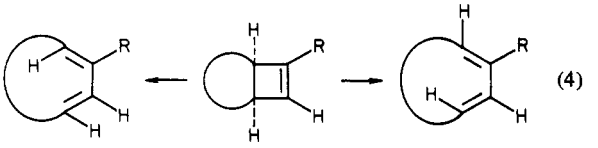
(3)

1a, $n = 2$
1b, $n = 6$

(net disrotatory opening) due to the strain encountered in trying to accommodate a trans double bond in a six-membered ring.[4]

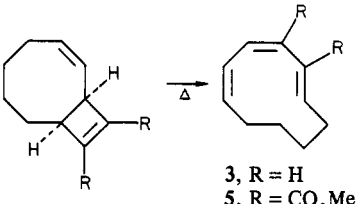
However, thermal valence isomerization of *cis*-bicyclo[6.2.0]-dec-9-ene (**1b**) yields the anticipated, symmetry-allowed *cis,-trans*-cyclodeca-1,3-diene, since the newly created monocyclic compound has sufficient freedom to permit the incorporation of a trans double bond.[5]

Due to the inherent symmetry of the aforementioned substituted cyclobutenes, conrotatory cleavage in either direction leads to the same product. Were the starting cyclobutene made dissymmetric, it would be expected that, in the absence of overriding steric interactions or generated strain, a mixture of both orbital-symmetry-allowed products (eq 4), resulting from nonequivalent



(4)

conrotatory opening of the rupturing α bond, would be obtained. Few such dissymmetric compounds have been studied. The thermal behavior of *cis*-bicyclo[6.2.0]deca-2,9-diene (**2**), an unsymmetrically substituted bicyclic cyclobutene whose related monocyclic 1,3-butadiene possessed a ring system sufficiently large to accommodate a trans double bond, has been studied. It has been reported[5] that cyclobutene **2** upon thermal isomerization gave rise, exclusively, to *trans,cis,cis*-cyclodeca-1,3,5-triene (**3**, eq 5). The related carbomethoxy derivative **4** gave a similar result.[6]



(5)

2, R = H
4, R = CO_2Me

3, R = H
5, R = CO_2Me

These findings of the exclusive formation of an internal cis double bond have never been adequately established or explained. A detailed study of the thermal behavior of unsymmetrical cis-fused cyclobutenes was undertaken in order to determine those factors, if any, controlling which mode of conrotatory ring opening is obtained. In this present study, a series of dissymmetric bicyclic cyclobutenes was prepared and the thermal chemistry of the materials examined.

Synthesis

The general synthetic procedure employed to prepare the compounds examined in this present study employed the carbene-mediated ring expansion of a cyclopropylcarbinyl carbene to

(1) This work was supported by Grant No. AM 00709 from the National Institute of Arthritis, Metabolism, and Digestive Diseases.
(2) Woodward, R. B., Hoffmann, R. "The Conservation of Orbital Symmetry"; Verlag Chemie: Weinheim/Bergstr., Germany; Academic Press: New York, 1971.
(3) Winter, R. E. K. *Tetrahedron Lett.* **1965**, 1207.
(4) Goldstein, M. L.; Leight, R. S.; Lipton, M. S. *J. Am. Chem. Soc.* **1976**, *98*, 5717.
(5) Radlich, P.; Fenical, W. *Tetrahedron Lett.* **1967**, 4901.
(6) McConaghy, J. S.; Bloomfield, J. J. *Tetrahedron Lett.* **1969**, 3719.

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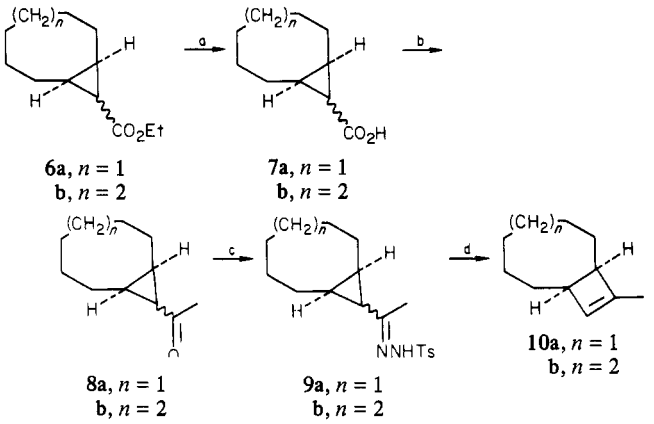
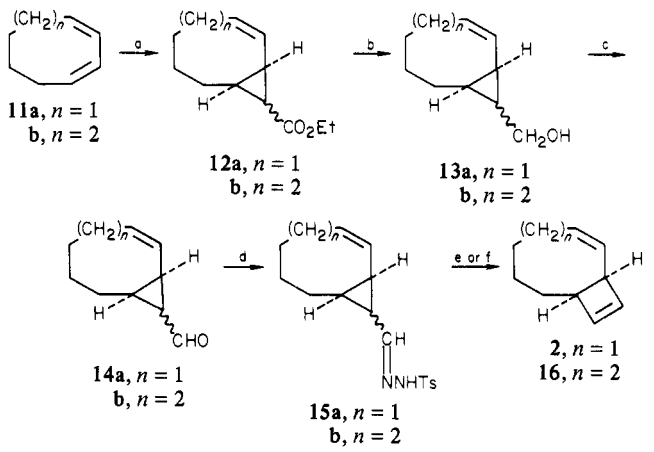
Scheme I[a]



[a] (a) NaOH, H_2O, 80 °C; (b) MeLi, 0 °C; (c) *p*-TsNHNH$_2$, MeOH, 0 °C; (d) NaH, diglyme, and 130 °C or *n*-BuLi, THF, and 130 °C.

Scheme II[a]



[a] (a) N_2CHCO_2Et, $CuSO_4$, 110 °C; (b) LAH, Et_2O; (c) $CrO_3 \cdot Py_2$ or PCC; (d) *p*-TsNHNH$_2$, MeOH; (e) NaH, diglyme, 130 °C; (f) NaH, diglyme, *hν*.

a cyclobutene.[5,7] Three general classes of dissymmetric bicyclic cyclobutenes were prepared.

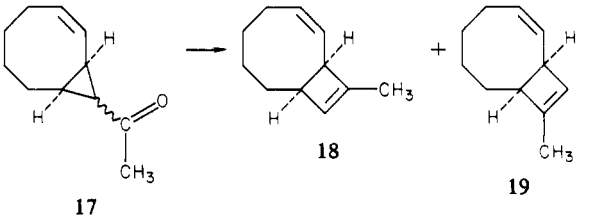
In the first class, a methyl group was used to serve as the element of dissymmetry, and the general synthetic route employed for the preparation of bicyclo[6.2.0]decene and bicyclo[7.2.0]-undecane derivatives is outlined in Scheme I. The methyl ketones **8a** and **8b** were obtained in excellent yield by reaction of acids **7a** or **7b** with 2 equiv of ethereal methyllithium and were converted to the tosylhydrazone intermediates **9a** and **9b**, respectively, by condensation with *p*-toluenesulfonylhydrazine in neutral methanolic solution. The sodium or lithium salts of these derivatives were pyrolyzed at 130 °C to yield the desired methylcyclobutenes **10a** and **10b**. The materials were purified by vapor-phase chromatography to remove small amounts (<5%) of *cis*-cyclooctene and *cis*-cyclononene, respectively.

In the second class of bicyclic cyclobutenes, an endocyclic double bond was used as the element of dissymmetry, and the general synthetic route employed for the preparation of the requisite bicyclic dienes and undecene is outlined in Scheme II. 1,3-Cyclooctadiene (**11a**) and 1,3-cyclononadiene (**11b**) were converted to the bicyclic esters **12a** and **12b**, respectively, by reaction with ethyl diazoacetate in the presence of copper sulfate. These materials were converted to the bicyclic aldehydes **14a** and **14b** via reduction to **13a** and **13b**, respectively, followed by oxidation. All attempts to convert the esters directly to the aldehydes proceeded in poor yield.

The tosylhydrazone **15a** in the bicyclo[6.1.0]nonene series, as its sodium salt, upon being heated to 130 °C afforded mainly

(7) Kirmse, W.; Pook, K. H. *Chem. Ber.* **1965**, *98*, 4022.

Scheme III



(70%) of the desired diene **2** as well as a lesser amount (30%) of 1,3-cyclooctadiene (**11a**). The diene **2** was thermally labile, and careful temperature control had to be observed during the course of the tosylhydrazone decomposition in order to avoid subsequent thermal rearrangement of the diene. The spectral data obtained for **2** are in agreement with the reported literature values.[5] In addition, the ^{13}C NMR resonance signals support the structural assignment.

The tosylhydrazone **15b** in the bicyclo[7.1.0]decane series when subjected to similar reaction conditions failed to produce any of the desired cyclobutene **16**. The reaction yielded, in addition to 1,3-cyclononadiene, other $C_{11}H_{16}$ isomeric compounds. By use of the more mild photochemical decomposition of the tosylhydrazone salt, the desired cyclobutene **16** was obtained. To obtain a pure sample of the diene **16**, however, it was necessary to chromatograph the reaction product on a silver nitrate impregnated silica gel column below room temperature in order to avoid rearrangement of the thermally labile cyclobutene. Examination of the NMR spectra of both the crude and the purified **16** revealed that no silver-promoted rearrangement had occurred during the chromatography. Furthermore, there is a striking similarity of both the ^1H NMR spectra and the ^{13}C NMR spectra for **2** and **16**.

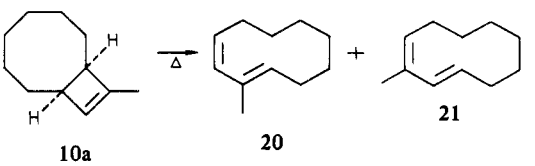
The third class of cyclobutenes used in this study combined the structural features of the previous two classes. The ester **12a** was saponified, and the resulting acid was converted to the methyl ketone **17** by reaction with methyllithium (Scheme III). The ketone **17** was converted to its tosylhydrazone, the sodium salt of which upon thermal decomposition yielded the two dienes **18** and **19** plus a trace amount of 1,3-cyclooctadiene. The isomeric dienes **18** and **19** were separated by chromatography on a 20% silver nitrate/silica gel column, and the mixture was found to contain 40% of **18** and 60% of **19**. The structural assignments were made on the basis of both the ^1H NMR and the ^{13}C NMR spectra.

It is of interest to note the small regiospecificity observed in the rearrangement of the inherently dissymmetric carbene intermediate generated from the tosylhydrazone derivative of **17**. The results obtained in this present study are in accord with an earlier report[8] that the predominant product results from participation of the stronger bond. However, since the ratio of products does not reflect any strong preference for either reaction pathway, it is suggestive that the transition state for the rearrangement is relatively early and does not feel any strong influence of the endocyclic double bond.

Results and Discussion

This series of appropriately labeled bicyclic cyclobutenes permitted the thermal chemistry of this class of compounds to be examined in detail.

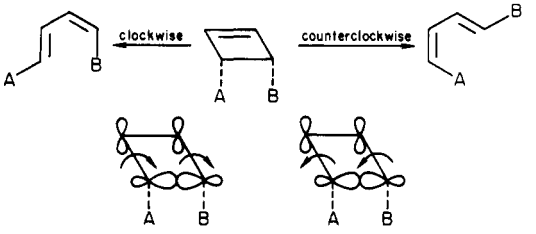
When a dilute benzene solution of **10a** was heated at 190 °C for 1.5 h, two new isomeric products, **20** and **21** (eq 6), were



(6)

(8) Bird, C. L.; Frey, H. M.; Stevens, I. D. R. *Chem. Commun.* **1967**, 707. Stevens, I. D. R.; Frey, H. L.; Bird, C. L. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 646.

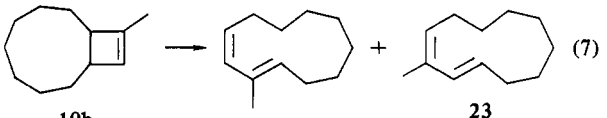
Scheme IV



formed in nearly equal amounts. The products were separated by chromatography on $AgNO_3$-impregnated silica gel. The diene **20** was eluted first and afforded spectra consistent with the proposed structure. Most notably, the presence of a vinyl methyl resonance at δ 1.73 (^{1}H NMR) and 16.81 (^{13}C NMR) is indicative of a trisubstituted double bond possessing an *E* configuration.[9] The absence of a trans double bond in the 970–990-cm^{-1} region of the infrared region completes the structural assignement for **20**.

The second compound eluted was assigned the structure **21**, again on the basis of spectral data. The presence of methyl resonance at δ 1.95 (^{1}H NMR) and δ 22.19 (^{13}C NMR) indicated a trisubstituted double bond with a *Z* configuration,[9] and the presence of absorption at 975 cm^{-1} indicated the presence of a trans-disubstituted double bond.

Nearly identical results were obtained for the next higher homologue, cyclobutene **10b**. The thermal opening proceeded under mild conditions (155 °C) to yield dienes **22** and **23** (eq 7) in about

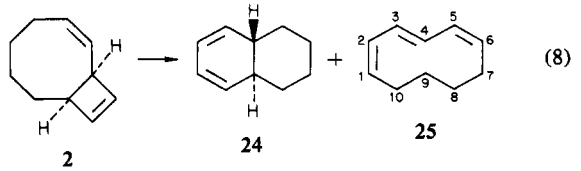


(7)

equal amounts. The structural assignments to the products were made by analogy to dienes **20** and **21**. As in the previous case, the position of the methyl resonances in both the ^{1}H NMR and ^{13}C NMR, coupled with the appearance or absence of the typical IR absorption for a trans-disubstituted double bond, lead to the assignments.

Thus, the thermally induced isomerizations of cis-fused bicyclic cyclobutenes **10a** and **10b** show that when the methylene chain is sufficiently large, the orbital-symmetry-allowed conrotatory opening of the cyclobutene occurs in both allowed directions (i.e., clockwise and counterclockwise) to yield two isomeric dienes. This concept is illustrated in Scheme IV.

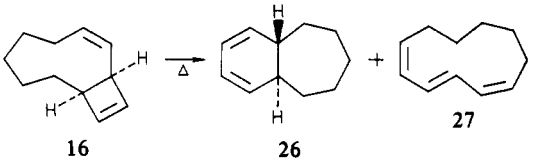
With the dual nature of the conrotatory opening of a cis-fused bicyclic cyclobutene established, attention was turned to the vinylcyclobutenes **2** and **16**. The thermal chemistry of diene **2** was reinvestigated, and it was found that when the compound in benzene solution was heated at 150 °C for 1 h, two isomeric products were obtained in a 4:6 ratio. A similar result was obtained when the diene **2** was heated in the vapor state; the previous study[5] had reported the formation of only a single compound. The two products were separated by preparative VPC, and the compound with the shorter retention time was *trans*-bicyclo[4.4.0]-deca-2,4-diene (**24**, eq 8). The structure was established by



(8)

comparison with an authentic sample.[10,12] The major product, **25**, possessed spectral properties in agreement with those properties previously reported,[5] i.e., the spectral characteristics consistent with a cyclic, conjugated triene with at least one trans-disubstituted double bond. The previous workers[5] had assigned this material the *trans,cis,cis*-1,3,5-cyclodecatriene structure **3**. However, some spectral features displayed by this major isomer cast doubt upon the structural assignment. In the ^{1}H NMR spectrum, the vinyl proton absorption showed a rather symmetrical coupling pattern with observed resonances at δ 6.25 (d, $J_{1,2}$ = 10.0 Hz, $H_{2,5}$), 6.11 (s, $W_{1/2}$ = 3.5 Hz, $H_{3,4}$), and 5.78 (td, $J_{1,2}$ = 10.0 Hz, $J_{1,10}$ = 7.0 Hz, $H_{1,6}$); the coupling constants were confirmed by double irradiation experiments. Perhaps more significantly, however, was that the ^{13}C NMR spectrum of **25** showed *only* five spectral lines when fully proton decoupled, a result indicative of a triene of high symmetry. On the basis of these spectral results, the major product was assigned the cis,trans,cis structure **25**.

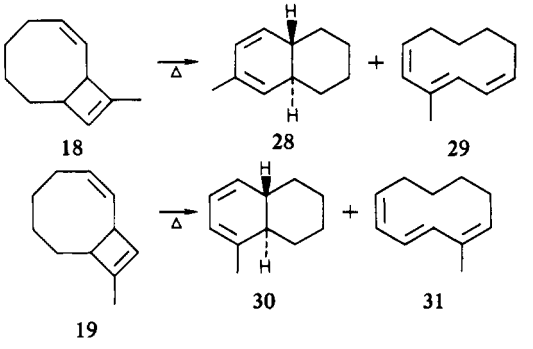
The one-carbon-higher homologue **16** also displayed a similar reaction pattern. Thermal activation of **16**, either in dilute diglyme solution or in the vapor state, gave rise to the formation of the known *trans*-bicyclo[5.4.0]undeca-8,10-diene (**26**)[10,12] and the triene **27**, in a 4:6 ratio (eq 9). The triene **27**, like triene **25**,



(9)

displayed symmetrical resonance patterns in both the ^{1}H NMR and ^{13}C NMR spectra. Since the isomeric *trans,cis,cis*-cycloundeca-1,3,5-triene is known,[12] an authentic sample was prepared and its ^{13}C NMR spectrum obtained. This triene, lacking an element of symmetry, displayed a ^{13}C NMR spectrum with a full 11-line pattern when fully proton decoupled, thereby confirming both the structures of the cis,trans,cis triene **27** and the isomeric trans,cis,cis triene.

Finally, the methyl-substituted dienes **18** and **19** were studied, and it was found that at 160 °C for 2 h both materials gave rise to a diene–triene mixture (eq 10 and 11). It is of interest to note



(10)

(11)

that the relative ratio of diene to triene products arising from a specific cyclobutene showed dependence upon the location of the methyl substituent. In the case of diene **18**, approximately a 1:1 mixture of diene **28** and triene **29** was obtained, whereas **19** afforded a 1:3 mixture of diene **30** and triene **31**, respectively. The structures of dienes **29** and **31** were established by a combination of ^{1}H NMR, ^{13}C NMR, and infrared spectroscopy.

As the structures of these dienes **28** and **30** were of paramount importance to the mechanistic interpretation of these thermally promoted isomerizations, the proposed structures were established, unambiguously, by the independent syntheses shown in Schemes

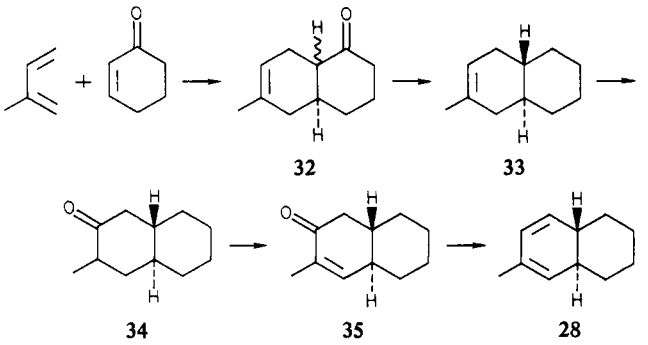
(9) In ^{13}C NMR spectroscopy, the methyl substituent on a trans double bond absorbs at a higher field (16–18 ppm) than a methyl substituent on a cis double bond (20–25 ppm). For general review of the ^{13}C NMR spectra of polyolefins, see: "Progress in the Chemistry of Organic Natural Products"; Springer-Verlag: New York, 1979; Vol. 36, pp 1–283.

(10) Olsen, E. G., Ph.D. Thesis, University of California at Berkeley, 1975.

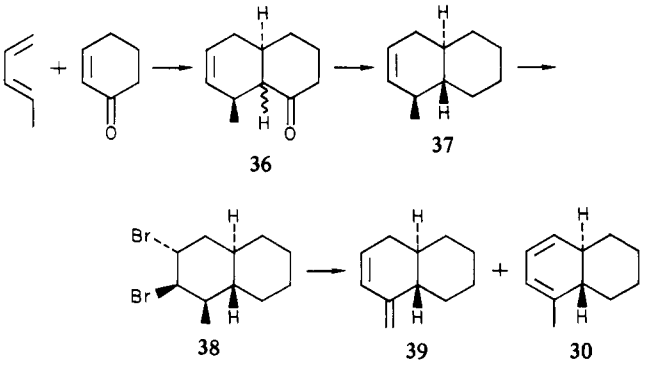
(11) It is worth noting that K. N. Mehrotra reported that heating **2** at 170 °C for 25 min gave only the diene **4**. It is not clear at this time how this worker and the earlier investigators[5] noted opposite specificity of product formation in the thermal reaction.

(12) Dauben, W. G.; Kellogg, M. S. *J. Am. Chem. Soc.* **1972**, *94*, 8951; *Ibid.* **1980**, *102*, 6188.

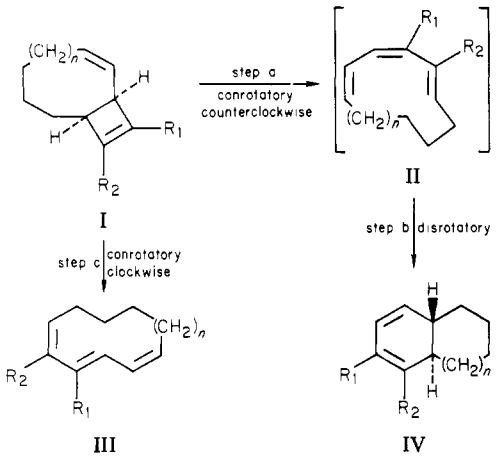
Scheme V



Scheme VI



Scheme VII



V and VI, the specifics of the synthesis being given in the Experimental Section.

In Scheme VII a mechanism to account for all the thermally induced results is presented, a mechanism based upon the dual nature of conrotatory ring opening which was demonstrated for **10a** and **10b**. Thus, conrotatory opening of the strained α bond of I in a counterclockwise sense (step a) affords a *trans,cis,cis*-triene, II. However, under reaction conditions required to isomerize the cyclobutene moiety of I, II undergoes a second facile rearrangement (step b) in a symmetry-allowed, disrotatory ($4n + 2$) ring closure to give the observed trans-fused 1,3-cyclohexadienyl derivative III. Conrotatory opening of the strained α bond of I in a clockwise manner (step c) leads to the formation of the isomeric and equally allowed *cis,trans,cis*-triene IV.

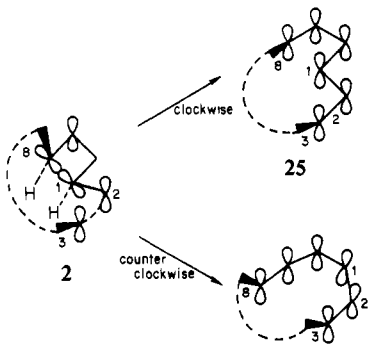
Support for the suggestion that medium-ring trienes possessing a trans,cis,cis configuration of the double bonds would not survive the isomerization temperatures used is present in the literature. Such trienes in nine-, ten-, and eleven-membered rings are known to close the cis-fused 1,3-cyclohexadienyl system at temperatures between −33 and +100 °C.[10,12-15] On the other hand, trienes with a trans central double bond are known to have high thermal stability.[16]

Table I. Product Ratio[a] of Cyclobutene Thermolysis

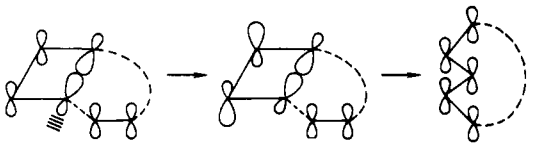
starting matl	ratio	starting matl	ratio
2	1.5	**18**	1.0
16	1.5	**19**	3.0

[a] Ratio of percent triene to percent cyclohexadiene.

Scheme VIII



Scheme IX



The distribution of cyclohexadiene to triene products obtained from the thermal isomerization of the corresponding bicyclic cyclobutenes is given in Table I. Following the above mechanism, one observes that these ratios reflect the efficiencies of the two conrotatory openings. It is found that this distribution reflects a slight preferential direction, and while further experimental data are required before such a preference can be fully understood, it is interesting to speculate on the observed trend.

Two plausible explanations, both based upon secondary orbital interactions, can be invoked to explain the results in Table I. First, the principle of least motion, a concept successfully employed to rationalize the apparent dichotomy of accordant vs. discordant photochemical opening of cyclohexadienes,[17] can be applied to the present system.

As illustrated in Scheme VIII, there is a conformation of **2** in which the double bond in the eight-membered ring (C_2–C_3) is in a position to participate in the rupture of the α-bond system. Consideration of the C_1 half of the C_1–C_8 σ bond and the C_2 p orbital reveals that a clockwise motion of C_1 (C_1 minor orbital to C_2 top orbital) to form the observed *cis,trans,cis*-triene **25** will result in far less movement of C_1 and require less reorganization of the methylene chain than a counterclockwise motion (C_1 minor orbital to C_2 top orbital) which leads to the formation of the thermally labile *trans,cis,cis*-triene. Furthermore, the movement of the C_1 lobe in a counterclockwise fashion forces it to become orthogonal to the C_2,C_3 π system at some point along the reaction coordinate. On the other hand, a clockwise motion of the C_1 lobe permits continuous overlap with the upper half of the C_2 p lobe throughout the reorganization process.

Second, the origin of this bias may be due to subtle secondary orbital interactions in the nonconjugated diene which results in an orbital distortion[18-20] of the π system as shown in Scheme IX.

(13) Vogel, E.; Crimme, W.; Dinne, E. *Tetrahedron Lett.* **1965**, 391.

(14) Dauben, W. G.; William, R. G.; McKelvey, R. A. *J. Am. Chem. Soc.* **1973**, *95*, 3932.

(15) Dauben, W. G.; Kellogg, M. S.; Seeman, J. I.; Vietmeyer, N. D.; Wendschuh, P. H. *Pure Appl. Chem.* **1973**, *33*, 192.

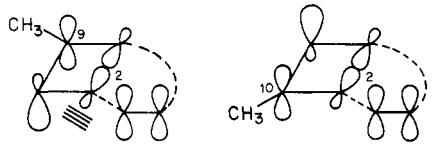
(16) Marvell, E. N.; Caple, G.; Schulte, B.; Pippin, W. *Tetrahedron* **1973**, *29*, 3789.

(17) Baldwin, J. E.; Krueger, S. M. *J. Am. Chem. Soc.* **1969**, *91*, 6444.

(18) Anh, N. T.; Eisenstein, J. M.; Lefour, M. E.; Trans, H. D. *J. Am. Chem. Soc.* **1973**, *95*, 6146.

The orbital topology thus obtained causes the σ framework to open in a fashion such that preferential overlap of the large centers of electron density occurs, resulting in the formation of a *cis,trans,cis* configuration of the double bonds.

It is instructive to recall that in the isomerization of the substituted monoolefin **10a** or **10b**, the methyl group had little influence as to which of the two allowed conrotatory modes of opening was followed, it being found that virtually an equal mixture of the *cis,trans*- and the *trans,cis*-2-methyl dienes were obtained. However, in the isomerization of the methyl-substituted dienes **18** and **19**, the position of the methyl group had a pronounced effect on the selectivity of the two allowed pathways, an effect reflected in the ratio of triene to cyclohexadiene product. Using the orbital distortion model presented above, coupled with the electronic influence of an electron-donating methyl group, it can be seen that in **19**, the C_9 methyl group enhances the electron



19 18

density of the distorted lower C_{10} lobe, resulting in increased interaction with the endocyclic C_2–C_3 double bond. This interaction, in turn, further favors the conrotatory mode, resulting in the formation of the *cis,trans,cis*-triene **31**, as is observed. Alternately, the C_{10} methyl group of **18** serves to decrease the C_{10}–C_2 interaction, thereby correcting the orbital distortion and permitting the two allowed modes for conrotatory ring opening to proceed with similar probability. The finding of about equal amounts of the products **28** and **29** is consistent with the postulate.

Experimental Section

General Methods. Infrared and ^{1}H NMR spectra were run in carbon tetrachloride as solvent unless otherwise noted. ^{13}C NMR spectra were run in deuteriochloroform unless otherwise noted, and the chemical shifts are reported in parts per million relative to tetramethylsilane as an internal standard, the multiplicity being given for off-resonance proton decoupling. Combustion analyses and mass spectral analyses were by the Analytical Laboratory, College of Chemistry, University of California at Berkeley.

The solvents used for reactions were dried and distilled prior to use when deemed necessary: diethyl ether and tetrahydrofuran from sodium benzophenone ketyl radical, dimethyl sulfoxide from calcium hydride, *N,N*-dimethylformamide and pyridine from barium oxide, diglyme from sodium hydride, dichloromethane and hexane from phosphorus pentoxide, pentane from potassium hydroxide.

Silver nitrate impregnated silica gel for column chromatography was prepared by mixing a solution of 125 g of silver nitrate in 750 mL of water with 450 g of silica gel (E. Merck), and the resulting mixture was shaken for 12 h. The water was removed from the mixture at reduced pressure and the impregnated silica gel dried at 130 °C in the dark. The corresponding TLC plates were prepared by spreading a slurry of 16 g of silica gel (with binder) in an aqueous solution of 5 g of silver nitrate upon microscope slides, followed by drying the slides in the dark at 110 °C.

The following columns were employed for vapor-phase chromatography: (A) 10 ft × $^1/_8$ in., 10% Carbowax 6000, 10% KOH on 60/80 Chromosorb W; (B) 10 ft × $^1/_8$ in., 5% Carbowax 20M, 5% KOH on 60/80 Chromosorb G; (C) 10 ft × $^1/_8$ in., 4% SF-96 on 70/80 Chromosorb G; (D) 6 ft × $^1/_8$ in., 10% SE-30 on 80/100 Chromosorb G; (E) 10 ft × $^1/_4$ in., 10% Carbowax 20M on 60/80 Chromosorb G; (F) 10 ft × $^1/_4$ in., 10% Carbowax 6000 on 60/80 Chromosorb W; (G) 10 ft × $^1/_4$ in., 5% Carbowax 6000, 5% Carbowax 1000 on 60/80 Chromosorb W; (H) 10 ft × $^1/_4$ in., 5% SE-30 on 60/80 Chromosorb G.

General Procedure for Preparation of Cyclopropanecarboxylic Esters. The general procedure of Kirmse was employed.[7] To a vigorously stirred slurry of anhydrous $CuSO_4$ (10 mol %) in the neat olefin or diene maintained at 100 °C was added, dropwise, ethyl diazoacetate (50–75 mol %) over a 2–3-h period. The mixture was heated at this temperature for an additional 30 min, cooled to room temperature, and filtered through Celite. The Celite layer was washed with ether, the combined organic material dried ($MgSO_4$), and the solvent removed by using a rotary evaporator. The residul dark red oil was distilled under reduced pressure to yield the desired cyclopropyl carboxylic ester.

***cis*-Bicyclo[6.2.0]deca-2,9-diene (2).**[5] To a stirred suspension of 3.05 g (64 mmol) of sodium hydride in 500 mL of anhydrous diglyme at room temperature was added, in one portion, 18.4 g (57.7 mmol) of tosylhydrazone **15a**, under N_2. The reaction mixture was heated at 130 °C until N_2 evolution ceased, cooled to 0 °C, and processed in the standard manner to yield 5.90 g of a clear, colorless oil, bp 70–85 °C (16 torr). The distillate upon VPC analysis (column A, 70–150 °C at 4 °C/min) was found to consist of 1,3-cyclooctadiene (31%), diene **2** (57%), *trans*-bicyclo[4.4.0]deca-2,4-diene (4%), and *cis,trans,cis*-cyclodeca-1,3,5-triene (**25**, 8%). A pure sample of diene **2** was obtained by preparative VPC (column F, 100 °C). The following spectral properties are given since no properties are listed in the literature: IR (neat) 3090, 3035, 1695, 1646, 1569, 799, 759, 716, 686 cm^{-1}; ^{1}H NMR δ 1.63 (m, 6), 1.93 (m, 2), 3.02 (m, 1), 3.71 (m, 1), 5.39 (dd, J = 11.5, 2.5 Hz, 1), 5.73 (m, 1), 6.00 (d, J = 2.5 Hz, 1), 6.08 (d, J = 2.5 Hz, 1); ^{13}C NMR δ 26.80 (t), 27.98 (t), 29.98 (t), 32.46 (d), 45.80 (d), 53.02 (d), 126.97 (d), 131.97 (d), 137.73 (d), 140.24 (d).

***cis*-Bicyclo[6.1.0]nonane-9-carboxylic Acid (7a).** The general procedure for the synthesis of cyclopropanecarboxylic esters was followed, and from 110 g (1.0 mol) of cyclooctene there was obtained 58.8 g (60%) of ester **6a** as a colorless oil: bp 78–82 °C (0.4 torr) [lit.[21] bp 100–105 °C (3 torr)]; IR 1724, 1130, 1019, 788 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.9–1.8 (m, 13), 1.23 (t, J = 7.0 Hz, 3), 2.09 (d, J = 9.5 Hz, 2), 4.24 (q, J = 7.0 Hz, 2); mass spectrum (70 eV), m/e 196 (parent).

A mixture of 19.6 g (0.1 mol) of ester **6a** and 8.13 g (0.34 mol) of sodium hydroxide in 200 mL of water was heated at 80 °C for 10 h with stirring, and the resulting solution was cooled to room temperature, extracted with ether, and acidified to pH 2 with 10% H_2SO_4, and the acid liberated was extracted with ether. The ethereal solution of the acid was processed in the standard fashion to yield 16.1 g (96%) of acid **7a** as a crystalline solid: mp 112–115 °C (lit.[22] mp 113–115 °C); IR (KBr) 3400–2200, 1682, 937 cm^{-1}; ^{1}H NMR δ 0.7–1.9 (m, 13), 2.18 (d, J = 9.5 Hz, 2), 10.75 (s, 1); mass spectrum (70 eV), m/e 168, 122, 121, 108, 41.

***cis*-Bicyclo[7.1.0]decane-10-carboxylic Acid (7b).** A solution of 4.2 g (0.02 mmol) of ethyl *cis*-bicyclo[7.1.0]dec-2-ene-2-carboxylate (**12b**) in 100 mL of 95% ethanol was hydrogenated at atmospheric pressure and room temperature over 80 mg of 5% Pd/C for 12 h. The mixture was filtered through Celite, the filtrate diluted with 300 mL of water, and the organic material extracted with ether. The solvent was removed under reduced pressure and the residue distilled using a Büchi-Kugelrohr apparatus to yield 3.95 g (92%) of **6a**: bp 70–80 °C (0.1 torr); IR 1730, 1165 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.90 (m, 1), 1.24 (t, J = 7.0 Hz, 3), 2.02 (d, J = 11 Hz, 2), 4.03 (q, J = 7.0 Hz, 2); mass spectrum (70 eV), m/e 210, 165, 122, 41. Anal. ($C_{13}H_{22}O_2$) C, H.

The ester was saponified as described for the preparation of **7a**, and the product recrystallized from petroleum ether to give 3.30 g (96%) of **7b** as a white crystalline solid: mp 137–138 °C; ^{1}H NMR δ 1.02 (m, 1), 1.50 (m, 14), 2.06 (d, J = 12 Hz, 2), 11.1 (s, 1); mass spectrum (70 eV), m/e 182, 164, 122, 107, 41. Anal. ($C_{11}H_{18}O_2$) C, H.

9-Acetyl-*cis*-bicyclo[6.1.0]nonane (8a). Under a nitrogen atmosphere was added 33.0 mL of a 1.84 M ethereal solution of methyllithium (2 mol as equiv), dropwise, to a stirred solution of 5.04 g (30 mmol) of **7a** in 200 mL of anhydrous ether at 0 °C over a 1.5-h period. The mixture was heated at reflux for 2.5 h, cooled to room temperature, and under an inert atmosphere added slowly to water with vigorous stirring. The organic materials were extracted with ether, the solution was dried ($MgSO_4$), and the solvent was removed by rotary evaporation. The residue was distilled by using a Büchi-Kugelrohr appparatus to yield 4.9 g (97%) of **8a** as a colorless oil: bp 70–80 °C (0.1 torr); IR (CCl_4) 2910, 1690, 1173, 960 cm^{-1}; ^{1}H NMR δ 1.0–1.8 (m, 13), 2.04 (m, 2), 2.17 (s, 2, *exo*-methyl ketone), 2.18 (s, 1, *endo*-methyl ketone); mass spectrum (70 eV), m/e 166, 151, 123, 108, 43. Anal. ($C_{11}H_{18}O$) C, H.

10-Acetyl-*cis*-bicyclo[7.1.0]decane (8b). By use of the method used to prepare **8a**, 2.73 g (15 mmol) of **7b** was converted into 2.25 g (85%) of **8b**: bp 82–85 °C (0.1 torr); IR 1681, 1420, 1350, 1168 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.1–2.0 (m, 17), 2.15 (s, $W_{1/2}$ = 1.5 Hz, 3); mass spectrum (70 eV), m/e 180, 165, 122, 43. Anal. ($C_{12}H_{20}O$) C, H.

9-Acetyl-*cis*-bicyclo[6.1.0]nonane Tosylhydrazone (9a). To a stirred slurry of 6.14 g (33.0 mmol) of *p*-toluenesulfonylhydrazine in 20 mL of 95% ethanol at 0 °C was added, dropwise, 4.98 g (30.0 mmol) of methyl

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ketone **8a** over a 15-min period. The resulting mixture was allowed to stir at 0 °C for 30 min and at room temperature for 1.0–2.0 h and was stored at 0 °C overnight. The precipitate was filtered, washed with cold ethanol, and air-dried to yield 8.95 g (90%) of a white crystalline solid: mp 158–159 °C dec; IR (KBr) 3180, 2890, 1623, 1592, 1495 cm^{-1}; ^1H NMR δ 0.7–2.1 (m, 13), 1.75 (s, $W_{1/2}$ = 1.5 Hz, 3), 2.00 (m, 2), 2.50 (s, $W_{1/2}$ = 3 Hz, 3), 7.24 (m, 1), 7.34 (d, J = 9 Hz, 2), 7.90 (d, J = 9 Hz, 2); mass spectrum (70 eV), m/e 334, 179. Anal. ($C_{18}H_{26}O_2N_2S$), C, H, N, S.

10-Acetyl-*cis*-bicyclo[7.1.0]decane Tosylhydrazone (9b). By use of the procedure used to prepare **9a**, 2.10 g (11.7 mmol) of methyl ketone **8b** was converted into 3.69 g (91%) of white, amorphous **9b**: mp 145–148 °C dec; ^1H NMR δ 0.9–2.3 (m, 16), 1.69 (s, exo, 1.8), 1.71 (s, endo, 1.2), 2.46 (s, $W_{1/2}$ = 2.0 Hz, 3), 7.33 (m, 3), 7.89 (d, J = 8 Hz, 2). Anal. ($C_{19}H_{28}O_2N_2S$) C, H, N, S.

9-Methyl-*cis*-bicyclo[6.2.0]dec-9-ene (10a). To a stirred slurry of 0.27 g (11.0 mmol) of sodium hydride in 150 mL of anhydrous diglyme was added 3.34 g (10.0 mmol) of **9a** in one portion under nitrogen. The mixture was heated at 130 °C until gas evolution ceased, cooled to 0 °C, and poured into ice-cold water and pentane (2:1 v/v). The separated aqueous layer was extracted with pentane, and the combined organic extracts were washed with water and dried ($MgSO_4$). The solvent was carefully removed at room temperature at water-aspirator pressure to yield 1.35 g (90%) of a clear colorless oil, bp 93 °C (16 torr). VPC analysis (column A) showed the presence of two compounds in a 3:97 ratio, in order of increasing retention time. The major component was isolated by preparative VPC (column H, 110 °C) and identified as **10a**: IR 3010, 1642, 1460, 1434, 812 cm^{-1}; ^1H NMR (CCl_4) δ 1.45 (m, 12), 1.58 (d, J = 1.5 Hz, 3), 2.50 (m, 2), 5.54 (q, J = 1.5 Hz, 1); ^{13}C NMR δ 13.74 (q), 25.49 (t), 25.87 (t), 26.34 (t), 27.56 (t), 30.47 (t), 30.61 (t), 44.95 (d), 48.83 (d), 130.58 (d), 148.06 (s); mass spectrum (70 eV), m/e 150, 135, 79; exact mass m/e 150.1380. Anal. ($C_{11}H_{18}$) C, H.

10-Methyl-*cis*-bicyclo[7.2.0]undec-10-ene (10b). By use of the procedure used to prepare **10a**, 1.74 g (5.0 mmol) of **9b** yielded 658 mg (81%) of a clear, colorless oil, bp (Büchi-Kugelrohr) 115–125 °C (16 torr). Analytical VPC (column A) revealed this oil to be a mixture of *cis*-cyclononene (3%) and **10b** (97%). Purification by preparative VPC (column H, 110 °C) led to extensive rearrangement. Spectral analysis was performed on the mixture: IR 1637, 1459, 1426, 807 cm^{-1}; ^1H NMR V 1.56 (m, 17), 2.64 (m, 2), 5.56 (q, J = 1.5 Hz, 1); ^{13}C NMR δ 13.64 (q), 24.66 (t), 24.81 (t), 25.49 (t), 26.94 (t), 27.23 (t), 27.33 (t), 27.86 (t), 46.99 (d), 50.58 (d), 130.84 (d), 147.87 (s); mass spectrum (70 eV), m/e 164, 149, 135, 121, 107, 93, 79; exact mass m/e 164.1570.

Ethyl *cis*-Bicyclo[6.1.0]non-2-ene-9-carboxylate (12a). The general procedure for the preparation of cyclopropanecarboxylic esters was followed, and from 151.5 g (1.40 mol) of *cis,cis*-cycloocta-1,3-diene there was obtained 68.9 g (51%) of **12a** as a clear, colorless oil: bp 75–77 °C (0.5 torr) [lit.[22] bp 89–95 °C (1 torr)]; IR 2857, 1736, 1149, 714 cm^{-1}; ^1H NMR (CCl_4) δ 0.9–2.7 (m, 11), 1.26 (t, J = 7 Hz, 3), 4.07 (1, J = 7.5 Hz, 2), 5.42 (m, 1), 5.80 (m, 1); mass spectrum (70 eV), m/e 194.

Ethyl *cis*-Bicyclo[7.1.0]dec-2-ene-10-carboxylate (12b). By use of the procedure used to prepare **12a**, 25.0 g (0.2 mol) of *cis,cis*-cyclonona-1,3-diene[23] yielded 12.7 g (36%) of **12b** as a clear, colorless oil: bp 82–85 °C (0.2 torr); IR 1724, 1156, 746 cm^{-1}; ^1H NMR (CCl_4) δ 0.4–2.9 (m, 13), 1.27 (t, J = 7.0 Hz, 3), 4.08 (q, J = 7.0 Hz, 2), 5.39 (dd, J = 9.5, 2.0 Hz, 1), 5.69 (brd, J = 9.5 Hz, 1); mass spectrum (70 eV), m/e 208, 163, 135, 79. Anal. ($C_{13}H_{20}O_2$) C, H.

9-(Hydroxymethyl)-*cis*-bicyclo[6.1.0]non-2-ene (13a). To a stirred slurry of 3.9 g (0.1 mol) of $LiAlH_4$ in 200 mL of anhydrous ether, under a nitrogen atmosphere, was added a solution of 19.4 g (0.1 mol) of **12a** in 20 mL of anhydrous ether over a 30-min period. The mixture was heated at reflux for 2 h, cooled to 0 °C, and treated, sequentially, with 3.9 mL of water, 3.9 mL of 3 N aqueous sodium hydroxide, and 12.0 mL of water. The solid aluminum salts were removed by suction filtration and were washed with ether. The filtrate was washed with water and with saturated sodium chloride solution and dried ($MgSO_4$). The sovlent was removed by using a rotary evaporator to afford 15.1 g (99%) of **13a** as a viscous, clear colorless oil: IR 3225, 2840, 1642, 1025, 704 cm^{-1}; ^1H NMR δ 0.25–2.5 (m, 11), 3.40 (d, J = 7.0 Hz, *exo*-hydroxymethyl), 3.43 (d, J = 7.0 Hz, *endo*-hydroxymethyl), 5.26 (d, J = 11.0 Hz, 1), 5.63 (m, 1); mass spectrum (70 eV), m/e 152. Anal. ($C_{10}H_{16}O$) C, H.

10-(Hydroxymethyl)-*cis*-bicyclo[7.1.0]dec-2-ene (13b). By use of the procedure used to prepare **13a**, 30.5 g (0.15 mol) of **12b** yielded 22.4 g (92%) of **13b** as a clear, colorless oil: IR 3365, 1660, 1050, 1035, 750 cm^{-1}; ^1H NMR (CCl_4–D_2O) δ 0.3–3.0 (m, 13), 3.44 (d, J = 6.5 Hz, *exo*-hydroxymethyl), 3.58 (d, J = 6.5 Hz, *endo*-hydroxymethyl), 5.50 (m, 2); mass spectrum (70 eV), m/e 166, 148, 135, 119, 41.

A small portion of **13b** was distilled via a Büchi-Kugelrohr apparatus for analysis; bp 85–90 °C (0.2 torr). Anal. ($C_{11}H_{18}O$) C, H.

***cis*-Bicyclo[6.1.0]non-2-ene-9-carboxaldehyde (14a).** To a stirred suspension of 38.7 g (0.18 mol) of pyridinium chlorochromate[24] in 225 mL of dichloromethane was added 15.2 g (0.1 mol) of **13a** in 50 mL of methylene chloride in one portion. The mixture was stirred at room temperature and processed in the standard fashion[24] to yield 12.0 g (81%) of **14a**: bp 76–77 °C (0.5 torr); IR 2932, 2857, 2717, 1706, 704 cm^{-1}; ^1H NMR (CCl_4) δ 0.7–2.8 (m, 11), 5.44 (d, J = 11.0 Hz, 1), 5.65 (m, 1), 9.26 (d, J = 3.5 Hz, 1); mass spectrum (70 eV), m/e 150.

***cis*-Bicyclo[7.1.0]dec-2-ene-10-carboxaldehyde (14b).** By use of the procedure used to prepare **14a**, 16.6 g (0.1 mol) of **13b** yielded 13.4 g (82%) of **14b**: bp (bulb-to-bulb) 80–90 °C (0.2 torr); IR 2775, 1715, 1035, 812, 715 cm^{-1}; ^1H NMR (CCl_4) δ 0.5–3.0 (m, 13), 5.50 (m, 2), 8.86 (d, J = 5.0 Hz, *exo*-aldehyde, 0.78), 9.38 (d, J = 5.0 Hz, *endo*-aldehyde, 0.22).

***cis*-Bicyclo[6.1.0]non-2-ene-9-carboxaldehyde Tosylhydrazone (15a).** By use of the procedure used to prepare **9a**, 11.5 g (76.6 mmol) of aldehyde **14a** was converted into 21.0 g (86%) of crude product which was recrystallized from 95% ethanol to yield 16.6 g (67%) of a white crystalline solid, mp 132–134 °C (lit.[22] mp 137–139 °C).

***cis*-Bicyclo[7.1.0]dec-2-ene-10-carboxaldehyde Tosylhydrazone (15b).** To a slurry of 8.24 g (44 mmol) of *p*-toluenesulfonylhydrazide in 30 mL of anhydrous methanol at 0 °C was added 6.95 g (0.039 mol) of aldehyde **14b**, dropwise, over a 10-min period. The resulting mixture was allowed to stir at 0 °C for 30 min and at room temperature for 2 h and was stored overnight at 0 °C. The solid was collected by suction filtration to give 10.2 g (80.0%) of **15b** as an off-white solid: mp 128–131 °C; IR (KBr) 1700, 1605, 1440, 1345, 810 cm^{-1}; ^1H NMR δ 0.6–2.8 (m, 13), 2.45 (s, $W_{1/2}$ = 2.0 Hz, 3), 5.46 (m, 2), 6.20 (d, J = 9.0 Hz, 0.22), 6.92 (d, J = 9.0 Hz, 0.78), 7.31 (m, 2), 7.80 (m, 2), 8.35 (m, 1). Anal. ($C_{18}H_{24}O_2N_2S$) C, H, N, S.

***cis*-Bicyclo[7.2.0]undeca-2,10-diene (16).** To a stirred suspension of 0.3 g (12.4 mmol) of sodium hydride in 200 mL of anhydrous diglyme at room temperature was added, in one portion, 3.75 g (11.3 mmol) of tosylhydrazone **15b**. The system was sealed with a U-tube partially filled with paraffin oil to monitor gas evolution. The mixture was stirred for 1.5 h at room temperature, at which point gas evolution had ceased. The homogeneous solution was transferred, under nitrogen, to a 250-mL irradiation reaction vessel which was fitted with a Hanovia quartz immersion well; the solution was irradiated with a 450-W Hanovia mercury light source through a Pyrex filter for 3 h at room temperature.[25] The mixture was diluted with 200 mL of water and the separated aqueous layer extracted with three 50-mL portions of pentane. The combined organic extract was washed with six 75-mL portions of water and dried ($MgSO_4$), and the solvent was removed by using a rotary evaporator to yield 1.4 g (86%) of a yellow oil. This oil was chromatographed on 150 g of 20% silver nitrate impregnated silica gel with a mixture of benzene/hexane with an increasing portion of ethyl acetate as the eluting solvent. Fractions (15 mL) 17–41 were combined, and the solvent was removed by using a rotary evaporator to yield 350 mg (21%) of **16** as a clear, colorless oil: IR 1865, 1655, 1575, 740, 720 cm^{-1}; ^1H NMR δ 0.77–2.75 (m, 10), 3.06 (dd, J = 11.5, 4.0 Hz, 1), 3.93 (m, 1), 5.44 (dd, J = 7.5, 2.0 Hz, 1), 5.63 (d, J = 7.5 Hz, 1), 5.96 (d, J = 3.0 Hz, 1), 6.08 (d, J = 3.0 Hz, 1); ^{13}C NMR δ 26.37 (t), 26.95 (t), 27.95 (t), 31.66 (t), 45.35 (d), 53.75 (d), 129.92 (d), 131.66 (d), 138.03 (d), 140.70 (d); exact mass 148.1254.

When the sodium salt of the tosylhydrazone was heated at 130 °C for 30 min, in the usual fashion, a mixture of three products was obtained: **11b** (25%), **26** (33%), and **27** (42%).

9-Acetyl-*cis*-bicyclo[6.1.0]non-2-ene (17). By use of the general procedure used to prepare **7a**, 26.0 g (0.134 mol) of ester **12a** yielded 20.0 g (89%) of a white waxy solid: mp 57–70 °C (lit.[22] mp 58–73 °C); IR (KBr) 3389–2277, 1675, 710 cm^{-1}; ^1H NMR δ 1.15 (m, 2), 1.3–2.7 (m, 9), 5.44 (d, J = 11.5 Hz, 1), 5.82 (m, 1), 4.83 (s, 1); mass spectrum (70 eV), m/e 166, 123, 121, 79, 43.

By use of the procedure used to prepare **8a**, 11.0 g (66.4 mmol) of the above acid gave 10.3 g (95%) of ketone **17** as a clear, colorless oil: bp 79 °C (0.4 torr); IR 2958, 2881, 1689, 1360, 714 cm^{-1}; ^1H NMR (CCl_4) 1.0–2.4 (m, 11), 2.19 (s, $W_{1/2}$ = 1.5 Hz, 3), 5.33 (d, J = 11.5 Hz, 1), 5.62 (m, 1); mass spectrum (70 eV) m/e 164, 149, 120, 43. Anal. ($C_{11}H_{16}O$) C, H.

The tosylhydrazone was prepared by following the procedure used to prepare **9a** and was a white solid: yield 28 g (97%); mp 159–160 °C dec; IR (KBr) 3105, 2857, 1618, 1438, 1383, 1154, 704 cm^{-1}; NMR 0.7–2.6 (m, 11), 1.73 (s, $W_{1/2}$ = 3.5 Hz, 3), 2.44 (s, $W_{1/2}$ = 2.5 Hz, 3), 5.32 (d, J = 11.5 Hz, 1), 5.71 (m, 1), 7.33 (d, J = 8 Hz, 2), 7.91 (d, J = 8 Hz,

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2). Anal. ($C_{18}H_{24}N_2O_2S$) C, H, N, S.

10-Methyl-*cis*-bicyclo[6.2.0]deca-2,9-diene (18) and **9-Methyl-*cis*-[6.2.0]deca-2,9-diene (19).** By use of the procedure used to prepare **10a**, 16.6 g of tosylhydrazone **17** yielded 6.35 g (86%) of a clear, colorless oil, bp 72 °C (4 torr). VPC analysis showed the product to be a 40:60 mixture of the two components, and a 1-g portion of this mixture was chromatographed on 200 g of 20% silver nitrate impregnated silica gel with 2% ethyl acetate, 49% hexane, and 49% benzene solutions as the eluting solvent. The initial column volume was discarded, and then 10-mL fractions were collected. Fractions 14–20 contained 302 mg of **18** as a clear oil: IR 1653 cm^{-1}; ^1H NMR δ 1.2–1.8 (m, 6), 1.68 (m, 1), 1.95 (m, 2), 2.76 (m, 1), 3.47 (m, 1), 5.25 (dd, J = 12.0, 2.5 Hz, 1), 5.45 (m, 1), 5.60 (m, 1); ^{13}C NMR δ 14.03 (q), 26.09 (t), 28.13 (t), 29.42 (t), 32.23 (t), 46.68 (d), 49.36 (d), 128.39 (d), 131.55 (d), 132.19 (d), 146.41 (s).

Fractions 23–26 contained 250 mg of about equal amounts of **18** and **19**. Fractions 27–29 contained 346 mg of **19** as an oil: IR 1653 cm^{-1}; ^1H NMR δ 1.2–1.8 (m, 6), 1.60 (m, 3), 1.93 (m, 2), 2.76 (m, 1), 3.49 (m, 1), 5.30 (dd, J = 12.0, 2.0 Hz, 1), 5.55 (m, 1), 5.67 (m, 1); ^{13}C NMR δ 13.98 (q), 25.97 (t), 26.26 (t), 29.27 (t), 32.23 (t), 42.52 (d), 53.69 (d), 127.53 (d), 128.94 (d), 131.66 (d), 148.89 (s).

Thermal Isomerization of 10a. A solution of 1.30 g (8.67 mmol) of **10a** (95% pure) in 4 mL of anhydrous benzene was placed in a thick-walled Pyrex tube sealed at one end. Under nitrogen, the tube was cooled to −78 °C, sealed, and allowed to warm to room temperature. The tube was totally immersed in a deep well oil bath at 190 °C for 1.3 h, cooled to −70 °C, and opened. The benzene solution was carefully concentrated at reduced pressure to yield 1.25 g (96%) of a clear colorless oil which by VPC analysis (column H, 110 °C) contained ≤5% of **10b**. A small portion (0.45 g) was chromatographed on 65 g of 20% $AgNO_3$-impregnated silica gel with a 1:1 mixture of benzene and hexane as the eluting solvent; fractions (4 mL) were collected every 16 min. Fraction 6 contained 6 mg of **10a**. Fractions 14–28 were combined to yield 110 mg of **20**: IR 1689, 1653, 908, 889, 733, 705 cm^{-1}; UV max (hexane) 225 nm (ϵ 4500); NMR δ 1.43 (m, 6), 1.73 (s, $W_{1/2}$ = 3.5 Hz, 3), 2.08 (m, 4), 5.58 (m, 1), 5.62 (td, J = 10.0, 6.0 Hz, 1), 6.11 (brd, J = 10.0 Hz, 1); ^{13}C NMR δ 16.81 (q), 23.26 (t), 25.24 (t), 25.73 (t), 26.84 (t), 28.11 (t), 29.12 (t), 129.29 (d), 131.28 (d), 132.63 (s), 135.51 (d); mass spectrum (70 eV), m/e 150. Fractions 44–60 contained 107 mg of **21**: IR 1617, 974, 808, 725 cm^{-1}; UV max (hexane) 227 nm (ϵ 5020); ^1H NMR δ 1.31 (m, 6), 1.95 (s, $W_{1/2}$ = 3.0 Hz, 3), 2.07 (m, 4), 5.25 (brt, J = 7.5 Hz, 1), 5.37 (td, J = 17.0, 7.5 Hz, 1), 6.25 (brd, J = 17.0 Hz, 1); ^{13}C NMR δ 22.19 (q), 23.25 (t), 24.03 (t), 26.79 (t), 29.37 (t), 34.51 (t), 124.33 (d), 131.65 (d), 132.58 (d), 137.63 (s); mass spectrum (70 eV), m/e 150.

Thermal Isomerization of 10b. Under conditions similar to those described for **10a** a solution of 540 mg (3.3 mmol) of **10b** in 2 mL of anhydrous benzene was heated at 155 °C for 1.3 h. The solvent was removed at reduced pressure and the residue chromatographed by using 20% $AgNO_3$-impregnated silica gel with a 1:1 mixture of benzene and hexane as the eluting solvent to separate the mixture. In the order of elution, 70 mg of **10b** was recovered followed by 124 mg of **22** [IR 2985, 2903, 1684, 1627, 1370, 725 cm^{-1}; UV max (methylcyclohexane) 229 nm (ϵ 4100); ^1H NMR δ 1.42 (m, 10), 1.74 (s, $W_{1/2}$ = 3.5 Hz, 3), 2.08 (m, 4), 5.48 (qt, J = 7.5, 1.5 Hz, 1), 5.56 (dt, J = 11.5, 7.0 Hz, 1), 5.93 (d, J = 11.5 Hz, 1); ^{13}C NMR δ 17.47 (q), 24.23 (t), 25.78 (t, 2 C), 26.08 (t), 26.21 (t), 27.14 (t), 27.72 (t), 128.56 (d), 130.31 (d), 133.07 (s), 134.52 (d); mass spectrum (70 eV), m/e 164, 149, 135, 121, 107, 93, 79; Exact mass m/e 164.1568], and finally 152 mg of **23**: IR 2903, 2837, 1679, 1622, 1446, 1371, 976, 853, 713 cm^{-1}; UV max (methylcyclohexane) 235 nm (ϵ 7400); ^1H NMR δ 1.48 (m, 8), 1.83 (s, $W_{1/2}$ = 3.5 Hz, 3), 2.10 (m, 4), 5.39 (t, J = 7 Hz, 1), 5.53 (td, J = 16.5, 7.0 Hz, 1), 6.28 (d, J = 16.5 Hz, 1); ^{13}C NMR δ 22.19 (q), 24.03 (t), 24.32 (t), 25.20 (t), 25.34 (t), 26.74 (t), 28.35 (t), 31.94 (t), 126.85 (d), 130.74 (d), 132.30 (d), 135.54 (s); mass spectrum (70 eV) m/e 164, 149, 135, 121, 108, 107, 93, 79; Exact Mass m/e 164.1565.

Thermal Isomerization of 2. For preparative purposes, the mixture of hydrocarbons obtained from the decomposition of **15a** was used directly without separation of isomers. In a typical experiment, 2.40 g of this mixture (~70% **2**, **24**, and **25**; ~30% **11a**) was dissolved in 4 mL of spectrograde benzene and, as described above, heated at 140–150 °C for 2 h. The solvent was removed at reduced pressure, and the residue was purified by preparative VPC (column F, 130 °C) to yield 296 mg (12% from **15a**) of **24**[10,12] and 550 mg (19% from **15a**) of **25**: IR 990, 974, 951, cm^{-1}; UV max (hexane) 278 nm (ϵ 6025); ^1H NMR δ 1.58 (m, 4), 2.28 (m, 4), 5.78 (td, J = 10.0, 7.0 Hz, 2), 6.11 (s, $W_{1/2}$ = 3.5 Hz, 2), 6.25 (d, J = 10.0 Hz, 2); ^{13}C NMR δ 24.76 (t), 24.92 (t), 129.86 (d), 131.05 (d), 133.15 (d); mass spectrum (70 eV), m/e 134, 117, 91.

In an analytical experiment, 5 mg of **2** (≥95% pure) was diluted with 15 μL of benzene-d_6 containing Me_4Si and sealed in a Pyrex tube at −78 °C under nitrogen. ^1H NMR analysis revealed an initial ratio of vinyl to nonvinyl hydrogen of 0.4. The tube was immersed in an oil bath equilibrated at 140 °C, removed after 30 min, and examined by ^1H NMR spectroscopy. The tube was returned to the oil bath for an additional 30 min, removed, and examined again by ^1H NMR. The results, listed below, showed a steady increase in the ratio of vinyl to nonvinyl

time, min	0	30	60
ratio (vinyl/nonvinyl)	0.40	0.52	0.60

hydrogen with a concomitant loss of the characteristic diallylic hydrogen (δ 3.71 ppm) of **2**. VPC analysis of the mixture after 60 min (column B) showed the formation of **24** and **25** in a relative ratio of 1:1.7, respectively, with ≤2% of **2**. The tube was resealed at −70 °C and placed in an oil bath at 170 °C for 2.0 h. VPC analysis (column B) showed no changed from the starting composition. In a similar fashion, 5 mg of **2** (≥95% pure) was placed in a thick-walled Pyrex tube (~10 mL capacity) and, under nitrogen, cooled to −78 °C. After several freeze–thaw cycles, the tube was evacuated to 0.05 mm, sealed, and allowed to warm to room temperature. The tube was immersed in an oil bath maintained at 140 °C for 1.5 h. VPC analysis (column B) of the contents revealed a product distribution ratio similar to that described in the analytical experiment described above (ratio **24**/**25** of 1:1.8).

Thermal Isomerization of 16. For preparative purposes, the product mixture obtained from the decomposition of **15b** was heated to 140 °C for 1.0 h. The products were isolated by preparative VPC (column F, 125 °C) to yield **11b** (25%), **26** (33%),[10,12] and **27** (42%): IR 1660, 1600, 990, 962, 824, 705 cm^{-1}; UV max (hexane) 274 nm (ϵ 6500); ^1H NMR δ 1.61 (m, 6), 2.18 (m, 4), 5.09–6.16 (m, 4), 6.28 (s, $W_{1/2}$ = 4.0 Hz, 2); ^{13}C NMR δ 23.93 (t), 25.10 (t), 25.49 (t), 128.16 (d), 128.88 (d), 134.52 (d); mass spectrum (70 eV), m/e 148, 98.

In an analytical experiment, a 1.0-μL sample of **16** (neat, ≥95% pure by spectral analysis) was injected into a preparative VPC instrument (column H) which was set at the following conditions: column temperature, 165 °C; injector temperature, 185 °C; detector temperature, 210 °C. The resulting chromatograms showed **26** and **27** were formed in an ~38:62 ratio, usp.

Thermal Isomerization of 18. A nitrogen-purged solution of 290 mg of **18** in 5 mL of anhydrous diglyme was heated, with stirring, at 160 °C for 2.0 h, cooled to room temperature, and diluted with 50 mL of water and 30 mL of pentane. The separated aqueous layer was extracted with two, 20-mL portions of pentane, and the united organic phase was washed with four 20-mL portions of water, dried ($MgSO_4$), and examined by VPC (column A). The results indicated the formation of two isomeric compounds in a relative ratio of 1:1.1 in order of increasing retention time. The mixture was separated by preparative VPC (column F, 110 °C). The material of shorter retention time was identified as **28**: IR 1642, 802, 779, 727 cm^{-1}; UV max (hexane) 264 nm (ϵ 3500); NMR δ 1.03–2.07 (m, 10), 1.74 (brs, $W_{1/2}$ = 5.0 Hz, 3), 5.30 (brs, $W_{1/2}$ = 4.0 Hz, 1), 5.58 (d, J = 10.0 Hz, 1), 5.80 (brd, $J \simeq$ 10 Hz, 1); ^{13}C NMR δ 20.88 (q), 26.66 (t), 26.79 (t), 32.19 (t), 32.57 (t), 40.93 (d), 41.07 (d), 127.83 (d), 128.02 (d), 131.66 (s), 133.36 (d); mass spectrum (70 eV), m/e 148. The material of longer retention time was identified as **29**: IR 1682, 1642, 1601, 807, 721 cm^{-1}; UV max (hexane) 273 nm (ϵ 9500); ^1H NMR δ 1.46 (m, 4), 1.66 (s, $W_{1/2}$ = 3.5 Hz, 3), 2.24 (m, 4), 5.45–6.65 (m, 5); ^{13}C NMR δ 16.94 (q), 22.23 (t), 23.55 (t), 25.92 (t), 27.14 (t), 128.70 (d), 129.42 (d), 131.57 (d), 132.97 (d), 133.51 (s), 134.38 (d); mass spectrum (70 eV), m/e 148.

Thermal Isomerization of 19. A nitrogen-purged solution of 240 mg of **19** in 6 mL of anhydrous diglyme was heated at 160 °C for 2.0 h with stirring, cooled to room temperature, and diluted with 50 mL of water and 20 mL of pentane. The separated aqueous phase was extracted with two, 20-mL portions of pentane, and the combined pentane fractions were washed with four 20-mL portions of water, dried ($MgSO_4$), and concentrated at reduced pressure. The residue was analyzed by VPC (column A) which revealed two isomeric compounds formed in a 1:3.1 ratio, in order of increasing retention time. The mixture was separated by preparative VPC (column F, 110 °C); the minor isomer was identified as **30**: IR 1652, 1595, 763, 706 cm^{-1}; UV max (hexane) 265 nm (ϵ 5010); ^1H NMR δ 1.02–2.15 (m, 10), 1.80 (brs, $W_{1/2}$ = 3.0 Hz, 3), 5.47 (brd, $J \simeq$ 8 Hz, 1), 5.73 (brs, $W_{1/2}$ = 5.5 Hz, 1), 5.82 (m, 1); ^{13}C NMR δ 19.91 (g), 26.70 (t), 27.04 (t), 29.56 (t), 32.92 (t), 40.83 (d), 43.35 (d), 120.55 (d), 124.14 (d), 131.12 (d), 139.97 (s); mass spectrum (70 eV), m/e 148. The major isomer was identified as **31**: IR 1688, 1639, 1600, 990, 976, 855, 680 cm^{-1}; UV max (hexane) 276 nm (ϵ 7600); ^1H NMR δ 1.50 (m, 4), 1.91 (s, $W_{1/2}$ = 4.0 Hz, 3), 2.25 (m, 4), 5.57 (qt, J = 7.5, 1.0 Hz, 1), 5.79–6.25 (m, 3), 6.49 (d, J = 16.8 Hz, 1); ^{13}C NMR δ 19.52 (q), 23.79 (t), 24.13 (t), 25.19 (t), 26.12 (t), 126.22 (d), 128.51 (d), 129.43 (d), 133.51 (d), 135.60 (d), 137.00 (s); mass spectrum (70 eV), m/e 148.

Thermal Isomerization of 18 and 19. A 5-mg mixture of **18** and **19** was diluted with 20 μL of benzene-d_6 and sealed in a 3-mm Pyrex tube.

Table II

retention time, min	compd	% mixture
8.64	28	27
8.94	18 + 19	6
9.45	30	9
10.08	29	29
10.39	31	29

The sealed tube was immersed in an oil bath maintained at 145 °C for 1.0 h. ^{1}H NMR spectral analysis showed that extensive rearrangement had occurred, as indicated by the increase in the ratio of vinyl to nonvinyl hydrogens and by the disappearance of the characteristic diallylic hydrogen resonance at 3.47 ppm. VPC analysis (column B) revealed the formation of **28**, **29**, **30**, and **31** in the relative amounts listed in Table II. The ratios of diene **30** to triene **31** and diene **28** to triene **29** were found to be identical with those obtained from the individual isomerizations of **19** and **18**, respectively. From the summation of the appropriate diene–triene pair (e.g., **28** plus **29** and **30** plus **31**) an approximation of the initial composition can be made as 59.6% **19** and 40.4% **18**.

time, min	0	60
ratio of vinyl/nonvinyl hydrogens	0.23	0.37

3-Methylbicyclo[4.4.0]dec-3-en-7-one (32). The procedure of Kitahara[26] was employed. To a vigorously stirred suspension of 0.65 g (5 mmol) of anhydrous aluminum chloride in 65 mL of anhydrous dichloromethane at 0 °C was added, dropwise, 5.60 g (50 mol) of freshly distilled cyclohex-2-en-1-one over a 30-min period. The mixture was stirred for 30 min at 0 °C, 6.80 g (100 mol) of 2-methylbuta-1,3-diene was added in one portion, the reaction vessel was sealed, and the reaction mixture was stirred for 4 days at room temperature. The resulting solution was treated with 200 mL of 2 N aqueous hydrochloric acid and the separated aqueous layer extracted with two 50-mL portions of carbon tetrachloride. The combined organic phases were washed successively with three 50-mL portions of water, 50 mL of saturated aqueous sodium bicarbonate solution, and 50 mL of saturated sodium chloride solution and dried ($MgSO_4$). The solvent was removed at aspirator pressure and the residue distilled to yield 3.35 g (41%) of **32** as a clear colorless oil: bp 92 °C (1.2 torr); IR 2880, 1705, 826 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.85–2.20 (m, 12), 1.61 (s, $W_{1/2}$ = 4.0 Hz, 3), 5.30 (m, 1); mass spectrum (70 eV), *m/e* 164.

2-Methylbicyclo[4.4.0]dec-3-ene (33). To a stirred solution of 27.2 mL of 86% hydrazine hydrate and 27.2 g of potassium hydroxide in 130 mL of triethylene glycol at room temperature and under nitrogen was added 14.0 g (85 mmol) of **32** in one portion. The solution was heated at 140 °C for 1 h and then to 220 °C. A two-phase distillate was collected by means of a variable takeoff condenser as the internal temperature approached 220 °C. The distillate was diluted with 100 mL of pentane and 50 mL of water and the separated aqueous layer extracted with two 20-mL portions of pentane. The combined organic phases were washed successively with five 50-mL portions of water, two 50-mL portions of saturated sodium bicarbonate, and 50 mL of saturated sodium chloride solution and dried ($MgSO_4$). The solvent was removed at reduced pressure to yield 11.2 g (90%) of a clear colorless oil which by VPC analysis (column B) was shown to be a mixture of *trans*- (80%) and *cis*- (20%) 3-methylbicyclo[4.4.0]dec-3-ene. The trans isomer could be obtained in pure form by preparative VPC (column G, 120 °C): IR 2870, 1438, 1365, 789 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.7–2.1 (m, 14), 1.63 (s, $W_{1/2}$ = 4 Hz, 3), 5.27 (s, $W_{1/2}$ = 6 Hz, 1); mass spectrum (70 eV), *m/e* 150. Anal. ($C_{11}H_{18}$) C, H.

4-Methylbicyclo[4.4.0]decan-3-one (34). To a stirred solution of 3.0 g (20.0 mmol) of **33** (as a mixture of cis and trans isomers) in 75 mL of anhydrous ether at room temperature was added 21.0 mL of a 0.98 M solution of borane in anhydrous tetrahydrofuran, dropwise, over a 20-min period under nitrogen. The clear colorless solution was heated to and maintained at 35 °C for 2 h, cooled to room temperature, and treated with 25 mL of water. A solution of 6.2 g (20.5 mol) of sodium dichromate dihydrate and 9.6 mL (81.9 mol) of concentrated sulfuric acid diluted to a 25-mL total volume with water was added dropwise at room temperature over a 25-min period and the dark green mixture heated at 30 °C for 2 h. The separated aqueous layer was extracted with two 25-mL portions of ether, and the combined organic layers were washed with two 100-mL portions of 5% aqueous sodium hydroxide solution, a 50-mL portion of 5% aqueous sodium bicarbonate solution, and 50 mL of saturated aqueous sodium chloride solution and dried ($MgSO_4$). The solvent was removed at reduced pressure and the residue bulb-to-bulb distilled to yield 2.30 g (69%) of a clear colorless oil which was identified as **34**: bp 75–80 °C (0.2 torr); IR 2880, 2820, 1606, 1459 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.77 (d, J = 6.0 Hz, *trans*-methyl, 2.4), 1.17 (d, J = 8.0 Hz, *cis*-methyl, 0.6), 2.7–0.7 (m, 15); mass spectrum (70 eV), *m/e* 166, 138, 136, 124, 123, 122.

4-Methylbicyclo[4.4.0]dec-2-en-3-one (35). To a stirred solution of 2.1 g (12.7 mmol) of **34** in 5 mL of carbon tetrachloride at room temperature under nitrogen was slowly added a solution of 1.9 g (13.8 mmol) of sulfuryl chloride in 5 mL of carbon tetrachloride over a 1.5-h period, and the resulting mixture was allowed to stir an additional 2 h at room temperature. The reaction mixture was extracted with three 5-mL portions of water and two 10-mL portions of saturated aqueous sodium bicarbonate, dried ($MgSO_4$), and concentrated at reduced pressure to give the α-chloro ketone as a clear yellow oil.

The oil was not purified further but diluted with 20 mL of anhydrous *N*,*N*-dimethylformamide and added to a mixture of 1.08 g (25.5 mol) of anhydrous lithium chloride and 3.76 g (50.8 mol) of anhydrous lithium carbonate. Under nitrogen, the resulting mixture was heated at 125 °C for 2 h, stirred overnight at room temperature, and diluted with 100 mL of water. The aqueous phase obtained was extracted with three 25-mL portions of pentane, and the combined pentane extracts were washed with five 50-mL portions of water and dried ($MgSO_4$). The solvent was evaporated by using a rotary evaporator and the residual red oil distilled using a Büchi-Kugelrohr apparatus to yield 1.33 (68%) of **35** as a clear colorless oil: bp 65–75 °C (0.2 torr); IR 2924, 2840, 1679, 1661, 1623, 1095, 870 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.8–2.8 (m, 12), 1.70 (s, $W_{1/2}$ = 4.5 Hz, 3), 6.36 (q, J = 1.5 Hz, trans isomer, 0.8), 6.66 (m, cis isomer, 0.2); mass spectrum (70 eV), *m/e* 164, 149, 136, 122, 121, 107, 69; exact mass *m/e* 164.1185.

3-Methyl-*trans*-bicyclo[4.4.0]deca-2,4-diene (28). A mixture of 0.82 g (5.0 mmol) of **35**, 1.07 g (5.3 mmol) of *p*-toluenesulfonylhydrazine, and 5 mL of 95% ethanol was heated at reflux for 20 min and cooled to room temperature, and the bulk of the solvent was removed at reduced pressure. The remaining red oil was triturated with pentane and taken up in 50 mL of ether, and the solution was extracted with three 20-mL portions of water and 20 mL of saturated aqueous sodium chloride solution. The organic layer was diluted with 100 mL of anhydrous benzene and the solution distilled at atmospheric pressure until the distillate reached 80 °C.

The remaining benzene solution was cooled to 0 °C under nitrogen, and 5.7 mL of a 1.8 M solution of methyllithium in ether[27] was added over a 20-min period with stirring. After the mixture was stirred for 30 min at 0 °C, 10 mL of water was added and the mixture diluted with 50 mL of pentane. The separated aqueous layer was extracted with two 10-mL portions of pentane, and the combined organic phases were washed with three 20-mL portions of water and dried over anhydrous $MgSO_4$. The solvent was removed at reduced pressure and the residue bulb-to-bulb distilled at reduced pressure to yield 0.26 g (34%) of a clear colorless oil, bp 110 °C (16 torr). The oil was further purified by preparative VPC (column G, 110 °C) to yield **28** contaminated with ≤8% of the cis isomer. The ^{13}C NMR of the mixture was identical with that obtained from **28** (via **18**) with the exception of the minor resonances associated with the cis isomer. The ^{1}H NMR spectra were identical.

2-Methylbicyclo[4.4.0]dec-3-en-7-one (36). To a vigorously stirred suspension of 2.7 g (20 mmol) of anhydrous aluminum chloride in 120 mL of anhydrous dichlormethane was added 19.2 g (200 mmol) of cyclohex-2-en-1-one over a 30-min period under nitrogen. The solution was stirred for 30 min at room temperature and treated with 40.8 g (600 mmol) of *trans*-penta-2,4-diene in one portion, the reaction vessel was sealed, and the contents were stirred for 5 days at room temperature. The resulting solution was treated with 300 mL of 2 N aqueous hydrochloric acid solution and the separated aqueous layer extracted with two 50-mL portions of carbon tetrachloride. The combined organic phases were washed successively with three 50-mL portions of water, 50 mL of saturated aqueous sodium bicarbonate solution, and 50 mL of saturated aqueous sodium chloride solution, dried over anhydrous $MgSO_4$, and concentrated at reduced pressure. The residual oil was distilled to afford 15.3 g (47%) of **36** as a 2:1 mixture of trans- and cis-fused isomers, respectively: bp 72 °C (0.5 torr); IR 3017, 2920, 1719 (cis), 1705 (trans), 741, 722 cm^{-1}; ^{1}H NMR (CCl_4) 0.95 (d, J = 6.5 Hz, *trans*-methyl), 1.16 (d, J = 6.5 Hz, *cis*-methyl), 1.35–2.90 (m, 13), 5.50 (m, 2); mass spectrum (70 eV), *m/e* 164, 131, 118, 105, 93.

2-Methyl-*trans*-bicyclo[4.4.0]dec-3-ene (37). A mixture of 26.4 mL of 85% hydrazine hydrate, 26.2 g of potassium hydroxide and 13.9 g (85

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mmol) of **36** in 125 mL of triethylene glycol under nitrogen was heated at 140 °C for 1 h. The temperature was increased to 250 °C (bath) and a two-phase distillate allowed to distill from the flask. The collected material was diluted with 50 mL of water and 50 mL of pentane. The separated aqueous layer was extracted with two 20-mL portions of pentane, and the combined organic phases were washed repeatedly with water, dried ($MgSO_4$), and concentrated at aspirator pressure. The residual oil was distilled at reduced pressure to yield 8.4 g (68%) of a clear, colorless oil, which by VPC analysis (column G, 110 °C) was ≥95% the trans isomer: bp 84–85 °C (25 torr); IR 2995, 1655, 756, 675 cm^{-1}; ^1H NMR (CCl_4) δ 0.7–2.25 (m, 13), 0.94 (d, J = 7.5 Hz, 3), 5.42 (m, 2); mass spectrum (70 eV), m/e 150, 135, 121, 109, 67. Anal. ($C_{11}H_{18}$) C, H.

***trans*-3,4-Dibromo-2-methyl-*trans*-bicyclo[4.4.0]decane (38).** To a stirred solution of 7.50 g (50 mmol) of **37** in 25 mL of chloroform at 0 °C was added dropwise a solution of 8.10 g (51 mmol) of bromine in 5 mL of chloroform over a 30-min period. The solution was stirred at 0 °C for 1 h, the cooling bath was removed, and 2 mL of water and sufficient sodium hydrogen sulfite to quench the excess bromine were added. The organic phase was washed with two 10-mL portions of water, dried over anhydrous $MgSO_4$, and concentrated at reduced pressure. The solid residue was recrystallized in a minimum amount of hot 95% ethanol to yield 12.8 g (83%) of **38** as white plate crystals: mp 39–40 °C; IR (KBr) 2890, 1358, 709 cm^{-1}; ^1H NMR δ 0.8–2.4 (m, 13), 1.01 (d, J = 7.0 Hz, 3), 4,56 (m, 1), 4.82 (q, J = 1.5 Hz, 1); mass spectrum (70 eV), m/e 312, 310, 308, 150, 135. Anal. ($C_{11}H_{18}Br_2$) C, H, Br.

2-Methyl-*trans*-bicyclo[4.4.0]deca-2,4-diene (30). To a stirred suspension of 2.03 g (18 mmol) of potassium *tert*-butoxide in 50 mL of anhydrous tetrahydrofuran at room temperature was added 0.93 g (3 mmol) of **38** in one portion. The resulting mixture was heated at reflux for 2 h, cooled to room temperature, and diluted with 100 mL of water. The separated aqueous phase was extracted with three 50-mL portions of pentane, and the combined organic layers were washed with five 50-mL portions of water and dried over anhydrous $MgSO_4$. The solvent was removed at reduced pressure and the residue distilled by using a Büchi-Kugelrohr apparatus to yield 0.37 g (83%) of a clear colorless oil which by VPC analysis (column A) was shown to be a mixture of 2-methyl-*trans*-bicyclo[4.4.0]deca-2,4-diene (**30**) and 2-methylene-*trans*-bicyclo[4.4.0]dec-3-ene (**39**) in a 55:45 ratio, respectively, by the following isolation procedure. The mixture was chromatographed on 15 g of silver nitrate impregnated silica gel by using benzene as the eluting solvent and collecting 3-mL fractions. Fraction 5 contained 100 mg of a clear colorless oil identified as **39** on the basis of the following spectral data: IR 3067, 3016, 1638, 1600, 892, 881, 778, 683 cm^{-1}; UV max (hexane) 230 nm (ε 14950); ^1H NMR δ 0.7–2.4 (m, 12), 4.83 (brs, $W_{1/2}$ = 5.0 Hz, 2), 5.70 (m, 1), 6.13 (d, J = 10.0 Hz, 1); ^{13}C NMR δ 26.12 (t), 26.41 (t), 28.98 (t), 33.98 (t), 34.27 (t), 38.88 (d), 42.43 (d), 108.60 (t), 128.51 (d), 130.50 (d), 147.68 (s); mass spectrum (70 eV), m/e 148.91. Anal. ($C_{11}H_{16}$) C, H.

Fractions 6 and 7 (150 mg) proved to be a mixture of dienes **39** and **30** in roughly equal amounts. Fractions 8 and 9 contained 110 mg of a clear colorless oil which was spectrally identical in every respect with diene **30** isolated from the thermal rearrangement of **19**.

***trans,cis,cis*-Cycloundeca-1,3,5-triene.** The compound was prepared by following published procedures:[12] ^{13}C NMR δ 25.54, 26.70, 27.28, 28.20, 30.25, 124.96, 126.56, 128.94, 131.08, 132.39, 135.21.

Phospho-Cope Rearrangement of Sodium Allylvinylphosphinate

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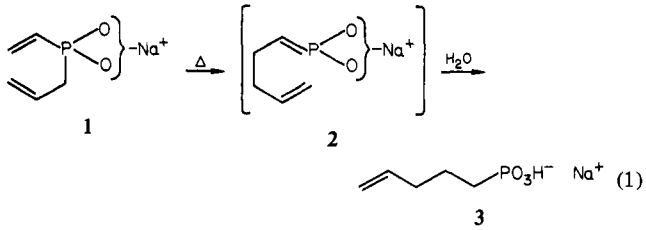
Abstract: Sodium allylvinylphosphinate (**1**) rearranges thermally to sodium hydrogen pent-4-enephosphonate (**3**) in virtually quantitative yield. The reaction probably constitutes a phospho-Cope rearrangement and presumably proceeds by way of the monomeric metaphosphonate **2** as a reactive intermediate. The half-time for the reaction is 4.67 h in water at 193.6 ± 1.0 °C and 6.03 h in ethanol. By contrast, ethyl allylvinylphosphinate reacts in ethanol to give a mixture of compounds; although some of the product expected for a phospho-Cope is present in the mixture, the rearrangement is slower than that of the anion by a factor of at least 16. The mechanistic implications of these facts are discussed.

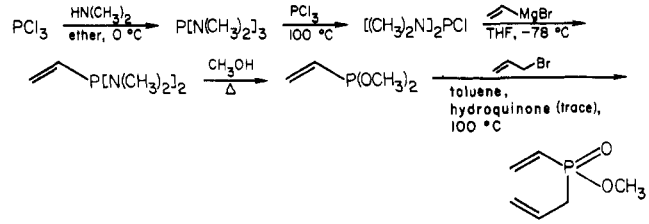
The Cope rearrangement has proved to be of great preparative and theoretical importance. The present research was designed to test whether an analogous reaction, where a PO_2^- unit is incorporated into the chain of carbon atoms, can be carried out. The simplest structure that comes into consideration for such a phospho-Cope rearrangement is the anion of allylvinylphosphinic acid.

When sodium allylvinylphosphinate is heated in water at temperatures near 200 °C, it undergoes a virtually quantitative rearrangement to sodium hydrogen pent-4-enephosphonate. This reaction probably consititutes a phospho-Cope rearrangement, and presumably proceeds as shown in eq 1 by way of a monomeric metaphosphonate as intermediate. (See, however, the Discussion for an alternative explanation.)



1 2 3

Scheme I



When **1** is heated in alcohol, the major product is ethyl hydrogen pent-4-enephosphonate, $CH_2{=}CH(CH_2)_3P{=}O(OH)(OC_2H_5)$ (**4**), the compound expected from addition of ethanol to the metaphosphonate **2**. When the ethyl ester of **1** is heated in alcohol, it undergoes rearrangement to yield diethyl pent-4-enephosphonate, but in poor yield and at a rate smaller than that for the anion by a factor of at least 16. This paper presents the data to support these statements and a discussion of the mechanism of the reaction.

Sodium allylvinylphosphinate was prepared from its methyl ester; the synthesis of the latter is outlined in Scheme I. The corresponding ethyl ester was prepared by an analogous series of reactions, substituting ethanol for methanol. Allylvinylphosphinic acid was prepared from its methyl ester by reaction with tri-

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