mmol) in glacial acetic acid (5 ml) at 16°. After 45 sec the mixture was filtered, the residue was washed well with ether, and the ether layer was washed to neutrality with aqueous $NaHCO_3$. The organic phase was dried over $MgSO_4$, evaporated, and separated by plc over silica gel using 20% acetone in hexane as eluent (two developments). The following zones were collected: R_f 0.7, 0.021 g of barbaralone and V (8 and 2% yield, respectively, by nmr analysis); R_f 0.5, 0.245 g of VIa (72%); R_f 0.4, 0.023 g of *anti*-9-bromotricyclo[3.3.0.0^{2,8}]non-6-en-3-one (VIb) (7%); mp 142–143°; ir ($CHCl_3$) 5.95 μ; nmr ($CDCl_3$, δ) 2.2–2.4 (mult, 5 H), 2.9 (br singlet, 1 H), 4.7 (br singlet, 1 H), 5.92 (doublet of doublets, J = 7 and 9 Hz, 1 H), 6.2 (doublet of multiplets, J = 9 Hz, 1 H); exact mass found for C_9H_9OBr, 213.98308 ± 0.0018 (calcd, 213.98175).

Conversion of VIb into IV with Base. The procedure for treatment of VIa with potassium *tert*-butoxide was followed using 0.005 g of VIb. By glpc analysis, IV was formed as the only volatile product, confirmed by peak enrichment.

Thermal Isomerization of 3,6-Dideuterio- and 1,2,7,8,9,9-Hexadeuterio-*cis*-bicyclo[6.1.0]nona-2,4,6-triene[1,2]

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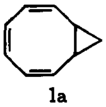
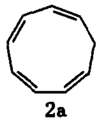
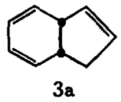
Contribution from the Department of Chemistry,
University of Oregon, Eugene, Oregon 97403. *Received January 3, 1972*

Abstract: Two deuterium-labeled analogs of *cis*-bicyclo[6.1.0]nona-2,4,6-triene have been synthesized and rearranged thermally to the corresponding *cis*-3a,7a-dihydroindenes. The labeling results show that a number of mechanistic formulations, "allowed" in terms of orbital symmetry theory and seemingly plausible, are not operative. Theoretical analysis leads to the conclusion that the rearrangement of bicyclo[6.1.0]nona-2,4,6-triene to dihydroindene may occur through the valence isomers bicyclo[5.2.0]nona-2,5,8-triene and *c,c,c,c*-cyclononatetraene, without intervention of any diradical intermediates.

Vogel and his collaborators synthesized *cis*-bicyclo-[6.1.0]nona-2,4,6-triene (**1a**) in 1961,[4-6] and discovered its rearrangement to *cis*-3a,7a-dihydroindene (**3a**). Cyclononatetraene (**2a**) was one proposed intermediate.


1a


2a


3a

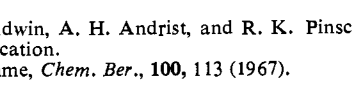
The comparative ease with which C-9-substituted derivatives of bicyclo[6.1.0]nona-2,4,6-triene may be synthesized has contributed to a rapid compilation of further instances of the conversion.[7-12] Some but not all[12] of these rearrangements may be related mechanistically to the parent hydrocarbon isomerization.

The same synthetic considerations, however, also contributed to a sustained absence of examples of the conversion of [6.1.0] systems having substitution at any of the other eight carbon atoms.

This paper outlines the current status of the mechanistic problems associated with the thermal isomerization of triene **1a** to *cis*-dihydroindene, describes the synthesis of 3,6-dideuterio- and 1,2,7,8,9,9-hexadeuteriobicyclo-[6.1.0]nona-2,4,6-triene, demonstrates in two independent ways the stereochemical course of the rearrangements of these hydrocarbons, and concludes that an orbital symmetry-disallowed yet state-conservative and energetically concerted isomerization from a folded conformer of bicyclo[5.2.0]nona-2,5,8-triene to *c,c,c,c*-cyclononatetraene is the key step in the overall rearrangement process.

A subsequent manuscript will detail our theoretical approach to this and related thermal rearrangements, in which seemingly implacable conflicts between orbital symmetry theory and stereochemical and kinetic fact are resolved.[13]

Background. Following the initial observation of the bicyclo[6.1.0]nonatriene to *cis*-dihydroindene conversion it was shown that 9,9-dideuteriobicyclo[6.1.0]-nonatriene (**1b**) rearranged to 1,1-dideuterio-*cis*-dihydroindene (**3b**).[14]



1b **3b**

The intervention of *c,c,c,c*-cyclonona-1,3,5,7-tetraene as an intermediate, suggested among other possibilities in the initial report[4] of the rearrangement, was supported by the finding that *anti*- and *syn*-9-methyl-*cis*-bicyclo[6.1.0]nonatriene and 9-methyl-*c,c,c,c*-cyclonona-1,3,5,7-tetraene all give the same or nearly the same

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[1] This work was supported by the Cities Service Oil Co., the DuPont Co., and the National Science Foundation.

[2] Preliminary reports: J. E. Baldwin and A. H. Andrist, *J. Amer. Chem. Soc.*, **93**, 4055 (1971); J. E. Baldwin, R. K. Pinschmidt, Jr., and A. H. Andrist, Autumn Meeting of the Chemical Society, York, Sept 1971, Abstract No. A23.

[3] National Institute of General Medical Sciences Predoctoral Fellow, 1968–1971.

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[5] E. Vogel, *Angew. Chem., Int. Ed. Engl.*, **2**, 1 (1963).

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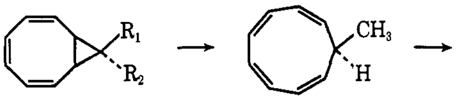
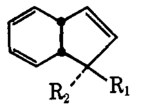
mixture of epimeric 1-methyl-*cis*-3a,7a-dihydroindenes.[15,16]



1c, $R_1 = CH_3$; $R_2 = H$
1d, $R_1 = H$; $R_2 = CH_3$

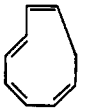
2c = 2d



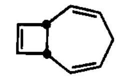
3c, $R_1 = CH_3$; $R_2 = H$
3d, $R_1 = H$; $R_2 = CH_3$

c,c,c,c-Cyclonona-1,3,5,7-tetraene (**2a**) was prepared in several laboratories and found to rearrange smoothly, as expected, to the cis bicyclic triene **3a**.[17-22]

Other valence isomers of **1** have been considered to be or demonstrated to be thermally accessible and thus potentially involved in the **1a** → **3a** conversion.



4a

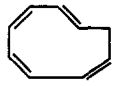


5

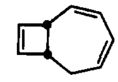
6

c,t,c,c-Cyclonona-1,3,5,7-tetraene (**4a**) has been trapped through Diels–Alder addition with 2,5-dimethyl-3,4-diphenylcyclopenta-2,4-dienone.[23] Bicyclo[5.2.0]nona-2,5,8-triene[24] (**5**) might be derived from **1a** through a *cis*-1,2-divinylcyclopropane type of Cope rearrangement, as occurs so readily in the isomerization of *cis*-bicyclo[6.1.0]nona-2,6-diene to *cis*-bicyclo[5.2.0]-nona-2,5-diene.[25] The cis,anti,cis isomer **6** has been trapped with good dienophiles such as maleic anhydride and acetylenedicarboxylate.[26,27]

t,c,c,c-Cyclononatetraene (**7**) has been suggested as a possible intermediate,[28] and *cis*-bicyclo[5.2.0]nona-2,4,8-triene (**8**), another valence isomer joined to triene **1a** through orbital symmetry-allowed processes, rearranges at 350° to *cis*-dihydroindene.[29]

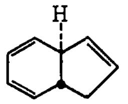


7



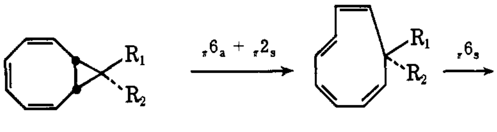
8

Bicyclo[6.1.0]nona-2,4,6-triene gives only a low yield of *trans*-3a,7a-dihydroindene (**9a**) along with the dominant cis product **3a**.[14,30]



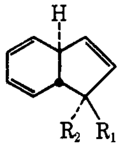
9a

For the 9,9-dimethyl and two isomeric 9-methyl-9-ethyl systems, though, trans product is formed exclusively;[31,32] each 9-methyl-9-ethyl isomer provides the same ratio of C(1) epimeric products (**9f** and **9g**).



1e, $R_1 = R_2 = CH_3$
f, $R_1 = C_2H_5$; $R_2 = CH_3$
g, $R_1 = CH_3$; $R_2 = C_2H_5$

4e
4f = 4g



9e, f, g

These rearrangements giving trans products offer no fundamental mechanistic quandaries, since starting materials and products may be linked by a sequence of reaction steps each allowed to be concerted in an orbital symmetry sense.[33]

The opposite seems true for the parent hydrocarbon rearrangement: at some stage in the overall process, production of *c,c,c,c*-cyclononatetraene through a valence isomerization of **1a** itself or an easily accessible isomer such as **4a**, **5**, or **6**, appears to occur in a disallowed fashion.

The problem this situation poses is severe: a thermal isomerization disallowed in terms of orbital symmetry theory (such as **5** → **2a** → **3a**) is faster than an immediately available alternative and fully concerted sequence (**1a** → **4a** → **9a**), an alternative that dominates the competitive situation totally in closely related cases. It has earned the rearrangement some notability as an unsolved mechanistic challenge.[12]

Three types of solutions to the problem might be considered.

First, it might be possible to muster a consistent rationale in terms of a diradical intermediate formalism.

Second, an orbitally concerted path of unusual and nonobvious character might be responsible for the apparent violation of reaction norms conforming to orbital symmetry theory.

Third, an orbitally nonconcerted but, in some other perspective, concerted mechanism might obtain.

Experimental Design Testing for Three [$_{\sigma}2_s + {}_{\sigma}2_a$] Mechanisms. The second of these three possibilities attracted our initial attention. The first already has

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(15) (a) P. Radlick and W. Fenical, *J. Amer. Chem. Soc.*, **91**, 1560 (1969); (b) see also A. G. Anastassiou and R. C. Griffith, *Chem. Commun.*, 1301 (1971).

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(23) A. G. Anastassiou and R. C. Griffith, *ibid.*, **93**, 3083 (1971).

(24) A 4-aza derivative of this system has been observed: S. Masamune and N. T. Castelluci, *Angew. Chem., Int. Ed. Engl.*, **3**, 582 (1964).

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(26) W. H. Okamura and T. W. Osborn, *J. Amer. Chem. Soc.*, **92**, 1061 (1970); C. S. Baxter and P. J. Garratt, *ibid.*, **92**, 1062 (1970).

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(29) M. Jones, Jr., and S. D. Reich, *ibid.*, **89**, 3935 (1967).

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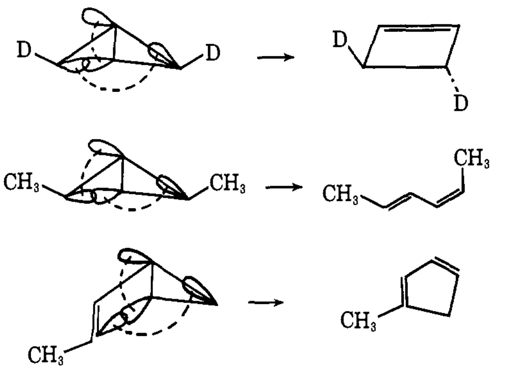
(31) S. W. Staley and T. J. Henry, *J. Amer. Chem. Soc.*, **91**, 1239 (1969); *ibid.*, **91**, 7787 (1969).

(32) S. W. Staley, *Intra-Sci. Chem. Rep.*, **5**, 149 (1971).

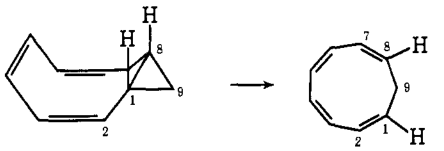
(33) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

many loyal proponents, and the third seemed too far a departure from commonly held conceptualizations and too nebulous a category. Further, experimental results in recent years have altered drastically notions of what geometrical and orbital contortions molecules may accommodate in order to react in an orbitally concerted fashion.[34–41]

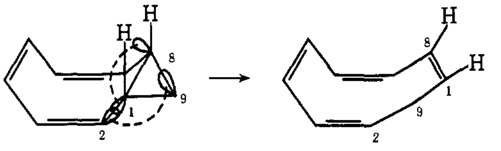
The thermal isomerization of deuterium[36] and methyl[37] labeled bicyclo[1.1.0]butanes, and the thermal conversion of 2-methylbicyclo[2.1.0]pent-2-ene to 1-methylcyclopentadiene[39] give some grounds for considering similar $[_\sigma 2_s + {}_\sigma 2_a]$ intramolecular cycloadditions as mechanistic possibilities for the bicyclononatriene rearrangement.



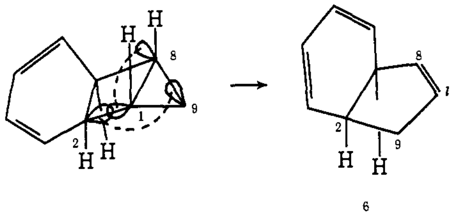
The disallowed mechanisms, represented by the disrotatory opening of the eight-electron system of bicyclo[6.1.0]nona-2,4,6-triene (eq 1) (or the four-electron system of isomer 5) and three symmetry-allowed (sa) mechanisms which were explicitly tested (eq 2, 3, 4) are shown: the enumeration of carbon atoms maintains the numbering of the original [6.1.0] skeleton.



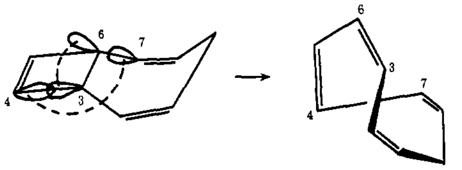
(1)



(2)



(3)



(4)

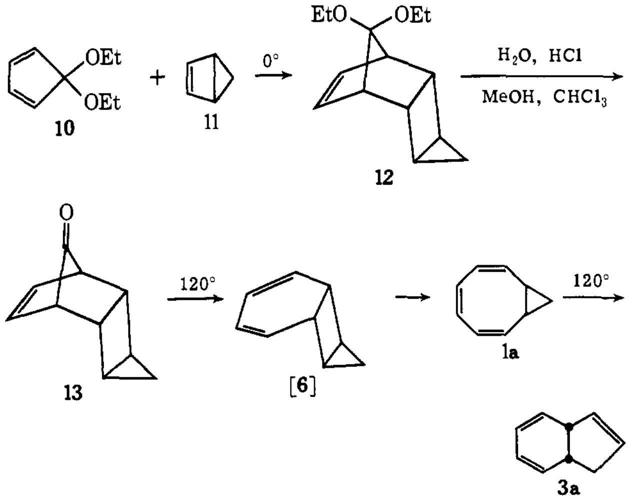
In the first $[_\sigma 2_s + {}_\sigma 2_a]$ case, the *c,c,c,c*-cyclononatetraene precursor to the more stable and observed *cis*-dihydroindene product has an altered connectivity: in the tetraene, the C-9 methylene unit separates C-1 and C-2, rather than C-1 and C-8. In the second sa possibility, the same connectivity change occurs and the original C-2 carbon is unambiguously located at the 7a position of dihydroindene. In the third sa mechanism, carbons 4 and 6 are permuted between starting material and tetraene.

Utilizing two bicyclo[6.1.0]nona-2,4,6-trienes specifically labeled with deuterium (3,6-d_2 and 1,2,7,8,9,9-d_6), these mechanistic possibilities have been put to experimental test.

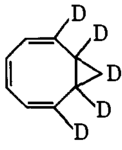
Results

Syntheses of the required bicyclononatrienes were accomplished using the route shown in Scheme I.

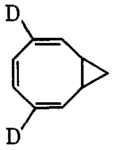
Scheme I



The accessibility[42] and dienophilic reactivity[43] of bicyclo[2.1.0]pent-2-ene (**10**) made possible this convenient route.[44] Using bicyclo[2.1.0]pent-2-ene-d_6[45] in this sequence led to 1,2,7,8,9,9-bicyclo[6.1.0]nona-2,4,6-triene (**1h**); using 2,5-dideuteriocyclopentadienone diethyl ketal as the Diels–Alder diene led to the 3,6-dideuterio triene (**1i**).



1h



1i

The predictions made by connectivity sustaining mechanisms and the three $[_\sigma 2_s + {}_\sigma 2_a]$ mechanisms listed above may be easily derived; the results are summarized in Table I.

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[34] J. A. Berson and G. L. Nelson, *J. Amer. Chem. Soc.*, **89**, 5503 (1967); 92, 1096 (1970).

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[40] J. E. Baldwin and M. A. Kaplan, *ibid.*, **93**, 3969 (1971); *ibid.*, **94**, 668 (1972).

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[42] A. H. Andrist, J. E. Baldwin, and R. K. Pinschmidt, Jr., *Org. Syn.*, in press.

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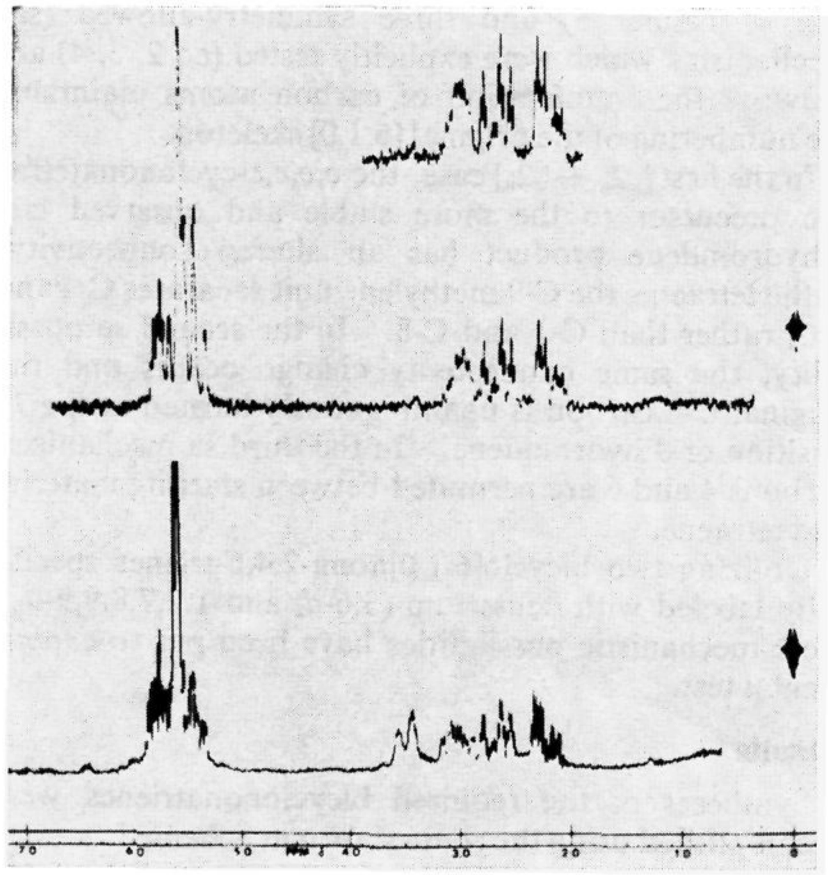
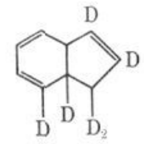
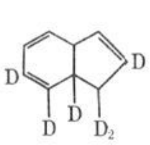
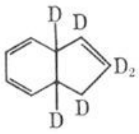
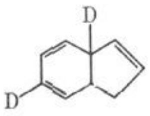
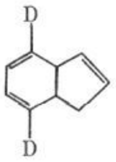
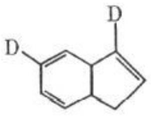
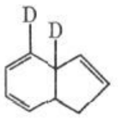
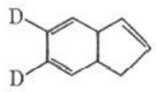
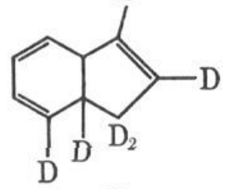


Figure 1. The nmr spectra of *cis*-3a,7a-dihydroindene (**3a**) (lower trace) and of dihydroindene-d_2 (**3i**) (upper traces).

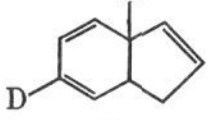
Table I. Predicted Products from the Thermal Rearrangement of Deuterated Bicyclo[6.1.0]nona-2,4,6-trienes

Mechanism, eq no.	Products, %				
	From 1h				
					
1	100				
2		50	50		
3			100		
4	100				
	From 1i				
					
1	100				
2		50	50		
3		100			
4				50	50

The dihydroindene-d_6 from thermolysis of **1h** had an nmr spectrum showing only a three-proton multiplet at δ 5.9–5.3 and a one-proton signal for H-3a at 3.48 ppm. This result excluded the mechanisms summarized in eq 2 and 3.



3h

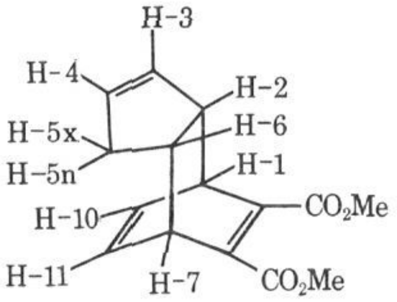


3i

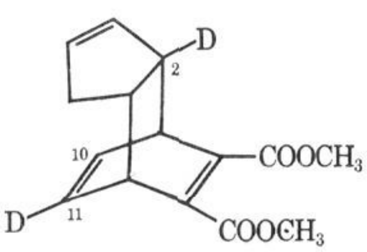
The dihydroindene-d_2 from thermolysis of **1i** had an nmr spectrum (in CS_2) showing absorption from five vinyl protons at δ 5.84–5.30, H-7a at 2.99, and the characteristic complex pattern for H-1x and H-1n at higher field (Figure 1). The absence of the H-3a signal, except for some absorption corresponding to incomplete deuteration in the starting material, is incompatible with the mechanisms of eq 2, 3 and 4. All three $[{}_\sigma 2_s + {}_\sigma 2_a]$ mechanisms considered are thus experimentally excluded.

Independent confirmation of this conclusion was obtained by preparing the dimethyl acetylenedicarboxylate adduct **14b** of **3i**.

The nmr spectrum of unlabeled adduct (**14a**) in



14a

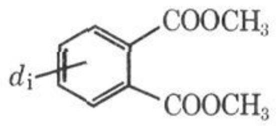


14b

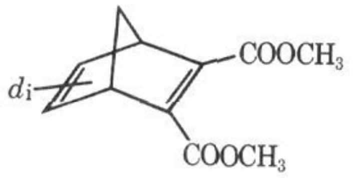
benzene-d_6 has absorptions at δ 6.05 (2, H-10, 11), 5.34 (1, H-3 or H-4), 5.21 (1, H-4 or H-3), 3.88 (2, H-1, 7), 3.47 (6, OCH_3), 2.97 (1, H-2), 2.48 (1, H-6), 2.08 (1, H-5x), and 1.53 ppm (1, H-5n). Estimations for some of the larger coupling constants in Hz are $J_{2,3} \cong J_{2,4} \cong 2$; $J_{2,6} = 8\text{–}9$; $J_{3,4} = 5.9$; $J_{3,5x} \cong J_{4,5x} \cong 2$; $J_{5n,5x} = 17$; $J_{5n,6} \cong 3.5$; $J_{5x,6} \cong 9.5$.

The nmr spectrum of the d_2 adduct in benzene-d_6 showed no appreciable signal at δ 2.97 for H-2, and a simplified H-10–H-11 vinyl proton signal at δ 6.09 ppm integrating for about 1 H instead of 2 H. The bridge protons appeared as a 1 H doublet, J = 6 Hz, superimposed on a second 1 H multiplet, placing the second deuterium at C-11 (**14b**).

Adduct **14b** was treated with more dimethyl acetylenedicarboxylate and allowed to stand at room temperature for 35 days. The two products **15** and **16** were



15



16

collected by glpc, as were samples of **12**, **12**-d_2, and the unlabeled analogs of **15** and **16**. The six samples were submitted for mass spectral analysis with a slow scan of the molecular ion regions. Significant M − 1 peaks in **12** and **16** limited the accuracy of the deuterium assay in these compounds but the predictions of Table II

Table II. Predicted Deuterium Distributions for the Thermolysis Products (**15** and **16**) from Adduct **14b**

Mechanism, eq no.	Compd	Predicted^a deuterium distribution, % d_0	d_1	d_2
1	**15**	6	94	
	16	6	94	
2	**15**	5	50	47
	16	50	48	
3	**15**	4	5	91
	16	100		
4	**15**	5	50	47
	16	50	48	

^{a} Based on adduct **12**-d_2 (4% d_0, 4.5% d_1, and 91.5% d_2).

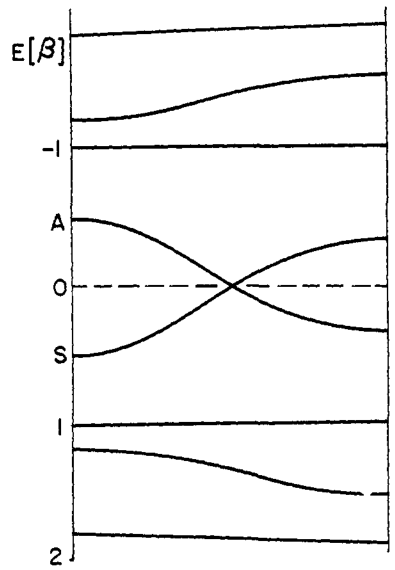
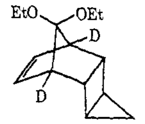
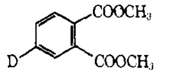
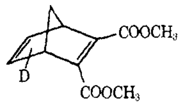


Figure 2. Molecular orbital correlation diagram for the conversion of bicyclo[5.2.0]nona-2,5,8-triene to *c,c,c,c*-cyclonona-1,3,5,7-tetraene.

and the results of Table III are nonetheless conclusive: no contribution from any of the three sa mechanisms could be detected.

Table III. Mass Spectral Analysis of Deuterium Distributions in Ketal **12**-d_2 and the Thermolysis Products (**15** and **16**) from **14b**

Compound	Ionizing voltage, eV	Deuterium distributions, %[a]		
		d_0	d_1	d_2
	70	4	4.5	91.5
	16	9.2	90.8	<0.2
	16	7.6	92.4	<0.2

[a] The spectra were obtained at slow scan; the reported values are based on averages of at least three scans, and have been corrected for natural abundance ^{13}C, ^{18}O, and significant M − 1 fragmentations, through comparisons with spectra obtained for unlabeled samples.

Conclusions

With the rigorous disproof of three allowed $[{}_\sigma 2_s + {}_\sigma 2_a]$ mechanisms (eq 2, 3, and 4) that might have removed the bicyclononatriene mechanistic stalemate, the situation reverts to an apparent impasse: a conflict between the dictates of orbital symmetry theory and the fact that a formally disallowed process of some sort is extremely facile.[46]

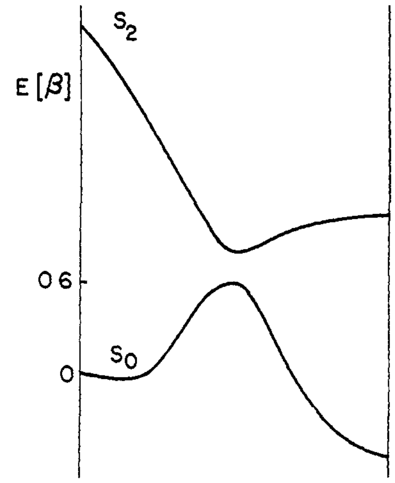
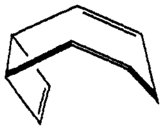


Figure 3. Electronic state correlation diagram for S_0 and S_2 for the conversion of bicyclo[5.2.0]nonatriene to cyclononatetraene.

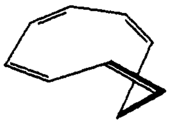
With the experimental assurance that the three allowed $[{}_\sigma 2_s + {}_\sigma 2_a]$ intramolecular cycloaddition mechanisms which seemed most plausible were not the key to the rearrangement and in light of the present dearth of postulated alternatives of an orbitally concerted sort, we considered alternative types of concerted mechanisms.[13]

Realizing[13] that state-conservative thermally-activated reactions may be either energetically concerted or nonconcerted, that they may be classified in terms of orbital symmetry theory as "allowed" or "disallowed," and that the four reaction types resulting from these two energetic and two orbital symmetry categories are all theoretically respectable possibilities, we scrutinized the isomerizations **5** → **2a** and **4a** → **2a** to gauge whether one or both might conceivably be facile and energetically concerted.

Starting from the folded conformer **17**, and using the most elementary Hückel molecular orbital methods and rough estimates of geometries intermediate between **17** and the symmetric *c,c,c,c*-cyclonona-1,3,5,7-tetraene (**18**), the results shown in Figures 2 and 3 were calculated. The state-correlation diagram of Figure 3 corresponds to a low activation energy energetically concerted reaction.



17



18

Hückel molecular orbital analysis of the isomerization of *c,t,c,c*-cyclonona-1,3,5,7-tetraene (**4a**) to the *c,c,c,c*-tetraene **2a** shows it to be far less likely. The molecular orbitals of octatetraene have no bonding level which drops in energy as they are transformed into the allyl plus pentadienyl orbitals (Figure 4). The corresponding state-correlation diagram (Figure 5) suggests more than twice as high an activation energy for **4a** → **2a** as for **5** → **2a** (**17** → **18**).

We accordingly view the isomerization of bicyclo[5.2.0]nona-2,5,8-triene to *c,c,c,c*-cyclonona-1,3,5,7-tetraene, the key to the rearrangement of bicyclo[6.1.0]nona-2,4,6-triene to *cis*-3a,7a-dihydroindene, as a state-conservative and energetically concerted conversion. The three stages of the rearrangement, **1a** → **4a** → **2a** → **3a**, three state-conservative isomerizations, may be conveniently labeled $[{}_\pi 2_s + {}_\sigma 2_s + {}_\pi 2_s]$(OS), $[{}_\pi 2_s + {}_\sigma 2_s)]$(CI), and $[{}_\pi 2_s + {}_\pi 2_s + {}_\pi 2_s]$(OS), giving in

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[46] Anastassiou and Griffith[23] estimate $\Delta H^{\ddagger}$ 26 kcal/mol and $\Delta S^{\ddagger}$ −5 eu for the rearrangement 1 → 3.

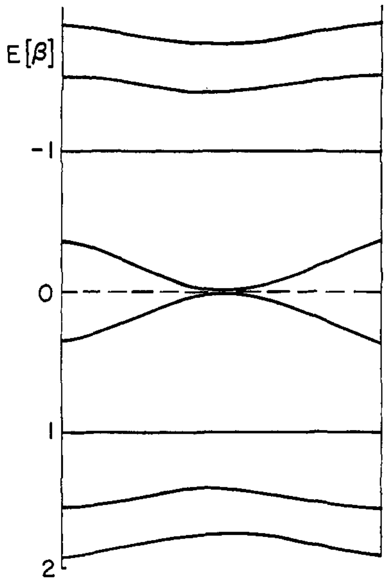

Figure 4. Molecular orbital correlation diagram for the conversion of *c,t,c,c*- to *c,c,c,c*-cyclononatetraene.

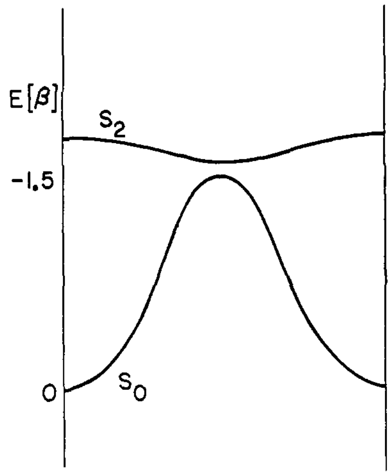

Figure 5. Electronic state correlation diagram for S_0 and S_2 for the conversion of *c,t,c,c*- to *c,c,c,c*-cyclononatetraene.

each case the stereochemistry of utilization of the two-electron components and the mechanism (orbital symmetry conservation or configuration interaction) through which the process manages state conservation.

Experimental Section

Nuclear magnetic resonance spectra were recorded on a Varian HA-100 instrument in the frequency sweep mode; double irradiation experiments employed a Hewlett Packard Model 200 ABR audio oscillator. Mass spectra were obtained on a CEC-110-21B spectrometer by Dr. S. Rottschaefer. Infrared spectra were recorded on Beckman IR 5 and IR 7 spectrophotometers.

A Varian Aerograph A-90-P3 was employed for glpc analyses and preparative separations; the following columns were used: A, 1.5 m × 6 mm 20% SE-30 on nonacid washed Chromosorb W (stainless steel); B, 105 cm × 6 mm 25% di-*n*-decyl phthalate on Chromosorb W (aluminum); C, 1 m × 6 mm 5% Apiezon L and 15% silicon rubber on Chromosorb W, treated with HMDS (copper); D, 0.5 m × 6 mm 10% DC-710 on Chromosorb W (aluminum).

Bicyclo[2.1.0]pent-2-ene and bicyclo[2.1.0]pent-2-ene-d_6 were prepared through photolysis of cyclopentadiene and cyclopentadiene-d_6,[47] using a modified version[42] of the original Brauman, Ellis, and van Tamelen technique.[48]

2,2,5,5-Tetradeuteriocyclopentanone diethyl ketal was prepared from 8.84 g of 2,2,5,5-tetradeuteriocyclopentanone,[49] 18.7 ml of ethyl orthoformate, 18 ml of EtOD, and dry hydrogen chloride. The combined reagents were stirred at 60° for 24 hr; the reaction mixture was then poured into aqueous sodium bicarbonate, and the organic phase was separated, dried over sodium sulfate, filtered, and distilled. The product, bp 61–65° (17 mm), amounted to 11.4 g (70%). The deuterium incorporation, as estimated nmr spectroscopically, was 90% of theory.

2,5-Dibromocyclopentanone diethyl ketal was secured through bromination of cyclopentanone diethyl ketal[50] with pyridinium hydrobromide perbromide in ethanol at 5°.[51,52]

2,5-Dibromo-2,5-dideuteriocyclopentanone diethyl ketal was prepared as described for the unlabeled analog[51,52] from 2.0 g (12.6 mmol) of dry 2,2,5,5-tetradeuteriocyclopentanone diethyl ketal and 8.0 g (25 mmol) of pyridinium hydrobromide perbromide to give 2.29 g of yellow oil (58% yield).

***endo,anti*-Tetracyclo[5.2.1.0^{2,6}.0^{3,5}]dec-8-en-10-one Diethyl Ketal (12).** To a vigorously stirred mixture of freshly sublimed (220°, 1 mm) potassium *tert*-butoxide (20.8 g, 190 mmol, Alfa Inorganics) and 75 ml of freshly distilled (from CaH_2) dimethyl sulfoxide (DMSO) at 5° was added 13.55 g (42.7 mmol) of 2,5-dibromocyclopentanone diethyl ketal in 25 ml of DMSO. The addition required 3 min and the temperature was maintained below 15° by occasional cooling in a Dry Ice–IPA bath. After stirring an additional 1 min, 100 ml of pentane at 0° was added and the mixture was poured onto 100 ml of ice and salt water. The pentane layer containing cyclopentadienone diethyl ketal (**10**) was decanted into a flask at −80°. The H_2O–DMSO layer was rapidly extracted with pentane. The combined pentane extracts and original organic phase were added to 0.5 g of bicyclo[2.1.0]pent-2-ene (**11**) in 20 ml of tetrahydrofuran at 4°. As judged by glpc analysis on column A, the Diels–Alder addition was complete within 1 hr (100% yield by glpc). The reaction mixture was concentrated by distillation (bp <56° (6 mm)) in a stream of dry nitrogen to give 1.208 g (79% recovery) of tetracyclic ketal **12**. After thorough purification by preparative glpc on column A, it had absorptions in the nmr at δ 6.02 (vinyl, t, 2.5 Hz, 2 H), 3.32 (methylene of *O*-ethyl, q, 7.0 Hz, 2 H), 3.30 (methylene of *O*-ethyl, q, 7.0 Hz, 2 H), 2.75 (C-1, 7, m, 2 H), 2.17 (C-2, 6, m, 2 H), 1.1 (C-3, 5, m, 2 H), 1.05 (methyl of *O*-ethyl, d of t, 7.0, $\Delta\nu$ = 0.75 Hz, 6 H), 0.77 (C-4 H_n, d of t, 4.0 and 1.5 Hz, 1 H), and 0.60 (C-4 H_x, d of t, 6.0 and 4.0 Hz, 1 H); M^+ at *m/e* 220.145 (calcd for $C_{14}H_{20}O_2$: 220.1463), base peak at *m/e* 117; and infrared bands in CCl_4 as follows: $\bar{\nu}_{C-H}$ at 3070, 3040, 2980, 2940 cm^{-1}, $\bar{\nu}_{C-O}$ at 1132, 1105, 1075, and 1060 cm^{-1}.

2,3,4,4,5,6-Hexadeuterio-*endo,anti*-tetracyclo[5.2.1.0^{2,6}.0^{3,5}]dec-8-en-10-one Diethyl Ketal (12-d_6). The hexadeuterio tetracyclic ketal **12**-d_6 was prepared as above supplanting bicyclo[2.1.0]pent-2-ene (**11**) with hexadeuteriobicyclo[2.1.0]pent-2-ene (**11**-d_6). The nmr spectrum of the product exhibited only C-1,7 methine protons at δ 2.75 (t, 2.5 Hz, 2 H) and vinyl protons at δ 6.11 (t, 2.5 Hz, 2 H) in addition to the two sets of absorptions for *O*-ethyl protons. The product was judged to be >95% d_6 material by nmr analysis.

1,7-Dideuterio-*endo,anti*-tetracyclo[5.2.1.0^{2,6}.0^{3,5}]dec-8-en-10-one Diethyl Ketal (12-d_6). Potassium *tert*-butoxide (Alfa Inorganics, 4 g) was powdered and sublimed at 195° (100 μ). Nitrogen was bubbled through 10 ml of dimethyl sulfoxide (dried over 4A molecular sieves) in an oven-dried 100-ml three-necked flask equipped with a thermometer. Some 2 or 3 g of the potassium *tert*-butoxide was rapidly scraped into the flask against a counter flow of nitrogen. The solution was cooled to 18° and 2.28 g of dibromodideuterio ketal in 3 ml of DMSO was added slowly over a 3- to 4-min period with vigorous stirring. The black mixture was kept near 22° with a bath of ice in brine and by the addition of a cold solution of bicyclopentene in THF. One min after the addition was finished, 15 ml of pentane at 0° was added; the resulting mixture was poured over 10 ml of ice and water in a separatory funnel, but not shaken. The layers were separated and the pentane solution was transferred to a flask at −78°. The aqueous layer was extracted with two addi-

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(47) Obtained using T. F. W. McKillop's procedure; *cf.* S. McLean, C. J. Webster, and R. J. D. Rutherford, *Can. J. Chem.*, **47**, 1555 (1969).

(48) J. I. Brauman, L. E. Ellis, and E. E. van Tamelen, *J. Amer. Chem. Soc.*, **88**, 846 (1966).

(49) T. B. Malloy, Jr., R. M. Hedges, and F. Fischer, *J. Org. Chem.*, **35**, 4256 (1970).

(50) J. Boeseken and F. Tellegren, *Recl. Trav. Chim. Pays-Bas*, **57**, 133 (1938).

(51) P. E. Eaton and R. A. Hudson, *J. Amer. Chem. Soc.*, **87**, 2769 (1965); E. L. Allred and C. Anderson, *J. Org. Chem.*, **32**, 1874 (1967).

(52) N. B. Chapman, J. M. Key, and K. J. Toyne, *ibid.*, **35**, 3860 (1970).

tional portions of cold pentane. The combined pentane solutions at −78° were decanted into a cold second portion of bicyclopentene in THF (about 300 mg of bicyclopentene in all). After 2 hr at 0°, the reaction mixture was washed twice with water and once with brine; it was then dried at 0° over 4A molecular sieves for 10 hr. The solution was filtered and concentrated by fractional distillation first at atmospheric and later at reduced pressure to give 1.026 g of orange-red oil. Distillation at aspirator pressure on a molecular still at 100° gave 475 mg of crude product (34% yield). The ketal was purified by glpc on column A at 140° (120 ml/min). A total of 105 mg of **12-*d*₂** with a retention time of 7 min was collected in CS_2 at −78°. The nmr spectrum had absorptions at δ 6.08 (s, 2), 3.27 (q, 2, $J = 7$ Hz), 3.26 (q, 2, $J = 7$ Hz), 2.70 (m, 0.16 ± 0.01), 2.12 (bs, 2), 1.02 (2 overlapping t, 6, $J = 7$ Hz), 1.0–1.1 (buried m, 2), 0.73 (dt, 1, $J \cong 4.2$, $J = 1.5$ Hz), and 0.60 ppm (td, 1, $J \cong 5.5$ Hz, $J \cong 4.2$ Hz); mass spectrum (70 eV) *m/e* 222, 120, 119, 118, 93, 92, 66; ir (neat) 3070 (m), 3040 (m), 2980 (s), 2940 (s), 1109 (d, s) cm^{-1}.

***endo,anti*-Tetracyclo[5.2.1.0^{2,6}.0^{3,5}]dec-8-en-10-one (13).**[44] The tetracyclic ketal (**12**, 0.471 g, 2.14 mmol) was subjected to hydrolysis in a solution of 2.0 ml of water, 0.4 ml of concentrated hydrochloric acid, 8.0 ml of methanol, and 4.0 ml of chloroform for 14 hr at room temperature. The reaction was quenched by the addition of potassium carbonate. Ether extraction followed by drying ($MgSO_4$) and concentrating gave 0.185 g (60%) of **13**. After thorough purification by preparative glpc on column D, it had absorptions in the nmr at δ 6.58 (vinyl, t, 2.5 Hz, 2 H), 2.83 (C-1, 7, quin, 2.5 Hz, 2 H), 2.34 (C-2, 6, m, 2 H), 1.15 (C-3, 5, d of quar, 6.0 and 1.5 Hz, 2 H), 0.74 (C-4 H_n, d of t, 4.5 and 1.5 Hz, 1 H), and 0.58 (C-4 H_x, d of t, 6.0 and 4.5 Hz, 1 H); M^+ at *m/e* 146, M − H at 145.118, M − CO at 118.078, base peak at 117; λ_{max} 319 nm (ϵ 141), 274 (1840), 255 (2910); and infrared bands in CCl_4 at 3020, 3000, 2945, 1810, and 1782 cm^{-1}.

Catalytic hydrogenation of **13** afforded *endo,anti*-tetracyclo[5.2.1.0^{2,6}.0^{3,5}]decan-10-one with the expected nmr spectrum, $\bar{\nu}_{C=O}$ (CCl_4) at 1788 and 1763 cm^{-1}, and M^+ at *m/e* 148.089.

2,3,4,4,5,6-Hexadeuterio-*endo,anti*-tetracyclo[5.2.1.0^{2,6}.0^{3,5}]dec-8-en-10-one (13-*d*₆). The hexadeuteriotetracyclic ketal **12-*d*₆** was hydrolyzed as above. After thorough purification by preparative glpc on column D, **13-*d*₆** showed nmr absorptions only for C-1 and C-7 methine protons at δ 2.83 (t, $J = 2.5$ Hz) and vinyl protons at 6.58 (t, $J = 2.5$ Hz), while $\bar{\nu}_{C=O}$ appeared at 1780 cm^{-1} in CCl_4.[44]

1,7-Dideuterio-*endo,anti*-tetracyclo[5.2.1.0^{2,6}.0^{3,5}]dec-8-en-10-one (13-*d*₂). The purified dideuterioketal (105 mg) was hydrolyzed 2 hr 50 min at 25° in a stirred mixture containing 1 ml of chloroform, 2 ml of methanol, 0.1 ml of 30% hydrochloric acid, and 0.4 ml of water. The reaction mixture was quenched with sodium carbonate, then partitioned between water and ether. The organic phase was dried over magnesium sulfate, filtered, and concentrated. The crude ketone was purified by glpc on column A at 95° (150 ml/min, injector and detector at 100°). The ketone was eluted at 4.6 min and was collected in CS_2 at −78° (41 mg, 59% isolated yield): nmr (CCl_4) δ 6.58 (s, 2), 2.87 (m, about 0.16), 2.30 (bs, 2), 1.24 (dm, 2, $J = 5.7$ Hz), 0.69 (dt, 1, $J \cong 4.4$, $J \cong 1.7$ Hz), and 0.54 ppm (td, 1, $J = 5.7$, $J \cong 4.4$ Hz); ir (neat) 3070 (w), 2980 (w), 2931 (m), 1790 (s), 1770 (s) cm^{-1}.

Thermolysis of *endo,anti*-Tetracyclo[5.2.1.0^{2,6}.0^{3,5}]dec-8-en-10-one (13). A 40-mg sample of **13**, thoroughly purified by preparative glpc on column D (105°, 100 ml min^{-1}), was sealed into a base-washed and oven-dried nmr tube along with 100 μl of CCl_4 after degassing on a vacuum line through four freeze–pump–thaw cycles at 10^{-4}–10^{-5} Torr. The nmr tube was heated in an oil bath at 120° while the disappearance of **13** and appearance of first *cis*-bicyclo[6.1.0]nona-2,4,6-triene (**1a**) and then *cis*-dihydroindene (**3a**) was monitored by nmr analysis. After 27 min (90% conversion), the tube was cooled and opened. Analysis by glpc on column B (105°, 120 ml min^{-1}) confirmed the presence of **1a** and **3a** in an approximate 1:4 ratio.

Thermolysis of 2,3,4,4,5,6-Hexadeuterio-*endo,anti*-tetracyclo[5.2.1.0^{2,6}.0^{3,5}]dec-8-en-10-one (13-*d*₆). A 25-mg sample of **13-*d*₆** was heated at 120° as described above. Preparative glpc collections on column B (105°, 120 ml min^{-1}) led to 8.4 mg of **1h**, 10.5 mg of **3h**, and 1.5 mg of hexadeuteriobicyclo[4.3.0]nona-3,5,7-triene. The nmr data for **3h** are given above.

Thermolysis of 1,7-Dideuterio-*endo,anti*-tetracyclo[5.2.1.0^{2,6}.0^{3,5}]-dec-8-en-10-one (13-*d*₂). The 41-mg sample of **13-*d*₂** and 70 μl of carbon tetrachloride (spectral grade, stored over sodium carbonate) containing a few per cent of TMS was sealed in a dry base-washed nmr tube after three freeze–pump–thaw (0.05 Torr) cycles. A reference spectrum was run, and the tube was heated for about 15 min in an air bath at 120°. Nmr analysis showed about 80% conversion of the ketone, giving dihydroindene and bicyclo[6.1.0]-nonatriene in an approximate ratio of 7:3. The nmr tube was opened and the major glpc peaks at 5.2, 6.8, and 9.1 min from co-injected air collected by preparative glpc on column B (105°, 120 ml min^{-1}). The second and third peaks were identified by glpc retention times as dihydroindene and bicyclo[6.1.0]nonatriene, respectively. The weak 2.9-mg sample of **1i** in CS_2 (*vs.* benzene reference at δ 7.35 ppm) showed nmr signals at δ 6.2–5.6 (m), 1.48 (m), 1.12 (m), and 0.12 ppm (m), with integral ratios of about 4.2:2.3:0.9:0.8. The dihydroindene sample was collected in CS_2; the nmr spectral data are given above and in Figure 1.

3a,7a-*cis*-Dihydroindene was prepared by thermolysis of bicyclo[6.1.0]nonatriene at 130°[4] and purified by glpc on column B at 120° (200 ml/min), and by the method of Alder and Flock.[53]

8,9-Dicarbomethoxytricyclo[5.2.2.0^{2,6}]undeca-3,8,10-triene (14a). To 36 mg (0.33 mmol) of dihydroindene in an nmr tube with 0.2 ml of CCl_4 was added 0.061 ml (0.67 mmol) of distilled dimethyl acetylenedicarboxylate. After 14 hr at 25° the solution showed greatly reduced dihydroindene nmr absorptions, small new peaks attributable to dimethyl phthalate and **16**, and peaks of a major new product at δ 6.24, 5.44, 4.0–3.5, and 3.1–1.6 ppm. Heating this sample for 90 min at 70° gave a 90% conversion to phthalate **15-*d*₀** and norbornadiene **16-*d*₀** leaving only about 10% of the new product by nmr.

A second sample consisting of 130 mg of dihydroindene (1.1 mmol) and 148 mg (1.04 mmol) of dienophile was allowed to stand 12 hr at room temperature. The low boiling materials were removed at reduced pressure (0.01–0.02 Torr for 1 hr) and the residue was subjected to thin layer chromatography at 0° and vacuum transfer to give nearly pure **14a**: nmr (CCl_4) δ 6.25 (dd, 2, $J = 3.6$, $J = 4.0$ Hz), 5.45 (m, 2), 3.90 (m, 2), 3.69 (s, 6), 3.02 (dm, 1, $J \cong 8$ Hz), 2.68 (dt, 1, $J \cong 9$, $J \cong 3$ Hz), 2.37 (ddm, 1, $J = 17$, $J \cong 10$ Hz), and 1.77 ppm (dm, 1, $J = 15$ Hz); uv λ_{max}^{EtOH} 222 nm (ϵ 6.3 × 10^3), end absorption; mass spectrum, no molecular ion, *m/e* 194, 163, 148, 120, 105, 104, 92, 91, 79 (base peak), 66. A second spectrum in benzene-*d*₆ and spin decoupling experiments helped give the assignments indicated above.

2,3-Dicarbomethoxynorbornadiene, prepared by the literature method,[54] had absorptions in the nmr (CCl_4) at δ 6.86 (t, 2, $J \cong 1.5$ Hz), 4.87 (m, 2), 4.71 (s, 6), 2.24 (bd, 1, $J = 7$ Hz), and 2.05 ppm (bd, 1, $J = 7$ Hz).

8,9-Dicarbomethoxy-2,11-dideuteriotricyclo[5.2.2.0^{2,6}]undeca-3,8,10-triene. To the nmr sample of purified dihydroindene-*d*₂ in CS_2 was added 50 μl (78 mg, 0.55 mmol) of freshly distilled dimethyl acetylenedicarboxylate. After 12 hr at 25° the sample showed only partial reaction by nmr. The solvent was removed at reduced pressure; the concentrated mixture was allowed to stand an additional 12 hr at 25° and then held at 25 μ for 2 hr to remove low boiling materials. An nmr spectrum of the product dissolved in benzene-*d*₆ showed absorptions at δ 6.09 (dm, about 1.2, $J = 6$ Hz), 5.35 (dt, 1, $J = 6$, $J \cong 2$ Hz), 5.19 (dt, 1, $J = 6$, $J \cong 2$ Hz), 3.85 (m, appears to be d, 1, $J = 6$ Hz superimposed on m, 1), 3.47 (s, 6), 2.48 (ddd, 1, $J = 9.6$, $J = 3$, $J = 4$ Hz), 2.07 (dddd, 1, $J = 17$, $J = 10$, $J \cong 2.0$, $J \cong 2.0$ Hz), and 1.50 ppm (dm, 1, $J = 17$ Hz). Traces of dimethyl phthalate and 2,3-dicarbomethoxynorbornadiene were also apparent.

Mass Spectral Analysis of the Products of 8,9-Dicarbomethoxy-2,11-dideuteriotricyclo[5.2.2.0^{2,6}]undeca-3,8,10-triene and Dimethyl Acetylenedicarboxylate. The small sample of **14b** was treated with 11 μl of distilled dimethyl acetylenedicarboxylate and stored for 35 days at room temperature. A few milligrams of each product, dicarbomethoxynorbornadiene-*d*₁ and dimethyl phthalate-*d*₁ in a 1:1 ratio, were collected by glpc using column C at 160° (120 ml/min). Retention times agreed with authentic unlabeled samples, 5.1 and 6.3 min after coinjected air, respectively. Slow scan mass spectra of the parent ion regions were obtained for reference and labeled samples of both compounds, and for the dideuterio ketal precursor **12-*d*₂**. The precursor **12-*d*₂** and the norbornadiene gave significant M − 1 peaks, even at 16 eV ionizing voltage. The results after correction for this and natural abundance ^{13}C and ^{18}O are shown in Table III.

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(53) K. Alder and F. H. Flock, *Chem. Ber.*, **87**, 1916 (1954).

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