A Mechanistic Alternative for the Thermal Antara–Antara Cope Rearrangements of Bicyclo[3.2.0]hepta-2,6-dienes and Bicyclo[4.2.0]octa-2,7-dienes[1]

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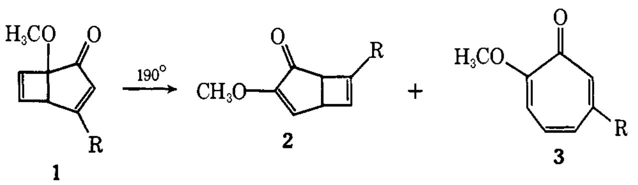
Abstract: Thermal rearrangements near 190° of various 1-methoxy-2-oxobicyclo[3.2.0]hepta-3,6-dienes to 3-methoxy-2-oxobicyclo[3.2.0]hepta-3,6-dienes having substituents at positions consistent with a Cope rearrangement formalism were first observed by Miyashi, Nitta, and Mukai in 1967. Similar rearrangements are now reported for 1-ethoxybicyclo[3.2.0]hepta-3,6-diene, 3-ethoxybicyclo[3.2.0]hepta-2,6-diene, and the degenerate rearrangement of a deuterium-labeled bicyclo[4.2.0]octa-2,7-diene. The degenerate rearrangement of 3,7-dideuteriobicyclo[3.3.0]-octa-2,6-diene does not occur even at 450° for 85 min; 1,5-dimethylbicyclo[3.3.0]octa-2,6-diene fails to isomerize at 350° for 11 hr to 3,7-dimethylbicyclo[3.3.0]octa-2,6-diene. These results are rationalized in terms stressing the decisively important mechanistic role played by the cyclobutene moiety in those systems which isomerize. The rearrangements are held to occur through conrotatory electrocyclic opening of the cyclobutene ring system, giving a cis,trans,cis monocyclic triene as intermediate, which then reverts to starting material or closes in the other direction to give the "Cope rearrangement" product.

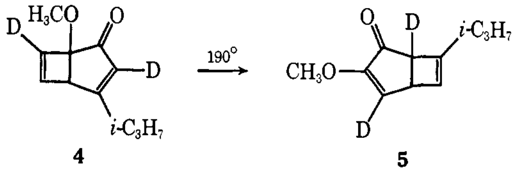
Thermal rearrangements of several bicyclo[3.2.0]-heptadienones were examined by Miyashi, Nitta, and Mukai[2] in 1967.



1 2 3

a, R = H
b, R = C_6H_5
c, R = i-C_3H_7

When **1a**, **1b**, or **1c** was heated in chloroform or methanol at 190°, it was converted into a mixture of the corresponding isomers **2** and **3**. Rearrangement of the 3,7-dideuterio derivative **4** gave only the 1,4-dideuterio product **5**, thus ruling out two possible mechanisms and favoring the Cope pathway.



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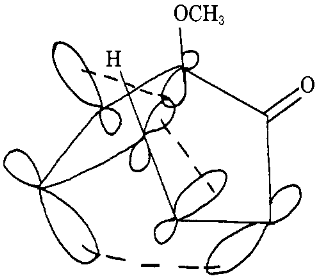
Analogs without the C_1 methoxy substituent showed no kinetically significant tendency to undergo a similar rearrangement.

Orbital symmetry considerations and an acute sense of stereochemical requirements led Woodward and Hoffmann[3] to view these rearrangements as examples of the symmetry-allowed but normally sterically unattainable trans–trans or antara–antara Cope rearrangement. In a prespective attempting to emphasize the three-dimensional relationships in the molecular system suffering rearrangement, the structure **6** may be seen to yield product **7** in a one-step concerted fashion[4] only when the C_1–C_5 bond is cleaved in a *suprafacial* disrotatory manner. Thus the process might be considered a $[{}_{\pi}2_a + {}_{\sigma}2_s + {}_{\pi}2_a]$ cycloreaction or, equivalently, an antara–antara [3,3] sigmatropic or antara–antara Cope rearrangement.



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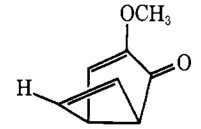

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Were this interpretation of the rearrangement correct, kinetic comparisons between suitably analogous systems such as hydrocarbons constrained to suffer Cope rearrangement in the normal supra–supra mode or in the antara–antara mode would give a valuable quantitative response to the question: to what extent can an orbital symmetry possibility for a reaction make up for an intrinsically poor orbital overlap situation?

Similar sorts of comparisons between geometrical isomers of the doubly bridged [14]annulene derivatives **8** and **9** have been made; temperature-dependent nmr studies indicate that the nearly planar π configuration of **8** behaves as an aromatic Hückel system, while the isomer **9** having relatively poor overlap between orbitals on C_1, C_{14}, and C_{13} and on C_6, C_7, and C_8 behaves as a mixture of valence isomers, equibrating only slowly

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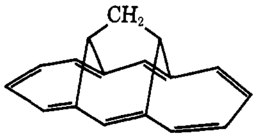
(1) Supported initially by Public Health Service Research Grant No. GM-16576, and completed with funds from National Science Foundation Grant No. GP 9259, the Cities Service Oil Co., the Du Pont Co., and the Petroleum Research Fund, administered by the American Chemical Society.

(2) T. Miyashi, M. Nitta, and T. Mukai, *Tetrahedron Lett.*, 3433 (1967).

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

(4) J. E. Baldwin and R. H. Fleming, *Fortschr. Chem. Forsch.*, **15** (3), 281 (1970).

at lower temperatures and undergoing reactions typical of a polyolefin.[5]



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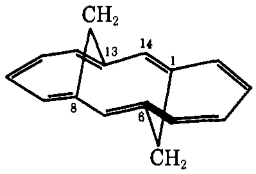

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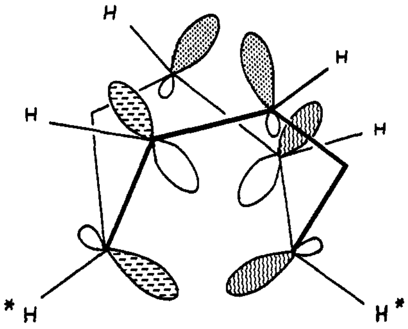
Both **8** and **9** correspond formally to the $(4n + 2)$ rule, but the overlap differences are sufficient to cause strikingly dissimilar physical and chemical characteristics. For rearrangements wherein different types of orbital symmetry allowed processes may be postulated, we expect in the same way overlap considerations to cause marked variations in reaction kinetics.[6]

There being apparently no other examples of antara–antara Cope rearrangements, and given the importance of the theoretical issue, further experimentation and analysis seemed warrented.

Results

Tests for Degenerate Rearrangements of Bicyclo[3.3.0]octa-2,6-dienes.[7] Our initial attempts to uncover new examples of "antara–antara Cope rearrangements" were within the bicyclo[3.3.0]octa-2,6-diene series. This system, being somewhat more flexible than a bicyclo[3.2.0]heptadienone, might, we imagined, make possible a more facile reaction; the orbitals on each end of the Cope system could approach one another without causing great angular distortions. The D_2 activated complex **10** would not necessitate a prohibitive strain energy.



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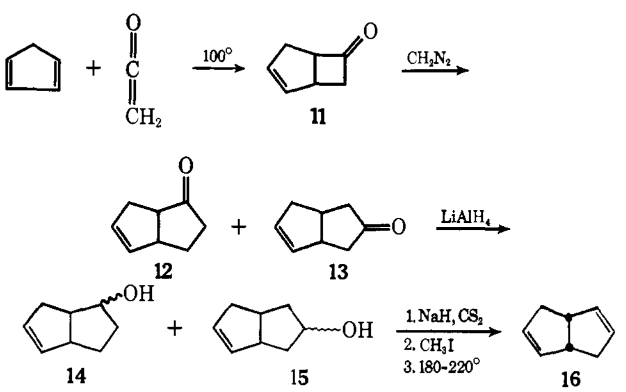
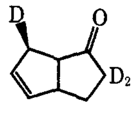
First, the unlabeled bicyclo[3.3.0]octa-2,6-diene was synthesized according to Scheme I. This route proved successful and was easily adapted to the preparation of labeled analogs. It depended, except for the diazomethane ring-expansion step, on earlier work by Roberts and Gorham;[8] the product **16** had infrared and nmr spectral properties in accord with the literature.[9]

Scheme I



The isomeric ketones **12** and **13** could be separated by glpc. Both showed molecular ion and M − CO peaks in their mass spectra at *m/e* 122 and 94, and carbonyl infrared bands at 1735 and 1730 cm^{-1}, respectively. In nmr spectra, both showed two vinyl protons at δ 5.7 ppm and an allylic methine proton at 3.5 as a broad multiplet; ketone **12** had many peaks in the 3.0–1.7-ppm region (7 H), while **13** had three protons at 2.65 and four methylene protons at 2.15 ppm.

Attempted deuterium exchange with ketone **12** in basic aqueous tetrahydrofuran led to incorporation of three deuterons: the 7 H upfield multiplet was reduced in relative intensity to 4.2 H. We interpret the exchange data in terms of product **17** and the homoenolization phenomenon uncovered by Nickon and coworkers.[10]



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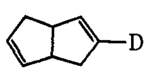
Bicyclo[3.3.0]octa-2,6-diene (**16**) exhibited a temperature invariant nmr spectrum up to 180°; thus, no facile degenerate antara–antara Cope rearrangement competes here with examples of fluctional isomeric supra–supra Cope rearranging molecules such as bullvalene[9,11–14] and semibullvalene[15–17] and, to test for rearrangement at higher temperatures, labeled derivatives of the diene **16** were required.

Reduction of ketone **13** after its separation by glpc from its isomer **12** with lithium aluminum deuteride gave through the Chugaev elimination route the 3-deuteriobicyclo[3.3.0]octa-2,6-diene (**18**). The nmr



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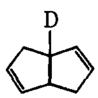

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[5] E. Vogel, lecture in Houston, Tex., Nov 13, 1968; *Proc. Robert A. Welch Found. Conf. Chem. Res.*, **12**, 215 (1969); E. Vogel, U. Haberland, and H. Günther, *Angew. Chem.*, **82**, 510 (1970); E. Vogel, A. Vogel, H.-K. Kübbeler, and W. Sturm, *ibid.*, **82**, 512 (1970).

[6] See C. Trindle (*J. Amer. Chem. Soc.*, **92**, 3251, 3255 (1970)) for a novel theoretical approach to concerted reactions giving a measure of relative degree of concertedness.

[7] Preliminary account: J. E. Baldwin and M. S. Kaplan, *Chem. Commun.*, 1354 (1969).

[8] J. D. Roberts and W. F. Gorham, *J. Amer. Chem. Soc.*, **74**, 2278 (1952).

[9] W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

[10] A. Nickon, J. L. Lambert, R. O. Williams, and N. H. Werstiuk, *J. Amer. Chem. Soc.*, **88**, 2728 (1966).

[11] W. von E. Doering and W. R. Roth, *Angew. Chem.*, **75**, 27 (1963).

[12] G. Schröder, *ibid.*, **75**, 722 (1963).

[13] M. Saunders, *Tetrahedron Lett.*, 1699 (1963).

[14] A. Alberhand and H. S. Gutowsky, *J. Amer. Chem. Soc.*, **87**, 4092 (1965).

[15] H. E. Zimmerman and G. L. Grunewald, *ibid.*, **88**, 183 (1966).

[16] J. Meinwald and H. Tsuruka, *ibid.*, **91**, 5877 (1969).

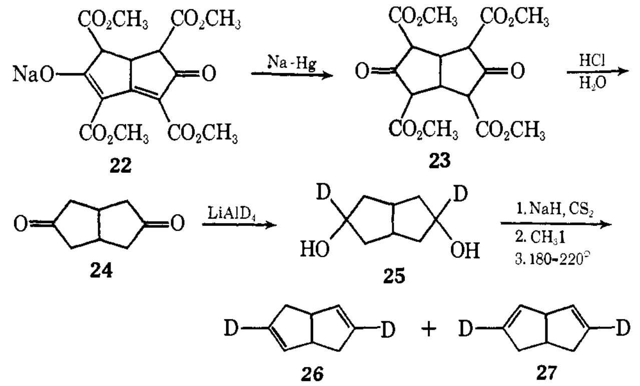
[17] H. E. Zimmerman, J. D. Robbins, and J. Schantl, *ibid.*, **91**, 5878 (1969).

spectrum of the 3-deuteriodiene **18** was in accord with expectations; the vinyl–bridgehead–methylene proton absorption at δ 5.4–5.7, 3.2–3.6, and 2.0–2.9 ppm had the expected 3:2:4 relative intensities (Figure 1).

Pyrolysis of small samples of the monodeuteriodiene **18** in sealed capillary tubes at 340–360° for 2 hr led to no sure indications of other hydrocarbons; the analytical glpc trace showed no new peaks appropriate to skeletally isomeric C_8 hydrocarbons, and the nmr spectrum obtained on the pyrolyzed sample in a capillary tube after glpc purification gave no marked change in the vinyl–bridgehead allylic methine proton absorption intensity. The observed ratios before and after pyrolysis, 1.55 ± 0.05 and 1.70 ± 0.06, correspond to at best a slight conversion to the bridgehead-deuterio system **19**; whether this modest change might be ascribed to the isomerization sought or to an experimental artifact—the pyrolysis at high pressures may have been subject to wall effects and the sensitivity of observed integral ratios to A-60 instrumental parameters for very small neat samples in 1.5-mm capillary tubes remains ill-defined—was not addressed directly. Rather, the experiment was taken as grounds for continuing the study with the 3,7-dideuteriodiene **26**, a substrate able to show a more significant change in nmr absorption intensities accompanying the putative rearrangement **26** $\rightleftharpoons$ **28**, conducting the pyrolyses at higher temperatures and lower pressures, and again subjecting the pyrolysate to glpc purification prior to nmr analysis.

3,7-Dideuteriobicyclo[3.3.0]octa-2,6-diene (**26**) was prepared through a seven-step sequence leading through Vossen's red salt **22**[18–20] and bicyclo[3.3.0]octa-3,7-dione[19] (**24**) as outlined in Scheme II. An alternative synthesis of intermediate **23** through the direct condensation of dimethyl β-ketoglutarate with glyoxal[21] was successful in low yield.

Scheme II



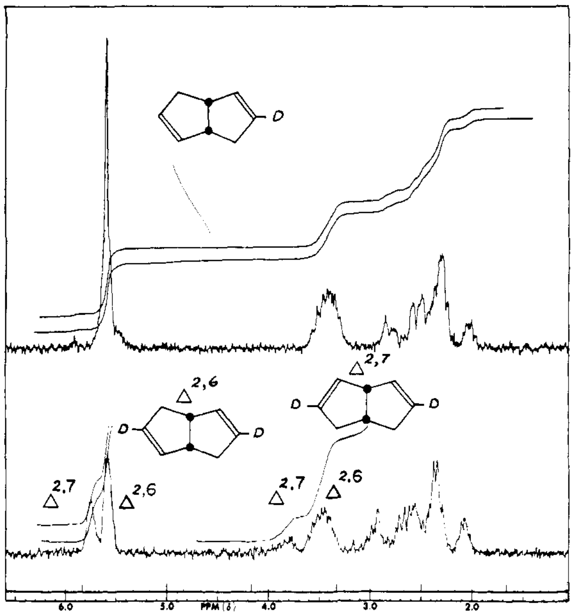
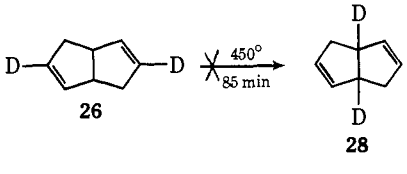


Figure 1. Nuclear magnetic resonance spectra at 60 MHz of 3-deuteriobicyclo[3.3.0]octa-2,6-diene (**18**) (above) and of a mixture of $\Delta^{2,6}$- and $\Delta^{2,7}$-3,7-dideuteriobicyclo[3.3.0]octadiene (**26** and **27**) (below).

The nmr spectrum of the diene obtained through the Chugaev pyrolysis revealed it to be a mixture of the desired $\Delta^{2,6}$-diene **26** and the isomeric $\Delta^{2,7}$-hydrocarbon **27** (Figure 1). That the monoxanthate derived from bicyclo[3.3.0]oct-6-en-3-ol (**15**) is pyrolyzed to the $\Delta^{2,6}$-diene **16**, while the dixanthate from dideuteriobicyclo[3.3.0]octa-3,7-diol (**25**) produces both $\Delta^{2,6}$- and $\Delta^{2,6}$-dienes (**26** and **27**), is an experimental fact we note with interest and without rationale.

The mixture of dienes was used without separation in pyrolysis experiments, since isomer **27** was expected to be unreactive and the alterations in nmr peak areas predictable for the antara–antara Cope rearrangement of **26** would be uncomplicated by the isomeric contaminant; as the rearrangement went to equilibrium the ratio of vinyl to bridgehead proton resonance signals would change from 1:1 to 3:1.



26 **28**

In the event, heating this mixture of **26** and **27** in the gas phase at 0.5 atm and 450° for 85 min gave a 91% return of dienes, according to glpc analysis, having an unaltered nmr spectrum, signifying no detectable conversion of **26** to **28**.

A further attempt to observe the rearrangement was made with 1,5-dimethylbicyclo[3.3.0]octa-2,6-diene, a system with a weaker C_1–C_5 bond and in principle permitting a more sensitive detection of the posited rearrangement product 3,7-dimethylbicyclo[3.3.0]-octa-2,6-diene by glpc analysis than would be possible

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(18) G. Vossen, Doctoral Dissertation, University of Bonn, 1910.

(19) P. Yates, E. S. Hand, and G. B. French, *J. Amer. Chem. Soc.*, **82**, 6347 (1960).

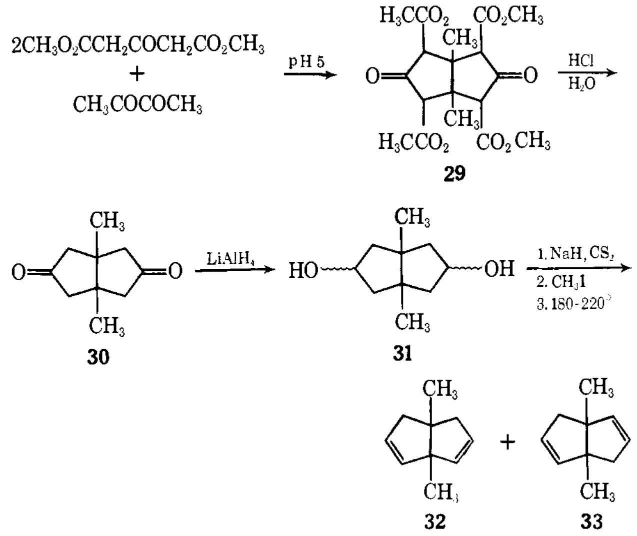
(20) E. R. Hanna, K. T. Finley, W. H. Saunders, Jr., and V. Boekelheide, *ibid.*, **82**, 6342 (1960).

(21) U. Weiss and J. M. Edwards, *Tetrahedron Lett.*, 4885 (1968).

by nmr spectroscopy for the degenerate deuterium-labeled case.

Synthesis of 1,5-dimethylbicyclo[3.3.0]octa-2,6-diene (**33**) was accomplished as outlined in Scheme III. The steps leading to the dione **30** had been realized by others,[21] and the rest of the sequence simply applied the route used above for the less substituted hydrocarbons.

Scheme III



Separation of the isomeric dienes **32** and **33** by glpc on a β,β'-oxydipropionitrile column afforded samples for spectroscopic examination. The hydrocarbon of shorter retention time showed two methyl singlets, at 0.94 and 0.95 ppm, a methylene peak at 2.15 (4 H), and vinyl protons centered at 5.35, and was accordingly assigned as **32**. In the second isomer, **33**, the methyl protons appeared as a sharp singlet at 0.95 ppm (6 H); the methylene and vinyl peaks came at 2.15 and 5.3 ppm.

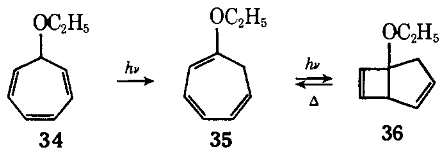
The isomer theoretically capable of an antara–antara Cope rearrangement, **33**, was heated in the gas phase at 350° for 11 hr; no change in its nmr spectrum was detected, although the darkened sample may have suffered some decomposition. At 450° at 0.5 atm for 70 min, the starting diene was partially converted to at least five other products, according to glpc analysis.

This inconclusive finding was not clarified through additional experimental work with diene **33** and the corresponding rearrangement product 3,7-dimethylbicyclo[3.3.0]octa-2,6-diene.

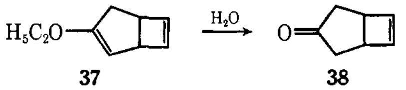
Rearrangements of Bicyclo[3.2.0]hepta-2,6-dienes. The observations of Miyashi, Nitta, and Mukai concerning the thermal rearrangement of 1-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one (**1**) to 3-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one (**2**) and 2-methoxytropone (**3**) were confirmed, quantitatively. A kinetic plot for our data appropriate to the reaction scheme assumed, that is, parallel and competitive irreversible first-order isomerizations,[22] gave an excellent correspondence.

To assess the significance of the oxo functionality in this conversion, 1-ethoxybicyclo[3.2.0]hepta-3,6-diene (**36**) was prepared and rearranged.

7-Ethoxycycloheptatriene (**34**), readily obtained through reaction of tropylium fluoroborate with ethanol,[23-25] may be isomerized photochemically[26] to the diene sought, **36**, by way of 1-ethoxycycloheptatriene (**35**).



The thermal reactivity of diene **36** has been examined briefly; when dropped into and swept with nitrogen through a vertically mounted pyrolysis column packed with Pyrex helices preheated to 340°, 1-ethoxycycloheptatriene (**35**) was obtained.[26] Under less drastic conditions we find that 3-ethoxybicyclo[3.2.0]hepta-2,6-diene (**37**), the product corresponding to an antara–antara Cope rearrangement, is also formed.



At 170° in a sealed tube, **36** gave products **37** and **35** in a 1:10 ratio. Kinetic behavior was in accord with parallel first-order reactions.[22]

The identity of the minor rearrangement product **37** was deduced from its molecular ion at *m/e* 136; low-intensity ultraviolet absorption maxima in ethanol at 297 (ϵ 20), 282 (32), 275 (24), and 258 nm (33), similar in wavelength and intensity to the ultraviolet absorption of the known 1-ethoxybicyclo[3.2.0]hepta-3,6-diene; nmr signals at δ 1.2–1.4 (3 H, t), 2.1–2.4 (2 H, m), 3.1–3.3 (1 H, m), 3.4–3.8 (3 H, m, $-OCH_2-$ and C_5–H), 5.4–5.5 (1 H, m C_4–H), and 5.95 and 6.2, AB quartet (J = 3 Hz); and facile hydrolysis to bicyclo[3.2.0]hept-6-en-3-one (**38**), having $\bar{\nu}$ 1740 cm^{-1}, *m/e* 108 (M^+), and nmr absorptions at δ 2.2–2.4 (4 H, m), 3.4–3.6 (2 H, m), and 6.2 (2 H, s).

When diene **37** was heated at 190° for 2.5 hr, it was 90% recovered; 8% of triene **35** and 2% of diene **36** had been formed, thus demonstrating the reversibility of the rearrangement.

The Degenerate Bicyclo[4.2.0]octa-2,7-diene Rearrangement. It appeared from the results with bicyclo[3.3.0]octa-2,6-dienes and various bicyclo[3.2.0]hepta-2,6-dienes that neither the oxo function nor an alkoxy group at C_1 was required for the rearrangement type, but that the cyclobutene moiety might be. We therefore sought an example of the rearrangement in a ring system having the minimum features thought required, and uncovered the degenerate bicyclo[4.2.0]octa-2,7-diene valence isomerization.[27]

The deuterium-labeled bicyclo[4.2.0]octa-2,7-diene **46** was prepared through the route shown in Scheme IV. A published synthesis of *cis*-bicyclo[4.2.0]oct-7-en-2-one,[28] followed by the Shapiro–Shechter ketone–olefin sequence[29-30] which, requiring no elevated tem-

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(22) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, p 160.

(23) G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Amer. Chem. Soc.*, **82**, 5846 (1960).

(24) K. Conrow, *Org. Syn.*, 43, 101 (1963).

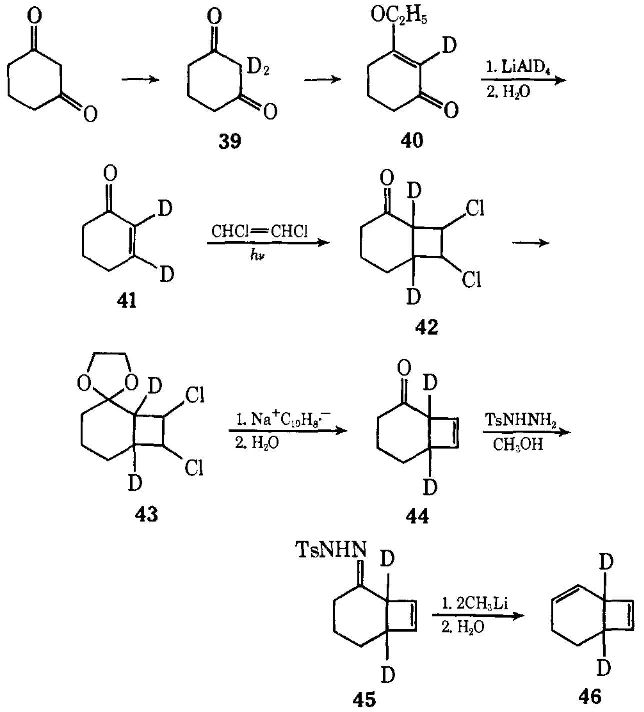
(25) K. Conrow, *J. Amer. Chem. Soc.*, **83**, 2343 (1961).

(26) G. W. Bordon, O. L. Chapman, R. Swindell, and T. Tezuka, *ibid.*, **89**, 2979 (1967).

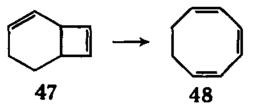
(27) Preliminary report: J. E. Baldwin and M. S. Kaplan, *Chem. Commun.*, 1560 (1970).

(28) C. G. Scouten, F. E. Barton, Jr., J. R. Burgess, P. R. Story, and J. F. Garst, *ibid.*, 78 (1969).

Scheme IV



peratures, was well suited to the system at hand, gave the required diene **46**. 2,3-Dideuteriocyclohex-2-en-1-one was obtained by modifying known procedures: deuterium exchange in cyclohexane-1,3-dione, formation of 2-deuterio-3-ethoxycyclohex-2-en-1-one,[31] and reduction with lithium aluminum deuteride.[32] The same sequence with unlabeled cyclohexenone gave the unlabeled bicyclo[4.2.0]octa-2,7-diene (**47**) needed for preliminary experiments. Though less efficient a route than the direct photoisomerization of 1,3,5-cyclooctatriene,[33,34] it served as a perfect model for the deuterium-labeling work.



The bicyclooctadiene **47** is known to suffer thermal rearrangement to 1,3,5-cyclooctatriene (**48**);[34] this process limits the observational possibilities accessible to one searching for a degenerate rearrangement. The longer or hotter the system is heated, the greater will be the progress of the degenerate isomerization toward equilibrium, but the smaller will be the absolute quantity of bicyclooctadiene **46** plus **49** available for observation!

The labeled material for the experiment was, according to its 100-MHz nmr spectrum, completely deuterated at C_6, but only 47 ± 3% labeled at C_1. Apparently back exchange occurred during preparation of the intermediate **40**, and perhaps later in the sequence.

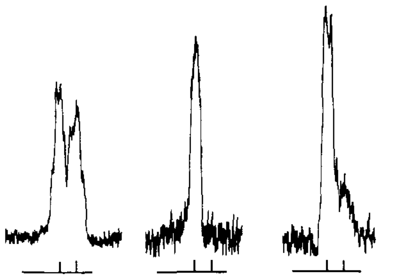
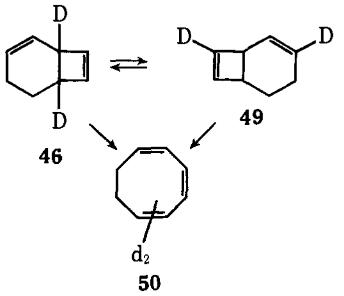


Figure 2. Nuclear magnetic resonance spectra at 100 MHz for bridgehead protons in bicyclo[4.2.0]octa-2,7-diene (**47**) at left, a mixture of 1,6-dideuterio- and 6-deuteriobicyclo[4.2.0]octa-2,7-diene (**46**) in the center, and, at the right, the mixture of **46** and **49** obtained through thermal rearrangement of **46** at 180°. The two hash marks in each tracing are at δ 3.24 and 3.12 ppm.

The allylic methyl C_6–*H* resonance at δ 3.05–3.2 and the doubly allylic C_1–*H* absorption at δ 3.2–3.35 observed for the unlabeled diene **47** appear in the labeled substrate **46** as a C_1–H signal of diminished intensity; the C_6–H absorption is absent (Figure 2).



Thermolysis of the dideuteriobicyclooctadiene **46** in the gas phase at 180° for 3 hr gave 55% cyclooctatriene and 45% starting material. The nmr spectrum of "starting material," however, after thorough purification by preparative glpc, showed a growth in absorption intensity for a C_6 proton, amounting to 27% of the total C_1–*H* plus C_6–*H* intensity (Figure 2). Thus the degenerate valence isomerization **46** → **49** does occur to a detectable extent.

Discussion

The 1,5-dimethylbicyclo[3.3.0]octa-2,6-diene system (**33**) failed to rearrange when heated to 350° for 11 hr. This result leads to the qualitative and tentative conclusion: the antara–antara Cope process converting **33** to the 3,7-dimethyl isomer may well require a comparatively high activation energy. Little of a more quantitative or conclusive nature may be said. Unanswered questions regarding the equilibrium mixture of the two isomers, detection limits for the isomer not observed and its stability with respect to other processes—questions which could have been answered only through synthesis of 3,7-dimethylbicyclo[3.3.0]octa-2,6-diene and further kinetic work—preclude definitive statements on the significance of the negative experiment at 350° or the fragmentations observed at 450°. A likely mode for rearrangement available to the dimethyl system **51** but not to the dideuteriobicyclooctadiene **26**, an intramolecular retroene process, could lead to a monocyclic triene **52** which, at 450°, might easily give rise to several additional isomers.

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(29) R. H. Shapiro and M. J. Heath, *J. Amer. Chem. Soc.*, **89**, 5736 (1967).

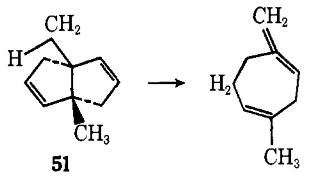
(30) G. Kaufman, F. Cook, H. Shechter, J. Bayless, and L. Friedman, *ibid.*, **89**, 5736 (1967).

(31) W. F. Gannon and H. O. House, *Org. Syn.*, 40, 41 (1960).

(32) W. F. Gannon and H. O. House, *ibid.*, 40, 14 (1960).

(33) O. L. Chapman, G. W. Bordon, R. W. King, and B. Winkler, *J. Amer. Chem. Soc.*, **86**, 2660 (1964).

(34) W. R. Roth and B. Peltzer, *Angew. Chem., Int. Ed. Engl.*, 3, 440 (1964).



51 **52**

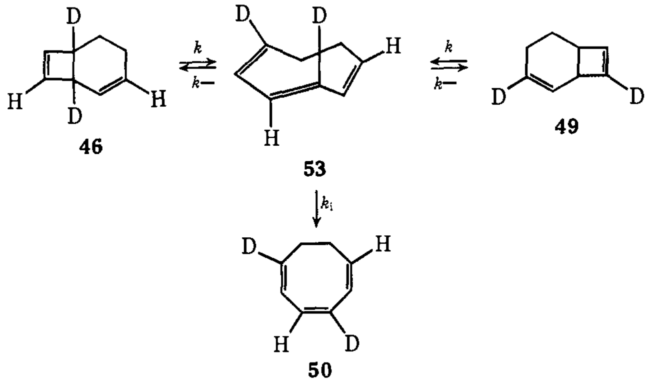
The "negative" experimental finding with the dideuterio substrate **26**, by contrast, may be treated much more surely. The equilibrium constant for the **26** ⇄ **28** interconversion as well as the detectability and stability with respect to other rearrangements for the unobserved product are known, thanks to the symmetry situtation obtaining for this degenerate process. Thus when, after 85 min at 450°, one recovers 91% of dideuteriobicyclo[3.3.0]octa-2,6-dienes, surely both **26** and **28** (if any) are collected, and the equilibrium has been approached from a thermodynamically feasible direction.

By making reasonable assumptions regarding detection limits and the preexponential Arrhenius term, a rough estimate of the minimum activation energy for the interconversion of **26** and **28** may be made. We assume that as little as 10% of **28** would have been seen; the 90:10 mixture of **26**:**28** would have given a 1.2:1 ratio of vinyl to bridgehead hydrogens in the nmr, a significant change from the original 1:1. Thus, the first-order rate constant for the isomerization at 450° must be less than 2×10^{-5} sec^{-1}. With a "normal" log A of 13, this corresponds to $E_a \approx 59$ kcal mol^{-1}. Compared with the "antara–antara Cope rearrangements" that are observed in bicyclic [3.2.0] and [4.2.0] systems, the bicyclo[3.3.0]octa-2,6-diene molecule would require at least 25 kcal mol^{-1} of additional activation energy! The magnitude of this difference in activation energy dwarfs the numerical imprecision of the estimate and unavoidably forces the issue: can the difference be associated with a mechanism available to the [3.2.0] and [4.2.0] dienes which, unlike the postulated antara–antara Cope process, is not accessible to the [3.3.0] dienes?

One alternative to the Cope explanation that discriminates in the proper sense between the various bicyclic dienes investigated is a mechanism based on initial conrotatory valence isomerization of the cyclobutene moiety to form a cis,trans,cis cyclic triene which then reverts to starting material, closes on the other cis double bond to give the rearranged bicyclic structure, or is converted irreversibly to the all-cis cyclic triene.

Scheme V, shown for the kinetically simple degenerate bicyclo[4.2.0]octa-2,7-diene case, is of course not appropriate for the [3.3.0] hydrocarbons which, lacking a cyclobutene unit, do not undergo this rearrangement.

Scheme V



The differential equations describing this situation, when subjected to the steady-state approximation d[**53**]/d$t \approx 0$, may be manipulated into the integrated forms shown, where all concentrations are in fractional terms, [**46**]t + [**49**]t + [**50**]t = 1; $k_0 \equiv (k_i k)/(k_i + 2k^-)$; and **50** includes all trienes, whatever the distribution of deuterium labels resulting from sequential 1,5-hydrogen shifts.

$$[\mathbf{46}]t = {}^1/_2(e^{-k_0 t} + e^{-kt})$$
$$[\mathbf{49}]t = {}^1/_2(e^{-k_0 t} - e^{-kt})$$
$$[\mathbf{50}]t = 1 - e^{-k_0 t}$$

From the data obtained for diene **46** at 180°, $k_0 = 0.75 \times 10^{-4}$ sec^{-1}. The ratio of relative peak intensities for C_1–H and C_6–H, 73:27, corresponds to a molar ratio **46**:**49** of 77:23 or to a fractional concentration of isomer **49** at the end of the pyrolysis of $0.23 \times 0.45 = 0.103$.

From the equations and the experimental data, $k = 1.3 \times 10^{-4}$ sec^{-1} and consequently $k_i/k^- = 2.7$.

In terms of the direct Cope rearrangement parallel first-order reaction scheme for these isomerizations

$$\mathbf{46} \underset{k_r}{\overset{k_r}{\rightleftarrows}} \mathbf{49}$$
$$\mathbf{46} \xrightarrow{k_t} \mathbf{50}$$
$$\mathbf{49} \xrightarrow{k_t} \mathbf{50}$$

the integrated rate expressions assume an identical form,[35] when $k' \equiv 2k_r + k_t$.

$$[\mathbf{46}]t = {}^1/_2(e^{-k_t t} + e^{-k' t})$$
$$[\mathbf{49}]t = {}^1/_2(e^{-k_t t} - e^{-k' t})$$
$$[\mathbf{50}]t = 1 - e^{-k_t t}$$

The rate constants derived are $k_t = 0.75 \times 10^{-4}$ sec^{-1} and $k_r = 0.28 \times 10^{-4}$; $k_t/k_r = 2.7$. Thus, either kinetic scheme is equally acceptable; a distinction between the two through accummulating additional or more precise kinetic data of the same kind is futile.

For the nondegenerate-substituted bicyclic[3.2.0]-hepta-3,6-dienes discussed above,[36] kinetic schemes with or without an intermediate cis,trans,cis cyclic triene are equally suitable; in one case, the product ratio would be determined by a partitioning of the intermediate, in the other by the relative rates of two parallel reactions of the bicyclic substrate.

The alternative mechanism outlined in Scheme V is properly discriminating between various kinds of bicyclic substrates, kinetically as adequate as the original direct Cope rearrangement hypothesis, and quite plausible in view of recent experimental findings. Thus, McConaghy and Bloomfield have shown that *cis*-bicyclo[4.2.0]oct-7-ene rearranges to *cis,trans*-1,3-cyclooctadiene which either recloses or isomerizes to *cis,-cis*-1,3-cyclooctadiene.[37] Photolysis of 1,3,5-cyclo-

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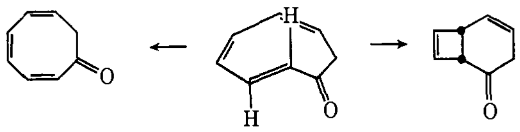
(35) Compare J. A. Berson, D. C. Tompkins, and G. Jones, II, *J. Amer. Chem. Soc.*, **92**, 5799 (1970).

(36) A. C. Day and M. A. Ledlie [*Chem. Commun.*, 1265 (1970)] have just reported that 1-hydroxybicyclo[3.2.0]hepta-3,6-dien-2-one undergoes a thermal rearrangement analogous to **1** → **2**.

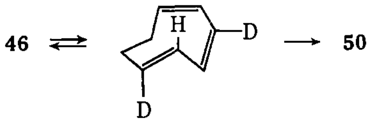
octatriene at 20°K in argon gives a strained isomer which reverts to starting material at room temperature.[38] The *cis,trans,cis*- and *trans,cis,cis*-trienes are likely structural formulations for this photoisomer. Cycloocta-2,4,6-trien-1-one at 77°K is photolyzed to the *trans,cis,cis*-trienone **54** which, on warming in the dark, gives both the *all-cis*-trienone **55** and bicyclo-[4.2.0]octa-2,7-dien-5-one (**56**).[39]



55 **54** **56**

The thermal behavior of **54** is an exact analogy to that postulated for the intermediate **53**.

The analogy also points toward another route to the triene **50** from labeled diene **46**; initial formation of the trans,cis,cis cyclic triene **57** could not give the deuterium scrambled and skeletally identical hydrocarbon **49**, but could continue to the *all-cis*-triene.



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Other circumstantial evidence that might favor interpretation of these rearrangements as occurring through short-lived cis,trans,cis cyclic trienes is being sought. Until further information is available, we favor this mechanism primarily because it does so naturally what the antara–antara Cope rearrangement rationale fails to do at all, namely, account for the great stability of bicyclo[3.3.0]octa-2,6-dienes with respect to this phenomenological rearrangement type. At the very least, the alternative mechanistic proposal here presented should serve to reopen discussion on the detailed course of one molecular rearrangement process. Such discussion has been lacking; the conversion may have been considered thoroughly understood and adequately systematized prematurely.

Experimental Section

Nuclear magnetic resonance spectra were recorded for solutions in deuteriochloroform on Varian A-60 or HA-100 instruments; mass spectra were secured on a CEC-110-21B spectrometer by Mrs. Mary Mitchell and Miss Susan Rottschaefer. Analytical and preparative glpc separations were done with Varian Aerograph A90-P3 and 1520 instruments using the following columns: A, 6 mm × 1 m Carbowax 20M, 20% on Chromosorb W; B, 10 mm × 6 m Carbowax 20M, 20% on Chromosorb W; C, 6 mm × 2.5 m β,β'-oxydipropionitrile, 21% on Chromosorb P; D, 6 mm × 2 m Carbowax 20M, 20% on non-acid-washed Chromosorb W; E, 6 mm × 1.5 m SE-30, 20% on 60–80 mesh Chromosorb W. The elemental analysis was done by Spang Microanalytical Laboratory, Ann Arbor, Mich.

Bicyclo[3.2.0]hept-2-en-6-one (11).[40] The crude bicyclic adduct from cyclopentadiene[41] and ketene was purified through the semicarbazone, mp 221–222° (lit.[40] mp 221–222°). Hydrolysis of the recrystallized semicarbazone, steam distillation, and distillation gave ketone **11**, bp 61–64° (20 mm) (lit.[40] bp 62–63.5° (20 mm)).

Bicyclo[3.3.0]oct-6-en-2-one (12) and Bicyclo[3.3.0]oct-6-en-3-one (13). Bicyclo[3.2.0]hept-2-en-6-one (1.08 g, 10 mmol) in 20 ml of chloroform and 15 ml of methanol was treated with excess ethereal diazomethane over 30 min at 0° with stirring. The progress of the reaction was monitored by glpc on column A at 135° as the reaction mixture was stirred at 0°; 5 hr after the addition of diazomethane, the starting material had disappeared. The reaction mixture was concentrated, and the bicyclic octenones were collected together on column B at 200°. The purified products amounted to 0.40 g. The isomeric bicyclic ketones were collected separately following another preparation on the same scale. The product of shorter retention time on column B at 200° proved to be bicyclo[3.3.0]oct-6-en-3-one (**13**) (247 mg): ir (film) 1730 cm^{-1}; nmr δ 2.0–2.25 (4 H, m, $-CH_2-$), 2.5–2.7 (3 H, m, allylic $-CH_2-$ and bridgehead H), 3.4–3.7 (1 H, m, allylic bridgehead H), 5.6–5.75 (2 H, broad s, vinyl); mass spectrum, *m/e* 122 (M$^+$). The ketone of longer retention time was the isomeric bicyclo[3.3.0]oct-6-en-2-one: ir (film) 1735 cm^{-1}; nmr δ 1.7–3.15 (7 H, m, $-CH_2-$ and bridgehead), 3.20–3.65 (1 H, m, allylic methine), 5.5–5.9 (2 H, broad s, vinyl); mass spectrum, *m/e* 122 (M$^+$).

Deuterium Exchange in Bicyclo[3.3.0]oct-6-en-2-one (12). The isomerically pure ketone (0.82 g), 7 ml of dry tetrahydrofuran, 2 ml of deuterium oxide, and a few milligrams of potassium carbonate were combined and heated to reflux under a drying tube. The reaction mixture was cooled, concentrated, and extracted (two 10-ml portions) with ether. The extracts were dried over magnesium sulfate, filtered, and concentrated. The nmr spectrum of the ketone **17** showed a diminished relative intensity of the multiplet at δ 1.7–3.15, from 7 H in the unlabeled ketone to 4.2 H in the exchanged product.

Bicyclo[3.3.0]oct-6-en-2-ol (14) and Bicyclo[3.3.0]oct-6-en-3-ol (15).[8] The purified mixture of bicyclo[3.3.0]oct-6-en-2-one and its 3-one isomer (0.40 g, 3.26 mmol) in 4 ml of dry ether was added over 20 min to 114 mg (3 mmol) of lithium aluminum hydride in 10 ml of ether under a nitrogen atomsphere with stirring. Following the addition, the reaction mixture was stirred at reflux 40 min and then cooled and quenched with 0.11 ml of water, 0.11 ml of 15% sodium hydroxide, and 0.34 ml of water. The resultant mixture was centrifuged; the ethereal layer was decanted, dried over magnesium sulfate, filtered, and concentrated to afford 0.27 g of product. Extraction of the precipitated salts with ether from a soxhlet thimble for 6 hr led to another 85 mg of alcohols; ir (film) 3400 cm^{-1}. The total yield was 0.35 g (87%); yields as high as 95% were realized in other runs.

Bicyclo[3.3.0]oct-6-en-2-yl and -3-yl Xanthates.[42] In a 25-ml round-bottomed flask equipped with magnetic stirrer, reflux condenser, drying tube, and dropping funnel was placed 74 mg (3.5 mmol) of sodium hydride in 10 ml of ether. The mixture of bicyclo-[3.3.0]oct-6-en-2-ols and -3-ols secured above (0.35 g, 2.84 mmol) in 2 ml of ether was added dropwise with stirring. After the addition, the reaction mixture was heated to reflux for 9 hr. After 3 hr of this period, 0.23 g (3 mmol) of carbon disulfide was added by syringe; after 6 hr, 0.43 g (3 mmol) of methyl iodide was added. The reaction mixture was cooled to room temperature and treated with 1 ml of water to dissolve some solid material. The ethereal layer was separated, washed with 0.5 ml of water, dried over magnesium sulfate, filtered, and concentrated; 0.51 g of yellow oil was obtained. Continuous extraction of the aqueous material with ether overnight gave another 40 mg of crude xanthate.

The infrared spectrum of the 0.55 g of product showed a sharp vinyl C-H stretching band at 3050 cm^{-1}, a $S-CH_3$ band at 1220 cm^{-1} (s), and C=S at 1060 cm^{-1} (s).

Bicyclo[3.3.0]octa-2,6-diene (16).[8] The crude mixture of xanthate esters obtained above (0.54 g) was placed in a microdistillation apparatus (Kontes Bantam-ware, No. K-284500). The oil bath was heated to 180° as the trap was cooled in Dry Ice–isopropyl alcohol. At 180–220°, gas evolved and a liquid product (215 mg) was collected over a 30-min period. Analysis by glpc on column A at 75° or column C at 70° revealed only one peak. The product bicyclo[3.3.0]octa-2,6-diene (**16**) was purified by preparation glpc on column A; it had a molecular ion peak at *m/e* 106 (C_8H_{10}) and spectral properties in agreement with literature citations.[8,9] The nmr spectrum in particular reveals the absence of the isomeric

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[37] J. S. McConaghy, Jr., and J. J. Bloomfield, *Tetrahedron Lett.*, 3719, 3723 (1969).

[38] P. Datta, T. D. Goldfarb, and R. S. Boikess, *J. Amer. Chem. Soc.*, **91**, 5429 (1969).

[39] L. L. Barber, O. L. Chapman, and J. D. Lassila, *ibid.*, **91**, 531 (1969).

[40] A. T. Blomquist and J. Kwiatek, *J. Amer. Chem. Soc.*, **73**, 2098 (1951).

[41] M. Korach, D. R. Nielsen, and W. H. Rideout, *Org. Syn.*, **42**, 50 (1962).

[42] Compare J. D. Roberts and C. W. Sauer, *J. Amer. Chem. Soc.*, **71**, 3925 (1949).

$\Delta^{2,7}$-diene: nmr σ 2.0–3.0 (4 H, m, methylene), 3.2–3.6 (2 H, m, allylic methine), 5.4–5.7 (4 H, broad singlet with some splitting, vinyl).

A variable-temperature nmr examination of bicyclo[3.3.0]octa-2,6-diene in α-chloronaphthalene gave no evidence for a degenerate rearrangement. The degassed sample showed the normal sharpening of peaks at temperatures up to 180°—nothing more.

3-Deuteriobicyclo[3.3.0]octa-2,6-diene (18). Isomerically pure bicyclo[3.3.0]oct-6-en-3-one, separated from the 2-one and purified by preparative glpc on column B at 200°, was reduced with lithium aluminum deuteride; the 3-deuterio-3-ol was converted to the xanthate ester and pyrolyzed, following the techniques used in the unlabeled series. From 247 mg of the ketone there was obtained 391 mg of xanthate. In another run, 920 mg of the 3-one gave 1.25 g of the ester. Pyrolysis of the first sample gave 140 μl of crude 95% pure 3-deuteriobicyclo[3.3.0]octa-2,6-diene. The second, larger sample gave diene which, after purification by glpc, amounted to 325 mg: nmr δ 2.0–2.9 (4 H, m, methylene), 3.2–3.6 (2 H, m, allylic methine), 5.4–5.7 (3 H, broad singlet, vinyl).

Pyrolysis of 3-Deuteriobicyclo[3.3.0]octa-2,6-diene. Several 5–10-μl samples of 3-deuteriobicyclo[3.3.0]octa-2,6-diene were degassed and sealed in acid- and base-washed capillary tubes to produce pyrolysis tubes 10–12 cm in length. The tubes were heated at 340–360° for 2 hr. The tubes were cooled and crushed in a vial containing 0.2 ml of ether. Analysis by glpc in column D at 115° showed only one volatile component other than ether. Collection of this peak and analysis by nmr in a capillary tube showed the glpc recovered material to be identical with the starting material. Several nmr integrations of the vinyl to methine peak areas gave 1.70 ± 0.06; the sample, before pyrolysis, showed a vinyl to methine peak area of 1.55 ± 0.05.

2,4,6,8-Tetramethoxycarbonylbicyclo[3.3.0]octa-3,7-dione (23).[43] Vossen's red salt[19] (40 g), 400 ml of water, 640 g of ice, and 800 ml of ether in a 5-l. three-necked round-bottomed flask was cooled in an ice bath and stirred mechanically. A few drops of 10% sulfuric acid was added to bring the pH to 3–4. An amalgam prepared from sodium (1.5 g) and mercury (585 g) was added in 2 min; the pH of the stirred reaction mixture was maintained at 3–4 for 2 hr, then brought to pH 1. The mercury was separated, and the aqueous layer was extracted with four 500-ml portions of ether. The ethereal extracts were dried over sodium sulfate, filtered, and concentrated to about 100 ml. The material separated from the concentrate after 12 hr in a freezer amounted to 21.6 g. An additional 3.2 g was secured through concentration of the mother liquor, trituration with ether, and recrystallization from methanol.

Another approach to dione **23**, condensation of dimethyl β-oxoglutarate with glyoxal,[21] was realized in 4% yield.

Bicyclo[3.3.0]octa-3,7-dione (24), mp 85–86° [lit.[19] mp 84–86°], was obtained in 97.5% yield through hydrolysis and decarboxylation of **23**.

3,7-Dideuteriobicyclo[3.3.0]octa-3,7-diol (25). Bicyclo[3.3.0]-octa-3,7-dione (2.76 g, 0.02 mol), dissolved in 50 ml of dry ether and 15 ml of tetrahydrofuran, was added dropwise to a stirred suspension of 840 mg (0.02 mol) of lithium aluminum deuteride in 25 ml of ether under nitrogen. The reaction mixture was worked up in the usual manner to give 2.81 g (98%) of an oil having an infrared spectrum appropriate to the diol; ir (film) 3300, 3400, 2260 cm^{-1}.

3,7-Dideuteriobicyclo[3.3.0]octa-2,6-diene (26) and 3,7-Dideuteriobicyclo[3.3.0]octa-2,7-diene (27). The crude dideuteriodiol (2.81 g) was converted and detailed above for the unlabeled case to the dixanthate, obtained as 4.3 g of foul smelling oil having the expected infrared spectral properties. Pyrolysis of the dixanthate at 180–220° gave 1.20 g of yellow liquid. Analysis by glpc on column C at 75° showed that the diene product was contaminated with traces of low boiling materials and some 25% of tetrahydrofuran, carried over from the previous step. Purified diene had infrared and nmr spectral characteristics appropriate to a mixture of $\Delta^{2,7}$- and $\Delta^{2,6}$-3,7-dideuteriobicyclo[3.3.0]octadiene (Figure 1).

Pyrolysis of 3,7-Dideuteriobicyclo[3.3.0]octa-2,6-diene. A base-washed 50-ml pyrolysis tube made from 22-mm Pyrex tubing was charged with 30 μl of the mixture of $\Delta^{2,6}$- and $\Delta^{2,7}$-dienes. The tube was degassed, sealed, and heated at 360° for 12 hr. The recovered sample was identified as starting material by nmr analysis. Another 30-μl sample heated at 450° for 85 min was recovered and analyzed on column D at 75°; 9% decomposition had occurred, 91% of the starting material remained. The latter was collected and purified by glpc and examined by nmr spectroscopy; the spectral characteristic of the pyrolyzed bicyclo[3.3.0]octadiene was indistinguishable from that of the starting mixture.

Dimethyl β-Oxoglutarate. The procedure of Findlay,[44] an improved version of the classic Adams prescription,[45,46] was followed in converting 96 g of dried citric acid to dimethyl β-oxoglutarate, bp 85° (1 mm), 48 g (55%).

1,5-Dimethyl-2,4,6,8-tetramethoxycarbonylbicyclo[3.3.0]octa-3,7-dione (29), obtained from dimethyl β-oxoglutarate and butanedione[21] in 49% yield, was sublimed at 140° (0.4 mm) and had mp 147–150° (lit.[21] mp 144–146°).

1,5-Dimethylbicyclo[3.3.0]octa-3,7-dione (30),[21] through hydrolysis of **29**, was secured in 88% yield. Sublimation gave colorless crystals of ill-defined melting point; the material became transparent in polarized light at about 158°, yet still appeared partially solid at 180° (lit.[21] mp 167–169°, not well defined).

1,5-Dimethylbicyclo[3.3.0]octa-3,7-diol (31). 1,5-Dimethylbicyclo[3.3.0]octa-3,7-dione (1.66 g, 0.01 mol) dissolved in 50 ml of anhydrous ether was added under nitrogen over 40 min to a stirred, refluxing solution of lithium aluminum hydride (0.38 g, 0.01 mol) in 25 ml of ether. After the addition, the solution was stirred at reflux another 90 min, cooled, and quenched through the sequential addition of 0.38 ml of water, 0.38 ml of 15% sodium hydroxide, and 1.14 ml of water. Filtration and concentration of the filtrate gave 1.04 g of white powder. Extraction of the salts precipitated through the quenching sequence with ether for 5 hr in a soxhlet led to an additional 0.32 g of diol. The total yield, 1.36 g, was 81% of theory; ir (film) 3300 cm^{-1}; mp (one recrystallization from $CHCl_3$) 141–145°.

1,5-Dimethylbicyclo[3.3.0]octa-2,6- and -2,7-diene. Dehydration of 1,5-dimethylbicyclo[3.3.0]octa-3,7-diol (**31**) through pyrolysis of its dixanthate ester was done in the usual manner. The diol (1.36 g) gave rise in turn to 3 g of crude dixanthate, contaminated with tetrahydrofuran, and to 0.51 g of mixed dienes. According to the glpc analysis, column C, this material was a 90–95% mixture of the $\Delta^{2,7}$-diene **32** (shorter retention time) and the $\Delta^{2,6}$-isomer **33**, mass spectrum *m/e* 134 (M^+). Spectral data for the glpc purified and collected dienes are given in the Discussion.

Pyrolysis of 1,5-Dimethylbicyclo[3.3.0]octa-2,6-diene. Several 10-μl samples of diene **33** were degassed, sealed in 12 cm × 1.5 mm capillary tubes, and heated at 340–360° for as long as 11 hr. The pyrolyzed hydrocarbon samples showed no change according to nmr analyses.

A 4-μl sample of **33** was degassed, sealed in a base-washed 18 cm × 7 mm tube, and heated at 450° for 70 min. Analysis of the pyrolysis mixture by glpc on column C at 80° showed the starting material and five new peaks of longer retention time.

1-Methoxybicyclo[3.2.0]hepta-3,6-dien-2-one (1a). A pure sample of diene **1a** was prepared from the photolysis of tropolone methyl ether[47] as described by Chapman and Dauben.[48] The diene was purified by preparative glpc using column A at 200°: ir ($CHCl_3$) 1710 cm^{-1}; HA-100 nmr δ 3.45 (3 H, s, $-OCH_3$), 3.85 (1 H, doublet of doublets, *J* = 3, <0.5 Hz, C_5–H), 6.1 (1 H, doublet *J* = 6 Hz, C_3–H), 6.35 (1 H, doublet, *J* = 3 Hz, C_7–H), 6.73 (1 H, doublet of doublets, *J* = 3, <0.5 Hz, C_6–H), 7.5–7.65 (1 H, doublet of doublets, *J* = 6, 3 Hz, C_4–H).

Rearrangement of 1a. A sample of glpc-purified dienone **1a** was dissolved in 250 μl of deuteriochloroform freshly distilled from potassium carbonate. The sample was placed in an nmr tube, degassed, and sealed. The tube was heated to 190° for various lengths of time and analyzed by nmr spectroscopy. Integration of the methoxyl proton areas for **1a**, **2a**, and **3a** at δ 3.45, 3.72, and 3.95 gave kinetic data in good accord with the assumed scheme.[22]

1-Ethoxybicyclo[3.2.0]hepta-3,6-diene (36).[26] The diene **36** was prepared in 94% yield (95% pure) by photolysis of 7-ethoxycycloheptatriene.[23–25] The glpc-purified material (column E at 110°) showed: ir (film) 3050, 2990, 2870, 1300, 1210, 1173, 1125, 1088, 785, 715 cm^{-1}; nmr δ 1.1–1.4 (3 H, t, $-OCH_2CH_3$), 2.5 (2 H, d, methylene), 3.4–3.8 (3 H, overlapping quartet and multiplet, OCH_2 and methine), 5.8 (2 H, s, cyclopentene vinyl), 6.3–6.4 (2 H, AB quartet, *J* = 3 Hz, cyclobutene); λ_{max}^{EtOH} 297 (ε 40), 283 (59), 274 (81), 258 (106).

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Pyrolysis of 1-Ethoxybicyclo[3.2.0]hepta-3,6-diene. Tubes of approximately 1.5-ml volume from 6-mm Pyrex tubing were washed, rinsed with dilute ammonia, and dried. Each tube was charged with 5 μl of 1-ethoxybicyclo[3.2.0]hepta-3,6-diene containing 10% toluene as an internal standard. The tubes were degassed and sealed at 10^{-3} mm. The pyrolyses at 170° were monitored by glpc using column E at 110°. Integration of peak areas with a planimeter gave kinetic data in good accord with expectations.[22]

Pyrolysis of 1-Ethoxycycloheptatriene. A 20-μl sample of 1-ethoxycycloheptatriene, shown by glpc analysis on column E to be at least 99% pure, was heated in a sealed tube at 170° for 10.8 hr. Analysis by glpc and nmr showed complete survival of the triene.

Pyrolysis of 3-Ethoxybicyclo[3.2.0]hepta-2,6-diene. A 7-μl sample of this diene, collected by glpc from the pyrolysis of 1-ethoxybicyclo[3.2.0]hepta-3,6-diene, was degassed and sealed at 10^{-3} mm in a 1.2-ml tube. Pyrolysis at 190° for 2.5 hr resulted in conversion of the starting material to 2% 1-ethoxybicyclo[3.2.0]hepta-3,6-diene, and 8% 1-ethoxycycloheptatriene; 90% of the original 3-ethoxybicyclo[3.2.0]hepta-2,6-diene remained unreacted.

Product from Pyrolysis of 1-Ethoxybicyclo[3.2.0]hepta-3,6-diene (36). The major product from the pyrolysis was identified as 1-ethoxycycloheptatriene (**35**) by nmr and ultraviolet data: $\lambda_{\max}^{\mathrm{EtOH}}$ 287 nm (ϵ 4510); nmr δ 1.2–1.4 (3 H, t, -OCH$_2$*CH*$_3$), 2.5–2.6 (2 H,d, C$_7$–H), 3.7–4.0 (2 H, q, OCH$_2$–), 5.3–5.6 (2 H, m, vinyl), 6.1–6.6 (3 H, m, vinyl).

The minor product was identified as 3-ethoxybicyclo[3.2.0]-hepta-2,6-diene (**37**) by mass spectral, ultraviolet, and nmr data; mass spectrum *m/e* 136 (M$^+$); $\lambda_{\max}^{\mathrm{EtOH}}$ 297 (ϵ 20), 282 (32), 275 (24), 258 (33); nmr (CCl$_4$) δ 1.2–1.4 (3 H, t, OCH$_2$*CH*$_3$), 2.1–2.4 (2 H, m, methylene), 3.1–3.3 (1 H, m, C-1 methine), 3.5–3.8 (3 H, m, O*CH*$_2$- and C-5 methine), 5.4–5.5 (1 H, m, C-4 vinyl), 5.95 and 6.2 (2 H, AB quartet, J = 3 Hz, cyclobutene vinyl). Hydrolysis of a sample of 3-ethoxybicyclo[3.2.0]hepta-2,6-diene in CDCl$_3$ with dilute HCl (30 min at room temperature) gave bicyclo[3.2.0]hept-6-en-3-one:[49] ir (CDCl$_3$) 1740 (C=O); nmr δ 2.2–2.4 (4 H, m, methylene), 3.4–3.6 (2 H, m, methine), 6.2 (2 H, s, vinyl); mass spectrum *m/e* 108 (M$^+$).

2,2-Dideuteriocyclohexane-1,3-dione (39). An 11.2-g sample of 1,3-cyclohexanedione (Aldrich) was placed in 20 ml of D$_2$O and stirred for 1 hr. The reddish solution obtained was extracted (three 20-ml portions) with chloroform. The chloroform extracts were combined and dried over MgSO$_4$. Filtration and concentration of the filtrate afforded 9.1 g of material containing 80% deuterium at C$_2$ by nmr analysis. Two cycles gave 7.9 g of material containing 95% deuterium at C$_2$.

2-Deuterio-3-ethoxycyclohex-2-enone (40). A solution of 10.8 g of 2,2-dideuteriocyclohexane-1,3-dione and 0.47 g of *p*-toluenesulfonic acid in 51 ml of *O*-deuterioethanol[50] and 185 ml of benzene was heated and concentrated by distillation over a 6-hr period. The residual yellow liquid was washed with four 15-ml portions of 10% sodium hydroxide saturated with sodium chloride. The organic layer was washed free of base with seven 10-ml portions of water. Concentration of the solution under vacuum followed by vacuum distillation of the residue gave 10.95 g (82.5%) of **40**, bp 69° (0.1 mm). Analysis by nmr and comparison with unlabeled material[31] showed 65% deuterium incorporation at C$_2$ (δ 5.3).

2,3-Dideuteriocyclohex-2-enone (41). A solution of 10.8 g (0.077 mol) of 2-deuterio-3-ethoxycyclohex-2-enone in 15 ml of dry ether was added dropwise to a mixture of 1.48 g (0.039 mol) of lithium aluminum deuteride (Stohler) in 50 ml of ether. The reaction and work-up, conducted as described for the preparation of the unlabeled prototype,[32] gave 3.05 g of product, bp 60–62° under aspirator vacuum. Analysis by nmr and comparison with unlabeled material[32] showed 60% deuterium at C$_2$ and 100% deuterium at C$_3$.

1,6-Dideuteriobicyclo[4.2.0]oct-7-en-2-one (44).[28] The photoadduct **42** was synthesized using 2,3-dideuteriocyclohex-2-enone in the same manner as the unlabeled substrate[28] in 77% yield. Formation of the ketal **43** followed by the published elimination reaction[28] using sodium dihydronaphthylide gave an 18% overall yield (from 2,3-dideuteriocyclohex-2-enone) of liquid, bp 45° (1 mm) (lit.[28] bp 71–75° (8.5 mm)).

1,6-Dideuterio-2-tosylhydrazonobicyclo[4.2.0]oct-7-ene (45). A 0.70-g (5.64-mmol) sample of pure 1,6-dideuteriobicyclo[4.2.0]-oct-7-en-2-one dissolved in 5 ml of anhydrous methanol was heated just to reflux and 1.05 g (5.64 mmol) of tosylhydrazine (Aldrich; recrystallized from benzene) was added. Upon cooling, the solution deposited 1.38 g (84%) of the colorless tosylhydrazone derivative, mp 145–148°.

1,6-Dideuteriobicyclo[4.2.0]octa-2,7-diene (46). A 100-ml three-necked flask equipped with gas inlet, mechanical stirrer, and dropping funnel was charged with 584 mg (2.0 mmol) of the deuterated tosylhydrazone and 10 ml of dry ether. To the stirred suspension of tosylhydrazone in ether under nitrogen was added dropwise at room temperature 4 ml of 1.2 *M* methyllithium in ether (Alfa). The suspension turned orange and gas was evolved. Some 30 min after the addition the reaction mixture was chilled in an ice bath and diluted cautiously with 3 ml of water. The colorless two-phased system was filtered, and the two layers of the filtrate were separated. The ethereal solution was dried (MgSO$_4$), filtered, and concentrated by careful distillation through a 10-cm Vigreux column. The residue showed a single major component when analyzed by glpc on column E at 90°. A total of 70 mg (32.5%) of the deuterated diene was collected in pure form through preparative glpc: nmr δ 1.2–2.1 (4 H, m, methylene), 3.2–3.35 (0.53 H, broad singlet, C$_1$–H), 5.7–5.9 (3 H, m, vinyl), 6.0–6.15 (1 H, d, vinyl).

Bicyclo[4.2.0]octa-2,7-diene (47). The same sequence employed to prepare labeled diene **46** was used to produce **47**. The unlabeled tosyhydrazone analogous to **45** was recrystallized from methanol and had mp 146–149°.

Anal. Calcd for C$_{15}$H$_{18}$N$_2$SO$_2$: C, 62.02; H, 6.24. Found: C, 62.21; H, 6.34.

The diene **47** produced from the tosylhydrazone by the Shapiro-Shechter[29,30] sequence had an identical nmr spectrum with that reported in the literature[33] for **47** prepared by photolysis of 1,3,5-cyclooctatriene.

Pyrolysis of Bicyclo[4.2.0]octa-2,7-diene.[34] A 6 mm × 17-cm pyrolysis tube was base washed, dried, and charged with 3 μl of unlabeled bicyclo[4.2.0]octa-2,7-diene. The sample was degassed and sealed at 10^{-5} mm. The 10-cm long sealed tube was heated at 180° for 1 hr, cooled, and opened. The recovered hydrocarbons, 2.9 μl, were analyzed by glpc on column E at 90°. The analysis showed starting material and one new product (21%) which was collected. The collected material from several runs was identified as 1,3,5-cyclooctatriene through nmr spectroscopy: nmr δ 2.4 (4 H, broad singlet with some additional splitting), 5.6–6.0 (6 H, m).

Gas-Phase Pyrolysis of 1,6-Dideuteriobicyclo[4.2.0]octa-2,7-diene. A 70-mg sample of labeled diene **46** was transferred on a vacuum line at 10^{-5} mm to a 200-ml break-seal flask, degassed, and sealed. The diene was heated at 180° for 3 hr, cooled, and transferred again on the vacuum line to a small collector. Analysis of the colorless pyrolysate by glpc (column E, 90°) showed 55% of a new product having the retention time of 1,3,5-cyclooctatriene and appropriate nmr signals: nmr δ 2.4 (1.26, broad singlet), 5.6–6.0 (1.00, m). The peak corresponding to starting material was collected by glpc and transferred on the vacuum line to an nmr tube containing 0.25 ml of 1:1 ethanol-free chloroform-deuteriochloroform. The nmr spectrum of this sample showed a new upfield shoulder at δ 3.05–3.2 which was not present before pyrolysis (Figure 2).

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