(hexane solution) in 110 ml of THF. The reaction mixture was stirred at room temperature for 19 hr and at 57° for 7 hr and the product was isolated with ether and purified by chromatography on 50 g of Fisher Alumina. The combined pentane fractions yielded 750 mg (76%) of olefins **25** and **26**, a 1:1 mixture according to the gas chromatogram. This mixture was separated by preparative gas chromatography to give the *trans*-hydroazulene **23**: $\delta_{\text{TMS}}^{\text{CCl}_4}$ 4.75 (vinyl H's) and 1.03 ppm ($CH_3$). *Anal.* Calcd for $C_{12}H_{20}$: C, 87.71; H, 12.29. Found: C, 87.9; H, 12.1.

The *cis*-hydroazulene **24** exhibited $\delta_{\text{TMS}}^{\text{CCl}_4}$ 4.69 (vinyl H's) and 0.73 ppm ($CH_3$). *Anal.* Calcd for $C_{12}H_{20}$: C, 87.71; H, 12.29. Found: C, 87.7; H, 12.2.

**Acknowledgments.** We are grateful to the National Institutes of Health for a predoctoral fellowship (FOl GM 41066 to W. F. H.) and the National Science Foundation for a research grant (GP 16234).

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# The Generation and Isomerization of *cis,trans,cis*-1,3,5-Cyclooctatriene at 180°[1]

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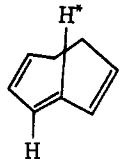
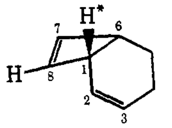
*Contribution from the Department of Chemistry, University of Oregon, Eugene, Oregon 97403.* *Received November 18, 1971*

**Abstract:** The Diels–Alder adduct from *cis,trans,cis*-1,3,5-cyclooctatriene and furan, *trans*-13-oxatricyclo-[8.2.1.0$^{2,9}$]trideca-3,7,11-triene, has been synthesized indirectly and pyrolyzed at 180°. The distributions of products, bicyclo[4.2.0]octa-2,7-diene and *cis,cis,cis*-1,3,5-cyclooctatriene, as a function of reaction time demonstrate that the initial detectable product is bicyclo[4.2.0]octa-2,7-diene. The putative initially formed $C_8$ hydrocarbon, *cis,trans,cis*-1,3,5-cyclooctatriene, is not directly partitioned between bicyclic and monocyclic isomers; it may lie along the reaction path of the degenerate bicyclo[4.2.0]octa-2,7-diene valence isomerization, but not on the path of the bicyclo[4.2.0]octa-2,7-diene to 1,3,5-cyclooctatriene conversion.

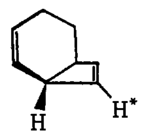
Two mechanistic problems are posed by the thermal isomerizations of bicyclo[4.2.0]octa-2,7-diene (**1**).



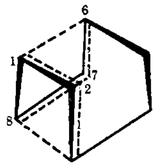
**2**



**1**



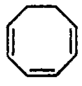
**1′**



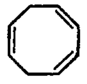
**3**

The automeric valence isomerization of this system may occur by way of *cis,trans,cis*-1,3,5-cyclooctatriene (**2**),[2,3] or possibly through a direct concerted cycloreaction, an antara,antara Cope rearrangement[4,5] with an orbital symmetry allowed transition-state electronic structure **3**.[6]

The isomerization of the bicyclic diene **1** to *cis,cis,cis*-1,3,5-cyclooctatriene (**4**)[7] might involve a direct disrotatory and orbital symmetry disallowed cyclobutene to butadiene valence isomerization, or some more subtle but symmetry-allowed pathway, such as an s,a intramolecular cycloaddition of C(1)–C(2) with C(6)–C(7),[8] or the intermediacy of *cis,trans,cis*-triene **2**. The latter might give *all-cis*-triene either through trans,cis isomerization of the strained double bond, or through 1,5-hydrogen migrations and another isomer, the *all-cis*-1,3,6-triene **5**.[7,9]



**4**



**5**

In the present work *cis,trans,cis*-1,3,5-cyclooctatriene has been generated at 180° and found to give bicyclo-[4.2.0]octa-2,7-diene (**1**), exclusively.

## Results

Synthesis of a thermally labile precursor of *cis,trans,-cis*-1,3,5-cyclooctatriene that would decompose at a convenient rate at 180° was desired.

In earlier work with deuterium-labeled bicyclo[4.2.0]-octa-2,7-dienes,[2,3] in which rates of deuterium scrambling and skeletal rearrangement to cyclooctatriene **4** were determined at 180°, there existed data sufficient for predicting quantitatively molar fractions of **1** and **4** as a function of time, given the rate at which *cis,trans,cis*-triene was produced. Thus, with a suitable precursor, the thermal behavior of *cis,trans,cis*-1,3,5-cyclooctatriene

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(1) Supported by the National Science Foundation, the Cities Service Oil Co., and the Du Pont Co.

(2) J. E. Baldwin and M. S. Kaplan, *Chem. Commun.*, 1560 (1970).

(3) J. E. Baldwin and M. S. Kaplan, *J. Amer. Chem. Soc.*, **93**, 3969 (1971).

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

(5) T. Miyashi, M. Nitta, and T. Mukai, *J. Amer. Chem. Soc.*, **93**, 3441 (1971).

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

(7) W. R. Roth and B. Peltzer, *ibid.*, 3, 440 (1964).

(8) Compare J. E. Baldwin and A. H. Andrist, *J. Amer. Chem. Soc.*, **93**, 4055 (1971); J. E. Baldwin, A. H. Andrist, and R. K. Pinschmidt, Jr., *ibid.*, in press.

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

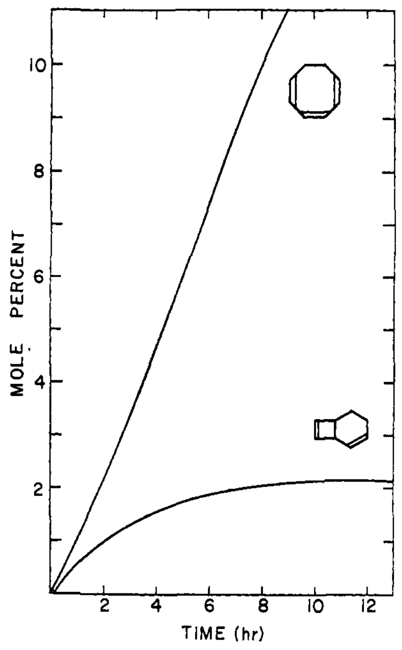
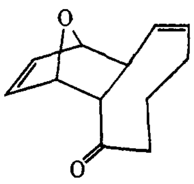


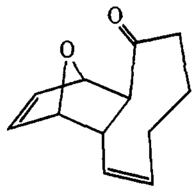
Figure 1. Mole percentages of diene **1** and triene **4** calculated according to Scheme I.

could be compared against theory, without the flexibility of a single disposable parameter.

Such a precursor was found and readily synthesized, taking advantage of the reported Diels–Alder adducts of furan and *trans,cis*-cycloocta-2,4-dien-1-one (**6**, **7**).[10]



**6**



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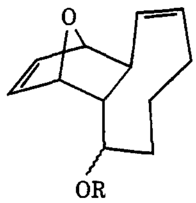

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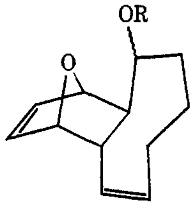
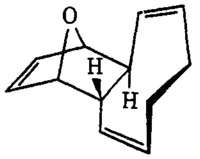


**9**

**a**, R = H
**b**, R = $CS_2CH_3$

These were prepared and then reduced with lithium aluminum hydride, and the mixture of alcohols (**8a**, **9a**) was converted to the corresponding xanthates (**8b**, **9b**). Pyrolysis of the xanthates at 200°, followed by preparative glpc, gave the Diels–Alder adduct of furan and *cis,trans,cis*-1,3,5-cyclooctatriene, *trans*-13-oxatricyclo-[8.2.1.$0^{2,9}$]trideca-3,7,11-triene (**10**).

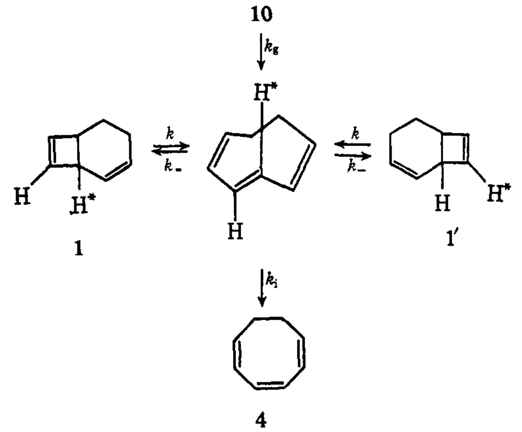


**10**

At 180°, triene **10** was found to decompose with a first-order rate constant equal to $4.2 \times 10^{-6}$ sec$^{-1}$. The observable decomposition products, bicyclo[4.2.0]octa-2,7-diene (**1**) and *all-cis*-cyclooctatriene (**4**), were identified through glpc and mass spectrometric comparisons against authentic samples.[11,12]

According to the mechanism in which *cis,trans,cis*-triene (**2**) is the intermediate in both the automeric and skeletal isomerizations of diene **1**, the partitioning ratio should be $2k_-/k_i$ (Scheme I).

**Scheme I**



From earlier work,[2,3] $k_i/k_- = 2.7$, and thus the initial product ratio from the partitioning of *cis,trans,cis*-triene **2** should be **1**/**4** = $2k_-/k_i = 0.74$. As the reaction giving *cis,trans,cis*-triene proceeds, and the isomerization **1** → **4** ($k_t = 0.75 \times 10^{-4}$ sec$^{-1}$)[3] occurs as well, the proportion of bicyclic **1** in the product mixture will decrease. Figure 1 gives the calculated percentages of **1** and **4**, based on Scheme I and $k_g = 4.2 \times 10^{-6}$ sec$^{-1}$.

If *cis,trans,cis*-triene **2** is intermediate for the **1** ⇌ **1'** equilibration, but does not give **4** directly, then Scheme II would apply. The initial mole fraction **1**/(**1** + **4**) would be 1.0, and it would decrease in a way characteristic of two consecutive first-order reactions.

**Scheme II**

$$\mathbf{10} \xrightarrow{k_g} \mathbf{2} \xrightarrow{\text{fast}} \mathbf{1} \xrightarrow{k_t} \mathbf{4}$$

The product ratios at low conversions were obtained using a capillary vpc column and flame-ionization detection. From the rate of decomposition of adduct **10**, the product ratios were converted into percentages; the results are listed in Table I and portrayed together with the predictions of Scheme II in Figure 2.

Table I. Mole Per Cent Data for Bicyclo[4.2.0]octa-2,7-diene (**1**) and 1,3,5-Cyclooctatriene (**4**), through Pyrolysis of Adduct **10** at 180°

| Time, hr | Diene **1**, % | Triene **4**, % |
|---|---|---|
| 1.5 | 1.7 | 0.6 |
| 2.5 | 2.5 | 1.3 |
| 5.0 | 3.9 | 3.4 |
| 5.0 | 4.2 | 3.1 |
| 11.0 | 4.9 | 10.4 |

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[10] T. S. Cantrell and J. S. Solomon, *J. Amer. Chem. Soc.*, **92**, 4656 (1970).

[11] O. L. Chapman, G. W. Bordon, R. W. King, and B. Winkler, *ibid.*, **86**, 2660 (1964).

[12] A. C. Cope, C. L. Stevens, and F. A. Hochstein, *ibid.*, **72**, 2510 (1950).

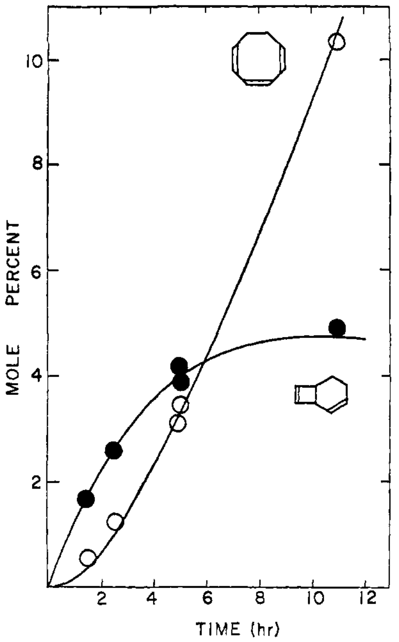


Figure 2. Mole percentages of diene **1** and triene **4** calculated according to Scheme II (solid lines) and experimental data (circles).

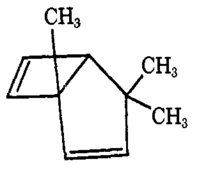
## Conclusions

The agreement between calculated and observed percentages of diene **1** and triene **4** produced through thermolysis of the furan plus *cis,trans,cis*-1,3,5-cyclooctatriene Diels–Alder adduct (Figure 2) is excellent, and there are clear differences between the observed kinetic behavior and that predicted according to Scheme I (Figure 1). The conclusion is, thermolysis of **10** gives **1**, and not both **1** and **4** in the ratio predicted for the common intermediate mechanism of Scheme I.

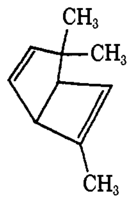
There is of course no conclusive evidence for generation of *cis,trans,cis*-1,3,5-cyclooctatriene from adduct **10**. The Diels–Alder retrogression **10** → **2** + furan is thermally allowed, and the conrotatory isomerization **2** → **1** is allowed: were the overall conversion to be achieved in a single step, the process could be formalized as an orbital-symmetry allowed but heretofore unexampled and unpostulated ${}_{\pi}2_s + {}_{\sigma}2_s + {}_{\sigma}2_a + {}_{\pi}2_s$ cycloreaction. The same ambiguity plagues many choices between one-step concerted and two-step, each-concerted mechanisms: when the intermediate, such as *cis,trans,cis*-triene **2** in the reaction $\mathbf{1} \rightleftharpoons \mathbf{1'}$ or **10** → **1** + furan, is sufficiently short-lived, kinetic distinctions are as impractical as orbital-symmetry theory is undiscriminating.

Thus, we conclude that if triene **2** is the initial product from thermolysis of adduct **10**, it gives bicyclo[4.2.0]-octa-2,7-diene as the sole isomerization product. And we believe that triene **2** as intermediate is a more likely alternative than a direct ${}_{\pi}2_s + {}_{\sigma}2_s + {}_{\sigma}2_a + {}_{\pi}2_s$ process.

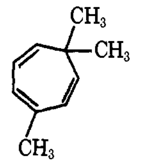
The mechanism by which bicyclooctadiene **1** gives triene **4**, if not by way of the intermediate **2**, might involve an s,a cycloreaction or a direct and orbital-symmetry disallowed isomerization. The former seems unlikely, since very similar reactions give products incompatible with this mechanistic alternative. 1,4,4-Trimethylbicyclo[3.2.0]hepta-2,6-diene (**11**) for instance is converted thermally to 2,2,6-trimethylbicyclo[3.2.0]hepta-3,6-diene (**12**) presumably by way of *cis,trans,cis*-3,7,7-trimethylcyclohepta-1,3,5-triene, as well as to 3,7,7-trimethyltropilidene (**13**).[13] The s,a cycloaddition between C(1)–C(2) and C(5)–C(6) would have given 2,7,7-trimethyltropilidene.



**11**



**12**



**13**

By default, then, the disallowed direct reaction **1** → **4** seems to be the prime mechanistic candidate.[8]

## Experimental Section

Nuclear magnetic resonance spectra were recorded for solutions in deuteriochloroform on a Varian HA-100 instrument; mass spectra were secured on a CEC-110-21B by Dr. Susan Rothschaefer. A Varian Aerograph 1520 with a 6 mm × 1.5 m 20% SE-30 on 60–80 mesh Chromosorb W column (column A) and a Perkin-Elmer F-11 with a 15-m squalene-coated capillary column (column B) were used for glpc work.

**2,4-Cyclooctadienone** was prepared from 1,3-cyclooctadiene (Cities Service Research and Development Co.) by way of 5-bromo-1,3-cyclooctadiene, 5-acetoxy-1,3-cyclooctadiene, and 5-hydroxy-1,3-cyclooctadiene.[10,14] The dienone had bp 43–44° (0.6 mm) [lit.[10] bp 44–46° (0.7 mm)] and spectral properties in accord with the literature.[10]

***trans*-13-Oxatricyclo[8.2.1.0$^{2,9}$]trideca-7,11-dien-3-ones (6, 7)**. A 2.0-g sample of 2,4-cyclooctadienone, at least 99% pure by glpc analysis (column A at 140°), in 175 ml of furan freshly distilled from lithium aluminum hydride, was placed in a Pyrex photolysis vessel. The solution was purged with nitrogen for 30 min and then irradiated for 4.3 hr, using a 450-W Hanovia lamp in a quartz-jacketed immersion well and a Pyrex filter. The reaction mixture was cooled in ice water during the photolysis. Furan was distilled from the photolysis reaction mixture, leaving 2.92 g (95%) of liquid residue. A small sample of the crude product mixture was distilled using a small molecular still (Kontes 284500) at 100–130° (0.2 mm); the distillate showed the anticipated[10] infrared and nmr spectral properties.

***trans*-13-Oxatricyclo[8.2.1.0$^{2,9}$]trideca-7,11-dien-3-ols (8a, 9a)**. The undistilled mixture of tricyclic ketones **6** and **7** (1.0 g, 5.26 mmol) in 30 ml of dry ether and 7 ml of dry tetrahydrofuran was added dropwise to a stirred slurry of 195 mg (5.14 mmol) of lithium aluminum hydride in 13 ml of dry ether under nitrogen over a period of 20–30 min. The reaction mixture was heated at reflux for 4 hr, cooled, and treated sequentially with 0.2 ml of water, 0.2 ml of 15% sodium hydroxide, and 0.8 ml of water. Filtration, drying over magnesium sulfate, filtration, and concentration gave 960 mg (95%) of a colorless oil; the hydroxyl band in the infrared for these alcohols as a film came at 3450 cm$^{-1}$.

***trans*-13-Oxatricyclo[8.2.1.0$^{2,9}$]trideca-3,7,11-triene (10)**. The crude mixture of alcohols **8a** and **9a** (1.64 g, 8.55 mmol) in 8 ml of dry ether was added to 210 mg of sodium hydride (8.75 mmol) in 40 ml of dry ether, and the slurry was stirred under dry nitrogen and heated at reflux for 5 hr. Carbon disulfide (8.75 mmol) was added by syringe, and the reaction mixture was heated at reflux an additional 4 hr. Methyl iodide (8.75 mmol) was added, and the reaction mixture was kept at reflux another 5 hr, then allowed to stand overnight at room temperature. Water (4 ml) was added dropwise with stirring to the cooled reaction mixture; the ethereal layer was separated and dried over magnesium sulfate. Filtration and concentration gave a clear pungent yellow oil, a mixture of xanthate esters (1055 and 1220 cm$^{-1}$ in the infrared), and some unconverted alcohols (3450 cm$^{-1}$).

A 1.3-g sample of the crude xanthates (**8b**, **9b**) was placed in a 5-ml round-bottomed flask and heated to 200°. The pressure was gradually lowered from 50 to 1 Torr after the temperature reached

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(13) J. E. Baldwin and M. S. Kaplan, *ibid.*, **94**, 668 (1972).

(14) A. C. Cope, S. Moon, C. H. Park, and G. L. Woo, *ibid.*, **84**, 4865 (1962).

200°. A yellow liquid (0.86 g) distilled through the short-path distillation head and was collected in a receiver cooled to −78°. Analysis by glpc (column A at 175°) showed the presence of low boiling impurities, the desired triene, and a broad peak at longer retention times which proved to be unreacted alcohols (**8a** and **9a**). The triene **10**, purified by preparative glpc, had mp 39–41°. The nmr spectrum showed six vinyl protons as three multiplets centered at $\delta$ 5.5, 5.95, and 6.5, two CHO protons as a multiplet from 4.7 to 5.0, and methylene protons at 1.4–3.0. Low-resolution mass spectrometry revealed the molecular ion at *m/e* 174 (0.35%), and other prominent ions at 106, 91, and 78 (base peak). Peak matching at high resolution identified the molecular ions as $C_{12}H_{14}O$ (calcd, 174.104; found, 174.106).

**Pyrolysis of *trans*-13-Oxatricyclo[8.2.1.0$^{2,9}$]trideca-3,7,11-triene (10) at 180°.** Several Pyrex 4-ml pyrolysis tubes were prepared, cleaned, base washed, and dried. Each was charged with about 2 mg of the tridecatriene **10**, degassed, and sealed. Pyrolyses at 180° gave rise to bicyclo[4.2.0]octa-2,7-diene (**1**) and 1,3,5-cyclooctatriene (**4**) identified through comparisons of retention times and peak shapes with authentic samples of **1**[11] and **4**[12] on glpc columns A and B, and through mass spectrometry, using a Varian Gnome mass spectrograph equipped with a gas chromatograph interface. Both hydrocarbons showed characteristic fragmentation patterns, with $M^+$ at *m/e* 106 and major peaks at 91 and 78.

Kinetic data were obtained with three neat samples of tridecatriene **10** and with two portions of a solution made up from a few milligrams of **10**, 15 μl of pentane, 20 μl of chloroform, and 1 μl of diphenyl ether, the internal standard. The degassed and sealed Pyrex ampoules were heated at 180° varying times, cooled at the bottom in liquid nitrogen, and opened; the walls of the tubes were washed with pentane, and the diluted samples were analyzed by glpc. Column B at 100° was used to determine the ratio of bicyclic (**1**) to monocyclic (**4**) products; the results are listed in Table II.

**Table II.** Fraction of Bicyclo[4.2.0]octa-2,7-diene (**1**) in Product Mixture from Pyrolysis at 180° of *cis,trans,cis*-Cycloocta-1,3,5-triene Precursor **10**

| Time, hr | Fraction = **1**/(**1** + **4**) |
|---|---|
| 1.5[a] | 0.75 |
| 2.5[a] | 0.67 |
| 5.0[a] | 0.53 |
| 5.0[b] | 0.57 |
| 11[b] | 0.32 |

[a] Neat precursor **10**. [b] Mixture containing triene **10**, pentane, chloroform, and diphenyl ether as internal standard.

The ratios of triene **10** to diphenyl ether were obtained through analysis on column A at 180°. The triene **10** was 7.4% reacted at 5 hr, and 15.5% converted at 11 hr.