

Cycloadditions. IV. Mechanism of the Photoisomerization of *cis,cis*-1,5-Cyclooctadiene to Tricyclo[3.3.0.0^{2,6}]octane¹

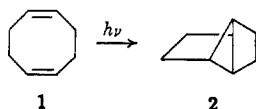
John E. Baldwin and Richard H. Greeley²

Contribution from the Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61803. Received May 22, 1965

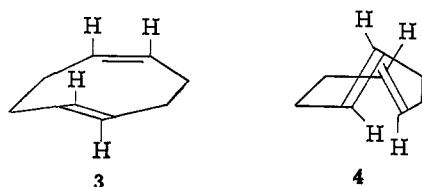
Photochemical rearrangement of 3-deuterio-*cis,cis*-1,5-cyclooctadiene gives a mixture of deuteriotricyclo[3.3.0.0^{2,6}]octane and unlabeled tricyclooctane. The results require intermolecular hydrogen transfer during the reaction. The reaction is interpreted as proceeding by way of free-radical intermediates.

Introduction

Photolyses of 1,5-hexadiene,³ *cis,cis*-1,5-cyclooctadiene,^{4,5} and myrcene⁶ all lead under appropriate conditions³⁻⁶ to the corresponding bicyclo[2.1.1]-hexanes. *cis,cis*-1,5-Cyclooctadiene (**1**), for instance, gives the interesting tricyclic hydrocarbon tricyclo[3.3.0.0^{2,6}]octane (**2**).^{4,5}



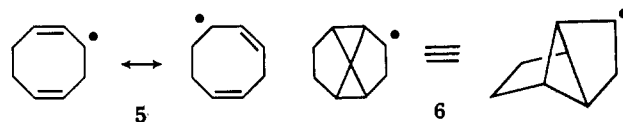
Mechanistic speculation on the conversion **1** → **2** has raised^{4,5} a number of questions which seemed well worth pondering. In particular, may photochemical isomerization of the *cis,cis*-diene **1** to a *cis,trans* form (**3**) or even a *trans,trans* structure **4** precede the intramolecular cycloaddition?⁷



If **4** should be the precursor of the tricyclooctane **2**, the baffling stereochemical aspects of the conversion **1** → **2** would be partially explained and *trans,trans*-1,5-cyclooctadiene (**4**) would become the stereochemically intriguing subject.

An alternative mechanism, however, involving neither a direct conversion **1** → **2** nor the indirect process **1** → **3** → **4** → **2** may be readily postulated. It is known⁸ that free-radical additions to *cis,cis*-1,5-cyclooctadiene readily give 2-substituted bicyclo[3.3.0]octanes. By analogy, then, loss of hydrogen from *cis,cis*-1,5-cyclo-

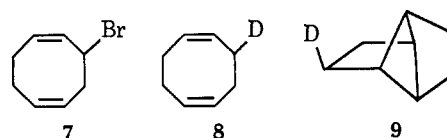
octadiene would produce a radical intermediate **5** potentially capable of isomerization to **6** and eventual production of **2**.



We addressed this mechanistic choice by studying the photochemical rearrangement of 3-deuterio-*cis,cis*-1,5-cyclooctadiene. The exclusively intramolecular mechanisms **1** → **2** or **1** → **3** → **4** → **2** would predict a deuterium distribution in the tricyclic product exactly identical with that of the starting labeled diene. The free-radical process is not strictly intramolecular and thus predicts some scrambling of label in the product. The results of this experimental test between intramolecular and intermolecular mechanistic pathways, described in the following section, prove consonant with the free-radical mechanism.

Results

Synthesis of 3-deuterio-*cis,cis*-1,5-cyclooctadiene (**8**) was accomplished by reducing 3-bromo-*cis,cis*-1,5-cyclooctadiene (**7**) with lithium aluminium deuteride.⁹



Photolysis of the labeled diene **8** in an ethereal solution saturated with cuprous chloride⁵ gave the deuteriotricyclooctane **9**.

On a strictly statistical basis, neglecting possible kinetic isotope effects, one would predict for the free-radical mechanism **1** → **5** → **6** → **2** that **5** and **6** would have seven-eighths of the deuterium label originally in the allylic positions of **1**; if **6** then abstracted a hydrogen from the solvent ether, the product **2** should similarly contain seven-eighths of the original label. The starting material, 3-deuterio-*cis,cis*-1,5-cyclooctadiene (**8**), was found to be 2.3% *d*₀, 96.7% *d*₁, and 1.0% *d*₂. The distribution of label in the saturated product derived from the labeled diene **8** predicted by the simple free-radical mechanism would be 14.4% *d*₀, 84.7% *d*₁, and 0.9% *d*₂. This prediction would have to be somewhat modified for various contingencies such as important kinetic isotope effects, radical chain transfer processes, or competitive hydrogen abstraction from solvent and rearrangement of the hypothetical, free-radical intermediate **5**.

(9) A. C. Cope, C. L. Stevens, and F. A. Hochstein, *J. Am. Chem. Soc.* **72**, 2510 (1950).

(1) Supported in part by the Petroleum Research Fund, administered by the American Chemical Society. Cycloadditions. III: J. E. Baldwin, G. V. Kaiser, and J. A. Romersberger, *J. Am. Chem. Soc.*, **87**, 4114 (1965).

(2) National Science Foundation Undergraduate Research Participant.

(3) R. Srinivasan, *J. Phys. Chem.*, **67**, 1367 (1963).

(4) R. Srinivasan, *J. Am. Chem. Soc.*, **85**, 819 (1963).

(5) R. Srinivasan, *ibid.*, **86**, 3318 (1964).

(6) R. S. H. Liu and G. S. Hammond, *ibid.*, **86**, 1892 (1964).

(7) Compare P. E. Eaton and K. Lin, *ibid.*, **86**, 2087 (1964); *ibid.*, **87**, 2052 (1965); E. J. Corey, M. Tada, R. LaMahieu, and L. Libit, *ibid.*, **87**, 2051 (1965).

(8) R. Dowbenko, *ibid.*, **86**, 946 (1964); *Tetrahedron*, **20**, 1843 (1964).

From the experimental data summarized in Table I, obtained at low electron voltages to render negligible $M - 1$ and $M - 2$ fragmentation peaks,¹⁰ the deu-

Table I. Relative Intensities of Ions in Mass Spectra of C_8H_{12} and $C_8H_{11}D$ Isomers

Compd.	Spec- trum	m/e (M)		
		108	109	110
C_8H_{12} ^a		1.000	0.088	
<i>cis,cis</i> -1,5-Cyclooctadiene (1)	707	1.000	0.085	
3-Deuterio- <i>cis,cis</i> -1,5-cyclooctadiene (8) (starting material)	708	0.024	1.000	0.095
Tricyclo[3.3.0.0 ^{2,6}]octane (2)	703	1.000	0.093	
Deuteriotricyclo[3.3.0.0 ^{2,6}]octane (9)	704	0.153	1.000	0.098
<i>cis,cis</i> -1,5-Cyclooctadiene (1)	885	1.000	0.088	
Deuterio- <i>cis,cis</i> -1,5-cyclooctadiene (recovered after reaction)	886	0.072	1.000	0.097

^a Expected abundance ratios: J. H. Beynon, "Mass Spectrometry and its Application to Organic Chemistry," Elsevier Publishing Co., Amsterdam, 1960, p. 494.

terium distributions for the $C_8H_{11}D$ isomers in Table II were calculated.¹¹ The deuterium distributions in Table II require intermolecular hydrogen exchange

Table II. Calculated Deuterium Distributions in $C_8H_{11}D$ Isomers

Compd.	$d_0, \%$	$d_1, \%$	$d_2, \%$
Deuterio- <i>cis,cis</i> -1,5-cyclooctadiene			
Starting material (8)	2.3	96.7	1.0
Recovered after reaction	6.7	92.4	0.9
Deuteriotricyclo[3.3.0.0 ^{2,6}]octane (9)	13.4	86.1	0.5

during the rearrangement process. The extent of hydrogen exchange in the diene recovered after the photochemical rearrangement is substantial but far too small to support a mechanism proceeding by hydrogen exchange in the diene, then intramolecular rearrangement to the tricyclooctane. The 13.4% d_0 , 86.1% d_1 , and 0.5% d_2 distribution of label in the tricyclooctane is in excellent agreement with the free-radical mechanism $1 \rightarrow 5 \rightarrow 6 \rightarrow 2$.

Discussion and Conclusions

The results of this study rule out any purely intramolecular mechanism for the photochemical isomerization of the diene **1** to the tricyclooctane **2** when the conversion is accomplished with an ethereal solution of diene, saturated with cuprous chloride. They are fully consistent with a mechanism involving the free radicals **5** and **6** as important reaction intermediates.

The obtusion of free-radical processes can hardly be regarded as surprising. The original work^{4,5} on the photochemical cycloaddition $1 \rightarrow 2$ utilized a low-pressure mercury lamp having strong emission at 2537 Å., corresponding to 113 kcal./mole, while the estimated¹² dissociation energy for a methylene carbon-hydrogen bond in the diene **1** is only 82 kcal./mole.

(10) K. Biemann, "Mass Spectrometry—Organic Chemical Application," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 209.

(11) Reference 10, pp. 224, 225.

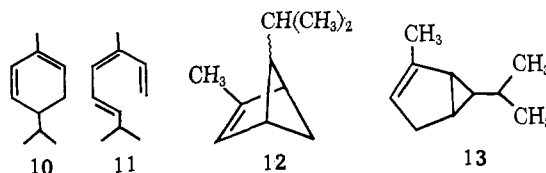
(12) By using 1-butene as a model: see P. S. Nangia and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 2773 (1964); K. W. Egger, D. M. Golden, and S. W. Benson, *ibid.*, **86**, 5420 (1964).

Thus the possibility of dissociation following photoexcitation of the diene may be considered likely.¹³

The free-radical mechanism for the formation of tricyclooctane **2** easily accommodates formation of polymer, dimers of the 1-ethoxyethyl radical, and other products observed in the reaction.⁵ Mercury-sensitized photolysis of 1,5-hexadiene in the vapor phase gives,³ in addition to bicyclo[2.1.1]hexane, "numerous other products believed to be of free-radical origin" emphasizing the possibility that in this case, too, a free-radical mechanism for the formation of cycloaddition product may obtain. Whether or not the sensitized photochemical isomerizations of 1,5-hexadiene,³ myrcene,⁶ or other 1,5-hexadienes proceed *via* free-radical intermediates is, of course, not answered by this study. There are enough dissimilarities in the stereochemical aspects of the hydrocarbons investigated³⁻⁶ and in the reaction conditions employed³⁻⁶ that extrapolation from the present results is not warranted. Further experimentation would be necessary in each case to settle the point. Nor do the results provide answers to all of the mechanistically important questions concerning the cycloaddition reaction $1 \rightarrow 2$. The role of cuprous chloride,⁵ possible radical chain processes, and other details of the free-radical mechanism remain unclarified.

The demonstrated intermolecular hydrogen exchange during the rearrangement, which we interpret as compelling evidence for free-radical intermediates **5** and **6**, may be interpreted otherwise by, for instance, postulating a radical in solution which removes hydrogens from starting material **1** and product **2** with a selectivity favoring abstraction from the tricyclooctane **2** by better than 2:1. But the relevant bond dissociation energies are about 82 kcal./mole for $1 \rightarrow 5 + H$ and 94 kcal./mole for $2 \rightarrow 6 + H$, thus making the postulated abstracting radical uniquely atypical. A rationale for the data based on such a postulated abstracting species is thermodynamically unreasonable.

Two rearrangements formally similar to the conversions of 1,5-hexadienes to bicyclo[2.1.1]hexanes have received recent attention. First, the report¹⁴ that α -phellandrene (**10**) may be photochemically converted through the triene **11** to a bicyclo[2.1.1]hexene (**12**) has been shown to be in error. The photoproduct is a dialkyl bicyclo[3.1.0]hex-2-ene (**13**).¹⁵



Second, 5,6-diphenyldibenzo[*a,e*]cyclooctatetraene (**14**) rearranges intramolecularly¹⁶ either thermally or photochemically to 5,11-diphenyldibenzo[*a,e*]cyclooctatetraene (**16**), presumably through the "twisted" intermediate **15**. Analogs give the same rearrangement. The stereochemical ramifications of the sequence $14 \rightarrow 15$ are in some ways similar to those for the hypo-

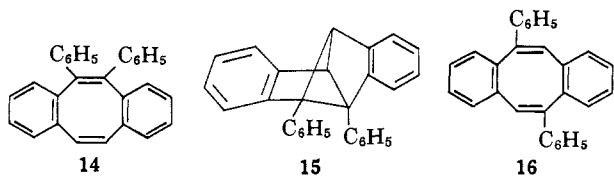
(13) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, pp. 533-535.

(14) K. J. Crowley, *J. Am. Chem. Soc.*, **86**, 5692 (1964).

(15) J. Meinwald, A. Eckell, and K. L. Erickson, *ibid.*, **87**, 3532 (1965).

(16) M. Stiles and V. Burckhardt, *ibid.*, **86**, 3396 (1964).

thetical scheme 1 → 3 → 4 → 2. The rearrangement seems remarkable¹⁶ indeed.



Experimental Section¹⁷

cis,cis-1,5-Cyclooctadiene from K & K Laboratories was redistilled through a 20-cm. Vigreux column; the center cut used below, b.p. 149° (754 mm.), was estimated >99% pure by g.l.p.c. analysis. Its n.m.r. spectrum showed absorptions at τ 4.49 and 7.67 in a 1:2 area ratio.

3-Bromo-*cis,cis-1,5-cyclooctadiene*⁹ was prepared from 47 g. (0.435 mole) of *cis,cis-1,5-cyclooctadiene*, 53 g. (0.298 mole) of N-bromosuccinimide, and 2 g. of benzoyl peroxide in 250 ml. of carbon tetrachloride under reflux with stirring for 3 hr. The reaction mixture was cooled and filtered; the filtrate was washed twice with aqueous sodium carbonate and twice with warm water. Distillation at reduced pressure gave 10 g. of unreacted diene and 30 g. (54%) of 3-bromo-*cis,cis-1,5-cyclooctadiene*, b.p. 94–95° (20 mm.). The infrared spectrum of this bromide was in good accord with the published⁹ spectrum.

(17) Perkin-Elmer Model 521, Varian A-60, and Atlas CH-4 spectrometers were used for determining infrared, nuclear magnetic resonance, and mass spectra. Mass spectra of labeled and unlabeled hydrocarbons were obtained using low electron energies (<12.5 e.v.) and wide slits. A Wilkins Model A-90-P and a 6 × 300 mm. β,β' -oxydipropionitrile column at 80° were used for g.l.p.c. estimation and isolation of hydrocarbons.

3-Deuterio-*cis,cis-1,5-cyclooctadiene*. To 15 ml. of ether and 0.805 g. of lithium aluminium deuteride (97%, Metal Hydrides, Inc.) in a three-necked flask fitted with a reflux condenser and addition funnel was added dropwise 7.887 g. of 3-bromo-*cis,cis-1,5-cyclooctadiene*. When the initial reaction subsided, the reaction mixture was refluxed for 24 hr. Excess deuteride was destroyed through cautious dropwise addition of water; the product was extracted with ether and isolated by distillation. There was obtained 3.456 g. (75%) of 3-deuterio-*cis,cis-1,5-cyclooctadiene*, b.p. 40–41° (20 mm.). After purification and isolation by g.l.p.c., this material was analyzed by mass spectrometry (cf. Tables I and II).

Tricyclo[3.3.0.0^{2,6}]octane. A solution of 2 g. of *cis,cis-1,5-cyclooctadiene* in 380 ml. of ether was saturated with cuprous chloride. The saturated solution was irradiated through a Vycor filter with a Hanovia high-pressure 450-w. mercury vapor lamp for 24 hr. Ether was removed by distillation through a 20-cm. glass helix packed column. The residue was fractionated and gave 0.79 g. (39.5%) of tricyclo[3.3.0.0^{2,6}]octane, b.p. 43° (26 mm.). The product was identified by its characteristic⁴ n.m.r. singlets at τ 8.18 and 8.27 in 1:2 area ratio.

Deuteriotricyclo[3.3.0.0^{2,6}]octane. Photolysis of 2.04 g. of 3-deuterio-*cis,cis-1,5-cyclooctadiene* following the procedure given above for the unlabeled diene gave 0.48 g. (24%) of product, b.p. 42° (25 mm.). The tricyclooctane and unreacted starting material were purified and isolated by g.l.p.c.; the mass spectrometric analyses for these hydrocarbons are given in Tables I and II.

The *sym*-Dibenzcyclooctatetraene Anion Radical and Dianion

Thomas J. Katz, Masayuki Yoshida, and L. C. Siew

Contribution from the Department of Chemistry, Columbia University, New York, New York 10027. Received April 29, 1965

sym-Dibenzcyclooctatetraene is easily reduced in tetrahydrofuran solution to the corresponding anion radical and dianion by lithium, sodium, or potassium metal. Polarographic reduction in 96% dioxane–water proceeds at low potentials suggesting that the interaction of unsaturated centers in the anions is considerable. The e.s.r. spectrum of the anion radical and the n.m.r. spectrum of the dianion are given and analyzed.

Introduction

While conjugation between the four double bonds of cyclooctatetraene is not appreciable and while the molecule does not exhibit aromatic properties,¹ the mono- and dialkali cyclooctatetraenides formed on reaction of cyclooctatetraene with alkali metals appear to owe their stability to π -electron delocalization and do

(1) R. A. Raphael, "Non-Benzenoid Aromatic Compounds," D. Ginsberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, Chapter VIII.

exhibit aromatic properties.² Thus, cyclooctatetraene is much easier to reduce than an unconjugated olefin,^{2d} it forms an anion radical^{2c} analogous to familiar benzenoid aromatic hydrocarbon anion radicals,³ and the dianion shows a proton n.m.r. peak at the low fields^{2a} characteristic of aromatic molecules.⁴

(2) (a) T. J. Katz, *J. Am. Chem. Soc.*, **82**, 3784 (1960); (b) *ibid.*, **82**, 3785 (1960); (c) T. J. Katz and H. L. Strauss, *J. Chem. Phys.*, **32**, 1873 (1960); H. L. Strauss and G. K. Fraenkel, *ibid.*, **35**, 1738 (1961); H. L. Strauss, T. J. Katz, and G. K. Fraenkel, *J. Am. Chem. Soc.*, **85**, 2360 (1963); (d) T. J. Katz, W. H. Reinmuth, and D. E. Smith, *ibid.*, **84**, 802 (1962); (e) H. P. Fritz and H. Keller, *Z. Naturforsch.*, **16b**, 231 (1961); *Chem. Ber.*, **95**, 158 (1962).

(3) M. C. R. Symons, *Advan. Phys. Org. Chem.*, **1**, 283 (1963).
(4) (a) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 180, 247 ff.; (b) G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5846 (1960); (c) T. Schaeffer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963); (d) B. P. Dailey, A. Garvin, and W. C. Neikam, *Discussions Faraday Soc.*, **34**, 18 (1962); (e) T. J. Katz and P. J. Garratt, *J. Am. Chem. Soc.*, **86**, 4876 (1964); *ibid.*, **85**, 2852 (1963); (f) T. J. Katz and J. Schulman, *ibid.*, **86**, 3169 (1964); (g) L. M. Jackman, F. Sond-