Mechanism of the Photoisomerization of
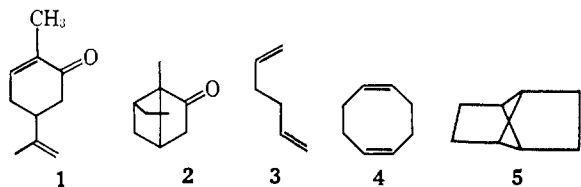## cis,cis-1,5-Cyclooctadiene to Tricyclo[3.3.0.0²,⁶]octane

Ivan Haller and R. Srinivasan

*Contribution from IBM Watson Research Center, Yorktown Heights, New York.
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Abstract: The mechanism of the photoisomerization of cis,cis-1,5-cyclooctadiene to tricyclo[3.3.0.0²,⁶]octane has been studied in the vapor phase as a mercury-sensitized reaction, and in ether solution with cuprous chloride as catalyst. In the gas phase the use of oxygen as a radical scavenger failed to eliminate the reaction. The reaction in the condensed phase was followed by the use of 1,5-cyclooctadiene-d_{12}. No loss of the deuterium label was detectable in either the tricyclooctane that was formed or in the cyclooctadiene that was recovered at conversions ranging from 23 to 70%. The reaction is best formulated as an intramolecular process and not as a free-radical reaction as proposed by Baldwin and Greeley.
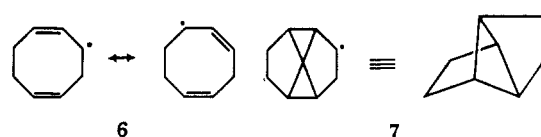
One of the interesting aspects of the photoisomerization of nonconjugated dienes to bicyclic systems is the variation in the geometry of the product with the nature of the diene and the conditions of the reaction. Systems which incorporate the 1,5-hexadiene group have received the greatest attention probably because they isomerize photochemically with ease to give rise to products which are not readily available by conventional methods.

Büchi and Goldmann[1] first showed that the photoisomerization of carvone[2] (1) gave a product derived from bicyclo[2.1.1]hexane (2) rather than the alternative bicyclo[2.2.0]hexane. This appears to hold true for 1,5-hexadiene[3] (3), myrcene,[4] and 1,5-cycloocta-

1   2   3   4   5

diene[5,6] (4) as well. The last example has drawn particular attention since the starting material is almost certainly cis,cis while the product, tricyclo[3.3.0.0²,⁶]octane (5), appears to be derived from $trans,trans$-cyclooctadiene. This particular reaction has been shown to occur in the vapor phase when sensitized by mercury ($^3P_1$) atoms[5] or in solution in ether in the presence of cuprous chloride as a catalyst.[6] The probable mechanisms of these processes have been discussed.[6]

Recently, Baldwin and Greeley[7] have proposed an alternative mechanism in which the formation of 5 from 4 would occur by "loss of hydrogen from cis,cis-1,5-cyclooctadiene (which) would produce a radical intermediate 6 potentially capable of isomerization to 7 and eventual production of 5."[8] They addressed themselves to this mechanistic choice by

(1) G. Büchi and I. M. Goldmann, *J. Am. Chem. Soc.*, **79**, 4741 (1957).
(2) G. Ciamician and P. Silber, *Chem. Ber.*, **41**, 1928 (1908).
(3) R. Srinivasan, *J. Phys. Chem.*, **67**, 1367 (1963).
(4) R. S. H. Liu and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 1892 (1964).
(5) R. Srinivasan, *ibid.*, **85**, 819 (1963).
(6) R. Srinivasan, *ibid.*, **86**, 3318 (1964).
(7) J. E. Baldwin and R. H. Greeley, *ibid.*, **87**, 4514 (1965).
(8) This quotation is taken *verbatim* from ref 7. Only the numbering of the structures has been altered to conform to this article.

6   7

studying the photochemical rearrangement of 3-deuterio-cis,cis-1,5-cyclooctadiene (8). Exclusively intramolecular mechanisms would predict a deuterium

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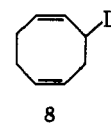
distribution in the tricyclic product exactly identical with that of the starting labeled diene. The free-radical process is not strictly intramolecular and thus predicts some scrambling of label in the product. The results of their experimental test between intramolecular and intermolecular mechanistic pathways, in their words,[7] "prove consonant with the free-radical mechanism."

A discussion of the experimental work of Baldwin and Greeley will be deferred to a later section. It is sufficient to mention here that their "free-radical mechanism" suggested to us that further experimentation on the photochemistry of 1,5-cyclooctadiene was necessary. We report here results on the photoisomerization of 1,5-cyclooctadiene-d_{12} in ether solution in the presence of cuprous chloride and on the mercury-sensitized isomerization of 1,5-cyclooctadiene in the gas phase under a variety of experimental conditions.

Experimental Section

1,5-Cyclooctadiene (K & K Laboratories) was fractionated on a spinning-band column. A small, constant-boiling middle fraction was used in these experiments. It contained 2% 4-vinyl-cyclohexene as the only impurity. 1,5-Cyclooctadiene-d_{12} was supplied by Merck Sharp and Dohme of Montreal. The total chemical impurities, as determined by vapor phase chromatography, amounted to 0.7%. The isotopic purity is given in Table I.

Vapor phase photolyses were carried out in a 6.4-cm long, 250-ml volume cylindrical quartz cell. A conventional vacuum line was used to evacuate and then fill the reaction vessel. The light source was an Ottawa style mercury resonance lamp, filtered with a 2-cm layer of water. In experiments with added gases, mixing of the reactants was achieved by agitating the mercury that was inside the cell. Analyses were conducted on a 2-m Ucon Oil 550 column (Perkin-Elmer R$_X$) at 90°.

Photolyses in ether solution (0.2%) were carried out in quartz test tubes 25 × 1.3 cm. The solutions were first saturated with

freshly prepared cuprous chloride, decanted, and introduced into the test tubes which were closed with serum caps. They were not degassed before irradiation. The light source (λ = 2537 A) has been described before.[6] At the end of the irradiation, most of the ether was distilled off; the C_8 fraction was separated into its components on a gas chromatographic column and analyzed for its deuterium content by mass spectroscopy. A Consolidated Engineering Co. 103-C mass spectrometer and a 21-620A mass spectrometer, which had been modified to allow the ionizing voltage to be reduced, were used in the analyses.

Results

In Table I, the deuterium contents of the product and of the starting material that was recovered from

Table I. Deuterium Content of Tricyclo[3.3.0.0^{2,6}]octane-d_{12} and 1,5-Cyclooctadiene-d_{12} as a Function of Conversion[a]

Conversion, %	1,5-Cyclooctadiene		Tricyclo[3.3.0.0^{2,6}]-octane	
	d_{12}	d_{11}	d_{12}	d_{11}
0	0.880	0.120	. . .	. . .
23	0.886	0.114	0.887	0.113
46	0.887	0.113	0.888	0.112
70	0.882	0.118	0.889	0.111

[a] Uncertainty in the analysis ±0.010.

the photoisomerization of 1,5-cyclooctadiene-d_{12} are presented as a function of conversion. Each line in the table was obtained in a separate run and averaged from two independent analyses. The useful radiation was almost entirely of 2537-A wavelength. Within experimental error, which was ±1%, there was no evidence for the loss of any of the deuterium atoms of the starting material in the tricyclooctane that was formed. Both mass spectrometers gave essentially identical results.

Qualitative studies of the mercury ($^3P_1$) sensitized isomerization of 1,5-cyclooctadiene have already been reported.[5,6] In this work, the reaction was studied quantitatively. The formation of 9 in addition to 5 has also been reported.[6] In Figure 1 the formation of

9

these two products is plotted as a function of added nitrogen. Since the vapor pressure of 1,5-cyclooctadiene at room temperature is less than 4 mm, the

Table II. Yields of Bicyclo[5.1.0]octene-3 and Tricyclo[3.3.0.0^{2,6}]octane in the Mercury-Photosensitized Reaction[a]

Gas or vapor	Pressure, mm	Time, min	Products, μmole/min Bicyclooctene	Tricyclooctane
None	. . .	3	0.65$_4$	0.08$_5$
Nitrogen[b]	6.4	3	0.65$_5$	0.11$_4$
	97.0	3	0.57$_9$	0.38$_2$
Oxygen	3.9	3	0.41$_7$	0.10$_3$
	97.0	30	0.00$_3$	0.01$_5$
	97.0	60	0.00$_8$	0.01$_6$
	97.0	140	0.00$_7$	0.01$_3$
Ether	15.0	3	0.45$_3$	0.19$_4$

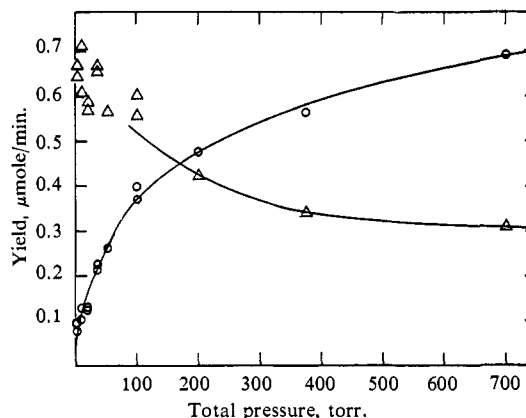[a] $P_{cyclooctadiene}$ = 3.6 mm, 2537 A, room temperature. [b] Average of two runs.

Figure 1. Product yields in the mercury-photosensitized reaction of cyclooctadiene in the presence of nitrogen ($\triangle$, bicyclooctene; $\bigcirc$, tricyclooctane).

total pressure in the system could be readily varied only by the addition of an inert gas.

In Table II, the yields of these products in the presence of oxygen and ether are reported. One run without any added material and two with nitrogen present are also included for comparison.

Discussion

It is best to examine the results of the mercury-sensitized reaction first since in the vapor phase it is relatively easy to scavenge free radicals efficiently. The data in Table II show that both oxygen and nitrogen, when present at pressures of the same order as of 1,5-cyclooctadiene, enhance the rate of formation of tricyclooctane and decrease the rate of formation of bicyclooctene. Thus oxygen behaves as an "inert" gas, its effect being wholly attributable to its efficiency in removing vibrational energy. Figure 1 extends the effect of nitrogen over a wider range of pressure. These curves are quite similar to the self-quenching curves that have been reported for 1,5-hexadiene[3] and 1,6-heptadiene.[9] The only difference lies in the failure to realize a maximum for the rate of formation of bicyclooctene.

The reactions of oxygen with aliphatic free radicals, especially in photochemical systems, have been reviewed.[10] In the present system the major point of interest is whether, in the presence of an efficient radical trap such as oxygen, the tricyclooctane (5) continues to be formed. The failure of 3.9 mm of oxygen to diminish the formation of tricyclooctane argues against the intermediacy of a long-lived free radical in its formation in this system.

When a considerable excess of oxygen is added, the rate of formation of tricyclooctane continues to be one-fifth of its value in the absence of any inert gas. In this instance three effects have to be taken into account. Oxygen would (i) tend to increase the yield by vibrationally deactivating excited molecules of 1,5-cyclooctadiene, (ii) tend to decrease the yield by quenching the triplet states of 1,5-cyclooctadiene, and (iii) tend to decrease the yield by quenching the triplet mercury atoms. The last effect is well known and well

(9) R. Srinivasan and K. A. Hill, J. Am. Chem. Soc., 87, 4988 (1965).
(10) See, for example, W. A. Noyes, Jr., Radiation Res. Suppl., 164 (1959).

documented.[11] The first effect is more evident at low pressure, as discussed above. The second effect may not be evident in instances in which the triplet of the olefin undergoes rapid rearrangement. This has been pointed out by Setser, Placzek, Cvetanović, and Rabinovitch.[12] It is significant to note that even a 30-fold excess of oxygen fails to eliminate the production of tricyclooctane. This reinforces the statement made previously,[5,6] *viz.*, that the mercury-photosensitized isomerizations to give tricyclooctane is partly, if not wholly, an intramolecular process.[13]

In the reaction in the condensed phase, as it was carried out in this study, 1,5-cyclooctadiene was present as a dilute solution in ether. As a result, the tricyclooctanyl radical (7) is more likely to abstract a hydrogen atom from the solvent than from the starting material or the product. It follows that when 1,5-cyclooctadiene-d_{12} is the starting material, the product must almost entirely be tricyclooctane-d_{11} if the mechanism of Baldwin and Greeley[7] is correct. Since the data in Table I show that none of this product is formed within experimental error, the transformation of 1,5-cyclooctadiene in the condensed phase must also be predominantly an intramolecular process.

Baldwin and Greeley[7] reported that "photolysis of the labeled diene (8) in an ethereal solution saturated with cuprous chloride gave the deuteriotricyclooctane (10)." Their starting material had the isotopic com-
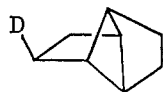

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position 2.3% d_0, 96.7% d_1, and 1.0% d_2. After they had photochemically converted an unstated portion of it, the recovered starting material had the isotopic composition 6.7% d_0, 92.4% d_1, and 0.9% d_2. The tricyclooctane that they obtained in this process had the composition 13.4% d_0, 86.1% d_1, and 0.5% d_2. The distribution of label in the saturated product derived from the labeled diene (8) predicted[7] by the simple free-radical mechanism would be 14.4% d_0, 84.7% d_1, and 0.9% d_2 if 8 had retained its label during the reaction. Any loss of label in 8 (as was actually observed) should lower the proportion of d_1 to d_0 in the product (10) over the predicted value if the free-

(11) W. A. Noyes, Jr., and P. A. Leighton, "Photochemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1941, p 224. A referee has pointed out that (by assuming a plausible value for the ratio of the quenching rate constants of O_2 and cylooctadiene) it can be readily seen that most of the decline in the yields of the products in the presence of 97 mm of oxygen is due to the quenching of $Hg(^3P_1)$ atoms by oxygen.

(12) D. W. Setser, D. W. Placzek, R. J. Cvetanović, and B. S. Rabinovitch, *Can. J. Chem.*, 40, 2179 (1962).

(13) All of the nonconjugated dienes which have been studied by mercury photosensitization undergo three primary processes, which in the case of 1,5-cyclooctadiene are

$(CH_2)_2CH=CH(CH_2)_3CH=CH$ +

$\dot{C}H_2CHCH=CH(CH_2)_2CH=CH$ + H
6

$Hg(^3P_1)$ ⟵→ **9**

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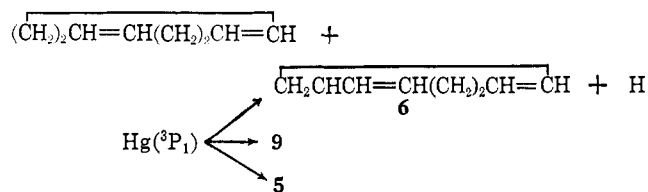
radical mechanism is applicable. Further, as stated by Baldwin and Greeley,[7] the predicted values "would have to be somewhat modified for various contingencies such as important kinetic isotope effects, radical chain transfer processes, or competitive hydrogen abstraction from solvent and rearrangement of the hypothetical, free-radical intermediate (6)."

Baldwin and Greeley concluded that "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 4 → 6 → 7 → 5."

To use a 1,5-cyclooctadiene that is completely deuterated is inherently a more sensitive test of free-radical intermediates such as 7 than the use of a monodeuterio compound such as 8. Our failure to find any loss of label in our starting material or in the photoproduct suggests that, at 2537 A, for the phototransformation 4 → 5 in ether solution in the presence of cuprous chloride, a free-radical mechanism, in which intermolecular hydrogen abstraction is an essential step, is almost completely ruled out.

The work of Baldwin and Greeley[7] seems deficient in two controls that are essential to its quantitative interpretation. The first is the use of a high-pressure mercury arc filtered by Vycor as the light source. The useful radiation must have extended from the transmission limit of Vycor to the long wavelength limit of absorption of cuprous chloride (3800 A). Both 1,5-cyclooctadiene and cuprous chloride would have simultaneously absorbed the incident light, as each absorbs in different regions over this range. Cremer[14] has shown that in ether saturated with cuprous chloride, photochemically initiated free-radical reactions lead to the formation of 2,3-diethoxybutane and 3-ethoxy-2-butanol. At 2537 A, in the presence of even 0.05 mole of 1,5-cyclooctadiene, this process is only one-twentieth as important as the photoisomerization of 4 to 5,[6] which is approximately in the same ratio as the optical densities of cuprous chloride (saturated) and 1,5-cyclooctadiene. At longer wavelengths, the optical density ratio is inverted, and the photoisomerization of 4 to 5 and radical attack on the solvent can be equally important. Clearly, radical attack on the 1,5-cyclooctadiene, as well as tricyclooctane, cannot be ruled out under these conditions.

The work of Baldwin and Greeley has also failed to report the loss in the label of their starting material and the isotopic composition of their product as a function of conversion.[15] It seems surprising that the composition of their photoproduct should have a *higher* d_1 content than the value that can be predicted on a statistical basis.

The first of these, which may give rise to the cyclooctadienyl radical (6), is the process most susceptible to pressure quenching, while the formation of 5 is promoted by an increase in pressure. Thus, at 4 mm[5] at 30° the chemical yield of 5 is less than 1%, while at 1 atm and 148° the chemical yield is 20% (R. Srinivasan, unpublished work). Further, under the latter condition, even 9 is undetectable, which clearly indicates that the free-radical split is an unimportant mode. It would be unreasonable to expect the free-radical split to be significant at even higher pressures which would correspond to photolysis in solution.

(14) S. Cremer, private communication.

(15) Baldwin and Greeley[7] have offered no explanation for the loss of the label in their starting diene on irradiation.