ular orbital which is otherwise found in odd alternant hydrocarbons. This results in different π-energies for the cation, radical, and anion, and hence in different ΔM values. In the approximation used here, ΔM for the p-methylbenzyl cation is greater, and ΔM for the p-methylbenzyl anion is smaller than ΔM for the benzyl system (0.721). These results are in qualitative agreement with the fact that p-methyl groups favor carbonium ion reactions but hinder reactions involving transition states which have carbanion character, such as ester hydrolysis.

The distances r_{ij} (Table IV) were calculated on the assumption that all carbon–carbon distances are equal to that in benzene,[20] including the pivot bond in biphenyl.

[CONTRIBUTION FROM THE IBM WATSON RESEARCH CENTER, YORKTOWN HEIGHTS, N. Y.]

Photochemical Transformations of 1,5-Cyclooctadiene

BY R. SRINIVASAN

Photolyses are reported of 1,5-cyclooctadiene: (i) by sensitization with mercury ($^3P_1$) atoms in the vapor phase, (ii) by direct irradiation in solution in the presence of cuprous chloride, and (iii) by irradiation in solution in a complexed state with rhodium chloride. The products from i are a polymer, bicyclo[5.1.0]octene-3 and tricyclo[3.3.0.0^{2,6}]octane. The polymer is believed to arise from a primary process which gives rise to free radicals. The other two products which are isomeric to 1,5-cyclooctadiene seem to be formed by intramolecular processes, analogs of which may be found in the photochemistry of 1,5-hexadiene. Process ii gives tricyclooctane in 30% yield while process iii gives 1,3-cyclooctadiene, bicyclo[4.2.0]octene-7, and 1,4-cyclooctadiene. It has been deduced that in ii the cuprous chloride acts merely as a catalyst for the isomerization reaction.

Introduction

Of all the aliphatic and alicyclic olefins which have hitherto been used as donor molecules in the formation of π-complexes with transition metal salts, 1,5-cyclooctadiene (1) is one of the best from the point of
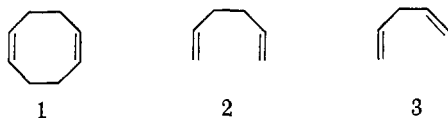

view of the stability of the complexes.[1] It was of interest to examine the photochemical behavior of these compounds, as the possibility of causing the photoisomerization of molecules in "frozen" conformations was visualized. The results of some of these studies are reported here. Photolysis of 1,5-cyclooctadiene by sensitization with mercury ($^3P_1$) atoms was also carried out to help compare the results that were obtained with the π-complexes with those obtained by a more conventional procedure.

Results

Mercury-Photosensitized Reaction.[2]—Mercury-sensitized photolysis of 1,5-cyclooctadiene in the vapor phase at 2537 Å.[2] gave rise to a polymeric liquid as the major product along with two compounds which together accounted for about 2 to 3% of the yield. Both compounds gave analytical figures and a molecular weight corresponding to the molecular formula C_8H_{12}. The first of these products had absorptions at 3.3 and 9.85 μ in its infrared spectrum, which suggested the presence of protons and carbons located in a cyclopropane ring.[3] The nuclear magnetic resonance spectrum of the compound showed a complex absorption

centered at 9.7 τ which confirmed the existence of cyclopropane protons in the molecule.[4] It is known that both 1,5-hexadiene (2)[5] and 1,4-pentadiene (3)[6] undergo two types of isomerizations on sensitization by mercury ($^3P_1$) atoms. One of these leads to cyclopropane derivatives, the products in the two cases being allylcyclopropane (4) and vinylcyclopropane (5), respectively. Cvetanovic and Doyle[7] have observed
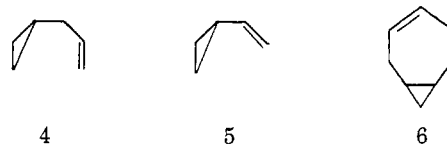
the isomerization of 1-butene to methylcyclopropane under similar conditions, but did not detect a corresponding isomerization in 2-butene. Although the double bonds in 1,5-cyclooctadiene are both symmetrically disubstituted, it is possible that the molecule undergoes an isomerization reaction that is analogous to those observed in linear terminal olefins. Thus, the structure of the first isomer that is formed is probably bicyclo[5.1.0]octene-3(6). This structure was compatible with the n.m.r. spectrum which showed four sets of absorptions of relative areas 2:4:2:4 which were centered at 4.35, 7.80, 8.25, and 9.70 τ, respectively. The first of these would correspond to the two olefinic protons, the second to the four allylic protons, the third to the two protons on the third methylene group, and the fourth to the four protons on the cyclopropane ring.

At about the time this work was completed, an independent synthesis of 6 by an alternative route was reported by Cope, Moon, and Park.[8] A comparison of

(1) R. G. Guy and B. L. Shaw, "Advances in Inorganic Chemistry and Radiochemistry," Vol. 4, edited by H. J. Emeleus and A. G. Sharpe, Academic Press, Inc., New York, N. Y., 1962, Chapter II.

(2) This part of the work was presented at the Symposium on "Reactions of the Triplet and Singlet States" held at the Conference of the Chemical Institute of Canada, Toronto, June 8, 1963.

(3) L. J. Bellamy, "Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1959, p. 29.

(4) J. B. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw–Hill Book Co., Inc., New York, N. Y., 1959, p. 236.

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

(6) R. Srinivasan, unpublished work; J. Meinwald, private communication.

(7) R. J. Cvetanovic and L. C. Doyle, J. Chem. Phys., 37, 543 (1962).

(8) A. C. Cope, S. Moon, and C. H. Park, J. Am. Chem. Soc., 84, 4850 (1962).

the infrared spectra of 6 from the two sources[9] indicated that the absorptions were essentially identical.

It has already been reported[10] that the second isomer was identified to be tricyclo[3.3.0.0.^{2,6}]octane (7) on the basis of its infrared, ultraviolet, and n.m.r.


7   8   9
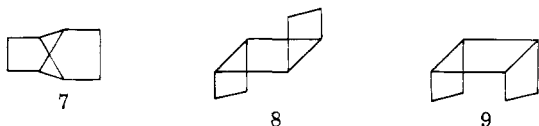
spectra. The assignment of this structure may be examined further at this point. Since the compound is saturated, its molecular formula requires that it be tricyclic. Those structures which require the presence of a cyclopropane ring are excluded by the spectral evidence.[10] Since the thermal decomposition of 7 in the temperature range from 330 to 350° gives rise to 1,5-cyclooctadiene (which undergoes further rearrangement),[11] it is reasonable to postulate that 7 is a valence tautomer of 1,5-cyclooctadiene. Besides 7, the structures 8 and 9 are also strong possibilities. It may be argued[10] that since only two kinds of protons were observed in the n.m.r. spectrum of the compound, structure 7 was the suitable one. It is possible that in both 8 and 9, although the two protons in each methylene group are nonequivalent, they may not be significantly different in their chemical shifts, or an accidental coincidence may give rise to only two absorptions from the three different groups of protons in each compound.

The problem was fortunately resolved when pure samples of 8 and 9, which had been prepared by the reduction of 10 and 11, respectively, by Nenitzescu, et al.,[12,13] became available. Neither 8 nor 9 showed any resemblance to 7 in their n.m.r. spectra, which


10   11   12
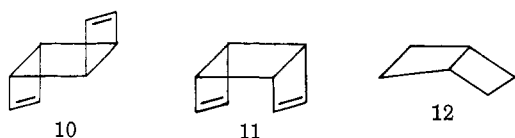
were related to the n.m.r. spectrum of bicyclo[2.2.0]-hexane (12).[14]

The mercury-photosensitized reactions of 1,5-cyclooctadiene and 1,5-hexadiene,[5] both of which have their olefinic groups separated by two carbon atoms, are entirely analogous. Reactions 1 and 2 are similar to
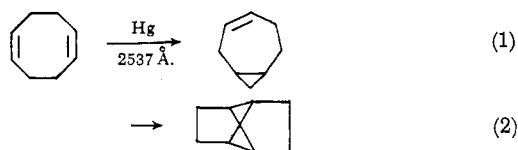

the formation of allyl cyclopropane and bicyclo[2.1.1]-hexane (13) from 1,5-hexadiene. As in 1,5-hexadiene, the polymerization of 1,5-cyclooctadiene is be-

lieved to be a free-radical chain process in which the initiating free radicals come from a primary process similar to 1 and 2. It follows that the high yield of the

13
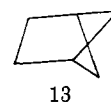
polymer is related to the low pressure (ca. 1 mm.) in the system at room temperature, a restriction that is dictated by the low vapor pressure of 1,5-cyclooctadiene. It was reasonable to expect that photoexcitation of 1,5-cyclooctadiene in a condensed phase would lead mainly to reaction from the low vibrational levels of the excited state which would favor reaction 2 almost exclusively.

Photolysis of 1,5-Cyclooctadiene–Cuprous Chloride.—Reaction between 1,5-cyclooctadiene and a solution of cuprous chloride in hydrochloric acid gives a precipitate of a complex of the empirical formula $C_8H_{12}CuCl$.[15] From X-ray studies, the structure of this compound in the solid state has been given as 14.[16]

14
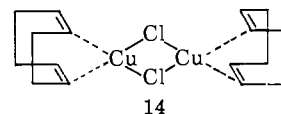
The solubility of the complex in ether was determined to be 0.06 g./l. at 25°, while that of pure cuprous chloride was 0.02 g./l.[17] Hydrocarbon solvents such as cyclohexane seemed to decompose the complex completely as a white precipitate slowly separated from the solution.

Photolysis of a solution of the complex in ether gave tricyclooctane (7) in 30% yield and small quantities of four compounds which were found to be products of radicals derived from the solvent. Since these compounds were formed (in different proportions) in the photolysis of a solution of cuprous chloride in ether in the absence of 1,5-cyclooctadiene, their structures will be discussed elsewhere.

Ultraviolet spectra of solutions of ether which contained cuprous chloride and 1,5-cyclooctadiene in various proportions are given in Fig. 1. In kinetic studies, instead of a solution of the complex, a saturated solution of cuprous chloride in ether to which known quantities of 1,5-cyclooctadiene had been added were used. In Table I the rates of formation of tricyclooctane (7) and two of the products from the solvent (referred to as A and A') are given.[17a]

From Fig. 1 it is seen that both cuprous chloride and 1,5-cyclooctadiene absorb weakly in the near ultraviolet spectrum, and that the spectrum of a mixture of the two is nearly additive. The spectrum of the complex 14 in solution (not shown in Fig. 1) was identical with that of the mixture. Whether this may be

(9) The author wishes to thank Professor A. C. Cope for the infrared spectrum of 6.

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

(11) A. A. Levi and R. Srinivasan, ibid., in press.

(12) M. Avram, E. Marica, and C. D. Nenitzescu, Chem. Ber., **92**, 1088 (1959); Tetrahedron Letters, **No. 1**, 21 (1961).

(13) The author wishes to thank Professor C. D. Nenitzescu for a generous gift of samples of 8 and 9.

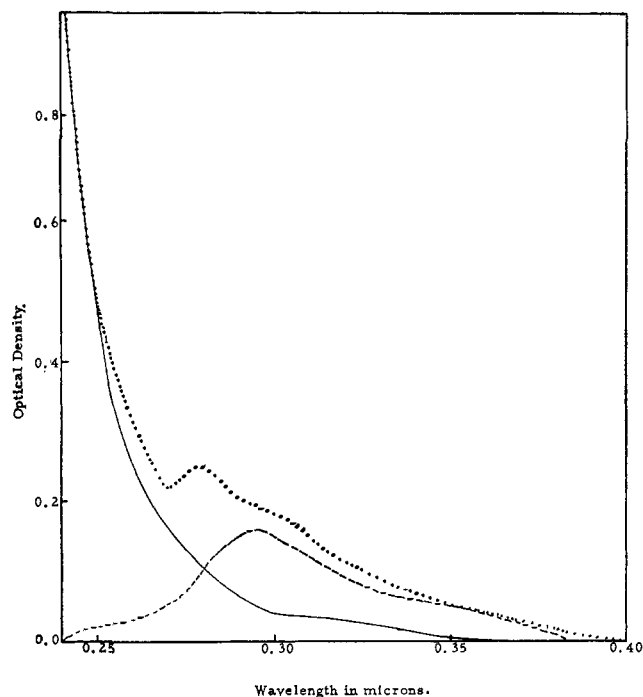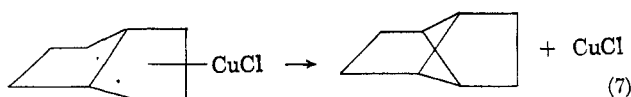(14) R. Srinivasan, J. Am. Chem. Soc., **83**, 4923 (1961).

(15) P. J. Hendra and D. B. Powell, Spectrochim. Acta, **17**, 913 (1961).

(16) J. H. Van den Hende and W. C. Baird, Jr., J. Am. Chem. Soc., **85**, 1009 (1963).

(17) The solubility of cuprous chloride in dioxane at 26.5° is reported to be 0.031 g./100 ml.; V. Heines and L. F. Yntema, Trans. Kentucky Acad. Sci., 785 (1938). Quoted by A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," 4th Ed., Vol. 1, D. Van Nostrand Co., Inc., New York, N. Y., 1958, p. 934.

(17a) NOTE ADDED IN PROOF.—Professor S. Cremer of Illinois Institute of Technology has informed the author that A and A' are stereoisomers of 2,3-diethoxybutane, and that the other two products derived from the solvent are stereoisomers of 3-ethoxy-2-butanol.
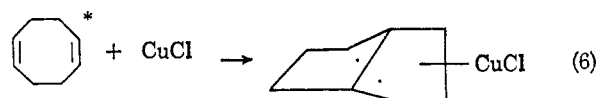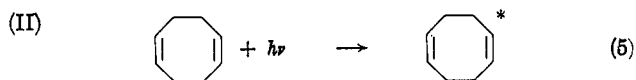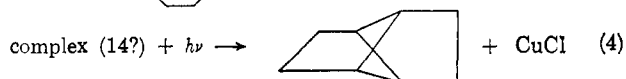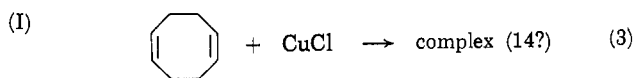
Fig. 1.—Ultraviolet spectra of 1,5-cyclooctadiene and cuprous chloride in ether; path length, 10 cm.: ———, 1,5-cycloocta-diene, 3.9 × 10³ M; ---------, cuprous chloride saturated at room temperature; ·······, saturated cuprous chloride and 3.9 × 10⁻³ M 1,5-cyclooctadiene.

taken as evidence for the complete dissociation of the complex or not is a questionable point. It is, however, clear that when an excess of 1,5-cyclooctadiene is added to the solution of the complex 14 in ether, the diene must absorb most of the radiation at 2537 Å.

Two mechanisms for the formation of tricyclooctane (7) may be considered:

(I)

 + CuCl ⟶ complex (14?)   (3)

complex (14?) + $h\nu$ ⟶ + CuCl   (4)

(II)

 + $h\nu$ ⟶   (5)

 + CuCl ⟶ —CuCl   (6)

—CuCl ⟶ + CuCl   (7)

The first mechanism requires that only that part of the radiation that is absorbed by a complex in solution leads to the formation of tricyclooctane. Since the maximum concentration of the complex can be only that of the cuprous chloride, it is possible to compute a quantum yield for tricyclooctane. The value was found to be of the order of 10.[18] Such a value seems irreconcilable with known ideas of photoisomerization.

(18) The quantum yield was calculated from a knowledge of the rate of formation of the product, the intensity of the incident radiation as measured with a uranyl oxalate actinometer, and the absorbance of the pure complex in solution.

TABLE I
### PHOTOLYSIS OF 1,5-CYCLOOCTADIENE IN THE PRESENCE OF CUPROUS CHLORIDE

2537 Å. radiation; room temperature; cylindrical cell, 20 cm. long, 0.7 cm. o.d.; solvent: diethyl ether

Cuprous chloride	1,5-Cyclo-octadiene, $M \times 10^3$	Relative optical density	Time, min.	Tri-cyclo-octane	A	A′
Satd.	Nil	1.0	180	0.0	2.0	4.5
Nil	3.8	7.4	180	0.0	1.3	2.0
Satd.	7.7	15.9	238	1.0	1.1	1.1
Satd.	23.0	45.7	300	2.7	1.0	0.8
Satd.	46.0	90.3	305	4.5	1.4	.6
Nil	45.6	89.3	300	0.2	1.5	.3

Again, if the complex has the structure 14, the formation of a tricyclooctane of structure 7 seems unlikely. The relative quantum yields for the formation of products A and A′ from the solvent are seen to be quite high when cuprous chloride alone is present and decreases steadily as the share of the radiation that is absorbed by the cuprous chloride in the mixture of cuprous chloride and 1,5-cyclooctadiene decreases. The evidence to prove that the formation or products A and A′ is related, for the greater part, to the radiation absorbed by the cuprous chloride will be presented in another publication.

The second mechanism requires that the quantum yield for tricyclooctane be calculated on the basis of the light absorbed by all of the 1,5-cyclooctadiene. This value was found to be of the order of 0.1. It also required that at constant concentration of cuprous chloride the quantum yield for tricyclooctane be constant. The 20% decrease that was observed with a 600% increase in intensity may be due to concentration gradients in the reaction cell, as the solution was not stirred during photolysis. In one experiment in which the concentration of cuprous chloride was increased by saturating with the salt after, rather than before, the 1,5-cyclooctadiene had been added, the rate of formation of tricyclooctane showed a sixfold increase. Unfortunately, the ultraviolet spectrum of the solution could not be determined as some of the cuprous chloride went into a fine suspension which scattered the ultraviolet radiation in the spectrometer.

Photolysis of 1,5-Cyclooctadiene–Rhodium Chloride.—A π-complex which is composed of two molecules of 1,5-cyclooctadiene to one of Rh₂Cl₂ was prepared by Chatt and Venanzi.[19] The structure of this material has been described as in 15 which is entirely similar to that of the π-complex with copper as the central atom.


15
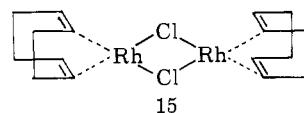
The solubility of this complex in ether was found to be of the order of that of the copper complex. The ultraviolet spectra of the solution, by itself and on the addition of some free 1,5-cyclooctadiene, are given in Fig. 2. The spectra is seen to be unchanged in position but intensified in the presence of an excess of

1,5-cyclooctadiene. The spectra is probably that of a complex which may have structure 15, although this is by no means certain. In the same figure, the ultraviolet spectrum of a solution that was saturated with the complex 15 in the presence of 1,5-cyclooctadiene in ether is also shown. The intensification of the spectra can be interpreted to indicate a higher concentration of the complex in this instance.

Photolysis of a solution of the complex 15 in ether at 2537 Å. caused the deposition of a brown precipitate. The supernatant liquid contained, in addition to unreacted starting material, three isomers of 1,5-cyclooctadiene. Two of these were identified to be 1,3-cyclooctadiene (16) and bicyclo[4.2.0]octene-7 (17) by comparison of their properties with those of authentic
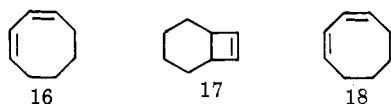
samples. The third isomer was most probably 1,4-cyclooctadiene (18) according to its infrared and n.m.r. spectra.[20]

Photolysis of the rhodium complex in solution in the presence of free 1,5-cyclooctadiene gave rise to the same organic compounds, but the formation of the precipitate (which was of inorganic origin) was not observed. It is reasonable to conclude from these results that the radiation is absorbed mainly by the rhodium complex of 1,5-cyclooctadiene, and that the diene isomerizes in its complexed state. In the presence of an excess of 1,5-cyclooctadiene the complex is presumably replaced readily as it is photolyzed. The formation of 1,3-cyclooctadiene (16) can be visualized to involve a series of bond shifts.
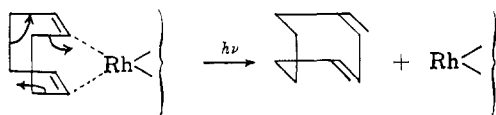
From the initially formed 1,3-cyclooctadiene (16) the bicyclo[4.2.0]octane-7 is probably generated by a second photochemical process which is well known.[21] The formation of 1,4-cyclooctadiene is more difficult to explain. It is possible to write a mechanism based on a deep-seated shift of electrons to account for this product, but the driving force for such a process is not obvious.

Experimental

Apparatus.—The light source was a bank of sixteen General Electric G8T5 lamps placed circularly around the reaction cell. Absorbed intensities were of the order of 10^{15}–10^{17} quanta/sec. at 2537 Å. Round-bottom quartz flasks of 2-l. capacity were used as reaction cells except in the kinetic studies with cuprous chloride. In the latter case, a cylindrical quartz cell 0.7 cm. o.d. and 20 cm. long was used.

Materials.—1,5-Cyclooctadiene from K and K Laboratories was distilled on a spinning band column (18 in.) before use. Ether (Mallinckrodt A.R. grade) was used as obtained. Cuprous chloride was prepared by the reduction of cupric chloride with copper and hydrochloric acid. $Rh_2Cl_2(C_8H_{12})_2$ was prepared as described by Chatt and Venanzi.[19]

Procedure. Mercury–Sensitized Decomposition.—The flask was charged with 1,5-cyclooctadiene (3.5 g.) and mercury (0.53 g.).

(20) A comparison of the spectra of this sample with those of a sample that was prepared by chemical routes from 1,5-cyclooctadiene suggests that the present compound may be a stereoisomer of the latter. The author is deeply grateful to Dr. J. Meinwald of Cornell University for the gift of a sample of 1,4-cyclooctadiene.

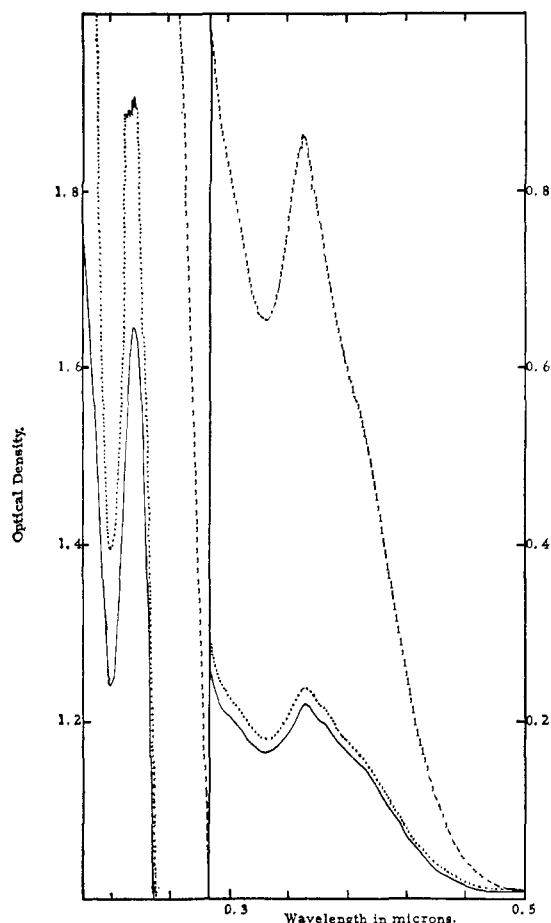(21) W. G. Dauben and R. L. Cargill, *J. Org. Chem.*, **27**, 1910 (1962).

Fig. 2.—Ultraviolet spectra of 1,5-cyclooctadiene–rhodium chloride complex in ether; path length, 1 mm.: ———, saturated solution of pure complex at room temperature; ······, saturated solution of pure complex with 1,5-cyclooctadiene (3.9×10^{-3} M) added; ———, 1,5-cyclooctadiene (3.9×10^{-3} M) saturated with complex at room temperature.

It was evacuated on a vacuum line to the vapor pressure of the diene (~1 mm.), detached from the line, and irradiated for 5 hr. After irradiation, the flask was connected to the vacuum line and all the volatile material (0.9 g.) was distilled off. The distillate consisted of unreacted 1,5-cyclooctadiene and the two reaction products which together amounted to 200 mg. Pure samples of bicyclo[4.1.0]octene-3 and tricyclo[3.3.0.0^{2,6}]octane were obtained by gas chromatographic separation on a Ucon oil column (Perkin-Elmer R_x) 2 m. long at 90. Tricyclo[3.3.0.0^{2,6}]-octane showed b.p. 123–124°, n^{25}D 1.4680, infrared (pure liquid) 3.3–3.45 (s), 7.77 (m), 8.13 (m), 9.12 (m), 11.03 (m), and 14.69 μ; for n.m.r. spectrum see ref. 10.

Photolysis of 1,5-Cyclooctadiene in the Presence of CuCl.—A solution of 1,5-cyclooctadiene (10 g.) in ether (2.5 l.) was saturated with cuprous chloride. The solution was decanted and irradiated for 21 hr. Since a black, finely divided precipitate separated and coated the wall of the vessel, the solution was filtered, resaturated with CuCl, and irradiated again in a clean vessel for another 18 hr. At that point about 50% of the 1,5-cyclooctadiene had been transformed. The reaction was stopped, the ether was distilled off, and the residue fractionated on a spinning band column. About 2.4 ml. of a fraction which was mostly tricyclooctane was collected (120–128°) and about 4 g. of 1,5-cyclooctadiene recovered. The first fraction was separated on a chromatographic column into tricyclooctane (1.4 g., 28%), and 1,5-cyclooctadiene (1.0 g.).

Photolysis of 1,5-Cyclooctadiene-Rh₂Cl₂.—A solution of 1,5-cyclooctadiene (5 g.) was added to ether (2 l.) saturated with the complex. The solution was photolyzed for 140 hr. The work-up of the solution was carried out as before: conversion, 20%; yield of bicyclo[4.2.0]octene-7, 20%; 1,4-cyclooctadiene, 23%. An appreciable amount of one of the products of free–radical attack on the solvent was also obtained.