

No apparent distinction can be made between the effects of complexing on rates of nucleophilic compared with general base mechanisms. For the types of systems described here, it is possible to determine, by the effect of complexing on rate, whether a reaction is intermolecular or intramolecular.

Kinetic Study of Complex Structure. The substrate-ligand complex system is at virtual equilibrium in the applications of the kinetic technique described here because the reactions to which the substrate are subjected are very slow relative to the complex association and dissociation reactions. Thus the kinetic approach yields the equilibrium stability constant in common with other methods for studying complexes. Since, however, the system is perturbed by causing it to undergo reaction, the procedure also permits a nonthermodynamic insight into the complex. This capability is the main reason the

kinetic method is an attractive alternative to conventional tools. A second reason is that it provides a method for the study of complexing tendencies of unstable compounds; the instability can be turned to advantage by utilizing it as the property measured in the kinetic study. In this paper the use of the kinetic method as a probe into organic complex structure has been developed. The quantity q_{11} is considered to be determined in part by the proximity of the ligand to the group being attacked. As the earlier discussion makes clear, q_{11} may also be a function of other reaction features, and its full interpretation must be based upon comparative studies with related systems.

Acknowledgment. This investigation was supported by Public Health Service Fellowship 5-F1-GM-34,063 from the National Institutes of Health.

Irradiation of *cis,cis*-1,5-Cyclooctadiene in the Presence of Copper(I) Chloride¹

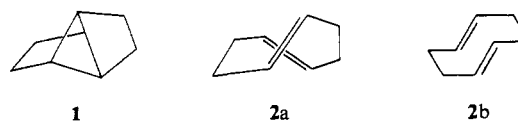
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Abstract: Irradiation of an oxygen-free pentane suspension of di- μ -chloro-bis(*cis,cis*-1,5-cyclooctadiene)dycopper(I) (**4**) at 254-m μ yields, in addition to tricyclo[3.3.0.0^{2,6}]octane (**1**), significant quantities of insoluble copper(I) complexes of *cis,trans*- and *trans,trans*-1,5-cyclooctadienes. Examination of the photochemical behavior of these dienes, and of their yields relative to the yield of **1** during the irradiation of **4**, indicates that a major part of the **1** formed has *cis,trans*-1,5-cyclooctadiene as a precursor. These data further suggest that a significant part of the photoconversion of *cis,trans*-1,5-cyclooctadiene to **1** may take place *via* the intermediacy of *trans,trans*-1,5-cyclooctadiene.

Transition metals catalyze the thermal and photochemical dimerization of a wide variety of olefins.³⁻⁸ One of the most interesting of the metal-catalyzed photochemical reactions is the conversion of *cis,cis*-1,5-cyclooctadiene to tricyclo[3.3.0.0^{2,6}]octane (**1**) by irradiation in the presence of copper(I) chloride, or by photosensitization with mercury (³P₁) atoms.^{3,4} Although the basic mechanism of the gas-phase, mercury-photosensitized reaction has been established,⁴ neither the mechanism(s) of the condensed-phase, copper-catalyzed photochemical reaction nor the nature of any intermediates in this reaction have yet been clearly defined.

The copper ion in the latter reaction might *a priori*



serve a variety of functions: *viz.*, as a photosensitizer, as a "template" controlling the stereochemistry of reaction of coordinated excited olefinic ligands, or as a catalyst facilitating carbon-carbon bond formation through mixing of appropriate metal orbitals with olefinic molecular orbitals.⁵ On the basis of quantum yield measurements, Srinivasan has suggested that the primary photochemical step under the homogeneous reaction conditions of his experiments involves absorption of light by uncomplexed *cis,cis*-1,5-cyclooctadiene. He further proposed that the copper(I) atom exerted its influence in the reaction in the subsequent stabilization of the initially formed excited state of the olefin by formation of a complex of unspecified structure (represented schematically by **3**).³ However, the appealing geometrical relation between **1** and the racemic conformation of *trans,trans*-1,5-cyclooctadiene (**2a**), and the complicated and quite different mechanism suggested for the superficially similar copper-catalyzed photochemical dimerization of norbornene,⁸

(1) Supported in part by the U. S. Army Research Office (Durham), Grant ARO(D)-31-124-435, and by the National Science Foundation, Grants GP-6222 and GP-7266.

(2) (a) National Science Foundation Predoctoral Fellow, 1964-1966; National Institutes of Health Predoctoral Fellow, 1966-1967. (b) Deceased June 4, 1966.

(3) R. Srinivasan, *J. Amer. Chem. Soc.*, **86**, 3318 (1964).

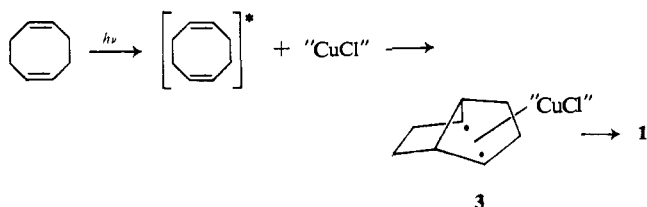
(4) I. Haller and R. Srinivasan, *ibid.*, **88**, 5084 (1966).

(5) F. D. Mango and J. H. Schachtschneider, *ibid.*, **89**, 2485 (1967).

(6) J. J. Mrowca and T. J. Katz, *ibid.*, **88**, 4012 (1966), and references therein.

(7) W. Merk and R. Pettit, *ibid.*, **89**, 4787, 4788 (1967).

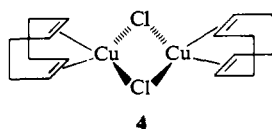
(8) D. J. Trecker, R. S. Foote, J. P. Henry, and J. E. McKeon, *ibid.*, **88**, 3021 (1966).



have led us to examine in detail several aspects of the photochemistry of *cis,cis*-1,5-cyclooctadiene in the presence of copper(I) chloride, under reaction conditions somewhat different from those described by Srinivasan. In this paper we report the isolation of significant quantities of *cis,trans*- and *trans,trans*-1,5-cyclooctadiene from this reaction, and present evidence pertinent to an understanding of the role of these compounds in the conversion of *cis,cis*-1,5-cyclooctadiene to **1**.⁹

Results

Isolation and Structure Proof of *trans,trans*-1,5-Cyclooctadiene. The starting material for the majority of our experiments has been the crystalline and well-characterized di- μ -chloro-bis(*cis,cis*-1,5-cyclooctadiene)dicopper(I) (**4**).¹⁰ Pentane rather than diethyl ether was used as the medium for our irradiations, in order to avoid the complicating free-radical side reactions encountered



by other workers during the irradiation of copper(I) chloride in ether.^{3,4,11} The use of **4** as starting material and pentane as medium for the irradiation unfortunately introduces several points of uncertainty in our experiments. In particular, it has not been possible to measure the solubility of **4** in pentane, since a suspension of **4** in this solvent dissociates in part to free *cis,cis*-1,5-cyclooctadiene and a solid nonstoichiometric 1,5-cyclooctadiene copper(I) complex. Further, we do not know exactly what fraction of the total *cis,cis*-1,5-cyclooctadiene present in the reaction mixture remains complexed with copper(I), either in solution or as suspended solid. Washing **4** with moderate quantities of pentane results in essentially quantitative extraction of cyclooctadiene from the complex (see the Experimental Section), and suggests that **4** should be appreciably dissociated under the conditions of these irradiations. Conversely the observation (*vide infra*) that *ca.* 10% of the starting *cis,cis*-1,5-cyclooctadiene can be recovered from the suspended pentane-insoluble copper containing solids at the conclusion of a typical irradiation, while *ca.* 50% is found in solution, indicates that at least 20% of the *cis,cis*-diene remains associated with solid copper(I). Thus, it appears likely that a suspension of what is nominally **4** in pentane

actually consists of a mixture of several species, and probably contains appreciable quantities of both complexed and uncomplexed *cis,cis*-1,5-cyclooctadiene; however, accurate estimates of the relative quantities of complexed and uncomplexed diene cannot be obtained from the available data.

In a typical experiment, a stirred, degassed pentane suspension of complex **4** was irradiated for *ca.* 24 hr at room temperature using low-pressure mercury lamps, and the solid material present at the end of the reaction was separated by filtration. The filtered solution was shown by glpc to contain *cis,cis*-1,5-cyclooctadiene and tricyclooctane **1** as major components, and *cis,cis*-1,4-cyclooctadiene, 4-vinylcyclohexene, and three unidentified components as minor constituents.¹² The solid material was composed of a mixture of copper(I) chloride and copper(I) olefin complexes. Treatment of this mixture with aqueous sodium cyanide solution liberated the olefinic components. Extraction and glpc analysis of the freed olefins indicated the presence of both *cis,cis*- and *cis,trans*-1,5-cyclooctadiene,¹³ as well as a small quantity of another component, to which we have assigned the *trans,trans*-1,5-cyclooctadiene structure **2** on the basis of the chemical and spectroscopic evidence which follows.

Compound **2** could be isolated in pure form by glpc under carefully controlled conditions. This compound proved to be very sensitive to traces of oxygen or acid, and slowly polymerized thermally even in the absence of these agents. It was indefinitely stable while frozen at -78° under an inert atmosphere, and reasonably stable in dilute solution in degassed aprotic solvents. It polymerized explosively on the addition of solvent that had not been deoxygenated. It was characterized by an odor similar to those of *cis,trans*-1,5-cyclooctadiene and *trans*-cyclooctene.

The infrared spectrum of **2** showed bands at 1615 ($\text{C}=\text{C}$ stretching vibration) and 985 cm^{-1} (*trans*-olefin bending vibration). No bands appeared in the 650–750- cm^{-1} region.¹⁴ The observed double-bond stretching frequency is lower than that of *cis,trans*-1,5-cyclooctadiene (1630 cm^{-1} in the ir spectrum; peaks of equal intensity at 1622 and 1635 cm^{-1} in the Raman spectrum¹³), which in turn is lower than that of *cis,cis*-1,5-cyclooctadiene (1655 cm^{-1} in the ir spectrum, and 1662 cm^{-1} in the Raman spectrum¹³).

The mass spectra of the 1,3-, 1,4-, and 1,5-cyclooctadienes are strikingly similar in the regions corresponding to fragments containing three, five, six, and seven carbon atoms (Figure 1). However, while the 1,3- and 1,4-cyclooctadienes show only small peaks in the region of m/e 50–55, the base peak of the 1,5-cyclooctadienes occurs at m/e 54 (butadiene molecular ion). The occurrence of M^+ at m/e 108 for **2** demonstrates that this compound has the same molecular formula as *cis,cis*- and *cis,trans*-1,5-cyclooctadienes. The observation of

(12) One of the unidentified side products is probably tricyclo[3.3.0.0^{2,4}]octane: *cf.* J. Meinwald and B. E. Kaplan, *ibid.*, **89**, 2611 (1967).

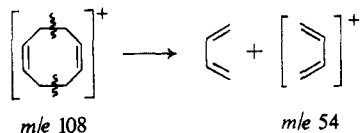
(13) A. C. Cope, C. F. Howell, J. Bowers, R. C. Lord, and G. M. Whitesides, *ibid.*, **89**, 4024 (1967). This photochemical reaction provides a practical synthesis for small quantities (50 mg or less) of *cis,trans*-1,5-cyclooctadiene.

(14) Bellamy reports the frequency range for *cis*-olefin bending vibrations as $725\text{--}675\text{ cm}^{-1}$: L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1958, pp 34–56.

(9) Part of this work has been communicated: G. M. Whitesides, G. L. Goe, and A. C. Cope, *ibid.*, **89**, 7136 (1967).

(10) H. L. Haight, J. R. Doyle, N. C. Baenziger, and G. F. Richards, *Inorg. Chem.*, **2**, 1301 (1963); X-ray structure: J. H. van den Hende and W. C. Baird, Jr., *J. Amer. Chem. Soc.*, **85**, 1009 (1963).

(11) J. E. Baldwin and R. H. Greeley, *ibid.*, **87**, 4514 (1965).



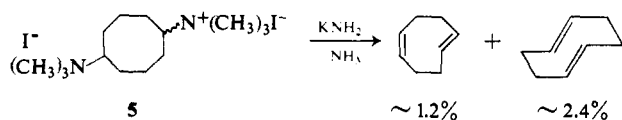
its base peak at *m/e* 54 supports the assignment of **2** as a 1,5-cyclooctadiene isomer. The fact that the mass spectra of **2** and *cis,cis*- and *cis,trans*-1,5-cyclooctadienes are distinguishable only by minor intensity differences is consistent with the proposal that **2** is *trans,trans*-1,5-cyclooctadiene, since the mass spectra of *cis* and *trans* olefins are usually almost identical.¹⁵

Chemical demonstration of the 1,5 arrangement of the double bonds in **2** was provided when its ozonolysis followed by oxidation with basic hydrogen peroxide afforded succinic acid in approximately 85% yield. Esterification of the crude acid with diazomethane yielded dimethyl succinate. The observation that no (< *ca.* 0.5%) dimethyl glutarate or adipate could be detected by gpc in the esterified acids from the ozonolysis reaction excludes a 1,4 or 1,3 arrangement of the double bonds in **2**.

The nmr spectrum of **2** showed resonances at δ 4.88 and 2.43 with relative areas 1:2. The low-field olefinic resonance is at higher field than the corresponding peaks of *cis,cis*-1,5-cyclooctadiene (δ 5.47) and *cis,trans*-1,5-cyclooctadiene (δ 5.7), and the high-field peak is somewhat downfield from the corresponding peaks of these isomers (δ 2.25 and 2.1, respectively). Although the upfield shift of the low-field resonance of **2** relative to the corresponding peaks of *cis,cis*- and *cis,trans*-1,5-cyclooctadienes is undoubtedly due to the shielding effect of the opposing double bond, data concerning the magnitude and anisotropy of shielding effects in the vicinity of carbon-carbon double bonds are not sufficiently quantitative to permit these shifts to be used in discussing the conformation of the compound.

In brief summary, these foregoing pieces of evidence clearly establish the structure of **2** to be *trans,trans*-1,5-cyclooctadiene: its mass spectrum shows it to be a C₈H₁₂ isomer and suggests that it is a 1,5-cyclooctadiene; its infrared spectrum shows the presence of one or more *trans*-disubstituted double bonds and demonstrates that it is neither *cis,cis*- nor *cis,trans*-1,5-cyclooctadiene; and its ozonolysis establishes the 1,5 position of the double bonds.

The low yield of *trans,trans*-1,5-cyclooctadiene obtained in the photoreaction is a major practical impediment to any proposed investigation of its chemistry. Accordingly, we briefly investigated the low-temperature modification¹⁶



of the Hofmann degradation of 1,5-bis(N,N-dimethylamino)cyclooctane dimethiodide¹⁷ (**5**) in an attempt to find a practical synthetic route to this compound. Treat-

(15) K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 151.

(16) G. Wittig and R. Polster, *Ann. Chem.*, **612**, 102 (1958).

(17) Z. Jacura, Ph.D. Thesis, Massachusetts Institute of Technology, 1962; A. C. Cope and Z. Jacura, unpublished.

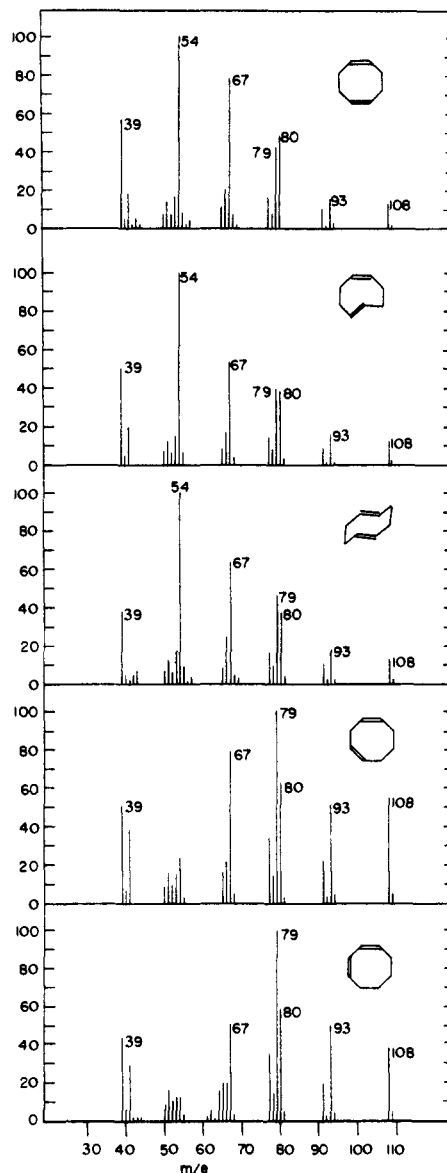


Figure 1. Mass spectra (ionizing voltage ~ 80 eV; inlet system at ambient temperature; source temperature $\sim 80^\circ$) of *cis,cis*-1,5-, *cis,trans*-1,5-, *trans,trans*-1,5-, *cis,cis*-1,4-, and *cis,cis*-1,3-cyclooctadienes.

ment of this methiodide with potassium amide in liquid ammonia did in fact yield both *cis,trans*- and *trans,trans*-1,5-cyclooctadienes in approximately 1.2 and 2.4% yields, respectively. No *cis,cis*-1,5-cyclooctadiene was observed. Hence, although this reaction does not provide a practical synthetic route to **2**, it does at least provide further confirming evidence for the assigned structure.

The ultraviolet spectrum of *trans,trans*-1,5-cyclooctadiene is remarkable. In both isoctane and diethyl ether solution the compound shows a peak at λ_{max} 246 μ m ($\epsilon \sim 1500$). In addition, it exhibits normal end absorption for a disubstituted olefin ($\epsilon_{210 \text{ m}\mu} \sim 1200$).¹⁸ The oscillator strength of the 246 μ m transition¹⁹ ($f \sim 0.05$) is sufficiently high that it seems unlikely that this transition is an olefin "mystery band" of unusually

(18) P. Bladon, H. B. Henbest, and G. W. Wood, *J. Chem. Soc.*, 2737 (1952).

high intensity.²⁰ Further, *cis,trans*-1,5-cyclooctadiene, *trans*-cyclooctene, and 9,9'-dehydrodianthracene,²¹ whose double bonds are also highly strained, show no abnormal uv absorption. Hence, the anomalous absorption exhibited by **2** is apparently not peculiar to the strained *trans* double bond. Models suggest that the double bonds in *cis,trans*-1,5-cyclooctadiene are held rather far apart,¹³ while those of both the racemic and *meso* conformations **2a** and **2b** of *trans,trans*-1,5-cyclooctadiene are constrained to be in close proximity. We believe, in the absence of other obvious explanations for this phenomenon, that the anomalous uv absorption in **2** is due to an interaction between the transannular double bonds.²²

Unfortunately, we are unable to determine unambiguously from either the uv or other available spectroscopic evidence whether the *trans,trans*-1,5-cyclooctadiene prepared by the copper-catalyzed photoreaction exists in conformation **2a** or **2b**. The high optical stabilities of resolved *trans*-cyclooctene²³ and of *cis,trans*-1,5-cyclooctadiene²⁴ suggest that the rate of interconversion of **2a** and **2b** should be slow. On the basis of the observation (*vide infra*) that **2** undergoes facile conversion to **1** rather than to tricyclo[4.2.0.0^{2,5}]octane on irradiation, we propose that **2a** is the conformation produced in the irradiation;²⁵ however, this proposal must obviously be considered tentative at this juncture.

Irradiation of 1,5-Cyclooctadiene Isomers. In considering possible mechanisms for the copper-catalyzed photochemical conversion of **4** to tricyclooctane **1**, it seemed conceivable that **1** might arise from an intramolecular thermal cycloaddition reaction of the strained and highly reactive double bonds of photochemically produced *trans,trans*- or *cis,trans*-1,5-cyclooctadiene. This hypothesis was examined and rejected on the basis of a brief examination of the thermal behavior of these two dienes.

(19) Calculated from an expression modified for unsymmetrical absorption bands

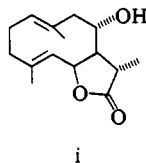
$$f = (1.62 \times 10^{-8}) \epsilon_{\max} (\nu_{\max} - \nu_i)$$

where ν_{\max} and ν_i are the frequencies (in cm^{-1}) of the absorption maximum and the long-wavelength side of the peak at half-band width. Cf. G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961, p 61.

(20) L. Lubezky and R. Kopelman, *J. Chem. Phys.*, **45**, 2526 (1966); M. B. Robin, R. R. Hart, and N. A. Kuebler, *ibid.*, **44**, 1803 (1966).

(21) N. M. Weinshenker and F. D. Greene, *J. Amer. Chem. Soc.*, **90**, 506 (1968).

(22) A transition occurring at *ca.* 210 $\text{m}\mu$ ($\log \epsilon \sim 4$) in a number of sesquiterpene lactones (*e.g.*, balchanolide (i), germacrone, and costunolide) has been attributed to a similar transannular interaction: F. Šorm



and L. Deloš, "Guaianolides and Germacranolides," Holden-Day, Inc., San Francisco, Calif., 1966; F. Šorm, *Pure Appl. Chem.*, **2**, 533 (1961).

(23) A. C. Cope and B. A. Pawson, *J. Amer. Chem. Soc.*, **87**, 3649 (1965).

(24) A. C. Cope, J. K. Hecht, H. W. Johnson, Jr., H. Keller, and H. J. S. Winkler, *ibid.*, **88**, 761 (1966).

(25) This proposal, if correct, carries no implication that **2a** or its copper(I) complex is necessarily more stable thermodynamically than **2b**, but simply requires either that it be produced more rapidly in the irradiation or that it be favored at photoequilibrium under these conditions. It may be a fortuitous coincidence that the same conformational isomer is apparently produced in the Hoffmann degradation of **5**.

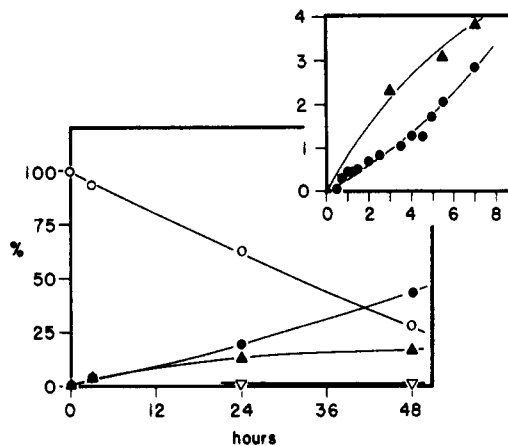


Figure 2. Yields of **1** (●), *cis,cis*-1,5-cyclooctadiene (○), *cis,trans*-1,5-cyclooctadiene (▲), and *trans,trans*-1,5-cyclooctadiene (▽), during the irradiation of **4** in pentane. The insert gives yields of **1** and *cis,trans*-1,5-cyclooctadiene on an expanded scale during the initial stages of the irradiation. The data of the two sets of plots were obtained in different experiments, and are not directly comparable, due to the effects of aging of the lamps.

Samples of *trans,trans*-1,5-cyclooctadiene which had been kept at room temperature until completely decomposed thermally showed no trace of **1** or of other of the cyclooctadiene isomers; only polymer was formed. Similarly, no trace of **1** could be detected on glpc of purified *trans,trans*-1,5-cyclooctadiene using an injection block temperature of 80° and column temperature of 60–65°. The compound was never exposed to higher temperatures.

Pyrolysis of samples of *cis,trans*-1,5-cyclooctadiene by injection into a glpc instrument having an injection port temperature of 275° resulted in the production of *cis,cis*-1,5-cyclooctadiene (12%), 4-vinylcyclohexene (5%), a compound (possibly *cis*-divinylcyclobutane) which decomposed to *cis,cis*-1,5-cyclooctadiene in the detector (10%),²⁶ and unidentified minor components; the remainder of the *cis,trans*-1,5-cyclooctadiene gave a single peak (84%) and decomposed to *cis,cis*-1,5-cyclooctadiene and 4-vinylcyclohexene on passage through the detector (300°). Although the minor components had retention times similar to **1** on the column used, no trace of **1** could be detected in the infrared spectrum of collected material²⁷





These data provide convincing evidence that **1** is not produced by an uncatalyzed thermal reaction of either *cis,trans*- or *trans,trans*-1,5-cyclooctadiene.²⁸ The possibility that **1** might be produced by a *copper-catalyzed*

(26) The retention time of this material was appreciably shorter than that of *cis,cis*-1,5-cyclooctadiene; however, material collected from the glpc had an ir spectrum identical with that of *cis,cis*-1,5-cyclooctadiene.

(27) Ziegler reported that heating a dilute solution of the compound subsequently shown¹³ to be *cis,trans*-1,5-cyclooctadiene at 110° yielded dimer (20%), polymer (43%), *cis,cis*-1,5-cyclooctadiene (12%), and *cis,cis*-1,3-cyclooctadiene (25%). Unfortunately, glpc techniques were not available for analysis of this reaction mixture, and the analyses are consequently somewhat suspect: cf. K. Ziegler, H. Sauer, L. Bruns, H. Froitzheim-Kühlhorn, and J. Schneider, *Ann. Chem.*, **589**, 122 (1954).

(28) Conversions of cyclooctadienes to tricyclooctanes apparently do occur in related systems. For perfluoro-1,5-cyclooctadiene, see M. Prober and W. T. Miller, Jr., *J. Amer. Chem. Soc.*, **71**, 598 (1949) and I. L. Karle, J. Karle, T. B. Owen, R. W. Broge, A. H. Fox, and J. L. Hoard, *ibid.*, **86**, 2523 (1964); for dibenzo[*a,e*]cyclooctadienes, M. Stiles and U. Burckhardt, *ibid.*, **86**, 3396 (1964); for possibly related reactions in [9]- and [10]annulene derivatives, see R. H. Mitchell and F. Sondheimer, *ibid.*, **90**, 530 (1968); *Tetrahedron Lett.*, 2873 (1968).

Table I. Irradiation of 1,5-Cyclooctadienes^a

Substrate	Irradiation time, hr	Yield, %						
				2	1			Other
<i>cis,cis</i> -1,5-COD	24	100	0	0	0	0	0	
<i>cis,cis</i> -1,5-COD ^b	72	Major	Trace ^c	0	0	0	0	Polymer
4	3	93	4	<1	3	0	0	
4	24	62	13	~1	19	1	1	
4	48	28	17	~1	43	5	7	
<i>cis,trans</i> -1,5-COD	2	19	0	0	0	0	0	Polymer
<i>cis,trans</i> -1,5-COD ^b	20	Major	Minor	0	Trace ^c	0	0	Polymer
<i>cis,trans</i> -1,5-COD + excess (CuCl) ₂	48	32	~20	~1	12	4	1	
2	1	0	0	0	70	0	0	Polymer

^a Irradiations were carried out in quartz vessels using low-pressure mercury lamps (2537 Å) in pentane solution except where noted. ^b Benzene solution. ^c Detectable by glpc, but yield < 1%. Identified by glpc retention time and ir spectrum.

thermal cycloaddition⁵ can be discarded on the grounds that both the copper(I) complexes of these dienes prepared in this work and the silver(I) complex of *cis,trans*-1,5-cyclooctadiene described previously^{1,3} are stable for extended periods of time in the absence of light. Hence **1** must be produced in a photochemical reaction.

In an effort to determine whether *cis,cis*-, *cis,trans*-, or *trans,trans*-1,5-cyclooctadiene was the immediate precursor to **1** in the photochemical reaction sequence, the relative yields of **1** and the three 1,5-cyclooctadienes were examined as a function of the length of time of irradiation of a suspension of **4** under typical photolysis conditions (Figure 2). The yields reported in this figure are total yields; they include both the hydrocarbons present in solution and the olefinic material bound to the insoluble copper(I) chloride.²⁹

Unfortunately it was not possible to monitor the yield of either *cis,trans*- or *trans,trans*-1,5-cyclooctadiene with high accuracy at very low conversions.³⁰ Nonetheless two significant facts emerge from the data in Figure 2. First, it is clear that the rate of formation of tricyclooctane **1** was initially slow, but became faster at higher conversions. Second, and more important, the initial rate of formation of *cis,trans*-cyclooctadiene was greater than that of **1**,³⁰ that is, the rate of formation of **1** appears qualitatively to depend on the concentration of *cis,trans*-1,5-cyclooctadiene. Despite the experimental uncertainties associated with the points in Figure 2, the data strongly suggest that **1** is not formed *directly* from either complexed or uncomplexed *cis,cis*-1,5-cyclooctadiene, but rather that *cis,trans*-1,5-cyclooctadiene is an intermediate in the reaction.

(29) It is of some importance in this connection to note that *cis,trans*- and *trans,trans*-1,5-cyclooctadienes were never detected free in the solution. The yields of these compounds summarized in Figure 2 are composed entirely of dienes bound to the insoluble copper(I) chloride suspended in the photolysis cell. That these olefins are found only in the solid residues in the irradiation, rather than free in solution, is consistent with the well-known high stability of complexes of cyclic *trans* olefins with copper(I) and silver(I): cf. M. A. Bennett, *Chem. Rev.*, **62**, 611 (1962). M. A. Muhs and F. T. Weiss, *J. Amer. Chem. Soc.*, **84**, 4697 (1962), have reported the equilibrium constants for complex formation between *cis*-cyclooctene, *trans*-cyclooctene, and *cis,cis*-1,5-cyclooctadiene and silver nitrate in ethylene glycol to be 14.4, >1000, and 75 l. mol⁻¹, respectively.

(30) The glass-column, low-temperature glpc used of necessity for the isolation and analysis of the *cis,trans*- and *trans,trans*-1,5-cyclooctadienes was unsuitable for reliable quantitative determinations of yields of these compounds less than approximately 2%. However, accurate determinations of the less sensitive **1** were possible using conventional glpc instruments (see Experimental Section).

In order to have a firmer basis for discussing the roles of these 1,5-cyclooctadienes as intermediates in the transformation of **4** to **1** and of the function of copper(I) in this reaction, we have briefly examined the photochemical behavior of each of the dienes. The products obtained in these experiments, along with typical results obtained on irradiation of *cis,cis*-1,5-cyclooctadiene and of **4** under comparable conditions, are summarized in Table I.

Under the conditions of these irradiations, *cis,cis*-1,5-cyclooctadiene is inert to photolysis in the absence of copper or a photosensitizer. On direct irradiation, *cis,trans*-1,5-cyclooctadiene is converted to *cis,cis*-1,5-cyclooctadiene in moderate yield (19%) but gives no **1** or **2**. As expected, *cis,cis*- and *cis,trans*-1,5-cyclooctadienes can be interconverted even in the absence of copper(I) by benzene-sensitized photochemical isomerization,³¹ however, benzene-sensitized isomerization of *cis,cis*- to *cis,trans*-1,5-cyclooctadiene appears qualitatively to be a much less efficient process than the conversion of *cis,trans*- to *cis,cis*-diene.^{32,33} Thus, with the possible exception of the benzene-sensitized irradiation of *cis,trans*-1,5-cyclooctadiene, no irradiation of *cis,cis*- or *cis,trans*-1,5-cyclooctadiene yields **1** in the absence of copper(I).

In contrast, direct irradiation of *trans,trans*-1,5-cyclooctadiene **2** yields **1** with high efficiency, with no other products detectable by glpc. This observation ensures that if **2** had been produced in the direct or benzene-sensitized irradiations of *cis,cis*- or *cis,trans*-1,5-cyclooctadiene, it would have been converted directly to the stable and easily detectable **1**. The fact that **1** is observed as a significant product in the irradiations of *cis,cis*- and *cis,trans*-1,5-cyclooctadienes only in the presence of copper(I) indicates clearly that copper(I) is a necessary reaction component for the production of **2**.

Discussion

Srinivasan's study of the *homogeneous* photochemical

(31) R. B. Cundall and T. F. Palmer, *Trans. Faraday Soc.*, **56**, 1211 (1960); R. B. Cundall, *Progr. Reaction Kinetics*, **2**, 208 (1964); R. B. Cundall and P. A. Griffiths, *Chem. Commun.*, 194 (1966); P. J. Kropp and H. J. Krauss, *J. Amer. Chem. Soc.*, **89**, 5199 (1967), and references therein; J. A. Marshall and R. D. Carroll, *ibid.*, **88**, 4092 (1966).

(32) For a related study of the photochemical isomerization of *cis,trans,trans*- to *cis,cis,trans*- and *trans,trans,trans*-1,5,9-cyclodecatrienes, see H. Nozaki, Y. Nisikawa, Y. Kamatani, and R. Noyori, *Tetrahedron Lett.*, 2161 (1965).

(33) The rapid formation of polymer in the benzene sensitized reactions may in part reflect photoaddition of the cyclooctadienes to benzene: cf. D. Bryce-Smith and A. Gilbert, *Chem. Commun.*, 643 (1966).

conversion of *cis,cis*-1,5-cyclooctadiene to **1** on irradiation in the presence of copper(I) chloride established, among other things, that only a very small fraction of the diene present in the ether solution was complexed with copper ion. Using arguments based on the optical densities of the various components of the irradiated solution, and on estimates of the quantum yields which would be required to describe the photochemical transformation of the complexed and uncomplexed forms of 1,5-cyclooctadiene into **1**, Srinivasan was able to demonstrate that *uncomplexed* diene was the primary light-absorbing species in solution under the conditions of his irradiations.

A choice of the primary light-absorbing species in the heterogeneous pentane suspension of **4** used in our experiments is unfortunately much more difficult, due both to the impracticability of meaningful quantum yield measurements under these conditions and to our inability to estimate either the solubility or dissociation constant of **4** in pentane. The last of these problems is particularly vexing, since **4**, if anything, appears to be *less* dissociated in heterogeneous pentane suspension than in homogeneous ether solution, and consequently appears relatively more likely to be the primary light-absorbing species in pentane than in ether. Nonetheless, both on the basis of the qualitative observation that a significant fraction of the *cis,cis*-1,5-cyclooctadiene present in a pentane suspension of **4** is free in solution, and on the basis of the obvious analogy between the system studied by Srinivasan and that investigated in this work, we will assume that uncomplexed *cis,cis*-1,5-cyclooctadiene is the primary light-absorbing species in irradiation of a pentane suspension of **4**.

Accepting this assumption, an uncomplexed electronically excited 1,5-cyclooctadiene is necessarily the first species formed on irradiation. This excited state, whatever its geometry, is certainly energetically capable of conversion to **1**. However, several observations suggest that the initially formed excited 1,5-cyclooctadiene, when generated under the conditions of our experiment, is converted to **1** in large measure by way of one or more stable intermediates.

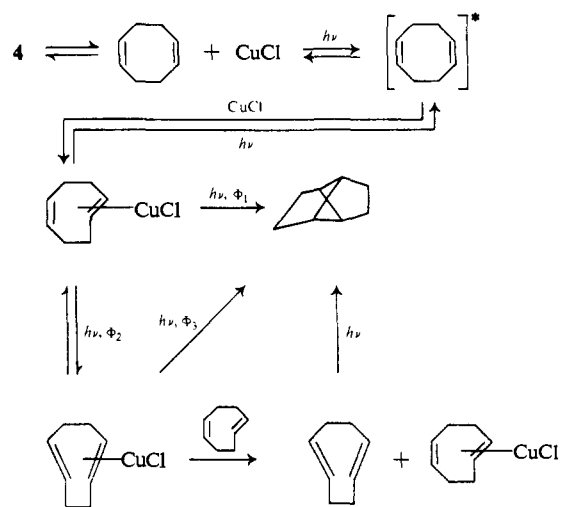
First, neither direct nor benzene-sensitized irradiation of *cis,cis*-1,5-cyclooctadiene, in the absence of copper(I) chloride but under conditions otherwise comparable to those of the copper-catalyzed photoreaction, yields detectable quantities of **1**.³⁴ Srinivasan has interpreted a similar observation under homogeneous conditions to mean that copper(I) functions in the photoreaction by coordination with the excited diene, and has suggested that **1** is obtained directly from this excited complex without a subsequent photochemical step. Although we cannot exclude a contribution from a pathway of this type in the irradiation of **4** in pentane, the isolation of *cis,trans*- and *trans,trans*-1,5-cyclooctadiene from this photoreaction, and the demonstration that these olefins are converted to **1** under the conditions of the reaction, suggest that it may be more profitable to rationalize the influence of the copper(I) on the basis of its ability to complex strongly with the ground-state *trans* double bonds of these dienes. Second, the relative yields of *cis,trans*-1,5-cyclooctadiene and of **1** observed at low

conversions of **4** (Figure 2) show that the rate of formation of **1** depends on the concentration of this diene in the irradiation mixture, and suggests that at least part of the **1** observed as a reaction product is derived from a photo-reaction of *cis,trans*-diene. The high steady-state concentration of *cis,trans*-1,5-cyclooctadiene observed during the latter stages of the irradiation (Figure 2), and the relatively high efficiency with which it is converted to **1** on irradiation in the presence of copper(I) chloride (Table I) indicate that a major portion of **1** has the *cis,trans*-diene as a precursor. Finally, the facile transformation of *trans,trans*-1,5-cyclooctadiene to **1** on irradiation, together with the observation that irradiation of *cis,trans*-1,5-cyclooctadiene in the presence of copper(I) chloride yields *trans,trans*-1,5-cyclooctadiene, raises the interesting possibility that the *trans,trans*-diene itself, despite its consistently low concentration, might give rise to a significant quantity of **1**.

Thus, we cannot rigorously exclude contributions to the conversion of **4** to **1** from either a direct photochemical reaction or from a less direct pathway involving conversion of uncomplexed *cis,cis*-1,5-cyclooctadiene to **1** via some undetected copper-complexed intermediate, but not involving *cis,trans*- or *trans,trans*-1,5-cyclooctadiene, on the basis of the relatively qualitative data available; however, it is clear from the accumulated data that an appreciable fraction of the **1** isolated at the conclusion of the reaction must have come in some fashion from *cis,trans*-1,5-cyclooctadiene.

On the basis of these data, we propose that the conversion of **4** to **1** should be described by some variant of the mechanism outlined in Scheme I. The most interest-

Scheme I



ing problem posed by this scheme concerns the role of *trans,trans*-1,5-cyclooctadiene in the formation of **1**. Under the conditions of the irradiations, both *cis,trans*- and *trans,trans*-1,5-cyclooctadienes are present in appreciable concentrations only as their copper(I) complexes. The major part of **1** might then be formed directly by irradiation of the *cis,trans*-1,5-cyclooctadiene copper(I) complex, or it might result from photochemical conversion of this complex to *trans,trans*-1,5-cyclooctadiene and subsequent photolysis of this latter compound. Ideally, examination of the rates of formation of **1** and of

(34) However Professor Harold Ward (Brown University) has obtained **1** on benzene-photosensitized irradiation of *cis,cis*-1,5-cyclooctadiene in the *vapor* phase: H. R. Ward, private communication.

trans,trans-1,5-cyclooctadiene at conversions well below the levels of Figure 2 would provide data which could be used to answer this question. Unfortunately the low steady-state concentration of the *trans,trans*-diene reached during the irradiation, and the appreciable experimental difficulties involved in analyzing small quantities of this compound, make a detailed quantitative yield study at very low concentrations impractical.

Alternatively, a knowledge of the absorption characteristics of the copper(I) complexes with *cis,trans*- and *trans,trans*-1,5-cyclooctadienes, and of the quantum yields Φ_1 , Φ_2 , and Φ_3 (Scheme I) describing the conversion of these complexes to **1** on irradiation, would permit an estimation of the relative rates of formation of **1** from each diene. Under the approximately steady-state conditions reached in the later stages of the photoreaction, the concentration of *cis,trans*-1,5-cyclooctadiene is approximately twenty times that of *trans,trans*-1,5-cyclooctadiene. On the other hand, the extinction coefficient of the 246-m μ transition of *trans,trans*-1,5-cyclooctadiene is sufficiently large that, if the extinction coefficients of the copper complexes of these dienes in the region of the emission maximum of the lamps are in the same ratio as the extinction coefficients of the uncomplexed dienes in this region, the *trans,trans*-1,5-cyclooctadiene complex should absorb a larger fraction of the incident light than the *cis,trans* complex. The quantum yield, Φ_3 , characterizing the internal cycloaddition of the *trans,trans*-1,5-cyclooctadiene copper(I) complex would be expected to be high.³⁵ Hence, with these assumptions, at one extreme of interpretation the rates of formation of **1** from *cis,trans*- and *trans,trans*-1,5-cyclooctadiene precursors should be approximately equal; at the other extreme, the major fraction of **1** might be formed from the *trans,trans*-diene. Unfortunately, carrying this approach through in a convincing quantitative manner requires a knowledge of the extinction coefficients of the diene-copper(I) complexes, and of the quantum yields of the individual steps in the presence of copper, and it is less than obvious how these numbers might be obtained practically in the heterogeneous reaction system of this study.

It is worthwhile pointing out explicitly that the conclusions reached in this paper are intended to apply only to the particular heterogeneous reaction system studied here. The vapor phase studies of Srinivasan^{3,4} and Ward³⁴ have demonstrated clearly that the presence of copper(I) is not a prerequisite for the photochemical conversion of 1,5-cyclooctadiene to **1**, and it seems entirely possible that the homogeneous copper-catalyzed photoreaction studied by Srinivasan⁴ may proceed by still another mechanism. Thus, it appears probable that a number of reaction pathways connect 1,5-cyclooctadiene and **1**, and that mechanistic conclusions drawn from studies of one system need necessarily have very little pertinence to other systems.

(35) The quantum yield of formation of oxetane from benzaldehyde in 4 *M* 2,3-dimethyl-2-butene has been found to be 0.527 (N. C. Yang, R. Loeschen, and D. Mitchell, *J. Amer. Chem. Soc.*, **89**, 5465 (1967)). The photocycloaddition of *trans*-stilbene and 2,3-dimethyl-2-butene (4 *M* in hexane) proceeds with a quantum yield of 0.538 (O. L. Chapman private communication). Although these quantum yields describe cycloaddition reactions proceeding from $n \rightarrow \pi^*$ and aromatic $\pi \rightarrow \pi^*$ excited states, respectively, and as such are not necessarily directly comparable to that describing the olefinic $\pi \rightarrow \pi^*$ cycloaddition presumed to be involved in the conversion of **2** to **1**, their high values do suggest that a low value for the last process is unlikely.

The correct description of the detailed function of the copper(I) in the reaction sequence of Scheme I remains a topic of speculation. The experiments reported here are not helpful in judging the correctness of Srinivasan's suggestion that the copper(I) serves to stabilize an electronic excited state of 1,5-cyclooctadiene.³ However, an alternative and attractive possibility raised by the isolation and examination of *cis,trans*- and *trans,trans*-1,5-cyclooctadienes is that the ability of copper(I) to form strong coordinate bonds with the ground-state *trans* double bonds of these dienes serves both to protect them from polymerization, and to shift the position of the photoequilibria between the three 1,5-cyclooctadiene isomers toward the sterically strained but strongly complexing *cis,trans*- and *trans,trans*-1,5-cyclooctadienes at the expense of the relatively unstrained but weakly coordinating *cis,cis*-1,5-cyclooctadiene.

Experimental Section

General. Melting points were determined on a Reichert hot-stage microscope and are uncorrected. All irradiations were conducted in quartz vessels using a Rayonet Photochemical Reactor equipped with RPR 2537A lamps. Solutions were concentrated at 0–5° (50–100 mm) with the aid of a rotary evaporator, except as noted. Infrared spectra were taken on a Perkin-Elmer Model 237B spectrometer. Mass spectra were taken on a Hitachi Perkin-Elmer Model RMU-6D mass spectrometer. Nmr spectra were obtained using Varian A-60 and HA-60 spectrometers. Ultraviolet spectra were taken on a Cary Model 14 recording spectrophotometer. Glpc analyses were carried out using the following columns and instruments: column A, 8 ft \times 0.25 in. 25% 4-nitro-4-methylpiperlonitrile (NMPN) on Chromosorb P, glass column operated isothermally at 65°;³⁶ column B, 8 ft \times 0.5 in. 10% 1,2,3-tris(2-cyanoethoxy)propane (TCEOP) on Chromosorb P, glass column operated isothermally at 65°;³⁶ column C, 12 ft \times 0.25 in. 5% XF 1150 (nitrile silicone fluid), 40–65° (F & M Model 810 gas chromatograph, thermal conductivity or flame ionization detector as noted); column D, 2 ft \times 0.25 in. 20% silicone rubber SE 30, temperature as noted (F & M Model 720 gas chromatograph). The areas of glpc peaks were determined by planimeter (columns A and B) or by Disc integrator (column C). Elemental analyses were performed by Dr. S. M. Nagy and associates. Pentane was purified by stirring with sulfuric acid, and distilled from barium oxide. All glassware was rinsed with concentrated ammonium hydroxide and distilled water, and dried before use.

Di- μ -chloro-bis(*cis,cis*-1,5-cyclooctadiene)dycopper(I) (**4**) was prepared using published procedures.¹⁰

Anal. Calcd for $C_{16}H_{24}Cu_2Cl_2$: C, 46.38; H, 4.57; Cl, 17.11. Found: C, 45.67, 45.48; H, 5.84, 5.90; Cl, 17.18, 17.21.

Pentane Washing of Complex 4. A 0.1-g sample of complex **4** was washed with five 5-ml portions of pentane and dried at 100 mm and room temperature for 2 hr.

Anal. Calcd for $C_{16}H_{24}Cu_2Cl_2$: C, 46.38; H, 4.57; Cl, 17.11. Found: C, 32.96; H, 4.57; Cl, 21.57 (~29% low in 1,5-cyclooctadiene).

The procedure was repeated with 15 5-ml portions of pentane.

Anal. Found: C, 1.42; H, 0.31; Cl, 34.04 (~97% low in 1,5-cyclooctadiene).

Irradiation of Complex 4. Complex **4** (0.5 g, 1.2 mmol) and 70 ml of pentane were placed in a 100-ml quartz vessel equipped with a nitrogen inlet and condenser, and irradiated for 24 hr with magnetic stirring. A stream of prepurified nitrogen previously saturated with pentane was bubbled through the suspension *via* a Teflon syringe needle; the agitation provided by this gas stream stirred the mixture and prevented caking of the solid on the walls of the vessel. The mixture was filtered and the solid was washed several times with pentane. Analysis of the concentrated filtrate by glpc

(36) Injection port and detector block temperatures were maintained at 80°. The glpc instrument used was of Massachusetts Institute of Technology Chemistry Department design. Attempts to use any of the available commercial instruments with metal columns for analysis or separation of mixtures containing **2** resulted in complete destruction of this compound.

using cyclooctane as an internal standard (column A) indicated the presence of *cis,cis*-1,5-cyclooctadiene (52%), tricyclo[3.3.0.0^{2,6}]-octane 1 (19%), *cis,cis*-1,4-cyclooctadiene (1.3%), and 4-vinylcyclohexene (1.9%).³⁷

The solid material³⁸ from the irradiation was shaken with a mixture of 25 ml of pentane and 25 ml of 15% aqueous sodium cyanide solution at 0°, and the hydrocarbon phase was separated. The aqueous layer was again extracted with 25 ml of cold pentane, and the combined pentane solutions were washed with cold water (25 ml), filtered quickly throughout Molecular Sieves (Linde 4A), and concentrated. The solutions were stored under nitrogen at 0°; all transfers and manipulations were carried out rapidly without protection from atmospheric oxygen. Analysis of the concentrate by glpc (column B) using cyclooctane as internal standard showed the presence of *cis,cis*-, *cis,trans*-, and *trans,trans*-1,5-cyclooctadienes in 10, 13, and 1% yields, respectively.

***trans,trans*-1,5-Cyclooctadiene (2).** The combined solid material³⁸ from 12 irradiations carried out as described above was stirred with 100 ml of 15% aqueous sodium cyanide solution at 0°, and the mixture was extracted with two 50-ml portions of cold pentane. The pentane solution was washed with 50 ml of cold water, filtered through Molecular Sieves (Linde 4A), and concentrated. The concentrate was kept at 0° in a nitrogen atmosphere during the time required for preparative glpc. The following components (retention times) were found in this concentrate (column B, helium flow 200 cc/min): *cis,trans*-1,5-cyclooctadiene (10.2 min), *trans,trans*-1,5-cyclooctadiene (13.5 min), and *cis,cis*-1,5-cyclooctadiene (15.3 min). The *trans,trans*-1,5-cyclooctadiene was isolated by preparative glpc and was kept in a Dry Ice-acetone bath until use. Compound 2 has ir (CCl₄) 2990 (s), 2940 (vs), 2925 (sh), 2850 (s), 1615 (m), 1440 (s), 1155 (s), 985 (s), 940 (m), 920 (m), 870 (w), and 840 (w) cm⁻¹; (CS₂) 780 (m) and 765 (m) cm⁻¹ (vs = very strong, s = strong, m = medium, w = weak, sh = shoulder). The carbon tetrachloride solution was allowed to stand at room temperature for 2 hr and the spectrum was run again. The bands at 2990, 1615, 1155, 985, 940, 920, and 840 cm⁻¹ had disappeared, the band at 1450 cm⁻¹ had broadened, the band at 870 cm⁻¹ was much stronger, and new bands had appeared at 1290, 1235, 1180, 1060, 1025, 900, 710, and 660 cm⁻¹. The nmr spectrum of 2 (1:1 CCl₄, TMS at -20°) showed broad (*ca.* 10–15 Hz) structureless peaks at δ 2.43 (8, CH₂) and 4.88 (4, CH). Uv³⁹ and mass spectra were obtained on samples freshly collected from glpc.

Irradiation of Complex 4 and Analysis at Low Conversion. The data presented in Figure 2 were obtained using the following procedure. A suspension of 0.500 g (1.2 mmol) of complex 4 in 70 ml of pentane containing a weighed amount of cyclooctane was irradiated in the usual manner. Periodically the lamps were extinguished and the nitrogen flow was stopped. A 2-ml sample of the supernatant solution was withdrawn, concentrated in a stream of nitrogen, and analyzed for tricyclooctane 1 and cyclooctane by glpc (column C, flame ionization detector).

After the desired number of aliquots had been taken, the reaction mixture was filtered and the solid washed with pentane until free of cyclooctane. The olefins were isolated from the solid in the usual manner, cyclooctane internal standard was added, and the mixture was analyzed by glpc (column B) for *cis,trans*-1,5-cyclooctadiene and cyclooctane.

Ozonolysis of 2. A sample (estimated³⁹ to be 15 mg, 0.14 mmol) of 2, prepared and collected from glpc as described above, was dissolved in 10 ml of methylene chloride. Into this solution, which was kept in a Dry Ice-isopropyl alcohol bath before and during ozonolysis, was bubbled ozonized oxygen until the blue color persisted (*ca.* 0.5 min), and the blue solution was allowed to

stand for 10 min. Nitrogen was bubbled through the solution to remove excess ozone. Methanol (30 ml) was added and the solution was allowed to warm to ice-bath temperature. To the stirred solution was added 5 ml of 20% aqueous sodium hydroxide solution, then 5 ml of 30% hydrogen peroxide was added dropwise over 10 min. Water (10 ml) was added, and the resulting mixture was stirred in the ice bath for 1 hr. The mixture was warmed gently on the steam bath, and methylene chloride was removed by distillation. The resulting solution was heated under reflux for 1 hr. Most of the methanol was removed by distillation, and the residue was cooled and made acidic with concentrated hydrochloric acid. This solution was extracted continuously with ether for 15 hr. The ether extract was dried and evaporated to yield 28 mg (85% of 0.28 mmol) of crude succinic acid, mp 169–176° (lit.⁴⁰ mp 182°). The crude diacid was esterified with ethereal diazomethane. The mass and ir spectra of a sample of the resulting dimethyl succinate, collected from glpc, corresponded to those of authentic material.

Hofmann Elimination on 1,5-Bis(dimethylamino)cyclooctane Dimethiodide (5).¹⁷ To 80 ml of liquid ammonia (distilled from sodium) were added a crystal of ferric nitrate and 0.5 g (12.8 mg-atoms) of potassium, and the mixture was stirred until the blue color disappeared. The amine methiodide (1.0 g, 2.08 mmol) was added and the resulting mixture was stirred for 2 hr under reflux. Ammonium sulfate (3 g) and 50 ml of ether were added, and the ammonia was evaporated quickly in a stream of nitrogen. Water was added to the residue, and the mixture was filtered and separated. The aqueous layer was extracted with ether, and the combined ether solutions were washed with water and aqueous copper(II) sulfate, then filtered through molecular sieves and concentrated. Glpc of the concentrated solution with the addition of cyclooctane internal standard showed the presence of *cis,trans*- (2.8 mg, 1.2%) and *trans,trans*-1,5-cyclooctadienes⁴¹ (5.6 mg, 2.4%) as the only volatile products.

Pyrolysis of *cis,trans*-1,5-Cyclooctadiene. A pentane solution of the diene, freshly prepared from its silver nitrate complex,¹³ was injected into a glpc (column C); the injection port temperature was 275° and the thermal conductivity detector temperature was 300°.³⁷

Irradiation of *cis,cis*-1,5-Cyclooctadiene in Benzene. A degassed solution of 2.0 g of the diene in 50 ml of benzene was irradiated for 72 hr. A white precipitate formed and was removed by filtration. Glpc (column A) of the filtrate showed the presence of *cis,cis*-1,5-cyclooctadiene, a trace (*ca.* 1%) of *cis,trans*-1,5-cyclooctadiene, and no tricyclooctane 1 (limit of detection 1%). Extraction of the solution with 1% aqueous silver nitrate solution, treatment of the aqueous extract with ammonium hydroxide, extraction with pentane,¹³ and glpc confirmed the presence of *cis,trans*-1,5-cyclooctadiene.³⁷

Direct Irradiation of *cis,trans*-1,5-Cyclooctadiene. A solution of 121 mg of the diene in 75 ml of pentane was irradiated at 1–15°. After 2 hr glpc analysis (column A) using cyclooctane as internal standard showed the presence of 19% *cis,cis*-1,5-cyclooctadiene, and trace amounts of other components. No dimer of *cis,trans*-cyclooctadiene⁴² was present by glpc (column C, 170°).

Irradiation of *cis,trans*-1,5-Cyclooctadiene with Excess Cuprous Chloride. A pentane solution of *cis,trans*-1,5-cyclooctadiene (*ca.* 120 mg, 1.1 mmol) was added to copper(I) chloride⁴³ (249 mg, 2.5 mmol) and the mixture was irradiated for 48 hr, then filtered and concentrated. The filtered solution, and the mixture of olefins liberated from the solid residue with aqueous sodium cyanide were analyzed by glpc (column A).

Irradiation of *cis,trans*-1,5-Cyclooctadiene in Benzene. A benzene solution (70 ml) of the diene (about 0.2 g) was prepared from the silver nitrate complex.¹³ The solution was irradiated for 20 hr at 10–15°, then concentrated. Pentane was added to precipitate most of the polymer, and the mixture was filtered, concentrated, and analyzed³⁷ by glpc (column B).

Irradiation of *trans,trans*-1,5-Cyclooctadiene. A pentane solution of the diene and 19.4 mg of cyclooctane internal standard was prepared. Glpc (column B) showed the solution to contain 16.7 mg of diene. The solution (10 ml) was irradiated for 1 hr, filtered, and concentrated by distillation. Glpc of the resulting

(37) Components were identified by comparison of glpc retention times and ir spectra of samples collected from glpc with those of authentic samples.

(38) This irradiated solid could be stored for more than a month in an atmosphere of dry nitrogen at ambient temperature without appreciable decomposition.

(39) The weight of the sample of 2 used for this determination was an estimate based on the known response factor for *cis,cis*-1,5-cyclooctadiene on the glpc instrument used for collection, and on the reproducible efficiency of collection for the *cis,cis*-diene. The thermal sensitivity of concentrated 2 was unfortunately such that more accurate measures of sample weights would have been difficult in practice. The estimated quantity of diene used in this experiment, and in consequence the calculated extinction coefficient, might be in error by as much as 20%.

(40) "Handbook of Chemistry and Physics," 46th ed, Chemical Rubber Co., Cleveland, Ohio, 1964, p C-548.

(41) The glpc retention time, ir and uv spectra of 2 prepared by this method were identical with those of 2 from the irradiation.

(42) R. Willstätter and H. Veraguth, *Chem. Ber.*, **38**, 1975 (1905).

(43) R. N. Keller and H. D. Wycoff, *Inorg. Syn.*, **2**, 2 (1946).

solution showed the presence of cyclooctane and 11.7 mg (70%) of tricyclooctane (2),³⁷ and no other components (limit of detection about 2%).

Acknowledgments. We would like to express our

appreciation to Dr. A. S. Mehta for preliminary experiments, to Mr. H. L. Mitchell for running mass spectra, and to Professor John Baldwin (University of Oregon) for a helpful discussion.

Halomethyl-Metal Compounds. XXV. α -Polyhaloalkyltin Compounds as Halocarbene Precursors¹

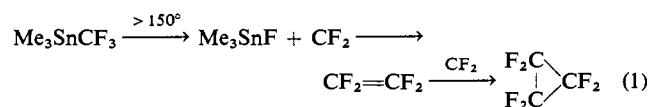
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Abstract: The thermolysis of a number of halomethyl-tin compounds in the presence of olefins has been investigated. Trimethyl(trichloromethyl)tin was found to be an effective CCl_2 transfer agent at 140° , and the action of sodium iodide in 1,2-dimethoxyethane at 85° induced CCl_2 transfer from this tin compound in fair yield. Trimethyl-(bromodichloromethyl)tin transferred CCl_2 to olefins very slowly at 80° , rapidly at 140° , but a small amount of decomposition to give Me_3SnCl and CClBr also was noted. In contrast, trimethyl(dichloromethyl)tin proved to be very stable thermally and it did not transfer CHCl at 140° . Trimethyl(α,α -dichlorobenzyl)tin appeared to transfer PhCCl to tetramethylethylene, but the initially formed cyclopropane was not isolated. Instead, 2,4-dimethyl-3-phenylpenta-1,3-diene, a product derived from ring opening of the latter and subsequent loss of hydrogen chloride, was obtained in 34% yield. When trimethyl(α,α -dichlorobenzyl)tin was pyrolyzed in the presence of cyclohexene, the major products were dimethyltin dichloride and styrene, and their formation could be explained in terms of a ($\text{Me} \rightarrow \text{C}$, $\text{Cl} \rightarrow \text{Sn}$) interchange in $\text{Me}_3\text{SnCCl}_2\text{Ph}$ before α elimination of a tin chloride. In the pyrolysis of bis(trimethyltin)bromochloromethane in the presence of cyclohexene at *ca.* 170° , the formation in low yield of 7-chloro-7-trimethyltinorcarane, bis(3-cyclohexenyl)methane, and 7,7'-bi(bicyclo[4.1.0]heptane) spoke for trimethyltinhalocarbene intermediates in the decomposition process. A similar reaction with bis(trimethyltin)-dibromomethane gave only 7,7'-bi(bicyclo[4.1.0]heptane), while bis(trimethyltin)dichloromethane was quite stable thermally.

Our previous investigations have demonstrated the outstanding utility of halomethyl-mercury compounds as divalent carbon transfer agents. Using the appropriate mercurials, CCl_2 ,³ CClBr ,³ CBr_2 ,³ CClF ,⁴ CHCl ,^{5,6} CHBr ,⁶ CH_2 ,⁷ and Me_3SiCCl ⁸ could be added to $\text{C}=\text{C}$ double bonds or inserted into various element-element single bonds. Such divalent carbon transfer from halomethyl-metal compounds appears to be a general reaction.⁹ In order to find out more concerning the factors which affect the nature of the divalent carbon transfer process, we have examined in some detail the thermolysis of a number of halomethyl-tin compounds in the presence of olefins which could serve as reactive

carbene traps. Organotin compounds were chosen as the subject for this study for several reasons. (1) Taking into account all that is known to date concerning such α -elimination reactions of metal halides from halomethyl-metal compounds,⁹ we would expect that the halomethyl-tin/olefin reaction would proceed by way of halocarbene intermediates, rather than a bimolecular reaction between the organometallic and the olefin. (2) Organotin starting materials for such a study can be prepared by a number of different routes.¹⁰⁻¹³ (3) The organotin halides produced in α elimination from halomethyltin compounds are easily removed from the reaction mixture by precipitation as the fluorides or as the ammonia adducts. (4) At the time this study was begun, the thermolysis of trimethyl(trifluoromethyl)tin had already been reported¹⁴ (eq 1) and we ourselves had made



this method for CF_2 generation more useful by appli-

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(2) National Institutes of Health Predoctoral Fellow, 1964-1968.

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