time through a spinning-band column, bp 65° (25 mm). Benzil (Matheson Coleman and Bell, reagent grade) was recrystallized from ethanol–water and then from ligroin, mp 96.5–96.8°. Chloroform (Matheson Coleman and Bell, Spectro quality) was used without further purification. Chrysene, recrystallized and sublimed, was supplied by Dr. J. R. Fox. *p*-Cyanobenzophenone was obtained from Dr. C.-H. Wu; it was recrystallized from ligroin–benzene, mp 115.5–116°. *p*-Diacetylbenzene (Aldrich, research grade) had been chromatographed on alumina and then recrystallized twice by Dr. A. A. Lamola. 4,4′-Dichlorobenzophenone (K and K Laboratories) was used without further purification; its phosphorescence spectrum was taken by Dr. A. A. Lamola and showed no trace of benzophenone. Fluorenone (Matheson Coleman and Bell, reagent grade) was recrystallized once from ligroin and once from ethanol, mp 83.8–84.5°. Maleic anhydride (Matheson Coleman and Bell, reagent grade) was sublimed at 45° (0.5 mm) immediately before use. Naphthalene (Matheson Coleman and Bell) was recrystallized twice from ethanol. Propiophenone (Matheson Coleman and Bell, reagent grade) was recrystallized from ligroin at −5° and then distilled at 0.5 mm through a Vigreux column; the fraction boiling at 63–64° was collected for use. Tetracyanoethylene (Aldrich, research grade) was recrystallized from ethyl acetate–chloroform. Thioxanthone was treated with carbon black and then recrystallized twice from methanol, mp 209°. Toluene (Matheson Coleman and Bell reagent grade) was shaken three times with concentrated sulfuric acid, dried over calcium chloride, and distilled from sodium. Triphenylene (Aldrich, research grade) was sublimed, mp 194–198°. Xanthone (Aldrich) was passed through an alumina column, eluted with benzene, and then recrystallized twice from methanol.

Procedures. Most irradiations were carried out in the "merry-go-round," an apparatus in which a number of tubes are rotated about a Hanovia immersion reactor containing a 450-w, medium-pressure lamp. The entire apparatus is placed in a constant-temperature water bath. The samples were placed in Pyrex culture tubes (13 mm o.d.) which had been constricted. The tubes were washed with Orvus soap, rinsed five times with distilled water and once with methanol, and dried at 125°. Solutions were prepared in volumetric flasks and 3- or 4-ml aliquots were added to the individual tubes. The samples were then degassed using three freeze–thaw cycles, with pumping at 5×10^{-4} mm, before being sealed off. The Pyrex tubes passed very little of the 2753- and 2804-A lines from the source and in most experiments with sensitizers a uranium–glass filter having virtually no transmission below 3300 A was used. No filter was used in experiments involving direct irradiation.

After irradiation the tubes were opened and the product was collected by suction filtration, washed with a few milliliters of cold reaction solvent, dried for 20 min at 115°, and weighed. The solubility of the adduct in all reaction solvents is too low for convenient measurement. However, varying amounts of product may have remained in the supernatant liquid by supersaturation, since crystal growth is very slow.

Some measurements of quantum yields were made using the collimated beam provided by the apparatus previously described.[9] Actinometry for runs with both systems was carried out by monitoring the reaction of benzophenone by benzhydrol.[9]

Acknowledgment. This work was supported in part by a grant from the National Science Foundation. W. M. H. also held summer fellowships provided by the Shell Oil Company and the National Science Foundation.

Radical Additions of Cl–CCl$_3$ to *cis*-Cyclooctene[1,2]

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Contribution from Coates Chemical Laboratories, Louisiana State University, Baton Rouge, Louisiana 70803. Received January 11, 1967

Abstract: Both photo- and thermally initiated additions of carbon tetrachloride to *cis*-cyclooctene give mainly stereoisomeric 1-chloro-4-(trichloromethyl)cyclooctanes, products of transannular addition. Small amounts of the stereoisomeric 1,2-addition products and several other minor products containing less chlorine per molecule are also formed. Peroxide-initiated addition of trichloromethanesulfonyl chloride (net addition of Cl–CCl$_3$) produces the 1,2- and 1,4-addition products in the ratio 30:70. The activation energy requirement for transannular hydrogen atom shift in this system is estimated to be approximately 18 kcal/mole. Selective dehydrochlorinations of the addition products have been achieved; potassium hydroxide in alcoholic dimethyl sulfoxide produces mostly chloro-(dichloromethylene)cyclooctanes, but alcoholic silver nitrate leads to (trichloromethyl)cyclooctenes.

Transannular hydride shifts during cationic reactions of medium-ring compounds were first reported in 1952[3] and are now considered to be characteristic of those compounds.[4] Although these rearrangements occur to small extents in unsubstituted cycloalkyl cations, they become extensive when the initial carbonium ion center is flanked by an electron-withdrawing substituent.[4] Examples of transannular reactions involving radical intermediates have been far fewer in number than those involving cationic intermediates. Some[5] but not all[6] radical additions to 1,5-cyclooctadiene yield mostly substituted bicyclo[3.3.0]octanes as products (transannular C=C participation), and thiol addition to norbornadiene gives both normal and transannular products.[7] Recently, reports of transannular hydrogen abstraction by the intermediate alkoxy radical formed during decomposition of 1-methylcyclooctyl hypochlorite[8] and transannular hydrogen migration to a

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(1) (a) Presented in part at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965; Abstracts, p 6S. (b) Based upon the Ph.D. dissertation submitted by T. M. C., Louisiana State University, Jan 1966. (c) A preliminary account of part of this research has been published: J. G. Traynham and T. M. Couvillon, *J. Am. Chem. Soc.*, 87, 5806 (1965).

(2) Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research (Grant No. 1817-A.)

(3) (a) A. C. Cope, S. W. Fenton, and C. F. Spencer, *J. Am. Chem. Soc.*, 74, 5884 (1952); (b) V. Prelog, K. Schenker, and H. A. Gunthard, *Helv. Chim. Acta*, 35, 1598 (1952).

(4) (a) V. Prelog and J. G. Traynham in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Division of John Wiley and Sons, Inc., New York, N. Y., 1963, Chapter 9; (b) A. C. Cope, M. M. Martin, and M. A. McKervey, *Quart. Rev.* (London), 20, 119 (1966).

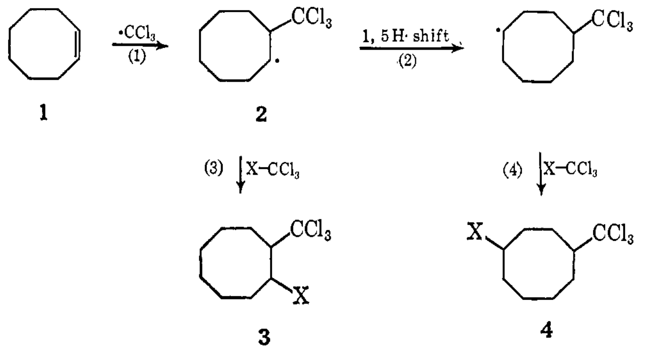
(5) R. Dowbenko, *J. Am. Chem. Soc.*, 86, 946 (1964).

(6) J. M. Locke and E. W. Duck, *Chem. Commun.*, 151 (1965).

(7) S. J. Cristol, G. D. Brindell, and J. A. Reeder, *J. Am. Chem. Soc.*, 80, 635 (1958).

(8) A. C. Cope, R. S. Bly, M. M. Martin, and R. C. Petterson, *ibid.* 87, 3111 (1965).

carbon radical center during radical additions to medium-ring olefins[9] have been reported. Only the latter rearrangement is directly comparable to the hydride shifts characteristic of medium-ring carbonium ion chemistry, and when those reports[9] appeared, our own investigations of radical additions to the simple medium-ring olefin, *cis*-cyclooctene, were substantially complete.[1a] We have described in detail the largely normal 1,2 addition of bromotrichloromethane to *cis*-cyclooctene.[1c,10] This paper describes our radical additions of Cl–CCl_3 (from carbon tetrachloride and from trichloromethanesulfonyl chloride) to *cis*-cyclooctene.[1c] These reactions are mainly transannular additions (product **4**), and a rough estimate of the activation energy for transannular hydrogen atom shift in 2-(trichloromethyl)cyclooctyl radical (**2**) has been made.

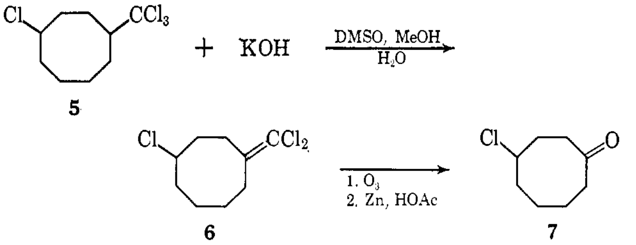


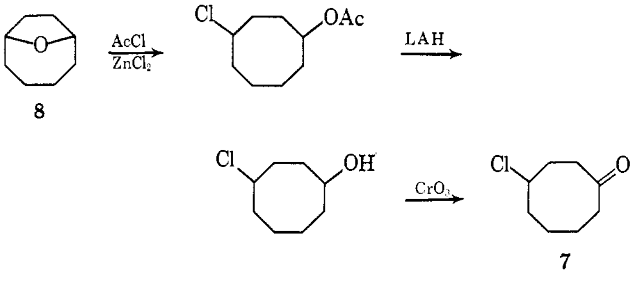
Additions of carbon tetrachloride to **1** have been carried out in different ways: photo- and thermally initiated reactions in the absence of any solvent other than excess carbon tetrachloride, and photoinitiated reaction with benzene solvent. Although the addition of benzene to the reaction mixture led to a higher conversion of cyclooctene to products and to less polymer formation, the over-all results of the three kinds of additions were substantially the same. The principal products were isomeric $C_9H_{14}Cl_4$ compounds, formed in yields of 59–71%; several minor products containing 1–3 chlorines per 8–9 carbons were obtained in combined yields of about 24–15%. Some hexachloroethane was isolated in each of the addition experiments, confirming the radical nature of the reactions.

Major Products. In contrast to a patent claim that the thermal addition of carbon tetrachloride to cyclooctene gives 1,2-addition product **3**,[11] our product mixtures from both kinds of additions consisted primarily of *cis*- and *trans*-1-chloro-4-trichloromethylcyclooctanes (**4**, X = Cl). This identity was established on the basis of nmr spectra, selective dehydrochlorinations, and conversion to 4-chlorocyclooctanone identical with an authentic sample.

The ratio of the areas of the nmr signals centered near -2.2 ppm (A) and -1.65 ppm (B)[12] is especially valuable for structure assignments in cycloalkane derivatives. The signals near -2.2 ppm (A) are associated with CH_2CX (X = electron-withdrawing substituent such as Cl or CCl_3) or with $CH_2C{=}C$, and those near -1.65 ppm (B) with more remote CH_2. For a 1,2-disubstituted cyclooctane such as **3**, the ratio A:B is 4:8;[10] for a 1,3 isomer, the ratio is 6:6, and for 1,4 and 1,5 isomers, it is 8:4.[13] The major fraction, $C_9H_{14}Cl_4$, from each of the CCl_4 additions gave an A:B ratio of nearly 8:4, clearly excluding normal 1,2 addition. That fraction, separated from lower boiling reaction products by careful distillations, was further separated into solid and liquid isomers by low-temperature fractional crystallization from methanol. The nmr spectra of these isomers are similar, and each exhibits an A:B ratio of about 8:4. The infrared spectra of the isomers are nearly the same but differ sufficiently at 10–11 μ for quantitative analysis. By comparison of the infrared spectra of the original $C_9H_{14}Cl_4$ product mixtures and standard mixtures prepared from the separated isomers, the original mixtures were estimated to consist of about 30% solid and 70% liquid isomers.[14]

When either the liquid or the solid isomer, or a mixture of them, was dehydrochlorinated with 1 molar equiv of potassium hydroxide in a mixed solvent, the same olefin, identified by infrared and nmr spectra as a chloro(dichloromethylene)cyclooctane, was produced. This result clearly identifies the solid and liquid isomers as geometrical, not position, isomers. Further identification of the olefin product as 1-chloro-4-(dichloromethylene)cyclooctane (**6**) was accomplished by ozonolysis of it to 4-chlorocyclooctanone, an authentic sample of which was synthesized independently from 9-oxabicyclo[4.2.1]nonane (**8**). This identification is completely in accord with the nmr A:B ratio for the original $C_9H_{14}Cl_4$ products and establishes that the radical addition of CCl_4 to cyclooctene proceeds mainly to give **5** (*cis* and *trans*).[15]





Bromotrichloromethane, on the other hand, adds equally exclusively to give *cis*- and *trans*-1-bromo-2-trichloromethylcyclooctane (**3**, X = Br).[10] Clearly the relative activation free energy requirements of the

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[9] (a) M. Fisch and G. Ourisson, *Chem. Commun.*, 407 (1965); (b) G. Ourisson, *Proc. Chem. Soc.*, 281 (1964).

[10] J. G. Traynham, T. M. Couvillon, and N. S. Bhacca, *J. Org. Chem.*, 32, 529 (1967).

[11] F. Reicheneder and H. Suter, German Patent 1,036,847 (Aug 21, 1958); *Chem. Abstr.*, **54**, 22416c (1960). Our experiments duplicated the reaction conditions described here as closely as possible.

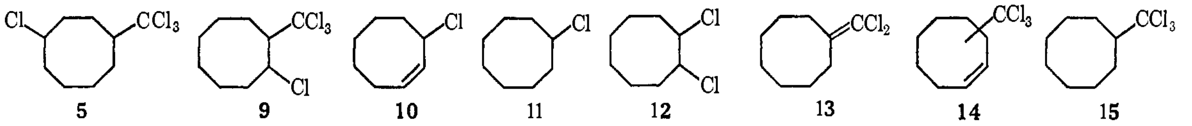
[12] All chemical shifts are relative to internal tetramethylsilane reference.

[13] Analytical use of nmr signal ratios similar to A:B has been described independently by C. L. McGehee and C. H. Sommers in "Developments in Applied Spectroscopy," Vol. 4, E. N. Davis, Ed., Plenum Press, New York, N. Y., 1965, p 405.

[14] The liquid fractions were subsequently shown to contain about 2–5% of the 1,2 isomer along with the 1,4 isomer.

[15] We have not yet firmly matched the labels *cis* and *trans* with the descriptions *solid* and *liquid* for isomeric **5**.

Table I. Product Distribution Data for CCl_4 Additions to *cis*-Cyclooctene



CCl_3–CCl_3

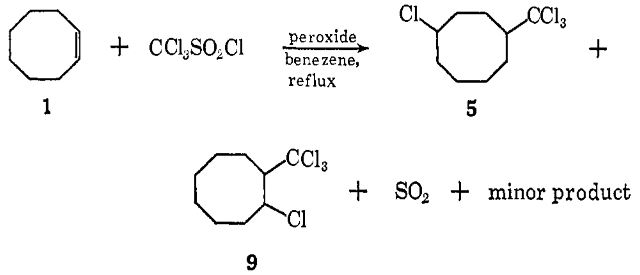
16

	Yield, mole %										
Conditions[a]	**5**s[d]	**5**l[d]	**9**[b]	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**[c]
Photoinitiated	26	41	3.8	0.7	0.6	1.3	2.6	3.4	5.0	0.07	3.0
Thermally initiated	20	38	1.2	0.9	8.2	1.2	0.36	8.0	0.3	0.07	5.1
Photoinitiated in benzene solution	22	46	5.0	0.13	1.1	1.7	5.1	1.5	0.9	0.9	3.3
CCl_3SO_2Cl addition	19	37	25	0.05	0.16	1.0	1.3	1.0	0.08	0.08	4.3

[a] See Experimental Section for details. [b] Both *cis* and *trans* isomers were obtained. [c] Other unidentified products. These figures exclude polymer and undistillable material. [d] **5**s = solid isomer, **5**l = liquid isomer.

alternate reactions of intermediate 2-(trichloromethyl)-cyclooctyl radicals (**2**), steps 2 and 3, determine the course of the over-all reaction. Abstraction of chlorine from carbon tetrachloride requires more energy than abstraction of bromine from bromotrichloromethane. An addition reagent with a radical chain transfer constant between those for Cl–CCl_3 and Br–CCl_3[16] would be expected to give more nearly equal amounts of products corresponding to **3** and **4**.

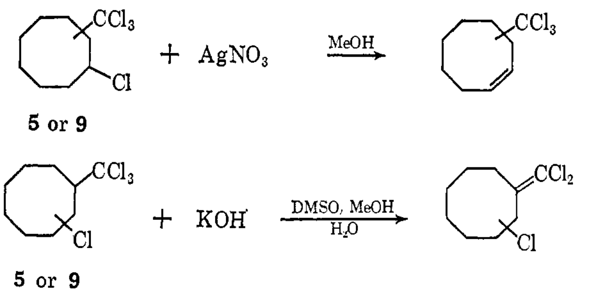
Benzoyl peroxide initiated addition of trichloromethanesulfonyl chloride[16] to **1** gave an 81% yield of $C_9H_{14}Cl_4$ product which was found by gas chromatography and nmr and infrared spectroscopic analyses to be about 70% **5** (67% liquid and 33% solid isomers) and 30% 1,2 isomer **9**. The nmr spectrum of the 1,2 isomer exhibits the expected A:B ratio of 4:8 and includes two multiplets for HCCl, separated by 18 cps and each equivalent to one H. These signals are virtually identical with those for the 1-bromo-2-trichloromethylcyclooctane (**3**, X = Br) obtained from $BrCCl_3$ addition;[10] decoupling experiments with that product identified it as a 1:1 mixture of *cis* and *trans* isomers.[10] Because of the correspondence of the spectra for **9** and **3** (X = Br), we conclude that **9** is also a 1:1 mixture of geometrical isomers (which was not resolved by gas chromatography). This unexpected composition is apparently surprisingly independent of the reagent ($BrCCl_3$ or CCl_3SO_2Cl) involved in the product-forming step (step 3).



Once the gas chromatography retention time and spectra for the 1,2-isomer mixture were at hand, careful reexamination of the data for the liquid 1,4 isomer from each CCl_4 addition revealed that it was contaminated by small amounts of **9** (2% from thermal addition, 5–7% from photoinitiated additions).

The yields of the major products (as well as the yields of the minor products described in the next section) obtained from the four additions to **1** are summarized in Table I.

In addition to the dehydrochlorination which established the geometrical isomerism of solid and liquid **5**, other selective dehydrochlorinations were carried out with both **5** and **9**. When dehydrochlorination is effected by alcoholic silver nitrate, a (trichloromethyl)-cyclooctene is the major product formed from both **5** and **9**, but with potassium hydroxide in mixed solvent a chloro(dichloromethylene)cyclooctane is the major one (different olefins from **5** and **9**). When mixtures of **5** and **9** were used with limited amounts of dehydrochlorinating reagent, **9** was consumed the more rapidly by potassium hydroxide, but **5** was consumed the more rapidly by silver nitrate. The differences in rates of reactions are apparently sufficiently large to offer promise for purification of one isomer at the expense of the other.



Minor Products. Several chlorine-containing products boiling lower than the $C_9H_{14}Cl_4$ isomers were obtained in very small amounts in each addition reaction. Although there were some differences among the four additions, the general picture for these minor products was consistent. These products were identified primarily by comparison of spectra and gas chromatography retention times with those of authentic samples (see Experimental Section for details). The product distribution data are summarized in Table I.

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[16] (a) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp 95, 157. The chain-transfer constant for CCl_3SO_2Cl is not accurately known but is apparently between the likely values for $BrCCl_3$ and CCl_4. (b) The relative ease of chain transfer by CCl_3SO_2Cl and CCl_4 is illustrated by the report that a 1:1 addition product is formed from CCl_3SO_2Cl and styrene, but only low molecular weight polymers are obtained with CCl_4 and styrene: E. C. Ladd and L. Y. Kily, U. S. Patent 2,606,213 (Aug 5, 1962); *Chem. Abstr.*, 47, 6440*h* (1962).

All of these products can be written as products of conventional radical reactions involving cyclooctene, CCl_4, and derived radical intermediates. The similarity of distribution among the four additions is not particularly helpful for considerations of mechanism details. Chlorocyclooctane is formed in significantly higher yield in the thermal addition than in the others, however, and this difference may stem from the fact that by-product HCl (which can add to **1**) was trapped in the sealed apparatus used for thermal addition but was lost by continuous nitrogen sweep in the others.

The extent to which allylic hydrogen abstraction accompanies addition of $\cdot CCl_3$ to cyclooctene is small (2–9% with CCl_4, 1% with CCl_3SO_2Cl). By contrast, radical reaction of CCl_4 with cyclohexene gives about equal amounts of addition and hydrogen abstraction.[17] Since the transition state for $\cdot CCl_3$ addition presumably resembles reactants while that for hydrogen abstraction is more like products,[18] the low extent of hydrogen abstraction from cyclooctene may signal relatively poor allylic stabilization for 2-cyclooctenyl radical compared to 2-cyclohexenyl radical.[19]

In connection with identification of one of the minor products, chloroform was added under radical conditions (photoinitiation) to cyclooctene with low conversion. The expected product,[20] (trichloromethyl)cyclooctane, was formed in about 20% yield and accompanied by chlorocyclooctane (10%) and (dichloromethyl)cyclooctane (41%). The predominance of this last product in the mixture is unexpected on the basis of previous reports of chloroform additions to olefins,[20] and we plan to investigate such additions further.

Energy Considerations. The driving force for the transannular rearrangement of **2** is the destabilization of a radical center by neighboring trichloromethyl substituent. This destabilization, which is relieved by the rearrangement, is estimated to amount to more than 3.5–4.0 kcal/mole. A tertiary radical is more stable than a secondary one by about that amount,[21] and rearrangement of the tertiary 1-(2,2,2-trichloroethyl)cyclodecyl radical to a secondary one has been reported.[9a]

The relative extents of transannular and vicinal radical addition depend on addend, temperature, and relative concentrations of cyclooctene and addend. The intermediate 2-substituted cyclooctyl radical is trapped effectively by good chain-transfer agents such as chlorine and bromotrichloromethane but not by carbon tetrachloride. The ratio of transannular **3** to vicinal **4** products was 17:1 for CCl_4 addition and about 1:34 for $BrCCl_3$ addition (addend:olefin molar ratio 4:1). These ratios lead to a calculated ratio of rate constants for bromine abstraction (from $BrCCl_3$) and for chlorine abstraction (from $ClCCl_3$) by 2-(trichloromethyl)cyclooctyl radical of 578:1, and the corresponding difference in free-energy change ($\Delta\Delta G^*$) is 4.04 kcal/mole (T = 317°K). The entropies of activation for the two processes should be quite similar except for the difference in symmetry numbers of CCl_4 (12) and $BrCCl_3$ (4), and ΔE_a is calculated to be about 5.5 kcal/mole. This amount of energy, 5.5 kcal/mole, is about 29% of the difference in bond energies (19 kcal/mole[21]) of the $Cl–CCl_3$ and $Br–CCl_3$ bonds being broken in the two processes.[22] The well-known Hirschfelder rule predicts that the activation energies for a series of similar exothermic radical-abstraction reactions should be proportional to the bond-dissociation energy of the bond being broken.[23] If the proportionality is extended for reactions of 2-(trichloromethyl)cyclooctyl radical to include not only halogen abstraction from $X–CCl_3$ but also (intramolecular) transannular hydrogen abstraction, ΔE_a for hydrogen and chlorine abstractions is estimated to be about 5.8 kcal/mole (0.29×20[21b]). Data for a good model of radical transfer involving **2** are not available, but activation energies for $Cl–CCl_3$ abstractions by polystyrene and poly(methyl acrylate) radicals are 12.3 and 13.3 kcal/mole, respectively.[16a] Using these energies as an approximation of E_a for **2** reacting with CCl_4, we estimate that E_a for transannular hydrogen abstraction in this system is about 18–19 kcal/mole).[24–27]

Although the amount of **4** from $Cl–CCl_3$ addition is small under any circumstances, the ratio of **4**:**3** is smaller at 150° (1:99) than at 44° (1:17), indicating that the transannular hydrogen migration does indeed have the higher activation energy.

Experimental Section

Gas chromatographic analyses were obtained with a Barber-Colman Model 20 instrument equipped with a hydrogen flame detector and a 100-ft capillary column coated with SE-96 silicone. Preparative gas chromatography was performed with a Wilkens Aerograph Autoprep Model A-700 instrument equipped with a $^3/_8$ in. × 20 ft silicone column. Nmr spectra were obtained with the assistance of Mr. R. Seab and Mr. W. Wegner on a Varian Associates HA-60 spectrometer, and all chemical shifts cited refer to tetramethylsilane as internal reference. Infrared spectra were obtained with Beckman IR-5 and IR-7 and Perkin-Elmer Models 21 and 137 instruments. Capillary melting points were obtained with a Thomas-Hoover apparatus and are uncorrected. Element microanalyses were performed by Mr. R. Seab in these laboratories.

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[17] (a) E. C. Kooyman and E. Farenhorst, *Rec. Trav. Chim.*, 70, 867 (1951); (b) S. Isralashvili and J. Shabatay, *J. Chem. Soc.*, 3261 (1951); (c) ref 16a, p 261; (d) E. S. Huyser, *J. Org. Chem.*, 26, 326 (1961).

[18] M. M. Martin and G. J. Gleicher, *J. Am. Chem. Soc.*, 86, 242 (1964).

[19] Addition to cyclooctene is apparently favorable, however. In a preliminary study of relative rates by competitive reactions, cyclooctene was consumed by $\cdot CCl_3$ 1.8 times as rapidly as cyclohexene: unpublished experiments by D. B. Stone.

[20] C. Walling and E. S. Huyser, *Org. Reactions*, 13, 91 (1963).

[21] (a) Reference 16a, p 51; (b) J. A. Kerr, *Chem. Rev.*, 66, 496 (1966).

[22] The activation energies for few chain-transfer reactions are accurately known.[16a]

[23] J. O. Hirschfelder, *J. Chem. Phys.*, 9, 645 (1941).

[24] This estimate depends importantly on the proportions of products 3 and 4 from the additions of $Br–CCl_3$ and CCl_4. The proportions we report were obtained in several experiments, and product ratios outside what we consider reasonable limits of experimental error do not drastically change the estimated activation energy for transannular hydrogen abstraction. For example, even if the ratio of 3:4 from CCl_4 addition were actually 9:1 and that from $BrCCl_3$ addition were actually 1:9, the same kind of calculation leads to an estimate of 17 kcal/mole for hydrogen abstraction.

[25] H. S. Johnson and C. Parr, *J. Am. Chem. Soc.*, 85, 2544 (1963), have calculated that the potential activation energy for hydrogen transfer between Me_2CH_2 and Me_2CH is 12 kcal/mole. This calculated energy however is slightly lower than the apparent activation energy for chlorine abstraction from CCl_4 by polystyryl radical[16a,22] and would be inconsistent with the product distribution data from our experiments.

[26] The activation energy for transannular *hydride* transfer between oxygenated carbons ($^-O–C–H \cdots C{=}O$) in the seven-membered ring of a dihydropleiadene has very recently been estimated to be about 24 kcal/mole: private communication from Professor P. T. Lansbury, Sept 1966. See P. T. Lansbury and F. D. Saeva, *J. Am. Chem. Soc.*, 89, 1890 (1967).

[27] The activation energy (E_a) for transannular hydrogen abstraction is higher than E_a for halogen abstraction from $XCCl_3$ by the 2-(trichloromethyl)cyclooctyl radical, but because of the more favorable entropy of activation for the unimolecular (transannular) reaction, the free energy of activation (ΔG^*) for the hydrogen-abstraction process is in between those for the two bimolecular, halogen-abstraction reactions.

Photoinitiated Addition of CCl_4. A solution of freshly distilled *cis*-cyclooctene (75 g, 0.68 mole) in carbon tetrachloride (75 g, 2.64 moles) was placed in a 500-ml quartz flask, deoxygenated with a nitrogen stream for 10 min, suspended in a Rayonet photochemical reactor, and irradiated with 2537-A light for a total of 40 hr. A nitrogen atmosphere was maintained over the reaction mixture during irradiation, and a cooling fan in the reactor kept the mixture at about 44°. After 20 hr, irradiation was interrupted so that the flask, which had become coated with a dark polymeric material, could be cleaned. The reaction mixture was returned to the flask, swept with nitrogen for 5 min, and irradiated for another 20 hr. The solution was concentrated on a rotary evaporator and then distilled at reduced pressure. Besides recovered cyclooctene (8 g, 11%), there were obtained 18.5 g of low-boiling products containing chlorine (fraction A) and 124 g (72%) of 1:1 addition product, bp 97–116° (0.2 mm) (fraction B).

Anal. Calcd for $C_9H_{14}Cl_4$: C, 40.95; H, 5.34. Found: C, 41.15; H, 5.75.

A portion of the distillate fraction B was dissolved in twice its volume of absolute methanol and chilled to −60°. The solid which separated was collected and recrystallized three times from methanol (−10 to −30°), mp 64–65.5°. It was subsequently identified as 1-chloro-4-(trichloromethyl)cyclooctane, **5s**.

Anal. Calcd for $C_9H_{14}Cl_4$: C, 40.95; H, 5.34. Found: C, 41.07; H, 5.78.

The liquid remaining from the crystallizations was distilled at reduced pressure to give a liquid isomer of the solid product, bp 127–130° (2 mm).

Anal. Calcd for $C_9H_{14}Cl_4$: C, 40.95; H, 5.34. Found: C, 41.02; H, 5.58.

The proportions of solid and liquid $C_9H_{14}Cl_4$ products isolated was 64% liquid:36% solid. The infrared spectra of both fractions exhibit strong absorptions for CCl_3 (12.8–13.5 μ) and absorptions for C–Cl (14.9 μ for solid, 14.81 μ for liquid). The spectra differ primarily in the relative intensities of peaks in the 7–11-μ region. Two absorption peaks proved useful for quantitative analysis: 10.2 (liquid) and 10.5 μ (solid). A plot of mole fraction of liquid isomer *vs.* the ratio of absorbance ($A_{10.2}$:$A_{10.5}$) for standard mixtures prepared from the separated solid and liquid products was a smooth curve. The ratio of absorbance for the original, unseparated distillate B corresponded to 64% liquid and 36% solid products (**5l** and **5s**, respectively).

A gas chromatogram indicated that the liquid product contained two isomeric products, the major one (92%) being subsequently identified as 1-chloro-4-(trichloromethyl)cyclooctane (**5l**) and the minor one (8%) as 1-chloro-2-(trichloromethyl)cyclooctane (**9**). The relative amounts of the three isomeric 1:1 addition products were 36% **5s**, 58.5% **5l**, and 5.5% **9**.

When the reaction was carried out with a solution of *cis*-cyclooctene (0.25 mole), carbon tetrachloride (3.2 moles), and benzene (100 g), little dark polymer was formed, the irradiation was not interrupted during 41 hr, and the conversion of cyclooctene to products was 93%. Product distribution nearly duplicated that obtained without benzene solvent. The yield of 1:1 addition product was 73%, and the distribution among the three isomers was 30% **5s**, 63% **5l**, and 7% **9**.

Thermally Initiated Addition of CCl_4. A mixture of *cis*-cyclooctene (61 g, 0.55 mole) and carbon tetrachloride (470 g, 3.1 moles) was heated in a Parr medium-pressure apparatus at 155° for 4.5 hr hr (100 psig). The mixture was concentrated on a rotary evaporator and distilled at reduced pressure. After a low-boiling fraction [15.1 g, 30–108° (1.4 mm)] had been collected, the major product, consisting of isomeric $C_9H_{14}Cl_4$ compounds, was obtained; 52 g [36%, bp 108–130° (1.4 mm)]. Infrared analysis (see above) of this fraction indicated that it consisted of 67% liquid and 33% solid products, which were subsequently separated by crystallization from methanol. The solid obtained was identical with that obtained from the photochemical experiments (mp 64–65.5°; the mixture melting point showed no depression). A gas chromatogram of the liquid portion indicated the presence of a small amount of isomer **2**. The distribution of the three isomeric 1:1 addition products was 33% **5s**, 65% **5l**, and 2% **9**.

Identification of 1:1 Addition Products. Nmr Spectra. The nmr spectrum of the liquid portion of the major product from the addition reactions consisted of multiplets centered near −4.23 ppm (area equivalent to one proton, HCCl), −2.6 ppm (1 H, $HCCCl_3$), −2.2 ppm (7.5 H, CH_2CCl and CH_2CCl_3), and −1.65 ppm (4.5 H, $CH_2CH_2CH_2$).[28] The nmr spectrum of the solid isomer isolated consisted of multiplets centered near −4.20 ppm (1 H, HCCl), −2.75 (1 H, $HCCCl_3$), −2.2 ppm (8 H, CH_2CCl and CH_2CCCl_3), and −1.65 ppm (4 H, $CH_2CH_2CH_2$). These spectra exclude 1,2-addition products **9**, which would give a signal at −1.65 ppm equivalent to 8 H, and one at about −2.2 ppm, equivalent to 4 H, exactly opposite to those obtained here. The fractional equivalence of these two signals for the liquid fraction is consistent with the gas chromatographic analysis, indicating contamination by a small amount of the 1,2 isomer.

Dehydrochlorination with KOH. A solution of the mixed 1:1 addition product (50 g, 0.19 mole) in DMSO (120 ml), methanol (35 ml), and water (5 ml) was added to a solution of potassium hydroxide (0.20 mole), water (10 ml), methanol (25 ml), and DMSO (25 ml). The mixture was stirred at 28° for 5 hr, methanol (50 ml) was added to obtain a homogeneous solution, and the solution was stirred for 3 hr more. It was poured into 300 ml of water and extracted with four 150-ml portions of petroleum ether. The combined organic material was washed thoroughly with water and concentrated by rotary evaporation. Gas chromatography indicated that some $C_9H_{14}Cl_4$ remained, but nearly all (about 82%) had been converted to a single olefinic product with detectable amounts of other products. Distillation gave a center cut at bp 121–123° (3.5 mm).

Anal. Calcd for $C_9H_{13}Cl_3$: C, 47.50; H, 5.76. Found: C, 47.53; H, 5.73.

The infrared and nmr spectra of the product were devoid of absorptions for olefinic hydrogens. The infrared spectrum did include intense absorptions for $C{=}CCl_2$ (6.23 and 11.1 μ) but none for CCl_3. The nmr spectrum included a quintet (J = 5.5 cps) at −4.1 ppm (1 H, HCCl) whose resolution was better at 60° than at room temperature. These data indicate that the dehydrochlorination product is a chloro(dichloromethylene)cyclooctane. The same product was obtained in approximately equal yields from equivalent but smaller scale dehydrochlorinations of the separated solid and liquid fractions.[29]

Ozonolysis of 6. Ozone (52 mmoles, about 5% in a stream of oxygen from a Welsbach T-23 ozonator) was passed during 5 hr into an ice-chilled CCl_4 solution of the chloro(dichloromethylene)cyclooctane (**6**, 10.0 g, 44 mmoles). The saturated solution was then allowed to stand for several hours at 0° before the solvent was removed on a rotary evaporator (temperature kept below 45°). The gummy residue was dissolved in 100 ml of acetic acid and reduced by the gradual addition at room temperature of powdered zinc (6.5 g) with vigorous stirring. The mixture was diluted with 200 ml of water and extracted three times with petroleum ether. The combined organic material was washed with water and sodium bicarbonate solution, dried, and concentrated. Gas chromatographic analysis indicated some starting olefin (varying amounts up to 30% in different experiments) together with the ozonolysis products. (In some experiments, the reaction mixture was separated by reduced pressure distillation; in others, it was examined directly by infrared spectroscopy and derivatization.) The ozonolysis mixture consisted of a minor product, a cyclooctenone (not conjugated, λ_{max} 1705 cm^{-1}), and a chlorocyclooctanone, the major product. The chlorocyclooctanone exhibited intense infrared absorption at 1706 cm^{-1}, clearly excluding 2-chlorocyclooctanone (C=O at 1714 and 1725 cm^{-1}).[30] The 2,4-dinitrophenylhydrazone was recrystallized three times from 95% ethyl alcohol, mp 150–152°. The infrared spectrum and melting point of this derivative were identical with those of the 2,4-dinitrophenylhydrazone of authentic 4-chlorocyclooctanone (synthesis described below).

Anal. Calcd for $C_{14}H_{17}N_4O_4Cl$: C, 49.34; H, 5.03. Found: C, 49.42; H, 5.54.

Independent Synthesis of 4-Chlorocyclooctanone (7). Addition of a small amount of zinc chloride (about 0.5 g) to a mixture of 9-oxabicyclo[4.2.1]nonane (**8**)[31,32] (2.6 g, 18 mmoles) and acetyl

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(28) Cyclooctane gives a single nmr signal at −1.65 ppm.

(29) Dehydrochlorinations with potassium hydroxide in aqueous ethanol or methanol were slow and gave complex mixtures of products. Potassium *t*-butoxide in DMSO gave a rapid, exothermic reaction which also led to a complex mixture of products. These product mixtures, which were unhelpful for structure identification, contained about 15–20% of the chloro(dichloromethylene)cyclooctane.

(30) C. Castinel, G. Chiurdoglu, M. L. Josien, J. Lascombie, and E. Vananduyt, *Bull. Soc. Chim. France*, 807 (1958).

(31) Prepared by the oxidation of cyclooctanol with lead tetraacetate: (a) R. M. Moriarty and H. C. Walsh, *Tetrahedron Letters*, 465 (1965); (b) A. C. Cope, M. Gordon, S. Moon, and C. H. Park, *J. Am. Chem. Soc.*, 87, 3119 (1965).

chloride (15 g) initiated a vigorous reaction[34] which was moderated by cooling the reaction flask in a water bath. After the initial reaction had subsided, the mixture was refluxed for 20 min. Gas chromatographic analysis indicated that no **8** remained in the mixture.[35] The mixture was diluted with petroleum ether, and the excess acetyl chloride was hydrolyzed with ice. Conventional separation and work-up gave a low-boiling fraction (about 1 g) whose infrared spectrum was characteristic for cyclooctenyl acetate and another fraction [2.5 g, bp 85–115° (2 mm)] whose spectrum was consistent with 4-chlorocyclooctyl acetate (λ_{max} 5.78, 8.1, and 14.9 μ). This chloro acetate (2.5 g, 12 mmoles) was reduced in ethyl ether solution with lithium aluminum hydride (0.35 g, 9 mmoles). Conventional work-up (acidic hydrolysis) and removal of solvent left crude 4-chlorocyclooctanol which was dissolved in acetone (25 ml) and oxidized directly at 0° with a chromic acid solution (1.5 g, 15 mmoles, of CrO_3 in 9 ml of 30% H_2SO_4). After the mixture was diluted with water and extracted with petroleum ether, the organic solution was washed thoroughly with water, dried with calcium chloride, and concentrated. Gas chromatographic analysis indicated that the principal constituent of the residual liquid had a retention time identical with that of the ketone obtained from the ozonolysis of **6**. The infrared spectrum (λ_{max} 1706 cm^{-1}), nmr spectrum (quintet at −4.15 ppm), and 2,4-dinitrophenylhydrazone derivative (mp 149–151.5°, the mixture melting point showed no depression) of this sample of 4-chlorocyclooctanone also matched the corresponding data for the ozonolysis product.

Reaction of Trichloromethanesulfonyl Chloride with Cyclooctene. During 1.5 hr, a solution of *cis*-cyclooctene (38 g, 0.35 mole) and benzoyl peroxide (8 g, 0.04 mole) in benzene (150 ml) was added to a refluxing solution of trichloromethanesulfonyl chloride (100 g, 0.45 mole, Eastman Practical Grade) in benzene (150 ml). Titration of evolved SO_2 with iodine indicated that 38% of the sulfonyl chloride had decomposed in 30 min after addition was complete. The mixture was refluxed for 15 hr to ensure complete decomposition of the peroxide. A gas chromatogram of the reaction mixture before distillation showed two principal products (85%) of relative area 30:70 and at least 18 minor components. Distillation at reduced pressure gave a small amount of low-boiling material and 75 g (81%) of mixed $C_9H_{14}Cl_4$ products, bp 90–114° (0.5 mm). The conversion of cyclooctene was greater than 96%. The mixture of products was analyzed by gas chromatography and infrared and nmr spectroscopy. The product distribution data are summarized in Table I.

The 1,2 and 1,4 isomers of $C_9H_{14}Cl_4$ (**5** and **9**) are resolved by gas chromatography (140°, 100-ft SE-96 silicone capillary column). The nmr spectrum of the $C_8H_{14}Cl_4$ mixture was used to confirm the gas chromatographic analysis. The integrated absorption centered at −4.75 ppm (HCCl, 1,2 isomer) was compared with that at −4.25 ppm (HCCl, 1,4 isomer), and the relative intensities of the absorptions to the left and right of −1.83 ppm were estimated (a 5:8 ratio is expected for the pure 1,2 isomer, a 9:4 ratio for the 1,4 isomer). The three analyses gave concordant results: 31% 1,2 isomer and 69% 1,4 isomer.

The infrared spectrum of the highest boiling $C_9H_{14}Cl_4$ fraction indicated that both the liquid and solid 1,4 isomers were present. The solid isomer was separated by fractional crystallizations, mp and mmp 64.5–65°. The liquid 1,4 and 1,2 isomers could not be separated cleanly by distillation, but repeated distillations through a 12-in. packed column gave fractions enriched in 1,2 isomer (77% purity) and 1,4 isomer (86% purity). The identity of the liquid 1,4 isomer was confirmed by comparison of its nmr and infrared spectra with those of previously identified samples (CCl_4 additions above). The nmr spectrum of the 1,2 isomer is almost identical with that of 1-bromo-2-(trichloromethyl)cyclooctane (1:1 *cis–trans* mixture);[10] it includes a pair of triplet-like signals (J = 5.5 cps) centered at −4.90 ppm (HCCl, *cis* isomer) and −4.60 ppm (HCCl, *trans* isomer). The ratio of signal intensity at −2.2 ppm to that at −1.65 ppm was 5:8 (after correction for 23% 1,4 isomer). The infrared spectrum of the 1,2 isomer was similar to the spectra of the two 1,4 isomers in the 7–11-μ region; the C–Cl absorption frequency was recorded at 690 cm^{-1} compared to 675 and 672 cm^{-1} for the liquid and solid 1,4 isomers, respectively.

Minor Products from Addition Reactions. The lower boiling fraction from the distillations of the addition reaction mixture were fractionally distilled at reduced pressure and analyzed primarily by gas chromatography. Few of the components responsible for the 11–14 gas chromatography peaks were isolated in sufficient quantity for complete identification, but seven have been rather firmly identified by comparisons of gas chromatographic retention times and infrared spectra with those of authentic samples. These minor products are described in order of increasing gas chromatography retention times; the estimated yields for the several addition reactions are summarized in Table I.

Hexachloroethane was identified by sublimation temperature (184°) and infrared spectrum.[36]

3-Chloro-1-cyclooctene had the same retention time as authentic chloride prepared from 2-cycloocten-1-ol and thionyl chloride. The distillate fraction rich in this component gave an immediate precipitate with cold alcoholic silver nitrate.

Chlorocyclooctane showed the same retention time as an authentic sample prepared by the addition of HCl to cyclooctene.

***trans*-1,2-Dichlorocyclooctane** showed the same retention time as an authentic sample prepared by the addition of chlorine to cyclooctene.[37,38]

Dichloromethylenecyclooctane was separated in about 91% purity by preparative gas chromatography; the infrared spectrum included only trace absorptions for C=CH and intense ones for $C{=}CCl_2$ (6.21 and 11.1 μ).

Anal. Calcd for $C_9H_{14}Cl_2$: C, 56.0; H, 7.3. Found: C, 55.3; H, 7.4.

A **(trichloromethyl)cyclooctene** was separated in low purity by preparative gas chromatography; the infrared spectrum included absorptions for C=CH (3.3 and 6.03 μ) and CCl_3 (13 μ, intense). The gas chromatographic retention time and infrared spectrum of this product were different from those of the 4-(trichloromethyl)-1-cyclooctene obtained by $AgNO_3$ dehydrochlorination of **5**.

(Trichloromethyl)cyclooctane was obtained in about 91% purity by preparative gas chromatography; the infrared spectrum included no absorptions for C=CH but an intense one at 13 μ for CCl_3. The nmr spectrum consisted of multiplets centered at −2.6 (1 H, $HCCCl_3$), −2.2 (4 H, CH_2CCCl_3), and −1.6 ppm (8 H, $CH_2CH_2CH_2$). Data for this product correspond to those of an authentic sample of (trichloromethyl)cyclooctane, prepared from chloroform and cyclooctene.

Dehydrohalogenation of 5 with $AgNO_3$. A mixture of **5s** (9.04 g, 34.2 mmoles), silver nitrate (6.00 g, 35 mmoles), and aqueous methanol (50 ml, 90 vol. % MeOH) was stirred at 45° for 4 hr, filtered from precipitated silver chloride, and diluted with ethyl ether. The ether solution was washed thoroughly with water, dried, and distilled. In addition to recovered starting material [4.0 g, 44%, bp 105–107° (0.2 mm)], a dehydrochlorination product was obtained in 93% yield (based on **5s** consumed), bp 74–80° (0.15–0.2 mm).

Anal. Calcd for $C_9H_{13}Cl_3$: C, 47.50; H, 5.76. Found: C, 47.40; H, 5.93.

The infrared spectrum of this product included absorptions for C=CH (3.30 μ), C=C (6.02 μ), and CCl_3 (12.8–13.6 μ, intense). The nmr spectrum included multiplet signals centered at −5.7 (2 H, C=CH with splitting virtually identical with the signal for *cis*-cyclooctene),[39] −2.6 (1 H, $HCCCl_3$), −2.2 (6 H, CH_2CCCl_3 and $CH_2C{=}C$), and −1.6 ppm (4 H, $CH_2CH_2CH_2$). The ratio of the signals at −5.7, −2.2, and −1.6 ppm is consistent only with 4-(trichloromethy)l-1-cyclooctene among the four isomeric (trichloromethyl)cyclooctenes. The precision of the integrated areas is such that a small contamination (<4%) by 5-(trichloromethyl)-1-cyclooctene would not be detected.

Similar treatment of **5l** with silver nitrate gave a 50% conversion to product whose infrared spectrum and gas chromatographic

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[32] The infrared spectrum of our product was identical with the published spectrum for 9-oxabicyclo[4.2.1]nonane[33] and gave no indication of contamination by the [3.3.1] isomer.

[33] A. C. Cope and B. C. Anderson, *J. Am. Chem. Soc.*, 79, 3892 (1957).

[34] A. C. Cope and A. Fournier, *ibid.*, 79, 3896 (1957), describe the comparable reaction between the oxide and acetyl bromide. We find that the reaction with the less-reactive acetyl chloride is facilitated by zinc chloride catalyst.

[35] In a previous experiment without zinc chloride, the 9-oxabicyclo[4.2.1]nonane was not consumed after 24-hr reflux with excess acetyl chloride.

[36] "Sadtler Index-Midget Edition," Sadtler Research Laboratory, Philadelphia, Pa., Spectrum No. 4546.

[37] E. A. Forbes, B. R. Gofton, R. P. Houghton, and E. S. Waight, *J. Chem. Soc.*, 4711 (1957).

[38] P. W. Havinga, *Rec. Trav. Chim.*, 81, 1053 (1962). This reference includes the infrared spectrum, which is identical with that of our authentic sample.

[39] G. V. Smith and H. Kriloff, *J. Am. Chem. Soc.*, 85, 2016 (1963).

retention time were identical with those of the 4-(trichloromethyl)-1-cyclooctene obtained from **5s**. The conversion of $C_9H_{14}Cl_4$ to dehydrochlorination product by silver nitrate solution was not increased substantially by prolonged heating.

Dehydrohalogenations of Mixed 1,2 and 1,4 Isomers of $C_9H_{14}Cl_4$. A. KOH in Mixed Solvent. A mixture prepared by adding a solution of potassium hydroxide (1.1 g, 21 mmoles) in 18 ml of solvent (DMSO–MeOH–H_2O, 10:5:3) to a solution of $C_9H_{14}Cl_4$ (4.4 g, 16.7 mmoles, 65% 1,2 isomers, 35% 1,4 isomers) in 5 ml of methanol and 35 ml of DMSO was stirred at room temperature for 6 hr. It was diluted with water and worked up as was the previous basic dehydrochlorination. After removal of solvent, the product mixture (3 g) was shown by gas chromatography to consist of five components (relative peak areas 9:5:54:18:13). The last two peaks corresponded in retention times to 1-chloro-4-(dichloromethylene)cyclooctane and 1-chloro-4-(trichloromethyl)cyclooctane, respectively. A peak corresponding to the starting 1,2 isomers was completely absent.

The major component (area 54) had a retention time indicative of 3 chlorine atoms per molecule.[40] The infrared spectrum of the product mixture showed only trace absorption for olefinic hydrogen, intense absorptions for $C{=}CCl_2$ at 6.23 and 11.02 μ, and weak absorption for CCl_3. Since **6** absorbs at 11.10 μ, the absorption at 11.02 μ can be attributed to the major component of the product mixture. This product is tentatively identified as 1-chloro-2-(dichloromethylene)cyclooctane. On the basis of retention time, the first product is tentatively identified as a (dichloromethylene)-cyclooctene. The 1,2 isomers of $C_9H_{14}Cl_4$ apparently undergo dehydrochlorination more rapidly under these conditions than do the 1,4 isomers.

B. Alcoholic $AgNO_3$. A mixture of $C_9H_{14}Cl_4$ (3.6 g, 13.6 mmoles, 65% 1,2 isomers, 35% 1,4 isomers) and silver nitrate (2.47 g, 16.6 mmoles) in aqueous methanol (50 ml, 90 vol. % MeOH) was refluxed for 5 hr, filtered, and diluted with water. Work-up as previously described gave 3 g of a product mixture shown by gas chromatographic analysis to consist of four components (relative peak areas 25:5:60:10). The last two peaks corresponded in retention times to the 1,2 and 1,4 isomers of $C_9H_{14}Cl_4$, respectively, and the first peak to 4-(trichloromethyl)-1-cyclooctene. On the basis only of retention time and product expected from **4**, the intermediate peak is tentatively associated with 3-(trichloromethyl)-1-cyclooctene. The 1,4 isomers undergo dehydrochlorination about six times more rapidly under these conditions than do the 1,2 isomers.

Photoinitiated Addition of Chloroform to Cyclooctene. A mixture of freshly distilled *cis*-cyclooctene (42 g, 0.38 mole) and chloroform (360 g, 3.0 moles) was placed in a quartz tube, deoxygenated with a stream of nitrogen for 15 min, and irradiated with 2537-A light for 65 hr. A slow stream of nitrogen swept over the mixture during the irradiation and into a trap containing a 10% aqueous sodium hydroxide solution. Distillation of the irradiated mixture gave recovered chloroform, cyclooctene (35 g, 83%), and a higher boiling product mixture (8 g) shown by gas chromatography to consist of three components. The most volatile of the three was separated by distillation [bp 40–42° (0.6 mm)] and identified as chlorocyclooctane by comparison with an authentic sample. Its nmr spectrum consisted of a well-resolved quintet ($J = 5.0$ cps) centered at -4.14 ppm (1 H, HCCl) and multiplets centered at -2.02 ppm (4 H, CH_2CCl), and -1.65 ppm (6 H, $CH_2CH_2CH_2$). The other higher boiling components were separated by preparative gas chromatography. The major one gave an analysis for $C_9H_{16}Cl_2$; its infrared spectrum showed absorption at 13.4 μ and none for $C{=}C$; its nmr spectrum consisted of a sharp doublet ($J = 3.0$ cps) at -5.07 ppm (1 H, $CHCHCl_2$) and multiplets at -2.1 ppm (1 H, $CHCHCl_2$) and -1.65 ppm (14 H, CH_2). This product is identified as (dichloromethyl)cyclooctane.

Anal. Calcd for $C_9H_{16}Cl_2$: C, 55.41; H, 8.25. Found: C, 55.77; H, 8.29.

The third product was identified by its analysis for $C_9H_{15}Cl_3$, its infrared spectrum (intense absorption at 13 μ), and its nmr spectrum (see above) as (trichloromethyl)cyclooctane.

The approximate yields of these three products, based on cyclooctene consumed, were 10% chlorocyclooctane, 41% (dichloromethyl)cyclooctane, and 20% (trichloromethyl)cyclooctane. Traces of hexachloroethane, *trans*-1,2-dichlorocyclooctane, and dichloromethylenecyclooctane were detected by gas chromatography. Treatment of the alkaline trap solution with acetic acid and silver nitrate gave silver chloride in molar amount, equivalent to the sum of the three major products.

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(40) Ranges of retention times for cyclooctane derivatives containing one, two, and three chlorines per molecule (C_8 or C_9), respectively, were separated by several minutes in our gas chromatographic analyses.