anisms for the Diels–Alder reaction[3] is not very profitable. Current viewpoints would postulate stabilizing overlap for the *endo* transition complex in either case. However, we do agree with Berson and Remanick[3c] that the question of the precise topography of the energy surface is not an irrelevant question.[3a,d] If one supposes that diradical intermediates could easily rotate before recombination or dissociation[17] a nonkinetic demonstration of the presence of diradical intermediates is possible.

In the *endo* dimer, breakage of one bond leads to a diallylic diradical intermediate which can reform the *endo* dimer by closure at either end of the two allylic systems, the product in either case being identical with the starting material. A reaction topologically equivalent to a degenerate Cope rearrangement[18] is possible. The *exo* compound is more interesting, in that it yields a diradical intermediate which after rotation can re-form *exo* dimer with configuration opposite to that of the starting material. We are presently studying the thermal decompositions of optically active *endo*- and *exo*-dicyclopentadiene in the hope of clarifying this problem.

Experimental Section

Materials.—*endo*-Dicyclopentadiene, mp 32.5°, was obtained commercially. *exo*-Dicyclopentadiene was prepared from the *endo* isomer using the procedure of Bartlett and Goldstein.[11a] The two isomers were separable by gas chromatography with a 6-ft, 5% SF96 oil on Chrom "W" column operating at room temperature and 14 psi. Retention times were 15.5 and 17.8 min for the *exo* and *endo* isomers, respectively. The commercial *endo*-dicyclopentadiene contained a very small amount (1%) of *exo*-dicyclopentadiene. Recrystallization removed the impurity. Our *exo* preparation was contaminated with 20% *endo* isomer. Because of the large difference in thermal reactivity for *exo*- and *endo*-dicyclopentadiene, pure *exo* isomer could be isolated by simply heating the mixture to 180° until all of the *endo* isomer had distilled as cyclopentadiene monomer.

Kinetic Experiments.—The stirred flow reactor system has been described in detail previously.[1,12] A controlled flow of inert gas is allowed to pass through a vaporizer containing the required isomer of dicyclopentadiene. Then the gas mixture flows into a spherical reactor, immersed in a constant temperature bath, and out through a soap-film flow meter. The gas stream can be sampled before and after the reactor, and the gas samples are analyzed by gas chromatography. At each temperature, three to five gas samples were analyzed at each of three to five flow rates. Known mixtures were used to calibrate the hydrogen flame detector and areas were determined with a mechanical integrator. Temperatures were measured with calibrated thermocouples and the electrical timer was checked against a calibrated stop watch.

Equilibration Studies.—One-gram samples of cyclopentadiene or *endo*-dicyclopentadiene were sealed into glass tubes and heated in an oil bath to 205°. The tubes were maintained at this temperature for periods of time ranging from 12 to 100 hr. The contents of the tubes were then analyzed for *exo*- and *endo*-dicyclopentadiene. In some cases a simple vacuum distillation was performed to separate dimeric and higher polymeric materials. Samples of the dimers were purified by gas chromatography, and submitted to E. W. Saybolt and Co., Inc., New Orleans, La., for determinations of heats of combustion. The results were imprecise.

Registry No.—*exo*-Dicyclopentadiene, 933-69-8; *endo*-dicyclopentadiene, 1755-01-7.

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(17) F. A. L. Anet, R. F. W. Bader, and A. r. d. Auwers, *J. Am. Chem. Soc.*, **82**, 3217 (1960).

(18) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

Preparation, Nuclear Magnetic Resonance Study, and Selective Dehydrohalogenations of 1-Bromo-2-trichloromethylcyclooctane[1]

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Photoinitiated addition of bromotrichloromethane to *cis*-cyclooctene gives 1-bromo-2-trichloromethylcyclooctane as the major addition product. Some 1-bromo-4-trichloromethylcyclooctane and appreciable amounts of 3-bromo-1-cyclooctene and trichloromethylcyclooctane are also formed. Nmr spectral studies have identified the major addition product (I) as a 50:50 mixture of *cis* and *trans* isomers. Solvent effects on the nmr spectra led to selective dehydrohalogenation experiments and the isolation of pure *trans* I.

As part of an investigation of radical rearrangements in medium-ring compounds, we have studied the radical addition of bromotrichloromethane to *cis*-cyclooctene. The major addition product is 1-bromo-2-trichloromethylcyclooctane (I); small amounts of the isomer, 1-bromo-4-trichloromethylcyclooctane (3–10% of the total addition product, depending on the mole ratio of the reactants), are also formed, apparently by a transannular radical rearrangement.[2] Nmr studies at 60 and 100 Mc, including decoupling experiments, clearly demonstrate that I is a 50:50 mixture of *cis* and *trans* isomers. While a mixture of geometric isomers is expected from a radical addition reaction,[3] formation of a 50:50 mixture from 2-trichloromethylcyclooctyl radical is surprising.

Bromotrichloromethane adds to olefins, under the influence of light, by a radical chain mechanism.[3] When a mixture of *cis*-cyclooctene and bromotrichloromethylcyclooctane is irradiated with 3500-A light, conversion of the olefin into reaction products is high. Besides the 1:1 addition products, 3-bromo-1-cyclooctene (II) and trichloromethylcyclooctane (III) are also formed in large and approximately equal amounts. Since 3-chloro-1-cyclooctene and trichloromethylcyclo-

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(1) (a) 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 1817-A4). (b) Abstracted in part from the Ph.D. dissertation of T. M. C., Louisiana State University, Jan 1966.

(2) See J. G. Traynham and T. M. Couvillon, *J. Am. Chem. Soc.*, **87**, 5806 (1965), and references cited there.

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

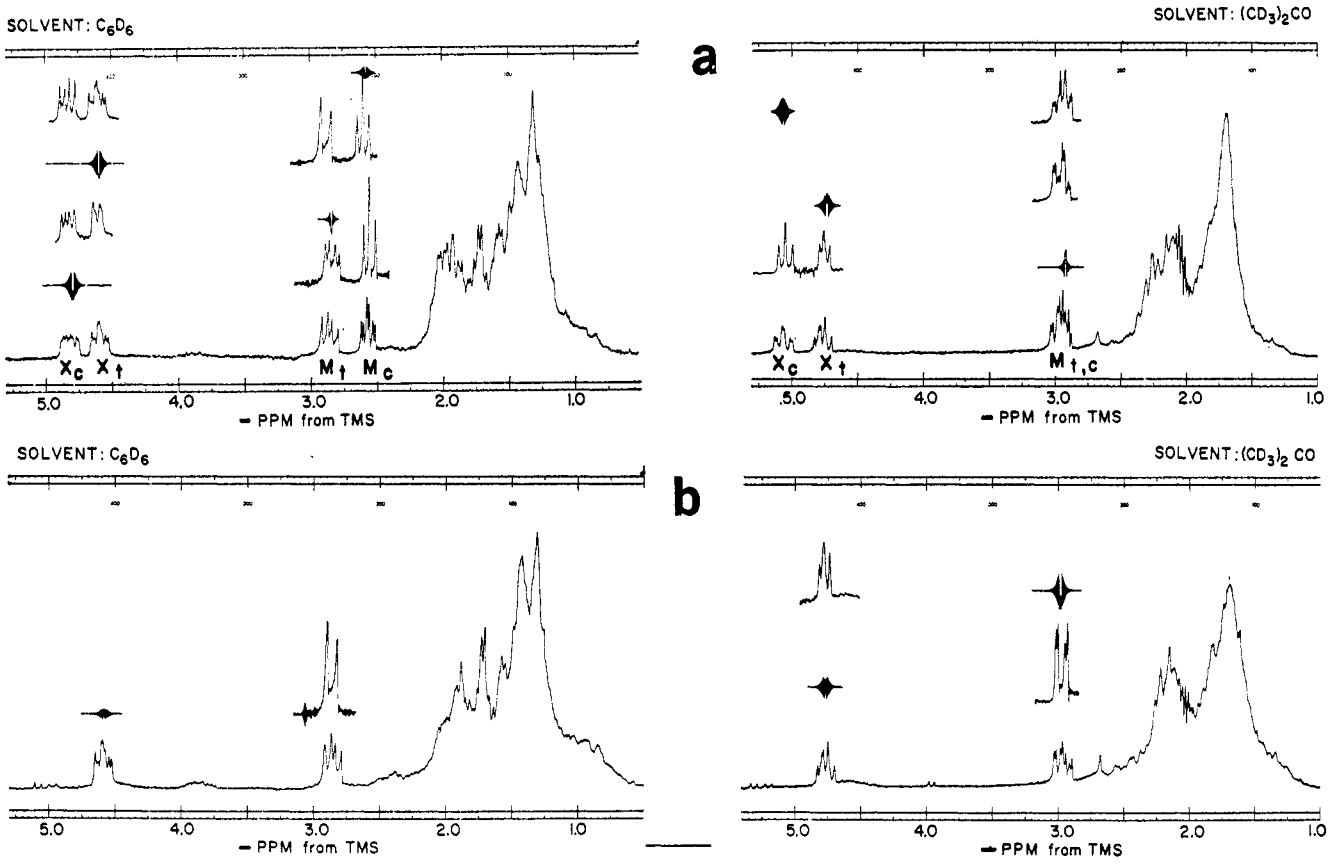
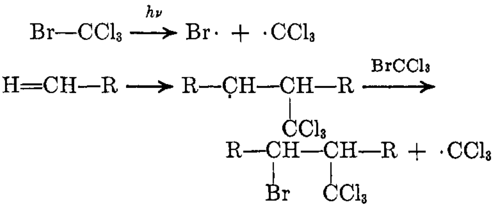


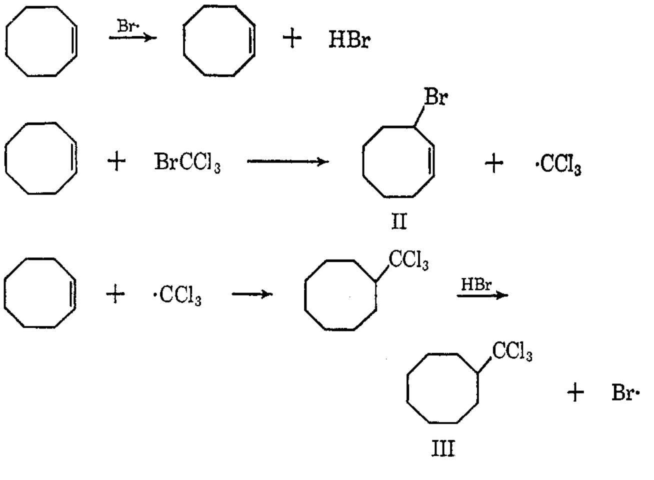
Figure 1.—Nmr spectra of (a) 1-bromo-2-trichloromethylcyclooctane (*cis* + *trans* mixture) at 100 Mc, and (b) *trans*-1-bromo-2-trichloromethylcyclooctane at 100 Mc.



$$Br{-}CCl_3 \xrightarrow{h\nu} Br\cdot + \cdot CCl_3$$

$$\cdot CCl_3 + R{-}CH{=}CH{-}R \longrightarrow R{-}\dot{C}H{-}\underset{CCl_3}{CH}{-}R \xrightarrow{BrCCl_3} R{-}\underset{Br}{CH}{-}\underset{CCl_3}{CH}{-}R + \cdot CCl_3$$

octane are formed in only very small amounts in the photoinitiated addition of carbon tetrachloride to *cis*-cyclooctene,[1b,2] hydrogen abstraction must be effected by radicals other than the common one, trichloromethyl. The following tentative scheme accounts for the much larger amount of hydrogen abstraction when bromotrichloromethane rather than carbon tetrachloride is used as the source of trichloromethyl radicals, as well as for the nearly equal amounts of II and III.



The 60-Mc nmr spectrum of I in carbon tetrachloride solution included a pair of multiplets (nearly triplets), of equal integrated areas, centered at −4.82 ppm and separated by 16 cps.[2] Although a doublet of triplets could be considered the expected signal from CH_2-$CHBrCHCCl_3$, the separation of 16 cps seemed extraordinarily large for a vicinal coupling constant.[4a] The nmr spectrum at 100 Mc included the two downfield multiplets at the same chemical shift positions, but with a separation of 29 cps. This result demonstrates that I (apparently homogeneous by gas chromatography) is actually a mixture of isomers. Further decoupling experiments, studies of solvent effects on the nmr spectra, and selective dehydrohalogenations demonstrated that I is a mixture of geometrical isomers, *cis*- and *trans*-1-bromo-2-trichloromethylcyclooctane. Some of the nmr spectra are reproduced in Figure 1. The dark beat patterns represent the irradiating frequency which led to the decoupled spectrum recorded on the same horizontal line.

The nmr spectrum of a benzene-d_6 solution includes four multiplet signals downfield from −2.5 ppm, each of which has an integrated area corresponding to 0.5 proton (peaks M_c, M_t, X_t, and X_c, Figure 1). We assign the pair of signals, M_c and M_t, to $HCCCl_3$ and the pair, X_t and X_c, to $HCBr$. Clearly signals M_c and X_c are coupled as are M_t and X_t. Irradiation near −2.3 ppm (CH_2CBr) provided decoupled spectra which permitted the pair of coupling constants, $J_{M_tX_t}$ and $J_{M_cX_c}$, to be discerned; they are 6–7 cps and 1–2 cps, respectively. On the basis of the relative magnitude of these coupling

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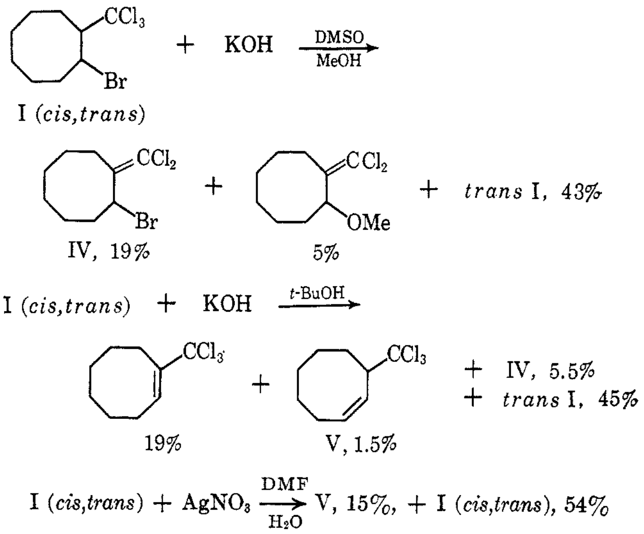
[4] J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965: (a) p 99, (b) p 117.

constants[5] and the dependence of J on dihedral angle,[4b] we consider signals M_c and X_c to come from the *cis* isomer and signals M_t and X_t from the *trans* isomer of 1-bromo-2-trichloromethylcyclooctane.

The other coupling constants responsible for the multiplicity of the signals from protons M and X cannot be equated with the splitting separations in the spectra because these separations change with variations in solvent and applied magnetic field. This phenomenon is common in systems containing three or more nuclei with similar chemical shifts.

The most striking feature of the nmr spectra obtained with different solvents is the unequal solvent dependence of the chemical shift of protons M_c compared with the other three signals beyond −2.5 ppm. Figure 1 illustrates the spectra of benzene-d_6 and acetone-d_6 solutions. Spectra of I, neat, in carbon tetrachloride and and in chloroform-d resemble the spectrum of I in benzene-d_6 in the appearance (but not precise chemical shifts) of the four signals beyond −2.5 ppm, but in dimethyl sulfoxide-d_6 solution as in acetone-d_6 solution, the signals for M_c and M_t coincide.[6] These comparisons suggested to us that protons M_c (*cis* isomer) are specifically deshielded by the oxygenated solvents, perhaps by hydrogen-bonding interactions, and that such solvents might promote stereoselective dehydrohalogenation of I. In basic solutions of *t*-butyl alcohol and of dimethyl sulfoxide (DMSO) (essentially E2 conditions), stereoselective dehydrohalogenations have indeed been achieved.[7] When I (50:50 *cis–trans* mixture) is treated in these solvents with 0.5 equiv of base, the *cis* isomer (whose nmr spectrum is more strongly affected by solvent) is specifically consumed, and pure *trans* I is isolated in nearly theoretical yield. (Figure 1 includes the nmr spectra of the recovered *trans* I.) Although the principal reaction in *t*-butyl alcohol solution is dehydrobromination and that in DMSO solution is dehydrochlorination, *trans* I remains unchanged in both solutions. By contrast, when dehydrohalogenation of I is promoted by 0.5 equiv of silver nitrate in aqueous dimethylformamide (DMF, E1 conditions), 3-trichloromethyl-1-cyclooctene (V) is the single dehydrohalogenation product,[9] and *cis* and *trans* I are consumed about equally. Apparently dehydrohalogenations of I through transition states involving minimum changes in the C–H_M bond are highly stereoselective.



Experimental Section

Gas chromatographic (gc) analyses were obtained with a Barber Coleman Model 20 instrument equipped with a hydrogen flame detector and a 100-ft capillary column coated with SE-96 silicone. Infrared spectra were obtained with Beckman IR-5 and IR-7 and Perkin-Elmer Model 21 and 137 instruments. Microanalyses were performed by Mr. R. Seab at Louisiana State University. Nmr spectra were obtained on Varian Associates HA-60 and HA-100 spectrophotometers;[10] all chemical shifts reported are relative to internal tetramethylsilane reference.

Addition of Bromotrichloromethane to *cis*-Cyclooctene.—A solution of cyclooctene[11] in freshly distilled bromotrichloromethane (1 mole of C_8H_{14}/4 moles of $BrCCl_3$) contained in a Pyrex tube was irradiated for 4 hr in a Rayonet photochemical reactor equipped with 3500-A lamps. The mixture was fractionally distilled through a short Vigreux column at reduced pressure; the density of the cyclooctene–bromotrichloromethane mixture collected in the trap corresponded to a recovery of 6% of the initial cyclooctene. The product mixture, distilling at 55–110° (0.25 mm), was collected in fractions, which were analyzed by gas chromatography and infrared and nmr spectroscopy. The sum of the yields of identified products was 92.5%. The major products are described below.

3-Bromo-1-cyclooctene (21%) immediately reacted with alcoholic silver nitrate: nmr (A/B, 6.2/4),[12] unsymmetrical vinyl proton signal at −5.75 ppm (1.8 H). Gc analysis revealed that this sample contained about 10% of a component of slightly longer retention time than 3-bromo-1-cyclooctene; this component is tentatively identified as **bromocyclooctane** (2%).

Trichloromethylcyclooctane was obtained in 24% yield: nmr (A/B, 4/8),[12] −2.6 ppm (1 H, $HCCCl_3$); intense absorption at 13 μ (CCl_3). *Anal.* Calcd for $C_9H_{15}Cl_3$: C, 47.2; H, 6.6. Found: C, 47.7; H, 6.9.

A mixture of **1-bromo-2-trichloromethylcyclooctane** (44%) and **1-bromo-4-trichloromethylcyclooctane** (1.5%) was obtained, bp 101–102° (0.17 mm). Nmr spectra of this sample[13] are reproduced in Figure 1 and discussed in the foregoing part of this article. The 1,2 isomer gave a single, unresolved peak in the gas chromatogram. *Anal.* Calcd for $C_9H_{14}BrCl_3$: C, 35.1; H, 4.6. Found: C, 35.0; H, 4.7.

When the photoinitiated addition of bromotrichloromethane to cyclooctene was carried out with the reactant mole ratio 1:1,

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[5] For 2,3-dihalonorbornanes and 4,5-dihalo-2-norbornenes, the nmr signals for both HCX in the (eclipsed) *trans* isomers are upfield from those in the *cis* isomers, but J_{trans} is still smaller than J_{cis}: (a) P. M. Subramanian, M. T. Emerson, and N. A. LeBel, *J. Org. Chem.*, **30**, 2624 (1965); (b) P Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1171 (1964).

[6] In some recent studies of conformationally rigid vicinal dihalides,[5] solvent effects were also more marked with *cis* isomers than with *trans* ones. In those studies, however, the upfield shift of $HCBr$ in benzene solution compared with carbon tetrachloride and chloroform solutions was about four to five times the shift observed for solutions of I, and, because of the nearly symmetrical compounds employed, no comparisons of solvent effects on different downfield protons (like $HCBr$ and $HCCCl_3$) could be made.

[7] A simple application of current theories about elimination reactions leads one to expect *cis* I to undergo dehydrobromination more rapidly than *trans* I but does not provide a choice for relative rates of dehydrochlorination. Even the magnitude of the rate difference for dehydrobromination is not easily predicted; present data do not permit one to specify with confidence the preferred conformation of substituted cyclooctanes[8] and the important H–C–C–Br torsion angles.

[8] (a) J. B. Hendrickson, *J. Am. Chem. Soc.*, **86**, 4854 (1964); (b) J. D. Dunitz and A. Mugnoli, *Chem. Commun.*, 166 (1966); (c) J. B. Hendrickson, paper presented at Symposium on Recent Advances in the Conformational Analysis of Mobile Systems, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

[9] Similar selective dehydrohalogenations of 1-chloro-4-trichloromethylcyclooctane have been reported;[2] the ring chlorine was removed by silver nitrate and an exocyclic chlorine by base in DMSO.

[10] We acknowledge with appreciation the assistance of Mr. W. Wegner (Louisiana State University) and Mr. R. Pitcher (Varian Associates), who obtained several of the spectra.

[11] Generously supplied by Columbian Carbon Co., Lake Charles, La.

[12] Ratio of integrated areas of nmr signals centered at −2.2 ppm (A, CH_2CBr, CH_2CCCl_3, and $HCCCl_3$) and −1.65 ppm (B, more remote methylenes).[2]

[13] The presence and amount of the 1,4 isomer in this sample was inferred from the integrated nmr spectrum, which included weak signals corresponding to those in the spectrum of 1-chloro-4-trichloromethylcyclooctane.[2]

the same products were formed in different proportions: 3-bromo-1-cyclooctene, 30%; bromocyclooctane, 3%; trichloromethylcyclooctane, 38%, 1-bromo-2-trichloromethylcyclooctane, 22%; and 1-bromo-4-trichloromethylcyclooctane, 2%. The conversion of cyclooctene into products was 77%, and the combined yield of identified products was 95%.

Selective Dehydrohalogenations of 1-Bromo-2-trichloromethylcyclooctane. A. With AgNO$_3$ in DMF.—A solution of silver nitrate (2.8 g, 0.016 mole) in aqueous dimethylformamide (20 ml, 70% DMF/30% H$_2$O v/v) was added dropwise to a warm (35°), stirred solution of I (0.0325 mole) in DMF (50 ml). Precipitation began quickly, and the mixture was stirred for 4 hr without additional heating. After dilution with water, the mixture was extracted three times with petroleum ether (bp 60–70°). The combined organic material was washed with water, dried, and distilled at reduced pressure. Nmr and gc analyses indicated that a single dehydrohalogenation product, C$_9$H$_{13}$Cl$_3$ (V), was formed and that 54% of the original I was recovered. *Anal.* Calcd for C$_9$H$_{13}$Cl$_3$: C, 47.4; H, 5.8. Found: 47.0; H, 5.9. Spectra of V indicate that it is 3-trichloromethylcyclooctene; nmr −5.7 (2 H, vinyl), −2.7 to −2.0 (5 H, HCCCl$_3$, CH_2C=C, and CH_2CCCl$_3$), and −1.62 ppm (6 H, CH$_2$CH_2CH$_2$). Infrared absorptions were recorded at 3.3 (vinyl C–H), 6.02 (C=C), and 12.6–13.2 μ (intense, CCl$_3$). The gc retention time of V is shorter than those of 4- and 1-trichloromethylcyclooctenes.

The nmr spectrum of the recovered I indicated that the sample was identical, within the experimental precision of the analysis, with the initial I.

B. With KOH in DMSO.—During 1.5 hr, a solution of potassium hydroxide (0.045 mole) in a mixed solvent (20 ml of DMSO, 5 ml of methanol, 5 ml of water) was added to a solution if I (0.065 mole) in DMSO (40 ml) and methanol (10 ml).[2] The mixture was stirred at room temperature for 18 hr longer, poured into 200 ml of water, and extracted three times with petroleum ether. Conventional work-up and distillation of the organic material gave a mixture of products in two fractions and another fraction of essentially pure *trans* I, bp 90–99° (0.12 mm), whose nmr spectrum is reproduced in Figure 1.

The nmr spectra of the first two distillate fractions included signals at −5.1 (complex six-peak multiplet, HCBrC=CCl$_2$), −4.65 (multiplet, HCBr in *trans* I), −3.1 ppm (sharp singlet, OCH_3). Infrared spectra of the same fractions included absorptions at 6.22 and 11.09 (C=CCl$_2$), 9.2 (methyl ether), and 12.7–13.4 μ (CCl$_3$). On the basis of concordant changes in the relative intensities of the absorptions in the nmr and infrared spectra of the distillate fractions, the components (and estimated yields based on initial I) were identified as follows: 1-bromo-2-dichloromethylenecyclooctane (19%), 1-methoxy-2-dichloromethylenecyclooctane (5%), and *trans* I (43%).

C. With *t*-BuOK in *t*-BuOH.—A mixture of potassium *t*-butoxide (0.035 mole), *t*-butyl alcohol (100 ml), methyl alcohol (10 ml), and I (0.052 mole) was stirred for 20 hr at room temperature, diluted with 100 ml of water, and extracted twice with petroleum ether. The combined organic material was washed thoroughly with water, dried with calcium chloride, and distilled. Besides solvent, four fractions (13.4 g total) boiling at 60–92° (0.12 mm) were collected; the final fraction, bp 91–92° (0.12 mm), 3.8 g (0.0123 mole), was virtually pure *trans* I. The fractions which were mixtures were analyzed by nmr and infrared spectroscopy and by gas chromatography. The recordings included nmr signals at −6.51 (well-resolved triplet,[14] J = 8.5 cps) as well as the previously mentioned ones at −5.1 (HCBrC=CCl$_2$) and −4.65 ppm (HCBr in *trans* I), and infrared absorptions at 3.3 and 6.1 (vinyl), 6.25 and 11.08 (C=CCl$_2$), and 12.7–13.4 μ (CCl$_3$). On the basis of concordant changes in the relative intensities of the absorptions in the nmr and infrared spectra and the relative peak areas in the gas chromatograms, the components (and estimated yields based on initial I) were identified as follows: 1-trichloromethyl-1-cyclooctene (19%), 1-bromo-2-dichloromethylenecyclooctane (5.5%), 3-trichloromethyl-1-cyclooctene (1.5%), and *trans* I (total yield 45%). Small amounts of alkoxycyclooctanes (see B above) appeared to be present in the mixtures also.

Registry No.—*trans* I, 7540-97-8; *cis* I, 7540-98-9; III, 7540-99-0; V, 7541-00-6; 1-bromo-4-trichloromethylcyclooctane, 7541-61-7.

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[14] The nmr spectra of several different 1-substituted cyclooctenes show a clean triplet signal for the single vinyl proton: A. C. Cope and R. B. Kinnel, *J. Am. Chem. Soc.*, **88**, 752 (1966); see in particular footnote 14 of that paper.

Base-Promoted Reactions of Epoxides. II. 3,4- and 5,6-Epoxycyclooctene[1]

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Received October 31, 1966

The rearrangement reactions of the title compounds promoted by lithium diethylamide have been examined. 3,4-Epoxycyclooctene produces 3-cyclooctenone and *cis*-bicyclo[3.3.0]oct-7-en-*endo*-2-ol. 5,6-Epoxycyclooctene gives a mixture of 2,4- and 3,5-cyclooctadienol as the initial product. These alcohols undergo facile thermal conversion into 3-cyclooctenone by a pathway involving 1,5-hydrogen migration. The details of the base-initiated rearrangements are discussed in the light of related studies.

In connection with our interest in the reactions of epoxides in strongly basic media, we have examined the transformations of 3,4-epoxycyclooctene (**1**) and 5,6-epoxycyclooctene (**2**) under such conditions. This study was prompted by the earlier work of Cope and co-workers,[2] who observed that *cis*-cyclooctene oxide (**3**) was largely isomerized to bicyclic alcohol **4** upon treatment with lithium diethylamide. This reaction, which is typical for a number of medium-ring epoxides, was demonstrated to proceed by an α-elimination mechanism that presumably involves transannular insertion of a carbenoid intermediate.[3] The present study was initiated to determine the effect of neighboring double bonds on the reactions of medium-ring epoxides with strong bases and, in particular, to ascertain whether intramolecular carbenoid addition to the olefinic bonds would occur. The predominance of transannular insertion reactions in the cyclooctyl system and the availability of the diene precursors of the epoxides directed our attention toward compounds **1** and **2**.

Subjecting **1** to reaction with excess lithium diethylamide in refluxing ether for 1 day resulted in a smooth conversion to a mixture of two products in an 8:92 ratio. The spectroscopic data for the minor component established that it was an unsaturated, non-

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[1] Part I: J. K. Crandall and Luan-Ho Chang, *J. Org. Chem.*, **32**, 435 (1967). A review of base-promoted rearrangements of unfunctionalized epoxides is included in this paper.

[2] A. C. Cope, H. H. Lee, and H. E. Petree, *J. Am. Chem. Soc.*, **80**, 2849 (1958).

[3] A. C. Cope, G. A. Berchtold, P. E. Peterson, and S. H. Sharman, *ibid.*, **82**, 6370 (1960).