

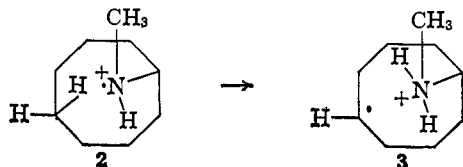
Proximity Effects. XXXIX. Transannular Radical Rearrangements in the Decomposition of 1-Methylcyclooctyl Hypochlorite¹

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A pronounced proximity effect has been observed in the photochemically induced rearrangement of 1-methylcyclooctyl hypochlorite at 0°. The mixture of primary products was shown to consist of *trans*-4-, *trans*-5-, *cis*-4-, and *cis*-5-chloro-1-methylcyclooctanol in yields of 28, 21, 7, and 3%, respectively. The two *trans*-chlorohydrins were unstable at room temperature and the mixtures were analyzed by indirect methods. The product of the competing ring-opening reaction, 9-chloro-2-nonanone, was formed in only 1% yield. Pyrolyses of the hypochlorite gave this ketone in yields as high as 15%, in addition to products resulting from thermal decomposition of the chlorohydrins. The structures of the new compounds resulting from this study were confirmed by independent syntheses.

The first example of a transannular radical rearrangement in a medium-sized ring was reported by Wawzonek and Thelan,⁵ who obtained N-methylgranatanine by irradiating a strongly acidic solution of N-chloro-N-methylcyclooctylamine. It seems clear from later mechanistic studies of the Hofmann-Löffler reaction⁶ that the radical ion **2** was an intermediate, and that it rearranged to **3** by abstraction of a hydrogen atom from the 5-position. As this requires a seven-membered



transition state (not ordinarily favored in this type of reaction⁶) and no products of attack at the 4-position were reported, a proximity effect must have operated. It was reported recently that the alkoxy radical rearrangement (Barton reaction) of cyclooctyl nitrite gave a product resulting from attack on a hydrogen atom in the 4-position (4-nitrosocyclooctanol dimer, characterized as 1,4-cyclooctanedione in 16% yield).⁷ In neither of these cases was it possible to determine the stereochemistry of a primary product.

We undertook the study of the decomposition of 1-methylcyclooctyl hypochlorite (Figure 1) to determine whether the 1-methylcyclooctyloxy radical **4** would

undergo an intramolecular rearrangement. It was also hoped that the stereochemical fate of the alkyl radicals could be determined by identifying initial products.

While this work was in progress it was predicted⁸ that photochemical intramolecular rearrangement of hypochlorites of appropriate structure would yield the respective halohydrins. Such rearrangements have been the subject of a number of recent communications.⁹ In all these cases hydrogen atoms were abstracted from positions such that a six-membered transition state was possible. Some of the reactions^{9b} were shown to proceed by radical chain reactions of long chain length.

Solutions of pure 1-methylcyclooctyl hypochlorite (**1**) in trichlorofluoromethane or carbon tetrachloride were obtained by treating 1-methylcyclooctanol with a large excess of hypochlorous acid. While the best of several attempts to isolate **1** (evaporation of a trichlorofluoromethane solution with added hydroquinone) gave only 97% pure material, analysis of the solutions by infrared spectroscopy showed the presence of less than 0.2% of unchanged 1-methylcyclooctanol and no other impurity (except solvent). 1-Methylcyclooctyl hypochlorite decomposed completely when refluxed in carbon tetrachloride solution under nitrogen for 12 hr. Two of the major components of the complex mixture of products, isolated by gas chromatography, were found to correspond to the molecular formula C₉H₁₆O. The supposition that they were 1,4- and 1,5-epoxy-1-methylcyclooctane (**5** and **6**, suggested by their infrared spectra) was confirmed by comparison with samples synthesized independently. 9-Chloro-2-nonanone (**7**), the product of the type of ring-opening rearrangement predominating in the decomposition of five- and six-membered cyclic tertiary hypochlorites,^{9b,10} was present only to the extent of 4–8%. The yield was increased to 15% when the hypochlorite **1** was pyrolyzed at 300°. While results were extremely variable, a major product of pyrolysis in carbon tetrachloride was usually a mixture of chlorolefins which was only partially separable by gas chromatography. The mixture contained isomers **12**, **13**, and **14**.

A similar mixture of products was obtained on irradiation of **1** in carbon tetrachloride at 0°, followed by

(1) Supported in part by a research grant (NSF-GP-1587) of the National Science Foundation. Paper XXXVIII: A. C. Cope, M. Brown, and G. L. Woo, *J. Am. Chem. Soc.*, **87**, 3107 (1965).

(2) National Institutes of Health Postdoctoral Fellow, 1959–1960.

(3) National Science Foundation Postdoctoral Fellow, 1958–1959.

(4) National Institutes of Health Postdoctoral Fellow, 1961–1962.

(5) S. Wawzonek and P. J. Thelan, *J. Am. Chem. Soc.*, **72**, 2118 (1950).

(6) E. J. Corey and W. R. Hertler, *ibid.*, **82**, 1657 (1960).

(7) P. Kabasakalian and E. R. Townley, *J. Org. Chem.*, **27**, 2918 (1962).

(8) D. H. R. Barton, J. M. Beaton, L. E. Geller, and M. M. Pechet *J. Am. Chem. Soc.*, **82**, 2640 (1960).

(9) (a) M. Akhtar and D. H. R. Barton, *ibid.*, **83**, 2213 (1961); (b) F. D. Greene, M. L. Savitz, H. H. Lau, F. D. Osterholtz, and W. N. Smith, *ibid.*, **83**, 2196 (1961); F. D. Greene, M. L. Savitz, F. D. Osterholtz, H. H. Lau, W. H. Smith, and P. M. Zanet, *J. Org. Chem.*, **28**, 55 (1963); (c) C. Walling and A. Padwa, *J. Am. Chem. Soc.*, **83**, 2207 (1961); (d) J. S. Mills and V. Petrow, *Chem. Ind. (London)*, 946 (1961).

(10) (a) T. L. Cairns and B. E. Englund, *J. Org. Chem.*, **21**, 140 (1956); (b) J. W. Wilt and J. W. Hill, *ibid.*, **26**, 3523 (1961).

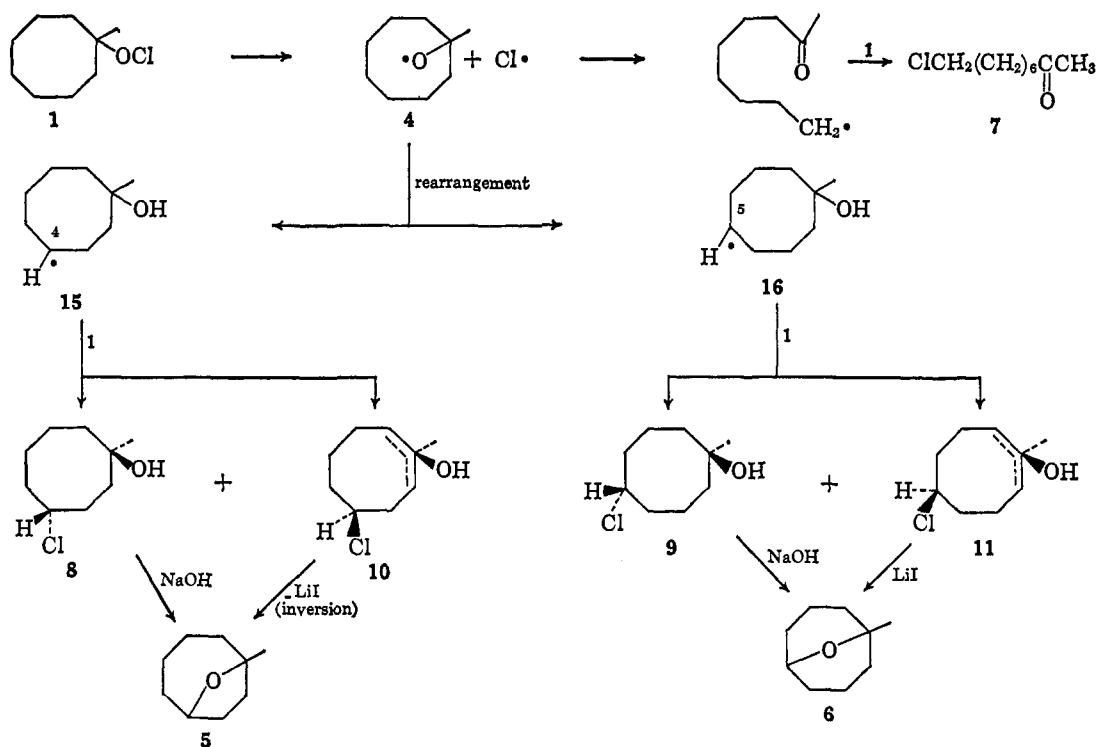


Figure 1. Decomposition of 1-methylcyclooctyl hypochlorite (1).

distillation of the solvent. To avoid further reaction and dehydration of the expected primary products, the chlorohydrins, the photolysis of **1** was carried out in trichlorofluoromethane at 0° and the solvent was removed and replaced by carbon disulfide below room temperature. The infrared spectrum and a negative Baeyer test for unsaturation were in accord with expectation for a mixture consisting mainly of chlorohydrins. However, decomposition at room temperature was so rapid as to frustrate all attempts to separate the mixture.

In a somewhat similar situation Bartlett,¹¹ by treating a mixture of *cis*- and *trans*-2-chlorocyclohexanol with aqueous alcoholic sodium hydroxide at room temperature, quantitatively converted the *trans* isomer to 1,2-epoxycyclohexane, thus facilitating isolation of the *cis*-chlorohydrin.

Under conditions similar to those of Bartlett the formation of epoxides **5** and **6** from photolysis products freshly prepared at 0° proceeded rapidly for 3 hr., then slowly for 3 days, after which time the concentrations of the products of interest did not change. Neutralized reaction mixtures were extracted with chloroform, and the concentrated extracts on analysis by gas chromatography showed three major peaks (the first due to 1-methylcyclooctanol) plus a number of poorly resolved minor components. The second major peak was separated into two components identified as 1,4- and 1,5-epoxy-1-methylcyclooctane (**5** and **6**), in yields of 28 and 21%, respectively, as determined by internal standards (see Experimental). The ratio **5/6** from five different photolyses was $(57 \pm 1)/(43 \pm 1)$. This meant that 28% of the hypochlorite was rearranged to *trans*-4-chloro-1-methylcyclooctanol (**8**) and 21% of *trans*-5-chloro-1-methylcyclooctanol (**9**). The formation of **8** was also confirmed by its

(11) P. D. Bartlett, *J. Am. Chem. Soc.*, **57**, 224 (1935).

isolation as a 3,5-dinitrobenzoate, m.p. 100° , from a photolysis product which had been treated with base for 2 hr. to destroy selectively the most unstable of the primary products. When this dinitrobenzoate was left in 0.2 *N* base at room temperature for 10 days it hydrolyzed and spontaneously cyclized to the 1,4-epoxide **5** in 88% over-all yield; this established both the position of the chlorine atom and its *trans* relationship to the hydroxyl group. The third major peak from analysis of the photolysis mixture by gas chromatography appeared to be a mixture of chlorohydrins from its elemental analysis and infrared spectrum. Attempts to separate the mixture by gas-liquid or liquid-solid chromatography failed. It was stable at 100° for 2 hr., was not affected by cold 0.2 *N* alkali, and when heated with alcoholic potassium hydroxide for 18 hr., gave none of the epoxides **5** or **6**, but decomposed instead into what appeared to be a mixture of unsaturated alcohols. Reaction with 3,5-dinitrobenzoic anhydride gave a mixture of dinitrobenzoates. One of them, m.p. 128 – 129° , was isolated by fractional crystallization, and on hydrolysis with weak base under conditions which led to epoxide formation with the *trans*-dinitrobenzoate of m.p. 100° gave a chlorohydrin. It seemed most probable that the chlorohydrins were a mixture of *cis*-4- and *cis*-5-chloro-1-methylcyclooctanol. This was proved by inversion of the chlorine atoms and facile cyclization of the resulting *trans*-chlorohydrins to the known and separable epoxides **5** and **6**. Inversion was accomplished by heating the chlorohydrins with lithium iodide in diglyme at 150° in the presence of calcium carbonate. A mixture of **5** and **6** in a ratio of 2:1 was obtained in 55% yield. Similar treatment of the chlorohydrin obtained on hydrolysis of the 3,5-dinitrobenzoate, m.p. 128 – 129° , gave only the 1,5-epoxide (**6**). Therefore the alcohol isolated was *cis*-5-

chloro-1-methylcyclooctanol (**11**), and the major component of the chlorohydrin mixture was the *cis*-4-isomer (**10**). If no other chlorohydrin was present the yield of **10** in the photolysis was about 7% and that of **11** about 3%.

The following arguments were used to exclude the presence of the isomeric 2-chloro- and 3-chloro-1-methylcyclooctanols in the photolysis products. Gas chromatography showed no peak at the retention time of 1,2-epoxy-1-methylcyclooctane; therefore less than 0.1% of *trans*-2-chloro-1-methylcyclooctanol could have been produced. It seemed improbable that, in the absence of the *trans*, only the *cis*-2- isomer would have been formed. In an effort to put an upper limit on the concentration of any 3-chloro-1-methylcyclooctanol formed, the mixture of chlorohydrins was dehydrated quantitatively with sodium bisulfate to a mixture of chloroolefins. The mixture was partially separated by gas chromatography into 4-chloro-1-methylcyclooctene (**13**) and a mixture presumed to be 5-chloro- and 6-chloro-1-methylcyclooctenes (**12** and **14**). The n.m.r. spectra (see Experimental) of each showed a vinyl proton as a triplet with no sign of the doublet expected for 3-chloro-1-methylcyclooctene. It seems safe to say that less than 1% of 3-chloro-1-methylcyclooctanol could have been present.

The yield of 1-methylcyclooctanol varied unaccountably among runs (2.5–13% in five reactions at 0°). The presence of the parent alcohol among the products of photolyses of alkyl hypochlorites has often been observed, but has not been given the attention it deserves. Perhaps it has been assumed that all of the alcohol found was present as an impurity in the original hypochlorite, an explanation which is unsatisfactory in this case. Formation of the alcohol may be related to the amount of adventitious water, for in one experiment in which water was deliberately added the yield of the alcohol rose to 30%. However, the yield of alcohol did not seem to correlate well with the effort made to ensure anhydrous conditions, and the question of its origin remains open. The yields of the various chlorohydrins were usually lower when the yield of the parent alcohol was high.

Only about 1% of the decomposition of **1** at 0° went by the ring-opening mechanism to form 9-chloro-2-nonanone. The complex mixture of volatile minor products only partially separable by gas chromatography accounted for 5–10% of the starting material. These, and products not sufficiently volatile for separation by gas chromatography, may be derived from intermolecular reactions of the hypochlorite, which were beyond the scope of the present study.

Thus a total of about 60% of the decomposition of 1-methylcyclooctyl hypochlorite proceeded *via* transannular radical rearrangements involving both the 4-position (35%) and the 5-position (24%). The hydrogen atoms at the single 5-position were about 1.4 times as reactive as those at the two 4-positions in spite of the requirement of a seven-membered transition state for hydrogen abstraction from C-5. From inspection of models it appears that when the cyclooctane ring is in the favored skewed crown conformation¹² the oxygen can approach a hydrogen atom on

(12) N. L. Allinger and S. Greenberg, *J. Am. Chem. Soc.*, **84**, 2394 (1962), and references cited therein.

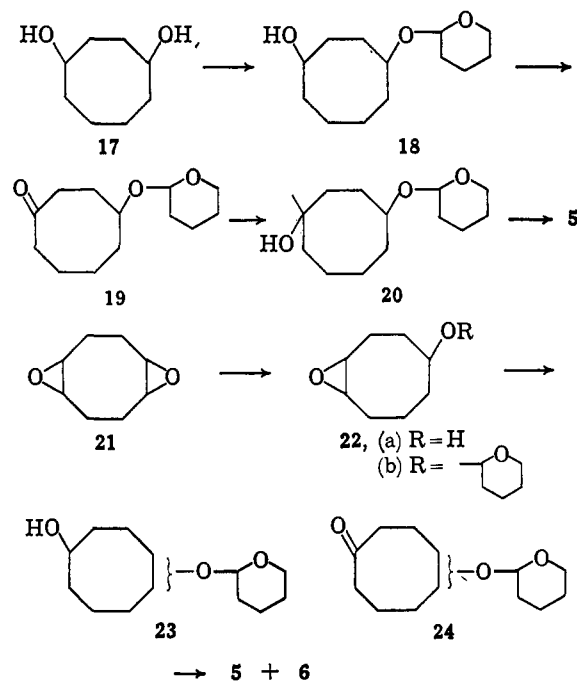


Figure 2. Syntheses of authentic samples.

C-5 easily, but cannot come close to one at C-4. Some less favored conformation is evidently necessary for a shift from C-4. The resulting radicals **15** and **16** apparently did not retain their original configuration (with the unpaired electron *cis* to the hydroxyl group) because the *trans*-chlorohydrins were the predominant primary products. The stereochemistry of the products probably is governed by the steric requirement of the bulky incoming 1-methylcyclooctyl hypochlorite molecule which furnishes the chlorine atom.¹³

Syntheses of the new compounds resulting from this study are summarized in Figure 2. *cis*-1,4-Cyclooctanediol¹⁴ was converted to a 2-tetrahydropyranyl ether by a phosphoryl chloride catalyzed reaction with 1 equiv. of dihydropyran, and the remaining hydroxyl group was oxidized with chromium trioxide–pyridine to give ketone **19**. The crude tertiary alcohol **20** obtained from **19** by a Grignard reaction gave the desired 1,4-epoxy-1-methylcyclooctane (**5**) directly when treated with hydrogen chloride in benzene. The epoxide was isolated by gas chromatography and proved to be identical with one of the two epoxides obtained from hypochlorite **1**.

cis,cis,syn-1,2,5,6-Diepoxcyclooctane¹⁵ (**21**) served as the starting material for synthesis of a mixture of epoxides **5** and **6**. One of the epoxide rings was cleaved in a sluggish reaction with lithium aluminum hydride to give the epoxyalcohol **22a**, characterized as its phenylurethan. The 2-tetrahydropyranyl ether (**22b**) of **22a** was treated with lithium aluminum hydride, yielding a mixture of 4- and 5-(2'-tetrahydropyranyloxy)-cyclooctanol. The mixture was then converted to a mixture of 1,4- and 1,5-epoxides **5** and **6** by the same

(13) Relation of the stereochemistry of these products to the mechanism of the atom transfer step may be complex (e.g., see F. D. Greene, C. C. Chu, and J. Walia, *J. Org. Chem.*, **29**, 1285 (1964)).

(14) A. C. Cope, S. W. Fenton, and C. F. Spencer, *J. Am. Chem. Soc.*, **74**, 5884 (1952).

(15) B. S. Fisher, Ph.D. Thesis, Massachusetts Institute of Technology, 1957. Cf. F. C. Frostick and B. Phillips, British Patent 793,150 (1958); *Chem. Abstr.*, **52**, 18268 (1958).

series of reactions employed for the synthesis of **5** from alcohol **18**. The epoxides were separated by gas chromatography. One of the two was identical with synthetic **5**; the other, which from the method of synthesis must be **6**, was identical with the second epoxide from the decomposition of hypochlorite **1**.

Alkylation of the sodium salt of ethyl acetoacetate with 1-chloro-6-iodohexane in refluxing toluene gave the keto ester **25**, which was cleaved by sulfuric acid to 9-chloro-2-nonanone (**7**).

Experimental¹⁶

1-Methylcyclooctanol. Cyclooctanone (126 g.) was converted to 1-methylcyclooctanol (135 g., 95% pure by gas chromatography on column C, 135°; cyclooctanone was the only impurity) using the method of Brown and Borkowski¹⁷ except that the reaction time was increased to 6 hr. One recrystallization from pentane gave 60 g. (42%), m.p. 33–34°, in which no cyclooctanone was detected by gas chromatography. A second recrystallization gave 39 g. of material of at least 99.8% purity, m.p. 35.0–35.5° (lit.¹⁷ 34–36°), which was used in most preparations of hypochlorite **1**.

The 3,5-dinitrobenzoate, prepared by Brewster's method,¹⁸ had m.p. 97–98° after recrystallization from ethanol.

Anal. Calcd. for C₁₆H₂₀N₂O₆: C, 57.13; H, 5.99. Found: C, 57.01; H, 6.06.

1-Methylcyclooctyl Hypochlorite (1). Using a modification of the method of Greene,¹⁹ a solution of 1-methylcyclooctanol (5.68 g.) in trichlorofluoromethane (60 ml.) was added during 15 min. with stirring to a solution of hypochlorous acid freshly prepared from 265 ml. of 0.76 *M* sodium hypochlorite solution ("Clorox") and 11.5 ml. of acetic acid at 0°. The mixture was stirred vigorously for 1.5 hr. at 0°, then extracted three times with ice-cold trichlorofluoromethane. The combined extracts were washed three times with cold 3% sodium bicarbonate, dried over potassium carbonate, and filtered. Iodometric titrations indicated that the yellow solution (171.4 g.) contained 7.0 g. (99%) of hypochlorite **1**. Similar preparations were made in carbon tetrachloride; solutions of **1** in either solvent were stable for several months when stored in the dark at –5° over potassium carbonate. When solutions of **1** in trichlorofluoromethane were evaporated in an effort to isolate the pure hypochlorite, titrations with thiosulfate usually showed that 13–35% of the active chlorine had been lost. Addition of small amounts of hydroquinone had a stabilizing effect, and evaporation of these solutions in an

(16) Melting points are corrected and boiling points uncorrected unless otherwise noted. Nuclear magnetic resonance spectra were recorded as 12% solutions in carbon tetrachloride using a Varian A-60 spectrometer; tetramethylsilane was the internal standard. Microanalyses were performed by Dr. S. M. Nagy and his associates and by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Gas chromatographic analyses and collections were carried out using 190 × 0.8 cm. Pyrex columns packed with 25–30% of stationary phase on 60–80 mesh support. The columns were: (A) silicone grease on firebrick (washed with 1% sodium hydroxide), (B) silicone grease on Celite, (C) 1,2,3-tris(2-cyanoethoxy)propane (TCEP) on firebrick, (D) 190 × 1.2-cm. column packed as for C, (E) silicone oil (Dow Corning No. 550) on firebrick. To prevent dehydration of tertiary alcohols a 20% solution of triethanolamine in methanol (0.1–0.2 ml.) was usually injected at least 30 min. before the start of an analysis.

(17) H. C. Brown and M. Borkowski, *J. Am. Chem. Soc.*, **74**, 1894 (1952).

(18) J. H. Brewster and C. J. Ciotti, Jr., *ibid.*, **77**, 6214 (1955).

(19) F. D. Greene, *ibid.*, **81**, 2688 (1959).

air stream at a pressure of 20–40 mm. gave **1** as a greenish yellow oil with percentages of active chlorine sometimes as high as 96–97% but occasionally as low as 92%. 2,4,6-Tri-*t*-butylphenol was somewhat less effective than hydroquinone as a stabilizer.

Infrared spectra of 10% solutions of **1** in carbon tetrachloride (0.1-mm. cell) showed no absorption in the carbonyl or hydroxyl regions. When a 5.0-mm. cell was used, a small peak was observable at 3580 cm.⁻¹, equal in intensity to that found in a 0.01% solution of 1-methylcyclooctanol. On adding enough of the alcohol to a 10% solution of **1** to make its concentration 0.05%, the 3580 cm.⁻¹ peak increased in size by the expected amount. Thus the amount of unchanged 1-methylcyclooctanol in 1-methylcyclooctyl hypochlorite was about 0.1 g./100 g. If the reaction time was reduced to 1 hr. the ratio of alcohol to hypochlorite was raised to 1.3 g./100 g.

Pyrolysis of Hypochlorite 1 in Carbon Tetrachloride. A. Carbon tetrachloride solutions of **1** (5–10%) were heated to reflux under nitrogen for 12 hr., after which time the active chlorine had disappeared and the solvent was removed by distillation. Gas chromatograms of the residual oil (column A or E, 175°) showed two major peaks and at least 20 smaller peaks, the relative areas of which varied considerably among different experiments.

The major peak of longer retention time²⁰ (*R* = 1.3, 25–50%), collected from column E, gave a positive Baeyer test and on analysis corresponded to C₉H₁₅Cl. It probably consisted of a mixture of at least three isomeric chloromethylcyclooctenes, as shown by partial separation on column C (90°).

Anal. Calcd. for C₉H₁₅Cl: C, 68.30; H, 9.56. Found: C, 68.39; H, 9.55.

The other major component, collected from column E (*R* = 0.65, 20–40%), was separated into two pure isomers by reinjection on column C (70°). The first eluted (60%), *n*^{25D} 1.3596, was identified as 1,4-epoxy-1-methylcyclooctane (**5**) by comparison of its infrared spectrum ($\nu_{\max}^{\text{CCl}_4}$ 1475, 1375, 1115, 1060, 1015, and 930 cm.⁻¹) and retention times (columns A, C, and E) with those of a synthetic sample.

Anal. Calcd. for C₉H₁₆O: C, 77.09; H, 11.50. Found: C, 76.81; H, 11.52.

The second isomer, *n*^{25D} 1.4663, $\nu_{\max}^{\text{CCl}_4}$ 1460, 1375, 1320, 1225, 1170, 1035, 960, 890, and 845 cm.⁻¹, was identified as 1,5-epoxy-1-methylcyclooctane (**6**) by similar comparisons.

Anal. Calcd. for C₉H₁₆O: C, 77.09; H, 11.50. Found: C, 76.86; H, 11.43.

An extremely variable component (*R* = 2.8, 0.25%) appeared from its infrared spectrum and retention time to be a mixture of isomeric chloro-1-methylcyclooctanols but was not further investigated.

9-Chloro-2-nonanone (7) (*R* = 2.3, 4–8%) was collected and identified by comparison of its infrared spectrum and retention time with those of authentic **7**.

B. At High Temperature. A simple distillation apparatus (15-cm. Claisen column) with a dropping funnel extending into the top of the still pot was used for this pyrolysis. The receiver was cooled to –80°, the still pot heated to 300° with a Woods metal bath,

(20) Retention times *R* are expressed relative to 1-methylcyclooctanol on column A (140–175°).

and a solution of hypochlorite **1** (1.5 g.) in trichlorofluoromethane (25 ml.) was added dropwise. The hypochlorite obviously decomposed long before being heated to 300°. The flask was removed when the addition was complete, and the product was distilled through a 30-cm. semimicro column. A fraction (b.p. 74–75° at 0.5 mm., 675 mg.) was found by gas chromatography (column A, 150°) to contain 230 mg. of ketone **7** (yield, 15%). The ketone was collected (n_D^{25} 1.4498) and identified as described previously. The semicarbazone, after recrystallization from aqueous methanol, had m.p. 111.5–112.5°.

Anal. Calcd. for $C_{10}H_{20}ClN_3O$: C, 51.39; H, 8.63. Found: C, 51.36; H, 8.40.

Photolysis of Hypochlorite 1. General Method. A solution of **1** in trichlorofluoromethane or carbon tetrachloride (0.2–0.4 *M*) in a Pyrex vessel was cooled to –70° and degassed several times, the oxygen being replaced by nitrogen. The solution was then brought to the desired temperature, usually 0°, and irradiated with a weak ultraviolet source (Burton Mfg. Co. Model 1910) or a tungsten lamp (100 w.) until a test for active chlorine (starch-iodide paper) was negative. The yellow color of **1** usually faded suddenly after an induction period of 10–20 min., and the reaction was complete within another hour. The solvent was quickly removed at room temperature under reduced pressure, leaving a colorless oil with the same weight ($\pm 1\%$) as the original hypochlorite. Analysis of one such crude product for total halogen showed that, within experimental error, no chlorine had been lost or gained (from the trichlorofluoromethane) during the reaction. When first isolated the photolysis products gave negative Baeyer tests and their infrared spectra exhibited strong absorption in the 3500-cm.⁻¹ region, a weak band at 1718 cm.⁻¹ and no peaks attributable to secondary decomposition products. After standing at room temperature for a few hours, a positive Baeyer test and a new peak in the infrared spectrum at 830 cm.⁻¹ indicated that olefins had formed, and the characteristic 1035-cm.⁻¹ band of epoxide **5** and 1060-cm.⁻¹ band of epoxide **6** appeared. Decomposition occurred during all attempts to separate the photolysis products by gas-liquid or liquid-solid chromatography.

Reaction of Photolysis Products with Alkali. The entire photolysis product was dissolved at once in 2 to 3 equiv. of sodium hydroxide solution (0.2 *N* in 80% ethanol, the number of moles of hypochlorite **1** present before photolysis being defined as 1 equiv.). The mixtures were allowed to stand at room temperature for at least 4 days. Titration of aliquots with hydrochloric acid showed that consumption of the base was rapid for 3 hr. (0.3–0.35 equiv.), then slow for 3 days (another 0.3 to 0.35 equiv.), and finally very slow after 3 days (0.1 equiv. during the next 50 days). When quantitative yield data were desired internal standards were added to the neutralized solutions. Mesitylene ($R = 0.4$)²⁰ and diphenylmethane ($R = 3.5$)²⁰ were chosen as standards after it had been established that essentially all of the volatile products of this reaction had retention times between 0.65 and 2.8 on column A.²⁰ The solution containing a standard was extracted four times with chloroform, the extracts were washed with 3% sodium bicarbonate solution and with water, then concentrated, and dried by careful distillation of

the wet chloroform through a 15-cm. Vigreux column. The resulting concentrate was separated by gas chromatography (column A, 140–150°) into three well resolved major components ($R = 0.65, 1.00,$ and 2.8) and a number of poorly resolved minor products ($R = 1.2$ – 2.3).

The foregoing applies to all photolyses carried out between 0 and –78°; the following data are from five photolyses at 0°. Four were irradiated in trichlorofluoromethane and the other in carbon tetrachloride; the products were treated with alkali for from 4 to 53 days. Quantitative gas chromatographic analysis of aliquots of one of these reaction mixtures taken after 4, 7, 9, and 16 days showed that the amounts of the three major products remained constant after 4 days in alkali.

The principal component of the three ($R = 0.65$) was shown to be a mixture of 1,4-epoxide **5** and 1,5-epoxide **6** by the methods described in the Pyrolysis section. The ratio of 1,4- to 1,5-epoxide as determined on column C (80°) was 57 ± 1 to 43 ± 1 . The ratio of **5** to **6** was reproducible to $\pm 1\%$ in every experiment, but the yields of individual photolysis products varied widely among experiments. The yield of **5** was 22–35% (av. 28%) while that of **6** was 16–27% (av. 21%).

The component of $R = 1.00$ was collected and identified as 1-methylcyclooctanol by its infrared spectrum. The yield of this alcohol varied between 2.5 and 13% (av. 8%).

The third major component ($R = 2.8$) was a mixture of *cis*-chloro-1-methylcyclooctanols and was obtained in 7–13% yield (av. 10%). Elucidation of the composition of this mixture is described in a subsequent section.

Anal. Calcd. for $C_9H_{17}ClO$: C, 61.18; H, 9.70. Found: C, 61.06; H, 9.52.

One of the minor products was 9-chloro-2-nonanone (**7**) ($1.2 \pm 0.3\%$ yield). It was collected and identified by infrared spectroscopy. The other minor products ($R = 1.2$ – 2.2) were not investigated.

There was no peak at $R = 0.89$ (the retention time of an authentic sample of *cis*-1,2-epoxy-1-methylcyclooctane²¹); a yield of 0.1% would have been detectable.

cis-Chloro-1-methylcyclooctanol Mixture. A. Stability. Samples of the mixture before and after heating in a sealed tube for 2 hr. at 100° showed no change on gas chromatographic analysis (a single peak on column A at 150°).

B. Chromatography. The mixture showed no sign of separation on eight different gas chromatography columns, nor could it be separated by chromatography on silica gel (thin-layer plates) or on alumina (activity II, elution chromatography). Much decomposition occurred on the alumina and recoveries were low.

C. Reaction with Lithium Iodide. The chlorohydrin mixture (19.0 mg., collected from column A), powdered calcium carbonate (62 mg.), and 1 ml. of a stock solution of 8.5% dry lithium iodide in diglyme were combined and stirred under nitrogen at 150° for 2 hr. Mesitylene (6.9 mg.) was added as an internal standard for gas chromatographic analysis, and the solution was diluted with water and extracted with

(21) A. C. Cope and P. E. Burton, *J. Am. Chem. Soc.*, **82**, 5442 (1960).

pentane. The combined pentane extracts were washed three times with saturated salt solution and once with water, dried over sodium sulfate, and concentrated to 1 ml. by distillation through a 15-cm. Vigreux column. Gas chromatography of the residue (column C, 80°) showed that the major products were the 1,4-epoxide **5** (36%) and the 1,5-epoxide **6** (19%); these were collected and identified by comparison of infrared spectra. Using column A at 150° no unchanged chlorohydrins and only 3% of chloroolefins were detected. Several unidentified substances of low retention time, presumably olefins, were the major by-products. When a similar mixture was heated at 82° for 16 hr. the yield of epoxides was 39%, and 19% of the chlorohydrin mixture was unchanged. When refluxing 2-butanone was used in place of diglyme the yield of epoxides after 15 hr. was only about 5% while the major product (~50%) was a mixture of chloroolefins; only small amounts of the chlorohydrins survived. In boiling acetone the rate of epoxide formation was extremely slow and competition from side reactions was excessive.

D. 3,5-Dinitrobenzoate of cis-5-Chloro-1-methylcyclooctanol. The product of a photolysis of **1** in trifluorochloromethane at 0° was treated with excess 0.2 *N* sodium hydroxide in 80% ethanol at room temperature for 16 days. The mixture was neutralized and extracted three times with chloroform. The extracts were washed with water and dried (sodium sulfate), the chloroform was evaporated, and most of the lower boiling products were removed by a rapid, short-path distillation (with sodium bicarbonate added to the pot) at 115° (0.1 mm.). The residual oil (445 mg.) which contained about 50% of the mixture of chlorohydrins (gas chromatography on column A at 145°) was added to a solution of 3,5-dinitrobenzoic acid (530 mg.) and *p*-toluenesulfonyl chloride (950 mg.) in pyridine (5 ml.) at 0°. After 2 hr. at 0° and 20 hr. at room temperature the mixture was poured onto ice and extracted with ether. The extracts were washed with 3% sodium bicarbonate and with water and dried over potassium carbonate, and the solvent was removed under reduced pressure. Leaching of the residue with ether left 614 mg. of crystals. Six recrystallizations from benzene-ether and from alcohol afforded about 25 mg. of the nearly colorless 3,5-dinitrobenzoate, m.p.²² 128–129°.

Anal. Calcd. for C₁₆H₁₉ClN₂O₆: C, 51.84; H, 5.17. Found: C, 51.67; H, 5.04.

The dinitrobenzoate (12.9 mg.) was mixed with 1.5 ml. of 0.2 *N* sodium hydroxide in 80% ethanol. After the mixture stood at room temperature with occasional shaking for 3 days the crystals had disappeared, and after 10 days mesitylene (2.6 mg.) and water were added and the mixture was extracted with four 1-ml. portions of chloroform. The extracts were washed with water, dried, and concentrated by distillation through a 15-cm. Vigreux column until 0.2 ml. remained. By gas chromatographic analysis (column A, 138°) the residue was found to contain a chlorohydrin (85% yield), presumably **11**; neither epoxide **5** nor **6** was detected. The remaining solution was allowed to evaporate spontaneously, and the resulting oil was

stirred under nitrogen for 2 hr. at 150° with lithium iodide in diglyme (0.5 ml. of an 8.5% solution) and powdered calcium carbonate (30 mg.), then cooled. Water was added, the mixture was extracted with pentane, and the extracts were washed several times with dilute salt solution and with water. Gas chromatography on columns C (85°) and A (140°) showed that 1,5-epoxy-1-methylcyclooctane (**6**) had been produced in good yield; no peak due to the 1,4-isomer was present.

E. Dehydration. The chlorohydrin mixture (5.3 mg.) was covered with powdered sodium bisulfate (35 mg.) and heated in a closed vial in a steam bath for 10 min. After cooling, an internal standard (5.8 mg. of diphenylmethane) was added and the mixture was leached with hot chloroform (four 0.1-ml. portions). Gas chromatographic analysis (column A, 140°) showed that the chloroform solution contained 4.8 mg. (100%) of a mixture of chloroolefins (*R* = 1.3). A sample from a similar reaction was collected from this column for analysis.

Anal. Calcd. for C₉H₁₅Cl: C, 68.30; H, 9.56. Found: C, 68.24; H, 9.45.

The chloroolefins were partially separated into two fractions on column D (80–90°). Fraction 1 (60–70%), a peak with a poorly resolved shoulder, gave no reaction with alcoholic silver nitrate. The n.m.r. spectrum was in accord with its formulation as a mixture of 5- and 6-chloro-1-methylcyclooctene (**12** and **14**); it exhibited a complex triplet at τ 4.6 (*J* = 7 c.p.s., 1 H), a broad multiplet at 6.0 (1 H), a singlet at 8.3 (3 H), and a complex multiplet between 7.5 and 8.5 (10 H). The mixture was not further investigated.

Fraction 2 (30–40%), *n*^{25D} 1.4942, was identified as 4-chloro-1-methylcyclooctene (**13**) on the basis of its n.m.r. spectrum. The spectrum was quite similar to that of fraction 1 in that it exhibited a complex triplet at τ 4.7 (*J* = 8 c.p.s., 1 H), a multiplet at 6.0 (1 H), and a singlet at 8.3 (3 H); however, the methylene protons between the vinyl proton and the proton on the carbon bearing the halogen atom appeared as a multiplet at τ 7.4–7.6 (2 H), distinct from the multiplet due to the other 8 methylene protons (7.7–8.7). A sample separated on column D was collected from column A (140°) for analysis.

Anal. Calcd. for C₉H₁₅Cl: C, 68.30; H, 9.56. Found: C, 68.39; H, 9.89.

All samples of **13** gave an immediate precipitate with alcoholic silver nitrate, indicating the presence of a small amount of an allylic chloride.

F. Reaction with Strong Base. The mixture of chlorohydrins (7.7 mg.), sealed in a tube with a solution of potassium hydroxide (10 mg.) in absolute ethanol (90 mg.), was heated at 100° for 18 hr. After cooling, saturated sodium chloride was added and the mixture was extracted with pentane (three 0.1-ml. portions). Qualitative gas chromatographic analysis (column A, 163°) indicated that about 10% of the chlorohydrins had survived while the remainder had been converted into an unidentified material, with *R* = 0.93.²⁰ On the basis of its infrared spectrum (bands in the 3500-cm.⁻¹ region, and at 1640 and 732 cm.⁻¹), it was probably a mixture of unsaturated 1-methylcyclooctanols resulting from dehydrohalogenation of the *cis*-chlorohydrins.

3,5-Dinitrobenzoate of trans-4-Chloro-1-methylcyclo-

(22) Taken on a Reichert hot-stage apparatus. In a capillary the m.p. was 117–122° dec.

octanol. 1-Methylcyclooctyl hypochlorite (3.20 g.) was photolyzed in trichlorofluoromethane (72 g.) at -78° . The oil (3.13 g.) remaining after evaporation of the solvent was treated with 0.2 *N* ammonium hydroxide in 80% ethanol (50 ml.) at room temperature for 2 hr. After distillation of most of the ethanol under reduced pressure below room temperature, 3% sodium bicarbonate was added and the mixture was extracted with ether. Evaporation of the ether extracts after washing with water and drying over potassium carbonate gave 2.68 g. of a pale yellow oil. This was dissolved in pyridine (5 ml.), added to an ice-cold solution of 3,5-dinitrobenzoic acid (1.75 g.) and tosyl chloride (3.13 g.) in pyridine (20 ml.), and then allowed to stand overnight at room temperature. The mixture was worked up in the usual manner,¹⁸ and 3.61 g. of crystalline product, m.p. $77-80^{\circ}$, was obtained. Three fractional crystallizations from alcohol and three from ether-pentane gave 300 mg. of the 3,5-dinitrobenzoate of **8**, m.p. $97-98^{\circ}$. The melting point was depressed by more than 30° by admixture with the dinitrobenzoate of 1-methylcyclooctanol, and was unchanged after four more recrystallizations. It was higher in a capillary ($99.6-100.4^{\circ}$) than on a hot stage ($97-98^{\circ}$).

Anal. Calcd. for $C_{16}H_{19}ClN_2O_6$: C, 51.84; H, 5.17. Found: C, 51.73; H, 5.10.

Treatment of a portion of the analytical sample (7.0 mg.) with 1.0 ml. of 0.2 *N* sodium hydroxide in 80% ethanol for 10 days at room temperature, followed by extraction with chloroform and gas chromatographic analysis using mesitylene as the internal standard (column C, 85°), indicated an 88% yield of the 1,4-epoxide **5**. Its identity was confirmed by infrared spectroscopy. A small amount (4.6%) of the 1,5-epoxide **6** also was present, showing that not all of the *trans*-5-chloro isomer had been removed by ten crystallizations. Similar treatment of material from the last three mother liquors gave the two epoxides in the same ratio. Gas chromatography of the product on column A (140°) showed that no chlorohydrins had survived the treatment with base.

Photolysis of 1 in Wet Trichlorofluoromethane. A photolysis of hypochlorite **1** (118 mg.) in trichlorofluoromethane (2.2 g.) was carried out at 0° in the manner described before except that 5 mg. of water was added (two phases). After 16 hr. there was still some active chlorine left, so the mixture was again degassed and irradiated for 2 hr., after which no active chlorine remained. After treatment with 0.2 *N* 80% ethanolic sodium hydroxide for 4 days gas chromatographic marker analysis (column A, 145°) showed that the yield of 1-methylcyclooctanol was 28.6 mg. (30%). The other products were a mixture of the 1,4- and 1,5-epoxides (33.1 mg., 35%), a mixture of the *cis*-chlorohydrins (5.5 mg., 4.7%), and the ketone **7** (1.7 mg., 1.4%). No previously unobserved products were apparent.

cis-4-(2'-Tetrahydropyranyloxy)cyclooctan-1-ol (**18**). A solution of *cis*-1,4-cyclooctanediol¹⁴ (**17**, 31.9 g.) and phosphoryl chloride (1 ml.) in anhydrous ether (4 l.) was heated to reflux while a solution of dihydropyran (19.3 g., 5% excess of 1 equiv.) in ether (500 ml.) was added during 18 hr.²³ The mixture was

made slightly alkaline with aqueous alcoholic sodium hydroxide and the solvents were removed under reduced pressure. Chromatography of the residue on two 2-lb. lots of Merck alumina afforded 12.3 g. of unidentified oil (presumably the diether of **17**, eluted with ether), 23.1 g. (46%) of the desired monoether **18**, and 9.7 g. (30%) of unchanged glycol **17** (eluted in that order with 5-10% methanol in ether). Short-path distillation of crude **18** over sodium carbonate gave a colorless, viscous oil, b.p. $133-137^{\circ}$ (0.3 mm.), n_D^{25} 1.4947, $\nu_{max}^{CS_2}$ 3590, 3440, 1205, 1135, 1115, 1080, 1055, 1025, and 990 cm^{-1} (the last seven bands are attributed to the tetrahydropyranyloxy group).

Anal. Calcd. for $C_{13}H_{24}O_3$: C, 68.38; H, 10.59. Found: C, 67.99; H, 10.38.

4-(2'-Tetrahydropyranyloxy)cyclooctan-1-one (**19**). Alcohol **18** (20 g.) was oxidized with chromium trioxide (35 g.) in pyridine.²⁴ The product was more easily isolated if considerable "Super-Cel" was added to the mixture before water was added. The product, after distillation, b.p. $120-127^{\circ}$ (0.3 mm.), was separated from a small amount of unchanged starting material by chromatography on alumina (Merck, special). Ketone **19** (13.2 g., 68% yield) was eluted with ether, and a sample purified by short-path distillation at 110° (bath temperature; 0.2 mm.) had n_D^{25} 1.4872, $\nu_{max}^{CS_2}$ 1700, 1205, 1135, 1115, 1080, 1055, 1025, and 1005 cm^{-1} .

Anal. Calcd. for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 69.29; H, 9.69.

1,4-Epoxy-1-methylcyclooctane (**5**). Ketone **19** (10 g.) was added to a Grignard reagent prepared from methyl iodide (14.2 g.), magnesium (2.4 g.), and ether (50 ml.), and the mixture was stirred for 1 hr. Water was added, the layers were separated, and the aqueous layer was extracted with ether. The residue after removal of ether was chromatographed on Merck alumina. After elution of unchanged **19** with ether-methanol (100:1), crude 4-(2'-tetrahydropyranyloxy)-1-methylcyclooctanol (**20**, 7.05 g., 66%) was eluted with ether-methanol (50:1). The infrared spectrum of crude **20** had no carbonyl absorption and showed the expected hydroxyl (3590 and 3380 cm^{-1}) and tetrahydropyranyloxy bands.

A slow stream of hydrogen chloride gas was bubbled through a solution of **20** (400 mg.) in dry benzene (4 ml.) for 1 hr. Water and potassium carbonate were added, and the mixture was extracted with ether. Most of the solvents were removed by distillation through a 50-cm., spinning-band column. Gas chromatography of the residue (column C, 80°), either alone or mixed with a sample of **5** from the hypochlorite decomposition, showed a single peak (except for solvents). The infrared spectra of collected samples of **5** from this source and from pyrolysis or irradiation of **1** were identical.

Anal. Calcd. for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.23; H, 11.48.

4,5-Epoxy-cyclooctanol (**22a**). Lithium aluminum hydride in ether (3.0 *M*, 150 ml.) was added under nitrogen to a stirred solution of *cis,cis,syn*-1,2,5,6-diepoxy-cyclooctane¹⁵ (**21**, 140 g.) in 750 ml. of ether. The mixture was heated to reflux and tetrahydrofuran was

(23) A modification of the method of W. E. Parham and E. L. Anderson, *J. Am. Chem. Soc.*, **70**, 4187 (1948).

(24) G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *ibid.*, **75**, 422 (1953).

added until the pot temperature reached 60°; this temperature was maintained for 18 hr. The mixture was cooled and to it were added successively water (17 ml.), 15% aqueous sodium hydroxide (17 ml.), and water (51 ml.). The mixture was filtered and the filter cake was washed with ether. The organic solution was washed with saturated sodium chloride solution and dried over magnesium sulfate, and the solvents were removed. Repeated fractional distillation of the residue through a 38-cm. Podbielniak column afforded 30.7 g. of crystalline hygroscopic epoxy alcohol **22a**, b.p. 115–126° (3 mm.), 90% pure by gas chromatographic analysis (column E, 160°). A collected sample melted at 52–61°. The phenylurethan, prepared from a 99% pure distillation fraction, b.p. 117–118° (3 mm.), had m.p. 141–142° after two recrystallizations from aqueous ethanol.

Anal. Calcd. for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 68.72; H, 7.54; N, 5.48.

Mixture of 4- and 5-(2'-Tetrahydropyranyloxy)cyclooctanol (23). Crude epoxy alcohol **22a** (23.0 g.) was converted to its 2-tetrahydropyranyl ether **22b** by treatment with dihydropyran (84 g.) and phosphoryl chloride (1 ml.) at 0° for 3 days. Distillation of the mixture after adjustment to pH 10 with ethanolic sodium ethoxide yielded 30.5 g. (83%) of **22b**, b.p. 103–108° (0.3 mm.). The infrared spectrum of this material showed no hydroxyl bands and exhibited typical 2'-tetrahydropyranyloxy bands in the 1000–1225-cm.⁻¹ region; it was used without further purification or characterization.

Crude **22b** (30.5 g.) was added to a solution of lithium aluminum hydride (28 g.) in tetrahydrofuran under nitrogen. The mixture was stirred at room temperature for 2 hr., then at the reflux temperature for 20 hr., and cooled. Water (3 ml.), 15% aqueous sodium hydroxide solution (3 ml.), and water (9 ml.) were added in that order and the product was isolated in the manner described for **22a**. Distillation afforded 27.2 g. (86%) of the mixture of alcohols **23**, b.p. 113–122° (0.2 mm.), n_D^{25} 1.4943. The infrared spectrum showed typical hydroxyl and 2-tetrahydropyranyloxy absorption and the absence of starting material. The analytical sample was dried over phosphorus pentoxide at 1 mm.

Anal. Calcd. for $C_{13}H_{24}O_3$: C, 68.31; H, 10.59. Found: C, 68.27; H, 10.31.

Mixture of 4- and 5-(2'-Tetrahydropyranyloxy)cyclooctanone (24). A portion (845 mg.) of the mixture of alcohols **23** was oxidized with chromium trioxide (1.1 g.) in the manner described for the oxidation of alcohol **18**. The mixture of ketones **24** (704 mg., 84%) was purified by short-path distillation at 0.1 mm. with a bath temperature of 110° and had n_D^{25} 1.4855, $\nu_{max}^{liq.}$ 1700 cm.⁻¹.

Anal. Calcd. for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 68.95; H, 9.94.

1,4- and 1,5-Epoxy-1-methylcyclooctane (5 and 6). A solution of the mixture of ketones **23** (325 mg.) in ether (5 ml.) was added during 20 min. at room temperature to the Grignard reagent prepared from magnesium (350 mg.) and methyl iodide (2 g.) in 30 ml. of ether. The mixture was stirred for 12 hr., then poured into cold saturated ammonium chloride solution and

extracted with ether. The combined ether extracts were filtered through "Super-Cel," washed with 0.1 N sodium thiosulfate and 3% sodium bicarbonate, and dried over potassium carbonate. Evaporation of the ether yielded a mixture of 4- and 5-(2'-tetrahydropyranyloxy)-1-methylcyclooctanols as a viscous yellow oil (289 mg., 83%) with a strong band at 3500 cm.⁻¹, characteristic 2-tetrahydropyranyloxy bands, and essentially no carbonyl absorption in its infrared spectrum. A portion of this material (146 mg.), dissolved in 5 ml. of benzene, was cooled to 5° and dry hydrogen chloride was bubbled through it slowly for 1 hr. Mesitylene (43.0 mg.) was added as a marker for gas chromatographic analysis and the mixture was washed with 3% sodium bicarbonate and with water, dried over sodium sulfate, and concentrated to about 2 ml. by distillation through a 15-cm. Vigreux column. Gas chromatographic analysis (column C, 80°) showed the presence of 20.4 mg. (24%) of a mixture of 1,4- and 1,5-epoxy-1-methylcyclooctane in a ratio of 3:2. Collected samples of the two epoxides had infrared spectra and retention times (columns A, 140° and C, 80°) identical with those of the two epoxides obtained from decomposition of 1-methylcyclooctyl hypochlorite.

Synthesis of 9-Chloro-2-nonanone (7). Ethyl acetoacetate (6.8 g.) was converted to its sodium salt by slow addition to a dispersion of sodium hydride (1.3 g.) in dry toluene (85 ml.).²⁵ 1-Chloro-6-iodohexane²⁶ (12.3 g.) was added and the slurry was stirred at the reflux temperature under nitrogen for 46 hr. The mixture was cooled, acidified with 1 N hydrochloric acid (4.5 ml.), and diluted with ether. The organic layer was separated, washed with water, and dried over magnesium sulfate, and the solvents were removed by distillation under reduced pressure. The alkylation product **25** appeared to be unstable above 150° but a fairly pure sample (3.3 mg.) was separated by gas chromatography (column B, 135°, retention time 75 min.). To this sample was added concentrated sulfuric acid (0.1 ml.), followed by water (0.1 ml.).²⁷ After 1 hr. the mixture was heated on a steam bath for 20 min., cooled, and extracted with ether. The extracts, after washing with 5% sodium bicarbonate and drying over potassium carbonate, were evaporated to give 1.7 mg. (73%) of 9-chloro-2-nonanone (**7**) which showed only one peak on gas chromatography (column A, 175°). Similar treatment of the crude alkylation product gave mixtures from which ketone **7** was easily separated by gas chromatography, the over-all yield from ethyl acetoacetate being about 17%. The ketone, a colorless oil at room temperature, crystallized when cooled with Dry Ice and melted at -16 to -15°, n_D^{25} 1.4492, $\nu_{max}^{CS_2}$ 1718 (C=O), 720 [(CH₂)₄], and 653 (C-Cl) cm.⁻¹.

Anal. Calcd. for $C_9H_{17}ClO$: C, 61.18; H, 9.70. Found: C, 61.19; H, 9.56.

One of the major by-products of the reaction was 1,6-diiodohexane.

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(26) R. A. Raphael and F. Sondheimer, *J. Chem. Soc.*, 2100 (1950).

(27) An adaptation of the method of A. B. Sen and P. M. Bhargava, *J. Indian Chem. Soc.*, **25**, 403, 539 (1948).