

## ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASS.]

Proximity Effects. XXXIV. Solvolysis of *cis*-Bicyclo[6.1.0]nonane<sup>1</sup>BY ARTHUR C. COPE AND GAR LOK WOO<sup>2</sup>

RECEIVED MARCH 29, 1963

The reaction of *cis*-bicyclo[6.1.0]nonane with formic acid gave a mixture of alcohols and olefins in which the products of transannular hydride shift, *cis*-4-methylcyclooctanol and 4-methylcyclooctene, predominated to the extent of 93%. For comparison purposes all of the isomeric methylcyclooctanones and methylcyclooctenes were synthesized. Stereospecific syntheses of *cis*- and *trans*-4-methylcyclooctanol were accomplished, and configurations were assigned to the 2-methylcyclooctanols. Possible mechanisms for the formation of the solvolysis products are discussed.

In our previous studies of solvolytic reactions resulting in extensive transannular shifts in medium ring compounds<sup>3a</sup> an oxygen function had been initially present in the cycloalkane derivative. It was of interest to investigate a simpler system not influenced initially by a polar function. *cis*-Bicyclo[6.1.0]nonane fulfilled this requirement and yet was reactive owing to the presence of the cyclopropane ring.<sup>3b</sup>

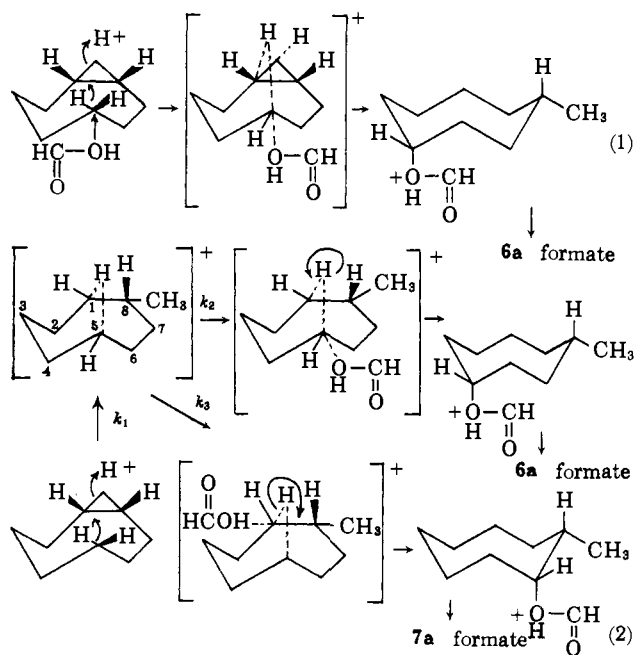
## Results and Discussion

*cis*-Bicyclo[6.1.0]nonane (1) was prepared from *cis*-cyclooctene, methylene iodide, and zinc-copper couple.<sup>4</sup> Reaction of *cis*-bicyclo[6.1.0]nonane and 98–100% formic acid at room temperature followed by alkaline hydrolysis gave in 92% yield a mixture of alcohols (77%) and olefins (23%). The mixture was separated into two fractions by chromatography on alumina. Catalytic hydrogenation of the olefin fraction afforded methylcyclooctane<sup>5</sup> as the only product, suggesting that the olefins were a mixture of methylcyclooctenes. Analysis of the olefin mixture by gas chromatography showed that it consisted of 1-methylcyclooctene<sup>5</sup> (2, 8%), 3-methylcyclooctene (3, 0.1%), 4-methylcyclooctene (4, 90%), and 5-methylcyclooctene (5, 2%).<sup>6</sup> The individual components were isolated by gas chromatography and identified by comparison of their infrared spectra with those of authentic samples.

Oxidation of the alcohol fraction with chromium trioxide in pyridine afforded a mixture of 2-methylcyclooctanone (9, 3%), 3-methylcyclooctanone (10, 1%), and 4-methylcyclooctanone (11, 96%), isolated by gas chromatography and identified by comparison of their infrared spectra with those of authentic samples. 4-Methylcyclooctanone was further characterized by the melting points and infrared spectra of the semicarbazone and 2,4-dinitrophenylhydrazone. Thus the positions of the methyl groups in the alcohols were established. Analysis of the mixture of alcohols by gas chromatography showed three peaks (in order of increasing retention time): a component with retention time identical with that of  $\alpha$ -methylcycloheptane methanol (0.2  $\pm$  0.1%), *cis*-2-methylcyclooctanol (7a, 3%), and an unresolved mixture (97%) of *cis*-4-methylcyclooctanol (6a) and 3-methylcyclooctanol (8). Components 6a (contaminated by 1% of 8 as determined by the oxidation experiment) and 7a were collected and identified

by comparison of their infrared spectra with those of authentic samples. *cis*-4-Methylcyclooctanol was further characterized as the acid phthalate. The configuration of the 3-methylcyclooctanol formed was not determined because it could be isolated only as the ketone.

Cleavage of *cis*-bicyclo[6.1.0]nonane with formic acid thus proceeded almost exclusively by a highly stereospecific transannular path. The simplest mechanism accounting for stereospecific formation of 6a is a one-step process (eq. 1) involving cleavage of the cyclopropane ring, 1,5- (or 1,3-) hydride shift and attack of a solvent molecule (or formate anion) on the opposite side of the departing hydride ion in a concerted manner. Alternatively, a two-step process involving formation of a nonclassical 1,5-bridged carbonium ion may be considered. This would provide a common intermediate for the formation of 7a (attack of a solvent molecule at



C-1) as well as for 6a (attack of a solvent molecule at C-5), as shown in eq. 2. The predominance of 6a relative to 7a may be rationalized in part on this basis because approach of a solvent molecule at C-1 is hindered by the methyl group. Alternatively, 7a might result from a 1,3-hydride shift involving C-1 and C-7 as shown in eq. 3. The process is represented here as concerted, but a two-stage process could also be considered. The presence of a small amount (1%) of 8 (undetermined configuration) in the product mixture can be rationalized by a 1,2-hydride shift to give the bridged

(1) Supported by a research grant (NSF-G5055) of the National Science Foundation. Paper XXXIII: A. C. Cope and J. K. Hecht, *J. Am. Chem. Soc.*, **85**, 1780 (1963).

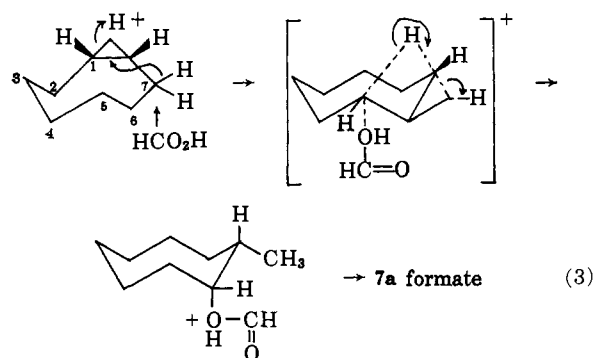
(2) National Institutes of Health Predoctoral Fellow, 1961–1962.

(3) (a) A. C. Cope, G. A. Berchtold, P. E. Peterson, and S. H. Sharman, *J. Am. Chem. Soc.*, **82**, 6366 (1960), and earlier papers in this series; (b) An investigation of the solvolysis of *trans*-bicyclo[6.1.0]nonane performed subsequently has been published (paper XXXIII).

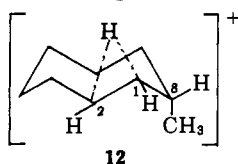
(4) (a) H. E. Simmons and R. D. Smith, *ibid.*, **81**, 4256 (1959); (b) R. S. Shank and H. Shechter, *J. Org. Chem.*, **24**, 1825 (1959).

(5) A. C. Cope and H. C. Campbell, *J. Am. Chem. Soc.*, **74**, 179 (1952).

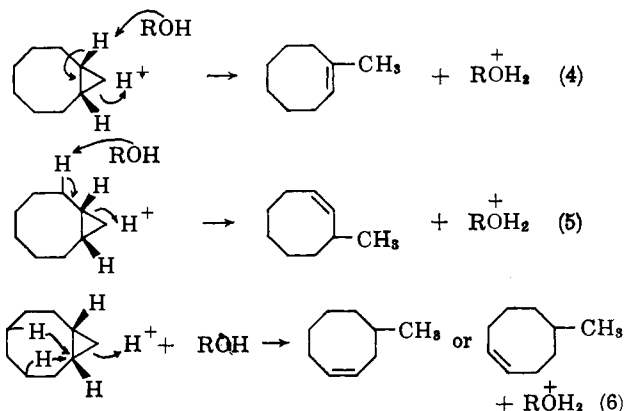
(6) The methylcyclooctenes all are understood to contain a *cis* double bond on the basis of methods of synthesis of the authentic samples.



carbonium ion 12 which can undergo nucleophilic attack at C-1 (yielding 7a) or at C-2 (yielding 8). This would imply that the configuration of 8 is *cis*.



The formation of 1- and 3-methylcyclooctenes can be most directly explained by a concerted elimination mechanism (eq. 4 and 5). The formation of 4- and 5-methylcyclooctenes can best be accommodated by a similar mechanism involving 1,3- or 1,5-transannular hydride shift (eq. 6).



Abstraction of a C-2 proton by a solvent molecule accompanied by a 1,3-hydride shift or of a C-6 proton accompanied by a 1,5-hydride shift leads to 4-methylcyclooctene. 5-Methylcyclooctene would arise by elimination of a C-4 proton accompanied by a 1,3- or a 1,5-hydride shift. Alternatively, a bridged (1,5- or 1,3-) nonclassical carbonium ion could yield the methylcyclooctenes by elimination of a  $\beta$ -proton and simultaneous formation of a conventional C-H bond.

The alcohols 6a and 7a were recovered unchanged when subjected individually to the conditions of the formolysis reaction and in neither case were any olefinic products detected. Thus the olefins did not arise by elimination of formic acid from initially produced formates. Olefins 2 and 3 were unchanged under the formolysis conditions while 4 and 5 after recovery were found to contain 0.5% and 5% of 2, respectively. This precluded the possibility of formation of 3, 4, or 5 by isomerization and showed that the amount of 2 formed by isomerization was insignificant.<sup>7</sup> No formic acid addition products were detected in the recovered olefins, indicating that the alcohols isolated from the formolysis reaction were not derived from olefins initially produced.

(7) Isomerization would involve a 1,3- or 1,5-hydride shift in the initially formed (secondary) carbonium ion to give a (tertiary) 1-methylcyclooctyl carbonium ion.

**Syntheses of Methylcyclooctanones and Methylcyclooctenes.**—2-Methylcyclooctanone (9) was prepared from cyclooctanone and diethyl oxalate by a procedure recently developed in this Laboratory.<sup>8</sup> An attempt to prepare the ketone from 1-pyrrolidylcyclooctanone<sup>9</sup> by the general method of Stork and co-workers<sup>10</sup> failed, probably due to extensive N-methylation. 3-Methylcyclooctanone (10) was synthesized by the cuprous chloride-catalyzed 1,4-addition of methylmagnesium iodide to 2-cycloocten-1-one. Catalytic hydrogenation of 4-methylenecyclooctanone (13), prepared from 1,4-cyclooctanedione and one equivalent of triphenylmethylenephosphorane, gave 4-methylcyclooctanone (11). Bicyclo[3.3.0]-1(5)-octen-2-one (the intramolecular condensation product of 1,4-cyclooctanedione) was isolated as the other major product in the preparation of 13. 5-Methylcyclooctanone (14) was prepared in several steps from 1,5-dibromo-3-methylpentane<sup>11</sup> (15), obtained from the corresponding glycol. Alkylation of acetonitrile with 15 afforded 5-methylnonanedinitrile (16) as well as the intramolecular alkylation product 4-methylcyclohexanecarbonitrile. The dinitrile 16 was cyclized to a mixture of 2-oxo-6-methylcyclooctanecarbonitrile (17) and 2-amino-6-methyl-1-cyclooctene-1-carbonitrile (18) which were each separately hydrolyzed to the same ketone 14.

1-Methylcyclooctene (2) was prepared by dehydration of 1-methylcyclooctanol.<sup>5</sup> Reaction of 3-bromocyclooctene with methylmagnesium iodide afforded 3-methylcyclooctene (3). Pyrolysis of the S-methyl xanthates of the 3-methylcyclooctanols obtained by lithium aluminum hydride reduction of the ketone 10 gave a mixture of 3-methylcyclooctene (37%) identical with 3 prepared above and 4-methylcyclooctene (63%) which was separated by gas chromatography. Lithium aluminum hydride reduction of 4-cyclooctene-1-carboxylic acid prepared by modification of the original procedure of Stork and Landesman<sup>12</sup> afforded 4-cyclooctene-1-methanol (19). The tosylate of 19 was reduced with lithium aluminum hydride to 5-methylcyclooctene (5). This olefin was also obtained from 5-methylcyclooctanone via the 5-methylcyclooctyl-S-methyl xanthates. The methylcyclooctenes are all assumed to be *cis* with respect to the double bond since pyrolysis of cyclooctyl-S-methyl xanthate gave 100% *cis*-cyclooctene.<sup>13</sup>

**Syntheses of *cis*- and *trans*-4-Methylcyclooctanol and Assignment of Configuration to the 2-Methylcyclooctanols.**—The bicyclic ketone 20 constituted the basis for the stereospecific syntheses of the 4-methylcyclooctanols summarized in Fig. 1. Ketone 20 was prepared from cyclopentanone and 1,4-bis-diazobutane by the procedure first reported,<sup>14</sup> although after the conclusion of our experiments a new synthesis appeared.<sup>15</sup> Oxidation of 20 with trifluoroperoxyacetic acid gave the lactone 21 which was reduced to the glycol 22 with lithium aluminum hydride. Lithium aluminum hydride reduction of the monotosylate 23 yielded pure *cis*-alcohol 6a.<sup>16</sup> Walden inversion of the *cis*-tosylate 24 with tetraethylammonium acetate gave the *trans*-acetate 25

(8) A. C. Cope, E. Ciganek, and J. Lazar, *J. Am. Chem. Soc.*, **84**, 2591 (1962).

(9) M. E. Kuehne, *ibid.*, **81**, 5400 (1959).

(10) G. Stork, R. Terrell, and J. Szmuszkovicz, *ibid.*, **76**, 2029 (1954).

(11) N. J. Leonard and Z. W. Wicks, *ibid.*, **68**, 2402 (1946).

(12) G. Stork and H. J. Landesman, *ibid.*, **78**, 5130 (1956); H. K. Landesman, Ph.D. Thesis, Columbia University, 1956.

(13) A. C. Cope and M. J. Youngquist, *J. Am. Chem. Soc.*, **84**, 2411 (1962).

(14) C. D. Gutsche and T. D. Smith, *ibid.*, **82**, 4067 (1960).

(15) G. Opitz and H. Mildnerberger, *Ann.*, **650**, 115 (1961).

(16) Similar stereospecific transformations in the cyclohexane series have been reported by D. S. Noyce and D. B. Denney, *J. Am. Chem. Soc.*, **74**, 5913 (1952), and H. L. Goering and C. Serres, Jr., *ibid.*, **74**, 5908 (1952).

which was reduced to the *trans*-alcohol **6b** with lithium aluminum hydride.

It appeared that the hydroboration-oxidation procedure of Brown and Zweifel<sup>17</sup> applied to 1-methylcyclooctene would provide a convenient stereospecific synthesis of *trans*-2-methylcyclooctanol. However, analysis of the product by gas chromatography revealed a mixture of alcohols which on oxidation by chromium trioxide-pyridine yielded a mixture of equal amounts of 2-methylcyclooctanone and 3-methylcyclooctanone.<sup>18</sup>

Assignment of configuration to the 2-methylcyclooctanols was based on three considerations. First, catalytic hydrogenation of 2-methylcyclooctanone in acidic medium afforded largely one alcohol which was purified by recrystallization of its hydrogen phthalate. Since such hydrogenations lead to a preponderance of the less stable (thermodynamically) epimer,<sup>19</sup> this alcohol was assigned the *cis* configuration **7a**. The *trans* isomer **7b** was obtained from **7a** by the Walden inversion procedure described for *trans*-4-methylcyclooctanol. The infrared spectra of **7a** and **7b** were significantly different in the fingerprint region.

Second, the methylcyclooctanol isolated from the reaction of dimethylmagnesium with *cis*-cyclooctene oxide was identical with 2-methylcyclooctanol (**7b**). The *trans* diaxial opening of epoxides by dimethylmagnesium and other nucleophilic reagents is well known and normally gives the *trans* isomer.<sup>20a-d</sup> Unexpectedly, however, treatment of *trans*-cyclooctene oxide with dimethylmagnesium also gave *trans*-2-methylcyclooctanol; none of the *cis* isomer was detected. Recovery of only unchanged *trans*-oxide (no *cis*) when the reaction was interrupted before completion precluded isomerization of *trans*- to *cis*-oxide under the reaction conditions. The anomaly may be rationalized in terms of the strain in the *trans*-oxide which by polarization of a C-O bond can impart a partial carbonium ion character to the carbon atom involved and cause the reaction to proceed with retention of configuration. Retention of configuration in acid-catalyzed ring opening of a number of oxides has been observed.<sup>21</sup>

These assignments of configuration to the 2-methylcyclooctanols were substantiated by a third observation. The epoxidation of 3-methylcyclooctene gave a single isomer, believed to be *trans*-3-methyl-1,2-epoxycyclooctane on the basis of approach of the oxidizing species from the least hindered side of the olefin.<sup>19b, 22</sup> Lithium aluminum hydride reduction of this epoxide gave two alcohols: a 2-methylcyclooctanol identical with the one previously assigned the *trans* configuration (**7b**) and a C<sub>9</sub>-alcohol with the same retention time as one of the isomers from the reduction of 3-methylcyclooctanone. This isomer therefore is believed to have the *trans* configuration. The absence of the other 3-methyl-

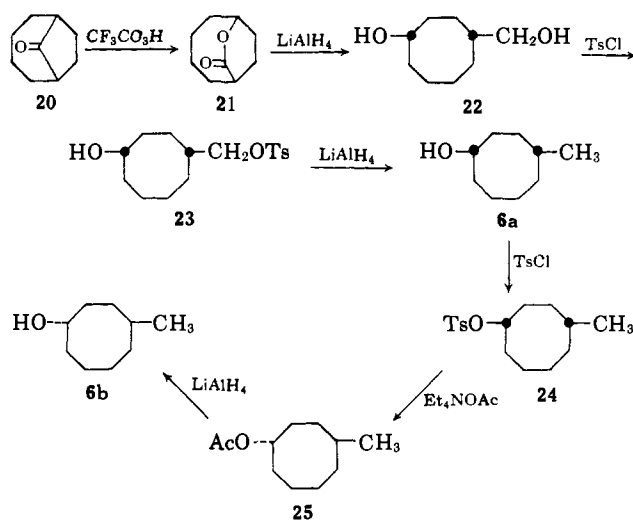


Figure 1.

cyclooctanol was interpreted as evidence for the homogeneity of the starting epoxide.

Attempts to relate the configurations of the 2-methyl- and 3-methylcyclooctanols to the 4-methylcyclooctanols (**6a** and **6b**) by catalytic hydrogenation of the bicyclo[6.1.0]nonan-2-ols and bicyclo[6.1.0]nonan-3-ols were unsuccessful. It was not possible to separate the *endo* and *exo* isomers, and moreover the bicyclic alcohols strongly resisted hydrogenation. Another approach, involving lithium aluminum hydride reduction of epoxides of the various methylcyclooctenes, was abandoned due to the inaccessibility of 4-methylcyclooctene and to uncertainty regarding the separability of the various isomeric oxides.

### Experimental<sup>23</sup>

***cis*-Bicyclo[6.1.0]nonane (1).**—A mixture of 201 g. of methylene iodide, 0.3 g. of iodine, 65.4 g. of freshly prepared zinc-copper couple,<sup>4b</sup> and 400 ml. of anhydrous ether was heated under reflux for 30 min. External heating was then discontinued and 49.0 g. of *cis*-cyclooctene in 25 ml. of dry ether was added at a rate sufficient to maintain refluxing. After addition was complete, the mixture was heated under reflux for 4 days. The solution was cooled, filtered, and washed successively with 3% hydrochloric acid, 10% sodium bicarbonate solution, and saturated sodium chloride solution. After drying (magnesium sulfate), the solvent was removed and the product was distilled through a 122-cm. Poddelniak column affording 32.8 g. (60%) of *cis*-bicyclo[6.1.0]nonane, shown to be 97% pure by gas chromatography (silicone oil, 165°). Distillation through a 46-cm. spinning-band column afforded 100% pure *cis*-bicyclo[6.1.0]nonane as shown by gas chromatography (silicone oil, 165°; MNPN, 30°, and SNTG, 65°), *n*<sub>D</sub><sup>25</sup> 1.4668, b.p. 89° (66 mm.) (lit.<sup>24</sup> b.p. 43° at 8 mm., *n*<sub>D</sub><sup>25</sup> 1.4622).

*Anal.* Calcd. for C<sub>9</sub>H<sub>16</sub>: C, 87.02; H, 12.98. Found: C, 87.01; H, 13.09.

**Reaction of *cis*-Bicyclo[6.1.0]nonane (1) and Formic Acid.**—In a typical experiment, a mixture of 1.889 g. of **1** and 8.813 g. of 98–100% formic acid was stirred at room temperature for 7 days. The reaction was followed by gas chromatography and was about 80% complete at the end of the third day. The mixture was diluted with 10 ml. of water and added with stirring and cooling to a cold solution of 25 g. of sodium hydroxide in 60 ml. of water. Stirring at room temperature was continued for 36 hr. The solution was then extracted five times with ether. The combined ether extracts were washed with water and dried over magnesium sulfate. Distillation in a short-path still at 12 mm. afforded 1.918 g. (91.7%) of a colorless liquid which was shown by gas chromatography (silicone oil, 150°) to consist of a mixture of olefins (23%) and alcohols (77%).

(23) Melting points are corrected and boiling points are uncorrected. Analyses were performed by Dr. S. M. Nagy and his associates. The equipment used for gas chromatography is described by A. C. Cope and P. E. Peterson, *J. Am. Chem. Soc.*, **81**, 1643 (1959). Stationary phases employed were 4-methyl-4-nitropimelonitrile (MNPN), silver nitrate-tetraethylene glycol (SNTG), Dow-Corning silicone oil No. 550, silicone grease, and 1,2,3-tris(2-cyanoethoxy)propane (TCEP).

(24) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **83**, 3159 (1961).

(17) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **81**, 247 (1959).

(18) After these experiments were completed, a report of similar anomalous results from the hydroboration-oxidation of 1-methylcyclooctene appeared (H. C. Brown and G. Zweifel, *ibid.*, **83**, 2544 (1961)), but no products were identified. The results were attributed to isomerization of the intermediate methylcyclooctylorganoborane.

(19) (a) W. Klyne, "Progress in Stereochemistry," Academic Press, Inc., New York, N. Y., 1954, p. 74; (b) A. C. Cope and R. W. Gleason, *J. Am. Chem. Soc.*, **84**, 1928 (1962); (c) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 243.

(20) (a) P. D. Bartlett and C. M. Berry, *J. Am. Chem. Soc.*, **56**, 2683 (1934); (b) A. Fürst and P. A. Plattner, *Helv. Chim. Acta*, **32**, 295 (1949); (c) B. G. Christensen, R. G. Strachan, N. R. Treuner, B. H. Arison, R. Hirschmann, and J. M. Chemerda, *J. Am. Chem. Soc.*, **82**, 3995 (1960); (d) A. C. Cope, H. H. Lee, and H. E. Petree, *ibid.*, **80**, 2849 (1958).

(21) (a) J. H. Brewster, *ibid.*, **78**, 4061 (1956); (b) J. H. Brewster and J. T. Rudesill, 135th National Meeting of the American Chemical Society, San Francisco, Calif., April 13–18, 1958, Abstracts of Papers, p. 8N.

(22) Reference 19c, p. 293.

A portion of this mixture (1.763 g.) was separated by chromatography on Woelm activity IV alumina into olefins (0.388 g., eluted with pentane) and alcohols (1.354 g., eluted with 0.5–0.6% ether in pentane) which were treated as described below.

**Identification of Olefins.**—The olefin fraction (124 mg.) on hydrogenation in the presence of 250 mg. of 10% palladium-on-Norit in 5 ml. of glacial acetic acid at atmospheric pressure and room temperature absorbed 101% of 1 molar equivalent of hydrogen. Ether (50 ml.) was added; the solution was filtered and washed with saturated sodium carbonate solution. After drying (magnesium sulfate) and removal of ether, distillation in a short-path still at 65 mm. and 130° (bath temperature) afforded 77 mg. (62%) of a colorless liquid,  $n_D^{25}$  1.4518, which was shown to be homogeneous by gas chromatography (MNPN, 65°). It was identified as methylcyclooctene by comparison of its infrared spectrum with that of an authentic sample ( $n_D^{25}$  1.4519).<sup>5</sup>

Gas chromatography of the olefin fraction (MNPN, 60°) showed the presence of 3-methylcyclooctene (<0.1%), 5-methylcyclooctene (1.7%), and a mixture of 1-methylcyclooctene (7.9%) and 4-methylcyclooctene (90.3%) which was separated into individual components on a SNTG column (55°). The methylcyclooctenes were identified by comparison of retention times and infrared spectra with authentic samples.

**Identification of Ketones from Oxidation of the Alcohols.**—The alcohols (60 mg.) were oxidized with 216 mg. of chromium trioxide in 2 ml. of pyridine.<sup>25</sup> The mixture was poured into 20 ml. of ice-water and extracted with four portions of ether. The combined ether extracts were washed successively with water, cold 6 N hydrochloric acid, 5% sodium bicarbonate solution, and again with water. Gas chromatography of the products (50 mg., 84%) showed the presence of 2-methylcyclooctanone (3.2%), 3-methylcyclooctanone (0.8%), and 4-methylcyclooctanone (96.0%), identified by comparison of their infrared spectra with those of authentic samples. 4-Methylcyclooctanone was further characterized by a semicarbazone (m.p. 159.6–160.2°) and a 2,4-dinitrophenylhydrazone (m.p. 125.0–126.8°). Neither derivative depressed the melting point of the respective authentic sample and the infrared spectra of the two pairs were superimposable.

**Identification of Alcohols.**—Gas chromatography (TCEP, 145°) of the alcohol fraction showed three peaks (in order of increasing retention time): a component (0.3%) with a retention time identical with that of  $\alpha$ -methylcycloheptanemethanol,<sup>26</sup> *cis*-2-methylcyclooctanol (**7a**, 3.3%), and an unresolved mixture of *cis*-4-methylcyclooctanol (**6a**, 95.6%) and 3-methylcyclooctanol (**8**, 0.8%), determined by the oxidation described previously). The alcohols **7a** and **6a** (contaminated by 0.8% of **8**) were isolated by gas chromatography and identified by infrared spectra. An acid phthalate prepared from a sample of this *cis*-4-methylcyclooctanol (recollected through a silicone grease column at 150°) had m.p. 116.6–117.6° after recrystallization from petroleum ether–methylene chloride. Its identity with an authentic sample was shown by mixture melting point and infrared comparison.

**2-Methylcyclooctanone (9)** was prepared in 86% yield by the method published<sup>8</sup> and had b.p. 97–98° (18 mm.),  $n_D^{25}$  1.4654–1.4657 (lit.<sup>8</sup> b.p. 86° at 12 mm.,  $n_D^{25}$  1.4656). Analysis by gas chromatography (TCEP, 135°) showed >99.5% purity. The semicarbazone had m.p. 139.1–140.4° (lit. m.p. 127–128°,<sup>27</sup> m.p. 134–135°<sup>28</sup>).

*Anal.* Calcd. for C<sub>10</sub>H<sub>18</sub>N<sub>3</sub>O: C, 60.87; H, 9.71; N, 21.30. Found: C, 60.80; H, 9.76; N, 21.40.

The 2,4-dinitrophenylhydrazone had m.p. 141.4–142.8° after recrystallization from 95% ethanol.

*Anal.* Calcd. for C<sub>15</sub>H<sub>20</sub>N<sub>4</sub>O<sub>4</sub>: C, 56.24; H, 6.29; N, 17.49. Found: C, 56.17; H, 6.06; N, 17.75.

**3-Methylcyclooctanone (10).**—To a solution of methylmagnesium iodide prepared from 0.8 g. of magnesium turnings in 30 ml. of dry ether and 5.3 g. of methyl iodide in 20 ml. of dry ether under nitrogen was added 45 mg. of cuprous chloride. The solution was cooled to 5° and a solution of 3.34 g. of 2-cycloocten-1-one<sup>28</sup> (98% pure) in 15 ml. of dry ether was added. Internal temperature was maintained at 5–8° during the addition, and stirring was continued overnight at room temperature. The mixture was poured into 50 g. of ice and cold 30% sulfuric acid was added (just enough to dissolve the hydroxide). The ether layer was separated and the aqueous layer was extracted twice with ether. The combined ether layers were washed with 10% sodium thiosulfate solution, dried over magnesium sulfate, and distilled through a semimicro column, affording 2.99 g. (79%) of 3-methylcyclooctanone, b.p. 93–94.5° (11 mm.), 97% pure by gas chromatographic analysis (TCEP, 128°). The ketone was purified by chromatography on alumina (Merck, Special, eluted

with 5% ether in pentane) and distilled at 87.5–88° (13 mm.),  $n_D^{25}$  1.4648, 2.40 g. (81% recovery). Gas chromatography showed that it was homogeneous.

*Anal.* Calcd. for C<sub>9</sub>H<sub>16</sub>O: C, 77.09; H, 11.50. Found: C, 77.09; H, 11.49.

The 2,4-dinitrophenylhydrazone had m.p. 148.0–149.2° dec. after recrystallization from aqueous ethanol.

*Anal.* Calcd. for C<sub>15</sub>H<sub>20</sub>N<sub>4</sub>O<sub>4</sub>: C, 56.24; H, 6.29; N, 17.49. Found: C, 56.04; H, 6.28; N, 17.47.

The semicarbazone was recrystallized from aqueous ethanol to a constant m.p. of 188.4–189.2°.<sup>29</sup>

*Anal.* Calcd. for C<sub>10</sub>H<sub>18</sub>N<sub>3</sub>O: C, 60.87; H, 9.71; N, 21.30. Found: C, 60.96; H, 9.71; N, 21.26.

**4-Methylenecyclooctanone (13).**—To 14.6 g. of methyltriphenylphosphonium bromide in 200 ml. of dry ether was added 28 ml. of a 1.42 M *n*-butyllithium solution in ether. The mixture was stirred under nitrogen for 3 hr. and then cooled in ice while 5.5 g. of 1,4-cyclooctanedione<sup>30</sup> in 50 ml. of dry ether was added during 5 min. Stirring was continued for an additional half-hour and the mixture was allowed to stand at room temperature overnight. Additional dry ether was added and the mixture was heated for 2 hr. at 65–67°. The solution was cooled and filtered and the solid was washed with ether and dissolved in 250 ml. of water. The aqueous solution was extracted three times with ether, and the combined ether solutions were dried (magnesium sulfate) and distilled under reduced pressure. A colorless liquid, 1.935 g., b.p. 103–115° (18 mm.), was obtained and was separated into three fractions by gas chromatography (TCEP, 136°). The first fraction, 146 mg., was a mixture of olefins that was not further investigated. The second, 678 mg. (11%), was homogeneous and consisted of the desired 4-methylenecyclooctanone. The third, 728 mg. (15%), was also homogeneous and was identified as bicyclo[3.3.0]-1(5)-octen-2-one by comparison of its infrared spectrum with that of an authentic sample.<sup>31</sup>

The nuclear magnetic resonance spectrum of 4-methylenecyclooctanone recollected by gas chromatography (silicone grease, 190°),  $n_D^{25}$  1.4844, showed the presence of two vinyl protons at 5.10 and 5.23  $\tau$  and twelve methylene protons between 7.56 and 8.66  $\tau$ .

*Anal.* Calcd. for C<sub>9</sub>H<sub>14</sub>O: C, 78.21; H, 10.21. Found: C, 78.39; H, 10.30.

Use of phenyllithium instead of *n*-butyllithium and addition of 1,4-cyclooctanedione at room temperature instead of at ice-bath temperature increased the yield of products (a 55:45 mixture of 4-methylenecyclooctanone and bicyclo[3.3.0]-1(5)-octen-2-one plus traces of olefins) to 72.5%.

**4-Methylcyclooctanone (11).**—4-Methylenecyclooctanone (**13**, 335 mg.) was hydrogenated at atmospheric pressure in the presence of 10% palladium-on-Norit (125 mg.) in 5 ml. of methanol, and absorbed 99% of the theoretical amount for one double bond. The suspension was filtered and the solvent was removed. The product after collection by gas chromatography (silicone oil, 190°) weighed 247 mg. (74%),  $n_D^{25}$  1.4659. Its homogeneity was demonstrated by gas chromatography on a TCEP column at 110°.

*Anal.* Calcd. for C<sub>9</sub>H<sub>16</sub>O: C, 77.09; H, 11.50. Found: C, 77.21; H, 11.74.

The semicarbazone had m.p. 159.7–160.4°<sup>29</sup> after recrystallization from aqueous ethanol.

*Anal.* Calcd. for C<sub>10</sub>H<sub>18</sub>N<sub>3</sub>O: C, 60.87; H, 9.71; N, 21.30. Found: C, 61.10; H, 9.52; N, 21.42.

The 2,4-dinitrophenylhydrazone had m.p. 127.2–128.4° after recrystallization from aqueous ethanol.

*Anal.* Calcd. for C<sub>15</sub>H<sub>20</sub>N<sub>4</sub>O<sub>4</sub>: C, 56.24; H, 6.29; N, 17.49. Found: C, 56.05; H, 6.14; N, 17.81.

**1,5-Dibromo-3-methylpentane (15) from 3-Methylpentane-1,5-diol.**—To 150 g. of 3-methylpentane-1,5-diol (Aldrich Chemical Co.) stirred and cooled to –5° was added 425 g. of phosphorus tribromide at a rate such that the internal temperature did not rise above 5°. The addition required about 4 hr. The solution was allowed to come to room temperature and stirring was continued overnight. It was then heated on a steam bath for 1.5 hr., cooled, and poured with shaking onto 800 g. of ice. The organic layer was washed with concentrated sulfuric acid, water, sodium carbonate solution, and again with water, and dried over magnesium sulfate. Distillation afforded 246 g. (80%) of colorless dibromide, b.p. 100.5–101° (10 mm.),  $n_D^{25}$  1.5055 (lit.<sup>10</sup> b.p. 97–98.5° at 10 mm.,  $n_D^{25}$  1.5073).

(29) The semicarbazone of the product (presumably a mixture of 3-methyl- and 4-methylcyclooctanones) of the reaction of 3-methylcycloheptanone and diazomethane had m.p. 165–166° (M. Mousseron and G. Manon, *Bull. soc. chim. France*, 392 (1949)).

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(31) A. C. Cope and W. R. Schmitz, *ibid.*, **72**, 3056 (1950).

(25) G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Am. Chem. Soc.*, **75**, 422 (1953).

(26) A. C. Cope and J. K. Hecht, *ibid.*, **85**, 1780 (1963).

(27) M. Godehot and G. Cauquil, *Compt. rend.*, **192**, 962 (1931).

(28) A. C. Cope, M. R. Kinter, and R. T. Keller, *J. Am. Chem. Soc.*, **76**, 2757 (1954).

**5-Methylnonanedinitrile (16).**—A suspension of 0.37 mole of sodium amide in 300 ml. of ether was prepared by the method of Cope and Hancock.<sup>32</sup> It was added in small portions during about 20 min. to a gently boiling stirred solution of 43.5 g. of the dibromide and 31 g. of redistilled acetonitrile in 100 ml. of anhydrous ether. Heating and stirring were continued until evolution of ammonia ceased. The sodium bromide was removed by filtration and the solvent and excess acetonitrile were removed by distillation. A mixture of products was distilled without fractionation, b.p. 49–148° (1.4–0.8 mm.). Redistillation through a spinning-band column yielded 5.58 g. (26.5%) of 4-methylcyclohexanecarbonitrile, b.p. 89–90.5° (18.5 mm.),  $n_D^{25}$  1.4451–1.4448 (lit.<sup>33</sup> b.p. 85–87° at 18 mm.,  $n_D^{25}$  1.448), and 4.68 g. (16%) of 5-methylnonanedinitrile, b.p. 115° (0.125 mm.),  $n_D^{25}$  1.4483–1.4496. The main fraction,  $n_D^{25}$  1.4483, was shown to be homogeneous by gas chromatography (silicone grease, 230°).

*Anal.* Calcd. for  $C_{10}H_{18}N_2$ : C, 73.12; H, 9.82; N, 17.06. Found: C, 73.10; H, 10.00; N, 17.19.

Modification of this procedure by adding acetonitrile to sodium amide in liquid ammonia as solvent followed by addition of the dibromide increased the yield of 5-methylnonanedinitrile to 27%, b.p. 152–153.5° (1.5–1.6 mm.),  $n_D^{25}$  1.4486–1.4484.

**Intramolecular Cyclization of 5-Methylnonanedinitrile.**—A solution of *n*-butyllithium prepared from 8.6 g. of lithium wire and 68.5 g. of *n*-butyl bromide in 200 ml. of dry ether was filtered into a flask containing 1000 ml. of dry ether and equipped with a high dilution apparatus.<sup>34</sup> While the solution was stirred mechanically under a nitrogen atmosphere and cooled externally, 93 g. of redistilled *N*-ethylaniline was added dropwise. The resulting lithium *N*-ethylanilide solution was heated under reflux for 1 hr. and then a solution of 35 g. of 5-methylnonanedinitrile in 750 ml. of dry ether was added through the high dilution apparatus at a rate of 1–2 drops per sec. at the reflux temperature. Complete addition required about 36 hr. Heating was continued for 45 min. longer; then the solution was cooled and decomposed with 500 ml. of water. The layers were separated and the aqueous layer was extracted with 500 ml. of ether. The combined ether extracts were shaken with 600 g. of ice and 300 ml. of concd. hydrochloric acid for 10 min.<sup>35</sup> The organic layer was then separated and the aqueous layer was extracted with two 250-ml. portions of ether. The combined extracts were filtered through sodium sulfate, dried over magnesium sulfate, and evaporated to an oily residue of ca. 29 g. No additional material was obtained by further extraction of the acidic aqueous layer. Distillation of the products through a 46-cm. spinning-band column afforded 7.3 g. (21%) of 2-oxo-6-methylcyclooctanecarbonitrile (17), b.p. 111–114° (0.65–0.80 mm.); 4.6 g. (13.1%) of 2-amino-6-methyl-1-cyclooctene-1-carbonitrile (18), b.p. 133.5–135° (0.7 mm.); and 1.3 g. (3.7%) of a mixture of these two compounds, b.p. 114–133.5° (0.8–0.7 mm.).

The nitrile 17 was recrystallized from petroleum ether–ether to a constant m.p. of 52.8–53.4°. It is unstable in air and must be stored with refrigeration or used immediately.

*Anal.* Calcd. for  $C_{10}H_{15}NO$ : C, 72.69; H, 9.15; N, 8.48. Found: C, 72.57; H, 9.08; N, 8.65.

The nitrile 18, recrystallized twice from petroleum ether–ether, had m.p. 93.7–94.2°.

*Anal.* Calcd. for  $C_{10}H_{16}N_2$ : C, 73.12; H, 9.82; N, 17.06. Found: C, 72.82; H, 9.75; N, 17.33.

**5-Methylcyclooctanone (14).**—A solution of 4.987 g. of 17 in 40 ml. of glacial acetic acid and 10 ml. of concd. hydrochloric acid was heated under reflux at 125–130° (bath temperature) for 36 hr. It was then cooled and diluted with 150 ml. of water and extracted three times with ether. The combined ether extracts were washed with water, then with small portions of 10% sodium carbonate solution, and dried over magnesium sulfate. Distillation of the crude product through a semimicro column afforded 3.645 g. (85.5%) of 5-methylcyclooctanone, b.p. 99.5–101° (19 mm.),  $n_D^{25}$  1.4642–1.4643. The fraction with  $n_D^{25}$  1.4643 was analyzed. The hydrolysis of 18 carried out in an analogous manner afforded the same ketone.

*Anal.* Calcd. for  $C_9H_{16}O$ : C, 77.09; H, 11.50. Found: C, 76.84; H, 11.56.

The semicarbazone had m.p. 176.8–177.4° after recrystallization from aqueous ethanol.

*Anal.* Calcd. for  $C_{10}H_{16}N_3O$ : C, 60.87; H, 9.71; N, 21.30. Found: C, 60.77; H, 9.77; N, 21.48.

The 2,4-dinitrophenylhydrazone had m.p. 131.6–132.0° after recrystallization from aqueous ethanol.

(32) A. C. Cope and E. M. Hancock, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 219.

(33) V. Grignard, E. Bellet, and C. Courtot, *Ann. chim.*, [9] **12**, 372 (1919).

(34) A. C. Cope and E. C. Herrick, *J. Am. Chem. Soc.*, **72**, 985 (1950).

(35) K. Ziegler, H. Eberle, and H. Ohlinger, *Ann.*, **604**, 94 (1933).

*Anal.* Calcd. for  $C_{15}H_{20}N_4O_4$ : C, 56.24; H, 6.29; N, 17.49. Found: C, 56.07; H, 6.27; N, 17.45.

**3-Methylcyclooctene (3).**—A solution of 29 g. of 3-bromocyclooctene<sup>36</sup> in 30 ml. of dry ether was added with stirring to 100 ml. of 3 *M* methylmagnesium iodide under a nitrogen atmosphere at a rate sufficient to maintain gentle reflux. The addition required ca. 40 min. Stirring was continued overnight at room temperature. The mixture was then poured slowly onto 200 g. of ice, and solid ammonium sulfate and water were added until the precipitate dissolved. The aqueous layer was extracted twice with ether and the combined ether solutions were washed with a solution of 25 ml. of concd. ammonium hydroxide in 75 ml. of water saturated with ammonium sulfate and then dried over magnesium sulfate. Distillation of the products through a 46-cm. spinning-band column under reduced pressure afforded a small forerun (0.159 g.), and then 6.331 g. (33%) of 3-methylcyclooctene, b.p. 77–78° (56 mm.),  $n_D^{25}$  1.4622–1.4627. The olefin was shown to be homogeneous by gas chromatography (TCEP at 50° and NMPN at 40°). A sample with  $n_D^{25}$  1.4622 was analyzed.

*Anal.* Calcd. for  $C_9H_{16}$ : C, 87.02; H, 12.98. Found: C, 87.16; H, 12.83.

**Reduction of 3-Methylcyclooctanone with Lithium Aluminum Hydride.**—3-Methylcyclooctanone, 914 mg., was reduced with 300 mg. of lithium aluminum hydride in ether by a procedure similar to the one described for reduction of 4-cyclooctene-1-carboxylic acid. Distillation through a semimicro column afforded 768 mg. (83%) of alcohol, b.p. 96–96.5° (9 mm.),  $n_D^{25}$  1.4756. Gas chromatography (TCEP, 135°) revealed a 3:2 mixture of isomers.<sup>37</sup>

**Preparation and Decomposition of 3-Methylcyclooctyl-S-methyl Xanthates.**—The xanthates were prepared by a procedure similar to that of Blomquist and Goldstein.<sup>38</sup> Sodium hydride (54%, dispersed in mineral oil), 1.60 g., was washed five times with dry benzene to remove the mineral oil. Then 20 ml. of dry benzene and 528 mg. of the mixture of 3-methylcyclooctanols were added. The mixture was heated under reflux with stirring for 29 hr., then cooled to room temperature, and 6 ml. of carbon disulfide was added. Heating under reflux was resumed for another 26 hr., then 13 g. of methyl iodide was added, and the mixture was heated under reflux for 21 hr. longer. The solution was cooled and filtered. The solid was washed with ether, and the combined washings and filtrate were washed with water and dried (magnesium sulfate). The solvent was evaporated at room temperature under reduced pressure to a constant weight (832 mg.).

The xanthates were pyrolyzed in a 50-ml. flask fitted with a reflux condenser. Bubbling occurred at about 160°. The heating bath was raised to 220° for 10 min. The products were distilled at atmospheric pressure and separated into two fractions by gas chromatography (silicone grease, 166°). The first fraction, 270 mg. (61%), consisted of a mixture of two olefins which was separated by gas chromatography (NMPN, 31°). The second fraction, 54 mg., was not investigated.

The olefin with shorter retention time (37%),  $n_D^{25}$  1.4621, was identified as 3-methylcyclooctene by comparison of its infrared spectrum with that of the authentic sample synthesized previously. The second olefin (63%),  $n_D^{25}$  1.4654, was therefore 4-methylcyclooctene, and had the same retention time as the major olefin product from solvolysis of *cis*-bicyclo[6.1.0]nonane; their infrared spectra were also identical.

*Anal.* Calcd. for  $C_9H_{16}$ : C, 87.02; H, 12.98. Found: C, 87.02; H, 12.82.

**2-N-Pyrrolidylbicyclo[3.3.1]nonan-9-one Methiodide.**—To a solution of 118 g. of 2-*N*-pyrrolidylbicyclo[3.3.1]nonan-9-one<sup>12</sup> in 100 ml. of dry ether was added 250 g. of methyl iodide. The mixture stood at room temperature for 2 hr., and was then filtered. To the filtrate was added 50 g. of methyl iodide, and after 5 hr. the solid was again collected. A third crop was obtained similarly. Recrystallization of the combined crops of crude methiodide (170 g., 85%) from acetone–ethanol afforded 161 g., m.p. 220.0–221.8°. An analytical sample was recrystallized twice from acetone–petroleum ether; m.p. 217.1–217.5°.

*Anal.* Calcd. for  $C_{14}H_{24}NOI$ : C, 48.14; H, 6.93; N, 4.01; I, 36.34. Found: C, 48.26; H, 6.92; N, 4.15; I, 36.30.

**4-Cyclooctene-1-carboxylic Acid.**—Some modifications of the procedure originally described by Landesman<sup>12</sup> for the preparation of this acid improved the yield considerably. A mixture of 17 g. of 2-*N*-pyrrolidylbicyclo[3.3.1]nonan-9-one methiodide and 32 ml. of 40% aqueous potassium hydroxide was heated with stirring at 125–130° (bath temperature) for 5 hr. It was then cooled and diluted with 30 ml. of water and extracted twice with ether. The aqueous layer was acidified with concd. hydrochloric

(36) A. C. Cope and L. L. Estes, Jr., *J. Am. Chem. Soc.*, **72**, 1128 (1950).

(37) The other pairs of methylcyclooctanols (2-, 4-, and 5-) failed to separate on TCEP. None of the pairs was separable on silicone grease.

(38) A. T. Blomquist and A. Goldstein, *J. Am. Chem. Soc.*, **77**, 1001 (1955).

acid with cooling to about pH 2 and extracted five times with ether. The combined ether extracts were washed twice with 10% sodium thiosulfate solution and dried over magnesium sulfate. Distillation afforded 3.14 g. (42%) of 4-cyclooctene-1-carboxylic acid, b.p. 125–126° (1.1 mm.), which gradually solidified. It was dissolved in a minimum volume of pentane and cooled in a Dry Ice bath. The solid, m.p. 34.2–35.0°, was collected immediately by suction filtration.

*Anal.* Calcd. for  $C_9H_{14}O_2$ : C, 70.10; H, 9.15. Found: C, 70.17; H, 9.17.

The yields of several similar preparations were between 38 and 42%. Prolonging the reaction time and the use of more base had no effect on the yield.

**4-Cyclooctene-1-methanol (19).**—A solution of 7.36 g. of 4-cyclooctene-1-carboxylic acid in 50 ml. of ether was added to a stirred suspension of 1.8 g. of lithium aluminum hydride in 100 ml. of ether and stirred for 2 hr. at room temperature and then for 1 hr. at reflux. The mixture was cooled, the excess hydride was decomposed with water, and 10% hydrochloric acid was added dropwise with stirring until the hydroxides were dissolved. The layers were separated and the aqueous layer was extracted three times with ether. The combined ether solutions were washed with 5% sodium carbonate solution and dried over magnesium sulfate. Distillation afforded 4.584 g. (65%) of 4-cyclooctene-1-methanol, b.p. 126.0–127.5° (20 mm.),  $n_D^{25}$  1.4930.

*Anal.* Calcd. for  $C_9H_{16}O$ : C, 77.09; H, 11.50. Found: C, 77.37; H, 11.54.

The hydrogen phthalate, recrystallized from aqueous ethanol, had m.p. 129.5–130.5°.

*Anal.* Calcd. for  $C_{17}H_{18}O_4$ : C, 70.81; H, 6.99. Found: C, 70.49; H, 6.98.

**5-Methylcyclooctene (5).**—To a solution of 3.815 g. of *p*-toluenesulfonyl chloride in 10 ml. of dry pyridine at 0° was added 1.4 g. of 4-cyclooctene-1-methanol dissolved in 5 ml. of dry pyridine. The mixture was kept in a refrigerator (5°) for 22 hr. Water (75 ml.) was added slowly to the cooled (ice-bath) solution and the mixture was extracted twice with ether. The ether extracts were washed twice with cold 6 *N* hydrochloric acid, three times with 5% sodium carbonate solution, and once with water. The ether solution was dried (magnesium sulfate), the solvent was removed under reduced pressure, and the thick oily tosylate was washed with cold 1:10 ether–pentane. It was dissolved in 25 ml. of dry ether and added over a period of 20 min. to a stirred suspension of 1.543 g. of lithium aluminum hydride in 35 ml. of dry ether at 0°. The temperature was maintained at 0° during the addition and for 3 hr. afterward. Stirring was continued at room temperature for 16 hr., then 150 ml. of ether was added and the excess hydride was decomposed with 10 ml. of water. The precipitate was removed by filtration, the layers in the filtrate separated, and the ether layer was dried over magnesium sulfate. After removal of the ether, distillation afforded 415 mg. (33.5% based on the alcohol used) of 5-methylcyclooctene, b.p. 85–86° (69 mm.),  $n_D^{25}$  1.4618. Gas chromatography on three different columns (TCEP at 40°, silicone oil at 70°, and NMPN at 50°) showed that the compound was homogeneous.

*Anal.* Calcd. for  $C_9H_{16}$ : C, 87.02; H, 12.98. Found: C, 87.25; H, 13.15.

**Reduction of 5-Methylcyclooctanone with Lithium Aluminum Hydride.**—5-Methylcyclooctanone (1.40 g.) was reduced with 0.38 g. of lithium aluminum hydride in ether. Distillation of the crude product through a semimicro column afforded 1.29 g. (91%) of a mixture of two alcohols,<sup>39</sup> b.p. 107–108° (10 mm.),  $n_D^{25}$  1.4762.

*Anal.* Calcd. for  $C_9H_{18}O$ : C, 75.99; H, 12.76. Found: C, 75.98; H, 12.72.

**Preparation and Thermal Decomposition of 5-Methylcyclooctyl-S-methyl Xanthates.**—The xanthates were prepared from 1.60 g. of 54% sodium hydride and 560 mg. of the mixture of 5-methylcyclooctanols by the procedure described for the 3-methylcyclooctyl-S-methyl xanthates. The crude xanthates (860 mg.) were pyrolyzed as described previously. Isolation of the products by gas chromatography (silicone oil, 105°) afforded 225 mg. (49%) of 5-methylcyclooctene,  $n_D^{25}$  1.4614, and 141 mg. (25%) of the original alcohols. Identity of this 5-methylcyclooctene with the 5-methylcyclooctene prepared from 19 was demonstrated by comparison of infrared spectra and retention times. Gas chromatography on two other columns (NMPN at 30° and NTNG at 60°) showed that this olefin was homogeneous.

**Hydroboration of 1-Methylcyclooctene.**—Excess diborane, generated according to Brown's procedure<sup>17</sup> from 1.3 g. of lithium aluminum hydride in ether and 20 ml. of boron trifluoride etherate, was bubbled with a slow stream of nitrogen into a solution of 1-methylcyclooctene (953 mg.) in dry tetrahydrofuran (4 ml.) cooled in an ice-bath. Nitrogen was bubbled through the solution to remove excess diborane after the reaction was com-

plete. The ice-cooled mixture was treated with 0.4 g. of sodium hydroxide in 3 ml. of water followed by 3.5 ml. of 30% hydrogen peroxide and allowed to stand at room temperature for 30 min. The solution was extracted three times with ether and the ether extracts were dried over magnesium sulfate. Distillation afforded 795 mg. (73%) of an alcohol (b.p. 104–106° at 16 mm.) that was shown to be a mixture by gas chromatography (TCEP, 131°). Oxidation of this mixture with chromium trioxide in pyridine by the procedure described previously afforded a mixture of equal amounts of two ketones, separated by gas chromatography (TCEP, 113°) and identified as 2-methylcyclooctanone and 3-methylcyclooctanone by a comparison of infrared spectra and retention times with those of authentic samples and by mixture melting points and infrared comparisons with authentic semicarbazones.

**Bicyclo[4.2.1]nonan-9-one (20).**—The reaction of 48 g. of cyclopentanone and 171 g. of crude *N,N'*-dicarbethoxy-*N,N'*-dinitroso-1,4-butanediamine<sup>40</sup> was carried out according to the procedure of Gutsche and Smith.<sup>14</sup> Distillation of the products through a 46-cm. spinning-band column afforded two fractions of the desired ketone. The first fraction, b.p. 140–144° (85 mm.), 3.12 g. of semi-solid, was found by gas chromatography (silicone grease, 165°) to be 93% pure. The second fraction, b.p. 144–145° (85 mm.), 6.14 g., was 98% pure. A portion collected by gas chromatography had m.p. 105.0–107.2° (lit.<sup>14</sup> m.p. 109–111°), and its infrared spectrum confirmed the presence of a cyclopentanone structure (1737  $cm^{-1}$ ). The 2,4-dinitrophenylhydrazine had m.p. 157.8–158.5° (lit. m.p. 159–160°<sup>14</sup> and 157–158°<sup>15</sup>).

**Lactone of *cis*-4-Hydroxycyclooctanecarboxylic Acid (21).**—The Baeyer–Villiger oxidation of bicyclo[4.2.1]nonan-9-one was carried out according to the procedure described by Emmons and Lucas<sup>41</sup> for methyl isobutyl ketone. The crude product (2.83 g.) obtained from 2.88 g. of ketone 20 (98% pure) was recrystallized from pentane, yielding 2.15 g. (67%) of lactone 21, m.p. 118.8–120.0°. Two recrystallizations from hexane afforded the analytical sample, m.p. 122.2–123.8°.

*Anal.* Calcd. for  $C_9H_{14}O_2$ : C, 70.10; H, 9.15. Found: C, 69.82; H, 9.03.

***cis*-4-Hydroxycyclooctanecarboxylic Acid.**—Lactone 21 (120 mg.) in a solution of sodium hydroxide (387 mg.) in 2 ml. of methanol and 3 ml. of water was heated on a steam-bath for 1 hr. The mixture, cooled in ice, was acidified to pH 2 with 6 *N* hydrochloric acid, and the hydroxy acid was extracted into methylene chloride (two 15-ml. portions). The combined extracts were dried over magnesium sulfate. The crude product, crystallized from acetonitrile (charcoal), m.p. 88.9–90.6°, weighed 68 mg. (51%). An analytical sample had m.p. 89.5–90.4°.

*Anal.* Calcd. for  $C_9H_{16}O_3$ : C, 62.76; H, 9.36. Found: C, 62.71; H, 9.61.

***cis*-4-Hydroxycyclooctanemethanol (22).**—A solution of 1.02 g. of 21 in 15 ml. of ether was added to a stirred suspension of 0.38 g. of lithium aluminum hydride in 30 ml. of ether. After addition was complete, the mixture was stirred overnight and then heated under reflux for 3 hr. The cooled mixture was decomposed with 20 ml. of nearly saturated ammonium chloride solution and 15 ml. of water (cold hydrochloric acid was added dropwise to break up emulsions). The aqueous layer was extracted twice with methylene chloride, and the ether layer and methylene chloride extracts were washed separately with 5% sodium bicarbonate solution and dried over magnesium sulfate. *cis*-4-Hydroxycyclooctanemethanol (761 mg.) was obtained as a viscous oil (76%). The bis-*p*-nitrobenzoate had m.p. 115.6–116.6° after recrystallization from ethanol–ethyl acetate.

*Anal.* Calcd. for  $C_{23}H_{24}O_8N_2$ : C, 60.52; H, 5.30; N, 6.14. Found: C, 60.31; H, 5.18; N, 6.37.

***cis*-4-Methylcyclooctanol (6a).**—A solution of 377 mg. of *p*-toluenesulfonyl chloride in 2 ml. of dry pyridine was added to a solution of 305 mg. of glycol 22 in 5 ml. of dry pyridine at 0°. The mixture was allowed to stand at 0° for 30 min. and at 3–5° overnight, then was poured into a mixture of 30 ml. of cold 6 *N* hydrochloric acid and 10 g. of ice. The mixture was extracted twice with methylene chloride, and the combined extracts were washed with water, dried over magnesium sulfate, and evaporated to a residue of 425 mg.

A solution of 425 mg. of this crude monotosylate in 5 ml. of ether was added to a stirred solution of 230 mg. of lithium aluminum hydride in 10 ml. of ether. The mixture was stirred at room temperature overnight and then heated under reflux for 1 hr. Water, 25 ml. of cold 10% hydrochloric acid, and 50 ml. of ether were added. The aqueous layer was extracted with ether and the combined extracts were washed with 5% sodium carbonate solution and dried over magnesium sulfate. The crude product (177 mg.) was purified by gas chromatography (silicone grease, 170°) yielding 102 mg. (53%) of 6a,  $n_D^{25}$  1.4784, shown to be homogeneous on a TCEP column (140°).

(40) C. M. Samour and J. P. Mason, *ibid.*, **76**, 441 (1954).

(41) W. D. Emmons and G. B. Lucas, *ibid.*, **77**, 2287 (1955).

(39) A. C. Cope and D. M. Gale, *J. Am. Chem. Soc.*, to be published.



*Anal.* Calcd. for  $C_9H_{18}O$ : C, 76.00; H, 12.75. Found: C, 76.18; H, 12.81.

The hydrogen phthalate, recrystallized from methylene chloride-petroleum ether, had m.p. 116.0–117.2°.

*Anal.* Calcd. for  $C_{17}H_{22}O_4$ : C, 70.32; H, 7.64. Found: C, 70.53; H, 7.70.

**trans-4-Methylcyclooctanol (6b).**—The oily tosylate (24) of *cis*-4-methylcyclooctanol (404 mg., obtained from 300 mg. of **6a** by the procedure described previously) was treated with 4.13 g. of tetraethylammonium acetate<sup>42</sup> in 20 ml. of dry acetone under reflux for 48 hr. The acetone was distilled and 15 ml. of water and 50 ml. of ether were added to the cooled residue. The ether extract was washed with saturated sodium bicarbonate solution and dried over magnesium sulfate. *trans*-4-Methylcyclooctyl acetate (25) was isolated by gas chromatography (silicone grease, 143°) in 25% over-all yield (98 mg.),  $n_D^{25}$  1.4551.

*Anal.* Calcd. for  $C_{11}H_{20}O_2$ : C, 71.69; H, 10.94. Found: C, 71.58; H, 11.07.

Reduction of **25** (91 mg.) with 110 mg. of lithium aluminum hydride in 10 ml. of refluxing ether afforded 49 mg. (70%) of **6b**,  $n_D^{25}$  1.4756, isolated by gas chromatography (silicone grease, 143°).

*Anal.* Calcd. for  $C_9H_{18}O$ : C, 76.00; H, 12.75. Found: C, 76.13; H, 12.62.

The acid phthalate had m.p. 132.4–133.2° after recrystallization from ether-petroleum ether.

*Anal.* Calcd. for  $C_{17}H_{22}O_4$ : C, 70.32; H, 7.64. Found: C, 70.07; H, 7.52.

**cis-2-Methylcyclooctanol (7a).**—A solution of 14.2 g. of **9** in 50 ml. of glacial acetic acid containing 2.2 g. of hydrogen chloride gas was hydrogenated in the presence of 1.45 g. of pre-reduced platinum oxide. Hydrogen uptake was about 120%. The filtered solution was poured into 200 ml. of ice-water and extracted three times with pentane. The pentane extracts were washed three times with saturated sodium bicarbonate solution and dried over magnesium sulfate. The product, 16.31 g., showed one peak on gas chromatography (TCEP, 142° and silicone grease, 140°). Treatment of this material (16.0 g.) with 3.5 g. of lithium aluminum hydride in 200 ml. of refluxing ether for 2 hr. afforded 10.1 g. (82%) of an alcohol, b.p. 83.5–86° (3 mm.),  $n_D^{25}$  1.4796–1.4801. An acid phthalate prepared in 88% yield from 9.39 g. of the alcohol had m.p. 123.0–124.5°. Four recrystallizations from hexane-ether afforded analytically pure material in 47.5% yield (9.0 g.), m.p. 126.0–127.1°.<sup>43</sup>

*Anal.* Calcd. for  $C_{17}H_{22}O_4$ : C, 70.32; H, 7.64. Found: C, 70.20; H, 7.75.

The analytically pure phthalate (5.8 g.) was heated under reflux overnight with 8 g. of sodium hydroxide in 25 ml. of water. The product was extracted with ether, dried, and distilled, affording 2.42 g. (85%) of **7a**,  $n_D^{25}$  1.4809.

*Anal.* Calcd. for  $C_9H_{18}O$ : C, 75.99; H, 12.76. Found: C, 75.83; H, 12.80.

*cis*-2-Methylcyclooctyl acetate, isolated in 75% yield by gas chromatography (silicone grease, 143°), had  $n_D^{25}$  1.4560.

*Anal.* Calcd. for  $C_{11}H_{20}O_2$ : C, 71.69; H, 10.94. Found: C, 71.48; H, 10.93.

**trans-2-Methylcyclooctanol (7b).**—Treatment of the tosylate prepared from 1.25 g. of **7a** with tetraethylammonium acetate as described previously yielded 833 mg. of crude *trans*-2-methylcyclooctyl acetate. A portion (100 mg.) was purified by gas chromatography (silicone grease, 138°),  $n_D^{25}$  1.4559.

*Anal.* Calcd. for  $C_{11}H_{20}O_2$ : C, 71.69; H, 10.94. Found: C, 71.81; H, 10.95.

Reduction of 733 mg. of the crude acetate with 0.50 g. of lithium aluminum hydride in 25 ml. of ether afforded 490 mg., separated by gas chromatography (silicone grease, 140°) into an olefin fraction (147 mg.) and *trans*-2-methylcyclooctanol (250 mg., over-all yield 23%),  $n_D^{25}$  1.4792.

*Anal.* Calcd. for  $C_9H_{18}O$ : C, 76.00; H, 12.75. Found: C, 76.06; H, 12.75.

The olefins, separated by gas chromatography (SNTG, 60°), consisted of 1-methylcyclooctene (80%) and 3-methylcyclooctene (20%).

The acid phthalate of **7b** had m.p. 119.4–120.6°<sup>43</sup> after recrystallization from ether-petroleum ether.

*Anal.* Calcd. for  $C_{17}H_{22}O_4$ : C, 70.32; H, 7.64. Found: C, 70.48; H, 7.84.

(42) J. Steigman and L. P. Hammett, *J. Am. Chem. Soc.*, **59**, 2536 (1937); A. C. Cope and A. Fournier, Jr., *ibid.*, **79**, 3896 (1957).

(43) Two acid phthalates of 2-methylcyclooctanols of undetermined stereochemistry have been reported: m.p. 104° and m.p. 119–120° [M. Godchet and M. Cauquil, *Chimie et Industrie*, Special No., 1019 (1933)]. The purity of these is questionable, since methylation of cyclooctanone by Godchet's procedure<sup>27</sup> is now known to give a mixture of ketones.<sup>8</sup>

**trans-3-Methyl-1,2-epoxycyclooctane.**—A mixture of 1.65 ml. of 40% commercial peracetic acid and 0.332 g. of sodium acetate trihydrate was added to 0.814 g. of 3-methylcyclooctene with vigorous swirling for about 10 min. The mixture was cooled to 0° and neutralized with 40% sodium hydroxide solution. The product was extracted with ether, washed with water, dried, and distilled. Gas chromatographic analysis (TCEP, 140°, and silicone grease, 140°) of the epoxide so obtained (0.756 g., 82%) showed that it was ca. 99% pure. An analytical sample,  $n_D^{25}$  1.4618, was collected by gas chromatography.

*Anal.* Calcd. for  $C_9H_{16}O$ : C, 77.09; H, 11.50. Found: C, 77.01; H, 11.58.

**Lithium Aluminum Hydride Reduction of trans-3-Methyl-1,2-epoxycyclooctane.**—The *trans*-epoxide (120 mg.) was treated with 135 mg. of lithium aluminum hydride in 3 ml. of refluxing ether for 4 hr. The mixture was cooled and decomposed with 5 ml. of water after 35 ml. of ether was added. The layers were separated, the aqueous layer was extracted with ether and the ether extracts were dried (magnesium sulfate). The mixture of products (110 mg.), separated by gas chromatography (TCEP at 120 and 134°), consisted of the following (in order of increasing retention time): unchanged epoxide (10%), *trans*-2-methylcyclooctanol (30%), and a third component (60%) with a retention time identical with one of the 3-methylcyclooctanols obtained from **10**. Comparison of infrared spectra showed that the 2-methylcyclooctanol isolated here is identical with that obtained by Walden inversion of **7a**. The third alcohol, presumably *trans*-3-methylcyclooctanol,  $n_D^{25}$  1.4767, was analyzed.

*Anal.* Calcd. for  $C_9H_{18}O$ : C, 76.00; H, 12.75. Found: C, 75.86; H, 12.87.

**Reaction of cis-Cyclooctene Oxide with Dimethylmagnesium.**—*cis*-Cyclooctene oxide<sup>44</sup> (230 mg.) was added to 250 ml. of a filtered dimethylmagnesium solution.<sup>45</sup> The solution was slowly distilled under nitrogen until nearly all solvent had been removed. The heating bath was maintained at  $150 \pm 5^\circ$  for 20 hr. (air-condenser). The mixture was cooled, diluted with 100 ml. of ether, and decomposed with 25 ml. of water. The ether layer was washed seven times with water and dried over magnesium sulfate. The products, separated by gas chromatography (TCEP, 136°, and silicone grease, 134°) and identified by comparison of infrared spectra, consisted of 2-cycloocten-1-ol<sup>20d</sup> (0.8%), unchanged *cis*-cyclooctene oxide (75%), unidentified substance (0.2%), and an alcohol (24%) identical with the 2-methylcyclooctanol (**7b**) prepared by Walden inversion of **7a**.

**Reaction of trans-Cyclooctene Oxide with Dimethylmagnesium.**—*trans*-Cyclooctene oxide (220 mg.) was treated with 250 ml. of filtered dimethylmagnesium solution exactly as described for the *cis*-oxide. Separation of the products by gas chromatography (TCEP, 120°, and silicone grease, 143°) and comparison of infrared spectra revealed the presence of 2-cycloocten-1-ol (4.5%),  $\alpha$ -methylcycloheptanemethanol<sup>26</sup> (45%), unidentified substance (0.5%), and an alcohol (50%) identical with **7b** prepared by Walden inversion of **7a**.

When *trans*-cyclooctene oxide and dimethylmagnesium were heated for only 2 hr., the *trans*-oxide was recovered unchanged (30% of the product mixture) while the relative composition of the other products remained approximately the same as before. (The *trans*-oxide was recovered on the silicone grease column; it rearranged to cycloheptanecarboxaldehyde on TCEP.)

**Stability of 2, 3, 4, 5, 6a, and 7a to Formic Acid.**—Compounds **2**, **3**, **4**, **5**, **6a**, **7a** were individually subjected to the conditions of formolysis of **1**. The products were analyzed by gas chromatography and identified by comparison of infrared spectra in the same manner as were the formolysis products. Results are summarized in the discussion.

**cis-Bicyclo[6.1.0]nonan-2-ol.**—The procedure was the same as the one described for *cis*-bicyclo[6.1.0]nonane; 3.5 g. of 2-cycloocten-1-ol<sup>40</sup> yielded 2.6 g. of bicyclic alcohol, b.p. 95–103° (8 mm.), contaminated by several minor components as shown by gas chromatography (silicone grease, 145°). Chromatography of 2.383 g. of this mixture on alumina (100 g., activity III) afforded fractions containing the impurities (1.023 g., eluted with pentane) and the alcohol (1.245 g., eluted with 10% ether in pentane). The alcohol fractions all showed identical behavior on gas chromatography (silicone grease at 145° or TCEP at 140°) and had identical infrared spectra, suggesting that they were one pure isomer. The combined alcohol fractions were redistilled for analysis, b.p. 98.5° (4 mm.),  $n_D^{25}$  1.4942.

*Anal.* Calcd. for  $C_9H_{16}O$ : C, 77.09; H, 11.50. Found: C, 76.94; H, 11.42.

The phenylurethan, recrystallized from petroleum ether, had m.p. 86.0–87.2°.

*Anal.* Calcd. for  $C_{16}H_{21}O_2N$ : C, 74.10; H, 8.16; N, 5.40. Found: C, 73.87; H, 7.94; N, 5.50.

(44) A. C. Cope, S. W. Fenton, and C. F. Spencer, *J. Am. Chem. Soc.*, **74**, 5885 (1952).

(45) A. C. Cope, *ibid.*, **57**, 2238 (1935).

*cis*-Bicyclo[6.1.0]nonan-3-ol.—By the same procedure used for *cis*-bicyclo[6.1.0]nonane, 2.57 g. of 3-cycloocten-1-ol<sup>46</sup> yielded 1.93 g. of a mixture found by gas chromatography (silicone grease, 145°) to consist of the original 3-cycloocten-1-ol (20%) and *cis*-bicyclo[6.1.0]nonan-3-ols (80%) in addition to a few minor components. Chromatography on alumina (100 g., activity III) removed the minor components (eluted with pentane). The mixture of alcohols (eluted with 4% ether in pentane) was collected in several fractions. The early alcohol fractions were enriched with a mixture of the bicyclic alcohols which were separated from 3-cycloocten-1-ol by gas chromatography (silicone grease, 140°). 3-Cycloocten-1-ol was identified by a comparison of infrared spectra.

The bicyclic alcohols (*endo* and *exo* mixture) could not be separated on silicone grease or TCEP (140°). However, the infrared spectra of the various alcohol fractions were different. A partial separation of the isomeric phenylurethans was accomplished.<sup>47</sup>

**Hydrogenation of *cis*-Bicyclo[6.1.0]nonane.**—*cis*-Bicyclo[6.1.0]nonane (90 mg.) was hydrogenated at atmospheric pres-

(46) A. C. Cope and P. E. Peterson, *J. Am. Chem. Soc.* **81**, 1643 (1959).

(47) G. L. Woo, Ph.D. Thesis, M. I. T., 1962.

sure in 5 ml. of glacial acetic acid containing 420 mg. of pre-reduced platinum oxide. No hydrogen uptake was observed after 7 hr. at room temperature. When the temperature was increased to 75°, uptake was 55% of the theoretical amount after 48 hr. The solution was filtered, diluted with 50 ml. of pentane, washed with water and 5% sodium bicarbonate solution, and dried over magnesium sulfate. The product (59 mg.) was shown by gas chromatography (silicone oil, 70°, and TCEP, 70°) to consist of methylcyclooctane (50%) and unchanged *cis*-bicyclo[6.1.0]nonane (50%), identified by comparison of infrared spectra with authentic samples.

**Attempted Hydrogenation of *cis*-Bicyclo[6.1.0]nonan-2-ol.**—When *cis*-bicyclo[6.1.0]nonan-2-ol (80 mg.) was hydrogenated as described above, no appreciable uptake was observed at 63° after 2 days. The alcohols were isolated through acetates which were collected by gas chromatography (silicone grease, 140°) and treated with lithium aluminum hydride. The regenerated alcohol (38 mg.) consisted largely of starting material, collected by gas chromatography (TCEP, 140°), and identified by a comparison of retention times and infrared spectra. A peak (less than 7%) corresponding to that of the 2-methylcyclooctanols was also present, but none corresponding to that of 3-methylcyclooctanols or cyclononanol was observed.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SAINT LOUIS UNIVERSITY, ST. LOUIS 4, MO.]

### Solvents of Low Nucleophilicity. III. The Effect of Remote Substituents in the Addition of Trifluoroacetic Acid to Substituted Alkenes<sup>1,2</sup>

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RECEIVED MARCH 22, 1963

First-order rates of addition of trifluoroacetic acid to 5-substituted 1-hexenes at 35 and 60° were determined for the substituents chloro, bromo, iodo, methoxy, acetoxy, trifluoroacetoxy, and cyano. Rate decreases by factors of 32.6, 167, and 311 compared to the rate for 1-hexene were observed for the reactions of the acetoxy, trifluoroacetoxy, and cyano substituted compounds, respectively, at 60°. Notable rate decreases were also observed in the reactions of *trans*-4-hexen-2-yl trifluoroacetate, 6-hepten-2-yl trifluoroacetate, and 7-octen-2-yl trifluoroacetate. The possibility that the large rate effects can be attributed at least in part to an enhancement of the inductive effect of substituents which form hydrogen bonds with the trifluoroacetic acid solvent is discussed.

The rates of addition of trifluoroacetic acid to a number of unbranched alkanes and cycloalkenes at 35° have recently been reported.<sup>3a,b</sup> The reactions may be regarded as typical carbonium ion reactions, which, in the case of terminal olefins, involve Markovnikov addition of a proton to the terminal carbon to give a secondary carbonium ion or its equivalent as an intermediate.<sup>4</sup> Accordingly, the addition of trifluoroacetic acid to olefins would be expected to be retarded by electron-attracting substituents near the potential cationic carbon atom, as is the case in other carbonium ion reactions.<sup>3a,b</sup> Since the sensitivity of the rates of carbonium ion reactions to electron-attracting substituents tends to be higher in solvents of low nucleophilicity, a study of such reactions in trifluoroacetic acid with its presumed very low nucleophilicity is of

particular interest. However, the work described in this paper was prompted originally not by such considerations but by the chance observation that 5-hexen-2-yl trifluoroacetate (**1g**, Fig. 1) was surprisingly unreactive toward trifluoroacetic acid. As may be seen from inspection of Fig. 1, the trifluoroacetoxy group in the presumed intermediate cation is on the fourth carbon from the positively charged carbon (counting the positive carbon as number one since it could conceivably have an attached substituent other than hydrogen).

Since it appeared that the finding of a large rate effect due to the presence of a functional group at a large distance from the reaction center would be of unusual interest, a study of the first-order rates of addition of trifluoroacetic acid to the trifluoroacetate **1g** and to other 5-substituted 1-hexenes at 35 and 60° was undertaken. Rates of reaction of *trans*-4-hexen-2-yl trifluoroacetate, 6-hepten-2-yl trifluoroacetate, 7-octen-2-yl trifluoroacetate, and of several unsubstituted alkenes were also determined. The results, given in Table I, confirmed the remarkably large rate retardation due to the presence of the trifluoroacetoxy group. The cyano and acetoxy groups were also found to cause large rate decreases.

**Product Studies.**—The products of the reaction of trifluoroacetic acid with 5-hexen-2-yl trifluoroacetate were shown to be those indicated in Fig. 2. On the basis of this and other studies, some of which are reported in the Experimental section, and also as a consequence of arguments based on the observed reaction rates which rule out various possible rearrangement reactions, it may be concluded that the main reaction observed for the substituted alkenes of Table I is in fact the addition of trifluoroacetic acid to the un-rearranged double bond. The role of the rearrange-

(1) (a) Presented in part at the 141st National Meeting of the American Chemical Society, Washington, D. C., March, 1962; (b) for a preliminary communication see P. E. Peterson and G. Allen, *J. Org. Chem.*, **27**, 2290 (1962).

(2) This paper is based on the Ph.D. research of G. Allen. The planning of the work was aided greatly by the opportunity which was afforded P. E. Peterson to spend the summer, 1961, in Professor R. W. Taft's research group at Pennsylvania State University where studies of inductive effects upon fluorine n.m.r. spectra were in progress which could be correlated with the work reported here. We are indebted to the donors of the Petroleum Research Fund of the American Chemical Society for a grant (PRF-790a) which made this phase of the work possible. G. Allen gratefully acknowledges a research assistantship provided by the Allied Chemical Corporation during the summer, 1962.

(3) (a) P. E. Peterson and G. Allen, *J. Org. Chem.*, **27**, 1505 (1962); (b) P. E. Peterson, *J. Am. Chem. Soc.*, **82**, 5834 (1960).

(4) The postulation of an intermediate as opposed to a positive transition state is primarily a matter of convenience. It may be noted, however, that the differences between addition and solvolysis reactions in trifluoroacetic acid were conveniently rationalized in terms of solvated cationic intermediates (*cf.* ref. 3b).

(5) (a) A. Streitwieser, Jr., *Chem. Rev.*, **56**, 571 (1956); (b) A. Streitwieser, *J. Am. Chem. Soc.*, **78**, 4935 (1956).