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Proximity Effects. XXXII. Ring Opening of *cis*- and *trans*-Cycloöctene Oxide in Alumina-catalyzed and Uncatalyzed Pyrolysis and in Reaction with Magnesium Bromide Etherate[1,2]

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Pyrolytic and Lewis acid-catalyzed ring opening of *cis*- and *trans*-cycloöctene oxide has been shown to afford a variety of products from transannular reactions. Pyrolysis on basic alumina resulted in oxidation–reduction reactions involving alcohols and carbonyl compounds. Possible mechanistic paths are discussed.

Isomerization of epoxides to carbonyl compounds on pyrolysis[4] and on treatment with Lewis acids[5] is a general reaction. This type of transformation has been investigated for the cycloöctene oxides to determine the extent of transannular processes. Rearrangements have been studied in pyrolysis with and without an alumina catalyst and in reaction with magnesium bromide etherate. The products were identified by comparison of their infrared spectra and gas chromatographic retention times with those of authentic samples. In some cases the authentic samples were synthesized.[6]

cis-Cycloöctene oxide afforded a mixture of thirteen products in a combined yield of 64.1% when passed over alumina (*p*H 8) at 280°. The compounds were separated by alumina chromatography and by gas chromatography on columns packed with 1,2,3-tris-β-cyanoethoxypropane (TCEP) and γ-methyl-γ-nitropimelonitrile (NMPN) on firebrick. They were identified as cycloöctanone (11.8%), cycloheptanecarboxaldehyde (1.6%), 2-cycloöcten-1-ol (1.8%), 3-cycloocten-1-ol (0.8%), 1,4-epoxycycloöctane (0.3%), 2-cycloöcten-1-one (1.1%), 3-cycloöcten-1-one (6.1%), cycloheptanemethanol (11.3%), 7-octen-1-ol (0.9%), 1,3-cycloöctadiene (26.0%), *cis*-cyclooctene (1.2%), methylenecycloheptane (0.3%) and an unidentified hydrocarbon (0.9%). Although the alumina employed was slightly basic, it is an amphoteric substance with sites for acid catalysis. Coördination with the epoxide oxygen atom could lead to the scheme shown in Fig. 1.

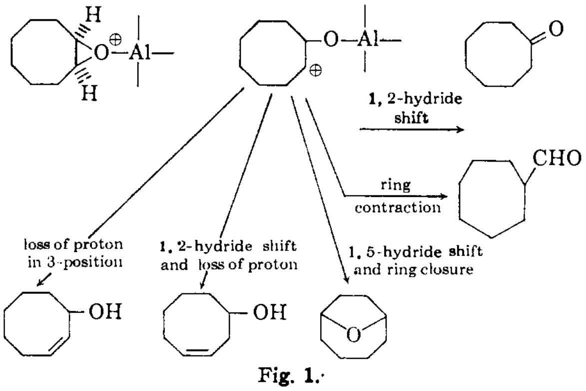


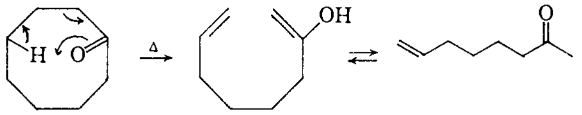
Fig. 1.

The alcohols and ketones not shown in Fig. 1 differ in oxidation state from the starting material and are probably formed in a reaction analogous to the reduction of carbonyl compounds with aluminum alkoxides.[7,8] This is shown in Fig. 2. *cis*-Cycloöctene and methylenecycloheptane are probably formed by dehydration of cycloheptanemethanol.[9]

$$\begin{array}{l}\text{cycloheptanecarboxaldehyde}\\ \text{7-octen-1-al}^{10}\\ \text{2-cycloöcten-1-ol}\\ \text{3-cycloöcten-1-ol}\end{array}\xrightarrow{Al_2O_3}\begin{array}{l}\text{cycloheptanemethanol}\\ \text{7-octen-1-ol}\\ \text{2-cycloöcten-1-one}\\ \text{3-cycloöcten-1-one}\end{array}$$

Fig. 2.

Uncatalyzed pyrolysis of *cis*-cycloöctene oxide at 590° gave in a combined yield of 64.1% a mixture of cycloöctanone (50.0%), cycloheptanecarboxaldehyde (9.1%), 7-octen-2-one (2.1%), 7-octen-1-al (0.4%), *trans*-methyl 2-methylcyclopentyl ketone (2.1%), and *cis*-methyl 2-methylcyclopentyl ketone (0.4%). Pyrolytic opening of the epoxide ring followed by or concerted with a 1,2-hydride shift or ring contraction could explain the formation of cycloöctanone and cycloheptanecarboxaldehyde. Cycloöctanone was pyrolyzed and was found to give 12.3% of 7-octen-2-one. The formation of 7-octen-2-one from cycloöctanone can be explained by a transannular reaction.



The pyrolyses of cyclononyl acetate and *trans*-cyclononene to 1,8-nonadiene[11] provide an analogy in the case of a nine-membered ring. 7-Octen-1-al is known to be formed in the pyrolysis of 3-cycloocten-1-ol.[12] Although 3-cycloöcten-1-ol was not isolated, its intermediacy is reasonable because it is converted to 7-octen-1-al at a lower temperature than is *cis*-cycloöctene oxide. Pyrolysis of cycloheptanecarboxaldehyde yields no 7-octen-1-al. The formation of the methyl 2-methylcyclopentyl

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[1] Supported in part by a research grant (NSF-G5055) of the National Science Foundation.

[2] Paper XXXI, A. C. Cope, P. Scheiner and M. J. Youngquist, *J. Org. Chem.*, to be published.

[3] National Institutes of Health Fellow, 1960–1961; Procter and Gamble Fellow, 1961–1962.

[4] W. Ipatiew and W. Leontowitsch, *Ber.*, **36**, 2016 (1903).

[5] S. M. Naqvi, J. P. Horwitz and R. Filler, *J. Am. Chem. Soc.*, **79**, 6283 (1957).

[6] Details of the syntheses are found in the Experimental section.

[7] W. von E. Doering and T. Aschner, *J. Am. Chem. Soc.*, **75**, 393 (1953).

[8] E. D. Williams, K. A. Krieger and A. R. Day, *ibid.*, **75**, 2404 (1953).

[9] M. A. Rozanov, *J. Russ. Phys. Chem. Soc.*, **61**, 2313 (1929); *C.A.*, **24**, 3766 (1930).

[10] 7-Octen-1-al was not isolated but is thought to be a possible intermediate.

[11] A. T. Blomquist and P. R. Taussig, *J. Am. Chem. Soc.*, **79**, 3505 (1957).

[12] N. A. LeBel, private communication.

ketones is unexpected and difficult to explain. Bicyclo[3.3.0]octan-2-ol was suspected as an intermediate, but pyrolysis of this alcohol yielded no ketones. Further pyrolysis of these ketones did not change their stereochemistry, showing that the percentages of the isomers which were isolated were the same as those originally formed.

Reaction of *cis*-cycloöctene oxide with magnesium bromide etherate without solvent at 70° gave in a combined yield of 54.6% a mixture of cycloheptanecarboxaldehyde (21.0%), cycloöctanone (9.0%), 1,4-epoxycycloöctane (8.8%) and *trans*-2-bromocycloöctanol (15.8%). Possible routes for the formation of these products are shown in Fig. 3.

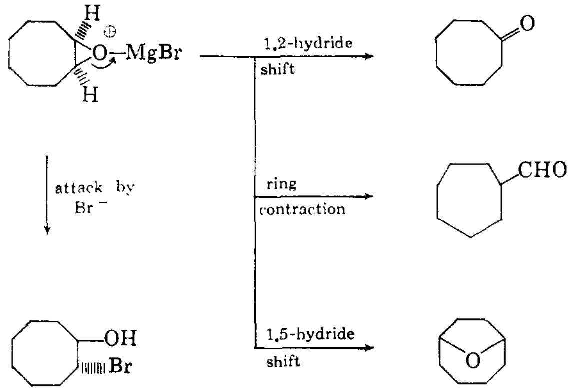

Fig. 3.

When the reaction was run in tetrahydrofuran, the amount of 1,4-epoxycycloöctane formed was less than 1%. The reaction mixture was more polar when no solvent was used than when tetrahydrofuran was present. This increase of transannular products as solvent polarity is raised has been observed previously in the solvolysis of *cis*-cycloöctene oxide with various acids.[13]

The products of pyrolysis of *trans*-cycloöctene oxide on alumina at 250° (obtained in a combined yield of 58.1%) were cycloheptanecarboxaldehyde (16.1%), cycloöctanone (5.1%), 2-cycloöcten-1-ol (3.8%), 7-octen-1-al (1.2%), *trans*-hexahydro-*o*-tolualdehyde (1.6%), 2-cycloöcten-1-one (1.6%), 3-cycloöcten-1-one (7.1%), *trans*-2-methylcyclohexanemethanol (1.9%), cycloheptanemethanol (12.9%) and 1,3-cycloöctadiene (6.8%). The formation of hexahydro-*o*-tolualdehyde from *trans*-cycloöctene oxide has been discussed previously.[14] The formation of *trans*-2-methylcyclohexanemethanol is analogous to the alumina-catalyzed reduction of cycloheptanecarboxaldehyde.

When *trans*-cycloöctene oxide was heated to 500° in the absence of catalyst, the products, obtained in a total yield of 73.8%, were cycloheptanecarboxaldehyde (38.2%), cycloöctanone (28.8%), *cis*-cycloöctene oxide (3.6%), 7-octen-1-al (1.6%), 1,4-epoxycycloöctane (1.1%) and *trans*-hexahydro-*o*-tolualdehyde (0.5%). The isomerization of *trans*-cycloöctene oxide to *cis*-cycloöctene oxide could have been caused by removal of a hydrogen atom from one of the atoms of the epoxide ring followed by reattachment. Alternatively, the epoxide ring may reclose in the *cis*-position after pyrolytic opening. The direction of the isomerization is not surprising in view of the greater thermodynamic stability of the *cis*-fused epoxide.

trans-Cycloöctene oxide reacted exothermically with a solution of magnesium bromide in ether at 15°. The products, obtained in a combined yield of 85.4%, were 1,4-epoxycycloöctane (25.2%), *trans*-hexahydro-*o*-tolualdehyde (24.3%), *cis*-hexahydro-*o*-tolualdehyde (4.2%), 1,3-cycloöctadiene (4.2%), 2-methylcycloheptanone (5.3%), 3-methylcycloheptanone (2.2%), 1-methylcyclohexanecarboxaldehyde (2.6%), an unidentified ether (2.7%) and a mixture of C_8-bromohydrins (14.7%). The formation of 2-methylcycloheptanone, 3-methylcycloheptanone and 1-methylcyclohexanecarboxaldehyde can be explained by rearrangement of the initially formed ion as shown in Fig. 4. The 1,3-cycloöctadiene is probably formed by loss of hydrogen bromide and water from one or more components of the bromohydrin fraction. The absence of cycloöctanone and cycloheptanecarboxaldehyde is striking and is probably caused by a conformational effect.

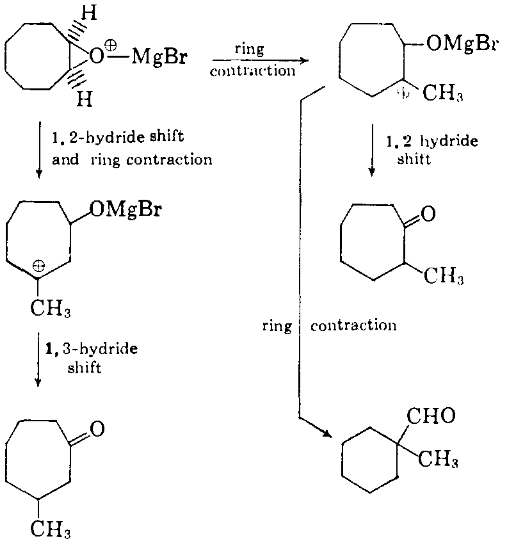

Fig. 4.

Experimental[15]

Pyrolysis of *cis*-Cycloöctene Oxide on Alumina.—A 50 × 1.2-cm. Pyrex tube containing 12 g. of alumina (8–14 mesh, *p*H 8) was heated at 270–280° for 1 hr. at 60 mm. to remove water. *cis*-Cycloöctene oxide (12.19 g.) was delivered in a stream of nitrogen with a contact time of 2 min. at 280° (the total time for the addition was 65 min.). The product mixture (10.05 g., 82.4%) was collected in a trap cooled in a Dry Ice–acetone bath. An additional 0.63 g. (5.2%) was recovered by washing the pyrolysis tube with hot methanol. Water was removed by decantation and the product mixture was distilled yielding 7.83 g. (64.1%).

A portion (2.79 g.) of this mixture was chromatographed on 110 g. of neutral alumina (activity I). Elution with pentane gave 1.18 g. of a mixture of hydrocarbons later shown to consist of 1,3-cycloöctadiene (26.0%), *cis*-cyclooctene[16] (1.2%), methylenecycloheptane (0.3%) and an

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[13] A. C. Cope, J. M. Grisar and P. E. Peterson, *J. Am. Chem. Soc.*, **81**, 1640 (1959).

[14] A. C. Cope, A. Fournier, Jr., and H. E. Simmons, Jr., *ibid.*, **79**, 3905 (1957).

[15] Melting points are corrected and boiling points are uncorrected. We are indebted to Dr. S. M. Nagy and his associates for analyses.

[16] The *cis*-cycloöctene oxide employed in the pyrolysis was shown by gas chromatography (TCEP, 120°) to be free of *cis*-cycloöctene.

unidentified hydrocarbon (0.9%). Elution with 5–10% ether-in-pentane gave 0.39 g. of a mixture containing cycloöctanone (11.8%), cycloheptanecarboxaldehyde (1.6%) and 1,4-epoxycycloöctane (0.3%). A more polar mixture (0.11 g.), eluted with 20–100% ether, contained 2-cycloocten-1-one (1.1%) and 3-cycloöcten-1-one (6.1%). Finally, 1.09 g. of a mixture of cycloheptanemethanol (11.3%), 2-cycloöcten-1-ol (1.8%), 3-cycloöcten-1-ol (0.8%) and 7-octen-1-ol (0.9%) was eluted with 10% methanol-in-ether. The compounds were identified by comparison of their infrared spectra and retention times (TCEP, 120°) with those of authentic samples. In addition, the retention times of the hydrocarbons were compared with those of authentic samples on an NMPN column at 29°. The percentages represent yields based on *cis*-cycloöctene oxide, and were calculated from peak areas on a TCEP column at 120°.

Cycloheptanemethyl Brosylate.—A sample of 0.055 g. of cycloheptanemethanol (then unidentified) was collected from a TCEP column and treated with 0.22 g. of *p*-bromobenzenesulfonyl chloride in the usual manner.[17] Recrystallization of the crude product (0.12 g.) from pentane gave 0.074 g. (50%) of cycloheptanemethyl brosylate, m.p. 46.3–49.2°. Two additional recrystallizations from pentane gave an analytical sample, m.p. 51.6–52.0°.

Anal. Calcd. for $C_{14}H_{19}BrO_3S$: C, 48.40; H, 5.53. Found: C, 48.18; H, 5.23.

Methylcycloheptane.—Cycloheptanemethyl brosylate (0.087 g.) was added to a solution of 0.075 g. of lithium aluminum hydride in 5 ml. of ether. After being heated under reflux for 1 hr., the mixture was cooled and 10 ml. of water was added. After filtration the water layer was extracted with two 5-ml. portions of ether and the ether extracts were dried over magnesium sulfate. The ether was removed through a semi-micro column to a volume of 0.3 ml. The product was collected from a silicone oil column at 94° and identified by comparison of its infrared spectrum with that of an authentic sample.

Lithium Aluminum Hydride Reduction of Cycloheptanecarboxylic Acid.—Cycloheptanecarboxylic acid (0.21 g.) was added to a solution of 0.15 g. of lithium aluminum hydride in 5 ml. of ether. The mixture was refluxed for 1 hr., then water (5 ml.) and 6 *N* hydrochloric acid (5 ml.) were added. The aqueous layer was extracted with four 10-ml. portions of ether and the combined ether extracts were dried over magnesium sulfate. Evaporation of the ether under reduced pressure yielded 0.14 g. (75%) of a colorless liquid, $n^{25}\text{D}$ 1.4726 (lit.[18] $n^{16}\text{D}$ 1.4748). A phenylurethan was prepared and had m.p. 66.2–66.8° after two recrystallizations from pentane.

Anal. Calcd. for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56. Found: C, 72.66; H, 8.65.

The sample of cycloheptanemethanol from pyrolysis gave a phenylurethan with m.p. 64.1–66.0°, which was not depressed on admixture with the authentic sample.

7-Octen-1-ol.—A solution of 0.40 g. of 7-octen-1-yl acetate[19] in 20 ml. of ether was added to a solution of 0.33 g. of lithium aluminum hydride in 10 ml. of ether and the mixture was stirred at room temperature for 45 min., then cooled in ice, and water and 10% hydrochloric acid were added. The aqueous layer was extracted with ether. The ether extracts were washed with saturated sodium bicarbonate solution and water and dried over magnesium sulfate. Distillation of the ether gave 0.28 g. (94%) of 7-octen-1-ol. A sample collected from a TCEP column at 120° had $n^{25}\text{D}$ 1.4426.

Anal. Calcd. for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 75.13; H, 12.61.

7-Octen-1-yl phenylurethan had m.p. 58.2–58.9° after two recrystallizations from pentane.

Anal. Calcd. for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56. Found: C, 72.93; H, 8.64.

Pyrolysis of *cis*-Cycloöctene Oxide (Uncatalyzed).—*cis*-Cycloöctene oxide (2.16 g.) was passed in a stream of nitrogen at 580–590° through a Pyrex tube filled with glass helices. The contact time was 4 min. (total time for the addition, 20 min.). The products, collected in a Dry Ice trap and distilled, amounted to 1.43 g. (66.3%). Analysis on a TCEP column at 120° showed six peaks, one of which was identified as unchanged *cis*-cycloöctene oxide by comparison of its infrared spectrum and retention time on TCEP with those of an authentic sample. The other peaks were identified as cycloöctanone (50.0%), cycloheptanecarboxaldehyde (9.1%), 7-octen-2-one (2.1%), *trans*-methyl 2-methylcyclopentyl ketone (2.1%) and a mixture (0.8%) of equal parts of 7-octen-1-al and *cis*-methyl 2-methyl-cyclopentyl ketone. Identifications were made by comparison of infrared spectra and retention times (TCEP, 120°) with those of authentic samples.

7-Octen-1-al.[20]—Sodium bicarbonate (2.20 g.) was added to a solution of 0.79 g. of 7-octen-1-yl brosylate (obtained as an oil from 7-octen-1-ol and *p*-bromobenzenesulfonyl chloride) in 7 ml. of dimethyl sulfoxide. The mixture was immersed in a bath at 150° for 5 min. under a nitrogen atmosphere. After cooling, the mixture was diluted with 20 ml. of water and extracted with three 10-ml. portions of pentane. The combined pentane extracts were washed with four 10-ml. portions of water, dried over magnesium sulfate, and concentrated. Short-path distillation of the residue gave 0.28 g. of a mixture of 82% of 7-octen-1-al and 18% of dimethyl sulfoxide. The yield of aldehyde determined by gas chromatography (TCEP, 120°) was 79%. A sample collected by gas chromatography was analyzed, $n^{25}\text{D}$ 1.4315.

Anal. Calcd. for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.85; H, 10.96.

A 2,4-dinitrophenylhydrazone, purified by filtration of a benzene solution through neutral alumina followed by recrystallization from aqueous methanol, had m.p. 95.1–96.0°.

Anal. Calcd. for $C_{14}H_{18}N_4O_4$: C, 54.89; H, 5.92. Found: C, 55.01; H, 6.08.

3-Carbethoxy-7-octen-2-one was prepared by a procedure similar to that used for 3-carbethoxyheptan-2-one.[21] Alkylation of ethyl acetoacetate with 5.00 g. of 5-bromo-1-pentene gave 3.37 g. (55%) of 3-carbethoxy-7-octen-2-one, b.p. 76–78° (0.5 mm.), $n^{25}\text{D}$ 1.4430.

Anal. Calcd. for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.57; H, 8.98.

7-Octen-2-one.—Saponification of 3-carbethoxy-7-octen-2-one (0.69 g.) followed by decarboxylation of the resulting acid according to the procedure used for 2-heptanone[22] gave 0.30 g. (68%) of 7-octen-2-one, b.p. 68–70° (21 mm.). The ketone formed a 2,4-dinitrophenylhydrazone, m.p. 63.6–64.0° (lit.[23] m.p. 65°) after recrystallization from aqueous ethanol.

Methyl 2-Methylcyclopentyl Ketone.—Methyl 2-methyl-1-cyclopentenyl ketone[24] (0.30 g.) was hydrogenated over 0.10 g. of palladium-on-carbon in 3 ml. of methanol until 99% of the theoretical amount of hydrogen was absorbed. Separation of the catalyst and removal of the solvent gave 0.30 g. (97%) of a mixture of saturated ketones. Analysis by gas chromatography (TCEP, 130°) showed 53% of the *cis* isomer ($n^{25}\text{D}$ 1.4453, lit.[25] $n^{25}\text{D}$ 1.4418) and 47% of the *trans* isomer ($n^{25}\text{D}$ 1.4390, lit.[25] $n^{25}\text{D}$ 1.4383). Equilibration[25] of the mixture with sodium ethoxide in ethanol gave a mixture containing 91% of the *trans* isomer and 9% of the *cis* isomer.

Pyrolysis of Cycloöctanone.—Cycloöctanone (0.80 g.) was pyrolyzed at 590° with a contact time of 4 min. to give 0.60 g. of a mixture containing 84.7% of cycloöctanone and 12.3% of 7-octen-2-one. The latter was identified by comparison of its infrared spectrum and retention time (TCEP, 120°) with those of an authentic sample.

Pyrolysis of Cycloheptanecarboxaldehyde.—Cycloheptanecarboxaldehyde (0.17 g.) was pyrolyzed at 590° with a contact time of 4 min. and at 500° with a contact time of 1 min., and was recovered essentially unchanged in both cases.

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[17] A. C. Cope and P. E. Peterson, *J. Am. Chem. Soc.*, **81**, 1643 (1959). This reference (footnote 24) also describes the equipment used for gas chromatography.

[18] E. E. Royals and A. H. Neal, *J. Org. Chem.*, **21**, 1448 (1956).

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

[20] This general method of preparing aldehydes is described by N. Kornblum, W. J. Jones and G. J. Anderson, *ibid.*, **81**, 4113 (1959).

[21] C. S. Marvel and F. D. Hager, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., p. 248.

[22] J. R. Johnson and F. D. Hager, *ibid.*, p. 351.

[23] L. Crombie and S. H. Harper, *J. Chem. Soc.*, 869 (1952).

[24] T. R. Marshall and W. H. Perkin, *ibid.*, **57**, 242 (1890).

[25] R. B. Turner, *J. Am. Chem. Soc.*, **72**, 878 (1950).

Pyrolysis of Methyl 2-Methylcyclopentyl Ketone.—A 0.10-g. sample of the mixture of isomers from hydrogenation of methyl 2-methyl-1-cyclopentenyl ketone was pyrolyzed at 590° with a contact time of 4 min. The isomer composition of the product was shown by gas chromatography (TCEP, 130°) to be the same as that of the starting material.

Pyrolysis of Bicyclo[3.3.0]octan-2-ol.—Bicyclo[3.3.0]octan-2-ol (0.10 g. of a mixture of the *endo* and *exo* isomers) was pyrolyzed at 590° with a contact time of 4 min. and gave only olefinic products.

Reaction of *cis*-Cycloöctene Oxide with Magnesium Bromide Etherate without Solvent.—To 1.45 g. of magnesium turnings in 20 ml. of ether was added dropwise 9.51 g. of bromine. Ether (20 ml.) was added and the mixture was stirred at room temperature for 0.5 hr. A solution of 5.00 g. of *cis*-cycloöctene oxide in 20 ml. of ether was added. The ether was distilled and the temperature was raised to 70°. The reaction was allowed to proceed for 24 hr. under a nitrogen atmosphere. The mixture was cooled in ice and 40 ml. of water and 50 ml. of ether were added. The aqueous layer was extracted three times with ether. The combined ether extracts were washed with saturated sodium bicarbonate solution and water and dried over magnesium sulfate. The ether was removed under reduced pressure, giving a dark liquid which was distilled through a semi-micro column. Two fractions were collected: (1) b.p. 58–70° (6 mm.), 2.11 g. (42.2%, calcd. for $C_8H_{14}O$); (2) b.p. 69–70° (0.3 mm.), 1.30 g. (15.8%, calcd. for $C_8H_{15}BrO$). The compounds in fraction 1 were separated by gas chromatography (TCEP, 120°) and identified by comparison of their infrared spectra and retention times with those of authentic samples. The products were cycloheptanecarboxaldehyde (21.0%), cyclooctanone (9.0%), 1,4-epoxycycloöctane (8.8%), and unchanged *cis*-cycloöctene oxide (3.4%). Fraction 2 was identified as *trans*-2-bromocycloöctanol by comparison of its infrared spectrum with that of an authentic sample prepared by treatment of *cis*-cycloöctene oxide with anhydrous hydrogen bromide.[26] It formed a 3,5-dinitrobenzoate, m.p. 93.4–94.0°, after two recrystallizations from chloroform-pentane, undepressed when mixed with an authentic sample, m.p. 93.5–94.4°. The infrared spectra of the derivatives were identical.

Reaction of *cis*-Cycloöctene Oxide with Magnesium Bromide in Tetrahydrofuran.—Bromine (9.51 g.) was added dropwise to 1.45 g. of magnesium turnings in 20 ml. of dry tetrahydrofuran. Another 20 ml. of tetrahydrofuran was added and the mixture was stirred at room temperature for 1 hr. A solution of 5.00 g. of *cis*-cycloöctene oxide in 30 ml. of tetrahydrofuran was added and the mixture was refluxed for 48 hr. under nitrogen. The mixture was cooled in ice, 20 ml. of saturated sodium sulfate solution was added, and the organic layer was separated and washed with saturated sodium bicarbonate solution. The aqueous layer was extracted with ether and the combined organic layers were washed with 20 ml. of saturated sodium sulfate solution and dried over magnesium sulfate. Concentration under reduced pressure gave a dark liquid which was distilled through a semi-micro column to give 3.18 g. (64%) of products, b.p. 48–77° (15 mm.). Comparison of retention times (TCEP, 120°) showed the same products in similar amounts as in the reaction without solvent, except that the yield of 1,4-epoxycycloöctane was less than 1%.

Pyrolysis of *trans*-Cycloöctene Oxide on Alumina.—*trans*-Cycloöctene oxide (1.89 g.) was pyrolyzed on 1.5 g. of alumina with a contact time of 15 sec. (the time required for addition was about 30 min.). Distillation of the material recovered from the cold trap (1.42 g.) gave 1.13 g. (59.8%). Elution of the pyrolysis tube with hot methanol gave an additional 0.18 g. (9.5%). The products were identified by comparison of their infrared spectra and retention times (TCEP, 120°) with those of authentic samples, except for *trans*-hexahydro-*o*-tolualdehyde, which was identified by lithium aluminum hydride reduction to *trans*-2-methylcyclohexanemethanol. The yields were 1,3 - cycloöctadiene (6.8%), *trans*-hexahydro-*o*-tolualdehyde (1.6%), 7-octen-1-al (1.2%), cycloheptanecarboxaldehyde (16.1%), cyclooctanone (5.1%), 2-cycloöcten-1-one (1.6%), 3-cycloöcten-1-one (7.1%), *trans*-2-methylcyclohexanemethanol (1.9%), cycloheptanemethanol (12 9%) and 2-cycloöcten-1-ol (3.8%). A small amount of *trans*-cycloöctene oxide (1.7%) was recovered.

Pyrolysis of *trans*-Cycloöctene Oxide (Uncatalyzed).—*trans*-Cycloöctene oxide (0.23 g.) was passed through a Pyrex tube filled with glass helices at 490–500° with a contact time of 1 min. (the time required for addition was 10 min.). The products (0.17 g., 73.8%), collected in a Dry Ice trap, were separated on a TCEP column at 110° and identified by comparison of their infrared spectra and retention times with those of authentic samples as cycloheptanecarboxaldehyde (38.2%), cycloöctanone (28.8%), *cis*-cycloöctene oxide (3.6%), 7-octen-1-al (1.6%) 1,4-epoxycycloöctane (1.1%). and *trans*-hexahydro-*o*-tolualdehyde (0.5%). The last two compounds did not separate on TCEP and were identified by comparison of the infrared spectrum and retention time of the mixture with those of authentic mixtures.

Reaction of *trans*-Cycloöctene Oxide with Magnesium Bromide Etherate.—A solution of magnesium bromide etherate was prepared by addition of 1.90 g. of bromine to 0.29 g. of magnesium turnings in 10 ml. of ether. The solution was cooled to 15° with an ice-bath and a solution of *trans*-cycloöctene oxide (1.00 g.) in 5 ml. of ether was added dropwise over a period of 10 min. The temperature rose to 26° during the addition. The mixture was stirred for 1 hr. at room temperature, then cooled in ice and 15 ml. of cold water added. The water layer was extracted with three 15-ml. portions of ether. The combined ether extracts were washed with saturated sodium bicarbonate solution and water and dried over magnesium sulfate. The ether was removed and the products were distilled through a short column. Two fractions were collected: (1) b.p. 31–76° (14–15 mm.), 0.77 g. (70.7%, calcd. for $C_8H_{14}O$); (2) b.p. 103–115° (1.5 mm.), 0.24 g. (14.7%, calcd. for $C_8H_{15}BrO$). The low-boiling fraction on analysis by gas chromatography (TCEP, 140°) showed six peaks. The major peak (49.5%) was identified (see below) as a mixture of 1,4-epoxycyclooctane (25.2%) and *trans*-hexahydro-*o*-tolualdehyde (24.3%). The other products, identified by comparison of their infrared spectra and retention times with those of authentic samples, were 1,3-cycloöctadiene (4.2%), *cis*-hexahydro-*o*-tolualdehyde (4.2%), 2-methylcycloheptanone (5.3%), 3-methylcycloheptanone (2.2%) and 1-methylcyclohexanecarboxaldehyde (2.6%). The 1-methyl-cyclohexanecarboxaldehyde was contaminated with an unidentified ether (2.7%).

The major peak in the gas chromatogram of the low-boiling fraction was collected (TCEP, 140°) and a solution of 0.048 g. of this mixture in 2 ml. of ether was added to a solution of 0.094 g. of lithium aluminum hydride in 2 ml. of ether. The mixture was allowed to stand for 15 min. The excess hydride was destroyed with water and 10% hydrochloric acid, and the aqueous layer was extracted twice with ether. The combined ether extracts were washed with saturated sodium bicarbonate solution and water and dried over magnesium sulfate. The ether was distilled, the products were collected from a TCEP column at 140°, and identified by comparison of their infrared spectra and retention times with those of authentic samples as 1,4-epoxycyclooctane (51%) and *trans*-2-methylcyclohexanemethanol (49%).

***cis*- and *trans*-2-Methylcyclohexanemethanol.**—A solution of 0.97 g. of *cis*-hexahydro-*o*-toluic acid[14] in 10 ml. of ether was added dropwise to a suspension of 1.04 g. of lithium aluminum hydride in 30 ml. of ether. The mixture was allowed to stand for 15 min., the excess hydride was destroyed with water and 10% sulfuric acid, and the aqueous layer was extracted with ether. The combined ether extracts were washed with saturated sodium bicarbonate solution and water and dried over magnesium sulfate. The ether was removed and the product was distilled through a semi-micro column, yielding 0.67 g. (77%) of *cis*-2-methylcyclohexanemethanol, b.p. 55–56° (0.9 mm.). *trans*-2-Methylcyclohexanemethanol was prepared in a similar manner from *trans*-hexahydro-*o*-toluic acid.[14]

***cis*-2-Methylcyclohexanemethyl Brosylate.**—Treatment of 0.37 g. of *cis*-2-methylcyclohexanemethanol with 1.38 g. of *p*-bromobenzenesulfonyl chloride[17] gave 0.75 g. of crude brosylate which was recrystallized from pentane giving 0.55 g. (54%) of material with m.p. 44.6–45.1°. An analytical sample had m.p. 44.6–45.1° after an additional recrystallization from pentane.

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[26] A. C. Cope and H. E. Johnson, *J. Am. Chem. Soc.*, **79**, 3889 (1957).

Anal. Calcd. for $C_{14}H_{19}BrO_3S$: C, 48.40; H, 5.53. Found: C, 48.64; H, 5.63.

cis-**Hexahydro-*o*-tolualdehyde.**—*cis*-2-Methylcyclohexanemethyl brosylate (0.25 g.) was dissolved in 5 ml. of dimethyl sulfoxide. Sodium bicarbonate (0.73 g.) was added and the mixture was immersed in a bath at 150° for 5 min. under a nitrogen atmosphere. After cooling in ice, water and pentane were added, and the water layer was extracted with pentane. The pentane layer was washed with water and dried over magnesium sulfate. The ether was evaporated and the product was collected from a TCEP column at 140°.

Hydroboration of 1-Methylcycloheptene.[27]—1-Methylcycloheptene (11.0 g.) was treated with diborane at 0° and the product was oxidized with alkaline hydrogen peroxide giving 6.8 g. (53%) of a mixture of alcohols, b.p. 56–57° (1.0 mm.). Analysis of this mixture (TCEP, 140°) showed two major peaks of approximately equal amounts. These compounds were collected and identified as *trans*-2-methylcycloheptanol and *trans*-3-methylcycloheptanol by comparison of their infrared spectra with those of authentic samples.[28] The formation of *trans*-3-methylcycloheptanol was unexpected. However, a similar rearrangement has been observed in the case of hydroboration of 1-methylcyclooctene.[27]

2-Methylcycloheptanone and 3-Methylcycloheptanone.—A solution of 1.27 g. of the above mixture of alcohols in 10 ml. of acetone was titrated to an orange-brown end-point with an 8 *N* solution of chromic anhydride in 30% sulfuric acid. The reaction was exothermic, causing the acetone to reflux gently. The acetone solution was decanted from the chromic salts and the product was isolated by adding 30 ml. of water, extracting with three 10-ml. portions of ether, washing the ether extracts with saturated sodium bicarbonate solution and water, and drying over magnesium sulfate. Distillation through a semi-micro column gave 0.86 g. (69%) of ketones, b.p. 79–80° (19 mm.), which were separated by gas chromatography (TCEP, 120°) and identified as 2-methylcycloheptanone (51%) and 3-methylcycloheptanone (49%) by the melting points of their 2,4-dinitrophenylhydrazones. 2-Methylcycloheptanone 2,4-dinitrophenylhydrazone had m.p. 119.2–120.3° (lit.[29,30] m.p. 121–122°). 3-Methylcycloheptanone 2,4-dinitrophenylhydrazone had m.p. 127.3–129.0° (lit.[31] m.p. 130.5–131.0°). Both derivatives were recrystallized from aqueous ethanol.

Purification and Identification of 1-Methylcyclohexanecarboxaldehyde.—The peak containing the aldehyde was collected from a TCEP column at 120° and injected onto a silicone oil column at 110°. The two peaks which separated were collected. The first compound (47%) was identified as 1-methylcyclohexanecarboxaldehyde by comparison of its infrared spectrum and retention time (TCEP, 120°) with those of an authentic sample. An infrared spectrum of the second peak (53%) contained no hydroxyl or carbonyl absorption, but showed strong ether absorption between 900 and 1200 cm.$^{-1}$.

1-Methylcyclohexanemethyl Brosylate.—1-Methylcyclohexanemethanol[32] (0.45 g.) was converted in 48% yield to the brosylate (0.59 g.), m.p. 60.8–61.4°, after one recrystallization from pentane. An analytical sample had m.p. 61.0–61.5° after an additional recrystallization from pentane.

Anal. Calcd. for $C_{14}H_{19}BrO_3S$: C, 48.40; H, 5.53. Found: C, 48.43; H, 5.36.

1-Methylcyclohexanecarboxaldehyde.—A solution of 0.10 g. of 1-methylcyclohexanemethyl brosylate in 2 ml. of dimethyl sulfoxide was treated with 0.30 g. of sodium bicarbonate at 150°. The aldehyde was collected from a TCEP column at 140°.

Composition of the High-boiling (Bromohydrin) Fraction.—The fraction with b.p. 103–105° (1.5 mm.) was dark in color, gave a positive Beilstein test, showed hydroxyl absorption in the infrared, and had n^{25}_{D} 1.5205. Purification using activated charcoal and drying under reduced pressure gave an analytical sample.

Anal. Calcd. for $C_8H_{15}BrO$: Br, 38.59. Found: Br, 38.33.

The bromohydrin fraction failed to give a crystalline 3,5-dinitrobenzoate.

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(32) 1-Methylcyclohexanemethanol was obtained by lithium aluminum hydride reduction of 1-methylcyclohexanecarboxylic acid. The acid was prepared from 2-methylcyclohexanol by the procedure of H. Koch and W. Haaf, *Ann.*, **618**, 251 (1958).

[A JOINT CONTRIBUTION FROM BELL TELEPHONE LABORATORIES, MURRAY HILL, N. J., AND THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY, NEW HAVEN, CONN.]

Structure of the 7-Norbornadienyl Carbonium Ion[1]

BY PAUL R. STORY[2a] AND MARTIN SAUNDERS[2b]

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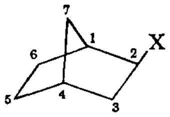
The first direct and detailed physical evidence for the structure of an aliphatic non-classical carbonium ion has been obtained from the nuclear magnetic resonance spectrum of 7-norbornadienyl fluoroborate. The spectrum in liquid sulfur dioxide and in nitromethane indicates an unsymmetrical structure. Rearrangement of the bicyclic skeleton is ruled out by conversion of the fluoroborate to the corresponding acetate and to the corresponding methyl ether.

Introduction

The solvolyses of certain related carbocyclic molecules including cyclopropyl carbinyl (I), norbornyl (II) and norbornenyl derivatives (III) have provided a fund of information concerning the nature of the carbonium ion intermediates and the subject of non-classical structures and charge delocalization in general.[3] Structures involving non-classical delocalization of electrons have been proposed for the intermediate carbonium ions hypothesized in these and other systems in order to explain remarkably enhanced rates of solvolysis of certain derivatives. The information obtained

I



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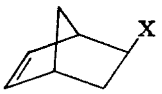
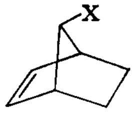


IIIa



IIIb

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(1) A portion of this work has been reported in preliminary form; P. R. Story and M. Saunders, *J. Am. Chem. Soc.*, **82**, 6199 (1960).

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(3) For comprehensive discussions see: (a) S. Winstein and E. M. Kosower, *J. Am. Chem. Soc.*, **81**, 4399 (1959); (b) R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver and J. D. Roberts, *ibid.*, **81**, 4390 (1959).