Similarly, 1.10 g. of triphenylethylene oxide yielded 0.76 g. (69%) of triphenylacetaldehyde, m.p. 98–102°. One recrystallization from absolute ethanol gave the pure aldehyde, 0.51 g. (46%), m.p. 104–105° (lit.[24] m.p. 105.5°).

Acknowledgment.—The assistance of a Brown University Faculty Summer Research Grant to one of the authors (E. R. T.) is gratefully acknowledged.

CAMBRIDGE, MASSACHUSETTS
PROVIDENCE, RHODE ISLAND

---

[24] S. Danilov, *Zhur. Russ. Fiz. Khim. Obshchestva*, **51**, 97 (1919); *C. A.*, **18**, 1488 (1924).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Proximity Effects. XII. Reaction of *cis*- and *trans*-Cycloöctene Oxide with Bases

BY ARTHUR C. COPE, HIOK-HUANG LEE[1] AND HARRIS E. PETREE

RECEIVED DECEMBER 12, 1957

The reaction of *cis*-cycloöctene oxide with the strong bases phenyllithium and lithium diethylamide has been shown to result in the formation of an intramolecular alkylation product, *endo-cis*-bicyclo[3.3.0]octan-2-ol (I) as the major product, and a smaller amount of 2-cycloöcten-1-ol (II). The reaction of *trans*-cycloöctene oxide with lithium diethylamide formed cycloheptanecarboxaldehyde, *exo-cis*-bicyclo[3.3.0]octan-2-ol (IV) and 2-cycloöcten-1-ol.

The acid-catalyzed solvolysis of cycloheptene oxide[2] and *cis*-[3] and *trans*-cycloöctene oxides[4] and the hydroxylation with performic acid of the nine-,[5] ten-[6] and eleven-membered[7] ring olefins are known to yield products other than the expected *trans*-1,2-glycols. Formation of the abnormal products has been explained as due to a transannular hydride shift for which the conformations of the medium-sized rings may be responsible. In the present paper, we report a different type of transannular reaction that takes place upon treatment of *cis*- and *trans*-cycloöctene oxides with strong bases.

When a mixture of *cis*-cycloöctene oxide and excess lithium diethylamide in ether was refluxed for forty-eight hours, and the products were separated by chromatography on alumina, they were found to be: 5.5% of recovered *cis*-cycloöctene oxide, 69.5% of a liquid alcohol, $C_8H_{13}OH$ (I), 16% of another liquid alcohol, $C_8H_{13}OH$ (II), and 2% of *trans*-1,2-cycloöctanediol, identified as the bis-*p*-nitrobenzoate. The major product I was identified as *endo-cis*-bicyclo[3.3.0]octan-2-ol by comparing its infrared spectrum with the spectrum of an authentic specimen,[8] and by preparation of identical *p*-nitrobenzoates from the two samples. The minor product II was identified by its infrared spectrum and *p*-nitrobenzoate as 2-cycloöcten-1-ol.[9]

This conversion of *cis*-cycloöctene oxide into the bicyclic alcohol I and 2-cycloöcten-1-ol through reaction with a base was first observed upon treating the oxide with an excess of phenyllithium. The bicyclic alcohol I was isolated in 50% yield, and 2-cycloöcten-1-ol in 27% yield. From a reaction mixture in which *cis*-cycloöctene oxide was present in 37% excess over phenyllithium, lower yields of I and II were obtained, 30% of the oxide was recovered and 13% of *trans*-1,2-cycloöctanediol was isolated. In neither case was 2-phenylcycloöctanol found among the products.

A base stronger than sodium ethoxide in ethanol is required for the transannular alkylation reaction leading from *cis*-cycloöctene oxide to I under the conditions that were investigated. When a mixture of *cis*-cycloöctene oxide and sodium ethoxide in absolute ethanol was refluxed for forty-eight hours, the products isolated were 81% of the recovered oxide, 7% of *trans*-1,2-cycloöctanediol and 3% of *trans*-2-ethoxycycloöctanol. The identity of the *trans*-2-ethoxycycloöctanol was established by comparison of its *p*-nitrobenzoate with the corresponding derivative obtained from an authentic sample prepared from the monosodium salt of *trans*-1,2-cycloöctanediol and ethyl iodide.

From the reaction of *trans*-cycloöctene oxide with lithium diethylamide, there was isolated 32% of cycloheptanecarboxaldehyde (III), identified as the 2,4-dinitrophenylhydrazone and semicarbazone. In addition there was isolated 68% of a mixture of liquid alcohols, with an infrared spectrum indicating that it contained 2-cycloöcten-1-ol and an alcohol of unknown structure. A *p*-nitrobenzoate prepared from the mixture was shown by mixed melting point to be the *p*-nitrobenzoate of *exo-cis*-bicyclo[3.3.0]octan-2-ol (IV).[8] Indirect separation of the mixture of II and IV was effected by treatment with phenyl isocyanate to form a mixture of phenylurethans, which was then ozonized. The ozonization product was treated with sodium borohydride and then with phenyl isocyanate. Chromatography on alumina of the mixture of phenylurethans that was formed separated as the major component the phenylurethan of *exo-cis*-bicyclo[3.3.0]octan-2-ol, identified by mixed melting point and comparison of the infrared spectrum with the spectrum of an authentic sample.[8] The minor component was similarly identified as 1,2,8-octanetriol tris-phenylurethan.[10] Based on this separation, the yields of II and IV from the reaction of *trans*-cycloöctene oxide with lithium diethylamide are calculated to be 10–15% and 55–60%, respectively.

---

(1) American Cyanamid Co. Fellow, 1955–1956.

(2) A. C. Cope, T. A. Liss and G. W. Wood, *Chemistry & Industry*, 823 (1956); THIS JOURNAL, **79**, 6287 (1957).

(3) A. C. Cope, S. W. Fenton and C. F. Spencer, *ibid.*, **74**, 5884 (1952).

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

(5) V. Prelog, K. Schenker and W. Küng, *Helv. Chim. Acta*, **36**, 471 (1953).

(6) V. Prelog and K. Schenker, *ibid.*, **35**, 2044 (1952).

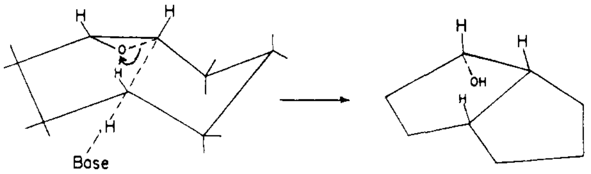
(7) V. Prelog and V. Boarland, *ibid.*, **38**, 1776 (1955).

(8) A. C. Cope, M. Brown and H. E. Petree, THIS JOURNAL, **80**, 2852 (1958).

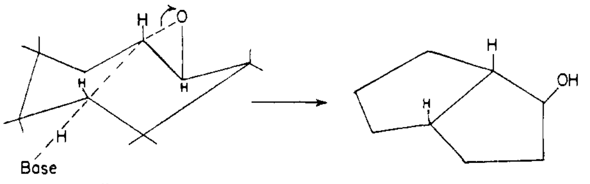
(9) A. C. Cope, M. R. Kinter and R. T. Keller, *ibid.*, **76**, 2757 (1954).

(10) A. C. Cope and G. W. Wood, *ibid.*, **79**, 3885 (1957).

The reactions in which the bicyclic alcohols I and IV are formed from *cis*- and *trans*-cycloöctene oxide, respectively, are intramolecular alkylations that occur at carbon atoms activated only by the epoxide group across the ring. The steric conformation of the rings must bring the carbon atoms that become united by a valence bond in the products sufficiently close together for this kind of activation by a "proximity effect" to suffice. It is hoped that a study of these reactions with deuterium-labeled epoxides will show which hydrogen is lost as a proton in the initial reaction with the base. At present, two reaction paths leading to the bicyclic alcohols appear to be possible. In the first, the base removes a proton from a carbon atom located across the ring from the epoxide group, with (probably concerted) opening of the epoxide by the carbanion so formed. If the epoxide ring opening proceeds with Walden inversion, as would be expected, the *cis*-oxide would lead to the *endo*-alcohol and the *trans*-oxide to the *exo*-alcohol, and these are the observed products. The most stable conformations of *cis*- and *trans*-cycloöctene oxides are unknown, but the formulas represent possible conformations in the form of transition states that would lead to the observed products.

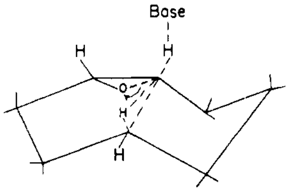


cis-cycloöctene oxide *endo*-alcohol I



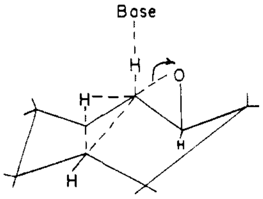
trans-cycloöctene oxide *exo*-alcohol IV

In a second possible reaction path, the proton is lost from one of the carbon atoms of the epoxide ring. Breaking of the bond between the oxygen atom and the carbon atom which has lost a proton to the base would form a "carbene" intermediate, which could then form a valence bond to the carbon atom across the ring, with transfer of hydrogen from the same carbon atom to the electron-deficient "carbene" carbon. In the following formulas representing possible transition states in this mechanism, the processes are represented as concerted, since the products are single stereoisomers.



cis-cycloöctene oxide

(⟶ *endo*-alcohol I)

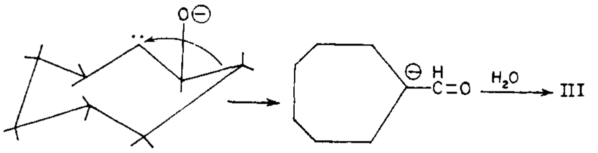


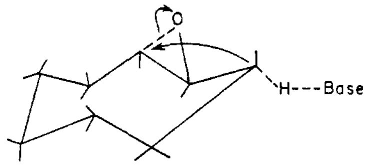
trans-cycloöctene oxide

(⟶ *exo*-alcohol IV)

Formation of 2-cycloöcten-1-ol from both *cis*- and *trans*-cycloöctene oxide and bases could result from removal of a proton either from a carbon atom one removed from the epoxide ring, or from a carbon atom attached to the epoxide ring. In the former case the intermediate would be a transitory carbanion, and in the latter a different carbanion that could form a "carbene." The conversion of certain epoxides to allylic alcohols by treatment with bases has been observed previously.[11]

The formation of cycloheptanecarboxaldehyde from the reaction of *trans*-cycloöctene oxide with lithium diethylamide was unexpected, although some precedent for this type of rearrangement exists in the reaction of the same base with *trans*-stilbene oxide, which yields diphenylacetaldehyde.[12] The reaction definitely occurs in the presence of the base rather than by an acid-catalyzed rearrangement during the isolation procedure, for *trans*-cycloöctene oxide was shown to be recovered unchanged after treatment with saturated aqueous ammonium chloride solution (used to hydrolyze intermediate lithium compounds in the reaction mixture from which cycloheptanecarboxaldehyde was isolated). The carbene intermediate previously mentioned could form the enolate of cycloheptanecarboxaldehyde by the path formulated below. An alkylation mechanism also might account for the formation of cycloheptanecarboxaldehyde, if a cyclopropanol could be formed by the electronic displacements shown in the following formula. Cyclopropanol is known to rearrange readily, forming propionaldehyde.[13]





Experimental[14]

Reaction of *cis*-Cycloöctene Oxide with Lithium Diethylamide.—*n*-Butyllithium was prepared by addition during 20 min. of 34.3 g. (0.25 mole) of *n*-butyl bromide to 4.3 g. (0.62 g.-atom) of lithium wire in 75 ml. of anhydrous ether at −10°. After the solution had been stirred at 0–10° for 1 hr., titration of aliquots indicated that 0.216 mole (86%) of *n*-butyllithium was present. Dry diethylamine (18.2 g., 0.25 mole) was added at −10° during 15 min. and the mixture was stirred for an additional 15 min. The ethereal solution of lithium diethylamide was decanted through a glass wool plug into a dry flask, 12.6 g. (0.1 mole) of *cis*-cycloöctene oxide[3] was added and the solution was stirred and refluxed under an atmosphere of nitrogen for 48 hr. The reaction mixture was cooled and poured into 700 ml. of ice and water, and the organic layer was separated. The aqueous layer was extracted with two 100-ml. portions of

---

(11) L. J. Haynes, I. Heilbron, E. R. H. Jones and F. Sondheimer, *J. Chem. Soc.*, 1583 (1947).

(12) A. C. Cope, P. S. Trumbull and E. R. Trumbull, This Journal, **80**, 2844 (1958).

(13) J. K. Magrane and D. L. Cottle, *ibid.*, **64**, 484 (1942); G. W. Stahl and D. L. Cottle, *ibid.*, **65**, 1782 (1943); J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 3176 (1951).

(14) Melting points are corrected and boiling points are uncorrected. We are indebted to Dr. S. M. Nagy and his associates for analyses.

ether and the ethereal solutions were combined and extracted with four 150-ml. portions of saturated ammonium chloride solution to remove diethylamine. After a final washing with water the ethereal solution was dried over anhydrous magnesium sulfate and concentrated. The residue was distilled through a semimicro column, giving 11.68 g. (93%) of liquid having b.p. 95–105° (21 mm.), n^{25}D 1.4809–1.4899.

A 7.0-g. aliquot of the above product was chromatographed over 475 g. of alumina of Grade II activity.[15] There was first eluted by hexane 0.39 g. of unreacted *cis*-cycloöctene oxide, which was identified by its infrared spectrum. Constituting the next band of the chromatogram was 4.66 g. of an oil, eluted by 5–50% ether in hexane, whose infrared spectrum was found to be identical with that of *endo-cis*-bicyclo[3.3.0]octan-2-ol (I).[8] *p*-Nitrobenzoates were prepared from the first and final cuts of this fraction; they melted at 87.2–87.7° and 85.5–86°, respectively, and showed no melting point depression when mixed with the authentic *p*-nitrobenzoate of I. The next 0.35 g. of oil, eluted by 50% ether in hexane, was found by comparison of its infrared spectrum with the spectrum of an authentic sample of 2-cycloöcten-1-ol (II)[9] to be a mixture of I and II, while the following 0.99 g. of oil, eluted by ether, had an infrared spectrum identical with the spectrum of II. However, the *p*-nitrobenzoate of this material melted at 92–96°, indicating that it was still contaminated with a small amount of I. Fractional recrystallization of this derivative from aqueous methanol separated the pure *p*-nitrobenzoate of 2-cycloöcten-1-ol, m.p. and mixed m.p. with an authentic sample 103–104°.

A final band of 0.17 g. of oil was eluted by 3–25% methanol in ether; a *p*-nitrobenzoate prepared from this fraction had m.p. 110–110.8°. Mixed with an authentic sample of *trans*-1,2-cycloöctanediol bis-*p*-nitrobenzoate (which had m.p. 112–112.7°),[16] it melted at 112–113.3°. The following yields of the products of *cis*-cycloöctene oxide with lithium diethylamide were calculated from a weight balance of the chromatographic cuts: recovered oxide, 5.5%; *endo-cis*-bicyclo[3.3.0]octan-2-ol (I), 69.5%; 2-cycloöcten-1-ol (II), 16%; and *trans*-1,2-cycloöctanediol, 2%. In another similar experiment, no *trans*-1,2-cycloöctanediol was obtained; the products, besides 20% of unreacted *cis*-cycloöctene oxide, were 68% of I and 12% of II. The *trans*-1,2-cycloöctanediol formed in some of these reaction mixtures is believed to result from the base-catalyzed hydrolysis of *cis*-cycloöctene oxide during the isolation procedure.

That no 2-diethylaminocycloöctanol was formed by this reaction was demonstrated by extraction of the product with 3 *N* hydrochloric acid. The acid extracts were made basic with sodium hydroxide and extracted with ether; no residue remained after distillation of the solvent.

Reaction of *cis*-Cycloöctene Oxide with Phenyllithium (in Excess).—Phenyllithium was prepared by the addition of 28.6 g. (0.175 mole) of bromobenzene in 400 ml. of anhydrous ether to 2.78 g. (0.4 g.-atom) of lithium wire in 200 ml. of anhydrous ether during 45 min. Dry benzene (200 ml.) was added and the ether removed by distillation. To the benzene suspension of phenyllithium was added 12.6 g. (0.1 mole) of *cis*-cycloöctene oxide, and the mixture was stirred and heated under reflux for 18 hr. The reaction mixture was cooled to 0° and decomposed by the addition of 100 ml. of ice-water. The organic layer was separated, and the aqueous layer was extracted once with ether. The organic portions were combined, washed with water and dried over anhydrous magnesium sulfate. The solvents were distilled through an 18-cm. Heligrid-packed column, followed by the product, 10.04 g. (83%) of an oil, b.p. 65–82° (5 mm.), n^{25}D 1.4906–1.5050. The distillation residue, 3.9 g. of a viscous brown oil, was chromatographed over 120 g. of alumina of Grade II activity. Biphenyl (1.1 g.) was separated. The polar material, eluted by methanol, was 2.2 g. of a viscous oil, from which no 2-phenylcycloöctanol could be isolated.

A 5.005-g. aliquot of the oil, b.p. 65–82° (5 mm.), n^{25}D 1.4906–1.5050, was chromatographed over 375 g. of alumina of Grade II activity. After removal of 0.18 g. of biphenyl, 2.59 g. of I was eluted by 0–10% ether in benzene and was identified by comparison of its infrared spectrum with the spectrum of an authentic sample, and by preparation of its *p*-nitrobenzoate, which melted at 86–86.4°. Mixed with an authentic sample of the *p*-nitrobenzoate of I, it melted at 85.5–86.3°.

Constituting the final portions of the chromatogram was 1.75 g. of material eluted by 40% ether in benzene and pure ether, with an infrared spectrum indicating that it was composed principally of II. However, since the *p*-nitrobenzoate of this material melted over the range 91–98°, a 1.22-g. portion was subjected to a second chromatographic separation over 125 g. of Grade II activity alumina. There was eluted by 20% ether in benzene 0.27 g. of oil with an infrared spectrum indicating that it was a mixture of I and II, followed by 0.65 g. of liquid, eluted by 20–50% ether in benzene, pure ether and 25% ethyl acetate in ether, with an infrared spectrum identical with the spectrum of II. The *p*-nitrobenzoate prepared from this fraction had m.p. 103.2–103.5° and showed no depression when mixed with the *p*-nitrobenzoate prepared from authentic II.

A weight balance of the chromatographic cuts, after correction for losses of material during concentration, enabled the calculation of a 6.25-g. (50%) yield of I and a 3.89-g. (27%) yield of II from this experiment.

When a 37% excess of *cis*-cycloöctene oxide was treated with phenyllithium under similar conditions, the products isolated besides I and II were 30% of unreacted oxide and 13% of *trans*-1,2-cycloöctanediol.

Reaction of *cis*-Cycloöctene Oxide with Sodium Ethoxide.—To the sodium ethoxide prepared from 100 ml. of absolute ethanol and 5.75 g. (0.25 g.-atom) of sodium was added 12.6 g. (0.1 mole) of *cis*-cycloöctene oxide. The resulting solution was refluxed in an atmosphere of nitrogen for 48 hr. The solvent was then distilled and the solid residue was poured into 300 ml. of ice and water. The product was extracted with two 100-ml. portions of ether and the ether extracts were dried and concentrated, giving 11.7 g. (93%) of a mushy solid possessing the odor of *cis*-cycloöctene oxide.

A 6.6-g. sample of the above product was chromatographed over 320 g. of alumina of Grade II activity. The major component, eluted by hexane and benzene, was 5.70 g. of *cis*-cycloöctene oxide, identified by its infrared spectrum. There was eluted next a band of 0.28 g. of an oil, n^{25}D 1.4630, which formed a *p*-nitrobenzoate, m.p. 60.6–61.2° after four recrystallizations from aqueous ethanol, and had the composition of the *p*-nitrobenzoate of a possible product of this reaction, *trans*-2-ethoxycycloöctanol.

Anal. Calcd. for $C_{17}H_{23}O_5N$: C, 63.53; H, 7.21. Found: C, 63.74; H, 7.10.

A final band of 0.55 g. of an oil, eluted by 1–50% methanol in ether and pure methanol was found by its infrared spectrum to be *trans*-1,2-cycloöctanediol. From a weight balance of the chromatographic cuts, the following yields were calculated for the products of reaction of *cis*-cyclooctene oxide with ethanolic sodium ethoxide: recovered oxide, 81%; *trans*-2-ethoxycycloöctanol, 3%; *trans*-1,2-cyclooctanediol, 7%.

***trans*-2-Ethoxycycloöctanol.**—A solution of 0.298 g. of *trans*-1,2-cycloöctanediol in 35 ml. of dry benzene was swirled for 10 min. with 0.05 g. of sodium hydride. Ethyl iodide (0.77 g.) was added and the mixture was refluxed for 24 hr. The reaction mixture was shaken with two 30-ml. portions of water and the benzene layer was dried and concentrated. The residue was chromatographed over 15 g. of Grade II activity alumina. A band of 14 mg. of a non-polar oil was first eluted by benzene and was not investigated. Next followed a band of 58 mg. of *trans*-2-ethoxycycloöctanol, eluted by 0–50% ether in benzene and pure ether. A final band of 28 mg. of unreacted *trans*-1,2-cycloöctanediol was then eluted by 1–50% methanol in ether.

The product was treated with 0.1 g. of *p*-nitrobenzoyl chloride in pyridine with the isolation of 35 mg. of a derivative which melted at 59.5–60° after two recrystallizations from aqueous ethanol. Mixed with the derivative isolated from the reaction products of sodium ethoxide and *cis*-cyclooctene oxide, it melted at 60–60.8°. Further proof of the identity of the two compounds was provided by the fact that their infrared spectra were superimposable.

Reaction of *trans*-Cycloöctene Oxide with Lithium Diethylamide.—*trans*-Cycloöctene oxide[4] (6.3 g., 0.05 mole) and 200 ml. of dry benzene were added to an ethereal solution of lithium diethylamide prepared from 0.118 mole of *n*-butyllithium in the manner described above. The ether and excess diethylamine were removed by distillation and the resultant mixture was stirred and refluxed in an atmosphere of

---

(15) H. Brockman, *Ber.*, **74**, 73 (1943).

(16) A. C. Cope, A. L. Keough, P. E. Peterson, H. E. Simmons, Jr., and G. W. Wood, THIS JOURNAL, **79**, 3900 (1957).

nitrogen for 72 hr. The products were isolated as in the experiment with the *cis*-oxide. The residue, after removal of the benzene, was distilled through a semimicro column, giving 5.26 g. (84%) of a liquid having b.p. 73–95° (10 mm.) and with an infrared spectrum containing a band at 1720 cm.$^{-1}$ and showing no absorption in the region 780 to 1000 cm.$^{-1}$ where *trans*-cycloöctene oxide absorbs strongly.

The distillate was chromatographed over 160 g. of alumina of Grade II activity. There was eluted by petroleum ether (30–60°) and 5% ether in petroleum ether (30–60°) 1.66 g. of a liquid (III), n^{25}D 1.4615–1.4622, with the strong odor characteristic of an aldehyde, which formed a 2,4-dinitrophenylhydrazone, m.p. 133.8–134.4° after two recrystallizations from aqueous ethanol. A mixed melting point of this derivative with an authentic sample of cycloheptanecarboxaldehyde 2,4-dinitrophenylhydrazone (which had m.p. 134.5–135.5°)[17] was 134–135°. The infrared spectra of the two compounds were also identical. That IV was cycloheptanecarboxaldehyde was further evidenced by the fact that its semicarbazone, m.p. 156–157°, did not depress the melting point of an authentic sample of cycloheptanecarboxaldehyde semicarbazone (m.p. 155–156.5°).[17]

A more polar material, 3.14 g. of a viscous liquid, was next eluted from the alumina by 15–50% ether in petroleum ether (30–60°). The first and final cuts of this liquid absorbed bromine in carbon tetrachloride solution. It also formed a *p*-nitrobenzoate, m.p. 72–74° after four recrystallizations from aqueous ethanol. A mixed melting point of this derivative with the *p*-nitrobenzoate of *exo-cis*-bicyclo[3.3.0]octan-2-ol (IV),[8] which had m.p. 76.9–77.8°, was 73–75°. That the liquid was a mixture of IV and some olefinic alcohol was further indicated by the fact that distillation through a semimicro column gave four fractions which had varying refractive indices (n^{25}D 1.4850–1.4890), with infrared spectra that were similar except for differences in the intensity of absorption at 710, 750 and 780 cm.$^{-1}$, which are characteristic absorption peaks of 2-cycloöcten-1-ol (II).

A fraction of the above distillate with n^{25}D 1.4880 weighing 648 mg. was treated with phenyl isocyanate. After removal of excess phenyl isocyanate under reduced pressure, the resultant viscous oil was chromatographed over 90 g. of alumina of Grade II activity. A total of 1.20 g. of solid was eluted by petroleum ether (30–60°) and ether in 6:1 and 2:1 ratios, and had m.p. 59–63°. Recrystallizations from pentane failed to yield a pure derivative. The phenylurethan mixture was finally separated by the ozonolysis experiment described below.

A solution of 880 mg. of the phenylurethan mixture described above in 25 ml. of ethyl acetate was cooled to −70° and a saturated solution of ozone in ethyl acetate (also at −70°) was added, with swirling, until a blue color persisted. A solution of 1.5 g. of sodium borohydride in 25 ml. of methanol was then added and the solution was allowed to warm slowly to room temperature. After 2 hr. the solution was poured into 50 ml. of 10% hydrochloric acid solution, and extracted with four 60-ml. portions of ether. The ethereal solutions were combined, dried over anhydrous magnesium sulfate, and concentrated. The residue was heated on a steam-bath for 10 min. with 1.0 g. of phenyl isocyanate. The gummy residue, after removal of excess phenyl isocyanate under reduced pressure, was chromatographed over 100 g. of alumina of Grade I activity. There was first eluted by benzene 96 mg. of an oil, which could not be crystallized, followed by 586 mg. of material which crystallized from cold pentane and had m.p. 70.6–72.2°. Three further recrystallizations from aqueous methanol raised the melting point to 74.8–75.6°. This was proved to be *exo-cis*-bicyclo[3.3.0]octan-2-ol phenylurethan by a mixed m.p. of 74.6–75.8° with an authentic sample,[8] and the fact that their infrared spectra were identical. The infrared spectrum of the oil (the first fraction in the chromatogram) was very similar to that of the phenylurethan of IV, except for minor differences which cannot be accounted for by the presence of the epimeric phenylurethan.

Next was eluted from the alumina by 10% methanol in ether, 287 mg. of a solid, m.p. 121–124°. After two recrystallizations from aqueous methanol, it melted at 134.4–136.2° and was identified as 1,2,8-octanetriol tris-phenylurethan by mixed melting point and by comparison of the infrared spectrum with the spectrum of an authentic sample.[10]

Based on the chromatographic separation described earlier and the ozonolysis experiment, the products of the reaction of *trans*-cycloöctene oxide with lithium diethylamide are: cycloheptanecarboxaldehyde, 32%; *exo-cis*-bicyclo[3.3.0]-octan-2-ol (IV), 55–60%; 2-cycloöcten-1-ol (II), 10–15%.

CAMBRIDGE, MASSACHUSETTS

---

[17] A. C. Cope, N. A. Nelson and D. S. Smith, THIS JOURNAL, **76**, 1100 (1954).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Proximity Effects. XIII. Stereochemistry of the *cis*-Bicyclo[3.3.0]octan-2-ols

BY ARTHUR C. COPE, MORTON BROWN[1a] AND HARRIS E. PETREE[1b]

RECEIVED DECEMBER 12, 1957

The known epimeric *cis*-bicyclo[3.3.0]octan-2-ols have been stereochemically related to the two epimeric *cis*-bicyclo[3.3.0]-octane-2-carboxylic acids. This has been achieved by the perbenzoic acid cleavage of the two methyl ketones prepared from the two acids, forming the corresponding alcohols. Absolute configurations have been assigned to these compounds on the basis of these transformations and mechanistic considerations.

Recent work in these laboratories[2] on the rearrangement that occurs when *cis*- and *trans*-cycloöctene oxide are treated with strong bases has resulted in the formation of two bicyclic alcohols, shown to be the epimeric *cis*-bicyclo[3.3.0]octan-2-ols (II and III). One of the alcohols, the one with the higher-melting phenylurethan (m.p. 76.9–77.8°), was tentatively assigned the *endo* configuration (II) because it was obtained by catalytic reduction of *cis*-bicyclo[3.3.0]octan-2-one (I), on the basis of the *cis* nature of catalytic reduction and the steric requirements of the bicyclo[3.3.0]octane ring system.[3]

It was of interest to determine the stereochemical configuration of these alcohols unequivocally by relating them to the epimeric *cis*-bicyclo[3.3.0]-octane-2-carboxylic acids.[4] One of these acids, m.p. 39.0–40.5°, was assigned the less stable *endo* configuration since it could be converted to a liquid isomer by treatment with hot alcoholic base or by refluxing with constant-boiling hydrochloric acid.

The alcohol I gave only an oily tosylate on treatment with *p*-toluenesulfonyl chloride in pyridine.

---

[1] (a) National Science Foundation Fellow 1955–1957; (b) National Science Foundation Fellow 1952–1954.

[2] A. C. Cope, H. H. Lee and H. E. Petree, THIS JOURNAL, **80**, 2849 (1958).

[3] A. C. Cope and T. Y. Shen, *ibid.*, **78**, 3177 (1956).

[4] A. C. Cope and M. Brown, *ibid.*, **80**, 2859 (1958).