

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*-cyclooctene 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_D^{25} 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_D^{25} 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-cycloocten-1-ol (II).

A fraction of the above distillate with n_D^{25} 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

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

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*-cyclooctene oxide with lithium diethylamide are: cycloheptanecarboxaldehyde, 32%; *exo-cis*-bicyclo[3.3.0]octan-2-ol (IV), 55–60%; 2-cycloocten-1-ol (II), 10–15%.

CAMBRIDGE, MASSACHUSETTS

[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}

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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 laboratories² on the rearrangement that occurs when *cis*- and *trans*-cyclooctene 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).

It did, however, give a crystalline *p*-nitrobenzenesulfonate and phenylurethan. Treatment of the tosylate with tetraethylammonium acetate in acetone and saponification of the crude acetate that was formed gave an epimeric alcohol tentatively designated as *exo-cis*-bicyclo[3.3.0]octan-2-ol (III). It gave a phenylurethan, m.p. 75.2–76.0°. Proof that III had an unrearranged carbon skeleton was obtained by oxidizing it with *N*-bromosuccinimide in aqueous acetone to the ketone I, identified as the 2,4-dinitrophenylhydrazone.⁵ Attempts to epimerize the alcohol III (through the tosylate and acetate) to II were unsuccessful, resulting in formation of a mixture of olefins arising from elimination of the tosylate group, which may have occurred in the attempted displacement with tetraethylammonium acetate or in the subsequent treatment of the reaction mixture with base. This unsuccessful attempt to displace the tosylate group in the tosylate of III is consistent with the *exo* configuration assigned to it. It has been shown that S_N2 reactions in these bicyclic ring systems are usually unsuccessful when the substituent is in an *exo* configuration³ and the reagent must approach from the hindered (*endo*) side of the molecule.

Synthesis of the *endo*- and *exo*-methyl ketones (IV and V) corresponding to the epimeric *cis*-bicyclo[3.3.0]octane-2-carboxylic acids was performed by the reaction of dimethylcadmium with the acid chlorides prepared from the two acids. The liquid ketones were shown to be different by comparison of their infrared spectra and preparation of dissimilar crystalline semicarbazones.

The acid and alcohol series were stereochemically related by perbenzoic acid oxidation of the two methyl ketones, employing a slight modification of a method used by Turner⁶ in the acetylcyclopentane series. Each ketone was treated for one week with an excess of a chloroform solution of perbenzoic acid. The acetate formed was saponified and after the unreacted ketone had been separated by chromatography, the bicyclic alcohol was isolated and identified as its crystalline phenylurethan. In this case the methyl ketone V arising from the base-stable acid (assigned the *exo* configuration) was oxidized to the alcohol III possessing the lower-melting phenylurethan (previously tentatively assigned an *exo* configuration). Similarly, the epimeric ketone IV gave the alcohol II with

the higher-melting phenylurethan, which therefore has the *endo* configuration.

cis-Bicyclo[3.3.0]octan-2-one (I) has been reduced with various reagents during the course of this work. It has been shown that catalytic reduction of I in the presence of *W*-7 Raney nickel proceeds with formation of the *endo* isomer II. Dauben, Fonken and Noyce⁷ in recent work on the stereochemistry of hydride reductions have found that in reductions of alkylcyclohexanones, lithium aluminum hydride, sodium borohydride and aluminum isopropoxide lead to the formation of increasing amounts of the axial (*cis*, less stable) isomer. In the cases studied, the composition of the mixture of isomers formed is determined by the steric requirements of the reducing agent and the stability of the possible products. In the case of the ketone I, reduction with sodium borohydride in methanol produced only the *endo* (less stable) alcohol II. Similar results were obtained with aluminum isopropoxide in isopropyl alcohol. However, when the alcohol II was heated under reflux for one week with a solution of aluminum isopropoxide in acetone and isopropyl alcohol, a mixture containing 61% of III and 39% of II was obtained.

These results show that even though the steric requirement of sodium borohydride is much less than aluminum isopropoxide, the ketone I is so greatly hindered to hydride attack from an *endo* position that the product is completely "steric approach controlled,"⁷ and the *endo*-alcohol II is formed. Its instability, relative to the *exo* isomer III, is shown by its partial conversion to III on heating under reflux with aluminum isopropoxide in acetone and isopropyl alcohol.

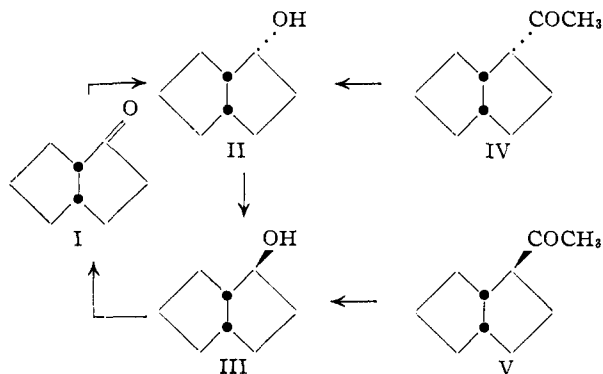
Experimental⁸

Methyl *exo-cis*-Bicyclo[3.3.0]oct-2-yl Ketone.—*exo-cis*-Bicyclo[3.3.0]octane-2-carboxylic acid (4.04 g.) was allowed to stand overnight with 10 g. of thionyl chloride. The excess thionyl chloride was removed under reduced pressure, and the residual acid chloride was taken up in 15 ml. of anhydrous benzene and used directly in the following preparation.

To an ethereal solution of methylmagnesium iodide prepared from 4.55 g. of methyl iodide and 0.72 g. of magnesium turnings contained in a 100-ml. three-necked flask equipped with stirrer, reflux condenser, dropping funnel and nitrogen inlet, was added in small portions 3.3 g. of anhydrous cadmium chloride. When the addition was complete, the mixture was heated under reflux for one hour, at which time a negative Gilman test was obtained. The ether was then distilled and replaced with 20 ml. of dry benzene. The above benzene solution of the crude acid chloride was added dropwise with stirring over 15 min., heated under reflux for 30 min., and then poured over 100 g. of ice and 10 ml. of concentrated sulfuric acid. The benzene layer was separated and the aqueous layer extracted with two 50-ml. portions of benzene. The combined extracts were washed with saturated sodium bicarbonate solution, dilute sodium thiosulfate solution, dried over magnesium sulfate and concentrated. Distillation of the residual oil through a semimicro column yielded 2.80 g. (70%) of liquid methyl *exo-cis*-bicyclo[3.3.0]oct-2-yl ketone, b.p. 94–95° (10 mm.), n_D^{25} 1.4655.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.86; H, 10.55.

This ketone (0.10 g.) was treated with 0.15 g. of semicarbazide hydrochloride and 0.22 g. of sodium acetate trihydrate in 2 ml. of hot 50% ethanol. The crude semicar-



(5) A. C. Cope and W. R. Schmitz, *THIS JOURNAL*, **72**, 3056 (1950).

(6) R. B. Turner, *ibid.*, **72**, 878 (1950).

(7) W. G. Dauben, G. J. Fonken and D. S. Noyce, *ibid.*, **78**, 2579 (1956).

(8) Melting points are corrected and boiling points are uncorrected.

bazone, 0.109 g. (80%), had m.p. 167.6–177.0° dec. Three recrystallizations from ethyl acetate raised the melting point to 181.0–182.4° dec.

Anal. Calcd. for $C_{11}H_{19}N_3O$: C, 63.12; H, 9.15. Found: C, 63.20; H, 9.36.

Peracid Cleavage of Methyl *exo-cis*-Bicyclo[3.3.0]oct-2-yl Ketone.—Methyl *exo-cis*-bicyclo[3.3.0]oct-2-yl ketone (1 g.) was allowed to stand for one week in a solution of 1.38 g. of perbenzoic acid in 47 ml. of chloroform. The unreacted peracid was destroyed by washing with dilute sodium thiosulfate solution and the benzoic acid was removed by washing with several portions of saturated sodium bicarbonate solution. The chloroform was evaporated and the oily residue heated under reflux for 30 min. in a solution of 1.5 g. of potassium hydroxide in 30 ml. of methanol. Most of the methanol was distilled and the remaining material diluted with 50 ml. of water and extracted with three 30-ml. portions of ether. The combined extracts were dried over magnesium sulfate and concentrated, yielding 0.73 g. of oil which was chromatographed on a 210×18 -mm. column of activity I alumina. The unreacted ketone, eluted with hexane, amounted to 0.041 g. (4%) and the crude *exo-cis*-bicyclo[3.3.0]octan-2-ol, eluted with 2–10% ether in hexane, amounted to 0.255 g. (31%). This alcohol yielded a crude phenylurethan, m.p. 71.8–75.2°, which, after three recrystallizations from hexane, melted at 75.0–75.9°. This derivative of *exo-cis*-bicyclo[3.3.0]octan-2-ol showed no depression in mixed melting point with the phenylurethan of III obtained by epimerization of II, which in turn had been prepared by catalytic reduction of I. Infrared spectra of the two samples of the phenylurethan were identical.

Methyl *endo-cis*-Bicyclo[3.3.0]oct-2-yl Ketone.—Two grams of *endo-cis*-bicyclo[3.3.0]octane-2-carboxylic acid was allowed to stand overnight with a threefold molar excess of thionyl chloride. The excess thionyl chloride was distilled under reduced pressure, and the residual acid chloride was taken up in 15 ml. of dry benzene and used directly in the following preparation.

Anhydrous cadmium chloride (3.3 g.) was added in small portions to a solution of methylmagnesium iodide prepared from 0.72 g. of magnesium turnings and 4.45 g. of methyl iodide. The benzene solution of the acid chloride was added and the reaction product isolated according to the method described above for the preparation of methyl *exo-cis*-bicyclo[3.3.0]oct-2-yl ketone. The liquid methyl *endo-cis*-bicyclo[3.3.0]oct-2-yl ketone, b.p. 108–111° (21 mm.), n_D^{20} 1.4735–1.4755, amounted to 1.33 g. (68%). An analytical sample had b.p. 110° (21 mm.), n_D^{20} 1.4735.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.70; H, 10.78.

Methyl *endo-cis*-bicyclo[3.3.0]oct-2-yl ketone (0.10 g.) was treated with 0.15 g. of semicarbazide hydrochloride and 0.22 g. of sodium acetate trihydrate in 2 ml. of hot 50% ethanol. The product, totaling 0.11 g. (83%), melted at 150.0–154.3° dec. Three recrystallizations from ethyl acetate gave an analytical sample, m.p. 159.0–161.1° dec.

Anal. Calcd. for $C_{11}H_{19}N_3O$: C, 63.12; H, 9.15; N, 20.08. Found: C, 62.84; H, 9.15; N, 19.98.

Peracid Cleavage of Methyl *endo-cis*-Bicyclo[3.3.0]oct-2-yl Ketone.—Methyl *endo-cis*-bicyclo[3.3.0]oct-2-yl ketone (1.02 g.) was allowed to stand for one week in a solution of 1.45 g. of perbenzoic acid in 49 ml. of chloroform. The product was isolated in the same manner as the *exo*-ketone and amounted to 0.88 g. of a dark oil that was chromatographed on a 230×18 -mm. column of activity I alumina. Unreacted ketone, eluted with hexane, amounted to 0.187 g. (18%), while the crude alcohol, eluted with 2–10% ether in hexane, amounted to 0.315 g. (38%). This alcohol gave a phenylurethan, m.p. 80.2–85.1°, which after three recrystallizations from hexane had m.p. 85.1–86.2° and was undepressed by admixture with the phenylurethan prepared from the alcohol obtained by catalytic or sodium borohydride reduction of *cis*-bicyclo[3.3.0]octan-2-one (I). Infrared spectra of the phenylurethans from both sources were identical.

***endo-cis*-Bicyclo[3.3.0]octan-2-ol.** (a) **By Catalytic Hydrogenation of *cis*-Bicyclo[3.3.0]octan-2-one (I).**—*cis*-Bicyclo[3.3.0]octan-2-one (3.0 g.) was dissolved in 25 ml. of absolute methanol and hydrogenated at 1 atm. using 0.2 g. of W-7 Raney nickel. Uptake of hydrogen was complete in 4 hr. The catalyst was separated, the solvent evapo-

rated, and the product distilled through a semimicro column, yielding 2.62 g. (88%) of *endo-cis*-bicyclo[3.3.0]octan-2-ol, b.p. 91–93° (12 mm.), n_D^{20} 1.4890.

Treatment of 0.5 g. of the above alcohol with 0.48 g. of phenyl isocyanate gave 0.69 g. (70%) of a white solid whose melting point remained at 86.4–87.0° during four recrystallizations from aqueous ethanol.

Anal. Calcd. for $C_{15}H_{19}NO_2$: C, 73.43; H, 7.80. Found: C, 73.58; H, 7.78.

(b) **By Sodium Borohydride Reduction of I.**—To a solution of 2.44 g. of sodium borohydride in 50 ml. of methanol was added a solution of 2.0 g. of *cis*-bicyclo[3.3.0]octan-2-one (I) in 20 ml. of methanol. The solution was allowed to stand at room temperature for 1 hr., most of the methanol was removed under reduced pressure, and the residue was cautiously acidified with cold dilute hydrochloric acid. The aqueous solution was extracted with three 30-ml. portions of ether, which were combined, washed with dilute sodium bicarbonate solution, dried over magnesium sulfate, concentrated, and distilled through a semimicro column, yielding 1.80 g. (89%) of *endo-cis*-bicyclo[3.3.0]octan-2-ol, b.p. 82–84° (7 mm.), n_D^{20} 1.4888. The infrared spectrum of this alcohol was identical with the spectrum of the alcohol obtained by catalytic reduction described above. The phenylurethan also was identical (mixed m.p. and infrared spectra).

(c) **By Meerwein-Ponndorf-Verley Reduction of I.**—A solution of 1.0 g. of *cis*-bicyclo[3.3.0]octan-2-one, 40 ml. of dry isopropyl alcohol and 6 g. of aluminum isopropoxide was distilled slowly through a 25-cm. fractionating column packed with one-eighth inch glass helices and equipped with a total reflux-partial takeoff head until the distillate produced no precipitate with 2,4-dinitrophenylhydrazine reagent (about 2 hr.). Most of the remaining alcohol was removed under reduced pressure, the residue acidified with cold 10% hydrochloric acid, and the product extracted with three 30-ml. portions of ether. The combined extracts were washed with saturated sodium bicarbonate solution, dried over magnesium sulfate, and the solvent was distilled. The residue on distillation through a semimicro column gave 0.80 g. (79%) of *endo-cis*-bicyclo[3.3.0]octan-2-ol, b.p. 92.5–94.0° (13 mm.), n_D^{20} 1.4903–1.4907. The infrared spectrum of the product was identical with the spectrum of the alcohol obtained by the two methods described above.

Equilibration of *exo*- and *endo-cis*-Bicyclo[3.3.0]octan-2-ol.—*endo-cis*-Bicyclo[3.3.0]octan-2-ol (2 g.) was heated under reflux for one week with a solution of 20 ml. of dry isopropyl alcohol, 0.2 ml. of acetone and 2 g. of aluminum isopropoxide. Most of the solvent was distilled, the residue cautiously acidified with cold dilute hydrochloric acid, and the product extracted with three 10-ml. portions of ether. The combined extracts were washed with saturated sodium bicarbonate solution, dried over magnesium sulfate and distilled, yielding 1.60 g. (80%) of a mixture of the epimeric *cis*-bicyclo[3.3.0]octan-2-ols, b.p. 91–93° (10 mm.), n_D^{20} 1.4878. Infrared analysis of the mixture, using the medium-strength band at 932 cm^{-1} present only in the *exo* isomer (see below), showed that the mixture contained 61% of the *exo* and 39% of the *endo* isomer.

***exo-cis*-Bicyclo[3.3.0]octan-2-ol.**—A 2.6-g. sample of *endo-cis*-bicyclo[3.3.0]octan-2-ol was added to 4.67 g. of *p*-toluenesulfonyl chloride in 10 ml. of dry pyridine and allowed to stand overnight. The solution was poured into 100 ml. of water and the resulting mixture was extracted with two portions of benzene. The benzene extracts were washed with 5% sodium carbonate solution, dilute hydrochloric acid and water, then dried over magnesium sulfate and concentrated. The residual *p*-toluenesulfonate was an oil which failed to crystallize from aqueous ethanol.

The oily *p*-toluenesulfonate (4.5 g., 78%) was heated under reflux with 3.5 g. of tetraethylammonium acetate in 75 ml. of acetone for 22 hr. Most of the acetone was distilled, and the residue was poured into 150 ml. of water. The *exo-cis*-bicyclo[3.3.0]oct-2-yl acetate was extracted with three portions of ether. The ether was distilled, and the residue was heated under reflux for 10 min. with 1.5 g. of potassium hydroxide in 30 ml. of methanol. Part of the methanol was distilled and the residue poured into 150 ml. of water. The product was extracted with three portions of ether, and the ether extracts were dried over magnesium sulfate, concentrated, and the residue was fractionally distilled through a semimicro column. After removal of a fore-run of 0.10 g. of material having b.p. 72.0–87.5° (12 mm.),

n_D^{25} 1.4695, the *exo-cis*-bicyclo[3.3.0]octan-2-ol distilled; 1.0 g. (39% over-all yield), b.p. 87.5–91.0° (12 mm.), n_D^{25} 1.4800–1.4831. The forerun decolorized bromine in carbon tetrachloride solution, and is believed to be a trace of olefin formed by elimination of the *p*-toluenesulfonate group during the step involving displacement with tetraethylammonium acetate. To assure complete removal of unsaturated material, two fractions having n_D^{25} 1.4830–1.4831 were redistilled through the same column. The resulting epimer had b.p. 79° (5 mm.) and n_D^{25} 1.4873–1.4883. Its infrared spectrum was quite unlike that of the *endo* isomer; it possessed characteristic bands at 932, 992, 1032 and 1105 cm^{-1} . A fraction with b.p. 79° (5 mm.) and n_D^{25} 1.4883 was analyzed.

Anal. Calcd. for $\text{C}_8\text{H}_{14}\text{O}$: C, 76.14; H, 11.18. Found: C, 75.98; H, 11.18.

exo-cis-Bicyclo[3.3.0]octan-2-ol phenylurethan was prepared by treatment of 0.18 g. of the above *exo*-alcohol with 0.26 g. of phenyl isocyanate, forming 0.15 g. of a white solid that melted at 75.0–75.2° after five recrystallizations from aqueous ethanol. A mixed melting point with the phenylurethan of the *endo*-alcohol was depressed to 59–71°.

Anal. Calcd. for $\text{C}_{15}\text{H}_{19}\text{O}_2\text{N}$: C, 73.43; H, 7.80. Found: C, 73.55; H, 7.81.

Oxidation of *exo-cis*-Bicyclo[3.3.0]octan-2-ol.—*exo-cis*-Bicyclo[3.3.0]octan-2-ol (0.101 g.) was dissolved in a solution of 15 ml. of reagent grade acetone, 1.5 ml. of water and one drop of glacial acetic acid. To this solution was added in one portion 0.605 g. of *N*-bromosuccinimide. The solution quickly turned pale yellow, then orange, then red, and after 4.5 hr. at room temperature became colorless again. Saturated sodium bicarbonate solution was added to neutralize the acid, the solution filtered, and the filtrate concentrated to about 5 ml. This solution was extracted with five 5-ml. portions of chloroform, which were combined, dried over magnesium sulfate and concentrated. The residual oil was taken up in 3 ml. of absolute ethanol and treated with 2,4-dinitrophenylhydrazine in ethanolic phosphoric acid. The crystalline product (0.244 g., 98%) was collected on a filter, air-dried, and then passed over 6 g. of activity II alumina in chloroform solution to remove excess 2,4-dinitrophenylhydrazine. The eluted product was recrystallized twice from ethanol and then had m.p. 111.2–

113.6°, undepressed by admixture with an authentic sample.⁵

***exo*- and *endo-cis*-Bicyclo[3.3.0]octan-2-ol *p*-Nitrobenzenesulfonates.**⁹—To a solution of 1.0 g. of the alcohol in 15 ml. of pyridine was added a 20% molar excess of *p*-nitrobenzenesulfonyl chloride at 0°, and the mixture was stored at 5° for 18 hr. The solution was poured onto 100 g. of ice, and the precipitate was collected on a filter, washed with water and dried at 0.02 mm. Recrystallization from warm 95% ethanol (prolonged heating was avoided) or hexane afforded the *p*-nitrobenzenesulfonate as prisms.

endo-p-Nitrobenzenesulfonate, m.p. 75°. *Anal.* Calcd. for $\text{C}_{14}\text{H}_{17}\text{O}_6\text{NS}$: C, 54.17; H, 5.52; N, 4.51. Found: C, 54.53; H, 5.72; N, 4.55.

exo-p-Nitrobenzenesulfonate, m.p. 77.8–78.0°. *Anal.* Calcd. for $\text{C}_{14}\text{H}_{17}\text{O}_6\text{NS}$: C, 54.17; H, 5.52; N, 4.51. Found: C, 54.36; H, 5.58; N, 4.48.

Attempted Epimerization of *exo-cis*-Bicyclo[3.3.0]octan-2-ol.—*exo-cis*-Bicyclo[3.3.0]octan-2-ol (0.50 g.) was treated with a 20% molar excess of *p*-toluenesulfonyl chloride in 5 ml. of pyridine at 0° for 20 hr. The solution was poured into 50 ml. of water and extracted with three 20-ml. portions of benzene. The combined extracts were washed with cold dilute hydrochloric acid, water and saturated sodium bicarbonate solution. The solvent was distilled and the residue heated under reflux for 24 hr. with a solution of 1.3 g. of tetraethylammonium acetate in 20 ml. of acetone. The solvent was distilled, 50 ml. of water added and the product extracted with three 20-ml. portions of ether. After evaporation of the ether, the residue was heated under reflux for 15 min. with a solution of 0.7 g. of potassium hydroxide in 30 ml. of methanol. The solvent was distilled, 20-ml. of water added and the product extracted with three 20-ml. portions of ether. The combined extracts were dried and concentrated; the residue on distillation afforded only olefinic hydrocarbon, b.p. 50–82° (22 mm.), n_D^{25} 1.4742, totaling 0.165 g. (positive unsaturation test with potassium permanganate). The infrared spectrum showed bands at 3030 (olefinic hydrogen) and at 1645 cm^{-1} (carbon-carbon double-bond stretching).

(9) We are indebted to Dr. T. Y. Shen for the preparation of these derivatives.

CAMBRIDGE, MASSACHUSETTS

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

Proximity Effects. XIV. The Reaction of *cis*- and *trans*-Cyclodecene Oxide with Lithium Diethylamide

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cis- and *trans*-Cyclodecene oxides were prepared from the corresponding olefins and treated with lithium diethylamide. *trans*-Cyclodecene oxide yielded 2-cyclodecen-1-ol and *cis-trans*-1-decalol. *cis*-Cyclodecene oxide yielded 2-cyclodecen-1-ol, *cis-cis*-1-decalol and an alcohol, $\text{C}_{10}\text{H}_{18}\text{O}$, which was shown to be a *cis*-bicyclo[5.3.0]decan-2-ol. The alcohol is assigned the *endo-cis* configuration because it also could be obtained by catalytic reduction of bicyclo[5.3.0]dec-1(7)-en-2-one.

Following the discovery that intramolecular alkylation or "bridging" occurs in the reaction of *cis*- and *trans*-cyclooctene oxides with strong bases,² the reaction of *cis*- and *trans*-cyclodecene oxides with lithium diethylamide was investigated to determine whether similar reactions occurred.

trans-Cyclodecene was prepared in 89% yield by the thermal decomposition of *N,N*-dimethylcyclodecylamine oxide.³ Although the infrared spectrum of the product was identical with the pub-

lished spectrum,⁴ vapor-phase chromatography showed that it contained 5.5% of the *cis* isomer. Extraction with 15% aqueous methanolic silver nitrate furnished *trans*-cyclodecene of 99.2–99.4% purity (*cis*-cyclodecene is less soluble in silver nitrate than the *trans* isomer). The cyclodecene obtained by heating cyclodecanol with phthalic anhydride, previously reported to be the *trans* isomer,⁴ was found in this work to have an infrared spectrum indicating that it was composed of approximately 62% *trans*- and 38% *cis*-cyclodecene in one experiment. The product of another similar preparation was analyzed by vapor-phase chroma-

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