$n^{25}\text{D}$ 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.), $n^{25}\text{D}$ 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 $n^{25}\text{D}$ 1.4830–1.4831 were redistilled through the same column. The resulting epimer had b.p. 79° (5 mm.) and $n^{25}\text{D}$ 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 $n^{25}\text{D}$ 1.4883 was analyzed.

Anal. Calcd. for $C_8H_{14}O$: 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 $C_{15}H_{19}O_2N$: 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 $C_{14}H_{17}O_5NS$: 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 $C_{14}H_{17}O_5NS$: 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.), $n^{25}\text{D}$ 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).

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[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, $C_{10}H_{18}O$, 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*-cyclooötene 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 published 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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[1] (a) National Science Foundation Fellow, 1955–1957; (b) American Cyanamid Co. Fellow, 1955–1956.

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

[3] A. C. Cope, D. C. McLean and N. A. Nelson, *ibid.*, **77**, 1628 (1955).

[4] A. T. Blomquist, R. E. Burge, Jr., and A. C. Sucsy, *ibid.*, **74**, 3636 (1952).

tography and found to contain 69% of *trans*- and 31% of *cis*-cyclodecene. A sample of this product after further heating with phthalic acid and phthalic anhydride was found to contain 62.8% *trans*- and 37.2% *cis*-cyclodecene. Evidently the rate of addition of the cyclodecanol to the molten phthalic anhydride is a critical factor in the composition of the product, since *trans*-cyclodecene partly isomerizes to the *cis*-olefin under the conditions of preparation by this method.

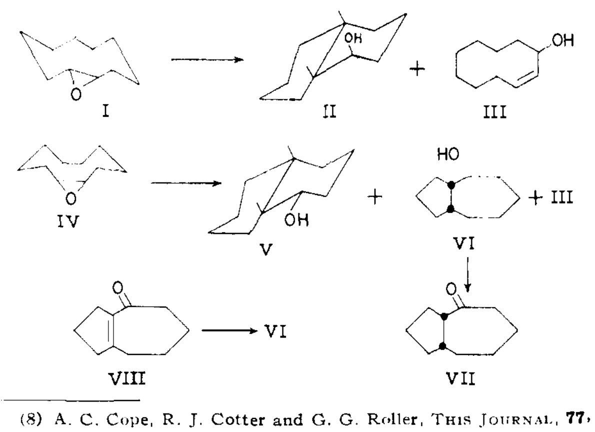
trans-Cyclodecene oxide[5] (I) was prepared in 83% yield from the pure olefin and 40% peracetic acid. The products obtained by heating the *trans*-oxide I with lithium diethylamide in boiling benzene were separated by chromatography on alumina, followed by crystallization. In this way two crystalline alcohols were isolated in relative amounts of 36% and 64%: II, $C_{10}H_{18}O$, m.p. 47.8–49.8°; and III, $C_{10}H_{18}O$, m.p. 50.4–51.4°. The major product III proved to be unsaturated, and on quantitative hydrogenation formed cyclodecanol. The alcohol III was identified as 2-cyclodecen-1-ol by comparison with an authentic sample prepared from cyclodecene by treatment with N-bromosuccinimide followed by silver acetate and saponification. The two samples had infrared spectra that were identical within experimental error, and formed identical *p*-nitrobenzoates (mixed m.p.). This alcohol previously had been reported as a liquid[6]; it is possible that the sample derived from I crystallized because it is formed as a single geometric isomer. The infrared spectrum of III suggests that the double bond is *trans* (strong absorption at 997 cm.$^{-1}$), but this assignment is only tentative.

The minor product II was a saturated secondary alcohol, which was oxidized by chromium trioxide in pyridine to *cis*-1-decalone, identified by comparison of the infrared spectrum with the spectrum of an authentic sample prepared by the oxidation of *cis-cis*-1-decalol (V) with the same reagent. Since the alcohol II was not identical with V (depression in mixed m.p.), it must be *cis-trans*-1-decalol. This conclusion was supported by preparation of the acid phthalate, m.p. 138.8–140.0°, in close agreement with the reported m.p. of 142°.[7] An attempt to prepare an authentic sample of *cis-trans*-1-decalol by treating *cis-cis*-1-decalyl-*p*-toluenesulfonate with tetraethylammonium acetate was unsuccessful, for elimination rather than displacement occurred and the product was 1,9-octalin. Reduction of *cis*-1-decalone with sodium borohydride gave a quantitative yield of *cis-cis*-1-decalol.

cis-Cyclodecene was prepared by the acid-catalyzed rearrangement of the *trans* isomer.[3,4] Vapor-phase chromatography showed that the product contained approximately 7% of *trans*-cyclodecene in addition to small amounts of *cis*- and *trans*-decalin. This mixture was enriched in the *cis*-olefin by two extractions with 15% aqueous methanolic silver nitrate, yielding a product containing less than 2% of *trans*-cyclodecene. *cis*-Cyclodecene oxide[5] was prepared from the olefin and 40% peracetic acid, and treated with lithium diethylamide in the same manner as the *trans* isomer. The products, separated by chromatography on alumina, were 9% of an oil (VI) that formed a crystalline *p*-nitrobenzoate with an elementary analysis corresponding to a derivative of an alcohol, $C_{10}H_{18}O$; 75% of crystalline *cis-cis*-1-decalol (V), identified by comparison with an authentic sample[8] (mixed m.p. and infrared spectra); and finally 16% of an oil that was identified by its infrared spectrum as a mixture of V and 2-cyclodecen-1-ol (III).

The alcohol VI was shown to be homogeneous by vapor-phase chromatography and gave a negative unsaturation test with tetranitromethane. Oxidation with the chromic anhydride–pyridine complex yielded an oily ketone that formed a 2,4-dinitrophenylhydrazone (m.p. 218.2–220° dec.) which was identical with the higher-melting derivative of cyclopentanocycloheptanone[9] (bicyclo[5.3.0]decan-2-one (VII), bridgehead configuration unknown). The alcohol VI was also obtained by catalytic reduction of bicyclo[5.3.0]dec-1(7)-en-2-one[10] (VIII) in the presence of platinum in ethanol. Thus alcohol VI may be assigned the structure *endo-cis*-bicyclo[5.3.0]decan-2-ol. The *cis* nature of catalytic reduction ensures that the ring fusion is *cis*, and in analogy with the catalytic reduction of *cis*-bicyclo[3.3.0]octan-2-one,[11] it is believed that the hydroxyl group is on the opposite side of the rings from hydrogen atoms at the point of ring fusion.

Formation of the epimeric *cis*-1-decalols from the reaction of *cis*- and *trans*-cyclodecene oxide with lithium diethylamide may be explained as a transannular alkylation at C_1 by an intermediate carbanion formed at sterically adjacent C_6 by loss of a proton, or as proceeding through a "carbene," as described for the analogous reactions of *cis*- and *trans*-cycloöctene oxide. However, if the latter route represents the correct mechanism, it should be noted that the entire process must be concerted, for an intermediate carbanion with the charge at



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[5] V. Prelog, K. Schenker and H. H. Gunthard, *Helv. Chim. Acta*, **35**, 1598 (1952).

[6] V. Prelog and K. Schenker, *ibid.*, **35**, 2045 (1952).

[7] W. Hückel, R. Danneel, A. Gross and H. Naab, *Ann.*, **502**, 99 (1933); these investigators report a higher melting point (55°) for *cis-trans*-1-decalol than was observed in the present work.

[8] A. C. Cope, R. J. Cotter and G. G. Roller, THIS JOURNAL, **77**, 3594 (1955).

[9] A. C. Cope and G. Holzman, *ibid.*, **72**, 3062 (1950).

[10] W. Hückel and A. Schnitzspahn, *Ann.*, **505**, 274 (1933).

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

the point of ring fusion adjacent to the hydroxyl group would be expected to form the more stable *trans*-decalin ring system rather than the observed *cis*-decalin derivatives.

Formation of bicyclo[5.3.0]decan-2-ol from the reaction of *cis*-cyclodecene oxide with lithium diethylamide can be explained in a similar fashion, *i.e.*, a transannular alkylation at C_1 by an intermediate carbanion formed at C_5. It is significant that both bicyclic alcohols (V and VI) formed from the *cis*-oxide have the same stereochemical configuration, indicative of a similar concerted mechanism in the formation of both.

Experimental[12]

2-Cyclodecen-1-ol (III).—A mixture of 15.0 g. of cyclodecanol[4] and 30 g. of phthalic anhydride was pyrolyzed according to the procedure of Blomquist, Burge and Sucsy.[4] The product obtained by distillation through a 30-cm. Vigreux column was 11.3 g. (88%) of a colorless liquid, b.p. 82–85° (22 mm.), n^{25}_{D} 1.4790, with an infrared spectrum indicating it to be a mixture of approximately 38% of *cis*- and 62% of *trans*-cyclodecene.

To a solution of 1.50 g. of the mixture of *cis*- and *trans*-cyclodecene described above in 10 ml. of carbon tetrachloride was added 1.95 g. of N-bromosuccinimide and 0.04 g. of benzoyl peroxide, and the mixture was refluxed on a steam-bath for 1 hr. The solid was separated by filtration and washed with two 5-ml. portions of carbon tetrachloride. The combined washings and filtrate were shaken first with 15 ml. of 5% sodium bicarbonate solution, then with two 15-ml. portions of water, and concentrated. The residue was dissolved in 5 ml. of glacial acetic acid and a suspension of 3.0 g. of silver acetate in 15 ml. of glacial acetic acid was added with stirring and cooling. The mixture was allowed to stand overnight and then was filtered to separate the silver bromide, which was washed with 10 ml. of acetic acid. The combined filtrates were concentrated under reduced pressure (15–20 mm.) and the residue was added to a solution of 5.0 g. of potassium hydroxide in 8 ml. of water and 8 ml. of methanol. The solution was allowed to stand for 12 hr. with occasional shaking and then was diluted with 50 ml. of water and extracted with four 20-ml. portions of ether. The ether extracts were dried and the residue after removal of the solvent was distilled through a semimicro column yielding 0.673 g. (40%) of 2-cyclodecen-1-ol, b.p. 80° (1 mm.), n^{25}_{D} 1.5020.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.65; H, 11.79.

2-Cyclodecen-1-ol *p*-nitrobenzoate was prepared from the alcohol and *p*-nitrobenzoyl chloride in pyridine and melted at 151.4–152.4° (lit.[6] m.p. 152°) after three recrystallizations from aqueous methanol.

***trans*-Cyclodecene.**—*trans*-Cyclodecene was prepared by decomposition of dimethylcyclodecylamine oxide.[3] A yield of 89% of a liquid, b.p. 77° (13 mm.), n^{25}_{D} 1.4792–1.4798, was obtained. The infrared spectrum of the liquid was identical with the published spectrum of *trans*-cyclodecene.[4] However, vapor-phase chromatography over a column of silver nitrate in diethylene glycol at 100° with helium as the eluent showed it to be a mixture of 94.5% *trans*-cyclodecene and 5.5% of *cis*-cyclodecene. The crude *trans*-cyclodecene was purified as follows.

To 250 g. of an aqueous solution of 30% silver nitrate was added an equal weight of methanol and 24.0 g. of crude *trans*-cyclodecene. The mixture was shaken for 10 min. and the small amount of precipitate that formed was separated by filtration. The filtrate was extracted with two 120-ml. portions of pentane, concentrated under reduced pressure to a smaller volume (*ca.* 400 ml.), and added with stirring to 200 ml. of concentrated ammonium hydroxide solution at 0°. The ammoniacal solution was extracted with four 150-ml. portions of pentane. The pentane solutions were combined, washed with 125 ml. of water and dried over anhydrous magnesium sulfate. The residue, after removal of the solvent, was distilled through a semimicro column, giving 4.85 g. (20%) of *trans*-cyclodecene, b.p. 77° (13 mm.), n^{25}_{D} 1.4792, with an infrared spectrum identical with the spectrum of the crude product. However, vapor-phase chromatography showed that it was 99.4% pure. From the original pentane extracts and the solid silver nitrate complex there was also recovered 16.5 g. (68%) of crude *trans*-cyclodecene, n^{25}_{D} 1.4740. Purification of this olefin by the same procedure, but with three extractions of the silver nitrate solution with 40-ml. portions of pentane gave a further 7.0 g. of *trans*-cyclodecene of 99.2% purity.

***trans*-Cyclodecene Oxide (I).**[5]—To 7.2 g. of *trans*-cyclodecene (99.3% purity) at 5° was added, with stirring over a period of 45 min., 20 ml. of 40% peracetic acid to which 2 g. of anhydrous sodium acetate had been added to neutralize the sulfuric acid present. The reaction mixture was stirred for an additional period of 2 hr. at 10–20° and allowed to remain at room temperature overnight. The solution was cooled to 0° and 40% sodium hydroxide was added dropwise, with stirring, until the mixture became basic to litmus. The mixture was extracted with four 100-ml. portions of ether. The ether solutions were combined, dried and concentrated. The residue was distilled through a 30-cm. spinning-band column, yielding 6.66 g. (83%) of *trans*-cyclodecene oxide, b.p. 94° (6 mm.), n^{25}_{D} 1.4780–1.4783, with an infrared spectrum identical with the published spectrum.[5]

Reaction of *trans*-Cyclodecene Oxide (I) with Lithium Diethylamide.—A mixture of 6.50 g. (0.0417 mole) of *trans*-cyclodecene oxide and lithium diethylamide (0.14 mole based on *n*-butyllithium) in benzene was refluxed under an atmosphere of nitrogen for 42 hr. and the products, 6.40 g. of liquid, b.p. 85–93° (2.5 mm.), were isolated in the manner described for the products of reaction of *cis*-cycloöctene oxide with lithium diethylamide.[2]

Chromatography of the products over 450 g. of alumina of Grade II activity gave as a single band eluted by ether 2.28 g. of an oil, followed by 3.68 g. of a solid that gave a positive test for unsaturation with bromine and melted at 47.4–49.2° after sublimation at 100° (15 mm.). Recrystallizations of the solid from petroleum ether (30–60°) gave a product, m.p. 50.4–51.4°, which was shown to have the composition $C_{10}H_{18}O$ by elemental analysis.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.64; H, 11.76.

Quantitative hydrogenation of the solid (described below) yielded cyclodecanol. The solid was identified as 2-cyclodecen-1-ol (III) by comparison of its infrared spectrum with the spectrum of the authentic sample described above. Additional evidence of the identity of the two compounds was supplied by the fact that a mixed melting point of their *p*-nitrobenzoates showed no depression.

The first two fractions (1.09 g.) of the minor product, 2.28 g. of an oil, were found by inspection of their infrared spectra to be an alcohol II different from III, while the infrared spectrum of the rest of the material (1.19 g.) indicated that it was II contaminated with about 12% of III. The alcohol II was crystallized from petroleum ether (30–60°) at 5° and had m.p. 47.8–49.8°, which was not raised by further recrystallization. The acid phthalate of II, prepared by heating a mixture of II and phthalic anhydride at 100–110° for 3 hr., melted at 138.8–140° after several recrystallizations from aqueous methanol. It corresponded in analysis to the acid phthalate of an alcohol possessing the molecular formula $C_{10}H_{18}O$.

Anal. Calcd. for $C_{18}H_{22}O_4$: C, 71.49; H, 7.33. Found: C, 71.62; H, 7.52.

Saponification of the acid phthalate by 40% aqueous methanolic potassium hydroxide regenerated II as a solid which crystallized slowly from petroleum ether (30–60°) at 5° and melted at 48–50°. Further recrystallization did not change the melting point.

Oxidation of II with chromium trioxide in pyridine and isolation of the ketone according to the procedure described below for the preparation of *cis*-1-decalone was found to give *cis*-1-decalone, identified by comparison of its infrared spectrum with that of the authentic ketone. Since admixture of II with a sample of *cis-cis*-1-decalol formed an oil, II is *cis-trans*-1-decalol.

Hydrogenation of 2-Cyclodecen-1-ol (III).—A solution of 172.8 mg. of III in 15 ml. of absolute ethanol was hydrogenated at room temperature in the presence of 80 mg. of prereduced platinum oxide with the absorption of 94% of

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

one equivalent of hydrogen in 3.5 hr. The solution was filtered and the solvent removed under reduced pressure (20 mm.). The residue was sublimed, yielding 165 mg. of cyclodecanol, m.p. 39.4–40.2° (lit.[13] m.p. 40–41°), identified by its *p*-nitrobenzoate, m.p. 114.6–115.2° (lit.[13] m.p. 116°) after three recrystallizations from methanol.

2-Cyclodecen-1-ol Phenylurethan.—A mixture of 81 mg. of 2-cyclodecen-1-ol (III), obtained from the reaction of *trans*-cyclodecene oxide with lithium diethylamide, and 100 mg. of phenyl isocyanate was heated on a steam-bath for 10 min. and allowed to stand overnight at room temperature. After removal of excess phenyl isocyanate at 50° and 0.1 mm., the residue was crystallized from aqueous methanol to give 120 mg. of the phenylurethan, m.p. 93–95°. An analytical sample was prepared by further recrystallization from aqueous methanol and melted at 94–95°.

Anal. Calcd. for $C_{17}H_{23}NO_2$: C, 74.96; H, 8.48; N, 5.12. Found: C, 75.01; H, 8.78; N, 5.17.

***cis*-Cyclodecene.**—A mixture of *cis*- and *trans*-cyclodecene (10.0 g., 0.0725 mole) was isomerized by treatment with β-naphthalenesulfonic acid (100 mg.).[3] Distillation through a semimicro column gave 8.30 g. (83%) of a liquid, b.p. 75–76° (15 mm.), n^{25}D 1.4820, identified as *cis*-cyclodecene by comparison of its infrared spectrum with the published spectrum of *cis*-cyclodecene. Analysis of this sample by vapor-phase chromatography showed the presence of 5–10% of the *trans* isomer and small amounts of *cis*- and *trans*-decalin, the formation of which had been observed earlier.[3] This mixture was enriched in the *cis*-olefin by two extractions with 15% aqueous methanolic silver nitrate solution, after which it contained less than 2% of *trans*-cyclodecene.

Isomerization of *trans*-Cyclodecene with Phthalic Anhydride and Phthalic Acid.—Cyclodecene (1.00 g.), containing 69% *trans*-cyclodecene and 31% *cis*-cyclodecene, was heated in a bath at 290° for 2 hr. with 0.20 g. of phthalic anhydride and 0.1 g. of phthalic acid. The product was taken up in pentane and washed with several portions of cold 20% potassium hydroxide solution. Distillation of the product and subsequent analysis by vapor-phase chromatography showed that the product consisted of 62.8% *trans*-cyclodecene and 37.2% *cis*-cyclodecene.

***cis*-Cyclodecene Oxide (IV).**—*cis*-Cyclodecene oxide was prepared by epoxidation of *cis*-cyclodecene (10.0 g.) with 40% peracetic acid (23 ml.) according to the procedure described above for the preparation of *trans*-cyclodecene oxide. The crude epoxide was separated from the accompanying decalin by distillation through a 30-cm. spinning-band column, which yielded 9.96 g. (90%) of *cis*-cyclodecene oxide, b.p. 99° (8 mm.), n^{25}D 1.4814 (lit.[5] b.p. 105° at 11 mm., n^{20}D 1.4847).

Reaction of *cis*-Cyclodecene Oxide with Lithium Diethylamide.—A mixture of 5.20 g. (0.09337 mole) of *cis*-cyclodecene oxide and lithium diethylamide (0.0992 mole, based on *n*-butyllithium) in 150 ml. of dry benzene was refluxed for 72 hr. under an atmosphere of nitrogen and the products, 4.26 g. of an oil, b.p. 116–120° (7 mm.), were separated in the manner described for the products of the reaction of *cis*-cyclooöctene oxide with the same base.[2]

The oil partially solidified at 5° and addition of a small amount of petroleum ether (30–60°) caused more precipitation. The solid was collected on a filter and washed thoroughly with two 10-ml. portions of 30–60° petroleum ether. In this way there was obtained 0.90 g. of crystalline material, m.p. 90–92°, which on recrystallization from hexane followed by sublimation melted at 93.0–93.4° and was identified as *cis-cis*-1-decalol (V) by mixed melting point and comparison of the infrared spectrum with the spectrum of an authentic sample.

The combined filtrates were concentrated and the residue, 3.20 g. of an oil, was chromatographed over 150 g. of alumina of Grade II activity. There was first eluted by 30% ether in petroleum ether (30–60°) 0.276 g. of an oil VI that formed a *p*-nitrobenzoate, m.p. 100.6–101.2° after several recrystallizations from aqueous methanol, which analyzed for the corresponding derivative of an alcohol, $C_{10}H_{18}O$.

Anal. Calcd. for $C_{17}H_{21}NO_4$: C, 67.30; H, 6.98; N, 4.62. Found: C, 67.44; H, 7.11; N, 4.72.

Next was eluted by the same solvent 2.33 g. of a solid identified as *cis-cis*-1-decalol (V) by its melting point and mixed melting point with an authentic sample, and finally, eluted by 30–60% ether in petroleum ether (30–60°), there was obtained 0.50 g. of oil with an infrared spectrum which indicated that it was a mixture of approximately equal parts of V and 2-cyclodecen-1-ol (III). From a weight balance of the chromatographic fractions, the yields of the various products from the reaction of *cis*-cyclodecene oxide with lithium diethylamide were calculated as: the alcohol VI, $C_{10}H_{18}O$, 9%; *cis-cis*-1-decalol, 83%; and 2-cyclodecen-1-ol, 8%.

Chromic Anhydride–Pyridine Oxidation of Bicyclo[5.3.0]-decan-2-ol (VI).—Chromic anhydride (0.3 g.) was added in small portions to 3 ml. of anhydrous pyridine at 15–20° and shaken until the yellow complex separated.[14] To the complex was added 0.20 g. of VI in 2 ml. of dry pyridine. The mixture was allowed to stand overnight with occasional shaking, diluted with 40 ml. of ice-water, and filtered through a mat of Super-Cel. The aqueous solution was extracted with four 40-ml. portions of ether, which were combined and washed with several portions of 2% hydrochloric acid and dilute sodium bicarbonate solution. After drying, concentration under reduced pressure yielded 0.31 g. of an oil which was treated with 0.30 g. of 2,4-dinitrophenylhydrazine in ethanolic sulfuric acid. The derivative, 0.34 g. (80%), was collected on a filter and had m.p. 183–191° dec. After four recrystallizations from ethanol it had m.p. 218.2–220° dec. (lit.[9] m.p. 219–220°), undepressed on admixture with an authentic sample of the 2,4-dinitrophenylhydrazone of cyclopentanocycloheptanone. The infrared spectra also were identical.

Catalytic Reduction of Bicyclo[5.3.0]dec-1(7)-en-2-one (VIII).—The ketone VIII was prepared from cyclodecan-1,6-dione.[10] Bicyclo[5.3.0]dec-1(7)-en-2-one (1.34 g.) was reduced catalytically in 20 ml. of ethanol in the presence of 0.2 g. of platinum oxide at 100° and 100 atm. The oily product was treated with *p*-nitrobenzoyl chloride in pyridine, forming a crude derivative, m.p. 90–94°. Two recrystallizations from aqueous methanol gave crystals of m.p. 99.8–100.6°. A mixed melting point with the *p*-nitrobenzoate of the alcohol VI isolated from the reaction of *cis*-cyclodecene oxide with lithium diethylamide was 100–101.2°. The infrared spectra of the two *p*-nitrobenzoates were identical.

Oxidation of *cis-cis*-1-Decalol.—To the chromium trioxide–pyridine complex[14] prepared from 300 mg. of chromium trioxide and 3 ml. of dry pyridine was added a solution of 200 mg. of V in 2 ml. of dry pyridine. The reaction mixture was shaken thoroughly, then stoppered and allowed to stand at room temperature overnight. The mixture was poured into 40 ml. of ice and water and extracted with four 25-ml. portions of ether. The combined extracts were washed first with 15% acetic acid solution, then with dilute sodium bicarbonate solution and finally with water. The solvent was removed under reduced pressure (20 mm.), and the liquid residue was shaken overnight with 5 ml. of saturated sodium bisulfite solution. The precipitate was collected on a filter, washed with three 20-ml. portions of ether, and added to 50 ml. of saturated sodium carbonate solution. The mixture was extracted with four 50-ml. portions of ether. The ethereal solutions were washed with water, dried and concentrated. A short-path distillation of the residue gave 102 mg. of a liquid with an infrared spectrum showing no absorption at 810, 900 and 1200 cm.$^{-1}$ where *trans*-1-decalone[7,15] absorbs strongly.

***cis-cis*-1-Decalol (V).**—To a stirred solution of 300 mg. of sodium borohydride in 5 ml. of methanol was added 1.10 g. of *cis*-1-decalone in 3 ml. of methanol at such a rate that the methanol refluxed gently. After the addition was complete, the solution was allowed to stand at room temperature for a further period of 2 hr. and then concentrated to dryness under reduced pressure. The solid residue was stirred for 15 min. with 30 ml. of 10% hydrochloric acid, collected by filtration, washed with water and dried. A yield of 0.968 g. (88%) of *cis-cis*-1-decalol, m.p. 88–90°, was obtained, which after one recrystallization from petroleum ether (30–60°) melted at 91–92° and did not depress the melting point of a sample prepared by the method of Hückel, Danneel, Gross and Naab.[7]

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[13] M. Kobelt, P. Barman, V. Prelog and L. Ruzicka, *Helv. Chim. Acta*, **32**, 256 (1949).

[14] G. I. Poos, G. E. Arth, R. E. Beyler and L. H. Sarett, THIS JOURNAL, **75**, 422 (1953).

[15] C. D. Gutsche and H. H. Peter, *ibid.*, **77**, 5933 (1955)

Attempted Epimerization of *cis-cis*-1-Decalol.—A solution of 6.0 g. of *cis-cis*-1-decalol in 15 ml. of dry pyridine was cooled to 0° and 8 g. of *p*-toluenesulfonyl chloride was added. The mixture was stored at 5° for 18 hr., then poured into 100 ml. of ice and water. The precipitate was collected by filtration, washed first with 10% sodium bicarbonate solution, then with water and dried. The tosylate (10.3 g.) melted at 95–97° without further purification (lit.[7] m.p. 96–98° dec.). It was dissolved in 50 ml. of acetone (reagent grade), to which was added 6 g. of potassium acetate and 10 g. of tetraethylammonium acetate monohydrate, and the mixture was heated under reflux for 40 hr. The solid was removed by filtration and washed thoroughly with acetone. The filtrate was concentrated to a sirupy residue, which was diluted with 200 ml. of water and extracted with three 100-ml. portions of petroleum ether (30–60°). Removal of the solvent left a liquid residue that was dissolved in 10 ml. of methanol and heated on a steam-bath for 20 min. with 10 ml. of 40% potassium hydroxide solution. The mixture was added to 100 ml. of water and extracted with four 75-ml. portions of ether. The ether solutions were combined, dried, and concentrated. The residue was distilled through a semimicro column giving 3.04 g. of 1,9-octalin, b.p. 83° (18 mm.), $n^{25}D$ 1.4945, with an infrared spectrum identical with the spectrum of an authentic sample.[7]

***trans-trans*-1-Decalol.**—*trans-trans*-1-Decalol was prepared according to the procedure of Dauben, Tweit and Mannerskantz.[16] The infrared spectrum of the *trans-trans*-1-decalol showed a band of medium intensity at 950 cm.$^{-1}$ which is not present in the spectrum of *cis-trans*-1-decalol (II). The acid phthalate of the *trans-trans*-1-decalol melted at 166.8–168° (lit.[6] m.p. 167°) after several recrystallizations from aqueous methanol.

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[16] W. G. Dauben, R. C. Tweit and C. Mannerskantz, THIS JOURNAL, **76**, 4421 (1954).

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

Proximity Effects. XV. The Reaction of Phenylmagnesium Bromide with Methyl Cycloöctene-1-carboxylate

BY ARTHUR C. COPE AND MORTON BROWN[1]

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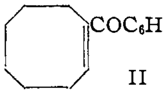
Addition of phenylmagnesium bromide to methyl cycloöctene-1-carboxylate has been shown to yield, besides the expected normal products, phenyl 2-phenylcycloöctyl ketone and methyl 2-phenylcycloöctane carboxylate, an abnormal product which has been shown by degradation and synthesis to be phenyl *endo-cis*-bicyclo[3.3.0]oct-2-yl ketone.

Certain reactions of medium-sized ring compounds have been shown to give rise to abnormal reaction products,[2] the formation of which has been ascribed to a "proximity effect" due to the conformation of the ring, which brings atoms that are unreactive by classical theory in such close proximity to the reactive center that they participate in the reaction.

Using the concept that development of a partial or full positive charge on one of the ring carbon atoms was responsible for the hydride ion shift that characterizes the transannular reaction that occurs in the solvolysis of epoxides with medium-sized carbocyclic rings, we have investigated another reaction in which a partially positively charged center is generated to determine whether a transannular reaction would occur. The reaction investigated was the addition of phenylmagnesium bromide to methyl cycloöctene-1-carboxylate (I). In such a case the incipient positive charge would be developed at the β-position in the conjugated system.

Methyl cycloöctene-1-carboxylate (I) was prepared from the crystalline acid[3] and treated with a 10% molar excess of phenylmagnesium bromide at −10°. The product, a yellow oil, was separated by means of Girard Reagent T into a "ketonic" fraction (approximately 1% yield) and a much larger "non-ketonic" fraction. The oily ketone was not analytically pure, but its infrared spectrum showed carbonyl absorption at 1667 cm.$^{-1}$ characteristic of a substituted acetophenone.[4] Analytical data on the crystalline 2,4-dinitrophenylhydrazone, m.p. 153.4–154.2°, indicated that it had the molecular formula $C_{21}H_{22}N_4O_4$. One possible structure considered for this ketone was phenyl 1-cycloöctenyl ketone (II). However, an independent synthesis of this ketone from 1-cycloöctenoyl chloride and diphenylcadmium gave a product which formed a 2,4-dinitrophenylhydrazone that was not identical with the corresponding derivative of the ketone isolated from the Grignard reaction.



II

The ketone formed from methyl cycloöctene-1-carboxylate subsequently was shown to be a phenyl *cis*-bicyclo[3.3.0]oct-2-yl ketone by a modified Barbier–Wieland degradation, involving in the final step oxidative cleavage to the known *cis*-bicyclo[3.3.0]octan-2-one (III), identified as the 2,4-dinitrophenylhydrazone. Determination of the configuration of the benzoyl group (*endo* or *exo*) relative to the hydrogen atoms at the point of ring fusion was accomplished by the synthesis of the epimeric ketones IV and V.

The "non-ketonic" fraction mentioned above partially crystallized on refrigeration to give a ketone, $C_{21}H_{24}O$, m.p. 135.5–136.5°. Although a crystalline 2,4-dinitrophenylhydrazone could not be obtained from this ketone by any of the usual methods, the infrared spectrum with absorption at 1667 cm.$^{-1}$ and the ultraviolet spectrum with a maximum at 243 mμ (ϵ_{max} 11,200, ethanol) gave evidence for the presence of a benzoyl group.[5] This ketone was shown to be phenyl 2-phenylcycloöctyl ketone (VI) by the same type of degrada-

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[1] National Science Foundation Fellow, 1955–1957.

[2] A. C. Cope, M. Brown and H. H. Lee, THIS JOURNAL, **80**, 2855 (1958), and preceding papers in this series and references cited therein.

[3] A. C. Cope, M. Burg and S. W. Fenton, *ibid*, **74**, 173 (1952).

[4] A. H. Soloway and S. L. Friess, *ibid.*, **73**, 5000 (1951); R. P. Barnes and G. E. Pinkney, *ibid.*, **75**, 479 (1953).

[5] M. Pestemer and E. Mayer-Pitsch, *Monatsh.*, **70**, 104 (1937).