for iodide ion, was concentrated under reduced pressure. The residue was heated for 4 hours at 0.8 mm.: decomposition of the quaternary base began at 70°, and the temperature gradually was raised to 125°. The distillate and residue were combined and treated with aqueous sodium hydroxide. The product was extracted with ether and distilled; the yield was 0.63 g. (37%) of a mixture of amines, b.p. 74–82° (2.5 mm.), $n^{25}\mathrm{D}$ 1.4914–1.4920. Analyses and the isolation of the two picrates described below showed that the mixture contained the normal product formed by Hofmann exhaustive methylation, 5-cyclodecen-1-yldimethylamine (XI). The tertiary amine IX formed by elimination of methanol from the quaternary base is believed to be the other component of the mixture, but it was not isolated.

5-Cyclodecen-1-yldimethylamine picrate was prepared from the mixture of amines described above and picric acid in ethanol and purified by recrystallization from ethanol to a constant melting point of 140–141.8°.

Anal. Calcd. for $C_{18}H_{26}N_4O_7$: C, 52.67; H, 6.39; N, 13.65. Found: C, 52.70, H, 6.59; N, 13.55.

Cyclodecyldimethylamine Picrate.—A solution of 0.326 g. of the mixture of amines described above in 5 ml. of glacial acetic acid was hydrogenated in the presence of 0.125 g. of prereduced platinum oxide. Absorption of hydrogen amounted to 67% of one molar equivalent, indicating that the mixture contained XI and IX in an approximate ratio of 2:1. Addition of picric acid in ethanol and recrystallization of the picrate to constant melting point from the same solvent gave cyclodecyldimethylamine picrate, m.p. 145.8–147.4°, which did not depress the m.p. of an authentic sample prepared from cyclodecanone.[10]

6-Aminocyclodecanone (IV).—A solution of 0.338 g. of 11-azabicyclo[4.4.1]-1-undecene in 10 ml. of 10% hydrochloric acid was heated under reflux for 1 hour, cooled, made basic with sodium hydroxide and extracted continuously with ether overnight. The extract was dried over sodium sulfate, concentrated, and purified by a short-path distillation at 0.5 mm. with a heating block temperature of 100°. The viscous distillate was a mixture of the aminoketone IV with the unsaturated amine III formed by partial dehydration during distillation. Calcd. for $C_{10}H_{19}NO$: C, 70.96; H, 11.32. Found: C, 72.95; H, 11.28. Another short-path distillation of the distillate completed the dehydration and yielded 0.14 g. of III, $n^{25}\mathrm{D}$ 1.5153. The identity of III from this source was established by comparing its infrared spectrum with the spectrum of a sample formed as a by-product in the reduction of 6-hydroxycyclodecanone oxime with sodium and *n*-butyl alcohol.

6-Aminocyclodecanone Benzenesulfonamide.—A solution of 0.26 g. of III in 10 ml. of 10% hydrochloric acid was heated under reflux for 1 hour and then concentrated to dryness. Benzenesulfonyl chloride (0.58 g.) and 8 ml. of 10% aqueous sodium hydroxide were added to the residue, and the mixture was shaken for 15 minutes. Water was added until the solid dissolved, and the basic solution was acidified with hydrochloric acid. The semi-solid which precipitated was treated with decolorizing carbon in ethanol, and recrystallized three times from absolute ethanol to a constant melting point of 93.6–94.6°. The yield of the benzenesulfonamide was 86 mg.

Anal. Calcd. for $C_{16}H_{23}NO_3S$: C, 62.11; H, 7.49; N, 4.53. Found: C, 61.81; H, 7.53; N, 4.62.

The semicarbazone of 6-aminocyclodecanone benzenesulfonamide was prepared by heating a solution of 56 mg. of the sulfonamide, 27 mg. of semicarbazide hydrochloride and 28 mg. of sodium acetate in aqueous ethanol on a steam-bath for 15 minutes. The crystals of the semicarbazone that separated on cooling were recrystallized three times from aqueous ethanol, and melted at 171.4–173° dec.

Anal. Calcd. for $C_{17}H_{26}N_4O_3S$: C, 55.70; H, 7.15; N, 15.30. Found: C, 55.70; H, 7.22; N, 15.24.

11-Deuterio-11-azabicyclo[4.4.1]-1-undecene.—A 0.32-g. sample of III was added to 5 ml. of 99.5% deuterium oxide which had been made basic (*p*H approximately 11) with a small amount of anhydrous sodium carbonate. The mixture was shaken at room temperature for 7 hours and then the amine was extracted continuously with dry ether overnight. The extract was dried over sodium sulfate, concentrated, and the residue was purified by short-path distillation at 10 mm. The infrared spectrum of the 11-deuterio compound is shown in Fig. 1. In a control experiment, the amine III was recovered unchanged when it was subjected to the conditions described above using water in place of deuterium oxide.

CAMBRIDGE, MASSACHUSETTS

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

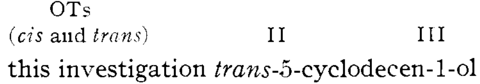
Proximity Effects. II. 1,9- and *cis*-1,2-Octalin from *trans*-5-Cyclodecen-1-yl *p*-Toluenesulfonate

BY ARTHUR C. COPE, ROBERT J. COTTER[1] AND GEORGE G. ROLLER[2]

RECEIVED JANUARY 24, 1955

trans-5-Cyclodecen-1-ol (VI) has been prepared from 6-aminocyclodecanol by the Hofmann exhaustive methylation procedure. Hydrogenation of the unsaturated alcohol VI in the presence of platinum yielded cyclodecanol, while with a palladium catalyst a mixture of cyclodecanol and cyclodecanone was produced, with hydrogen transfer from the carbinol group to the double bond of VI forming the saturated ketone. *trans*-5-Cyclodecen-1-yl *p*-toluenesulfonate (II) was heated with diethylaniline, and formed a mixture of *cis*-1,2- and 1,9-octalins, identified by their infrared spectra and by conversion to crystalline *cis*-glycols with osmium tetroxide. The occurrence of 1,6-bridging forming the octalin ring system rather than a double bond on elimination of *p*-toluenesulfonic acid from the tosylate II is explained by the spatial proximity of the double bond to the tosylate group, and is similar in some respects to the *iso*-steroid rearrangement.

Both stereoisomeric 1,6-cyclodecanediol di-*p*-toluenesulfonates have been shown to form mixtures of 1,9- and 9,10-octalin rather than cyclodecadienes on heating with diethylaniline.[3] If the elimination of *p*-toluenesulfonic acid from the ditosylates I occurs in two steps, the intermediate would be 5-cyclodecen-1-yl *p*-toluenesulfonate (II, *cis* or *trans*) or 9-decalyl *p*-toluenesulfonate (III, *cis* or *trans*), the first formed by a normal 1,2- and the second by 1,6-elimination of *p*-toluenesulfonic acid.



I (*cis* and *trans*) II III

In this investigation *trans*-5-cyclodecen-1-ol (VI) has been prepared, and the reaction of its *p*-toluenesulfonate (II) with diethylaniline has been studied. A mixture of the *cis* and *trans* isomers of 6-aminocyclodecanol, prepared by reduction of 6-hydroxycyclodecanone oxime,[4] was converted to a mixture

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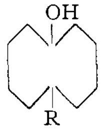
[1] American Cyanamid Co. Fellow, 1953–1954.

[2] Arthur D. Little Fellow, 1948–1949.

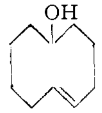
[3] A. C. Cope and G. Holzman, THIS JOURNAL, **72**, 3062 (1950).

[4] A. C. Cope, R. J. Cotter and G. G. Roller, *ibid.*, **77**, 3590 (1955).

of *cis*- and *trans*-6-dimethylaminocyclodecanol (IV, 80%) by treatment with formic acid and formaldehyde. The methiodide V was obtained from the tertiary amine and methyl iodide in 98% yield. Thermal decomposition of the corresponding quaternary base yielded 5-cyclodecen-1-ol (VI, 87%). The double bond in the unsaturated alcohol VI is believed to have the *trans* configuration; it was introduced by the Hofmann exhaustive methylation reaction, which is known to form *trans*-cyclodecene in the closely related thermal decomposition of cyclodecyltrimethylammonium hydroxide.[5] Moreover, the infrared absorption spectrum of VI (Fig. 1) shows the strong, characteristic absorption of a *trans*-olefin at 10.18 μ as well as less intense absorption at 14.18 μ that is characteristic of ten-membered cyclic hydrocarbons.[5]



IV, R = $N(CH_3)_2$
V, R = $N(CH_3)_3I$



VI

Evidence establishing the carbon skeleton and the presence of one double bond in the alcohol VI was obtained by quantitative reduction in the presence of Adams platinum catalyst in methanol, which resulted in the absorption of 97% of one molar equivalent of hydrogen and formed cyclodecanol. Unexpectedly, the hydrogenation of VI in the presence of a palladium catalyst in methanol or acetic acid resulted in absorption of only 64 to 76% of one molar equivalent of hydrogen, and only 39% of one equivalent when VI was stirred with the palladium catalyst in ethanol in a nitrogen atmosphere for 6.5 hours before hydrogenation. These results were shown to be due to partial conversion of VI to cyclodecanone in the presence of palladium by the showing of a strong carbonyl band at 5.85 μ in the infrared spectrum of the reduction product, and by its conversion to cyclodecanone semicarbazone in high yield. Reductions of olefins by alcohols, decalin or other relatively easily dehydrogenated compounds in the presence of hydrogenation catalysts have been observed previously.[6] The exceptional ease of such a reduction in the present case may be explained by the spatial proximity of the secondary alcohol and olefin groups in VI, favoring an intramolecular hydrogen transfer. Presumably a similar transfer occurs in the presence of platinum, but was not observed because the cyclodecanone formed was reduced to cyclodecanol with hydrogen and platinum.

trans-5-Cyclodecen-1-ol (VI) failed to yield a tosylate on treatment with *p*-toluenesulfonyl chloride and pyridine at room temperature, but did form a crystalline tosylate II that was isolated in 29% yield when the reaction was conducted at 0–5°, and in 45% yield with a reaction temperature of −10°. These results probably are explained by the rapidity with which the tosylate II reacts with pyridine, eliminating *p*-toluenesulfonic acid. The tosylate II decomposes rapidly a few degrees above its melting point of 63°, or more slowly at room temperature, forming *p*-toluenesulfonic acid and a hydrocarbon. The hydrocarbon formed was not investigated, but from the results described below is presumed to be a mixture of octalins.

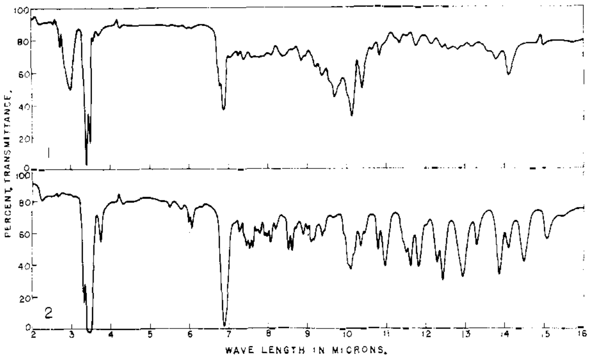


Fig. 1.—Infrared absorption spectra: curve 1, *trans*-5-cyclodecen-1-ol (VI) as a solution (100 mg./ml.) in carbon tetrachloride in the region 2–12 μ and in carbon disulfide in the region 12–16 μ, in a 0.091-mm. cell; curve 2, mixture of octalins from the reaction of *trans*-5-cyclodecen-1-yl *p*-toluenesulfonate with diethylaniline, without solvent in a 0.032-mm. cell.

trans-5-Cyclodecen-1-yl *p*-toluenesulfonate was heated with diethylaniline at 160–170° for 45 minutes. This temperature undoubtedly is much higher than is required for the elimination of *p*-toluenesulfonic acid, but was chosen in order to use the conditions under which the stereoisomeric ditosylates (I) formed a mixture of 1,9- and 9,10-octalin.[3] A mixture of hydrocarbons with the composition $C_{10}H_{16}$ was isolated as the reaction product in 59% yield. The mixture absorbed 99–102% of one molar equivalent of hydrogen in the presence of a palladium catalyst, and the reduction product was shown to be a mixture of *cis*- and *trans*-decalin by comparison of its infrared spectrum with the spectrum of an authentic mixture. The decalin obtained showed no infrared absorption at 10.5 μ, at which wave length cyclopentanocycloheptane (bicyclo[5.3.0]decane) has an absorption band of medium intensity.[7] This evidence shows that the octalin mixture contained no appreciable amount of a bicyclo[5.3.0]decene. The fact that the octalin mixture absorbed one molar equivalent of hydrogen in quantitative reductions as well as absence of absorption bands at 12.76 and 13.94 μ characteristic of cyclodecane in the infrared spectrum of the decalins formed in the reduction, indicated little if any contamination of the octalins by cyclodecadienes. The infrared spectrum of the octalin mixture (Fig. 1) shows two distinct olefinic bands at 6.0 and 6.08 μ, corresponding exactly to bands in the spectra of 1,9-octalin and *cis*- or *trans*-1,2-octalin (Fig. 2). However, *trans*-1,2-octalin has strong infrared bands at 11.37 and 12.73 μ which are not present in the spectrum of the octalin mixture derived from

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(5) A. T. Blomquist, R. E. Burge, Jr., and A. C. Sucsy, THIS JOURNAL, **74**, 3636 (1952).

(6) See, for example, H. Adkins, L. M. Richards and J. W. Davis, *ibid.*, **63**, 1320 (1941).

(7) Reported for *cis*-bicyclo[5.3.0]decane by E. Kováts, A. Fürst and H. H. Günthard, *Helv. Chim. Acta*, **37**, 534 (1954), and observed in the present work for the isomer or mixture of isomers obtained by Wolff–Kishner reduction of a mixture of *cis*- and *trans*-bicyclo[5.3.0]-2 decanones (ref. 3).

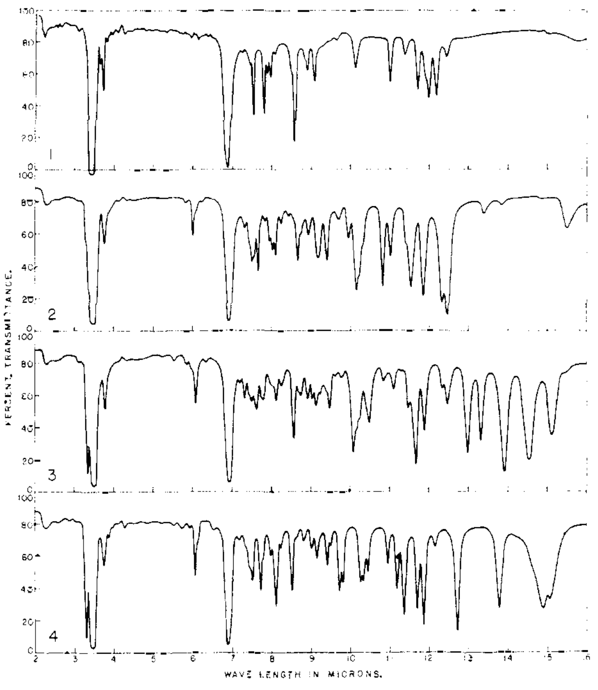
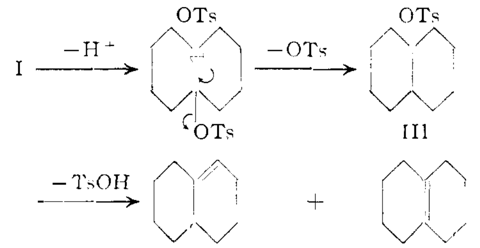


Fig. 2.—Infrared absorption spectra: curve 1, 9,10-octalin; curve 2, 1,9-octalin; curve 3, *cis*-1,2-octalin containing approximately 10% of 1,9-octalin; curve 4, *trans*-1,2-octalin, all as pure liquids in a 0.032-mm. cell.

the tosylate II, while all of the bands present in the infrared spectra of 1,9- and *cis*-1,2-octalin are present. Comparison of the relative intensities of the 6.0 and 6.08 μ bands of the mixture with the spectra of mixtures of these hydrocarbons of known composition showed that they were present in approximately equal amounts. An unknown impurity is responsible for absorption bands of the mixture at 11.0, 12.8 (shoulder) and 14.1 μ. These bands cannot be due to the presence of 9,10-octalin, which absorbs in the 11.0 μ region, but not at 12.8 or 14.1 μ; moreover, the absorption bands of 9,10-octalin at 8.6, 12.0 and 12.2 μ are not present in the spectrum of the octalin mixture derived from II.

Chemical evidence confirming the identity of 1,9- and *cis*-1,2-octalin in the mixture of octalins formed from the tosylate II was obtained by treating the mixture with osmium tetroxide and pyridine.[8] Hydrolysis of the resulting mixture of osmic esters formed a mixture of *cis*-glycols that was separated by adsorption on alumina followed by elution with 2% methanol in ether. Decalin *cis*-1,9-diol was eluted first and after recrystallization melted at 83–84°. This glycol was identical according to mixed melting point and comparison of infrared spectra with a sample prepared from pure 1,9-octalin and osmium tetroxide. The present work provides no evidence concerning the stereochemical configuration of the glycol, but the principles of conformational analysis[9] and the assumption that the osmium tetroxide attacks the double bond from the least hindered side indicate that a probable configuration would be one in which the C_9 hydroxyl is axial, the C_1-hydroxyl is equatorial, and the ring fusion is *cis*.[10] Continued elution yielded *cis*-decalin *cis*-1,2-diol, which after recrystallization melted at 85.4–85.8° and was identical according to mixed melting point and comparison of infrared spectra with an authentic sample prepared from *cis*-1,2-octalin and osmium tetroxide. Although the two glycols have nearly the same melting point, they crystallize in different forms and show a large depression in mixed melting points. From steric considerations, the most likely configuration for the *cis*-glycol derived from *cis*-1,2-octalin is the one in which the C_1-hydroxyl is equatorial and the C_2-hydroxyl is axial.[9,10]

Isolation of a mixture of 1,9- and *cis*-1,2-octalin from the reaction of the tosylate II with diethylaniline, and the fact that the mixture contained little if any 9,10-octalin, shows that II cannot be the sole intermediate in the reaction of the ditosylate I with diethylaniline, in which 9,10-octalin is one of the products.[3] The reaction of the ditosylate I (a mixture of the two stereoisomers) with diethylaniline was repeated on a small scale, in order to examine the infrared spectrum of the mixture of octalins formed. The spectrum of the mixture showed that it contained *cis*-1,2-octalin and possibly a small amount of *trans*-1,2-octalin, in addition to the 9,10-octalin and 1,9-octalin previously identified in the mixture by conversion to crystalline nitrosochlorides.[3] Accordingly the tosylate II can be and probably is one of the intermediates in the reaction of the ditosylates I with diethylaniline. Other possible intermediates are *cis*-5-cyclodecen-1-yl *p*-toluenesulfonate and 9-decalyl *p*-toluenesulfonate (III, *cis* or *trans*). The latter compound is inaccessible at present because of the difficulty of preparing tosylates of tertiary alcohols, but the product expected from its reaction with bases would be a mixture of 1,9- and 9,10-octalin.



Kinetic studies of the mechanism of reaction of the tosylate II with bases forming octalins are planned, as well as examination of the products of solvolysis of II with hydroxylic solvents to determine whether rearrangement products containing the decalin ring system are formed. The similarity of the reaction of II with diethylaniline forming octalins to the reactions of derivatives of 3-hydroxy-Δ^5-steroids forming *iso*-steroids[11] (6-substituted-3,5-cyclosteroids) is apparent, and intermediates[12] of similar type may be involved. A probable first step in the conversion of the tosylate II to octalins is the elimination of tosylate ion, with the double

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[8] R. Criegee, *Ann.*, **522**, 75 (1936); R. Criegee, E. Büchner and W. Walther, *Ber.*, **73B**, 571 (1940).

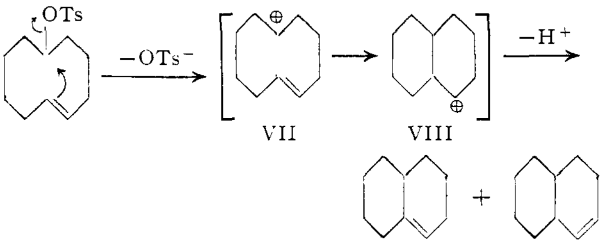
[9] H. D. Orloff, *Chem. Revs.*, **54**, 426 (1954).

[10] Discussed in the Ph.D. thesis of Robert J. Cotter, Massachusetts Institute of Technology, 1954.

[11] M. Hafez, G. Halsey and E. Wallis, *Science*, **110**, 474 (1949); C. W. Shoppee and G. Summers, *J. Chem. Soc.*, 3361 (1952).

[12] S. Winstein and R. Adams, THIS JOURNAL, **76**, 838 (1948).

bond exerting a driving force, forming the ion VIII. Ion VII is a possible intermediate for which there is no evidence at present. The fact that the product contains no *trans*-1,2-octalin does not prove that the ring juncture is formed in a stereospecific manner leading solely to VIII with a *cis* ring fusion, although that may be the case, for the isomer of ion VIII with a *trans* ring juncture might lose a proton exclusively from the 9-position, forming 1,9-octalin.

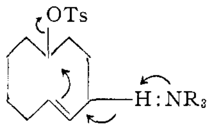


VII VIII

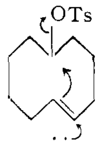
Reactions of 1-substituted *trans*-decalins that might proceed through a carbonium ion (VIII, *trans* ring fusion) might show whether such an ion would eliminate a proton to yield 1,9-octalin exclusively. The reaction of *trans*-1-decalylamine (axial amino group) with nitrous acid forms a mixture of *trans*-1,2- and 1,9-octalin.[8] However, this evidence is inconclusive, since it has been shown that the reactions of cyclohexylamines with nitrous acid do not always proceed through carbonium ions.[13] *trans*-1-Decalyl *p*-toluenesulfonate (axial ester group) forms a mixture of *trans*-1,2- and 1,9-octalin on heating with ethanol,[14] but it is not known to what extent this reaction proceeds through a carbonium ion.

If *cis*- and *trans*-1,2-octalin are comparable to 3,4-disubstituted cyclohexenes,[15] the *trans* isomer should have a more stable conformation than the *cis* form. Since *cis*- rather than *trans*-1,2-octalin is formed, it may be inferred that participation by the double bond in the process in which the tosylate group is eliminated exerts some steric control over the resulting ring fusion. Models of the tosylate II show that it can assume conformations which would explain the formation of either a *cis* or a *trans* ring juncture, as well as products from 1,5-bridging (which were not observed). *cis*-1,2-Octalin was shown to be stable to the conditions of the reaction of the tosylate II with diethylaniline, and consequently is not an intermediate in the formation of 1,9-octalin.

In the preceding discussion of the formation of octalins from the tosylate II, the base is assumed to function initially in the ionization of the tosylate, for example by solvation of the ions formed, rather than to participate in a bimolecular process, such as removal of a proton from IX. Other reaction paths can be formulated in which the base participates; kinetic data should furnish information concerning the role of the base. Formula IX shows removal of an allylic hydrogen as a proton by the base in a process leading to 1,2-octalin. Formula X shows a path by which a quaternary compound could be formed, and subsequent loss of the tertiary amine and a proton from C_2 or C_9 could explain formation of 1,2- and 1,9-octalin.



IX



X NR_3

Four of the isomeric octalins were prepared as follows for comparison with the mixture obtained from the tosylate II. 1-Naphthol was hydrogenated to a mixture of stereoisomeric 1-decalols in 92% yield in the presence of a ruthenium catalyst. The *cis*-1-decalol isomer melting at 93° was separated by crystallization and converted to the methyl xanthate, which on pyrolysis formed *cis*-1,2-octalin containing about 10% of 1,9-octalin.[14,16] Oxidation of the 1-decalol mixture with chromic acid yielded a mixture of *cis*- and *trans*-1-decalones (81%), which was isomerized with sodium methoxide to the *trans* isomer, and converted to *trans*-1-decalone oxime in 72% yield. Sodium and ethanol reduction of the oxime yielded *trans*-1-decalylamine (93%), which was converted to *trans*-1,2-octalin by the Hofmann exhaustive methylation procedure (75% over-all from the primary amine). Hydrogenation of the *trans*-1,2-octalin to *trans*-decalin, identified by its infrared spectrum,[17] proved that the ring juncture remained *trans* in the final steps leading to the olefin. 9,10-Octalin was regenerated from its nitrosochloride, and 1,9-octalin was prepared from *cis*-9-decalyldimethylamine through the amine oxide.[18]

Experimental[19]

6-Dimethylaminocyclodecanol (IV).—A mixture of 8.8 g. of 6-aminocyclodecanol (a mixture of *cis* and *trans* isomers, m.p. 70–97°, obtained by reduction of 6-hydroxycyclodecanone oxime with sodium and *n*-butyl alcohol,[4] 15 g. of 88% formic acid and 13 g. of 37% formalin was heated slowly to 90°. The source of heat was removed and, after the evolution of carbon dioxide ceased, the solution was heated at 100° for 14 hours. The cooled solution was acidified with 50 ml. of 3 *N* hydrochloric acid and concentrated to dryness under reduced pressure. The residue was made basic with 50 ml. of 10% sodium hydroxide and heated under reflux for 2 hours. The mixture was cooled, made strongly acidic with 3 *N* hydrochloric acid, filtered, made strongly basic with solid sodium hydroxide and extracted with ether. The ether extracts were dried over sodium sulfate, concentrated and the residue was distilled through a semi-micro column. The yield of 6-dimethylaminocyclodecanol (a mixture of *cis* and *trans* isomers) was 8.2 g. (80%), b.p. 122–123° (0.48 mm.), $n^{25}D$ 1.5013–1.5022. A sample with $n^{25}D$ 1.5022 from a similar preparation that had been treated with benzenesulfonyl chloride and excess aqueous sodium hydroxide to remove any traces of the primary and secondary amines present as contaminants was analyzed.

Anal. Calcd. for $C_{12}H_{25}NO$: C, 72.30; H, 12.64; N, 7.03. Found: C, 72.05; H, 12.76; N, 6.95.

6-Dimethylaminocyclodecanol methiodide (V) was prepared by heating a solution of 3.74 g. of 6-dimethylaminocyclodecanol and 10.5 g. of freshly distilled methyl iodide in

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[13] J. A. Mills, *J. Chem. Soc.*, 260 (1953); W. G. Dauben, R. C. Tweit and C. Mannerskantz, THIS JOURNAL, **76**, 4420 (1954).

[14] W. Hückel, W. Tappe and G. Legutke, *Ann.*, **543**, 209 (1940).

[15] D. H. R. Barton, R. C. Cookson, W. Klyne and C. W. Shoppee, *Chemistry & Industry*, 21 (1954).

[16] W. Hückel and H. Naab, *Ann.*, **502**, 136 (1933).

[17] J. Seidman, *Anal. Chem.*, **23**, 559 (1951).

[18] R. A. Pike, Ph.D. Thesis, Massachusetts Institute of Technology, June, 1953; to be published.

[19] Melting points are corrected and boiling points are uncorrected. We are indebted to Dr. S. M. Nagy and his associates for analyses. Infrared spectra were determined with a Baird double beam recording spectrometer, model B, with a sodium chloride prism.

25 ml. of dry methanol under reflux for 2 hours. The solution was concentrated to a volume of a few ml. and the methiodide (a mixture of *cis* and *trans* isomers, m.p. 120–138°, 6.3 g., 98%) was precipitated by adding ethyl acetate. An analytical sample composed largely of one stereoisomer was crystallized from methanol by addition of ethyl acetate; m.p. 150–152°.

Anal. Calcd. for $C_{13}H_{28}NOI$: C, 45.75; H, 8.27; N, 4.10; I, 37.19. Found: C, 45.98; H, 8.35; N, 4.18; I, 37.48.

trans-**5-Cyclodecen-1-ol (VI).**—The freshly precipitated silver hydroxide prepared from 15 g. of silver nitrate was added to a solution of 5.0 g. of 6-dimethylaminocyclodecanol methiodide in 80 ml. of dry methanol. The mixture was digested by warming, allowed to stand at room temperature for 45 minutes and filtered. The filtrate, which gave a negative test for iodide ion with silver nitrate, was concentrated under reduced pressure. The quaternary base was decomposed by heating at 120–125° and 0.5 mm. in a flask attached to a semi-micro column, and the distillate was redistilled, yielding 1.96 g. (87%) of *trans*-5-cyclodecen-1-ol, b.p. 77–78° (0.25 mm.), $n^{25}\text{D}$ 1.5030–1.5050. A fraction with $n^{25}\text{D}$ 1.5050 from a similar preparation was analyzed.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.66; H, 11.63.

Hydrogenation of *trans*-**5-Cyclodecen-1-ol.**—A solution of 155.3 mg. of *trans*-5-cyclodecen-1-ol in 10 ml. of dry methanol was hydrogenated in the presence of 0.12 g. of prereduced platinum oxide. Reduction ceased after 97% of one molar equivalent of hydrogen had been absorbed in 9 hours. After filtration to separate the catalyst, concentration yielded cyclodecanol, m.p. 39.5–41.5° (lit.[20] m.p. 40–41°).

Hydrogenations of *trans*-5-cyclodecen-1-ol in the presence of palladium-on-Norit resulted in absorption of less than one molar equivalent of hydrogen. In one experiment designed to determine the reason for this unexpected result, a solution of 124.3 mg. of *trans*-5-cyclodecen-1-ol in 10 ml. of absolute ethanol was stirred in a nitrogen atmosphere for 6.5 hours in the presence of 0.20 g. of 10% palladium-on-Norit. The nitrogen was then replaced by hydrogen and the remaining unsaturated alcohol was reduced. The reduction ceased after absorption of 39% of one molar equivalent of hydrogen, indicating that 61% of the unsaturated alcohol had been converted to a compound not readily reducible under these conditions. The catalyst and solvent were removed, and the residue was dissolved in aqueous ethanol and treated with 0.20 g. of semicarbazide hydrochloride and 0.30 g. of sodium acetate. Cyclodecanone semicarbazone was isolated from the reaction mixture in a yield of 90 mg. (87%, assuming that 61% of the cyclodecenol was converted to cyclodecanone), m.p. and mixed m.p. with an authentic sample, 202–205°. Conditions for a more complete conversion of *trans*-5-cyclodecen-1-ol to cyclodecanone in the presence of palladium were not determined.

trans-**5-Cyclodecen-1-yl** *p*-**Toluenesulfonate (II).**—A solution of 2.55 g. of *trans*-5-cyclodecen-1-ol in 10 ml. of dry pyridine was cooled to −10°, and 3.61 g. of *p*-toluenesulfonyl chloride was added slowly. The mixture was allowed to stand at −10° for 24 hours with intermittent shaking, and then was acidified by addition of 25 ml. of cold 3 *N* hydrochloric acid. The oil that separated solidified on further cooling, and the crude solid was recrystallized from ether at −10°. The yield of the tosylate after recrystallization was 2.3 g. (45%), m.p. 61–63°. A sample from another preparation, m.p. 62.2–63.2°, that was recrystallized from ether–petroleum ether was analyzed.

Anal. Calcd. for $C_{17}H_{24}O_3S$: C, 66.20; H, 7.84. Found: C, 66.01; H, 8.13.

Reaction of *trans*-**5-Cyclodecen-1-yl** *p*-**Toluenesulfonate (II) with Diethylaniline.**—A solution of 1.77 g. of *trans*-5-cyclodecen-1-yl *p*-toluenesulfonate in 10 ml. of freshly distilled diethylaniline was heated at 160–170° for 45 minutes. The mixture was cooled, dissolved in 175 ml. of ether, and the solution was washed with five 20-ml. portions of cold 10% sulfuric acid, two 20-ml. portions of water and dried over magnesium sulfate. The solution was concentrated and the residue was distilled through a semi-micro column, yielding 0.461 g. (59%) of a mixture of hydrocarbons, b.p. 65–70° (11 mm.), $n^{25}\text{D}$ 1.4882–1.4944. A fraction with $n^{25}\text{D}$ 1.4928 was analyzed.

Anal. Calcd. for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.03; H, 11.78.

Hydrogenation of a 126-mg. sample of the mixture of hydrocarbons with $n^{25}\text{D}$ 1.4938 in 7 ml. of glacial acetic acid in the presence of 120 mg. of 10% palladium-on-Norit resulted in absorption of 102% of one molar equivalent of hydrogen. The catalyst was separated by filtration and the filtrate was neutralized with 10% sodium hydroxide in a 50-ml. volumetric flask. Water was added, followed by 3 ml. of ether, so that the ethereal layer was in the neck of the flask. The mixture was shaken and allowed to stand overnight. The ethereal layer was withdrawn with a capillary pipet, concentrated, and the residue was distilled in a short-path still, yielding 58 mg. of decalin, $n^{25}\text{D}$ 1.4716, with an infrared spectrum essentially identical with the spectrum of a mixture of *cis*- and *trans*-decalins.

The results of the hydrogenation described above, together with comparison of the infrared spectrum of the mixture of hydrocarbons obtained by treating II with diethylaniline with the spectra of several of the isomeric octalins, indicated that the mixture was composed of approximately equal parts of 1,9-octalin and *cis*-1,2-octalin. The presence of these two olefins in the mixture was confirmed by hydroxylation with osmium tetroxide. A 370-mg. sample of the mixture of hydrocarbons (obtained from II and diethylaniline) with $n^{25}\text{D}$ 1.4896 was dissolved in 25 ml. of dry ether containing 1.5 ml. of dry pyridine, and a solution of 1 g. of osmium tetroxide in 50 ml. of dry ether was added. A mixture of the osmic esters precipitated in a few minutes, and was allowed to stand in the dark for 24 hours with occasional shaking. The solid was separated by filtration, dissolved in 45 ml. of chloroform, and stirred vigorously for 2.5 hours with a solution of 2 g. of potassium hydroxide and 2 g. of mannitol in 20 ml. of water. The layers were separated, and the aqueous layer was extracted with two 20-ml. portions of chloroform. The combined chloroform solutions were dried over magnesium sulfate, concentrated, and the residue was distilled in a short-path still at 0.5 mm. with a heating block temperature of 125°. The liquid distillate was dissolved in dry benzene and chromatographed on 4.5 g. of alumina (grade I–II)[21] in a 38 × 1-cm. column. The glycols were eluted with 2% methanol in ether, and the eluate was separated into 15-ml. fractions. The first two fractions contained 49 mg. of decalin *cis*-1,9-diol, which after four crystallizations from 35–60° petroleum ether was analytically pure and melted at 83–84°. A mixed melting point with an authentic sample described below (m.p. 83.6–84.6°) showed no depression. The next twelve fractions of the eluate yielded 104 mg. of *cis*-decalin-*cis*-1,2-diol, which after three crystallizations from 35–60° petroleum ether melted at 85.4–85.8°, and gave no depression in a mixed m.p. with an authentic sample (m.p. 86.2–87°) described below. A mixed m.p. of the 1,9- and 1,2-diols separated as described above showed a marked depression (to 58–66°), as did a mixture of the two authentic samples. The total yield of glycols from the mixture of octalins was 33%.

1-Decalols.—A solution of 100 g. of α-naphthol in 400 ml. of absolute ethanol was hydrogenated in the presence of 1 g. of ruthenium dioxide (Baker and Co., Newark, N. J.) at 110° and 1600–1100 p.s.i. in 3.5 hours. The catalyst was separated by filtration, the filtrate was concentrated under reduced pressure, and the residue was distilled through a short still-head, yielding 98.8 g. (92%) of a mixture of stereoisomeric 1-decalols, b.p. 100–105° (7 mm.), which partially crystallized on standing at room temperature. The *cis*-1-decalol isomer described[22] as melting at 93° was obtained from 48.5 g. of the mixture of stereoisomeric 1-decalols by crystallization from 175 ml. of 35–60° petroleum ether, which was allowed to cool slowly to room temperature. After two more crystallizations from the same solvent the yield was 15.5 g., m.p. 91.6–92°. No attempt was made to separate all of this isomer that was present in the mixture, or to identify the other isomers that were present.

cis-**1,2-Octalin.**—The methyl xanthate of the *cis*-1-decalol isomer described above was prepared by a procedure similar to the one described for the preparation of methyl *cis*-2-

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

[21] H. Brockmann and H. Schodder, *Ber.*, **74B**, 73 (1941).

[22] W. Hückel, R. Danneel, A. Gross and H. Naab, *Ann.*, **502**, 99 (1933).

phenylcyclohexyl xanthate,[23] except that the sodium alkoxide was prepared with sodium hydride in benzene. The yield was 60%, m.p. 86.6–87.2° after one recrystallization from dry methanol (ref. 16 reports a yield of 25% and m.p. 86°). A 6.9-g. sample of the xanthate was heated in a flask (attached to a reflux condenser) in a bath at 210–220° for 30 minutes and at 250–260° for 15 minutes, after which the evolution of gases had ceased. The residue was purified by washing it through a column containing 10 g. of silica gel with 200 ml. of 35–60° petroleum ether. The effluent was concentrated and the residue was distilled through a semi-micro column, yielding 2.48 g. (64%) of *cis*-1,2-octalin, b.p. 72–73° (14 mm.), n^{25}D 1.4890–1.4900. The infrared spectrum of the product (n^{25}D 1.4900, Fig. 2) showed that it contained approximately 10% of 1,9-octalin, in agreement with refs. 14 and 16.

cis-**Decalin**-*cis*-**1,2-diol**.—A 307-mg. sample of *cis*-1,2-octalin was treated with 1 g. of osmium tetroxide in 30 ml. of ether containing 1.5 ml. of pyridine by the procedure described above for hydroxylation of the mixture of octalins derived from II, and the osmic ester was hydrolyzed to the glycol in the same way. After three recrystallizations from a mixture of dry ether and 35–60° petroleum ether, *cis*-decalin-*cis*-1,2-diol was isolated in a yield of 0.17 g. (44%) as colorless needles with a constant m.p. of 86.2–87°.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.65. Found: C, 70.42; H, 10.48.

Decalin-*cis*-**1,9-diol**.—1,9-Octalin, n^{25}D 1.4928, was prepared from *cis*-9-N,N-dimethylaminodecalin through the amine oxide (not isolated) by a method described by Pike.[18] A 343-mg. sample of the 1,9-octalin was treated with 1 g. of osmium tetroxide in ether containing 1.5 ml. of pyridine and the resulting osmic ester was hydrolyzed by the procedure described for hydroxylation of the mixture of octalins obtained from II and diethylaniline. The product that was isolated by a short-path distillation crystallized and amounted to 0.23 g. (54%). After three crystallizations from 35–60° petroleum ether and sublimation, the decalin-*cis*-1,9-diol melted at 83.6–84.6°.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.65. Found: C, 70.23; H, 10.50.

trans-**1-Decalone Oxime**.—A mixture of *cis*- and *trans*-1-decalones was prepared from the 1-decalols obtained by hydrogenation of α-naphthol in the presence of ruthenium (described above) by oxidation with chromic acid[24]; the yield was 76 g. (81%), b.p. 104–106° (10 mm.), n^{25}D 1.4915 (from 93.5 g. of 1-decalols). The mixture of 1-decalones (76 g.) was heated under reflux for 0.5 hour with the sodium methoxide prepared from 12 g. of sodium and 450 ml. of dry methanol, in order to convert the mixture to the *trans* isomer. A slurry of 91 g. of hydroxylamine hydrochloride, 100 g. of sodium acetate, 250 ml. of water and 200 ml. of methanol was added, and the mixture was heated under reflux for 2 hours. After cooling, the mixture was poured into 2 l. of ice water and the oxime was separated by filtration. It was recrystallized from 1 l. of 95% ethanol and air-dried; the yield was 60 g. (72%), m.p. 167–168° (lit.[24] m.p. 168°).

trans-**1-Decalyldimethylamine**.—*trans*-1-Decalylamine was prepared by the reduction of *trans*-1-decalone oxime with sodium and absolute ethanol in a yield of 93%, b.p. 94–96° (10 mm.), n^{25}D 1.4890. The amine formed an N-benzoyl derivative melting at 199.4–200.2° (lit.[16] m.p. 195°), and is the stereoisomer described as melting at −1°.[16] A 5-g. sample of this *trans*-1-decalylamine was methylated by adding it to a mixture of 10.5 g. of 85% formic acid and 10.5 g. of 37% formalin with cooling in ice, followed by heating until carbon dioxide evolution began, and further heating at 100° for 24 hours after the spontaneous reaction subsided. The mixture was cooled, acidified with 40 ml. of 3 *N* hydrochloric acid and concentrated to dryness under reduced pressure. The residue was made basic with 40 ml. of 20% sodium hydroxide, and 10 ml. of benzenesulfonyl chloride was added. The mixture was shaken and, after no more benzene sulfonyl chloride was present (by odor), 75 ml. of water was added followed by concentrated hydrochloric acid until the *p*H was 1. The solution was concentrated to dryness under reduced pressure, and 40 ml. of 20% sodium hydroxide was added to the residue. The product was extracted with ether, and the extracts were dried over sodium sulfate and concentrated. Distillation of the residue through a semi-micro column yielded 5.73 g. (96%) of *trans*-1-decalyldimethylamine, b.p. 107–108° (11 mm.), n^{25}D 1.4822.

Anal. Calcd. for $C_{12}H_{23}N$: C, 79.59; H, 12.77; N, 7.73. Found: C, 79.72; H, 12.73; N, 7.88.

trans-**1-Decalyldimethylamine picrate** was prepared from the amine and picric acid in 95% ethanol and recrystallized three times from the same solvent; m.p. 155–155.6°.

Anal. Calcd. for $C_{18}H_{26}N_4O_7$: C, 52.67; H, 6.39; N, 13.65. Found: C, 52.38; H, 6.36; N, 13.65.

trans-**1-Decalyldimethylamine methiodide** was prepared by heating a solution of 25.5 g. of the tertiary amine and 70 g. of methyl iodide in 125 ml. of dry methanol under reflux for 2 hours. The solution was concentrated and the residue was crystallized from dry acetone, yielding 36.2 g. (80%) of the methiodide, m.p. 190° dec. (lit.[16] dec. begins at 180°).

Anal. Calcd. for $C_{13}H_{26}IN$: C, 48.30; H, 8.11; N, 4.33. Found: C, 48.34; H, 8.22; N, 4.23.

trans-**1,2-Octalin**.—The silver oxide freshly prepared from 36 g. of silver nitrate was added to a solution of 13.7 g. of *trans*-1-decalyldimethylamine methiodide in 150 ml. of dry methanol. The mixture was warmed on a steam-bath with occasional swirling for 1 hour and filtered to separate the silver iodide and silver oxide, which were washed with methanol. The filtrate was concentrated under reduced pressure and the residual quaternary base was decomposed by heating at 125° and 4 mm. The distillate, which was collected in a trap cooled with liquid nitrogen, was treated with 20 ml. of cold 20% hydrochloric acid. The hydrocarbon layer was combined with ethereal extracts of the aqueous layer and washed with sodium bicarbonate solution, water and dried over sodium sulfate. The solution was concentrated and the residue was distilled through a semi-micro column, yielding 4.48 g. (78%) of *trans*-1,2-octalin, b.p. 70.5° (14.5 mm.), n^{25}D 1.4819–1.4827. A sample of this olefin which was reduced quantitatively in the presence of 10% palladium-on-Norit in glacial acetic acid absorbed 97.3% of one molar equivalent of hydrogen and yielded *trans*-decalin, with the infrared spectrum characteristic of that hydrocarbon and free from the bands characteristic of *cis*-decalin.[17]

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[23] E. R. Alexander and A. Mudrak, THIS JOURNAL, **72**, 1812 (1950).

[24] W. Hückel, *Ann.*, **441**, 1 (1925).