[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Studies in the Terpene Series. XXI.[1a] The Thermal Isomerization of 6,6-Dimethylnorpinane at Atmospheric Pressure

BY HERMAN PINES AND N. E. HOFFMAN[1b]

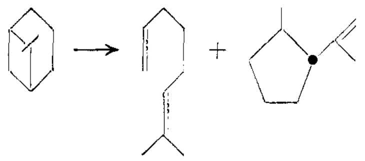
RECEIVED MARCH 17, 1954

At 500° and atmospheric pressure, 6,6-dimethylnorpinane isomerizes to 7-methyl-1,6-octadiene and 1-methyl-*trans*-2-isopropenylcyclopentane. The structures of these products are proved by degradation to known compounds. The structure of methyl-*trans*-2-methylcyclopentyl ketone obtained from acetylation of cyclohexane was proved.

The study of the thermal reaction of 6,6-dimethylnorpinane, 6,6-dimethylbicyclo[3.1.1]heptane, was undertaken to find whether a reaction analogous to the reaction of pinane[1] occurred and, if so, whether under similar conditions the distribution of monoölefin and diolefin products was the same in both reactions.

Results and Discussion

At 500° and atmospheric pressure 6,6-dimethylnorpinane (I) isomerizes to 7-methyl-1,6-octadiene (II) and 1-methyl-*trans*-2-isopropenylcyclopentane (III). The distribution of the products of the reaction under the flow rate conditions used was approximately 50% II, 20% III, 20% unreacted I and 10% high and low boiling material.



I II III

These results are based on the following method of investigation. The products of the reaction were fractionally distilled into small cuts (distillation curve in Fig. 1), and samples of these cuts were quantitatively hydrogenated to determine the degree of unsaturation of each. The results of these hydrogenations are shown in Table I. It should be noted that an H number below 1 indicates the presence of 6,6-dimethylnorpinane in the sample. Chromatographic separation of 6,6-dimethylnorpinane on silica gel gave the amount of that compound in the products. Quantitative hydrogenations corrected for the amount of 6,6-dimethylnorpinane present gave the amount of II and III present in the products.

Chromatographic separation also was used to isolate the pure products of the reaction because the presence of unreacted 6,6-dimethylnorpinane made separation by distillation unfeasible.

The rise in boiling point and fall in refractive index at the end of the distillation as shown in the distillation curve (Fig. 1) could possibly be the result of the presence of 1-methyl-*cis*-2-isopropenylcyclopentane.

Structure Proof of 7-Methyl-1,6-octadiene.—Catalytic hydrogenation of the diolefin obtained by chromatographic separation of the diolefin-rich distillation cuts of the reaction products gave a saturated hydrocarbon whose infrared spectrogram was identical to that of pure 2-methyloctane.[2]

TABLE I

QUANTITATIVE HYDROGENATIONS OF THE PRODUCTS FROM THE THERMAL REACTION OF 6,6-DIMETHYLNORPINANE

% Distilled	H number[a]	B.p., °C.	$n^{20}D$
8	1.90	143.3	1.4377
31	1.70	144.4	1.4403
53	1.28	146.7	1.4467
72	0.87	148.5	1.4510
100	0.34	152.2	1.4510

[a] Defined as moles of hydrogen absorbed per mole of 6,6-dimethylnorpinane and its isomers.

TABLE II

CHARACTERISTIC INFRARED BANDS OF COMPOUNDS II AND III IN MICRONS

Compound II	λ = 6.07, 6.92, 7.23, 7.40, 7.54, 7.75, 8.13, 8.43, 8.60, 8.93, 9.63, 10.04, 10.95, 11.62, 11.93, 13.57
Compound III	λ = 6.07, 6.92, 7.27, 7.45, 7.64, 7.83, 8.04, 8.45, 8.58, 8.86, 9.17, 9.68, 9.83, 10.07, 10.98, 11.25, 12.60

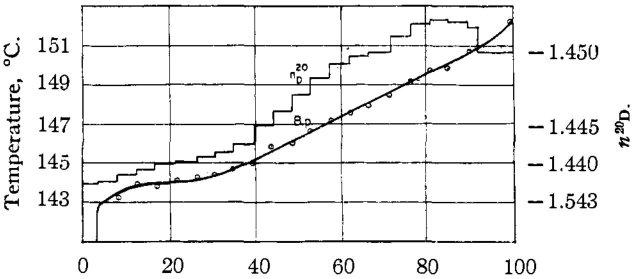


Fig. 1.—Distillation 6,6-dimethylnorpinane products 500° reaction.

The infrared spectrogram of the diolefin showed the presence of a vinyl group from absorption bands at 10.04 and 10.95 microns,[3] but the spectrogram gave no clear indication of the other type of double bond present in the diolefin.

The location of the double bonds in the diolefin was proved by ozonolysis using hydrogen peroxide in aqueous acetic acid for hydrolysis. The products of the ozonolysis reaction were carbon dioxide, showing the presence of a vinyl group, diacetone

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(1a) For the previous paper of this series, see H. Pines, N. E. Hoffman and V. N. Ipatieff, THIS JOURNAL, **76**, 4412 (1954).

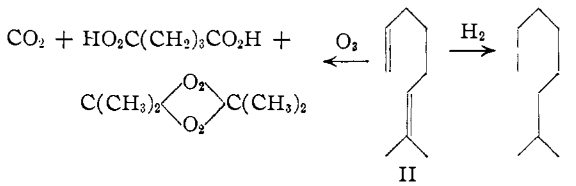
(b) Universal Oil Products Company Predoctoral Fellow, 1950–1953.

(2) Catalog of Selected Infrared Absorption Spectrograms, A.P.I. Research Project 44.

(3) H. L. McMurry and V. Thorton, *Anal. Chem.*, **24**, 318 (1952).

peroxide, showing the presence of an isopropylidene group, and glutaric acid.

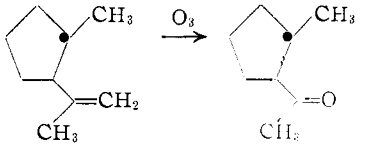
The hydrogenation and ozonolysis results proved the structure of the diolefin II was 7-methyl-1,6-octadiene. The following scheme of reactions summarizes the proof of structure



II

Structure Proof of 1-Methyl-*trans*-2-isopropenylcyclopentane.—The pure cyclic monoölefin III was obtained by chromatographic separation of the center cuts from the distillation of the products of the reaction. The infrared spectrogram of this monoölefin showed the type of double bond present was $R_1R_2C{=}CH_2$ from the absorption band at 11.25 μ.[3]

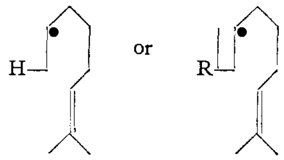
Ozonolysis of this cyclic monoölefin gave formaldehyde and a methyl ketone as was shown by a positive iodoform test. The infrared spectrum of this ketone was identical to the ketone prepared by reacting cyclohexane with acetyl chloride in the presence of aluminum chloride.[4] The latter ketone was proved to be methyl *trans*-2-methylcyclopentyl ketone. Furthermore, the melting points of the semicarbazones of the two ketones were practically the same and a mixed melting point showed no depression. This degradation reaction, shown below, proved the structure of the cyclic monoölefin III to be 1-methyl-*trans*-2-isopropenylcyclopentane.



Discussion.—Comparison of the thermal reactions of pinane and 6,6-dimethylnorpinane shows that pinane isomerizes to a diolefin faster than 6,6-dimethylnorpinane and the diolefin from pinane cyclizes faster than the diolefin from 6,6-dimethylnorpinane. According to the mechanism proposed for the pinane reaction,[1] a biradical is an intermediate in the formation of the diolefin. Pinane gives IV and 6,6-dimethylnorpinane gives V as intermediate. The difference in ease of formation of these biradicals could be the result of a stabilizing inductive effect of the methyl group beta to the free radical in the ring. The difference in the distribution of cyclic and aliphatic products in the pinane and 6,6-dimethylnorpinane could be the result of a decrease in the rate of cyclization because of (1) a lower concentration of diolefin in the case of 6,6-dimethylnorpinane and (2) a less easily formed radical of the type

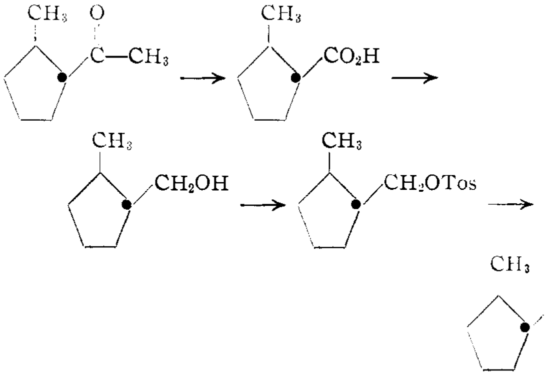
IV

V



Proof of Structure of Methyl *trans*-2-Methylcyclopentyl Ketone.—This ketone was prepared by the method of Nenitzescu and Ionescu.[4] Nenitzescu and Vantu reported that degradation of the acetyl group of this ketone to a methyl group gives 1-*trans*-2-dimethylcyclopentane.[4a] It was the results of this degradation which put the reported structure of the ketone somewhat in doubt because the physical properties—boiling point, refractive index and density—of the dimethylcyclopentane obtained were not those now accepted as the true values for 1-*trans*-2-dimethylcyclopentane.[5]

The present study was undertaken to determine if the reported structure of the saturated ketone obtained by acetylation of cyclohexane was correct. The acetyl group of the ketone was degraded to a methyl group by hypobromite oxidation of the ketone to a carboxylic acid, lithium aluminum hydride reduction of the acid to an alcohol, and lithium aluminum hydride reduction of the *p*-toluenesulfonate ester of the alcohol to a hydrocarbon. The physical properties of the hydrocarbon obtained by degradation—boiling point, refractive index, density and infrared spectrum[2]—were identical to those of 1-*trans*-2-dimethylcyclopentane.



It seems certain that the previously assigned structure of this ketone, methyl *trans*-2-methylcyclopentyl ketone, was correct.

Experimental

Preparation of 6,6-Dimethylnorpinane.—The 6,6-dimethylnorpinane was prepared by the hydrogenolysis of myrtanol.[6] The 6,6-dimethylnorpinane, distilled on a Podbielniak Hypercal column, had the following properties: b.p. 151.0–152.0° (750 mm.), $n^{20}D$ 1.4605.

Apparatus and Procedure.—The apparatus and procedure previously described was used for the thermal reaction study.[1] Reaction of 186 g. of 6,6-dimethylnorpinane at

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[4] C. D. Nenitzescu and C. N. Ionescu, *Ann.*, **491**, 207 (1931).

[4a] C. D. Nenitzescu and G. G. Vantu, *Bull. soc. chim.*, [5] **2**, 2209 (1936).

[5] Selected Values of Properties of Hydrocarbons and Related Compounds, A.P.I. Research Project 44.

[6] V. N. Ipatieff, G. J. Czajkowski and H. Pines, THIS JOURNAL, **73**, 4098 (1951).

500° and a liquid flow rate of 50–60 ml./hr. gave 182 g. of liquid product and 0.39 l. of gas not condensable at −78°. The products were fractionated on a Podbielniak Hypercal distilling column and the residue from this distillation was further fractionated on a Piros Glover spinning band column. The final residue amounted to 5 g. The distillation curve is in Fig. 1. Chromatographic separation on silica gel by the technique of Mair and Forziati[7] was used for further separation.

Analysis for Unsaturation.—The method previously described[1] was used for quantitative hydrogenation.

Structure Proof of 7-Methyl-1,6-octadiene (II). A. Isolation and Properties.—Chromatographic separation on silica gel of a 15-ml. sample of reaction product, b.p. 143.3–144.1°, gave the pure diolefin, b.p. 143.5–144.0°, $n^{20}\mathrm{D}$ 1.4369, $d^{20}{}_4$ 0.7533; *MR*D calcd. 42.83, found 43.19.

Anal. Calcd. for C_9H_{16}: C, 87.02; H, 12.98. Found: C, 87.08; H, 13.06.

B. Hydrogenation of II.—Hydrogenation of two 0.6-g. samples of pure II at room temperature and atmospheric pressure using 1 ml. of glacial acetic acid and 0.05 g. of platinum oxide catalyst each time was carried out and the hydrocarbon product had the properties: b.p. 143.0–144.0°, $n^{20}\mathrm{D}$ 1.4034, $d^{20}{}_4$ 0.7121; *MR*D calcd. 43.76, found 43.96. This compound's infrared spectrogram was identical to that of 2-methyloctane.[8]

C. Ozonolysis of II.—A 7.0-g. sample of the distilled reaction product, H number 1.90, was dissolved in 75 ml. of methylene chloride and ozonized at −78°. After completion of ozonation the solvent was removed by vacuum, and the ozonide was dissolved in 20 ml. of glacial acetic acid. The acetic acid solution was added to a solution of 25 g. of 30% hydrogen peroxide in 30 ml. of water maintained at 95–98° over a period of one hour. After addition the solution was maintained at 95–98° for 15 hours.

Carbon dioxide evolved during hydrolysis was detected by precipitation of barium carbonate from a saturated solution of barium hydroxide.

During hydrolysis of the ozonide, 0.21 g. of diacetone peroxide, m.p. 131–132°, collected on the reflux condenser of the ozonide hydrolysis flask. On striking, the diacetone peroxide exploded.

After hydrolysis, the solution of ozonolysis products was distilled to remove excess water–acetic acid solution. Salting out the first 10 ml. of distillate with sodium carbonate gave no organic layer. After distilling off 60 ml. of water–acetic acid solution, the ozonolysis products solution was vacuum distilled on a steam-bath. The residual oil from vacuum distillation solidified on cooling to room temperature to give 5.0 g., 67% yield, of glutaric acid, m.p. 95.5–97.5° after three recrystallizations from benzene; neut. equiv. calcd. 66, found 66.

Anal. Calcd. for $C_5H_8O_4$: C, 45.42; H, 6.10. Found: C, 45.50; H, 6.10.

Its *p*-bromophenacyl ester recrystallized from 95% ethanol melted at 135.5–136.5°.

Anal. Calcd. for $C_{21}H_{18}O_6Br_2$: C, 47.94; H, 3.44. Found: C, 47.72; H, 3.62.

Structure Proof of 1-Methyl-*trans*-2-isopropenylcyclopentane (III). A. Isolation and Properties.—Chromatographic separation on silica gel of the center cuts from the distillation of the products of pyrolysis, b.p. 145.5–152.1°, gave I, II and III. Compound III had the following properties: b.p. 149–150°, $n^{20}\mathrm{D}$ 1.4496.

Anal. Calcd. for C_9H_{16}: C, 87.02; H, 12.98. Found: C, 86.70; H, 12.75.

B. Ozonolysis of III.—Ten grams of III obtained by chromatographic separation of the reaction products was ozonized and hydrolyzed with zinc in aqueous acetic acid according to the procedure of Henne and Hill.[8] Unfortunately during distillation on a Piros Glover column, the ozonolysis products exploded. Before the explosion 1.8 g. of ketone was distilled, b.p. 167–168°, $n^{20}\mathrm{D}$ 1.4414. This ketone's infrared spectrogram was identical to that of methyl *trans*-2-methyl-cyclopentyl ketone.[5] The ketone gave a positive iodoform test.

Anal. Calcd. for $C_7H_{12}O$: C, 76.14; H, 11.18. Found: C, 75.76; H, 10.78.

The semicarbazone of the ketone after recrystallization from 95% ethanol, melted at 159.5–161.5°.

Anal. Calcd. for $C_9H_{17}N_3O$: C, 58.98; H, 9.35; N, 22.93. Found: C, 59.29; H, 9.15; N, 23.21.

A mixture of the semicarbazones of this ozonolysis product and methyl *trans*-2-methylcyclopentyl ketone melted at 158.5–160.5°.

Proof of Structure of Methyl *trans*-2-Methylcyclopentyl Ketone. Acetylation of Cyclohexane.—The procedure followed for the acetylation of cyclohexane was that used by Nenitzescu and Ionescu except that the reaction time was shortened to 17 hours.[8] From 300 g. of acetyl chloride, 600 g. of aluminum chloride and 2 l. of cyclohexane was obtained after fractionating on a Podbielniak Hypercal distilling column 141 g., 30% yield, of methyl *trans*-2-methylcyclopentyl ketone, b.p. 166.9–167.3°, $n^{20}\mathrm{D}$ 1.4406, $d^{20}{}_4$ 0.8956; *MR*D calcd. 36.95, found 37.16.

Anal. Calcd. for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.28; H, 11.35.

Its semicarbazone, recrystallized from ethanol-water solution, melted at 159.0–161.0°.

Anal. Calcd. for $C_9H_{17}N_3O$: N, 22.93. Found: N, 23.35.

***trans*-2-Methylcyclopentanecarboxylic Acid.**—Sodium hypobromite oxidation of 88 g. of methyl *trans*-2-methylcyclopentyl ketone using 228 g. of sodium hydroxide, 327 g. of bromine and 2 l. of water gave 51 g., 58% yield, of *trans*-2-methylcyclopentanecarboxylic acid, b.p. 111° (8 mm.), $n^{20}\mathrm{D}$ 1.4504, $d^{20}{}_4$ 1.0275; *MR*D calcd. 33.87, found 33.52; neut. equiv. calcd. 128, found 128.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.23; H, 9.24.

The amide of the acid was recrystallized from benzene, and melted at 151–152°.

Anal. Calcd. for $C_7H_{13}NO$: N, 11.01. Found: N, 11.50.

***trans*-2-Methylcyclopentylmethanol.**—Reduction of 40 g. of *trans*-2-methylcyclopentanecarboxylic acid with 14.5 g. of lithium aluminum hydride in the usual manner[9] gave 30 g., 86% yield, of *trans*-2-methylcyclopentylmethanol, b.p. 103° (53 mm.), $n^{20}\mathrm{D}$ 1.4533, $d^{20}{}_4$ 0.9144; *MR*D calcd. 33.86, found 33.78.

Anal. Calcd. for $C_7H_{14}O$: C, 73.63; H, 12.36. Found: C, 73.71; H, 12.31.

Its α-naphthylurethan, recrystallized from water–ethanol solution, melted at 98.5–99.5°.

Anal. Calcd. for $C_{18}H_{21}NO_2$: C, 76.29; H, 7.47; N, 4.94. Found: C, 76.51; H, 7.44; N, 5.01.

***trans*-2-Methylcyclopentylcarbinyl *p*-Toluenesulfonate.**—This ester was prepared from 42 g., 0.22 mole of *p*-toluenesulfonyl chloride and 25 g., 0.22 mole, of *trans*-2-methylcyclopentylmethanol according to the procedure described previously.[1] The tosylate, 42 g., 72% yield, $n^{20}\mathrm{D}$ 1.5030, failed to crystallize on standing.

Reduction of *trans*-2-Methylcyclopentylcarbinyl *p*-Toluenesulfonate.—The procedure was similar to that used by Cram.[10] Three solutions, each containing 14 g. of lithium aluminum hydride, 14 g. of *trans*-2-methylcyclopentylcarbinyl *p*-toluenesulfonate and 330 ml. of anhydrous ether, and each placed in a 1-liter erlenmeyer flask, were allowed to stand 15 hours. Each solution was hydrolyzed while cooled with ice with 200 ml. of ether containing 25 ml. of methanol, followed by 25 ml. of water, and finally 400 ml. of 10% sulfuric acid. The three ether solutions after separation from the acid washings were combined and dried over sodium carbonate. The ether was removed by distillation. The residue from ether distillation after being washed with 50 ml. of water followed by 50 ml. of 10% sodium hydroxide was dried over sodium and then distilled to give 8.0 g., 51% yield, of hydrocarbon. This hydrocarbon contained a trace of olefin as was shown by a permanganate test.[11] Chromatographic separation over silica gel using absolute ethanol as an eluant gave a saturated hydrocarbon, b.p. 91–92°, $n^{20}\mathrm{D}$ 1.4120, $d^{20}{}_4$ 0.7515; *MR*D calcd. 32.33, found 32.40. The infrared spectrogram of this hydrocarbon was identical to that of 1,*trans*-2-dimethylcyclopentane.[6]

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(7) B. J. Mair and A. F. Forziati, *J. Research Natl. Bur. Standards*, **32**, 151, 165 (1944).

(8) A. L. Henne and P. Hill, This Journal, **65**, 752 (1943).

(9) R. Nystrom and W. G. Brown, *ibid.*, **69**, 1197 (1947).

(10) D. J. Cram, *ibid.*, **74**, 2152 (1952).

(11) V. N. Ipatieff, W. W. Thompson and H. Pines, *ibid.*, **70**, 1658 (1948).

Anal. Calcd. for C_7H_{14}: C, 85.63; H, 14.37. Found: C, 85.50; H, 14.31.

Acknowledgment.—The authors wish to thank Dr. A. Rudin and Mr. G. Bô of this Laboratory for preparing part of the 6,6-dimethylnorpinane used in this work and Miss H. Beck for the elemental analyses.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Decahydronaphthoic Acids and their Relationship to the Decalols and Decalylamines.[1] A Stereochemical Study of the Reaction of Nitrous Acid with Decalylamines

BY WILLIAM G. DAUBEN, ROBERT C. TWEIT AND CHRISTINA MANNERSKANTZ

RECEIVED JANUARY 25, 1954

The preparation of *cis–cis*-1-, *trans–trans*-1- and *trans–cis*-2-decahydronaphthoic acids in pure form has been achieved. The *cis*-decalyl derivative was obtained by catalytic hydrogenation and the *trans*-materials were prepared from the corresponding chlorides *via* carbonation of the Grignard reagent. The structures of the acids were assigned on the basis of stereospecific elimination reactions, conformational analysis as applied to reaction rates and by catalytic hydrogenation. The three acids were degraded, with stereochemical retention, to decalols and decalylamines. The steric courses of the deamination of decalylamines with nitrous acid has been re-examined and possible mechanisms of this reaction as applied to alicylic compounds have been discussed.

The reaction of aliphatic primary amines with nitrous acid to yield alcohols and olefins has been extensively investigated and in the acyclic series (containing no neighboring participating groups[2]) the stereochemical results can be adequately explained by assuming an SN1 type of reaction process[3] involving the intermediate formation of a diazonium ion. For example, it has been shown that when an optically active acyclic primary amine is allowed to react with nitrous acid, the products of

$$\text{L-RNH}_2 + \text{HONO} \longrightarrow \text{RN}_2^{\oplus}\text{OH}^{\ominus} \longrightarrow \text{D-ROH} + \text{DL-ROH} + \text{olefins}$$

the reaction are unsaturated hydrocarbons and an alcohol of inverted configuration. In the alicyclic series, however, such a reaction consistency is not to be found. In the simplest case, that is with *cis*- and *trans*-4-methylcyclohexylamine,[4] it has been reported that whereas the *cis*-amine yielded inverted alcohol and olefins, the *trans*-isomer gave rise to a single product, the *trans*-alcohol. This pattern of one isomer yielding only an alcohol with retention of configuration while its epimer gives largely inverted alcohol and olefin is the usual picture seen upon examination of the reaction of the other epimeric alicyclic amines with nitrous acid.[5] It is evident that in any two alicyclic epimers the conformation of the substituent is different and viewed in this manner various workers[6,7] have formulated the rule that when the amino group is in an equatorial conformation pure retention results while for an axial[8] conformation both inversion and elimination occur. Therefore, such a reaction as deamination is an example of conformational control.

In all of the cases cited by Mills[6] and Bose[7] in the cyclohexyl, menthyl and *trans*-decalyl series, the configurational relationship between the amine and the alcohol has been arbitrarily assigned. In order to utilize such data as an aid to the postulation of a mechanism of deamination, it is desirable to know these configurations with certainty. Accordingly, work was undertaken to establish firmly such relationship of epimers and the interest was centered on the decalin series since all 8 possible isomers of the 1- and 2-substituted decalins have been studied under deamination conditions by Hückel.[9] Also, it was noted that in this decalin series certain discrepancies existed which tended to cast doubt upon the generalized conformational postulates referred to above.[6,7]

The results obtained in the *cis*-2-decalin series have been reported earlier[1] and in such work the steric relationship between the alcohol and the amine was established by degradation of a common intermediate, the decahydro acid, by stereospecific processes. The methods utilized were to convert the acid to a methyl ketone with methyllithium followed by cleavage of the ketone with perbenzoic acid and degradation of the acid to an amine with hydrazoic acid. To employ these same methods

$$\begin{tikzcd} & \text{RCOCH}_3 \arrow[r] & \text{ROCOCH}_3 \\ \text{RCOOH} \arrow[ur] \arrow[r] & \text{RNH}_2 & \end{tikzcd}$$

in the *cis*-1, *trans*-1 and *trans*-2 series necessitated the preparation of pure isomeric acids in each series.

Preparation of Decahydronaphthoic Acids.—Previous investigators have reported the preparation of several isomeric decahydronaphthoic acids

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[1] For the previous paper in this series, see THIS JOURNAL, **73**, 1504 (1951).

[2] For a detailed discussion of such a series of compounds, see M. Mousseron, M. Mousseron-Canet and R. Jacquier, *Ann. chim.* (*Paris*), [12] **8**, 5 (1953).

[3] P. Brewster, F. Hiron, E. D. Hughes, C. K. Ingold and P. A. D. Rao, *Nature*, **166**, 178 (1950); C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1950, p. 395.

[4] M. M. Claudon, *Bull. soc. chim. France*, 627 (1950).

[5] Examples of such reactions are: menthyl and neomenthylamine, isomenthyl and neoisomenthylamine (J. Read, A. M. R. Cook and M. I. Shannon, *J. Chem. Soc.*, 2223 (1926); J. Read and G. J. Robertson, *ibid.*, 2168 (1927)), carvomenthyl and neocarvomenthylamine (R. G. Johnston and J. Read, *ibid.*, 1138 (1935); and A. K. Bose, *Experientia*, **8**, 458 (1952)).

[6] J. A. Mills, *J. Chem. Soc.*, 260 (1953).

[7] A. K. Bose, *Experientia*, **9**, 256 (1953).

[8] The term *axial* is employed here in place of *polar* in conformity with the recent suggestion of D. H. R. Barton, O. Hassel, K. S. Pitzer and V. Prelog (*Science*, **119**, 49 (1954)) with regard to those bonds in a cyclohexyl ring which are parallel to the axis of threefold symmetry.

[9] W. Hückel, *Ann.*, **533**, 1 (1938).