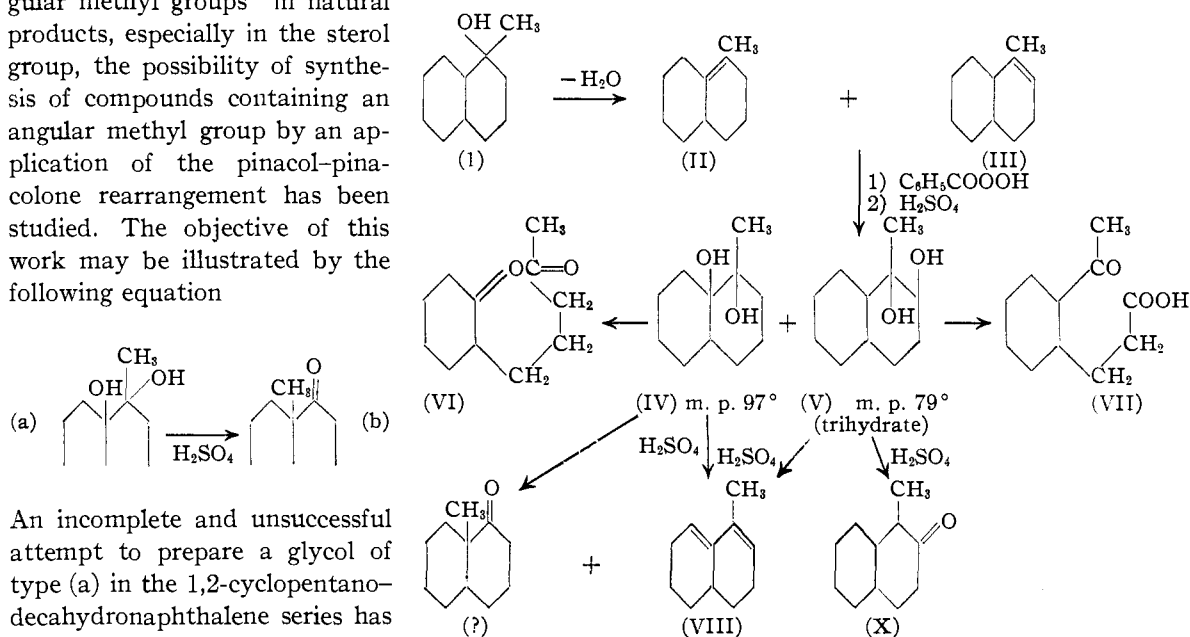


[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

## The Synthesis and Rearrangement of Some Decahydro- and Tetrahydronaphthalenediols

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In view of the significant occurrence of "angular methyl groups" in natural products, especially in the sterol group, the possibility of synthesis of compounds containing an angular methyl group by an application of the pinacol-pinacolone rearrangement has been studied. The objective of this work may be illustrated by the following equation



An incomplete and unsuccessful attempt to prepare a glycol of type (a) in the 1,2-cyclopentano-decahydronaphthalene series has been described by Robinson and Slater,<sup>3</sup> who had in mind a synthesis along similar lines.

A suitable test of the feasibility of the above synthesis seemed to lie in the decahydronaphthalene series, mainly because the stereochemical problems were minimized and the necessary starting materials were more readily available.

Some experiments were carried out in the tetrahydronaphthalene series also, the object being to determine the conditions under which the reactions to be applied to the decahydronaphthalene series could be carried out. It was found, however, that the behavior of the tetrahydronaphthalene derivatives is strikingly different from that of the corresponding decahydro compounds, probably due to the influence of the aromatic ring in compounds of the former type.

The reactions carried out in the decahydro-

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(3) Robinson and Slater, *J. Chem. Soc.*, **143**, 376 (1941).

The starting materials, *cis*- and *trans*- $\alpha$ -decalols, were obtained by catalytic reduction of aryl  $\alpha$ -tetralol<sup>4</sup> and  $\alpha$ -naphthol,<sup>5</sup> respectively. In both cases oxidation to the corresponding  $\alpha$ -decalones could be carried out either by chromic anhydride<sup>4</sup> or by aluminum isopropylate with satisfactory yields. It was noted in this connection that the isomerization of *cis*- $\alpha$ -decalone to *trans*- $\alpha$ -decalone reported by Hückel<sup>4</sup> did not take place under any of the conditions described by this author, and that a mixture of  $\alpha$ -decalones could be separated into its stereoisomeric components by fractional crystallization of the semicarbazones, followed by hydrolysis or by chromatographic adsorption methods. The conversion of the  $\alpha$ -decalones to the corresponding *cis*- and *trans*-1-methyl-decahydronaphthol-1 was effected by reaction with methylmagnesium iodide.

Dehydration of 1-methyl-decahydronaphthol-1

(4) Hückel, *Ann.*, **441**, 1 (1925).

(5) The reduction of  $\alpha$  naphthol was kindly carried out by Mr. G. F. Hager through the courtesy of Professor H. Adkins. It should be noted that the product of this reaction is chiefly *trans*  $\alpha$ -decalol rather than the *cis*-form as had been indicated by Adkins in an earlier paper (*THIS JOURNAL*, **60**, 664 (1938)).

(6) Robinson and Koebner, *J. Chem. Soc.*, **143**, 566 (1941).

(I) gave a mixture of 1-methyl- $\Delta^{1,9}$ -octahydronaphthalene (II) and 1-methyl- $\Delta^{1,2}$ -octahydronaphthalene which could not be separated by fractional distillation. Oxidation of this mixture with perbenzoic acid in chloroform solution, and acid hydrolysis of the epoxides thus obtained gave a complex mixture of glycols from which two pure crystalline compounds could be isolated: a trihydrate of m. p.  $79^\circ$  (V) and an anhydrous compound of m. p.  $97^\circ$  (IV). The structure of these compounds was proved by cleavage with lead tetraacetate in glacial acetic acid solution. The former (V) gave an aldehyde and the corresponding acid (VII), thus proving the presence of a secondary hydroxyl group in the glycol, while a diketone (VI) giving a positive iodoform test was obtained from the anhydrous glycol (IV) thus proving its ditertiary character.

The rearrangement of the glycols was carried out on heating with dilute sulfuric acid. The main product obtained on rearrangement of 1-methyl-1,2-*trans*-dihydroxy-*trans*-decahydronaphthalene trihydrate (V) was of ketonic nature, while a small amount of a conjugated diene was also present in the reaction mixture. The structure of the ketone (X) was proved by a Clemmensen reduction, followed by a vapor phase dehydrogenation<sup>7</sup> over palladized charcoal.<sup>8,9</sup> 1-Methylnaphthalene was obtained, thus indicating that the methyl group had not migrated in the formation of the ketonic rearrangement product. The nature of the by-product (XI) and its unsaturated character were indicated by its molecular refraction and unsaturated properties; the position of the double bonds was assumed on the basis of Bergmann's rule<sup>10</sup> according to which, in presence of acid, conjugated double bonds in condensed ring systems migrate to different rings.

The rearrangement of 1-methyl-1,9-*trans*-dihydroxy-decahydronaphthalene gave a conjugated diene (VIII) as the main product, while a very small amount of ketonic material was also obtained. As in the previous case, the structure of the diene was assumed to be as shown without further proof. The structure of the ketone could not be conclusively proved, due to the minute amount of material available. *cis*-9-

Methyldecalone has been reported by several workers<sup>11,12,13,14,15</sup> to give a semicarbazone melting at  $223$ - $225^\circ$ , while the semicarbazone of the *trans*-isomer is reported by Nenitzescu<sup>11</sup> to melt at  $185^\circ$ . The product obtained from this reaction gave a semicarbazone melting at  $200$ - $202^\circ$ . This melting point could not be raised by repeated fractional crystallization of this product from various solvents. Since our product does not give iodoform when treated with sodium hydroxide and iodine, it is believed not to be the 1-acetyl-hexahydroindane that might result from formation of a five-membered ring on rearrangement. The only remaining possible structures are 9-methyldecalone or a compound containing a 7-membered ring (1-methyl-bicyclo-decane-(4,3,1)-10-one). Of these two possibilities the former seems more likely. Further experiments are being carried out in connection with the structure of this product.

### Experimental

**1-Methyl-*cis*-decahydronaphthol-1 (I).**—A solution of 7.0 g. of *cis*- $\alpha$ -decalone in 100 cc. of dry ether was added to the methylmagnesium iodide prepared from 16.9 g. of methyl iodide and 2.8 g. of magnesium turnings in 100 cc. of dry ether. The mixture was then refluxed for two hours, poured into 400 g. of cracked ice, acidified with 6 *N* hydrochloric acid. The product was extracted with ether, dried over anhydrous sodium sulfate and distilled: b. p.  $76$ - $77^\circ$  (12 mm.),  $n_D^{25}$  1.4912, yield 6.95 g. (90%).

*Anal.* Calcd. for  $C_{11}H_{20}O$ : C, 7.86; H, 11.90. Found: C, 78.5; H, 11.82.

1-Methyl-*trans*-decahydronaphthol-1, prepared in an identical manner, had the following physical constants: b. p.  $93^\circ$  (5 mm.),  $n_D^{25}$  1.4928.

**1-Methyl- $\Delta^{1,2}$ -*trans*-octahydronaphthalene (III) and 1-Methyl- $\Delta^{1,9}$ -octahydronaphthalene (II).**—Twenty-five grams of 1-methyl-*trans*-decahydronaphthol-1 was heated for two hours at  $120$ - $130^\circ$  with 20 g. of anhydrous potassium bisulfate. After cooling to room temperature, the product was extracted with ether, dried over sodium sulfate and fractionally distilled through a 30-cm. Podbielniak column. The fraction boiling at  $65^\circ$  (5 mm.) weighed 14.3 g. and was a mixture of the two isomeric 1-methyl octalins:  $n_D^{25}$  1.4960.

*Anal.* Calcd. for  $C_{11}H_{18}$ : C, 88.0; H, 12.00. Found: C, 87.8; H, 12.32.

There was recovered 8.7 g. of unchanged 1-methyl-*trans*-decahydronaphthol-1 which brings the yield of hydrocarbons up to the theoretical amount, calculated on the basis of the amount of tertiary alcohol used up in the reaction.

**1-Methyl-1,2-epoxy-*trans*-decahydronaphthalene and 1-Methyl-1,9-epoxy-decahydronaphthalene.**—A solution of

(7) Zelinsky and Pawlow, *Ber.*, **56**, 1249 (1923).  
 (8) Zelinsky and Turowa-Pollak, *ibid.*, **58**, 1292 (1925).  
 (9) Linstead, Millidge, Thomas and Walpole, *J. Chem. Soc.*, **139**, 1151 (1937).  
 (10) W. Bergmann and Hirschmann, *J. Org. Chem.*, **4**, 40 (1939).

(11) Nenitzescu, Cioranescu and Prsemetsky, *Ber.*, **73**, 313 (1940).  
 (12) Chang Kong Chuang, *ibid.*, **69**, 1494 (1936).  
 (13) Cook and Lawrence, *J. Chem. Soc.*, **139**, 814 (1937).  
 (14) Elliot and Linstead, *ibid.*, **140**, 660 (1938).  
 (15) Pfentl and Bogert, *J. Org. Chem.*, **6**, 669 (1941).

18 g. of perbenzoic acid (a 20% excess) in 500 cc. of chloroform was cooled to 0°, and 17 g. of the above 1-methyl-octahydronaphthalene mixture were added with shaking at 0°. After standing for four hours at 0°, titration indicated that only the 20% excess perbenzoic acid remained. The solution was washed with 8% sodium hydroxide and with water, dried over sodium sulfate and distilled. The mixture of epoxides was a constant boiling, colorless liquid of pleasant menthol-like odor; b. p. 83° (7 mm.);  $n_{D}^{22}$  1.4820; yield, quantitative.

*Anal.* Calcd. for  $C_{11}H_{18}O$ : C, 79.5; H, 10.84. Found: C, 79.4; H, 11.12.

**1-Methyl-1,2-trans-dihydroxy-trans-decahydronaphthalene Trihydrate (V).**—Twenty-one and eight-tenths grams of the above 1-methyl-epoxy-trans-decahydronaphthalene mixture was added to 218 g. of 10% sulfuric acid at 0°. After shaking the reaction mixture for thirty minutes at 0–10°, a white semi-solid mass separated out and the mixture was allowed to stand in the ice box overnight. The solid was filtered on sintered glass, washed with three 50-cc. portions of ether and small amounts of ice-cold acetone. The white crystalline product thus obtained weighed 11 g. (yield, 36%). Recrystallization from aqueous acetone gave a product melting at 79°. The m. p. of this product could not be raised by fractional recrystallization from an ethyl acetate-petroleum ether mixture or water. When the glycol trihydrate was left in a vacuum desiccator over calcium chloride, it reverted to the corresponding anhydrous glycol. This was a colorless viscous oil which readily took up water from the air to give the crystalline trihydrate of m. p. 79°. The water of hydration was determined by vacuum drying over phosphorus pentoxide at 60°.

*Anal.* Calcd. for  $C_{11}H_{20}O_2 \cdot 3H_2O$ :  $H_2O$ , 22.7. Found:  $H_2O$ , 22.6. Calcd. for  $C_{11}H_{20}O_2 \cdot 3H_2O$ : C, 55.5; H, 10.92. Found: C, 55.5; H, 10.85.

**1-Methyl-1,9-trans-dihydroxy-decahydronaphthalene (IV).**—The filtrate and ether washings remaining after the isolation of the 1-methyl-1,2-trans-dihydroxy-trans-decahydronaphthalene trihydrate were treated as follows. The ether layer was separated, the aqueous layer was repeatedly extracted with a 50% ether–50% ethyl acetate mixture, and the combined extracts were dried over anhydrous potassium carbonate. Fractional distillation through a 30-cm. Podbielniak column gave 4.3 g. of low boiling, impure dehydration and rearrangement products of the glycols present in the mixture (as indicated by analytical data). The fraction boiling at 109–110° (3 mm.) weighed 3.5 g. and immediately solidified in colorless rhombic colorless plates of 1-methyl-1,9-trans-dihydroxy-decahydronaphthalene (yield, 15% of the theoretical, calculated on the basis of the total amount of 1-methyl-epoxy-decahydronaphthalene hydrolyzed).<sup>16</sup> After several recrystallizations from an ethyl acetate–low boiling petroleum ether mixture, the glycol melted sharply at 97°.

(16) The total yield of 1-methyl-trans-dihydroxy-decahydronaphthalenes which could be isolated on cleavage of the 1-methyl-epoxy-trans-decahydronaphthalene mixture was 50% of the theoretical: while the yields of 1-methyl-1,2-trans-dihydroxy-trans-decahydronaphthalene trihydrate could always be reproduced, the amount of 1-methyl-1,9-trans-dihydroxydecahydronaphthalene which could be isolated varied considerably in different preparations, depending mainly on the conditions of distillation.

It did not form a hydrate, and was very insoluble in water, very soluble in ether, acetone and benzene.

*Anal.* Calcd. for  $C_{11}H_{20}O_2$ : C, 71.7; H, 10.86. Found: C, 71.5; H, 10.86.

**Lead Tetraacetate Cleavage of 1-Methyl-1,2-trans-dihydroxy-trans-decahydronaphthalene Trihydrate.**—Two grams of 1-methyl-1,2-trans-dihydroxy-trans-decahydronaphthalene trihydrate was added to 120 cc. of a saturated solution of crystalline lead tetraacetate in aldehyde-free glacial acetic acid (corresponding to 3.8 g., or a slight excess, of lead tetraacetate). After heating for twenty-four hours at 40–45°, titration indicated that only the slight excess of lead tetraacetate remained. This was destroyed by addition of a few drops of glycerol, and the acetic acid was then removed under reduced pressure. Water was added to the residue, and 6 cc. of 30% sulfuric acid was added. The lead sulfate was filtered and thoroughly washed with ether. The ether layer was separated from the filtrate, and the aqueous layer was extracted with ether. The combined ether extracts were washed with 4% sodium hydroxide and with water, dried over sodium sulfate. After removing the ether, there remained 0.7 g. of a viscous pale yellow oil which was crude  $\beta$ -(2-acetyl-cyclohexyl)-propionaldehyde: it gave iodoform (m. p. 119°, mixed m. p. 119°) when treated with iodine and sodium hydroxide; it gave positive Schiff, Fehling and Tollens tests and readily gave a precipitate when treated with semicarbazide hydrochloride and sodium acetate in aqueous alcohol solution. It was not further purified.

The alkaline washings were acidified, and extracted with ether. After drying the ether extracts and removing the ether, 0.6 g. of a viscous yellow oil remained. This gave a positive iodoform test and had a neutralization equivalent of 199 (calculated for  $\beta$ -(2-acetyl-cyclohexyl)-propionic acid (VII) 198). It was distilled (at a pressure below 0.2 mm., bath temperature 140–150°) as a viscous colorless oil which slowly solidified on cooling.

*Anal.* Calcd. for  $C_{11}H_{18}O_3$ : C, 66.6; H, 9.09. Found: C, 66.6; H, 8.99.

The pseudo-benzyl thiourea salt of the  $\beta$ -(2-acetylcyclohexyl)-propionic acid crystallized from ethanol in small colorless needles of m. p. 156.5–157.5°.

**Lead Tetraacetate Cleavage of 1-Methyl-1,9-trans-dihydroxydecahydronaphthalene.**—One gram of 1-methyl-1,9-trans-dihydroxydecahydronaphthalene was added to 71 cc. of a saturated solution of lead tetraacetate in aldehyde-free glacial acetic acid (corresponding to 2.4 g., or the calculated amount of lead tetraacetate). After standing for ten hours at 40–45°, the solution gave no color with starch-iodide, thus indicating that the reaction was complete. After removing the acetic acid, and adding water and sulfuric acid to the residue, the lead sulfate was filtered, well washed with ether, and the ether layer was separated from the filtrate. The aqueous layer was extracted with ether. The combined ether extracts were washed with 2% sodium hydroxide and with water, dried over anhydrous sodium sulfate, and distilled. The colorless liquid thus obtained weighed 0.9 g., and was 1-( $\gamma$ -acetopropyl)-cyclohexanone-2 (VI). It gave a positive iodoform test, negative Schiff, Tollens and Fehling tests. It could be distilled without decomposition at 1 mm. (bath temp. 170–175°),  $n_{D}^{20}$  1.4818.

*Anal.* Calcd. for  $C_{11}H_{18}O_2$ : C, 72.5; H, 9.89. Found: C, 72.1; H, 9.75.

The 1-( $\gamma$ -acetopropyl)-cyclohexanone-2 readily gave a semicarbazone which was very insoluble in most organic solvents and melted with decomposition at 207–209°.

*Anal.* Calcd. for  $C_{13}H_{22}O_2N_2$ : N, 28.73. Found: N, 26.83. Calcd. for  $C_{12}H_{20}O_2N_2$ : N, 17.57.

**Rearrangement of 1-Methyl-1,2-trans-dihydroxy-trans-decahydronaphthalene Trihydrate (V).**—Sixteen grams of the glycol trihydrate was heated for four hours with 200 cc. of 30% sulfuric acid. After cooling to room temperature, the mixture was extracted with ether and the ether extracts were washed and dried over sodium sulfate. The products of the reaction were fractionally distilled through a 30-cm. modified Craig column.

The fraction boiling at 82° (10 mm.) weighed 1 g. It readily decolorized dilute aqueous potassium permanganate and was assumed to be 1-methyl-3,4,5,6,7,10-hexahydronaphthalene (VIII). It was redistilled over sodium to give a colorless liquid of hydrocarbon-like odor;  $n_D^{20}$  1.5308. It was not further investigated. The fraction boiling at 98° (10 mm.) weighed 4.9 g. It had a menthol-like odor, and readily reacted with reagents specific for a carbonyl group. It was 1-methyl-2-keto-trans-decahydronaphthalene (X) as proved by the following experiments;  $n_D^{20}$  1.4852.

*Anal.* Calcd. for  $C_{11}H_{18}O$ : C, 79.5; H, 10.84. Found: C, 79.2; H, 10.71.

Semicarbazone recrystallized from ethanol—m. p. 208–209° (dec.).

*Anal.* Calcd. for  $C_{12}H_{21}N_3O$ : N, 18.83. Found: N, 18.70. The oxime recrystallized from ethanol m. p. 149°; 2,4-dinitrophenylhydrazone, m. p. 170–171° (dec.).

**1-Methyl-trans-decahydronaphthalene (Clemmensen reduction of 1-methyl-2-keto-trans-decahydronaphthalene).**—One gram of 1-methyl-2-keto-trans-decahydronaphthalene (X) was added to a suspension of amalgamated zinc (from 20 g. of granulated zinc and 40 cc. of 5% mercuric chloride) in 7 cc. of 12 *N* hydrochloric acid, and the mixture was refluxed for twelve hours, 1 cc. of 12 *N* hydrochloric acid being added every hour. After cooling to room temperature, the product was extracted with ether, washed, dried and distilled; b. p. 54° (4 mm.);  $n_D^{20}$  1.4720; yield 0.7 g. (80% of the theoretical).

**Catalytic Dehydrogenation of 1-Methyl-trans-decahydronaphthalene.**—The reaction tube of Pyrex glass (30 cm. long and 10 mm. in diameter) was packed with a mixture of palladized charcoal<sup>8,9</sup> and asbestos, and heated electrically to 350° in a slow current of hydrogen. The gas stream was then stopped, and 0.6 g. of 1-methyl-trans-decahydronaphthalene was added over a period of two and one-half hours; 270 cc. of hydrogen was evolved (80% of the theoretical amount) and a colorless liquid distilled slowly into the receiver; the apparatus was then swept out with hydrogen for two hours.

The distillate, 1-methylnaphthalene, was isolated as the picrate which crystallized in orange-yellow needles of m. p. 140°. This was recrystallized from ethanol to constant m. p. 141–142° (reported m. p. for 1-methylnaphthalene picrate, 141–142°).

**Rearrangement of 1-Methyl-1,9-trans-dihydroxydecahydronaphthalene (IV).**—Two and three-tenths grams of

the anhydrous glycol of m. p. 97° (IV) was refluxed for four hours with 50 cc. of 30% sulfuric acid. After extracting with ether, washing and drying over sodium sulfate, the products were fractionated through a 30-cm. modified Craig column. The fraction boiling at 82° (7 mm.) weighed 0.95 g. and readily decolorized dilute aqueous potassium permanganate. It was assumed to be 1-methyl-3,4,5,6,7,10-hexahydronaphthalene (VIII);  $n_D^{20}$  1.5352,  $d_4^{20}$  0.9516; molecular refraction calcd. for  $C_{11}H_{17}$ , 48.76; found, 48.77.

*Anal.* Calcd. for  $C_{11}H_{17}$ : C, 88.6; H, 11.41. Found: C, 88.4; H, 11.03.

From the higher boiling fraction (b. p. 85–92° (7 mm.)), 80 mg. of crude semicarbazone could be isolated on treating with semicarbazide hydrochloride and sodium acetate in aqueous alcohol solution. After repeated crystallizations from methanol and chloroform, this semicarbazone melted with decomposition at 200–202°.

The ketone could be regenerated from the semicarbazone on heating with aqueous oxalic acid. The product thus obtained was a colorless liquid of pleasant decalone-like odor, which gave no iodoform when treated with sodium hydroxide and iodine.

**1-Methyl-3,4-dihydronaphthalene.**—Fifty grams of 1-methyl-1,2,3,4-tetrahydronaphthol-1 (prepared from tetralone and methylmagnesium iodide as described by Auwers<sup>17</sup>) was heated for two hours at 120–130° with 30 g. of anhydrous potassium bisulfate. After cooling to room temperature and separating the aqueous layer, the water-potassium bisulfate layer was extracted with ether. The combined extracts were dried, the ether distilled and the residue<sup>18</sup> fractionated *in vacuo*. 1-Methyl-3,4-dihydronaphthalene was obtained in quantitative yield as a colorless liquid of naphthalene-like odor; b. p. 84° (5 mm.);  $n_D^{25}$  1.5742.

*Anal.* Calcd. for  $C_{11}H_{12}$ : C, 91.6; H, 8.33. Found: C, 91.3; H, 8.28.

**1-Methyl-1,2-epoxy-1,2,3,4-tetrahydronaphthalene.**—Attempts to isolate the epoxide prepared from 1-methyl-3,4-dihydronaphthalene by the action of perbenzoic acid were unsuccessful. Only polymeric material and the ketonic rearrangement product, 1-methyl-2-keto-3,4-dihydronaphthalene, could be isolated. Seventeen grams (0.11 mole) of 1-methyl-3,4-dihydronaphthalene was added to a solution of 17 g. (0.12 mole) of perbenzoic acid in chloroform solution at 0°. After standing for two and one-half hours at 0° the reaction was complete as indicated by titration. The solution was washed with 8% sodium hydroxide solution and then with water, dried and distilled. The fraction boiling at 96–102° (2 mm.) weighed 12 g. and readily gave a semicarbazone on treatment with semicarbazide hydrochloride and sodium acetate in dilute alcohol. This semicarbazone after recrystallization from methanol melted at 194° with decomposition.<sup>19</sup> The

(17) Auwers, *Ann.*, **415**, 163 (1918).

(18) Although Auwers reported<sup>17</sup> that the formation of 1-methyl-3,4-dihydronaphthalene from the corresponding carbinol was difficult even under drastic conditions, it was found in the present investigation that the carbinol was dehydrated quantitatively under mild conditions.

(19) Recently Cornforth, Cornforth and Robinson, *J. Chem. Soc.*, **144**, 689 (1942), have prepared this substance and they report the melting point of the semicarbazone as 200–202° with decomposition.

ketone was regenerated by treatment of this derivative with aqueous oxalic acid and showed the following physical constants: b. p. 103° (3 mm.);  $n_D^{25}$  1.5485,  $n_D^{20}$  1.5494.

*Anal.* Calcd. for  $C_{11}H_{12}O$ : C, 82.5; H, 7.50. Found: C, 82.3; H, 7.67.

**1-Methyl-1,2-cis-dihydroxy-1,2,3,4-tetrahydronaphthalene.**—A solution of 7 g. of potassium permanganate in 425 cc. of acetone and 25 cc. of water was added over a period of six hours to a stirred solution of 7 g. of 1-methyl-3,4-dihydronaphthalene in 25 cc. of acetone cooled to  $-40^\circ$ . After the addition was complete the mixture was stirred for one hour at  $-40^\circ$  and then allowed to warm up to room temperature. The manganese dioxide was filtered and the filtrate saturated with carbon dioxide. After filtering the potassium bicarbonate and evaporating the acetone on the steam-bath, 200 cc. of water was added to the residue and the resulting oil extracted with ether. The ether extracts were then washed, dried and fractionally distilled. A fore-fraction of 2.2 g., b. p. 82° (4 mm.), was unchanged hydrocarbon ( $n_D^{25}$  1.5738) and the fraction distilled at 135–140° (4 mm.) yielded 3.3 g. of the expected glycol as a viscous liquid which slowly crystallized on long standing. The yield was 60% of the theoretical based on the amount of the hydrocarbon that had reacted.<sup>20</sup>

*Anal.* Calcd. for  $C_{11}H_{14}O_2$ : C, 74.2; H, 7.86. Found: C, 74.2; H, 7.86.

**1-Methyl-2-keto-1,2,3,4-tetrahydronaphthalene.**—A solution of 4.3 g. of the above glycol in 45 cc. of 30% sulfuric acid was refluxed for two and one-half hours. After cooling, the mixture was extracted with ether, washed with sodium bicarbonate solution, dried and distilled *in vacuo*. The first fraction yielded 1.7 g. of unchanged starting material; the fraction boiling at 105–107° (3 mm.) was found to be 1-methyl-2-keto-1,2,3,4-tetrahydronaphthalene, a colorless, pleasant-smelling liquid. The semicarbazone prepared in the usual manner melted at 194° with decomposition. The ketone regenerated from this derivative as described above showed physical properties identical with those of the rearrangement product of 1-methyl-1,2-epoxy-1,2,3,4-tetrahydronaphthalene. A direct comparison of the physical properties of this ketone with those of the other possible rearrangement product, 2-methyl-1-keto-tetrahydronaphthalene, and a similar comparison of

(20) Under seemingly identical conditions the yield in this reaction varied widely, perhaps due to difficulties in temperature control.

the semicarbazones (m. p. of 2-methyl-1-ketotetrahydronaphthalene 199°) confirmed the structure of this ketone. A determination of the ultraviolet absorption spectrum also indicated the absence of the conjugation to be expected of an  $\alpha$ -tetralone derivative.<sup>21</sup>

**2-Methyl-1-keto-1,2,3,4-tetrahydronaphthalene.**—Since the values for the physical constants of this substance as reported in the literature differ<sup>22</sup> it was necessary to synthesize it for comparison with the rearrangement product of 1-methyl-1,2-hydroxy-1,2,3,4-tetrahydronaphthalene. This synthesis was carried out by alkylating  $\alpha$ -tetralone by means of sodamide and methyl iodide in benzene solution. The mixture of sodium  $\alpha$ -tetralone and methyl iodide was refluxed for five hours, decomposed with water, extracted with ether, dried and distilled. The product, a mixture of  $\alpha$ -tetralone and the methylated ketone was further purified by fractional crystallization of the semicarbazones. The properties of 2-methyl-1-ketotetrahydronaphthalene obtained by regeneration of the semicarbazone (m. p. 199°) were: b. p. 98° (3 mm.);  $n_D^{25}$  1.5585.

*Anal.* (semicarbazone) Calcd. for  $C_{12}H_{13}N_3O$ : N, 19.35. Found: N, 19.45.

### Summary

1. Isomeric tertiary alcohols, mono-unsaturated hydrocarbons, and epoxides of the decahydronaphthalene series, containing a methyl group in position 1 have been prepared and studied as intermediates leading to the synthesis of glycols.

2. 1,2- and a 1,9-glycol derived from 1-methyl-decahydronaphthalene have been isolated and characterized and their rearrangement studied.

3. The rearrangement of 1-methyl-1,2-dihydroxy-1,2,3,4-tetrahydronaphthalene has also been investigated.

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(21) The absorption spectrum was obtained through the courtesy of Dr. M. M. McLean.

(22) Schroeter, *Ber.*, **51**, 1600 (1918); Krollpfeiffer and Schager *ibid.*, **56**, 631 (1923); Brunner and Grof, *Monatsh.*, **64**, 79 (1934).