0.02 mole) was dissolved in 120 ml. of 95% ethanol. To this solution was added 3.5 g. (0.02 mole) of silver nitrate dissolved in 80 ml. of a solution of 60 parts ethanol and 40 parts water. After the resulting reaction mixture was heated to reflux for one hour, the precipitated silver bromide was filtered and washed. After drying, the silver bromide weighed 3.6 g. (97%).

Most of the organic solvent was evaporated under reduced pressure and the remaining mixture was extracted with ether. After the ether was evaporated the neutral organic material was separated into a ketonic and non-ketonic fraction using Girard[16] reagent. The non-ketonic fraction was saponified using the procedure of Rubin[14] for esters of II to give 0.74 g. (18%) of 1-phenylcyclohexanecarboxylic acid, m.p. 123–124°.

After an aliquot had been withdrawn, the remaining neutral ketonic fraction was distilled to give 0.8 g. of pure 1-cyclohexenyl phenyl ketone, m.p. 32–34°, the melting point of which was not depressed by addition of an authentic sample. Titration of the aliquot of neutral material with bromine indicated the presence of 68% of unsaturated compound. An infrared spectrum of the neutral ketonic fraction indicated no significant amount of α-hydroxyketone (IV) had formed.

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[16] M. E. Smith, B. Chase and R. Rhodes, THIS JOURNAL, **66**, 1547 (1944).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

The Configuration of Isocamphenilanol[1]

BY WYMAN R. VAUGHAN AND RANDOLPH PERRY, JR.

RECEIVED MARCH 25, 1952

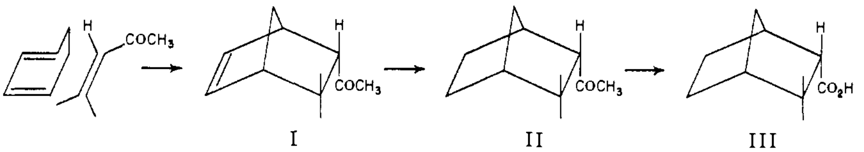
Evidence is presented for the assignment of an *endo* configuration to the lower melting isomer of the epimeric pair of alcohols related to camphenilanic and isocamphenilanic acids. The names camphenilanol and isocamphenilanol are suggested for the corresponding alcohols.

The confusion arising from an early study[2] of the acids obtained by oxidation of camphene and camphene derivatives was only partially resolved by the explicit demonstration of the *endo* configuration of isocamphenilanic acid.[3] While this proof of configuration inferentially established the identity of camphenilanic acid[2,4] there appeared to be no satisfactory way of relating the apparently stereoisomeric camphenanic and isocamphenanic acids to these substances. The esters of all four acids gave the same alcohol on reduction with sodium and alcohol thus suggesting the stereoisomeric character of the acids as opposed to structural differences, and this appeared to be confirmed by saponification of the ester of isocamphenanic acid, which afforded a mixture of camphenilanic and isocamphenilanic acids. In view of this evidence and the nature of the steric problem it is only possible to conclude that camphenanic acid, too, must constitute another such mixture.[5]

Inasmuch as esters of the pure acids as well as of mixtures of them appeared to give the same alcohol on sodium and alcohol reduction, nothing could be said of the configuration of this alcohol (m.p. 77°, acid phthalate m.p. 153°).[2] A presumably epimeric, lower melting alcohol[6,7] had been prepared by reduction of the enolacetate of camphenilanaldehyde, but here again conclusions as to configuration are equivocal.

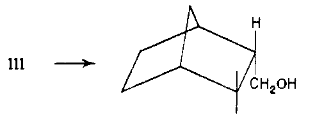
Recently the two epimeric alcohols were prepared for the first time in substantially pure state and with adequate data on derivatives to enable comparative identification. However, unequivocal assignment of configuration was not possible, since the reactions used[8] were essentially those previously described[2,6] and thus are subject to the same objections. It is only possible to infer that since the yield and purity of the higher melting alcohol (81°) obtained by sodium and alcohol reduction of methyl camphenilanate (*exo*) are superior to those reported for similar reduction of the epimeric isocamphenilanate (*endo*), the higher melting isomer probably has the *exo* configuration.

In connection with other studies in this field the present investigators had occasion to prepare one of these alcohols by a route which leaves no doubt as to its configuration. Mesityl oxide was allowed to react with cyclopentadiene, produced *in situ* by thermal depolymerization of the dimer, and the resulting unsaturated ketone (I) was reduced catalytically to the saturated ketone (II) which then was converted to isocamphenilanic acid (III) by the haloform reaction. The acid thus obtained corresponded in all respects with that more directly produced by the addition of β,β-dimethylacrylic acid to cyclopentadiene followed by reduction.[3]



I II III

Reduction of III by lithium aluminohydride afforded an excellent yield of an alcohol, IV, melting at 58–60°. Purification through the acid phthal-



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[1] Presented in part before the Organic Division of the American Chemical Society at Buffalo, March 26, 1952.

[2] G. G. Henderson and M. M. J. Sutherland, *J. Chem. Soc.*, **105**, 1710 (1914).

[3] G. Komppa and O. Komppa, *Ber.*, **69B**, 2606 (1936).

[4] J. Bredt and W. Jagelki, *Ann.*, **310**, 112 (1900).

[5] *Cf.* P. Lipp, private communication, "Beilstein," Vol. V, 1 Suppl., p. 83.

[6] F. W. Semmler, *Ber.*, **42**, 962 (1909).

[7] P. Lipp, H. Dessauer and E. Wolf, *Ann.*, **525**, 271 (1936).

[8] W. Hückel and H. Schultze, *ibid.*, **575**, 32 (1951).

ate (m.p. 156.0–156.7°, reported[8] 153.5–154.0°) furnished a sample of the alcohol melting at 65–66° (reported[8] 68°). The 4-nitrobenzoate melted sharply at 106.5–107.0° (reported[8] 103°). Thus there seems to be little doubt that the alcohol presently reported is Hückel's "isocamphanol II" (m.p. 68°).[9]

Inasmuch as it has been demonstrated that lithium aluminohydride reduction does not affect racemizable asymmetric centers,[10] the configuration of the lower melting "isocamphanol II" is clearly established as *endo*. In view of this it would seem appropriate to call it isocamphenilanol and to name the higher melting isomer camphenilanol, thus preserving the generic relationships with the related isocamphenilanic and camphenilanic acids.[11]

Acknowledgment.—The senior author is indebted to the Executive Board of the Horace H. Rackham School of Graduate Studies for the grant of a Summer Faculty Research Fellowship which enabled him to undertake the present study.

Experimental[12]

2,2-Dimethyl-3,6-*endo*-methano-Δ^4-cyclohexenyl Methyl Ketone (5,6-Dehydro-*endo*-3-camphenilyl Methyl Ketone) (I).—A mixture of 135 ml. (1 mole) of freshly distilled dicyclopentadiene and 650 ml. (5.7 moles) of mesityl oxide was heated in an autoclave at 160° for 12 hours, after which the system was allowed to cool spontaneously overnight and the mixture was fractionated at reduced pressure. There was recovered 569 ml. of mesityl oxide (37–43° at 18 mm.); and 68 g. (0.42 mole) of adduct (100–105° at 18 mm.) was obtained. Based upon available cyclopentadiene this represents a 21% yield; however, based upon mesityl oxide actually consumed it represents a 60% yield. A small portion was carefully refractionated for analysis: b.p. 74° at 4 mm., 53° at 1 mm.; n^{25}D 1.4807; sp. gr.$^{28}_{28}$ 0.9698.

Anal. Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.42; H, 9.52.

Attempts to prepare the usual carbonyl derivatives were not pursued when it became apparent that difficultly separable mixtures of geometric isomers were produced, even with 2,4-dinitrophenylhydrazine.

2,2-Dimethyl-3,6-*endo*-methanocyclohexyl Methyl Ketone (Isocamphenilyl Methyl Ketone, *endo*-3-Camphenilyl Methyl Ketone) (II).—A solution of 34 ml. (0.20 mole) of the preceding unsaturated ketone in 100 ml. of glacial acetic acid was hydrogenated at room temperature and 3 atm. using 0.20 g. of Adams catalyst. The theoretical volume of hydrogen (0.2 mole) was absorbed rapidly (6 minutes) with the evolution of considerable heat, and there was no evidence of further hydrogen uptake upon continued shaking. Fractionation of the product afforded 31.6 ml. (0.183 mole) of product (91%) boiling at 51–53° at 0.90 mm. Refractionation at 52–53° at 0.90 mm. was carried out to provide the analytical sample: n^{25}D 1.4749; sp. gr.$^{28}_{28}$ 0.9606.

Anal. Calcd. for $C_{11}H_{18}O$: C, 79.47; H, 10.91. Found: C, 79.46; H, 10.52.

Preparation of derivatives again appeared to yield mixtures, but a semicarbazone was obtained in reasonably pure condition, m.p. 201.6–203.0° from ethanol.

Anal. Calcd. for $C_{12}H_{21}N_3O$: C, 64.54; H, 9.48; N, 18.82. Found: C, 64.93; H, 9.20; N, 18.81.

Isocamphenilanic Acid (*endo*-**3-Camphenilanecarboxylic Acid**)[13] (**III**).—A vigorously refluxing mixture of isocamphenilyl methyl ketone (5 ml., 0.03 mole), and 15 ml. of water containing 1 g. of potassium hydroxide and a crystal of "Nacconol" was treated with a large excess (0.15 mole) of potassium hypochlorite solution, added dropwise over 0.5 hr. Refluxing was continued for an hour after which the chloroform, carbon tetrachloride and unchanged ketone were removed by steam distillation. The reaction mixture was then cooled to room temperature and with efficient external cooling was strongly acidified with 1:2 sulfuric acid. Isocamphenilanic acid first separated as an oil and then solidified; yield 2.92 g., 60%. Additional acid (0.43 g.) was obtained by returning the steam distillate to the reaction flask and repeating the haloform reaction; thus an over-all yield of 70% of the crude acid can be obtained. The reaction product melted at 109–112° and after recrystallization from 30–40° petroleum ether or aqueous alcohol there was obtained a beautifully crystalline product, m.p. 118.0–118.5° cor., reported[3] 118°.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.58; H, 9.59.

Isocamphenilanol (*endo*-**3-Camphenilylmethanol**) (**IV**).—A solution of 4.23 g. (0.025 mole) of isocamphenilanic acid in ether was added dropwise to excess lithium aluminohydride in ether. The reaction mixture was then treated cautiously with ethanol to destroy the excess hydride, and the usual method of processing afforded 3.85 g. of crude alcohol, m.p. 58–60° before and after sublimation. Conversion to the acid phthalate was achieved in 82.5% yield by refluxing the sublimed product with 4.5 g. of phthalic anhydride in 10 ml. of reagent benzene for 10 hr.[2] After several recrystallizations from ether–petroleum ether, isocamphenilyl acid phthalate melted somewhat higher than previously reported; m.p. 156.0–156.7°, previously 153.5–154.0°.[8]

Anal. Calcd. for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.65; H, 7.18.

Saponification of the acid phthalate afforded a sample of the alcohol which, after sublimation, melted at 65–66°, reported 68°.[2]

The 4-nitrobenzoate was prepared and recrystallized from aqueous methanol, and melted at 106.5–107.0°, somewhat higher than the previously reported value, 103°.[8]

Anal. Calcd. for $C_{17}H_{21}NO_5$: C, 67.30; H, 6.98; N, 4.62. Found: C, 67.50; H, 6.81; N, 4.80.

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[9] The slight differences in recorded melting points may be due to the lack of corrections and to the notoriously high cryoscopic constants in this series which render difficult the obtaining of reproducible melting points from one laboratory to another.

[10] D. S. Noyce and D. B. Denney, THIS JOURNAL, **72**, 5743 (1950).

[11] *Cf.* Sir John Simonsen, "The Terpenes," Vol. II, Second Edition, Cambridge University Press, 1949, pp. **277**, 294.

[12] Melting points uncorrected unless otherwise stated. Microanalyses by Clark Microanalytical Laboratory, Urbana, Illinois

[13] The authors are indebted to Mr. C. E. Smith, Jr., who studied the conditions for this reaction.