veloped by two of the present authors,[6] however, gave good results. Antimetabolite tests showed no inhibition of growth of *E. coli*, *Staph. aureus*, or *Strep. varidans in vitro* by 1:2000 dilution of either 2- or 6-fluoronicotinic acid. These tests were carried out by the Lilly Research Laboratories. Testing of the fluoronicotinamides is in progress.

### Experimental

**2-Fluoro-3-methylpyridine.**—To a solution of 80 g. (0.74 mole) of redistilled 2-amino-3-methylpyridine[7] in 310 g. of 40% fluoboric acid contained in an ice-cooled 1500 ml. beaker, 51 g. (0.74 mole) of sodium nitrite was gradually added in small portions with mechanical stirring. When the addition was complete, the solution was stirred for an additional thirty minutes at ice-bath temperature, and was then warmed to 45° to ensure complete decomposition. The solution was neutralized with sodium carbonate and steam-distilled. The yellow oil which separated from the distillate was removed and the remaining water layer extracted with ether. The oil and ether extracts were combined, dried over anhydrous sodium sulfate, and the ether removed. Distillation of the residue gave 39.5 g. (48%) of 2-fluoro-3-methylpyridine, b. p. 150.5–151.0° at 757 mm.

*Anal.* Calcd. for $C_6H_6NF$: C, 64.9; H, 5.4; N, 12.6. Found: C, 64.7; H, 5.6; N, 12.5.

**2-Fluoronicotinic Acid.**—A mixture of 38 g. (0.33 mole) of 2-fluoro-3-methylpyridine, 126 g. (0.80 mole) of potassium permanganate, and 1.5 l. of water contained in a 3-liter three-necked flask, fitted with condenser and sealed stirrer, was refluxed gently for four hours. The mixture was first steam-distilled to remove unreacted 2-fluoro-3-methylpyridine (8.0 g.) and then filtered hot. The resulting solution was evaporated to approximately 700 ml., cooled in an ice-bath, and acidified with concentrated hydrochloric acid. The precipitate which formed was filtered, dried, and recrystallized from water to yield 23.0 g. (49% based on starting methyl compound or 63% based on amount reacted) of 2-fluoronicotinic acid, m. p. 164–165°,[8] with decomposition.

*Anal.* Calcd. for $C_6H_4O_2NF$: C, 51.1; H, 2.9; N, 9.9; F, 13.5. Found: C, 51.2; H, 3.1; N, 9.9; F, 13.7.

**2-Fluoronicotinamide.**—A solution of 28.2 g. (0.20 mole) of 2-fluoronicotinic acid in 250 ml. of thionyl chloride was refluxed for forty-five hours. The excess thionyl chloride was then removed under reduced pressure, and the residue of 2-fluoronicotinyl chloride, b. p. 84.0–85.0° at 4 mm., was dissolved at once in 115 ml. of dry benzene. Dry ammonia was bubbled through the solution for thirty minutes and the solids formed were removed by filtration. These were extracted with dry acetone, the solvent was taken off, and the remaining yellow crystals were recrystallized from water. The yield of pure 2-fluoronicotinamide, m. p. 120.9–122.0° was 67.5%.

*Anal.* Calcd. for $C_6H_5ON_2F$: C, 51.4; H, 3.6; N, 20.0. Found: C, 51.4; H, 3.5; N, 19.8.

Approximately the same yield was obtained when the acid chloride was prepared by reaction of the acid with phosphorus pentachloride in phosphorus oxychloride solvent.

**2-Fluoro-5-methylpyridine.**—This compound was prepared according to the directions given for 2-fluoro-3-methylpyridine, except that 2-amino-5-methylpyridine was the starting material. A 46% yield of pure product, b. p. 155–156° at 752 mm., was obtained.

*Anal.* Calcd. for $C_6H_6NF$: C, 65.0; H, 5.4; N, 12.6. Found: C, 64.7; H, 5.5; N, 12.8.

**6-Fluoronicotinic Acid.**—This product was obtained in 60% yield, based on starting 2-fluoro-5-methylpyridine (71% based on that reacted), according to the method described for the preparation of the 2-fluoro-isomer. It was purified by sublimation and melted at 146–147° with decomposition.

*Anal.* Calcd. for $C_6H_4O_2NF$: C, 51.1; H, 2.9; N, 9.9; F, 13.5. Found: C, 51.0; H, 3.1; N, 9.8; F, 13.8.

**6-Fluoronicotinamide.**—Prepared in 65% yield from 6-fluoronicotinic acid by the method described for the 2-fluoro-isomer, this compound melted at 166.2–167.0°, after recrystallization from water.

*Anal.* Calcd. for $C_6H_5ON_2F$: C, 51.4; H, 3.6; N, 20.0. Found: C, 51.4; H, 3.8; N, 19.7.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF KANSAS
LAWRENCE, KANSAS

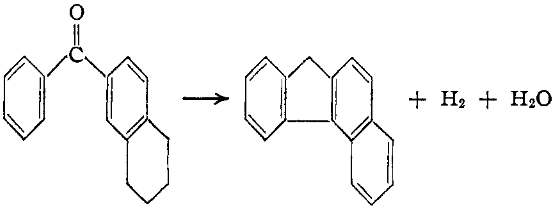
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NORTH CAROLINA
CHAPEL HILL, N. C.

RECEIVED SEPTEMBER 23, 1948

## Aromatic Cyclodehydrogenation. VIII. Experiments with 2-Benzoyl-5,6,7,8-tetrahydronaphthalene[1]

BY MILTON ORCHIN,[2] E. O. WOOLFOLK[2] AND LESLIE REGGEL[2]

A possible convenient two-step synthesis of 3,4-benzfluorene, II, consists of its formation by direct cyclization of 2-benzoyl-5,6,7,8-tetrahydronaphthalene, I. The latter is readily available, since acylating agents substitute exclusively at the 6-position of 1,2,3,4-tetrahydronaphthalene. In the respect that the conversion would involve a cyclization of a diaryl ketone, accompanied by loss of water, the reaction bears a superficial resemblance to the Elbs reaction. Although no suitable catalyst has been found for the Elbs reaction,[3] it seemed reasonable to expect, in the present instance, that a chromia-on-alumina catalyst would combine dehydration and cyclization activity. It has been found that vapor-phase treatment of I over such a catalyst at 450-470° gave, as a major product, 2-benzylnaphthalene. Only a little of the expected 3,4-benzfluorene was formed, accompanied by a small quantity of 2,3-benzfluorene. Both benzfluorenes were probably formed *via* 2-benzylnaphthalene, the former by cyclization into the 1-position and the latter by closure at the 3-position.



I II

Liquid-phase treatment of 2-benzoyl-5,6,7,8-

---

(6) Roe and Hawkins, THIS JOURNAL, 69, 2443 (1947).

(7) Obtained from the Reilly Tar and Chemical Corporation.

(8) Melting points are corrected.

(1) Article not copyrighted.

(2) Organic Chemist, Bureau of Mines, Office of Synthetic Liquid Fuels, Research and Development Branch, Pittsburgh, Pa.

(3) For a review of this reaction see Fieser in "Organic Reactions," John Wiley & Sons, N. Y., Vol. I, p. 129.

tetrahydronaphthalene, I, in the presence of a palladium-on-charcoal catalyst also gave principally 2-benzylnaphthalene. An analogous internal dehydrogenation–hydrogenation has been reported with 2-acetyl-5,6,7,8-tetrahydronaphthalene.[4] Treatment of I with sulfur in the liquid phase gave 2-benzoylnaphthalene, in agreement with the work reported by Barbot.[5] In general, it appears that sulfur dehydrogenation of a hydroaromatic compound containing oxygen seldom results in elimination of oxygen. With palladium-on-charcoal, however, the hydrogen liberated from one part of a molecule during dehydrogenation is frequently used in the hydrogenation or hydrogenolysis of another susceptible portion of the molecule and may in suitable cases even be transferred intermolecularly.[6] It is of interest to note that, even in the vapor-phase reaction mentioned above, such an intramolecular dehydrogenation–hydrogenation occurred.

### Experimental[7]

**2-Benzoyl-5,6,7,8-tetrahydronaphthalene, I.**—This compound was prepared from benzoyl chloride and tetrahydronaphthalene according to the directions of Scharwin,[8] except that nitrobenzene was used as the solvent instead of carbon disulfide. Purification by crystallization from methanol gave pure I, m. p. 40.4–41.2°, which has previously been reported[8] as an oil.

**Sulfur Dehydrogenation of I.**—A mixture of 10 g. of I and 2.7 g. of sulfur was heated at 200–270° for seventy minutes. The crude product was distilled, and the distillate (7.8 g.) was chromatographed on alumina–celite whereby 5.8 g. of phenyl 2-naphthyl ketone was isolated. Crystallization from ethanol gave colorless crystals, m. p. 81.4–81.8°. A stable picrate could not be prepared.[9]

**Palladium Dehydrogenation of I.**—A mixture of 10 g. of I and 0.09 g. of 30% palladium-on-charcoal[10] was heated gradually from 220 to 320° over a period of ninety-five minutes. Vacuum distillation of the product gave 8.2 g. of oil. Chromatography of the crude product on alumina gave as a first, less strongly adsorbed fraction, 6.1 g. (66%) of 2-benzylnaphthalene, which after crystallization from ethanol was obtained as thick, colorless prisms, m. p. 54.3–55.3°. The picrate had a melting point of 94.2–95.0°.[11] The more strongly adsorbed fractions from the chromatogram gave 1.6 g. (16%) of phenyl 2-naphthyl ketone.

**Chromia-on-Alumina Dehydrogenation of I.**—During three and one-half hours, 15 g. of I was passed over 92 g. of the chromia-on-alumina catalyst[10] at 450–470°, using the apparatus previously described.[10] The product, a mixture of green oil and water, weighed 12.03 g. It was dissolved in benzene, the water distilled off, and an aliquot containing 4.83 g. chromatographed on alumina–supercel. The percolate fractions gave 0.12 g. of naphthalene, identified by melting point and mixed melting point. The column was extruded and divided into three sections. The bottom portion (non-fluorescent, least strongly adsorbed) gave 3.28 g. of 2-benzylnaphthalene, identified by melting point and mixed melting point of the hydrocarbon and its picrate. The intermediate purple-fluorescent band gave 0.07 g. of material, identified as 3,4-benzfluorene by its ultraviolet absorption spectrum.[12] The uppermost, green-fluorescent band gave 0.02 g. of material, identified as 2,3-benzfluorene by its ultraviolet absorption spectrum.[12] It is of interest to note that the separation of 3,4- and 2,3-benzfluorene was easily achieved by chromatography, whereas the separation of 1,2- and 2,3-benzfluorene is extremely difficult.[13]

---

(4) Newman and Zahm, This Journal, **65**, 1097 (1943).

(5) Barbot, *Bull. soc. chim.*, [4] **47**, 1314 (1930).

(6) Orchin, This Journal, **66**, 535 (1944).

(7) All melting points corrected.

(8) Scharwin, *Ber.*, **35**, 2511 (1902).

(9) Rousset, *Bull. soc. chim.*, [3] **15**, 71 (1896), reported the melting point of the ketone as 82° and stated that a picrate was formed which had a melting point of 112–113°.

(10) Orchin, Reggel, Friedel and Woolfolk, Bureau of Mines T. P. 708. This preparation is essentially the catalyst-*d* of Linstead and Thomas, *J. Chem. Soc.*, 1127 (1940).

(11) These properties are in agreement with those listed in Heilbron, "Dictionary of Organic Compounds," Vol. 3, p. 432 (1943).

(12) We wish to thank Dr. R. A. Friedel and Mrs. Lois Harnack for the spectra determinations. The comparison spectrum for 3,4-benzfluorene was obtained from the work of Mayneord and Roe, *Proc. Roy. Soc.* (*London*), **A158**, 634 (1937); that for 2,3-benzfluorene was obtained from a sample in our possession.[13]

(13) Orchin and Reggel, This Journal, **70**, 1245 (1948). A forthcoming paper will discuss the ultraviolet spectra and fine structure of the three benzfluorenes.

OFFICE OF SYNTHETIC LIQUID FUELS
RESEARCH AND DEVELOPMENT BRANCH
U. S. DEPARTMENT OF INTERIOR
BUREAU OF MINES
CENTRAL EXPERIMENT STATION
PITTSBURGH, PA.

RECEIVED SEPTEMBER 16, 1948

---

## 1,2-Diphenylcyclohexane

BY STANLEY M. PARMERTER[1]

Although several preparations of 1,2-diphenylcyclohexane have been reported[2,3,4,5] subsequent investigations[6,7] have shown that the product was actually the 1,4-isomer.

The synthesis of 1,2-diphenylcyclohexane has now been accomplished by an unequivocal method. The reaction between phenylmagnesium bromide and 2-phenylcyclohexanone produced a carbinol which was dehydrated to a diphenylcyclohexene. Hydrogenation of the diphenylcyclohexene with palladium–on–charcoal catalyst yielded 1,2-diphenylcyclohexane, which the author presumes to be the *cis*-form.

### Experimental

**Diphenylcyclohexene.**—A solution of 62 g. (0.36 mole) of 2-phenylcyclohexanone[8] in 300 cc. of absolute ether was added in ninety minutes to a stirred, refluxing solution of phenylmagnesium bromide, prepared from 63 g. (0.40 mole) of bromobenzene and 9.7 g. (0.40 g. atom) of magnesium turnings in 250 cc. of absolute ether. After an additional two hours of stirring and refluxing, the mixture was left overnight at room temperature. The mixture was then decomposed with ammonium chloride solution and the product was extracted in two 300-cc. portions of ether. The dried ether solution upon evaporation left the crude carbinol which was dehydrated by stirring with an equal volume of 85% phosphoric acid for four hours on the steam-bath. The acid mixture was diluted with water and the product taken up in benzene. Distillation of the benzene solution gave a fraction of 64 g. boiling at 170–188° (10 mm.). Upon recrystallization from methanol there was obtained 44.5 g. (53%) of colorless needles, m. p. 50–52°. An analytical sample melted at 51–52°.

---

(1) Present address: Eastman Kodak Co., Rochester, N. Y.

(2) Kursanoff, *Ann.*, **318**, 309 (1901).

(3) Gustavson, *Compt. rend.*, **146**, 640 (1908).

(4) Bodroux, *Ann. chim.*, [10] **11**, 511 (1929).

(5) Wertyporoch and Sagel, *Ber.*, **66**, 1306 (1933).

(6) Nenitzescu and Curcaneanu, *ibid.*, **70**, 346 (1937).

(7) Corson and Ipatieff, This Journal, **60**, 747 (1938).

(8) Price and Karabinos, *ibid.*, **62**, 1159 (1940).