cooled in an ice-bath and saturated with dry hydrogen chloride. To this, 30 g. of calcium chloride was added, the mixture was allowed to stand at room temperature for twenty-four hours and the solid material was removed by filtration. The liquid was a yellow oil with a very unpleasant odor. The compound was unstable at high temperatures, boiling at 158–160°, 16 mm.

β-(Benzylseleno)-alanine.—Ten grams of benzyl chloromethyl selenide was refluxed for four hours with 15 g. of sodium phthalimidomalonic ester in the presence of toluene. The toluene was removed *in vacuo*, the compound recrystallized and the white crystals were collected. The compound was unstable at high temperatures and a melting point could not be determined. Fifteen grams of the compound was suspended in 100 ml. of an ethyl alcohol and water mixture (1:1) and 10 ml. of dioxane added. Two drops of phenolphthalein solution was added and the mixture was heated to 50°. Fifteen ml. of 5 *N* sodium hydroxide solution was added dropwise with stirring at a rate to maintain a temperature of 55–60°. When all of the alkali had been added the temperature of the solution was brought up to 70°. The solution was stirred constantly while the temperature was allowed to drop to room temperature. Hydrochloric acid was added until the solution was acid to phenolphthalein and the solution was distilled to half volume *in vacuo*. Water was added to make a total volume of 150 ml. and 20 ml. of concentrated hydrochloric acid was added with the evolution of carbon dioxide. The solution was heated for one and one-half hours, more hydrochloric acid added and heating continued for two more hours. The solution was taken to dryness, the residue dissolved in water and ammonium hydroxide was added until a neutral reaction was obtained with congo red. The precipitate which consisted of β-(benzylseleno)-alanine and phthalic acid was removed by filtering, suspended in boiling ethyl alcohol and again filtered. This was repeated until all of the phthalic acid had been removed leaving the β-(benzylseleno)-alanine as a white, crystalline residue, m. p. 185°; yield, 59%.

Anal. Calcd. for $C_{10}H_{13}O_2NSe$: Se, 30.52; C, 47.0; H, 5.07; N, 5.41. Found: Se,[9] 30.03; C, 47.0; H, 5.5; N,[10] 5.42.

β,β′-Diselenodialanine.—Three and one-half grams of β-(benzylseleno)-alanine was cleaved with concentrated hydriodic acid after digesting for forty-eight hours while air was bubbled through the mixture. Yellow hexagonal plates were obtained, m. p. 215° with decomposition; yield, 0.32 g.

Anal. Calcd. for $C_6H_{12}O_4N_2Se_2$: Se, 47.27. Found: Se, 47.10.

Summary

Two syntheses of the selenium analog of cystine are described which furnish additional evidence that selenium analogs may be substituted for the sulfur compounds used in published methods for the preparation of *dl*-cystine. In the first method α-amino-β-chloropropionic acid was treated with barium hydrogen selenide or calcium hydrogen selenide and the product was oxidized to produce the selenium analog of cystine. In the second method, the Gabriel synthesis of amino acids was used to produce the selenium analog from benzyl chloromethyl selenide and sodium phthalimidomalonic ester.

(10) J. K. Parnas and R. Wagner, *Biochem. Z.*, **125**, 253 (1931).

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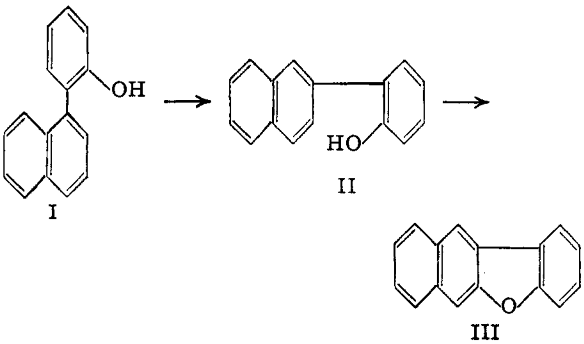
[CONTRIBUTION FROM THE U. S. BUREAU OF MINES, CENTRAL EXPERIMENT STATION]

Aromatic Cyclodehydrogenation. VII. Rearrangements in the Phenylnaphthalene Series[1]

BY MILTON ORCHIN[2] AND LESLIE REGGEL[2]

It was shown previously[3] that liquid-phase treatment of 2′-hydroxy-1-phenylnaphthalene, I, with a palladium-on-charcoal catalyst resulted in cyclodehydrogenation to 1,9-benzoxanthene. It was of interest to study the behavior of I under the vapor-phase conditions used in earlier cyclodehydrogenation studies.

Treatment of I with a chromia–alumina catalyst at 490° gave a mixture of conversion products. The first compound to be isolated from this mixture had properties and composition consistent with its formulation as the hitherto unknown 2′-hydroxy-2-phenylnaphthalene, II. It had a higher melting point than I and on treatment with diazotized *p*-nitroaniline gave a color identical with that observed for I under the same conditions. The ultraviolet absorption spectrum of II differed from that of I in the same manner as the spectrum of 2-phenylnaphthalene differed from that of 1-phenylnaphthalene.[4] Although none of this evidence fixes the position of the hydroxyl group, the isolation of compound III supports its placement in the *ortho* position, as shown in II.



I II III

A second compound isolated from the reaction mixture had properties identical with those reported[5] for benzo[b]naphtho[2,3-*d*]furan, III

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(1) Published by permission of the Director, U. S. Bureau of Mines.

(2) Organic Chemist, Central Experiment Station, U. S. Bureau of Mines, Pittsburgh, Pennsylvania.

(3) Orchin, THIS JOURNAL, in press.

(4) Friedel, Orchin and Reggel, *ibid.*, **70**, 199 (1948).

(5) Robinson and Mosettig, *ibid.*, **61**, 1148 (1939).

(brazan); direct comparison with a sample of brazan kindly furnished by Dr. E. Mosettig confirmed the identity. The formation of III from I can be explained by the rearrangement of I to II followed by the intramolecular loss of hydrogen between the hydroxyl group and the naphthalene nucleus.[3] The ultraviolet absorption spectrum of brazan is shown in Fig. 1.[6]

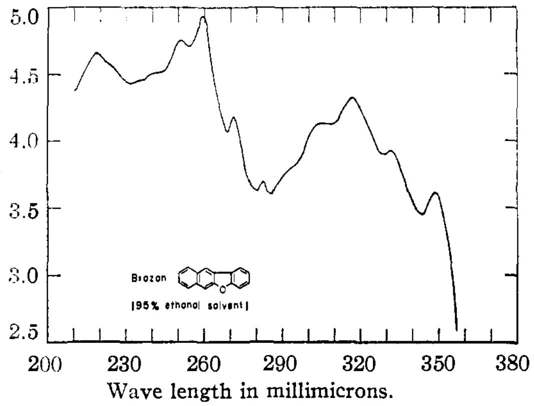
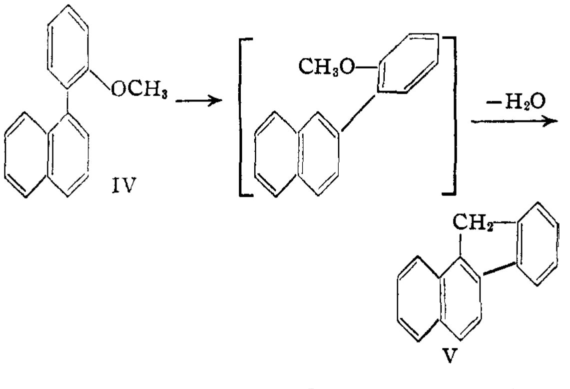


Fig. 1.—Ultraviolet absorption spectrum of brazan.

2-Phenylnaphthalene was also isolated from the reaction products.

Treatment of 1-*o*-anisylnaphthalene, IV, with a chromia–alumina catalyst at 510–520° gave a mixture of products from which it was exceedingly difficult to separate pure compounds. The hydrocarbon fraction of the products appeared to be a mixture of 1,2- and 2,3-benzfluorene (ultraviolet absorption spectra) and indeed one fraction, on oxidation, gave a ketone the color and melting point of which were identical with that reported[7] for authentic 1,2-benzfluorenone. The transformation of IV to 1,2-benzfluorene, V, may be explained by assuming the shift of the anisyl group in IV to the *beta* position to give the indicated intermediate, followed by a most unusual intramolecular loss of water (cyclodehydration) to V. The presence of 2,3-benzfluorene can be accounted for by assuming cyclodehydration of the intermediate into the beta position of the naphthalene nucleus.



Although the various fractions from IV were examined intensively by ultraviolet spectra, no evidence was found for the presence of fluoranthene or a substituted fluoranthene. We have previously shown[8] that 1-phenylnaphthalene undergoes cyclodehydrogenation to fluoranthene in good yield, and that there is only slight migration of the phenyl group to give 2-phenylnaphthalene. The present work makes it appear probable that in some cases migration of a group from the 1- to the 2-position of the naphthalene nucleus takes precedence over cyclodehydrogenation involving the 8-position.

Experimental[9]

Apparatus and Catalysts.—The apparatus used was similar to that employed in earlier experiments.[10] The catalyst tube was vertical and was heated by means of a standard combustion furnace. A detailed drawing and photograph of the apparatus will be found in a Bureau of Mines publication.[11] The catalyst, designated as Cr-181, was purchased from the Harshaw Chemical Company, Cleveland, Ohio.[8]

Conversion of 2′-Hydroxy-1-phenylnaphthalene, I.—During the course of two hours, 7.1 g. of molten I[3] was passed over 76 g. of catalyst at 490°. The partly crystalline material in the receiver weighed 6.18 g. This material was refluxed for a short time with a small volume of petroleum ether and the insoluble material filtered to give 1.4 g., melting point 78–91°. Three recrystallizations gave 0.47 g. of colorless crystals, m. p. 96.2–96.8°. *Anal.* Calcd. for $C_{16}H_{12}O$: C, 87.2; H, 5.5. Found: C, 87.7; H, 5.7. When this compound was tested with diazotized *p*-nitroaniline,[12] it produced a deep color identical with that obtained when I was similarly treated. The infrared absorption spectrum of the compound showed a strong band in the 2.8 micron region, indicating the presence of a hydroxyl group. The compound is regarded as 2′-hydroxy-2-phenylnaphthalene, II. The ultraviolet absorption spectrum of this compound has been reported.[4] Ferric chloride tests in aqueous and alcoholic solutions were negative with both 2′-hydroxy-1-phenyl- and 2′-hydroxy-2-phenylnaphthalene.

All mother liquors were combined and chromatographed on alumina–celite. Two percolate fractions were collected, the column extruded, and arbitrarily cut into four fractions. The first percolate fraction on evaporation gave a small (unweighed) quantity of material with the odor and appearance of naphthalene; it was discarded. Evaporation of the second percolate fraction gave 0.7 g. of material which after one crystallization from methanol was obtained as colorless crystals, m. p. 99.4–102.2°; mixed melting point with authentic 2-phenylnaphthalene[4] showed no depression. The fractions on the chromatographic column were called 3, 4, 5, and 6 in order of increasing strength of adsorption. Fraction 3 on elution gave 0.22 g. of an obvious mixture which was not investigated. Fraction 5 (0.10 g.) was also not investigated. Fraction 6 consisted of 4.57 g. of a very viscous liquid which was probably a mixture of I and II. Frac-

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[6] We wish to thank Mrs. Lois Harnack and Mrs. Lois Pierce for the spectra measurements. It is a pleasure to acknowledge the very valuable assistance of Dr. Robert A. Friedel in the interpretation of the data.

[7] Cook and Hewett, *J. Chem. Soc.*, 365 (1934); Kruber, *Ber.*, **70B**, 1556 (1937).

[8] Orchin and Reggel, THIS JOURNAL, **69**, 505 (1947).

[9] All melting points corrected. All analyses were microanalyses performed by G. L. Stragand, University of Pittsburgh.

[10] Orchin, *Ind. Eng. Chem., Anal. Ed.*, **17**, 673 (1945).

[11] Orchin, Reggel, Friedel and Woolfolk, Bureau of Mines Technical Paper, in press.

[12] Fieser, "Experiments in Organic Chemistry," D. C. Heath & Co., Boston, Mass., 2nd edition, 1941, p. 259.

tion 4 gave 0.12 g. of material, which, after two recrystallizations from ethanol, was obtained as colorless plates, m. p. 209.2–209.8°. *Anal.* Calcd. for $C_{16}H_{10}O$: C, 88.1; H, 4.6. Found: C, 88.3; H, 5.1. This material was identical (melting point, mixed melting point, ultraviolet absorption spectrum) with a sample of brazan obtained from Dr. E. Mosettig (secured from the Gesellschaft fur Teerverwertung).[13] It has been reported[5] that brazan does not form a picrate. We have found that the *s*-trinitrobenzene complex of brazan is very unstable, but that it readily forms a complex with 2,4,7-trinitrofluorenone[14] in the usual manner. The complex crystallized from benzene–alcohol in orange needles, m. p. 215.2–216.0°. *Anal.* Calcd. for $C_{29}H_{15}N_3O_8$: C, 65.3; H, 2.8. Found: C, 66.5; H, 3.0.

Conversion of 1-*o*-Anisylnaphthalene, IV.—During two and one-half hours, 11.25 g. of molten IV[8] was passed over 98 g. of catalyst at 510–520°. The partly crystalline product weighed 6.4 g. Four recrystallizations gave 0.22 g. of material which still had not reached a constant melting point. The material was converted to the trinitrofluorenone[14] complex, the orange needles recrystallized twice, and then decomposed by chromatography on alumina. The recovered hydrocarbon portion, melting point 203.0–205.2°, was still impure and was shown by ultraviolet absorption spectra (Fig. 2) to be a mixture of 1,2-benzfluorene and 2,3-benzfluorene.[15] About 0.08 g. of the impure material was refluxed with 0.20 g. of sodium dichromate dihydrate in 5 cc. of acetic acid for fifteen minutes, the mixture poured into water, and extracted with benzene. The benzene solution was extracted with sodium carbonate and the neutral portion chromatographed on alumina. Two bands were observed, separated, and eluted. The bottom orange colored band consisted of 29 mg.; recrystallization gave orange crystals, m. p. 129.4–132.4°. *Anal.* Calcd. for $C_{17}H_{10}O$: C, 88.7; H, 4.4. Found: C, 88.4; H, 4.3. The analysis, melting point, and appearance of this compound are consistent with that of 1,2-benzfluorenone.[7] The upper yellow band from the chromatography of the oxidation products consisted of 27 mg. and could not be recrystallized. The ultraviolet absorption spectrum was very similar to that of authentic 2,3-benzfluorenone.

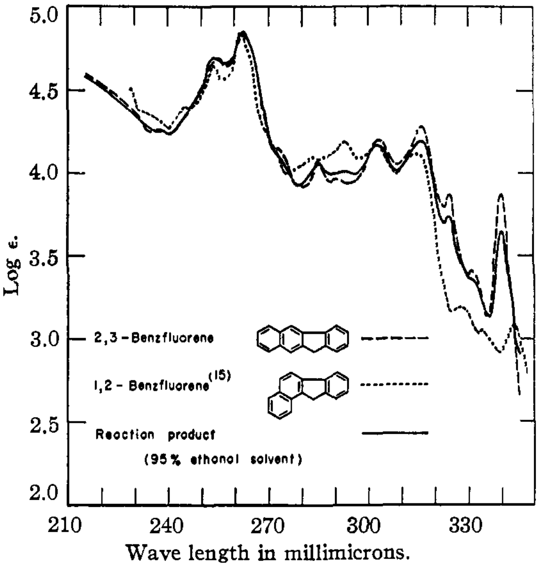

Fig. 2.—Ultraviolet absorption spectra.

The mother liquor containing 6.3 g. of the conversion product was evaporated to dryness. A methoxyl determination indicated that only a very small amount (2%) of this mixture could be unchanged starting material. All the product was dissolved in benzene and extracted with Claisen alkali. The alkali-soluble fraction weighed 2.5 g.; ultraviolet absorption spectrum indicated it was principally 2′-hydroxy-1-phenylnaphthalene, I. Chromatography of the neutral fraction (4.0 g.) gave 0.02 g. of naphthalene, 0.06 g. of 2-phenylnaphthalene, a third fluorescent fraction of 2.7 g. and a fourth fraction of 0.3 g. The ultraviolet absorption spectrum of fraction 4 indicated that it was a mixture of 1,2- and 2,3-benzfluorenes. The ultraviolet absorption spectrum of fraction 3 indicated principally a mixture of 1,2- and 2,3-benzfluorenes with some 1,9-benzoxanthene, but no pure compounds could be isolated by crystallization of the mixture, of the T. N. F. complexes, chromatography, or crystallization of the T. N. B. complexes.

Summary

Vapor phase treatment of 2′-hydroxy-1-phenylnaphthalene over a chromia–alumina catalyst gave a mixture of products from which a compound of the probable structure of 2′-hydroxy-2-phenylnaphthalene was isolated. There was also obtained benzo[b]naphtho[2,3-*d*]furan (brazan).

Vapor phase treatment of 1-*o*-anisylnaphthalene gave a mixture of products among which 1,2- and 2,3-benzfluorene were shown to be present. These compounds were probably formed by the migration of the anisyl group to the *beta* position followed by an unusual type of cyclodehydration between the methoxyl group and the aromatic nucleus.

PITTSBURGH, PENNSYLVANIA RECEIVED OCTOBER 14, 1947

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(13) A strictly unambiguous proof of structure of brazan is still lacking since, as Robinson and Mosettig have indicated, their synthesis gave two isomers, one of which was identical with the German commercial sample and to which they therefore assigned the structure of benzo[b]naphtho[2,3-*d*]furan (brazan).

(14) Orchin and Woolfolk, THIS JOURNAL, **68**, 1727 (1946).

(15) The ultraviolet absorption spectrum of 2,3-benzfluorene was obtained from a carefully purified authentic sample in our possession. The spectrum of 1,2-benzfluorene was obtained from the work of Mayneord and Roe, *Proc. Roy. Soc.* (*London*), **A158**, 634 (1937). Since the latter spectrum was determined in chloroform solution, we determined the spectrum of 2,3-benzfluorene in both alcohol and chloroform; band shifts were of the order of 1-3 mμ, and extinction coefficients were practically identical. On this basis the small band shifts could be safely applied to the corresponding bands in 1,2-benzfluorene, to produce a reliable spectrum of this compound in alcohol for comparison purposes. The spectra of the two benzfluorenes are very similar; the chief differences are not found in the location of band maxima, but in the extinction coefficients. The coefficients of our sample are intermediate between those of the two benzfluorenes.