

Anal. Calcd. for $C_{26}H_{16}O_3$: C, 82.96; H, 4.29. Found: C, 82.71, 82.80; H, 4.40, 4.34.

When 0.31 mole of benzoyl chloride was used (0.26 mole dibenzofuran), a 37.1% yield of pure 2-benzoyldibenzofuran was obtained and no diketone was isolated. The use of 0.85 mole of benzoyl chloride gave 32.8% of pure 2,8-dibenzoyldibenzofuran and no monoketone was found.

Reaction of 2-Dibenzofuryllithium with Benzonitrile.—A solution of *n*-butyllithium⁸ was prepared from 6.7 g. (0.05 mole) of *n*-butyl bromide in 25 ml. of dry ether and 1.4 g. (0.2 g. atom) of lithium in 25 ml. of dry ether. The solution of organometallic compound was added to a solution of 3.0 g. (0.012 mole) of 2-bromodibenzofuran in 50 ml. of dry benzene. After a 30-min. period of stirring and refluxing, 2.06 g. (0.02 mole) of benzonitrile in 7 ml. of dry ether and 7 ml. of dry benzene was added. After an additional hour of refluxing, the bright red reaction mixture which now gave a negative color test⁶ for an organometallic compound was hydrolyzed with ice-water, followed by concd. hydrochloric acid.

The ether layer was dried, then the solvent was removed by distillation. The tarry residue was extracted several times with hot water and the insoluble material was recrystallized from ethanol. The 1.55 g. of crude ketone was recrystallized twice more from ethanol to give 1.3 g. (36.4%) of 2-benzoyldibenzofuran, m.p. 134–135°. There was no depression of melting point when this material was mixed with the benzoyldibenzofuran obtained in the Friedel-Crafts reaction.

Reaction of Phenyllithium with 2-Dibenzofurancarboxylic Acid Diethylamide.—To a solution of 2.0 g. (0.0075 mole) of 2-dibenzofurancarboxylic acid diethylamide⁷ in 50 ml. of dry ether was added a solution of phenyllithium⁸ prepared from 0.3 g. (0.042 g. atom) of lithium and 1.5 g. (0.01 mole) of bromobenzene in 25 ml. of dry ether. After a 2-hour period of refluxing, the reaction mixture was poured onto Dry Ice. After treatment of the ethereal solution with alkali solution, the basic extract was acidified to give 0.85 g. (38.5%) of 2-benzoyl-*x*-dibenzofurancarboxylic acid (?), m.p. 265–266° after recrystallization from ethanol-water.

Anal. Calcd. for $C_{26}H_{16}O_4$: neut. equiv., 317. Found: neut. equiv., 315, 320.

From the ethereal solution was obtained a non-acidic gum which melted at 136–137° after recrystallization from ethanol. A mixed melting point determination indicated this product to be 2-benzoyldibenzofuran.

Esterification of the 2-benzoyl-*x*-dibenzofurancarboxylic acid (?) with diazomethane gave 2-benzoyl-*x*-carbomethoxydibenzofuran (?), m.p. 189–190° from ethanol.

Anal. Calcd. for $C_{27}H_{18}O_4$: OCH_3 , 9.40. Found: OCH_3 , 9.44.

2-Benzoyldibenzofuran Oxime.—From 5.45 g. (0.020 mole) of 2-benzoyldibenzofuran and 1.53 g. (0.025 mole) of hydroxylamine hydrochloride in 150 ml. of ethanol and 20 ml. of pyridine was obtained 5.54 g. of oxime, m.p. range 151–158°. Recrystallization from ethanol-water yielded 3.41 g. (59.3%) of white needles, m.p. 158–159.5°. ⁹

Anal. Calcd. for $C_{19}H_{13}NO_2$: C, 79.43; H, 4.56; N, 4.88. Found: C, 79.55, 79.34; H, 4.57, 4.59; N, 4.94, 4.84.

2,8-Dibenzoyldibenzofuran Dioxime.—The oximation of 3.76 g. (0.010 mole) of 2,8-dibenzoyldibenzofuran with 1.53 g. (0.022 mole) of hydroxylamine hydrochloride in 150 ml. of ethanol and 20 ml. of pyridine gave a 99.2% yield (4.03 g.) of crude dioxime, m.p. 229° dec. Recrystallization from a large volume of acetone raised the melting point to 231.5–232° dec. ¹⁰

(5) H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, *THIS JOURNAL*, **71**, 1499 (1949).

(6) H. Gilman and F. Schulze, *ibid.*, **47**, 2002 (1925).

(7) Unpublished studies by H. B. Willis.

(8) R. G. Jones and H. Gilman in R. Adams, "Organic Reactions," Vol. 6, John Wiley and Sons, Inc., New York, N. Y., 1951, Chap. 7, p. 353.

(9) In one experiment, a product melting at 182–183° was obtained. This compound, which analyzed correctly for the desired oxime, may have been the isomeric *syn*-phenyl oxime or merely a crystalline form different from that obtained in other preparations of the monoxime.

(10) A melting point of 234–235° has been reported¹ for this compound, but no analytical data were given.

Anal. Calcd. for $C_{26}H_{18}N_2O_3$: C, 76.84; H, 4.46; N, 6.89. Found: C, 76.57, 76.58; H, 4.61, 4.55; N, 6.74, 6.81.

2-Dibenzofurancarboxylic Acid Anilide.—To a solution of 2.87 g. (0.01 mole) of 2-benzoyldibenzofuran oxime in 200 ml. of dry benzene was added 3.12 g. (0.015 mole) of phosphorus pentachloride. The green solution was stirred at room temperature for 12 hours. Subsequent to hydrolysis, the benzene layer was separated and washed with sodium carbonate solution. Evaporation of the benzene left 2.81 g. (98.0%) of a pink powder, m.p. 160–164°. Two recrystallizations from ethanol raised the melting point of the amide to 164–165.5°. A mixed melting point with the original oxime was 128–164°.

Anal. Calcd. for $C_{19}H_{13}NO_2$: C, 79.43; H, 4.56; N, 4.88. Found: C, 79.39, 79.48; H, 4.44, 4.45; N, 4.99, 4.96.

Hydrolysis of the anilide was accomplished by refluxing a solution of 1.00 g. of anilide in 20 ml. of concd. sulfuric acid, 50 ml. of glacial acetic acid and 80 ml. of water for 8 hours. Dilution with a large volume of water gave 0.59 g. of acid, m.p. range 220–240° softening at 190°. Solution in alkali and reprecipitation by acid followed by two recrystallizations from glacial acetic acid yielded white needles, m.p. 252–255°. There was no depression of melting point with an authentic specimen of 2-dibenzofurancarboxylic acid.

2-Benzamidodibenzofuran.—A reaction mixture consisting of 1.83 g. (0.010 mole) of 2-aminodibenzofuran,¹¹ 3 ml. of benzoyl chloride and 0.5 g. of sodium hydroxide in 100 ml. of water was stirred for 10 hours at room temperature. The suspended material was removed by filtration and washed thoroughly with warm dilute hydrochloric acid. The 1.94 g. (67.6%) of crude amide had a melting point range of 178–183°. Two recrystallizations from ethanol-water, followed by vacuum sublimation and another recrystallization from ethanol-water yielded small needles, m.p. 185–186°.

Anal. Calcd. for $C_{19}H_{13}NO_2$: C, 79.43; H, 4.56; N, 4.88. Found: C, 79.03, 79.08; H, 4.68, 4.62; N, 5.07, 5.05.

2,8-Dibenzamidodibenzofuran.—A suspension of 1.98 g. (0.010 mole) of 2,8-diaminodibenzofuran¹² and 3 ml. of benzoyl chloride in a solution of 1.2 g. (0.030 mole) of sodium hydroxide in 100 ml. of water was stirred for 3.5 hours at room temperature. The solid material was removed by filtration and washed with warm dilute hydrochloric acid, then with large amounts of water. The 1.30 g. (32.0%) of diamide melted at 293–296° after two recrystallizations from glacial acetic acid and one recrystallization from acetone-water.

Anal. Calcd. for $C_{26}H_{18}N_2O_3$: C, 76.83; H, 4.46; N, 6.87. Found: C, 76.48, 76.56; H, 4.80, 4.72; N, 6.85, 6.92.

(11) H. Gilman, G. E. Brown, W. G. Bywater and W. H. Kirkpatrick, *THIS JOURNAL*, **56**, 2473 (1934).

(12) J. Swislawsky, *Iowa State Coll. J. Sci.*, **14**, 92 (1939); *C. A.*, **34**, 6273 (1940).

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A Novel Cyclization Reaction of a Hydroxyquinone

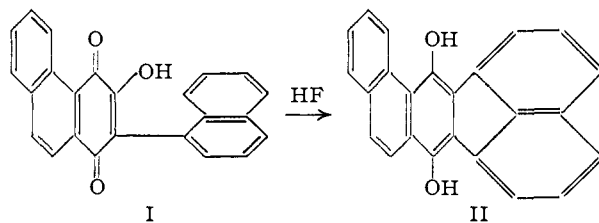
By HAROLD E. ZAUGG

RECEIVED APRIL 15, 1954

Since the hydroxyl group in 3-hydroxy-2-(α -naphthyl)-1,4-phenanthrenequinone (I)¹ bears a vinylogous relationship to the hydroxyl group of a carboxylic acid, cyclization involving the peri-position of the 2-naphthyl substituent appeared feasible. Treatment of the quinone I with anhydrous hydrogen fluoride did indeed effect ring closure, but to the hydroquinone II rather than to the corresponding quinone. The structure of II was es-

(1) H. E. Zaugg, R. T. Rapala and M. T. Leffer, *THIS JOURNAL*, **70**, 3224 (1948).

established by analysis, by its lack of color and by the fact that it forms a diacetate. Apparently, stabilization of the hydroquinone II relative to the corresponding quinone results from fusion of the highly strained five-membered ring to the quinoid center. That fused five-membered rings do indeed increase the oxidation potentials of such quinoid systems has been noted by a number of investigators.²⁻⁵



Experimental

7,14-Dihydroxyacenaphtho[1,2-b]phenanthrene (II).—One gram of 3-hydroxy-2-(α -naphthyl)-1,4-phenanthrene-quinone (I)¹ was added to 80 g. of anhydrous hydrogen fluoride in a copper alloy container. After stirring well

- (2) L. F. Fieser, *THIS JOURNAL*, **50**, 439 (1928).
- (3) R. T. Arnold and H. E. Zaugg, *ibid.*, **63**, 1317 (1941).
- (4) C. F. Koelsch and E. J. Prill, *ibid.*, **67**, 1296 (1945).
- (5) T. Posternak and R. Castro, *Helv. Chim. Acta*, **31**, 536 (1948).

with a copper wire, a tight fitting closure was screwed to the container. After standing at room temperature overnight, the mixture was poured into ice and the product was taken up in ether, washed successively with water, sodium bicarbonate solution, and more water, and then dried over anhydrous magnesium sulfate. Filtration, removal of the ether by distillation and trituration of the residue with pentane gave 0.7 g. of crude material which after two recrystallizations from benzene (charcoal treatment was included in the first crystallization) gave nearly colorless crystals, m.p. 175–177°.

Anal. Calcd. for $C_{24}H_{14}O_2$: C, 86.21; H, 4.22. Found: C, 86.21; H, 4.59.

The product is insoluble in aqueous sodium bicarbonate but dissolves in a large volume of aqueous potassium hydroxide.

7,14-Diacetoxyacenaphtho[1,2-b]phenanthrene.—A solution of 0.5 g. of crude II in 10 cc. of acetic anhydride containing 0.5 g. of anhydrous potassium acetate and a few pieces of 20-mesh zinc was heated on the steam-bath for 45 minutes. After pouring into water and standing overnight the solid product remaining was collected by filtration and dried. The 0.6 g. of crude material obtained in this way was recrystallized three times from heptane to give the pure diacetate, m.p. 180–182°.

Anal. Calcd. for $C_{28}H_{18}O_4$: C, 80.37; H, 4.34. Found: C, 80.39; H, 4.89.

Acknowledgment.—The author is grateful to Mr. E. F. Shelberg for the microanalyses.

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COMMUNICATIONS TO THE EDITOR

MULTIPLE PROSTHETIC GROUPS IN CYTOCHROME C

Sir:

The well known cytochrome *c* preparation of Keilin and Hartree¹ has been purified further by Margoliash,² who employed a column chromatographic procedure which appears to eliminate both a non-cytochrome *c* hemoprotein and an enzymatically inactive cytochrome *c*. In spite of the high degree of purity of the product and its homogeneity on the column employed, observations recorded in this paper demonstrate that two closely related hemo-hemins may be derived from the preparation and that they probably represent two molecular species of cytochrome *c*.

The "enzymatically active" fraction of cytochrome *c* prepared by the Margoliash procedure was subjected to the silver treatment of Paul³ for the removal of hemin. The hemin solution so obtained was evaporated to dryness, dissolved in chloroform, and chromatographed on the silicic acid column described by Morrison and Stotz.⁴ Eluent from the column was distributed in the tubes of an automatic fraction collector and the concentration of hemin in each aliquot was determined by its optical density

(1) D. Keilin and E. F. Hartree, *Proc. Roy. Soc. (London)*, **B122**, 298 (1937).

(2) E. Margoliash, *Biochem. J.*, **56**, 529 (1954).

(3) K. G. Paul, *Acta Chem. Scand.*, **5**, 389 (1951).

(4) M. Morrison and E. Stotz, *J. Biol. Chem.*, in press.

at 410 m μ . The resulting chromatogram as illustrated shows two distinct peaks, representing two hemins derived from the purified cytochrome *c*.

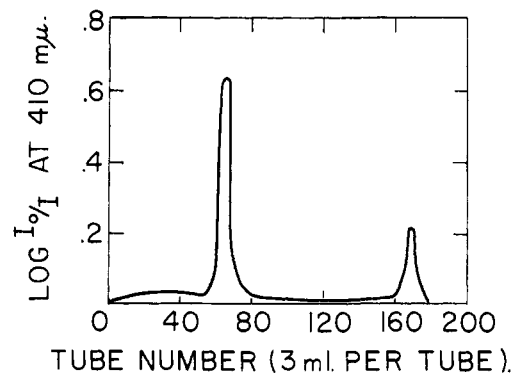


Fig. 1.

Paper chromatograms employing modifications of the solvent systems of Chu, *et al.*,⁵ confirmed the results of column chromatography. Also each hemin fraction obtained from column chromatography resulted in a single fraction upon re-chromatographing on the silicic acid column. The porphyrins derived from the hemin fractions gave identical spectra typical of hematoporphyrin, with absorption bands at 404, 504, 536, 572 and 625 m μ . The spec-

(5) T. C. Chu, A. A. Green and E. J. Chu, *ibid.*, **190**, 643 (1951).