colored oil which, when recrystallized from methanol, yielded 0.30 g. of a solid that melted at 70°. The solid was recrystallized again from an ethanol–water solution containing a trace of sodium hydroxide to a m.p. of 72°. It was shown to contain iodine and nitrogen by an element test. The yield was *ca.* 7%.

Anal. Calcd. for $C_{12}H_{16}NO_2I$: C, 43.26; H, 4.84; N, 4.20. Found: C, 43.80; H, 4.93; N, 4.34.

The solid unextracted by hexane was dissolved in hot benzene. The benzene solution was evaporated down to a solid that weighed 0.69 g. and melted at 160–165°. It was recrystallized from a mixture of ethanol and benzene containing a trace of sodium hydroxide to crystals of m.p. 166–169°. The results of an element test showed that they contained nitrogen but no iodine. The yield was 15%.

Anal. Calcd. for $C_{13}H_{22}N_2O_2$: C, 72.45; H, 7.43; N, 9.39. Found: C, 72.58; H, 7.41; N, 9.45.

***trans*-2,5-Bis-(aminomethyl)-*p*-dioxane (XVI).**—Two grams (0.0054 mole) of *trans*-2,5-bis-(iodomethyl)-*p*-dioxane and 30 ml. of concd. ammonium hydroxide were heated in a sealed tube for three hours at 140°. The solution obtained was boiled to expel excess ammonia and to reduce the volume. Solid sodium hydroxide was then added and the dark-colored solid that precipitated out was filtered and extracted by hot ethanol. The ethanol solution was evaporated down to a solid that was sublimed under 11 mm. of pressure. The sublimate consisted of 0.50 g. (63%) of colorless crystals of m.p. 134°.

Anal. Calcd. for $C_6H_{14}N_2O_2$: N, 19.17. Found: N, 18.83.

Usual procedures were used to convert this amine to a dibenzamide XVIII, m.p. 235°, identical in most properties to that reported by Stoehr, although his melting point was 229°. On one occasion we used a sample of diamine unpurified by sublimation and duplicated Stoehr's melting point.[6]

Anal. Calcd. for $C_{20}H_{22}O_4N_2$: N, 7.91. Found: N, 7.93.

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NOTES

The Benzoylation of Dibenzofuran

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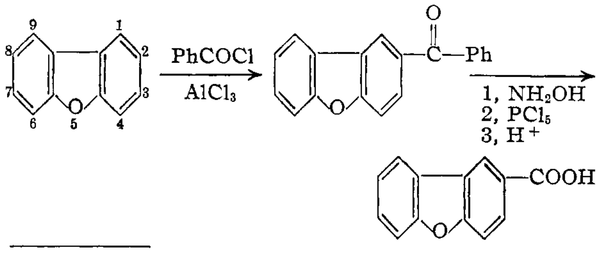
The benzoyldibenzofuran obtained as a result of the action of benzoyl chloride on dibenzofuran has been reported[1] as having the melting point 167–168°.

We have found that the Friedel–Crafts reaction of dibenzofuran with an excess of benzoyl chloride yields two ketones, one melting at 136–138°, the other at 167–168.5°.

Analysis of the two ketones and their oximes indicated that the compound melting at 136–138° is a monobenzoyldibenzofuran, while the higher melting ketone (apparently the compound obtained by Borsche and Bothe) is a dibenzoyldibenzofuran.

The structure of the monoketone has been established as 2-benzoyldibenzofuran by virtue of the fact that this compound was also obtained when (1) benzonitrile was treated with 2-dibenzofuryllithium and (2) phenyllithium was allowed to react with 2-dibenzofurancarboxylic acid diethylamide. Further proof of the structure was afforded by conversion of the ketoxime to an amide *via* the Beckman rearrangement, the amide yielding 2-dibenzofurancarboxylic acid on acid hydrolysis.



It is assumed that the diketone is 2,8-dibenzoyldibenzofuran.[2] Though the dioxime was prepared, it could not be rearranged to the diamide. Several attempts to do so yielded in each instance material which melted over a wide range and which could not be purified by recrystallization.

2-Benzamidodibenzofuran and 2,8-dibenzamidodibenzofuran, the products to be expected from the Beckmann rearrangement of the *syn*-phenyl oximes,[3] have been prepared.

Experimental[4]

Benzoylation of Dibenzofuran.—The Friedel–Crafts reaction of 43.7 g. (0.26 mole) of dibenzofuran with 59.0 g. (48.7 ml., 0.42 mole) of benzoyl chloride and 53.0 g. of aluminum chloride in 400 ml. of nitrobenzene was carried out at room temperature for 14 hours. Subsequent to hydrolysis, the nitrobenzene was removed by steam distillation. The residue after washing with a 5% solution of sodium hydroxide and then with methanol weighed 76.8 g. and melted over the range 110–128°. Recrystallization from ethanol–benzene and then from glacial acetic acid (three times) gave a product which melted over the range 130–136°, softening at 115°. Chromatography from benzene solution on an alumina column and recrystallization from glacial acetic acid of all fractions melting above 130° gave 28.2 g. (39.8%) of white needles, m.p. 134–137.5°. A sample of **2-benzoyldibenzofuran** purified for analysis by recrystallization from glacial acetic acid melted at 136–138°.

Anal. Calcd. for $C_{19}H_{12}O_2$: C, 83.80; H, 4.44. Found: C, 83.72, 83.72; H, 4.50, 4.56.

The mother liquors from the ethanol–benzene recrystallization of the monobenzoyl compound were worked up to give 2.94 g. (3.0%) of **2,8-dibenzoyldibenzofuran,** m.p. 167–168.5°, after two recrystallizations from glacial acetic acid.

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[1] W. Borsche and W. Bothe, *Ber.*, **41**, 1940 (1908).

[2] Both diacetylation [H. Gilman, P. T. Parker, J. C. Bailie and G. E. Brown, THIS JOURNAL, **61**, 2836 (1939)] and dipropionylation [Ng. Ph. Buu-Hoi and R. Royer, *Rec. trav. chim.*, **67**, 175 (1948)] give 2,8-disubstituted dibenzofurans.

[3] The *anti*-phenyl configuration has been assigned by us to the 2-benzoyldibenzofuran oxime reported in this note because of the generalization [B. Jones, *Chem. Revs.*, **35**, 335 (1944)] that *trans* migration occurs in the Beckmann rearrangement.

[4] All melting points are uncorrected.

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*-butyllithium[5] 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 test[6] 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 diethylamide[7] in 50 ml. of dry ether was added a solution of phenyllithium[8] 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 $C_{20}H_{12}O_4$: 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 $C_{21}H_{14}O_4$: 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]

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-diaminodibenzofuran[12] 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.

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(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 reported[1] for this compound, but no analytical data were given.

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

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

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A Novel Cyclization Reaction of a Hydroxyquinone

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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-

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