The *anilide* (II. $R_1 = H$; $R_2 = CONHC_6H_5$), obtained in the usual way, crystallized from ethanol as colorless prisms, m.p. 164.5–165.2°.

Anal. Calcd. for $C_{18}H_{15}O_4N$: C, 69.9; H, 4.89; N, 4.53. Found: C, 70.1; H, 5.09; N, 4.44.

The *methyl ester* (II. $R_1 = H$; $R_2 = COOCH_3$), from the acid chloride and methanol, crystallized from a mixture of methanol and petroleum ether (b.p. 30–60°) as pale yellow needles, m.p. 79–81°.

Anal. Calcd. for $C_{13}H_{12}O_5$: C, 62.9; H, 4.88. Found: C, 62.76; H, 4.74.

2,3-Dihydro-8-methoxybenzo[1,2-b,5,4-b']difuran (II. $R_1 = R_2 = H$). II($R_1 = H$, $R_2 = CO_2H$) (10.0 g.) was heated at 255–280° (oil bath) in an apparatus arranged for distillation under reduced pressure. A colorless distillate was collected between 50 and 120 mm. A solution of this distillate in ether was filtered to remove an insoluble white solid and was then washed with 5% sodium hydroxide. After drying and evaporation of solvent, the residue distilled from 109°/0.45 mm. to 120°/1.1 mm. to give 5.09 g. (62.5% yield) of colorless liquid. Redistillation gave a fraction, b.p. 115°/1 mm., a drop of which, in concd. sulfuric acid, gave a cherry red color at room temperature and a deep blue color after gentle warming.

Anal. Calcd. for $C_{11}H_{10}O_3$: C, 69.5; H, 5.30. Found: C, 69.2; H, 5.24.

4,6-Dibromo-2,3-dihydroxanthotoxin (I. $R_1 = R_2 = Br$). A. Bromine (3.20 g.; 0.02 mole) was added to a stirred solution of 2.18 g. (0.01 mole) of I($R_1 = R_2 = H$) in 35 ml. of chloroform. After standing for 2 hr., the solution was concentrated to dryness on a steam bath and the light yellow residue gave pale yellow felted needles, m.p. 267.6–268.1°, after recrystallization from 1-butanol.

Anal. Calcd. for $C_{12}H_8O_4Br_2$: C, 38.3; H, 2.14; Br, 42.5. Found: C, 38.5; H, 2.25; Br, 42.5.

B. Bromine (0.48 g.; 0.003 mole) was added to a stirred solution of 0.72 g. (0.003 mole) of I($R_1 = Br$; $R_2 = H$)[2] in 25 ml. of chloroform. After 2 hr., crystallization from the reaction mixture began and, the next day, 0.56 g. (62% yield) of colorless felted needles, m.p. 268.7–269.7°, were collected. A mixed melting point with the sample from A showed no depression and the two samples had identical infrared spectra.

4-Bromo-6-carboxy-2,3-dihydro-8-methoxybenzo[1,2-b,5,4-b']difuran (II. $R_1 = Br$; $R_2 = CO_2H$). The method used for the preparation of II($R_1 = H$; $R_2 = COOH$) was applied to I($R_1 = R_2 = Br$) and gave a quantitative yield of crude product, m.p. 254.5° dec. Crystallization from ethanol gave a sample, m.p. 261.5° dec.

Anal. Calcd. for $C_{12}H_9O_5Br$: C, 46.0; H, 2.90; Br, 25.5. Found: C, 46.2; H, 2.59; Br, 26.0.

4-Amino-2,3-dihydroxanthotoxin (I. $R_1 = NH_2$; $R_2 = H$). A solution of 18.50 g. of 4-aminoxanthotoxin[2] in 400 ml. of dimethylformamide, plus 5.0 g. of 5% palladium on charcoal, was shaken under 60 pounds of hydrogen pressure until 1 equivalent of hydrogen had been absorbed (*ca.* 7 hr.). After filtration, the reaction mixture was diluted with 4 l. of water to obtain a green precipitate, which gave 8.57 g. (46% yield) of stocky yellow needles, m.p. 243–245°, after recrystallization from ethanol. The reported[2] m.p. of 214–216° was obtained by mixing some starting material with the product.

The *ethyl carbamate* (I. $R_1 = NHCO_2C_2H_5$; $R_2 = H$) was obtained from the amine and ethyl chloroformate. It crystallized from ethanol as colorless felted needles, m.p. 216–216.5°.

Anal. Calcd. for $C_{15}H_{15}O_6N$: C, 59.0; H, 4.95; N, 4.59. Found: C, 58.8; H, 5.14; N, 4.75.

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Action of Grignard Reagents. XIX. Action of Phenylmagnesium Bromide on 4,5-Benzocoumaran-2,3-dione

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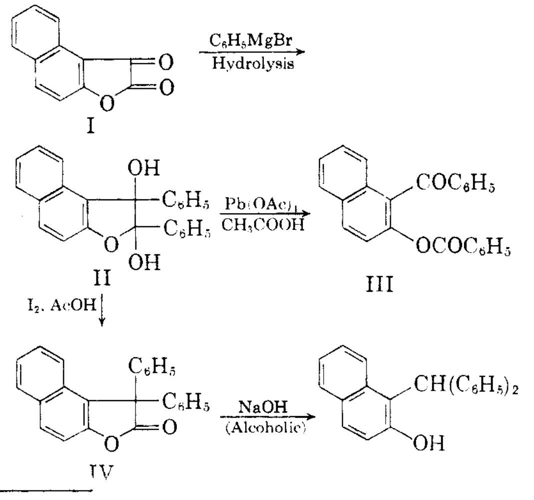
Coumaran-2,3-dione, in its reactions, shows the chemical properties associated with both lactones and 1,2-diketones.[1] Although the reaction of isatin, the nitrogen analog of coumaran-2,3-dione, with organomagnesium compounds has been thoroughly studied,[2] no work has been reported concerning the action of coumaran-2,3-dione with the same reagent.

We now have investigated the behavior of 4,5-benzocoumaran-2,3-dione (I) toward the action of phenylmagnesium bromide. Thus, when the colored I was treated with an excess of this reagent, a colorless product was obtained for which structure II is assigned. The isolation of the comparatively stable glycol II is in contrast with the behavior of isatin toward the same reagent, whereby, the nonisolable glycol undergoes rearrangement by excess of Grignard reagent[2b] or acid[2c] to the indoxyl or to the oxindole. Meanwhile, it simulates



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[1] *Heterocyclic Compounds*, ed. by R. C. Elderfield, Vol. 2, p. 41, John Wiley and Sons, Inc., New York, 1951.

[2] (a) M. Kohn, *Monatsh.*, **31**, 747 (1910); (b) M. Kohn and A. Osterstzer, *Monatsh.*, **32**, 905 (1911); **34**, 789, 1741 (1913); (c) F. J. Myers and H. G. Lindwall, *J. Am. Chem. Soc.*, **60**, 2153 (1938); (d) B. Witkop and A. Ek, *J. Am. Chem. Soc.*, **73**, 5664 (1951).

the behavior of acenaphthenequinone toward the action of the same reagent to give 1,2-diphenyl-1,2-dihydroxyacenaphthene.[3]

The structure of II was inferred from the fact that it was colorless and gave the correct analytical values. It was insoluble in aqueous sodium hydroxide and did not develop color with ferric chloride. Treatment of II with lead tetraacetate in glacial acetic acid effected its oxidation with the formation of the benzoyl derivative of 1-benzoyl-2-naphthol (III). Furthermore, II underwent a pinacol rearrangement[4] by the action of iodine in glacial acetic acid solution, to give the corresponding lactone of 2-hydroxy-1-naphthyldiphenylacetic acid.

Whereas IV was proved to be stable toward the action of a mixture of acetic acid and hydrochloric acid, it has been readily opened by the action of hot alcoholic sodium hydroxide solution to give 1-benzhydryl-2-naphthol (V). V was as many sterically hindered phenols,[5] insoluble in aqueous alkali and gave the color test for sterically hindered phenols.[6]

EXPERIMENTAL

Action of phenylmagnesium bromide on 4,5-benzocoumaran-2,3-dione (I). To a Grignard solution (prepared from 0.8 g. of bromobenzene and 40 ml. of dry ether) was added 1 g. of I[7] and 30 ml. of dry benzene. The color of I was discharged and the reaction mixture was refluxed (water-bath) for 2 hr. and kept overnight at room temperature. It was then decomposed with cold saturated ammonium chloride solution, to which were added a few drops of concd. hydrochloric acid; the resulting oil was washed several times with hot petroleum ether (b.p. 60–80°), after which the product solidified as a colorless substance. This was crystallized from benzene (or ethanol) as colorless uniform crystals, m.p. 182°; yield is *ca.* 87%.

Anal. Calcd. for $C_{24}H_{18}O_3$: C, 81.35; H, 5.08. Found: C, 81.22; H, 5.10.

II gave a green color with concd. sulfuric acid. It was insoluble in aqueous sodium hydroxide solution and developed no color with ferric chloride. It was easily soluble in hot benzene.

Behavior of 2,3-diphenyl-2,3-dihydroxy 4,5-benzocoumaran (II): (a) *Lead tetraacetate.* In a procedure similar to that described by Crigee,[8] a solution of II (0.5 g.) in freshly distilled glacial acetic acid (50 ml.), was treated with freshly prepared lead tetraacetate (7.0 g.). The reaction mixture was shaken for 20 hr. at room temperature. It was then heated (water-bath) for 15 min., cooled, and poured into ice-cold water, then extracted with ether, dried over anhydrous sodium sulfate, and evaporated. The oily residue, so obtained, was scratched until it turned into a colorless powder. Upon crystallization from ethanol it gave colorless crystals, m.p. 96°; yield is *ca.* 58%.

Anal. Calcd. for $C_{24}H_{16}O_3$: C, 81.81; H, 4.54. Found: C, 81.72; H, 4.61.

III was identified as 1-benzoyl-2-naphthylbenzoate (mixed melting point with an authentic sample[9] showed no depression).

III was insoluble in aqueous sodium hydroxide solution, gave no color with alcoholic ferric chloride, and developed a brown color with concd. sulfuric acid.

(b) *Iodine and acetic acid.* In a procedure similar to that described by Bachmann,[10] III (1.0 g.) was dissolved in glacial acetic acid (5 ml.) and iodine (0.01 g.) was added. The reaction mixture was refluxed (sand-bath) for 5 min. till the solution was clear red. Upon cooling IV separated in a crystalline form. The product was filtered with suction, washed with a small amount of glacial acetic acid and crystallized from the same solvent into colorless uniform crystals, m.p. 191°, (colorless melt). Mixed melting point with an authentic sample[11,12] showed no depression; yield is *ca.* 78%.

Anal. Calcd. for $C_{24}H_{16}O_2$: C, 85.71; H, 4.76. Found: C, 85.15; H, 4.54.

IV gave a brown color with concd. sulfuric acid. It was insoluble in aqueous sodium hydroxide solution, and gave no color with ferric chloride.

Action of hydrochloric acid on IV. A solution of IV (0.2 g.) in a mixture of glacial acetic acid (10 ml.) and concd. hydrochloric acid (*d.* 1.18) (3 ml.) was refluxed (sand-bath) for 5 hr. Recrystallization of the product from acetic acid gave unchanged IV (melting point and mixed melting point) in nearly quantitative yield.

Action of alcoholic sodium hydroxide on IV. Compound IV (0.6 g.) was dissolved in boiling ethanol (100 ml.), then aqueous 5% sodium hydroxide solution (6 ml.) was added. The reaction mixture was refluxed (water-bath) for 6 hr., cooled, and filtered. The filtrate was acidified with dilute hydrochloric acid and left overnight. The compound that separated was extracted with ether. The oily residue, obtained after evaporating the ether solution, was washed twice with petroleum ether (b.p. 60–80°) and the colorless substance obtained (0.22 g.) was crystallized from a mixture of 6 ml. petroleum ether (b.p. 60–80°) and a few drops of benzene.

1-Diphenylmethyl-2-naphthol (V) separated in colorless uniform crystals, m.p. 109°, (deep yellow melt).

Anal. Calcd. for $C_{23}H_{18}O$: C, 89.03; H, 5.80. Found: C, 89.01; H, 5.45.

V gave a yellow color with concd. sulfuric acid and developed no color with ferric chloride. It was insoluble in aqueous sodium hydroxide.

V gave the color test (blue) for sterically hindered phenols.[6]

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[3] P. D. Bartlett and R. F. Brown, *J. Am. Chem. Soc.*, **62**, 2927 (1940); E. J. Moriconi, W. F. O'Connor, L. P. Kuhn, E. A. Keneally, and F. T. Wallenberger, *J. Am. Chem. Soc.*, **81**, 6472 (1959).

[4] *Cf.* the pinacol rearrangement of 1,2-diphenyl-1,2-dihydroxyacenaphthene to 2,2-diphenyl-1-ketoacenaphthene by the action of aqueous sulfuric acid (ref. 3 and *Steric Effects in Organic Chemistry*, ed. by M. S. Newman, John Wiley and Sons, Inc., New York, 1956, p. 254.

[5] G. H. Stillson, D. W. Sawger, and C. K. Hunt, *J. Am. Chem. Soc.*, **67**, 303 (1945); A. Schönberg, A. Mustafa, and A. F. A. Shalaby, *J. Am. Chem. Soc.*, **77**, 5766 (1955).

[6] *Cf.* V. M. Platkovskaya and S. G. Vatkins, *J. Appl. Chem.* (*U.S.S.R.*) **10**, 202 (1937); *Chem. Abstr.*, **31**, 4232 (1937).

[7] M. Giua and V. de Franciscis, *Gazz. chim. ital.*, **54**, 509 (1924).

[8] R. Crigee, *Ber.*, **64**, 260 (1931).

[9] O. Dischendorfer and E. Ofenheimer, *Monatsh.*, **74**, 140 (1943).

[10] W. E. Bachmann, *Org. Syntheses*, **Coll. Vol. II**, 73 (1950).

[11] R. Geipert, *Ber.*, **37**, 664 (1904).

[12] C. O. Guss, *J. Am. Chem. Soc.*, **73**, 608 (1951).