Redistillation yielded a colorless fraction identical in boiling point, refractive index, density and infrared absorption spectrum with the 2-chloroethyl methanesulfinate prepared by the reaction of pure methanesulfinyl chloride with ethylene oxide.

The reaction between I and ethylene oxide was repeated with the order of addition reversed. Ethylene oxide (0.66 mole) was placed in the flask fitted with stirrer and held at −20°, while 0.66 mole of I was added dropwise. On distilling the mixture there was obtained 16.4 g. (0.166 mole, 76%) of ethylene dichloride, 19.0 g. (0.202 mole, 92%) of methyl disulfide and 26.3 g. (0.184 mole, 84%) of 2-chloroethyl methanesulfinate.

The preparation of 2-chloroethyl methanesulfinate. Ethylene oxide (10 g., 0.23 mole) was passed into 19.7 g. (0.2 mole) of well stirred methanesulfinyl chloride[6] cooled to −20°. When all had been added the mixture was allowed to warm to room temperature and was distilled at reduced pressure. The colorless product weighed 23.4 g. (82%) and boiled at 108–110° (22 mm.). A middle fraction boiled unchanged at 110° (22 mm.), n_D^{25} 1.4760, d_4^0 1.3276 and d_4^{25} 1.2998.

Anal. Calcd. for $C_3H_7ClO_2S$: C, 25.27; H, 4.95; Cl, 24.86; S, 22.48. Found: C, 25.84; H, 6.02; Cl, 24.65; S, 22.2.

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Bromination of Dihydroxanthotoxin. Synthesis of Furocoumarans

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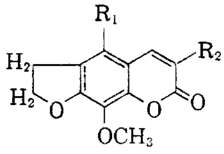
Recently, there was reported[2] the isolation of a monobromo substituted derivative of 2,3-dihydroxanthotoxin (I. $R_1 = R_2 = H$), which was not the 4-bromo isomer (I. $R_1 = Br$; $R_2 = H$), but which gave a compound $C_{12}H_{10}O_5$ on treatment with 6*N* sodium hydroxide. While the present work was in progress, Horton and Paul[3] suggested II ($R_1 = H$, $R_2 = CO_2H$) as the structure of $C_{12}H_{10}O_5$, which could be expected from the action of sodium hydroxide on 6-bromo-2,3-dihydroxanthotoxin (I. $R_1 = H$; $R_2 = Br$). Our results confirm the latter suggestion, because a sample of $C_{12}H_{10}O_5$, obtained by the procedure of Brokke and Christensen,[2] was easily converted to an acid chloride (II. $R_1 = H$; $R_2 = COCl$), an anilide (II. $R_1 = H$; $R_2 = CONHC_6H_5$), and a methyl ester (II. $R_1 = H$; $R_2 = CO_2CH_3$). Its infrared spectrum showed absorption at 2690, 2580, 2520, 2490, and 2350 cm.$^{-1}$ (OH, bonded, acid) and at 1670, 1680 (sh) cm.$^{-1}$ (C=O, acid). On heating under reduced pressure, the compound lost a molecule of carbon dioxide, as would be expected for structure II ($R_1 = H$; $R_2 = COOH$). The resultant furocoumaran (II. $R_1 = R_2 = H$) gave a deep blue color on warming with concentrated sulfuric acid, which is analogous to the behavior reported[4] for other similarly constituted benzofurans. These results establish 6-bromo-2,3-dihydroxanthotoxin (I. $R_1 = H$; $R_2 = Br$) as the product of reaction between 2,3-dihydroxanthotoxin and one equivalent of bromine.



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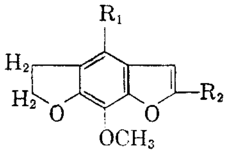

II

Treatment of 2,3-dihydroxanthotoxin with two equivalents of bromine produced a dibromo derivative. It has been assigned structure I ($R_1 = R_2 = Br$) because it was also obtained by bromination of 4-bromo-2,3-dihydroxanthotoxin[2] (I. $R_1 = Br$; $R_2 = H$) and because treatment with sodium hydroxide converted it to $C_{12}H_9O_5Br$, which must have structure II ($R_1 = Br$; $R_2 = COOH$). While repeating some of the earlier work, a sample of 4-amino-2,3-dihydroxanthotoxin (I. $R_1 = NH_2$; $R_2 = H$) was obtained, which melted at 243–245° instead of the reported[2] 214–216°. A mixture of this compound and 4-aminoxanthotoxin melted at 214–216°. The aminodihydro compound was also converted to the corresponding ethyl carbamate (I. $R_1 = NHCO_2C_2H_5$; $R_2 = H$).

EXPERIMENTAL[5]

2,3-Dihydroxanthotoxin (I. $R_1 = R_2 = H$). Xanthotoxin (28.50 g.) dissolved in 355 ml. of glacial acetic acid at 45° and the solution, plus 2.5 g. of 5% palladium on charcoal, was shaken under 60 pounds hydrogen pressure until 1 equivalent of hydrogen had been absorbed (*ca.* 20 min.). After removing the catalyst and concentrating the solution, the product crystallized and was finally obtained as colorless needles (20.85 g.; 69%), m.p. 159.3–159.5°, after recrystallization from acetic acid; reported[2]: 31% yield, m.p. 160–161°.

6-Bromo-2,3-dihydroxanthotoxin (I. $R_1 = H$; $R_2 = Br$). This compound was prepared according to the method of Brokke and Christensen[2] who report m.p. 202–203°. A sample, m.p. 207.5°, was obtained.

6-Carboxy-2,3-dihydro-8-methoxybenzo[1,2-b,5,4-b′]difuran (II, $R_1 = H$; $R_2 = CO_2H$) was prepared according to Brokke and Christensen,[2] who report m.p. 264–268°. A sample, m.p. 267.5° dec., was obtained from ethanol.

The *acid chloride* (II. $R_1 = H$; $R_2 = COCl$) was obtained by adding small portions of phosphorus pentachloride to a suspension of 46.8 g. of II($R_1 = H$; $R_2 = CO_2H$) in 2 l. of chloroform until a clear solution was obtained. Concentration under reduced pressure left a residue which was obtained as 19.8 g. (40% yield) of yellow needles, m.p. 133.5–134.5°, after two recrystallizations from dry xylene.

Anal. Calcd. for $C_{12}H_9O_4Cl$: C, 57.0; H, 3.59; Cl, 14.0. Found: C, 57.6; H, 3.32; Cl, 13.85.

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[1] To whom inquiries concerning this paper should be addressed.

[2] M. E. Brokke and B. E. Christensen, *J. Org. Chem.* **23,** 589 (1958).

[3] W. J. Horton and E. G. Paul, *J. Org. Chem.* **24,** 2000 (1959).

[4] Hantzch, *Ber.*, **19,** 2933 (1886).

[5] All melting points are corrected.

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.

Acknowledgment. This work was made possible by the Paul B. Elder Co., Bryan, Ohio, who supplied xanthotoxin (9-methoxypsoralene) and by financial assistance under a grant from the National Science Foundation (NSF-G5795). Micro analyses and spectral analyses were contributed by the Upjohn Co., Kalamazoo, Michigan, and are gratefully acknowledged.

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

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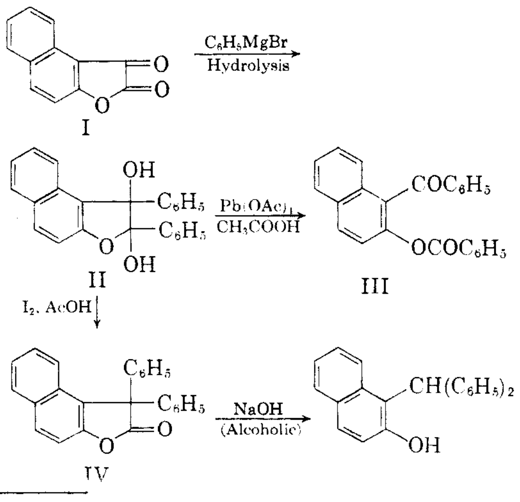
Coumaran-2,3-dione, in its reactions, shows the chemical properties associated with both lactones and 1,2-diketones.[1] Although the reaction of isatin, the nitrogen analog of coumaran-2,3-dione, with organomagnesium compounds has been thoroughly studied,[2] no work has been reported concerning the action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