1.76 (m, γ, δ-CH_2CH_2), 4.32 (d, J = 3 Hz, α-H), 4.25 (m, β-H), 3.86 (s, $COOCH_3$); MPW, R_f 0.55 (pink); PW, R_f 0.87.

Anal. Calcd for $C_7H_{13}Cl_2N_2O_3$: C, 33.74; H, 7.28; Cl, 28.46; N, 11.25. Found: C, 33.86; H, 7.41; Cl, 28.66; N, 11.22.

Sodium Methoxide Treatment of Oxazoline (*cis* **15**).—Pure oxazoline (*cis* **15**) (68 mg, 0.18 mmol) was dissolved in 10 ml of dry methanol, 1.0 ml of 0.88 *N* sodium methoxide was added, and the solution was allowed to stand for 20 min. Then 2.5 ml of water was added and the solution was refluxed for 30 min. When cooled, the solution was acidified to congo red with concentrated HCl and allowed to stand for 4 hr. The pH of the solution was adjusted to *ca.* 10 which after 10 min was reacidified with concentrated HCl and evaporated at 40° under vacuum until an oil began to form in the liquid. Methanol was added until the oil dissolved. Water was then added and the solution was scratched to induce crystallization. The product was collected by centrifugation and dried under vacuum at 46°: weight 62 mg (93%); mp 172–173° dec. The infrared spectrum was identical with that of *threo*-N,N′-dibenzoyl-β-hydroxylysine (*threo* **14a**), the starting material from which this oxazoline was prepared.

Direct Acid Hydrolysis of Oxazoline (*cis* **15**).—The oxazoline (*cis* **15**) (83 mg, 0.23 mmol) was dissolved in 10 ml of methanol, 1.2 ml of 1 *N* HCl was added, and the solution was allowed to stand 18 hr to convert the oxazoline into the O-benzoyl compound. After the solution had been made basic with about 1.2 ml of *N* NaOH and had stood 10 min, enough base was added to bring the total volume of base to 3 ml and the solution was refluxed 30 min. The solution was then cooled to room temperature, acidified with concentrated HCl, and evaporated to an oily solid residue. After washing the residue twice with water, it was dissolved in 2 ml of methanol and diluted with 8 ml of water. This solution was then evaporated under vacuum to about 3 ml, after which a solid slowly crystallized from the solution. After centrifugation and drying at 46° under vacuum, 14 mg of *erythro*-N,N′-dibenzoyl-β-hydroxylysine (*erythro* **14a**) was collected, mp 159–162° dec. The infrared spectrum of this product was identical with *erythro* **14a**.

Registry No.—**6a**, 19991-86-7; **6b**, 19991-87-8; **8** hydrochloride, 19991-88-9; **10a**, 19991-89-0; **10b**, 19991-90-3; *erythro* **12a** hydrobromide, 19991-91-4; *threo* **12a** hydrobromide, 19991-92-5; *erythro* **12b** dihydrochloride, 19991-93-6; *threo* **12b** dihydrochloride, 19991-94-7; **13** hydrochloride, 19991-95-8; *erythro* **14a**, 19991-96-9; *threo* **14a**, 19991-97-0.

Synthetic Furocoumarins. IX. A New Synthetic Route to Psoralen[1]

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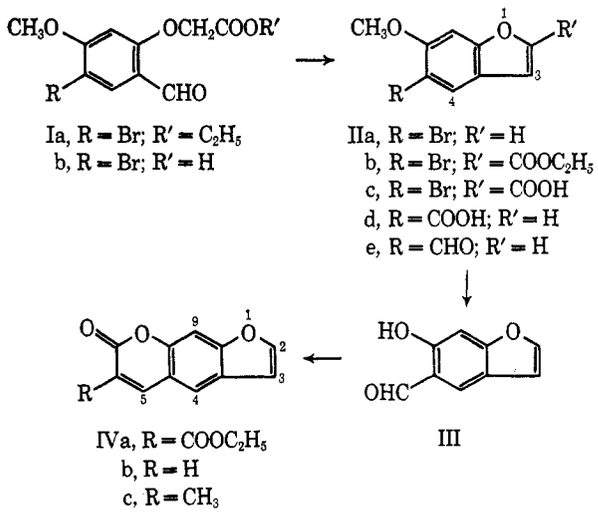
Practical syntheses of psoralen (IVb) and 3-methylpsoralen (IVc) from β-resorcylaldehyde are described. Bromination of ethyl (2-formyl-5-methoxyphenoxy)acetate gave the 4-bromo derivative Ia, which was saponified and simultaneously cyclized and decarboxylated to 5-bromo-6-methoxybenzofuran (IIa). Lithium–bromine interchange and then formylation and demethylation gave 5-formyl-6-hydroxybenzofuran (III), which was condensed with diethyl malonate to furnish psoralen after hydrolysis and decarboxylation of the Knoevenagel product IVa. Condensation of III with propionic anhydride furnished 3-methylpsoralen (IVc) directly.

Unfavorable directive effects associated with syntheses of psoralens unsubstituted in the 9 position have limited yields of the naturally occurring phototoxin psoralen (IVb, Scheme I) to 1–4% over-all from resorcinol or β-resorcylaldehyde.[3] However, Chatterjee and Sen recently reported a 15% conversion of resorcinol into psoralen.[4] Although their scheme now is the route of choice to psoralen itself, the synthesis lacks the versatility of the novel Scheme I, which represents a 14% conversion of β-resorcylaldehyde into psoralen.

Ethyl (4-bromo-2-formyl-5-methoxyphenoxy)acetate (Ia) was prepared both by bromination of ethyl (2-formyl-5-methoxyphenoxy)acetate[5] and by alkylation of 5-bromo-2-hydroxy-*p*-anisaldehyde.[6] Saponification of the ester Ia and then decarboxylative cyclization in acetic acid–acetic anhydride[7] gave the bromobenzofuran IIa and a trace quantity of a carboxylic acid identified as IIc by the independent synthesis of IIc from the ester Ia by base-catalyzed cyclization.

SCHEME I



To investigate the lithium–halogen interchange, the bromobenzofuran (IIa) was treated with butyllithium and then Dry Ice. This gave the carboxylic acid IId in quantitative yield. Earlier investigation of direct metalation with butyllithium of 6-methoxybenzofuran[8] and then carbonation (Dry Ice) indicated (thin layer chro-

(1) Part VIII: K. D. Kaufman, R. C. Kelly, and D. C. Eaton, *J. Org. Chem.*, **32**, 504 (1967). Preliminary communication: L. R. Worden and K. D. Kaufman, presented at the First International Congress of Heterocyclic Chemistry, Albuquerque, N. M., June 1967.

(2) (a) To whom inquiries should be directed. (b) National Science Foundation Undergraduate Research Participant (Grant No. GE-4097).

(3) (a) E. Späth, B. L. Manjunath, M. Pailer, and H. S. Jois, *Ber.* **69**, 1087 (1936); (b) E. C. Horning and D. B. Reisner, *J. Amer. Chem. Soc.*, **70**, 3619 (1948); (c) R. T. Foster, A. Robertson, and A. Bushra, *J. Chem. Soc.*, 2254 (1948); (d) T. R. Seshadri and M. S. Sood, *Indian J. Chem.*, **1**, 291 (1963).

(4) D. K. Chatterjee and K. Sen, *Sci. Cult.* (Calcutta), **33**, 528 (1967).

(5) R. Andrisano, F. Duro, and G. Pappalardo, *Boll. Sci. Fac. Chim. Ind. Bologna*, **14**, 96 (1956).

(6) M. G. S. Rao, C. Srikantia, and M. S. Iyengar, *J. Chem. Soc.*, 1578 (1929); *Chem. Abstr.*, **23**, 4681 (1929).

(7) A. W. Burgstahler and L. R. Worden, *Org. Syn.*, **46**, 28 (1966).

(8) H. Dumont and St. v. Kostanecki, *Ber.*, **42**, 911 (1909).

matography) the formation of at least seven bicarbonate-soluble products.

Treatment of the bromobenzofuran (IIa) with butyllithium and then N-methylformanilide furnished the aldehyde IIe, which was demethylated to the key intermediate, 5-formyl-6-hydroxybenzofuran (III).[9] Condensation of this intermediate with diethyl malonate gave ethyl 3-psoralencarboxylate (IVa), which was hydrolyzed in glacial acetic acid–concentrated hydrochloric acid[10] and then decarboxylated with copper–bronze to psoralen (IVb). This sample was identical (melting point, mixture melting point, infrared and ultraviolet spectra) with an authentic sample of the natural product obtained from the Pharmaceutical Department of Sandoz Ltd., Basle, Switzerland, to whom we express our appreciation.

Perkin condensation of the aldehyde III with propionic anhydride furnished the new furocoumarin, 3-methylpsoralen (IVc).

Experimental Section[11]

Ethyl (4-Bromo-2-formyl-5-methoxyphenoxy)acetate (Ia). A. From Ethyl (2-Formyl-5-methoxyphenoxy)acetate.—Partial methylation of β-resorcylaldehyde with methyl iodide and K_2CO_3 in acetone furnished 2-hydroxy-*p*-anisaldehyde of mp 41.5–43° in 62% yield by steam distillation of the alkali-soluble portion of the organic residue obtained from the reaction (lit.[12] mp 41–42°).

Alkylation of 2-hydroxy-*p*-anisaldehyde with ethyl bromoacetate according to Andrisano and coworkers[6] furnished ethyl (2-formyl-5-methoxyphenoxy)acetate of mp 63–65.5° in quantitative yield (lit.[6] mp 68–69°, no yield stated). This material was sufficiently pure for use in the next step.

A stirred solution of 8.9 ml (0.17 mol) of bromine in 0.4 l. of glacial acetic acid was added at room temperature over a period of 15 min to a stirred solution of 39.0 g (0.164 mol) of ethyl (2-formyl-5-methoxyphenoxy)acetate in 0.2 l. of glacial acetic acid. The resulting solution was stirred for an additional 45 min and then diluted by the slow addition of 1.5 l. of ice water. The white, flocculent precipitate was stirred for 45 min, collected, and washed with water. The dried white powder weighed 49.8 g (96%) and was of sufficient purity for use in the next step, mp 117.5–120°.

The **semicarbazone** crystallized from a large volume of ethanol, mp 241.5–242.5°.

Anal. Calcd for $C_{13}H_{16}BrN_3O_5$: C, 41.72; H, 4.31; N, 11.23. Found: C, 41.90; H, 4.49; N, 10.99.

B. From 5-Bromo-2-hydroxy-*p*-anisaldehyde.—5-Bromo-2-hydroxy-*p*-anisaldehyde was prepared both by bromination of 2-hydroxy-*p*-anisaldehyde (see part A) according to Rao and coworkers[6] (73%) and by bromination of β-resorcylaldehyde according to Seshadri and Varadarajan[13] to give 5-bromo-β-resorcylaldehyde of mp 173–175.5° in 22% yield (lit.[13] mp 175–176°, no yield of pure material stated). Partial methylation with dimethyl sulfate then furnished 19% 5-bromo-2-hydroxy-*p*-anisaldehyde, mp 116–119° (lit.[13] mp 120–121°, no yield stated).

A mixture of 2.00 g (8.66 mmol) of 5-bromo-2-hydroxy-*p*-anisaldehyde, 1.2 ml (11 mmol) of ethyl bromoacetate, 15.6 g (11.3 mmol) of potassium carbonate, and 50 ml of acetone was stirred under reflux for 21 hr, then cooled and filtered. Evaporation of the acetone left a solid residue, which was leached thoroughly with ether. The ether was washed with cold 5% sodium hydroxide, dried, and evaporated to leave 1.81 g (66%) of a light yellow material which smelled strongly of ethyl bromoacetate. Crystallization from ligroin (bp 100–115°) and then carbon tetrachloride afforded 0.63 g (23%) of the ester Ia of mp 121.5–123.5°. An additional crystallization from carbon tetrachloride gave an analytical sample of long, white needles of mp 123.5–124.5°.

Anal. Calcd for $C_{12}H_{13}BrO_5$: C, 45.44; H, 4.13; Br, 25.20. Found: C, 45.40; H, 4.45; Br, 25.21.

(4-Bromo-2-formyl-5-methoxyphenoxy)acetic Acid (Ib).—A mixture of 49.5 g (0.156 mol) of the ethyl ester Ia, 500 ml of 95% ethanol, and 625 ml (0.625 mol) of 1 *N* aqueous sodium hydroxide was stirred under reflux for 1 hr, and then *ca.* 200 ml of solvent was removed by distillation. The resulting yellow solution was cooled to 0° and poured into a mixture of 200 ml of ice water and 53 ml (0.620 mol) of concentrated hydrochloric acid. The yellow precipitate was collected, washed with several portions of water, and dried to give 43.1 g (95%) of the acid Ib, mp (instantaneous) 218° dec. A small sample was recrystallized three times from glacial acetic acid for analysis, mp (instantaneous) 222° dec.

Anal. Calcd for $C_{10}H_9BrO_5$: C, 41.56; H, 3.14; Br, 27.66. Found: C, 41.67; 3.39; Br, 27.82.

5-Bromo-6-methoxybenzofuran (IIa).—A mixture of 5.00 g (0.0173 mol) of (4-bromo-2-formyl-5-methoxyphenoxy)acetic acid (Ib), 5.00 g (0.0609 mol) of powdered anhydrous sodium acetate, 125 ml of acetic anhydride, and 25 ml of glacial acetic acid was stirred under reflux for 2 hr and then poured onto 1 kg of cracked ice. Alternate portions of 20% aqueous sodium hydroxide and ice were added until the mixture was distinctly basic. The basic mixture was thoroughly extracted with ether, and the ether was washed with 5% aqueous sodium hydroxide, dried (brine and then $MgSO_4$), and evaporated to leave 3.40 g of a light brown oil that crystallized upon being cooled. The solid was chromatographed on 25 g of acid-washed alumina (eluted with 30–60° petroleum ether) to give 3.01 g (77%) of 5-bromo-6-methoxybenzofuran as light yellow crystals of mp 51–55°, which were sufficiently pure for use in the next step. Two crystallizations of a small sample from methanol gave white needles of mp 55–56°: ultraviolet λ_{max} (95% ethanol) 244 mμ (log ε 3.94), 252 (3.92), 292 (3.75), and 302 (3.68); nmr (CCl_4) τ 2.35 (s, 1, C_4-**H**), 2.56 (d, 1, J = 2 Hz, C_2-**H**), 3.05 (s, 1, C_7-**H**), 3.44 (d, 1, J = 2 Hz, C_3-**H**), and 6.13 (s, 3, CH_3).

Anal. Calcd for $C_9H_7BrO_2$: C, 47.60; H, 3.11; Br, 35.20. Found: C, 47.64; H, 3.25; Br, 35.50.

Acidification with concentrated hydrochloric acid of the aqueous layers from the ether extractions gave only trace amounts of 5-bromo-6-methoxy-2-benzofurancarboxylic acid (IIc).

Ethyl 5-Bromo-6-methoxy-2-benzofurancarboxylate (IIb) and 5-Bromo-6-methoxy-2-benzofurancarboxylic Acid (IIc).—A sodium ethoxide solution was prepared from 0.75 g (0.033 mol) of sodium and magnesium-dried[14] ethanol. To 5 ml of this solution was added 1.00 g (3.15 mmol) of the ester Ia and 10 ml of magnesium-dried ethanol. The solution was refluxed for 15 min and then cooled in an ice bath. A yellow precipitate which had formed during the course of the reaction dissolved when 25 ml of water was added cautiously to the reaction mixture, but a new light yellow crystalline precipitate appeared and was collected and dried, 0.20 g, mp 99–100°. Recrystallization from dilute ethanol gave 0.16 g (17%) of the ester IIb as off-white, slender needles of mp 100.5–101.5°.

Anal. Calcd for $C_{12}H_{11}BrO_4$: C, 48.18; H, 3.71; Br, 26.72. Found: C, 48.23; H, 3.76; Br, 26.34.

Acidification of the filtrate from which the 0.20-g precipitate had been collected gave 0.41 g of a mixture of 5-bromo-6-methoxy-2-benzofurancarboxylic acid (IIc) and (4-bromo-2-formyl-5-methoxyphenoxy)acetic acid (Ib). Fractional crystallization of the mixture from 95% ethanol gave 0.17 g (20%) of the benzofurancarboxylic acid IIc as a bright yellow, amorphous solid of instantaneous mp 284–285°. Sublimation followed by another crystallization from 95% ethanol gave a white solid of instantaneous mp 289.5–291.5°.

Anal. Calcd for $C_{10}H_7BrO_4$: C, 44.31; H, 2.60; Br, 29.48. Found: C, 44.42; H, 2.90; Br, 29.50.

(9) P. Karrer, A. Glattfelder, and Fr. Widmer [*Helv. Chim. Acta*, **3**, 541 (1920)] formylated 6-hydroxybenzofuran and obtained a material which they believed to be 5-formyl-6-hydroxybenzofuran, but which failed to yield psoralen when condensed with acetic anhydride. Robertson and coworkers[3c] later suggested that Karrer, *et al.*, had obtained the 2-formyl derivative. The synthesis described in this paper established unequivocally that the substance in question was not 5-formyl-6-hydroxybenzofuran since our material differs widely in chemical and physical properties from that reported by Karrer, Glattfelder, and Widmer.

(10) E. L. Eliel, M. T. Fisk, and T. Prosser, *Org. Syn.*, **36**, 3 (1956).

(11) Melting points (capillary) below 225° are corrected. Infrared, ultraviolet, and (in some cases) nuclear magnetic resonance spectra of most of the compounds described below are on file. Photocopies will be supplied on request.[2a] In nmr descriptions, s = singlet, d = doublet.

(12) E. Ott and E. Nauen, *Ber.*, **55**, 920 (1922). The authors prepared the same compound in 50% yield by partial alkylation with dimethyl sulfate.

(13) T. R. Seshadri and S. Varadarajan, *J. Sci. Ind. Res.*, **11B**, 39 (1952).

(14) H. Lund and J. Bjerrum, *Ber.*, **64**, 210 (1931).

6-Methoxy-5-benzofurancarboxylic Acid (IId).—To a solution of 0.500 g (2.20 mmol) of 5-bromo-6-methoxybenzofuran (IIa) in 10 ml of anhydrous ether was added 2.00 ml (2.32 mmol) of 1.16 *N* butyllithium[15] in ether. The reaction flask was stoppered and the reaction mixture, which became warm, was swirled for 2 min and then poured onto crushed Dry Ice. More ether was added, the solid carbon dioxide was allowed to evaporate, and the ether was extracted thoroughly with 5% sodium bicarbonate. The white solid recovered from the extract by acidification, extraction with ether, and removal of the ether was washed with three small portions of ether to remove adhering butyric acid: yield 0.42 g (99%); mp 140–141°. Crystallization of a small sample from dilute ethanol gave feathery needles of mp 144.5–145°.

Anal. Calcd for $C_{10}H_8O_4$: C, 62.50; H, 4.20. Found: C, 62.33; H, 4.11.

5-Formyl-6-methoxybenzofuran (IIe).—To a solution of 47.6 g (0.209 mol) of 5-bromo-6-methoxybenzofuran (IIa) in 0.8 l. of anhydrous ether was added rapidly 260 ml (0.21 mol) of 0.82 *N* butyllithium[15] in ether. The reaction mixture was stirred slowly for about 0.25 min and then added over a period of 5 min to a stirred solution of 55.5 g (0.411 mol) of redistilled N-methylformanilide in 0.5 l. of anhydrous ether. After being stirred for an additional 15 min, the ether solution was washed with water and then with 5% hydrochloric acid (four 200-ml portions). The ether was dried ($MgSO_4$) and evaporated to give a yellow oil which crystallized upon overnight refrigeration. Chromatography on 1.2 kg of silica gel (4-in.-diameter column, elution with 50% benzene in hexane) and then crystallization from cyclohexane afforded 25.45 g (69%) of 5-formyl-6-methoxybenzofuran as off-white crystals of mp 88.5–90°: nmr (CCl_4) τ −0.35 (s, 1, CHO), 2.03 (s, 1, C_4-**H**), 2.52 (d, 1, J = 2.5 Hz, C_2-**H**), 3.04 (s, 1, C_7-**H**), 3.32 (d, 1, J = 2.5 Hz, C_3-**H**), and 6.07 (s, 3, CH_3). Recrystallization of a small sample from ligroin (bp 60–90°) gave white needles of unchanged melting point.

Anal. Calcd for $C_{10}H_8O_3$: C, 68.18; H, 4.58. Found: C, 67.96; H, 4.61.

5-Formyl-6-hydroxybenzofuran (III).—Granular anhydrous aluminum chloride (3.05 g, 22.9 mmol, J. T. Baker Co. No. 0504) that had been powdered and then weighed rapidly in an open container on a dry day was added to 200 ml of freshly distilled, reagent grade 1,2-dichloroethane (Eastman Kodak Co., no. EK-132) in a flask protected with a drying tube. The straw-colored solution was warmed and stirred until *ca.* half the aluminum chloride had dissolved. Then 2.00 g (11.4 mmol) of 5-formyl-6-methoxybenzofuran (IIe) was added, and the resulting orange solution was heated under reflux for 1.25 hr. The mixture turned considerably darker during the course of the reflux period and slowly deposited a fine, brown precipitate after the first 0.5 hr. After the reflux period the reaction mixture was allowed to cool to room temperature and then was poured into a separatory funnel that contained 0.2 l. of 10% hydrochloric acid. Ether was added to bring the organic phase to the surface, the clear aqueous layer was discarded, and the ether solution was extracted repeatedly with 50-ml portions of 5% sodium hydroxide until the alkaline extracts remained colorless. The combined, cooled extracts were acidified, and the resulting flocculent tan precipitate was taken up in either. The ether was dried ($MgSO_4$) and evaporated to give a tan residue, which was leached with 200 ml of boiling ligroin (bp 60–90°). The filtered ligroin solution was evaporated to dryness to leave 1.67 g (91%) of 5-formyl-6-hydroxybenzofuran as a pale yellow solid of mp 106.5–107.5°. Although this material was pure enough for use in the next step, a small sample was crystallized from ligroin (bp 60–90°) with activated carbon and then from 95% ethanol to give white needles of unchanged melting point.

(15) The reagent was prepared according to G. Wittig in "Newer Methods of Preparative Organic Chemistry," Vol. 1, Interscience Publishers, New York, N. Y., 1948, p 575, and standardized according to H. Gilman and A. H. Haubein, *J. Amer. Chem. Soc.*, **66**, 1515 (1944). Butyllithium now is commercially available.

Anal. Calcd for $C_9H_6O_3$: C, 66.67; H, 3.73. Found: C, 66.89; H, 3.91.

The **semicarbazone** crystallized from 95% ethanol in lustrous, light yellow plates of instantaneous mp 283°. The melt resolidified immediately to a light orange solid.

Anal. Calcd for $C_{10}H_9N_3O_3$: C, 54.79; H, 4.14; N, 19.17. Found: C, 55.02; H, 4.38; N, 19.11.

Ethyl 3-Psoralencarboxylate (IVa).—A mixture of 0.162 g (1.00 mmol) of 5-formyl-6-hydroxybenzofuran (III) and 2.0 ml of absolute ethanol was warmed to effect solution of the benzofuran, and then 0.18 ml (1.2 mmol) of diethyl malonate and 0.03 ml of piperidene were added with an accompanying red coloration. The reaction mixture was heated under reflux for 15 min and allowed to cool whereupon the product crystallized. Filtration furnished 0.216 g (84%) of orange plates, mp 151–152.5°. Two recrystallizations of a small portion from methanol for analysis gave long orange needles of mp 153–154°.

Anal. Calcd for $C_{14}H_{10}O_5$: C, 65.12; H, 3.90. Found: C, 65.04; H, 4.22.

Psoralen (IVb).—A mixture of 1.00 g (3.87 mmol) of ethyl 3-psoralencarboxylate (IVa), 7.5 ml of glacial acetic acid, and 3.5 ml of concentrated hydrochloric acid was heated under reflux for 2 hr and poured onto 25 g of crushed ice to furnish 0.87 g (98%) of the corresponding acid as a yellow powder of mp 258–261°. Two recrystallizations of a small sample from 1,2-dichloroethane gave yellow needles of mp 264.5–265.5° for which a satisfactory analysis was not obtained.

A mixture of 0.200 g (0.868 mmol) of crude 3-psoralencarboxylic acid, 0.500 g of copper–bronze powder (E. H. Sargent Co., No. SC-11552), and 3.0 ml of freshly distilled quinoline was heated under reflux for 10 min, allowed to cool, diluted wth 50 ml of ether, and then filtered to remove the copper–bronze. The ether solution was extracted repeatedly with 6 *N* hydrochloric acid until further extracts remained colorless. Evaporation of the dried ether layer gave a brown solid which upon sublimation at 145° (0.45 mm) and then recrystallization from dilute ethanol furnished 0.097 g (60%) of psoralen as long white needles of mp and mmp 165.5° (no range), infrared and ultraviolet spectra[16] identical with those of an authentic sample received from Sandoz Ltd.

3-Methylpsoralen (IVc).—A mixture of 0.486 g (3.0 mmol) of 5-formyl-6-hydroxybenzofuran (III), 0.572 g (6.0 mmol) of sodium propionate (Eastman Kodak practical grade), and 0.78 ml (6.1 mmol) of freshly distilled propionic anhydride was heated at 178–181° (oil-bath temperature) for 9 hr, cooled, and then stirred overnight with 15 ml of 3 *N* aqueous sodium acetate to decompose excess anhydride. The reaction mixture was worked up by ether extraction. Extraction of acidic materials with sodium bicarbonate solution and then drying and evaporation of the ether furnished a dark-colored solid which was sublimed at 170° (0.3 mm). Crystallization of the sublimate from ethanol furnished 0.279 g (47%) of 3-methylpsoralen as colorless needles of mp 235–235.5°. Recrystallization for analysis of a small sample from ethanol did not change the melting point.

Anal. Calcd for $C_{12}H_8O_3$: C, 71.99; H, 4.03. Found: C, 71.86; H, 4.38.

Registry No.—Ia, 20073-14-7; Ia semicarbazone, 20073-15-8; Ib, 20073-16-9; IIa, 20073-17-0; IIb, 20073-18-1; IIc, 20073-19-2; IId, 20073-20-5; IIe, 20073-21-6; III, 20073-22-7; III semicarbazone, 20073-23-8; IVa, 20073-24-9; IVb, 66-97-7; IVc, 20073-26-1.

Acknowledgment.—We thank the Upjohn Co., Kalamazoo, Mich., for determination of combustion data and nmr spectra.

(16) See D. K. Chatterjee, R. M. Chatterje, and K. Sen [*J. Org. Chem.*, **29**, 2467 (1964)] for a reproduction of the ultraviolet spectrum of psoralen.