A. 2,3-Tolylene Diisocyanate (Va) from 2,3-Tolylenediamine (Ia).—Dry o-dichlorobenzene (150 ml) was heated at 150° in a round-bottomed flask under a blanket of nitrogen and saturated with phosgene, while agitating. 2,3-Tolylenediamine (20 g) was dissolved in 200 ml of dry o-dichlorobenzene at 90-100° and added slowly at this temperature through a dropping funnel over a period of 4 hr, while simultaneously passing phosgene into the flask. The molar ratio of phosgene to o-TDA was approximately 20:1. Feeding of phosgene and rapid stirring of the reaction mixture at 150° was continued for 14 hr after addition of the diamine had been completed. Hydrogen chloride, formed during the reaction, and excess phosgene were withdrawn through a water-cooled reflux condenser.

The reaction mixture was then purged with nitrogen at 150° for 2 hr, insolubles were removed by filtration, and the filtrate worked up by distillation. After removal of the solvent, a liquid distilled slowly into the receiver, where it polymerized rapidly to a solid material, 8.19 g or 28.6% of theory calculated for Va. Heating of the polymer between 250 and 300° under 15 mm pressure resulted in gradual depolymerization and distillation of 6.5 g of 2,3-tolylene diisocyanate (Va), n^{25} D 1.5650 (2.4-tolylene diisocyanate, lit. n^{25} D 1.5654). When subjected (2,4-tolylene diisocyanate, lit. n^{25} D 1.5654). When subjected to vapor phase chromatography, this product eluted at the same retention time as standard solutions of the 2,4- and 2,6-tolylene diisocyanates in o-dichlorobenzene under identical conditions. The infrared spectrum of compound Va displayed absorption at 4.45 μ , indicative for isocyanato groups and had peaks at 12.9 and 13.9 μ , characteristic for 1,2,3-substituted benzene derivatives: mass spectrum (70 eV) m/e (relative intensity of 2,3 isomer, relative intensity of 2,4/2,6 isomer mixture) 174 (100, 100), 146 (26.5, 25.0), 132 (18, 17.5), 118 (33, 17), 91 (40, 16), 39 (15.5, 12.5). The observed differences at 118 and 91 are believed to be due to the different isomer configuration. A molecular ion observed at m/e 148 and fragment ions associated with this molecular ion must be due to small amounts of a protonated entity in the product, very likely 4-methylbenzimidazolone, which could have been formed by traces of moisture. The residue (about 1.6 g) obtained by thermal cleavage of the polymer showed strong infrared absorption at 5.85 and 7.05 μ , indicating that partial, irreversible trimerization to isocyanurates had occurred.

Polymerization of the freshly distilled sample of Va proceeded relatively slowly and could be followed by the increase in the infrared absorption at 5.65 and 5.75 μ . The sample had completely polymerized after 2 hr.

Reaction of Va with water at room temperature resulted in the formation of 4-methylbenzimidazolone (IIIa), identified by melting point and infrared spectrum.

B. 3,4-Tolylene Diisocyanate (Vb) from 3,4-Diaminotolylene (Ib).—The procedure described for the preparation and isolation of Va was repeated, except that 300 ml of o-dichlorobenzene were saturated with phosgene and 20 g of 3,4-diaminotolylene was dissolved in 500 ml of o-dichlorobenzene. The yield of distilled diisocyanate Vb was 1.6 g or 5.5% of theory, n^{25} D 1.5615. When subjected to vapor phase chromatography, Vb displayed the same retention time as Va. The infrared spectrum of this product displayed strong absorption at 4.45 μ , indicative for isocyanato groups, and had peaks at 11.4 and 12.3 μ , characteristic for 1,2,4-substituted benzene derivatives. A freshly distilled sample of Vb polymerized completely within 20 min.

C. o-Tolylene Diisocyanates V from 4- and 5-Methylbenzimidazolone (III).—A stirred solution of 10 g of 4-methylbenzimidazolone (IIIa) in 1000 ml of dry o-dichlorobenzene at 150° was treated with phosgene for 9 hr. Excess phosgene was then removed by passing nitrogen through the reaction mixture at 160° for 2 hr. The solvent was removed by distillation and the resulting residue subjected to vapor phase chromatography, which indicated a 3% yield of diisocyanate Va.

A solution of 10 g of 5-methylbenzimidazolone (IIIb) in 500 ml of dry o-dichlorobenzene was phosgenated at 155° for 6 hr. The reaction product was purged with nitrogen at 150° for 2 hr and the solvent was removed by distillation. Vapor phase chromatography of the residue indicated that disocyanate Vb had been formed in 15% yield of the theory.

Vb had been formed in 15% yield of the restdue interact the information of the second in 15% yield of the theory. D. 2,3-Tolylene Diisocyanate (Va) from 2,3-Tolyleneallophanoyl Chloride (IVa).—A sample of IV (1 g) was heated in 15 ml of dry o-dichlorobenzene at 175-180° for 20 min. After hydrogen chloride evolution had ceased, the solution was subjected to vapor phase chromatography, which indicated that 2,3-tolylene diisocyanate had been formed in a 35% yield. An infrared spectrum of the solution showed strong absorption at 4.45 μ , indicative for the presence of free isocyanato groups.

o-Tolylene Diisocyanate Polymers.—Both the 2,3- and the 3,4-tolylene diisocyanate derived polymers are insoluble in the common solvents, but can be dissolved in 100% sulfuric acid. The intrinsic viscosity in sulfuric acid of the polymer derived from the 2,3 and 3,4 isomers were found to be 0.18 and 0.12, respectively. Mass spectroscopy showed the presence of tolylene diisocyanate as the predominant component (m/e 174). Combustion analyses were in good agreement with the values calculated for tolylene diisocyanate: λ (infrared) of 2,3-tolylene diisocyanate polymer 4.45, 5.65, 5.75, 7.5, 7.7, 9.6, 10.9, 12.9, 13.6; λ (infrared) of 3,4-tolylene diisocyanate polymer 4.45, 5.65, 5.75, 7.45, 7.8, 9.2, 9.3, 10.6, 11.85, 12.3, 13.1, 13.7, 14.4.

Anal. Calcd for $(C_9H_6O_2N_2)_n$: C, 62.07; H, 3.47; N, 16.09. Found: C, 61.42; H, 3.86; N, 15.79.

2,3-Tolyleneallophanic Acid Methyl Ester (VI).—A few drops of freshly distilled 2,3-tolylene diisocyanate were added to an excess of methanol. After a short time, crystals started to precipitate. Filtration and recrystallization of the filter cake from methanol gave VI: mp 207.5-209°; λ (infrared) 3.18, 5.75, 5.80, 6.98, 7.42 μ .

5.80, 6.98, 7.42 μ . *Anal.* Calcd for C₁₀H₁₀N₂O₃: C, 58.24; H, 4.87; N, 13.60. Found: C, 57.66; H, 4.97; N, 13.72.

2,3-Tolyleneallophanoylanilide (VII).—A few drops of freshly distilled 2,3-tolylene diisocyanate were added to an excess of aniline. The resulting white crystals were recrystallized from methanol to give VII: mp 238-240°; λ (infrared) 3.12, 3.24, 5.80, 5.86, 7.4 μ .

Anal. Calcd for $C_{15}H_{18}N_3O_2$: C, 67.40; H, 4.90; N, 15.72. Found: C, 67.85; H, 5.36; N, 15.76.

Registry No.—4-Methylbenzimidazalone, 19190-68-2; IVa, 19190-69-3; Va, 7373-19-5; Vb, 13879-33-9; VIa, 19190-72-8; VIIa, 19190-73-9.

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Synthesis of the Dibenzo[b,g]oxocin System

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The medium-ring heterocyclic systems, like the corresponding carbocycles, are of considerable chemical interest for studies on aromaticity,² transannular interactions³ and reactions,⁴ conformation⁵ and other properties. The partially or fully unsaturated molecules are of particular interest in this respect.⁶ Much less is known of the heterocyclic systems than of the carbocycles, however, because of the lesser synthetic availability of the heterocycles. In this paper we wish to report a synthesis of the dibenzo[b,g]oxocin system.

The starting materials used in the synthesis were di-o-tolyl ether (1a) and 2-carboxy-2'-methyldiphenyl

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ether (2), which have been prepared by the coppercatalyzed condensation of the potassium or sodium salt of o-cresol with o-bromotoluene⁷ and with potassium o-chlorobenzoate⁸ (Ullmann ether synthesis⁹).



In repeating these preparations, one new observation worthy of note was made. When potassium o-bromobenzoate was treated with the potassium salt of o-cresol in the presence of excess o-cresol, the ether 2 was formed in good yield under the usual Ullmann conditions without the addition of the copper catalyst. Addition of copper powder to the initial reaction mixture resulted in no improvement in the yield. When potassium o-chlorobenzoate was used instead of the bromo compound, even with the addition of copper, no ether was formed and unreacted starting materials were recovered. The reaction of the potassium salt of o-cresol with an equivalent amount of o-bromotoluene in excess o-cresol, without added copper, afforded di-o-tolyl ether in 20%yield. This yield was raised to 81%, however, when a threefold excess of potassium o-cresylate was employed. These results are of interest because a number of workers have reported that the Ullmann ether synthesis fails completely in the absence of added catalytic copper,⁹⁻¹¹ and several studies have been made to determine the form of the active copper species and other aspects of the mechanism.¹¹⁻¹⁵ There is no obvious rationalization for the success of the uncatalyzed reaction in our hands. It is possible that the use of a severalfold excess of the phenol as solvent was the decisive factor. It has been noted that the choice of solvent can have a dramatic effect upon the rate and yield of the Ullmann ether synthesis^{11,15} and on related reactions.¹⁶ Another possibility is that the reactions were actually catalyzed by small amounts of impurities. The reactants used were of reagent grade or purified by redistillation, but no unusual precautions were taken to remove traces of metals or other contaminants. Enhancement of the rate of the copper-catalyzed reaction by impurities present in the solvent has been noted previously.¹⁴ Further study of this subject is desirable. It would be convenient if general conditions for the preparation of diaryl ethers without the presence of copper could be developed, as reduction of the halide and other side reactions are sometimes promoted by the copper.11,15

Di-o-tolyl ether was converted to a dibromo derivative in 44% yield by treatment with N-bromosuccinimide by

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the procedure of Wenner.¹⁷ The nuclear magnetic resonance spectrum of the product showed it to have the symmetrical structure 1b. This was confirmed by the preparation of 1b by the alternative route described below. This dibromo compound was converted by reaction with sodium cvanide to the dinitrile 1c, which was not isolated but was hydrolyzed directly to the diacid 3a. The dimethyl ester of this acid 3b was used



for the ring closure experiments. This ester was also prepared by an alternative route, starting from ether 2. Oxidation of 2 by potassium permanganate converted it to the known¹⁸ dicarboxylic acid 4a. Reaction of 4a with thionyl chloride yielded the known diacid chloride 4b, whose melting point differed from that reported in the literature.¹⁸ As the properties of methyl ester and amide derivatives of 4b agreed with those previously reported, it is likely that the discrepancy is due to the existence of 4b in isomorphic forms. The diacid chloride 4b was converted to the diester 3b via the Arndt-Eistert sequence.¹⁹ The intermediate didiazo ketone 4c was decomposed using silver oxide in methanol to afford 3b. The over-all yield of 3b from 2 by this route was 27%. This was inferior to the first route in which the diester 3b was produced from 1a in 32%over-all yield. A further correlation between the two pathways was established by lithium aluminum hydride reduction of diacid 4a to the dialcohol 1d, which on treatment with HBr gave dibromide 1b.

The diester 3b was cyclized to the dibenzoxocin derivative 5 by use of the Dieckmann reaction under high dilution conditions.²⁰ With potassium t-butoxide as catalyst, the yield, based upon diester consumed, was 21%. When the reaction was attempted in dimethyl sulfoxide with the use of dimethylsulfinyl carbanion as catalyst,²¹ no Dieckmann product could be isolated. A superior set of conditions for the preparation of 5 was discovered inadvertently, however.



An attempt was made to close a nine-membered ring by acyloin reaction of diester 3b, using a dispersion of

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sodium in xylene under high dilution conditions. No acyloin product was isolated, but a 32% yield of Dieckmann product 5 was obtained. Several cases have been recorded previously in which Dieckmann products have been isolated from attempted acyloin reactions.²² In the present case, the phenyl rings in 3b undoubtedly enhanced the acidity of the protons α to the carbonyl groups and so favored the Dieckmann reaction, as opposed to the acyloin condensation.

In our initial preparation of the dibenzoxocin 5 under Dieckmann conditions, the nuclear magnetic resonance spectrum of the product indicated it to be essentially in the enol form depicted. On subsequent Dieckmann runs, and with the preparation under acyloin conditions, the compound was found to contain approximately 15-20% of the keto form **6a**. It was homogeneous on thin layer chromatography. For further characterization, this product was hydrolyzed and decarboxylated in dilute hydrochloric acid in 87% yield to a sharpmelting product with the properties expected of the cyclic ketone 6b. When the same hydrolysis of 6a was attempted in aqueous base, ring cleavage occurred, with the formation of the diacid 3a. Ketone 6b was also formed from 5 during an attempted analysis of the latter compound by gas chromatography.

Compound 5 appears to be the first reported dibenzoxocin derivative. No fully unsaturated derivative of the parent compound, oxocin, has as yet been reported, although a number of partly saturated derivatives, and the fully saturated oxocane have been prepared.5,23

Experimental Section

Infrared spectra were obtained with a Perkin-Elmer Infracord spectrophotometer. Nuclear magnetic resonance spectra were determined using a Varian A-60 spectrometer using tetramethylsilane as internal reference. Mass spectra were obtained with a Varian M-66 mass spectrometer. An Aerograph 90-P3 instrument was used for gas chromatography. Melting points were determined with a Thomas-Hoover Unimelt apparatus and are uncorrected. Elemental analyses were performed by Mr. George I. Robertson, Florham Park, N.J., except for that of 5 which was obtained from M-H-W Laboratories, Garden City, Mich. Thin layer chromatography plates were made from Adsorbosil to which 1% Radelin phosphor was added. The plates were 0.25-mm thick and were visualized by means of ultra-The violet light.

Di-o-tolyl Ether (1a) .- A mixture of 133 g (0.777 mol) of o-bromotoluene, 345 g (2.36 mol) of the dry potassium salt of o-cresol, and 235 g (2.17 mol) of o-cresol was heated at 200-210° with stirring, for 11 hr. To the resulting glassy mass was added 500 ml of 4.4 N NaOH and 200 ml of hexane. The organic layer was separated, dried (MgSO₄), and evaporated. The residue was distilled and gave 124 g (81%) of di-o-tolyl ether (1a): bp 148-149° (14 mm) (lit.7 bp 146-147 (3 mm)); ir (neat), 6.75, 8.11, 13.3 μ ; nmr (CDCl₃), δ 2.23 (s, 6, CH₃), 6.55–7.30 (m, 8, aromatic).

2-Carboxy-2'-methyldiphenyl Ether (2).-A mixture of 119.5 g (0.50 mol) of dry potassium o-bromobenzoate, 163 g (1.52 mol) of o-cresol, and 29 g (0.50 mol) of 95% sodium methoxide was heated with stirring for 1 hr at 170-180°. The resulting glassy mass was dissolved in water and acidified with concentrated HCl. Sufficient ether was added to dissolve the precipitate that formed, and the organic layer was separated and extracted repeatedly with 5% sodium bicarbonate solution.

Acidification of the aqueous extracts precipitated the crude product which, upon recrystallization from ethanol-water, gave 78 g (68%) of acid 2: mp 134-135° (lit.⁸ 135°); ir (KBr), 3.4-

4.0 (acid OH), 5.90 (C=O), 6.75, 8.10, 13.1, and 13.4 µ; nmr (CDCl₃), δ 2.25 (s, 3, CH₃), 6.6 (m, 7, aromatic H, except proton ortho to CO₂H), 8.25 (q, 1, J = 2 Hz, H ortho to CO₂H), 10.6 (s, broad, 1, CO_2H).

2,2'-Bis(bromomethyl)diphenyl Ether (1b). A. Preparation from 1a.—A mixture of 109 g (0.552 mol) of 1a, 400 ml of carbon tetrachloride, 205 g (1.15 mol) of N-bromosuccinimide, and 1 g of dibenzoyl peroxide was heated at reflux, with stirring for 24 hr. The suspension was filtered, and the filtrate was evaporated to dryness. The residue was recrystallized from hexane to afford 89 g of the dibromo compound 1b, mp 86-90°. Another recrystallization from hexane gave pure 1b: mp 90-91°; ir (KBr), 6.77, 6.94, 8.10, 13.25 μ ; nmr (CDCl₃), δ 4.65 (s, 4, CH₂Br), 6.8–7.6 (m, 8, aromatic); tlc, R_f (hexane) 0.18. Anal. Calcd for C₁₄H₁₂Br₂O: C, 47.16; H, 3.37; Br, 44.89. Found: C, 46.95; H, 3.37; Br, 44.81.

B. Preparation from 1d.--Anhydrous hydrogen bromide was bubbled, for 1 hr, into a stirred suspension of 3.10 g of dialcohol 1d in 150 ml of benzene and the solution was then allowed to stand for 16 hr. The solution was dried (MgSO₄), and the benzene was evaporated under vacuum to yield 4.70 g (98%) of crystalline material, mp 86-89°. Recrystallization from hexane gave pure 1b, mp 90-91°, whose ir spectrum was identical with the one obtained by the alternative preparation above.

(Diphenyl ether)-2,2'-diacetic Acid (3a).—A mixture of 70.0 g of dibromide 1b (0.196 mol), 400 ml of ethanol, 150 ml of water, and 26.4 g (0.54 mol) of sodium cyanide was refluxed, with stirring, for 48 hr. A small aliquot was removed and water was added to it, causing precipitation of a white solid: ir (KBr), 2.95 (N-H), 4.44 (CN), 6.03 (C=O) μ . The ir indicated that some hydrolysis of the expected dinitrile to the corresponding amide had occurred.

Hydrolysis of the above mixture to the diacid was accomplished by the addition of 19.0 g (0.475 mol) of sodium hydroxide in 50 ml of water to the cooled solution and refluxing overnight. The ethanol was then removed by distillation. The cooled solution was filtered and partially acidified with concentrated hydrochloric acid. This resulted in the precipitation of a small quantity of dark, impure material, which was removed by filtration. Acidification of the filtrate gave 50.0 g (91%) of a light red product, mp 192-199°. Recrystallization of 40 g of this material from 80 ml of nitrobenzene gave 35 g of the pure, colorless diacid 3a: mp 202-204°; ir (KBr), 3.0-4.0 (acid OH), 5.89 (C=O), 8.10, 13.1 μ . Anal. Calcd for C₁₆H₁₄O₅: C, 67.13; H, 4.98. Found: C,

67.61; H, 5.08.

To a suspension of 28.4 g of this acid in 400 ml of 95% ethanol was added a solution in ether of diazomethane (prepared from N,N'-dimethylterephthalamide²⁴) until the yellow color of diazomethane persisted in the receiver. The excess diazomethane, the ether, and the alcohol were removed under vacuum. Dis-tillation of the residue gave 11.29 g (86%) of the diester 3b: bp 172-175° (3 mm); ir (neat), 5.74 (C=O), 8.10, 8.65; nmr (CDCl₃), § 3.60 (s, 6, OCH₃), 3.70 (s, 4, CH₂C=O), 6.70-7.40 (m, 8, aromatic); molecular weight (mass spectrum), 314; tlc $(CHCl_3), R_f 0.9.$

2,2'-Dicarboxydiphenyl Ether (4a).—A mixture of 38.5 g (0.17 mol) of 2, 82 g (0.51 mol) of potassium permanganate, 140 g (3.5 mol) of sodium hydroxide, and 2 l. of water was heated at 95-100°, with stirring, for 20 min and allowed to cool. Ethanol (60 ml) was added, and the precipitate of MnO_2 was removed by filtration. The filtrate was acidified with 200 ml of concentrated HCl to give 39 g (mp $225-228^{\circ}$) of product, which was collected by filtration. Recrystallization of 27 g of this product from 500 ml of tetrachloroethane gave 24.5 g (80%) of diacid 4a: mp 228-229.5° (lit.¹⁸ 230°); ir (KBr), 3.4-4.0 (acid OH), 5.85, 6.00, 8.10, 13.2 (o-C₆H₄) μ ; nmr (CF₃CO₂H), δ 7.0–7.9 (m, 6, aromatic, except H ortho to CO_2H), 8.25 (q. 2, J = 2, 6 Hz, H ortho to O_2H).

2,2'-Bis(hydroxymethyl)diphenyl Ether (1d).-The procedure of Nystrom and Brown²⁵ for acids of low solubility in ether was followed. Five grams (19.4 mol) of the diacid 4a, in an extraction thimble, was inserted in a Soxhlet extractor containing 225 ml of anhydrous ether and 3.0 g (96.7 mol) of lithium aluminum hydride. After refluxing for 30 hr the flask was cooled, and water slowly was added, followed by 100 ml of 10% H₂SO₄. The

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organic layer was separated, washed with water, dried (MgSO₄), and evaporated to yield 4.1 g (93%) of crude product. Recrystallization from benzene gave pure dialcohol 1d: mp 98.5–99.5°; ir (KBr), 3.10 (OH), 6.78, 6.91, 8.15, 9.70, 13.2 μ ; nmr (CDCl₃), δ 3.3 (s, broad, 2, OH), 4.65 (s, 4, CH₂), 6.80–7.50 (m, 8, aromatic).

Anal. Caled for C₁₄H₁₄O₈: C, 73.04; H, 6.09. Found: C, 73.18, H, 6.15.

(Diphenyl ether)-2,2'-dicarbonyl Chloride (4b).—A mixture of 250 ml of SOCl₂ (redistilled) and 24.2 g of the diacid 4a was heated at reflux for 2 hr, and 150 ml of solvent was then removed by distillation. Hexane (300 ml) was added and the mixture was cooled at 5° for 4 hr. The precipitate was filtered and washed with hexane to yield 22.0 g (80%) of 4b: mp 91–93° (lit.¹⁸ 161°); ir (KBr), 5.63, 5.67 (C=O), 8.06, 13.1 μ ; methyl ester 4c: mp 64–65.5° (lit.¹⁸ 65.5°); amide 4d: mp 264–266° (lit.¹⁸ 265°).

Arndt-Eistert Synthesis of Dimethyl (Diphenyl ether)-2,2'-Diacetate (3b).—To a solution of 6.0 g (0.020 mol) of 4b in 40 ml of dry dioxane was added diazomethane solution (0.14 mol) in ether, prepared from N,N'-dinitroso-N,N'-dimethylterephthalamide,²⁴ and the reaction mixture was allowed to stand overnight. The solvents were removed by distillation, leaving 6.0 g of didiazo ketone 4c as a gummy yellow solid: ir (KBr), 4.74 (N=N), 6.24 (C=O), 8.20, 13.3 μ . This was dissolved in 110 ml of methanol, heated at 60°, and over 2.5 hr a slurry prepared from 0.7 g of silver oxide in 20 ml of methanol was added to it. The mixture was refluxed for 16 hr and filtered through a bed of Celite. On evaporation of the methanol, 6.0 g of a brown oil, which showed ir absorption at 5.78 (ester) and 5.91 (ketone) μ was obtained.

The ketone impurity was removed in the following manner. A mixture of 3.5 g of the crude reaction product, 2.3 g of trimethylaminoacetoxyhydrazide chloride (Girard's T Reagent), 40 ml of methanol, and 40 ml of acetic acid was refluxed for 45 min, and then ether and water were added. The ether layer was separated, washed with water, 10% NaHCO₃, and water, dried (MgSO₄), and evaporated. This afforded 1.4 g (38%) of pale yellow oil with ir absorption at 5.78 but not at 5.91 μ . Distillation of the oil gave the colorless liquid diester **3b**, with properties identical with the material prepared by esterification of the diacid **3a** (above).

4-Carbomethoxy-5-hydroxydibenzo[b,g]-6H-oxocin (5). A. Preparation by the Dieckmann Reaction.-A cyclic high-dilution apparatus,²⁶ fitted with a constant-addition dropping funnel and То high-speed stirrer, and flushed with nitrogen, was employed. a refluxing mixture of 300 ml of dry xylene and 2.05 g (0.0183 mol) of potassium t-butoxide, was added 2.86 g (0.0091 mol) of diester 3b in 115 ml of xylene, over 30 hr. After cooling, 5 ml of glacial acetic acid in 5 ml of xylene was added drop by drop, followed by 50 ml of water. The two-phase mixture was filtered, and the organic layer was separated, washed with water, dried $(MgSO_4)$, and evaporated to give 1.64 g of a thick red oil. A portion of this oil (1.53 g) was introduced onto a column, prepared from 39 g of Mallincrodt Silicar, 200-325 mesh, and eluted with benzene-hexane mixtures, gradually increasing the benzene content. With benzene-hexane (90:10) 372 mg (21%) of a white crystalline solid, 5, was eluted. An analytical sample was prepared by several recrystallizations from hexane: mp 94-100°; ir (KBr), 6.06, 6.18, 6.98, 8.20 μ ; nmr (CDCl₃), δ 3.32 (m, 2, CH₂), 3.75 (S, 3, OCH₃), 7.00-7.50 (m, 8, aromatic), 12.88 (s, 1, 1.20) Inspection of molecular models of 5 revealed that the OH). methylene protons were not equivalent; a singlet for them in the nmr was not expected. In subsequent preparations, the product 5 had the following properties: mp 94-99°; ir (KBr), 5.75, 5.82 μ , in addition to the bands listed above; nmr (CDCl₃), δ 3.65 (m, CH₂CO), 4.71 (s, CHCO₂CH₃), in addition to the bands listed above; molecular weight (mass spectrum), 282; the ratio of aromatic to nonaromatic protons in the nmr was 8:6 and the ratio of CHCO₂CH₃ to OH protons was 1:4.

Anal. Calcd for $C_{17}H_{14}O_4$: C, 72.34; H, 4.96. Found: C, 72.56; H, 5.07.

Upon continued elution of the above chromatography column with benzene, 667 mg of starting diester **3b** was recovered.

B. Preparation under Acyloin Conditions.—The apparatus and procedure was the same as in the Dieckmann reaction, using 600 ml of xylene and 7.70 g of a 40% 5- μ dispersion of sodium in toluene and adding 8.35 g (0.0266 mol) of the diester 3b in 150 ml of xylene over 26 hr. The work-up was similar to that used in the Dieckmann reaction. Twenty milliliters of glacial acetic acid in an equal volume of xylene was added, and the final oil (6.37 g) was applied to 470 g of Silicar column. With benzene-hexane (90:10) 200 mg of di-o-tolyl ether was eluted. Elution with benzene-hexane (95:5) yielded a crystalline product 5 (2.42 g, 32%). Its properties agreed with those of the partly ketonic product of the Dieckmann reaction, described above.

5-Oxodibenzo[g,g]-4H,6H-oxocin (6b).—In a flask were combined 160 mg of 5, 6 ml of 95% ethanol, and 6 ml of 3 N hydrochloric acid. The mixture was refluxed overnight and then allowed to cool to room temperature and poured into a beaker containing 7 g of ice. The precipitate that formed (110 mg, 87%) was collected by filtration and purified by recrystallization from hexane to give 6b as white crystals: mp 84.5°; ir (KBr), 5.85 (C=O), 8.18, 13.30 μ ; nmr (CDCl₃), δ 3.76 (s, 4, CH₂), 7.10-7.60 (m, 8, aromatic); molecular weight (mass spectrum), 224.

Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.36; H, 5.37. Found: C, 80.58; H, 5.31.

Upon injection of a solution of 5 into a gas chromatograph (Carbowax or silicone grease column, 190-230°), only one major peak was detected. The compound was collected and its ir and nmr spectra were found to correspond to those of 6b.

Registry No.—1b, 10038-43-2; 1d, 10038-40-1; 3a, 18993-57-2; 3b, 18993-58-3; 5, 19019-48-8; 6b, 18993-59-4.

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Quinoline Synthesis by o-Amino Ketone-Propiolate Addition¹

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The significant synthetic utility of dimethyl acetylenedicarboxylate adducts of amines,^{2,3} anthranilates,⁴ anthranilamides,⁵ o-aminobenzophenones,⁶ and thiosalicyclic acid derivatives⁷ in heterocyclic synthesis has been documented in previous contributions from this laboratory. The lack of reactivity displayed by propiolate and phenylpropiolate esters in addition reactions with these ortho-substituted aromatic amines has also been noted.^{3,6}

In light of published reports on the preparation of

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