ml). Hycanthone was collected as yellow prisms: 2.71 g (71%); mp 95–98° (lit.[3] mp 101–102.5°); uv max (EtOH) 223 mμ (log ε 4.27), 234 (4.35), 257 (4.65), 331 (3.93), 441 (3.91); ir (KBr) 1600 cm^{-1} (C=O); nmr ($CDCl_3$) δ 10.1 (t, 1, NH), 8.40 (m, 1, peri H), 7.30 (m, 4, aromatic H), 6.30 (d, 1, aromatic H), 4.60 (s, 2, CH_2O), 3.76 (s, 1, OH), 2.33–3.50 (m, 8, 4 NCH_2), 1.08 (t, 6, 2 CH_3).

Anal. Calcd for $C_{20}H_{24}N_2O_2S$: C, 67.38; H, 6.78; N, 7.85; S, 8.99. Found: C, 67.20; H, 6.76; N, 7.85; S, 9.05.

Registry No.—**1**, 38605-72-0; **2**, 6469-87-0; **3**, 13420-58-1; **5**, 38615-62-2; **7**, 3105-97-3; **8**, 38615-64-4; **8** 2HCl, 38615-65-5; **9**, 38615-66-6; **9** HCl, 38615-67-7; **10**, 3613-13-6; **11**, 32484-50-7; thiophenol, 108-98-5; 2,6-dichlorobenzonitrile, 1194-65-6; thiosalicylic acid, 147-93-3; *m*-bromochlorobenzene, 106-37-2; *N,N*-diethyl-*N'*-methylethylenediamine, 104-79-0.

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Synthesis of Aminobenzofurans and Aminonaphtho[1,2-*b*]furans

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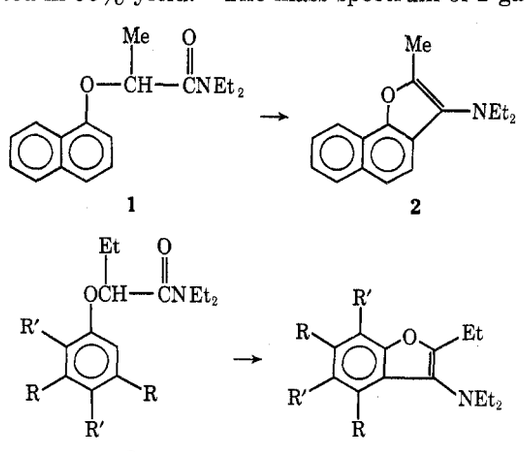
The synthesis of benzofurans and naphthofurans by the ring closure of α-aryloxy carbonyl compounds and their corresponding acetals has been well documented.[1] However, the ring closure of α-aryloxyamides has not been presented. We wish to report a new synthesis of aminonaphtho[1,2-*b*]furan (**2**) and aminobenzofurans (**4**) by a cyclodehydration of aryloxyamides.[2,3] When *N,N*-diethyl-2-(1-naphthyloxy)propionamide (**1**) was treated with phosphorus oxychloride, compound **2** was isolated in 90% yield. The mass spectrum of **2** gave a molecular ion at *m/e* 253 which is equivalent to a loss of water from **1**. The ir spectrum of **2** showed no carbonyl group. The nmr spectrum of **2** showed a sharp singlet at δ 2.50 ppm corresponding to a methyl group, and the aromatic protons were reduced from seven to six protons. From a comparison of the aromatic region of the nmr spectra of **1** (δ 6.72–8.40 ppm) and **2** (δ 7.22–8.35 ppm), it is obvious that the proton at the 2 position was replaced.[4] These spectral data suggest **2** to be 2-methyl-3-(*N,N*-diethylamino)naphtho[1,2-*b*]furan. Similarly, the reaction of aryloxyamides **3** gave benzofurans **4**.



a, R = Cl; R' = H
b, R = H; R' = Cl

The reaction is believed to involve an electrophilic attack by the carbonyl carbon at a position ortho to the ether group. Attempts were made to use phosphorus pentoxide, zinc chloride, and polyphosphoric acid as dehydrating agents, but the yield was poor.

Experimental Section

The nmr spectra were obtained on a Varian HA-60-IL spectrometer in deuteriochloroform solution with tetramethylsilane as an internal reference. The mass spectra were measured on a Varian MAT CH-5 spectrometer. Melting points are uncorrected. Elemental analyses were performed on a Perkin-Elmer 240 Elemental Analyzer.

Preparation of α-Aryloxyamides. General Procedure.—The α-aryloxy acids were prepared from the corresponding phenol or naphthol and the α-halo acid according to the procedure of Koelsch.[5] The α-aryloxy acids were converted to their corresponding acid chlorides by reaction with phosgene at 50° in toluene using 0.1 mol of dimethylformamide per 1 mol of acid. After HCl evolution ceased, excess phosgene was removed by purging with dry nitrogen. The α-aryloxyamides were prepared by addition of the acid chloride solution to a mixture of diethylamine and triethylamine (each in 10% excess) in toluene at 10–15°. After complete acid chloride addition, the solution was stirred at 45° for 1 hr. Upon cooling, the reaction mixture was washed successively with 2% HCl solution and water. The organic phase was dried over anhydrous magnesium sulfate and then evaporated to obtain α-aryloxyamides. Compounds **1**, **3a**, and **3b** prepared in this method are listed in Table I.

TABLE I
PREPARATION OF α-ARYLOXYAMIDES[a]

Compd	Yield, %	Mp or bp, °C (mm)
1	98	78–79
3a	82	63.5–64.5
3b	84	133–135 (0.06)

[a] Satisfactory analytical values (±0.35% for C, H) were reported for **1**, **3a**, and **3b**.

Preparation of Aminobenzofurans and Aminonaphtho[1,2-*b*]furans. General Procedure.—The aryloxyamide (0.05 mol) and phosphorus oxychloride (0.15 mol) in 50 ml of toluene were refluxed for 5 hr. The resulting reaction mixture was quenched in cold water (15–20°) and then treated with 100 ml of 5% sodium carbonate solution. The toluene layer was separated, dried over anhydrous magnesium sulfate, and then evaporated to obtain an oil which was either distilled under reduced pressure or purified by tlc.

2-Methyl-3-(*N,N*-diethylamino)naphtho[1,2-*b*]furan (**2**) had nmr spectrum ($CDCl_3$) δ 1.00 (t, 6 H, methyl), 2.50 (s, 3 H, methyl), 3.15 (q, 4 H, methylene), and 7.22–8.35 (m, 6 H, aromatic); mass spectrum *m/e* 253 (parent ion); picrate (ethanol) mp 154–155°.

Anal. Calcd for $C_{23}H_{22}N_4O_8$: C, 57.26; H, 4.56; N, 11.62. Found: C, 57.34; H, 4.52; N, 11.60.

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2-Ethyl-3-(*N*,*N*-diethylamino)-4,6-dichlorobenzofuran (4a) had nmr spectrum ($CDCl_3$) δ 0.95 (t, 6 H, methyl), 1.25 (t, 3 H, methyl), 2.79 (q, 2 H, methylene), 3.08 (q, 4 H, methylene), 7.18 (d, 1 H, aromatic), and 7.28 (d, 1 H, aromatic); picrate (ethanol) mp 148.5–149.5°.

Anal. Calcd for $C_{20}H_{20}N_4O_8Cl_2$: C, 46.60; H, 3.88; N, 10.87. Found: C, 46.30; H, 3.81; N, 10.72.

2-Ethyl-3-(*N*,*N*-diethylamino)-5,7-dichlorobenzofuran (4b) had nmr spectrum ($CDCl_3$) δ 0.91 (t, 6 H, methyl), 1.24 (t, 3 H, methyl), 2.77 (q, 2 H, methylene), 3.03 (q, 4 H, methylene), 7.17 (d, 1 H, aromatic), and 7.40 (d, 1 H, aromatic); picrate (ethanol) mp 172–173°.

Anal. Calcd for $C_{20}H_{20}N_4O_8Cl_2$: C, 46.60; H, 3.88; N, 10.87. Found: C, 46.15; H, 3.87; N, 10.68.

Registry No.—**1**, 15299-99-7; **2**, 38740-02-2; **2** picrate, 38740-03-3; **3a**, 38740-04-4; **3b**, 38740-05-5; **4a**, 38740-06-6; **4a** picrate, 38740-07-7; **4b**, 38740-08-8; **4b** picrate, 38740-09-9.

Reexamination of the Claisen–Schmidt Condensation of Phenylacetone with Aromatic Aldehydes[1]

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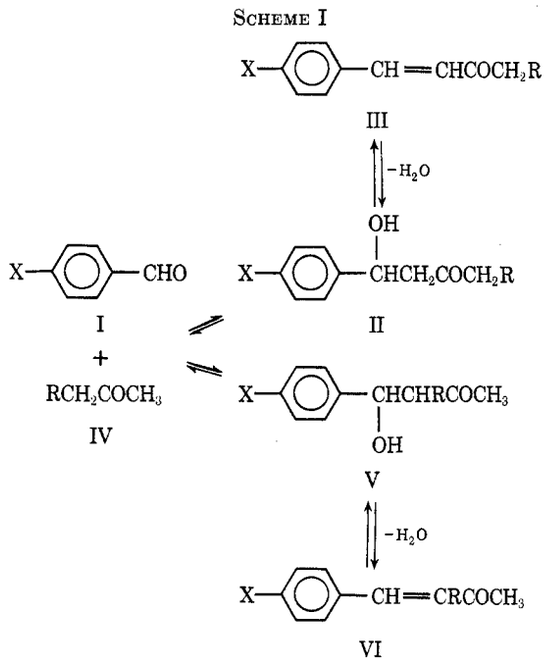
Although the base-catalyzed reaction of aldehydes with ketones of the type RCH_2COCH_3 can, in principle, occur with two possible orientations (Scheme I) the

SCHEME I



a, X = H; R = H
b, X = H; R = CH_3
c, X = OCH_3; R = H
d, X = H; R = C_6H_5
e, X = CH_3; R = C_6H_5
f, X = OCH_3; R = C_6H_5
g, X = Cl; R = C_6H_5
h, X = NO_2; R = C_6H_5

condensation of aromatic aldehydes with such ketones usually occurs at the methyl group.[2] It has been shown[3-6] that the rate-determining step in reactions of this type involves the condensation process, namely, attack by an enolate ion of IV at the carbonyl group of I. In basic solution methyl-*n*-alkyl ketones form approximately equal amounts of the two isomeric enolates while branched alkyl groups favor the less highly substituted enolate;[7] hence a mixture of both unsaturated ketones, III and VI, would be expected from the base-catalyzed condensations of the ketones IV with aldehydes. Because this is not the case, the *product*-determining step is believed to involve large rate differences in the competing dehydrations of the intermediate ketols, II and V. For example, the reaction of 2-butanone (IVb) with benzaldehyde affords the unsaturated ketone IIIb exclusively.[4,5] Independent synthesis of ketols IIb and Vb followed by treatment with base revealed that Vb retrogressed to reactants[5] while both dehydration and retrogression occurred with IIb.[4,5] The exclusive formation of methyl condensation products is usually observed only when reaction conditions are vigorous enough to cause dehydration of the intermediate ketols. Under milder conditions ketols II and V can both be isolated in reactions of aromatic aldehydes with 2-butanone.[5,8,9] The preferential cleavage of type V ketols to reactants has been attributed to steric hindrance to dehydration imposed by bulky R groups.[4,5,10,11]

A reaction frequently cited[12,13] as involving exclusive methyl condensation is the hydroxide-catalyzed condensation of phenylacetone (IIId) with benzaldehyde;[14,15] substituted benzaldehydes have also been reported to afford unsaturated ketones corresponding to methyl condensation only.[16] Since the more highly substituted enolate of phenylacetone is strongly favored in basic solution[7] these results have prompted the belief[12,13] that ketol Vd must undergo retrogression in preference to dehydration.

We have examined the base-catalyzed reaction of phenylacetone with several aromatic aldehydes under similar conditions to those reported previously and have quantitatively determined the components of the crude products using glc and nmr analysis. In every reaction but one, unsaturated ketones corresponding to both possible modes of condensation were produced. The results are shown in Table I.[17] The relative mole ratios of III:VI were determined by glc analysis, using pure samples of the unsaturated ketones as standards. Samples of VI were prepared independently by the piperidine-catalyzed condensa-

(1) The receipt of a Lafayette College Research Fund grant in support of this research is gratefully acknowledged.

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(17) See Experimental Section.