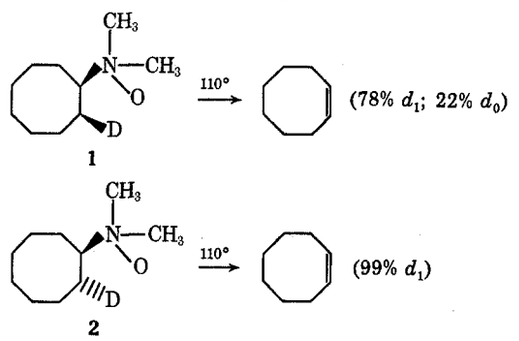
beyond doubt.[2] Although there is good evidence[1,3] that the pyrolysis of an amine oxide involves syn-elimination, this mechanism has never been rigorously tested by deuterium-labeling experiments. Since considerable emphasis has been placed on this reaction we now report unequivocal deuterium-labeling evidence that establishes the mechanism of the Cope elimination as a 100% syn elimination.

The specifically labeled *N,N*-dimethylcyclooctylamines were prepared according to the method of Coke.[4] The amine oxides were prepared by oxidation of the labeled tertiary amines with 36% hydrogen peroxide affording *cis*- and *trans*-*N,N*-dimethylcyclooctyl oxide-2-d_1. Pyrolysis of the cis-2-d_1 oxide **1** at 110° (11 mm) afforded *cis*-cyclooctene that had retained 78% of its initial deuterium content (Scheme I).

SCHEME I



From these data a syn k_H/k_D of 3.5 may be calculated. The deuterium content was analyzed by mass spectrometry on a sample purified by gas chromatography. Pyrolysis of the trans-2-d_1 oxide **2** afforded *cis*-cyclooctene that had retained 100% (within experimental error) of the deuterium initially present in the amine oxide, providing unequivical evidence for an exclusive syn elimination.

The complete absence of *trans*-cyclooctene (gc analysis) in the pyrolyses of **1** and **2** is worthy of comment. The stereoselective formation of cis olefin has been taken[3a,5] as evidence for the intramolecular cyclic mechanism, because the atoms eliminated would be in a preferred planar transition state. This reaction may be considered an analog of the ylide mechanism in which an α' oxy anion rather than the carbanion basic center is involved. We recently reported[6] that *trans*-cyclooctene can be readily formed by an α',β elimination in liquid ammonia using KNH_2 as the base (syn k_H/k_D = 5.89). Thus, a cyclic intramolecular transition state to form the more strained (~9 kcal/mol relative to the cis isomer) trans olefin is not precluded in the cyclooctyl system. Therefore the cis/trans ratio observed in these reactions should not be used as an indication of the mechanism involved.[7] As an alternate explanation we suggest that the exclusive formation of *cis*-cyclooctene is a manifestation of the weakly basic oxy anion. In the Cope elimination both C–H and C–N bond cleavage may be well advanced at the transition state with considerable development of double-bond character. However, with the strongly basic nitrogen ylide[6] there might be more C–H cleavage than C–N cleavage in the transition state. In support of this suggestion, stabilized benzyl ylides[7] and sulfonium ylides[8] also afford the thermodynamically favored cis olefin. Thus, in the present case product development control results in exclusive formation of the cis stereoisomer.

(2) J. Zavada, J. Krupicka, and J. Sicher, *Collect. Czech. Chem. Commun.*, **31**, 4273 (1966); J. Sicher, *Angew. Chem., Int. Ed. Engl.*, **11**, 200 (1972).

(3) (a) C. H. DePuy and R. W. King, *Chem. Rev.*, **60**, 431 (1960); (b) M. R. V. Sahyun and D. J. Cram, *J. Amer. Chem. Soc.*, **85**, 1263 (1963).

(4) J. L. Coke and M. C. Mourning, *J. Amer. Chem. Soc.*, **90**, 5561 (1968).

(5) A. C. Cope, R. A. Pike, and C. F. Spencer, *J. Amer. Chem. Soc.*, **75**, 3213 (1953).

(6) (a) R. D. Bach and D. Andrzejewski, *J. Amer. Chem. Soc.*, **93**, 7118 (1971); (b) R. D. Bach, K. W. Bair, and D. Andrzejewski, *ibid.*, **94**, 8608 (1972).

(7) G. Wittig and R. Polster, *Justus Liebigs Ann. Chem.*, **612**, 102 (1958); C. L. Bumgardner, *J. Org. Chem.*, **27**, 1035 (1962).

Experimental Section

Mass spectral analyses were performed on an MS-902 mass spectrometer. *cis*-Cyclooctene and *N,N*-dimethylcyclooctylamine were purified by preparative gas chromatography and analyzed at 11 eV. The deuterium analyses were corrected for 83.3% and the 86.7% isotopic purity of the starting compounds, *N,N*-dimethyl-*cis*- and *N,N*-dimethyl-*trans*-cyclooctylamine-2-d_1. The *cis*-cyclooctene and the labeled amines were collected on a 6-ft 10% SE-30 column at 150° prior to mass spectral analysis. Gas chromatographic analyses of the reaction mixtures were carried out with a 6-ft 10% NMPN column at 80°.

The *cis*-cyclooctene was obtained as a gift from Columbian Carbon Co. *trans*-Cyclooctene was prepared as reported previously.[9] *cis*- and *trans*-cyclooctene were converted to *cis*- and *trans*-cyclooctylamine-2-d_1, bp 80–81° (20 mm), according to the procedure of Coke and Mourning.[4] The Clark–Eschweiler procedure described by Icke[4,10] was used to prepare the specifically labeled *N,N*-dimethylcyclooctylamines.

***N,N*-Dimethyl-*cis*-cyclooctylamine-2-d_1 Oxide.**—To a stirring solution of 1 ml of reagent methanol was added 0.028 g (0.180 mmol) of *N,N*-dimethyl-*cis*-cyclooctylamine-2-d_1[4] and 30 μl (1.3 mmol) of 36% hydrogen peroxide. After 3 days at room temperature the solvent was removed by rotary evaporation, affording the crude amine oxide as a viscous oil.

***N,N*-Dimethyl-*trans*-cyclooctylamine-2-d_1 Oxide.**—The above procedure was repeated on 0.028 g of *N,N*-dimethyl-*trans*-cyclooctylamine-2-d_1 affording the trans labeled amine oxide as a viscous oil.

Cope Elimination.—The crude amine oxides were heated at 110° (11 mm) and the temperature was slowly raised to 120° over a 30-min period. The pyrolysis products were collected in a cold trap in a pentane solution and washed with 10% HCl. The *cis*-cyclooctene was isolated by preparative gas chromatography. The product composition was at least 99.9% *cis*-cyclooctene with none of the trans isomer being observed by gc analysis.

Registry No.—**1**, 38645-04-4; **2**, 38645-05-5.

Acknowledgment.—We wish to express our appreciation to donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

(8) V. Franzen and H. J. Schmidt, *Chem. Ber.*, **94**, 2937 (1961).

(9) A. C. Cope and R. D. Bach, *Org. Syn.*, **49**, 39 (1969).

(10) R. N. Icke, B. B. Wisegarver, and G. A. Alles, "Organic Syntheses," Collect. Vol. III, E. C. Hornung, Ed., Wiley, New York, N. Y., 1955, p 723.

The Synthesis of Hycanthone

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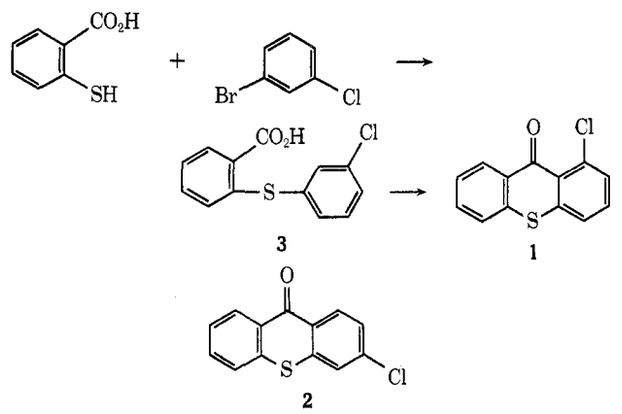
Hycanthone (**7**), a schistosomicidal agent, was first prepared by Rosi, *et al.*, by microbiological oxidation of the corresponding 4-methylthioxanthenone,

lucanthone.[1-3] We now wish to report a chemical synthesis of hycanthone from 1-chlorothioxanthen-9-one (1). Although Mahishi, *et al.*,[4] claim to have prepared pure 1 by cyclization of *o*-[(*m*-chlorophenyl)-thio]benzoic acid (3) (Scheme I), we found that the

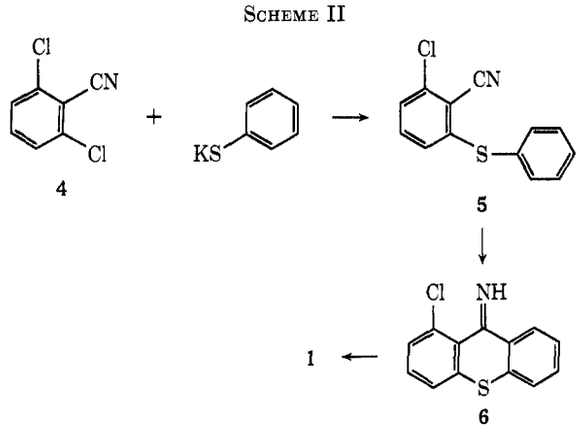
SCHEME I



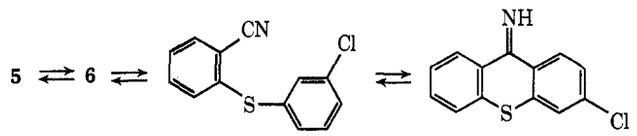
product was an approximately 50:50 mixture of 1 and 3-chlorothioxanthen-9-one (2).[5,5a]

We, therefore, prepared 1 by an alternate route (Scheme II) which was designed to afford pure 1.

SCHEME II



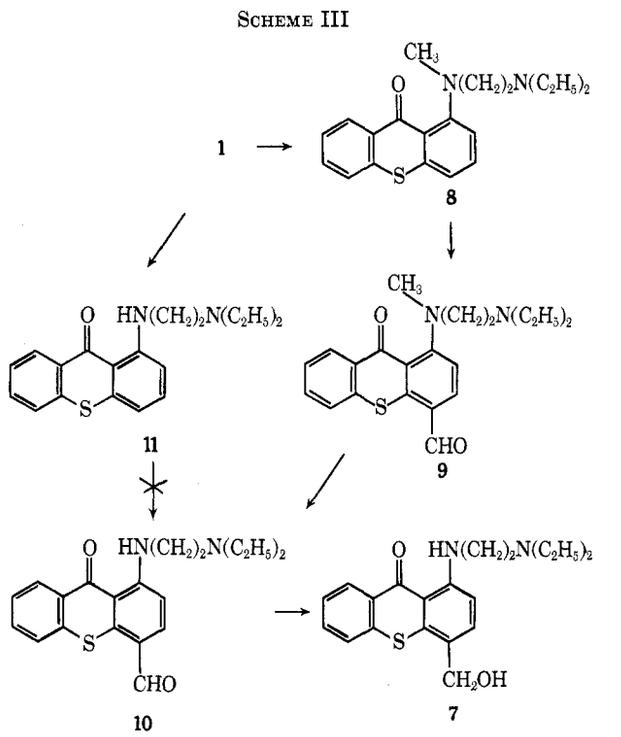
2-Chloro-6-(phenylthio)benzonitrile (5) was easily prepared from 2,6-dichlorobenzonitrile (4) and potassium thiophenolate in DMSO. A similar preparation of 5 has been reported utilizing 2-chloro-6-nitrobenzonitrile in place of 4.[6] The nitrile 5 was cyclized in polyphosphoric acid and the imine intermediate 6 was hydrolyzed in water to give a 66% yield of the desired chloro compound 1. Optimum yields of 1 were obtained when the PPA cyclization was carried out at 150–170°. As the cyclization temperature was raised above this range, increasing amounts of the 3-chloro isomer 2 formed and at 260° 2 was the sole product produced. The formation of 2 is presumably a result of the following temperature-dependent reactions.



An attempt was made to prepare 2-chloro-6-(phenylthio)benzoic acid from 2,6-dichlorobenzoic acid and thiophenol. Unreacted acid was recovered when the reaction was run in refluxing DMF. When this same reaction was run with a copper catalyst present (Ullmann conditions), no acidic procduts were obtained and gas chromatography revealed the presence of *m*-dichlorobenzene, indicating that decarboxylation had occurred. In an attempt to block this decarboxylation the reaction was run with methyl 2,6-dichlorobenzoate in place of the corresponding acid. Although none of the desired sulfide formed, gas chromatography indicated the presence of thioanisole. The ester apparently behaved as an alkylating agent to form thioanisole and 2,6-dichlorobenzoic acid.[7]

The synthesis of hycanthone (7) from 1 is shown in Scheme III.

SCHEME III



Compound 8 was prepared by treating 1 with *N*,*N*-diethyl-*N'*-methylethylenediamine in refluxing pyridine. This same reaction can be run on the mixture of 1- and 3-chlorothioxanthen-9-ones, obtained from cyclization of 3, since the 3 isomer 2 is unreactive in refluxing pyridine. The chlorine atom of 2 can, however, be displaced in refluxing DMF. Reaction of 8 with phosphorus oxychloride in DMF (Vilsmeier conditions)

(1) D. Rosi, G. Peruzzotti, E. W. Dennis, D. A. Berberian, H. Freele, and S. Archer, *Nature (London)*, **208**, 1005 (1965).

(2) H. Mauss, *Ber.*, **81**, 19 (1948).

(3) D. Rosi, G. Peruzzotti, E. W. Dennis, D. A. Berberian, H. Freele, B. F. Tullar, and S. Archer, *J. Med. Chem.*, **10**, 867 (1967).

(4) N. B. Mahishi, P. B. Sattur, and K. S. Nargund, *J. Karnatak Univ.*, **2** (1), 50 (1957); *Chem. Abstr.*, **53**, 14101 (1959).

(5) A recent patent reports the preparation of the isomeric 3-chlorothioxanthen-9-one by essentially the same procedure employed by Mahishi, *et al.*: British Patent 1,000,509 (1965); *Chem. Abstr.*, **58**, 12518*f* (1963).

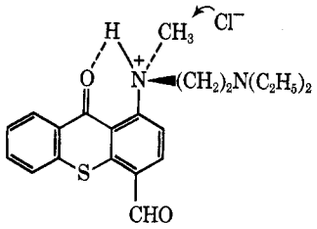
(5a) NOTE ADDED IN PROOF.—A recent paper reports essentially the same mixture of 1 and 2 obtained by us by cyclization of 3 in strong acid. These authors also describe an unambiguous synthesis of 1 starting with 6-chloroanthranilic acid: I. Okabayashi, *et al.*, *Yakugaka Zasshi*, **92**, 1386 (1972).

(6) British Patent 951,651 (1964); *Chem. Abstr.*, **61**, P5575*b* (1964).

(7) A similar hydrolysis was reported recently: P. A. Bartlett and W. S. Johnson, *Tetrahedron Lett.*, 4459 (1970).

afforded the aldehyde **9** with no evidence of formylation in the 2 position of the thioxanthene ring. A similar Vilsmeier reaction on **11** did not yield the desired aldehyde **10**. The *N*-methyl group of **8** functions, therefore, as a protecting group allowing formylation in the 4 position. The methyl group of **9** was then removed with pyridine hydrochloride to yield compound **10**, which has been reported previously as a by-product in the microbiological oxidation of lucanthone.[3] Sodium borohydride reduction of **10** afforded hycanthone[8] in 15% overall yield from pure **1**.

The demethylation of **9** presumably proceeds in the following manner.



The peri oxygen atom may stabilize this intermediate through hydrogen bonding. Attack of the chloride ion on the methyl group then yields **10**. There was no evidence of N-dealkylation of the other, more hindered, alkyl group.

Experimental Section

All melting points are corrected. Thin layer chromatograms were developed on precoated silica gel F-254 Merck plates. Gas chromatograms were recorded on a Hewlett-Packard Model 5750 gas chromatograph. The ir spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer and the nmr spectra were determined on a Varian Model A-60 or a Varian HA-100 spectrometer.

Elemental analyses were performed by Istranal Laboratories, Rensselaer, N. Y., or Galbraith Laboratories, Inc., Knoxville, Tenn.

2-Chloro-6-(phenylthio)benzonitrile (5).—Thiophenol (13 ml, 0.15 mol) in DMSO (50 ml) was dripped into a cooled suspension of potassium *tert*-butoxide (13.0 g, 0.15 mol) in DMSO (300 ml). 2,6-Dichlorobenzonitrile (19.0 g, 0.11 mol) in DMSO (300 ml) was added dropwise to this mixture with stirring over a 30-min period. The reaction mixture was heated on a steam bath for 2.5 hr and then poured into cold H_2O (1 l.) and allowed to stand while the oily product solidified. Recrystallization from ethanol (125 ml) yielded white prisms, 19.5 g (72%), mp 67–72° (lit.[6] mp 66–67°).

1-Chlorothioxanthen-9-one (1).—Compound **5** (25 g, 0.10 mol) was suspended in PPA (2.5 l.) and heated with vigorous stirring for 6 hr at 150–170°. The reaction mixture was allowed to cool to 90° and poured into an ice–water (12 l.) mixture with stirring. The aqueous mixture was warmed on a steam bath for several hours and cooled (ice bath), and **1** was collected by filtration (sintered glass). Recrystallization from isopropyl alcohol (125 ml) afforded **1** as pale yellow needles: 14.0 g (56%); mp 112.5–114.0° (lit.[4] mp 146°]; uv max (EtOH) 221 mμ (log ε 4.19), 258 (4.62), 293 (3.70), 303 (3.72), 380 (3.75); ir (KBr) 1638 cm^{-1} (C=O); nmr ($CDCl_3$) δ 8.40 (m, 1, peri H), 7.15–7.55 (m, 6, aromatic H).

Anal. Calcd for $C_{13}H_7ClOS$: C, 63.28; H, 2.85; Cl, 14.37; S, 12.99. Found: C, 63.28; H, 2.98; Cl, 14.39; S, 13.11.

***o*-[(*m*-Chlorophenyl)thio]benzoic Acid (3).**—Thiosalicylic acid (30 g, 0.19 mol), copper bronze (1.86 g), KI (1.75 g, 0.010 mol), and K_2CO_3 (40.5 g, 0.29 ml) were combined in DMF (450 ml). The mixture was warmed to 100° and *m*-bromochlorobenzene (40.8 g, 0.21 mol) in DMF (25 ml) was added. The reaction mixture was refluxed for 18 hr and then poured into an ice–water (1.0 l.) mixture. The aqueous mixture was charcoaled, filtered, and made acidic (3 *N* HCl). **3** was collected and recrystallized from glacial acetic acid (300 ml), 30.4 g (61%), mp 186–194° (lit.[4] mp 192–194°).

1 and 3-Chlorothioxanthen-9-one (2).—Compound **3** (16.3 g, 0.061 mol) was suspended in concentrated H_2SO_4 (50 ml) and stirred at ambient temperatures for 2 hr. The reaction mixture was poured into an ice–water mixture (300 ml) and the crude products were collected by filtration, 15.2 g (100%), mp 150–165°. Vpc analysis of this mixture showed it to be a 52:48 mixture of **1** and **2**.[9] Pure **2** was also prepared by an unambiguous synthesis.[4] A portion of the above mixture was recrystallized several times from isopropyl alcohol to yield **2**, mp 171–173° (lit.[4] mp 176°).

1-{[2-(Diethylamino)ethyl]methylamino}thioxanthen-9-one (8).—Compound **1** (5.0 g, 0.020 mol), *N*,*N*-diethyl-*N'*-methylethylenediamine (3.26 g, 0.025 mol), and pyridine (15 ml) were refluxed for 36 hr. The solvents were removed under reduced pressure and the residue was dissolved in 10% aqueous acetic acid (40.0 ml), charcoaled, filtered, and extracted with methylene dichloride (40.0 ml). The aqueous layer was made basic with 35% aqueous NaOH solution (15.0 ml) and extracted with methylene dichloride (300 ml). The organic layer was dried, filtered, and concentrated to an oil, 3.41 g (50%). This oil was converted to its dihydrochloride and recrystallized from acetonitrile: 1.10 g; mp 160.5–161.0°; uv max (EtOH) 262 mμ (log ε 4.54), 315 (3.61), 322 sh (3.60), 375 (3.42), 428 (3.56); ir ($CHCl_3$) 1605 cm^{-1} (C=O); nmr (D_2O) δ 7.65–9.00 [m, 7, aromatic H), 5.13 (s, 2, exchanged H's), 4.58 (m, 2, NCH_2), 3.87 (s, 3, NCH_3), 3.33–4.08 (m, 6, 3 NCH_2), 1.70 (t, 6, 2 NCH_3).

Anal. Calcd for $C_{20}H_{26}Cl_2N_2OS$: C, 58.10; H, 6.33; N, 6.77; S, 7.75. Found: C, 57.65; H, 6.37; N, 7.04; S, 7.63.

Compound **8** could also be prepared from a mixture of **1** and **2** using the procedure described above, partitioning the unreacted **2** and **8** between an organic layer (chloroform) and aqueous acetic acid. This also provides a useful synthesis for pure 3-chlorothioxanthen-9-one (**2**).

1-{[2-(Diethylamino)ethyl]amino}thioxanthen-9-one (11).—Compound **11** was prepared from a mixture of **1** and **2** using the general procedure outlined in the synthesis of **8**. Thus a mixture (26 g, 0.10 mol) of **1** and **2** yielded 15 g (88.5% from **1**) of **11** as yellow plates when recrystallized from ethanol, mp 83–85°, ir (KBr) 1605 cm^{-1} (C=O).

Anal. Calcd for $C_{19}H_{22}N_2OS$: C, 69.89; H, 6.79; N, 8.58. Found: C, 69.83; H, 6.84; N, 8.28.

1-{[2-(Diethylamino)ethyl]methylamino}-9-oxothioxanthene-4-carboxaldehyde (9).—Compound **8** (10 g, 0.029 mol) was dissolved in DMF (70 ml), and phosphorus oxychloride (5.5 ml, 0.06 mol) was slowly added as the temperature rose to 55°. The reaction mixture was heated on a steam bath for 1 hr, cooled, and poured into ice water (200 ml). The mixture was made basic with 35% aqueous sodium hydroxide (30 ml) and extracted with chloroform (300 ml) to yield **9** isolated as its hydrochloride: 7.4 g (63%); mp 202–204°; uv max (EtOH) 256 mμ (log ε 4.39), 272 sh (4.21), 301 (4.15), 333 (4.20), 415 (3.83); ir (KBr) 1655 cm^{-1} (HC=O), 1605 (C=O); nmr (D_2O) δ 9.30 (s, 1, CHO), 6.65–8.35 (m, 6, aromatic H), 5.18 (s, 1, exchanged H), 3.33–4.83 (m, 8, 4 NCH_2), 2.95 (s, 3, NCH_3), 1.71 (t, 6, 2 CH_3).

Anal. Calcd for $C_{21}H_{25}ClN_2O_2S$: C, 62.28; H, 6.22; N, 6.91. Found: C, 62.25; H, 6.22; N, 7.00.

1-{[2-(Diethylamino)ethyl]amino}-9-oxothioxanthene-4-carboxyaldehyde (10).—Compound **9** (5.4 g, 0.013 mol), as its hydrochloride, was heated in pyridine hydrochloride (25 g, 0.216 mol) at 140° for 1 hr and then treated with H_2O and made basic with 35% aqueous sodium hydroxide. Extraction with ether yielded **10**, which was recrystallized from isopropyl acetate (50 ml), 3.85 g (91%), mp 118–120° (lit.[3] mp 119.4–120.6°).

1-{[2-(Diethylamino)ethyl]amino}-4-(hydroxymethyl)thioxanthen-9-one, Hycanthone (7).—The aldehyde **10** (3.80 g, 12 mmol) was dissolved in methanol (50 ml) and treated with sufficient sodium borohydride at room temperature to reduce **10** to **7** as evidenced by tlc examination. (Plates were sprayed with a solution of 2,4-dinitrophenylhydrazine and the addition of sodium borohydride was terminated when no aldehyde was evident.) Methanol was removed and the residue was taken up in benzene and washed with water until the pH was 8.0. The benzene solution was dried ($MgSO_4$), filtered, and concentrated to a yellow solid which was recrystallized from isopropyl acetate (45

(8) The conversion of **10** to hycanthone has been previously described; see ref 3.

(9) All vpc analyses were run utilizing a glass column, 0.25 in. × 4 ft, and packed with 3% OV-1 as the stationary phase.

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.

Acknowledgments.—The authors wish to express appreciation to our associates, Drs. R. Kullnig and S. Clemans and their coworkers, for the spectroscopic data reported in this paper.

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

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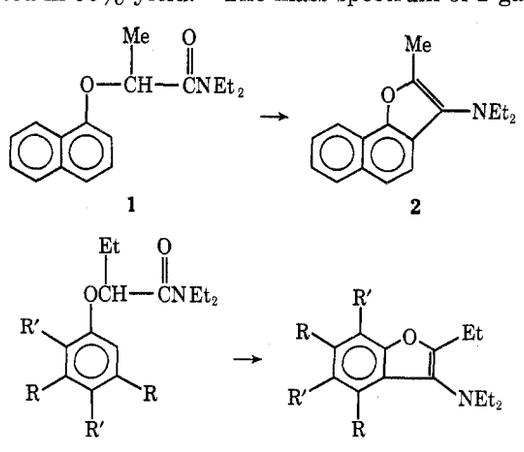
Received November 17, 1972

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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