recovered in almost quantitative yield: bp 89–90 °C (0.5 mm), mp 40–43 °C [lit.[7] bp 95–101 °C (2.5–3.5 mm)]; NMR δ 2.33 (s, 3 H, Me), 2.65 (s, 6 H, Me), 7.03 (s, 2 H, aromatic H). Anal. Calcd for $C_9H_{11}ClS$: C, 57.89; H, 5.94; Cl, 18.99; S, 17.17. Found: C, 57.80; H, 5.91; Cl, 19.08; S, 17.12.

General Methods for Preparing Unsymmetrical Aryl Sulfides. The following procedures are typical of the methods used to prepared unsymmetrical aryl sulfides.

Method A. To a solution of the appropriate aromatic substrate (0.01 mol) in $EtNO_2$ (10 mL) was added an equimolar amount of arenesulfenyl chloride in $EtNO_2$ (10 mL) dropwise under N_2, with stirring. Stirring was continued until the evolution of HCl was complete (0.5–1 h). Removal of solvent under reduced pressure left crude crystals of the corresponding sulfide, which was recrystallized from ethanol to constant melting point (Table I).

Method B. A solution of arenesulfenyl chloride (0.01 mol) in $EtNO_2$ (10 mL) was added dropwise to a mixture of mesitylene (0.01 mol) and $SnCl_4$ (2 drops) in $EtNO_2$ (10 mL) under conditions identical to those described for method A. Workup consisted of removing the solvent in vacuo, washing the residue with a 1:1 ethanol–hydrochloric acid mixture (5 mL) and water, drying, and recrystallizing from ethanol. Only sulfide **8** was a liquid, which was purified by high-vacuum distillation (Table I).

Remarkably, in the attempt to prepare sulfide **6** by this procedure, **1,3-bis(mesitylthio)-2,4,6-trimethoxybenzene** [mp 174–175 °C (from ethanol)] was isolated as the major product: NMR δ 2.27 (s, 6 H, Me), 2.37 (s, 12 H, Me), 3.63 (s, 6 H, OMe), 3.74 (s, 3 H, OMe), 6.20 (s, 1 H, aromatic H), 6.90 (s, 4 H, aromatic H). Anal. Calcd for $C_{27}H_{32}O_3S_2$: C, 69.19; H, 6.88; S, 13.68. Found: C, 69.05; H, 6.85; S, 13.59.

Reaction of 3c with S_2Cl_2 To Produce Trisulfide 24. In a red glass flask, equipped with a magnetic stirring bar, a reflux condenser, an N_2 inlet, and a dropping funnel were placed a solution of **3c** (16.8 g, 0.1 mol) in CS_2 (40 mL) and iron powder (ca. 5 mg). The mixture was cooled at 0 °C, and under N_2 a solution of S_2Cl_2 (1.35 g, 0.01 mol) in CS_2 (10 mL) was added dropwise with stirring. Stirring was continued until the evolution of HCl was judged complete. After removal of solvent and subsequent steam distillation of the reaction mixture to remove the excess **3c**, a residue was left. It was extracted with $CHCl_3$, dried (Na_2SO_4), and concentrated under reduced pressure to give the trisulfide **24** (2.8 g, 65% yield) as a yellow crystalline powder, mp 176–177 °C (from AcOH). The analytical and spectral data of this product were identical with those of an authentic sample (see below).

2,4,6-Trimethoxythiophenol (26). To a stirred mixture of **24** (2.15 g, 5 mmol) and Zn powder (5 g) suspended in benzene (40 mL) and cooled in an ice-bath was added 37% HCl (50 mL) dropwise under stirring. When the addition of the acid was complete, the reaction mixture was stirred until the Zn had dissolved. The benzene layer was separated, washed with water, dried (Na_2SO_4), and concentrated under reduced pressure to give the desired thiol (1.6 g, 80% yield) as pale yellow prisms: mp 58–59 °C; NMR δ 3.75 (s, 1 H, SH), 3.79 (s, 3 H, OMe), 3.87 (s, 6 H, OMe), 6.15 (s, 1 H, aromatic H). Anal. Calcd for $C_9H_{12}O_3S$: C, 53.98; H, 6.04; S, 16.01. Found: C, 53.81; H, 6.02; S, 15.87.

Bis(2,4,6-trimethoxyphenyl) Trisulfide (24). A solution of SCl_2 (0.26 g, 2.5 mmol) in anhydrous Et_2O (20 mL) was added dropwise with stirring at 0 °C to a solution of thiol **26** (1 g, 5 mmol) in Et_2O (50 mL). The mixture was flushed with N_2 and stirred until the evolution of HCl subsided. The crude trisulfide **24** (1 g, 70% yield) was collected by filtration and recrystallized from AcOH to afford a yellow powder: mp 176–177 °C; NMR 3.87 (s, 6 H, OMe), 3.91 (s, 12 H, OMe), 6.17 (s, 4 H, aromatic H). Anal. Calcd for $C_{18}H_{22}O_6S_3$: C, 50.21; H, 5.15; S, 22.34. Found: C, 50.07; H, 5.09; S, 22.27.

Reaction of 3d with S_2Cl_2 To Produce Disulfide 25. Compound **3d** (16.16 g, 0.08 mol) and S_2Cl_2 (1.35 g, 0.01 mol) in CS_2 (100 mL) were reacted in the presence of catalytic amounts of iron powder under conditions identical with those described for the sulfuration of **3c**. On removal of the solvent, the residue was thoroughly washed with Et_2O to leave crude crystals of disulfide **25** (3.2 g, 68% yield) as yellow prisms, mp 196–198 °C (from AcOH). The analytical and spectral data of this product were identical with those of an authentic sample (see below).

3-Chloro-2,4,6-trimethoxythiophenol 27. This compound (mp 80–82 °C) was obtained in 87% yield by reduction of **25** with Zn and 37% HCl using a procedure identical with that followed for the preparation of thiol **26**: NMR δ 3.87 (s, 1 H, SH), 3.90 (s, 9 H, OMe), 6.35 (s, 1 H, aromatic H). Anal. Calcd for $C_9H_{11}ClO_3S$: C, 46.05; H, 4.72; Cl, 15.11; S, 13.66. Found: C, 45.84; H, 4.68; Cl, 15.24; S, 13.57.

Bis(3-chloro-2,4,6-trimethoxyphenyl) Disulfide (25). The thiol **27** (0.58 g, 2.5 mmol), dissolved in Me_2SO[8] (5 mL), was stirred for 24 h at room temperature. When the mixture was poured into brine, the disulfide precipitated in almost quantitative yield. It was collected by filtration, washed with water, and recrystallized from AcOH: mp 196–198 °C; NMR δ 3.77 (s, 12 H, OMe), 3.97 (s, 6 H, OMe), 6.35 (s, 2 H, aromatic H). Anal. Calcd for $C_{18}H_{20}Cl_2O_6S_2$: C, 46.25; H, 4.31; Cl, 15.17; S, 13.72. Found: C, 46.11; H, 4.30; Cl, 15.03; S, 13.64.

Method C. To a solution of *p*-nitrochlorobenzene (1.57 g) in EtOH (10 mL) was added an equimolar amount of the appropriate potassium thiolate dissolved in water (minimum amount) in one portion. The mixture was refluxed for 0.5 h and cooled. The precipitate obtained was collected by filtration, washed with water, dried, and recrystallized from EtOH to a constant melting point.

Registry No. 2a, 14575-12-3; **2b**, 931-59-9; **2c**, 933-00-6; **2d**, 933-01-7; **3a**, 108-67-8; **3b**, 7051-13-0; **3c**, 621-23-8; **3d**, 67827-56-9; **4**, 5324-71-0; **5**, 77189-83-4; **6**, 77189-84-5; **7**, 77189-85-6; **8**, 33667-80-0; **9**, 75787-00-7; **10**, 41280-62-0; **11**, 77189-86-7; **12**, 34678-74-5; **13**, 77189-87-8; **14**, 77189-88-9; **15**, 77189-89-0; **16**, 77189-90-3; **17**, 77189-91-4; **18**, 77189-92-5; **19**, 77189-93-6; **20**, 77189-94-7; **21**, 77210-79-8; **22**, 77189-95-8; **23**, 77189-96-9; **24**, 77189-97-0; **25**, 77189-98-1; **26**, 77189-99-2; **27**, 77190-00-2; 1,3-bis(mesitylthio)-2,4,6-trimethoxybenzene, 77190-01-3; *p*-nitrochlorobenzene, 100-00-5; potassium 2,4,6-trimethylthiophenol, 77190-02-4; potassium 3-chloro-4,6-dimethoxythiophenol, 77190-03-5; potassium 2,4,6-trimethoxythiophenol, 77190-04-6; potassium 3-chloro-2,4,6-trimethoxythiophenol, 77190-05-7; thiomesitol, 1541-10-2.

Supplementary Material Available: NMR spectral assignments for compounds **4-23** (1 page). Ordering information is given on any current masthead page.

(7) W. E. Truce and O. L. Norman, *J. Am. Chem. Soc.*, **75**, 6023 (1953).

(8) C. N. Yannios and J. V. Karabinos, *J. Org. Chem.*, **28**, 3246 (1963).

Formation and Fragmentation of 10-(Diethoxymethyl)-9-anthrone and Its Derivatives

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Received December 15, 1980

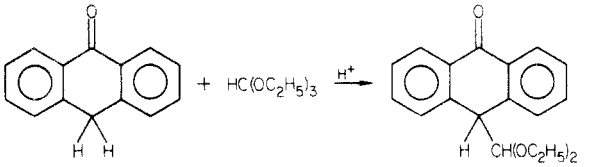
Carbonyl compounds, particularly those that are readily enolized, are commonly converted to their enol ethers by reaction with trialkyl orthoformates in the presence of acidic catalysts.[1,2] It seemed reasonable to expect that the reaction of anthrone with ortho esters would serve as a convenient and general synthesis of 9-alkoxyanthracenes. The acid-catalyzed reaction of anthrone with triethyl orthoformate was therefore examined.

Reaction of anthrone with a 1 molar equiv of triethyl orthoformate in the presence of sulfuric acid resulted principally in recovery of unchanged anthrone. Reaction

(1) H. W. Post, "The Chemistry of Aliphatic Orthoesters", Reinhold Publishing Co., New York, 1943, Chapter 3.
(2) R. H. DeWolfe, "Carboxylic Ortho Acid Derivatives", Academic Press, New York, 1970.

0022-3263/81/1946-2795$01.25/0

with a 10 molar excess of the ortho ester at reflux resulted in formation of 10-(diethoxymethyl)-9-anthrone (1) in 65% yield. Unreacted anthrone, together with a small amount of anthroquinone, was recovered, but no evidence could be obtained for formation of 9-ethoxyanthracene.

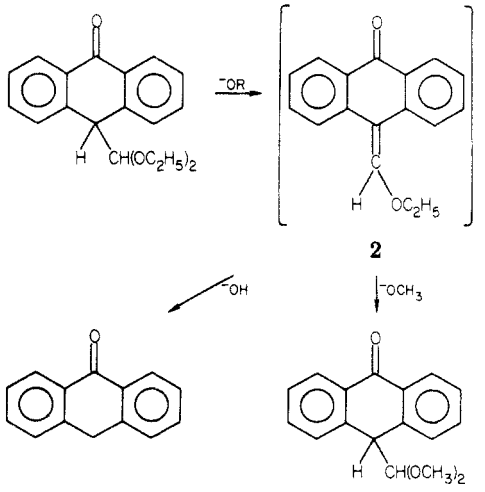


1

The structure of 1 was established from its chemical reactions (see below), its elemental analysis, and its IR and NMR spectra. The NMR spectrum of 1 (in $CDCl_3$) was initially more misleading than helpful, since it showed a two-proton singlet at δ 4.42, nearly unchanged from the methylene signal in the spectrum of anthrone. Furthermore, the signals for the *O*-methylene protons appeared as a very complex multiplet, which initially suggested the presence of two different ethoxy groups in the product. However, the NMR spectrum of 1 in pyridine solution showed the signal at δ 4.4 resolved into two doublets (J = 2.8 Hz). These signals could therefore be assigned to the protons at C-10 and the diethoxymethyl group of 1. The spectrum of 1-*10-d*, formed by reaction of triethyl orthoformate with anthrone-*10,10-d*$_2$, showed the upfield doublet converted to a singlet and the downfield doublet much reduced in size, in accordance with this assignment. Once the structure of 1 was determined, it was realized that the complex signals for the *O*-methylene groups are due to the enantiotopic nature of the ethoxy groups.

Hydrolysis of 1 in dilute aqueous acid resulted in quantitative regeneration of anthrone. No evidence for formation of anthrone-10-carboxaldehyde (or its tautomers)[3] could be obtained under the mildest of hydrolysis conditions. Reaction of 1 with a dilute solution of sulfuric acid in absolute ethanol similarly yielded anthrone in quantitative yield. Ethyl orthoformate could be detected among the products, showing that formation of 1 could easily be reversed.

Reaction of 1 with sodium hydroxide in aqueous methanol also converted it back to anthrone, presumably via the dialkoxymethylene derivative 2. However, no evidence



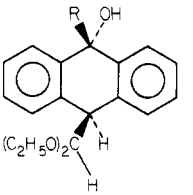
2

for formation of 2 in either acid or basic solutions could be obtained. Reaction with sodium ethoxide in ethanol converted 1 to a dark yellow, insoluble material whose structure could not be determined. Reaction of 1 with sodium methoxide in anhydrous methanol gave low yields of anthrone and the alkoxy exchange product 10-(dimethoxymethyl)-9-anthrone, accompanied by an insoluble material resembling that formed by reaction of 1 with sodium ethoxide solution.

Formation of 1 from reaction of anthrone with triethyl orthoformate was unexpected, since reactions of ketones with ortho esters normally yield ketals or enol ethers.[1,2] Condensation of ortho esters at α-carbons of ketones normally takes place only in acetic anhydride solution, since the anhydride will prevent addition of alcohol to the ketone carbonyls. Under these conditions, the products obtained are usually alkoxymethylene derivatives rather than dialkoxymethyl derivatives, except when loss of alcohol to form the alkoxymethylene derivatives cannot occur.[1,4]

The absence of any apparent ketal or enol ether from reaction of anthrone with triethyl orthoformate is presumably a result of the general lack of reactivity of anthrones in nucleophilic addition reactions, which is evidenced by the very high temperatures needed for reaction with primary amines.[5] Formation of the dialkoxymethylanthrone in place of the alkoxymethylene derivative can be attributed to decreased resonance interaction between the alkoxy and carbonyl groups of an alkoxymethylene ketone when an aromatic ring is interposed between them.

Ketone 1 seemed likely to be a useful intermediate for formation of substituted anthracene-9-carboxaldehydes. The reactions of 1 with phenyllithium and methyllithium were therefore carried out to form the corresponding tertiary alcohols.



5, R = C_6H_5
6, R = CH_3

The product of reaction with phenyllithium, **5**, was obtained as an apparent single isomer which could be recrystallized without difficulty from hexane–benzene. Its NMR spectrum differed from that of 1 (aside from the additional signals for the phenyl and hydroxy groups) in that the doublet for either the proton at C-10 or the dialkoxymethyl proton had been shifted upfield by ca. 0.5 ppm compared to the other doublet. In the NMR spectrum of the product obtained from reaction of phenyllithium with 1-*10-d*, the upfield doublet was converted to a singlet, and the signal for the downfield doublet was markedly reduced in size, so that the downfield and upfield signals could be assigned to the C-10 and diethoxymethyl protons, respectively. The marked shift in the position of the diethoxymethyl proton signal is attributed to shielding by the phenyl group at C-9, so alcohol **5** is assigned the *E* structure, with cis (pseudoaxial) phenyl and diethoxymethyl groups.

Alcohol **6**, obtained from reaction of 1 with methyllithium, also appeared to consist of a single stereoisomer. It could be recrystallized from hexane at low temperature,

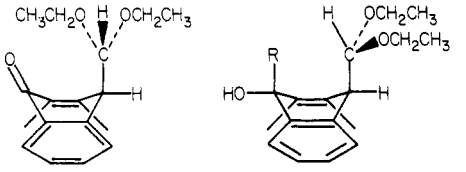
(3) L. Nédélec and J. Rigaudy, *Bull Soc. Chim. Fr.*, 1204 (1960); G. L. Buchanan and D. B. Jhaveri, *J. Org. Chem.*, **26**, 4295 (1961).

(4) Reference 2, Chapter 4.

(5) K. H. Meyer and H. Schlösser, *Justus Liebigs Ann. Chem.*, **420**, 126 (1920).

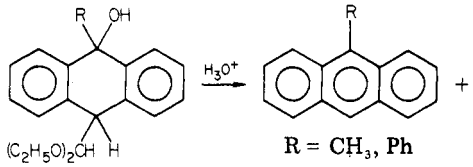
but decomposed to form 9-methylanthracene on attempted recrystallization from warm hexane. Alcohol **6**, like **5**, appears to have the *E* configuration, since the methyl singlet in the spectrum of **6** appears at almost the same position as in the spectrum of 9-methyl-9,10-dihydro-9-anthrol[6] and less than 0.1 ppm downfield from the reported position of the methyl signal of *cis*-9,10-dimethyl-9,10-dihydroanthracene.[7] The methyl groups in these compounds appear to exist predominantly in quasi-axial positions, while signals for quasi-equitorial methyl groups in 9,10-dihydroanthracenes appear at lower field positions.[7,8]

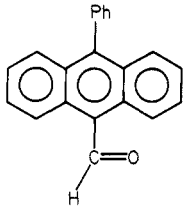
It is of some interest that the very small coupling constant (2.8 Hz) for the C-10 and diethoxymethyl protons in **1** is increased to 5 Hz in the spectrum of **6**, and to 8 Hz in the spectrum of **5**. Ketone **1** thus appears to exist largely in conformations such as **7** in which the bonds to the two vicinal protons are almost at right angles to each other. Conversion of C-9 to a quaternary carbon changes the preferred conformation (particularly when R is a bulky phenyl group) to **8**, to minimize transannular repulsions.



7 **8**

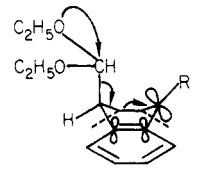
Reaction of alcohols **5** and **6** with acid was expected to result in dehydration to form 10-methyl- and 10-phenylanthracene-9-carboxaldehyde. However, **6** was converted quantitatively to 9-methylanthracene by reaction with dilute aqueous acid. No evidence for formation of the aldehyde could be detected. Reaction of alcohol **5** with acid gave a mixture of 9-phenylanthracene and 10-phenylanthracene-9-carboxaldehyde in a molar ratio of 9 to 1.





The almost exclusive occurrence of fragmentation, rather than dehydration, in acid-catalyzed reactions of **5** and **6** can be attributed to the fact that the bond between the pseudoaxial diethoxymethyl group and C-10 in each alcohol is nearly coplanar with the aromatic π bonds and the p orbital of a carbonium ion at C-9. In contrast, the bond to the pseudoequatorial proton at C-10 is almost orthogonal to the π systems.

Loss of a diethoxymethyl group in preference to loss of the C-10 proton is characteristic of **1** as well as of its derivatives. This was demonstrated by reaction of **1-*10-d*** with aqueous acid. Monodeuterated anthrone was obtained, showing that fragmentation of **1** is more rapid than enolization of either **1** or anthrone.



Experimental Section

General Procedures. All melting points are uncorrected. NMR spectra were recorded on a Perkin-Elmer Model R12A spectrometer in deuteriochloroform solution, using Me_4Si as an internal standard unless otherwise noted. IR spectra were recorded on a Perkin-Elmer Model 727 spectrometer. VPC analyses were carried out on a Varian Model 2400 charomatograph, using a 6 ft × $^1/_8$ in. 1% SE-30 column. Analyses were carried out by the Microanalytical Laboratory, University of Massachusetts, Amherst, MA.

10-(Diethoxymethyl)-9-anthrone. Anthrone (5.0 g, 0.026 mol) was suspended in triethyl orthoformate (50 mL, ca. 0.3 mol) and four drops of concentrated sulfuric acid were added. The mixture was refluxed (145 °C) for 20 h, while being protected from atmospheric moisture by a drying tube. VPC analysis indicated that about 15% of the anthrone remained unreacted. The mixture was allowed to cool to room temperature and filtered free of a small amount of precipitate (0.39 g.). The solid was identified by its NMR spectrum and VPC analysis as a mixture of anthrone and anthraquinone in a 3:1 molar ratio. The filtrate was shaken with 200 mL of water until most of the organic liquid (triethyl orthoformate) had dissolved, leaving a gummy solid residue. The mixture was extracted with methylene chloride, the organic layer dried over magnesium sulfate, and the solvent evaporated to give 7.3 g of brown solid. Recrystallizations from hexane–benzene and then from hexane yielded 5.1 g (0.0017 mol, 65%) of 10-(diethoxymethyl)-9-anthrone as pale yellow crystals, mp 100.5–102 °C. Two additional crystallizations from hexane raised the melting point to 104–104.5 °C. The IR spectrum (in mineral oil) of 10-(diethoxymethyl)-9-anthrone showed a carbonyl stretching peak at 1660 cm^{-1}. Its NMR spectrum ($CDCl_3$) showed absorptions at δ 0.97 (t, J = 7.5 Hz, 6 H), ca. 3.3 (m, 4 H), 4.42 (s, 2 H), 7.4–7.7 (m, 6 H), and 8.2–8.4 (m, 2 H). In pyridine solution, the singlet at δ 4.42 separated into doublets at δ 4.60 and 4.57 (J = 2.8 Hz). Anal. Calcd for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found: C, 77.18; H, 7.12.

Anthrone-*10,10-d*$_2$. Anthrone (3.0 g, 0.0155 mol) was suspended in a mixture of ethylene glycol dimethyl ether (10 mL) and deuterium oxide (20 mL). Sulfuric acid (0.50 g) was added and the mixture refluxed for 17 h. It was cooled to room temperature and extracted with methylene chloride. The methylene chloride layer was washed with sodium bicarbonate solution, dried over magnesium sulfate, and filtered, and the solvent evaporated under vacuum to yield 2.9 g of anthrone-*10,10-d*$_2$. Its NMR spectrum was identical with that of anthrone except that the singlet at δ 4.3 had an area equivalent to only 0.18 H, by comparison with the signal at δ 8.3 (protons at C-1 and C-8).

10-(Diethoxymethyl)-9-anthrone-*10-d*. Anthrone-*10,10-d*$_2$ was converted to the diethoxymethyl derivative as described above. Its NMR spectrum (in pyridine) showed principally a singlet (1 H) at δ 4.60 and a residual doublet (ca. 0.15 H) at δ 4.56.

Reaction of 10-(Diethoxymethyl)-9-anthrone with Sodium Methoxide Solution. 10-(Diethoxymethyl)-9-anthrone (1.0 g, 0.0051 mol) was dissolved in 20 mL of anhydrous methanol and 5 mL of a 1 M solution of sodium methoxide in methanol was added. The solution turned deep orange in color. After 20 min the solution was diluted with 25 mL of methylene chloride and acidified with 50% aqueous acetic acid. A yellow precipitate formed which was insoluble in methylene chloride, water, or chloroform. The methylene chloride solution was washed with water, dried over magnesium sulfate, and filtered, and the solvent evaporated to give a pale yellow oil which crystallized on standing overnight. Chromatography on silica gel, eluting with hexane–

(6) B. Miller and V. C. Marhevka, *Tetrahedron Lett.*, 895 (1981).
(7) R. G. Harvey, L. Arzadon, J. Grant, and K. Urberg, *J. Am. Chem. Soc.*, **91**, 4535 (1969).
(8) L. R. C. Barclay and R. A. Chapman, *Can. J. Chem.*, **43**, 1754 (1965).

methylene chloride, yielded anthrone (0.031 g, 3%) and 10-(dimethoxymethyl)-9-anthrone (0.064 g, 0.239 mol, 5%), mp 144–146 °C (from hexane–benzene). Its NMR spectrum showed signals at δ 8.3 (2 H, m), 7.55 (6 H, m), 2.35 (1 H, d, J = 3.0 Hz), 2.40 (1 H, d, J = 3.0 Hz), and 3.15 (6 H, s). Anal. Calcd for $C_{17}H_{16}O_3$: C, 76.13; H, 5.98. Found: C, 75.79; H, 6.06.

10-(Diethoxymethyl)-9-hydroxy-9-methyl-9,10-dihydroanthracene (6). A 1.56 M solution of methyllithium in ether (3 mL, 4.68 mmol) was added to a solution of 10-(diethoxymethyl)-9-anthrone (0.50 g, 1.68 mmol) in 15 mL of anhydrous ether. The solution was stirred, allowed to stand at room temperature for 5 min, and then poured into water. The organic layer was separated and dried over magnesium sulfate, and the solvent evaporated under vacuum to yield 10-(diethoxymethyl)-9-hydroxy-9-methyl-9,10-dihydroanthracene as a yellow oil (0.53 g, 1.69 mmol) which crystallized on standing overnight in the refrigerator. Its NMR spectrum showed peaks at δ 7.90–7.65 (m, 2 H), 7.50–7.15 (m, 6 H), 4.31 (1 H, d, J = 5 Hz, proton at acetal carbon), 4.05 (1 H, d, J = 5 Hz, proton at C-10), 3.80–2.85 (m, 4 H) 2.45 (s, 1 H, hydroxy proton), 1.63 (s, 3 H), and 1.00 (6 H, t, J = 7 Hz). Attempted recrystallization from warm hexane converted the product to 9-methylanthracene (0.39 g).

In another run, 0.27 g of the alcohol was dissolved in anhydrous ether, cooled to −78 °C, and filtered to give 0.09 g of pale yellow powder, which decomposed on melting to yield 9-methylanthracene. The NMR spectrum of the recrystallized material was essentially identical with that of the unrecrystallized reaction product.

Reaction of methyllithium with 10-(diethoxymethyl)-9-anthrone-*10-d* gave **6**-*10-d*. Its NMR spectrum showed a 0.14-H doublet at δ 4.05 and a singlet (together with a small doublet) at δ 4.3 (1 H).

Reaction of 10-(Diethoxymethyl)-9-methyl-9,10-dihydroanthracene with Acid. Hydrochloric acid solution (1.2 M, 1 mL) was added to a solution of 10-(diethoxymethyl)-9-hydroxy-9-methyl-9,10-dihydroanthracene (0.25 g, 0.80 mmol) in 10 mL of acetone. The solution was shaken for 1 min, diluted with water, and extracted with methylene chloride. The methylene chloride solution was washed with water, dried over magnesium sulfate, and filtered, and the solvent evaporated to give 0.15 g (0.78 mmol, 98%) of 9-methylanthracene. IR, NMR, and vapor-phase chromatographic analyses showed no evidence for the presence of 10-methylanthracene-9-carboxaldehyde.

10-(Diethoxymethyl)-9-hydroxy-9-phenyl-9,10-dihydroanthracene (5). A 1.90 M solution of phenyllithium in ether (2.3 mL, 4.37 mmol) was added to a solution of 10-(diethoxymethyl)-9-anthrone (0.60 g, 2.03 mmol) in 20 mL of ether. The dark phenyllithium color disappeared in about 5 min. The solution was then poured into water, the layers were separated, the ether layer was washed with water, dried over magnesium sulfate, and filitered, and the solvent was evaporated to give 0.72 g of yellow oil which crystallized on standing at room temperature. The product was recrystallized from benzene–hexane to give 0.43 g of 10-(diethoxymethyl)-9-hydroxy-9-phenyl-9,10-dihydroanthracene (1.15 mmol, 57%) as yellow needles, mp 149–151 °C. The NMR spectrum showed signals at δ 8.17–7.95 (m, 2 H), 7.7–7.2 (m, 6 H), 7.20 (s, 5 H), 4.05 (d, J = 8 Hz, 1 H, proton at C-10), 3.45 (d, J = 8 Hz, 1 H, diethoxymethyl proton), 2.43–4.05 (m, 4 H), 1.52 (s, 1 H, hydroxy proton), and 0.87 (t, J = 8 Hz, 6 H). Anal. Calcd for $C_{25}H_{26}O_3$: C, 80.18; H, 7.00. Found: C, 80.30; H, 7.17.

Reaction of 10-(diethoxymethyl)-9-anthrone-*10-d* with phenyllithium gave 10-(diethoxymethyl)-10-hydroxy-10-phenyl-9,10-dihydroanthracene-*10-d*. Its NMR spectrum showed a reduced intensity for the doublet at δ 4.05 and a singlet (together with a small doublet) at δ 3.45.

Reaction of 10-(Diethoxymethyl)-9-hydroxy-9-phenyl-9,10-dihydroanthracene with Acid. Hydrochloric acid solution (1.2 M, 1 M) was added to a solution of 10-(diethoxymethyl)-9-hydroxy-9-phenyl-9,10-dihydroanthracene (0.20 g, 0.54 mmol) in 5 mL of acetone. The mixture was shaken for 1 min, diluted with 20 mL of water, and extracted with methylene chloride, the organic layer washed with water, dried over magnesium sulfate and filtered, and the solvent evaporated to give 0.17 g of yellow gum which solidified on scratching and trituration with petroleum ether. Vapor-phase chromatography at 235 °C showed two peaks with retention times of 3.3 and 7.9 min. These products were isolated and identified as 9-phenylanthracene and 10-phenylanthracene-9-carboxaldehyde.[9]

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for a grant in support of this work.

Registry No. 1, 77224-36-3; *trans*-**5**, 77224-37-4; *trans*-**6**, 77224-38-5; *trans*-**6**-*10-d*, 77224-39-6; anthrone, 90-44-8; triethyl orthoformate, 122-51-0; anthrone-*10,10-d*$_2$, 77224-40-9; 10-(diethoxymethyl)-9-anthrone-*10-d*, 77224-41-0; 10-(dimethoxymethyl)-9-anthrone, 77224-42-1; 9-methylanthracene, 779-02-2; 10-(diethoxymethyl)-9-hydroxy-9-phenyl-9,10-dihydroanthracene-*10-d*, 77224-43-2; 9-phenylanthracene, 602-55-1; 10-phenylanthracene-9-carboxaldehyde, 54458-81-0.

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A Chiral Ligand for Lithium

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Received September 12, 1980

Our continuing interest in the area of asymmetric induction[1] has led naturally to the design and construction of chiral ligands for synthetically important alkali metals such as lithium and mangesium. Such cations certainly play a significant role in the addition of organometallic reagents to ketones and aldehydes,[2] and relatively recent evidence implicates the cation as being intimately involved in the transition state of the reduction of carbonyl compounds by complex metal hydrides.[3] Chiral ligands for the cation would provide for diastereoselection between the otherwise enantiotopically related faces of a ketone or aldehyde. The report of a rather extensive effort in this area by Mukaiyama[4] serves as the impetus for this publication of our research with a similar ligand.

Our approach to the design of a ligand for lithium was predicated on two considerations: the ligand should be bidentate so as to afford, at the minimum, two additional binding sites to the metal—one for the carbonyl system and the other for a nucleophilic group such as the carbon chain of an alkyl lithium; while a tertiary amine would be desirable as a ligand, the carbon trisubstitution at nitrogen would afford less freedom in design for stereodifferentiation than a disubstituted oxygen or sulfur ligand site. The ligand **1** (Figure 1) was one outcome of these deliberations, and its preparation in enantiomerically enriched form proceeded as outlined. The tetrahydrofuryl amine used was outlined by resolution of racemic material by a known procedure.[5] The optical rotation for the starting amine was within experimental error the same as that previously reported. We were also able to prepare **1** by the reaction of pyrrolidine with the methanesulfonate ester to tetrahydrofurfuryl alcohol, and in greatly superior yield.

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0022-3263/81/1946-2798$01.25/0