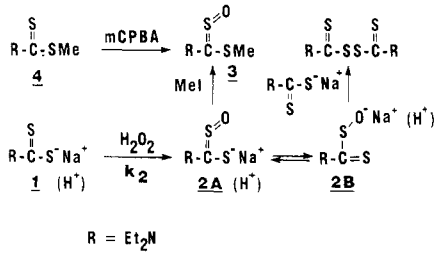
Scheme I



synthesis of **3** was carried out according to the method of Zwanenburg;[10a] i.e., the oxidation of methyl diethyldithiocarbamate (**4**) with 1 equiv of *m*-CPBA.

These results, especially ii–iv, clearly eliminate the possible formation of diethyldithiocarbamic acid *N*-oxide. Many aminosulfines have been prepared by the oxidation of tertiary thioamides with hydrogen peroxide without forming *N*-oxides.[13] Consequently, it seems clear that the oxidation of **1a** and **1b** by hydrogen peroxide took place on sulfur atom to afford the corresponding *S*-oxides.

A kinetic study showed the oxidation of **1a,b** by hydrogen peroxide is first order in both [**1**] and [hydrogen peroxide]. No effect of sodium salt on the rate constant was observed (k_2: **1a**, 6.67 M^{-1} s^{-1}; **1b**, 6.47 M^{-1} s^{-1}, at 22.5 °C).

There are two tautomers available for **2**. Appearance of the C=S=O bands at 965 and 1005 cm^{-1} for **2b** and disappearance of the S–H bands at 2310 and 2420 cm^{-1}, observed for **1b**, suggest certain interaction between oxygen and hydrogen. The formation of the methyl ester by the treatment of **2a** with methyl iodide indicates involvement of the structure of **2A**. On the other hand, exclusive formation of disulfiram in the reaction of **1a** with **2a** suggests participation of sulfenic acid form **2B**. All these observations are summarized in Scheme I.

Finally, one must be very careful to interpret the inhibitory effect of **1a** when used as a copper trapping reagent in redox-related enzymatic reactions.[14] Further study on the structure and reactivity of **2** is under way in this laboratory.

Experimental Section

^1H NMR spectra were determined on Hitachi R-40 (90 MHz) and JEOL FX-90 spectrophotometers in $CDCl_3$ solvent using tetramethylsilane as internal standard. Mass spectra were recorded on a JEOL JMS-D300 mass spectrometer. IR spectra were obtained on a JASCO IR-810 spectrophotometer. UV spectra were obtained on a Hitachi U-3200 spectrophotometer. Solvents and reagents were commercially available and, unless otherwise noted, were used without further purification.

Oxidation of Sodium Diethyldithiocarbamate (1a) by Hydrogen Peroxide. A solution of **1a** (trihydrate, 100 mg, 0.44 mmol) in methanol (10 mL) at 0 °C was treated with 50 μL of hydrogen peroxide (30% in H_2O) for a minute. UV spectrum of the reaction mixture showed complete conversion of **1a** to **2a**. Evaporation of the solvent gave 95 mg of **2a** (89%): TLC (Al_2O_3) R_f 0 (by $CHCl_3$); UV (MeOH) 265 nm (log ε 4.31), 330 (3.89); IR_{neat} 3400, 1480, 1410, 1375, 1355, 1260, 1210, 1140, 1010 (sh), 990, 920 cm^{-1}.

Acidification of 2a. The residue, **2a**, obtained above was dissolved in an ice-cold phosphate buffer solution (pH 3.3, 0.02 M) and extracted by methylene chloride. Only one spot (**2b**) on SiO_2–TLC (R_f 0.75, by AcOEt) was observed. Visible spectrum of **2b** was identical with that of **2a**. Evaporation of the solvent gave 92 mg of **2b**: IR_{neat} 3400, 1585, 1410, 1375, 1350, 1265, 1195, 1140, 1005, 965, 910 cm^{-1}; ^1H NMR 4.03 (q, 4 H, J = 7.0 Hz), 1.33 ppm (t, 6 H, J = 7.0 Hz); MS (CI), m/e (relative intensity) 166 (M^+ + 1, 15), 150, 148, 118, 116, 104 (base).

Oxidation of diethyldithiocarbamic acid (**1b**) was carried out by the procedure employed for the oxidation of **1a** to give **2b** in 92% isolated yield.

Methylation of 1b by Methyl Iodide. A methanol solution (10 mL) of **1b** (100 mg, 0.44 mmol) was treated with 1.5 equiv of methyl iodide at 0 °C for 12 h. After the usual workup, the product **3** was isolated by Al_3O_2–PTLC (Bz) in 80% yield: ^1H NMR 3.90 (q, 4 H, J = 7.2 Hz), 2.83 (s, 1.1 H), 2.22 (s, 1.9 H), 1.26 ppm (t, 6 H, J = 7.2 Hz); IR_{neat} 3400, 1490, 1425, 1200, 1150, 1025, 1000 (sh), 960, 900 cm^{-1}; HRMS for $C_6H_{13}NOS_2$ requires 179.0418, found, 179.0426.

Preparation of Methyl Diethyldithiocarbamate (4). Methyl iodide (500 mg, 3.3 mmol) was added to an acetone solution (12 mL) of **1a** (500 mg, 2.2 mmol) at 0 °C, and the reaction mixture was stirred for 12 h at 0 °C. The solvent was evaporated in vacuo, and the residue was dissolved in CH_2Cl_2. The solution was washed with water and the product **4** was isolated by Al_2O_3 column chromatography (Bz/$CHCl_3$ = 3, R_f 0.2) in 82% yield: ^1H NMR 4.05 (q, 2 H, J = 7.1 Hz), 3.75 (q, 2 H, J = 7.1 Hz), 1.59 (s, 3 H), 1.29 (t, 6 H, J = 7.1 Hz); IR_{neat} 1480, 1410, 1260, 1200, 1140, 910 cm^{-1}; MS (EI), m/e 163 (M^+, base), 116, 91, 88, 60; HRMS for $C_6H_{13}NS_2$ requires 163.0406, found, 163.0446.

Oxidation of Methyl Diethyldithiocarbamate (4). A methylene chloride solution (15 mL) containing **4** (50 mg, 0.30 mmol) and *m*-chloroperbenzoic acid (50 mg, 0.28 mmol) was stirred for 24 h at 0 °C. Methyl diethyldithiocarbamate *S*-oxide was isolated by Al_2O_3–PTLC (CH_2Cl_2) in 32% yield. All physical properties are consistent with those of **3**.

Reaction of 1a and 2a. Hydrogen peroxide (30% in H_2O, 25 μL) was introduced to a methanol solution (10 mL) containing **1a** (50 mg, 0.22 mmol) at 0 °C in one portion and stirred for a minute followed by addition of **1a** (50 mg, 0.22 mmol). The resulting was evaporated, and the residue was dissolved in CH_2Cl_2 and washed with water. The product, disulfiram, was isolated by column chromatography on silica gel Bz) in 78% yield: ^1H NMR 4.03 (q, 8 H, J = 7.4 Hz), 1.6–1.2 ppm (m, 12 H).

Kinetics. A methanol solution (1.8 mL) of **1a** (or **1b**) (1.88 × 10^{-4} M) in UV cuvette was placed to a spectrophotometer at 22.5 ± 0.5 °C. The reaction was initiated by addition of 3 equiv of hydrogen peroxide and monitored by absorbance changes at 330 nm. Second-order rate constants for the oxidation of **1a** and **1b** were 6.67 ± 0.19 and 6.47 ± 0.09 M^{-1} s^{-1}, respectively.

Acknowledgment. We are grateful to Professors Shigeru Oae (Okayama University of Science, Japan) and Tokuji Kimura (Wayne State University) for their helpful discussions.

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Syntheses of 9,10-Disubstituted Anthracenes Derived from 9,10-Dilithioanthracene

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The class of anthracenes disubstituted at the central ring (the 9- and 10-positions) has been proven useful in studies ranging from ESR[1] to artificial receptor design[2] to polymer synthesis.[3] As a part of our studies of structural effects on the retro-Diels–Alder reaction,[4] we required several

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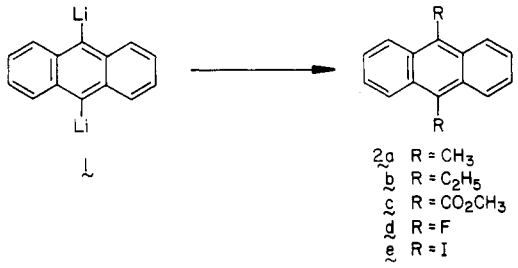
Scheme I



9,10-disubstituted anthracenes that were (a) expensive, (b) available only via long or low-yielding syntheses, or (c) previously unknown. We now report that reactions of 9,10-dilithioanthracene permit facile syntheses of the corresponding dimethyl-, diethyl-, dicarbomethoxy-, difluoro-, diiodo-, and diacetylanthracenes.

9,10-Dilithioanthracene (1) can be made by the halogen–metal exchange of 9,10-dibromoanthracene, which is itself made easily by the bromination of anthracene.[5] This halogen–metal exchange has been reported several times previously,[2,6,7] but the range of electrophiles with which reaction could be accomplished has not been examined. We find that a select, but important set of compounds can be made by using this route (Scheme I). The reaction of 9,10-dilithioanthracene with methyl iodide has been reported to afford 9,10-dimethylanthracene (**2a**) in 16% yield;[6] we find that optimizing the conditions of this reaction increases the yield to 59% of the isolated product. Similarly, reaction with ethyl iodide affords 9,10-diethylanthracene (**2b**) in 33% yield; alkylations with *n*-propyl and *n*-butyl iodides provide 9,10-di-*n*-propyl- (mp 138.5–139.5 °C) and 9,10-di-*n*-butylanthracenes (mp 105–106 °C) in 51 and 38%, respectively. Not surprisingly, attempted reactions with isopropyl and *tert*-butyl halides afforded only anthracene itself after aqueous workup. Quenching of 9,10-dilithioanthracene with CO_2 has been reported previously to provide the corresponding dicarboxylic acid.[2] Conversion to the diacid chloride with $SOCl_2$ and workup with methanol afforded 9,10-dicarbomethoxyanthracene (**2c**), made previously by reduction of anthracene to the dianion, reaction with CO_2 to provide the dihydro dicarboxylic acid, esterification, and dehydrogenation.[8-11]

Of the 9,10-dihaloanthracenes, the dichloro[12] and dibromo[5] derivatives can be made easily and are both purchasable. Five syntheses of 9,10-difluoroanthracene (**2d**) have been reported previously, each of which presents experimental challenges. The reaction of 1,4-difluoro-2,5-dibromobenzene with *n*-butyllithium followed by trapping of the dehydrobrominated intermediates with furan affords the bisadduct in 5% yield, which could be hydrogenated and dehydrated to give **2d**.[13] Reaction of anthraquinone with SF_4 yields 9,9,10,10-tetrafluoro-9,10-dihydroanthracene;[14] defluorination with iron gauze provides the desired product in 5% yield.[15] Reaction of 9-fluoro-10-bromoanthracene, available by bromination of 9-fluoroanthracene, with Mg affords the Grignard reagent; reaction with perchloryl fluoride gives the difluoride in an unspecified yield percent.[16] A seven-step route from octahydroanthracene also provides the difluoride.[17] Finally, electrolysis of anthracene in an acetonitrile solution of $(CH_3)_4NF{\cdot}2HF$ gives 9,10-difluoroanthracene in 0.1% yield.[18] We find that reaction of 9,10-dilithioanthracene with *N*-*tert*-butyl-*N*-fluorobenzenesulfonamide[19,20] yields difluoride **2d** in one step in 60% yield after column chromatography. Attempted reaction with *N*-fluoro-2,4,6-trimethylpyridinium triflate[21] led only to proton abstraction and anthracene formation; in fact, the literature suggests that lithium salts are not good starting materials for fluorinations with the *N*-fluoropyridinium triflates.[21a] Attempted reaction of 9,10-dilithioanthracene with XeF_2 (−78 → +23 °C) afforded a complex mixture of products, one of which as the desired difluoride (**2d**) as confirmed by mass spectrometry and TLC comparison with an authentic sample. Surprisingly, 9,10-diiodoanthracene (**2e**) has not been reported previously; we were able to make this new compound easily by reaction of **1** with molecular iodine.

9,10-Bis(trimethylsilyl)anthracene, which may be prepared by the methods of Harvey,[22] Lehmkuhl,[23] and Roberts,[24] can also be prepared by the reaction of 9,10-dilithioanthracene with trimethylsilyl chloride in the presence of TMEDA as reported recently by Raston.[25] The direct silylation reaction of **1** with no added TMEDA was attempted in this laboratory using widely varying conditions without success. Following a communication with Prof. Raston, we repeated the reaction with added TMEDA and did obtain a sample of 9,10-bis(trimethylsilyl)anthracene via the one-step process. This direct silylation is certainly the method of choice for the preparation of 9,10-bis(trimethylsilyl)anthracene at the present time.

Finally, we attempted to prepare 9,10-diacetylanthracene (**5**) using a direct Friedel–Crafts acylation of anthracene as has been reported previously;[26] we did make the modification of using CH_2Cl_2 instead of CS_2 as solvent. The product we isolated showed a ^{13}C NMR spectrum identical with that reported,[26] but was inconsistent with the pattern expected for a compound with D_{2h} symmetry. On the basis of its ^1H NMR spectrum, we were able to assign structure **4** to the product of direct acylation under Friedel–Crafts conditions. Somewhat surprisingly, compound **1** did not react with either acetic anhydride or acetyl chloride at room temperature to provide **5** directly; in addition, quenching with acetone leads only to anthracene.

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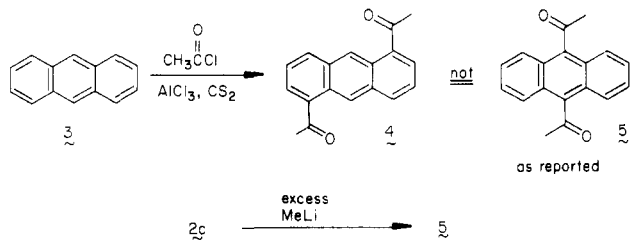

We were able to prepare 9,10-diacetylanthracene from the 9,10-dicarbomethoxy derivative (**2c**) by reaction with excess methyllithium. Notably, an anticipated second addition of methyllithium to **5** to afford the tertiary alcohol did not occur, due likely to an orthogonal orientation of the acetyl groups to the anthracene framework and shielding by the peri hydrogens.

In summary, the reactions of 9,10-dilithioanthracene with selected electrophiles provide access to a variety of 9,10-disubstituted anthracene derivatives in one- or two-step sequences. Of particular importance is a short synthesis of 9,10-difluoroanthracene in 60% from 9,10-dibromoanthracene in a one-pot reaction.

Experimental Section

General. Melting points were taken on an Electrothermal melting point apparatus and are uncorrected. Microanalyses were carried out at Canadian Microanalytical Service, New Westminster, BC. Mass spectra were obtained by use of a Kratos-30 mass spectrometer. FT-NMR spectra at 11.75 T (500 MHz) or 7.0 T (300 MHz) were obtained on equipment funded in part by NIH Grant 1 S10 RR01458-01A1. We thank Mr. Richard Weisenberger and Dr. C. E. Cottrell for their assistance in obtaining mass and high-field ^1H NMR spectra, respectively, at The Ohio State University Chemical Instrumentation Center and Mr. Carl Engelman for other NMR assistance. Thionyl chloride was distilled freshly from triphenyl phosphite prior to use.

9,10-Dilithioanthracene (1). A minor modification of the procedure reported by Herrmann and co-workers[2] was used. For example, 9,10-dibromoanthracene (2.0 g, 5.95 mmol) was placed in a dry 100-mL round-bottom flask along with 20 mL of anhydrous diethyl ether. To the stirred mixture was added *n*-butyllithium (6.0 mL of a 2.6 M solution in hexane,[27] 15.6 mmol) via syringe dropwise over the course of 30 min. The resulting mixture was stirred for an additional 10 min and used directly in subsequent reactions.

9,10-Dimethylanthracene (2a). To a mixture of **1** prepared as described from dibromoanthracene (3.0 g, 8.9 mmol) was added iodomethane (2.0 mL, 32 mmol) dropwise. The solution was heated to reflux for 18 h, allowed to cool, washed with H_2O (4 × 10 mL), dried over $MgSO_4$, and finally evaporated to a yellow solid under reduced pressure. The resulting solid was purified by flash chromatography on silica gel eluting with hexane to yield, after pooling and evaporation of the appropriate fractions, yellow crystals (1.08 g, 59%): mp 182.5–184 °C (lit.[28] mp 180–181 °C); R_f 0.26 (hexane on silica); ^1H NMR ($CDCl_3$) δ 3.15 (s, 6, CH_3), 7.55 (dd, 4, Ar–H), 8.35 (dd, 4, Ar–H). High-resolution mass spectrum: calcd for $C_{18}H_{14}O_2$, 206.110; measured, 206.112.

9,10-Diethylanthracene (2b). To a mixture of **1** prepared as described from 9,10-dibromoanthracene (3.0 g, 8.9 mmol) was added iodoethane (3.0 mL, 37 mmol). The resulting solution was heated to reflux for 15 h, washed with H_2O (4 × 7 mL), dried over $MgSO_4$, and finally evaporated under reduced pressure to a thick yellow oil. The oil was subjected to column chromatography on silica (eluting with hexane) and finally crystallized from absolute ethanol to afford yellow crystals (679 mg, 33%): mp 142–144 °C (lit.[29] mp 144–145 °C); R_f 0.29 (hexane on silica); ^1H NMR ($CDCl_3$) δ 1.39 (t, 6, CH_2CH_3), 3.49 (q, 4, CH_2CH_3), 7.41–7.78 (dd, 4, Ar–H), 8.28–8.63 (dd, 4, Ar–H). High-resolution mass spectrum: calcd for $C_{18}H_{18}$, 234.141; measured, 234.145.

9,10-Dicarbomethoxyanthracene (2c). A solution of 9,10-anthracenedicarboxylic acid (1.0 g, 4.4 mmol)[2] and thionyl chloride (50 mL) was brought to reflux for 1.5 h and then the thionyl chloride was removed in vacuo. Anhydrous methanol (60 mL) was added, and the solution was heated to reflux for 2.5 h and then evaporated to dryness. The solid was taken up in ether, and washed with aqueous sodium bicarbonate and finally H_2O. The ether layer was dried over $MgSO_4$ and evaporated to dryness. Recrystallization from methanol yielded 903 mg (88% yield) of yellow crystals: mp 175–176 °C; ^1H NMR ($CDCl_3$) δ 4.15 (s, 6, OCH_3), 7.48–7.65 (dd, 4, Ar–H), 7.94–8.08 (dd, 4, Ar–H). High-resolution mass spectrum: calcd for $C_{18}H_{14}O_4$, 294.0892; measured, 294.0895.

Anal. Calcd for $C_{18}H_{14}O_4$: C, 73.46; H, 4.76. Found: C, 73.19; H, 4.80.

9,10-Difluoroanthracene (2d). A mixture of **1** prepared as described from 9,10-dibromoanthracene (100 mg, 0.3 mmol) was cooled to −78 °C, and *N-tert*-butyl-*N*-fluorobenzenesulfonamide (0.9 mmol) in 0.5 mL of anhydrous ether was added. The solution was allowed to continue to stir and to warm slowly to room temperature. It was finally quenched with aqueous NH_4Cl, and the ether layer was given an aqueous workup. The ether layer was dried over $MgSO_4$ and evaporated to dryness, and the resulting solid was subjected to flash chromatography on silica gel with hexane solvent. The first bright fluorescent band to emerge was collected and pooled to give upon evaporation 40 mg (60%) of a yellow crystalline solid whose NMR spectra and melting point are identical with those found in a previous citing: mp 164–165 °C (lit.[17] mp 164–165 °C); R_f 0.56 (hexane on silica); ^1H NMR ($CDCl_3$) δ 7.53–7.56 (dd, 4, Ar–H), 8.22–8.27 (m, 4, Ar–H). High-resolution mass spectrum: calcd for $C_{14}H_8F_2$, 214.059; measured, 214.059.

9,10-Diiodoanthracene (2e). To a mixture of **1** prepared as described from 9,10-dibromoanthracene (3.0 g, 8.93 mmol) were added iodine crystals (7.5 g, 30 mmol) through the top of the condenser over the course of 5 min. The mixture was stirred for an additional 15 min until the color was a dark brown and then transferred to a separatory funnel where it was washed 5 times with a 25% (w/w) solution of sodium thiosulfate in water. The crude product was filtered, dried in a vacuum oven at 80 °C, and finally recrystallized twice from CCl_4, (100 mL) to give 1.82 g (47%) of yellow needles: mp 254–255 °C; ^1H NMR ($CDCl_3$) δ 7.55 (dd, 4, Ar–H), 8.55 (dd, 4, Ar–H). High-resolution mass spectrum: calcd for $C_{14}H_8I_2$, 429.872; measured, 429.873.

Anal. Calcd for $C_{14}H_8I_2$: C, 39.10; H, 1.88; I, 59.02. Found: C, 39.21; H, 1.90; I, 59.04.

9,10-Diacetylanthracene (5). To a stirred solution of 9,10-dicarbomethxoyanthracene (**2c**; 100 mg, 0.43 mmol) in anhydrous diethyl ether (25 mL) at −78 °C was added methyllithium (1.0 mL of a 1.4 M solution in diethyl ether, 1.4 mmol),[30] and the solution was allowed to warm to ambient temperature overnight. The resulting solution was quenched with ammonium chloride and then work up with H_2O extraction. The ether layer was dried over $MgSO_4$ and evaporated to dryness. Recrystallization from ethanol afforded yellow crystals (329 mg, 58%): mp 248.5–249.5 °C; ^1H NMR ($CDCl_3$) δ 2.8 (s, 6, CH_3), 7.5–7.7 (dd, 4, Ar–H), 7.8–8.0 (dd, 4, Ar–H); ^{13}C NMR δ 33.8 ($COCH_3$), 124.9 and 126.8 (aromatic *C*–H), 125.9 (quaternary Ar–*C*), 138.3 (aromatic *C*–CO), 207.4 (*C*=O). High-resolution mass spectrum: calcd for $C_{18}H_{14}O_2$, 262.099; measured, 262.099.

Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.21; H, 5.37. Found: C, 82.42; H, 5.38.

Acknowledgment. Helpful discussions with Prof. Robert Filler (Illinois Institute of Technology) and Prof. Ronald Harvey (University of Chicago) are acknowledged with pleasure. The financial support of the National Science Foundation is acknowledged with gratitude.

Supplementary Material Available: Details concerning the preparation of *N*-fluoro-*N-tert*-butylbenzenesulfonamide (2 pages). Ordering information is given on any current masthead page.

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