amount of amine) of the phenoxyacetic acid **4** was added as a 1.0 M solution in anhydrous THF. After stirring at −78 °C for 15 min an excess of the ketone or aldehyde electrophile (twice the amount of the acid) was added as a 3.0 M solution in anhydrous THF. The solution was stirred at −78 °C for 15 min to 12 h, poured on 2–3 volumes of crushed ice, and transferred into a separatory funnel. After extraction with 2 × 15 mL of ethyl ether to remove neutral products, the aqueous layer was acidified with 10% HCl to pH ~3 and extracted with 4 × 20 mL of ethyl ether. The combined ether extracts were dried over $MgSO_4$ and the solvent rotoevaporated at 30 °C, first at 25 mm and finally at 1 mm. The residue was recrystallized from the appropriate solvent. The yields, physical constants, and spectral data are summarized in Table I.

General Method for the Preparation of α-Phenoxy-β-lactones 2. The β-hydroxy-α-phenoxycarboxylic acid **3** (1 mol) was dissolved in 10–20 mL of anhydrous pyridine, placed into a 50-mL stoppered Erlenmeyer flask, cooled to 0 °C and 2 mol of benzensulfonyl chloride was added. When the β-hydroxy acid **3** contains 1 mol of water of crystallization, 3 mol of benzenesulfonyl chloride must be used. After storing overnight in the refrigerator, the mixture was poured onto 3–4 volumes of crushed ice and extracted with 4 × 15 mL of ethyl ether. The combined ether extracts were washed with 2 × 20 mL of saturated bicarbonate and 1 × 20 mL of water and dried over $MgSO_4$. The solvent was rotoevaporated at 30 °C, first at 25 mm and finally at 1 mm, and the residue was recrystallized from the appropriate solvent. When the β-lactone **2** failed to crystallize, it was purified by silica gel chromatography at ca. −20 °C. The yields, physical constants, and spectral data are given in Table II.

General Method for the Preparation of Enol Ethers 1. Thermal Decarboxylation of the β-Lactones 2. The β-lactone (1.0 mmol) was placed into a 10-mL, one-necked, round-bottomed flask, provided with a gas outlet tube, and heated to 150 °C in an oil bath until cessation of CO_2 evolution. After cooling to room temperature, the enol ether product was distilled at reduced pressure or recrystallized from the appropriate solvent. The reaction yields, physical constants, and spectral data are given in Table III.

Direct Dehydrocarbonation of β-Hydroxy Acids 3. A 100-mL one-necked, round-bottomed flask, provided with a spin-bar and condenser with a gas outlet tube which was protected with a $CaCl_2$ drying tube, was charged with 2.0 mmol of the β-hydroxy-α-phenoxycarboxylic acid **3** in ca. 15 mL of anhydrous pyridine. To this solution was added 4.0 mmol of benzenesulfonyl chloride (6.0 mmol in the case of **3** containing 1.0 mmol of water of crystallization) and the mixture was stirred at 50–55 °C overnight. The dark mixture was poured onto 4–5 volumes of crushed ice and extracted with 2 × 15 mL of ethyl ether. The combined ether extracts were washed with 1 × 10 mL of 10% HCl, then with 1 × 10 mL of saturated $NaHCO_3$, and finally with 2 × 10 mL of water. After drying over $MgSO_4$, the solvent was rotoevaporated at 30 °C (30 mm). The residue was purified by distillation at reduced pressure or recrystallized from the appropriate solvent.

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Registry No.—Acetone, 67-64-1; cyclopentanone, 120-92-3; tricyclo[3.3.1.1^{3,7}]decanone, 700-58-3; benzaldehyde, 100-52-7; diphenylmethanone, 119-61-9; 9*H*-fluoren-9-one, 486-25-9; **4**, 122-59-8; LDA, 411-54-0; lithium α-phenoxy-α-lithioacetate, 67774-23-6.

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Modified Crown Ether Catalysts.
1. Synthesis of Alkanoyl-, Aroyl-, and α-Hydroxyalkylbenzo Crown Ethers[1]

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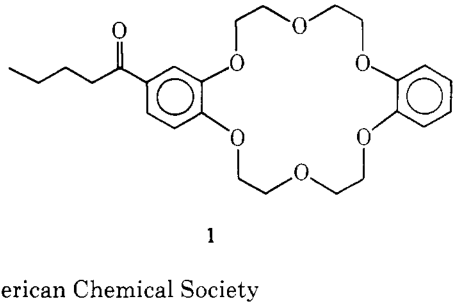
Crown ethers bearing lipophilic substituents were prepared for testing as improved catalysts. Fifteen alkanoylbenzo crown ethers were prepared in yields of 50–92%. The most satisfactory method of acylation proved to be treatment of the benzo crown with a slight excess of carboxylic acid and 1 equiv of phosphorus pentoxide in anhydrous methanesulfonic acid. Several of the resulting ketones were reduced in high yield to the corresponding alcohols with sodium borohydride in ethanol.

The recent report by Hautala and Hastings[2] on the preparation of 2,3-(4′-valeroylbenzo)-11,12-benzo-18-crown-6 (**1**) has prompted us to report the results of work which has been progressing in our laboratories.



1

Crown ethers are well known for their ability to form strong complexes with alkali metal and organic cations (log K_s for the 18-crown-6·K^+ complex in methanol is 6.0).[3] They have been used to dissolve potassium permanganate in benzene ("purple benzene"),[4] to stabilize diazonium salts,[5] and to bring

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Table I. Acylated Benzo Crown Ethers [a]

compd	method (solvent)	% yield[b]	mp, °C[c]
3	A (CH_2Cl_2)	0	
	B	63	95–96.5 (lit.[16] 96–97)
5	B	55	49–51
6	A (CH_2Cl_2)	50[d]	
7	A (CH_2Cl_2)	0	
	A (nitrobenzene)	0[e]	
	B	86	200–208
8	B	72	149–159 (174–182)
9	B	88	154–160 (169–179)
10	B	85	146–159
11	A (nitrobenzene	*d, e*	
12	A (nitrobenzene)	*d, e*	
13	A (nitrobenzene)	*d, e*	
	B	75	117–129
14	A (nitrobenzene)	*d, e*	
	B	71	123–127 (144–146)
15	B[g]	0	
	C	75	112–122
16	C	91	166–169 (175–180)
17	B	0[e]	
18	B	0[e]	
19	B	0[e]	
20	A (nitrobenzene)	85	150–160
21	A (CH_2Cl_2)	60	86–95[f]
	B	84	78–91[f]

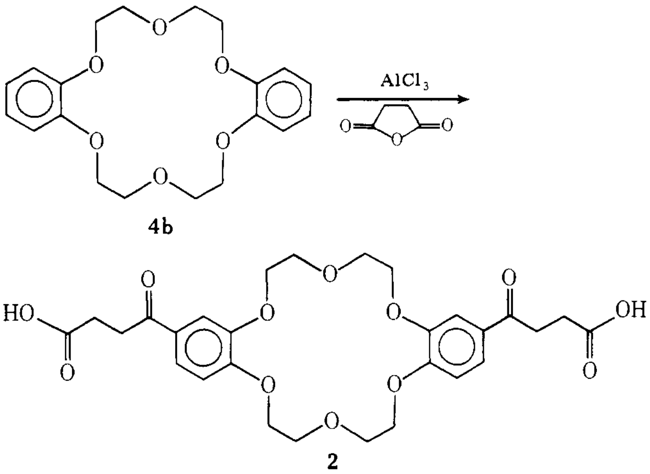
[a] Satisfactory analytical data (±0.4% for C, H) were reported for all new compounds. [b] No attempt was made to optimize yields. [c] In several cases, partial fractional crystallization occurred. The melting points of each fraction are reported. Satisfactory analytical data were reported on each fraction. [d] NMR and IR indicated only partial reaction. Products were not isolated and characterized. [e] The remainder of the product was polymeric. [f] The product of method A was recrystallized from ethyl acetate, while the product of method B was recrystallized from ethanol. The lower melting isomer is more soluble in ethyl acetate and was partially lost in the case of method A, resulting in a lower yield and higher melting point for this method. Satisfactory elemental analyses were obtained for both fractions, and the infrared and NMR spectra of both fractions were essentially identical. [g] Reaction was allowed to proceed for 5 days.

about the reaction of a variety of alkali metal salts with organohalides under very mild conditions. Successful catalysis has been reported with potassium phenoxides,[6] potassium phosphide,[7] potassium salts of protected amino acids,[8] potassium chromate,[9] and many others. Reviews of the catalytic reactivity of crown ethers in these and many other types of reactions have been published.[10] Crown ethers have also been demonstrated to facilitate the transport of alkali metal salts in liquid membrane cells.[11]

Considerable attention has been given to correlations between the size of the crown ether cavity, the diameter of the alkali metal cation, and binding constants of crown ethers with alkali metal cations as parameters affecting their catalytic activity.[3] For effective catalysis to occur, however, a reasonably stable ligand–cation complex must not only form, but must be soluble in the reaction medium. Landini and coworkers[12] have demonstrated that in two-phase systems dibenzo- and dicyclohexo-18-crown-6 are vastly superior to 18-crown-6 as catalysts. This is presumed to be due to the greater affinity of the more lipophilic crowns toward the organic reaction solvent. This is particularly significant in view of the lower binding constants of dibenzo-18-crown-6 with alkali metal cations. More recently, Cinquini, Tundo, and Montanari[13] have extended this work to show that 18-crown-6 and 1,10-diaza-18-crown-6 bearing large hydrocarbon substituents have catalytic activity dramatically higher than the parent crowns.

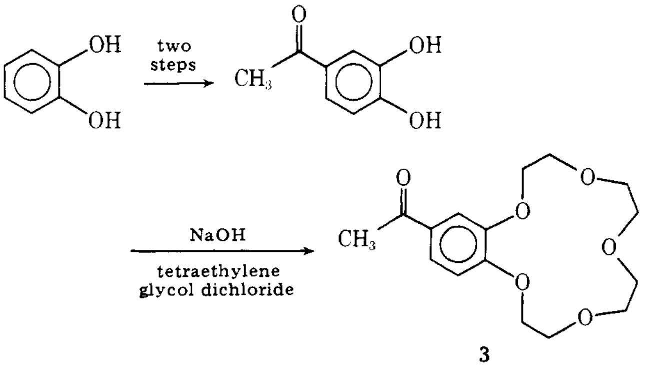
In our laboratories, we commenced a program to synthesize substituted benzo crown ethers because (1) dibenzo-18-crown-6 is readily prepared in high yield from inexpensive materials using simple techniques and (2) the aromatic rings in these compounds should be very reactive toward electrophilic substitution. Thus, a large number of variously substituted benzo crown ethers should be readily available from the single intermediate dibenzo-18-crown-6. It should also be noted that while dibenzo-18-crown-6 has rarely been used as a catalyst because of its lower solubility and lower binding constants for alkali cations, alkylated dibenzo-18-crown-6 compounds are reported to have binding constants for sodium ion nearly as high as those of 18-crown-6 for potassium ion[3] and much higher solubilities in common organic solvents.

A variety of methods have been developed for electrophilic acylation of reactive aromatic systems. Nearly all of these methods involve catalysis by Lewis acids such as aluminum chloride or boron trifluoride. In the case where the aromatic ring is fused to a crown ether, a potential difficulty is apparent. The Lewis acid catalyst and/or the reactive electrophilic intermediate may be complexed and consequently deactivated by the crown ether. Despite an earlier published suggestion that aluminum chloride should prove useful in the acetylation of dibenzo-18-crown-6,[14] our experience with this catalyst in the attempted acylation of dibenzo-18-crown-6 with succinic anhydride was negative. Recently, Ragsdale and Powell have made a preliminary report that this reaction can be carried out in moderate yield using mixed solvents, low temperature, and long reaction time (7 days); however, isolation of the product was complicated by complexation of the aluminum salt by the product.[15] The preparation of 4′-acetylbenzo-15-crown-5 (**3**), 2,3-(4′-acetylbenzo)-11,12-benzo-18-crown-6,



4b

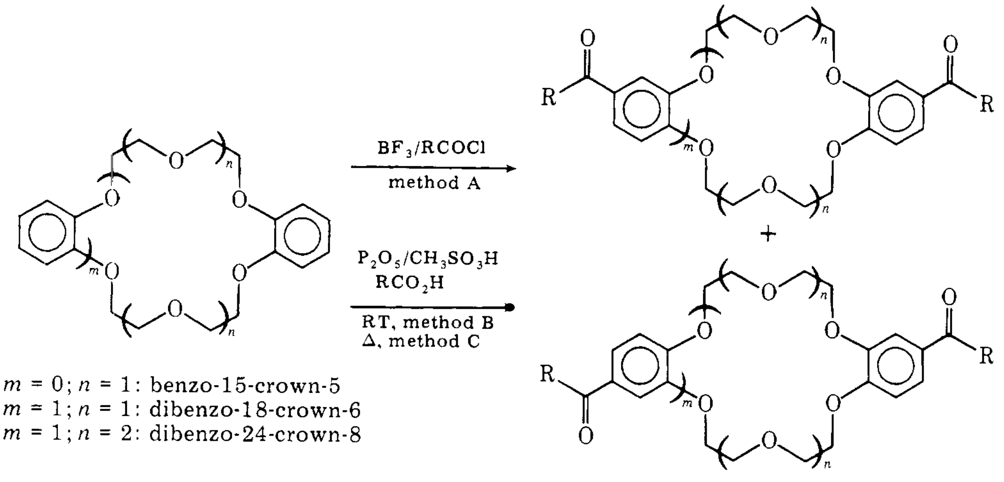
2



3

22% overall yield

Scheme I



4a, $m = 0$; $n = 1$: benzo-15-crown-5
b, $m = 1$; $n = 1$: dibenzo-18-crown-6
c, $m = 1$; $n = 2$: dibenzo-24-crown-8

3, $m = 0$; $n = 1$; R = CH_3
5, $m = 0$; $n = 1$; R = n-C_6H_{13}
6, $m = 0$; $n = 1$; R = n-C_9H_{19}
7, $m = 1$; $n = 1$; R = CH_3
8, $m = 1$; $n = 1$; R = n-C_3H_7
9, $m = 1$; $n = 1$; R = $(CH_3)_2CH$
10, $m = 1$; $n = 1$; R = $(CH_3)_3C$
11, $m = 1$; $n = 1$; R = n-C_6H_{13}
12, $m = 1$; $n = 1$; R = benzyl
13, $m = 1$; $n = 1$; R = n-C_9H_{19}
14, $m = 1$; $n = 1$; R = n-$C_{13}H_{27}$
15, $m = 1$; $n = 1$; R = n-$C_{17}H_{35}$
16, $m = 1$; $n = 1$; R = phenyl
17, $m = 1$; $n = 1$; R = $ClCH_2$
18, $m = 1$; $n = 1$; R = $BrCH_2CH_2$
19, $m = 1$; $n = 1$; R = CF_3
20, $m = 1$; $n = 2$; R = CH_3
21, $m = 1$; $n = 2$; R = n-C_9H_{19}

and 4′-acetylbenzo-18-crown-6 from 3′,4′-dihydroxyacetophenone by initial acetylation of catechol followed by cyclization with a bis(chloroethyl) ether to form the crowns has previously been reported.[16]

Due to our previous experiences with aluminum chloride catalized reactions, initial emphasis in this research centered on acylation of the crown ethers with acid chlorides using boron trifluoride as the Lewis acid catalyst (method A, Scheme I). This method proved useful for the acylation of dibenzo-24-crown-8 (i.e., **21**; see Table I) in chlorinated solvents; however, dibenzo-18-crown-6 could not be acylated with this catalyst. Benzo-15-crown-5 reacted slowly with large acid chlorides (i.e., **6**), but no product was obtained from the attempted preparation of 4′-acetylbenzo-15-crown-5 (**3**). In the latter case, a colorless crystalline product, unstable to air or water, was isolated. The material decomposed to the starting benzo-15-crown-5 in water. This unstable material could be a complex between the intermediate acylonium ion (**22**) and the crown ether which would be analogous to the well-known complex between acetonitrile (**23**) and 18-crown-6.[17]

$$\underset{\textbf{22}}{{}^{+}O{\equiv}C{-}CH_3} \qquad \underset{\textbf{23}}{N{\equiv}C{-}CH_3}$$

Several reactions were also carried out in nitrobenzene (**7**, **11–14**, and **20**). No insoluble complexes were observed in this solvent. Again, the acylation of dibenzo-24-crown-8 proceeded smoothly (i.e., **20**); however, this method proved unworkable for the acylation of dibenzo-18-crown-6. In most cases (**11–14**) the reaction products were rapidly converted to polymeric materials, and in the case of the attempted preparation of 2,3,11,12-bis[4′(5′)-acetylbenzo]-18-crown-6 (**7**) only black polymeric material was obtained. Treatment of dibenzo-18-crown-6 with boron trifluoride in nitrobenzene, but in the absence of acid chloride, returned starting material.

Polyphosphoric acid proved useful for the acylation of dibenzo-18-crown-6 with carboxylic acids when the reaction was carried out at room temperature; however, at higher temperatures white polymeric material was obtained. At room temperature, polyphosphoric acid is extremely difficult to handle; therefore, Eaton's reagent[18] (phosphorus pentoxide dissolved in anhydrous methanesulfonic acid) was substituted for it (method B). To minimize polymer formation, only the minimum amount of condensing agent which effected complete condensation was used. Use of this reagent readily afforded acylated benzo crown ethers with both linear and branched aliphatic substituents, ranging from two to ten carbons (**3**, **6–10**, **13**, and **21**; Table I). This method represents a significant improvement over the method of Smid and coworkers[16] in overall yield, number of steps, and ease of operation (see above). On the other hand, attempts to react halogenated aliphatic acids in this manner always yielded polymeric products (**17–19**).

Method B proved unworkable with larger aliphatic acids. The attempted preparation of 2,3,11,12-bis[4′(5′)-stearoylbenzo]-18-crown-6 (**15**) yielded only starting materials after a 5-day reaction time. Gently warming the reaction mixture (60–70 °C) for 15–20 min effected a complete conversion to the desired product (method C). The myristoyl and benzoyl derivatives of dibenzo-18-crown-6 (**14** and **16**) were prepared in similar fashion.

Diacylation of dibenzo crown ethers leads to two isomeric products, and it is of interest to note that the two isomers do not appear to cocrystallize. Although no deliberate attempt was made to separate the two isomers, partial fractional crystallization was observed in several cases (**8**, **9**, **14**, and **16**). The melting ranges of the mixed isomer products were broad. It was noted, however, that samples of the mixed isomers nearly always exhibited two distinct melting points rather than a continual broad melting range.

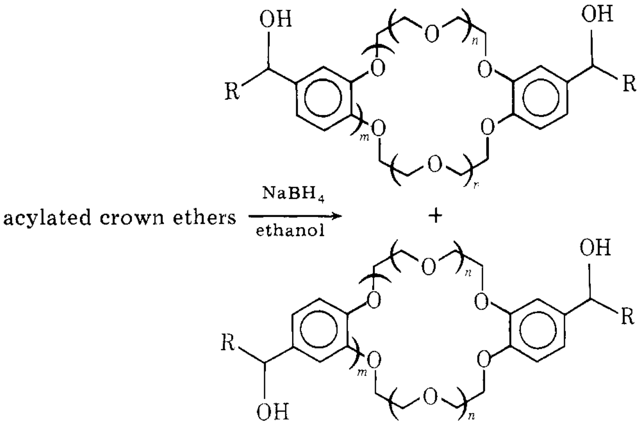
Several of the products obtained were also reduced to the corresponding alcohols in high yield.

These new alkanoyl- and α-hydroxyalkylbenzo crown ethers are being tested as solubilizers for potassium permanganate in chloroform and as transfer agents for potassium and sodium nitrate through a thick chloroform membrane. Work is currently under way to further modify the aliphatic side chains and screen the resulting products for activity in these tests. The potentially improved catalytic activity of these compounds is also being investigated at the present time.

Experimental Section

Equipment and Data. All melting points were obtained with a Thomas-Hoover Unimelt capillary melting point apparatus and are uncorrected. All infrared spectra were obtained with a Beckman

Table II. α-Hydroxyalkylbenzo Crown Ethers [a]



24, $m = 0$; $n = 1$; R = $n\text{-}C_6H_{13}$
25, $m = 1$; $n = 1$; R = CH_3
26, $m = 1$; $n = 1$; R = $n\text{-}C_9H_{19}$
27, $m = 1$; $n = 1$; R = $n\text{-}C_{13}H_{27}$
28, $m = 1$; $n = 2$; R = CH_3
29, $m = 1$; $n = 2$; R = $n\text{-}C_9H_{19}$

compd	% yield	mp, °C
24	92	oil
25	84	164–167
26	100	120–122 (132–143)
27	100	111–117
28	89	oil
29	75	88–92

[a] Satisfactory analytical data (±0.4% for C, H) were reported for all compounds.

Acculab I, and all NMR spectra were obtained with a Varian EM 390 spectrophotometer. Molecular weights were determined by vapor phase osmometry in chloroform using an Hitachi Perkin-Elmer 115 molecular weight apparatus. All elemental analyses were performed by M-H-W Laboratories, Phoenix, Ariz.

Explicit details of each preparation are not supplied. For yields and melting point data, refer to Tables I and II. Explicit details of preparations which are representative of each of the methods discussed and of specific types of results cited in this paper are presented below.

Preparation and Standardization of the Condensing Agent for Use in Method B. A mixture of 83 g of phosphorus pentoxide and 695 mL (1030 g) of methanesulfonic acid, anhydrous (Pennwalt), was stirred until all of the solids were dissolved (about 36 h). A mixture of 3.6 g (0.01 mol) of dibenzo-18-crown-6, 1.2 g (0.02 mol) of acetic acid, and 13 g of the condensing agent was stirred for 6 h. The reaction mixture was worked up in the usual manner (vide infra, method B). The NMR spectrum of the crude product indicated that 50% reaction had occured. It was therefore assumed that 13 g of condensing agent was required to bring about the condensation of 0.01 mol of carboxylic acid, and this figure was used in determining the optimum amount of condensing agent to use in all subsequent reactions.

Attempted Preparation of 4′-Acetylbenzo-15-crown-5 (3): Method A. A mixture of 5 g (0.0185 mol) of benzo-15-crown-5 and 1.6 g (0.0210 mol) of acetyl chloride was dissolved in 50 mL of methylene chloride and saturated with boron trifluoride. Within a few minutes the solution turned red-brown, and after 30 min a red-brown layer separated (lower). After 4 h, boron trifluoride addition was discontinued and the mixture was stirred vigorously for 12 h. Samples were taken from each layer and treated with water. Infrared spectra of both samples indicated that no reaction occurred. After standing for 72 h, colorless leafy crystals formed in the lower layer. These decomposed rapidly to a gummy purple powder on standing in air. Treatment with water, extraction into methylene chloride, and evaporation of the solvent yielded benzo-15-crown-5 (**4a**), which was identified by its infrared spectrum. Repetition of the attempted synthesis in refluxing dichloroethane yielded an intractable black tar.

Method B. A mixture of 5.4 g (0.02 mol) of benzo-15-crown-5 (**4a**) and 1.3 g (0.022 mol) of acetic acid was dissolved in 27 g of condensing agent and stirred at room temperature for 6 h. The reaction mixture slowly turned dark red. It was poured into 100 mL of water, neutralized with sodium bicarbonate, and extracted three times with 50 mL of methylene chloride. The organic extracts were combined, washed with water, dried over sodium sulfate, and evaporated to yield 4.6 g (74%) of a gummy, light gray solid. Recrystallization from hexane yielded 3.9 g (63%) of fluffy white crystals, mp 95–96.5 °C (lit.[17] mp 96–97 °C).

2,3,11,12-Bis[4′(5′)-acetylbenzo]-24-crown-8 (20): Method A. A mixture of 4.5 g (0.01 mol) of dibenzo-24-crown-8 and 2 g (0.025 mol) of acetyl chloride was dissolved in 50 mL of nitrobenzene. The solution was saturated with boron trifluoride and stirred overnight. The reaction mixture was poured into 1 L of *n*-hexane, and the minimum amount of benzene required to make the two solvents miscible was added. The solution was allowed to stand overnight, and the sticky, dark brown product which had precipitated was removed by decanting away the solvent. The material was triturated with hot hexane to yield 5.7 g (100%) of a tan powder which retained the odor of nitrobenzene. The product was dissolved in a minimum of refluxing benzene, and the hot solution was decanted from the tarry residue. The product was precipitated from the cooled benzene solution by the addition of an equal volume of *n*-hexane to give 4.5 g (85%) of a light yellow powder, mp 150–160 °C. Anal. Calcd for $C_{28}H_{36}O_{10}$: C, 63.14; H, 6.81; M_r 532. Found: C, 63.33; H, 6.72; M_r 509.

2,3,11,12-Bis[4′(5′)-decanoylbenzo]-18-crown-6 (13): Method B. A mixture of 3.6 g (0.01 mol) of dibenzo-18-crown-6, 3.5 g (0.02 mol) of decanoic acid, and 27 g of condensing agent was stirred for 4.5 h at room temperature, during which time the reaction mixture turned cherry red. After pouring the mixture onto 50 g of ice, an equal volume of water was added and the mixture was stirred overnight. The crude tan product was removed by filtration, dissolved in 75 mL of methylene chloride, and washed four times with dilute sodium hydroxide solution and then repeatedly with water. The organic phase was separated and dried over anhydrous sodium sulfate. Evaporation of the solvent gave 6.1 g (92%) of light tan product, mp 117–129 °C. The product was recrystallized from 250 mL of boiling ethanol to yield 5.0 g (74%) of gelatinous meterial which dried to a light yellow powder. It was observed that approximately 50% of the sample melted from 117 to 119.5 °C. The remainder melted between 127 and 129 °C, with no melting being observed between 117 and 127 °C. Anal. Calcd for $C_{40}H_{60}O_8$: C, 71.82; H, 9.04; M_r 669. Found: C, 71.60; H, 9.21; M_r 675.

2,3,11,12-Bis[4′(5′)-myristoylbenzo]-18-crown-6 (14): Method C. A mixture of 3.6 g (0.01 mol) of dibenzo-18-crown-6, 4.6 g (0.02 mol) of myristic acid, and 27 g of condensing agent was stirred at room temperature for 48 h. The reaction mixture slowly turned dark cherry red. The infrared spectrum of a sample removed from the reaction showed only a small band at 1675 cm^{-1} and a substantial band at 740 cm^{-1} (four adjacent aromatic hydrogens), indicating that only slight reaction occurred. The reaction mixture was warmed to 60 °C in a water bath and maintained at this temperatue for 20 min. The infrared spectrum of a sample removed from the reaction showed no band at 740 cm^{-1}. The reaction mixture was worked up in the same manner as **13**. The crude yellow product (6 g, 75% yield) was heated in 100 mL of boiling ethyl acetate, and 1.46 g of white insoluble material was removed by filtration (fraction A), mp 144–146 °C. The infrared spectrum showed two carbonyl bands at 1680 and 1663 cm^{-1}. The ethyl acetate solution was decolorized with Norit A, filtered, and cooled to give a gelatinous precipitate which was difficult to filter. There was thus obtained 4.1 g of a light tan product (fraction B), mp 123–127 °C. The infrared spectrum showed only one carbonyl band at 1680 cm^{-1}. Both fractions had identical NMR spectra and are presumed to be isomers. The overall yield of both fractions was 5.46 g (71%). Anal. Calcd for $C_{48}H_{76}O_8$: C, 73.80; H, 9.81. Found (fraction A): C, 73.63; H, 9.90. Found (fraction B): C, 73.64; H, 9.87.

2,3,11,12-Bis[4′(5′)-(1″-hydroxydecyl)benzo]-18-crown-6 (29). An excess of sodium borohydride was carefully added to a stirred slurry of 16.5 g of **21** in 200 mL of ethanol. The mixture was stirred for 3 h at room temperature and then for 30 min at 50 °C. The solution was filtered to remove a fluffy inorganic precipitate, neutralized with dilute sulfuric acid, and combined with 300 mL of methylene chloride. The organic solution was washed four times with 150 mL of water, dried over sodium sulfate, and evaporated. The waxy cream-colored product was triturated with a minimum of acetone, filtered, and washed with cold ethanol to yield 12.4 g (75%) of a white powder: mp 88–92 °C; IR 3985, 2936, 2881, 2860, 1515, 1271, 1238, 1150, and 1137 cm^{-1}. Anal. Calcd for $C_{44}H_{72}O_{10}$: C, 69.44; H, 9.54. Found: C, 69.06; H, 9.75.

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Registry No.—**3**, 41757-95-3; **4a,** 14098-44-3; **4b,** 14187-32-7; **4c,** 14174-09-5; **5,** 67722-63-8; **6,** 67722-64-9; **7** isomer 1, 67722-65-0; **7** isomer 2, 67722-66-1; **8** isomer 1, 67722-67-2; **8** isomer 2, 67722-68-3; **9** isomer 1, 67722-69-4; **9** isomer 2, 67722-70-7; **10** isomer 1, 67722-71-8; **10** isomer 2, 67722-72-9; **13** isomer 1, 67722-73-0; **13** isomer 2, 67722-74-1; **14** isomer 1, 67722-75-2; **14** isomer 2, 67722-76-3; **15** isomer 1, 67722-77-4; **15** isomer 2, 67722-78-5; **16** isomer 1, 67722-79-6; **16** isomer 2, 67722-80-9; **20** isomer 1, 67722-81-0; **20** isomer 2, 67722 82-1; **21** isomer 1, 67722-83-2; **21** isomer 2, 67722-84-3; **24,** 67722-85-4; **25** isomer 1, 67722-86-5; **25** isomer 2, 67722-87-6; **26** isomer 1, 67722-88-7; **26** isomer 2, 67722-89-8; **27** isomer 1, 67722-90-1; **27** isomer 2, 67722-91-2; **28** isomer 1, 67722-92-3; **28** isomer 2, 67722-93-4; **29** isomer 1, 67722-94-5; **29** isomer 2, 67722-95-6; acetyl chloride, 75-36-5; heptadecanoyl chloride, 2528-61-2; decanoyl chloride, 112-13-0; butanoyl chloride, 141-75-3; 2-methylpropanoyl chloride, 79-30-1; 2,2-dimethylpropanoyl chloride, 3282-30-2; benzeneacetyl chloride, 103-80-0; myristoyl chloride, 112-64-1; stearoyl chloride, 112-76-5; benzoyl chloride, 98-88-4; chloroacetyl chloride, 79-04-9; 3-bromopropanoyl chloride, 15486-96-1; trifluoroacetyl chloride, 354-32-5.

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Model Studies of the Thioindigo Chromophore

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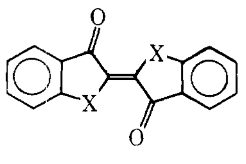
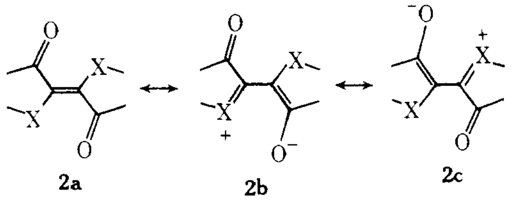
X-ray diffraction methods have been used to study the crystal structures of *trans*-$\Delta^{2,2'}$-bis(4,4-dimethylthiolan-3-one) (**4**) and *trans*-3,4-bis(methylthio)-3-hexene-2,5-dione (**6**) as model compounds for the thioindigo chromophore. The central region of the thiolanone molecule (**4**) and the upper $SC{=}CC{=}O$ half of **6** are reasonably planar, but $CH_3...CH_3$ nonbonded interactions have produced considerable out-of-plane distortions of the $CH_3C{=}O$ and CH_3S groups in the lower part of **6.** Bond lengths reflect some conjugative interactions, but involvement of the $C{=}O$ groups is small. It is concluded that the extent of merocyanine-like interactions between sulfur and oxygen (viz., $SC{=}CC{=}O \leftrightarrow S^+{=}CC{=}CO^-$) is small and that the ground state structure can be represented best as a hybrid of structures $SC{=}CC{=}O \leftrightarrow {}^+S{=}CC^-C{=}O$.

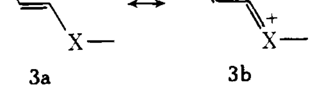
Since the elucidation of the structure of indigo (**1a**) and its synthesis,[1] there has been considerable interest in the relationship between molecular (and electronic) structure and color in the class of compounds **1a–d.** Theories advanced on the relationship between structure and color[2] generally were unable to rationalize how the deep color of the indigo dyes is related to the relatively compact mesomeric system. Klessinger and Luttke,[4] however, have shown with HMO and PPP calculations that the 10 π-electron system embodied in **2** should have the same spectroscopic properties as the indigo dyes. According to their work, the ground state electronic structures of the indigos can be represented as a resonance hybrid of canonical forms **2a–c,** similar to the merocyanines (**3**).[5] Accordingly, removal of the benzene rings in **1** should not change the basic characteristics of the electronic transitions and other properties typical of the indigos. This idea has been tested by the synthesis of **4**,[6] which has the same planar configuration as the thioindigo chromophore. The compound has similar chemical properties to thioindigo (**1b**),[6-8] and the long



1a, X = NH; λ_{max} 588 nm
b, X = S; λ_{max} 541 nm
c, X = Se; λ_{max} 558 nm
d, X = O; λ_{max} 410 nm



2a **2b** **2c**



3a **3b**

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