carboxylate, 52917-64-3; butyl bicyclo[4.1.0]heptane-7-carboxylate, 61452-50-4; ethyl bicyclo[6.1.0]nonane-9-carboxylate, 72258-12-9; 4-(ethoxycarbonyl)tricyclo[4.4.0.0^{3,5}]decane, 72258-13-0; 3-(ethoxycarbonyl)tricyclo[3.2.1.0^{2,4}]octane, 72258-14-1; ethyl 2-acetoxycyclopropanecarboxylate, 72229-07-3; 7-(ethoxycarbonyl)-2-oxabicyclo[4.1.0]hexane, 72229-08-4; ethyl 2-(1-propenyl)cyclopropanecarboxylate, 16783-15-6; ethyl 2-ethenyl-3-methylcyclopropanecarboxylate, 51607-42-2; ethyl 2-ethenyl-2-methylcyclopropanecarboxylate, 21304-31-4; ethyl 2-(1-methylethenyl)cyclopropanecarboxylate, 18864-65-8; ethyl 2-(3-butenyl)cyclopropanecarboxylate, 61452-53-7; 7-(ethoxycarbonyl)bicyclo[4.1.0]hept-2-ene, 61452-52-6; 7-(ethoxycarbonyl)bicyclo[6.1.0]non-4-ene, 59891-06-4; 3-(ethoxycarbonyl)tricyclo[3.2.1.0^{2,4}]oct-6-ene, 59811-70-0; 1-octene, 111-66-0; 1-hexyne, 693-02-7; methyl 2-hexylcyclopropanecarboxylate, 72229-09-5; ethyl 2-decylcyclopropanecarboxylate, 15898-93-8; methyl 2-butyl-2-cyclopropenecarboxylate, 67500-40-7.

Study of the Electrochromism of Methoxyfluorene Compounds

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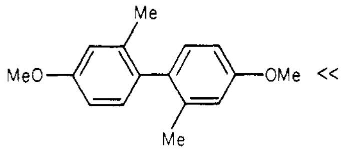
The electrochemical and electrochromic properties of a variety of polysubstituted fluorene compounds have been studied. The 2,7- and 2,3-dimethoxy-, 2,3,6,7-tetramethoxy-, and 2,3,4,5,6,7-hexamethoxyfluorenes are highly reversible electrochromic materials. One-electron oxidation of these materials yields deeply colored, stable radical cations. The structure–property relationships observed for the electrochemical and absorption behavior of these materials are discussed.

Electrochromism, a reversible optical absorption change induced in a material by an applied electric field or current, has been observed in a relatively large number of organic and inorganic substances.[1] In general, widespread applications have not been realized due to a variety of material problems, including poor electrochemical nucleic; between the colored and colorless states, low optical efficiencies, electrode incompatibilities, etc. However, increasing technological demands (e.g., low-power, nonemissive information displays) prompt the need for highly reversible, optically efficient electrochromic materials. The ultimate development of these systems will require better understanding of the relationships of molecular structure to the electrochemical and electrochromic behavior of materials. In the present study we describe these properties for a new class of organic electrochromic materials, namely, the polymethoxylated fluorenes.

In a series of papers describing the oxidation of methoxybiphenyls and related compounds,[2-5] Parker and coworkers noted the unusual stability of the corresponding radical cations and dications. They observed a direct relationship between the stability of the oxidation products and the planarity of the aromatic nuclei; e.g., the relative stabilities of the radical cations of compounds **1**–**3**, were found to be as shown. Of interest for the present study, the radical cation of the methylene-bridged biphenyl **3** was reportedly a deep blue color and displayed a half-life of approximately 6 h in nitrobenzene solution.[2] These observations prompted us to investigate further the electrochromism of bridged biphenyl compounds.

Results and Discussion

Important structures for subsequent discussion are either indicated as shown or are in Table I.



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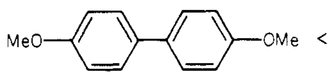

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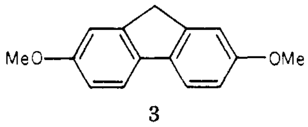

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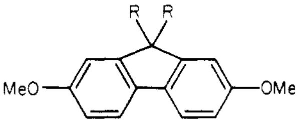

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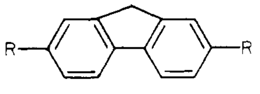
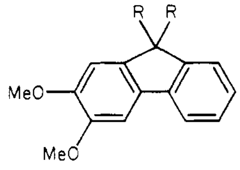
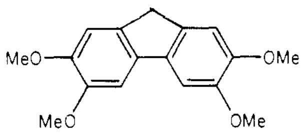
4, R = Me



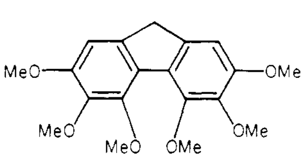
5, R = NH_2
6, R = O_2CCH_3
7, R = OCH_2Ph



12, R = H
13, R = Me



14



15

Cyclic Voltammetry Data. The previous reports of Parker et al.[2-5] established the ability of methoxy substituents to stabilize the oxidation products of fluorene materials. We have extended these studies to a variety of

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(1) I. F. Chang, B. L. Gilbert, and T. I. Sun, *J. Electrochem. Soc.*, **122**, 955 (1975).

(2) A. Ronlân, J. Coleman, O. Hammerlich, and V. D. Parker, *J. Am. Chem. Soc.*, **96**, 845 (1974).

(3) A. Ronlân, O. Hammerlich, and V. D. Parker, *J. Am. Chem. Soc.*, **95**, 7132 (1973).

(4) A. Ronlân and V. D. Parker, *J. Chem. Soc., Chem. Commun.*, 33 (1974).

(5) A. Nilsson, U. Palmquist, A. Ronlân, and V. D. Parker, *J. Am. Chem. Soc.*, **97**, 3540 (1975).

0022-3263/80/1945-0702$01.00/0

Table I. Voltammetric Oxidation of Substituted Fluorenes[a]

compd	E_{Pa}^{1} [c]	E_{Pc}^{1} [c]	E_{Pa}^{2} [c]	E_{Pc}^{2} [c]	ΔE, mV[d]	reversibility,[f] %
3	0.91	0.79	1.41	1.28	500	99 (30[b])
4	0.96	0.84	1.50	1.36	540	99 (70[b])
5[b]	0.43	0.37	0.72	0.65	290	92
6[b]	1.66[e]		2.14[e]			
7	1.14	1.08	1.48[e]		340	
8[g]	0.96[e]					
9[h]	1.54[e]					
10[i]	1.23[e]					
11[j]	1.34[e]					
12	0.90	0.81	1.52[e]		620	99
13	1.04	0.92	1.66[e]		620	99
14	0.76	0.65	1.25	1.15	490	99
15	0.87	0.81	1.22	1.16	350	99

[a] Unless otherwise noted 1.0 mM in CH_2Cl_2/TFAn/TFA (95:2.5:2.5) containing n-Bu_4NBF_4 (0.1 M). [b] 1.0 mM in MeCN containing n-Bu_4NBF_4 (0.1 M). [c] In volts vs. the aqueous saturated calomel electrode, measured at a sweep rate of 200 mV/s. [d] $E_{Pa}^{1} = E_{Pa}^{2} = \Delta E$. [e] No reverse peak. [f] $(Q_{redn}/Q_{oxidn})100$. [g] 4-Azafluorene. [h] 1-Methoxyfluorene. [i] 2-Methoxyfluorene. [j] 4-Methoxyfluorene.

substituents and substitution patterns to determine the key structural unit(s) required for the desired electrochemical stability. Our results of cyclic voltammetric (CV) measurements for a number of substituted fluorenes are summarized in Table I. Irreversible cyclic voltammograms were observed for the parent unsubstituted fluorene as well as for the acetoxy and aza derivatives **6** and **8**, respectively. The monomethoxyfluorenes **9**–**11** also displayed irreversible oxidations, suggesting that a minimum of two such substituents are necessary for stabilization of the radical cation. The dimethoxy derivatives **3**, **4**, **12**, and **13**, the diamino derivative **5**, the bis(benzyloxy) derivative **7** and the tetra- and hexamethoxy derivatives **14** and **15** undergo reversible or quasi-reversible one-electron oxidations at a sweep rate of 200 mV/s. In several cases the peak separations for the anodic and cathodic processes ($E_{Pa}^{1} - E_{Pc}^{1}$) deviated from the theoretical 60 mV for reversible electrochemical reaction; however, the ratio of peak currents was in all cases approximately 1. A second reversible or quasi-reversible one-electron oxidation peak was observed only for compounds **3**, **4**, **5**, **14**, and **15**. It should be noted that the reversible two-electron process could be observed for compounds **3**, **4**, **14**, and **15** only when the system was rigorously anhydrous (e.g., employing trifluoroacetic anhydride as a water scavenger).[6]

The peak potentials of the first oxidation (E_{Pa}^{1}) for the monomethoxy analogues **9**–**11** confirm that electron-donating substituents located ortho or para to the biphenyl linkage are more effective at reducing the oxidation potential than a meta substituent. As shown by compounds **3** and **10** the two para substituents exert a greater electron-donating influence than one (i.e., E_{Pa}^{1} of 0.91 and 1.23 V, respectively). A surprisingly low E_{Pa}^{1} value of 0.90 V was observed for the meta,para-substituted analogue **12**, comparable, in fact, to that observed for the para,para derivative **3** (0.91 V). The electron-donating influence is further manifested in the low oxidation potential of the tetramethoxy compound **14**. This trend is reversed, however, for the hexamethoxyfluorene **15** for which E_{Pa}^{1} was approximately 110 mV higher than that for the tetramethoxy compound **14**. This may be a result of the distortion from planarity which results from steric crowding of the methoxy substituents in **15**, thus reducing their donating ability.

Table II. Electronic Absorption Spectral Data[a]

cation radical of	λ_{max}, nm	ϵ, L cm^{-1} mol^{-1}	rel optical efficiency[c]
3	385	20 400	1
	400	31 200	
	411	40 400	
	690	16 000	
	758	20 800	
4	385	32 800	1.2
	695	18 400	
	760	24 800	
5[b]	360	16 800	
	609	11 000	
	820	13 800	
12	600	6 200	0.2
13	597	11 300	0.3
14	412	11 600	0.08
	612	3 100	
15	415	44 300	1.1
	635	20 100	
	688	28 000	
2	415	21 000	
	425	23 500	
	732	12 500	
	804	21 000	

[a] Unless otherwise indicated CH_2Cl_2:TFAn:TFA (95:2.5:2.5). [b] MeCN. [c] See text for explanation.

Coulometry Data. Having determined the cyclic voltammetric reversibilities of the polymethoxyfluorenes, we utilized coulometric measurements to study the stability of the fluorene radical cations on longer time scales. A 1 mM solution of the electrochromic material in a preelectrolyzed solvent was electrolyzed at a constant potential (120 mV more anodic than E_{Pa}^{1}) for a time sufficient to oxidize approximately 80% of the material. The darkly colored solution was kept for approximately 10 min and the electrolysis then reversed. Reversibility was computed as the $(Q_{redn}/Q_{oxidn})100$ averaged over repeated cycles. As indicated in Table I, reversibilities of greater than 99% were determined for the methoxy fluorene derivatives **3**, **4**, and **12**–**15** in CH_2Cl_2/trifluoroacetic anhydride/trifluoroacetic acid (95:2.5:2.5). For comparison, the well-known electrochromic material heptylviologen[1] yields electrochemical reversibilities of 80–85% (H_2O, CH_3CN) in a similar examination. A 92% reversibility was obtained for the diaminofluorene **5** measured in CH_3CN. The coulometric reversibilities measured for the methoxyfluorenes were sensitive to the presence of water. For example, a reversibility of approximately 30% was obtained for compound **3** in wet acetonitrile compared to a value of 95% obtained under anhydrous conditions. The role of the benzylic hydrogens of the fluorene nucleus in the decomposition pathways is suggested by the data for the 2,7-dimethoxyfluorene (**3**) and its 9,9-dimethyl analogue **4**. Coulometric reversibilities of approximately 30% are observed for the methylene-bridged compound **3** in wet CH_3CN compared to a value of greater than 70% for the geminally substituted derivative **4**.

Electronic Absorption Data. The electronic absorption spectral data for the radical cations of the substituted fluorenes are given in Table II. In bulk electrolysis experiments of 1 mM solutions, all of the materials display the persistent deep blue coloration of the radical cations. No change in the absorbance at λ_{max} for compounds **3**, **4**, and **12**–**15** was observed for periods of several hours. This is consistent with the radical cation stabilities determined

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(6) O. Hammerlich and V. D. Parker, *Electrochim. Acta*, 18, 537 (1973).

by coulometry. Closer inspection of the data in Table II indicates a strong structure dependence of both the absorption maxima and the extinction coefficients for the colored species.

Structure–property relationships for color in organic molecules have been the topic of extensive discussion.[7] It is well-known that in neutral species the introduction of methoxy substituents in direct conjugation with the main chromophores of the organic compound results in a dramatic bathochromic shift of the long-wavelength absorption band. Similar behavior has been observed for the radical cation species in the present study. An interesting comparison is made between the radical cation of 2,7-dimethoxyfluorene (**3**) and the unbridged analogue 4,4′-dimethoxybiphenyl (**2**). A hypsochromic shift of the lowest energy absorption bands is observed on forcing the coplanarity of the two rings via the methylene bridge of **3** (804 and 732 nm for **2** vs. 758 and 690 nm for **3**) while the intensities of the absorptions do not vary appreciably. Comparison of the 2,7-diamino compound **5** and the dimethoxy analogue **3** indicates the expected bathochromic shift for the stronger electron-donating substituent (820 vs. 758 nm) and a significant lowering of the absorption intensity. Compared to the 2,7-dimethoxy derivative **3** [758 nm (ϵ 20800)], the 2,3-dimethoxyfluorene (**12**) and 2,3,6,7-tetramethoxyfluorene (**14**) radical cations are both strongly blue-shifted [600 nm (ϵ 6200) and 612 nm (ϵ 3100), respectively], and the extinction coefficients are dramatically reduced. These effects are presumed due to the influence of the meta methoxy groups. Consistent with this conclusion is the somewhat reduced shift observed for the hexamethoxy derivative **15** [688 nm (ϵ 28000)] in which two additional ortho substituents are present. As expected, the substitution of geminal methyl groups at the fluorene bridge position had no effect on the position of the absorption maxima; however, an increase of approximately 5000 in the extinction coefficient of the lowest energy absorption was observed (e.g., **3** vs. **4** and **12** vs. **13**).

Optical Efficiency Data. A key issue in the evaluation of electrochromic materials is the optical efficiency (i.e., optical density per coulomb). In Table II the relative optical efficiencies of the methoxy fluorenes are given. The values were obtained from a comparison of the total area under the absorption curves in the visible region at a constant concentration of the radical cation. The values have been normalized to 2,7-dimethoxyfluorene (**3**). A striking structure–efficiency relationship is evident from the data. The meta effects noted earlier, i.e., hypsochromic shift of the long-wavelength absorption and reduction in extinction coefficient, result in a dramatic reduction in optical efficiency for compounds **12–14**.

Conclusion

The electrochromism of methoxy-substituted fluorenes has been extensively investigated. The polymethoxy derivatives **3**, **4**, and **12–15** are highly reversible electrochromic materials. A strong dependence of the optical properties on substitution pattern was observed such that high optical efficiencies were observed for compounds **3**, **4**, and **15** and significantly lower values for **12–14**.

Experimental Section

Standard equipment and techniques were employed in the electrochemical experiments described. Electrolyses were carried out in a divided cell to avoid contributions of radical anions to the absorption spectra. All melting points are uncorrected. Microanalyses were carried out by Childers Laboratories. NMR spectra were recorded on a Varian HA-100 spectrometer using tetramethylsilane as an internal standard. Electron-impact mass spectra were obtained at 70 eV by using an AEI MS-30 spectrometer. Reagent-grade solvents were purified by being passed through neutral alumina (Woelm W-200) prior to electrochemical analyses. Trifluoroacetic acid and anhydride were used as purchased. Compounds **8** (Aldrich), **9** (Chemical Procurement Labs), and **11** (Pfaltz and Bauer, Inc.) were obtained from commercial sources. Compounds **6**, **7**, and **10** were prepared by standard procedures from 2,7-dihydroxyfluorenone (Ash Stevens Inc.) and 2-hydroxyfluorene (Chemical Procurement Labs).

2,7-Dimethoxyfluorene (3). 2,7-Dihydroxyfluorenone (5 g, 23.5 mmol), *p*-toluenesulfonic acid (1 g), and 10% Pd/C (1 g) in ethanol (250 mL) were shaken under 50 psi of hydrogen overnight. The reaction mixture was hot filtered through Celite and the filtrate evaporated to dryness. The resulting solids were dissolved in ethyl acetate, and the organic layer was washed with water, dried, and concentrated. The crude product was dissolved in dimethyl sulfoxide containing 2mL of a 50% aqueous NaOH solution. Dimethyl sulfate (8 g) was added dropwise, keeping the temperature below 10 °C with ice cooling. After 15 min the reaction was poured into water, and the solids were removed. Recrystallization from acetone gives the desired product: 3.4 g (64%); mp 166–167 °C (lit.[3] mp 168–168.5 °C).

2,7-Dimethoxy-9,9-dimethylfluorene (4). 2,7-Dimethoxyfluorene (1 g, 4.4 mmol) and diisopropylamine (8 mL) in dry tetrahydrofuran (20 mL) were reacted at −78 °C with 1 equiv of *n*-butyllithium. The solution was warmed to −30 °C for several minutes, cooled to −78 °C, and further reacted with 1 equiv of methyl iodide. The butyllithium/methyl iodide sequence was repeated once more. Standard workup, followed by preparative-layer chromatography (hexane/ethyl acetate, 9:1), gave the 9,9-dimethyl derivative: 0.65 g (58%); mp 85–86.5 °C; NMR ($CDCl_3$) δ 1.45 (3 H, s), 3.90 (3 H, s), 6.74 (H_3, dd, $J_{3,4} = 9$ Hz, $J_{1,3} = 2$ Hz), 6.91 (H_1, d, $J_{1,3} = 2$ Hz), 7.40 (H_4, d, $J_{3,4} = 9$ Hz); mass spectrum, *m/e* 254 (M^+). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.39; H, 7.91.

2,3-Dimethoxyfluorene (12). Toluenesulfonanthranilic acid[6] (15 g, 51 mmol) was dissolved in carbon disulfide (300 mL), and phosphorus pentachloride (12 g, 57 mmol) was added slowly. The stirred mixture was heated at 50 °C for 30 min and then cooled to 20 °C. Veratrole (21.7 g, 0.16 mol) was added followed by portionwise addition of aluminum chloride (12 g, 0.09 mol), maintaining the temperature below 25 °C.[8] After being heated at reflux for 4 h, the mixture was poured into water and extracted with chloroform. The dried extracts were concentrated, and the residue was recrystallized from ethanol. The mixture of dimethoxy-2′-toluenesulfamidobenzophenones was obtained in 95% yield: NMR ($CDCl_3$) δ 2.20 (3 H, s), 3.82 (3 H, s), 3.92 (3 H, s), 7.15 (11 H, m), 9.5 (1 H, br s). The mixture (5.0 g, 12.3 mmol) was dissolved in a 1:1 solution of acetic acid and sulfuric acid (20 mL) and heated on a steam bath until small aliquots remained clear upon addition of water. Water (15 mL) was added and the hot solution filtered. A 6% aqueous sodium nitrite solution (15 mL) was added and the mixture heated until the vigorous nitrogen evolution ceased.[9] Extraction of the aqueous solution with ether and evaporation of the ether gave a residue which was heated with 10% aqueous sodium hydroxide (25 mL). Reextraction with ether, drying, and evaporation gave a crude mixture. Column chromatography (hexane/ethyl acetate, 4:1) resulted in 0.4 g (13%) of a mixture of 1,2- and 3,4-dimethoxyfluorenone (assignment based on ^1H NMR) and 1.95 g (66%) of 2,3-dimethoxyfluorenone: mp 156–157 °C; NMR ($CDCl_3$) δ 3.80 (3 H, s), 3.90 (3 H, s), 6.80 (1 H, s), 7.0 (1 H, s), 7.21 (4 H, m). 2,3-Dimethoxyfluorenone was reduced by using the procedure described for preparation of **3**. The product, 2,3-dimethoxyfluorene (**12**), was recrystallized from ethanol: mp 161–162 °C; NMR ($CDCl_3$) δ 3.82 (2 H, s), 3.95 (3 H, s), 4.05 (3 H, s), 7.10 (1 H, s), 7.30 (5 H, m). Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.81; H, 6.28. Found: C, 79.65; H, 6.19.

2,3-Dimethoxy-9,9-dimethylfluorene (13). The conversion of **12** into **13** was performed as described for the preparation of

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(7) J. Griffiths, "Colour and Constitution of Organic Molecules", Academic Press, London, 1976.

(8) H. J. Scherfele, Jr., and D. F. Detar, "Organic Syntheses", Collect. Vol. IV, Wiley, New York, 1963, p 34.

(9) F. Ullman and H. Bleir, *Chem. Ber.*, **35**, 4279 (1902).

compound 3. The product was recrystallized from ethanol: mp 143–145 °C; NMR ($CDCl_3$) δ 1.40 (6 H, s), 3.85 (6 H, s), 6.80 (1 H, s), 7.20 (5 H, m). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.09. Found: C, 80.15; H, 7.25.

2,3,6,7-Tetramethoxyfluorene (14). 6-Bromoveratraldehyde (2.45 g, 0.01 mol) was heated with copper powder (2.5 g) at 220 °C for 16 h. The chloroform solubles were purified by chromatography (hexane/ethyl acetate, 5:1). Minor amounts of tetramethoxy dialdehyde coupling product were eluted first followed by 2,3,6,7-tetramethoxyfluorenone as a red-orange solid: mp 206–207 °C (lit. mp 207–208.5,[8] 203 °C[10]). Reduction as before gave 2,3,6,7-tetramethoxyfluorene (14) (recrystallization from ethanol): mp 193–194 °C (lit.[11] mp 196 °C). Anal. Calcd for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34. Found: C, 71.05; H, 6.21.

2,3,4,5,6,7-Hexamethoxyfluorene (15). 2,3,4,5,6,7-Hexamethoxyphenanthrene[12] (1.92 g, 5.4 mmol) in dioxane/water (9:1, 10 mL) was mixed with osmium tetraoxide in dioxane (2 mL of a 20 mg/mL standard solution). The reaction was heated at 50 °C for 1 h, and then sodium periodate (1.5 g) was added in portions over a period of 2 h. Heating at 50 °C was continued for 48 h. The cooled reaction mixture was extracted with ether and the extract washed with saturated sodium bicarbonate followed by 3% aqueous sodium sulfide. The washed extract was dried and concentrated to yield the hexamethoxy dialdehyde as an essentially pure oil (90%): NMR ($CDCl_3$) δ 3.54 (3 H, s), 3.90 (6 H, s), 7.32 (1 H, s), 9.44 (1 H, s). Without further purification the dialdehyde was treated with copper powder (2 g) at 220 °C overnight. 2,3,4,5,6,7-Hexamethoxyfluorenone was obtained as a red solid (33%): mp 143–145 °C; NMR ($CDCl_3$) δ 3.85 (6 H, s), 3.91 (3 H, s), 6.98 (1 H, s); IR ν (NaCl) 1695 cm^{-1} (C=O). Reduction with hydrogen as described afforded the desired 2,3,4,5,6,7-hexamethoxyfluorene (15) (recrystallization from ethanol): mp 132–133 °C; NMR ($CDCl_3$) δ 3.66 (1 H, s), 3.82 (3 H, s), 3.85 (3 H, s), 3.88 (3 H, s), 6.76 (1 H, s). Anal. Calcd for $C_{19}H_{22}O_6$: C, 65.69; H, 6.67. Found: C, 65.81; H, 6.82.

Registry No. 2, cation radical, 34539-20-3; **3**, 42523-30-8; **3**, cation radical, 51548-21-1; **4**, 70278-85-2; **4**, cation radical, 72442-87-6; **5**, 525-64-4; **5**, cation radical, 72442-88-7; **6**, 18675-95-1; **7**, 72442-89-8; **8**, 244-99-5; **9**, 26060-14-0; **10**, 2523-46-8; **11**, 26060-13-9; **12**, 42523-12-6; **12**, cation radical, 72442-90-1; **13**, 72442-91-2; **13**, cation radical, 72442-92-3; **14**, 51487-65-1; **14**, cation radical, 65989-21-1; **15**, 70278-86-3; **15**, cation radical, 72442-93-4; 2,7-dihydroxyfluorenone, 42523-29-5; 2-hydroxyfluorene, 2443-58-5; methyl iodide, 74-88-4; toluenesulfonanthranilic acid, 6311-23-5; veratrole, 91-16-7; dimethoxy-2′-(toluenesulfamido)benzophenone, 72453-52-2; 1,2-dimethoxyfluorenone, 42523-09-1; 3,4-dimethoxyfluorenone, 23346-81-8; 2,3-dimethoxyfluorenone, 2041-27-2; 6-bromoveratraldehyde, 5392-10-9; 2,3,6,7-tetramethoxyfluorenone, 58532-06-2; 2,3,4,5,6,7-hexamethoxyphenanthrene, 63557-97-1; 2,3,4,5,6,7-hexamethoxyphenanthren-9,10-dial, 63557-99-3; 2,3,4,5,6,7-hexamethoxyfluorenone, 72442-94-5.

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(10) M. Hanoaka, H. Sassa, C. Shimezawa, and Y. Arata, *Chem. Pharm. Bull.*, **23**, 2478 (1975).

(11) T. Dreyfuss, *Gazz. Chim. Ital.*, **68**, 92 (1938); *Chem. Abstr.*, **32**, 6238 (1939).

(12) E. Ghera, Y. Ben-David, and D. Becker, *Tetrahedron Lett.*, 463 (1977).

(13) R. Pappo, D. S. Allen, Jr., R. U. Lemieux, and W. S. Johnson, *J. Org. Chem.*, **21**, 478 (1956).

Micellar Effects on the Base-Catalyzed Oxidative Cleavage of a Carbon–Carbon Bond in 1,1-Bis(*p*-chlorophenyl)-2,2,2-trichloroethanol

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The base-catalyzed oxidative cleavage of 1,1-bis(*p*-chlorophenyl)-2,2,2-trichloroethanol (Dicofol) results in the formation of chloroform and 4,4′-dichlorobenzophenone. The reaction was studied in the presence of hexadecyltrimethylammonium bromide (CTAB) and hexadecyldimethyl(2-hydroxyethyl)ammonium bromide (CHEDAB), and catalytic factors of 200- and 345-fold, respectively, were obtained. The experimental results are rationalized in terms of an increase of the concentration of the reagents in the micellar phase. Sodium dodecyl sulfate (NaLS) inhibits the reaction, and dodecylcarnitine chloride (LCC) essentially does not alter the rate. The catalysis by cationic surfactants (CTAB, CHEDAB) is inhibited by added salts. The effectiveness of the salts in decreasing the rate constant is $NaCl < NaBr < NaNO_3 < Na_2SO_4 < NaOTs$. The activation parameters for 4.0×10^{-3} M CTAB ($\Delta H^{\ddagger} = 27.7$ kcal/mol, $\Delta G^{\ddagger} = 19.8$ kcal/mol, $\Delta S^{\ddagger} = 25.9$ eu) and for 1.0×10^{-1} M CTAB ($\Delta H^{\ddagger} = 26.7$ kcal/mol, $\Delta G^{\ddagger} = 20.8$ kcal/mol, $\Delta S^{\ddagger} = 19.6$ eu) indicate that the rate decrease observed at high surfactant concentration is due to an entropic contribution to the free-energy term.

1,1-Bis(*p*-chlorophenyl)-2,2,2-trichloroethanol, Kelthan or Dicofol, is a pesticide used on a commercial scale. It has also been identified as a metabolite in the enzymatic degradation of 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane, DDT. Several other products have been confirmed in the enzymatic transformation of DDT. Scheme I presents a commonly accepted mechanism for this degradation.[1]

According to this scheme, the formation of 4,4′-dichlorobenzophenone (DBP) occurs through several steps, without participation of Dicofol. However, from a purely chemical point of view, it would be very plausible to postulate the formation of DBP upon treatment of Dicofol with base. Indeed, the presence of three chlorine atoms on C-2 should result in the stabilization of a developing carbanion. Thus, the ionization of Dicofol in the presence of base would result in the formation of an alkoxide ion which would later lead to an oxidative carbon–carbon bond cleavage and produce DBP and chloroform. This type of oxidative carbon–carbon bond cleavage reaction involving a tertiary alcohol is well documented and has been described extensively in the literature.[2-4]

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(1) For reviews see: Korte, F.; Klein, W. *Pharma Int., Engl. Ed.* **1971**, *5*, 12. Kuhr, R. CHEMTECH **1976**, 316. Khan, M.; Gassman, M.; Haque, R. *Ibid.* **1976**, 62.

(2) March, J. "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure", 2nd ed.; McGraw-Hill Kogakusha: Tokyo, 1977; pp 525–6.

0022-3263/80/1945-0705$01.00/0