Derivatives of 1,8-Diphenylanthracene[1]

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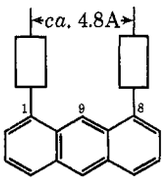
Two additional polyphenylated anthracenes, the 1,8,10-triphenyl derivative **5** and the 1,8,9,10-tetraphenyl derivative **6**, have been prepared by reaction of the diphenylquinone **2** with phenyllithium followed by reduction and dehydration. Mononitration of 1,8-diphenylanthracene (**1d**) yielded the 10-nitro derivative **13**. Derivatives **12** of 1,8-diphenylanthracene with a substituent at C-9, a location allowing interaction of the substituent with the π orbitals of the two phenyl rings, were obtained by the methylation or acetylation of the anthrone **11**. Studies of the oxidation and reduction of the various hydrocarbons **1**, **5**, **6**, and **20** by polarography and cyclic voltammetry provided a measure of the relative ease of adding or removing one or more electrons from these hydrocarbons. In general, the cation radicals and dianions formed were relatively unstable, but the anion radicals had substantial lifetimes even in partially aqueous solutions.

In earlier publications,[2] we have described the preparation of various derivatives of anthracene **1** and naphthalene **20** with phenyl substituents in one or more of the peri positions C-1, C-8, and C-9.[3] Of special interest were those compounds **1c**, **1e**, and **20b** with two or more adjacent phenyl substituents held in a sterically crowded face-to-face relationship to one another and 1,8-phenylanthracene (**1d**), a molecule that exists primarily in a conformation (see Chart I) with the two phenyl rings approximately perpendicular to the plane of the anthracene ring. This latter molecule offers the interesting possibility that appropriate substituents at C-9 will be in an environment that is shielded from attack by external reagents and yet in a favorable location for interaction with the π orbitals of the two phenyl rings. This paper describes several methods that we have explored for the introduction of substituents at the 9 position of the 1,8-diphenylanthracene system and describes certain physical properties of the derivatives prepared by us.

CHART I

CONFORMATION OF 1,8-DIPHENYLANTHRACENE (**1d**)



The most useful intermediate that we have found for preparing various 1,8-diphenylanthracene derivatives is the diphenylquinone **2** (Scheme I), prepared from the diodide **19d** and a lithium di- or triphenylcuprate.[2] Several other possible synthetic precursors (Chart II), including **18**, **19b**, and **19c**, were prepared but were found to be less satisfactory than the diiodoquinone **19d**. As expected from earlier reduction studies,[2] reaction of the quinone **2** with a limited amount of phenyllithium introduced a phenyl group at the less hindered C-10 carbonyl group to form the keto alcohol **3**. With excess phenyllithium the diol **4** became the major product. Each of these alcohols **3** and **4** could be reduced and dehydrated to form the polyphenylanthracene derivatives **5** and **6**. The nmr spectra of these derivatives (see Experimental Section) were analogous to those observed previously[2] for the phenylanthracene derivatives **1d** and **1e**. In the triphenyl

SCHEME I

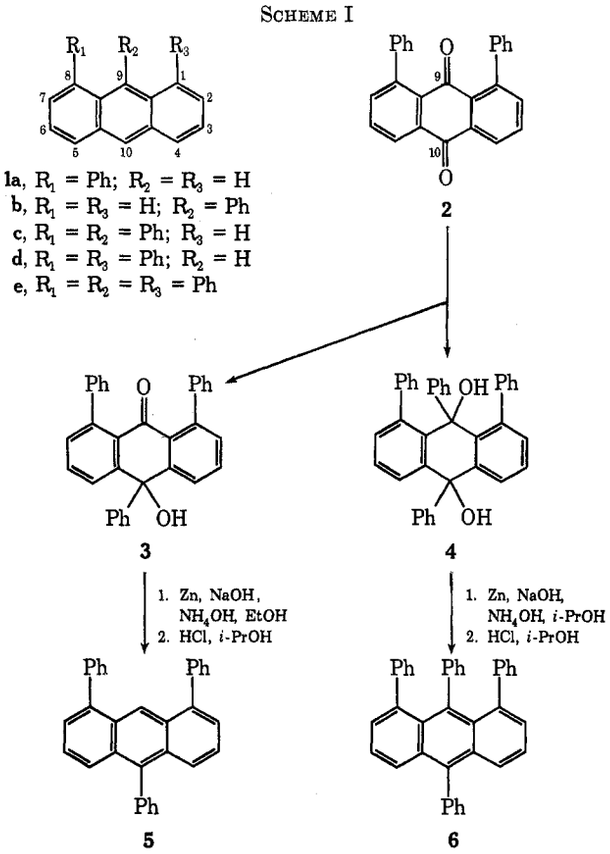
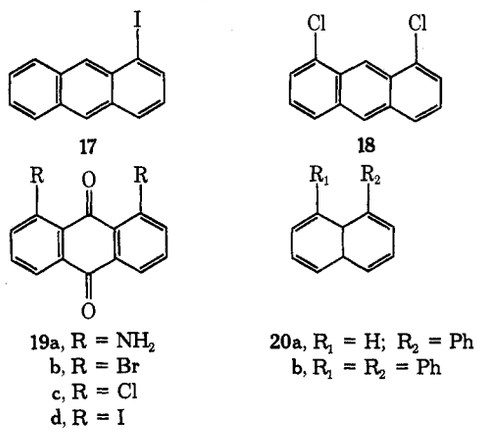


CHART II



(1) This research has been supported by Public Health Service Grant No. RO1-CA-12634 from the National Cancer Institute.

(2) H. O. House, D. G. Koepsell, and W. J. Campbell, *J. Org. Chem.*, **37**, 1003 (1972), and references cited therein.

(3) For a review of the properties of naphthalenes with peri substituents, see V. Balasubramaniyan, *Chem. Rev.*, **66**, 567 (1966).

derivative **5**, with no phenyl rings in a crowded face-to-face arrangement, all of the phenyl signals were at relatively low field (δ 7.1–7.9) analogous to the spectrum observed for 1,8-diphenylanthracene (**1d**). In the tetraphenyl derivative **6**, the signal for one phenyl group (at C-10) was in the usual low-field location (δ 7.60) but the remaining three phenyl groups (at C-1, C-8, and C-9) exhibited relatively high-field signals (δ 6.3–6.9) analogous to the spectrum observed for 1,8,9-triphenylanthracene (**1e**).

One satisfactory method for preparing 1,8-diphenylanthracene derivatives with C-9 substituents consisted of the O-methylation or the O-acetylation of the anthrone **11** to form the derivatives **12** (Scheme II). Table I summarizes the locations of the nmr methyl signals for the C-9 methoxy or acetoxyl substituent when two (**12**), one (**10**), or no (**8**) adjacent phenyl substituents are present. The substantial upfield shift (*ca.* 2 ppm) of the methyl signal in the diphenylanthracene derivatives **12** indicates that the C-9 substituents are suitably located to be capable of interaction with the π orbitals of the two phenyl rings.[4]

SCHEME II

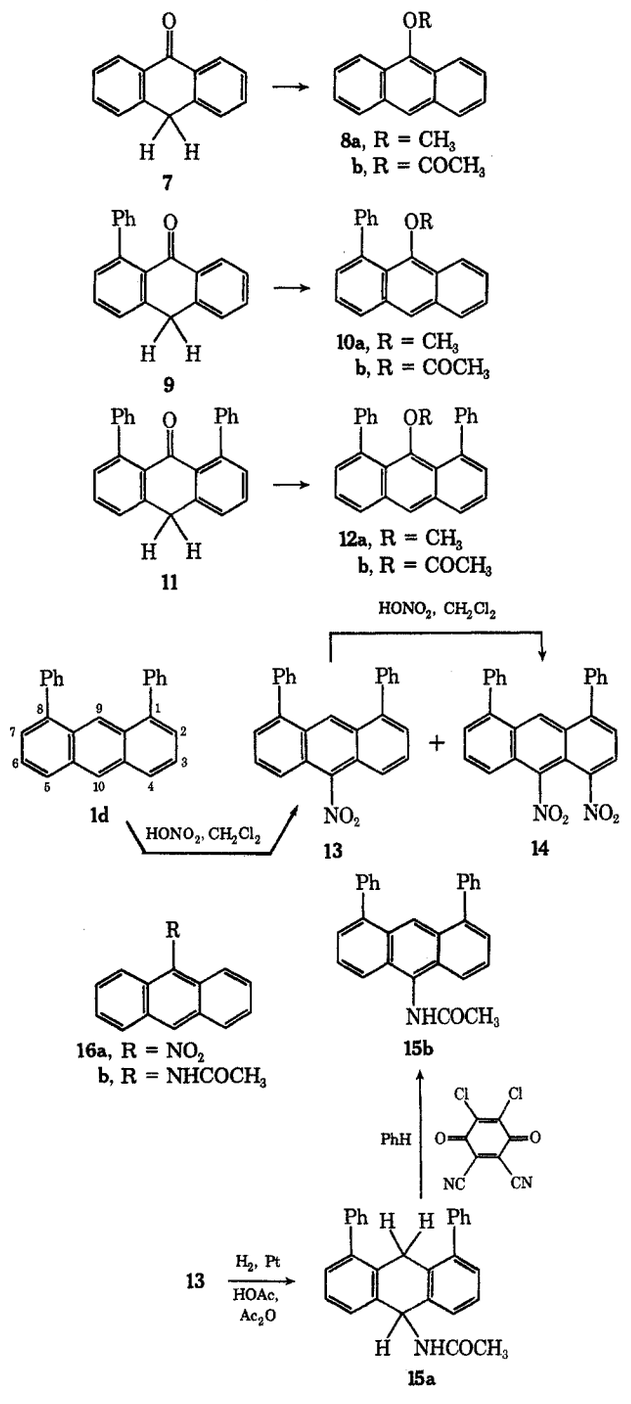


TABLE I

NMR METHYL SIGNALS FOR THE 9-METHOXYANTHRACENES AND THE 9-ACETOXYANTHRACENES

Functional group	δ values (CDCl3 solutions) 8	10	12
CH_3CO_2	2.53	1.52	0.28
CH_3O	4.10	3.25	2.37

To examine the preferred site of electrophilic substitution in 1,8-diphenylanthracene (**1d**), the hydrocarbon was subjected to nitration under mild conditions. Like anthracene, which undergoes nitration to form the 9-nitro derivative **16a**, we expected the major product to be either the 10-nitro derivative **13** or possibly the 9-nitro isomer. In fact, the mononitro compound proved to be **13** and further nitration led to substitution at C-4 in the anthracene ring to form the dinitro derivative **14**. Thus, there appears to be appreciable steric hindrance to electrophilic substitution at C-9 in the hydrocarbon **1d**. The location of the nitro group in **13** was established by hydrogenation and acetylation to form the dihydroamide **15a**. Dehydrogenation with dichlorodicyanobenzoquinone yielded the aromatic amide **15b**. Since the nmr spectrum of the amide **15b** exhibited a methyl signal (at δ 2.80) comparable in location to the signal from 9-acetamidoanthracene (2.34), we conclude that the acetamide function is at C-10 (structure **15b**) and not at C-9, where a distinct upfield shift (*ca.* 2 ppm) would be expected (*cf.* **12b**, Table I).

The ease of reduction and of oxidation of the various hydrocarbons **1**, **5**, **6**, and **20** were compared by the polarographic measurements summarized in Tables II and III. The potentials required for oxidation to the cation radical and for reduction to the anion radical were both relatively insensitive to the number and the location of the phenyl substituents. The second reduction potential (corresponding to reduction of the anion radical to a dianion) was also relatively insensitive to the location and number of phenyl substituents present except for the two anthracene derivatives **1e** and **6**. For these materials, each of which has three phenyl groups in adjacent peri positions (C-1, C-8, and C-9), the second reduction potential was *ca.* 0.3 V less negative than would be expected from the values for related materials. This second reduction step may be facilitated by the formation of a nonplanar dianion which relieves strain in these sterically crowded molecules.

The lifetimes of the various ions formed by oxidation and reduction were estimated from the cyclic voltammetry studies summarized in Table IV. In general, both the dianions and the cation radicals were very reactive with half-lives of the order of 10^{-2} sec or less. However, the anion radicals were relatively

(4) Because the two C-9 substituents described (CH_3O– and CH_3COO–) are not linear, the methyl groups are probably not located properly to exhibit the maximum upfield shift from the ring currents of the two adjacent phenyl rings.

TABLE II

POLAROGRAPHIC OXIDATION POTENTIALS FOR PHENYL DERIVATIVES OF NAPHTHALENE AND ANTHRACENE IN $CHCl_2$ CONTAINING 0.2 M n-$Pr_4N^+CF_3SO_3^-$

Compd (concn, $M \times 10^3$)	$E_{1/2}$ vs. sce, V	n value
Naphthalene (0.60)	1.76[a]	0.7
20a (0.67)	1.67	0.7
20b (0.63)	1.64	0.7
Anthracene (1.2)	1.35[b]	0.8
1a (0.66)	1.35	0.7
1b (1.2)	1.32[b]	0.7
1c (0.61)	1.30	0.7
1d (1.6)	1.34	0.7
1e (0.46)	1.25[c]	0.6
5 (0.41)	1.30	0.7
6 (0.62)	1.21[d]	0.8

[a] The reported value in CH_3CN containing $NaClO_4$ is 1.54 V: E. S. Pysk and N. C. Yang, *J. Amer. Chem. Soc.*, **85**, 2124 (1963). [b] The reported values in DMF containing n-Bu_4NI are 1.34 V for anthracene and 1.30 V for **1b**: A. J. Bard, K. S. V. Santhanam, J. T. Maloy, J. Phelps, and L. O. Wheeler, *Discuss. Faraday Soc.*, **45**, 167 (1968). [c] A second poorly defined wave was also observed at *ca.* 1.60 V. [d] A second poorly defined wave was also observed at *ca.* 1.67 V.

TABLE III

POLAROGRAPHIC REDUCTION POTENTIALS FOR PHENYL DERIVATIVES OF NAPHTHALENE AND ANTHRACENE IN DMF CONTAINING 0.5 M n-$Bu_4N^+BF_4^-$

Compd (concn, $M \times 10^3$)	$E_{1/2}$ vs. sce, V (n value) First wave	Second wave
Naphthalene (15.2)[a]	−2.49 (0.9)	
20a (9.2–13.7)[a]	−2.37 (0.9)	−2.61 (1.3)
20b (3.5)[a,b]	−2.23 (1.0)	−2.50 (1.2)
Anthracene (8.9)[a]	−1.93 (1.0)	−2.48 (0.9)
1a (3.5)[a,c]	−1.86 (1.0)	−2.35 (1.1)
1b (7.8)[a]	−1.87 (1.0)	−2.43 (0.9)
1c (1.9)[a,d]	−1.83 (0.9)	−2.21 (1.0)
1d (3.2)[a]	−1.84 (0.9)	−2.34 (1.1)
1e (2.7)[a]	−1.83 (0.9)	−2.05 (1.2)
5 (0.50–0.64)	−1.79 (1.0)	−2.28 (1.0)
6 (0.91–1.1)	−1.77 (0.9)	−2.00 (1.2)

[a] Data from ref 11. [b] A third wave was observed at −2.78 V. [c] A third wave was observed at −2.70 V. [d] A third wave was observed at −2.69 V.

stable (half-lives typically 30 sec or more), not only in anhydrous media but also in the presence of added 1 M H_2O. Consequently, it would appear practical to isolate salts of certain of these anion radicals provided that they are kept in an oxygen-free environment. A study of the properties of certain of these anion radicals will be subject of a separate paper.

Experimental Section[5]

1,8-Diphenyl-9,10-anthraquinone (2).—The following procedure represents an improvement on the previously reported[2] method. The CuBr used in this procedure was purified by first dissolving 35 g of commercial CuBr (Fisher Scientific Co.) in 150 ml of saturated aqueous KBr followed by decolorizing with charcoal and dilution with 1000 ml of H_2O. The CuBr that precipitated was collected, washed successively with EtOH and with hexane, and then dissolved in 125 ml of freshly distilled n-Bu_2S [bp 74–75° (14 mm)]. The resulting solution was filtered through a sintered glass funnel to remove *ca.* 0.3 g of insoluble residue and the filtrate was then heated to 140–160° under 10–20 mm pressure to remove the n-Bu_2S, leaving 27.5 g of purified CuBr. Spectrographic analysis indicated that this procedure removed small amounts of impurities containing Fe, Mg, Ag, Pb, Sn, and Ca. A solution of Li_2Ph_3Cu was prepared by treating 3.50 g (24.4 mmol) of purified CuBr with 76.6 mmol of PhLi in 170 ml of Et_2O. This solution was cooled to −10° and a cold solution of 2.00 g (4.35 mmol) of the diiodoquinone **19d** in 600 ml of THF was added rapidly with stirring. After the resulting solution had been stirred at −10° for 4 min, a stream of oxygen was bubbled through the reaction solution for 7 min while the temperature was maintained at 0 to −10°. The resulting mixture was treated with aqueous NH_4Cl + NH_3 (pH 8), the organic layer was separated, and the aqueous phase was extracted with Et_2O. The combined organic solutions were concentrated and the residual yellow semisolid was triturated with ether to remove 0.4 g of an insoluble, high-melting by-product. The Et_2O solution was concentrated and the residue was heated to 60–70° (0.05 mm) to remove the bulk of the relatively volatile biphenyl. The residue (1.567 g) was chromatographed on silica gel with CH_2Cl_2 as an eluent to separate 818 mg (52%) of the crude diphenylquinone **2**, mp 190–196°. Recrystallization (*i*-PrOH) afforded the pure quinone **2**, mp 200–201°. A small amount (20 mg) of the starting diiodide **19d** was also recovered from the chromatography column.

Preparation of the Triphenyl- and Tetraphenylanthracenes 5 and 6.—To a solution of 1.005 g (2.79 mmol) of the quinone **2** in 80 ml of PhH was added 3.0 ml of an Et_2O solution containing 3.3 mmol of PhLi. The resulting solution was stirred at 25° for 30 min and poured into aqueous NH_3 and NH_4Cl (pH 8). The combined organic layer and CH_2Cl_2 extract of the aqueous phase were concentrated to leave 1.34 g of yellow semisolid. Trituration with CH_2Cl_2 left 231 mg of the crude diol **4**, which was recrystallized (EtOH) to separate 149 mg (10%) of the diol **4** in fractions melting within the range of 266–271.5°.

Repetition of this reaction with 319 mg (0.89 mol) of the quinone **2** in 10 ml of PhH and excess PhLi (17.7 mmol in 16 ml of Et_2O) afforded 319 mg (70%) of the diol **4** as white needles from EtOH, mp 262–272.5°.

Recrystallization from EtOH separated one stereoisomer of the diol **4** as white needles: mp 282.5–283.5°; ir (KB pellet) 3480 and 3350 cm^{-1} (OH); uv (95% EtOH) intense end absorption (ϵ 80,000 at 210 mμ) with an inflection at 222 mμ (ϵ 53,300); mass spectrum m/e (rel intensity) 516 (M^+, 0.5) 483 (43), 482 (100), 405 (24), and 326 (18).

Anal. Calcd for $C_{38}H_{28}O_2$: C, 88.34; H, 5.46. Found: C, 88.15; H, 5.60.

The residue (1.088 g) from the mother liquors, after separating the diol **4**, was chromatographed on silica gel with $CHCl_3$ as the eluent. The early chromatographic fractions were triturated with hexane and fractionally recrystallized from EtOH to separate 82 mg (6%) of a second stereoisomer of the diol **4** as white needles: mp 276–277.5°; ir (KBr pellet) 3490 cm^{-1} (OH); uv (95% EtOH) intense end absorption (ϵ 62,000 at 210 mμ) with inflections at 223 mμ (ϵ 48,000) and 265 (7800); nmr (C_6D_6) δ 5.9–8.1 (multiplet, OH and aryl CH); mass spectrum m/e (rel intensity) 516 (M^+, 1), 501 (25), 500 (38), 499 (16), 483 (34), 469 (29), 468 (100), 424 (28), and 423 (67). On tlc (silica gel coating, CH_2Cl_2 eluent) the R_f values for the isomeric diols **4** were 0.76 (mp 276–277.5°) and 0.10 (mp 282.5–283.5°).

Anal. Calcd for $C_{38}H_{28}O_2$: C, 88.34; H, 5.46. Found: C, 88.22; H, 5.76.

The mother liquors from the early chromatographic fractions and the intermediate chromatographic fractions were crystallized from EtOH to separate 146 mg (15%) of the starting quinone **2**, mp 196–199°. The later chromatographic fractions were recrystallized from EtOH or from MeOH to separate 385 mg (32%) of the hydroxy ketone **3**, mp 221–225°. Recrystallization from MeOH afforded the pure ketol **3** as colorless prisms: mp 227–228°; ir ($CHCl_3$) 3570 (OH) and 1678 cm^{-1} (conjugated C=O); uv max (95% EtOH) 222 mμ (shoulder ϵ 43,000) and 291 (10,200); nmr ($CDCl_3$) δ 7.85 (2 H d of d, J = 1.8 and 8 Hz, aryl CH), 7.55 (2 H t, J = 8 Hz, aryl CH), 7.1–7.4 (17 H m, aryl CH), and 3.07 (1 H s, OH); mass spectrum m/e (rel intensity) 438 (M^+,

(5) All melting points are corrected and all boiling points are uncorrected. Unless otherwise stated $MgSO_4$ was employed as a drying agent. The ir spectra were determined with a Perkin-Elmer Model 237 or Model 257 infrared recording spectrophotometer fitted with a grating. The uv spectra were determined with a Cary Model 14 or a Perkin Elmer Model 202 recording spectrophotometer. The nmr spectra were determined at 60 MHz with a Varian Model A-60 or Model T-60 nmr spectrometer. The chemical shift values are expressed in δ units (parts per million) relative to a Me_4Si internal standard. The mass spectra were obtained with an Hitachi (Perkin-Elmer) or a Varian Model M-66 mass spectrometer. All reactions involving strong bases or organometallic intermediates were performed under a nitrogen atmosphere.

TABLE IV

STUDIES OF THE OXIDATION (0.2 M n-$Pr_4N^+CF_3SO_3^-$ IN CH_2Cl_2) AND REDUCTION (0.5 M n-$Bu_4N^+BF_4^-$ IN DMF) OF PHENYL DERIVATIVES OF NAPHTHALENE AND ANTHRACENE BY CYCLIC VOLTAMMETRY

Compd (concn, $M \times 10^3$)	Potentials (vs. sce) and half-lives (values obtained with added H_2O)[a] — Reduction				Oxidation	
	$E_{1/2}$, V	$t_{1/2}$, sec	$E_{1/2}$, V	$t_{1/2}$, sec	$E_{1/2}$, V	$t_{1/2}$, sec
Naphthalene	−2.56	>30			1.81	<0.1
(3.0–13.5)	(−2.55)	(>30)				
20a (4.0–4.4)	−2.36	3	−2.59	$<10^{-2}$		
	(−2.37)	(2)	(2.37)			
20b (2.9–5.4)	−2.25	~13	−2.51[b]	$<10^{-2}$	1.59	$<10^{-2}$
	(−2.25)	(7)	(−2.50)			
Anthracene	−1.96	>30	−2.53	<0.02	1.35	<0.05
(1.0–12.0)	(−1.95)	(>30)	(−2.47)			
1a (2.3–2.9)	−1.91	>30	−2.40[c]	$<10^{-2}$		
	(−1.90)	(>30)	(−2.35)			
1b (1.0–6.2)	−1.93	>30	−2.47	<0.03	1.31	7×10^{-3}
	(−1.93)	(>30)	(−2.42)		(1.31)	(7×10^{-3})
1c (1.0–2.9)	−1.90	>30	−2.34[d]	<0.04		
	(−1.88)	(>30)	(−2.23)			
1d (1.9–4.1)	−1.88	>30	−2.37[e]	<0.04	1.30	7×10^{-3}
	(−1.88)	(>30)	(−2.30)		(1.29)	(3×10^{-3})
1e (2.9–4.4)	−1.85	3	−2.03[f]	$<10^{-2}$	1.26	0.05
	(−1.85)		(−2.00)		(1.23)	(0.04)
5 (0.6–0.7)	−1.81	~22	−2.31[c]	$<10^{-2}$		
6 (0.9–1.1)	−1.77	~8	−2.03[g]	$<10^{-2}$		

[a] The solutions for reduction contained 1.0 M H_2O and the solutions for oxidation contained 0.2 M H_2O. [b] An additional peak was observed at −2.80 V. [c] An additional peak was observed at −2.75 V. [d] An additional peak was observed at −2.72 V. [e] An additional peak was observed at −2.76 V. [f] An additional peak was observed at −2.79 V. [g] An additional peak was observed at −2.78 V.

48), 437 (39), 422 (60), 421 (100), 420 (39), 361 (24), 344 (29), and 171 (16).

Anal. Calcd for $C_{32}H_{22}O_2$: C, 87.64; H, 5.06. Found: C, 87.43; H, 4.99.

A mixture of 253 mg (0.58 mmol) of the ketol **3**, 1.0 g of Zn dust (activated with 6 mg of $CuSO_4$),[6] 2 ml of aqueous 28% NH_3, 12 ml of aqueous 30% NaOH, and 20 ml of EtOH was refluxed with stirring for 24 hr. An additional 500 mg of Zn dust was added and refluxing and stirring were continued for 39 hr more. The reaction mixture was filtered and both the residue and the filtrate were extracted with CH_2Cl_2. The combined CH_2Cl_2 extracts were concentrated and a solution of the residual white solid and 3 ml of aqueous 12 M HCl in 100 ml of i-PrOH was refluxed for 45 min. The resulting solution was concentrated and the residue was partitioned between aqueous $NaHCO_3$ and CH_2Cl_2. The organic phase was dried, concentrated, and chromatographed on silica gel with CH_2Cl_2 as the eluent. The early fractions contained 92 mg (38%) of the triphenylanthracene **5**, mp 189–192°. Recrystallization (EtOH) separated the pure hydrocarbon **5** as yellow needles: mp 194–195°; ir ($CHCl_3$) no absorption in the 3- or 6-μ regions attributable to OH or C=O groups; uv max (95% EtOH) 214 mμ (ϵ 44,800), 261 (101,000), 343 (shoulder, 3660), 361 (7720), 380 (11,800), and 400 (10,300); nmr ($CDCl_3$) δ 8.66 (1 H, partially resolved multiplet, aryl CH at C-9), 7.1–7.9 (21 H m, aryl CH); mass spectrum m/e (rel intensity) 406 (M^+, 100) and 325 (11).

Anal. Calcd for $C_{32}H_{22}$: C, 94.54; H, 5.46. Found: C, 94.24; H, 5.77.

The later chromatographic fractions from the reaction mixture afforded 47 mg (23%) of the quinone **2**, mp 195–199° (believed not to have been an impurity in the starting ketol **3**), and 44 mg (17%) of the starting ketol **3**, mp 217–220°.

A mixture of 319 mg (0.62 mmol) of the diol **4**, mp 262–272°, 2.5 g of Zn dust (activated with 15 mg of $CuSO_4$),[6] 5 ml of aqueous 28% NH_3, 25 ml of aqueous 30% NaOH, and 60 ml of i-PrOH was refluxed with stirring for 48 hr. The resulting mixture was filtered, the filtrate was treated with an additional 500 mg of Zn dust and 25 ml of i-PrOH, and refluxing and stirring were continued for 48 hr more. The previously described isolation procedure was followed, including reaction of the reduced intermediate with 3 ml of aqueous 12 M HCl in 100 ml of boiling i-PrOH for 45 min. The crude organic product was chromatographed on silica gel with a hexane–CH_2Cl_2 (7:3, v/v) eluent. Recrystallization of the early fractions from hexane separated 86 mg (29%) of the tetraphenylanthracene **6** as pale yellow plates: mp 220–221°; ir ($CHCl_3$) no absorption in the 3- or 6-μ regions attributable to OH or C=O groups; uv max (95% EtOH) 229 mμ (inflection, ϵ 34,000), 270 (71,500), 369 (inflection, 7750), 391 (11,800), and 409 (11,000); nmr ($CDCl_3$) δ 7.5–7.8 (7 H m, two anthracene CH and C-10 phenyl at δ 7.60), 6.9–7.4 (4 H m, anthracene CH), and 6.3–6.9 (15 H m, three phenyl groups at C-1, C-8, and C-9); mass spectrum m/e (rel intensity) 483 (20), 482 (M^+, 100), 405 (13), and 326 (10).

Anal. Calcd for $C_{38}H_{26}$: C, 94.57; H, 5.43. Found: C, 94.65; H, 5.40.

Later fractions from the chromatography of the reaction mixture contained (ir analysis) 205 mg (64%) of the crude diol **4**, mp 243–250°.

Preparation of the 9-Acetoxyanthracene Derivatives 8b, 10b, and 12b.—A mixture of 3.013 g (15.5 mmol) of anthrone (**7**), 5 ml of Ac_2O, and 20 ml of collidine was heated to 100° for 2.5 hr and then cooled and poured with stirring into a mixture of ice and aqueous HCl. The resulting suspension was filtered and the residue was fractionally crystallized from EtOH to separate 309 mg (10%) of the starting anthrone **7**, mp 286–288°, and 2.22 g (60%) of the acetate **8b** as white needles, mp 134–137°. Recrystallization afforded the pure acetate **8b**: mp 135.5–137° (lit.[7] mp 130–133°); ir ($CHCl_3$) 1765 cm^{-1} (ester C=O); uv max (95% EtOH) 216 mμ (ϵ 11,300), 219 (11,000), 246 (shoulder, 101,000), 252 (192,000), 315 (shoulder, 1320), 329 (2980), 345 (5800), 363 (8780), and 383 (8150); nmr ($CDCl_3$) δ 8.30 (1 H s, aryl CH at C-10), 7.2–8.1 (8 H m, aryl CH), and 2.53 (3 H s, CH_3CO); mass spectrum m/e (rel intensity) 236 (M^+, 3), 194 (51), 193 (31), 165 (100), 164 (24), 163 (43), 139 (17), and 43 (52).

The same reaction and isolation procedures were followed with 241 mg (0.89 mmol) of the anthrone **9**, 1 ml of Ac_2O, and 3 ml of collidine. Recrystallization of the crude product from EtOH separated 219 mg (79%) of the acetate **10b**, mp 188–194°. The pure acetate **10b** crystallized from EtOH as colorless prisms: mp 194–195°; ir ($CHCl_3$) 1764 cm^{-1} (ester C=O); uv max (95% EtOH) 214 mμ (ϵ 21,800), 256 (127,000), 319 (shoulder, 1270), 335 (3060), 351 (6090), 369 (9150), and 389 (7970); nmr ($CDCl_3$) δ 8.40 (1 H s, aryl CH at C-10), 7.1–8.2 (12 H m, aryl CH), and 1.52 (3 H s, CH_3CO); mass spectrum m/e (rel intensity) 312 (M^+, 3), 270 (80), 269 (42), 268 (84), 241 (38), 240 (20), 239 (100), 237 (38), 213 (20), and 43 (39).

(6) E. Martin, *J. Amer. Chem. Soc.*, **58**, 1438 (1936).

(7) J. S. Meek, P. A. Monroe, and C. J. Bouboulis, *J. Org. Chem.*, **28**, 2572 (1963).

Anal. Calcd for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16. Found: C, 84.59; H, 5.24.

A comparable reaction of 232 mg (0.802 mmol) of the anthrone **11** with 1 ml of Ac_2O and 3 ml of collidine for 4.5 hr yielded 258 mg of crude product. Recrystallization from EtOH afforded 203 mg (65%) of the acetate **12b**, mp 274–282°. An additional recrystallization from EtOH afforded the pure acetate as white needles: mp 282–282.5°; ir ($CHCl_3$) 1760 cm^{-1} (ester C=O); uv max (95% EtOH) 213 mμ (ε 31,000), 261 (133,000), 342 (shoulder, 3280), 359 (6520), 377.5 (9540), and 398 (7920); nmr ($CDCl_3$) δ 8.48 (1 H s, aryl CH at C-10), 8.02 (2 H d of d, J = 1.6 and 8.4 Hz, aryl CH), 7.1–7.6 (14 H m, aryl CH), and 0.28 (3 H s, CH_3CO); mass spectrum, m/e (rel intensity) 388 (M^+, 4), 347 (17), 346 (100), 345 (22), 344 (28), 313 (16), 268 (21), 239 (19), and 43 (19).

Anal. Calcd for $C_{25}H_{20}O_2$: C, 86.57; H, 5.19. Found: C, 86.27; H, 5.10.

Preparation of the 9-Methoxyanthracene Derivatives 8a, 10a, and 12a.—To a refluxing solution of 259 mg (0.96 mmol) of the anthrone **9** and 6 ml of aqueous 20% NaOH in 8 ml of *i*-PrOH was added, portionwise with stirring, 1.21 g (6.5 mmol) of MeOTs. The resulting mixture was refluxed for 20 min and then diluted with 15 ml of H_2O and allowed to cool. The crude crystalline product (167 mg) that separated was collected and recrystallized from EtOH to separate 154 mg (57%) of the methoxyanthracene **10a** as pale yellow plates: mp 138.5–139.5°; ir ($CHCl_3$) no absorption in the 3- or 6-μ regions attributable to OH or C=O groups; uv max (95% EtOH) 212 mμ (ε 23,000), 258 (105,000), 340 (shoulder, 3090), 356 (5960), 375 (8620), and 394 (7720); nmr ($CDCl_3$) δ 8.30 (1 H s, aryl CH at C-10), 7.1–8.2 (12 H m, aryl CH), and 3.25 (3 H s, OCH_3); mass spectrum m/e (rel intensity) 285 (23), 284 (M^+, 100), 270 (18), 269 (99), 268 (91), 229 (15), and 124 (20).

Anal. Calcd for $C_{21}H_{16}O$: C, 88.70; H, 5.67. Found: C, 88.47; H, 5.95.

A comparable reaction with 190 mg (0.55 mmol) of the anthrone **11**, 6 ml of aqueous 20% NaOH, 8 ml of *i*-PrOH, and 1.21 g (6.5 mmol) of MeOTs yielded 115 mg (60%) of the methoxyanthracene **12a** as pale yellow needles from EtOH: mp 241–242.5°; ir ($CHCl_3$) no absorption in the 3- or 6-μ regions attributable to OH or C=O groups; uv max (95% EtOH) 215 mμ (ε 31,900), 254 (shoulder, 67,600), 262 (112,000), 346 (shoulder, 3280), 369 (6760), 384 (9530), and 406 (8300); nmr ($CDCl_3$) δ 8.35 (1 H s, aryl CH at C-10), 7.1–8.2 (16 H m, aryl CH), and 2.37 (3 H s, OCH_3); mass spectrum m/e (rel intensity) 361 (30), 360 (M^+, 100), 346 (16), 345 (69), 344 (49), and 268 (12).

Anal.. Calcd for $C_{27}H_{20}O$: C, 89.97; H, 5.59. Found: C, 89.79; H, 5.70.

The same procedure was applied[8] to anthrone (**7**) to produce 9-methoxyanthracene (**8a**) in 51% yield as yellow needles from *i*-PrOH: mp 95–96° (lit.[7] mp 95–96°); nmr ($CDCl_3$) δ 7.3–8.5 (9 H m, aryl CH) and 4.10 (3 H s, OCH_3).

Nitration of Anthracene and 1,8-Diphenylanthracene (1d).—A mixture of 968 mg (10.8 mmol) of aqueous 70% HNO_3, 8 ml of CH_2Cl_2, and 306 mg (1.72 mmol) of anthracene was stirred at 0–3° for 1 hr and then partitioned between CH_2Cl_2 and aqueous $NaHCO_3$. The organic layer was dried and concentrated and the residual yellow oil (432 mg) was chromatographed on silica gel with PhH as an eluent. The early fractions, containing (tlc) 9-nitroanthracene (**16a**), were recrystallized from EtOH to separate 208 mg (55%) of the nitro derivative **16a** as yellow needles: mp 145.5–147.5° (lit.[9] mp 146°); ir ($CHCl_3$) 1520 and 1370 cm^{-1} (NO_2); uv (95% EtOH) 217 mμ (ε 14,300), 245 (shoulder, 102,000), 250 (120,000), 333 (shoulder, 2480), 347 (3840), 364 (4640), 383 (3950), and 402 (shoulder, 2180); nmr ($CDCl_3$) δ 8.51 (1 H s, aryl CH at C-10) and 7.2–8.1 (8 H m, aryl CH); mass spectrum m/e (rel intensity) 223 (M^+, 100), 193 (48), 177 (69), 176 (76), 165 (51), 151 (21), and 88 (34).

To a refluxing solution of 1.018 g (4.52 mmol) of the nitro compound **16a** in 20 ml of HOAc was added, dropwise and with stirring, a solution of 8 g of $SnCl_2 \cdot 2H_2O$ in 8 ml of aqueous 12 *M* HCl. The resulting solution was refluxed for 30 min, cooled, and filtered to separate the amine–tin complex. This residue was washed with HOAc and then triturated with aqueous NH_3 and extracted repeatedly with Et_2O. The Et_2O extract was concentrated and the residual crude amine was dissolved in 30 ml of cold (0°) Ac_2O. This cold solution was stirred for 15 min and then poured onto ice and allowed to stand. The crude amide **16b** (835 mg or 78%, mp 282–284°) was collected and recrystallized from PhH to separate the pure amide **16b** as 737 mg of white needles: mp 283–284° dec (lit.[10] mp 280–281°); ir (KBr pellet) 3190 (amide NH) and 1637 cm^{-1} (amide C=O); uv max (95% EtOH) 214 mμ (ε 14,000), 247 (shoulder, 95,600), 253 (158,000), 315 (shoulder, 1160), 330 (2740), 346 (5350), 364 (7700), and 383.5 (6950); nmr ($C_6D_5NO_2$ at 120°) δ 8.34 (1 H s, aryl CH at C-10), 7.2–8.3 (8 H m, aryl CH), and 2.34 (3 H s, CH_3CO); in $Cl_2CHCHCl_2$ solution at *ca.* 35° the *C*-methyl singlet is located at δ 1.83. In $CDCl_3$ solution, the methyl signal appears as two peaks at δ 1.68 and 2.49, suggesting that in this solvent both the acetamido and acetimido tautomers are present. Exposure of this $CDCl_3$ solution to gaseous HCl resulted in a change in the relative positions and intensities of the peaks with the predominant peak appearing at δ 2.18, mass spectrum m/e (rel intensity) 235 (M^+, 38), 194 (18), 193 (100), 192 (28), and 43 (26).

A cold (0°) mixture (two phases) of 204 mg (0.619 mmol) of 1,8-diphenylanthracene (**1d**), 15 ml of CH_2Cl_2, and 500 mg (5.5 mmol) of aqueous 70% HNO_3 was stirred for 2 hr at 0° and then for 20 min at 25°. After the mixture had been treated with $NaHCO_3$, the CH_2Cl_2 solution was separated and stirred with an additional 500 mg (5.5 mmol) of aqueous 70% HNO_3 for 2 hr at 0° and 30 min at 25°. Solid $NaHCO_3$ was again added and the CH_2Cl_2 solution was separated, concentrated, and chromatographed on silica gel with CH_2Cl_2 as the eluent. The early fractions were combined and recrystallized from hexane to separate 111 mg (48%) of the nitro derivative **13**, mp 245–252°. Recrystallization from EtOH afforded the pure nitro compound **13** as yellow needles: mp 250.5–252°; ir ($CHCl_3$) 1525 and 1367 cm^{-1} (NO_2); uv max (95% EtOH) 257 mμ (ε 71,700), 359 (shoulder, 3840), 382 (5190), and 400 (shoulder, 4770); nmr ($CDCl_3$) δ 8.75 (1 H s, aryl CH at C-9), 7.95 (2 H, d of m, J = 8 Hz, aryl CH at C-4 and C-5), and 7.3–7.8 (14 H m, phenyl CH and aryl CH at C-2, C-3, C-6, and C-7); mass spectrum m/e (rel intensity) 376 (26), 375 (M^+, 100), 345 (11), 329 (14), 328 (14), and 326 (18).

Anal. Calcd for $C_{26}H_{17}NO_2$: C, 83.18; H, 4.56; N, 3.73. Found: C, 83.15; H, 4.65; N, 3.65.

The later chromatography fractions (41 mg or 16%) contained the crude dinitro compound **14**, mp 193.5–195°. Recrystallization from hexane and then from EtOH separated the pure dinitro compound **14** as orange prisms: mp 199–200°; ir ($CHCl_3$) 1530 and 1355 cm^{-1} (NO_2); uv max (95% EtOH) 245 mμ (ε 30,400), 272 (44,500), and 426 (8420); nmr ($CDCl_3$) δ 8.83 (1 H s, aryl CH at C-9), 8.0–8.4 [2 H, a doublet (J = 8 Hz) of multiplets for the proton at C-5 and a doublet (J = 7.5 Hz) for the proton at C-3], and 7.1–8.0 (13 H m, phenyl CH and aryl CH at C-2, C-6, and C-7); mass spectrum m/e (rel intensity) 420 (M^+, 26), 375 (18), 374 (71), 345 (21), 344 (82), 316 (66), 315 (100), 314 (28), 313 (70), and 239 (18).

Anal. Calcd for $C_{26}H_{16}N_2O_4$: C, 74.28; H, 3.84; N, 6.66. Found: C, 74.31; H, 3.87; N, 6.55.

A 21.2-mg (0.057 mmol) sample of the mononitro compound **13** was treated at 25° for 2.5 hr with a mixture of 2 ml of CH_2Cl_2 and 0.2 g (2 mmol) of aqueous 70% HNO_3. The crude product, isolated as previously described, was recrystallized from EtOH to separate 15.1 mg (63%) of the dinitro compound **14**, mp 197.5–198.5°, identified with the previously described sample by a mixture melting point determination and by comparison of nmr and mass spectra.

A solution of 113 mg (0.302 mmol) of the nitro compound **13** in 85 ml of HOAc and 15 ml of Ac_2O was hydrogenated for 10 hr at 25° and atmospheric pressure over the catalyst from 100 mg of Pt_2O. The resulting mixture was filtered and concentrated and the residue was chromatographed on silica gel with $CHCl_3$ as an eluent. Recrystallization of the appropriate chromatographic fractions from EtOH separated 95 mg (80%) of the crude dihydroamide **15a** as white needles: mp 235–240°; ir ($CHCl_3$) 3430 (NH) and 1670 cm^{-1} (amide C=O); uv (95% EtOH) shoulders at 235 mμ (ε 20,800) and 260 (7930) with intense end absorption (ε 64,100 at 210 mμ); nmr ($CDCl_3$) δ 7.0–7.6 (16 H m, aryl CH), 6.0–6.4 (2 H m, NH and CH), 3.5–4.2 (2 H m, benzylic CH_2), and 2.17 (3 H s, CH_3CO). A solution of 88 mg (0.23 mmol) of the crude dihydro amide **15a** and 58 mg (0.26 mmol) of 2,3-dichloro-5,6-dicyanobenzoquinone in 7 ml of PhH

(8) This experiment was performed in our laboratories by Dr. David S. Crumrine.

(9) O. Dimroth, *Ber.*, **34**, 219 (1901).

(10) J. Rigaudy, H. Canquis, G. Izout, and J. Baranne-Lafont, *Bull. Soc. Chim. Fr.*, 1842 (1961).

was refluxed for 24 hr and then the solvent was removed. The residue was chromatographed on silica gel with first CH_2Cl_2 and then $CHCl_3$ as eluents. The fractions containing the crude amide **15b** were recrystallized from EtOH to separate 40 mg (46%) of the crude amide **15b** as colorless plates, mp 319–323°. Recrystallization afforded the pure amide **15b**: mp 324–325.5°; ir (KBr pellet) 3240 (NH) and 1650 cm^{-1} (amide C=O); uv max (95% EtOH) 212 mμ (ε 39,800), 260 (111,000), 362 (6880), 380.5 (10,500), and 400.5 (9030); mass spectrum *m/e* (rel intensity), 387 (M^+, 86), 345 (84), 344 (31), 190 (28), and 43 (100); nmr ($C_6D_5NO_2$) δ 7.2–8.6 (17 H m, aryl CH) and 2.80 (3 H s, CH_3CO); in $Cl_2CHCHCl_2$ solution the *C*-methyl singlet was at δ 1.89. As was the case with the model amide **16b**, a solution of the amide **15b** in $CDCl_3$ exhibited two peaks at δ 2.52 and 1.75; after exposure of the solution to gaseous HCl, the major peak was located at δ 2.03.

Anal. Calcd for $C_{28}H_{21}NO$: C, 86.79; H, 5.46; N, 3.62. Found: C, 86.52; H, 5.40; N, 3.45.

Preparation of the Halogenated Anthracene Derivatives 17, 18, and 19b.—A cold (0°) solution of 15.0 g (77.7 mmol) of 1-aminoanthracene in a mixture of 40 ml of concentrated H_2SO_4, 55 ml of H_2O, and 125 g of ice was diazotized at −10° by treatment with a solution of 14.0 g (203 mmol) of $NaNO_2$ in 60 ml of H_2O. The cold (−10°) slurry of the red diazonium salt was treated with a solution of 55 g (330 mmol) of KI in 75 ml of H_2O and the resulting mixture was warmed to complete the reaction with the diazonium salt. The crude solid product (37.5 g) was collected and chromatographed on silica gel with PhH as an eluent. The early fractions, containing (tlc) the iodide **17**, were washed with aqueous $Na_2S_2O_3$, dissolved in CH_2Cl_2, dried, concentrated, and triturated with Et_2O to separate 6.66 g (27%) of the iodide **17**, mp 81–96°. Recrystallization from EtOH separated the pure iodide **17** as yellow plates: mp 102.3–103°; ir ($CHCl_3$) no absorption in the 3- or 6-μ regions attributable to OH or C=O groups; uv max (95% EtOH) 217 mμ (ε 12,600), 252 (130,000), 317 (shoulder, 1340), 331 (3020), 347 (5770), 365 (8170), and 385 (7780); nmr ($CDCl_3$) δ 8.61 (1 H s, aryl CH), 8.23 (1 H s, aryl CH), and 6.9–8.1 (7 H m, aryl CH); mass spectrum *m/e* (rel intensity) 304 (M^+, 100), 177 (36), 176 (29), and 88 (14).

Anal. Calcd for $C_{14}H_9I$: C, 55.29; H, 2.98; I, 41.73. Found: C, 55.46; H, 2.99; I, 41.53.

A mixture of 2.515 g (9.10 mmol) of the dichloroquinone **19c**, 12.5 g of Zn dust, and 50 ml of aqueous 20% NH_3 was heated on a steam bath with stirring for 30 min and then cooled and filtered. The residue and the filtrate were each extracted with CH_2Cl_2 and the combined CH_2Cl_2 extracts were concentrated. A solution of the residual white solid in 250 ml of *i*-PrOH containing 2 ml of aqueous 12 *M* HCl was refluxed for 3 hr and then concentrated and partitioned between CH_2Cl_2 and aqueous $NaHCO_3$. The organic layer was concentrated and the residue was recrystallized from *i*-PrOH to separate 1.655 g (74%) of the dichloride **18**, mp 149–157°. Recrystallization afforded the pure dichloride **18** as pale yellow needles: mp 156.5–158°;[11] ir ($CHCl_3$) no absorption in the 3- or 6-μ regions attributable to OH or C=O groups; uv max (95% EtOH) 218 mμ (ε 12,600), 252 (113,000), 256 (113,000), 319 (shoulder, 1340), 333 (2950), 350 (5550), 368 (8060), and 388 (7320); nmr ($CDCl_3$) δ 9.19 (1 H s, aryl CH), 8.35 (1 H s, aryl CH), and 7.2–8.0 (6 H m, aryl CH); mass spectrum *m/e* (rel intensity) 250 (12), 248 (70), 246 (M^+ for ^{35}Cl, 100), 176 (23), 123 (12), and 68 (13).

Anal. Calcd for $C_{14}H_8Cl_2$: C, 68.05; H, 3.22; Cl, 28.80. Found: C, 67.78; H, 3.26; Cl, 28.69.

An attempt to apply this same reduction procedure to the diiodoquinone **19d** resulted in the reductive cleavage of the C–I bonds to form anthracene in 68% yield.

A solution of 5.48 g (24.5 mmol) of the diamine **19a** in a mixture of 27 ml of concentrated H_2SO_4, 35 ml of H_2O, and 78 g of ice was diazotized at −15° by the slow addition of a solution of 8.8 g (128 mmol) of $NaNO_2$ in 38 ml of H_2O. To the resulting cold (−15°) suspension was added a slurry of CuBr, prepared from 4.70 g (18.8 mmol) of $CuSO_4 \cdot 5H_2O$, 1.5 g (23.6 mg-atom) of Cu, 11.6 g (113 mmol) of NaBr, 2.4 ml of concentrated H_2SO_4, and 100 ml of H_2O. The resulting mixture was heated to 80° and then cooled and made basic with NaOH. The crude solid product was collected, washed successively with aqueous 10% HCl, aqueous $NaHCO_3$, and water, and then dried. Chromatography on silica gel with PhH as the eluent separated 1.237 g (14%) of the crude dibromoquinone **19b**, mp 213–225°. Recrystallization from EtOH separated the pure dibromide **19b** as yellow needles: mp 233–234°; ir ($CHCl_3$) 1685 cm^{-1} (conjugated C=O); uv max (95% EtOH) 213 mμ (ε 28,800), 255 (33,800), 351 (4480), and 416 (shoulder, 774); nmr ($CDCl_3$) δ 8.28 (2 H, d of d, J = 7.6 and 1.3 Hz, aryl CH at C-4 and C-5), 8.06 (2 H, d of d, J = 1.3 and 7.6 Hz, aryl CH at C-2 and C-7), and 7.55 (2 H t, $J \cong 8$ Hz, aryl CH at C-3 and C-6); mass spectrum *m/e* (rel intensity) 368 (52), 366 (100), 364 (M^+ for ^{79}Br, 50), 150 (90), 75 (64), and 74 (29).

Anal. Calcd for $C_{14}H_6Br_2O_2$: C, 45.94; H, 1.65; Br, 43.66. Found: C, 45.89; H, 1.73; Br, 43.90.

Polarographic Measurements of Oxidation and Reduction Potentials.—These measurements were obtained at 25° with a Heath polarograph, Model EU-402V. The reductions were performed at a dropping Hg electrode with a Pt counterelectrode in purified DMF[12] employing 0.5 *M* n-$Bu_4N^+BF_4^-$[12] as the supporting electrolyte and with a saturated calomel reference electrode that made contact with the reaction solution through intervening salt bridges containing aqueous 1 *M* $NaNO_3$ and 0.5 *M* $Et_4N^+BF_4^-$ in DMF. The oxidations were performed at a rotating Pt wire anode (0.1 mm diameter, 600 rpm) with a fixed Pt counterelectrode in CH_2Cl_2 containing 0.2 *M* n-Pr_4N^+-$CF_3SO_3^-$[13] as the supporting electrolyte. The CH_2Cl_2 was purified by washing successively with aqueous 5% Na_2CO_3 and with H_2O and drying over $CaCl_2$. The solvent was then distilled under N_2 at atmospheric pressure and collected at 40–40.5°. The Pt wire anode was cleaned before each use by successive treatment with aqueous H_2CrO_4 and with aqueous 12 *M* HCl as described by Adams[14] and then rinsed successively with H_2O, acetone, and CH_2Cl_2. The reference was a saturated calomel electrode with intervening salt bridges containing aqueous 1 *M* $NaNO_3$ and 0.5 *M* n-$Bu_4N^+BF_4^-$ in DMF. The $E_{1/2}$ values (*vs.* sce) and the n values were obtained from plots of E *vs.* log $[i/(i_d - i)]$ and are presented in Tables II and III. Certain of the reduction potential values in Table III were described in an earlier paper.[2]

Oxidation and Reduction Measurements by Cyclic Voltammetry.—The polarographic module employed was a custom-made module utilizing solid-state amplifiers that followed the typical three-electrode design such as that found in a Heath polarograph. For slow scans the internal circuitry of the module was employed and for fast scans an external triangular wave form generator was employed to drive the polarography module. The current–potential curves were displayed on a storage oscilloscope (Tektronix RM 564 fitted with two differential amplifiers, type 2-A63) and were photographed with a Tektronix oscilloscope camera fitted with a Polaroid back. The potentials were calibrated against a previously calibrated digital voltmeter (United Systems Corp., Series 180) and the sweep time calibrations were made with the oscilloscope fitted with a previously calibrated time base (Tektronix type 2-B67). The oxidation measurements employed a spherical Pt anode (typical diameter 1.25 mm) that had been cleaned by heating it in an air–H_2 flame. For reduction measurements, the cathode was the same spherical Pt electrode described above that had been coated with Hg as previously described.[15] The same solvents, supporting electrolytes, counterelectrodes, and reference electrodes that were used in the above polarographic measurements were employed for these studies. The nitrogen was purified as previously described[15] and the electrolysis cell was of all-glass construction with provision for passing purified nitrogen either through or over the solution being measured. The entire electrolysis cell was kept in a grounded steel drum during measurements to minimize electrical interference. In those reduction measurements where cathodic (E_{pc}) and anodic (E_{pa}) waves were observed, the value of the reduction potential ($E_{1/2}$) was taken to be $^1/_2$ ($E_{pc} + E_{pa}$); as expected, the value corresponded to the cathodic potential where the cathodic

(11) E. Bergmann and A. Weizmann [*J. Amer. Chem. Soc.*, **60**, 1801 (1938)] have reported the dichloride **18** to melt at 185°.

(12) H. O. House, E. Feng, and N. P. Peet, *J. Org. Chem.*, **36**, 2371 (1971).

(13) K. Rousseau, G. C. Farrington, and D. Dolphin, *J. Org. Chem.*, **37**, 3968 (1972).

(14) R. N. Adams, "Electrochemistry at Solid Electrodes," Marcel Dekker, New York, N. Y., 1969, pp 201–202.

(15) K. W. Bowers, R. W. Giese, J. Grimshaw, H. O. House, N. H. Kolodny, K. Kronberger, and D. K. Roe, *J. Amer. Chem. Soc.*, **92**, 2783 (1970).

current had reached 85% of its peak value (i_{pc}).[16] Where no anodic current peak (i_{pa}) was observed, an estimate of the value of $E_{1/2}$ was obtained from the cathodic potential at which i_c reached 85% of the maximum value, i_{pc}. Comparable procedures were followed to obtain the oxidation potentials. Half-life estimates for the various oxidized and reduced species were obtained by a previously described procedure[15] in which the scan rates and switching potentials (E_λ) in reductions were adjusted until $i_{pa} = 1/2(i_{pc})$. The half-life for reduced species was than taken to be the elapsed time as the potential was swept from E_{pc} to E_λ to E_{pa}. In instances where the intermediate was either too unstable or too stable to allow a variation in i_{pa} with time, the minimum or maximum values of the half-life were estimated. Comparable procedures were followed for the oxidations. The results of these measurements are summarized in Table IV. The effect of added H_2O on the stability of various oxidized and reduced species was explored by adding known amounts of H_2O (1.0 *M* for reductions and 0.2 *M* for oxidations) to the anhydrous solution and then repeating the measurements previously described.

(16) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964); **37**, 178 (1965).

Registry No.—**1a**, 1714-09-6; **1b**, 602-55-1; **1c**, 1714-19-8; **1d**, 33522-35-9; **1e**, 33522-39-3; **2**, 33522-27-9; **3**, 38305-27-0; *cis*-**4**, 38309-51-2; *trans*-**4**, 38309-52-3; **5**, 38305-28-1; **6**, 38305-29-2; **7**, 90-44-8; **8a**, 2395-96-2; **8b**, 784-04-3; **9**, 1714-15-4; **10a**, 38305-34-9; **10b**, 38305-35-0; **11**, 33522-37-1; **12a**, 38305-37-2; **12b**, 38305-38-3; **13**, 38305-39-4; **14**, 38305-40-7; **15a**, 38305-30-5; **15b**, 38305-31-6; **16a**, 602-60-8; **16b**, 37170-96-0; **17**, 22362-90-9; **18**, 14381-66-9; **19a**, 129-42-0; **19b**, 38313-16-5; **19c**, 82-43-9; **19d**, 30877-00-0; **20a**, 605-02-7; **20b**, 1038-67-1; anthracene, 120-12-7; 1-anthramine, 610-49-1.

The Reaction of Cyclic α-Ketal Acids with Phosphorus Pentachloride. A New Stereospecific Route to Esters of Halohydrins

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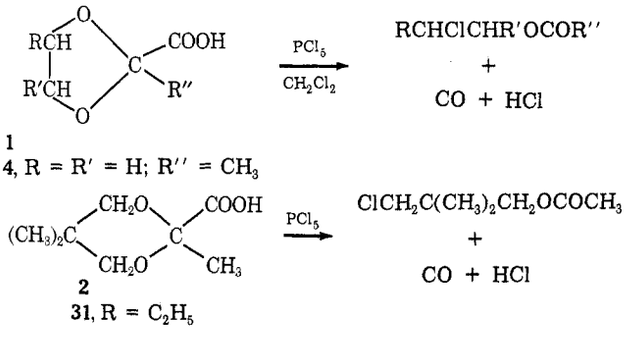
Treatment of a number of cyclic α-ketal acids containing 1,3-dioxolane, 1,3-dioxane, and 1,3-dioxepane rings with phosphorus pentachloride in methylene chloride yielded esters of 1,2-, 1,3-, and 1,4-chlorohydrins, respectively. Evidence is presented to show that 2-chloro-2-methyl-1,3-dioxolane (**5**) and 2-chloro-2,5,5-trimethyl-1,3-dioxane (**9**) are formed directly at −60° from 2-carboxy-2-methyl-1,3-dioxolane (**4**) and 2-carboxy-2,5,5-trimethyl-1,3-dioxane (**8**), respectively. On warming to 0° **5** and **9** rearrange to 2-chloroethyl acetate (**6**) and 3-chloro-2,2-dimethylpropyl acetate (**10**), respectively. Similar reactions with optically active 1,3-dioxolanes yield stereospecific products in which inversion of configuration occurs at the carbon–oxygen bond which is converted to a carbon–chlorine bond. In unsymmetrical 1,3-dioxolanes, the regiospecific products of the reaction are those predicted by assuming an SN2 type mechanism for opening of the 1,3-dioxolane ring. The synthetic utility of these reactions for the synthesis of optically active epoxides is demonstrated.

In a preliminary communication, the conversion of several 2-carboxy-1,3-dioxolanes (**1**) and a 2-carboxy-1,3-dioxane (**2**) into esters of halohydrins by treatment



1

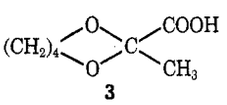
4, R = R' = H; R'' = CH_3

2

31, R = C_2H_5

with phosphorus pentachloride in methylene chloride were described.[2] A more detailed account of this and additional work is presented herein.

The preparation of the requisite 2-carboxy-1,3-dioxolanes and 1,3-dioxanes from diols and pyruvic and benzoylformic acids was accomplished in moderate yields under acid catalysis by either or both of two methods: A, treatment of the α-keto acid with excess diol; and B, treatment of the diol with excess α-keto acid.[3] When method A was used an alkaline treatment was needed during the work-up to hydrolyze any ester formed. Yields of 1,3-dioxanes were better than those of 1,3-dioxolanes (see Table I, Experimental Section). In the only case of a 1,4-diol studied, 1,4-butanediol and pyruvic acid reacted to give 2-carboxy-2-methyl-1,3-dioxapane (**3**) in 63% yield. In a few cases, benzoylformic acid afforded α-ketal acids in about the same yields as when pyruvic acid was used.



3

The reactions of the cyclic acids above described with phosphorus pentachloride or thionyl chloride in methylene chloride took place rapidly at room temperature or below. The evolution of hydrogen chloride and carbon monoxide occurred rapidly under all conditions. Comparable results were obtained when a suspension of the dried sodium salts of **1** and **2** in methylene chloride was treated with thionyl chloride or phosphorus pentachloride. In two cases when thionyl chloride was used, the results were qualitatively the same but the yields of pure halo esters obtained were inferior. Accordingly, in all further work only phosphorus pentachloride was used.

With regard to the mechanism of the reaction, we wished to know whether the acid chloride was formed and lost carbon monoxide or an alternate path was involved. Accordingly, a solution of 2-carboxy-2-

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(2) M. S. Newman and C. H. Chen, *J. Amer. Chem. Soc.*, **94**, 2149 (1972).

(3) E. Vogel and H. Schinz, *Helv. Chim. Acta*, **33**, 116 (1950).