Reactions of the 1,8-Diphenylanthracene System[1]

Herbert O. House,* Nabih I. Ghali, John L. Haack, and Don VanDerveer

School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

Received November 29, 1979

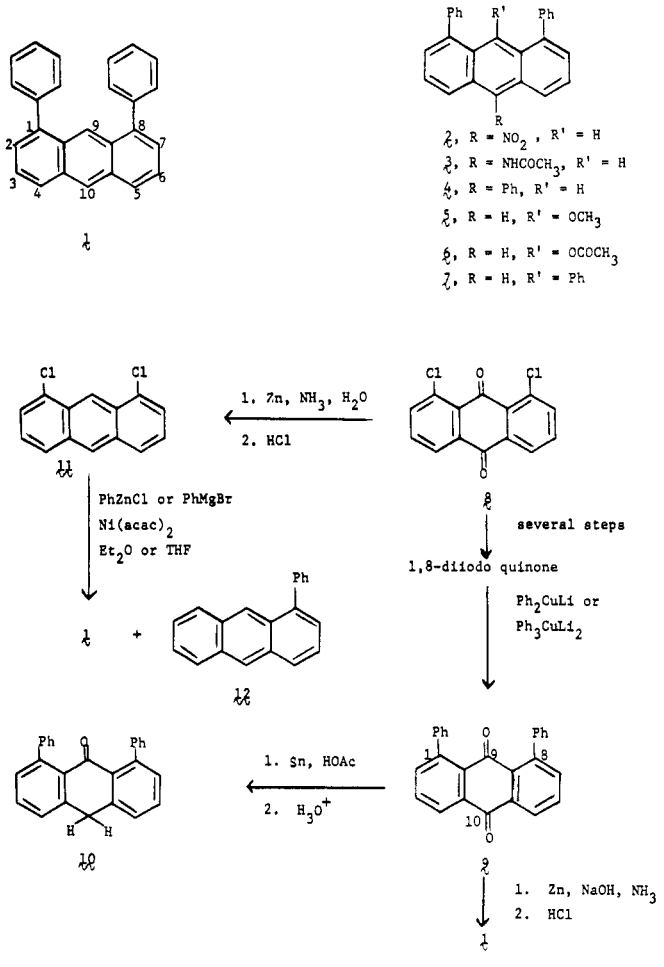
An improved synthesis of 1,8-diphenylanthracene (**1**) is described along with various reactions of this hydrocarbon, including electrophilic substitution reactions, oxidations, and addition of *n*-BuLi. The molecular geometry of a derivative, 10-bromo-1,8-diphenylanthracene (**20**), was determined by X-ray crystallography. Of the various routes explored for forming 9-substituted 1,8-diphenylanthracenes, only the addition of certain organometallic reagents to the 9-anthrone **10** was satisfactory.

Our interest in the 1,8-diphenylanthracene system **1** (Scheme I) arises from the expectation that the favored conformation of this hydrocarbon **1** will have both phenyl rings approximately perpendicular to the plane of the anthracene system. Such a conformation offers the possibility of conferring unusual physical and chemical properties upon atoms or functional groups held in a position approximately 3 Å above atom C(9) of the anthracene ring. Substituents in this position would be located in a rather special microenvironment that would be geometrically favorable for interaction with the π orbitals of the two phenyl rings and would be at least partially shielded from interaction with external ligands. This paper describes a more efficient synthesis of 1,8-diphenylanthracene (**1**), the molecular geometry of the corresponding 10-bromo derivative, and the present status of our effort to find synthetically practical methods for introducing substituents at position C(9) of the 1,8-diphenylanthracene system.

Earlier publications[2] described preparative routes to 1,8-diphenylanthracene (**1**) and certain of its derivatives, **2**–**7**, by conversion of the dichloroquinone **8** to the corresponding diiodide followed by reaction with one of the cuprate reagents Ph_2CuLi or Ph_3CuLi_2 to form the diphenylquinone **9**. This quinone **9** could be reduced and dehydrated to form either the anthrone **10** or the hydrocarbon **1**.

We have now found that the parent hydrocarbon **1** may be prepared more efficiently by reduction and dehydration of the quinone **8** to form 1,8-dichloroanthracene (**11**) followed by coupling with either PhMgBr or PhZnCl in the presence of a catalytic amount of a nickel derivative.[3] Use of other reduction procedures (see Scheme II) with the quinone **8** formed, after acid-catalyzed dehydration, one or both of the anthrones **13** and **14**. The diphenylquinone **9** was readily obtained by oxidation of the hydrocarbon **1** with chromic acid. Although the hydrocarbon **1** was readily converted to the peroxide **16** by photosensitized oxidation, we were unsuccessful in finding a satisfactory method for converting the peroxide **16** directly to the anthrone **10**. Instead, various mixtures of the quinone **9**, the diol **17**, and one of the ketols **18** or **19** were obtained. In any event, the parent hydrocarbon **1** and the quinone **9** are now readily obtained from the dichloroquinone **8**.

Scheme I



Earlier NMR and UV measurements[2] suggested that 1,8-diphenylanthracene (**1**) and its derivatives, like 1,8-diphenylnaphthalene,[4] exist predominantly in a conformation with the two phenyl rings approximately perpendicular to the plane of the anthracene ring. To gain further evidence on this point, we converted the hydrocarbon **1** into its 10-bromo derivative **20** (Scheme III) for X-ray crystallographic analysis. It should be noted that electrophilic substitution by bromine at C-10 was to be ex-

(1) This research has been supported by Public Health Service Grant R01-GM-20197 from the National Institute of General Medical Science. The execution of this research was also assisted by Institutional Research grants from the National Science Foundation for the purchase of a mass spectrometer and a Fourier transform NMR spectrometer.

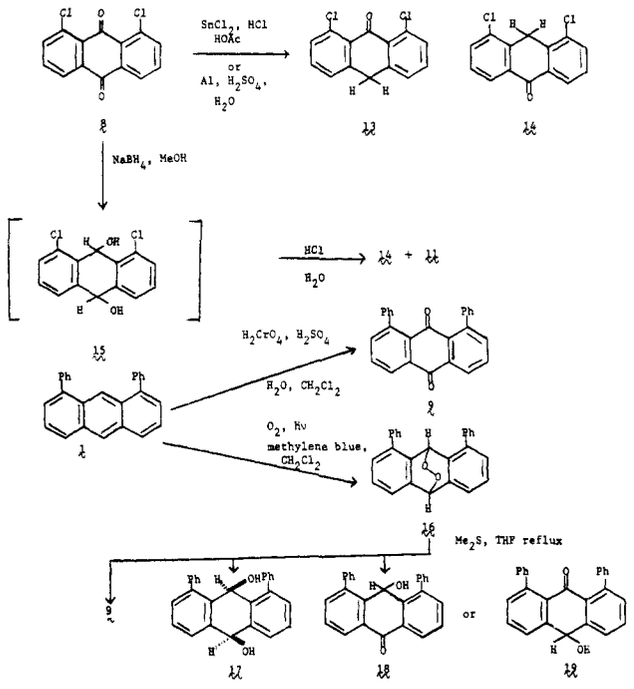
(2) (a) House, H. O.; Koepsell, D. G.; Campbell, W. J. *J. Org. Chem.* **1972**, *37*, 1003. (b) House, H. O.; Koepsell, D.; Jaeger, W. *Ibid.* **1973**, *38*, 1167.

(3) This coupling reaction involving catalytic amounts of Ni(0) and Ni(II) intermediates has been studied by several groups. For leading references, see: (a) Corey, E. J.; Semmelhack, M. F.; Hegedus, L. S. *J. Am. Chem. Soc.* **1968**, *90*, 2416; (b) Morrell, D. G.; Kochi, J. K. *Ibid.* **1975**, *97*, 7262; (c) Kende, A. S.; Liebeskind, L. S.; Braitsch, D. M. *Tetrahedron Lett.* **1975**, 3375; (d) Clough, R. L.; Mison, P.; Roberts, J. D. *J. Org. Chem.* **1976**, *41*, 2252; (d) Negishi, E.; King, A. O.; Okukado, N. *Ibid.* **1977**, *42*, 1821.

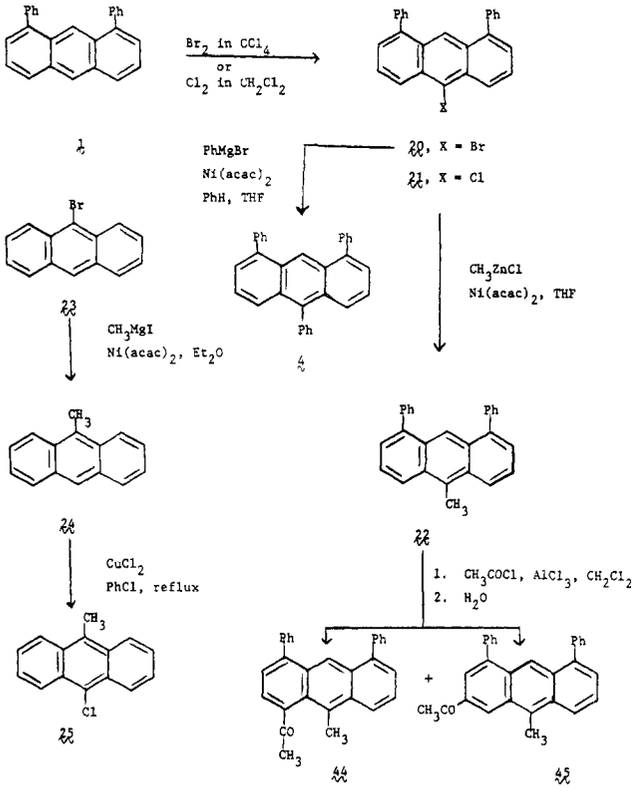
(4) For leading references to earlier studies and crystal structures for 1,8-diphenylnaphthalene and its derivatives, see: ref 2a; Clough, R. L.; Kung, W. J.; Marsh, R. E.; Roberts, J. D. *J. Org. Chem.* **1976**, *41*, 3603.

0022-3263/80/1945-1807$01.00/0

Scheme II



Scheme III



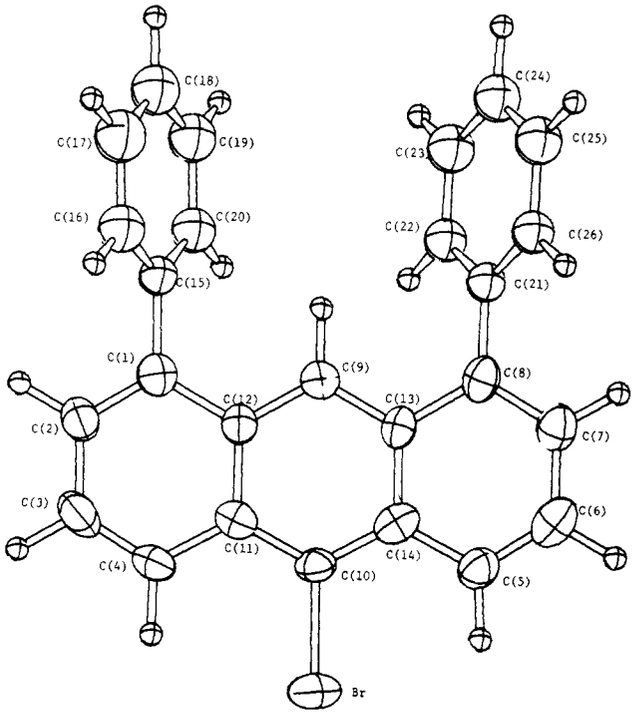


Figure 1. Perspective view from the side of the molecular structure of the bromide **20**.

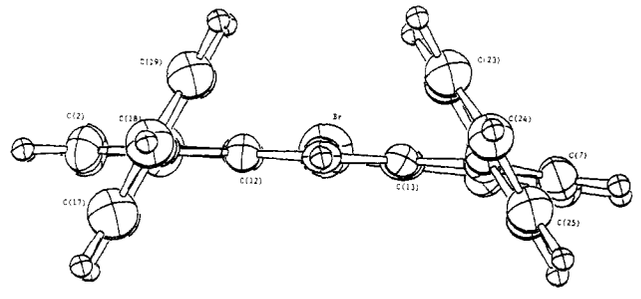


Figure 2. Perspective view from the top of the molecular structure of the bromide **20**.

pected on the basis of our earlier observation[2b] that nitration of the hydrocarbon 1 formed the 10-nitro derivative **2**. Reaction of the bromide **20** with PhMgBr in the presence of a catalytic amount of $Ni(acac)_2$ to form the known[2] 1,8,10-triphenylanthracene (**4**) confirmed our expectation.

Two perspective views of the structure of the bromide **20** are presented in Figures 1 and 2; the bond lengths and bond angles for this structure are listed in Table I. The axes of the two phenyl rings passing through the C-1 and C-8 positions of the anthracene ring are approximately parallel with the following interatomic distances: C(1)–C(8), 4.979 Å; C(15)–C(21), 5.127 Å; C(18)–C(24), 5.485 Å. In the crystal, each phenyl ring is twisted 55–56° from the plane of the anthracene ring. The observation that the two phenyl rings were not approximately parallel to one another was initially surprising. However, upon consideration of the intermolecular interactions present in the crystal, the reason for this geometry in the crystal became apparent. As illustrated in Figure 3, each molecule of the bromide **20** is packed in the crystal in such a way that carbon atoms C(16), C(17), C(25), and C(26) of the phenyl rings in one molecule are at approximately the sums of the van der Waals radii from carbon atoms C(6) and C(7) (and the associated hydrogen atoms) in a second molecule. We presume that in solution, this molecule would adopt a conformation with the two phenyl rings approximately parallel to one another.

As noted above direct electrophilic substitution on 1,8-diphenylanthracene, exemplified by nitration to form compound **2**[2b] and bromination to form bromide **20**, results in initial introduction of a C(10) substituent. Similarly, chlorination formed the 10-chloro derivative **21**. Dinitration introduced the second nitro group at C(4), and our efforts to effect dibromination formed a complex mixture from which we were unsuccessful in isolating any pure substance. Since the chlorination of 9-methylanthracene (**24**) was known[5] to form the 10-chloro-9-methyl

Table I. Molecular Geometry of the Bromoanthracene 20[a]

A. Bond Lengths

atoms	dist, Å	atoms	dist, Å
C10-Br	1.931 (5)	C1-C15	1.485 (6)
C1-C2	1.365 (7)	C15-C16	1.395
C2-C3	1.408 (7)	C16-C17	1.395
C3-C4	1.365 (7)	C17-C18	1.395
C4-C11	1.443 (7)	C18-C19	1.395
C10-C11	1.404 (7)	C19-C20	1.395
C10-C14	1.402 (7)	C15-C20	1.395
C5-C14	1.437 (7)	C8-C21	1.486 (6)
C5-C6	1.333 (7)	C21-C22	1.395
C6-C7	1.408 (7)	C22-C23	1.395
C7-C8	1.376 (7)	C23-C24	1.395
C8-C13	1.438 (7)	C24-C25	1.395
C9-C13	1.405 (6)	C25-C26	1.395
C9-C12	1.397 (6)	C21-C26	1.395
C1-C12	1.452 (6)	C11-C12	1.445 (7)
C13-C14	1.429 (7)		

B. Bond Angles

atoms	angle, deg	atoms	angle, deg
C15-C1-C2	118.7 (4)	C9-C13-C14	119.0 (5)
C2-C1-C12	118.9 (5)	C8-C13-C14	119.0 (5)
C15-C1-C12	122.4 (4)	C8-C13-C9	121.9 (5)
C1-C2-HC2	118.7 (3)	HC9-C9-C12	118.4 (3)
C3-C2-HC2	118.7 (3)	C12-C9-C13	123.1 (5)
C1-C2-C3	122.6 (5)	HC9-C9-C13	118.4 (3)
C2-C3-HC3	119.7 (3)	C1-C12-C11	118.8 (5)
HC3-C3-C4	119.8 (3)	C9-C12-C11	118.9 (5)
C2-C3-C4	120.5 (5)	C1-C12-C9	122.2 (5)
C3-C4-HC4	119.8 (3)	C8-C21-C22	120.6 (2)
HC4-C4-C11	119.9 (3)	C8-C21-C26	119.4 (2)
C3-C4-C11	120.3 (5)	C22-C21-C26	120.0
C4-C11-C12	118.7 (5)	HC17-C17-C16	120.0
C4-C11-C10	124.7 (5)	C16-C17-C18	120.0
C10-C11-C12	116.5 (5)	HC17-C17-C18	120.0
C11-C10-Br	117.2 (4)	HC18-C18-C17	120.0
Br-C10-C14	117.5 (4)	C17-C18-C19	120.0
C11-C10-C14	125.3 (5)	HC18-C18-C19	120.0
C10-C14-C13	117.0 (5)	C18-C19-C20	120.0
C10-C14-C5	124.7 (5)	HC19-C19-C20	120.0
C5-C14-C13	118.3 (5)	C18-C19-HC19	120.0
HC5-C5-C14	119.2 (3)	C15-C20-C19	120.0
HC5-C5-C6	119.2 (3)	C15-C20-HC20	120.0
C6-C5-C14	121.6 (5)	C19-C20-HC20	120.0
C1-C15-C16	119.3 (2)	HC22-C22-C23	120.0
C1-C15-C20	120.7 (2)	HC22-C22-C21	120.0
C16-C15-C20	120.0	C21-C22-C23	120.0
HC16-C16-C17	120.0	HC23-C23-C22	120.0
HC16-C16-C15	120.0	C22-C23-C24	120.0
C15-C16-C17	120.0	HC23-C23-C24	120.0
HC6-C6-C5	119.9 (3)	HC24-C24-C23	120.0
HC6-C6-C7	119.9 (3)	C23-C24-C25	120.0
C5-C6-C7	120.2 (5)	HC24-C24-C25	120.0
C6-C7-C8	122.0 (5)	C24-C25-C26	120.0
HC7-C7-C6	119.0 (3)	HC25-C25-C26	120.0
HC7-C7-C8	119.0 (3)	C24-C25-HC25	120.0
C13-C8-C21	122.1 (4)	C21-C26-C25	120.0
C7-C8-C13	118.7 (5)	C21-C26-HC26	120.0
C7-C8-C21	119.1 (5)	C25-C26-HC26	120.0

[a] Numbers in parentheses indicate estimated standard deviations in the least significant digit.

derivative **25** in good yield, we explored both the bromination and the chlorination of the 10-methyldiphenylanthracene **22**. However, we again obtained rather complex mixtures of products from which we were unable to isolate a 9-halo derivative. Acetylation of this hydrocarbon **22** with CH_3COCl and $AlCl_3$ formed a mixture of the two

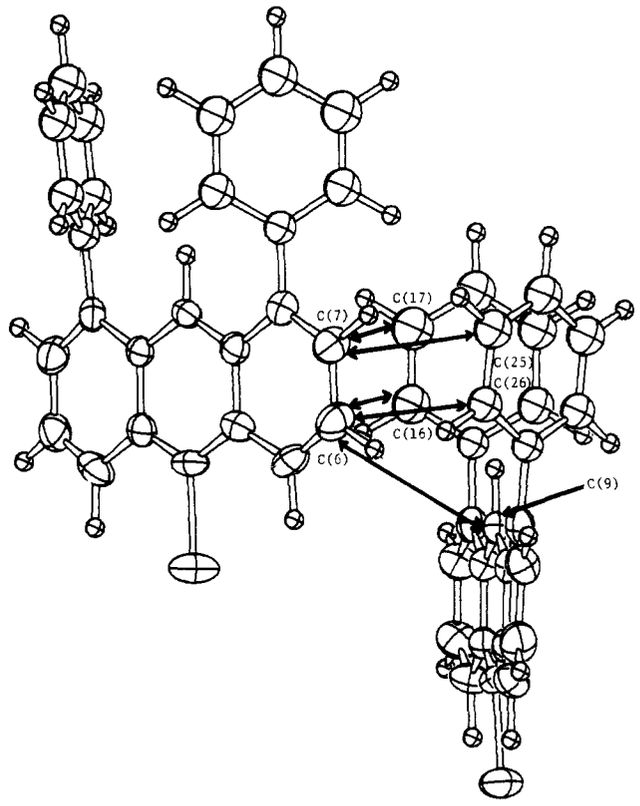
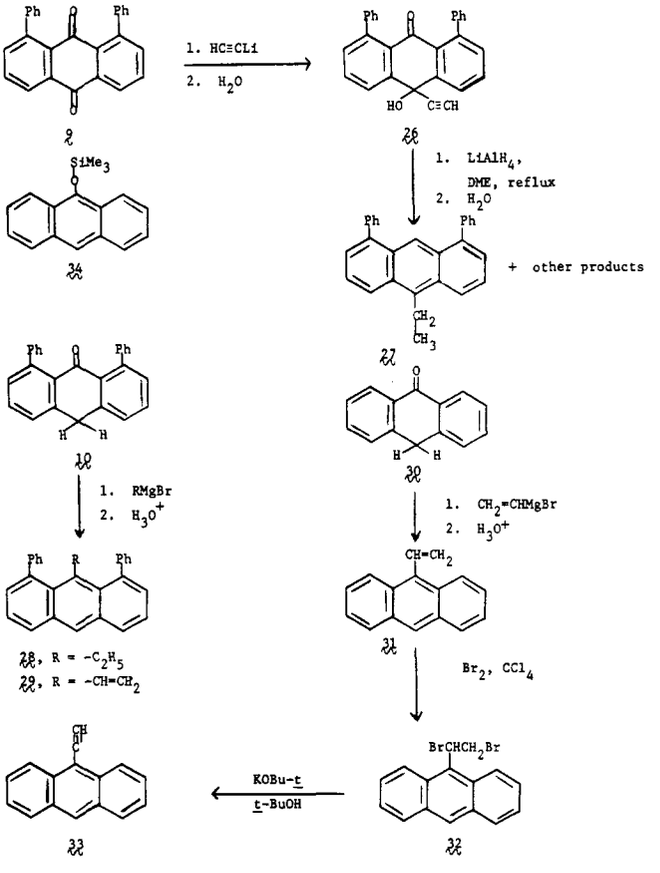


Figure 3. Perspective view of two molecules of the bromide **20**. The distances for the designated interactions are as follows: C(7)–C(17), 3.977 Å; C(7)–C(25), 3.945 Å; C(6)–C(16), 3.900 Å; C(6)–C(26), 3.757 Å; C(6)–C(9), 3.640 Å.

Scheme IV



monoacetyl derivatives **44** and **45**. This combination of experiments discouraged us from examining other electrophilic substitution reactions as a method for introducing

(5) Mosnaim, D.; Nonhebel, D. C.; Russel, J. A. *Tetrahedron* **1969**, *25*, 3485.

a substituent at C(9) of the hydrocarbon 1.

We turned our attention to addition reactions involving the quinone 9 and the related anthrone 10 (Scheme IV). As might have been anticipated from the earlier addition[2] of PhMgBr to the C(10) position of the quinone 9, reaction of the quinone with ethynyllithium formed the ketol 26 that was reduced and dehydrated to form the 10-ethyl compound 27.

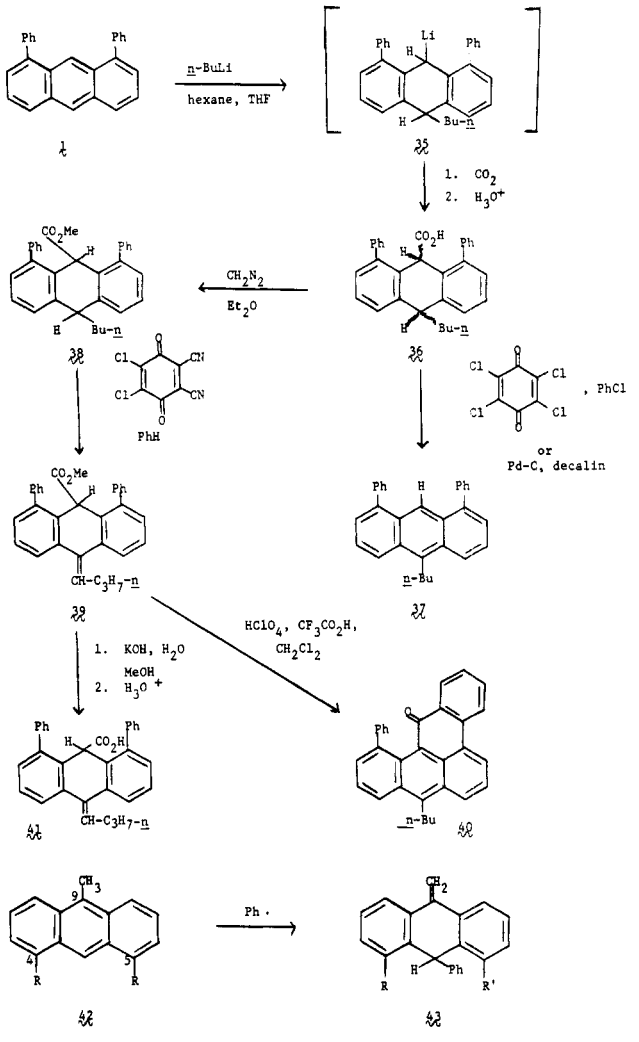
Reaction of the anthrone 10 with either EtMgBr or CH_2=CHMgBr followed by acid-catalyzed dehydration afforded the 9-ethyl and 9-vinyl derivatives 28 and 29. A similar reaction with PhLi was used previously[2a] to form the 9-phenyl derivative 7. Unfortunately, our efforts to effect the same type of reaction with either HC≡CLi or HC≡CMgBr resulted only in conversion of the anthrone 10 to its enolate; acidification regenerated the starting anthrone 10. This same problem has been observed[6] in various attempts to add ethynyl organometallic reagents to anthrone (30). Enol (or enolate) formation was also a complication in our effort to convert anthrone (30) to its cyanohydrin by reaction with Me_3SiCN in the presence of a catalytic amount of cyanide ion.[7] Rather than the desired cyanohydrin derivative, we obtained the trimethylsilyl enol ether 34.

Since 9-vinylanthracene (31) was readily prepared from anthrone (30) and CH_2=CHMgBr, we explored conversion of the vinyl derivative 31 to the acetylene 33 by a bromination–dehydrobromination sequence. This sequence proved to be a satisfactory route to 9-ethynylanthracene (33). Unfortunately, our efforts to effect a comparable conversion starting with the vinyldiphenylanthracene 29 have been thwarted by the formation of a complex mixture upon reaction of the vinyl compound 29 with bromine.

We were attracted by the reports[8] of successful addition of alkyllithium reagents such as EtLi and *n*-BuLi to anthracene since it appeared likely that use of such an addition with the diphenylanthracene 1 would form the 9-lithio derivative 35 (Scheme V). This expectation proved correct and allowed us to obtain the dihydro acid 36. Unfortunately, dehydrogenation of the acid 36 was accompanied by decarboxylation to form the 10-(*n*-butyl)-anthracene 37. However, initial formation of the ester 38 prevented decarboxylation during the dehydrogenation step, but we were surprised to find that the dehydrogenated product 39 contained an exocyclic C=C rather than a fully aromatized anthracene. Attempts to isomerize the unsaturated ester 39 with acid resulted either in no change or, with sufficiently vigorous conditions, in intramolecular acylation to form the fully aromatic ketone 40. Reaction with methanolic KOH slowly saponified the ester 39 to form the corresponding unsaturated acid 41. These results are similar to the observation[9] that 9-methylanthracenes with 4- or 5-substituents (e.g., 42) react with phenyl radicals (from PhN_2^+) to give 9-methylene derivatives 43; in the absence of 4- or 5-substituents the fully aromatized anthracene derivatives were formed.

Thus, among the methods we have examined, the only satisfactory route to 9-substituted derivatives of the 1,8-diphenylanthracene system 1 has been the addition of certain organometallic reagents to the anthrone 10.

Scheme V



Experimental Section[10]

Preparation of 9-Vinylanthracene (31). Reduction of anthraquinone with either $SnCl_2$ and aqueous HCl in HOAc[11] or Al powder and H_2SO_4[12] yielded anthrone (30) as white needles: mp 154–155 °C (lit.[11b] mp 154–155 °C); IR ($CHCl_3$) 1660 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 8.2–8.5 (2 H, m, aryl CH), 7.2–7.6 (6 H, m, aryl CH), 4.30 (2 H, s, CH_2); UV max (95% EtOH) 259 nm (ε 18 900), 268 (17 600), 308 (4400).

To 140 mL of a THF solution containing[13] 121 mmol of CH_2=CHMgBr was added, dropwise and with stirring during 3 h, a solution of 20.0 g (103 mmol) of anthrone (30) in 200 mL of THF. The resulting yellow solution was stirred for an additional 30 min and then partitioned between Et_2O and aqueous 10% HCl.

(6) Reid, W. In "Newer Methods of Preparative Organic Chemistry"; Foerst, W., Ed.; Academic Press: New York, 1968; Vol. 4, p 106.

(7) This procedure for cyanohydrin formation was developed by: Evans, D. A.; Hoffman, J. M.; Truesdale, L. K. *J. Am. Chem. Soc.* **1973**, *95*, 5822.

(8) (a) Zieger, H. E.; Shaeffer, D. J.; Padronaggio, R. M. *Tetrahedron Lett.* **1969**, 5027. (b) Shaeffer, D. J.; Zieger, H. E. *J. Org. Chem.* **1969**, *34*, 3958. (c) Zieger, H. E.; Gelbaum, L. T. *Ibid.* **1972**, *37*, 1012.

(9) Cromarty, F. M.; Henrequez, R.; Nonhebel, D. C. *J. Chem. Res. (S)* **1977**, 309.

(10) 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 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 proton NMR spectra were determined at 60 MHz with a Varian Model A-60 or Model T-60-A NMR spectrometer, and the ^{13}C NMR spectra were determined at 100 MHz with a JEOL Fourier transform spectrometer, Model PFT-100. The chemical shift values are expressed in δ values (parts per million) relative to a Me_4Si internal standard. The mass spectra were obtained with a Hitachi Perkin-Elmer Model RMU-7 or a Varian Model M-66 mass spectrometer. All reactions involving strong bases or reactive organometallic intermediates were performed under a nitrogen atmosphere.

(11) (a) Fatiadi, A. J.; Sager, W. F. "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. 5, p 595. (b) Meyer, K. H. *Ibid.* 1932; Collect. Vol. 1, p 60.

(12) Barnett, E. B.; Matthews, M. A. *J. Chem. Soc.* **1923**, 123, 2549.

(13) Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165.

The crude product, 21 g of yellow brown solid, was chromatographed on silica gel with a hexane–PhH eluent (1:1 v/v) to separate in the early fractions 12.93 g (61%) of the olefin **31** as a yellow solid, mp 62–63 °C. Recrystallization from EtOH afforded the pure olefin **31** as yellow plates: mp 64.5–65.5 °C (lit.[14] mp 64–67 °C); IR (CCl_4) 1620 (C=C), 980, 930 cm^{-1} (CH=CH_2); UV max (95% EtOH) 253 nm (ε 133 000), 337 (sh, 2400), 352 (4600), 368 (6600), 386 (5900); ^1H NMR ($CDCl_3$) δ 7.2–8.5 (10 H, m, aryl and vinyl CH), 5.97 (1 H, dd, J = 2.5, 12 Hz, vinyl CH), 5.68 (1 H, dd, J = 2.5, 18 Hz, vinyl CH); mass spectrum, m/e (relative intensity), 204 (M^+, 100), 203 (94), 202 (54), 103 (13), 102 (28), 100 (11), 88 (14); ^{13}C NMR ($CDCl_3$, multiplicity in off-resonance decoupling) 132.8 (s and d, 2 C atoms), 130.7 (s, 2 C atoms), 128.6 (s, 2 C atoms), 127.9 (d, 2 C atoms), 125.6 (d), 125.3 (d, 2 C atoms), 124.6 (d, 2 C atoms), 124.3 (d, 2 C atoms), 122.0 (t) ppm.

A PhH solution of the later chromatographic fractions was extracted with a solution containing 10% KOH in $HOCH_2CH_2OH$. This basic extract was acidified with aqueous 10% HCl and extracted with CH_2Cl_2 to separate 3.15 g (16%) of the starting anthrone, mp 150–152 °C.

Attempts to add a THF solution of HC≡CLi[15] or HC≡C-MgBr[16] to anthrone (**30**) resulted in recovery of the starting ketone as had been reported previously.[6]

Preparation of the Dibromide 32 and the Acetylene 33. To a cold (−20 °C) solution of 1.008 g (4.94 mmol) of the olefin **31** in 20 mL of CCl_4 was added, dropwise with stirring and cooling during 30 min, 3.15 mL of a CCl_4 solution containing 4.90 mmol of Br_2. The resulting pale yellow solution was allowed to warm to 25 °C and concentrated to leave 1.703 g (95%) of the dibromide **32** as a yellow solid, mp 102–103 °C. Recrystallization from a pentane–CCl_4 mixture separated 1.497 g (83%) of the pure dibromide **32** as yellow prisms: mp 104–105 °C (lit.[17] mp 112 °C); UV max (95% EtOH) 257 nm (ε 82 500), 365 (6800), 382 (9950), 401 (8500); ^1H NMR (CCl_4), δ 5.6–7.2 (9 H, m, aryl CH), 4.9–5.2 (1 H, m, CHBr), 2.6–3.2 (2 H, m, CH_2Br); mass spectrum, m/e (relative intensity) 366 (M^+, 1), 364 (M^+, 2), 362 (M^+, 1), 284 (11), 282 (10), 204 (25), 203 (100), 202 (60), 89 (20); ^{13}C NMR ($CDCl_3$) 35.4 (CH_2Br), 45.2 (CHBr), and a series of partially resolved peaks in the region 121.9–131.4 ppm (aryl C atoms).

Anal. Calcd for $C_{16}H_{12}Br_2$: C, 52.78; H, 3.32; Br, 43.89. Found: C, 52.70; H, 3.34; Br, 43.83.

The reaction of 1.234 g (6.05 mmol) of the olefin **31** with 6.05 mmol of Br_2 in 34 mL of CCl_4 at −20 °C as described above yielded 2.201 g of the crude dibromide **32**, mp 102–103 °C. A solution of this dibromide **32** in 20 mL of anhydrous THF was added to a solution of KO-t-Bu prepared from 0.60 g (15 mmol) of K and 15 mL of anhydrous t-BuOH. The resulting yellow slurry was stirred at 25 °C for 4 h and then filtered and concentrated. The residual orange-brown solid (1.46 g) was chromatographed on neutral alumina with a PhH–hexane eluent (1:1 v/v) to separate 1.201 g of the crude acetylene **33** as an orange solid. Recrystallization from pentane separated 1.003 g (82%) of the acetylene **33** as yellow prisms, mp 73–74 °C. An additional recrystallization from pentane, including treatment with decolorizing carbon, gave the pure acetylene **33** as pale yellow prisms: mp 75.5–76 °C (lit.[18] mp 71–75 °C,[17] 73.5–74 °C,[18a] 76–76.5 °C[18b]); IR (CCl_4) 3300 (acetylenic CH), 2100 cm^{-1} (C≡C); UV max (95% EtOH) 249 nm (sh, ε 81 300), 257 (149 000), 343 (3080), 361 (6900), 380 (11 300), 400 (10 700); ^1H NMR ($CDCl_3$) δ 7.1–8.7 (9 H, m, aryl CH), 3.91 (1 H, s, C≡CH); mass spectrum, m/e (relative intensity) 202 (M^+, 100), 200 (23), 101 (28), 100 (21), 88 (15); ^{13}C NMR ($CDCl_3$, multiplicity in off-resonance decoupling) 132.4 (s, 2 C atoms), 130.2 (s, 2 C atoms), 127.9 (d, 2 C atoms), 127.5 (d), 125.8 (d, 4 C atoms), 124.8 (d, 2 C atoms), 115.3 (s), 80.0 (d) ppm.

Anal. Calcd for $C_{16}H_{10}$: C, 95.02; H, 4.98. Found: C, 94.76; H, 5.20.

Preparation of the Quinone 9. A. From 1,8-Diiodo-9,10-anthraquinone. Previously described procedures[2] were used to convert the commercially available dichloroquinone 8 (Aldrich Chemical Co.) to the corresponding diiodoquinone; reaction of this diiodoquinone with Ph_2CuLi[2] formed the diphenylquinone **9**.

B. From the Anthracene 1. A mixture of 3.95 g (11.9 mmol) of the anthracene **1**, 16.0 g (54.4 mmol) of $K_2Cr_2O_7$, 100 mL of PhCl, 50 mL of H_2O, 40 mL of HOAc, and 10 mL of concentrated H_2SO_4 was refluxed with stirring for 48 h, cooled, and extracted with CH_2Cl_2. The CH_2Cl_2 extract was washed with H_2O, dried, and concentrated to leave 4.19 g of crude product as a yellow solid, mp 194–199 °C. Recrystallization from i-PrOH separated 3.46 g of the quinone **9** as fine yellow needles, mp 200–201 °C (lit.[2a] mp 200–201 °C). An additional 0.25 g (total yield 3.71 g, 86%) of the quinone **9**, mp 199–200 °C, was recovered from the mother liquors.

Preparation of the Dichloroanthracene 11. By use of a previously described procedure,[2b] 10.0 g (36.1 mmol) of the quinone **8** was reduced with 50.0 g (765 mmol) of Zn dust and 200 mL of aqueous 28% NH_3 with a 3-h reaction time at 100 °C. A CH_2Cl_2 solution of the resulting crude solid was combined with the CH_2Cl_2 extract of the supernatant liquid and the mixture dried and concentrated. The residual crude white solid was dissolved in a mixture of 500 mL of i-PrOH and 50 mL of aqueous 12 M HCl. After the resulting solution had been refluxed for 3 h, it was concentrated and partitioned between CH_2Cl_2 and aqueous $NaHCO_3$. The organic layer was dried and concentrated to leave 10.5 g of the crude anthracene **11** as a yellow solid, mp 150–160 °C. This material was recrystallized from a CH_2Cl_2–hexane mixture to separate 7.059 g (79%) of the anthracene **11** as pale yellow needles, mp 156–157 °C (lit.[2b] mp 156.5–158 °C). This material was identified with the previously described[2b] sample by comparison of IR and NMR spectra and by a mixture melting point determination.

Preparation of the Anthracene 1. A. With PhZnCl. Reaction of 19 mL of a 0.68 M ethereal solution of anhydrous $ZnCl_2$ (13 mmol)[19] with 15 mL of an Et_2O solution containing 13 mmol of PhLi (0.87 M) afforded a 0.38 M solution of PhZnCl in Et_2O. To a solution of 201 mg (0.812 mmol) of the anthracene **11** and 9.5 mmol of PhZnCl in 25 mL of Et_2O was added, dropwise and with stirring during 30 min, a solution of 50 mg (0.19 mmol) of anhydrous Ni(acac)$_2$ (Research Organic/Inorganic Chemical Corp.) in 20 mL of THF. The initially yellow solution, which turned dark brown during the addition of the Ni(acac)$_2$, was stirred at 25 °C for an additional 30 min, hydrolyzed with aqueous 2 M HCl, and extracted with CH_2Cl_2. After the organic extract had been dried and concentrated, the residual yellow solid (359 mg) was chromatographed on silica gel with a hexane eluent to separate 171 mg (64%) of the anthracene **1**, mp 188–189 °C. Recrystallization from hexane afforded 153 mg of the pure anthracene **1** as colorless needles, mp 191–192 °C (lit.[2a] mp 191.5–193 °C). This product was identified with a previously described[2a] sample by comparison of IR and NMR spectra.

B. With PhMgBr. To a solution of 10.00 g (36.1 mmol) of the anthracene **11** and 170 mmol of PhMgBr in 200 mL of THF was added, dropwise and with stirring during 2 h, a solution of 50.1 mg (0.195 mmol) of Ni(acac)$_2$ in 10 mL of THF. During this addition the solution gradually turned black [presumably colloidal Ni(0)]. After the addition was complete, the black reaction mixture was stirred for an additional 1 h, quenched with 20 mL of aqueous 3 M HCl, and steam distilled (to remove Ph–Ph). The residual mixture was extracted with CH_2Cl_2. The organic extract was washed with aqueous $NaHCO_3$, dried, and concentrated to leave 14.47 g of crude product as a yellow solid, mp 139–146 °C, containing (TLC, silica gel coating with a PhH–hexane eluent, 1:9 v/v) the starting dichloride **11** (R_f 0.23), the diphenyl derivative **1** (R_f 0.20), and the monophenyl derivative **12** (R_f 0.31). The crude product was recrystallized from a CH_2Cl_2–hexane mixture to separate 5.80 g of the diphenyl derivative **1** as white needles, mp

(14) Hawkins, E. G. E. *J. Chem. Soc.* **1957**, 3858.
(15) Midland, M. M. *J. Org. Chem.* **1975**, *40*, 2250.
(16) Skattebol, L.; Jones, E. R. H.; Whiting, M. C. "Organic Syntheses"; Wiley: New York, 1963; Collect. Vol. 4, p 792.
(17) Rappoport, Z.; Shulman, P.; Thuval (Shoolman), M. *J. Am. Chem. Soc.* **1978**, *100*, 7041.
(18) (a) Michel, R. H. *J. Polym. Sci., Polym. Chem. Ed.* **1967**, *5*, 920. (b) Akiyama, S.; Ogura, F.; Nakagawa, M. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 3443. (c) Okamoto, Y.; Chellappa, K. L.; Kundu, S. K. *J. Org. Chem.* **1972**, *37*, 3185. These authors have reported the acetylene **33** to be a red-orange solid, mp 110–112 °C. Although the nature of this solid is not clear, we have noted that when the acetylene **33** is allowed to stand at 25 °C in contact with air it polymerizes with formation of a red color.

(19) This $ZnCl_2$ solution was prepared as described by: Auerbach, R. A.; Crumrine, D. S.; Ellison, D. L.; House, H. O. *Org. Synth.* **1973**, *54*, 49.

191.5–193 °C (lit.[2a] mp 191.5–193 °C). The residue (7.09 g, mp 159–169 °C) from the mother liquors was chromatographed on silica gel with $CHCl_3$–hexane mixtures as eluents. The early fractions (2.396 g, mp 105–109 °C) were recrystallized from isopropyl alcohol to separate 1.172 g (13% yield) of the monophenyl derivative **12** as white prisms, mp 116–117 °C (lit.[2a] mp 116–117 °C), that were identified with an authentic sample by comparison of IR, UV, NMR, and mass spectra. The later chromatographic fractions (1.904 g) were crystallized from CH_2Cl_2–hexane to separate 1.195 g of the diphenyl derivative **1**, mp 191–192.5 °C (total yield 6.995 g or 59%). The diphenyl derivative **1** was identified with a previously described[2a] sample by comparison of IR, UV, and NMR spectra.

Reduction of the Anthraquinone 8. A. With $SnCl_2$ and HCl. A solution of 5.56 g (20.1 mmol) of the quinone **8**, 13.90 g (61.5 mmol) of $SnCl_2 \cdot H_2O$, 15 mL of aqueous 12 M HCl, and 90 mL of HOAc was refluxed with stirring for 5 h, during which time a brown solid separated and then redissolved to give a yellow solution. After the mixture had been diluted with H_2O and filtered, a solution of the collected solid in CH_2Cl_2 was washed with aqueous $NaHCO_3$, dried, and concentrated to leave 5.01 g of crude solid product, mp 153–165 °C. A 1.015-g portion of the crude product was chromatographed on silica gel with a PhH–hexane eluent (3:1 v/v). The early chromatographic fractions contained 570 mg of the crude anthrone **14**, mp 188–190 °C. Recrystallization from a CH_2Cl_2–hexane mixture separated 339 mg of the pure anthrone **14** as colorless needles, mp 198–199 °C (lit.[20] mp 198 °C). An additional 193 mg (total yield 532 mg or 50%) of the anthrone **14**, mp 196–197 °C, was recovered from the mother liquors: IR ($CHCl_3$) 1666 cm^{-1} (C=O); UV max (cyclohexane) 220 nm (ϵ 16 000), 227 (15 500), 235 (12 900), 264 (15 800), 301 (3220), 310 (2830), 314.5 (3760); ^1H NMR ($CDCl_3$) δ 8.28 (2 H, dd, J = 2, 8 Hz, aryl CH), 7.2–7.8 (4 H, m, aryl CH), 4.18 (2 H, s, benzylic CH_2); mass spectrum, m/e (relative intensity) 264 (M^+, 22), 262 (M^+, 30), 229 (46), 228 (26), 227 (100), 201 (26), 199 (62), 164 (32), 163 (72).

Anal. Calcd for $C_{14}H_8Cl_2O$: C, 63.89; H, 3.06; Cl, 26.94. Found: C, 63.86; H, 3.06; Cl, 26.91.

The later chromatography fractions contained 434 mg of the crude anthrone **13**, mp 160–162 °C. Recrystallization from a CH_2Cl_2–hexane mixture separated 234 mg of the pure anthrone **13** as colorless needles, mp 167–168 °C (lit.[12] mp 167 °C). An additional 136 mg (total yield 370 mg or 35%) of the anthrone **13**, mp 165–166 °C, was obtained from the mother liquors: IR ($CHCl_3$) 1685 cm^{-1} (C=O); UV (95% EtOH), intense end absorption (ϵ 15 700 at 218 nm) with a maximum at 275 nm (ϵ 11 400) and a point of inflection at 310 nm (ϵ 3380); ^1H NMR ($CDCl_3$) δ 7.1–7.5 (6 H, m, aryl CH), 4.18 (2 H, s, benzylic CH_2); mass spectrum, m/e (relative intensity) 264 (M^+, 35), 262 (M^+, 58), 229 (35), 227 (100), 201 (35), 200 (28), 199 (95), 198 (25), 164 (30), 163 (82).

B. With Al and H_2SO_4. Following a previously described procedure,[12] a mixture of 10.0 g (36.1 mmol) of the quinone **8**, 3.00 g (111 mmol) of Al powder, and 110 mL of concentrated H_2SO_4 was stirred overnight at 25 °C. The resulting greenish yellow suspension was poured into an ice–H_2O mixture and then filtered. A CH_2Cl_2 solution of the residual solid was washed with aqueous $NaHCO_3$, dried, and concentrated to leave 9.23 g of yellow solid (mp 135–148 °C) that contained (TLC, silica gel coating with a PhH–hexane eluent, 1:1 v/v) the quinone **8** (R_f 0.19), the anthrone **14** (R_f 0.28), and the anthrone **13** (R_f 0.14). The product was chromatographed to separate, after recrystallization, 658 mg (7%) of the anthrone **14** (mp 196–197 °C) and 5.16 g (54%) of the anthrone **13** (mp 167–168 °C). Both products **13** and **14** were identified with the previously described samples by mixture melting point determinations and comparison of NMR spectra.

C. With $NaBH_4$. By use of a previously described procedure,[21] a cold (0–5 °C) suspension of 2.61 g (9.40 mmol) of the quinone **8** in 70 mL of MeOH was treated, portionwise and with stirring during 15 min, with 1.00 g (26.4 mmol) of $NaBH_4$. After the mixture had been stirred for 2.75 h, during which time a solution was obtained, it was poured into water and filtered. The crude solid product was stirred and heated on a steam bath with 90 mL of aqueous 5 M HCl for 8 h and then diluted with cold H_2O and filtered. After a CH_2Cl_2 solution of the residual solid had been washed with aqueous $NaHCO_3$ and concentrated, the residual solid (2.32 g, mp 190–196 °C) was chromatographed on silica gel to separate 192 mg of the crude anthracene **11** (mp 149–152 °C), 885 mg of the crude anthrone **14** (mp 190–195 °C), and 1.12 g of the crude diol **15**. This crude diol **15** was again heated with aqueous 5 M HCl for 9 h, and the crude neutral product (1.11 g, mp 190–193 °C) was chromatographed to separate 184 mg of the crude anthracene **11** (mp 150–153 °C) and 808 mg of the crude anthrone **14** (mp 190–193 °C). Recrystallization of appropriate combined fractions separated 358 mg (15%) of the anthracene **11** (mp 155–156 °C) and 1.53 g (62%) of the anthrone **14** (mp 197–198 °C). None of the anthrone **13** was isolated.

Reduction of the Anthraquinone 9. To a refluxing mixture of 701 mg (1.95 mmol) of the anthraquinone **9**, 500 mg (4.21 mmol) of granular Sn, and 15 mL of HOAc was added, dropwise and with stirring during 2 h, a solution of 4 mL of aqueous 12 M HCl in 4 mL of HOAc. The resulting pale yellow solution was refluxed with stirring for an additional 1 h and then poured into an ice–water mixture. The crude solid anthrone **10** was collected on a filter and then dissolved in CH_2Cl_2 and washed successively with aqueous $NaHCO_3$ and with H_2O. After the organic solution had been dried and concentrated, the residual crude anthrone **10** (649 mg, mp 152–160 °C) was recrystallized from hexane to separate 485 mg (72%) of the pure anthrone **10** as colorless needles, mp 167–168 °C (lit.[2a] mp 167.5–168.5 °C), with spectral properties corresponding to those previously described.[2a]

Preparation of the Bromide 20. To a solution of 1.01 g (3.06 mmol) of the anthracene **1** in 50 mL of CH_2Cl_2 was added, dropwise and with stirring, 15 mL of a CCl_4 solution containing 3.9 mmol of Br_2. The resulting yellow solution was washed consecutively with aqueous $Na_2S_2O_3$, with aqueous $NaHCO_3$, and with H_2O, dried, and concentrated. The crude product, 1.163 g of yellow solid (mp 225–226 °C), contained (TLC, silica gel coating with a PhH–hexane eluent, 1:9 v/v) the bromide **20** (R_f 0.29), but none of the starting material **1** (R_f 0.21) was detected. Recrystallization from PhH separated 717 mg of the pure bromide **20** as yellow prisms, mp 226–227 °C; an additional 303 mg (total yield 1.02 g or 82%) of bromide **20** (mp 225.5–226.5 °C) was recovered from the mother liquor. The spectral properties of the bromide **20** are as follows: UV max (95% EtOH) 254 nm (sh, ϵ 63 000), 262 (112 000), 368 (sh, 7400), 387 (11 600), 407 (9250); ^1H NMR ($CDCl_3$) δ 8.4–8.7 (3 H, m, aryl CH), 7.2–7.9 (14 H, m, aryl CH); mass spectrum, m/e (relative intensity) 410 (M^+, 100), 408 (M^+, 100), 330 (26), 329 (33), 328 (36), 327 (29), 326 (30), 163 (25), 157 (25), 84 (28), 69 (25), 57 (40), 49 (41), 44 (30), 43 (34), 41 (43).

Anal. Calcd for $C_{26}H_{17}Br$: C, 76.29; H, 4.19; Br, 19.52. Found: C, 76.30; H, 4.24; Br, 19.53.

To establish the structure of the bromide **20**, we treated a solution of 1.365 g (3.34 mmol) of the bromide and 25.2 mmol of PhMgBr in 50 mL of PhH and 30 mL of THF, dropwise and with stirring during 2 h, with a solution of 30 mg (0.12 mmol) of $Ni(acac)_2$ in 10 mL of THF. The resulting solution, which gradually turned black [presumably colloidal Ni(0)], was stirred overnight, quenched with 10 mL of aqueous 3 M HCl, and steam distilled. The CH_2Cl_2 extract of the residue was dried and concentrated to leave 1.56 g of yellow solid, mp 170–176 °C. Recrystallization from hexane separated 768 mg of the anthracene **4** as yellow prisms, mp 195.5–196 °C (lit. mp[2b] 194–195 °C). The residue (598 mg) from the mother liquors was subjected to preparative TLC (silica gel with a PhH–hexane eluent, 1:9 v/v) to separate an additional 259 mg of the anthracene **4**, mp 195–196 °C (total yield 1.027 g or 76%). This product was identified with a previously described[2b] sample of the anthracene **4** by comparison of IR, UV, and NMR spectra.

Preparation of the Peroxide 16. A solution of 522 mg (1.58 mmol) of the anthracene **1** and 11 mg of methylene blue in 150 mL of CH_2Cl_2 in a Pyrex vessel was irradiated for 4 h with the light from two 300-W tungsten bulbs while a slow stream of O_2 was passed through the reaction solution. The resulting solution was concentrated, and the residual solid (534 mg) was chromatographed on silica gel with a PhH eluent to separate 38 mg of early fractions containing (TLC, silica gel coating with PhH as eluent) a mixture of the starting material **1** (R_f 0.71) and the

(20) Barnett, E. B.; Cook, J. W.; Matthews, M. A. *Recl. Trav. Chim. Pays-Bas* **1926**, *45*, 68.
(21) Criswell, T. R.; Klanderman, B. H. *J. Org. Chem.* **1974**, *39*, 770.

peroxide **16** (R_f 0.38). Subsequent fractions contained (TLC) 458 mg of the peroxide **16**, mp 170–173 °C dec.

Recrystallization from a CH_2Cl_2–hexane mixture afforded 383 mg (67%) of the pure peroxide **16** as colorless needles: mp 173–174 °C dec; IR ($CHCl_3$), no OH or C=O absorption; UV max (95% EtOH) 232 nm (ϵ 38 300); ^1H NMR ($CDCl_3$) δ 7.0–7.6 (16 H, m, aryl CH), 6.56 (1 H, partially resolved multiplet, benzylic OCH), 6.11 (1 H, partially resolved multiplet, benzylic OCH); mass spectrum, *m/e* (relative intensity) 362 (M^+, 100), 346 (55), 333 (30), 331 (25), 330 (80), 149 (40), 121 (20), 105 (30), 77 (35), 57 (24), 55 (25), 43 (23), 41 (28), 40 (48).

Anal. Calcd for $C_{26}H_{18}O_2$: C, 86.16; H, 5.01. Found: C, 85.98; H, 5.04.

Preparation of the Vinylanthracene 29. To 20 mL of a THF solution containing 14 mmol of CH_2=CHMgBr was added, dropwise and with stirring during 2 h, a solution of 1.116 g (3.23 mmol) of the anthrone **10** in 30 mL of THF. The resulting brown to red-brown solution was stirred overnight and then poured into aqueous 1 M HCl. After the acidic mixture had been stirred at 25 °C for 15 min, it was extracted with PhH. The organic extract was washed successively with aqueous $NaHCO_3$ and with H_2O, dried, and concentrated to leave 1.013 g of the crude product as a yellow solid, mp 190–197 °C. Recrystallization from a CH_2Cl_2–hexane mixture separated 436 mg of the anthracene **29** as yellow needles, mp 214–215 °C. The residue from the mother liquors was chromatographed on silica gel with a PhH–hexane eluent to separate in the early fractions an additional 102 mg of the anthracene **29**, mp 213–214 °C (total yield 538 mg or 47%). Later fractions from the chromatography contained 139 mg (13% recovery) of the starting anthrone **10**, mp 166–168 °C. The spectral properties of the vinylanthracene **29** are as follows: UV max (95% EtOH) 263 nm (ϵ 80 000), 355 (sh, 4800), 385 (7030), 403 (6710); mass spectrum, *m/e* (relative intensity) 357 (31), 356 (M^+, 100), 355 (36), 279 (31), 277 (25), 276 (20), 163 (21), 149 (54), 104 (20), 91 (20), 69 (25), 57 (40), 56 (35), 55 (51), 44 (28), 43 (48), 41 (40), 40 (56), 39 (30); ^1H NMR ($CDCl_3$) δ 8.42 (1 H, s, aryl CH), 7.2–8.1 (16 H, m, aryl CH), 5.76 (1 H, dd, J = 6, 9 Hz, vinyl CH), 4.05 (1 H, dd, J = 1, 6 Hz, vinyl CH), 3.81 (1 H, dd, J = 1, 9 Hz, vinyl CH).

Anal. Calcd for $C_{28}H_{20}$: C, 94.34; H, 5.66. Found: C, 94.24; H, 5.73.

As had been observed with anthrone (**30**), an attempt to add HC≡CMgBr in THF solution to the anthrone **10** by reaction overnight at 25 °C resulted in the recovery of 86% of the starting anthrone, mp 166–167 °C.

Reaction of the Peroxide 16 with Me_2S. A solution of 1.50 g (4.15 mmol) of the peroxide **16** and 10 mL of Me_2S in 30 mL of THF was refluxed overnight and then concentrated to leave 1.67 g of crude product as a yellow solid, mp 167–178 °C. This product contained (TLC, silica gel coating with an EtOAc–PhH eluent, 1:9 v/v) the quinone **9** (R_f 0.67), the ketol **18** or **19** (R_f 0.53), and the diol **17** (R_f 0.45). The crude product was chromatographed on silica gel by employing first PhH and then EtOAc–PhH (1:9 v/v) as the eluent. The early fractions (299 mg, mp 167–173 °C) were recrystallized from *i*-PrOH to separate 201 mg (13%) of the quinone **9** as yellow needles, mp 200–201 °C.

Subsequent fractions contained 833 mg of crude ketol **18** or **19** as a pale yellow solid, mp 160–166 °C. Recrystallization from a CH_2Cl_2–hexane mixture separated 538 mg (36%) of the pure ketol **18** or **19** as colorless prisms: mp 169–170 °C dec; IR (KBr pellet) 3390 (OH), 1672 cm^{-1} (C=O); UV max (95% EtOH) 236 nm (ϵ 34 500), 288 (10 400); mass spectrum, *m/e* (relative intensity) 362 (M^+, 23), 360 (46), 359 (70), 347 (30), 346 (100); ^1H NMR ($CDCl_3$) δ 8.0–8.4 (2 H, m, aryl CH at C-4 and C-5), 7.0–7.9 (14 H, m, aryl CH), 5.91 (1 H, d, J = 6 Hz, benzylic CH), 2.03 (1 H, d, J = 6 Hz, OH, exchanged with D_2O); ^{13}C NMR ($CDCl_3$, multiplicity in off-resonance decoupling) 184.6 (s), 141.7 (s, 2 C atoms), 138.9 (s, 2 C atoms), 138.4 (s, 2 C atoms), 134.3 (s, 2 C atoms), 131.5 (d, 2 C atoms), 128.4 (d, 4 C atoms), 127.9 (d, 2 C atoms), 127.5 (d, 4 C atoms), 126.9 (d, 2 C atoms), 126.5 (d, 2 C atoms), 60.6 (d) ppm. The presence of a low-field multiplet in the ^1H NMR spectrum (δ 8.0–8.4) is characteristic of H atoms at C-4 and C-5 when a C=O function is present at C-10. Consequently, the ketol has been tentatively assigned structure **18**; however, the isomeric structure **19** has not been rigorously excluded.

Anal. Calcd for $C_{26}H_{18}O_2$: C, 86.16; H, 5.01. Found: C, 86.13; H, 5.01.

The final fractions from this chromatography contained 334 mg of the diol **17** as a white solid, mp 170–172 °C dec. Successive recrystallizations from PhH and from EtOAc separated the pure diol **17** as 209 mg (14%) of colorless prisms: mp 171–172 °C dec; IR (KBr pellet) 3300 cm^{-1} (br, OH); UV max (cyclohexane), 229 nm (ϵ 30 000); mass spectrum, *m/e* (relative intensity) 347 (55), 346 (100), 331 (25), 330 (84), 78 (52). Because of the insolubility of the diol **17** we were unsuccessful in attempts to obtain useful NMR spectra.

Anal. Calcd for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53. Found: C, 85.57; H, 5.56.

Preparation of Trimethylsilyl Cyanide.[22] To a cold (5 °C) solution of 52.0 g (0.48 mol) of Me_3SiCl (distilled from CaH_2) and 60.0 g (0.60 mol) of Et_3N in 1000 mL of Et_2O was added, through a gas-inlet tube with stirring during 1 h, 18 g (0.66 mol) of anhydrous HCN.[23] After the resulting solution had been allowed to warm to 25 °C and allowed to stand overnight, the $Et_3NH^+Cl^-$ was removed by filtration and washed with Et_2O. The combined organic filtrates were concentrated by distillation of the Et_2O through a 30-cm Vigreux column. Distillation of the residual liquid separated 30.0 g (63.0%) of Me_3SiCN as a colorless liquid: bp 116–117 °C (lit.[22] bp 117–118 °C); IR (CCl_4) 2190 cm^{-1} (C≡N). When the same product was prepared by an alternative method[24] from reaction of 15.50 g (143 mmol) of Me_3SiCl, 12.1 g (186 mmol) of KCN, and 393 mg (1.48 mmol) of 18-crown-6 polyether in 20 mL of CH_2Cl_2 for 36 h, the yield of Me_3SiCN was 2.387 g (17%).

Reaction of Anthrone (30) with Me_3SiCN. A solution of 1.759 g (9.07 mmol) of anthrone, 4.301 g (43.4 mmol) of Me_3SiCN, 10 mg (0.15 mmol) of KCN, and 25 mg (0.095 mmol) of 18-crown-6 polyether in 50 mL of anhydrous PhH was refluxed with stirring for 16 days and then concentrated under reduced pressure. The residual tan solid (1.958 g, mp 100–109 °C) was chromatographed on silica gel with a PhH–hexane eluent (1:9 v/v) to separate early fractions containing 1.059 g of the anthracene **34**, mp 106–107 °C. Recrystallization from hexane afforded 968 mg (41%) of the pure anthracene **34** as white needles: mp 107.5–108.5 °C (lit.[25] mp 105–106 °C); UV max (cyclohexane) 247 nm (ϵ 51 000), 252 (58 100), 258 (62 400), 340 (sh, 2690), 359 (5290), 378 (7630), 400 (5900); ^1H NMR ($CDCl_3$) δ 7.7–8.4 (5 H, m, aryl CH), 7.2–7.6 (4 H, m, aryl CH), 0.32 (9 H, s, Me_3SiO); ^{13}C NMR ($CDCl_3$, multiplicity in off-resonance decoupling) 146.9 (s), 131.7 (s, 2 C atoms), 127.5 (d, 2 C atoms), 124.6 (d, 2 C atoms), 123.5 (d 2, C atoms), 123.0 (s, 2 C atoms), 122.4 (d, 2 C atoms), 118.9 (d), 0.9 (q, 3 C atoms) ppm; mass spectrum, *m/e* (relative intensity) 266 (M^+, 38), 73 (100).

Anal. Calcd for $C_{17}H_{18}OSi$: C, 76.63; H, 6.82. Found: C, 76.61; H, 6.82.

Subsequent chromatographic fractions contained 842 mg of anthrone (**30**), mp 153–157 °C. Recrystallization from hexane separated 793 mg (45%) of pure anthrone, mp 155–156 °C.

Reaction of the Quinone 9 with Lithium Acetylide. A cold (−70 °C) solution of lithium acetylide (prepared by adding 20 mL of a hexane solution containing 30 mmol of *n*-BuLi to 100 mL of cold (−78 °C) THF saturated with acetylene) was added, dropwise and with stirring, to a solution of 2.013 g (5.59 mmol) of the quinone **9** in 100 mL of THF. After the resulting mixture had been refluxed for 3 h, it was washed with H_2O, dried, and concentrated to leave 2.457 g of pale yellow solid, mp 205–208 °C. Recrystallization from a CH_2Cl_2–hexane mixture separated 1.306 g of the pure ketol **26** as colorless needles, mp 209–210 °C; an additional 0.575 g (total yield 1.881 g or 87%) of ketol **26** (mp 208–209 °C) was recovered from the mother liquor. The spectral properties of the ketol **26** are as follows: IR ($CHCl_3$) 3560, 3595 (OH), 3305 (acetylenic CH), 1685 cm^{-1} (C=O); UV max (95% EtOH) 222 nm (ϵ 26 800), 286 (9870); ^1H NMR ($CDCl_3$) δ 8.12 (dd,

(22) The procedure of: Uznanski, B.; Stec, W. J. *Synthesis* **1978**, 154.
(23) The anhydrous HCN was prepared by the procedure of: Brauer, G. "Handbuch der Preparativen Anorganischen Chemie"; Ferdinand Enke, Verlag: Stuttgart, 1960; Vol. 1, p 584.
(24) See ref 7 and: Zubrick, J. W.; Dunbar, B. I.; Durst, H. D. *Tetrahedron Lett.* **1975**, 71.
(25) Bouas-Laurent, H.; Lapouyade, R.; Brigand, C.; Desvergne, J. P. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1970**, *270*, 2167.

J = 2, 8 Hz, aryl CH), 7.0–7.7 (14 H, m, aryl CH), 3.10 (1 H, s, OH, exchanged with D_2O), 2.81 (1 H, s, C≡CH); mass spectrum, m/e (relative intensity) 386 (M^+, 30), 385 (100), 384 (99), 369 (15), 368 (43), 367 (75), 359 (15), 358 (17), 291 (11), 184 (10).

Anal. Calcd for $C_{28}H_{18}O_2$: C 87.02; H, 4.69. Found: C, 87.17; H, 4.91.

Reduction of the Ketol 26. A solution of 905 mg (2.33 mmol) of the ketol **26** and 1.00 g (26.3 mmol) of $LiAlH_4$ in 100 mL of DME was refluxed for 24 h, cooled, and treated with 1 mL of H_2O followed by 2 g of $MgSO_4$. The resulting mixture was filtered from the insoluble salts, and the filtrate was concentrated to leave 810 mg of yellow solid (mp 90–100 °C) that contained (TLC with silica coating and a PhH eluent) the starting ketol **26** (R_f 0.10), the anthracene **27** (R_f 0.75), and several additional unidentified components. This material was chromatographed on silica gel with a CH_2Cl_2–hexane eluent (1:4 v/v) to separate 89 mg of early fractions containing the anthracene (**27**), mp 205–207 °C. Recrystallization afforded 80 mg (10%) of the pure anthracene **27** as pale yellow needles: mp 207–208 °C; IR (KBr pellet), no absorption attributable to OH or C=O groups; UV max (95% EtOH) 263 nm (ε 99 200), 345 (2980), 364 (6260), 383 (9850), 402 (8350); ^1H NMR ($CDCl_3$) δ 8.50 (1 H, br s, aryl CH), 8.31 (2 H, dd, J = 2, 10 Hz, aryl CH), 7.1–7.7 (14 H, m, aryl CH), 3.72 (2 H, q, J = 7 Hz, benzylic CH_2), 1.50 (3 H, t, J = 7 Hz, CH_3); mass spectrum, m/e (relative intensity) 359 (M + 1, 28), 358 (M^+, 100), 343 (80), 328 (24).

Anal. Calcd for $C_{28}H_{22}$: C, 93.81; H, 6.19. Found: C, 93.82; H, 6.14.

Preparation of the Anthracene 28. To a solution of 9.6 mmol of EtMgBr in 10 mL of THF was added, dropwise and with stirring during 30 min, a solution of 657 mg (1.90 mmol) of the anthrone **10** in 30 mL of THF. After the resulting solution had been stirred overnight, it was partitioned between aqueous 2 M HCl and PhH. The organic layer was washed successively with aqueous $NaHCO_3$ and with H_2O, dried, and concentrated to leave 670 mg of yellow solid (mp 230–235 °C) containing (TLC, silica gel coating with a PhH eluent) the anthracene **28** (R_f 0.78) and the anthrone **10** (R_f 0.36). This material was chromatographed on silica gel with a CH_2Cl_2–hexane eluent (1:9 v/v). The early fractions contained 320 mg of the crude anthracene **28**, mp 280–285 °C. Recrystallization from a CH_2Cl_2–hexane mixture separated 191 mg of pure anthracene **28** as yellow needles, mp 288–289 °C; an additional 98 mg (total yield 289 mg or 43%) of the same product (mp 287–289 °C) was recovered from the mother liquors. The spectral properties of the anthracene **28** are as follows: IR (KBr pellet), no absorption attributable to OH or C=O functions; UV max (95% EtOH) 268 nm (ε 89 500), 377 (5390), 395 (7670), 417 (6390); ^1H NMR ($CDCl_3$) δ 8.37 (1 H, s, aryl CH), 8.02 (2 H, dd, J = 3, 9 Hz, aryl CH), 7.2–7.7 (14 H, m, aryl CH), 2.16 (q, J = 7 Hz, benzylic CH_2), 0.15 (3 H, t, J = 7 Hz, CH_3); mass spectrum, m/e (relative intensity) 359 (M + 1, 30), 358 (M^+, 100), 341 (20), 329 (47).

The later chromatographic fractions (313 mg) were recrystallized to separate 301 mg (46% recovery) of the starting anthrone **10**, mp 167–168 °C.

Anal. Calcd for $C_{28}H_{22}$: C, 93.81; H, 6.19. Found: C, 93.75; H, 6.21.

Preparation of the Acid 36. A cold (0 °C) solution of 2.176 g (6.59 mmol) of the anthracene **1** and 15 mmol of n-BuLi in 10 mL of hexane and 100 mL of THF[8] was stirred at 0 °C for 1 h and then siphoned into cold (−78 °C), anhydrous Et_2O saturated with CO_2. The resulting mixture was acidified with aqueous 1 M HCl, and the organic layer was washed with aqueous $NaHCO_3$ (the acid **36** is insoluble in aqueous $NaHCO_3$), dried, and concentrated. The residual pale yellow solid (2.259 g, mp 265–268 °C dec) contained (TLC, silica gel coating with a PhH eluent) the acid **36** (R_f 0.10) and the starting anthracene **1** (R_f 0.75). Recrystallization from a CH_2Cl_2–hexane mixture separated 1.532 g of the acid **36** (a mixture of stereoisomers) as fine white crystals (mp 276–277 °C dec) accompanied by 594 mg (total yield 2.126 g or 75%) of less pure acid **36**: mp 274–276 °C dec; IR ($CHCl_3$) 2900–3200 (br, associated OH), 1700 cm^{-1} (carboxyl C=O); UV max (95% EtOH) 212 nm (ε 51 400), 240 (sh, 14 900); ^1H NMR ($CDCl_3$) δ 7.0–7.4 (17 H, m, OH and aryl CH), 5.30 (1 H, s, benzylic CH), 3.6–4.2 (1 H, m, benzylic CH of two stereoisomers), 0.7–2.0 (9 H, m, aliphatic CH); mass spectrum, m/e (relative intensity) 432 (M^+, 2), 388 (22), 387 (81), 332 (24), 331 (100), 330 (40).

Anal. Calcd for $C_{31}H_{28}O_2$: C, 86.08; H, 6.53. Found: C, 86.07; H, 6.80.

A mixture of 1.039 g (2.41 mmol) of the acid **36**, 1.001 g (4.07 mmol) of chloranil, and 100 mL of PhCl was refluxed with stirring for 3 days and then concentrated to leave 2.09 g of brown solid containing (TLC, silica gel coating with a PhH eluent) the acid **36** (R_f 0.10), chloranil (R_f 0.75), and the anthracene **37** (R_f 0.87). Chromatography on silica gel with CH_2Cl_2–hexane (1:9 v/v) as an eluent separated early fractions containing 452 mg of the crude anthracene **37**, mp 182–186 °C. Recrystallization from a CH_2Cl_2–hexane mixture afforded 402 mg (43%) of the pure anthracene **37** as yellow needles: mp 185–186 °C; IR ($CHCl_3$), no absorption attributable to OH or C=O groups; UV max (95% EtOH) 261 nm (ε 102 200), 347 (3240), 368 (6800), 385 (10 530), 398 (8900); ^1H NMR ($CDCl_3$) δ 8.52 (1 H, s, aryl CH), 8.36 (2 H, dd, J = 1.5, 10 Hz, aryl CH), 7.0–7.7 (14 H, aryl CH), 3.74 (2 H, t, J = 8 Hz, benzylic CH_2), 0.8–2.2 (7 H, m, aliphatic CH); mass spectrum, m/e (relative intensity) 387 (M + 1, 24), 386 (M^+, 74), 344 (28), 343 (100), 331 (41), 165 (23).

Anal. Calcd for $C_{30}H_{26}$: C, 93.22; H, 6.78. Found: C, 93.13; H, 6.84.

A similar attempt to dehydrogenate 222 mg (0.514 mmol) of the acid **36** with 20 mg of 5% Pd/C catalyst in 70 mL of refluxing decalin for 24 h resulted in the isolation of 193 mg (97%) of the anthracene **37**, mp 185–186 °C.

Preparation of the Unsaturated Ester 39. A solution of 2.00 g (4.6 mmol) of the acid **36** (a mixture of stereoisomers) in 50 mL of THF was added to 100 mL of an Et_2O solution containing 8.6 mmol of CH_2N_2. After the resulting solution had been allowed to stand for 3 h, it was concentrated to leave 2.06 g of the crude ester **38**, mp 120–123 °C. Recrystallization separated 2.03 g (98%) of the pure ester **38** (presumably a mixture of stereoisomers) as colorless needles: mp 130–131 °C; IR ($CHCl_3$) 1728 cm^{-1} (ester C=O); UV (95% EtOH) 235 nm (sh, ε 16 600); ^1H NMR ($CDCl_3$) δ 7.0–7.4 (16 H, m, aryl CH), 5.32 (1 H, s, benzylic CH), 3.8–4.2 (1 H, m, benzylic CH), 3.39 (3 H, s, OCH_3), 0.7–1.8 (9 H, m, aliphatic CH); mass spectrum, m/e (relative intensity) 466 (M^+, <1), 388 (55), 387 (34), 386 (100), 344 (24), 330 (65), 329 (85), 328 (20).

Anal. Calcd for $C_{32}H_{30}O_2$: C, 86.06; H, 6.77. Found: C, 86.35; H, 6.88.

A red solution of 2.53 g (5.69 mmol) of the ester **38** and 1.30 g (5.72 mmol) of 2,3-dichloro-5,6-dicyanobenzoquinone in 100 mL of PhH was refluxed for 6 h, and the resulting yellow suspension was cooled and filtered through a short column of silica gel with a CH_2Cl_2–hexane mixture (1:1 v/v) as the eluent. The resulting eluent was concentrated to leave 2.41 g of yellow solid (mp 85–93 °C) containing (TLC, silica gel coating with an EtOAc–hexane eluent, 1:9 v/v) the unsaturated ester **39** (R_f 0.58) but none of the starting ester **38** (R_f 0.61). Recrystallization from hexane afforded 2.04 g (81%) of the unsaturated ester **39** as colorless fine crystals: mp 103–104 °C; IR ($CHCl_3$) 1731 cm^{-1} (ester C=O); UV max (95% EtOH) 232 nm (ε 39 400); mass spectrum, m/e (relative intensity) 444 (M^+, 10), 386 (32), 385 (100), 343 (34); ^1H NMR ($CDCl_3$) δ 7.0–7.6 (16 H, m, aryl CH), 6.16 (1 H, t, J = 7 Hz, vinyl CH), 5.32 (1 H, s, benzylic CH), 3.39 (3 H, s, OCH_3), 2.61 (2 H, q, J = 7 Hz, allylic CH_2), 1.2–1.9 (2 H, m, CH_2), 0.97 (3 H, t, J = 7 Hz, CH_3); ^{13}C NMR ($CDCl_3$, multiplicity in off-resonance decoupling) 171.0 (s), 140.5 (s, 2 C atoms), 140.2 (s, 2 C atoms), 136.3 (s), 135.9 (s), 133.4 (s), 131.3 (s), 130.2 (s), 128.6 (d, 5 (?) C atoms), 127.6 (d, 5 (?) C atoms), 126.5 (d, 3 C atoms), 125.8 (d, 2 C atoms), 123.0 (d, 2 C atoms), 52.0 (q), 45.8 (d), 31.8 (t), 23.4 (t), 13.9 (q) ppm.

Anal. Calcd for $C_{32}H_{28}O_2$: C, 86.45; H, 6.35. Found: C, 86.36; H, 6.42.

A solution of 489 mg (1.09 mmol) of the ester **39** and methanolic NaOMe, prepared from 0.10 g (4.3 mmol) of Na and 15 mL of MeOD, was heated to reflux and then stirred at 25 °C for 5 days. After the resulting mixture had been neutralized with CH_3CO_2D, the ester **39** was recovered (471 mg, mp 101–103 °C) and recrystallized from CH_2Cl_2–hexane to separate 453 mg (93% recovery) of the unchanged ester **39**, with NMR absorption indicating the absence of any appreciable deuterium incorporation.

A solution of 1.05 g (2.36 mmol) of the ester **39** and 1.00 g (15.2 mmol) of KOH in 20 mL of H_2O and 40 mL of MeOH was refluxed for 48 h. After the mixture had been acidified with aqueous HCl

and then extracted with CH_2Cl_2, the organic extract was washed with H_2O, dried, and concentrated to leave 982 mg of crude solid (mp 220–228 °C) that contained (TLC, silica gel coating with a CH_2Cl_2–hexane eluent, 1:4 v/v) the acid **41** (R_f 0.10) and a small amount of the starting ester **39** (R_f 0.57). Chromatography on silica gel with hexane–CH_2Cl_2 mixtures as the eluent separated initial fractions containing 85 mg of the crude ester **39**. Recrystallization from hexane afforded 65 mg (6% recovery) of the ester **39**, mp 103–104 °C. Subsequent chromatographic fractions (866 mg) were combined and recrystallized from hexane to separate 850 mg (83%) of the acid **41** as fine colorless crystals: mp 231–232 °C dec; IR ($CHCl_3$) 2800–3200 (br, carboxyl OH), 1705 cm^{-1} (carboxyl C=O); UV max 236 nm (ϵ 41 600); ^1H NMR ($CDCl_3$) δ 10.33 (1 H, br, OH), 6.8–7.6 (16 H, m, aryl CH), 6.06 (1 H, t, J = 7 Hz, vinyl CH), 5.23 (1 H, s, benzylic CH), 2.52 (2 H, q, J = 7 Hz, allylic CH_2), 1.36 (2 H, quintet, J = 7 Hz, CH_2), 0.68 (3 H, t, J = 7 Hz, CH_3); mass spectrum, m/e (relative intensity) 430 (M^+, 23), 385 (100), 343 (32); ^{13}C NMR ($CDCl_3$, multiplicity in off-resonance decoupling) 176.8 (s), 140.5 (s), 140.3 (s, 2 C atoms), 139.6 (s, 2 C atoms), 136.1 (s), 135.4 (s), 132.6 (s), 130.6 (s and d, 2 C atoms), 128.3 (d, 4 C atoms), 127.3 (d, 4 C atoms), 126.6 (d, 2 C atoms), 126.3 (d, 2 C atoms), 125.7 (d, 2 C atoms), 122.7 (d, 2 C atoms), 45.3 (d), 31.5 (t), 23.0 (t), 13.4 (q) ppm.

Anal. Calcd for $C_{31}H_{26}O_2$: C, 86.48; H, 6.09. Found: C, 86.76; H, 6.20.

A 1.35-g (3.14 mmol) sample of the acid **41** in 70 mL of THF was allowed to react with excess ethereal CH_2N_2. The crude neutral product (1.44 g, mp 100–104 °C) was recrystallized from a CH_2Cl_2–hexane mixture to separate 1.355 g (97%) of the ester **39** (mp 103–104 °C) that was identified with the previously described sample by a mixture melting point determination and by comparison of IR and NMR spectra.

A solution of 2.003 g (4.51 mmol) of the ester **39**, 23 mmol of $HClO_4$, and 4 mL of H_2O in a mixture of 10 mL of CF_3CO_2H and 20 mL of CH_2Cl_2 was stirred at 25 °C for 3 days and then partitioned between CH_2Cl_2 and H_2O. After the organic layer had been washed successively with aqueous $NaHCO_3$ and with H_2O, it was dried and concentrated to leave 1.93 g of red solid (mp 130–139 °C) that contained (TLC, silica gel with a CH_2Cl_2 eluent) the ketone **40** (R_f 0.48) along with small amounts of the starting ester **39** (R_f 0.78) and several other minor, rapidly eluted components. The material was chromatographed on silica gel with a CH_2Cl_2–hexane eluent to separate 1.552 g of the crude ketone **40** as an orange solid, mp 193–195 °C. Recrystallization from a CH_2Cl_2–hexane mixture separated 1.501 g (81%) of the pure ketone **40** as orange microcrystals: mp 198–199 °C; IR ($CHCl_3$) 1642 cm^{-1} (conj C=O); UV max (95% EtOH) 247 nm (ϵ 51 200), 281 (47 100), 385 (3230), 475 (11 400); mass spectrum, m/e (relative intensity) 412 (M^+, 100), 395 (19), 370 (31), 369 (55), 355 (25), 339 (22); ^1H NMR ($CDCl_3$) δ 7.0–8.6 (15 H, m, aryl CH), 3.63 (2 H, t, J = 7 Hz, benzylic CH_2), 0.7–2.2 (7 H, m, aliphatic CH); ^{13}C NMR ($CDCl_3$, multiplicity in off-resonance decoupling) 185.5 (s), 144.8 (s), 143.5 (s), 141.0 (s), 133.8 (s), 133.1 (s), 131.2 (s), 131.0 (d, 1 (?) C atom), 130.8 (d, 1 (?) C, atom), 128.0 (d, 2 C atoms), 127.6 (s, 2 C atoms), 127.0 (s, 2 C atoms), 126.9 (d, 1 (?) C atom), 126.1 (d, 2 C atoms), 125.8 (d, 2 (?) C atoms), 125.6 (d, 2 (?) C atoms), 124.5 (d and s, 2 C atoms), 123.5 (d), 123.2 (d), 121.6 (d), 34.0 (t), 29.1 (t), 23.3 (t), 13.9 (q) ppm.

Anal. Calcd for $C_{31}H_{24}O$: C, 90.26; H, 5.86. Found: C, 89.96; H, 6.06.

Preparation of the Chloroanthracene 21. To a cold (0 °C) solution of 1.06 g (3.21 mmol) of the anthracene **1** in 100 mL of CH_2Cl_2 was added, dropwise and with stirring, a solution of Cl_2 in CH_2Cl_2. The addition was stopped when TLC analysis (silica gel coating with a CH_2Cl_2–hexane eluent, 1:9 v/v) indicated that all the starting anthracene **1** (R_f 0.40) had been converted to the chloride **21** (R_f 0.51). The resulting solution was washed successively with aqueous $Na_2S_2O_3$ and with aqueous $NaHCO_3$, dried, and concentrated. The residual solid (1.169 g, mp 210–215 °C) was recrystallized from *i*-PrOH to separate 1.039 g (89%) of the chloride **21** as pale yellow microcrystals: mp 213–214 °C; IR (KBr pellet), no absorption attributable to OH or C=O groups; UV max (95% EtOH) 253 nm (sh, ϵ 61 300), 261 (117 000), 347 (sh, 3390), 367 (6790), 384 (10 400), 408 (8680); ^1H NMR ($CDCl_3$) δ 8.4–8.7 (3 H, m, aryl CH), 7.2–7.8 (14 H, m, aryl CH); mass spectrum, m/e (relative intensity) 366 (M^+, 33), 365 (31), 364 (M^+, 100), 329 (21), 328 (26), 326 (22).

Anal. Calcd for $C_{26}H_{17}Cl$: C, 85.57; H, 4.70; Cl, 9.71. Found: C, 85.51; H, 4.75; Cl, 9.68.

Preparation of the Anthracene 22. By mixing 20 mL of an Et_2O solution containing 13.6 mmol of anhydrous $ZnCl_2$[19] with 16 mL of an Et_2O solution containing 12.8 mmol of MeLi, we obtained a mixture of an ethereal solution of MeZnCl and a precipitate of LiCl. To this mixture was added a solution of 1.401 g (3.43 mmol) of the bromide **20** and 25 mg (0.1 mmol) of $Ni(acac)_2$ in 100 mL of THF. The resulting brown solution was stirred at 25 °C for 24 h and then partitioned between Et_2O and aqueous HCl. After the organic layer had been washed with aqueous $NaHCO_3$, dried, and concentrated, the residual solid (1.108 g, mp 160–161 °C) was chromatographed on silica gel with a CH_2Cl_2–hexane eluent (1:9 v/v). The product (993 mg present in the early fractions) was recrystallized from a CH_2Cl_2–hexane mixture to separate 779 mg (66%) of the anthracene **22** as yellow prisms: mp 176–177 °C; IR ($CHCl_3$), no absorption attributable to OH or C=O groups; UV max (95% EtOH) 261 nm (ϵ 109 700), 345 (sh, 3250), 363 (6580), 382 (9670), 408 (7700); ^1H NMR ($CDCl_3$) δ 8.45 (1 H, br s, aryl CH), 8.25 (2 H, dd, J = 8, 1.5 Hz, aryl CH), 7.0–7.6 (14 H, m, aryl CH), 3.14 (3 H, s, aryl CH_3); mass spectrum, m/e (relative intensity) 345 (30), 344 (M^+, 100), 330 (10), 329 (10), 328 (13).

Anal. Calcd for $C_{27}H_{20}$: C, 94.15; H, 5.85. Found: C, 93.90; H, 6.08.

In a similar reaction, a solution of 1.039 g (2.85 mmol) of the chloride **21** and 25 mg (0.1 mmol) of $Ni(acac)_2$ in 100 mL of PhH was mixed with 10 mL of an Et_2O solution containing 9.5 mmol of MeMgBr. After the resulting brown solution had been refluxed for 6 h, it was subjected to the previously described isolation procedure to separate 690 mg (70%) of the anthracene **22**, mp 176–177 °C.

Preparation of 9-Methylanthracene (24). A mixture of 8.911 g (50.0 mmol) of anthracene, 22.34 g (100 mmol) of anhydrous $CuBr_2$, and 300 mL of CCl_4 was refluxed for 16 h,[26] cooled, filtered to remove most of the CuBr, and then chromatographed on silica gel with PhH as the eluent. The rapidly eluted material (11.93 g, mp 90–96 °C) was recrystallized from *i*-PrOH to separate 9.39 g (73%) of the bromide **23** as yellow needles: mp 98–99 °C (lit.[27] mp 98–99 °C); IR ($CHCl_3$), no absorption attributable to OH or C=O groups; UV max (95% EtOH) 246 nm (ϵ 86 500), 252 (142 000), 337 (2720), 354 (5450), 372 (8530), 390 (7340); ^1H NMR ($CDCl_3$) δ 8.3–8.6 (2 H, m, aryl CH), 7.7–8.1 (1 H, m, aryl CH), 7.1–7.7 (6 H, m, aryl CH); mass spectrum, m/e (relative intensity) 258 (M^+, 95), 256 (M^+, 100), 177 (52), 176 (50), 88 (40); ^{13}C NMR ($CDCl_3$, multiplicity in off-resonance decoupling) 131.2 (s, 2 C atoms), 129.7 (s, 2 C atoms), 127.7 (d, 2 C atoms), 126.7 (d, 3 C atoms), 126.3 (d, 4 C atoms), 124.7 (d, 2 C atoms), 121.5 (s) ppm.

A solution of 2.50 g (9.73 mmol) of the bromide **23** and 25 mg (0.1 mmol) of $Ni(acac)_2$ in 100 mL of PhH was mixed with 20 mL of an Et_2O solution containing 19.0 mmol of MeMgI, and the resulting brown mixture was refluxed for 3 h. After the organic solution had been washed successively with aqueous HCl, with aqueous $NaHCO_3$, with aqueous $Na_2S_2O_3$, and with H_2O, it was dried and concentrated. The residual crude product (1.682 g, mp 65–73 °C) was recrystallized twice from MeOH to separate 1.409 g (75%) of the anthracene **24** as colorless needles: mp 78–79 °C (lit.[28] mp 79–80 °C); IR ($CHCl_3$), no absorption attributable to OH or C=O groups; UV max (95% EtOH) 251 nm (sh, ϵ 102 400), 256 (197 000), 316 (sh, 650), 330 (2310), 347 (5250), 365 (8930), 385 (8410); ^1H NMR ($CDCl_3$) δ 7.0–8.0 (9 H, m, aryl CH), 2.83 (3 H, s, CH_3); mass spectrum, m/e (relative intensity) 192 (M^+, 100), 191 (56), 190 (10), 189 (24); ^{13}C NMR ($CDCl_3$, multiplicity in off-resonance decoupling) 130.7 (s, 2 C atoms), 129.4 (s, 2 C atoms), 128.3 (d, 2 C atoms), 124.4 (d and s (?), 4 C atoms), 123.9 (d, 4 C atoms), 13.7 (q) ppm.

A solution of 495 mg (2.58 mmol) of the anthracene **24** and 700 mg (5.22 mmol) of $CuCl_2$ in 50 mL of PhCl was refluxed for 1 h,[26] cooled, filtered (to remove CuCl), and concentrated. The crude product (553 mg of yellow liquid) contained (TLC, silica gel coating

(26) The halogenation procedure described in ref 5.
(27) Barnett, E. D. B.; Cook, J. W. *J. Chem. Soc.* **1924**, *125*, 1084.
(28) Gerdil, R.; Lucken, E. A. C. *Helv. Chim. Acta* **1961**, *44*, 1966.

with a PhH–hexane eluent, 1:9 v/v) a mixture of the starting material **24** (R_f 0.47) and the chloro derivative **25** (R_f 0.50). Chromatography on silica gel with a hexane eluent separated 505 mg of the crude product **25**, mp 180–181 °C. Recrystallization from *i*-PrOH afforded 498 mg (85%) of the pure chloroanthracene **25** as yellow needles: mp 180–181 °C (lit.[5] mp 180–181 °C); UV max (95% EtOH) 252 nm (ε 79 800), 259 (157 000), 326 (1030), 341 (2500), 358 (4560), 378 (8550), 399 (8320); ^{1}H NMR ($CDCl_3$) δ 7.7–8.3 (4 H, m, aryl CH), 6.9–7.4 (4 H, m, aryl CH), 2.86 (3 H, s, aryl CH_3); mass spectrum, *m/e* (relative intensity) 228 (M^+, 33), 227 (23), 226 (M^+, 100), 225 (26), 191 (57), 189 (41); ^{13}C NMR ($CDCl_3$, multiplicity in off-resonance decoupling) 129.9 (s, 2 C atoms), 129.1 (s), 127.9 (s, 2 C atoms), 126.6 (s), 125.5 (d, 2 C atoms), 124.8 (d, 4 C atoms), 124.3 (d, 2 C atoms), 14.1 (q) ppm.

Acetylation of the Methylanthracene 22. A solution of 550 mg (4.14 mmol) of $AlCl_3$ and 315 mg (4.04 mmol) of CH_3COCl in 50 mL of anhydrous CH_2Cl_2 was added to a solution of 1.380 g (4.00 mmol) of the methylanthracene **22** in 60 mL of anhydrous CH_2Cl_2. After the resulting red solution had been stirred at 25 °C for 18 h, it was partitioned between H_2O and CH_2Cl_2. The organic layer was dried and concentrated to leave 1.436 g of crude solid product (mp 138–150 °C) that contained (TLC, silica gel with a CH_2Cl_2–hexane eluent, 1:1 v/v) the starting hydrocarbon **22** (R_f 0.57), the ketone **45** (R_f 0.17), the ketone **44** (R_f 0.15), and one or more unidentified components that remained at the origin of the TLC plate. The crude product was chromatographed on silica gel with a CH_2Cl_2–hexane eluent (2:3 v/v) to separate 537 mg of early fractions (mp 175–177 °C) containing the unchanged hydrocarbon **22**. Recrystallization of this material afforded 501 mg (36% recovery) of the hydrocarbon **22** (mp 176–177 °C) that was identified with a previously described sample by a mixture melting point determination and by comparison of IR and NMR spectra. The later chromatographic fractions (803 mg of red solid, mp 183–191 °C) contained (NMR analyses) an approximately equal mixture of ketones **44** and **45**. This mixture of ketones was separated by repeated preparative TLC employing a silica gel coating with a CH_2Cl_2–hexane eluent (2:3 v/v). The more rapidly eluted ketone **45** (213 mg of yellow solid, mp 183–187 °C) was recrystallized from CH_2Cl_2–hexane to separate 198 mg (13%) of the ketone **45**, mp 189–190 °C. An additional recrystallization from CH_2Cl_2–EtOH gave the pure ketone **45** as yellow prisms: mp 197–198 °C; IR ($CHCl_3$) 1685 cm^{-1} (conjugated C=O); UV max (95% EtOH) 218 nm (ε 31 000), 248 (27 300), 263 (sh, 42 500), 272 (53 200), 297 (32 400), 340 (2680), 357 (4530), 376 (6290), 405 (5830), 421 (5640);[29] mass spectrum, *m/e* (relative intensity) 387 (30), 386 (M^+, 100), 343 (26), 328 (13), 43 (11); ^{1}H NMR ($CDCl_3$) δ 8.97 (1 H, partially resolved multiplet, aryl CH at C-4), 8.46 (1 H, s, aryl CH at C-9), 8.2–8.4 (1 H, m, aryl CH at C-5), 7.88 (1 H, d, J = 1.6 Hz, shown to be coupled to the signal at 8.97 by decoupling, aryl CH at C-2), 7.2–7.6 (12 H, m, aryl CH), 3.24 (3 H, s, aryl CH_3, broadened slightly by long-range coupling), 2.77 (3 H, s, $COCH_3$). When a 0.4 M solution of the ketone **45** in $CDCl_3$ was treated with successive increments of Eu(fod)$_3$ (0.004–0.02 M), the three signals at δ 8.97 (aryl CH at C-4), 7.88 (aryl CH at C-2), and 2.77 ($COCH_3$) were shifted rapidly to lower field, and the signal at δ 3.24 (aryl CH_3) was shifted relatively slowly to lower field. These NMR data confirm the assigned structure **45**.

Anal. Calcd for $C_{29}H_{22}O$: C, 90.12; H, 5.74; mol wt 386.1671. Found: C, 89.76; H, 6.06; mol wt 386.1679 (mass spectrum).

The later fractions from the preparative TLC separation contained 193 mg of the crude ketone **44**, mp 205–207 °C. Recrystallization from CH_2Cl_2–CCl_4 separated 179 mg (12%) of the ketone **44**, mp 210–211 °C. An additional recrystallization from CH_2Cl_2–EtOH gave the ketone **44** as fine orange crystals: mp 216–217 °C; IR ($CHCl_3$) 1682 cm^{-1} (conjugated C=O); UV max (95% EtOH) 215 nm (ε 30 800), 266 (46 400), 270 (47 400), 396 (sh, 7290), 408 (7390);[29] mass spectrum, *m/e* (relative intensity) 387 (25), 386 (M^+, 100), 373 (20), 372 (72), 344 (22), 343 (75), 141 (20), 119 (25), 117 (35), 69 (20); ^{1}H NMR ($CDCl_3$) δ 8.50 (1 H, s, aryl CH at C-9), 8.1–8.4 (1 H, m, aryl CH at C-5), 7.6–7.8 (2 H, m, aryl CH, including signal for C-3 proton), 7.2–7.6 (12 H, m, aryl CH), 2.97 (3 H, s, aryl CH_3), 2.77 (3 H, s, $COCH_3$). A 0.21 M solution of the ketone **44** was treated with successive increments of Eu(fod)$_3$ (0.002–0.01 M). The rate of downfield shift of various signals was in the following order: δ 2.77 ($COCH_3$) > δ 7.7 (aryl CH at C-3) > δ 2.97 (aryl CH_3). As the C-3 aryl signal at δ 7.7 was shifted downfield, the coupling constant (J = 7 Hz) could be observed.

Anal. Calcd for $C_{29}H_{22}O$: C, 90.12; H, 5.74; mol wt 386.1671. Found: C, 88.89; H, 6.06; mol wt 386.1691 (mass spectrum).

Crystal Structure of the Bromoanthracene 20. A. Data Collection. A crystal of the bromide **20** with approximate dimensions 0.55 × 0.20 × 0.15 mm was mounted on a glass fiber by using epoxy cement such that the longest crystal dimension, 0.55 mm, was approximately parallel to the fiber axis. Unit cell parameters and the orientation matrix were determined on a Syntex $P2_1$ four-circle diffractometer equipped with a graphite monochromator (Bragg 2θ angle 12.2°) using Mo Kα radiation at a takeoff angle of 6.75°. Fifteen reflections whose 2θ values ranged from 3.71 to 13.82° were machine centered and used in least-squares refinement of the lattice parameters and the orientation matrix. The unit cell parameters obtained were a = 19.544 (5) Å,[30] b = 11.062 (4) Å, c = 9.774 (2) Å, α = 93.14 (2)°, β = 93.78 (2)°, γ = 117.02 (3)°, and V = 1870 (1) Å^3. The calculated density of 1.45 g cm^{-3} for four formula units per unit cell agrees with the experimental density of 1.43 g cm^{-3} measured by the flotation method with a mixture of CCl_4 and hexane. ω scans of several low 2θ angle reflections gave peak widths at half-height of less than 0.18°, indicating a satisfactory mosaic spread for the crystal. Axial photographs indicated that the crystal belonged to the triclinic system. Intensity data for the zero and upper levels were collected at a rapid scan rate and the intensities examined for systematic absences; none were found. This is consistent only with the space groups $P1$ or $P\bar{1}$ (No. 1 or 2).[31] Assuming the later space group, a successful refinement was obtained.

Intensity data were collected by using θ–2θ scans with an X-ray source and monochromator settings identical with those used for determining the unit cell parameters. A variable scan rate of from 2.02 to 29.30°/min was used, and a scan width of 2.0° was sufficient to collect all the peak intensity. Stationary background counts were measured at the beginning (B_1) and at the end (B_2) of each scan with a total background to scan time ratio, TR, of 1.0. No significant fluctuations were observed in the intensities of three standard reflections (006, 040, 500) monitored every 97 reflections. Intensities were calculated from the total scan count (CT) and background counts by the relationship of eq 1. The

$$I = CT - TR(B_1 + B_2) \quad (1)$$

intensities were assigned standard deviations according to the formula in eq 2, for a total of 6612 reflections collected in a

$$\alpha(I) = [CT + (TR)^2(B_1 + B_2)]^{1/2} \quad (2)$$

complete hemisphere (±h,±k) of data out to 2θ = 50°; 4529 were accepted as statistically above background on the basis that F was greater than 3σ(F). Lorentz and polarization corrections were made in the usual way.

B. Solution and Refinement of the Structure. Computations were performed by using standard programs;[32] all computations were carried out on the CDC Cyber 74 system. For structure factor calculations the scattering factors were taken from Cromer and Waber's tabulation.[33] The scattering factor(s) for all atoms except hydrogen were corrected for the real and imaginary anomalous dispersion components.[33] The agreement factors were defined in the usual way as in eq 3 and 4.

(29) (a) Lutskii, A. E.; Antropova, L. A.; Kaneoskaya, Z. M. *Theor. Expt. Chem. (Engl. Transl.)* **1971**, 222. These authors report the following UV maxima (EtOH) for the acetylanthracenes: 1-acetylanthracene, 252 nm (ε 83 200), 322 (2630), 334 (4000), 365 (9000), 385 (10 200), 408 (4000); 2-acetylanthracene, 260 nm (ε 63 100), 326 (2700), 340 (6310), 358 (5900), 380 (3170). Similar values for these acetylated anthracenes have been reported by: (b) Martynoff, M.; Chauvin, M.; Grumez, M.; Lefevre, N. *Bull. Soc. Chim. Fr.* **1958**, 164; (c) Gore, P. H.; Hoskins, J. A. *J. Chem. Soc.* **1965**, 5744; Gore, P. H.; Thadani, C. K. *J. Chem. Soc. C* **1966**, 1279.

(30) Numbers in parentheses here and elsewhere in this paper indicate estimated standard deviations in the least significant digit(s).

(31) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1952; Vol. I.

(32) Programs utilized were Sheldrick's SHELX-76 program and Johnson's ORTEP program.

(33) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99–101, 149–50.

$$R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o| \quad (3)$$

$$R_w = [\Sigma(|F_o| - |F_c|)w^{0.5}]/\Sigma(|F_o|)w^{0.5} \quad (4)$$

In all least-squares refinements, the quantity minimized was $w(|F_o| - |F_c|)^2$. A weighting scheme based on counting statistics ($w = 2.4580[\sigma(F)^2 + 0.000436F^2]^{-1}$ was employed for calculating R_w and in least-squares refinement.

The structure was solved by using Patterson techniques. The total number of parameters varied were 321 for 4529 observations. The phenyl rings were refined as rigid groups, and their carbon temperature factors were refined isotropically. An overall isotropic temperature factor was assigned to the phenyl hydrogen atoms. Parameters varied included a scale factor, coordinates of all remaining atoms except hydrogen atoms (which were refined in the riding mode), and anisotropic thermal parameters for all atoms other than hydrogen atoms, and an overall isotropic temperature factor was applied to the hydrogen atoms. The full-matrix least-squares refinement converged at $R = 0.0713$ and $R_w = 0.0623$.

There are two pairs of crystallographically nonequivalent molecules per unit cell. However, the bond lengths and bond angles do not differ significantly between these two molecules. Therefore, only the bond distances and bond angles for one of the molecules is presented in Table I. The final atomic coordinates and thermal parameters for both molecules are available as supplementary material in Table II, and the list of calculated and observed structure factors is available from the authors as Table III.

Registry No. 1, 33522-35-9; 4, 38305-28-1; 8, 82-43-9; 9, 33522-27-9; 10, 33522-37-1; 11, 14381-66-9; 12, 1714-09-6; 13, 50259-93-3; 14, 63605-29-8; 15, 73274-95-0; 16, 73274-96-1; 17, 73274-97-2; 18, 73274-98-3; 19, 73274-99-4; 20, 73275-00-0; 21, 73275-01-1; 22, 73275-02-2; 23, 1564-64-3; 24, 779-02-2; 25, 19096-07-2; 26, 73275-03-3; 27, 73275-04-4; 28, 73275-05-5; 29, 73275-06-6; 30, 90-44-8; 31, 2444-68-0; 32, 68941-26-4; 33, 13752-40-4; 34, 28871-54-7; 36 (isomer 1), 73275-07-7; 36 (isomer 2), 73275-08-8; 37, 73275-09-9; 38 (isomer 1), 73275-10-2; 38 (isomer 2), 73275-11-3; 39, 73275-12-4; 40, 73275-13-5; 41, 73275-14-6; 44, 73275-15-7; 45, 73275-16-8; anthraquinone, 84-65-1; 1,8-diiodo-9,10-anthraquinone, 30877-00-0; lithium acetylide, 1111-64-4; anthracene, 120-12-7; CH_2=CHBr, 593-60-2; Me_3SiCN, 7677-24-9; EtBr, 74-96-4.

Supplementary Material Available: Table II, containing atomic coordinates and thermal parameters (2 pages). Ordering information is given on any current masthead page.

Synthetic Routes to Derivatives of Polycyclic Aromatic Hydrocarbons Using Isobenzofurans as Transient Reactive Intermediates

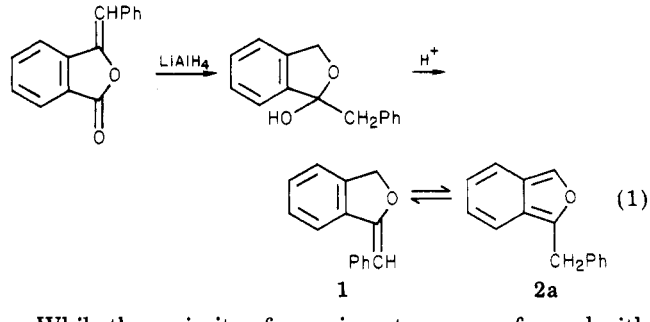
James G. Smith,* Sudha S. Welankiwar, Barry S. Shantz, Eric H. Lai, and Noreen G. Chu

The Guelph-Waterloo Centre for Graduate Work in Chemistry, Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1

Received August 16, 1979

The known equilibrium between the tautomers benzalphthalan (1) and 1-benzylisobenzofuran (2) has been exploited as a synthetic route to novel substituted polycyclic aromatic compounds. The isobenzofuran was captured in a series of Diels–Alder reactions to provide epoxy-bridged Diels–Alder adducts. Aromatization of these adducts by dehydration was generally effected by using catalytic amounts of toluenesulfonic acid. Alternatively, trimethylsilyl chloride/sodium iodide was found superior in those cases where acid catalysis was unsatisfactory. The Diels–Alder adducts formed by using quinones were best aromatized under mild basic conditions (sodium acetate/methanol). When aromatization resulted in increased nonbonded interactions among the substituents attached to the developing polycyclic aromatic system, mixtures containing the desired aromatic compound and a product in which dehydration did *not* yield the new aromatic ring resulted. This problem was obviated by using basic conditions to isomerize the product mixture to the fully aromatic derivative.

1,3-Diarylisobenzofurans have been frequently used as intermediates for the synthesis of substituted polycyclic compounds.[1] More recently, less stable isobenzofurans have been generated as transient intermediates and utilized for the same purposes.[2] Earlier, we demonstrated[3] that the readily available benzalphthalan (1) (eq 1) existed in equilibrium with its tautomer 1-benzylisobenzofuran (**2a**) and the latter could be captured in Diels–Alder reactions. In this paper, the possibility of using this as a route to substituted polycyclic aromatic compounds is explored.



(1)

1 2a

While the majority of experiments were performed with the readily accessible **2a** (via 1), several successful reactions were obtained with isobenzofurans bearing substituent groups in the benzo or benzyl aromatic ring (i.e., Scheme I, **2b–d**). A variety of dienophiles were used to capture the isobenzofurans, and the results of these experiments are summarized in Table I and Scheme I. Reaction temperatures ranged from 35 °C for the more reactive dienophiles such as maleic anhydride to 80–140 °C for the less reactive dienophiles such as acrylonitrile. In one case, *trans*-1,2-

(1) See, for example: (a) E. Bergmann, *J. Chem. Soc.*, 1147 (1938); (b) J. A. Berson, *J. Am. Chem. Soc.*, **75**, 1240 (1953); (c) M. P. Cava and J. P. Van Meter, *J. Org. Chem.*, **34**, 538 (1969); (d) E. D. Bergmann, Sh. Blumberg, P. Bracha, and Sh. Epstein, *Tetrahedron*, **20**, 195 (1964); (e) A. Etienne, A. Spire, and E. Toromanoff, *Bull. Soc. Chim. Fr.*, 750 (1952).

(2) M. Hamaguchi and T. Ibata, *Chem. Letters*, 287 (1976); R. Faragher and T. L. Gilchrist, *J. Chem. Soc., Perkin Trans. 1*, 336 (1976); A. S. Kende, D. P. Curran, Y. Tsay, and J. E. Mills, *Tetrahedron Lett.*, 3537 (1977); L. Contreras, C. E. Slemon, and D. B. MacLean, *ibid.*, 4237 (1978); H. P. Plaumann, J. G. Smith, and R. Rodrigo, *J. Chem. Soc., Chem. Commun.*, in press.

(3) J. G. Smith and R. T. Wikman, *J. Org. Chem.*, **39**, 3648 (1974).

0022-3263/80/1945-1817$01.00/0