The Synthesis of Some Diphenyl and Triphenyl Derivatives of Anthracene and Naphthalene[1]

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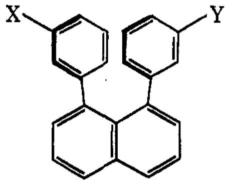
Coupling reactions of lithium diphenylcuprate and appropriate aryl halides have been developed to provide efficient syntheses of 1,8-diphenylnaphthalene (**1d**), 1-iodo-8-phenylnaphthalene (**3**), 1-phenyl-9,10-anthraquinone (**13**), and 1,8-diphenyl-9,10-anthraquinone (**15**). Appropriate transformations of the anthraquinones **13** and **15** yielded 1,8-diphenylanthracene (**22**), 1,9-diphenylanthracene (**25**), and 1,8,9-triphenylanthracene (**26**). The spectroscopic properties of all these phenylated anthracenes and naphthalenes are consistent with the existence of these molecules in conformations with the phenyl rings parallel to one another and perpendicular to the plane of the anthracene or naphthalene ring.

Earlier publications[3-8] have described preparative routes to anthracene and naphthalene derivatives which contain at least two aryl substituents at adjacent peri positions. Particularly in the naphthalene series, it has been common to obtain these substances by constructing alicyclic intermediates with the necessary carbon skeleton. Aromatization has then been accomplished by a combination of dehydration and/or dehydrogenation steps. These synthetic pathways have provided a sufficient variety of 1,8-diarylnaphthalene derivatives to show (uv, nmr, and dipole moment measurements)[3b,c] that in solution these molecules exist primarily in the conformation illustrated in structure **1** with the aryl rings approximately parallel to one another and approximately perpendicular to the plane of the naphthalene nucleus. In derivatives (*e.g.*, **1a**) with meta-substituted aryl rings, the energy barrier to rotation of the substituted ring ($\Delta G^{\ddagger} = 16$ kcal/mol at 25°) is sufficiently low that it is not practical to separate cis and trans isomers of structures such as **1b** or **1c** at room temperature. A complete X-ray crystallographic analysis of the parent hydrocarbon, 1,8-diphenylnaphthalene (**1d**),[9] has shown this molecule to have the dimensions and packing pattern in the crystal illustrated in Figure 1. Both previous X-ray crystallographic measurements with other naphthalene derivatives[8,10] and various speculations and calculations concerning similar compounds[6b,11] suggest that this hydrocarbon should be deformed to alleviate the nonbonding interaction between the two phenyl rings. It will be seen in Figure 1 that this relief of strain is distributed among deformation of the naphthalene ring, a splaying out of the two phenyl rings, and a rotation of the phenyl rings so that the approximately parallel planes of the two phenyls are at an angle of approximately 70° to the plane of the naphthalene ring. As a result the meta positions and, especially, the para positions of the phenyl rings are relatively distant from one another and our earlier failure to convert the diacid **1c** to a cyclic anhydride[3b] is understandable.



1a, $X = H$; $Y = C(CH_3)_2OH$
b, $X = Y = CO_2CH_3$
c, $X = Y = CO_2H$
d, $X = Y = H$

To pursue further the chemical and physical properties of the aryl-substituted naphthalenes and anthracenes, we sought more direct synthetic routes to these substances. Although the Ullmann coupling of 1,8-diiodonaphthalene (**2**) and iodobenzene in the presence of copper powder did not provide a useful route to 1,8-diphenylnaphthalene,[12] coupling of the diiodide **2** with performed organocopper(I) derivatives[12,13] was more effective. Thus, a small-scale reaction of the diiodide **2** with a reagent preformed from phenyllithium and copper(I) bromide led to the formation of 1,8-diphenylnaphthalene (**1d**) in 47% yield.[13] However, in our subsequent attempts to use this process for the synthesis of the diphenylnaphthalene **1d** the reaction proved very capricious, sometimes producing the hydrocarbon **1d** but more frequently yielding the known monophenyl iodide **3**.[14] After considerable experimentation, we found that the course of the reaction was critically dependent on the proportions of phenyllithium and copper(I) bromide used to prepare the copper reagent. When the reagent was prepared by reaction of 2 mol of phenyllithium with slightly more

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(2) Department of Chemistry, Georgia Institute of Technology, Atlanta, Ga. 30332.

(3) (a) H. O. House, R. W. Magin, and H. W. Thompson, *J. Org. Chem.* **28**, 2403 (1963); (b) H. O. House and R. W. Bashe, II, *ibid.*, **30**, 2942 (1965); **32**, 784 (1967); (c) H. O. House, W. J. Campbell, and M. Gall, *ibid.*, **35**, 1815 (1970).

(4) (a) A. S. Bailey, G. A. Dale, A. J. Shuttleworth, and D. P. Weizmann, *J. Chem. Soc.*, 5110 (1964); (b) A. S. Bailey and A. J. Shuttleworth, *ibid.*, *C*, 1115 (1968).

(5) S. C. Dickerman, D. deSouza, and P. Wolf, *J. Org. Chem.*, **30**, 1981 (1965).

(6) (a) E. D. Bergmann, S. Blumberg, P. Bracha, and S. Epstein, *Tetrahedron*, **20**, 195 (1964); (b) M. Rabinovitz, I. Agranat, and E. D. Bergmann, *Tetrahedron Lett.*, 4133 (1965).

(7) (a) C. Dufraisse and Y. Lepage, *C. R. Acad. Sci.*, **258**, 1507, 5447 (1964); (b) Y. Lepage and O. Pouchot, *Bull. Soc. Chim. Fr.*, 2342 (1965).

(8) For a review, see V. Balasubramaniyan, *Chem. Rev.*, **66**, 567 (1966).

(9) A. S. Parkes and R. A. Ogilvie, unpublished work. The details are available in the Ph.D. dissertation of R. A. Ogilvie, Massachusetts Institute of Technology, 1971.

(10) M. B. Jameson and B. R. Penfold, *J. Chem. Soc.*, 528 (1965).

(11) A. I. Kitaigorodsky and V. G. Dashevsky, *Tetrahedron*, **24**, 5917 (1968).

(12) R. W. Bashe, II, Ph.D. Dissertation, Massachusetts Institute of Technology, 1966.

(13) See G. M. Whitesides, W. F. Fischer, Jr., J. San Filippo, Jr., R. W. Bashe, and H. O. House, *J. Amer. Chem. Soc.*, **91**, 4871 (1969), and references cited therein.

(14) W. A. Henderson, Jr., R. Lopresti, and A. Zweig, *ibid.*, **91**, 6049 (1969). We are grateful to Dr. Henderson for providing us with a sample of their material for comparison with our product.

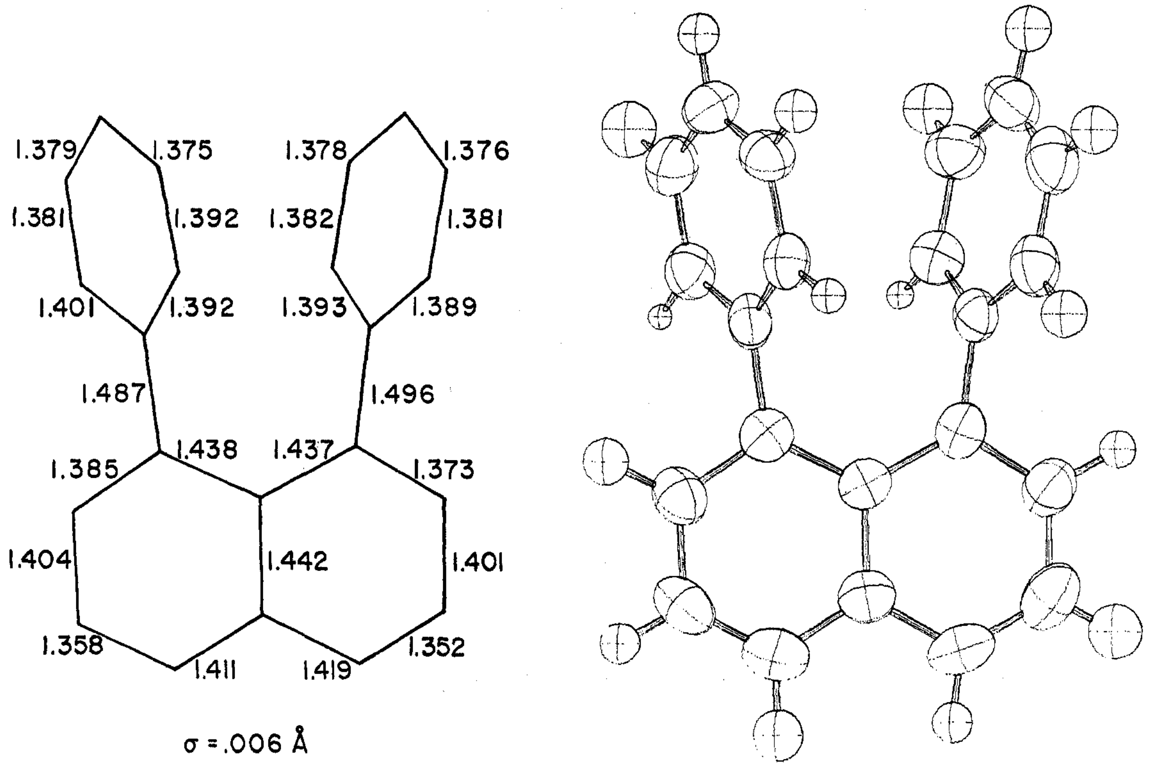
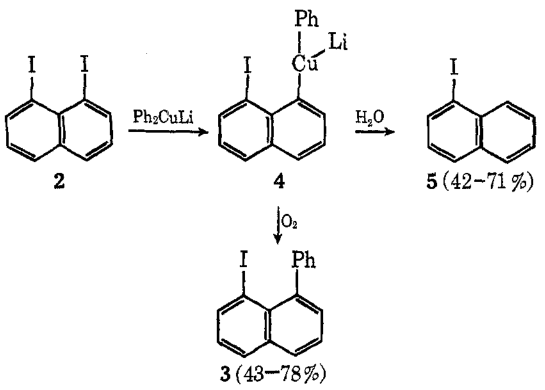


Figure 1.—Bond lengths and a perspective view perpendicular to the naphthalene ring of 1,8-diphenylnaphthalene as determined by X-ray cystallography (ref 9).

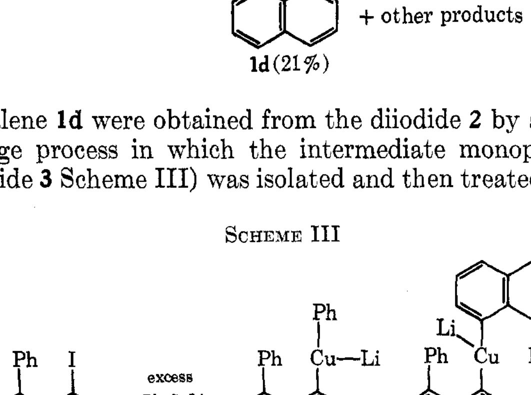
than 1 mol of copper(I) bromide, a solution containing only a reagent having the stoichiometry Ph_2CuLi was obtained. As indicated in Scheme I, an excess of this

SCHEME I



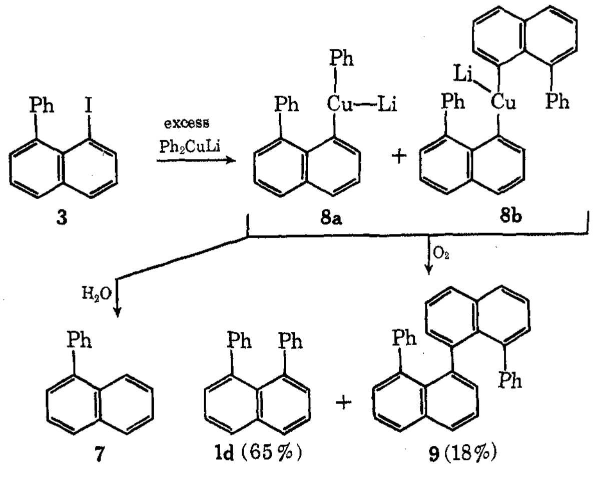
reagent reacted rapidly at only one position of the diiodide **2** to form an intermediate cuprate with the stoichiometry implied in structure **4**. As expected,[13] hydrolysis of this intermediate formed 1-iodonaphthalene (**5**) and oxidation yielded mainly the monophenyl monoiodide **3**. However, if even a slight excess of phenyllithium was present a more reactive species was apparently generated which reacted further with the monocuprate **4**. Scheme II illustrates the results of treating the diiodide **2** with a copper reagent having the apparent stoichiometry Ph_3CuLi_2 (from 3 mol of PhLi and 1 mol of CuBr). In this case a biscuprate species such as **6** was apparently formed, since hydrolysis yielded mainly naphthalene whereas oxidation produced the diphenyl derivative **1d** and other higher molecular weight materials.

SCHEME II



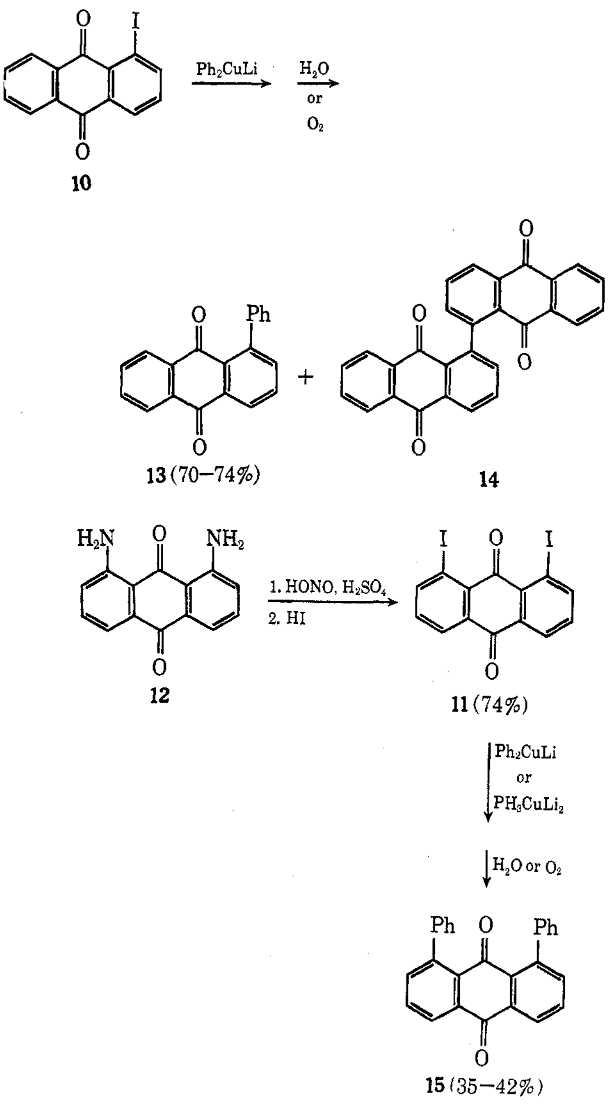
The highest overall yields of the diphenylnaphthalene **1d** were obtained from the diiodide **2** by a two-stage process in which the intermediate monophenyl iodide **3** Scheme III) was isolated and then treated with

SCHEME III

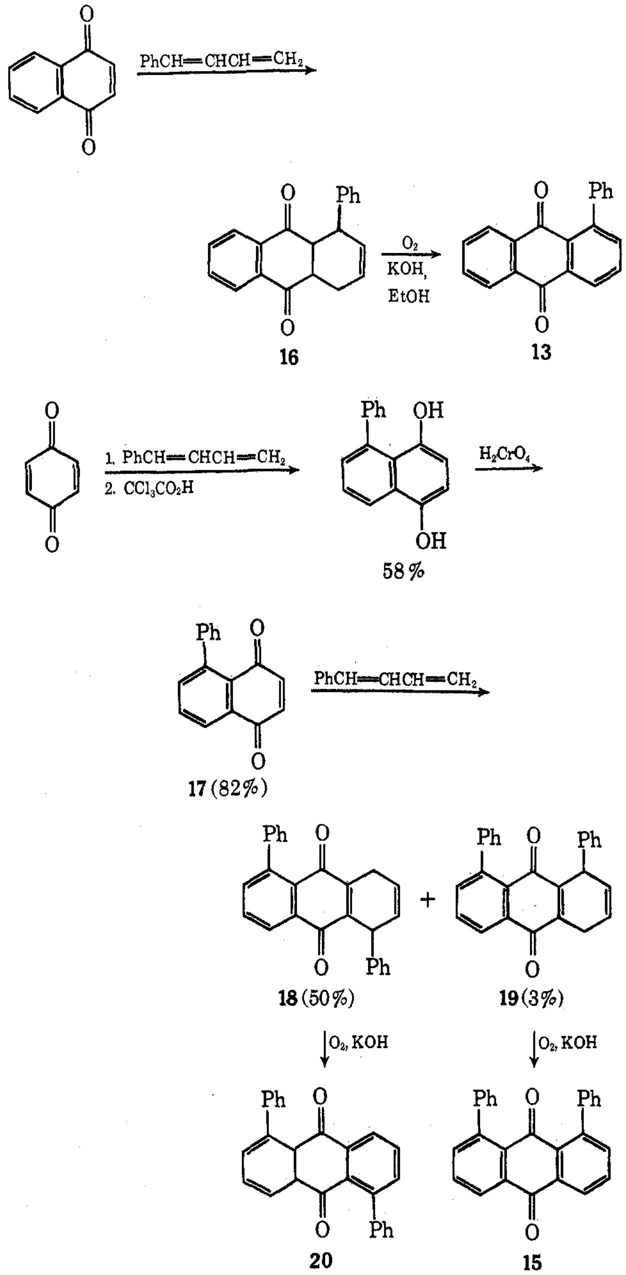


excess lithium diphenylcuprate. Oxidation of the intermediate mixture of cuprates **8** produced the hydrocarbons **1d** and **9**. When equimolar amounts of the cuprate and the iodide **3** were used, an unusually high percentage of the symmetrical coupling product **9** was produced. This suggests that formation of the symmetrical cuprate intermediate **8b** may be favored by a special type of stabilization involving coordination of the metal with the adjacent phenyl rings. The nature of the cuprate **8b** is under investigation and will be reported elsewhere.

SCHEME IV



SCHEME V



With this background, we were led to explore syntheses of various phenylated anthracenes which were based on the reaction of lithium diphenylcuprate with iodoquinones **10** and **11** (Scheme IV). As indicated, the diiodoquinone **11** was readily available from the corresponding diamine **12**. The phenylquinones **13** and **15** were obtained much more easily by this procedure than by the alternative Diels–Alder procedure summarized in Scheme V. The reactions of the iodoquinones **10** and **11** with lithium diphenylcuprate or dilithium triphenylcuprate differed from the reactions with the iodonaphthalenes in that halogen–metal exchange was much faster (complete in less than 30 sec at 0°) and C–C bond formation occurred relatively rapidly even when no oxidant was added to the reaction mixture prior to hydrolysis. Although these coupling reactions might be supposed to follow a pathway analogous to the conjugate addition of cuprates to α,β-unsaturated carbonyl compounds,[15] we found that reaction of the diiodoquinone **11** with Ph_3CuLi_2 for 25–30 sec at 0° followed by hydrolysis without prior oxidation yielded a mixture containing primarily 9,10-anthraquinone (42%) accompanied by smaller amounts of the phenylquinone **13** (9%) and the diphenylquinone **15** (14%). Use of the same reaction conditions with oxidation *before* hydrolysis produced the diphenylquinone **15** in 42% yield. Therefore, we believe that these iodoquinone coupling reactions follow a path analogous to other aryl iodides[13] in which initial metal–halogen exchange (possibly preceded by electron transfer) forms a diaryl (or triaryl) cuprate. Subse-

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[15] (a) H. O. House, W. L. Respess, and G. M. Whitesides, *J. Org. Chem.*, **31**, 3128 (1966); (b) H. O. House and W. L. Fischer, Jr., *ibid.*, **33**, 949 (1968).

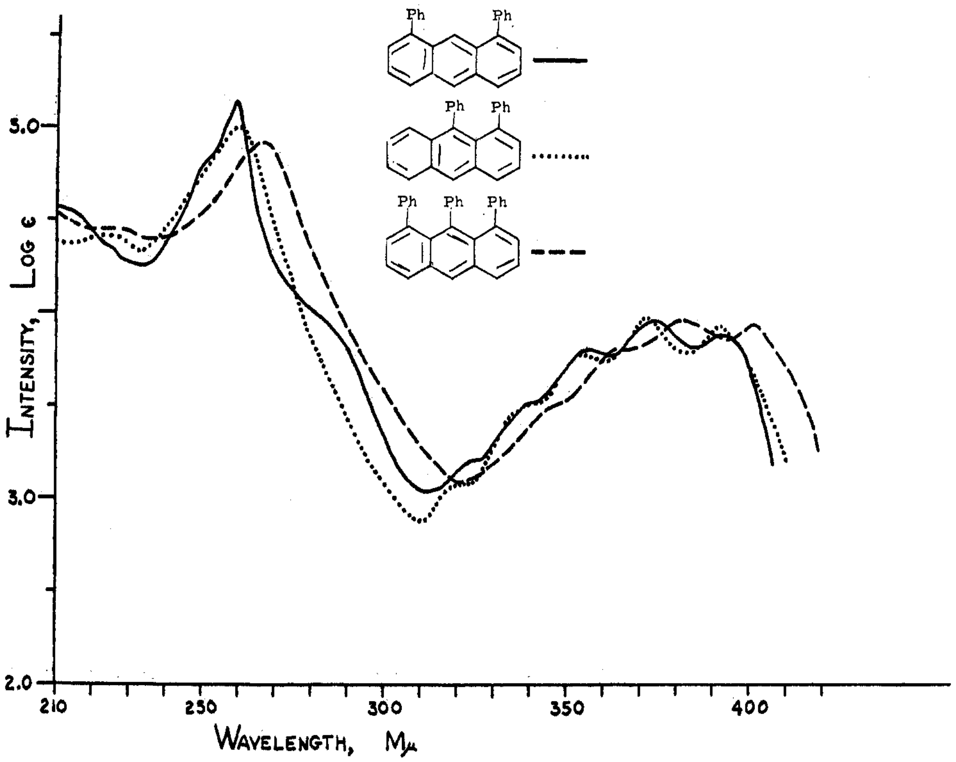

Figure 2.—The electronic spectra of the phenylated anthracenes **22**, **25**, and **26** determined in 95% EtOH.

quent oxidation of this cuprate intermediate, either by added oxygen or by one of the quinones present in the reaction mixture, leads to formation of the new C–C bond.

The reaction scheme VI, devised and used previously to prepare compounds **21**, **23**, and **25**,[5] was equally useful for the new compounds **22**, **24**, and **26** and for the conversion of anthrone to the known 9-phenylanthracene (**27**).

The electronic and nmr spectra of the diphenylanthracenes **22** and **25** and the triphenylanthracene **26** are compared in Figures 2 and 3. As had been observed for 1-phenylnaphthalene and the 1,8-diphenyl derivative **1d**, the electronic spectra (Figure 2) of the anthracenes **22**, **25**, and **26** resemble closely the spectra of anthracene and the monophenyl derivatives **21** and **27**, the principal differences being a shift of the low-intensity peaks in the region 300–400 mμ to slightly longer wavelengths. These shifts in peak positions are related primarily to the number of phenyl substituents present, and no special effect on the electronic spectrum arises from having two phenyl groups on adjacent peri positions. The similarity among these electronic spectra is consistent with the idea that each of these molecules exists in a conformation with the phenyl groups approximately perpendicular to the anthracene ring so that π-orbital overlap between the aromatic rings is slight. Comparison of the nmr spectra (Figure 3) reveals that the 1,8-diphenylanthracene (**22**), like the monophenyl compounds **21** and **27**, has no nmr absorption at higher field than δ 7.0. In the 1,9-diphenyl compound, the resonance for the two presumably parallel phenyl rings is shifted above δ 7.0. In the triphenyl derivative **26**, the resonance for all the phenyl rings is shifted above δ 7.0 and the phenyl substituent at C-9 with adjacent parallel phenyl substituents on each side is shifted upfield to δ 6.36.

The polarographic reduction potentials for the various naphthalene, anthraquinone, and anthracene derivatives prepared in this study were measured and are summarized in Table IV. Although further studies will be required to characterize the species being produced, each of the materials exhibits two reduction waves which probably correspond to the successive reduction of each compound to a radical anion and to a dianion.[16] In general, the half-wave potentials for the hydrocarbons became less negative by about 0.05–0.1 V for each phenyl substituent added. The only unusual case was the triphenyl derivative **26**; in this case the half-wave potential for the first reduction step had the value expected but the value for the second wave was significantly less negative than the above generalization would predict. We do not yet know whether this result is explained by relief of strain in the presumably nonplanar anthracene ring of the dianion or by a rapid further reaction of the dianion in this case. We hope to resolve this question with cyclic voltammetry and product studies which are in progress.

Experimental Section[17]

1,8-Diiodonaphthalene (2).—By use of a modification of the procedure described by Shechter and coworkers[18] in which pure 1,8-diaminonaphthalene in aqueous 4.1 *M* H_2SO_4 was diazotized

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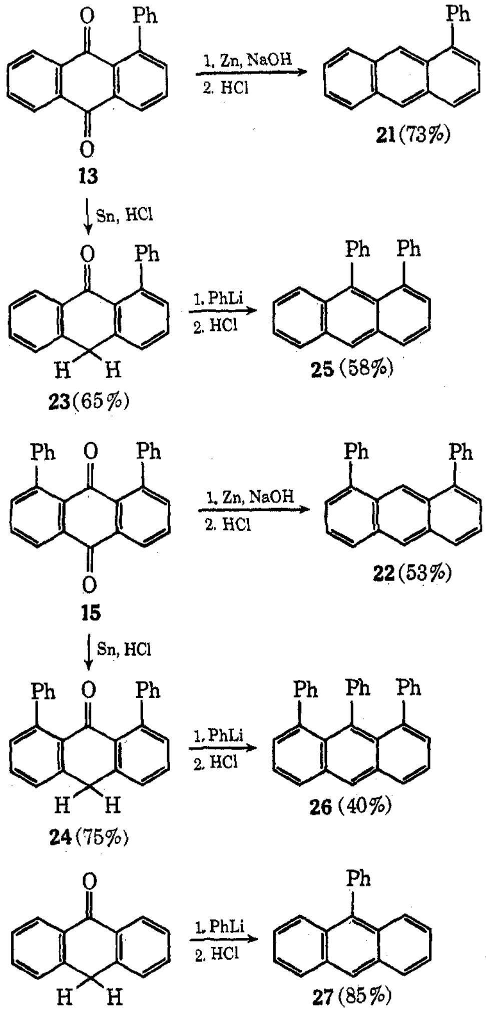
[16] For related studies, see (a) L. H. Klemm, C. D. Lind, and J. T. Spence, *J. Org. Chem.*, **25**, 611 (1960); (b) A. J. Bard, K. S. V. Santhanam, J. T. Maloy, J. Phelps, and L. O. Wheeler, *Discuss. Faraday Soc.*, 167 (1968).

[17] All melting points are corrected and all boiling points are uncorrected. Unless otherwise stated magnesium sulfate was employed as a drying agent. The infrared spectra were determined with a Perkin-Elmer Model 237 or Model 257 infrared recording spectrophotometer fitted with a grating. The ultraviolet 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 shifts are expressed in δ values relative to a tetramethylsilane internal standard. The mass spectra were obtained with an Hitachi Perkin-Elmer mass spectrometer. All reactions involving strong bases or organometallic intermediates were performed under a nitrogen atmosphere.

[18] B. Bossenbroek, D. C. Sanders, H. M. Curry, and H. Shechter, *J. Amer. Chem. Soc.*, **91**, 371 (1969).

SCHEME VI



at −10° rather than at 5°, we obtained the pure diiodide 2 in 55% yield. In agreement with these workers, our efforts to obtain the diiodide 2 by stepwise diazotization[19] of the diamine resulted in low yields. The following procedure was found most satisfactory for preparation of the diiodide 2. Technical grade (Aldrich) 1,8-diaminonaphthalene (100 g) was distilled from 5 g of zinc dust, and the distillate [bp 183–187° (4–5 mm)] was crystallized from hexane to separate 83.8 g (0.53 mol) of the pure diamine as white needles, mp 63–65.5°. A suspension of this diamine salt in 975 ml of aqueous 6.9 *M* H_2SO_4 was cooled to −20° and then a solution of 108 g (1.59 mol) of $NaNO_2$ in *ca.* 400 ml of H_2O was added, dropwise and with stirring, while the temperature of the mixture was kept at −15 to −20°. As soon as the addition was complete a solution of 538 g (3.24 mol) of KI in *ca.* 450 ml of H_2O was added, dropwise and with stirring. During this addition the reaction mixture was kept at −15 to −20° and additional portions of concentrated H_2SO_4 were added as needed to keep the reaction mixture from freezing. The resulting mixture was warmed to 80°, rapidly and with stirring, and then cooled to 20° and made alkaline by the addition of solid NaOH. The mixture was filtered and the black solid residue was collected, pulverized, and extracted with several portions of boiling Et_2O (total volume 3 l.). The ethereal solution was washed successively with aqueous 10% HCl, saturated aqueous $Na_2S_2O_3$, and dilute aqueous NaOH and then dried and concentrated. The residual brown solid (147.6 g) was recrystallized from hexane to separate 126.6 g (63%) of the pure diiodide 2 as tan prisms, mp 108.5–110° (lit.[18] mp 109°), as well as 10.0 g (5%) of less pure fractions melting within the range 102.5–108.5°; ir ($CHCl_3$), no absorption attributable to OH or C=O in the 3- or 6-μ region; uv max (95% EtOH) 237 mμ (ε 47,000), 299 (6900), 311 (8000), and 325 (6200); nmr ($CDCl_3$) δ 8.38 (2 H, d of d, *J* = 7.5 and 1.3 Hz), 7.79 (2 H, d of d, *J* = 7.5 and 1.3 Hz), and 7.03 (2 H t, *J* = 7.5 Hz); mass spectrum *m/e* (rel intensity) 380 (54, M^+), 253 (38), and 126 (100).

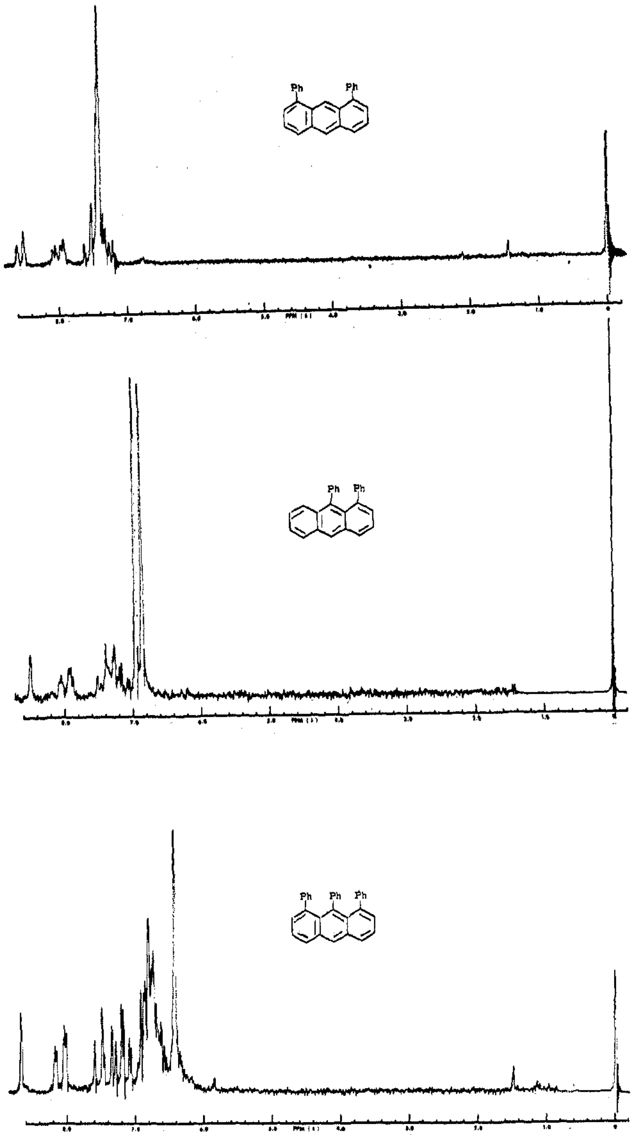


Figure 3.—The nmr spectra of the phenylated anthracenes **22, 25,** and **26** determined in $CDCl_3$.

1-Iodo-8-phenylnaphthalene (3).—A cold (0°) solution of lithium diphenylcuprate,[13] prepared from 3.78 g (26.3 mmol) of CuBr and 52.7 mmol of phenyllithium in 60 ml of Et_2O, was added over 2.5 min to a cold (−5°), stirred suspension of 5.00 g (13.2 mmol) of the diiodide 2 in 70 ml of Et_2O. The resulting solution was stirred in an ice bath for 3 min and then a stream of oxygen was passed over the surface of the liquid, with vigorous stirring and cooling, for 20 min. The resulting black colored mixture was partitioned between Et_2O and an aqueous solution of NH_3 and NH_4Cl and the ethereal phase was dried and concentrated. The residue was chromatographed on 170 g of silica gel with hexane as an eluent. After separation of the early fractions containing iodobenzene and biphenyl, the crude iodide 3 was eluted as 2.43 g of pale yellow liquid. Crystallization from hexane afforded 1.847 g (43%) of the iodide 3 as pale yellow needles, mp 63–65°. Recrystallization narrowed the melting range to 64–65° (lit.[14] mp 65–65.5°); ir (CCl_4) no absorption attributable to OH or CO functions in the 3- or 6-μ regions; uv max (95% EtOH) 214 mμ (ε 38,000), 232 (38,000), and 301 (9700); nmr ($CDCl_3$) δ 6.6–8.3 (multiplet, aryl CH); mass spectrum *m/e* (rel intensity) 330 (50, M^+), 203 (100), 202 (62), 102 (26), and 101 (34). This material was identified with an authentic sample[14] by comparison of ir spectra, glpc retention times, and a mixture melting point.

To establish the optimum conditions for this coupling reaction a number of small-scale experiments were performed. In one representative set of experiments a cold (0°) solution of 2.00

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(19) R. Scholl, C. Seer, and R. Weitzenböck, *Ber.*, **43**, 2202 (1910).

mmol of $LiPh_2Cu$ in 10 ml of Et_2O was treated with a solution of 380 mg (1.00 mmol) of the diiodide **2** and 114 mg of bibenzyl (an internal standard) in 10 ml of ether. The resulting solutions were either stirred at 0° or refluxed and aliquots were removed periodically. The aliquots were either hydrolyzed directly with an aqueous solution of NH_3 and NH_4Cl or they were first stirred at 0° under an oxygen atmosphere and then hydrolyzed. In each case the final ethereal solution remaining after hydrolysis was dried and analyzed by glpc. The glpc analysis (silicone gum, SE-52, on Chromosorb P) was started at 100° with a programmed temperature rise of 5°/min. Under these conditions the retention times and the various components were iodobenzene, 5.0 min; naphthalene, 8.2 min; biphenyl, 12.2 min; bibenzyl, 15.0 min; 1-iodonaphthalene (**5**), 17.5 min; 1-phenylnaphthalene (**7**), 22.2 min; 1-iodo-8-phenylnaphthalene (**3**), 29.0 min; 1,8-diphenylnaphthalene (**1d**), 31.0 min. The glpc equipment was calibrated with known mixtures of authentic samples. The results of these analyses are summarized in Table I.

TABLE I

REACTION OF 0.1 *M* $LiPh_2Cu$ WITH 0.05 *M* 1,8-DIIODONAPHTHALENE (**2**) IN ETHER SOLUTION

Temp, °C	Reaction time, min	Isolation procedure[a]	Product yields, % **5**	**3**	**1d**
0	1	H_2O	71	33	
		O_2, H_2O		66	4
0	10	H_2O	69	31	
		O_2, H_2O		78	
0	180	H_2O	59	5	
		O_2, H_2O		69	4
Reflux	1	O_2		55	4
Reflux	30	O_2		3	10
Reflux	180	O_2			6
		H_2O			3

[a] Aliquots of the reaction mixture were either hydrolyzed (H_2O) or oxidized with oxygen and then hydrolyzed (O_2, H_2O).

In a similar set of experiments a cold (3-6°) solution of 2.00 g (5.37 mmol) of the diiodide **2** and 393 mg of bibenzyl in 35 ml of ether was treated with 10 ml of an Et_2O solution containing 5.4 mmol of $LiPh_2Cu$ and stirred for 1 min. After aliquots had been removed for the previously described hydrolysis or oxidation and glpc analysis, an additional 10-ml portion of $LiPh_2Cu$ (5.4 mmol) in Et_2O was added and the processes were repeated. The results of these experiments are summarized in Table II.

TABLE II

REACTION OF 0.06–0.12 *M* 1,8-DIIODONAPHTHALENE (**2**) WITH 0.12–0.72 *M* $LiPh_2Cu$ AT 3–6° IN ETHER SOLUTION

$LiPh_2Cu$, equiv	Reaction time, min	Isolation procedure[a]	Product yields, % **2**	**5**	**3**	**3** + **5**	**7**	**1d**	**1d** + **7**
1.0	1	O_2, H_2O	59	7	31	38	2		2
		H_2O	43	16	25	41			
2.0	4	O_2, H_2O		7	63	70		4	4
		H_2O		42	36	78	3	1	4
3.0	7	O_2, H_2O		7	71	78	5	15	20
		H_2O		47	23	70	11	5	16
4.0	10	O_2, H_2O			66	66		21	21
		H_2O		55	14	69	17	6	23
5.0	13	O_2, H_2O		5	59	64	4	25	29
		H_2O		50	13	63	22	7	29
6.0	16	O_2, H_2O		5	44	59	6	28	34
		H_2O		52	6	58	23	6	29
6.0	20[b]	O_2, H_2O		3	41	44	5	27	32

[a] Aliquots of the reaction mixture were either hydrolyzed (H_2O) or oxidized and then hydrolyzed (O_2, H_2O). [b] The entire remaining reaction mixture was oxidized and then hydrolyzed.

In another set of experiments a cold (0°) solution of 500 mg (1.32 mmol) of the diiodide **2** and a weighed amount of bibenzyl (*ca.* 100 mg) in 4.5 or 5.5 ml of Et_2O was treated with a solution of either 1.97 mmol of $LiPh_2Cu$ in 5.5 ml of Et_2O (from 3.95 mmol of PhLi and 292 mg or 2.02 mmol of CuBr) or 3.94 mmol of Li_2Ph_3Cu in 14.5 ml of Et_2O (from 576 mg or 3.94 mmol of CuBr and 11.82 mmol of PhLi). After the resulting solution had been stirred at 0° for 2.0 min, 2.0-ml aliquots were removed for the previously described hydrolysis or oxidation and glpc analysis. The remaining mixture from the reaction with $LiPh_2Cu$ was treated with an additional 1.24 mmol of PhLi and then stirred for 2.0 min at 0°. Aliquots were either hydrolyzed or oxidized and then subjected to glpc analysis. The results of these experiments are summarized in Table III.

TABLE III

REACTION OF 0.07–0.13 *M* 1,8-DIIODONAPHTHALENE (**2**) WITH EITHER $LiPh_2Cu$ OR Li_2Ph_3Cu FOR 2 MIN AT 0° IN ETHER SOLUTION

Cuprate (concn, *M*)	Isolation procedure[a]	Product yields, % **3**	**5**	**7**	**1d**	Naphthalene
$LiPh_2Cu$	H_2O	9	62	2	1	5
(0.2)	O_2, H_2O	60		1	3	
$LiPh_2Cu$ (0.2)	H_2O			3		67
+ PhLi (0.2)	O_2, H_2O				21	
Li_2Ph_3Cu	H_2O	1		8	1	68
(0.2)	O_2, H_2O				27	1

[a] Aliquots of the reaction mixtures were either hydrolyzed (H_2O) or oxidized with oxygen and then hydrolyzed (O_2, H_2O).

Reaction of the Iodide 3 with Lithium Diphenylcuprate.—To a cold (−2 to −5°) solution of 90.9 mmol of $LiPh_2Cu$ in 250 ml of Et_2O was added, dropwise and with stirring over 3 min, a solution of 5.00 g (15.2 mmol) of the iodide **3** in 50 ml of Et_2O. The resulting mixture was stirred in an ice bath for 3 min and then oxidized by passing oxygen over the surface of the cold solution, with vigorous stirring, for 30 min. After the reaction mixture had been partitioned between Et_2O and an aqueous solution of NH_3 and NH_4Cl, the ethereal phase was dried and concentrated. Chromatography on silica gel separated 2.959 g (69.8%) of the crude diphenylnaphthalene **1d** (eluted with hexane) which was recrystallized from hexane to afford 2.77 g (65.4%) of pure 1,8-diphenylnaphthalene (**1d**) as white needles, mp 149.5–151° (lit.[3a] mp 149–150°). A later fraction (0.818 g), eluted with mixtures of Et_2O and hexane, was recrystallized from hexane to separate 0.525 g (18%) of the dinaphthyl derivative **9** as white prisms: mp 210.5–212°; ir ($CHCl_3$) no OH or C=O absorption in the 3- and 6-μ regions; uv max (95% EtOH) 221 mμ (ϵ 58,000), 248 (shoulder, 29,000), 285 (11,000), and 315 (12,000); nmr ($CDCl_3$) δ 6.8–7.7 (12 H m, naphthyl CH) and 6.0–6.8 (10 H m, phenyl CH); mass spectrum *m/e* (rel intensity) 406 (100, M^+), 405 (21), and 215 (16).

Anal. Calcd for $C_{32}H_{22}$: C, 94.54; H, 5.46. Found: C, 94.56; H, 5.40.

To obtain an authentic sample of the dinaphthyl derivative **9**, a mixture of 300 mg (0.91 mmol) of the iodide **3** and 225 mg of copper bronze was heated to 150–180° with stirring for 19 hr. The resulting mixture was cooled and extracted with ether. The crude extract was chromatographed on silica gel to separate 141.8 mg of crude solid (eluted with Et_2O–hexane mixtures) which was recrystallized from hexane to separate 56.6 mg (31%) of the binaphthyl **9**, mp 210–212.5°. This product was identified with the previously described sample by a mixture melting point determination and by comparison of ir, uv, and nmr spectra.

In a subsequent experiment, a cold (0°) solution of 0.76 mmol of $LiPh_2Cu$ in 2.0 ml of Et_2O was added to a cold (0°) solution of 500 mg (1.52 mmol) of the iodide **3** in 0.5 ml of Et_2O. The resulting solution was stirred while oxygen was passed over the surface for 5 min and the reaction mixture was subjected to the usual isolation procedure. Crystallization of the crude organic product from hexane separated 121 mg (39%) of the dinaphthyl **9**, mp 210–211°. Chromatography on silica gel separated an additional 18 mg of the dimer **9**, mp 209–210° (total yield 139 mg or 45%). Analysis (tlc, silica gel coating) of the remaining mother liquors suggested that a small amount of 1,8-diphenylnaphthalene (**1d**) was also present.

5-Phenyl-1,4-naphthoquinone (17).—Following a published procedure,[20] *trans*-1-phenyl-1,3-butadiene was obtained as a colorless liquid: bp 61–63° (3 mm); $n^{23}D$ 1.6064 [lit.[20] bp 78–81°

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[20] O. Grummitt and E. I. Becker, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 771.

(8 mm); n^{25}D 1.607–1.608]; ir (CCl_4) 1630 (C=C), 945 (trans CH=CH), and 895 cm^{-1} ($C=CH_2$); nmr (CCl_4) δ 7.0–7.5 (5 H m, aryl CH), 6.0–6.8 (3 H m, vinyl CH), and 5.0–5.5 (2 H m, vinyl CH).

A solution of 5.00 g (38 mmol) of the diene and 4.50 g (42 mmol) of *p*-benzoquinone in 50 ml of PhH was refluxed for 8.5 hr. The reaction mixture was treated[21b] with a solution of 0.1 g of CCl_3CO_2H in 3 ml of PhH and refluxing was continued for 4 hr. The resulting solution was concentrated under reduced pressure and the residue was triturated with CH_2Cl_2 to leave 5.21 g (58%) of the crude hydroquinone, mp 157–163°. Recrystallization from an EtOAc–hexane mixture afforded the pure 5-phenyl-1,4-dihydroxynaphthalene as colorless prisms: mp 169.5–171° (lit.[21] mp 170°); ir (Nujol mull) 3250 cm^{-1} (broad, associated OH); uv max (95% EtOH) 215 mμ (shoulder, ε 17,500) and 295 (3900); nmr (CD_3COCD_3) δ 7.0–8.0 (7 H m, 5 aryl CH and 2 OH, exchanged with D_2O), 6.4–6.8 (2 H m, aryl CH), 5.7–6.2 (2 H m, vinyl CH), 4.6–5.0 (1 H m, benzylic CH), and 3.3–3.8 (2 H m, allylic CH_2); mass spectrum *m/e* (rel intensity) 238 (M^+, 35), 165 (40), 160 (69), 152 (30), 147 (83), 131 (54), 115 (74), 105 (37), 103 (42), 91 (51), 77 (100), 63 (34), 55 (82), 51 (77), and 39 (42).

A solution of 5.00 g (21 mmol) of this hydroquinone in 22.5 ml of HOAc was treated with a solution of 14 g of $Na_2Cr_2O_7$ and 0.7 ml of H_2SO_4 in 9 ml of H_2O and the resulting solution was heated on a steam bath with stirring for 10 min. The reaction mixture was cooled and poured into ice water. Filtration separated 4.13 g (82%) of the naphthoquinone **17** as an orange solid, mp 167–171°. Recrystallization from MeOH separated the pure quinone **17** as orange plates: mp 169.5–170°; ir (CCl_4) 1675 cm^{-1} (conjugated C=O); uv max (95% EtOH) 246 mμ (ε 22,000) and 352 (2420); nmr ($CDCl_3$) δ 8.16 (1 H, d of d, *J* = 6.8 and 2.0 Hz, aryl CH), 7.0–7.9 (7 H m, aryl CH), and 6.6–7.0 (2 H m, CH of quinone); mass spectrum *m/e* (rel intensity) 234 (M^+, 63), 233 (100), 205 (16), 152 (11), and 76 (12).

Anal. Calcd for $C_{16}H_{10}O_2$: C, 82.04; H, 4.30. Found: C, 81.91; H, 4.09.

Reaction of the Naphthoquinone 17 with 1-Phenylbutadiene.—A solution of 3.00 g (12.8 mmol) of the naphthoquinone **17** and 2.00 g (15.4 mmol) of the 1-phenylbutadiene in 40 ml of PhH was refluxed for 104 hr. On standing at 25° the reaction mixture deposited 3.055 g of crude solid, mp *ca.* 215–330°, followed by 130 mg of solid, mp 156–160°. Recrystallization of the higher melting solid from $CHCl_3$–MeOH afforded 2.302 g (50%) of the dihydroquinone **18** as yellow plates, mp 228–229° (softens) and 356–358° (completely melts). We presume that this melting behavior arises from a partial or complete conversion of the dihydroquinone **18** to the quinone **20** during the melting point determination. The dihydroquinone has the following properties: ir ($CHCl_3$) 1660, 1655 (shoulder) (conjugated C=O), and 1625 cm^{-1} (C=C); uv max (95% EtOH) 249 mμ (ε 24,000) and 348 (3230); nmr ($CDCl_3$) δ 8.10 (1 H, d of d, *J* = 2.4 and 7.2 Hz, aryl CH at C-8), 7.0–7.8 (12 H m, aryl CH), 5.7–6.2 (2 H m, vinyl CH), 4.6–5.0 (1 H m, benzylic CH), and 2.9–3.5 (2 H m, allylic CH_2); mass spectrum *m/e* (rel intensity), 362 (49, M^+), 228 (28), 226 (41), 181 (33), 153 (38), 152 (100), 151 (45), 77 (68), and 51 (51).

Anal. Calcd for $C_{26}H_{18}O_2$: C, 86.16; H, 5.01. Found: C, 86.26; H, 4.90.

The mother liquors from crystallization of **18** and the lower melting solid from the initial crystallization were each crystallized from hexane to separate 140 mg (3%) of the dihydroquinone **19** as yellow needles: mp 160–161°; ir ($CHCl_3$) 1665, 1655 (shoulder) (conjugated C=O), and 1630 cm^{-1} (C=C); uv max (95% EtOH) 248 mμ (ε 22,200) and 353 (2020); nmr ($CDCl_3$), δ 8.03 (1 H d of d, *J* = 2.4 and 6.8 Hz, aryl CH at C-6), 6.6–7.8 (12 H m, aryl CH), 5.6–6.3 (2 H m, vinyl CH), 4.5–5.0 (1 H m, benzylic CH), and 3.2–3.5 (2 H m, allylic CH); mass spectrum *m/e* (rel intensity) 362 (100, M^+), 360 (43), 359 (58), and 344 (23).

Anal. Calcd for $C_{26}H_{18}O_2$: C, 86.16; H, 5.01. Found: C, 85.99; H, 5.28.

A solution of 597 mg (1.7 mmol) of the dihydroquinone **18** and 3.0 g of KOH in 30 ml of EtOH and 30 ml of PhH was refluxed for 3 hr, during which time a slow stream of O_2 was passed through the solution. The resulting mixture was cooled, diluted with H_2O, and filtered to separate 392 mg (66%) of the quinone **20** as yellow crystals: mp 352–355° (lit. mp 345°,[21b] 355°[21a]); ir (KBr pellet) 1675 cm^{-1} (conjugated C=O); uv max ($CHCl_3$) 256 mμ (ε 40,500), 270 (inflection, 21,800), and 347 (4680); mass spectrum *m/e* (rel intensity) 360 (68, M^+), 359 (100), 358 (38), and 179 (45).

A solution of 44 mg (1.2 mmol) of the hydroquinone **19** and 0.1 g of KOH in 15 ml of EtOH was refluxed for 5 hr while a slow stream of O_2 was passed through the solution. The solution was cooled, filtered (to separate some quinone **15**), concentrated, and partitioned between CH_2Cl_2 and H_2O. The organic phase was dried and concentrated. The combined residues from filtration and extraction were recrystallized from EtOH to separate 25 mg (57%) of the quinone **15** as yellow needles, mp 197.5–199.5°. Recrystallization raised the melting point to 199.5–201°; this product was identified with a subsequently described sample of the quinone **15** by a mixture melting point determination and by comparison of ir spectra.

1-Iodo-9,10-anthraquinone (10).—1-Aminoanthraquinone (20 g, 90 mmol) was converted to 16.4 g of the crude iodo derivative **10**, mp 195–199°, as previously described.[22] Sublimation (175–185° and 3 mm) afforded the pure iodoquinone **10** as orange needles: mp 204.5–205.5° (lit.[22] mp 204–205°; ir ($CHCl_3$) 1680 cm^{-1} (C=O); uv max (95% EtOH) 213 mμ (ε 22,200), 254 (32,300), and 363 (4750); uv max ($CHCl_3$) 257 (ε 31,900) and 367 (ε 3730); nmr ($CDCl_3$) δ 8.1–8.6 (4 H m, aryl CH), 7.7–8.1 (2 H m, aryl CH), and 7.40 (1 H t, *J* = 7.2 Hz, aryl CH); mass spectrum *m/e* (rel intensity) 334 (19, M^+), 179 (31), 151 (100), 150 (52), 76 (37), 75 (20), 74 (43), and 50 (34).

1-Phenyl-9,10-anthraquinone (13). A. Coupling with Lithium Diphenylcuprate.—To a solution of $LiPh_2Cu$, from 867 mg (6.04 mmol) of CuBr and 12.0 mmol of PhLi in 30 ml of Et_2O, was added a solution of 499 mg (1.49 mmol) of 1-iodoanthraquinone (**10**) in 30 ml of tetrahydrofuran. The resulting red solution was stirred for 20 min and the O_2 was passed over the surface of the solution with stirring for an additional 20 min. The yellow-brown reaction mixture was partitioned between Et_2O and aqueous NH_4Cl and NH_3 and the organic phase was separated, dried, and concentrated. Trituration of the residue with hexane left 230 mg (54%) of the phenylquinone **13**, mp 178.5–179.5°. Recrystallization from isopropyl alcohol separated the pure quinone **13** as yellow needles: mp 179.9–180.5° (lit.[21a] mp 177°); ir ($CHCl_3$) 1675 cm^{-1} (C=O); uv max (95% EtOH) 254 mμ (ε 46,400), 272 (shoulder, 17,600), and 335 (4520) with intense end absorption (ε 32,900 at 210 mμ); uv max ($CHCl_3$) 256 mμ (ε 45,800), 274 (shoulder, 18,500), and 335 (4760); nmr ($CDCl_3$) δ 7.0–8.6 (multiplet, aryl CH); mass spectrum *m/e* (rel intensity) 284 (52, M^+), 283 (100), 226 (18), and 113 (17). Chromatography of the mother liquors on silica gel (deactivated with water) separated an additional 81 mg (total yield 74%) of the 1-phenylquinone **13** in fractions eluted with CH_2Cl_2. From a similar reaction, employing 4.12 g (12.3 mmol) of the iodide **10** and 49.5 mmol of $LiPh_2Cu$ in a mixture of 225 ml of tetrahydrofuran and 90 ml of Et_2O the yield of the 1-phenylquinone was 880 mg (25%) and 1.43 g of an insoluble by-product, 1,1′-dianthraquinone (**14**), was obtained. Recrystallization from PhBr afforded the pure dimer **14** as yellow needles: mp 436–438° (lit.[23] mp 435–435.5°); ir (KBr pellet) 1660 cm^{-1} (C=O); uv max ($CHCl_3$) 254 mμ (ε 68,700), 276 (shoulder, 37,300), and 343 (7960). An authentic sample of this dimer was prepared[23] by reaction of 1.50 g (4.5 mmol) of the iodide **10** and 590 mg of copper powder in 3 ml of refluxing $PhNO_2$ for 3 hr. The dimer **14** was separated as 352 mg (38%) of tan solid, mp 436–438°, which was identified with the previously described sample by a mixture melting point determination and comparison of ir spectra. In subsequent small-scale coupling reactions with the iodide **10** and $LiPh_2Cu$, the isolation of the pure 1-phenylquinone **13** in *ca.* 70% yield was found to be facilitated when the original reaction was not subject to oxidation (with O_2) before hydrolysis. Apparently the 1-phenylquinone **13** is formed in the reaction mixture without oxidation.

B. Use of a Diels–Alder Reaction.—A mixture of 3.43 g (21.7 mmol) of 1,4-naphthoquinone and 4.00 g (30.8 mmol) of 1-phenylbutadiene was heated to 170–180° for 5 hr and then cooled and triturated with MeOH. The residual crude 1-phenylquinone **13**, mp 173–175°, amounted to 1.65 g (27%). Recrystallization (*i*-PrOH) afforded the pure quinone, mp 177.5–

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(21) (a) C. Weizmann, E. Bergmann, and L. Haskelberg, *J. Chem. Soc.*, 391 (1939); (b) E. A. Braude, J. S. Fawcett, and A. A. Webb, *ibid.*, 1049 (1954).

(22) A. E. Goldstein, *J. Amer. Chem. Soc.*, **61**, 1600 (1939).

(23) F. Ullmann and W. Minajeff, *Ber.*, **45**, 687 (1912).

178.5°, which was identified with the previously described material by a mixture melting point determination. The MeOH mother liquors from the separation deposited 3.38 g of the crude 1,4-dihydroquinone **16**, mp 110–138°. Recrystallization from isopropyl alcohol separated a sample of the pure dihydroquinone **16**: mp 139–140° (lit.[21b] mp 139°); ir ($\mathrm{CHCl_3}$) 1665 cm^{-1} (C=O); uv max (95% EtOH) 247 mμ (ε 19,500), 264 (shoulder, 11,600), and 334 (3280); uv max ($\mathrm{CHCl_3}$) 251 mμ (ε 18,400), 264 (shoulder, 12,700), and 335 (3140), nmr ($\mathrm{CDCl_3}$) δ 7.4–8.2 (4 H m, aryl CH), 7.0–7.4 (5 H m, aryl CH), 5.94 (2 H, two center lines of AB pattern, vinyl CH), 4.6–5.0 (1 H m, benzylic CH), and 3.2–3.5 (2 H m, allylic $\mathrm{CH_2}$); mass spectrum *m/e* (rel intensity) 286 (100, M$^+$), 284 (30), 283 (55), 268 (30), 257 (30), 209 (22), 181 (24), 152 (36), 77 (40), and 76 (24).

A solution of 2.325 g of this dihydroquinone **16** and 1.0 g of KOH in 200 ml of refluxing EtOH was oxidized by passing $\mathrm{O_2}$ through the solution for 1.5 hr. The solution was cooled and diluted with $\mathrm{H_2O}$ to precipitate 1.648 g of the crude quinone **13**, mp 174–177°.

1-Phenylanthracene (21).—A mixture of 739 mg (26 mmol) of the 1-phenylquinone **13**, 4.0 g of Zn dust (activated with 20 mg of $\mathrm{CuSO_4}$[24]), 40 ml of aqueous 30% NaOH, 5 ml of concentrated aqueous $\mathrm{NH_3}$, and 20 ml of EtOH was refluxed with stirring for 58 hr and then cooled and partitioned between $\mathrm{H_2O}$ and $\mathrm{CH_2Cl_2}$. The organic layer was separated and concentrated and a solution of the residue in 100 ml of isopropyl alcohol was treated with 2 ml of concentrated aqueous HCl and heated to boiling. The hot solution was filtered, concentrated, and then washed with water to leave a residue which was chromatographed on silica gel. The fractions eluted with benzene were recrystallized from MeOH to separate 479 mg (73%) of the anthracene **21** as pale yellow needles, mp 108–112°. Recrystallization from hexane gave the pure hydrocarbon **21**: mp 114–115° (lit.[5] mp 116–117°); ir ($\mathrm{CCl_4}$) no OH or C=O absorption in the 3- and 6-μ regions; uv max (95% EtOH), 255 mμ (ε 141,000), 347 (6240), 365 (8420), and 384 (7630); nmr ($\mathrm{CDCl_3}$) δ 8.42, 8.48 (two 1 H s, aryl CH at C-9 and C-10), and 7.1–8.1 (12 H m, aryl CH); mass spectrum *m/e* (rel intensity) 254 (100, M$^+$), 253 (51), 252 (42), 126 (28), and 113 (17).

1-Phenyl-9-anthrone (23).—Reduction of 1.276 g (4.49 mmol) of the 1-phenylquinone **13** with 1.624 g of granular Sn and 9 ml of concentrated aqueous HCl in 30 ml of HOAc as previously described[5] yielded 776 mg (65%) of the crude anthrone **23**, mp 188–195°. Successive recrystallization from PhH and from $\mathrm{CHCl_3}$ separated the pure anthrone **23** as colorless needles: mp 194–195.5° (lit.[5] mp 196–197.5°); ir ($\mathrm{CHCl_3}$) 1665 cm^{-1} (C=O); uv max (95% EtOH) 262.5 mμ (ε 19,000) and 310 (4620) with intense end absorption (ε 23,500 at 210 mμ); nmr ($\mathrm{CDCl_3}$) δ 8.0–8.3 (1 H m, aryl CH at C-8), 7.0–7.7 (11 H m, aryl CH), and 4.40 (2 H s, benzylic $\mathrm{CH_2}$); mass spectrum *m/e* (rel intensity) 270 (74, M$^+$), 269 (100), 268 (29), 239 (26), and 134 (23).

1,9-Diphenylanthracene (25).—Following a known procedure,[5] 245 mg (0.91 mmol) of the anthrone **23** was converted to 174 mg (58%) of crude diphenylanthracene **25**, mp 179–185°. Recrystallization from hexane afforded the pure hydrocarbon **25** as pale yellow needles: mp 184.5–185° (lit.[5] mp 183.5–184°); ir ($\mathrm{CHCl_3}$) no OH or C=O absorption in the 3- and 6-μ regions; uv max (95% EtOH) 224 mμ (ε 25,500), 260 (101,000), 338 (shoulder, 3050), 354 (6100), 371 (9550), and 392 (8700); nmr ($\mathrm{CDCl_3}$) δ 8.53 (1 H s, aryl CH at C-10), 7.8–8.2 (2 H m, aryl CH), 7.1–7.6 (5 H m, aryl CH), 6.95 (5 H s, phenyl CH), and 6.88 (5 H s, phenyl CH); mass spectrum *m/e* (rel intensity) 330 (70, M$^+$), 253 (88), 252 (100), and 250 (33).

1,8-Diiodo-9,10-anthraquinone (11).—Following previously described procedures,[25] a mixture of 60.0 g (217 mmol) of 1,8-dichloro-9,10-anthraquinone, 111.0 g (650 mmol) of *p*-toluenesulfonamide, 48 g of KOAc, 3.0 g of $\mathrm{Cu(OAc)_2}$, and 600 ml of $\mathrm{PhNO_2}$ was refluxed with stirring for 5 hr. The resulting solution was cooled to separate 37.0 g of the crude bissulfonamide, mp 266–269°. After removal of the $\mathrm{PhNO_2}$ from the mother liquor by steam distillation, an additional 31.7 g (total yield 68.7 g or 58%) of the bissulfonamide, mp 259–268°, was obtained. Recrystallization from benzene afforded the pure bissulfonamide as yellow needles: mp 269.5–270.5° (lit.[25] mp 264–264.5°); ir ($\mathrm{CHCl_3}$) 3170 (broad, associated NH), 1674 and 1622 cm^{-1} (C=O); uv max (95% EtOH) 230 mμ (ε 46,000), 261 (28,400), and 432 (9120); nmr ($\mathrm{CDCl_3}$) δ 11.82 (2 H s, NH), 7.0–8.3 (14 H m, aryl CH), and 2.37 (6 H s, aryl $\mathrm{CH_3}$). A solution of 37.0 g (67.7 mmol) of the bissulfonamide in 200 ml of concentrated $\mathrm{H_2SO_4}$ was heated on a steam bath for 1 hr and then poured onto ice and neutralized with NaOH. The resulting precipitate was triturated with $\mathrm{H_2O}$ to leave 15.38 g (95%) of the diamine **12** as a red solid, mp 265–268°. Recrystallization from benzene afforded the pure diamine **12** as maroon needles: mp 269–270.5° (lit.[25] mp 262–264°); ir (KBr pellet) 3440 and 3300 (NH) and 1591 cm^{-1} (C=O); uv max (95% EtOH) 233 mμ (ε 46,100), 278 (13,900), 310 (5950), and 513 (10,700); nmr (pyridine-d_5 at 79°) δ 7.3–8.7 (8 H m, aryl CH and two NH) and 4.15 (2 H broad, NH); mass spectrum *m/e* (rel intensity), 238 (100, M$^+$), 209 (21), 183 (29), 182 (33), 181 (31), 154 (56), 127 (32), 91 (41), 77 (37), 65 (36), 64 (34), 63 (42), 52 (27), and 39 (33).

To a cold (−15°) mixture prepared from 12.24 g (51.5 mmol) of the diamine **12**, 55 ml of concentrated $\mathrm{H_2SO_4}$, 72 ml of $\mathrm{H_2O}$, and 160 g of ice was added, dropwise with stirring and cooling, a solution of 18.0 g of $\mathrm{NaNO_2}$ in 78 ml of $\mathrm{H_2O}$. The resulting mixture (an orange slurry) was stirred at −15° for 30 min and then a solution of 72 g of KI in 96 ml of water was added, dropwise with stirring and cooling. The resulting mixture was warmed to 80° and then cooled and made basic with NaOH. The solid product was collected and washed successively with aqueous 10% HCl, saturated aqueous $\mathrm{Na_2S_2O_3}$, and aqueous $\mathrm{NaHCO_3}$. The residual brown solid (26.44 g, mp 270–276°) was chromatographed on silica with PhH as the eluent to separate 16.66 g (74%) of the diiodide **11** as red-orange needles: mp 282–283°; ir (KBr pellet), 1675 and 1660 cm^{-1} (shoulder) (C=O); uv max (95% EtOH) 224 mμ (ε 31,100), 261 (25,800), and 367 (4940); uv max ($\mathrm{CHCl_3}$) 263 mμ (ε 25,800) and 371 (4930); mass spectrum *m/e* (rel intensity) 460 (100, M$^+$), 368 (23), 305 (23), 149 (42), 75 (48), and 74 (20).

Anal. Calcd for $\mathrm{C_{14}H_6I_2O_2}$: C, 36.54; H, 1.31; I, 55.17. Found: C, 36.53; H, 1.49; I, 55.22.

1,8-Diphenyl-9,10-anthraquinone (15).—A solution of 2.003 g (4.35 mmol) of the diiodide **11** in 650 ml of THF was cooled to 0° and then a solution of $\mathrm{Li_2Ph_3Cu}$ (from 3.75 g or 26.2 mmol of CuBr and 77.9 mmol of PhLi) in 129 ml of $\mathrm{Et_2O}$ was added rapidly (15 sec) with stirring. The resulting solution was stirred for 10 sec and then $\mathrm{O_2}$ was bubbled through the solution with stirring for 7 min. The resulting mixture was partitioned between $\mathrm{Et_2O}$ and aqueous $\mathrm{NH_4Cl}$ and $\mathrm{NH_3}$. The crude organic product was chromatographed on silica gel and the fractions (eluted with $\mathrm{CH_2Cl_2}$) contained 657 mg (42%) of the diphenyl quinone **15**, mp 196–200°. This material was recrystallized from isopropyl alcohol to separate the quinone **15** as 610 mg of pale yellow needles: mp 200–201°; ir ($\mathrm{CHCl_3}$) 1680 (shoulder) and 1672 cm^{-1} (C=O); uv max (95% EtOH) 218 mμ (ε 33,700), 253.5 (40,600), and 349 (4700); uv max ($\mathrm{CHCl_3}$) 255 mμ (ε 40,500) and 349 (4340); nmr ($\mathrm{CDCl_3}$) δ 8.1–8.4 (2 H m, aryl CH at C-4 and C-5), 7.4–7.8 (4 H m, aryl CH), and 7.29 (10 H s, phenyl CH); mass spectrum *m/e* (rel intensity), 360 (67, M$^+$), 359 (100), 302 (22), 300 (25), 283 (30), 151 (22), and 150 (20).

Anal. Calcd for $\mathrm{C_{26}H_{16}O_2}$: C, 86.65; H, 4.48. Found: C, 86.52; H, 4.70.

The reaction was repeated with 1.003 g (2.18 mmol) of the diiodide **11** in 340 ml of THF and 16 ml of an $\mathrm{Et_2O}$ solution containing $\mathrm{Li_2Ph_3Cu}$ (from 1.25 g or 8.72 mmol of CuBr and 26 mmol of PhLi). After a reaction time of 30 sec at 0° the reaction mixture was partitioned between $\mathrm{Et_2O}$ and aqueous $\mathrm{NH_4Cl}$ and $\mathrm{NH_3}$ without prior treatment with $\mathrm{O_2}$. The $\mathrm{Et_2O}$ layer was concentrated and the residue was dissolved in $\mathrm{CH_2Cl_2}$, at which time 57 mg of 9,10-anthraquinone, mp 284–286°, separated. The $\mathrm{CH_2Cl_2}$ solution was chromatographed on silica gel employing $\mathrm{CH_2Cl_2}$ and $\mathrm{CH_2Cl_2}$–$\mathrm{Et_2O}$ mixtures as the eluents to separate 112 mg (14%) of the diphenylquinone **15** (mp 197–200°), 56 mg (9%) of the crude phenylquinone **13** (mp 170–178°), and 135 mg (total yield 192 mg or 42%) of 9,10-anthraquinone (mp 283–287°). Recrystallization of the crude phenylquinone **13** from isopropyl alcohol raised the melting point to 178–179.5°. The samples of 9,10-anthraquinone and the phenylquinone **13** were identified with authentic samples by mixture melting point determinations and comparison of ir spectra. In another experiment the reaction of 1.001 g (2.18 mmol) of the diiodide **11** and $\mathrm{LiPh_2Cu}$ (from 2.50 g or 17.5 mmol of CuBr and 35.1 mmol of PhLi) in 87 ml of $\mathrm{Et_2O}$ for 30 min at 25° followed by hydrolysis (without prior oxi-

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

(25) N. R. Rao, K. H. Shah, and K. Venkataraman, *Proc. Indian Acad. Sci., Sect. A*, **34**, 355 (1951).

dation) yielded 272 mg (35%) of the diphenylquinone **15**, mp 200–201°.

1,8-Diphenylanthracene (22).—A mixture of 275.7 mg (0.766 mmol) of the diphenylquinone **15**, 1.5 g of Zn powder (activated with 8 mg of $CuSO_4$),[24] 16 ml of aqueous 30% NaOH, 2 ml of concentrated aqueous NH_3, and 20 ml of EtOH was refluxed with stirring for 52 hr and then cooled and extracted successively with CH_2Cl_2 and hexane. The combined organic extracts were dried and concentrated and a solution of the residue in 300 ml of isopropyl alcohol was treated with 3 ml of concentrated aqueous HCl and then heated to boiling. The hot solution was filtered and cooled to separate 222 mg of crude product, mp 178–180°. Concentration of the mother liquor left an additional 82 mg of crude product. The chromatography of the crude product on silica gel separated 134 mg (53%) of the diphenylanthracene **22**, mp 190–192°. Recrystallization from hexane afforded the pure hydrocarbon **22** as white needles: mp 191.5–193°; ir (KBr pellet) no OH or C=O absorption in the 3- or 6-μ region; uv max (95% EtOH) 211 mμ (ϵ 36,900), 251 (shoulder, 65,400), 259 (127,000), 356 (6500), 374 (9440), and 394 (7850); nmr ($CDCl_3$) δ 8.55 and 8.46 (two 1 H singlets, aryl CH at C-9 and C-10), 7.97 (2 H, d of d, J = 7.2 and 2.4 Hz, aryl CH at C-4 and C-8), and 7.1–7.7 (14 H m, aryl CH); mass spectrum m/e (rel intensity) 330 (100, M^+) and 252 (14).

Anal. Calcd for $C_{26}H_{18}$: C, 94.51; H, 5.49. Found: C, 94.70; H, 5.47.

1,8-Diphenyl-9-anthrone (24).—A mixture of 697.1 mg (1.94 mmol) of the diphenylquinone **15**, 504 mg of granular Sn, and 13.5 ml of HOAc was heated under reflux with stirring for 2 hr, during which time 3.3 ml of concentrated aqueous HCl was added dropwise to the mixture. The resulting mixture was partitioned between H_2O and CH_2Cl_2 and the organic layer was separated and concentrated. Recrystallization of the residue from hexane separated 500 mg (75%) of the anthrone **24** as white needles, mp 166–167.5°. Recrystallization from hexane raised the melting point to 167.5–168.5°: ir (CCl_4) 1680 cm^{-1} (C=O); uv max (95% EtOH) 234 mμ (ϵ 25,600), 283 (12,100), and 311 (shoulder, 6030) with intense end absorption (ϵ 45,300 at 210 mμ); nmr ($CDCl_3$) δ 7.1–7.6 (16 H m, aryl CH) and 4.26 (2 H s, benzylic CH_2); mass spectrum m/e (rel intensity) 346 (66, M^+), 345 (100), 344 (20), 268 (20), and 239 (21).

Anal. Calcd for $C_{26}H_{18}O$: C, 90.14; H, 5.24. Found: C, 90.14; H, 5.28.

1,8,9-Triphenylanthracene (26).—A solution of 605 mg (1.74 mmol) of the anthrone **24** in 77 ml of PhH was treated with 32.5 ml of an Et_2O solution containing 34.8 mmol of PhLi. The resulting mixture, from which a yellow precipitate settled, was stirred at 25° for 2 hr and then acidified with aqueous 10% HCl. The resulting mixture was refluxed for 30 min and then cooled and extracted with PhH. After the organic extracts had been washed with H_2O and concentrated, the residue (242 mg) was chromatographed on 50 g of silica gel. The early fractions, eluted with PhH, contained 395 mg (56%) of the crude triphenylanthracene **26**, mp 225–230°. Recrystallization from hexane separated 323 mg of the pure anthracene **26** as yellow prisms: mp 230–231°; ir ($CHCl_3$) no OH or C=O absorption in the 3- and 6-μ regions; uv max (95% EtOH) 227 mμ (shoulder, ϵ 28,300), 266 (82,700), 363 (6460), 381 (10,480), and 401 (8940); nmr ($CDCl_3$) δ 8.62 (1 H s, aryl CH at C-10), 8.02 (2 H, d of d, J = 7.0 and 1.6 Hz, aryl CH at C-4 and C-5), 6.4–7.6 (14 H m, aryl CH), and 6.36 (5 H partially resolved multiplet, CH for phenyl group at C-9); mass spectrum m/e (rel intensity) 406 (100, M^+), 329 (65), 328 (28), 327 (20), and 326 (22).

Anal. Calcd for $C_{32}H_{22}$: C, 94.54; H, 5.46. Found: C, 94.61; H, 5.44.

Later fractions from the chromatographic separation, eluted with PhH and with PhH–CH_2Cl_2 mixtures, contained 216 mg (36% recovery) of the crude starting anthrone **24**, mp 157–163°, which was identified with an authentic sample by a mixture melting point determination and by comparison of ir spectra.

9-Phenylanthracene (27).—To a solution of 503 mg (2.59 mmol) of 9-anthrone in 120 ml of PhH was added 23 ml of an Et_2O solution containing 25 mmol of PhLi. The resulting mixture was stirred for 2 hr at 25° and then acidified with aqueous 10% HCl. This mixture was refluxed for 30 min and then cooled and extracted with PhH. The combined organic solutions were washed with H_2O and concentrated. Recrystallization of the residue (782 mg) from hexane separated 542 mg (83%) of the crude anthracene **27**, mp 148–156°. Recrystallization from EtOH afforded the pure phenylanthracene **27** as pale yellow plates: mp 156–157° (lit. mp 155–157°,[26] 151–152°[5]); uv max (95% EtOH) 255 mμ (ϵ 140,000), 331 (3800), 347 (7100), 365 (10,500), and 385 (10,100); nmr (CCl_4), δ 8.39 (1 H s, aryl CH at C-10) and 7.0–8.2 (13 H m, aryl CH); mass spectrum, m/e (rel intensity) 254 (100, M^+), 253 (40), 252 (39), and 126 (15).

Polarographic Reduction of the Naphthalene and Anthracene Derivatives.—These measurements were obtained at 25° with a Heath polarograph (Model EU-402V) employing either a 0.30 M or a 0.50 M solution of n-$Bu_4N^+BF_4^-$ in $(CH_3)_2NCHO$ as the solvent and supporting electrolyte.[27] The reference, a saturated calomel electrode, made contact with the solution through intermediate salt bridges containing aqueous 1 M $NaNO_3$ and 0.5 M $Et_4N^+BF_4^-$ in $(CH_3)_2NCHO$. The $E_{1/2}$ values (*vs.* sce) and the αn values, obtained from plots of E *vs.* log $[i/(i_d - i)]$, are presented in Table IV.

TABLE IV

POLAROGRAPHIC REDUCTION POTENTIALS FOR THE NAPHTHALENE AND ANTHRACENE DERIVATIVES IN $(CH_3)_2NCHO$ CONTAINING 0.30 M OR 0.50 M n-Bu_4NBF_4

Compd	First wave		Second wave	
(concn, $M \times 10^3$)	$E_{1/2}$ *vs.* sce, V	αn value	$E_{1/2}$ *vs.* sce, V	αn value
Naphthalene (15.2)	−2.49[a]	0.90		
7 (9.2–13.7)	−2.37[b]	0.87	−2.61	1.3
1d (3.5)[c]	−2.23	0.98	−2.50	1.2
9 (7.1)	−2.27	0.94	−2.56	1.0
Anthraquinone (8.3)	−0.82	0.99	−1.50	0.95
13 (3.4)	−0.85	1.2	−1.54	1.1
15 (4.5)	−0.92	0.93	−1.62	0.91
Anthracene (8.9)	−1.93[d]	0.98	−2.48	0.94
21 (3.5)[e]	−1.86[f]	0.98	−2.35	1.1
27 (7.8)	−1.87[g]	0.99	−2.43	0.93
22 (3.2)	−1.84	0.94	−2.34	1.1
25 (1.9)[h]	−1.83[i]	0.92	−2.21	1.0
26 (2.7)	−1.83	0.90	−2.05	1.2

[a] Reported −2.46 V.[16a] [b] Reported −2.40 V.[16a] [c] A wave was also observed at −2.78 V (αn = 1.5). [d] Reported −1.96 V,[16a] −1.92 V.[16b] [e] A wave was also observed at −2.70 V (αn = 1.2). [f] Reported −1.89 V,[16a] −1.88 V.[16b] [g] Reported −1.92 V,[16a] −1.86 V.[16b] [h] A wave was also observed at −2.69 V (αn = 1.1.). [i] Reported −1.85 V.[16b]

Registry No.—**1d**, 1038-67-1; **2**, 1730-04-7; **3**, 25308-69-4; **7**, 605-02-7; **9**, 33522-22-4; **10**, 3485-80-1; **11**, 30877-00-0; **12**, 129-42-0; **13**, 1714-14-3; **14**, 914-20-5; **15**, 33522-27-9; **16**, 33522-28-0; **17**, 33522-29-1; **17** (dihydroxy derivative), 33522-30-4; **18**, 33522-31-5; **19**, 33522-32-6; **20**, 33522-33-7; **21**, 1714-09-6; **22**, 33522-35-9; **23**, 1714-15-4; **24**, 33522-37-1; **25**, 1714-19-8; **26**, 33522-39-3; **27**, 602-55-1; $LiPh_2Cu$, 23402-69-9; Li_2Ph_3Cu, 33520-60-4; *trans*-1-phenyl-1,3-butadiene, 16939-57-4; bissulfonamide, mp 266–269°, 33522-40-6.

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