formed during the ozonation. The product was isolated as above and analyzed by gas chromatography for *cis* and *trans* isomers.

Ozonation of *trans*-3-Hexene.—The addition of ozone to *trans*-3-hexene, 99.95% *trans,* in the absence of a solvent resulted in a violent explosion shortly after the ozonation was started whereby a dark-colored precipitate formed. When 3 vol. of *n*-pentane per volume of *trans*-3-hexene was used, the ozonation could be carried out to completion. To 20 ml. (13.6 g., 0.0162 mole) of *trans*-3-hexene in 60 ml. of hexane was added 7.6 g. (0.16 mole) of ozone. Distillation gave 4.7 g. of *trans*-3-hexene ozonide, b.p. 39.5° at 18 mm. A high yield of polymeric material was obtained, 13.7 g. The crude product was dissolved in ether and shaken with sodium bicarbonate solution to remove any propionic acid. After drying over magnesium perchlorate and removing the ether, the ozonide was distilled; b.p. 38.5° at 22 mm., n^{25}_{D} 1.4023, d^{20}_{4} 0.9781.

Anal. Calcd.: active O, 12.10. Found: active O, 11.95.

Ozonation of 2,5-Dimethyl-3-hexene.—To 20 ml. (14.2 g., 0.127 mole) of 2,5-dimethyl-3-hexene, 99.8% *cis,* in 40 ml. of *n*-pentane was added 6.0 g. (0.125 mole) of ozone to completion. The product was twice distilled, b.p. 66° at 23 mm. 2,5-Dimethyl-3-hexene ozonide (19 g.) was obtained in high yield (95%); n^{25}_{D} 1.4115, d^{20}_{4} 1.0398. There was almost no polymeric material.

To 15 ml. (10.7 g., 0.095 mole) of 2.5-dimethyl-3-hexene, 99.9% *trans,* in 45 ml. of *n*-pentane was added 4.7 g. (0.098 mole) of ozone to completion. The product was twice distilled and 9.6 g. of 2,5-dimethyl-3-hexene ozonide was obtained; b.p. 63–64° at 22 mm., n^{25}_{D} 1.4103, d^{20}_{4} 1.0376. The polymeric product weighed 5.5 g.

Ozonation of *trans*-3-Hexene in *n*-Butyraldehyde.—To 60 ml. (40.6 g., 0.485 mole) of 3-hexene, 99.95% *trans,* in 180 ml. (147 g.) of *n*-butyraldehyde was added 23.0 g. (0.48 mole) of ozone. Distillation gave 28 g. of monomeric ozonides and 46 g. of residue. The ozonides were dissolved in an equal volume of ether and shaken with sodium bicarbonate solution. After drying over magnesium perchlorate and removing the ether, the product was redistilled. The fraction boiling at 48–49° at 7 mm. was 3-heptene ozonide, n^{25}_{D} 1.4059, d^{20}_{4} 0.9619.

Anal. Calcd. for $C_7H_{14}O_3$: C, 57.45; H, 9.60; O, 32.83; active O, 10.94. Found: C, 57.5; H, 9.75; O, 33.0; active O, 10.85.

Identification of Ozonides by Reduction with Triphenylphosphine.—3-Hexene ozonide was reduced as follows. 3-Hexene (0.4 g., 3.03 mmoles) ozonide was mixed with 1.2 ml. of *n*-heptane and 1.2 g. (4.58 mmoles) of triphenylphosphine was added. The mixture was heated in a sealed tube for 60 min. in boiling water which completely reduced the ozonide. The tube was cooled in cold water which caused crystallization of triphenylphosphine oxide. The supernatant liquid was analyzed by gas chromatography. Two peaks were observed, corresponding to *n*-heptane (solvent) and propionaldehyde. The latter was identified by comparison of the retention time with an authentic sample of propionaldehyde and the addition of propionaldehyde to the reaction mixture and repeated chromatographic analysis. Similar experiments were made with the other ozonides. After it has been established that the reduction of ozonides by triphenylphosphine led exclusively to the corresponding carbonyl compounds, the unnatural ozonides could be identified in the same manner.

Preparation of 2-Butene Ozonide (Isomer B).—Triphenylphosphine (4.37 g., 0.0167 mole) was added to 25 ml. of *n*-pentane. After solid carbon dioxide was added to remove the air, the flask was connected to an effective reflux condenser and a slow stream of nitrogen was bubbled over the solution. Butene ozonide (5.2 g., 0.050 mole) was added. The ozonide was obtained by the ozonation of 2-butene (94% *trans,* 5% *cis*) and contained 13% of isomer A and 87% of isomer B. The triphenylphosphine dissolved upon shaking and triphenylphosphine oxide started to precipitate after a few minutes, whereupon acetaldehyde began to boil. After standing for 16 hr. at room temperature, the triphenylphosphine oxide was filtered off and the solution was distilled through a short column. After removal of the 2-pentane, 2.0 g. of 2-butene ozonide was obtained, b.p. 48° at 58 mm. G.l.c. analysis indicated that the product was free of component A; n^{25}_{D} 1.3815.

Preparation of 2,5-Dimethyl-3-hexene Ozonide (Isomer A).—2,5-Dimethyl-3-hexene ozonide (4.4 g., 0.0275 mole) prepared from the *trans* olefin (99.9% *trans*) was added to 25 ml. of *n*-pentane and treated with 4.32 g. (0.0165 mole) of triphenylphosphine. The mixture was heated for 5–10 min. in a water bath to achieve complete solution, whereupon triphenylphosphine began to precipitate. The mixture was allowed to stand for 16 hr. at room temperature and the triphenylphosphine oxide was filtered off. After removing the *n*-pentane, the remaining ozonide was distilled; 2.4 g., b.p. 61° at 21 mm., n^{25}_{D} 1.4100, d^{20}_{4} 1.0370. Gas chromatography indicated that the more readily reducible form was removed.

Acknowledgment.—The authors wish to thank Dr. K. W. Greenlee for preparation of the olefins, Mr. W. R. Flint for technical assistance, and Mr. J. L. Patrick for the determination of the *cis* and *trans* content of the olefins.

Synthesis and Spectra of Di- and Polyphenylanthracenes

S. Carlton Dickerman, Derek de Souza, and Philip Wolf

Department of Chemistry, New York University, New York, New York

Received February 18, 1965

Three diphenylanthracenes (1,9, 1,10, and 2,10) and 1,9,10-triphenylanthracene have been prepared and an improved synthesis of 1,4,9,10-tetraphenylanthracene is reported. N.m.r. spectra confirm the presence of face-to-face arrangements of the benzene rings in three of these compounds. Ultraviolet spectra of phenylanthracenes (9, 1, and 2), diphenylanthracenes (1,9, 1,10, 2,10, 2,9, 1,4, and 9,10), 1,9,10-triphenylanthracene, and 1,4,9,10-tetraphenylanthracene have been measured in methylene chloride. The red shifts in the long wave-length bands associated with di- and polyphenyl substitution are essentially additive for the entire series including those derivatives which possess parallel benzene rings. Gas–liquid chromatography of the six diphenylanthracenes has been investigated and retention times are reported.

In connection with problems arising from studies of homolytic arylation of anthracene we required authentic samples of the five diphenylanthracenes that have in common a 9-phenyl group. The 9,10 and 2,9 isomers were known but the 1,9-, 1,10-, and 2,10-diphenylanthracenes had not been described. Recent interest (*vide infra*) in the physical properties, particularly ultraviolet spectra, of systems containing perpendicular π-electron systems suggested inclusion of the polyphenylanthracenes.

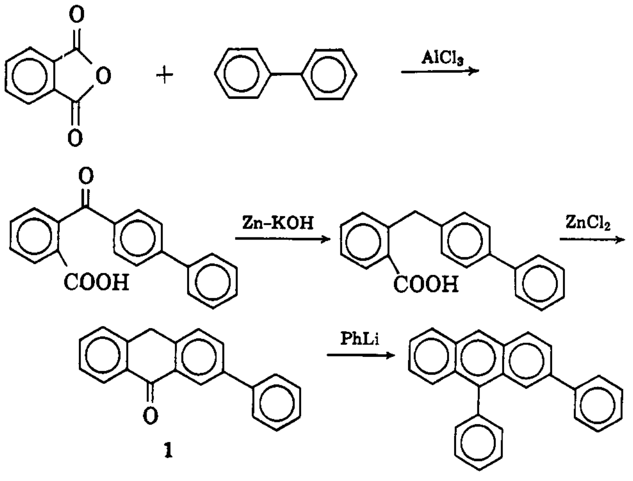
A general route to diphenylanthracenes involves the preparation of the appropriate phenylanthrone followed by addition of phenylmagnesium bromide or phenyllithium. For example, 2,9-diphenylanthracene (**2**) has been prepared from biphenyl and phthalic anhydride by the sequence of reactions given in Scheme I.[1,2] Similar methods afforded 1,10- and 2,10-diphenylanthracenes (**6** and **10**) and are illustrated

(1) R. Scholl and W. Neovius, *Ber.*, **44**, 1075 (1911).

(2) Y. Hirshberg and L. Haskelberg, *Trans. Faraday Soc.*, **39**, 45 (1943).

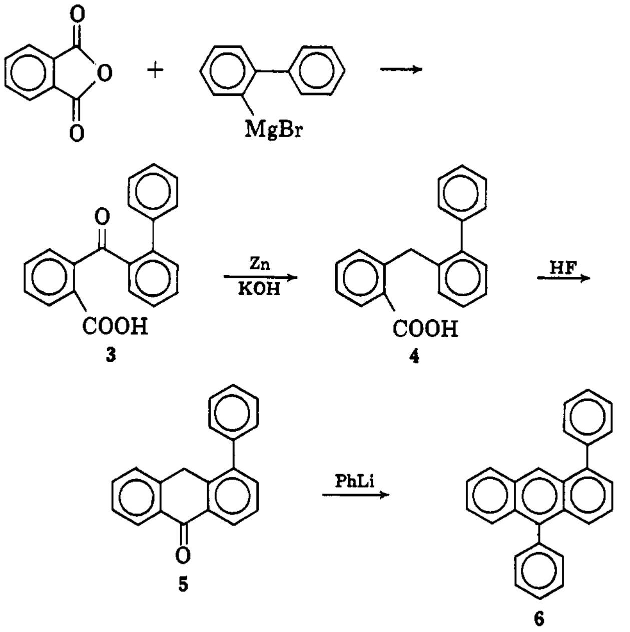
SCHEME I

2,9-DIPHENYLANTHRACENE (2)



SCHEME II

1,10-DIPHENYLANTHRACENE (6)



in Schemes II and III. In the synthesis of 2,10-diphenylanthracene (**10**), cyclization might have occurred both *ortho* and *para* to the phenyl group.[3] However, only 2-phenyl-10-anthrone (**9**) was isolated and the hydrocarbon **10** derived from the anthrone **9** was homogeneous by g.l.c. The isomeric anthrone **12** would have produced 1,9-diphenylanthracene (**13**) which is easily differentiated from the 2,10 isomer by this technique (see Table I). Both benzoylbenzoic acids **3** and **7** were recovered from attempted cyclizations in hydrogen fluoride; this observation is in agreement with previous studies which have indicated that hydrogen fluoride is not effective when the ring system under attack contains strongly electron-attracting groups.[4]

Synthesis of 1,9-diphenylanthracene (**13**) presented a different problem in that the required anthrone is not accessible, at least directly, by the general method described above. However, 1-phenylanthraquinone is readily available from 1-aminoanthraquinone[5] and it was decided to investigate tin and acid reduction of this compound in the hope that steric factors would diminish the reactivity of the hindered carbonyl group. This expectation proved to be correct and 1,9-diphenylanthracene (**13**) was prepared as indicated in Scheme IV.

SCHEME III

2,10-DIPHENYLANTHRACENE (10)

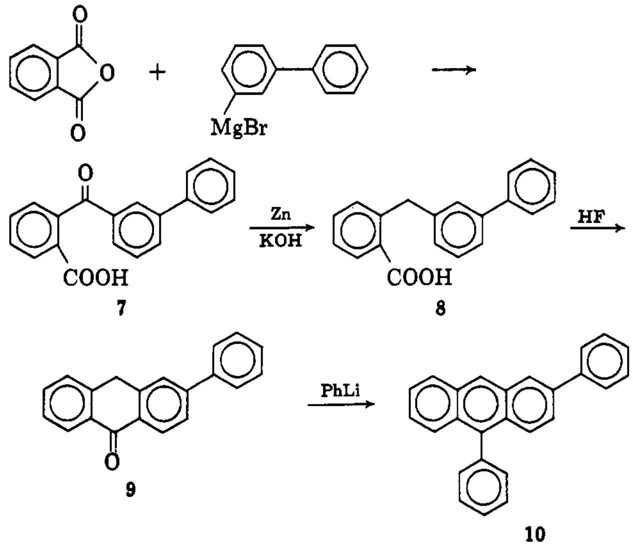


TABLE I

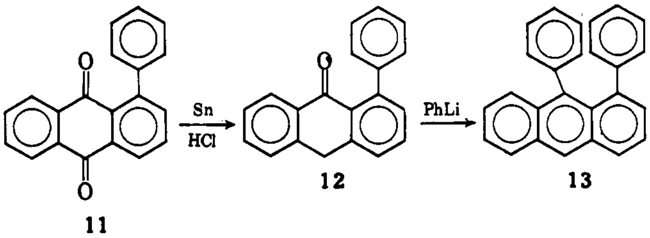
GAS-LIQUID CHROMATOGRAPHY OF DIPHENYLANTHRACENES

Compd.	M.p., °C.	Retention time, min.[a]
9,10	249–250	4.4
1,9 (**13**)	183–184	5.7
1,10 (**6**)	176–177	6.0
1,4	173–174	7.8
2,9 (**2**)	166–167	9.6
2,10 (**10**)	173–174	12.6

[a] On a 6 ft. × 0.25 in. stainless steel column prepared with Dow Corning FS-1265, 10% w./w. on Chromosorb P, at column temperature of 260°, flow rate of 200 cc./min., and injection port temperature of 330°.

SCHEME IV

1,9-DIPHENYLANTHRACENE (13)



Column chromatography of both 2-phenyl-9-anthrone (**1**) and 2-phenyl-10-anthrone (**9**) on basic alumina afforded 2-phenylanthraquinone. These reactions represent additional examples of air oxidations which are catalyzed by basic alumina.[6]

---

(3) The hydrogen fluoride method of forming cyclic ketones and the effects of substituents on the direction of closure have been reviewed by W. S. Johnson, *Org. Reactions*, **2**, 114 (1944).

(4) L. F. Fieser and E. B. Hershberg, *J. Am. Chem. Soc.*, **61**, 1271 (1939).

(5) V. A. Puchkov, *Chem. Abstr.*, **55**, 19877 (1961); *Zh. Vses. Khim. Obshchestva im D. I. Mendeleeva*, **6**, 238 (1961).

(6) (a) R. M. Roberts, C. Barter, and H. Stone, *J. Phys. Chem.*, **63**, 2077 (1959); (b) Y. Matsumoto and E. Funakubo, *J. Chem. Soc. Japan, Pure Chem. Sect.*, 731 (1951); (c) Y. Matsumoto, *ibid.*, 733 (1951); (d) J. H. Pinckard, A. Chatterjee, and L. Zechmeister, *J. Am. Chem. Soc.*, **74**, 1603 (1952).

TABLE II

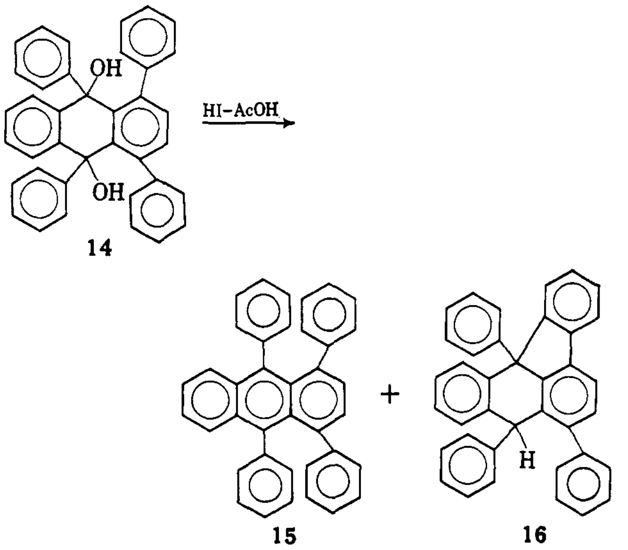
ULTRAVIOLET SPECTRA OF PHENYL DERIVATIVES OF ANTHRACENE

Position(s) of phenyl	Absorption maxima, mμ (log ε)[a]							Shift, mμ[b]
None[c]	253		312	326	343	360	380	
1-[c]	258 (5.14)		315 (3.08)	333 (3.45)	349 (3.74)	367 (3.92)	387 (3.84)	7
2-[c]	261 (4.72)	281 (4.85)	319 (3.15)	334 (3.45)	350 (3.70)	368 (3.82)	389 (3.67)	9
9-[c]	259 (5.13)		318 (3.09)	332 (3.46)	350 (3.78)	368 (3.97)	387 (3.93)	7
9,10-[c]	259 (5.02)		323 (3.19)	338 (3.54)	354 (3.88)	372 (4.09)	392 (4.11)	12
1,4-[c]	260 (5.02)		320 (3.19)	337 (3.52)	354 (3.82)	371 (3.99)	391 (3.93)	11
1,9-	260 (5.21)		319 (3.29)	336 (3.56)	353 (3.89)	371 (3.98)	391 (3.93)	11
1,10-	259 (5.12)		322 (3.27)	336 (3.66)	354 (3.91)	372 (4.10)	392 (4.05)	12
2,9-[c]	265 (4.77)	283 (4.88)	322 (3.18)	339 (3.55)	356 (3.81)	374 (3.86)	395 (3.88)	15
2,10-	266 (5.08)	282 (5.17)	321 (3.19)	337 (3.51)	355 (3.76)	373 (3.81)	393 (3.83)	13
1,9,10-	268 (4.97)		328 (3.11)	345 (3.52)	364 (3.86)	383 (4.06)	403 (4.03)	23
1,4,9,10-[c]	277 (4.86)						408 (4.08)	28

[a] Solvent: methylene chloride. [b] In the longest wave-length band relative to anthracene. [c] For spectra in other solvents, see "Organic Electronic Spectral Data," Vol. 1, M. J. Kamlet, Ed., Interscience Publishers, Inc., New York, N. Y., 1960.

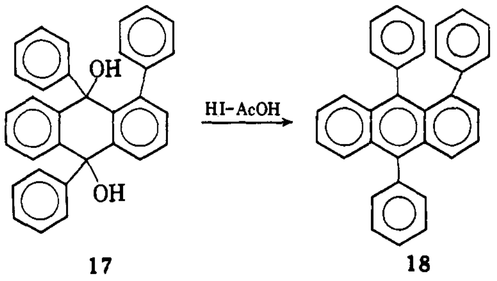
SCHEME V

1,4,9,10-TETRAPHENYLANTHRACENE (**15**)



SCHEME VI

1,9,10-TRIPHENYLANTHRACENE (**18**)



The initial route to 1,4,9,10-tetraphenylanthracene (**15**) is indicated in Scheme V and has presented problems.[7] The difficulty here and with a similar synthesis of rubrene is associated with the formation of an isomeric hydrocarbon in the reductive aromatization of the tetraphenyldiol. Separation of the mixture of hydrocarbons **15** and **16** is at best tedious. Since the mechanism of aromatization presumably involves reduction of carbonium ions, it seemed reasonable to expect that a high concentration of iodide ion would favor formation of **15** at the expense of **16**. This is difficult to achieve using potassium iodide; however, 50% hydriodic acid in acetic acid proved to be effective and 1,4,9,10-tetraphenylanthracene was isolated without recourse to fractional crystallization.[8] The same reagent proved to be equally effective in converting the diol **17**, which had been described previously,[6] to 1,9,10-triphenylanthracene (**18**) (Scheme VI).

N.m.r. spectra of 1,9-diphenylanthracene (**13**), 1,9,-10-triphenylanthracene (**18**), and 1,4,9,10-tetraphenylanthracene (**15**) exhibit two resonance signals between τ 2.81 and 3.10 superimposed on complex multiplet absorption. If the major signal from the phenyl protons in 1,10-diphenylanthracene (**6**) at τ 2.43 is used as the reference for this series of compounds, the resulting shifts are comparable in magnitude and direction to those observed for 2,2-paracyclophane[9] and 1,8-diphenylnaphthalene.[10] Such shifts have been attributed to shielding of each set of phenyl protons by an adjacent parallel benzene ring.[9,10] A similar interpretation with an additional factor, nonequivalency of the two sets of phenyl protons, accounts for the two upfield signals exhibited by the three derivatives of anthracene.

The homogeneity of each of the diphenylanthracenes was confirmed by gas-liquid chromatography and retention times, determined with mixtures, are given in Table I. These data reveal that the order of elution is determined by the positions of the phenyl groups and corresponds to the pattern 9 before 1 before 2.

The ultraviolet spectra of anthracene and ten derivatives, all determined in methylene chloride, are recorded in Table II. Phenyl substitution produces a shift in all the absorption maxima to longer wave lengths and the effects on the longest wave-length bands, produced by the introduction of two or more phenyl groups, are essentially additive and independent of the presence of face-to-face benzene rings. However, adherence of the spectra of 1,4,9,10-tetraphenylanthracene (**15**) to the additivity relationship may be fortuitous in view of the loss in fine structure of the long wave-length band exhibited by this compound.

---

[7] C. Weizmann, E. Bergmann, and L. Haskelberg, *J. Chem. Soc.*, 391 (1939).

[8] Another route to 1,4,9,10-tetraphenylanthracene (reduction of the corresponding methyl ether) which circumvents the formation of the isomeric hydrocarbon has been described by C. Weizmann and E. Bergmann, *ibid.*, 494 (1939).

[9] (a) J. S. Waugh and R. W. Fessenden, *J. Am. Chem. Soc.*, **79**, 846 (1957); (b) D. J. Cram, C. K. Dalton, and G. R. Knox, *ibid.*, **85**, 1088 (1963).

[10] H. O. House, R. W. Magin, and H. W. Thompson, *J. Org. Chem.*, **28**, 2403 (1963).

Furthermore, both the naphthalene and naphthacene analogs of **15**, 1,4,5,8-tetraphenylnaphthalene[11] and 5,6,11,12-tetraphenylnaphthacene (rubrene),[12] exhibit considerably larger shifts than predicted on the basis of additivity. Although the ultraviolet spectra of both 1,9-diphenylanthracene and 1,8-diphenylnaphthalene[10] do not reveal any interaction between the respective phenyl groups, 5,6-diphenylnaphthacene does show an enhanced shift of about 4 mμ which has been attributed to face-to-face interaction.[13]

Theoretical interpretation of these and the earlier findings presents an interesting problem. For example, 1,8-diphenylnaphthalene, 1,9-diphenylanthracene, and 5,6-diphenylnaphthacene possess phenyl groups which must be oriented essentially perpendicular to a polycyclic π-system. Nevertheless, all of these compounds exhibit the pattern of ultraviolet absorption characteristic of the parent arene at substantially longer wave lengths and with increased intensity. House and co-workers[10] have discussed this problem with respect to 1,8-diphenylnaphthalene, and Jaffé and Chalvet[13] have interpreted the spectra of 5,6-diphenylnaphthacene and other compounds in terms of resonance interaction of perpendicular π-systems. However, it is difficult to reconcile this type of interpretation with the observation that the ultraviolet spectrum of 9,10-diphenylanthracene is essentially uneffected by nitro and methoxy substituents in the phenyl groups.[14]

Experimental[15]

2,9-Diphenylanthracene (2).—The literature method of preparation[2] was modified by using the hydrogen fluoride method of cyclization. After column chromatography on alumina and recrystallization from *n*-hexane, the hydrocarbon melted at 165–166°, lit.[2] m.p. 165–166°.

2-(2-Phenylbenzoyl)benzoic Acid (3).—The Grignard reagent prepared from 11.7 g. (0.05 mole) of 2-bromobiphenyl and 1.32 g. (0.055 g.-atom) of magnesium in 100 ml. of ethyl ether was added with stirring to 7.4 g. (0.05 mole) of phthalic anhydride in 150 ml. of warm benzene. After heating to reflux, the mixture was stirred for 3 hr. and poured into a mixture of ice and hydrochloric acid. The organic phase was separated and was extracted with potassium carbonate solution. Acidification of the alkaline extract gave a gum that solidified. The solid was digested with two portions of boiling water to remove phthalic acid and gave 10.8 g. (72%) of product, m.p. 163–164°. Recrystallization from acetic acid afforded an analytical sample of m.p. 164–165°.

Anal. Calcd. for $C_{20}H_{14}O_3$: C, 79.46; H, 4.67. Found: C, 79.73; H, 4.80.

2-(2-Phenylbenzyl)benzoic Acid (4).—A solution of 10.4 g. of 2-(2-phenylbenzoyl)benzoic acid in 1000 ml. of 1 *N* sodium hydroxide was added to 79 g. of zinc dust which had been activated by treatment with dilute aqueous copper sulfate. The mixture was stirred at gentle reflux for 50 hr. and was filtered. Acidification of the filtrate gave a solid that was digested in boiling water; yield 9.39 g. (90%) of colorless product of m.p. 190–191°.

Anal. Calcd. for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.35; H, 5.73.

1-Phenyl-10-anthrone (5).—A suspension of 15.6 g. of 2-(2-phenylbenzyl)benzoic acid in liquid hydrogen fluoride was prepared in a polyethylene beaker and was allowed to stand in a hood until the hydrogen fluoride had evaporated. The orange residue of solid was washed with water, dilute ammonium hydroxide, and again with water. After drying, the product was recrystallized from methanol and gave 6.00 g. (41%) of yellow compound, m.p. 140–141°.

Anal. Calcd. for $C_{20}H_{14}O$: C, 88.86; H, 5.22. Found: C, 89.29; H, 5.26.

1-Phenylanthracene.—A mixture of 3.00 g. of 1-phenyl-10-anthrone, 10 ml. of 2 *N* sodium hydroxide, 0.6 g. of activated zinc dust, and 7 ml. of toluene was refluxed for 43 hr. The toluene layer, which exhibited an intense blue fluorescence, was separated and was washed with water. Evaporation of the toluene gave a residue that was chromatographed on alumina (Merck) in 1:1 benzene–hexane and afforded 2.65 g. (94%) of 1-phenylanthracene, m.p. 111–113°, lit.[16] m.p. 110–112°. A second chromatography on alumina (Woelm) and recrystallization from ethanol raised the melting point to 116–117°.

1,10-Diphenylanthracene (6).—Phenyllithium prepared from 1.05 g. of bromobenzene in 30 ml. of ethyl ether was added with stirring to a solution of 0.180 g. of 1-phenyl-10-anthrone in 30 ml. of benzene. The mixture was refluxed for 1 hr., cooled, and acidified with dilute hydrochloric acid. After heating and stirring for an additional hour, the benzene layer was separated and was subjected to steam distillation to remove biphenyl. The nonvolatile residue was dissolved in a minimum amount of benzene and was chromatographed on alumina (Woelm) using 1:1 benzene–hexane as eluent; yield 0.181 g. (82%). After recrystallization from acetone–methanol 1,10-diphenylanthracene was obtained as colorless needles of m.p. 175–176°. The n.m.r. spectra[17] showed strong absorption due to phenyl protons at τ 2.43 superimposed on a complex multiplet.

Anal. Calcd. for $C_{26}H_{18}$: C, 94.51; H, 5.49. Found: C, 94.27; H, 5.49.

2-(3-Phenylbenzoyl)benzoic acid (7) was prepared from 3-biphenylylmagnesium bromide and phthalic anhydride, by the procedure described for 2-(2-phenylbenzoyl)benzoic acid. The yield amounted to 46% and the analytical sample melted at 204–205° after recrystallization from acetic acid.

Anal. Calcd. for $C_{20}H_{14}O_2$: C, 79.46; H, 4.67. Found: C, 79.27; H, 4.88.

2-(3-Phenylbenzyl)benzoic Acid (8).—Reduction of 2-(3-phenylbenzoyl)benzoic acid with activated zinc dust and sodium hydroxide by the procedure given for 2-(2-phenylbenzyl)benzoic acid gave the desired compound in a yield of 73%. Recrystallization from cyclohexane afforded an analytical sample of m.p. 128–129°.

Anal. Calcd. for $C_{20}H_{16}O_2$: C, 81.31; H, 5.59. Found: C, 83.17; H, 5.67.

2-Phenyl-10-anthrone (9).—A solution and/or suspension of 1.00 g. of 2-(3-phenylbenzyl)benzoic acid in 25 ml. of liquid hydrogen fluoride in a polyethylene beaker was allowed to remain in a hood at room temperature until the hydrogen fluoride had evaporated. The colored residue was dissolved in chloroform and this solution was washed with water, dilute ammonium hydroxide, and again with water. After drying with anhydrous sodium sulfate, the chloroform was evaporated, and the residue was crystallized by trituration with methanol. Recrystallization from 10:1 cyclohexane–acetone afforded the anthrone as yellow needles of m.p. 149–150°, yield 0.57 g. (61%).

Anal. Calcd. for $C_{20}H_{14}O$: C, 88.86; H, 5.22. Found: C, 88.91; H, 5.11.

Phenylanthraquinones.—Chromatography of both 2-phenyl-10-anthrone (**9**) and 2-phenyl-9-anthrone (**1**) in benzene on basic alumina gave 2-phenylanthraquinone, m.p. 161–162°, lit.[1] m.p. 162–163°. Chromatography of 1-phenyl-10-anthrone (**5**) on basic alumina (Merck) in benzene gave yellow plates of 1-phenylanthraquinone, m.p. 174–175°, lit.[7] m.p. 177°.

2,10-Diphenylanthracene (10).—The procedure described above for the 1,10 isomer was employed. 2-Phenyl-10-anthrone (0.244 g., 0.9 mmole) in 10 ml. of benzene was added to phenyllithium prepared from 0.293 g. (0.0425 g.-atom) of lithium metal and 3.14 g. (0.02 mole) of bromobenzene in 35 ml. of ethyl ether. After 1 hr., the mixture was acidified with dilute cold sulfuric acid, and the organic layer was separated, washed free of acid,

---

[11] E. D. Bergmann, S. Blumberg, P. Bracha, and S. Epstein, *Tetrahedron*, **20**, 195 (1964).

[12] R. G. Douris, *Ann. chim.*, **4**, 479 (1959).

[13] H. H. Jaffé and O. Chalvet, *J. Am. Chem. Soc.*, **85**, 1561 (1963).

[14] S. C. Dickerman, M. Klein, and G. B. Vermont, *J. Org. Chem.*, **29**, 3695 (1964).

[15] All melting points are corrected. Microanalyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y. All n.m.r. spectra were measured with a Varian Model A-60 spectrophotometer. Ultraviolet spectra were obtained with a Cary Model 15 spectrophotometer. Gas–liquid chromatography was studied with an F and M Model 500 instrument.

[16] J. C. Cook, *J. Chem. Soc.*, 1087 (1930).

[17] In methylene chloride relative to tetramethylsilane.

and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and after digestion in methanol gave 0.225 g. (75%) of yellow product. Recrystallization from ethanol gave pale yellow crystals, m.p. 173–174°.

Anal. Calcd. for $C_{26}H_{18}$: C, 94.57; H, 5.43. Found: C, 94.08; H, 5.86.

1-Phenylanthraquinone (11).—The procedure of Puchkov[5] was modified by diazotizing 1-aminoanthraquinone (Aldrich) in concentrated hydrochloric acid.[18] 1-Aminoanthraquinone was dissolved in concentrated sulfuric acid and reprecipitated by the addition of water. Eight grams (36 mmoles) of the amine was diazotized with sodium nitrite in 30 ml. of concentrated hydrochloric acid at 40°. A slurry of the diazonium salt was added to a mixture of 300 ml. of benzene, 50 ml. of water, and 30 g. of sodium acetate. After stirring for 1 hr. at room temperature, the mixture was refluxed with stirring for 2 hr. The organic phase was separated, washed with water, dried, and treated with Norit. Evaporation of the benzene left a solid residue which was recrystallized from acetone to yield 5.6 g. (55%) of 1-phenylanthraquinone, m.p. 178.5–179.5°, lit.[5] m.p. 177°.

1-Phenyl-9-anthrone (12).—A mixture of granular tin (0.74 g., 0.0062 g.-atom) in 10 ml. of glacial acetic acid and 1.0 g. (36 mmoles) of 1-phenylanthraquinone was heated to boiling and 5 ml. of concentrated hydrochloric acid was added dropwise over a period of 2 hr. at reflux temperature.[19] After cooling, 100 ml. of water was added and the mixture was extracted with methylene chloride. The extract was dried and decolorized, and the solvent was removed under reduced pressure. Recrystallization of the residue from benzene gave 0.35 g. (38%) of yellow crystals, m.p. 196.0–197.5°.

Anal. Calcd. for $C_{20}H_{14}O$: C, 88.86; H, 5.22. Found: C, 88.63; H, 5.09.

1,9-Diphenylanthracene (13).—Phenyllithium prepared from 1.1 g. (0.16 g.-atom) of lithium metal and 12 g. (0.082 mole) of bromobenzene in 60 ml. of ethyl ether was filtered into a solution of 1.09 g. (4 mmoles) of 1-phenyl-9-anthrone in 150 ml. of benzene. The reaction mixture was stirred under nitrogen for 2 hr. at ambient temperature, and most of the ether was removed by distillation. After acidification with dilute hydrochloric acid the two-phase mixture was refluxed for 30 min. The benzene layer was separated, washed, dried, and concentrated to a volume of about 25 ml. Chromatography of this solution on alumina (Woelm, neutral, activity I) with 1:2 benzene–hexane gave a product which melted over a range and probably contained biphenyl. Digestion with three portions of 25:2 hexane–benzene afforded 0.850 g. (70%) of 1,9-diphenylanthracene as a colorless microcrystalline solid of m.p. 183.5–184.0°. The n.m.r. spectra showed strong absorption due to phenyl protons at τ 3.02 and 3.10 superimposed on a complex multiplet.

Anal. Calcd. for $C_{26}H_{18}$: C, 94.51; H, 5.49. Found: C, 94.15; H, 5.49.

1,4,9,10-Tetraphenylanthracene (15).—Phenyllithium prepared from 1.56 g. (0.23 g.-atom) of lithium metal and 17.4 g. (0.119 mole) of bromobenzene in 80 ml. of ethyl ether was filtered (nitrogen) into a solution of 1.0 g. (2.8 mmoles) of 1,4-diphenylanthraquinone in a mixture of 60 ml. of benzene and 100 ml. of ethyl ether. After stirring under nitrogen for 30 min. at ambient temperature and at reflux for 1 hr., the mixture was acidified with dilute hydrochloric acid. The organic phase was separated, washed with water, and dried over sodium sulfate, and the solvent was evaporated. A clear oil remained which crystallized on trituration with hexane. The crude diol (14) (1.34 g.), m.p. 170–190°, was recrystallized from benzene to yield colorless crystals, m.p. 188–190°.[20] The diol (0.5 g.) was added with stirring to a hot solution of 1.0 g. of concentrated hydriodic acid (50%), 50 ml. of glacial acetic acid, and 6 ml. of hypophosphorous acid (50%). The mixture was heated for 20 min. at about 80° during which time a yellow solid crystallized. After cooling in an ice–salt bath, the solid was isolated by filtration and was recrystallized from acetone; the yield of bright yellow needles was 0.271 g. (54% based on quinone), m.p. 202–203°, lit.[7] m.p. 205°. The n.m.r. spectra showed strong absorption due to phenyl protons at τ 2.81 and 3.09 superimposed on a complex multiplet.

1,9,10-Triphenylanthracene (18).—1-Phenylanthraquinone was converted to 1,9,10-triphenyl-9,10-dihydro-9,10-anthracenediol (17) with phenyllithium. The crude diol (m.p. 156–192°, lit.[7,20] m.p. 238°) was treated with a mixture of acetic, hydriodic, and hypophosphorous acids as was described for 1,4,9,10-tetraphenylanthracene. After recrystallization from acetone, the product was isolated as pale yellow needles of m.p. 205–206° and in a yield of 34% based on quinone. The n.m.r. spectra showed strong absorption at τ 3.02 and 3.10 superimposed on a complex multiplet.

Anal. Calcd. for $C_{32}H_{22}$: C, 94.55; H, 5.45. Found: C, 94.74; H, 5.34.

1,4-Diphenylanthracene.—After chromatography on alumina and recrystallization from ethanol, 1,4-diphenylanthracene[7,21] melted at 174–175°, lit.[7] m.p. 170°.

Reference Compounds.—The following hydrocarbons were prepared by standard methods and were purified by chromatography on alumina and subsequent recrystallization: 9,10-diphenylanthracene, m.p. 250°, lit.[22] m.p. 249–250°; 2-phenylanthracene, m.p. 212°, lit.[7] m.p. 207°; 9-phenylanthracene, m.p. 151–152°, lit. m.p. 155–157°[23] and 152–153°.[24] 1-Phenylanthracene is listed separately in the Experimental section.

Acknowledgment.—This research was supported in part by a Frederich Gardner Cottrell Grant from the Research Corporation. We also wish to thank Professor Lester Friedman for helpful discussion and for a generous gift of 3-bromobiphenyl.

---

[18] A. Schaarschmidt, *Ber.*, **49**, 2678 (1916).

[19] Adapted from the preparation of 9-anthrone reported by K. H. Meyer in "Organic Syntheses," Coll. Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 60.

[20] 1,4,9,10-Tetraphenyl-9,10-anthracenediol (**14**) has been reported[7] to melt at 240°. Presumably, this melting point refers to one of the two possible configurational isomers.

[21] E. Bergmann, L. Haskelberg, and F. Bergmann, *J. Org. Chem.*, **7**, 303 (1942).

[22] C. K. Ingold and P. G. Marshall, *J. Chem. Soc.*, 3080 (1926).

[23] E. D. Barnett, J. W. Cook, and I. G. Nixon, *ibid.*, 512 (1927).

[24] P. L. Julian, W. Cole, and J. G. Schager, *J. Am. Chem. Soc.*, **71**, 2060 (1949).