

Synthesis and Conformations of Dibenzylanthracenes. Evidence for the 1,4-Benzylation of Anthracene

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Four new dibenzylanthracenes (1-4) have been prepared by benzylation of anthracene with 2,5-dimethylbenzyl chloride, 2,4,6-trimethylbenzyl chloride, and 2,3,5,6-tetramethylbenzyl chloride or by reacting 9,10-bis(chloromethyl)anthracene with *p*-xylene or mesitylene using Friedel-Crafts reactions. Evidence is presented for the 1,4-benylation of anthracene which is attributed to steric hindrance effects preventing the attack of 9,10 positions, normally the most reactive. The structural assignments and the conformational preferences of the compounds prepared were achieved by the interpretation of the uv and nmr spectra combined with *a priori* estimates of the ring current magnetic effects.

We have been interested in the Friedel-Crafts benzylation of alkylbenzenes¹ and the conformational properties² of the reaction products (diphenylmethanes and dibenzylbenzenes). During our work we have had the opportunity to propose in several instances that steric hindrance effects play a major role in determining the substitution position in the aromatic substrate.^{3,4} We report here evidence for the 1,4-benylation of anthracene which, again, can be interpreted in terms of steric effects.

Although some benzyl- and dibenzylanthracenes have been reported in the literature,⁵ little work has appeared as yet on the benzylation of anthracene using Friedel-Crafts reactions,⁶ and many of the compounds mentioned have been obtained by reduction of the corresponding ketones,⁷ hydroboration of anthrone derivatives,⁸ or by reaction of anthracene with benzyl radicals.⁹

Some Japanese workers⁶ have prepared, using Friedel-Crafts reactions, some dibenzylanthracenes which they, without considering alternative structures, assigned the 9,10 structure. Instead, 9,10- or 1,4-dibenzylanthracenes, respectively, were obtained by us because of the steric hindrance exhibited by the benzylating agent used. The structural relationship of dibenzylanthracenes with some of the dibenzylbenzenes already studied² has allowed us to assign the conformational preferences of the compounds prepared and also helped us in the finer details of their structure proof.

Discussion

Four new dibenzylanthracenes were prepared according to Scheme I reported below and their structural

(1) G. Montaudo, P. Finocchiaro, S. Caccamese, and F. Bottino, *J. Chem. Eng. Data*, **16**, 249 (1971).

(2) G. Montaudo, S. Caccamese, and P. Finocchiaro, *J. Amer. Chem. Soc.*, **93**, 4202 (1971).

(3) P. Finocchiaro, *Tetrahedron*, **27**, 581 (1971).

(4) G. Montaudo, P. Finocchiaro, S. Caccamese, and F. Bottino, *J. Polym. Sci., A-1*, **8**, 2475 (1970).

(5) (a) J. M. Cook, *J. Chem. Soc.*, 2160 (1926); (b) E. de B. Barnett, J. M. Cook, and J. L. Wiltshire, *ibid.*, 1724 (1927); (c) E. de B. Barnett and J. L. Cook, *ibid.*, 566 (1928); (d) E. Bergman and S. Fujise, *Justus Liebig's Ann. Chem.*, **480**, 188 (1930); (e) M. Imoto, T. Iguchi, F. Sakurai, T. Kuraya, S. Yoshioka, T. Uehara, and J. Itakura, *Makromol. Chem.*, **43**, 189 (1961); (f) T. Nakaya, T. Tomomoto, and M. Imoto, *Bull. Chem. Soc. Jap.*, **39**, 1551 (1966).

(6) M. Imoto and T. Nakaya, *ibid.*, **36**, 785 (1963).

(7) P. Rona and U. Feldman, *J. Chem. Soc.*, 1737 (1958).

(8) M. Rabinovitz and G. Salemnik, *J. Org. Chem.*, **33**, 3935 (1968).

(9) (a) A. L. Beckwith and W. A. Waters, *J. Chem. Soc.*, 1001 (1957); (b) K. Sisido, Y. Udô, and H. Nozaki, *J. Amer. Chem. Soc.*, **82**, 434 (1960); (c) K. C. Bass and P. Nababing, *J. Chem. Soc.*, 4396 (1965); (d) A. L. J. Beckwith, W. B. Renfrow, and J. K. Teubner, *Tetrahedron Lett.*, 3463 (1968); (e) S. Gibson, A. D. Mosnaim, D. C. Nonhebel, and J. A. Russel, *Tetrahedron*, **25**, 5047 (1969).

assignment was made unambiguously by uv and nmr spectra (see next section). The importance of using short reaction times and mild catalyst (SnCl_4 or ZnCl_2), combined with excess of hydrocarbon to minimize isomerization and polymerization reactions, has been already stressed.¹ All the reactions were run in nitroethane, *i.e.*, under nonisomerizing conditions.¹⁰

As reported in Scheme I, compound 2 can be obtained only by benzylating mesitylene with 9,10-bis(chloromethyl)anthracene. Instead, a compound which exhibits different characteristics, identified as 1,4-disubstituted anthracene (compound 3), is obtained by benzylating anthracene with 2,4,6-trimethylbenzyl chloride.

The 1,4-benylation of anthracene (see also compound 4) is best rationalized in terms of steric effects which prevent the attack of the anthracene nucleus at the 9 and 10 positions, normally the most reactive.¹¹ The presence of two ortho methyls prevents 2,4,6-trimethylbenzyl chloride and 2,3,5,6-tetramethylbenzyl chloride from attacking the 9 and 10 positions, while this is not the case with 2,5-dimethylbenzyl chloride where only one ortho position is substituted and the steric effect is weaker. In fact, the same product (1) is obtained by the two alternative routes.

Compound 4 has already been prepared,⁶ but it was erroneously assigned the 9,10 structure. By repeating the procedure by the Japanese workers, we have obtained a compound which proved to be identical with 4.

Structure Proof and Conformational Properties.—

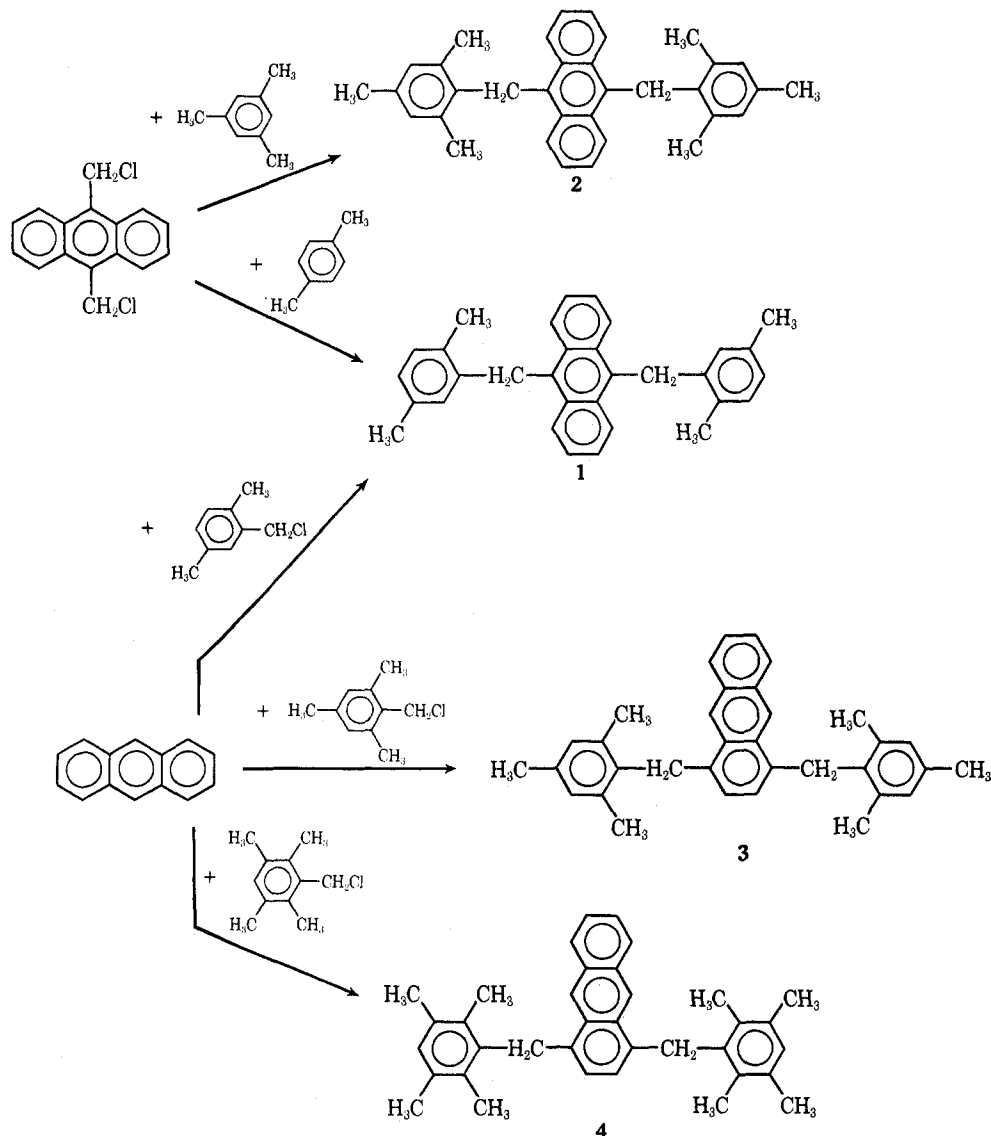
The uv and nmr spectral characteristics of compounds 1-4 are reported in Table I, together with those of some reference compounds. The uv spectra of compounds 1 and 2 show a definite red shift in the anthracene absorption bands (300-380 $m\mu$), which, as well recognized,¹² is characteristic of the 9,10-disubstituted anthracenes. The nmr spectra unambiguously confirm the structure of compounds 1 and 2. In fact, compound 1 shows an AA'BB' multiplet (8.12, 7.41 ppm) due to anthracene protons 1-8. The 9 and 10 protons, which should appear as a singlet at about 8.40 ppm (Table I), are absent. The two vicinal xylyl protons (AB system) appear at 7.40 ppm, while the ortho xylyl proton resonates as a singlet at 6.24 ppm. The same situation is found for compound 2. Anthracene pro-

(10) G. A. Olah and J. A. Olah, *J. Org. Chem.*, **32**, 1612 (1967).

(11) F. A. Drahowzal in "Friedel-Crafts and Related Reactions," Vol. II, part 1, G. A. Olah, Ed., Interscience, New York, N. Y., 1964, p 431.

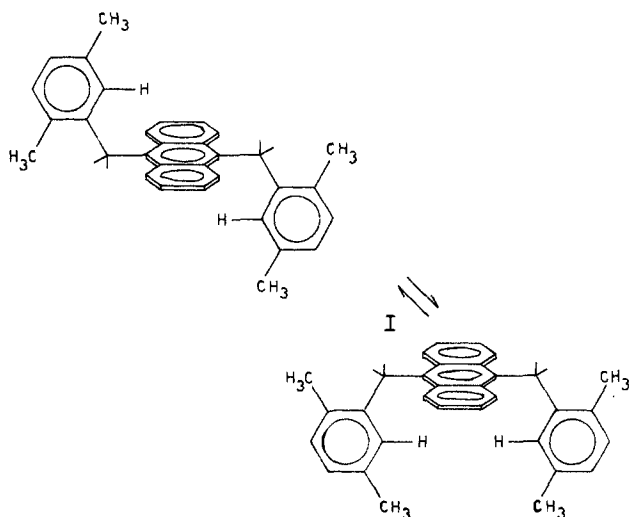
(12) H. H. Jaffé and M. Orchin in "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962, p 317.

SCHEME I



tons 1–8 appear as an AA'BB' system and the 9 and 10 protons are absent.

The conformational preference of compounds **1** and **2** can be assigned on the basis of the structural relationship between dibenzylanthracenes and dibenzylbenzenes already studied.² Compound **1** is predicted to



exist preferentially in the conformations **I** (two rapidly interconverting rotamers) where the ortho xylyl hydrogens lie above and below the anthracene ring and experience its diamagnetic shielding.

The experimental value of 6.24 ppm for these ortho hydrogens in compound **1** indicates a diamagnetic shielding¹³ of about 0.96 ppm (with respect to the other nuclear xylyl protons) which can be explained by the predominance of the less hindered molecular conformations **I**. This is also confirmed by the paramagnetic deshielding experienced by the ortho methyl groups² (2.64 ppm) in compound **1** with respect to the averaged value (1.96 ppm; see below) of the ortho methyls in compound **2**.

Conformations **I** are analogous to that found² for bis(2,5-dimethylbenzyl)durene which differs from compound **1** only because the durene ring replaces anthracene, indicating that as far as the steric effect is concerned the anthracene is equivalent to a durene ring.

(13) For polynuclear hydrocarbons the estimated ring current effect is somewhat higher than those for benzene case. The theoretical shieldings predicted for anthracene are 1.2–1.5 times higher with respect to benzene.¹⁴

(14) N. Jonathan, S. Gordon, and B. P. Dailey, *J. Chem. Phys.*, **36**, 2443 (1962).

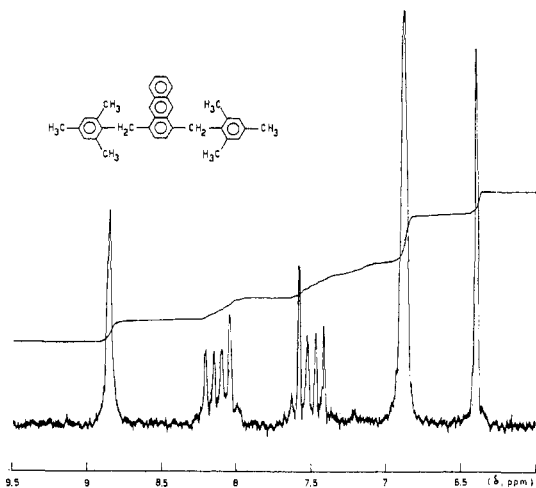


Figure 1.—Nmr spectrum (aromatic region) of compound 3.

In compound 2 conformations of type I become unfavorable because of the steric repulsion between methyls and the π -electron cloud of the anthracene ring, so that mesityl rings are forced into a skew position. Averaging must necessarily occur in this case because the coexistence of equivalent conformations with equal population causes each ortho methyl to be exchanged from a shielded position to a deshielded one.

Coming now to the compounds 3 and 4, the uv and nmr spectra clearly rule out a 9,10-disubstituted structure. The uv spectra (Table I) come close to that of 1,4-dimethylantracene and show marked differences from the spectra of 9,10-disubstituted anthracenes. The nmr spectra (Table I, Figure 1) reveal the 9,10-anthracene protons resonating at 8.86 and 8.84 ppm, respectively, and the methylene protons resonating at higher field value (about 4.50 ppm) with respect to the compounds 1 and 2 (4.90 ppm),¹⁵ an AA'BB' system (with halved intensity with respect to that of compounds 1 and 2), and two other signals (singlet) which resonate at higher field value (3, 6.43, 6.91 ppm; and 4, 6.38, 6.88 ppm). The singlet at about 6.90 ppm belongs to mesitylene (3) or durene (4) nuclear protons² and the other must belong to anthracene protons.

These data rule out all alternative structures, but the 1,4 and 2,3 types (1,5 type cannot account for the 6.40 ppm singlet and for the AA'BB' system; 1,2 type might account for the AA'BB' system but not for the 6.40 ppm singlet, etc.). In fact, 1,4 and 2,3 type structures should give roughly the same nmr pattern (*i.e.*, the four anthracene protons 5 to 8 should appear as an AA'BB' system, protons 9 and 10 as a singlet, and protons 2 and 3 or 1 and 4, respectively, should appear as a singlet).

Although a 2,3-disubstituted structure might be *a priori* excluded on steric grounds, the analysis of finer details of the nmr spectra permits assignments of the structure of compounds 3 and 4 as 1,4 disubstituted.

In fact, on the basis of structural relationship between dibenzylanthracenes and dibenzylbenzenes discussed above, we can predict *a priori* for compounds 3 and 4 that 1,4 and the alternative 2,3 type structures should

(15) Methyl and methylene signals in the 9 and 10 positions are usually found shifted downfield with respect to those from other anthracene positions.¹⁵

(16) M. D. Bentley and M. J. S. Dewar, *J. Org. Chem.*, **35**, 2707 (1970).

TABLE I
NMR and UV Spectra of 9,10- and 1,4-Anthracene Derivatives

Compd	UV, λ_{max} (ϵ_{max})		Nmr, δ , ppm										Ref				
	H _{1,4}	H _{3,3'}	H _{5,3}	H _{5,3'}	H _{6,7}	H _{6,7'}	H _{9,10}	H _{6',6''}	H _{5',5''}	H _{4',4''}	H _{3',3''}	CH ₂					
Anthracene	310 (1120), 325 (2510), 339 (5020), 357 (7600), 378 (7600)	378 (7600)	7.98 ^b	7.43 ^b	7.43 ^b	7.43 ^b	8.38 ^c	3.03									
9,10-Dimethyl	323 (1000), 339 (7600), 357 (6030), 377 (9780), 387 (9120)	387 (9120)	7.98 ^b	7.43 ^b	7.41 ^b	7.41 ^b	8.38 ^c	3.03									
9,10-Dibenzyl	345 (3500), 360 (7600), 380 (13,100), 400 (13,380)	400 (13,380)	7.98 ^b	7.43 ^b	7.41 ^b	7.41 ^b	8.38 ^c	3.03									
9,10-Di(CH ₂ -p-xylyl)	330 (1050), 345 (3000), 361 (6800), 381 (12,100), 403 (12,100)	403 (12,100)	7.98 ^b	7.43 ^b	7.41 ^b	7.41 ^b	8.38 ^c	3.03									
9,10-Di(CH ₂ -mesityl)	332 (1300), 348 (3450), 364 (7900), 384 (16,700), 408 (17,050)	408 (17,050)	7.98 ^b	7.43 ^b	7.20 ^b	7.20 ^b	8.06 ^b	2.69									
1,4-Dimethyl	315 (1175), 330 (2830), 345 (5625), 364 (8710), 382 (7930)	382 (7930)	7.98 ^b	7.43 ^b	6.43 ^c	6.43 ^c	8.15 ^b	2.69									
1,4-Di(CH ₂ -mesityl)	319 (1700), 333 (3600), 348 (6250), 366 (10,300), 388 (9280)	388 (9280)	7.98 ^b	7.43 ^b	6.38 ^c	6.38 ^c	8.12 ^b	2.69									
1,4-Di(CH ₂ -duryl)	319 (1300), 334 (3100), 349 (6250), 368 (10,100), 388 (9000)	388 (9000)	7.98 ^b	7.43 ^b	6.38 ^c	6.38 ^c	8.12 ^b	2.69									

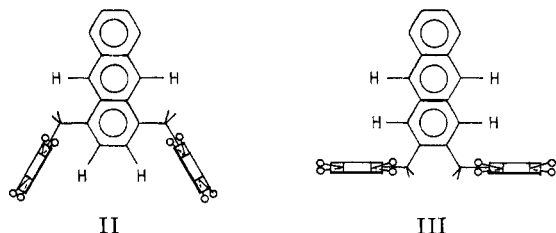
^a Values in italics denote methyl singlets. ^b AA'BB' system. ^c Singlet. ^d AB system. ^e W. Carruthers, H. N. M. Stewart, P. G. Hansell, and K. M. Kelly, *J. Chem. Soc. C*, 2607 (1967). ^f W. L. Mosby, *J. Org. Chem.*, **18**, 966 (1953).

TABLE II
OBSERVED AND CALCULATED MAGNETIC SHIELDINGS (PPM) FOR CONFORMER II AND III

	H _{2,5} ^a	H _{9,10} ^a	H _{1,4} ^a	$\Delta^{2,3}$		$\Delta^{1,1'}$		$\Delta^{9,10}$	
				Obsd ^b	Calcd ^c	Obsd ^b	Calcd ^c	Obsd ^b	Calcd ^c
Anthracene	7.43	8.38	7.98						
Conformer II {	6.43	8.86		+1.00	+0.98			-0.48	-0.17
4	6.38	8.84		+1.05	+0.98			-0.46	-0.17
Conformer III {		8.86	6.43			+1.55	+0.80	-0.48	+0.26
4		8.84	6.38			+1.60	+0.80	-0.46	+0.26

^a Experimental values from Table I. ^b Computed as the difference between the chemical shifts of the hydrogens in compounds **3** and **4** and those of the corresponding protons in anthracene. ^c Calculated through the Johnson and Bovey tables.¹⁷

exist predominantly in the less hindered molecular conformations II and III, respectively.



This in turn permits calculation through the Johnson and Bovey tables¹⁷ of the magnetic shieldings induced by the benzene rings for the anthracene protons of the two structures considered. For conformer II, the chemical shift differences (Δ values, Table II) computed from the experimental values are in good agreement with the calculated ones. On the contrary, Δ values computed for conformer III (Table II) cannot be reconciled with the calculated figures.¹⁸ Based on the above arguments, a structure of type 1,4 can be safely assigned to compounds **3** and **4**, which exist in the preferred conformation II.

Experimental Section

The ¹H nmr spectra were recorded with TMS as internal standard on a Varian A-60 or HA-100 spectrometer in CDCl₃ (Table I). They are reported in parts per million on the δ scale. All uv spectra were recorded in toluene on a Hitachi Perkin-Elmer EPS-3t spectrometer (Table I). The infrared spectra were determined in Nujol with a Perkin-Elmer 237 instrument. Molecular weight determinations were obtained by vpo, in *o*-dichlorobenzene at 130° using a Mechrolab 302 thermoelectric osmometer. The melting points are uncorrected and were determined with a Kofler microscope hot stage.

The following chloromethyl derivatives were prepared according to the literature: 2,5-dimethylbenzyl chloride,¹⁹ 2,3,5,6-tetramethylbenzyl chloride,²⁰ 2,4,6-trimethylbenzyl chloride,²¹ and 9,10-bis(chloromethyl)anthracene.²²

(17) C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

(18) The paramagnetic shielding experienced by the anthracene 9 and 10 protons cannot be rationalized on the basis of conformer III, where a diamagnetic shielding is reasonably to be expected.

(19) C. D. Shacklett and H. A. Smith, *J. Amer. Chem. Soc.*, **73**, 766 (1951).

(20) R. R. Aitken, G. M. Bagder, and J. W. Cook, *J. Chem. Soc.*, 331 (1950).

(21) R. C. Fuson and N. Rabjohn, *Org. Syn.*, **25**, 65 (1945).

9,10-Bis(2,5-dimethylbenzyl)anthracene (1).—This product was synthesized in one of two ways: by reacting 2,5-dimethylbenzyl chloride (7.7 g, 0.05 mol) with anthracene (8.90 g, 0.05 mol) dissolved in nitroethane (200 ml) at 50° with stannic chloride as a catalyst (0.5 ml 0.0043 mol) for 2 hr [yield 1.6 g (15%)]; or, in good yield (3.3 g, 80%), by reacting 9,10-bis(chloromethyl)anthracene (2.75 g, 0.01 mol) with *p*-xylene (50 g, 0.42 mol) in nitroethane (50 ml) at 100° for 2 min, with stannic chloride (0.1 ml, 0.00087 mol) as a catalyst. In both cases the mixture was poured into methanol (1:10). The precipitate was filtered off, washed with dilute hydrochloric acid, water, and methanol, and dried *in vacuo*. The crude product was crystallized from toluene. This work-up was also followed for the other products: yellow microcrystalline powder; mp 284–286°; ir spectrum (Nujol) 1610, 1030, 995, 950, 810, 795, 745, 730, 660 cm⁻¹.

Anal. Calcd for C₃₂H₃₀: C, 92.71; H, 7.29; mol wt, 414.6. Found: C, 92.89; H, 7.11; mol wt (vpo), 415.0.

9,10-Bis(2,4,6-trimethylbenzyl)anthracene (2).—To a stirred solution of 9,10-bis(chloromethyl)anthracene (3.0 g, 0.011 mol) and mesitylene (40 g, 0.33 mol) in nitroethane (50 ml) was added at 100° anhydrous zinc chloride (0.13 g, 0.001 mol) dissolved in nitroethane. The mixture was reacted for 30 sec. After work-up as above there was obtained 3.52 g (72%) of a yellow microcrystalline powder: mp 255–257° (toluene); ir spectrum (Nujol) 1610, 1030, 1010, 950, 840, 780, 770, 730, 640 cm⁻¹.

Anal. Calcd for C₃₄H₃₄: C, 92.26; H, 7.74; mol wt, 442.6. Found: C, 92.44; H, 7.58; mol wt (vpo), 440.3.

1,4-Bis(2,4,6-trimethylbenzyl)anthracene (3).—To a stirred solution of 2,4,6-trimethylbenzyl chloride (14 g, 0.083 mol) and anthracene (9 g, 0.051 mol) in nitroethane (200 ml) was added at 50° stannic chloride (0.5 ml, 0.0045 mol). The mixture was allowed to react for 3 hr. After work-up as above there was obtained 7 g (38%) of white microcrystalline powder: mp 270–272° (toluene); ir spectrum (Nujol) 1610, 1300, 1200, 1130, 1025, 950, 870, 850, 740, 700 cm⁻¹.

Anal. Calcd for C₃₄H₃₄: C, 92.26; H, 7.74; mol wt, 442.6. Found: C, 92.38; H, 7.63; mol wt (vpo), 451.0.

1,4-Bis(2,3,5,6-tetramethylbenzyl)anthracene (4).—To a stirred solution of 2,3,5,6-tetramethylbenzyl chloride (3.75 g, 0.021 mol) and anthracene (12.5 g, 0.07 mol) in nitroethane (200 ml) was added at 50° stannic chloride (0.5 ml, 0.0043 mol). The mixture was reacted for 2 hr. After work-up as above there was obtained 3.0 g (58%) of white microcrystalline powder: mp 378–379° (toluene); ir spectrum (Nujol) 1630, 1080, 1015, 890, 870, 750, 740, 710 cm⁻¹.

Anal. Calcd for C₃₆H₃₆: C, 91.86; H, 8.14; mol wt, 470.7. Found: C, 91.70; H, 8.30; mol wt (vpo), 470.0.

Registry No.—**1**, 30690-21-2; **2**, 30690-22-3; **3**, 30690-23-4; **4**, 30690-24-5.

(22) M. W. Miller, R. W. Amidon, and P. O. Tawney, *J. Amer. Chem. Soc.*, **77**, 2845 (1955).