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REACTIONS OF THE 9-MESITYL-9-BORAANTHRACENE ANION*

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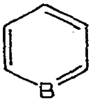
Summary

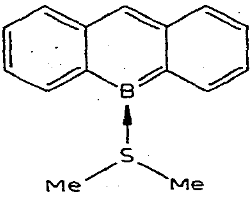
The synthesis of 9-mesityl-9,10-dihydro-9-boraanthracene is described. Proton abstraction with organolithium reagents gave the title anion, which was converted with various electrophiles into derivatives substituted at C-10. UV spectra indicated the absence of intramolecular coordination of oxygen-containing substituents at C-10 to the Lewis acidic boron centre. The preparation and some properties of the fulvenoid 9-mesityl-10-methylene-9,10-dihydro-9-boraanthracene and its reaction with tert-butyllithium are reported.

Introduction

No derivative of borin (I) with two-coordinate boron has been isolated to date [1]. Recently Jutzi [2] described a dimethyl sulfide adduct of 9-boraanthracene (II), but apart from the UV spectrum gave no experimental evidence to con-



(I)



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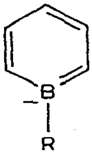

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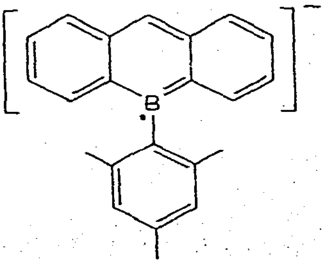

(IV)

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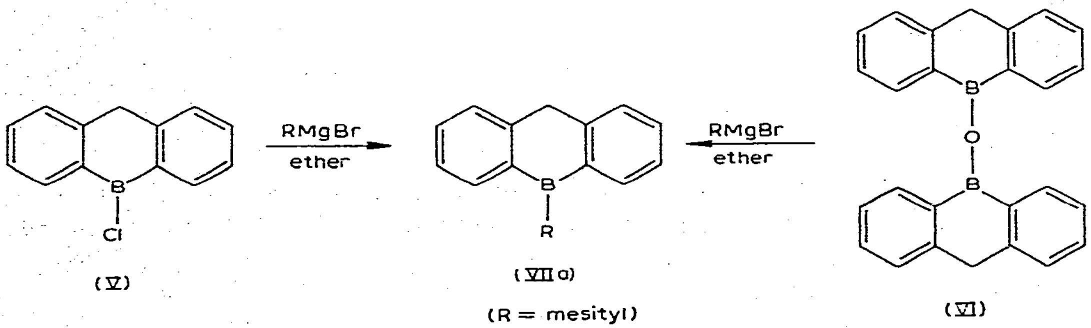
* Taken in part from the thesis of R. van Veen, Vrije Universiteit, Amsterdam (1974).

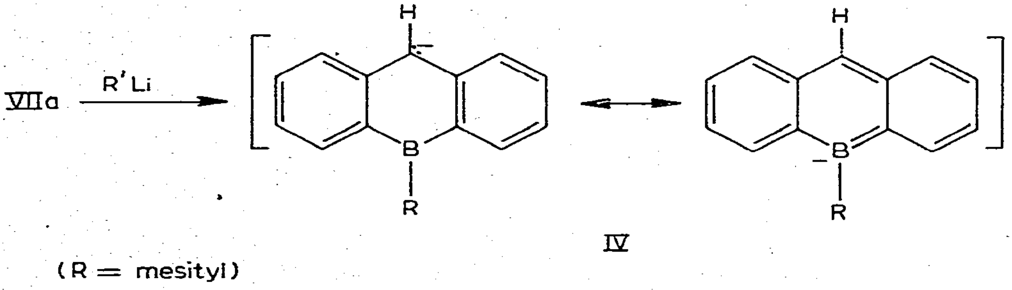
firm the proposed structure. The anionic analogues III with three-coordinate boron (being isosteric with the well-known borazaro compounds [3-6]) promised to possess a higher stability, and offer a better chance of isolation. Ashe and Shu [7] elegantly synthesized the 1-phenylborabenzene anion III (R = Ph). In a preliminary communication [8] we reported the synthesis of the 9-mesityl-9-boraanthracene anion (IV). In this paper we wish to present the preparation of IV in detail and some of its reactions.

Results and discussion

We obtained 9-mesityl-9,10-dihydro-9-boraanthracene (VIIa) on treatment of 9-chloro-9,10-dihydro-9-boraanthracene (V) [1] or of the corresponding borinic anhydride (VI) [1] with an excess of mesitylmagnesium bromide in ether.

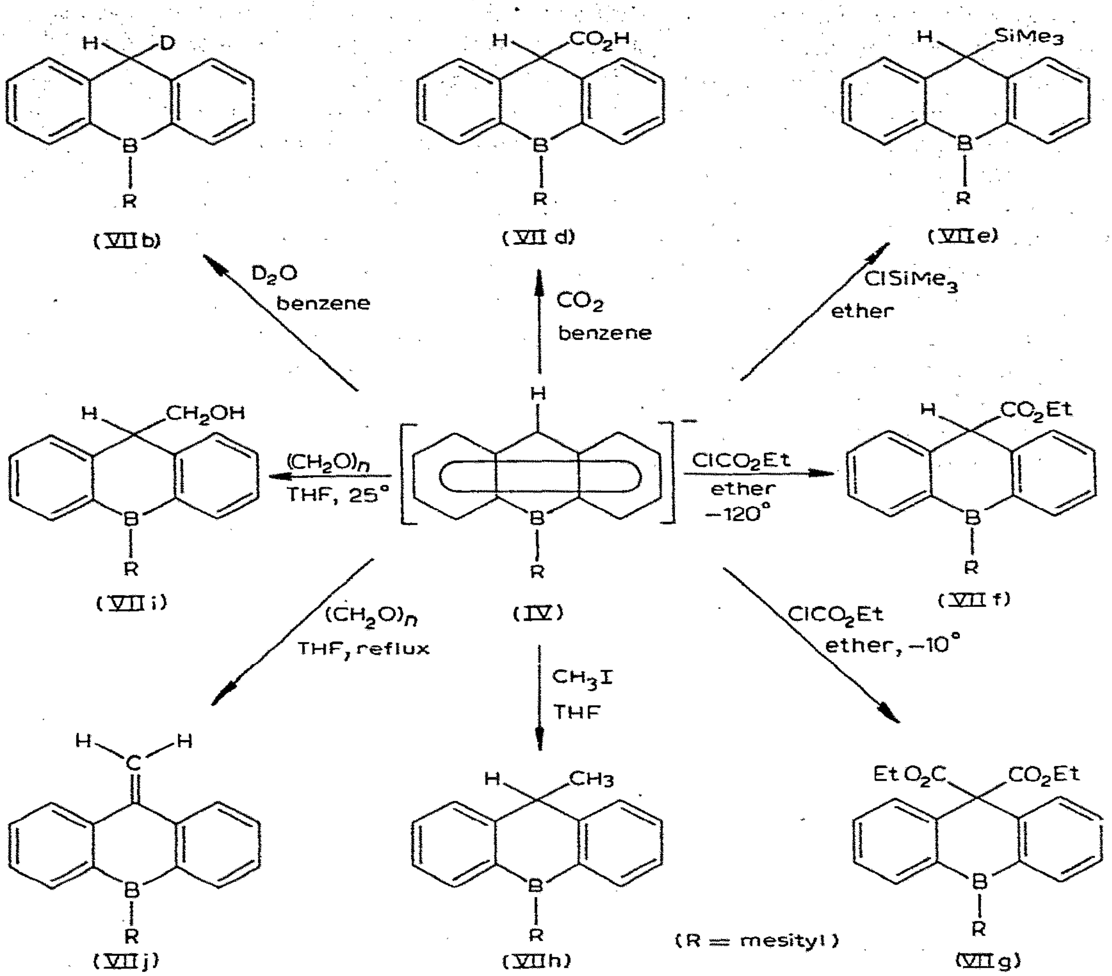


By the introduction of the bulky mesityl group and the resulting increase in crowding at boron we aimed at eliminating the formation of lithium borates as a possibly interfering reaction [9]. Our results indicate that this steric shielding of boron was effective, at least towards organolithium reagents [9]: when VIIa was treated with tert-butyllithium in benzene or with n-butyllithium in ether or tetrahydrofuran, the 9-mesityl-9-boraanthracene anion (IV) was formed by abstraction of a proton from C-10; we obtained no evidence (product analysis) for the formation of lithium borates with tetracoordinate boron. However, cyclohexylamine did attack at the boron atom [10].



The conversions of IV with various electrophilic reagents leading to derivatives substituted at C-10 are summarized in Scheme 1. In all instances an excess of n- or tert-butyllithium and a large excess of electrophilic reagent was used.

SCHEME 1

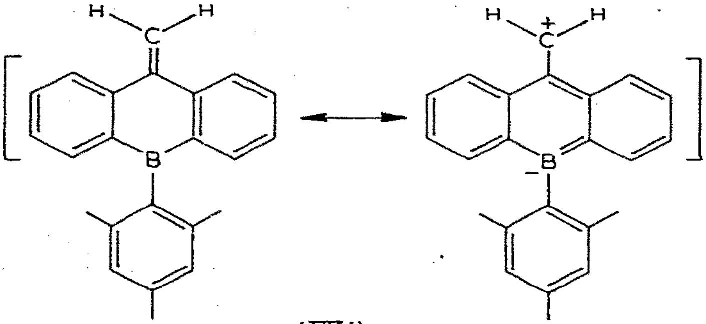


When IV in benzene was treated with deuterium oxide, VIIb (isotopic purity 90%; see Experimental) was isolated in 64% yield; VIIa and its 10,10-dideuterio-derivative VIIc were present in only 5%, indicating that proton transfer between VIIb and unreacted IV is not rapid in this solvent (compare, however, the formation of VIIf and VIIg).

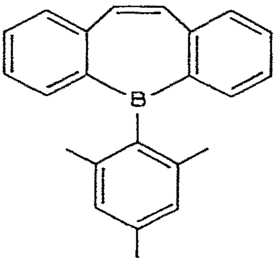
When carbon dioxide was passed over a solution of IV in benzene, VIId was formed and isolated in 64% yield as the hemihydrate; VIId was difficult to purify because of its ready decarboxylation to VIIa. As IV is a highly stabilized anion [10] it is reasonable to assume that the stability of IV is a major factor contributing to the instability of VIId towards decarboxylation.

Treatment of IV in ether solution with chlorotrimethylsilane gave 96% of VIIe. The reaction of IV with ethyl chloroformate in ether proved to be strongly dependent on the temperature; addition of the reagent to a partially frozen solution of IV yielded 98% of VIIf, whereas VIIg was obtained in 88% yield when the reaction was conducted at about - 10°. The formation of VIIg presumably takes place via VIIf, which in the presence of an excess of base is rapidly deprotonated at C-10 to yield ultimately VIIg, suggesting that at least at higher temperatures deprotonation of VIIf at C-10 is effectively competing with the addition reaction of the excess of n-butyllithium to the large excess of ethyl chloroformate; we assume that at low temperatures the excess of n-butyllithium is destroyed by the ethyl chloroformate, whereas the stabilized and hence less reactive IV is only converted to VIIf at higher temperatures.

Reaction of IV with methyl iodide in tetrahydrofuran at —70° gave 76% of VIIh. Treatment of IV with paraformaldehyde in tetrahydrofuran at room temperature yielded 79% of VIIi; however, when the reaction mixture was refluxed, the expected conversion to 10,10-bis(hydroxymethyl)-9-mesityl-9,10-dihydro-9-boraanthracene did not occur, but dehydration took place to VIIj. The chemistry of VIIj is expected to resemble that of the fulvenes [12], due to the possibly extensive delocalization of the π-electrons of the exocyclic double bond into the boraanthracene part of the molecule; the extent of this delocalization might be comparable to that in fulvene itself, if judged by the p*K* values of the parent compounds VIIa (p*K* 15.8 [10]) and cyclopentadiene (p*K* 14-15 [13], p*K* 18.0-18.5 [14]).



(VIIj)



(VIII)

Whereas the visible spectra of the 9-boraanthracene and fluorenyl anions bear a close resemblance [10], the correspondence between the UV spectra of VIIj (see Fig. 1) and dibenzofulvene [15] is much less pronounced. The UV spectrum of VIIj is not very similar to those of the dibenzotropylium ions [16], but shows a striking resemblance to those of xanthone [17] and acridone [18] and to those of the 10,9-boroxaro- [17] and 10,9-borazaroanthracene [19] systems, strongly suggesting an important contribution of the polarized resonance structure in VIIj. In all these compounds we find a tendency from an aromatic, anthracene-like system which in terms of resonance structures is accomplished by an electron shift from a donor to an acceptor; due to the particular structures involved this is accompanied by an opposite polarization between central ring and exocyclic double bond in xanthone and acridone (ring positively charged) and VIIj (ring negatively charged). As VIIa is much more acidic than fluorene [10] [p*K* 22.8], the difference of the UV spectra of VIIj and dibenzofulvene is not surprising. As the other available evidence (^{1}H NMR, IR, and mass spectra; elemental analysis) did not rule out the alternative dibenzoborepin structure VIII, further support for structure VIIj was desirable. When VIIj in benzene solution was treated with an equivalent amount of tert-butyllithium, the

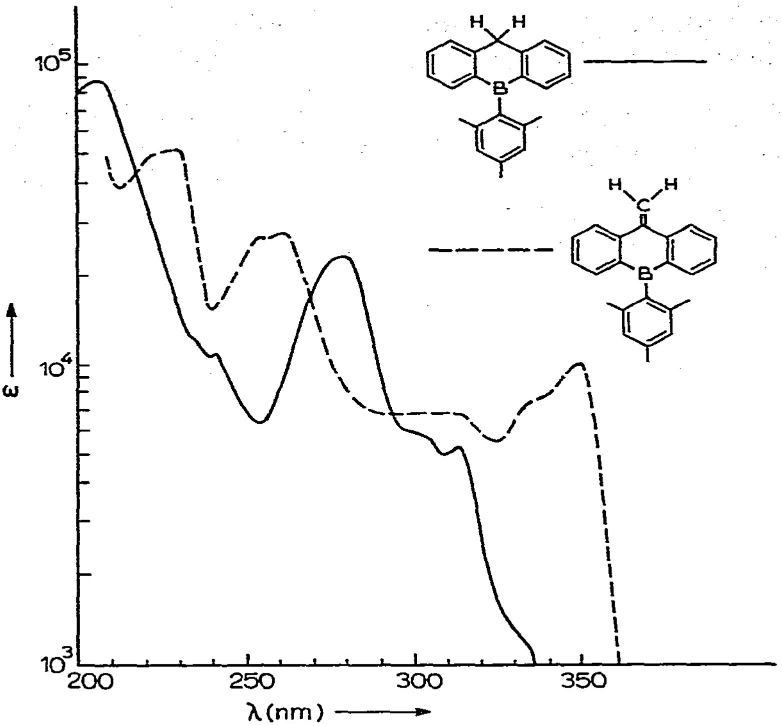
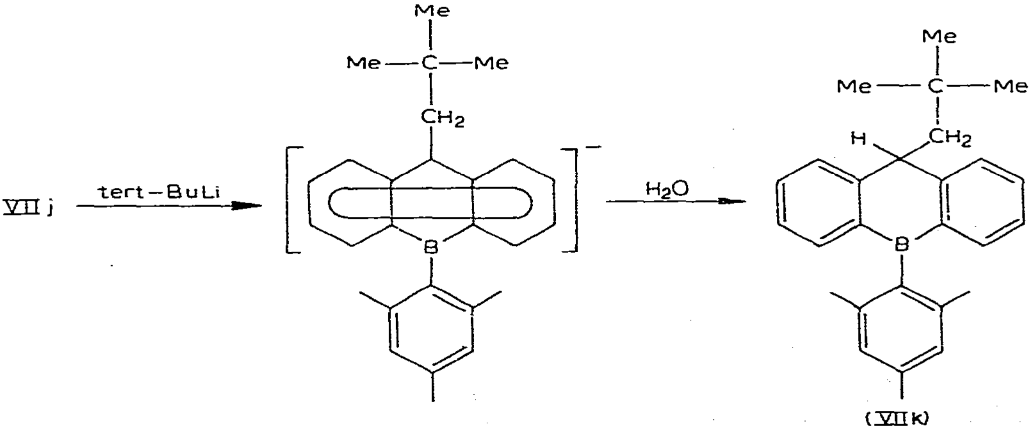


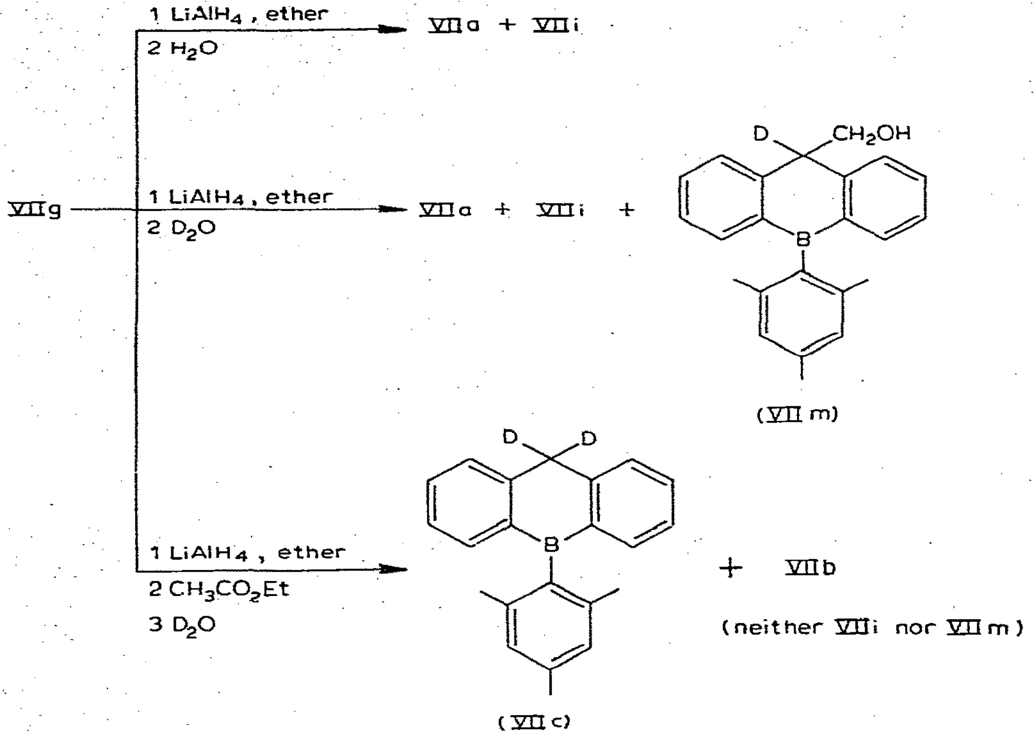
Fig. 1. UV spectra of VIIa and VIIj in n-hexane.

visible spectra of the carbanion produced (in benzene and in cyclohexylamine) were very similar to those of IV [10], suggesting a corresponding π-electronic system; after hydrolysis VIIk was isolated in 57% yield.



An interesting feature of the ^{1}H NMR spectra of VIIe and VIIk, which had already been observed with the 10-phenylsubstituted analogue [20], is that at room temperature there are two peaks arising from the mesitylenic *ortho*-methyl groups, indicating that rotation around the B—C(mesitylenic) bond is slow on the NMR time-scale. In the other compounds described in this paper, containing less bulky substituents at C-10, the two above mentioned methyl groups gave rise to one peak only, confirming the suggestion [20] that the inhibition of rotation has a steric origin.

Whereas the reduction of VIIf with lithium aluminum hydride in ether gave VIIi in 98% yield, the analogous conversion of VIIg turned out to be a complex reaction clearly deserving further study. The formation of VIIa and VIIc, respectively, might suggest the intermediacy of species with two Al—C(10) bonds (see Experimental for details).



A comparison of the mass spectra of VIIa, VIIb, and VIIc (see Table 1) proved that the mesityl group and one hydrogen atom are lost from the molecular ion, whereas elimination of the mesityl group and one deuterium (from C-10) is of minor importance, a conclusion which is in accordance with the re-

TABLE 1

MASS SPECTRA OF VIIa, VIIb, AND VIIc

m/e	Relative intensity (%)			*m/e*	Relative intensity (%)		
	VIIa	VIIb	VIIc		VIIa	VIIb	VIIc
175	42.3			295	14.6		
176	100	39.3		296	50.4	16.8	
177	38.5	100	51.7	297	12.4	48.3	14.9
178		30.0	100	298		14.3	38.0
179			25.3	299			9.3

TABLE 2

UV SPECTRA OF SOME 9-MESITYL-9,10-DIHYDRO-9-BORAANTHRACENES[a]

VIIa	241 (11000, max)	278 (23200, max)	303 (5400, sh)	313 (5300, max)	334 (1180, sh)
VIIh	243 (10100, sh)	280 (24000, max)	302 (7640, sh)	312 (5890, sh)	335 (1240, sh)
IX[b]	242 (13000, sh)	281 (24400, max)	304 (6800, sh)	313 (5900, sh)	336 (1270, sh)
VIIf	244 (10500, sh)	281 (22900, max)	sh[c]	309 (4950, sh)	339 (1120, sh)
VIIg	246 (13900, sh)	283 (22300, max)	sh[c]	312 (4420, sh)	341 (1180, sh)
VIIi	247 (9630, sh)	282 (23100, max)	303 (7570, sh)	314 (5190, sh)	340 (1170, sh)

[a] Solvent n-hexane, values tabulated as λ in nm (ϵ). [b] IX is 9-mesityl-10-phenyl-9,10-dihydro-9-boraanthracene [20]. [c] Shoulders at about 300 nm.

sults for the 9-mesityl-10-phenyl-9,10-dihydro-9-boraanthracene system [20] (IX) (for metastable ions see Experimental). These results exclude the boraanthracene-structures [1] at least for the majority of the $(M-\text{mesitylene})^{+\cdot}$ ions.

It was conceivable that in derivatives with an oxygen-containing substituent at C-10, i.e. VIId, VIIf, VIIg, VIIi and VIIm, transannular coordination might occur. Whereas IR and ^{1}H NMR spectra gave no clear-cut indication, the UV spectra proved this interaction to be of no importance. The higher wavelength bands in the UV spectra of triarylboranes are associated with the empty 2*p* orbital at boron; these bands disappear when boron is complexed by a nucleophile [21-23]. The UV spectra of VIIa (Fig. 1) and those of both the oxygen-free and oxygen-containing derivatives (Table 2) were extremely similar in shape so that transannular coordination, if present at all, must be negligible.

All compounds described in this paper are crystalline solids which can be handled in air, at least for several hours, without appreciable oxidation, VIIj being the most air-sensitive, particularly in solution. As VIIa seemed to be light-sensitive, all compounds were stored under nitrogen in the dark.

Experimental

All melting points are uncorrected and were determined in sealed capillaries under nitrogen. The IR spectra were obtained with a Perkin—Elmer model 237 spectrophotometer, the ^{1}H NMR spectra with a Varian A-60 spectrometer (internal TMS as a reference), the UV spectra with a Perkin—Elmer 137 spectrophotometer under nitrogen in a vessel described elsewhere [10], and the mass spectra with a Varian MAT CH5 mass spectrometer at 70 eV.

9-Mesityl-9,10-dihydro-9-boraanthracene (VIIa)

(a). From 9-chloro-9,10-dihydro-9-boraanthracene (V) [1]. A filtered solution of 14.5 mmol of mesitylmagnesium bromide [24] in 9 ml of ether was added under nitrogen to a thoroughly stirred solution of 1.53 g (7.20 mmol) of V in 30 ml of ether at - 70°. After standing overnight at room temperature, the deep-red mixture was hydrolyzed with dil. HCl. The ether layer was separated, washed with water, and evaporated in vacuum. Vacuum sublimation of the residue at 120°/0.1 mm gave 1.8687 g (88%) of pure VIIa, m.p. 131-134°. (Found: C, 89.61; H, 7.45; B, 3.44. $C_{22}H_{21}B$ (296.20) calcd.: C, 89.20; H, 7.15; B, 3.65%.) ^{1}H NMR (CCl_4): δ 7.78-7.58 (m, 2, aryl protons), 7.53-7.03 (m, 6, aryl protons), 6.82 (s, 2, mesitylenic aryl protons), 4.47 (s, 2, CH_2), 2.33 (s, 3, *p*-CH_3), 1.95 ppm (s, 6, *o*-CH_3). Mass spectrum (see Table 1): $C_{22}H_{21}{}^{11}B$, *m/e* found: 296.1751, calcd.: 296.1736; for the transition $296 \xrightarrow{*} 176$ a metastable ion was observed at *m/e* 104.7, calcd.: 104.68. UV spectrum (n-hexane): see Fig. 1 and Table 2.

(b). From bis(9,10-dihydro-9-bora-9-anthryl) oxide (VI) [1]. In a nitrogen-swept 500 ml three-necked flask crude VI, prepared [1] from 20 g (84 mmol) of 9-(2-aminoethoxy)-9,10-dihydro-9-boraanthracene [1, 25], was dissolved in 400 ml of toluene. After distilling off 350 ml of toluene and cooling to room temperature, 300 ml of dry ether was added. Then the solution was cooled to —70° and a filtered solution of the Grignard reagent prepared [24] from 48 g (241 mmol) of 2-bromomesitylene in 150 ml of ether was quickly added. After standing overnight at room temperature and work-up as described above, the

crude product was recrystallized from 16 g of n-hexane at - 20°, yielding 18.6020 g of pure VIIa, m.p. 131-134°. From the mother liquor another 1.1173 g of VIIa was obtained by chromatography over an alumina column using pet. ether (60-80°) as an eluent. Total yield 79%, based on the ethanolamine ester. The compound was shown by its IR and ^{1}H NMR spectra to be identical with an authentic sample (see above).

Reactions of the 9-mesityl-9-boraanthracene anion (IV)

After refluxing the solutions of VIIa for 5 min in a dry nitrogen-swept three-necked flask, provided with a reflux condenser and a magnetic stirrer, and cooling to room temperature, an excess of tert- or n-butyllithium was quickly added by means of a Schlenk burette.

(a). 10-deutero-9-mesityl-9,10-dihydro-9-boraanthracene (VIIb). To a solution of 274.5 mg (0.93 mmol) of VIIa in 50 ml of dry benzene 2 ml of 2*N* tert-butyllithium (4 mmol) in n-pentane was added. After stirring for 45 min, 1 ml of D_2O (D-content $\geqslant$ 99.75%) was added in one portion. Usual work-up and vacuum sublimation at 120°/0.1 mm gave 177.5 mg (64%) of a mixture containing 5% of VIIa, 90% of VIIb, and 5% of VIIc (estimated from ^{1}H NMR and mass spectral data), m.p. 126-133°. Mass spectrum (see Table 1), for the transition $297 \xrightarrow{*} 177$ a metastable ion was observed at m/e 105.5, calcd.: 105.52. IR and ^{1}H NMR spectra were very similar to those of VIIa with the expected differences due to the presence of deuterium.

(b). 10-carboxy-9-mesityl-9,10-dihydro-9-boraanthracene (VIId). To a solution of 291.9 mg (0.99 mmol) of VIIa in 20 ml of dry benzene, 1.1 ml of 2*N* tert-butyllithium (2.2 mmol) in n-pentane was added. After 45 min, carbon dioxide was passed over the thoroughly stirred solution until the deep-red colour changed into bright yellow. After evaporation in vacuum, the residue was dissolved in water. After filtration over Hyflo, the filtrate was carefully acidified with dil. HCl. The precipitate was filtered, washed with water, and dried in vacuum over phosphorus pentoxide at 40° for 12 h. Yield: 221.3 mg (64%) of the hemihydrate of VIId, m.p. 168-171° (dec.). (Found: C, 79.28; H, 6.10; B, 2.89. $C_{23}H_{21}BO_2 \cdot 1/2H_2O$ (349.22) calcd.: C, 79.10; H, 6.35; B, 3.10%.) ^{1}H NMR ($CDCl_3$): δ 7.78-7.15 (m, 8, aryl protons), 6.92 (s, 2, mesitylenic aryl protons), 6.37 (variable, s, 2, hydroxylic protons), 5.36 (s, 1, methine proton), 2.38 (s, 3, p-CH_3), 1.98 ppm (s, 6, o-CH_3). Mass spectrum, m/e (%): 44 (60.0), 175 (26.8), 176 (100), 177 (24.3), 295 (8.6), 296 (28.6), 297 (7.2); for the transition $296 \xrightarrow{*} 176$ a metastable ion was observed at m/e 104.7, calcd.: 104.68. IR spectrum (KBr), ν_{max} in cm^{-1}: 2960 s, broad; 1700 vs (CO_2H). Attempts to purify VIId by crystallization or sublimation invariably gave VIIa.

(c). 9-mesityl-10-trimethylsilyl-9,10-dihydro-9-boraanthracene (VIIe). To a solution of 2.0852 g (7.04 mmol) of VIIa in 70 ml of dry ether 9 ml of 2.25 *N* n-butyllithium in n-hexane was added. After cooling in an ice-salt bath, 10 ml of freshly distilled chlorotrimethylsilane was added in one portion. After stirring for 5 min, the mixture was refluxed for another 5 min and then evaporated in vacuum. The residue was dissolved in toluene and water. After separation, the toluene layer was washed with water and evaporated in vacuum. Vacuum sublimation of the residue at 172°/0.1 mm gave 2.4913 g (96%) of VIIe as a glass. Crystallization from 8 g of pet. ether (28-40°) at - 70° yielded 1.8210 g of crys-

talline VIIe, m.p. 109-111°. (Found: C, 81.57; H, 8.08. $C_{25}H_{29}BSi$ (368.38) calcd.: C, 81.51; H, 7.94%.) ^1H NMR (CCl_4): δ 7.83-6.88 (m, 8, aryl protons), 6.82 (s, 2, mesitylenic aryl protons), 4.40 (s, 1, methine proton), 2.33 (s, 3, *p*-CH_3), 2.12 (s, 3, *o*-CH_3), 1.78 (s, 3, *o*-CH_3), −0.17 ppm (s, 9, trimethylsilylic protons). Mass spectrum, *m/e* found: 368.2129, $C_{25}H_{29}{}^{11}B^{28}Si$ calcd.: 368.2132. IR spectrum (KBr), ν_{max} in cm^{-1}: 830 vs ($SiMe_3$).

(d). 10-carbethoxy-9-mesityl-9,10-dihydro-9-boraanthracene (VIIf). To a solution of 2.4628 g (8.31 mmol) of VIIa in 50 ml of dry ether 5 ml of 2.25 *N* n-butyllithium (11.25 mmol) in n-hexane was added. After freezing the solution in liq. N_2, 25 ml of freshly distilled ethyl chloroformate was added in one portion. The cooling bath was removed and the reaction mixture, which was thoroughly stirred as soon as possible, warmed to room temperature within 10 min and then immediately acidified with dil. HCl (delay in acidifying resulted in product contaminated with the diester VIIg). After separation, the ether layer was washed with pet. ether (28-40°), yield: 3.0004 g (98%) of VIIf, m.p. 133-136°. Recrystallization from n-hexane raised the m.p. to 139.5-140.0°. (Found: C, 81.53; H, 6.87; B, 2.90. $C_{25}H_{25}BO_2$ (368.26) calcd.: C, 81.53; H, 6.84; B, 2.94%.) ^1H NMR (CCl_4): δ 7.73-7.10 (m, 8, aryl protons), 6.80 (s, 2, mesitylenic aryl protons), 5.31 (s, 1, methine proton), 3.94 [q(*J* 7.1 Hz), 2, OCH_2], 2.33 (s, 3, *p*-CH_3), 1.98 (s, 6, *o*-CH_3), 1.01 ppm [t(*J* 7.1 Hz), 3, ester CH_3]. Mass spectrum $C_{25}H_{25}{}^{11}BO_2$ *m/e* found: 368.1947, calcd.: 368.1948. IR spectrum (CCl_4), ν_{max} in cm^{-1}: 1730 vs (C=O). Mixtures of VIIf and VIIg could be separated easily by chromatography over an alumina column using toluene for the elution of VIIf and chloroform to elute VIIg; generally, recrystallizations of such mixtures were not satisfactory.

(e). 10,10-dicarbethoxy-9-mesityl-9,10-dihydro-9-boraanthracene (VIIg). To a solution of 1.4892 g (5.03 mmol) of VIIa in 50 ml of dry ether 9 ml of 2.25 *N* n-butyllithium (20.25 mmol) in n-hexane was added. After cooling in an ice-salt bath, 25 ml of freshly distilled ethyl chloroformate was added as quickly as possible. Then the cooling bath was removed and the mixture stirred for 2.5 h at room temperature. After acidification with dil. HCl and separation, the ether layer was washed with water and evaporated in vacuum. The residue was washed with pet. ether (28-40°), yield: 1.9511 g (88%) of VIIg, m.p. 150-152°. Recrystallization from ether and vacuum sublimation at 175°/0.1 mm raised the m.p. to 155-156.5°. (Found: C, 76.50; H, 6.71; B, 2.35. $C_{28}H_{29}BO_4$ (440.32) calcd.: C, 76.37; H, 6.64; B, 2.46%.) ^1H NMR (CCl_4): δ 7.81-7.11 (m, 8, aryl protons), 6.81 (s, 2, mesitylenic aryl protons), 4.07 [q(*J* 7.1 Hz), 4, OCH_2], 2.33 (s, 3, *p*-CH_3), 1.94 (s, 6, *o*-CH_3), 1.05 ppm [t(*J* 7.1 Hz), 6, ester CH_3]. Mass spectrum $C_{28}H_{29}{}^{11}BO_4$, *m/e* found: 440.2166, calcd.: 440.2159. IR spectrum (CCl_4), ν_{max} in cm^{-1}: 1740 vs, 1765 s (C=O).

(f). 9-mesityl-10-methyl-9,10-dihydro-9-boraanthracene (VIIh). To a solution of 2.3828 g (8.04 mmol) of VIIa in 50 ml of dry tetrahydrofuran 6 ml of 2.25 *N* n-butyllithium (13.5 mmol) in n-hexane was added. After cooling to - 70°, 10 ml of methyl iodide was added in one portion. Then the bath was removed and the mixture was stirred for 45 min at room temperature. After evaporation in vacuum, the residue was dissolved in ether and dil. HCl. The ether layer was separated, washed with water, and evaporated in vacuum. The crude product was recrystallized from 8 g of n-hexane at - 20°; yield: 1.8523 g (74%) of VIIh,

m.p. 163-167° [from the mother liquor another 58.9 mg (2%) of VIIh was obtained by chromatography over an alumina column using pet. ether (40-60°) as an eluent]. (Found: C, 88.94; H, 7.65; B, 3.44. $C_{23}H_{23}B$ (310.22) calcd.: C, 89.04; H, 7.47; B, 3.48%.) ^1H NMR (CCl_4): δ 7.71-7.01 (m, 8, aryl protons), 6.81 (s, 2, mesitylenic aryl protons), 4.36 [q(J 7.3 Hz), 1, methine proton], 2.33 (s, 3, p-CH_3), 1.98 (s, 6, o-CH_3), 1.56 ppm [d(J 7.3 Hz), 3, 10-CH_3]. Mass spectrum, m/e (%): 189 (34.8), 190 (100), 191 (26.1), 294 (20.3), 295 (70.0), 309 (28.5), 310 (76.3), 311 (20.6); $C_{23}H_{23}{}^{11}B$, m/e found: 310.1873, calcd.: 310.1893; for the transitions $310 \xrightarrow{*} 295$ and $310 \xrightarrow{*} 190$ the corresponding metastable ions were observed at m/e 280.6 (calcd.: 280.87) and m/e 116.5 (calcd.: 116.50), respectively.

(g). 10-hydroxymethyl-9-mesityl-9,10-dihydro-9-boraanthracene (VIIi). To a solution of 506.4 mg (1.71 mmol) of VIIa in 20 ml of dry tetrahydrofuran 1.5 ml of 2.25 N n-butyllithium (3.4 mmol) in n-hexane was added. After 5 min 120.9 mg of air-free paraformaldehyde was added in one portion. After another 10 min water was added and the mixture evaporated in vacuum. The residue was dissolved in ether and dil. HCl. After separation, the ether layer was washed with water and evaporated in vacuum. The residue was chromatographed over an alumina column. After elution with toluene (yielding a yellow impurity), VIIi was eluted with ether. The crude product was recrystallized from pet. ether (60-80°), yield 438.0 mg (79%) of VIIi, m.p. 138-139°. (Found: C, 84.68; H, 7.29; B, 3.07. $C_{23}H_{23}BO$ (326.22) calcd.: C, 84.68; H, 7.11; B, 3.31%.) ^1H NMR (CCl_4): δ 7.77-7.06 (m, 8, aryl protons), 6.82 (s, 2, mesitylenic aryl protons), 4.31 [t(J 6 Hz), 1, methine proton], 3.58 [d(J 6 Hz), 2, OCH_2], 2.33 (s, 3, p-CH_3), 1.96 (s, 6, o-CH_3), 1.43 ppm (s, 1, OH). Mass spectrum, m/e (%): 175 (22.7), 176 (76.1), 294 (28.7), 295 (100), 296 (57.9), 326 (23.5); $C_{23}H_{23}{}^{11}BO$, m/e found: 326.1840, calcd.: 326.1842; for the transitions $326 \xrightarrow{*} 296$ and $296 \xrightarrow{*} 176$ the corresponding metastable ions were observed at m/e 268.8 (calcd.: 268.92) and m/e 104.6 (calcd.: 104.68), respectively. IR spectrum (CCl_4), ν_{max} in cm^{-1}: 3590 m (O—H).

(h). 9-mesityl-10-methylene-9,10-dihydro-9-boraanthracene (VIIj). To a solution of 1.2546 g (4.24 mmol) of VIIa in 40 ml of dry tetrahydrofuran, cooled in an ice-bath, 10 ml of 2.25 N n-butyllithium (22.5 mmol) in n-hexane was added. After 10 min 5 g of air-free paraformaldehyde was added in one portion. After reflux for 75 min and cooling to room temperature, water was added and the mixture was evaporated in vacuum. The residue was dissolved in toluene and water. After separation, the toluene layer was washed with water and evaporated in vacuum. The residue was chromatographed over a silica-gel column using toluene as an eluent; yield: 971.6 mg (74%) of VIIj. Recrystallization from 3.3 g of ether under nitrogen in the dark gave 503.1 mg of VIIj as pale yellow-rose crystals, m.p. 163-164°. (Found: C, 89.36; H, 6.94; B, 3.62. $C_{23}H_{21}B$ (308.21) calcd.: C, 89.62; H, 6.87; B, 3.51%.) ^1H NMR (CCl_4): δ 8.12-7.91 (m, 2, aryl protons), 7.75-7.12 (m, 6, aryl protons), 6.83 (s, 2, mesitylenic aryl protons), 6.22 (s, 2, methylenic protons), 2.33 (s, 3, p-CH_3), 1.96 ppm (s, 6, o-CH_3). Mass spectrum, m/e (%): 163 (21.6), 204 (45.4), 292 (25.4), 293 (78.6), 307 (31.7), 308 (100), 309 (25.7); $C_{23}H_{21}{}^{11}B$, m/e found: 308.1744, calcd.: 308.1736; for the transition $308 \xrightarrow{*} 293$ a metastable ion was observed at

m/e 278.7, calcd.: 278.86. UV spectrum (n-hexane, see Fig. 1), λ_{max} in nm (ϵ_{max}): 229 (51700), 255 (26800), 261 (27500), 310 (6960), 336 (7550, sh), 350 (10050).

Reductions with lithium aluminum hydride

(a). Reduction of VIIf. A solution of 991.9 mg (2.69 mmol) of VIIf in 40 ml of dry ether was added under nitrogen within 10 min to 1.0123 g of lithium aluminum hydride in 40 ml of ether. After reflux for 45 min, the mixture was cooled in an ice-salt bath and hydrolyzed with ethanol, water, and dil. HCl. The ether layer was separated, washed with water, and evaporated in vacuum, yield: 862.9 mg (98%) of crude VIIi, m.p. 130-133°. Recrystallization from ether/pet. ether (28-40°) at - 20° raised the m.p. to 138-139°. The compound was shown by its IR and ^{1}H NMR spectra to be identical with an authentic sample (see above).

(b). Reduction of VIIg. Under nitrogen a solution of 699.4 mg (18.4 mmol) of lithium aluminum hydride in 20 ml of dry ether was refluxed for 10 min. After cooling to room temperature, a solution of 528.9 mg (1.20 mmol) of VIIg in 20 ml of dry ether was added during 10 min (locally transitory yellow-orange colour). After reflux for 45 min, the mixture was cooled in an ice-salt bath and hydrolyzed with water and dil. HCl. After usual work-up, the crude product was chromatographed over an alumina column. Elution with toluene gave 16.4 mg (5%) of VIIa, and elution with ether gave 147.6 mg (38%) of VIIi. The product from an identical reaction mixture was chromatographed over a silica-gel column using toluene and chloroform as eluents, yielding VIIa and VIIi again, but no 10,10-bis(hydroxymethyl)-9-mesityl-9,10-dihydro-9-boraanthracene could be identified among the other fractions. When an identical reaction mixture, after reflux and cooling in an ice-salt bath, was treated with 20% DCl in D_2O (D-content $\geqslant$ 99%), again VIIa was obtained, but instead of VIIi, a mixture of VIIi and VIIm was isolated (78-91% deuterium incorporation at C-10; estimated from ^{1}H NMR and mass spectral data). When the excess of lithium aluminum hydride was destroyed with ethyl acetate prior to deuteriolysis, we isolated a mixture containing 91% of VIIc and 9% of VIIb (estimated from ^{1}H NMR and mass spectral data), m.p. 130-133° (neither VIIi nor VIIm were present among the other products according to ^{1}H NMR). Mass spectrum (see Table 1), for the transition $298 \xrightarrow{*} 178$ a metastable ion was observed at *m/e* 106.3, calcd.: 106.37. During the hydrolysis stage the reaction mixtures showed a dark green colour or contained a bright yellow precipitate, both of which vanished at the end of acidification. The compounds were identified by their IR and ^{1}H NMR spectra.

9-mesityl-10-neopentyl-9,10-dihydro-9-boraanthracene (VIIk)

In a vessel described elsewhere [10] 41.0 mg (0.133 mmol) of VIIj in 10 ml of dry benzene was treated with 100 μl of 1.4 *N* tert-butyllithium (0.140 mmol) in n-pentane under nitrogen. After measuring the visible spectrum, the benzene was pumped off and 10 ml of cyclohexylamine [10] was vacuum transferred into the vessel. After measuring the visible spectrum again, 100 μl of water was injected. After the usual work-up, the crude product was purified by TLC over silica-gel, using pet. ether (60-80°). The yield was 27.7 mg (57%) of VIIk as a (partly crystalline) glass. (Found: C, 87.53; H, 9.17; B, 2.84. $C_{27}H_{31}B$ (366.33) calcd.: C, 88.52; H, 8.53; B, 2.95%.) ^{1}H NMR (CCl_4): δ 7.72-6.98 (m, 8, aryl protons), 6.83 (s, 2, mesitylenic aryl protons), 4.43 [t(J 6 Hz), 1, methine proton], 2.35 (s, 3, p-CH_3), 2.08 (s, 3, o-CH_3), 1.98 [d(J 6 Hz), 2, CH_2], 1.93 (s, 3, o-CH_3), 0.72 (s, 9, CMe_3). Mass spectrum $C_{27}H_{31}{}^{11}B$, m/e found: 366.2531, calcd.: 366. 2519.

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