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ATTEMPTED SYNTHESIS OF DIBENZO[*b,e*]BORIN (9-BORAANTHRACENE) AND ITS FORMATION UNDER ELECTRON IMPACT

R. VAN VEEN AND F. BICKELHAUPT
Scheikundig Laboratorium der Vrije Universiteit, De Lairessestraat 174, Amsterdam-Z. (The Netherlands)

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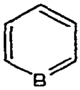
SUMMARY

Derivatives of 9,10-dihydro-9-boraanthracene were synthesized from *o,o'*-bis(bromomagnesio)diphenylmethane and substituted dichloroaminoboranes. Chemical elimination experiments did not lead to 9-boraanthracene. This compound, which possibly is aromatic in character was easily formed, however, from dihydro precursors under electron impact.

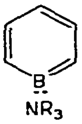
INTRODUCTION

Strong evidence exists in numerous types of compounds that boron is capable of double bond formation by $p_\pi - p_\pi$ interaction[1,2]. It is therefore remarkable that little is known on heterocyclic aromatic compounds containing boron as the only hetero atom. In spite of increasing interest in the last ten years, success was only achieved in the case of the borepin derivatives[3-5]. Eisch and Gonsior[6] reported on an attempt to synthesize triphenylboracyclopropene, but their results were not unambiguous.

No derivative of borin (I) has been prepared to date, although considerable resonance stabilization might be expected for this type of compound. If the unfavorable empty orbital at boron were a source of instability, stabilization could occur by coordination with a suitable Lewis base, as *e.g.* in (II).



(I)



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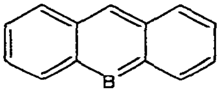
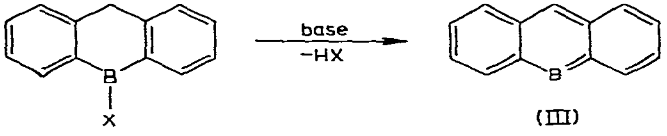


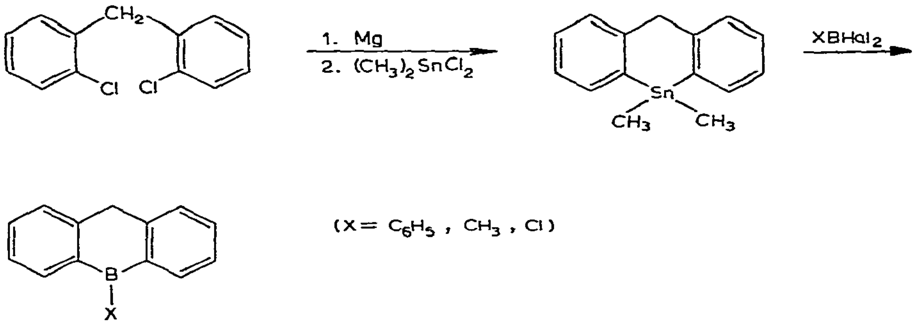
(III)

In connection with our investigations of 9-phospha-[7], 9-sila-[8], and 9-arsaanthracenes[9] we were interested in the corresponding 9-boraanthracene {dibenzo[*b,e*]-borin, (III)} or its base adduct. An approach which had been successfully used in the earlier cases was the elimination of hydrogen halide from a suitable dihydro precursor and we hoped that elimination of hydrogen halide from (IV) (X = Hal) would lead to the desired heterocycle (III).



(IV) (III)

Compounds of type (IV) have recently been described by Jutzi[10]. Interaction of the di-Grignard reagent from *o,o'*-dichlorodiphenylmethane with dimethyltin dichloride afforded 9,9-dimethyl-9,10-dihydro-9-stannaanthracene, which by reaction with boron dihalides was converted to (IV).



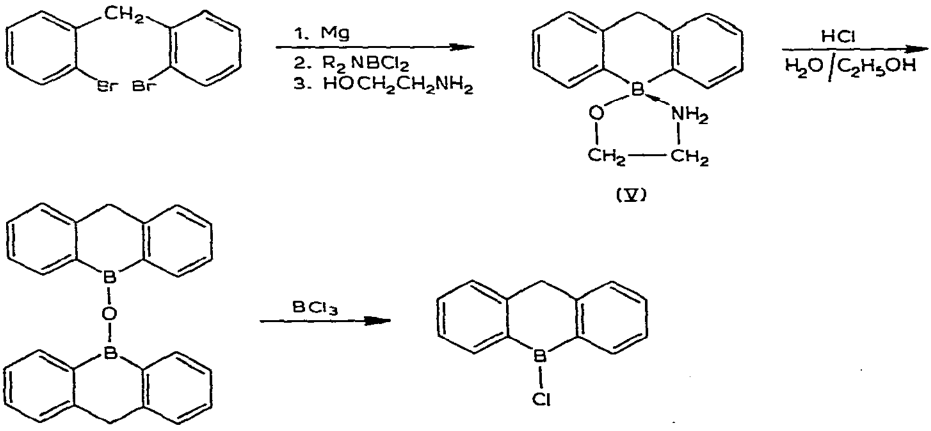
(IV)

($X = C_6H_5$, CH_3, Cl)

In this paper we wish to present an alternative preparation of (IV) and its application in aromatization attempts.

RESULTS AND DISCUSSION

We achieved the formation of the ring system of (IV) in one step by a procedure analogous to that used by Coates and Livingstone[11], *i.e.* addition of (diethylamino)- or (diphenylamino)boron dichloride to the tetrahydrofuran solution of the di-Grignard reagent from *o,o'*-dibromodiphenylmethane. The ring-closed product was isolated in 71% yield as the ethanolamine ester (V):



(V) (VI) (VII)

By a method analogous to that used by Letsinger and Skoog[12], (V) was converted to the corresponding anhydride (VI) in 96% yield. When treated with boron trichloride in chloroform solution according to Abel *et al.*[13], (VI) afforded 9-chloro-9,10-dihydro-9-boraanthracene [(VII); (IV), X=Cl] in 95% yield.

The structures of (V), (VI), and (VII) were confirmed by elemental analyses, by ^1H NMR, IR and mass spectra, and by their degradation and interconversion reactions (see experimental part).

Elimination of hydrogen chloride from (VII) did not lead to (III). When (VII) was treated with 150% excess triethylamine in ether solution in a sealed high vacuum system, there seemed to be no formation of (III), as indicated by the absence of an anthracene-type UV spectrum of the reaction mixture, although 45% triethylamine hydrochloride was isolated. Similarly 1,5-diazabicyclo[5.4.0]undec-5-ene in toluene solution did not give the desired reaction. When treated with conc. sulfuric acid in air-free conditions (VI) and (VII) gave yellow solutions but no indication of aromatization (UV spectrum).

Possibly the failure to aromatize (VII) by the action of base is caused by the Lewis acid character of the boron atom which leads preferentially to addition of the base at the boron atom[14], whereas the corresponding tricyclic phosphorus and arsenic compounds, having a Lewis base center at the hetero atom, undergo elimination rather easily. However, the available evidence does not rule out the possibility that a lower tendency to aromatization itself is the chief cause of our negative results.

On the other hand, the mass spectra of (VI) and (VII) indicate that (III) is readily formed under electron impact. In the mass spectra of *e.g.* (VII) there are signals due to the ions (VII)$^{+\cdot}$ (m/e =214, 32.1%; m/e=213, 42.9%; m/e=212, 100%; m/e= 211, 94.3%); (III)$^{+\cdot}$ (m/e=176, 88.7%; m/e=175, 28.2%); fluorene$^{+\cdot}$ (m/e=166, 6.6%); fluorenyl$^+$ (m/e=165, 40.0%); (III)$^{2+}$ ($m/2e$=88, 29.8%; $m/2e$=87.5, 8.9%); (HCl)$^{+\cdot}$ (m/e=38, 10.3%; m/e=36, 30.9%). For the transition (VII)$^{+\cdot}$→(III)$^{+\cdot}$ a group of metastable ions was observed; strongest peak at m/e=146.2, calcd.: 146.21 for the isotopically most abundant transition:

$$(C_{13}H_{10}{}^{11}B^{35}Cl)^{+\cdot} \xrightarrow{-H^{35}Cl} (C_{13}H_9{}^{11}B)^{+\cdot}$$

For additional peaks see the experimental section.

In contrast to the analogous ion of dibenzo[*b,e*]phosphorin[7], but in agreement with the arsenic analogue[9], the ion (III)$^{+\cdot}$ is not the base peak. The relatively strong occurrence of (III) as mono- and dipositive ion suggests, however, a rather high degree of stabilization once it is formed.

EXPERIMENTAL

All melting points are uncorrected. The IR spectra were obtained with a Perkin–Elmer model 237 spectrophotometer, the NMR spectra with a Varian A-60 spectrometer, the UV spectra with a Perkin–Elmer 137 spectrophotometer and the mass spectra with the Varian MAT CH5 mass spectrometer at 70 eV.

9-(2-*aminoethoxy*)-9,10-*dihydro-9-boraanthracene* (*V*)

In a nitrogen atmosphere 72.1 mmole R_2NBCl_2($R=C_2H_5$, C_6H_5) in 280 ml toluene was added to a filtered solution of the di-Grignard reagent prepared from

23.5 g (72.1 mmole) *o,o'*-dibromodiphenylmethane in 350 ml tetrahydrofuran. After evaporation to dryness *in vacuo*, the residue was dissolved in a mixture of 200 ml water and 200 ml ether. After separation the ether layer was treated with 25 ml 2-aminoethanol. Filtration of the precipitate, washing with ether and water, and drying in vacuo yielded 12.6 g of crude (V).

Recrystallization from 250 ml 96% ethanol afforded 9.56 g (V), m.p. 170–176°. Further evaporation of the mother liquor yielded another fraction of 2.64 g (V). Total yield 71%. (Found: C, 73.39; H, 6.92; B, 4.72; N, 6.06. $C_{15}H_{16}BNO$ calcd.: C, 75.98; H, 6.81; B, 4.56; N, 5.91%.) IR spectrum (KBr), ν_{max} in cm^{-1}: 3320 m, 3280 s, 3220 m (N–H); 1460 m (CH_2); 1440 s (B–aryl); 1195 s, 1180 m, 1160 s (N→B); 1070 s (C–O).

Reaction of (V) with H_2O_2[12]. Addition of 2.5 ml water, 5 ml acetic acid, and 5 ml 30% H_2O_2 to 206.5 mg (V) and shaking for 10 min afforded a colourless solution. After addition of 30 ml water the mixture was cooled in an ice-bath and sodium bicarbonate was added until no further product crystallized. Filtration, washing with water, and drying *in vacuo* yielded 151.4 mg *o,o'*-dihydroxydiphenylmethane (87%), m.p. 114.8–115.4°, identified by its IR[15], UV[16], and ^1H NMR spectra.

Bis(9,10-dihydro-9-bora-9-anthryl) oxide (VI)

Addition of 125 ml 1 *N* HCl to a solution of 2.0 g (V) in 125 ml 96% ethanol and 25 ml 6 *N* HCl, cooling in an ice-bath, filtration of the precipitate, washing with water, and drying in vacuo yielded 1.49 g crude (VI) (96%), m.p. 208–225°. Vacuum sublimation afforded pure (VI), m.p. 232–235°. (Found: C, 84.19; H, 5.72; B, 5.47. $C_{26}H_{20}B_2O$ calcd.: C, 84.39; H, 5.45; B, 5.84%.) IR spectrum (KBr), ν_{max} in cm^{-1}: 1450 s (CH_2); 1440 s (B–aryl); 1325 s, 1310 s (B–O). ^1H NMR ($CDCl_3$, internal TMS), δ in ppm: 7.98–7.75 (m, 4, aryl protons), 7.55–7.02 (m, 12, aryl protons), 4.47 (s, 4, CH_2). Mass spectrum, *m/e* (%): 149 (6.2), 150 (19.0), 151 (19.2), 152 (5.2), 165 (21.0), 166 (6.9), 174 (9.5), 175 (17.2), 176 (50.5), 177 (40.4), 178 (6.9), 183.5 (7.9), 184 (17.6), 184.5 (8.7), 185 (7.4), 191 (4.7), 192 (4.9), 193 (17.6), 194 (10.4), 263 (5.6), 264 (19.2), 265 (23.2), 266 (36.4), 267 (7.7), 368 (14.1), 369 (60.6), 370 (100), 371 (27.2). (Under some conditions of measurement, *m/e* 176 becomes the base peak).

Reaction of (VI) with:

(*a*). hydrogen peroxide, as described for (V), yielded 67% *o,o'*-dihydroxydiphenylmethane, m.p. 117–118°.
(*b*). bromine in methanol solution afforded *o,o'*-dibromodiphenylmethane, identified by its IR and ^1H NMR spectra.
(*c*). 2-aminoethanol in an ethanol/water mixture gave (V).

9-chloro-9,10-dihydro-9-boraanthracene (VII)

Under nitrogen, 6 ml boron trichloride was condensed into a solution of 7.35 g crude (VI) in 60 ml dry chloroform at −30°. After standing overnight at room temperature, the solution was concentrated to about 30 ml by distillation. After filtration under nitrogen the mixture was distilled in vacuo to yield 7.99 g (VII) (95%), b.p. 122–125° (0.1 mm), m.p. 95.0–97.5°. (Found: C, 73.75; H, 4.91; B, 5.60; Cl, 16.06. $C_{13}H_{10}BCl$ calcd.: C, 73.48; H, 4.74; B, 5.09; Cl, 16.69%.) IR spectrum ($CHCl_3$), ν_{max} in cm^{-1}: 1450 s (CH_2); 1440 s (B–aryl); 900 s (B–Cl). ^1H NMR (CCl_4, external TMS), δ in ppm: 8.84–8.58 (m, 2, aryl protons); 8.13–7.75 (m, 6, aryl protons); 4.70

(s, 2, CH_2). Mass spectrum, *m/e* (%): 36 (30.9), 38 (10.3), 71 (4.3), 75 (7.3), 87 (9.5), 87.5 (8.9), 88 (29.8), 105 (9.9), 106 (5.5), 139 (4.2), 148 (5.7), 149 (8.2), 150 (11.5), 165 (40.0), 166 (6.6), 174 (12.3), 175 (28.2), 176 (88.7), 177 (15.7), 185 (6.8), 209 (8.3), 210 (21.8), 211 (94.3), 212 (100), 213 (42.9), 214 (32.1), 215 (4.1); ($C_{13}H_9{}^{11}B$, found: 176.0787, calcd.: 176.0794; metastable peak: see discussion). Hydrolysis of (VII) afforded (VI). Some of our data for (VII) (m.p. and ^1H NMR spectrum) are at variance with those of Jutzi[10].

Aromatization attempts

Reactions with amines

(*a*). In a sealed high vacuum system 59.77 mg 1,5-diazabicyclo[5.4.0]undec-5-ene in 0.798 ml degassed toluene was added to a degassed solution of 75.4 mg (VII) in 10 ml toluene. A minute amount of precipitate was formed and the UV absorption shifted to shorter wavelengths. Raising the temperature did not change the UV spectrum of the mixture.

(*b*). In a sealed high vacuum system 59.23 mg triethylamine in 0.98 ml degassed toluene was added to a degassed solution of 52.4 mg (VII) in 10 ml ether. A white precipitate was formed, but in the UV spectrum there was only an end absorption above at least 320 mμ. The vacuum system was opened under nitrogen, the ether solution decanted and the precipitate washed with ether. The precipitate was dissolved in chloroform, and identified by its IR spectrum as triethylammonium chloride. (Found: Cl, 26.34. $C_6H_{16}ClN$ calcd.: Cl, 25.75%.) The total yield of $(C_2H_5)_3N \cdot HCl$ was 15.1 mg (45%). The ether solution was evaporated to dryness; the ^1H NMR spectrum of the residue indicated that it was a complex mixture.

Reactions with sulfuric acid

(*a*). In a sealed high vacuum system 63.9 mg (VII) was suspended in 10 ml conc. sulfuric acid, which had been made air-free by degassing. The mixture bubbled vigorously and turned yellow. In the UV spectrum there was only an end absorption above 300 mμ.

(*b*). Under the same conditions, as described for (VII), (VI) gave similar results.

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REFERENCES

1 D. S. Matteson, in R. J. Brotherton and H. Steinberg (Eds.), *Progress in Boron Chemistry*, Vol. 3, Pergamon, Oxford, 1970, pp. 117–135.

2 M. F. Lappert, in E. L. Muetterties (Ed.), *The Chemistry of Boron and Its Compounds*, Wiley, New York, 1967, pp. 482–495.

3 E. E. van Tamelen, G. Brieger and K. G. Untch, *Tetrahedron Lett.*, 8 (1960) 14.

4 A. J. Leusink, W. Drenth, J. G. Noltes and G. J. M. van der Kerk, *Tetrahedron Lett.*, 14 (1967) 1263.

5 S. Gronowitz, P. Gassne and B. Yom-tov, *Acta Chem. Scand.*, 23 (1969) 2927.

6 J. J. Eisch and L. J. Gonsior, *J. Organometal. Chem.*, 8 (1967) 53.

7 P. de Koe and F. Bickelhaupt, *Angew. Chem.*, 79 (1967) 533; 80 (1968) 912; *Angew. Chem. Int. Ed. Engl.*, 6 (1967) 567; 7 (1968) 889.

8 G. L. van Mourik and F. Bickelhaupt, *Recl. Trav. Chim. Pays-Bas*, 88 (1969) 868.

9 H. Vermeer and F. Bickelhaupt, *Angew. Chem.*, 81 (1969) 1052; *Angew. Chem. Int. Ed. Engl.*, 8 (1969) 992. See also: P. Jutzi and K. Deuchert, *Angew. Chem.*, 81 (1969) 1051; *Angew. Chem. Int. Ed. Engl.*, 8 (1969) 991.
10 P. Jutzi, *J. Organometal. Chem.*, 19 (1969) P1.
11 G. E. Coates and J. G. Livingstone, *J. Chem. Soc.*, (1961) 4909.
12 R. L. Letsinger and I. H. Skoog, *J. Amer. Chem. Soc.*, 77 (1955) 5176.
13 E. W. Abel, S. H. Dandegaonker, W. Gerrard and M. F. Lappert, *J. Chem. Soc.*, (1956) 4697.
14 P. I. Paetzold and H. G. Smolka, *Chem. Ber.*, 103 (1970) 289.
15 R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, (1947) 1260.
16 R. F. Hunter, R. A. Morton and A. T. Carpenter, *J. Chem. Soc.*, (1950) 441.