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SYNTHESIS OF 5-AND 6-MEMBERED CARBON–BORON HETEROCYCLES BY PYROLYSIS OF PYRIDINE–ARYLBORANES

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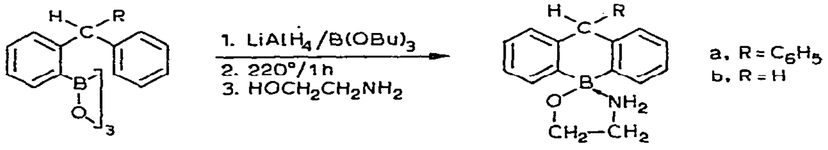
SUMMARY

Pyrolysis of pyridine(2-benzylphenyl)borane and pyridine(2-benzhydrylphenyl)borane yielded the 9,10-dihydro-9-boraanthracene system. The ring-closed products were isolated as the ethanolamine esters. An analogous conversion of pyridine-2-biphenylylborane gave pyridine-9-borafluorene.

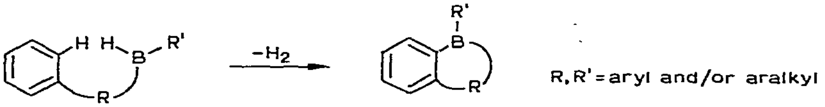
INTRODUCTION

In a recent publication[1] we reported the synthesis of the 10-phenyl-9,10-dihydro-9-boraanthracene system (IIa) from tris(2-benzhydrylphenyl)boroxin (Ia) by pyrolysis with lithium aluminum hydride and tributyl borate. We suggested that the cyclization might proceed via the corresponding primary arylborane.



(I) (II)

Several analogous attempts to cyclize (Ib), however, did not yield any (IIb). Köster[2] described the pyrolysis of some aralkyl- and arylboranes (III), which



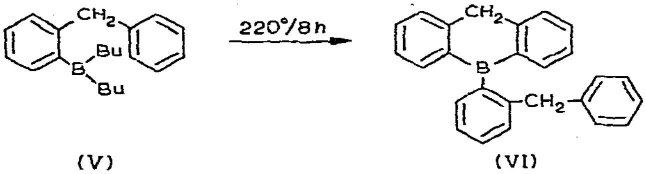
(III) (IV)

cyclized to (IV). In a later publication Köster[3] reported the analogous cyclization of (aralkylmethylamino)boranes to boron–nitrogen heterocycles.

RESULTS AND DISCUSSION

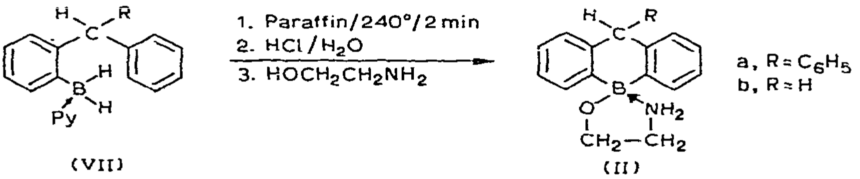
As we are interested in the 9,10-dihydro-9-boraanthracene system[1,4,5], we tried to arrive at this system, in analogy to Köster's method, by pyrolysis of di-n-butyl(2-benzylphenyl)borane (V). The only pure product which we could isolate, was

9-(2-benzylphenyl)-9,10-dihydro-9-boraanthracene (VI), the 2-benzylphenyl group on boron being a result of ligand exchange[2,6].



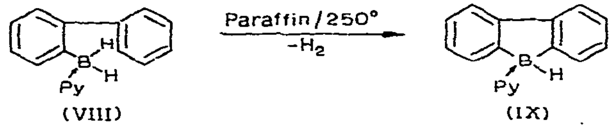
At this point we decided to explore the pyrolysis of appropriately substituted pyridine–arylboranes, the reversible thermal dissociation of which would produce the desired primary arylboranes as intermediates[7], in order to find an attractive synthesis of systems such as (II). Indeed, heating of pyridine(2-benzylphenyl)borane and pyridine-2(benzhydrylphenyl)borane (VII) lead to the formation of derivatives of the boraanthracene system which could be more easily used for further synthetic variations at the boron atom than (VI).

Short pyrolysis of (VII) in liquid paraffin as a solvent afforded the corresponding heterocycles, isolated as the ethanolamine esters (II) in 45–60% yield. The reaction,

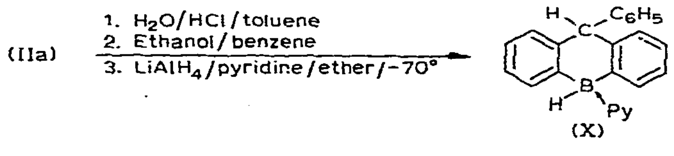


as indicated by the gas evolution, apparently begins at about 190°, but is performed advantageously at 240–250° (possibly in order to minimize side reactions such as ligand exchange[2,6]). Pyrolysis of the pure compounds, without solvent, gave the cyclized products in a few per cent yield only, together with much polymeric material. The role of the solvent is obviously that of a diluent, which prevents intermolecular reactions.

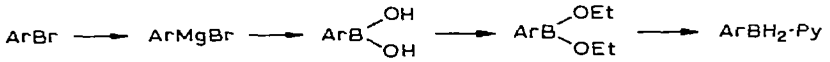
As an extension of this ring closure reaction, we undertook the pyrolysis of pyridine-2-biphenylylborane (VIII) to the corresponding 5-membered heterocycle. In this case, attempts to isolate the ethanolamine ester resulted in low yields of impure material, presumably due to protolysis of the B–C(aryl)-bond in the hydrolysis step. However, it was possible to isolate the initial reaction product, pyridine-9-borafluorene (IX) in 66% yield.



The pyridine-derivatives of the corresponding boraanthracene-system (II) can be obtained by Hawthorne's procedure for the preparation of pyridine–diarylboranes[8], as exemplified by the conversion of (IIa) to (X):



The ring closure of the pyridine–arylboranes described in this paper may formally be considered as a variation of Köster's general scheme for the cyclization of compounds of type (III)[2]. Our method forms, however, an attractive alternative because of the ready accessibility of the air-stable pyridine–arylboranes. These can be easily prepared from the corresponding aryl bromides via the crude aryl boronic acids (or their anhydrides) which are transformed to the crude diethyl esters followed by reduction according to the method of Hawthorne[9], with lithium aluminum hydride in ether at −70° in the presence of an excess of pyridine:



$$\mathrm{ArBr} \longrightarrow \mathrm{ArMgBr} \longrightarrow \mathrm{ArB(OH)_2} \longrightarrow \mathrm{ArB(OEt)_2} \longrightarrow \mathrm{ArBH_2{\cdot}Py}$$

Not only are the required monobromides, ArBr, more readily available than the dihalides used in previous syntheses of system (II)[4,10], but conversely, compounds of type (II) can now be used to prepare (by reaction with bromine[1]) the dibromides needed for the synthesis of other organometallic tricyclic ring systems[11].

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, unless otherwise specified) and the mass spectra with a Varian MAT CH5 mass spectrometer at 70 eV.

Pyridine-(di)arylboranes

According to the procedure of Hawthorne[9] the following compounds were synthesized:

(*a*). *Pyridine-2-biphenylylborane* (*VIII*). Prepared from 2-biphenylylboronic acid[12]. Yield (based on the boronic acid) 42% (VIII), m.p. 64–65°. (Found: C, 83.45; H, 6.75; B, 4.23; N, 5.73. $C_{17}H_{16}BN$ calcd.: C, 83.29; H, 6.58; B, 4.41; N, 5.72%.) IR spectrum (KBr), ν_{max} in cm^{-1}: 2320 s (BH), 1620 s (Py). ^{1}H NMR ($CDCl_3$) δ: 8.31–8.03 (d, 2, 2- and 6-pyridine protons), 7.93–6.96 (m, 12, aryl protons), ≈5.97–0.93 ppm (2, estimated from the integrated spectrum, BH_2). Mass spectrum $C_{17}H_{16}{}^{11}BN$, *m/e* found: 245.1383, calcd.: 245.1376. (Hydrolysis of the aluminum precipitate and the crystallization mother liquor with dil. HCl afforded 49% 2-biphenylylboronic acid).

(*b*). *Pyridine(2-benzhydrylphenyl)borane* (*VIIa*). Prepared from tris(2-benzhydrylphenyl)boroxin[1]. Yield (based on the boroxin) 63% (VIIa) m.p. 144–146°. (Found: C, 85.76; H, 6.78. $C_{24}H_{22}BN$ calcd.: C, 85.98; H, 6.62%.) IR spectrum (KBr), ν_{max} in cm^{-1}: 2320 s (BH), 1620 s (Py). ^{1}H NMR ($CDCl_3$), δ: 8.38–8.18 (d, 2, 2- and 6-pyridine protons), 7.83–6.89 (m, 17, aryl protons), 6.35 (s, 1, methine proton), ≈5.92–0.78 ppm (2, estimated from the integrated spectrum, BH_2). Mass spectrum $C_{24}H_{22}{}^{11}BN$, *m/e* found: 335.1847, calcd.: 335.1845.

(*c*). *Pyridine(2-benzylphenyl)borane* (*VIIb*). Prepared from crude tris(2-benzylphenyl)boroxin (see below). Yield (based on the diethanolamine ester) 56–63% (VIIb), m.p. 74.0–74.5°. (Found: C, 83.26; H, 6.83; B, 4.07; N, 5.37. $C_{18}H_{18}BN$ calcd.: C, 83.42; H, 7.00; B, 4.17; N, 5.41%.) IR spectrum (KBr), ν_{max} in cm^{-1}: 2320 s (BH), 1620 s (Py). ^{1}H NMR ($CDCl_3$), δ: 8.39–8.18 (d, 2, 2- and 6-pyridine protons), 7.78–6.90 (m, 12, aryl protons), 4.12 (s, 2, CH_2), ≈5.88–0.97 ppm (2, estimated from the integrated spectrum, BH_2). Mass spectrum $C_{18}H_{18}{}^{11}BN$, *m/e* found: 259.1531, calcd.: 259.1532. (Hydrolysis of the aluminum precipitate and the crystallization mother liquor with dil. HCl afforded 29–32% starting diethanolamine ester).

(*d*). *Pyridine-10-phenyl-9,10-dihydro-9-boraanthracene* (*X*). The azeotropic esterification of bis(10-phenyl-9,10-dihydro-9-bora-9-anthryl)oxide[1] was followed by the reduction of the crude ethyl ester as decribed by Hawthorne[8]. Yield [based on (IIa)] 89% (X), m.p. 204–206°, (Recrystallization is possible from toluene.) (Found: C, 86.08; H, 6.14; B, 3.13; N, 4.04. $C_{24}H_{20}BN$ calcd.: C, 86.50; H, 6.05; B, 3.24; N, 4.20%.) IR spectrum (KBr), ν_{max} in cm^{-1}: 2320 s (BH), 1610 (Py).

Pyrolysis experiments

(*a*). 9-(*2-benzylphenyl*)-9,10-*dihydro-9-boraanthracene* (*VI*). Under a nitrogen atmosphere a filtered solution of (2-benzylphenyl)lithium, prepared from 27.70 g (94.2 mmol) 2-iododiphenylmethane and 2 g lithium wire (288 mmol) in 150 ml ether, was added to 12.90 g (80.4 mmol) di-n-butylchloroborane in 70 ml ether. After standing overnight the ether was removed in vacuum. The residue was extracted with 200 ml cyclohexane. After removal of the solvent, the residue was heated in an oil-bath to 220° for 8 h under nitrogen. Distillation yielded 3.74 g (27%) (VI), b.p. 175–176°/0.01 mmHg. Vacuum sublimation afforded purified product, m.p. 117–120°. (Found: C, 90.08; H, 6.68; B, 3.42. $C_{26}H_{21}B$ calcd.: C, 90.71; H, 6.15; B, 3.14%.) ^1H NMR (CCl_4, external TMS), δ: 8.17–7.05 (m, 17, aryl protons), 4.78 (s, 2, ring CH_2), 4.22 ppm (s, 2, benzyl CH_2). Mass spectrum $C_{26}H_{21}{}^{11}B$, *m/e* found: 344.1747, calcd.: 344.1736.

(*b*). 9-(*2-aminoethoxy*)-9,10-*dihydro-9-boraanthracene* (*IIb*). In a nitrogen-swept 250 ml three-necked flask, provided with a mechanical stirrer and thermometer, 175 ml liquid paraffin was heated to 250° and then cooled to room temperature. After addition of 7.2860 g (28.1 mmol) (VIIb), the thoroughly stirred mixture was heated (by IR) in 6 min to 245°, maintained for 1.5 min at 245 ± 5°, and cooled to room temperature in a liquid nitrogen bath. Then 50 ml 6 *N* HCl was added. After stirring for 3 min, the reaction mixture was transferred into a 750 ml Erlenmeyer flask with 200 ml toluene and stirring continued for 1 h. After vacuum filtration, the organic layer was separated, washed with water and concentrated in vacuum. The residue was dissolved in 160 ml ether and added to a solution of 25 ml ethanolamine in 125 ml water. After standing overnight at room temperature, the precipitate was filtered, washed with water and ether, and dried in vacuum. Average yield was 61% (IIb), m.p. 170–175°, identical with an authentic[4] sample in m.p. and IR spectrum.

(c). 9-(*2-aminoethoxy*)-10-*phenyl-9,10-dihydro-9-boraanthracene* (*IIa*). 470.9 mg (1.4 mmol) (VIIa) in 9 ml liquid paraffin, was pyrolyzed and worked up as described under (*b*). The evaporation residue was dissolved in 30 ml ether and added to a solution of 2 ml ethanolamine in 10 ml water. After standing overnight at room temperature, the precipitate was filtered, washed with water and ether, and dried in vacuum, yielding 201.1 mg (46%) (IIa), m.p. 226–231°, identical with an authentic[1] sample in m.p. and IR spectrum.

(*d*). *Pyridine-9-borafluorene* (*IX*). Analogous to the procedure as described under (*b*), 397.8 mg (1.6 mmol) (VIII) in 20 ml liquid paraffin was heated (by IR) in 3 min to 250° and immediately cooled to room temperature in a liquid nitrogen bath.

After addition of 0.2 ml dry pyridine and 80 ml petr. ether 28–40° and stirring for 1 h, the precipitate was filtered and dissolved in 3 ml toluene. This solution was added to a mixture of 20 ml ether and 70 ml petroleum ether 28–40° and filtered. On slowly cooling to −70°, 232.9 mg (IX) crystallized from the solution, m.p. 117–118.5°. From the mother liquor another crop of (IX) (28.2 mg) was obtained. Total yield 66%. (Found: C, 82.64; H, 6.01; B, 4.02; N, 5.35. $C_{17}H_{14}BN$ calcd.: C, 83.99; H, 5.80; B, 4.45; N, 5.76%.) IR spectrum (KBr), ν_{max} in cm^{-1}: 2340 s (BH), 1620 s (Py). ^1H NMR ($CDCl_3$), δ: 8.53–8.30 (d, 2, 2- and 6-pyridine protons), 7.83–6.75 ppm (m, 11, aryl protons). Mass spectrum $C_{17}H_{14}{}^{11}BN$, m/e found: 243.1227, calcd.: 243.1219.

2-benzylphenylboronic acid, diethanolamine ester [2-(*2-benzylphenyl*)-1,3,6,2-*dioxazaboracyclooctane*]

Under a nitrogen atmosphere a filtered solution of the Grignard reagent from 132.19 g (534.9 mmol) 2-bromodiphenylmethane in 500 ml ether was added in 45 min to a thoroughly stirred solution of 500 ml tributyl borate in 500 ml ether at −70°. After standing overnight at room temperature the mixture was hydrolyzed with excess 2*N* HCl. The organic layer was separated and the water layer extracted with ether. The combined organic layers were concentrated in vacuum; several times 50 ml portions of water were added and this mixture again evaporated in vacuum to remove the butanol. The residue was dissolved in 200 ml warm abs. ethanol. Then a solution of 50 g diethanolamine in 60 ml abs. ethanol was added in one portion. After standing overnight at 4°, the precipitate was filtered, washed with ether and dried in vacuum, yielding 118.37 g (79%) diethanolamine ester of 2-benzylphenylboronic acid, m.p. 202–204°. (Found: C, 72.46; H, 7.09; B, 3.88; N, 5.10. $C_{17}H_{20}BNO_2$ calcd.: C, 72.62; H, 7.17; B, 3.84; N, 4.98%.) IR spectrum (KBr), ν_{max} in cm^{-1}: 3130 s (NH). ^1H NMR [$(CD_3)_2SO$], δ: 7.81–6.60 (m, 10, aryl protons and NH), 4.22 (s, 2, benzyl CH_2), 4.07–3.62 (m, 4, OCH_2), 3.43–2.65 ppm (m, 4, NCH_2). The ester was converted to:

(*a*). *Tris(2-benzylphenyl)boroxin*. At room temperature 3.5674 g (12.7 mmol) diethanolamine ester was thoroughly stirred for 3 h in a mixture of 50 ml toluene, 40 ml water and 5 ml conc. HCl. After separation, the organic layer was washed with water and evaporated to dryness in vacuum. The residue was recrystallized from petr. ether 80–100°, yielding 2.1998 g (89%) tris(2-benzylphenyl)boroxin, m.p. 124–126.5°. Vacuum sublimation raised the m.p. to 131–132°. (Found: C, 80.76; H, 5.69; B, 5.29. $C_{39}H_{33}B_3O_3$ calcd.: C, 80.47; H, 5.71: B, 5.57%.) IR spectrum (KBr), ν_{max} in cm^{-1}: 1340 vs. (BO). ^1H NMR (CCl_4), δ: 7.98–7.77 (m, 3, aryl protons), 7.50–6.81 (m, 24, aryl protons), 4.44 ppm (s, 6, CH_2). Mass spectrum $C_{39}H_{33}{}^{11}B_3O_3$, m/e found: 582.2686, calcd.: 582.2709. Crystallization of the boroxin from water yielded 2-benzylphenylboronic acid, m.p. 94.0–94.5°. (Found: C, 73.44; H, 6.33. $C_{13}H_{13}BO_2$ calcd.: C, 73.63; H, 6.18%.)

(*b*). *2-benzylphenol*. 1.1521 g (4.1 mmol) diethanolamine ester was converted to the crude tris(2-benzylphenyl)boroxin, which was stirred for 4 h at room temperature in 40 g methanol with 10 ml 30% H_2O_2. Working up yielded 749.1 mg (99%) 2-benzylphenol, m.p. 19–22°. (Labile form, lit.[13] m.p. 22–23°).

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