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CONTRIBUTIONS TO THE CHEMISTRY OF BORON

CLVI *. A CONVENIENT ROUTE TO 9-BORAFLUORENES

CHAITANYA K. NARULA ** and HEINRICH NÖTH*
Institut für Anorganische Chemie der Universität München, Meiserstrasse 1, 8000 München 2 (F.R.G.)

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Summary

A convenient high yield synthesis is reported for 9-halo-9-borafluorene from *o,o'*-mercurated diphenyl and boron halides. These in turn are easily converted into methoxy-, methylthio- and diethylamino derivatives.

9-Borafluorene provides a good example of the incorporation of a boron atom into an aromatic π-electron system. 9-Chloro-9-borofluorene was synthesized as early as in 1963 [2], but its chemistry remained undeveloped due to the unusually difficult, multistep synthesis. The yield was only 5% based on 5-bromoaniline as one of the starting materials. A similar procedure was later employed to prepare 9-alkyl-9-borafluorenes [3]. The report that 9-fluoro-9-borafluorene was obtained from 2,2'-dilithiobiphenyl and $BF_3 \cdot OEt_2$ remains doubtful in the absence of any experimental details and characterization [4], especially since Wittig and Herwig obtained lithium bis(2,2'-biphenyl)borate from this reaction [5].

Our current interest in tricoordinated boron cations [6–9] prompted us to study cations derived from 9-borafluorene, since electron delocalization increases the stability of these cations [10,11]. We now report a convenient high yield one step route to 9-borafluorenes involving reaction of *o,o'*-biphenylmercury, **1** [12], with boron trihalides. Surprisingly, this simple reaction has not previously been investigated although the mercury compound has been known since 1954 [13].

Boron trifluoride etherate fails to react with *o,o'*-biphenylmercury to give the corresponding 9-fluoro-9-borafluorene. In contrast, **1** and BCl_3 readily give **2**, as a yellow solid, its spectral characteristics are similar to those previously reported. The halides **3** and **4** are orange and red, respectively. A comparison of their ^{11}B NMR shifts reveal that the order of total shielding at boron is Cl < I < Br, but the shift differences are small (~ 4 ppm). Since reported values of $\delta(^{11}B)$ for diphenylboron

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[*] For part CLV see ref. 1.

[**] Alexander-von-Humboldt fellow.

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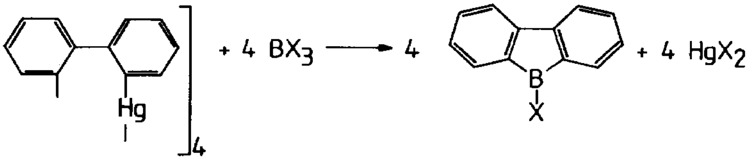
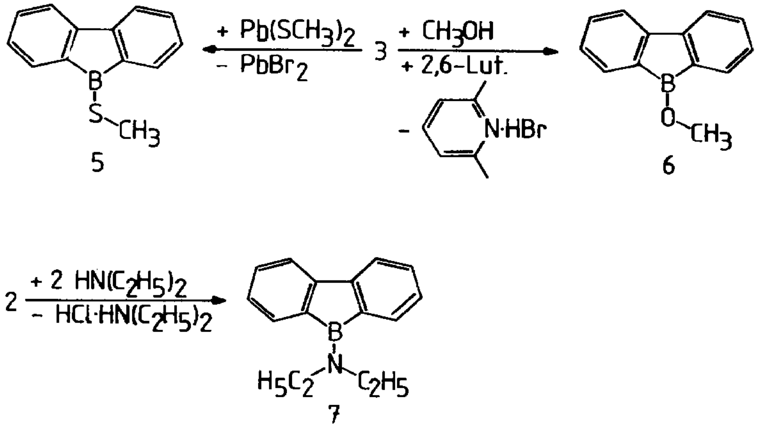


X	Cl	Br	I
	2	3	4

bromide vary considerably [14], no reliable comparison can be made between the two series of compounds.

Since previous reports were concerned only with the synthesis of **2** and a series of 9-alkyl-9-borafluorenes we also prepared representative alkoxy-, mercapto- and amino-derivative. Conventional reactions gave satisfactory results.



Interestingly, the ^{11}B NMR shift of 9-methylmercapto-9-borafluorene **5** is comparable to that of **2**. This situation differs from that with the analogous diphenylboron derivatives, for which the boron atom is more shielded in the diphenylboron chloride. The methoxy derivative **6** shows an ^{11}B chemical shift similar to Ph_2BOCH_3 ($\delta(^{11}B)$ 53.6 ppm). In contrast, the boron atom in 9-diethylamino-9-borafluorene **7** is more shielded than in diethylaminodiphenylborane ($\delta(^{11}B)$ 42.7 ppm) [14].

Experimental

All manipulations were carried out under rigorously anhydrous conditions in a high vacuum system and/or under oxygen-free dinitrogen using Schlenk techniques. Solvents were carefully dried and stored under N_2. *o,o'*-Diphenyl mercury was prepared by a published procedure [12].

NMR spectra were recorded on a JEOL FX 90 or Bruker WP 200 PFT multinuclei NMR spectrometer. Chemical shifts refer to internal TMS (^1H, ^{13}C) and external $BF_3 \cdot OEt_2$ (^{11}B). Elemental analyses were carried out in the Microanalytical Laboratory of this Institute.

9-Chloro-9-borafluorene (2)

BCl_3 (7.72 g, 65.9 mmol) was condensed into a stirred suspension of *o,o'*-biphenyl mercury (23.2 g, 16.4 mmol) in hexane (100 ml) at −78°C. The mixture was then slowly brought to room temperature and stirred overnight. Mercuric chloride was filtered off, the solvent was stripped from the filtrate, and the residue was distilled, b.p. 92°C/0.4 torr. Yield 9.7 g **2** (75%). Analyses Found C, 74.49, H, 5.04. $C_{12}H_8BCl$ calcd.: C, 72.63, H, 4.06%. $\delta(^{11}B)$ 61.5 ppm, $\delta(^{1}H)$ ($CDCl_3$) 6.67–7.43m ppm.

9-Bromo-9-borafluorene (3)

This was made from *o,o'*-biphenyl mercury (16.1 g, 11.4 mmol) and BBr_3 (11.42 g, 45.5 mmol) by the procedure described for **2**. Yield: 8.25 g **3** (75%); b.p. 126°C/0.5 torr; m.p. 86°C. Analyses Found C, 62.42, H, 4.25. $C_{12}H_8BBr$ calcd.: C, 59.34. H, 3.32%. $\delta(^{11}B)$ 65.8 ppm; $\delta(^{1}H)$ ($CDCl_3$): 6.87–7.38m ppm.

9-Iodo-9-borafluorene (4)

This was similarly made from *o,o'*-biphenylmercury (4.72 g, 3.35 mmol) and BI_3 (5.23 g, 13.36 mmol). Yield: 2.98 g **4**, (77%); b.p. 138°C/0.5 torr, m.p. 64°C. Analyses: Found: C, 47.39, H, 2.80; $C_{12}H_8BBr$ calcd.: C, 48.72, H, 2.78; $\delta(^{11}B)$ 64 ppm; $\delta(^{1}H)$ ($CDCl_3$): 6.89–7.56 m ppm.

9-Methylmercapto-9-borafluorene (5)

9-Bromo-9-borafluorene (0.925 g, 3.80 mmol) was added to a suspension of bis(methylthio)lead (0.58 g, 1.92 mmol) and the mixture was boiled under reflux for 1 h. The lead bromide formed was filtered off and the filtrate concentrated to a volume of ~ 15 ml. On cooling to −20°C compound **5** precipitated. The supernatant liquid was removed with a syringe and the solid residue dried in vacuo. Yield: 0.74 g **5**, (92%), m.p. 144°C. Analyses Found: C, 70.21, H, 5.13. $C_{13}H_{11}BS$ calcd.: C, 74.32, H, 5.28%. $\delta(^{11}B)$ 61.9 ppm; $\delta(^{1}H)$ (C_6D_6): 0.695 (3H), 6.60–7.88 m (8H) ppm.

9-Methoxy-9-borafluorene (6)

To a hexane solution (~ 30 ml) of 9-bromo-9-borafluorene (0.908 g, 3.73 mmol) at −78°C was added a solution of 2,4-lutidine (0.4 g, 3.73 mmol) in hexane (~ 10 ml). The yellow precipitate of 2,6-lutidine-9-bromo-9-borafluorene was filtered off, washed with hexane, and dried in vacuo. Yield: 0.85 g (65%). Addition of 0.5 ml of methanol to a hexane suspension of the adduct resulted into immediate methanolysis; the 2,6-lutidine hydrochloride was filtered off and volatiles were removed from the filtrate. Yield: 0.38 g **6** (81%). Analyses Found C, 77.1, H, 4.92: $C_{13}H_{11}BO$ calcd.: C, 80.47, H, 5.71%. $\delta(^{11}B)$ 46.0 ppm; $\delta(^{1}H)$ ($CDCl_3$): 4.07 (3H), 6.88–7.46 m (8H) ppm.

9-Diethylamino-9-borafluorene (7)

Diethylamine (0.50 g, 7.76 mmol) was added at −78°C to 9-chloro-9-borafluorene (0.764 g, 3.84 mmol) in hexane (50 ml). The mixture was brought to room temperature and refluxed for 2 h. A white precipitate was filtered off and the filtrate evaporated to leave the product. Yield 0.68 g **7**, (75%); m.p. 68°C. Analyses Found: C, 78.49, H, 7.59, N, 5.10. $C_{16}H_2BN$ calcd.: C, 81.73, H, 7.72, N, 5.96%. $\delta(^{11}B)$ 38.5 ppm; $\delta(^{1}H)$ ($CDCl_3$): 1.25 t (6H), 3.519 (4H), 6.99–7.59 ppm, m (8H) ppm.

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