

Heteroaromatic Boron Compounds. XVI. Some New Heteroaromatic Borohydrides

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Dedicated to Professor K. A. Jensen on his 70th birthday

5-Methyl-4,5-borazarothieno[2,3-*c*]pyridine (*2c*) and 6-methyl-7,6-borazarothieno[3,2-*c*]pyridine (*3c*) have been synthesized. They showed no reducing or hydroborating properties.

It has previously been demonstrated that 3,2-borazaropyridines, such as *1* and their thienofused analogues (*2a*, *3a*), from which they are prepared by Raney-nickel desulfurization, show pronounced aromatic properties.¹ Their dipole moments, UV and NMR spectra gave strong evidence that these compounds are isoelectronic with the corresponding pyridines. Aromatic substitution reactions could be carried out with these compounds^{2–6} (for a recent review on boron-containing heterocycles *cf.* Ref. 7). We were therefore interested to find out if the aromatic nature of these ring systems was reflected in the reactivity and other properties of the corresponding boron hydrides.

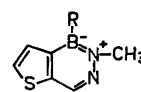
Aromatic boron hydrides have been prepared in 1958 by Dewar by reduction of the corresponding B–Cl compound with lithium aluminium hydride in ether, as in the syntheses of 10,9-borazarophenanthrene⁸ and 2,1-borazaronaphthalene.⁹ Alternatively, the B–OCH₃ derivative or some other ether was reacted with lithium aluminium hydride and aluminium chloride, as in the syntheses of 5,6-borazobenz[*a*]anthracene,¹⁰ 5,4-borazapyrene¹¹ and 3,4-methyl-4,3-borazaroisquinoline.¹² Dewar and coworkers, however, did not study the reactions of these borohydrides. We used the latter approach for the synthesis of 5-methyl-

4,5-borazarothieno[2,3-*c*]pyridine (*2c*) and 6-methyl-7,6-borazarothieno[3,2-*c*]pyridine (*3c*), which were obtained from *2a* and *3a* via the butoxy derivatives, *2b* and *3b*, in high yield. The latter compound was crystalline, m.p. 30 °C. The compounds showed strong absorption in the IR spectrum at 2550 and 2540 cm⁻¹, characteristic of B–H stretching.¹³ These compounds are most probably monomers, since absorption at 1600 cm⁻¹, considered characteristic for dimers with B–H–B bridges,¹⁴



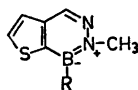
1

R = OH or CH₃
R = H or CH₃



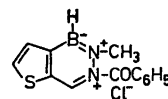
2

a R = OH
b R = OC₄H₉
c R = H

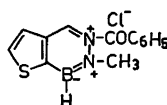


3

a R = OH
b R = OC₄H₉
c R = H



4



5

was not observed. Also in the mass spectrometer these compounds were monomeric.

The NMR spectra were in accordance with the suggested structures, although the B-H resonance could not be observed, most probably due to the high quadrupole moment of the boron.¹² However, indirect evidence for the presence of the BH group was obtained in the form of long-range coupling to one of the thiophene hydrogens, which persisted when the resonance from all other protons were decoupled, and therefore must be due to the B-H proton. The thiophene hydrogen to which it couples is most probably the 3-hydrogen. The assignment is based on chemical shift comparison with the shifts of 2- and 3-bromo-7,6-borazarothieno[3,2-c]pyridines.¹⁵ Also the theory of the shortest zig-zag path for this long-range coupling¹⁶ supports this assignment. Similar long-range couplings have been observed in 4,5-borazarothieno[2,3-c]pyridines.¹⁷ Both *2c* and *3c* are very stable compounds and could be stored at room temperature under nitrogen for several years without discoloration or decomposition. They reacted very slowly with water or alcohols under evolution of hydrogen to give the corresponding B-OH or B-alkoxy derivatives. The reaction of *2c* with eight equivalents of butanol at 30 °C was followed by NMR. We found that after 4 h 75 % had reacted to give *2b*. *2c* and *3c* did not react with benzaldehyde, acetone, ethyl acetate or benzyl cyanide in anhydrous ether. Only starting material was recovered after 150 h at 25 °C. In the reaction of *2c* and *3c* with benzoyl chloride, a white precipitate was immediately formed, which most probably is the benzo-ylated derivative (*4* and *5*, respectively), as treatment with water caused hydrogen evolution and the formation of *2a* and *3a*, respectively, besides benzoic acid. It is well-known that 1-hexyne reacts easily with boranes such as disiamylborane.¹⁷ However, *2c* and *3c* did not react with 1-hexyne. Only starting material was recovered after 150 h at 25 °C.

It is thus obvious that the boron hydrides *2c* and *3c* show no reducing power nor are they active as hydroborating agents. This behaviour thus provides additional evidence for the aromatic nature of the 3,2-borazaropyridines.

EXPERIMENTAL

Microanalyses were carried out at Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim, a.d. Ruhr. IR spectra were recorded with a Perkin-Elmer 257 grating infrared spectrophotometer. ¹H NMR spectra were recorded with a Varian A-60 spectrometer. The MS were recorded on an LKB A 9000 spectrometer. GLC analyses were carried out on a Perkin-Elmer 900 gas-chromatograph using a flame ionization detector.

6-Methyl-7,6-borazarothieno[3,2-c]pyridine (3c). A solution of 10.4 g (0.0625 mol) of 7-hydroxy-6-methyl-7,6-borazarothieno[3,2-c]pyridine¹⁷ in 150 ml of butanol and 100 ml of benzene in a flask connected with a water separator was refluxed for 6 h. The solvents were distilled off, finally at 0.13 Pa. The residue, which still contained 3.4 g of butanol, was dissolved in 500 ml of anhydrous ether cooled to -20 °C, and 1.25 g (0.0325 mol) of lithium aluminium hydride suspended in 300 ml of anhydrous ether was added dropwise under nitrogen during 15 min with vigorous stirring. Then 0.625 g of aluminium chloride in 100 ml of anhydrous ether was added. The temperature was allowed to rise to room temperature and the mixture was refluxed for 2 h. The precipitate was allowed to sediment and the supernatant was transferred with nitrogen pressure through a glass filter to a flask and the ether was evaporated over nitrogen, giving the title compound as colorless needles. The product was sublimed at 75 °C/0.25 Pa and the sublimation apparatus opened in a glove box, yielding 7.2 g (77 %) of the title compound, m.p. 30 °C; IR (KBr) B-H 2540 cm⁻¹; NMR (CDCl₃): δ 7.73 (1, d, H-2, *J*₂₃ = 5.0 Hz), 7.34 (1, dd, H-3, *J*₂₃ = 5.0 Hz, *J*₃₇ = 0.6 Hz), 8.43 (1, s, H-4), 3.88 (3, s, NCH₃); *m/e* (%): 150 (100), 149 (42), 122 (47), 121 (14). (Found: C 48.54; H 4.89; B 7.01; N 18.89; S 21.5. Calc. for C₆H₇BN₂S: C 48.04; H 4.71; B 7.20; N 18.67; S 21.37).

5-Methyl-4,5-borazarothieno[2,3-c]pyridine (2c). From 10.4 g (0.0625 mol) of 4-hydroxy-5-methyl-4,5-borazarothieno[2,3-c]pyridine,¹⁷ 0.65 g (0.0172 mol) of lithium aluminium hydride and 0.625 g of aluminium chloride, 8.35 g (89 %) of the title compound, b.p. 84.0–85.5 °C/0.65 Pa was obtained in the same way as described above; IR (KBr): B-H 2550 cm⁻¹; NMR (CDCl₃): δ 7.40 (2, s, thiophene protons), 8.45 (1, s, 7-H), 3.85 (3, s, NCH₃); *m/e* (%): 150 (100), 149 (40), 122 (51), 121 (15). (Found: C 48.21; H 4.80; B 7.11; N 18.70; S 21.48. Calc. for C₆H₇BN₂S: C 48.04; H 4.71; B 7.20; N 18.67; S 21.37).

Grants from the Swedish Natural Science Research Council (to S.G.) and the Royal Physiographic Society in Lund (to A.M.) are gratefully acknowledged.

REFERENCES

1. Gronowitz, S. and Maltesson, A. *Acta Chem. Scand.* 25 (1971) 2435.
2. Namtvedt, A. *Acta Chem. Scand.* 22 (1968) 1611.
3. Gronowitz, S. and Maltesson, A. *Chem. Scr.* 2 (1972) 79.
4. Gronowitz, S. and Maltesson, A. *Acta Chem. Scand. B* 29 (1975) 457.
5. Gronowitz, S. and Maltesson, A. *Acta Chem. Scand. B* 29 (1975) 461.
6. Gronowitz, S. and Roos, C. *Acta Chem. Scand. B* 29 (1975) 1036.
7. Gronowitz, S. *J. Heterocyclic Chem.* 12S (1975) 17.
8. Dewar, M. J. S., Kubba, V. P. and Pettit, R. *J. Chem. Soc.* (1958) 3073.
9. Dewar, M. J. S. and Dietz, R. *J. Chem. Soc.* (1959) 2725.
10. Dewar, M. J. S. and Poesche, W. H. *J. Am. Chem. Soc.* 85 (1963) 2253.
11. Dewar, M. J. S. and Poesche, W. H. *J. Org. Chem.* 29 (1964) 1757.
12. Dewar, M. J. S. and Dougherty, R. C. *J. Am. Chem. Soc.* 86 (1964) 433.
13. Bellamy, L. J., Gerard, W., Lappert, M. F. and Williams, R. L. *J. Chem. Soc.* (1958) 2412.
14. Köster, R. In Steinberg, H. and McCloskey, A. L., Eds., *Progress in Boron Chemistry*, Pergamon, Oxford 1969, Vol. I, p. 289.
15. Gronowitz, S. and Glennow, C. *To be published.*
16. Banwell, C. N. and Sheppard, N. *Discuss. Faraday Soc.* 34 (1962) 115.
17. Gronowitz, S. and Namtvedt, J. *Acta Chem. Scand.* 21 (1967) 2151.
18. Brown, H. C. *Hydroboration*. Benjamin, New York 1962.

Received April 20, 1977.