



[2,3-c]pyridine (III).<sup>5</sup> As III is easily obtained<sup>6</sup> from commercially available 3-bromothiophene, this method appears to be a preparatively useful route to 3,2-borazaropyridines, making possible a detailed study of the chemistry of this new system.

Our structural proof for IV is based on a correct elementary analysis for  $C_6H_{11}BN_2OS$ , and on the MS-spectrum, which shows strong peaks at  $m/e = 137-138$ , corresponding to the molecular ions. Further, this spectrum shows strong peaks at  $m/e = 122-123$  and  $m/e = 110-111$ , which correspond to  $[M-CH_3]^+$  and  $[M-HCN]^+$ . The last fragmentation is characteristic for nitrogen-containing heterocyclic compounds.

The structural proof is further based on the completely resolved NMR-spectrum. The NMR-spectrum in deuteriochloroform shows six bands; two doublets at 2.34  $\tau$  and 3.03  $\tau$ , two singlets at 4.40  $\tau$  and 6.39  $\tau$ , a quartet at 7.53  $\tau$  and a triplet at 8.82  $\tau$ , with relative intensities of 1:1:1:3:2:3, respectively. The bands at 7.55  $\tau$  and 8.82  $\tau$  can be assigned to the ethyl group and show a coupling constant of 7.5 c/s. The bands at 4.40  $\tau$  and 6.39  $\tau$  can be assigned to the OH and N-CH<sub>3</sub> hydrogens, respectively. The bands at 2.34  $\tau$  and 3.03  $\tau$ , which show a coupling constant of 4.4 c/s, can be assigned to the 5- and 6-hydrogens. If the band at 3.03  $\tau$ , which is rather broad, belongs to the 5-hydrogen, the broadening can be due to a small long-range coupling to the methylene hydrogens in the ethyl group. Decoupling brought about by irradiation of the methylene group caused better resolution of the 3.03  $\tau$  band indicating coupling between the 5-hydrogen and the methylene hydrogens. The band at lowest field (2.34  $\tau$ ) must therefore belong to the 6-hydrogen. In analogy with pyridine, it is also to be expected that the resonance of the hydrogen at the azomethine carbon occurs at lowest field.

The UV-spectrum of IV in ethanol shows maxima at 228  $m\mu$  ( $\epsilon$  2410) and at 273  $m\mu$  ( $\epsilon$  7930) and shows resemblance to the UV-spectrum of 3-hydroxypyridine in ethanol.<sup>7</sup> It is most probable that the measured spectrum is that of the ethyl ether as compounds of this type undergo exchange of RO groups attached to boron very rapidly. No change was observed in the UV-spectrum of IV in 1 N hydrochloric acid and 1 N sodium hydroxide over a period of one week. This, together with

the fact that the double bond in the boron-containing ring remained intact during the desulphurization of III, indicates that IV is an aromatic compound of considerable stability.

*Experimental.* 4-Ethyl-3-hydroxy-2-methyl-3,2-borazaropyridine. To a solution of 6.64 g (0.04 mole) of 4-hydroxy-5-methyl-4,5-borazathieno[2,3-c]pyridine<sup>5</sup> in 200 ml of ethanol was added 60 g of Raney nickel catalyst (LS-S-32). After refluxing for 3 h, the catalyst was filtered off and the filtrate evaporated *in vacuo*. The residue (4.0 g) was chromatographed on a silica gel column and eluted with ether. The first fraction was evaporated *in vacuo* and the residue recrystallized from hexane, giving 2.7 g (49 %) of 4-ethyl-3-hydroxy-2-methyl-3,2-borazaropyridine in colourless crystals, m.p. 63–70°C. Upon standing or distillation, some ether formation occurred. UV (ethanol):  $\lambda_{max} m\mu$  ( $\epsilon \times 10^{-3}$ ) 228 (2.41); 273 (7.03). NMR (CDCl<sub>3</sub>):  $\tau_6$  2.34,  $\tau_5$  3.03,  $\tau_{OH}$  4.40,  $\tau_{NCH_3}$  6.39,  $\tau_{CH_2CH_3}$  7.55–8.82;  $J_{65} = 4.40$  c/s, and  $\tau_{CH_2CH_3} = 7.75$  c/s. (Found: C 52.04; H 7.49; N 20.84. Mol.wt. 137–138. Calc. for  $C_6H_{11}BN_2OS$  (138.0): C 52.22; 7.04; N 20.29). The NMR-spectrum was obtained on a Varian A-60 NMR-spectrometer using tetramethylsilane as internal standard. The IR-spectrum was obtained on a Perkin Elmer 257 grating infrared spectrophotometer. The UV-spectra were obtained on a Unicam SP 800 ultraviolet spectrophotometer. The MS-spectrum was obtained on an LKB-9000 mass-spectrometer using a direct inlet system. The elementary analyses were carried out by Miss Ilse Beetz, Mikroanalytisches Laboratorium, Kronach.

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