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Heteroaromatic Boron Compounds. XII. On the Halogenation of 3,2-Borazaropyridines under Non-acidic Conditions

SALO GRONOWITZ* and ALF MALTESSON**

Division of Organic Chemistry, Chemical Center, University of Lund, Box 740, S-220 07 Lund 7, Sweden

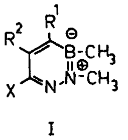
Derivatives of 3,2-borazaropyridines can conveniently be brominated by bromine in pyridine-carbon tetrachloride and iodinated by iodine chloride in pyridine-acetonitrile. The benzo- and thieno-fused ring systems react at the remaining C – H group of the boron-nitrogen containing ring. While derivatives of 5-ethyl-3,2-borazaropyridine give a mixture of the 4- and 6-isomer upon attempted monobromination, iodination occurs selectively in the 4-position. The 5-ethyl derivative easily gives the 4,6-dibromo and 4,6-diiodo derivatives, when excess reagents are used. 4-Ethyl-3,2-borazaropyridines are only monobrominated or iodinated in the 6-position.

The isoelectronic pyridines are not halogenated with the above mentioned reagents. Possible mechanism for the facile halogenation of 3,2-borazaropyridines are discussed.

In a previous short communication we mentioned that the new aromatic boron-containing heterocycle 3,2-borazaropyridine could be brominated by molecular bromine in carbon tetrachloride-pyridine as solvent.[1] From 2,3-dimethyl-4-ethyl-3,2-borazaropyridine (Ia), the 6-bromo derivative (Ib) was obtained, while 2,3-dimethyl-5-ethyl-3,2-borazaropyridine (Ic) gave a mixture of approximately the same amounts of the 4- (Id) and 6- (Ie) bromo derivatives, in addition to the 4,6-dibromo derivative (If). It has previously also been found that bromine in acetic acid brominates benzo- [2] and thieno-fused 3,2-borazaropyridines [3] in the boron-nitrogen containing ring.

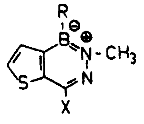
We have now undertaken a more detailed study of the bromination and iodination of 3,2-borazaropyridines and their benzo- and thieno-fused derivatives under non-acidic conditions.

We found that both B – OH derivatives, such as 4-hydroxy-5-methyl-4,5-borazarothieno[2,3-*c*]pyridine (IIa) and 7-hydroxy-6-methyl-7,6-borazarothieno[4,3-*c*]pyridine (IIIa), and B – CH_3 derivatives, such as 4,5-dimethyl-4,5-



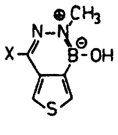
I

a. $R^1 = C_2H_5; R^2 = H;$ $X = H$
b. $R^1 = C_2H_5; R^2 = H;$ $X = Br$
c. $R^1 = H;$ $R^2 = C_2H_5;$ $X = H$
d. $R^1 = Br;$ $R^2 = C_2H_5;$ $X = H$
e. $R^1 = H;$ $R^2 = C_2H_5;$ $X = Br$
f. $R^1 = Br;$ $R^2 = C_2H_5;$ $X = Br$
g. $R^1 = C_2H_5; R^2 = H;$ $X = I$
h. $R^1 = I;$ $R^2 = C_2H_5;$ $X = H$
i. $R^1 = I;$ $R^2 = C_2H_5;$ $X = I$



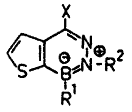
II

a. $R = OH; X = H$
b. $R = CH_3; X = H$
c. $R = OH; X = Br$
d. $R = CH_3; X = Br$



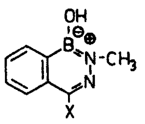
III

a. $X = H$
b. $X = Br$



IV

a. $R^1 = CH_3; R^2 = CH_3; X = H$
b. $R^1 = CH_3; R^2 = CH_3; X = Br$
c. $R^1 = OH; R^2 = H;$ $X = H$
d. $R^1 = OH; R^2 = H;$ $X = Br$
f. $R^1 = CH_3; R^2 = CH_3; X = I$



V

a. $X = H$
b. $X = Br$

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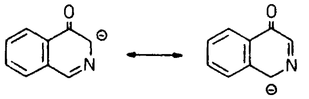
* To whom correspondence should be addressed.

** Taken in part from the Ph. D. thesis of A. Maltesson, University of Lund 1974.

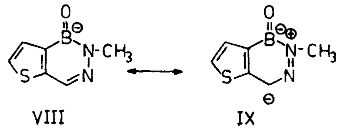
borazarothieno[2,3-c]pyridine (IIb) and 6,7-dimethyl-7,6-borazarothieno[3,2-*c*]pyridine (IVa), react with one equivalent of bromine in pyridine-carbon tetrachloride to give monobromo derivatives IIc, IIIb, IId, and IVb, respectively, in 70 – 80 % yield. In all cases substitution occurred at the only C – H position of the boron-nitrogen containing ring. The structures followed directly from the NMR spectra.

However, N – H derivatives such as 7-hydroxy-7,6-borazarothieno[3,2-*c*]pyridine (IVc) gave a low yield of the 4-bromo derivative (IVd), when one equivalent of bromine was used, and much starting material was recovered. This could be circumvented by using two equivalents of bromine, but the yield was still only 52 %. It is possible that *N*-bromination complicated the reaction. Also 4-hydroxy-3-methyl-4,3-borazaroisoquinoline (Va) [4] was brominated to the 1-bromo derivative (Vb) in high yield with one equivalent of bromine under these conditions. The structure was determined by comparison of its NMR spectrum with that of 1-bromo-4-methyl-4,3-borazaroisoquinoline [2,5] and by oxidative degradation to benzoic acid. In general the bromination method described above gave higher yield than bromination in acetic acid.

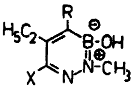
We made several attempts to obtain dibromination by using excess bromine and longer reaction time, but it was not possible to introduce bromine in the fused thiophene or benzene part with this reagent. This is also in accordance with the observation by Roos [6] that 5,7-dimethyl-4-hydroxy-4,5-borazarothieno-[2,3-c]pyridine, in which the reactive 7-position is blocked by a methyl group, is not brominated by the bromine-pyridine adduct in carbon tetrachloride.



VI VII



VIII IX



X

a. R = H ; X = H
b. R = Br; X = H
c. R = H ; X = Br
d. R = Br; X = Br

In order to obtain some information on the mechanism of this bromination, we reacted 3,4-dimethylisoquinoline [7] which bromine in pyridine-carbon tetrachloride, but only starting material was recovered. It is possible that this is due to the fact that the base strength of 3,4-dimethylisoquinoline* is greater than that of pyridine and that the pyridine bromine adduct is only transformed to the isoquinoline adduct. We therefore used 2,4,6-trimethylpyridine,[9] which should be a stronger base than 3,4-dimethylisoquinoline, as solvent. However, also in this case no bromination occurred. On the other hand, it has been shown that 4-hydroxyisoquinoline in aqueous sodium hydroxide is smoothly monobrominated to 3-bromo-4-hydroxyisoquinoline by bromine in aqueous sodium hydroxide, and dibrominated to the 1,3-dibromo derivative with excess bromine.[10] However, IIa did not react under these conditions and was recovered unchanged. It is probable that the activation for electrophilic substitution in the phenolate ion, as expressed in resonance structures VI and VII, is not effectively transmitted in the 3,2-borazaropyridine system (VIII and IX), as indicated by structure IX, which involves several charged atoms.**

As mentioned above bromination of Ic led to a mixture of 4- and 6-bromosubstituted derivatives, which could not be separated by fractional distillation. Similarly bromination of the B – OH derivative 5-ethyl-3-hydroxy-2-methyl-3,2-borazaropyridine (Xa) gave with one equivalent of bromine a mixture of 4-bromo- (Xb), 6-bromo- (Xc), and 4,6-dibromo-5-ethyl-3-hydroxy-2-methyl-3,2-borazaropyridine (Xd) in

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* The base-strength of this compound is estimated from that of isoquinoline and the known effects of methyl groups (*cf.* Ref. 8).

** It should be pointed out that the similarity of the UV spectra of the B – OH derivatives of 3,2-borazaropyridines in acid and alkaline media has been taken as evidence that these acids are proton acids and not Lewis acids.[4,11]

the proportions 1:1:2. In this case, it was even more difficult to separate the isomers, as they could not be distilled and the B – OH compounds partially formed anhydrides during the work-up.

With excess bromine, dibromination of both Ic and Xa, in the 4- and 6-position could be achieved to give If and Xd, respectively, in high yields. However, the purification of the latter compound caused some difficulty. Attempts to substitute Ia in the 5-position by using excess bromine and more forced conditions failed. Neither did the isoelectronic 2,3,4-[12] and 2,3,5-trimethylpyridines[13] react under these conditions.

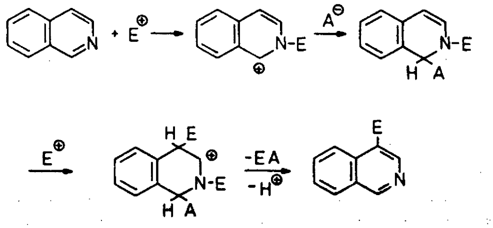
We then investigated the possibility of iodination of 3,2-borazaropyridines. Our hope was also to obtain crystalline derivatives suitable for X-ray analysis of these new heterocyclic systems. Attempts to react IVa with iodine in carbon tetrachloride-pyridine failed, perhaps due to the poor solubility of iodine in this solvent system. We found, however, that smooth iodination of IVa occurred, using iodine chloride in acetonitrile-pyridine as solvent, yielding 6,7-dimethyl-4-iodo-7,6-borazarothieno[3,2-*c*]pyridine (IVf) in 92 % yield. In analogy with the bromination reaction, it is assumed that the iodine chloride-pyridine complex is the iodinating agent. We found that the monocyclic derivative Ia was also smoothly iodinated with this reagent, yielding 2,3-dimethyl-4-ethyl-6-iodo-3,2-borazaropyridine (Ig). The use of excess iodine chloride and forced conditions did not give disubstitution. According to GLC and NMR Ic is selectively iodinated in the 4-position, giving 2,3-dimethyl-5-ethyl-4-iodo-3,2-borazaropyridine (Ih) in 60 % yield. The structure follows from its NMR spectrum [δ 7.57 (H-6)]. The use of excess iodine chloride in the reaction with Ic gave the crystalline (m.p. 37 – 38 °C) 4,6-diiodo-2,3-dimethyl-5-ethyl-3,2-borazaropyridine (Ii) in 74 % yield. An X-ray analysis of this compound is in progress.

From the investigations on the substitution reactions of 3,2-borazaropyridines hitherto carried out, the following picture is emerging. In strongly acidic solutions in which the 3,2-borazaropyridines are highly protonated, the monocyclic derivatives do not react,[14] while the benzo- or thieno-fused systems undergo substitution in the benzene[5] or thiophene ring.[15] The isoelectronic monocyclic pyridines, in contrast to the 3,2-borazaropyridines, undergo electrophilic substitution smoothly under these conditions.[14] It thus seems clear that the 3,2-borazaropyridinium ion is more deactivated towards electrophilic substitution than the pyridinium ion. Under slightly acidic or non-acidic conditions, on the other hand, as shown above, and in previous papers, both the monocyclic and fused 3,2-borazaropyridines react in the boron-nitrogen containing ring,[1,3,16] while the corresponding isoelectronic pyridines do not react.

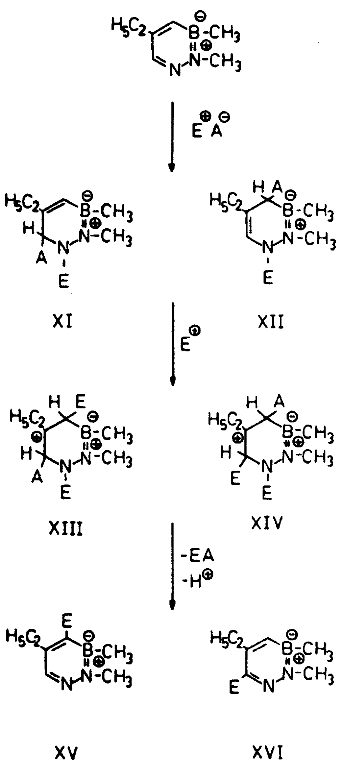
It appears probable that substitution of the pyridines in strongly acidic solution follows the normal mechanism for electrophilic substitution *via* the Wheland intermediate. The mechanism of the substitution under non-acidic conditions is more uncertain. A direct electrophilic substitution on the free bases seems somewhat unlikely, as it is then difficult to understand why protonation should reverse the order of reactivity of the monocyclic 3,2-borazaropyridines compared to the isoelectronic pyridines. Also the dependence of the isomer distribution on the nature of the reagent, substitution occurring predominantly in the 6-position upon nitration and in the 4-position on iodination, with intermediate results for bromination, is hardly expected for "normal" electrophilic substitution through a Wheland intermediate.

However, HMO calculations on the parent 3,2-borazaropyridine system using the ω-technique gave the highest π-electron densities and super-delocalizabilities for the 4- and 6-positions. This indicates that these positions should be the most reactive in electrophilic substitution.

In isoquinoline different substitution patterns are obtained under acidic and non-acidic conditions. Thus, bromination of isoquinoline in the presence of aluminium chloride gives a mixture



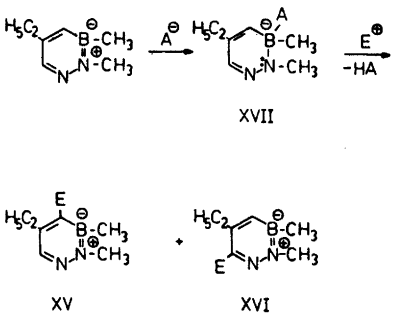
Scheme 1.



Scheme 2.

of 5-bromo- and 5,8-dibromoisoquinoline,[17] while bromination with bromine in pyridine-carbon tetrachloride yields 4-bromoisoquinoline.[18] For the latter reaction Brown and Harcourt [19] have suggested an addition-substitution-elimination mechanism shown in Scheme 1.

A somewhat analogous mechanism can be perceived for the substitution of 3,2-borazaropyridines (Scheme 2). 1,2- and 1,4-Addition to the formal conjugated azomethine bond give XI and XII, respectively, which are attacked by the electrophile in positions 4- and 6- to give intermediates such as XIII and XIV, which lose EA and H^+ to give the products. The reason that the isoelectronic pyridines do not react in the same way may depend upon the fact that the primary addition is slow and/or that the more basic pyridines attack the α-position of the *N*-pyridine complex, giving ring-opened products. Except for *N*-nitropyridinium tetrafluoroborate, which with pyridine gives a derivative of glutaconaldehyde,[20] similar ring-opened products have also been observed from the adduct of cyanogen bromide and pyridine [21,22] and from the adducts of pyridine with sulfur trioxide, chlorosulfonic acid and ethyl chlorosulfonate.[23,24]



Scheme 3.

Another possible mechanism which utilizes the characteristic properties of boron is indicated in Scheme 3. The nucleophile attacks at boron, transforming the 3,2-borazaropyridine in principle into a cyclic α,β-unsaturated hydrazone (XVII). It is known that certain hydrazones are nitrated with amylnitrite [25] and brominated with bromine in acetic acid at the azomethine bond.[26] Therefore, substitution at the 6-position to give XVI and at the vinylogous position to give XV could also be a possibility. We have in vain tried to detect intermediate addition products by the NMR technique. However, this does not exclude the above mechanism, since intermediate addition products can be present in low "steady-state" concentrations.

It appears to us that the problem of proving the mechanism(s) which are valid under non-acidic conditions is a difficult task, demanding extensive theoretical and experimental studies. Knowledge of the reaction mechanism is obviously of great importance for a deeper understanding of the isomer distributions obtained in nitration and halogenation of 3,2-borazaropyridines.

EXPERIMENTAL

7-Bromo-4-hydroxy-5-methyl-4,5-borazarothieno[2,3-c]*pyridine (IIc).* To a mixture of 9 ml of anhydrous pyridine (dried and distilled from potassium hydroxide) and 15 ml of carbon tetrachloride (distilled from phosphorus pentoxide), 1.66 g (0.10 mol) of 4-hydroxy-5-methyl-4,5-borazarothieno[2,3-*c*]pyridine [11] was added, and 1.70 g (0.011 mol) of bromine in 20 ml of anhydrous carbon tetrachloride was added dropwise with stirring during 15 – 20 min. A yellow precipitate formed, and the mixture was refluxed for 1.5 h. The precipitate was filtered off and washed with carbon tetrachloride. The combined carbon tetrachloride phases were extracted with water, dried over magnesium sulfate and the solvent evaporated. The residual sirupy oil (2.3 g) which upon scratching crystallized, was recrystallized from 35 ml (30 %) of aqueous acetic acid, yielding 1.8 g (73 %) of the title compound, m.p. 93 – 95 °C. After solidification it melted at 204.5 °C probably due to anhydride formation during the melting process. NMR (CD_3COCD_3): δ 7.85 (H-2 and H-3), 3.63 (NCH_3). [Found: C 29.44; H 3.08; Br 33.01; N 10.68; S 12.72. Calc for C_6H_6BBrOS (244.9): C 29.43; H 2.47; Br 32.63; N 11.48; S 13.08.]

7-Bromo-4,5-dimethyl-4,5-borazarothieno[*2,3-*c]*pyridine (IId)*. From 1.64 g (0.10 mol) of 4,5-dimethyl-4,5-borazarothieno[2,3-*c*]pyridine [11] and 1.70 g (0.011 mol) of bromine, 2.3 g of crude product was obtained in the same way as described above. Recrystallization from 75 % aqueous ethanol gave 1.9 g (78 %) of the title compound, m.p. 75.0 – 76.0 °C. NMR ($CDCl_3$): δ 7.63 (H-2 and H-3), 3.80 (NCH_3), 0.93 (BCH_3). [Found: C 34.42; H 3.26; Br 32.96; N 11.45; S 13.22. Calc. for C_7H_8BBrS (242.9): C 34.61; H 3.32; Br 32.89; N 11.53; S 13.20.]

4-Bromo-6,7-dimethyl-7,6-borazarothieno[*3,2-*c]*pyridine (IVb)*. In the same way as described above, 2.3 g of crude product was obtained from 1.64 g (0.010 mol) of 6,7-dimethyl-7,6-borazarothieno[3,2-*c*]pyridine,[14] 1.70 g (0.011 mol) of bromine and the appropriate amounts of pyridine and carbon tetrachloride. Recrystallization from 75 % aqueous ethanol yielded 2.0 g (82 %) of the title compound, m.p. 79.0 – 80.5 °C. NMR ($CDCl_3$): δ 7.47 and 7.73 (H-2 and H-3 or H-3 and H-2, J_{23} 5.0 Hz), 3.75 (NCH_3), 0.90 (BCH_3). [Found: C 34.64; H 3.29; B 4.39; Br 32.92; N 11.50; S 13.25. Calc. for $C_7H_8BBrN_2S$ (242.9): C 34.61; H 3.22; B 4.45; Br 32.89; N 11.53; S 13.20.]

4-Bromo-7-hydroxy-7,6-borazarothieno[*3,2-*c]*-pyridine (IVd)*. In the same way as described above, 1.52 g (0.010 mol) of 7-hydroxy-7,6-borazarothieno[3,2-*c*]pyridine [27] and 3.2 g (0.020 mol) of bromine in pyridine-carbon tetrachloride gave after recrystallization from 30 % aqueous acetic acid 1.2 g (52 %) of the title compound, m.p. 95.0 – 98.0 °C. When only 1.7 g (0.011 mol) of bromine was used, 1.1 g of a 1:1 mixture of the title compound and 7-hydroxy-7,6-borazarothieno[3,2-*c*]pyridine was obtained according to NMR analysis. NMR (CD_3COCD_3): δ 7.53 and 8.03 (H-2 and H-3 or H-3 and H-2, J_{23} 5.0 Hz). [Found: C 25.87; H 2.06; Br 34.20; N 12.04; S 13.63. Calc. for $C_5H_4BBrN_2OS$ (230.9): C 26.01; H 1.74; Br 34.61; N 12.13; S 13.89.]

4-Bromo-7-hydroxy-6-methyl-7,6-borazarothieno[*3,4-*c]*pyridine (IIIb)*. In the same way as described above 1.7 g (70 %) of the title compound, m.p. 92.0 – 94.0 °C after recrystallization from 35 – 40 ml (30 %) of aqueous acetic acid, was obtained from 1.66 g (0.010 mol) of 7-hydroxy-6-methyl-7,6-borazarothieno[3,4-*c*]-pyridine,[11] and 1.70 g (0.011 mol) of bromine in pyridine and carbon tetrachloride. NMR (CD_3SOCD_3): δ 7.97 (H-1), 8.47 (H-3, J_{13} 2.8 Hz), 9.00 (OH), 3.42 (NCH_3). [Found: C 29.35; H 2.86; Br 33.10; N 11.19; S 12.84. Calc. for $C_6H_6BBrN_2OS$ (244.9): C 29.43; H 2.47; Br 32.63; N 11.48; S 13.08.]

1-Bromo-4-hydroxy-3-methyl-4,3-borazaroisoquinoline. (Vb). From 1.60 g (0.010 mol) of 4-hydroxy-3-methyl-4,3-borazaroisoquinoline [4] and 1.70 g (0.011 mol) of bromine in pyridine-carbon tetrachloride, 1.85 g (77 %) of the title compound, m.p. 99.5 – 100 °C (141.0 – 142.0 °C after resolidification and remelting) was obtained after recrystallization from 30 % aqueous acetic acid in the same way as described above. NMR (CD_3COCD_3): δ 7.83 (m, arom.), 3.58 (NCH_3). [Found: C 39.94; H 3.26; Br 33.21; N N 11.49. Calc. for $C_8H_8BBrN_2O$ (238.9): C 40.22; H 3.38; Br 33.45; N 11.73.] Oxidation of the title compound with potassium permanganate in alkaline solution yielded benzoic acid (25 %) having the same IR spectrum as an authentic sample.

Attempted bromination of 3,4-dimethylisoquinoline. When 0.79 g (0.0050 mol) of 3,4-dimethylisoquinoline [7] and 0.85 g (0.0065 mol) of bromine in pyridine-carbon tetrachloride were reacted as described above, only starting material was detected by GLC. The same was true when 2,4,6-trimethylpyridine was used instead of pyridine as cosolvent.

4,6-Dibromo-2,3-dimethyl-5-ethyl-3,2-borazaropyridine (If). From 2.52 g (0.0185 mol) of 2,3-dimethyl-5-ethyl-3,2-borazaropyridine [14] in 25 ml of anhydrous carbon tetrachloride, and 9 ml of anhydrous pyridine and 8.8 g (0.055 mol) of bromine in 15 ml of anhydrous carbon tetrachloride, 4.1 g (75 %) of the title compound, b.p. 84 – 86 °C/0.5 mmHg was obtained, when the procedure given for IIc was followed. it had the same spectroscopic properties as a previously described sample.[1]

Bromination of 5-ethyl-3-hydroxy-2-methyl-3,2-borazaropyridine. When 1.38 g (0.010 mol) of 5-ethyl-3-hydroxy-2-methyl-3,2-borazaropyridine [14] was reacted with 1.70 g (0.11 mol) of bromine in pyridine-carbon tetrachloride and the product worked up as described for IIc, 1.6 g of crude product was obtained, which according to NMR and GLC consisted of a mixture of starting material and of mono- and dibromo derivatives. The compounds could not be separated.

4,6-Dibromo-3-hydroxy-2-methyl-3,2-borazaropyridine (Xd). When 1.38 g (0.010 mol) of 5-ethyl-3-hydroxy-2-methyl-3,2-borazaropyridine [14] and 3.2 g (0.020 mol) of bromine in pyridine-carbon tetrachloride were reacted in the usual way, the crude product did not crystallize. Purification was achieved by sublimation *in vacuo*. At the cold finger 2.0 g (68 %) of the title compound collected as a colourless, very viscous syrup. NMR ($CDCl_3$): δ 1.13 (CH_3), 2.83 (CH_2), 3.55 (NCH_3). [Found: C 25.87; H 3.14; Br 52.34; N 9.15. Calc. for $C_6H_9BBr_2N_2O$ (295.8): C 24.36; H 3.07; Br 54.03; N 9.47.]

Attempted bromination of 2,3,4-trimethylpyridine and 2,3,5-trimethylpyridine. 1.21 g (0.010 mol) of 2,3,4-trimethylpyridine [12] and the same amount of 2,3,5-trimethylpyridine [13] were each reacted with 1.70 g (0.011 mol) of bromine in pyridine and carbon tetrachloride for 24 h and worked up as described above. More than 90 % of unchanged starting material was recovered, and no bromo derivatives were detected by GLC.

6,7-Dimethyl-4-iodo-7,6-borazarothieno[*3,2-*c]*-pyridine (IVf).* To a solution of 1.64 g (0.010 mol) of 6,7-dimethyl-7,6-borazarothieno[3,2-*c*]-pyridine [14] in 15 ml of anhydrous acetonitrile (distilled from phosphorus pentoxide) and 6 ml of anhydrous pyridine, 1.63 g (0.010 mol) of iodine chloride in 15 ml of anhydrous acetonitrile was added dropwise with stirring and the mixture refluxed for 6 h. GLC analysis (BDS, 10 %, 200 °C) showed that about 60 % of the starting material had reacted. The mixture was therefore allowed to stand overnight, an additional 1.63 g (0.010 mol) of iodine chloride in 15 ml of anhydrous acetonitrile was added, and the mixture refluxed for 3 h. The red solution was allowed to cool and was evaporated to one fourth of its original volume. Four volumes of ether were added and the pyridinium hydrochloride which precipitated was filtered off and washed with ether. The combined ether phases were washed twice with thiosulfate solution, twice with water, dried and evaporated. Recrystallization of the residue from 80 % aqueous ethanol yielded 2.66 g (92 %) of the title compound in colourless crystals, m.p. 80.0 – 81.0 °C. NMR ($CDCl_3$): δ 7.37 and 7.69 (H-2 and H-3 or H-3 and H-2, J_{23} 4.8 Hz), 3.78 (NCH_3), 0.92 (BCH_3). [Found: C 28.89; H 2.78; B 3.72; I 43.84; N 9.65. Calc. for $C_7H_8BIN_2S$ (289.9): C 28.99; H 2.78; B 3.68; I 43.76; N 9.66.]

2,3-Dimethyl-5-ethyl-4-iodo-3,2-borazaropyridine (Ih). To a solution of 1.00 g (0.0074 mol) of 2,3-dimethyl-5-ethyl-3,2-borazaropyridine [14] in 15 ml of anhydrous acetonitrile and 4 ml of anhydrous pyridine, 2.4 g (0.0147 mol) of iodine chloride in 15 ml of anhydrous acetonitrile was added dropwise with cooling. The mixture was then refluxed for 30 min. GLC analysis (BDS, 10 %, 90 – 200 °C), showed no trace of starting material, but only monoiodinated and about 5 % of diiodinated product (mass spectra). The mixture was worked up as described above, yielding 1.72 g of crude product, which upon distillation *in vacuo* gave 1.15 g (60 %) of the title compound, b.p. 122 – 124 °C/10 mmHg. The reaction was also carried out with carbon tetrachloride instead of acetonitrile as solvent giving the same result. NMR ($CDCl_3$): δ 7.57 (H-6), 1.15 (CH_3), 2.70 (CH_2), 3.75 (NCH_3), 0.87 (BCH_3). [Found: C 32.15; H 4.69; B 4.08; I 48.51. Calc. for $C_7H_{12}BIN_2$ (261.9): C 32.10; H 4.62; B 4.13; I 48.45.]

4,6-Diiodo-2,3-dimethyl-5-ethyl-3,2-borazaropyridine (Ii). To a solution of 1.0 g (0.0074 mol) of 2,3-dimethyl-5-ethyl-3,2-borazaropyridine [14] in 15 ml of anhydrous acetonitrile and 5 ml of anhydrous pyridine, 3.58 g (0.0221 mol) of iodine chloride in 15 ml of anhydrous acetonitrile was added with stirring and the mixture refluxed for 2 h. GLC analysis showed that about 50 % mono- and 50 % diiodo derivatives had been formed. Therefore, 1.2 g (0.074 mol) of iodine chloride was added and the mixture refluxed for 1 h. The mixture was worked up as described above, yielding a yellow oil which crystallized on standing overnight. Recrystallization from 95 % ethanol at – 30 °C gave 2.1 g (74 %) of the title compound as colourless crystals, m.p. 37.5 – 38 °C. NMR ($CDCl_3$): δ 1.13 (CH_3), 3.03 (CH_2), 3.72 (NCH_3), 0.87 (BCH_3). [Found: C 21.72; H 2.90; B 2.80; I 65.37; Calc. for $C_7H_{11}BI_2N_2$ (287.8): C 21.68; H 2.86; B 2.79; I 65.45.]

2,3-Dimethyl-4-ethyl-6-iodo-3,2-borazaropyridine (Ig). To a solution of 1.0 g (0.0074 mol) of 2,3-dimethyl-4-ethyl-3,2-borazaropyridine [14] in 15 ml of acetonitrile and 4 ml of pyridine, 2.4 g (0.0147 mol) of iodine chloride was added and the mixture refluxed for 1.5 h and worked up as described above, yielding 1.05 g (55 %) of the title compound, b.p. 122 – 123 °C/10 mmHg. NMR ($CDCl_3$): δ 7.23 (H-5), 1.10 (CH_3), 2.50 (CH_2-4), 3.68 (NCH_3), 0.67 (BCH_3). [Found: C 32.03; H 4.67; B 4.21; I 48.38. Calc. for $C_7H_{12}BIN_2$ (261.9): C 32.10; H 4.62; B 4.13; I 48.45.]

GLC analyses were carried out on a Varian model 1400 or a Perkin-Elmer 900 gas chromatograph. NMR spectra were recorded on a Varian A 60 NMR spectrometer and mass spectra were obtained with an LKB A-9000 mass spectrometer. Elemental analyses were carried out by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim/Ruhr.

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