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Heteroaromatic Boron Compounds

II. Synthesis, NMR-Spectra and Hydrolytic Stability of Some Borazarothienopyridines

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Several members of a new boron-containing heterocycle, 7,6-borazarothieno[3,2-c]pyridine (IV), have been synthesized through the reaction of 3-formyl-2-thiopheneboronic acid with hydrazines. Also, some additional 4,5-borazarothieno[2,3-c]pyridines (I) have been prepared through reaction of 2-formyl-3-thiopheneboronic acid with hydrazines. Studies of their NMR-spectra and of their alkaline and acid hydrolysis indicate marked aromaticity in these systems, in contrast to the 7,6-borazarothieno[3,4-c]pyridines obtained upon reacting 4-formyl-3-thiopheneboronic acid with hydrazines.

In the first paper of this series,[1] it was demonstrated that 2-formyl-3-thiopheneboronic acid gave the cyclic derivatives (Ia) and (Ic) with hydrazine and phenylhydrazine, respectively, while 4-formyl-3-thiopheneboronic acid gave a cyclic derivative with hydrazine (IIa) but the open normal phenylhydrazone (III) with phenylhydrazine.

It was also found that IIa underwent hydrolytic ring-opening much more easily than Ia. The larger tendency towards ring-closure and the greater stability towards hydrolysis of the 2,3-annulated system was taken as evidence for aromatic stabilization of the boron-containing ring of the 4,5-borazarothieno[2,3-c]pyridine ring system. This conclusion was based on the known difference in aromaticity of thianaphthene and isothianaphthene.

We have now prepared a third system, 7,6-borazarothieno[3,2-c]pyridine, derived from 3-formyl-2-thiopheneboronic acid, and have studied the influence of the R group on the formation and hydrolytic stability of these cyclic compounds.

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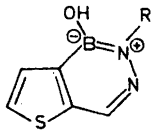


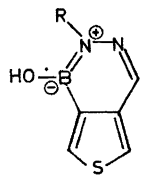
I

a R = H

b R = CH_3

c R = C_6H_5

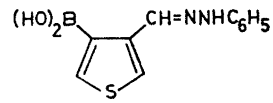
d R = p-C_6H_4COOH



II

a R = H

b R = CH_3



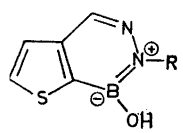
III

7,6-Borazarothieno[3,2-c]pyridines. 3-Formyl-2-thiopheneboronic acid was prepared in 50 % yield through metalation of 3-thiophenealdehyde ethylene acetal with butyllithium, which occurs in the 2-position,[2] followed by reaction with butyl borate and hydrolysis. The structure is evident from its NMR-spectrum in DMSO. The thiophenic hydrogen resonances occur as a hard-coupled AB-spectrum centered at 2.34 τ, with $J_{45} = 4.7$ c/s, the CHO peak at -0.12 τ. As in 4-bromo-3-thiophenealdehyde[3] no long-range coupling to the 5-hydrogen can be observed. The hydroxyl resonance occurs at 3.26 τ.

Reaction of 3-formyl-2-thiopheneboronic acid with hydrazine, methylhydrazine, phenylhydrazine, and *p*-carboxyphenylhydrazine lead to the cyclic derivatives IV in almost quantitative yields. The structures were evident from their NMR-spectra and mass-spectra.

The NMR-spectrum of IVa in dimethyl sulphoxide showed five bands with the same relative intensities at -0.25 τ, 1.60 τ, 1.72 τ, 1.88 τ, and 2.39 τ. The two last mentioned bands are split into doublets with a coupling constant of 5.0 c/s, characteristic of 2,3-di-substituted thiophenes.[3] The relatively broad band at 1.72 τ is assigned to the B—OH group. Comparison with the NMR-spectra of Ia and its N-substituted derivatives (*cf.* below) leads to the assignment of the band at -0.25 τ to the NH and of the 1.60 τ band to the CH hydrogen.

The NMR-spectrum of IVb in DMSO shows five bands with the relative intensities of 1:1:1:1:3 at 1.27 τ, 1.80 τ, 1.92 τ, 2.42 τ, and 6.38 τ, respectively.



IV

a R = H

b R = CH_3

c R = C_6H_5

d R = p-C_6H_4COOH

Table 1. NMR-spectral data of 7,6-borazarothieno[3,2-c]pyridines in DMSO.

Substituent	$\tau_{2 \text{ or } 3}$	$\tau_{3 \text{ or } 2}$	τ_R	$\tau_{R'}$	τ_4	J_{23}
IV , R = H	1.88	2.39	1.72	−0.25	1.60	5.0 c/s
IV , R = CH_3	1.92	2.42	1.27	6.38	1.80	5.0 »
IV , R = C_6H_5	1.80	2.40	0.83	2.40	1.57	4.8 »
IV , R = *p*-C_6H_4COOH	1.77	2.30	0.61 [a]	1.87−2.13	1.54	5.0 »
VIII	1.88	2.35	9.08	−1.50	1.43	5.0 »

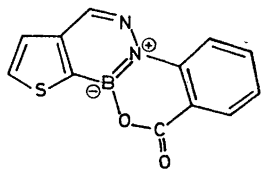
[a] Contains also the COOH group absorption.

The band at 6.38 τ belongs to the CH_3 group, while the two bands at 1.92 τ and 2.42 τ are ascribed to the thiophenic ring-hydrogens as they are split into doublets with a coupling of 5.0 c/s. The bands at 1.27 τ and 1.80 τ could be assigned by studying the effect of addition of water on the NMR-spectrum in tetrahydrofuran. In this case the spectrum shows in the aromatic region a singlet at 1.95 τ and the two thiophenic doublets at 2.23 τ and 2.65 τ, the high-field line of the low field doublet being overlapped by an additional sharp band. Addition of water to the tetrahydrofuran solution causes migration of the latter singlet. As solvents usually have little influence on the shifts of CH hydrogen resonances it follows that the band at 1.80 τ in DMSO can be assigned to the CH and the band at 1.27 τ to the OH group. Also the NMR-spectra and elementary analyses of IVc and IVd (*cf.* Table 1) are in agreement with cyclic structures.

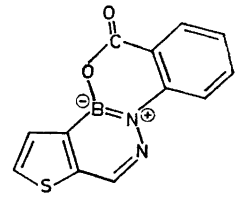
The reaction of 3-formyl-2-thiopheneboronic acid with *o*-carboxyphenylhydrazine resulted in further elimination of water yielding the tetracyclic lactone V. Its structure follows from the absence of the characteristic IR-absorption in the 3.0—4.0 μ region due to carboxylic OH-stretching.

In this region the IR-spectrum shows only a weak absorption due to aromatic CH-stretching at 3.2 μ. The carbonyl stretching at 5.74 μ falls in the ester region.

4,5-Borazarothieno[2,3-c]pyridines. To demonstrate the general scope of this ring-closure reaction 2-formyl-3-thiopheneboronic acid was reacted with some additional hydrazines. Reaction with methylhydrazine yielded the cyclic compound Ib as was evident from its NMR-spectra in DMSO and tetrahydro-



V



VI

furan. The NMR-spectrum in DMSO showed four bands with relative intensities of 1:1:2:3 at 1.42 τ, 1.75 τ, 2.18 τ, and 6.40 τ, respectively. No splittings are observed in these bands. It is obvious that the band at 2.18 τ stems from the two thiophenic hydrogens, as in aqueous tetrahydrofuran two doublets are observed at 2.27 τ and 2.43 τ with a coupling constant of 5.0 c/s. The band at 1.75 τ in DMSO is assigned to the 7-hydrogen, as the band at 1.95 τ in tetrahydrofuran does not migrate upon addition of water. This identifies the band at 1.42 τ as that of the B-OH group.

Reaction of 2-formyl-3-thiopheneboronic acid with *p*-carboxyphenylhydrazine gives the cyclic compound Id. The combined OH and COOH band occurs at 0.66 τ and the 7-hydrogen resonance at 1.46 τ. The four phenyl hydrogens and the two thiophenic hydrogens give rise to a complex band. Two doublets with a splitting of 9.1 c/s characteristic for *para*-substituted benzenes [4] are observed at 1.85 τ and 2.12 τ, the latter doublet being partly overlapped by the very hard-coupled AB-spectrum of the thiophenic hydrogens. From chemical shift considerations the band at 1.85 τ is assigned to the hydrogens *ortho* to the carboxylic group.

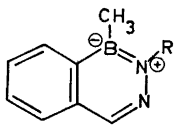
Finally, reaction of *o*-hydrazinobenzoic acid with 2-formyl-3-thiopheneboronic acid yielded the cyclic lactone (VI). Elementary analysis, and IR-spectra are consistent with this structure.

2,4-Dinitrophenylhydrazones. In contrast to the above findings reaction of both 2-formyl-3-thiopheneboronic acid and 3-formyl-2-thiopheneboronic acid with 2,4-dinitrophenylhydrazine led to the normal 2,4-dinitrophenylhydrazones. This was evident from the elementary analysis and IR-spectra. While the cyclic phenyl derivatives have a broad, very poorly resolved band in the 3.0—4.0 μ region, the 2,4-dinitrophenylhydrazones show two sharp bands at 3.05 μ and 3.22 μ, which can be assigned to NH- and CH-stretchings, respectively. The difficult solubility of the 2,4-dinitrophenylhydrazones made an investigation of their NMR-spectra impracticable. The behaviour of the formylthiopheneboronic acids is quite similar to that of *o*-formylbenzeneboronic acid,[5,6] which also gives a normal hydrazone with 2,4-dinitrophenylhydrazine. The above-mentioned results are in accordance with Dewar's proposal [7] that strongly electron-attracting substituents on the nitrogen destabilize the cyclic forms, as these substituents offer a competing route for delocalization of the *p*-electron pair of the nitrogen atom.

7,6-Borazarothieno[3,4-c]pyridines. As mentioned above, we had already earlier found that, whereas phenylhydrazine gave a normal derivative with 3-formyl-4-thiopheneboronic acid,[1] unsubstituted hydrazine gave a cyclic one. The results now obtained with methylhydrazine might indicate that this is general for aliphatic hydrazines. The NMR-spectrum (DMSO) is in accordance with structure IIb and shows five bands with relative intensities of 1:1:1:1:3 at 1.26 τ, 1.60 τ, 1.96 τ, 2.01 τ, and 6.53 τ, respectively. The band at 6.53 τ is assigned to the CH_3 group hydrogens and that at 1.26 τ to the OH hydrogen. The band at 1.60 τ appears as a quartet with splittings of 3.0 c/s and 0.9 c/s. Assuming that the latter long-range coupling is of the same type as in 3-thiophenealdehydes [8] this would identify the resonance at 1.60 τ as that of hydrogen 1; also the theory of shortest zig-zag path leads to this assignment. The splitting of 3.0 c/s is characteristic of J_{25} in thiophenes [3]

and its appearance in the doublet at 1.96 τ identifies this band as that of hydrogen 3, while the doublet with a splitting 0.9 c/s at 2.01 τ is that of hydrogen 4. The different numbering in the simple thiophenes and in the 7,6-borazarothieno[3,4-c]pyridines should be noted. The shifts are very similar to those of IIa, and also the IR-spectrum in the 3.0—4.0 μ region is very similar to the spectra of the other cyclic N-methyl derivatives, IIb and IVb. However, we experienced difficulties in getting correct elementary analysis for IIb, which was also the case with the 2,4-dinitrophenylhydrazone derived from 3-formyl-4-thiopheneboronic acid, which had the same open normal structure as the 2,4-dinitrophenylhydrazones of the two other *o*-formylthiopheneboronic acid.

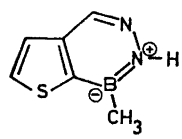
B-Alkylsubstituted borazarothienopyridines. Different N-substituted borazarothienopyridines are thus easily obtained by changing the hydrazine component, making it possible to study the influence of N-substituents on the stability and reactivity of these ring-systems. Variation of substituents on the boron atom is somewhat more difficult. Dewar *et al.*[7] prepared 4-methyl-



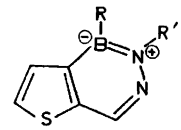
VII

a R=H

b R=CH_3



VIII



IX

a R=CH_3, R′=H

b R=R′=CH_3

c R=C_4H_9, R′=H

4,3-borazaro-isoquinoline (VIIa) by treating the anhydride of 4-hydroxy-4,3-borazaro-isoquinoline with methyl magnesium bromide in tetrahydrofuran and in the preparation of 3,4-dimethylborazaro-isoquinoline (VIIb), they treated the B-hydroxy derivatives directly with excess methyl magnesium bromide. However, our attempts to prepare the B-CH_3 derivative of IVa in this manner failed, only starting material being recovered. We therefore converted our hydroxy compounds to butyl esters by refluxing with butanol and then reacting the crude esters with Grignard reagents. In this way, 7-methyl-7,6-borazarothieno[3,2-c]pyridine (VIII), 4-methyl-4,5-borazarothieno [2,3-c]pyridine (IXa), 4,5-dimethyl-4,5-borazarothieno[2,3-c]pyridine (IXb), and 4-butyl-4,5-borazarothieno[2,3-c]pyridine (IXc) were obtained in good yields.

The NMR-spectra of these compounds (Tables 1 and 2) are in complete agreement with the suggested structures and show B-CH_3 resonance at high field (at 9.10 τ).

Table 2. NMR-spectral data of 4,5-borazarothieno[2,3-c]pyridines in DMSO.

Substituent	$\tau_{2 \text{ or } 3}$	$\tau_{3 \text{ or } 2}$	τ_R	$\tau_{R'}$	τ_7	J_{23}	J_{37}
R = OH, R′ = H[1]	2.28	2.21	1.81	−0.29	1.81	5.3 c/s	0.5 c/s
R = OH, R′ = CH_3	2.18	2.18	1.42	6.40	1.75		
R = OH, R′ = C_6H_5[1]	2.08	2.08	1.05	2.50	1.57		
R = OH, R′ = *p*-C_6H_5COOH	2.06	1.99	0.66 [a]	1.85–2.12	1.46		
R = CH_3, R′ = H	2.39	2.11	9.10	−1.45	1.38	5.0 c/s	0.5 c/s
R = C_4H_9, R′ = H	2.34	2.08	8.47–9.00	−1.50	1.30	5.0 c/s	
R = CH_3, R′ = CH_3	2.45	2.17	9.08	6.24	1.47	5.0 c/s	0.5 c/s

[a] Contains also the COOH group absorption.

The mass-spectra of borazarothienopyridines show a strong peak at the molecular ion, but the B-OH compounds also always show a weaker peak at $2M-H_2O$. This is probably the molecular ion from the ether formed during the introduction of the samples.

NMR-spectra. The NMR-spectral data for the 7,6-borazarothieno[3,2-c] pyridines and the 4,5-borazarothieno[2,3-c]pyridines are collected in Tables 1 and 2, respectively. In the 4,5-borazarothieno[2,3-c]pyridines the thiophenic hydrogens mostly show hard-coupled spectra and in many cases the two resonances coincide. In the 2-formyl-3-thiopheneboronic acid used as starting material, there is a larger shift between the thiophenic hydrogens (τ_5 = 1.89 ppm, τ_4 = 2.46 ppm).[1] As the mechanism of long-range coupling is not known, it is difficult to decide to which thiophenic hydrogen the 7-hydrogen couples.

In 3-formyl-2-thiopheneboronic acid on the other hand, the thiophenic hydrogen resonances are hard-coupled, centered at 2.34 τ, while a shift of about 0.5 ppm is observed in the 7,6-borazarothieno[3,2-c]pyridines. In this case no long-range coupling permitting us to make assignments is observed, neither is any long-range coupling observed in 3-formyl-2-thiopheneboronic acid. Normally, a coupling to the 5-hydrogen is observed in 3-thiophenealdehydes, but its absence is not without precedence, as no long-range coupling was found in 4-bromo-3-thiophenealdehyde.[3] It is known that the formyl group long-range couplings are dependent on the conformation of this group and are greatly influenced by hydrogen bonding.[9] Quantum chemical calculations [10] indicate a greater difference in electron density between the 2- and 3-carbon in the 7,6-borazarothieno[3,2-c]pyridines than in the 4,5-borazarothieno[2,3-c]pyridines, the 2-position having the lower density. This might indicate that the lowest field band in the 7,6-borazarothieno[3,2-c]pyridines belongs to hydrogen 2. We hope to verify this by preparing appropriate derivatives substituted in the thiophene ring. Finally, as mentioned before, the presence of long-range couplings in the two 7,6-borazarothieno[3,4-c] pyridines hitherto known allows an assignment of the thiophenic hydrogens.

The shifts of the NH and N-CH_3 groups are of great importance in elucidating the aromatic nature of the 2,3-annulated systems. It is assumed that the dipolar structures in I and IV are of importance if aromatic stabilization occurs, while in the 3,4-annulated system such stabilization is of much less importance, in accordance with the properties of isothionaphthene. The nitrogen is therefore more positive in I and IV than in II and a corresponding low-field shift of the NH resonance is expected in Ia and IVa as compared to IIa. It was also found that the NH resonance of Ia and IVa occurred at $-0.29\ \tau$ and $-0.25\ \tau$, respectively, in dilute DMSO solution, while that of IIa occurred at $0.65\ \tau$. The positive charge on the nitrogen is partially neutralized by the electron-donating +M effect of the OH group, changing to weaker +M groups as alkyl causes a shift of the NH resonance to $-1.50\ \tau$ in VIII, IXa, and IXc.

Also the N-CH_3 resonances fall 0.13—0.25 ppm towards lower field in the 2,3-annulated system than in the 3,4-annulated system and considerably lower than the N-CH_3 resonance of 3-thiophenealdehyde methylhydrazone ($7.18\ \tau$).

Hydrolysis of the borazarothienopyridines. Although the NMR-spectral data discussed above give clear evidence for the greater aromatic stabilization in the 2,3-annulated systems, a study of the stability of these ring-systems towards acidic and alkaline hydrolysis would yield additional information.

It has been found by Brown *et al.*[11] that 2-thiopheneboronic acid is deboronated 120 times faster than the 3-acid and 8.5×10^5 times faster than benzeneboronic acid in perchloric acid. However, the presence of electron-attracting groups stabilize the C-B bond to an appreciable extent. 3-Formyl-2-thiopheneboronic acid is completely deboronized to 3-thiophenealdehyde after two hours' reflux with concentrated hydrochloric acid, while the same treatment of 2-formyl-3-thiopheneboronic acid and 4-formyl-3-thiopheneboronic acid leads to 65 % and 50 % recovery of the starting acids, respectively, the difference in reactivity of the α- and β-positions being thus evident. Alkaline hydrolysis occurs much more easily and two hours' reflux with 2 N sodium hydroxide leads to complete deboronation in all three *o*-formylthiopheneboronic acids. The products isolated are the thiophenecarboxylic acids and the thenyl alcohols besides traces of the thiophene aldehydes, deboronation thus being accompanied by Cannizzaro reaction. Treatment with 2 N sodium hydroxide at room temperature for 24 h differentiated between the 3-formyl-2-thiopheneboronic acid and the two formyl-substituted 3-thiopheneboronic acids, as the latter were recovered in about 70 % yield, while the 2-acid was completely deboronated.

Ring-closure to the borazarothieno derivatives from 3-formyl-2-thiopheneboronic acid and 2-formyl-3-thiopheneboronic acid leads to increased stability towards hydrolysis. It was found earlier that Ia was not hydrolyzed by conc. hydrochloric acid. This is also the case with IVa. The contrast is even more marked in the present case, as 3-formyl-2-thiopheneboronic acid is completely deboronated under the same conditions.

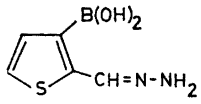
The difference in reactivity of boron in the 2- and 3-position is also noticeable in the cyclic compounds upon alkaline hydrolysis. While Ia was found to be stable when refluxed for 2 h with 2 N sodium hydroxide. IVa vas completely deboronated, the azine of 3-thiophenealdehyde, identified by comparison with

an authentic sample, being isolated in 71 % yield. Furthermore, the presence of hydrazine in the filtrate was shown by the addition of benzaldehyde, which yielded the azine of benzaldehyde. This indicates that it is not the N—N bond which is broken in the ring-opening but that first the hydrazone is formed which disproportionates into the azine and free hydrazine.

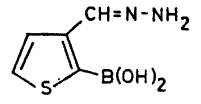
However, that ring-closure led to increased stability even towards alkaline hydrolysis in the 7,6-borazarothieno[3,2-c]pyridine system is evident from the fact that when IVa was treated with 2 N sodium hydroxide at room temperature for 24 h, it was recovered in 87 % yield, while 3-formyl-2-thiopheneboronic acid deboronated completely by this treatment.

The question if it is the C—B bond or the B—N bond which is first broken in the alkaline hydrolysis of IVa is of course still open. However, the differences in stability between Ia and IVa might indicate that the breaking of the C—B bond is the ring-opening step. Since the B—N bonds in the anions derived from Ia and IVa are similar in character, they should not differ greatly in their tendencies towards ring-opening to give open hydrazones (X—XI). These hydrazones would disproportionate to the azine boronic acids XII and XIII, which then possibly (at least in the case of XIII) could deboronate.

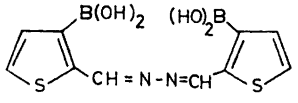
However, hydrolytic ring-opening of the B—N bond occurs in the alkaline hydrolysis of IIa. Refluxing for 2 h with 2 N sodium hydroxide gave both the boronic acid azine XIV and the 3-thiophenealdehyde azine XV; continued hydrolysis yields only XV. All attempts to detect XIII when treating IVa



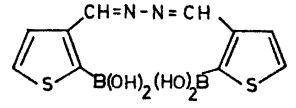
X



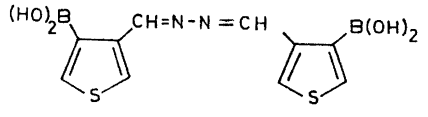
XI



XII

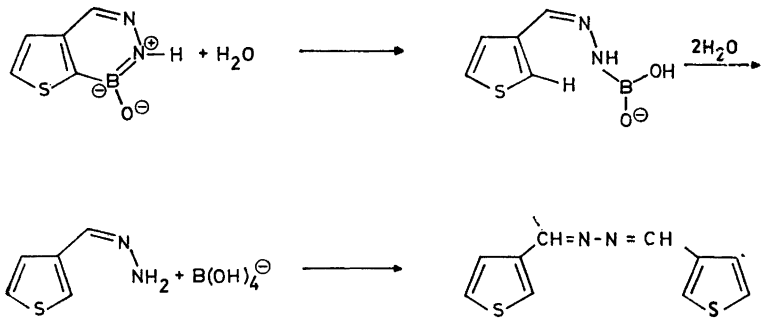


XIII



XIV

with more dilute sodium hydroxide, or using shorter reation times and lower temperatures, failed. It would therefore seem probable that the hydrolytic ring-opening of IVa proceeds as indicated in the reaction scheme below and differs from that of IIa:



XV

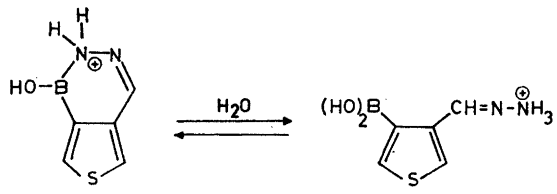
We assume that IVa manifests its acidic properties by losing a proton, as the UV-spectra of IVa and of its anion are very similar, as also seems to be the case with 4-hydroxy-4,3-borazaro-isoquinoline.[7] Normally, boronic acids co-ordinate a hydroxyl ion.[12,13] as is also assumed in the mechanism of the base-catalyzed protodeboronation of some benzeneboronic acids.[14]

The quite different behaviour of Ia and IIa towards 2 N sodium hydroxide testifies to the much greater aromatic stabilization in the 2,3-annulated system than in the 3,4-annulated one.

The methyl derivatives Ib and IIb behaved similarly. While Ib was stable against 2 N sodium hydroxide, IIb yielded under the same conditions the methylhydrazone of 3-thiophenealdehyde. Also the apparently different type of ring-opening in IIa and IVa is of interest in this connection.

Gronowitz and Bugge[1] found that the 3,4-annulated system IIa was easily hydrolyzed by 2 N hydrochloric acid, yielding a product in 81 % yield which at that time was not identified. We have now found that this compound is identical with the azine of 4-formyl-3-thiopheneboronic acid (XIV) also obtained in the alkaline hydrolysis. The structure follows from the NMR-spectrum (DMSO). The band at 0.95 is assigned to the CH hydrogen, the two doublets at 1.53 τ and 1.73 τ with a coupling of 3.0 c/s are assigned to the thiophenic hydrogens and the band at 5.50 τ to the $B(OH)_2$ hydrogens.

We made, however, the surprising observation that when IIa was refluxed for 2 h with concentrated hydrochloric acid, neutralized rapidly with solid sodium bicarbonate, and the precipitate filtered off at once, IIa was recovered in high yield. Small amounts of 4-formyl-3-thiopheneboronic acid were also isolated. On the other hand, if the strongly acidic solution is diluted with water, 4-formyl-3-thiopheneboronic acid azine separates out. This could indicate that in strongly acidic solution the protonated cyclic form is in equilibrium with the conjugate acid of the hydrazone (XVII) and that XVII



XVI XVII

further hydrolysed to 4-formyl-3-thiopheneboronic acid. Raising the pH either causes disproportionation to the azine (which reaction is blocked in strongly acidic solutions) to proceed more rapidly than ring-closure or *vice versa*. In the case of Ia and IVa, ring-closure is apparently more rapid than disproportionation, as starting material is recovered. The fact that Ib and IVb in 2 N hydrochloric acid give hydrochlorides which analyse correctly for the hydrated form supports the view that these compounds exist in the form of protonated open hydrazones. It is, however, evident that the structure could be the cyclic one containing a mole of crystal-water; the NMR-spectra do not help us to decide between these alternatives. It is also somewhat unexpected that no *o*-formylthiopheneboronic acids were found as with IIa. It is obvious that further investigations are needed before this point can be clarified.

The alkaline hydrolysis of IVb is complicated by the formation of 3-thiophenealdehyde azine and 3-thiophenecarboxylic acid. It was verified that the methylhydrazone of 3-thiophenealdehyde prepared directly from methylhydrazine and 3-thiophenealdehyde also gave the azine on treatment with 2 N sodium hydroxide. Probably the methylhydrazone is demethylated to the hydrazone, which then disproportionates.

The phenyl derivatives Ic and IVc were less stable towards hydrolysis and qualitative tests hardly showed greater stability than those of the corresponding formylthiopheneboronic acids. The lower stability is expected theoretically, as the phenyl ring offers an alternative route for the delocalization of the *p*-electrons on the nitrogen, thus destabilizing the B—N π-bond and reducing the aromatic nature. In the extreme case, when a strong electron-attracting group such as the 2,4-dinitrophenyl group is on the nitrogen, ring-closure does not occur.

The B-methyl compounds VIII and IX show similar ring-stability as the corresponding B—OH compounds. The weak spot is the B—CH_3-bond. Especially IXb gives both on acid and on alkaline hydrolysis Ib as the only isolated product, while VIII and IXa only give traces of the B—OH compounds, most of the starting materials being recovered upon acid hydrolysis. On alkaline hydrolysis, IXa is recovered in good yield while VIII is deboronated completely, giving the azine of 3-thiophenealdehyde. Similar differences between 4,3-dimethyl-4,3-borazaroisoquinoline and 4-methyl-4,3-borazaroisoquinoline were found by Dewar *et al.*[7] They believed that steric effects were responsible for the facile cleavage of the B—CH_3 bond in the dimethyl compound.

It is thus evident that the hydrolytic stability increases when going from 7,6-borazarothieno[3,4-c]pyridines to 7,6-borazarothieno[3,2-c]pyridines to 4,5-borazarothieno(2,3-c]pyridines. It seems highly probable that the additional stability of the two latter systems is due to the aromatic nature of these condensed heterocycles. Both systems undergo aromatic substitution reactions, such as nitration and bromination, and some results have recently been published.[15,16]

Further investigations on the substitution reactions of the borazarothienopyridines as well as mass spectral studies of their fragmentation pattern are in progress.

EXPERIMENTAL

3-Formyl-2-thiopheneboronic acid. To a stirred solution of 15.6 g (0.10 mole) of 2-(3-thienyl)-1,3-dioxolane [2] in 100 ml of anhydrous ether was added dropwise under nitrogen 93 ml of 1.20 N ethereal butyllithium. After being refluxed for 15 min, the mixture was cooled to −70°C and 28.7 (0.125 mole) of butyl borate in 150 ml of ether was added as rapidly as possible under vigorous stirring. The mixture was stirred for 4 h at −70°C, the cooling bath removed and when the temperature had risen to 0°C, 200 ml of 1 N hydrochloric acid was added carefully. The mixture was stirred for one hour, the ether phase was separated and the aqueous layer extracted three times with ether. The combined ether phase was extracted with 200 ml of 1 N sodium carbonate and the aqueous layer immediately acidified with 4 N hydrochloric acid to pH 1, which caused the precipitation of crystals. The extraction with sodium carbonate solution was repeated until acidification gave no further precipitation. The dried precipitate (9.5 g) was recrystallized from aqueous ethanol, yielding 8.0 g (50 %) of 3-formyl-2-thiopheneboronic acid as pale yellow needles, which decomposed on heating. NMR (DMSO): $\tau_{CHO} = -0.12$ ppm, $\tau_{4,5} = 2.25$ ppm, 2.42 ppm, $\tau_{OH} = 3.26$ ppm, $J_{45} = 4.70$ c/s. (Found: C 38.91; H 3.25. Calc. for $C_5H_5BO_3S$ (156.0): C 38.50; H 3.24).

7-Hydroxy-7,6-borazarothieno[3,2-c]pyridine. To 3.12 g (0.020 mole) of 3-formyl-2-thiopheneboronic acid in 10 ml of ethanol and 100 ml of ether was added dropwise with stirring 2 ml of 99 % hydrazine in 10 ml of ethanol. The solution was evaporated to dryness on a water-bath, yielding a crystalline residue in quantitative yield. Recrystallization from aqueous ethanol yielded 2.7 g (89 %) of 7-hydroxy-7,6-borazarothieno[3,2-c]-pyridine having the same IR-spectrum as the crude product. M.p. 140−143°C. Cooling and reheating the sample gave m.p. of 184−185°C. NMR: *cf.* Table 1. (Found: C 39.65; H 3.41; N 8.55. Mol. wt. 152. Calc. for $C_5H_5BN_2OS$ (152.0): C 39.51; H 3.32; N 8.43).

7-Hydroxy-6-methyl-7,6-borazarothieno[3,2-c]pyridine. To 3.12 g (0.020 mole) of 3-formyl-2-thiopheneboronic acid in 20 ml of ethanol was added dropwise 1 ml of methyl hydrazine in 10 ml of ethanol. The same work-up as described above yielded 2.8 g (85 %) of the title compound in colourless crystals, m.p. 135−143°C after recrystallization from aqueous ethanol. NMR: *cf.* Table 1. (Found: C 43.38; H 4.25; N 16.56. Mol. wt. 166. Calc. for $C_6H_7BN_2OS$ (166.0): C 43.41; H 4.25; N 16.87).

7-Hydroxy-6-phenyl-7,6-borazarothieno[3,2-c]pyridine. To 1.56 g (0.010 mole) of 3-formyl-2-thiopheneboronic acid in 10 ml of ethanol was added dropwise with stirring 1.5 ml of phenylhydrazine dissolved in 10 ml of ethanol. The mixture was heated to boiling and water added dropwise until all was dissolved. On cooling, 1.99 g (87 %) of the title compound separated out. Recrystallization from aqueous ethanol did not change its IR spectrum. M.p. 102−120°C (decomp.). NMR: *cf.* Table 1. (Found C 58.32; H 4.06; N 12.38. Mol. wt. 228. Calc. for $C_{11}H_9BN_2OS$ (228.1): C 57.92; H 3.98; N 12.28).

6-(p-Carboxyphenyl)-7-hydroxy-7,6-borazarothieno[3,2-c]pyridine. To a hot solution of 3.12 g (0.020 mole) of 3-formyl-2-thiopheneboronic acid in 10 ml of ethanol was added dropwise with stirring a warm solution of 3.2 g (0.021 mole) of *p*-hydrazinobenzoic acid in 2 ml of conc. hydrochloric acid and 50 ml of water. A crystalline precipitate started to form. The mixture was allowed to stand overnight at −20°C, the product (5.2 g, 96 %) was filtered off, washed with water and dried. Recrystallization from glacial acetic acid did not change the IR spectrum and yielded 4.5 g (83 %) of the title compound

in white crystals, m.p. 235—237°C. NMR: *cf.* Table 1. (Found C 53.39; H 3.38; N 10.32. Mol. wt. 272. Calc. for $C_{12}H_9BN_2O_3S$ (272.1): C 52.97; H 3.33; N 10.29).

6-(o-Carboxyphenyl)-7-hydroxy-7,6-borazarothieno[3,2-c]pyridine lactone. To 1.56 g (0.010 mole) of 3-formyl-2-thiopheneboronic acid in 20 ml of ethanol was added dropwise with stirring a hot solution of 2.0 g (0.011 mole) of *o*-hydrazinobenzoic acid hydrochloride in 10 ml of water. A crystalline precipitate started to form. The mixture was allowed to stand overnight at —20°C, the product (2.48 g, 97 %) was filtered off, washed with water and dried. Recrystallization from ethanol did not change the IR spectrum and yielded 1.48 g (58 %) of the title compound in colourless crystals, m.p. 197—200°C. (Found: C 56.51; H 2.95; N 11.10. Mol. wt. 254. Calc. for $C_{12}H_7BN_2O_2S$ (254.1): C 56.72; H 2.78; N 11.02).

4-Hydroxy-5-methyl-4,5-borazarothieno[2,3-c]pyridine. To 15.6 g (0.10 mole) of 2-formyl-3-thiopheneboronic acid [1] in 100 ml of hot ethanol was added dropwise 8 ml of methylhydrazine in 20 ml of ethanol and the reaction mixture worked-up as described above for the isomeric compound. Recrystallization from aqueous ethanol yielded 13.5 g (81 %) of the title compound in colourless crystals, m.p. 115—135°C. Cooling the sample and reheating gave m.p. of 172—175°C. NMR: *cf.* Table 2. (Found: C 43.26; H 4.26; N 16.83. Mol. wt. 166. Calc. for $C_6H_7BN_2OS$(166.0): C 43.41; H 4.25; N 16.87).

5-(p-Carboxyphenyl)-4-hydroxy-4,5-borazarothieno[2,3-c]pyridine. To 3.12 g (0.020) mole of 2-formyl-3-thiopheneboronic acid in 50 ml of hot ethanol was added 3.2 g (0.021 mole) of *p*-hydrazinobenzoic acid and the mixture worked-up as described above for the isomeric compound. Recrystallization of the crude product (5.1 g, 94 %) from glacial acetic acid yielded 4.5 g (83 %) of the title compound in colourless crystals, m.p. 258—260°C. NMR: *cf.* Table 2. (Found: C 52.61; H 3.35; N 10.40. Mol. wt. 272. Calc. for $C_{12}H_9BN_2O_3S$ (272.1): C 52.97; H 3.33; N 10.29).

5-(o-Carboxyphenyl)-4-hydroxy-4,5-borazarothieno[2,3-c]pyridine lactone. 1.56 g (0.010 mole) of 2-formyl-3-thiopheneboronic acid and 2.0 g (0.011 mole) of *o*-hydrazinobenzoic acid were reacted as described above for the preparation of the isomeric compound. Recrystallization from ethanol yielded 1.1 g (43 %) of the title compound in colourless crystals, m.p. 214—215°C. (Found: C 57.01; H 2.98; N 11.03. Mol. wt. 254. Calc. for $C_{12}H_7BN_2O_2S$ (254): C 56.72; H 2.78; N 11.02).

3-Formyl-2-thiopheneboronic acid-2,4-dinitrophenylhydrazone. To 0.39 g (2.5 mmole) of 3-formyl-2-thiopheneboronic acid in 5 ml of ethanol was added dropwise with stirring 0.52 g (2.6 mmole) of 2,4-dinitrophenylhydrazine in a mixture of 10 ml of ethanol and 1 ml of conc. sulphuric acid. An orange crystalline precipitate was obtained in quantitative yield. Recrystallization from aqueous ethanol did not change its IR spectrum and yielded 0.50 g (60%) of the title compound in orange coloured crystals, m.p. 250—253°C (decomp.). (Found: C 40.23; H 2.78; N 16.62. Calc. for $C_{11}H_9BN_4O_6S$ (336.1): C 39.31; H 2.70; N 16.66).

2-Formyl-3-thiopheneboronic acid-2,4-dinitrophenylhydrazone. From 2-formyl-3-thiopheneboronic acid applying the same procedure as above, the title compound was obtained as orange crystals in 54 % yield after recrystallization from aqueous ethanol, m.p. 265—270°C (decomp.). (Found: C 39.54; H 2.96; N 16.80. Calc. for $C_{11}H_9BN_4O_6S$ (336.1): C 39.31; H 2.70; N 16.66).

4-Formyl-3-thiopheneboronic acid-2,4-dinitrophenylhydrazone. The same procedure applied to 4-formyl-3-thiopheneboronic acid [1] yielded 0.54 g (64 %) of orange crystals, m.p. 260—270°C (decomp.). In spite of repeated recrystallizations a satisfactory analysis could not be obtained. (Found: C 38.15; H 2.56; N 15.80. Calc. for $C_{11}H_9BN_4O_6S$ (336.1): C 39.31; H 2.70; N 16.66).

7-Hydroxy-6-methyl-7,6-borazarothieno[3,4-c]pyridine. To 3.12 g (0.020 mole) of 4-formyl-3-thiopheneboronic acid in 20 ml of ethanol was added dropwise with stirring 1 ml of methylhydrazine. Evaporation of solvent yielded a crystalline residue which was recrystallized from aqueous ethanol yielding 2.0 g (60 %) of the title compound in colourless crystals, m.p. 110—120°C. NMR (DMSO): $\tau_{OH} = 1.26$ ppm, $\tau_1 = 1.60$ ppm, $\tau_3 = 1.96$ ppm, $\tau_4 = 2.01$ ppm, $\tau_{CH_3} = 6.53$ ppm, $J_{13} = 3.0$ c/s, $J_{14} = 0.9$ c/s. In spite of repeated recrystallizations a satisfactory elementary analysis could not be obtained although NMR and mass-spectra clearly show that the title compound is the main product. (Found: C 41.47; H 4.08; N 15.80. Mol. wt. 166. Calc. for $C_6H_7BN_2OS$ (166.0): C 43.41; H 4.25; N 16.87).

7-Methyl-7,6-borazarothieno[3,2-c]pyridine. 6.08 g (0.040 mole) of 7-hydroxy-7,6-borazarothieno[3,2-c]pyridine was refluxed for 6 h with 150 ml of butanol in a flask connected with a Dean-Stark trap. Excess butanol was removed *in vacuo* and the remaining oil was dissolved in 200 ml of anhydrous ether and cooled to 0°C. To this solution was transferred with nitrogen 100 ml of 1 N ethereal methylmagnesium iodide cooled to 0°C. A yellowish precipitate was formed. The mixture was refluxed for one hour and then poured into 200 ml of cold 1 N hydrochloric acid. The ether phase was separated, the aqueous layer neutralised to pH 7 with solid sodium bicarbonate and then extracted twice with ether. The combined ether phase was dried and evaporated *in vacuo*, leaving a crystalline residue. Crystallization from aqueous ethanol yielded 4.3 g (70 %) of 7-methyl-7,6-borazarothieno[3,2-c]pyridine in colourless needles, m.p. 80.5—82.5°C. NMR-spectrum: *cf.* Table 1. (Found: C 48.29; H 4.82; N 18.91. Mol. wt. 150. Calc. for $C_6H_7BN_2S$ (150.0): C 48.04; H 4.71; N 18.67).

4-Methyl-4,5-borazarothieno[2,3-c]pyridine. From 6.08 g (0.040 mole) of 4-hydroxy-4,5-borazarothieno(2,3-c]pyridine, butanol, and 0.10 mole of methylmagnesium iodide solution, the title compound was obtained in the same way as described above. Recrystallizing the crude product (5.2 g, 87 %) from ethanol yielded 3.8 g (63 %) of analytically pure 4-methyl-4,5-borazarothieno[2,3-c]pyridine as pale yellow needles, m.p. 62—63°C, having the same IR spectrum as the crude product. NMR: *cf.* Table 2. (Found: C 48.07; H 4.57; N 18.87. Mol. wt. 150. Calc. for $C_6H_7BN_2S$ (150.0): C 48.04; H 4.71; N 18.67).

4,5-Dimethyl-4,5-borazarothieno[2,3-c]pyridine. From 11.5 g (0.070 mole) of 4-hydroxy-5-methyl-4,5-borazarothieno[2,3-c]pyridine, 150 ml of butanol and 0.175 mole of ethereal methylmagnesium iodide, the title compound was obtained in the same way as described above. As the residue after evaporation of the ether did not crystallize, it was distilled *in vacuo* yielding 7.8 g (68 %) of 4,5-dimethyl-4,5-borazarothieno[2,3-c]pyridine, b.p. 59—70°/0.01 mm Hg. A fraction b.p. 62—64°/0.01 mm Hg, $n_D^{18} = 1.6008$, was analysed. NMR: *cf.* Table 2. (Found: C 51.08; H 5.58; N 17.17. Mol. wt. 164. Calc. for $C_7H_9BN_2S$ (164.0): C 51.27; H 5.53; N 17.07).

4-Butyl-4,5-borazarothieno[2,3-c]pyridine. From 1.3 g (0.008 mole) of 4-hydroxy-4,5-borazarothieno[2,3-c]pyridine, butanol and 0.05 mole of ethereal butylmagnesium bromide, the title compound was obtained as described above. Recrystallization from aqueous ethanol yielded 0.5 g (33 %) of 4-butyl-4,5-borazarothieno[2,3-c]pyridine as pale yellow needles, m.p. 56.5—57.5°C NMR: *cf.* Table 2. (Found: C 56.24; H 6.39; N 14.82. Mol. wt. 192. Calc. for $C_9H_{13}BN_2S$ (192.1): C 56.27; H 6.82; N 14.58).

3-Thiophenealdehyde azine. To 1.0 g of 3-thiophenealdehyde in a mixture of 10 ml of ethanol and 10 ml of ether was added 1.0 ml of 99 % hydrazine in 5 ml of ethanol. The reaction mixture was evaporated to dryness and the residue recrystallized from aqueous methanol, yielding 0.89 g (90 %) of the crystalline title compound, m.p. 153—154°C. (Found: C 54.49; H 3.67; N 12.95; S 28.87. Calc. for $C_{10}H_8N_2S_2$ (220.3): C 54.52; H 3.66; N 12.71; S 29.11).

3-Thiophenealdehyde methylhydrazone. 11.2 g (0.10 mole) od 3-thiophenealdehyde was dissolved in ethanol and refluxed for 2 h with excess methylhydrazine. Distillation *in vacuo* yielded 9.0 g (64 %) of the methylhydrazone, b.p. 135—137°/13 mm Hg, $n_D^{25} = 1.6347$. NMR (DMSO): $\tau_{CH} = 2.44$ ppm, $\tau_{thiophenic} = 2.60$ ppm, $\tau_{N-CH_3} = 7.18$ ppm. (Found: C 51.35; H 5.59; N 19.01; S 22.05. Calc. for $C_6H_8N_2S$ (140.2): C 51.40; H 5.75; N 19.97; S 22.87).

Protodeboronation of formylthiopheneboronic acid: In conc. hydrochloric acid: 1.0 g of 2-formyl-3-thiopheneboronic was refluxed for 2 h with 20 ml of conc. hydrochloric acid. After cooling to room temperature the solution was extracted three times with 50 ml portions of ether. The combined ether phase was dried over magnesium sulphate and the ether evaporated *in vacuo*. The crystalline residue (0.65 g, 65 %) was shown by IR-spectroscopy to be idential with the starting material. Treating 4-formyl-3-thiopheneboronic acid in the same way yielded 0.47 g (47 %) of starting material. Treating 3-formyl-2-thiopheneboronic acid in the same way afforded an oil which was identified by IR as 3-thiophenealdehyde. The characteristic peaks of the starting acid were absent in the IR spectrum of the product.

In water. 1.0 g of 2-formyl-3-thiopheneboronic acid in 50 ml of water was refluxed for 24 h and worked up as above, yielding 0.80 g (80 %) of the starting acid as identified by IR.

Treating 4-formyl-3-thiopheneboronic acid in the same way afforded 0.50 g (50 %) of this acid. The same treatment given to 3-formyl-2-thiopheneboronic acid yielded an oil identified by IR as 3-thiophenealdehyde. No acid could be detected.

2 N sodium hydroxide. 1.0 g of 2-formyl-3-thiopheneboronic acid in 50 ml of 2 N sodium hydroxide was refluxed for 2 h. The resulting dark mixture was cooled and extracted three times with 75 ml portions of ether. The combined ether phase was dried and evaporated to dryness. An oil was obtained which was identified by IR as 2-thenyl alcohol. The *α-naphthyl urethane* had m.p. 145—147°C. (Lit. value [17] m.p. 148). The IR spectrum of the product had weak absorption at 6.0 μ indicating the presence of small amounts of 2-thiophenealdehyde, which was verified by the addition of 2,4-dinitrophenylhydrazine reagent.

The aqueous layer from the hydrolysis was acidified with hydrochloric acid to pH 1 and extracted with three 50 ml-portions of ether. The combined ether phase was dried over magnesium sulphate and evaporated *in vacuo* to dryness, giving 0.314 g (75 %) of 2-thiophenecarboxylic acid, m.p. 124—128°C, having the same IR spectrum as an authentic sample. Literature value [18] m.p. 129—130°C.

The same treatment given to *4-formyl-3-thiopheneboronic acid* yielded 3-thenyl alcohol; the α-naphthyl urethane had m.p. 131—133°C. (Lit. value [19] m.p. 132—133°C) and 0.247 g (60 %) of 3-thiophenecarboxylic acid, m.p. 132—138°C. (Lit. value [20] m.p. 138°C).

The same treatment given to 3-formyl-2-thiopheneboronic acid yielded 3-thenyl alcohol (naphthyl urethane, m.p. 131—133°C) and 0.366 g (90 %) of 3-thiophenecarboxylic acid, m.p. 134—138°C.

2-Formyl-3-thiopheneboronic acid (0.5 g) was dissolved in 25 ml of 2 N sodium hydroxide and the mixture worked up after standing at room temperature for 24 h. No residue was obtained from the ether extract of the alkaline solution. From the ether extract of the acidic solution, 0.34 g (68 %) of 2-formyl-3-thiopheneboronic acid was recovered.

Treating 4-formyl-3-thiopheneboronic acid in the same way gave 0.35 g (70 %) of the starting material.

Upon treating 3-formyl-2-thiopheneboronic acid in the same way the characteristic smell of 3-thiophenealdehyde could be noticed after a few minutes. The same work-up as described above yielded 3-thenyl alcohol and 0.165 g (80 %) of 3-thiophenecarboxylic acid, identified as described above.

Acid hydrolysis of borazarothienopyridines. General procedure. 1.0 g material in 25 ml of conc. hydrochloric acid or in 50 ml of 2 N hydrochloric acid was refluxed for 2 h. After cooling to room temperature, the mixture was neutralised to pH 7 through addition of solid sodium bicarbonate, which caused precipitation. The products were identified by IR-spectroscopy.

When Ia and IVa were refluxed with conc. hydrochloric acid or 2 N hydrochloric acid and worked up as described above, the starting material was recovered in 82—84 % yield in all cases.

When VIII and IXa were treated with conc. hydrochloric acid, starting material was recovered in 85 % and 74 % yield, respectively. In addition, small amounts of a mixture of the respective B-methyl and B-hydroxyl derivatives were precipitated when adjusting the pH to 7.

When IXb was refluxed with conc. hydrochloric acid, only Ib was obtained when neutralizing the mixture.

IIa was refluxed with 2 N hydrochloric acid. Upon cooling, 0.82 g (81 %) of 4-formyl-3-thiopheneboronic acid azine was obtained, which decomposed on heating. NMR (DMSO): τ_{OH} = 5.50 ppm, τ_{CH} = 0.95 ppm, $\tau_{2,5}$ = 1.53 ppm — 1.73 ppm, J_{25} = 3.0 c/s. (Found: C 39.50; H 3.48; N 8.96. Calc. for $C_{10}H_{10}B_2N_2O_4S_2$ (308.0): C 38.99; H 3.27; N 9.09). Extraction of the filtrate with ether and evaporation of the dried ether extract yielded traces of 4-formyl-3-thiopheneboronic acid.

When IIa in conc. hydrochloric acid was refluxed, no precipitate was obtained upon cooling. Extraction with ether and evaporation to dryness of the ether phase yielded 10 mg of 4-formyl-3-thiopheneboronic acid. Neutralization of the aqueous phase to pH 7

caused 0.84 g (84 %) of starting material to precipitate out. If water was added to the strongly acidic solution after extraction with ether, 0.81 g (81 %) of 4-formyl-3-thiopheneboronic acid azine precipitated out.

When Ib was refluxed with 2 N hydrochloric acid, and after cooling to room temperature, the pH was adjusted to pH 6, 1.06 g (80 %) of a compound precipitated out. This compound was either 2-formyl-3-thiopheneboronic acid methylhydrazone hydrochloride (A) or 4-hydroxy-5-methyl-4,5-borazarothieno[2,3-c]pyridine hydrochloride monohydrate (B). M.p. 225—228°C after recrystallization from ethanol. NMR (DMSO): τ_{NH} (A) or τ_{OH} (B) = −2.20 ppm, τ_{CH} = 0.50 ppm, $\tau_{2,3}$ = 1.43 − 1.76 ppm, $\tau_{N\text{-}CH_3}$ = 5.72 ppm, J_{23} = 5.0 c/s. (Found: C 32.89; H 4.66; N 12.76. Calc. for $C_6H_9BN_2O_2S.HCl$ (220.5): C 32.68; H 4.57; N 12.07).

Alkaline hydrolysis of borazarothienopyridines. General procedure: 1.0 g of substrate was dissolved in 50 ml of 2 N sodium hydroxide, the reaction mixture was refluxed for 2 h, cooled to room temperature, and then worked up by the following procedures.

A. If this treatment caused precipitation, the crystals were filtered off and characterised.

B. If this treatment caused oily material to separate, the mixture was extracted with ether, the ether extract was dried over magnesium sulphate and the solvent evaporated *in vacuo*.

C. The filtrate or the water phase was neutralized to pH 7 with conc. hydrochloric acid. If precipitation occurred, the crystals were filtered off and characterised.

D. The filtrate was acidified to pH 1 with conc. hydrochloric acid and then extracted with ether. The ether phase was dried over magnesium sulphate and the solvent evaporated *in vacuo*.

The products were identified by IR-spectroscopy and melting points.

Result: Ia and Ib both gave 0.75 g (75 %) of starting material, while Ic yielded 0.81 g (92 %) of 2-thiophenealdehyde phenylhydrazone, m.p. 128—135°C. (Lit. value [22] m.p. 134—135°C).

IXa gave 0.70 g (70 %) of starting material, and from the ether extracts of the acidified solution. 0.05 of a mixture of Ia and IXa were obtained.

IXb gave 0.32 g (32 %) of Ib as the only isolated product.

IVa gave 0.52 g (71 %) of 3-thiophenealdehyde azine, m.p. 150—154°C, as the only isolated product. Addition of benzaldehyde, dissolved in ethanol, to the aqueous phase yielded 0.43 g (63 %) of benzaldehyde azine, m.p. 87—90°C. (Lit. value [21] m.p. 93°C). When allowing a solution of 1.0 g of IVa in 50 ml of 2 N sodium hydroxide to stand for 24 h at room temperature, 0.87 g (87 %) of the starting material was recovered upon working up in the usual manner.

VII yielded 0.58 g (79 %) of 3-thiophenealdehyde azine.

IVb gave 3-thiophenealdehyde methylhydrazone. When the isolated methylhydrazone was dissolved in a little ethanol and allowed to stand, 0.06 g of 3-thiophenealdehyde azine crystallized out. In addition, traces of 3-thiophenecarboxylic acid were isolated upon evaporation of the ether extract obtained after acidifying the water phase.

IVc yielded 0.83 g (93 %) of 3-thiophenealdehyde phenylhydrazone, m.p. 131—135°C. (Lit. value [23] m.p. 138°C).

IIa gave 0.20 g (28 %) of 3-thiophenealdehyde azine and 0.49 g (48 %) of 4-formyl-3-thiopheneboronic acid azine.

After refluxing IIa with 2 N sodium hydroxide for 10 h, only 3-thiophenealdehyde azine was isolated, IIb gave 3-thiophenealdehyde methylhydrazone.

NMR-spectra were recorded with a Varian A—60 NMR spectrometer. Chemical shifts are given as τ-values, tetramethyl silane serving as internal standard. IR-spectra were recorded on a Beckman IR-5 A infrared spectrophotometer. The elementary analyses were carried out by Miss Ilse Beetz, Mikroanalytisches Laboratorium, Kronach. Mass-spectra were obtained using an LKB—9000 mass-spectrometer.

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