The Tautomeric Structures of Some Alkylsubstituted 3-Hydroxythiophenes

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It has been shown earlier by NMR-spectroscopy that most 2-hydroxythiophenes exist as $\alpha\beta$- and $\beta\gamma$-unsaturated γ-thiolactones.[1-4] The investigation is now extended to the tautomeric structure of 3-hydroxythiophenes, which hitherto are little known.[5]

The 3-hydroxythiophenes can be prepared by hydrogen peroxide oxidation of the carbon-boron bond of the corresponding thiopheneboronic acids. This method for the preparation of the hydroxythiophenes gives acceptable yields and has also been used for the preparation of the corresponding acetates.

The IR-spectrum of unsubstituted 3-hydroxythiophene has been interpreted by Ford and Mackay[6] to show that it exists as a mixture of both the hydroxy and the oxo forms. Due to the great instability of this compound, it has not yet been possible to determine the proportion between the two forms by NMR-spectroscopy. In order to get a more stable system, a methyl group was introduced into the 2-, 4- and 5-position, respectively. Of the compounds so obtained the 2-isomer appeared to be the most stable. Its NMR-spectrum showed a tautomeric mixture consisting of 80 % of 2-methyl-3-hydroxythiophene and 20 % of 2-methyl-4-thiolen-3-one (I). When the 2-substituent is *tert.* butyl the amount of the enol form is reduced to 55 % (III). The oxo form is even more favoured when there is a methyl group in both the 2- and 5-position (III). Then the composition is 70 % of 2,5-dimethyl-4-thiolen-3-one and 30 % of 2,5-dimethyl-3-hydroxythiophene. This variation in the proportions of the tautomeric mixtures is in agreement with the expected hyperconjugative effect of the substituents.

The 2-methyl-3-hydroxythiophene system, in contrast to the two other compounds described above, is rapidly converted into a dimer as indicated by mass-spectroscopy. The structure of this

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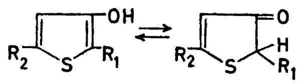
Table 1. τ-Values (ppm) and ring coupling constants (c/s) of the hydroxy forms in carbon disulphide solution.

Compound	H_4	H_5	OH	R_1	R_2	J_{45}
2-Methyl-3-hydroxythiophene	3.57	3.28	3.79	7.85		5.5
2-*tert.*-Butyl-3-hydroxythiophene	3.55	3.35	3.63	8.68		5.5
2,5-Dimethyl-3-hydroxythiophene	3.85	—	3.35	7.91	7.75	—

Table 2. τ-Values (ppm) and ring coupling constants (c/s) of the 4-thiolen-3-one forms in carbon disulphide solution.

Compound	H_4	H_5	H_2	R_1	R_2	J_{45}
2-Methyl-4-thiolen-3-one	3.93	1.72	6.47	8.54		6.0
2-*tert.*-Butyl-4-thiolen-3-one	4.00	1.79	6.60	8.96		6.2
2,5-Dimethyl-4-thiolen-3-one	4.15	—	6.32	8.56	7.67	—

dimer and the mechanism for the dimerisation is under investigation.



I	80	20
II	55	45
III	30	70

I $R_1 = CH_3$, $R_2 = H$
II $R_1 = t\text{-}Bu$, $R_2 = H$
III $R_1 = R_2 = CH_3$

Experimental. 2-Methyl-3-hydroxythiophene. 49 g of butyl borate in 150 ml absolute ether was added in a single portion to 2-methyl-3-thienyllithium which had been prepared from 160 ml 1.05 N butyllithium and 26.5 g (0.15 mole) of 2-methyl-3-bromothiophene[7] in 100 ml absolute ether at $-70°$. The mixture was stirred at $-60°$ for 4 h and then allowed to warm slowly to 0°. The reaction mixture was decomposed with 120 ml of cold 2 N hydrochloric acid. The aqueous layer was extracted twice with ether and the combined ethereal phases were extracted with 100 ml of cold 2 N sodium hydroxide solution. Acidification of the alkaline solution with cold 2 N sulphuric acid gave the boronic acid which was immediately dissolved in ether.

90 ml of 10 % hydrogen peroxide solution was added with stirring at room temperature to the ethereal boronic acid under nitrogen. When the addition was complete the mixture was refluxed for half an hour, and after cooling the layers were separated. The water layer was extracted with ether and the combined ethereal phases were washed five times with 15 ml portions of cold water, or until the water phase did not oxidize ferrous ammonium sulphate, and dried over magnesium sulphate. Distillation *in vacuo* under nitrogen yielded 8.3 g (49 %) of the tautomeric 2-methyl-3-hydroxythiophen (I) b.p. 92–98°/12 mm Hg, $n_D^{20} = 1.5460$. *Acetate* b.p. 86°/10 mm Hg, $n_D^{20} = 1.5123$. (Found: C 53.60; H 5.08; S 20.33. Calc. for $C_7H_8O_2S$ (156.19): C 53.82; H 5.16; S 20.53).

The NMR-spectra were recorded in carbon disulphide solution on a Varian Associate model HR 60 high resolution spectrometer.

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Studies on the Chemistry of Lichens

22* The Chemistry of the Genus *Siphula*. I

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The lichen genus *Siphula* has its main distribution in the southern hemisphere although one species, *S. ceratites*, occurs mainly in northern Scandinavia. The genus consists only of sterile species and hence the taxonomical questions are far from simple. A thorough chemical investigation might therefore, in this case, be of special value. So far, only *S. ceratites* has been chemically investigated by Bruun[1] and by Lindberg *et al.*[2] Recently Miss Annick Mathey has made an independent investigation of some species belonging to the genus *Siphula* using Asahina's microcrystallisation method.[3]

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