

the spectrum of the acid form. This indicates changes in the double bond structure of the pyridine nucleus or possibly in the C=N bond of the oxime group. Both of these possibilities support a contribution of structure III.

The dipole moment and infrared data indicate that the basic form of a N-methylpyridinium-2-aldoxime salt is a resonance hybrid of structures II and III, and that the ionized form predominates, but that the contribution of the quinoid structure is obvious.

*Experimental.* The preparation of the basic form of N-methylpyridinium-2-aldoxime was performed by means of an anion-exchanger (Dowex 2, 20–50 mesh). The column was regenerated by 0.5 M sodium hydroxide solution and washed with methanol. A solution of 5 g of the iodide (2-PAM) in 500 ml of methanol was introduced into the anion-exchanger and the flow rate was kept at about one drop/sec. The dark yellow eluate was concentrated by evaporation under vacuum to a volume of 75–100 ml. By addition of ether to the concentrated solution the basic form was precipitated. The precipitate was filtered off and purified by repeated reprecipitations. Because the product is discoloured by air and light, it had to be dried in a dark vacuum-exsiccator. Yield 50 %. (Found: C 61.5; H 5.86. Calc. for  $C_7H_8N_2O$ : C 61.8; H 5.92).

*Dipole moment measurements.* Preliminary experiments showed that the solubility of the basic form was very low in benzene and carbon tetrachloride but about 2.5 % in chloroform. Because of its slight solubility in nonpolar solvents an accurate determination of its dipole will not be successful. Thus for the calculation of the dipole moment the simplified method described by Guggenheim<sup>6</sup> will give a sufficient accuracy. The dielectric constants of five different concentrations of the compound in chloroform were determined by means of a "Dekameter 03" (Dr. N. Slevogt, Germany) at 25°C. In order to check the method of calculation and the instrument, the dipole moment of p-nitrosodimethylaniline was determined. It was found to be 5.5 D in chloroform solution and 7.1 D in benzene solution. The latter value agrees well with 6.9 D which has been given by Le Fèvre<sup>7</sup> for this compound in benzene solution.

*Infrared spectrophotometric measurements.* The infrared spectra of the basic form of N-methylpyridinium-2-aldoxime and of its iodide were recorded between 2 and 11  $\mu$  on a Perkin-Elmer spectrophotometer, Model 21. The pellet

technique was used, and 1 mg of sample was ground mechanically with 300 mg of potassium bromide.

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## Unsaturated $\gamma$ -Thiolactones II\*. The Structures of 3- and 4-Methyl-2-thienols

ANNA-BRITTA HÖRNFELDT and  
SALO GRONOWITZ

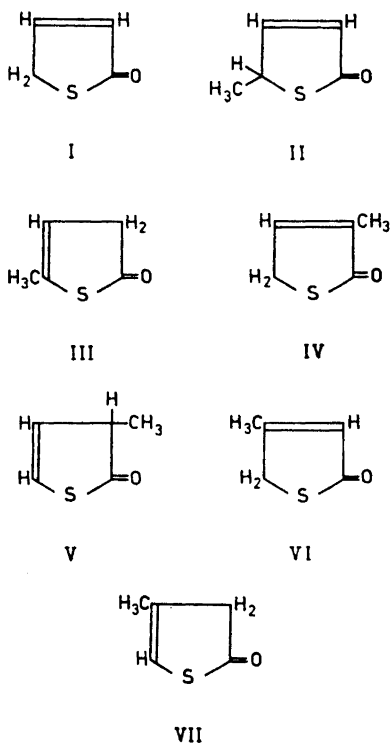
*Institute of Chemistry, University of Uppsala,  
Uppsala, Sweden*

It has earlier been shown by NMR-studies that 2-thienol exists in the liquid state as 3-thiolen-2-one (I), and that two tautomeric thiolactone forms of 5-methyl-2-thienol can be prepared, both of which rearrange to an equilibrium mixture consisting of 85 % 5-methyl-3-thiolen-2-one (II) and 15 % 5-methyl-4-thiolen-2-one (III)<sup>1</sup>.

We have now extended the investigation of the tautomeric structure of hydroxythiophenes to the two remaining methyl substituted 2-thienols. 3-Methyl-2-thienol was obtained in good yield through hydrogen peroxide cleavage<sup>2</sup> of 3-methyl-2-thiophenboronic acid, which has been prepared through the reaction of 3-methyl-2-thiophenemagnesium bromide with butyl borate. In a similar way, 4-methyl-2-thienol contaminated with smaller amounts of the

\* Part I. Ref.<sup>1</sup>

3-methyl isomer was obtained through metalation of 3-methylthiophene with butyllithium<sup>3</sup> followed by the reaction with butyl borate and peroxide oxidation. This method for the preparation of hydroxythiophenes gives acceptable yields and has also been used by us for the preparations of 2-thienol and the tautomeric forms of 5-methyl-2-thienol, as well as for the preparation of the acetate of the very unstable 3-hydroxythiophene, which was obtained in 30 % yield calculated on 3-bromothiophene. Hydroxythiophenes appear to be available also through acid-catalyzed dealkylation of *t*-butoxythiophenes<sup>4</sup>.



The NMR-spectrum at 60 Mc/s showed that 3-methyl-2-hydroxythiophene exists as 3-methyl-3-thiolen-2-one (IV). Its spectrum showed three bands at  $\tau = 2.70$  ppm,  $\tau = 6.03$  ppm and  $\tau = 8.07$  ppm, with relative intensities of 1:2:3, respectively, and belong thus to the CH-, CH<sub>2</sub>- and CH<sub>3</sub>-groups of (IV). From the completely resolved spectrum the following coupling constants are obtained:

$J_{\text{CH}-\text{CH}_2} = 1.5$  c/s,  $J_{\text{CH}-\text{CH}_3} = 3.0$  c/s and  $J_{\text{CH}_2-\text{CH}_3} = 1.9$  c/s.

The spectrum of 4-methyl-2-hydroxythiophene consists of three bands at  $\tau = 3.89$  ppm,  $\tau = 5.98$  ppm and  $\tau = 7.77$  ppm with the relative intensities of 1:2:3. The coupling constants are  $J_{\text{CH}-\text{CH}_2} = 1.5$  c/s,  $J_{\text{CH}-\text{CH}_3} = 1.5$  c/s and  $J_{\text{CH}_2-\text{CH}_3} = 0.75$  c/s. From the relative intensities alone it is impossible to determine whether this compound exists as (VI) or (VII). Through a comparison of the chemical shifts of the CH<sub>3</sub>-group in this compound and in (I-IV) and of the coupling constants it is evident that this compound is 4-methyl-3-thiolen-2-one (VI). In contrast to the case of the 5-methyl isomer it has not yet been possible to obtain the other thiolactone form (V) of 3-methyl-3-thiolen-2-one by acidifying an alkaline solution.

(IV) reacted in its enol form to give esters and could also be condensed with benzaldehyde in the 5-position to give 5-benzylidene-3-methyl-3-thiolen-2-one.

**Experimental.** *3-Methyl-3-thiolen-2-one.* The Grignard reagent from 35.5 g (0.2 mole) of 3-methyl-2-bromothiophene<sup>5</sup> was added dropwise to 46.4 g (0.2 mole) of butyl borate in 80 ml absolute ether under nitrogen at  $-70^\circ$ . The resulting solution was allowed to warm slowly to  $0^\circ$ . The reaction mixture was decomposed with 120 ml of cold sulphuric acid. The aqueous layer was extracted with 200 ml of 1 N cold NaOH and the alkaline solution was acidified with 2 N cold sulphuric acid. The boronic acid was filtered off and immediately dissolved in 250 ml of ether.

135 ml of 10 % hydrogen peroxide was added with stirring to the ethereal boronic acid under nitrogen. When the addition was complete the mixture was refluxed for one hour and the layers separated. The water layer was extracted with ether and the combined ethereal phases were washed five times with 15 ml of 10 % ferrous ammonium sulphate solution, once with water, and dried over MgSO<sub>4</sub>. Distillation *in vacuo* under nitrogen yielded 9.8 g (43 %) of 3-methyl-3-thiolen-2-one, b.p.  $96-98^\circ/8$  mm Hg, mp.  $35-36^\circ$ . (Found: C 52.13; H 5.25; S 27.80; Calc. for C<sub>5</sub>H<sub>4</sub>OS (114.19): C 52.60; H 5.20; S 28.09).

*5-Benzylidene-3-methyl-3-thiolen-2-one.* 2.3 g (0.02 mole) of 3-methyl-3-thiolen-2-one and 2.2 g (0.02 mole) of benzaldehyde in 20 ml of cold absolute alcohol was treated with gaseous hydrogen chloride yielding 3.0 g (70 %) of 5-benzylidene-3-methyl-3-thiolen-2-one mp.

133–134° (Found: C 70.97; H 4.99; S 15.93. Calc. for  $C_{12}H_{10}OS$  (202.27) C 71.25; H 4.98; S 15.85).

*3-Acetoxythiophene.* 65 g of butyl borate in 170 ml absolute ether was added in a single portion to 3-thienyllithium which had been prepared from 190 ml 1.15 N butyllithium and 32.6 g (0.2 mole) of 3-bromothiophene<sup>6</sup> in 50 ml absolute ether at  $-70^{\circ}$ . The mixture was stirred at  $-60^{\circ}$  for 4 h and the boronic acid<sup>7</sup> isolated and oxidized as above. After the ethereal phases had been washed with ferrous sulphate they were extracted with 80 ml of cold sodium hydroxide solution. The alkaline solution was shaken vigorously for 5 min with crushed ice and 15 ml of acetic anhydride, and then extracted with ether. Distillation *in vacuo* under nitrogen yielded 8.5 g (30 %) of 3-acetoxythiophene b.p.  $82-84^{\circ}/10$  mm Hg  $n_D^{20} = 1.5200$  (Found: C 50.65; H 4.40; S 22.21. Calc. for  $C_6H_6O_2S$  (142.18) C 50.68; H 4.26; S 22.56).

The NMR-spectra were recorded in deuteriochloroform-cyclohexane solution on a Varian Associate model A 60 high resolution spectrometer.

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## A Tetragonal Form of Zirconium Oxide Sulfide, ZrOS

F. JELLINEK

*Laboratory of Inorganic Chemistry, University of Groningen, Netherlands, and Institute of Chemistry, University of Uppsala, Sweden*

In his study of the system Zr–S Schönberg<sup>1</sup> found a tetragonal phase with cell dimensions  $a = 3.55$  Å;  $c = 6.31$  Å and space group  $P 4/nmm-D_{4h}^2$ , to which he ascribed a composition of ZrS and a structure of the *B* 11 type. Several reinvestigations of the system Zr–S have been undertaken since, e.g. by Hahn and co-workers<sup>2</sup>, by McTaggart and Wadsley<sup>3</sup> and by the present author. All these investigators agree that ZrS has a cubic superstructure of the NaCl type; no indications were found for the existence of a tetragonal monosulfide, nor indeed for any tetragonal phase in the system Zr–S. (Tetragonal "Zr<sub>4</sub>S<sub>3</sub>"<sup>2</sup>) has shown to be a ternary phase of composition ZrSiS<sup>4</sup>.)

In view of these discrepancies a re-examination of Schönberg's X-ray diagrams of the system Zr–S was undertaken. It was confirmed that in several of his preparations a tetragonal phase with the dimensions and symmetry derived by Schönberg was present. However, all preparations which contain this phase had been partly oxidized: the tetragonal phase was always accompanied by considerable proportions of cubic ZrOS and in some cases even by ZrO<sub>2</sub>. It seemed probable, therefore, that the tetragonal phase also contains oxygen.

From the symmetry it is evident that the unit cell must contain an even number of all kinds of atoms; from spatial considerations a unit-cell content of  $2 \times$  ZrOS seems the most probable. This hypothesis is strongly supported by the fact the ThOS, UOS and NpOS have the same symmetry and similar cell dimensions as the tetragonal zirconium oxysulfide; the unit cells of ThOS, UOS and NpOS contain two formula units and the structures are of the PbFCl (*E* 0<sub>1</sub>)-type<sup>5</sup>. It seems most probable, therefore, that the alleged tetragonal ZrS is a new modification of ZrOS, and that its structure is also of the PbFCl type. Zr and S are situated in positions 2(c):  $0\frac{1}{2}z$ ;  $\frac{1}{2}0z$ ; oxygen in position 2(a):  $0\ 0\ 0$ ;  $\frac{1}{2}\frac{1}{2}0$ .