

with perpendicular polarization. Experimental and methodical details about this type of linear dichroism studies can be found elsewhere.¹⁻⁴ From the fact that the dichroic ratio $R_D = A(\parallel)/A(\perp)$ increases when passing from 300 to 400 nm, it can be concluded that the transition responsible for the shoulder at about 400 nm has a considerably higher degree of parallel polarization than the transition indicated at higher energy (at least in the visualized range). The extraordinary high R_D (4-5) which has been obtained in a few cases with high stretch ratio (major problem: fragility of film) implies a very high degree of orientation (f is at least 0.5-0.8).^{2,3}

From the high degree of orientation and from our experience of the dependence of the orientation effect on the molecular shape, it can be concluded that the chromophore must be situated on a long molecule, i.e. probably on the PVA molecule itself. The requirement of optical anisotropy in the complex (we assume that the transition is connected with the copper atom) makes us rule out the cubic configurations $\text{Cu}(\text{O}-)_6$ (regularly octahedral) and $\text{Cu}(\text{O}-)_4$ (tetrahedral). There remains *trans*- $\text{Cu}(\text{O}-)_2(\text{NH}_3)_2$ (planar), *trans*- $\text{Cu}(\text{O}-)_2(\text{NH}_3)_4$ and *trans*- $\text{Cu}(\text{O}-)_4(\text{NH}_3)_2$. The last mentioned arrangement might be obtained with four polymer chains parallel to the N-Cu-N axes but is not very probable. In the other alternatives, the O-Cu-O axes should be parallel to the direction of orientation, i.e. parallel to the polymer chain. However, it seems difficult to force a copper atom on the line between two adjacent enol oxygens (assuming the Cu-O distance to be 1.9 Å).^{6,7} As a final alternative there remains the possibility that the discussed band is a product of coupling between a series of transitions along the polymer chain. In that case the individual transitions can be allowed to form non-zero angles to the chain axis but still a chelatic bonding is required unless the transitions are not charge transfers between the copper atoms or between the oxygen atoms along the chain.

If a sheet of PVA is soaked in 20 ml 1 M CuSO_4 and 3 ml 25 % NH_3 for 10 min it will become dark green but will keep its size. However, if CuCl_2 is used instead (the same pH, 9.0) the sheet will expand 1.3 times, and have a gluey appearance. Its colour will be blue, changing to dark green after washing with water, but will thereafter give the same spectrum as the product

obtained from CuSO_4 (Fig. 1). The reasons for these peculiarities have not yet been elucidated but it seems probable that the counter ion may influence the formation of intra- and intermolecular hydrogen bonds.

It should finally be noted that the spectrum of our compound resembles the spectra which have been reported for certain "complexes between cuprammonium and glycosides" (see Ref. 9 and references therein). These have been supposed to be 1:1 complexes but their composition seems still to be unknown.

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Unsaturated γ -Thiolactones

XVI. Alkylation of the Thallium Salt of the 5-Methyl-2-hydroxythiophene System

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In previous work, the 5-methyl-2-hydroxythiophene system was alkylated with methyl iodide and dimethyl sulphate¹ by means of the ion pair extraction method developed by Brändström *et al.*² Using this

method, a large number of different anions may be extracted into a chloroform or methylene chloride phase as the counter ion in an ion pair with the tetrabutylammonium cation (Q). In the methylation with methyl iodide the 3-position of the 5-methyl-2-hydroxythiophene system was found to be the most reactive, giving mono- as well as dialkylated products. However, when the alkylating agent was changed from methyl iodide to dimethyl sulphate, *O*-alkylation was the dominant reaction.

Recently, Pedersen and Lawesson have shown that the thallium salt of the 5-methyl-2-hydroxythiophene system, upon treatment with methyl iodide, gives the same yield and exhibits a reaction pattern similar to that of the alkylation of the Q salt with methyl iodide.³ These results are in contrast to those obtained by Taylor, Hawks and McKillop, who found that the thallium salt of β -dicarbonyl compounds gave mono *C*-alkylated products with alkyl iodides in essentially quantitative yield, even in cases where dialkylation and *O*-alkylation could be competitive reactions.⁴ The results obtained by Pedersen and Lawesson are, however, in accord with our earlier results,⁵ which show that there is a more pronounced tendency toward *C*-alkylation in the 2-hydroxythiophene system than in phenols.

As the Q-salt of the 5-methyl-2-hydroxythiophene system showed different reactivities when treated with methyl iodide and dimethyl sulphate, it was of interest to examine the behaviour of the thallium salt when treated with dimethyl sulphate. In this case, we found that the reaction product consisted of 98 % of 5-methyl-2-methoxythiophene compared to 90 % when the Q salt was treated with dimethyl sulphate. The ion pair extraction method is, however, much more convenient, as the reaction takes place almost instantaneously while the reaction time for the thallium salt was 45 h.

The results of the various alkylations are given in Table 1. It is obvious that the rather large discrepancy between our results and those obtained by Pedersen and Lawesson for the methylation of the thallium salt is due to the different methods of analyzing the reaction product. Pedersen and Lawesson used a thin-layer chromatography technique, whereas we used analytical gas chromatography.

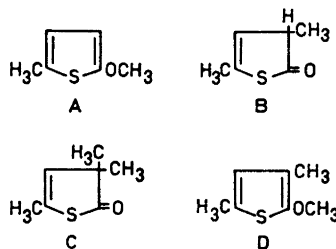
The procedure used for the methylation with methyl iodide, continuous extraction in a Soxhlet apparatus, could not be

applied to the dimethyl sulphate methylation. Even after 94 h no alkylation product could be detected, and the thallium salt was recovered unchanged. This is probably due to the low solubility of the thallium salt and the high boiling point of dimethyl sulphate. The best results were obtained when the reaction was performed as described in the experimental part.

It is thus evident that it is the nature of the alkylating agent and not the ambident carbanion and its counter ion that is the main factor in determining the position of alkylation in the 2-hydroxythiophene system and this might also be possible in the β -diketone systems investigated by Taylor and coworkers.⁴

Table 1. Relative percentage of products in the alkylation of the Q- and thallium salts of the 5-methyl-2-hydroxythiophene system with methyl iodide and dimethyl sulphate.

	A	B	C	D
Q salt methyl iodide ¹	12	86	2	—
Q salt dimethyl sulphate ¹	90	4	2	4
Tl salt methyl iodide ³	10	80	10	—
Tl salt methyl iodide	32	65	3	—
Tl salt dimethyl sulphate	99	1	—	—



Experimental. Methylation of the thallium salt of the 5-methyl-2-hydroxythiophene system with dimethyl sulphate. 12.7 g (0.04 mol) of the

thallium salt of the 5-methyl-2-hydroxythiophene system³ was carefully added to a solution of 10.1 g (0.08 mol) of dimethyl sulphate and 250 ml of dry petroleum ether (b.p. 30–50°). The reaction mixture was refluxed for 45 h with vigorous stirring. After cooling, the reaction mixture was filtered, and VPC analysis showed that the crude product contained 98 % 5-methyl-2-methoxythiophene, 1 % 3,5-dimethyl-3-thiolen-2-one and 1 % 5-methyl-thiolen-2-one. The retention times and spectroscopic data were identical with those of authentic samples.^{5–7} The filtrate was extracted with 2 N sodium hydroxide solution and water and dried over magnesium sulphate. Distillation gave 4.0 g (78 %) of 5-methyl-2-methoxythiophene, b.p. 65–67°/15 mmHg, n_D^{20} = 1.5254 (Lit.:⁸ b.p. 51–52°/10 mmHg, n_D^{17} = 1.5216).

The NMR spectra were obtained with a Varian A–60 high resolution spectrometer. The IR spectra were recorded on a Perkin-Elmer Model 257 instrument. The gas chromatograph used was a Perkin-Elmer 900 analytical instrument with an OV 17 column. The quantitative analyses were calibrated with respect to the sensitivity of the detector for the different compounds.

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