# REACTIONS OF METAL HALIDE-ALKOXIDES

## XXV.* SYNTHESIS OF ESTERS OF THIOPHENE-2,5-DIGLYOXYLIC ACID

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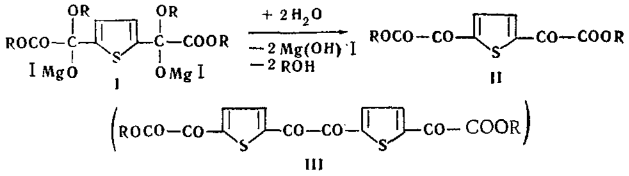
A method has been developed for the synthesis of esters of thiophene-2,5-diglyoxylic acid from iodomagnesium derivatives of thiophene-2,5-dicarbinols. The formation of products of the second stage of the reaction – 2,2'-di(alkoxalyl)-5,5'-oxalyldithiophenes – has also been established. The IR spectra of the compounds obtained have been studied.

As established previously [1-3], halogenomagnesium derivatives of alkoxymethanols containing a thienyl radical have a high thermal stability because of the formation of a coordination bond between the sulfur and magnesium atoms and decompose only at an elevated temperature (110-115°C). These facts concerning thermal stability were obtained on the basis of the method of synthesizing esters of thiophene-2,5-diglyoxylic acid (II) given below.

As is well known, 2,5-diiodothiophene forms diiodomagnesium compounds with a yield reaching 80%. We have established that the reaction of this magnesium derivative of thiophene with esters of oxalic acid under the usual conditions of organomagnesium reactions (at the boiling point of an ethereal solution) forms stable iodomagnesium derivatives of di(alkoxy carbinols) which are converted by hydrolysis into esters of thiophene-2,5-diglyoxylic acid (II). The 2,2'-dialkoxalyl-5,5'-oxalyldithiophenes (III) were obtained as by-products.



Raising the temperature of the reaction to 110-115°C (replacing the ether by toluene) in order to cause the decomposition of the halogenomagnesium derivative of the alkoxy carbinol referred to above and so to obtain esters of thiophene-2,5-diglyoxylic acid did not lead to satisfactory results. The reason for this is, as stated previously [1], the formation of a coordination bond between the sulfur and magnesium atoms, a shift of electrons on the sulfur atom to the magnesium atoms, a probable weakening of the aromatic properties of the thienyl radical, and, as a result of this, the resinification of the product. The results of the investigations are given in Table 1.

In order to confirm the structure of the compounds synthesized, their IR spectra were recorded. The spectrum of thiophene-2,5-diglyoxylic acid, the molecule of which is symmetrical, has the absorption bands only of two carbonyl groups: a ketone group (≈1680 $cm^{-1}$) and an ester carbonyl (≈1740 $cm^{-1}$). Some decrease in the frequency of the absorption of the ketonic carbonyl as compared with [5] is explained by the conjugation of this group with the 2,5-thienylene radical and the increase in this frequency in comparison with esters of $\alpha$-thienylglyoxylic acid is due to the weaker interaction of these groups with the 2,5-thienylene radical because of the competing action of the glyoxylic acid residues.

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*For Communication XXIV, see [7].

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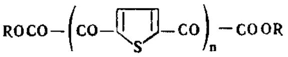
TABLE 1 

| R | $n$ | mp, °C | Empirical formula | S, % |  | Yield, % |
|---|---|---|---|---|---|---|
|  |  |  |  | found | calc. |  |
| $C_2H_5$ | 1 | 61—62 | $C_{12}H_{12}O_6S$ | 11,50 | 11,24 | 48 |
| $C_2H_5$ | 2 | 150—151 | $C_{18}H_{14}O_8S_2$ | 15,31 | 15,18 | 5 |
| $n$-$C_3H_7$ | 1 | 70—71 | $C_{14}H_{16}O_6S$ | 10,58 | 10,26 | 38 |
| $i$-$C_3H_7$ | 1 | 52—53 | $C_{14}H_{16}O_6S$ | 10,47 | 10,26 | 40 |
| $n$-$C_4H_9$ | 1 | 60—61 | $C_{16}H_{20}O_6S$ | 9,62 | 9,42 | 39 |
| $n$-$C_4H_9$ | 2 | 141—142 | $C_{22}H_{22}O_8S_2$ | 13,48 | 13,38 | 6 |
| $i$-$C_4H_9$ | 1 | 63—64 | $C_{15}H_{20}O_6S$ | 9,73 | 9,42 | 45 |
| $i$-$C_4H_9$ | 2 | 157—158 | $C_{22}H_{22}O_8S_2$ | 13,53 | 13,38 | 3 |
| $n$-$C_5H_{11}$ | 1 | 59—60 | $C_{18}H_{24}O_6S$ | 8,82 | 8,70 | 25 |
| $i$-$C_5H_{11}$ | 1 | 67—68 | $C_{18}H_{24}O_6S$ | 8,81 | 8,70 | 29 |

The spectra of the 2,2'-dialkoxalyl-5,5'-oxalyldithiophenes exhibit, besides the absorption bands of the ketonic and ester groups, an absorption band with a maximum at the ≈1670 $cm^{-1}$ ascribed to the stretching vibrations of the $C=O$ groups present between the thiophene rings. In all the spectra there is an absorption band at 3100 $cm^{-1}$ which may be ascribed to the stretching vibrations of the C– H bond of the thienyl radical [6].

## EXPERIMENTAL

The reaction of 2,5-diiodothiophene with magnesium was carried out in the presence of ethyl bromide taken in twofold excess. The reaction mixture separated into layers: the lower layer consisted of thiophene-2,5-di(magnesium iodide) and the upper layer of ethylmagnesium bromide. The lower layer was added to an ethereal solution of oxalic ester taken in equimolecular amount. The resulting mixture was heated for 2 h and was then hydrolyzed with water and 10% hydrochloric acid. A precipitate of 2,2'-dialkoxalyl-5,5'-oxalyldithiophene usually appeared at the boundary between the ethereal and aqueous layers, and this was separated off and purified by recrystallization from carbon tetrachloride. The ethereal layer was separated from the aqueous layer and washed with sodium bicarbonate solution and with water and was then dried with sodium sulfate. After the solvent had been distilled off, the residue was distilled in vacuum and purified by recrystallization from petroleum ether. Hydrolysis of the esters gave thiophene-2,5-diglyoxylic acid with mp 183-184°C (from benzene). Found %: S 13.72; COOH 38.2. $C_8H_4O_6S$. Calculated %: S 14.05; COOH 38.4.

The IR spectra were taken in paraffin oil on an IKS-14 spectrophotometer.

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