

STUDIES IN THE THIOPHENE SERIES. IV.*

ELECTROCHEMICAL BROMINATION IN METHANOLIC AMMONIUM BROMIDE SOLUTION

M. NĚMEC, J. ŠROGL and M. JANDA

*Department of Organic Chemistry,
Institute of Chemical Technology, Prague 6*

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During anodic oxidation of thiophene and 2-acetylthiophene in methanolic ammonium bromide solution bromination takes place under formation of bromo derivatives of thiophene and 2-acetylthiophene without the formation of methoxylated products.

As part of the comparison of the reactivity of furan derivatives with their sulfur analogues we investigated electrochemical oxidation of thiophene and 2-acetylthiophene in methanol in the presence of ammonium bromide. During this reaction in the furan series formation of 2,5-dimethoxy-2,5-dihydrofuran derivatives takes place (with the exception of negatively substituted derivatives). The course of this reaction is explained by the primary formation of bromine by anodic oxidation of bromide anion, its subsequent 1,4-addition to the furan nucleus, and the termination of the reaction by methanolysis¹. The probability that the primary reaction on the electrode is the oxidation of bromide is supported by the fact that the yields of the products are almost independent of the nature of the anode². If the mentioned mechanism is accepted then it is evident that our measurements represent in fact a comparison of the ability of both types of heterocycles for 1,4-addition.

The electrochemical oxidation was carried out under similar conditions as the methoxylation of the furan series³. In the case of thiophene 24% of 2-bromothiophene and 6.4% of 2,5-dibromothiophene were isolated from the reaction mixture in addition to the unreacted thiophene, while 5-bromo-2-acetylthiophene was isolated from the reaction mixture in a 12% yield in addition to the starting substance after the oxidation of 2-acetylthiophene. The results show that in contrast to furan compounds the derivatives of thiophene do not behave as conjugated dienes, but that electrophilic substitution of the thiophene nucleus takes place as in the case of aromatic systems. As the anodic half-wave potentials of thiophene⁴ and furan⁵ are very similar these results may be considered as support for the mechanism of the alkoxylation of furan proposed by Clauson-Kaas and coworkers¹. The course of the reaction comprising

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the formation of methoxyl radicals⁶ is not probable because we were unable to prove the presence of the methoxylated thiophene product in the reaction mixture.

EXPERIMENTAL

Temperature data were not corrected. The PMR spectra were measured on a Tesla BS 477 (60 MHz) spectrometer. Gas chromatographic analyses were carried out with Chrom II using FID, column length 160 cm, diameter 0.6 cm, nitrogen as carrier gas. The electrolytic cell⁷ was composed of a coaxial graphite anode and a nickel cathode and it was cooled externally by a mixture of carbon dioxide-butanol. 2-Acetylthiophene was prepared by a known method⁸ as were also standards of bromothiophenes⁸.

Electrobromination of Thiophene

A solution of 16.8 g (0.2 mol) of thiophene and 20 g of ammonium bromide in 300 ml of methanol was electrolysed at a constant current of 4.0 A and -25 to -35°C for 11 h in the cooling bath. After the end of the electrolysis methanol was eliminated by distillation under reduced pressure and the residue extracted with ether. The extract was dried over magnesium sulfate and evaporated *in vacuo*. The residue was distilled to yield 14.1 g of a product, b.p. $50-90^{\circ}\text{C}/15$ Torr. Its rectification through a filled column gave 7.7 g (24%) of 2-bromothiophene and 3.1 g (6.4%) of 2,5-dibromothiophene, b.p. 151 and 210°C . The products were identified gas chromatographically, by comparison of their elution times with those of standards, using two different fillings (Carbowax 20 M and neopentyl glycol sebacate, both 20% on Chromosorb W). For $\text{C}_4\text{H}_3\text{BrS}$ (163.0) calculated: 29.47% C, 1.85% H, 49.01% Br, 19.67% S; found: 30.30% C, 2.04% H, 48.80% Br, 19.79% S. PMR: 2.75–3.28 τ (m). For $\text{C}_4\text{H}_2\text{Br}_2\text{S}$ (241.9) calculated: 19.86% C, 0.83% H, 66.06% Br, 13.25% S; found: 20.50% C, 1.00% H, 65.61% Br, 13.38% S. PMR: 3.22 τ (s).

Electrobromination of 2-Acetylthiophene

A solution of 12.6 g (0.1 mol) of 2-acetylthiophene and 20 g of ammonium bromide in 300 ml of methanol was electrolysed for 12 h and worked up in the same manner as above. Distillation of the residue gave 7.0 g of a product, b.p. $70-100^{\circ}\text{C}/15$ Torr. Its rectification gave 2.45 g (12%) of 5-bromo-2-acetylthiophene which after crystallisation from heptane had b.p. 90°C . For $\text{C}_6\text{H}_3\text{BrOS}$ (205.1) calculated: 35.14% C, 2.46% H, 38.97% Br, 15.64% S; found: 35.97% C, 2.65% H, 38.50% Br, 15.87% S. PMR: 7.50% τ (3 H, s), 2.92 τ (1 H, d, $J = 4.0$ Hz), 2.58 τ (1 H, d, $J = 4.0$ Hz). The magnitude of the coupling constant and the differences of the chemical shifts of both thiophene protons are, for a given substitution, characteristic of hydrogens in the positions 3 and 4 of the thiophene nucleus⁹.

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