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Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Abstract

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CHEMISTRY

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RADIATION METHOD FOR THE SYNTHESIS OF NEW DERIVATIVES OF HETEROCYCLIC COMPOUNDS

(Presented by Academician S. S. Medvedev on 29 V 1961)

Among methods for the synthesis of heterocyclic compounds, in particular for the thiophene, furan, and similar series, there are no data on the existence of a method consisting in the preparation of substances dimerized with simultaneous hydrogenation of the heteroring in one part and oxidation to an oxoheterocycle in the other. Great prospects in this direction are opened by the use of ionizing radiation for the radiation-chemical synthesis of organic substances in aqueous solutions, in particular heterocyclic compounds.

Fig. 1. Dependence of the concentration of the precipitate on the absorbed dose

Fig. 2. U.-v. spectra: **a** —products of irradiation of thiophene in 5% NaOH, **b** —furan in water; **v**, **g** —in ethanol solution: **v** —22$' 44' *—tetranitro—*55' *—dimethyl—*33' *—dithienyl,* ∗∗*g*∗∗—22' 55' *—tetramethyl—*44' *—dicarboxylicacid* — 33' $-dithienyl

As is known (^{1}), when water is irradiated with ionizing radiation, the OH and H radicals that arise, as well as excited water molecules, are capable of entering into oxidation-reduction reactions with impurities—dissolved substances. However, the nature of the impurities, the products formed, their concentration, and also various conditions may influence whether one process or another is carried out.

Figure 3 and Figure 4

Figure 3: Figure 3 and Figure 4

For our investigation we selected the systems: thiophene—water, furan—water in a ratio of 1:1000. Irradiation was carried out in sealed glass ampoules with Co^{60} γ-radiation at a dose rate from 8 to 648 r/sec. The water (pH 5—7) used for irradiation was purged for one hour with purified nitrogen. The experiments were conducted at room temperature.

In a series of experiments with thiophene—water, the insoluble product formed after irradiation, which was a stable white suspension, was coagulated with sodium chloride and, after centrifugation, dried in vacuo and weighed. The yield of precipitate is equal to 1 mole/100 eV at a dose rate of 648 r/sec. Along with the accumulation of precipitate along OA (Fig. 1), a simultaneous accumulation of a small amount of thienol (2) occurs, then, with increasing

the dose its amount decreases, which indicates the participation of thiophenol molecules in the process of precipitate formation. The precipitate is almost insoluble in nonpolar solvents, but dissolves well in alkaline solutions, in cyclohexanol, in cyclohexanone, and partially in alcohols. The dried precipitate is oxidized by a boiling solution of $KMnO_4$. When the alkaline solution of the precipitate is combined with n-nitroaniline, a yellow coloration is formed, characteristic of oxy compounds.

Figure 2a presents the UV absorption spectra of the precipitate in 5% $NaOH$. For comparison, known (3) UV spectra of substituted $33'$-dithienyls are also given there. Gas analysis showed that the amount of gas evolved (hydrogen), at a dose rate of 8 r/sec, increases with increasing pH of the solution. At pH 0.4, $G_{H_2} = 0.3$ mol./100 eV (Fig. 3, 1).

Fig. 3. Hydrogen yield as a function of dose: 1 —pH 0.4; 2 —pH 9; 3 —in the presence of 10^{-2} M Fe^{2+}

Fig. 4. Nuclear magnetic resonance spectrum of the broad line

With the introduction of Fe^{2+} into the system (10^{-2} M, pH 0.4), the hydrogen yield* increased to 1.2-1.3 mol./100 eV (curve 3).

In the IR spectra** of the precipitate, the following are clearly visible: absorption bands of the thiophene ring at 700 cm^{-1} and 1235 cm^{-1}, of thiophan $—CH_2$ (2860 cm^{-1}) (4), the OH group (3250 cm^{-1}), $—C—O—$ in the system $—C—OH$, and weak bands at 3000 cm^{-1} (aromatic CH) and 1440 cm^{-1} (aliphatic CH) (5). The melting point of the precipitate is $130 \pm 3°C$, and the molecular weight is 186 ± 4.

The experimental data make it possible to propose the following mechanism of the process: first, radicals H and OH add to thiophene molecules

$$C_4H_4S + H^{\cdot} \rightarrow \dot{C}_4H_5S, \qquad C_4H_4S + \dot{O}H \rightarrow \dot{C}_4H_4OHS.$$

Collision of the radicals formed with one another leads to the formation of a hydrogenated product with an added oxy group:

$$\dot{C}_4H_5S + \dot{C}_4H_4OHS \rightarrow SC_4H_5 - C_4H_4OHS \quad \text{(2-hydro-2}'\text{-oxy-33}'\text{-dithienyl)}$$

This scheme is also confirmed by the fact that, upon acceptance of even one of the radicals (tetralin, glycerin, Mn^{7+}, Fe^{2+}, Fe^{3+}, Cu^{1+}, O_2), precipitation is not observed, i.e., the above-mentioned mechanism is suppressed.

The results*** of microanalysis are as follows:

Found, %: C 51.57; H 5.37; S 33.94; O 9.12
Calculated, %: C 51.58; H 5.4; S 34.4; O 8.58

A nuclear magnetic resonance spectrum of the broad line (Fig. 4) of 2-hydro-2′-oxy-33′-dithienyl was recorded.

* The hydrogen analysis was carried out by B. F. Bogatikov.
** The IR spectrum was kindly recorded by N. A. Slovokhotova at the L. Ya. Karpov Institute.
*** The microanalysis of the precipitate was carried out under the direction of A. V. Zimin.

From the series of experiments furan—water, the UV spectrum of the product in water is presented (Fig. 2b). Several other experiments that were carried out make it possible to assume an analogous mechanism in this case as well.

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