

UV absorption spectra of methanol solutions of the compounds were recorded with SF-4 and Spektromom-203 spectrophotometers. The use of other solvents was hindered by the very poor solubility of some of the compounds even in such solvents as dioxane and dichloroethane. In addition, as seen from the data in [11], replacement of the solvents has practically no effect on the character of the spectra of the azomethines. Hydrolysis was carried out in methanol containing concentrated hydrochloric acid at pH 1.5.

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EFFECT OF PROTONATION OF 2,2'-DITHIENYL CARBONYL COMPOUNDS ON THE DIRECTION OF SUBSTITUTION DURING NITRATION

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The nitration of 5-formyl- and 5-acetyl-2,2'-dithienyls by the action of potassium nitrate in 60-95% sulfuric acid solutions was studied. An increase in the acidity of the medium and a decrease in the reaction temperature from +30°C to -30°C lead to an increase in the percentage of the 5'-nitro isomer in the mixture.

The problems involved in the change in the direction of orientation during electrophilic substitution in the thiophene series have been previously elucidated [1]. In particular, Ya. L. Gol'dfarb and co-workers [2, 3] have studied the effect of protonation of the carbonyl group on the direction of substitution during the nitration of 2-formylthiophene and 2-acetylthiophene and have shown that the percentage of the 4-nitro isomer increases as the sulfuric acid concentration increases.

In the case of 5-substituted 2,2'-dithienyls the typical electrophilic substitution reactions take place in the 5' and 3' positions [4], and the ratio of the resulting isomers depends to a considerable extent on the character of the substituent. Thus nitro isomers (5'-NO₂/3'-NO₂) are formed in ratios of 1.58:1 and 1:2, respectively, in the nitration of 5-formyl-2,2'-dithienyl (I) [5] and 5-acetyl-2,2'-dithienyl (II) [6] with copper nitrate in acetic anhydride at 8-10°C.

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TABLE 1. Quantitative Ratios of the 5'-Nitro and 3'-Nitro Isomers in the Nitration of 5-Formyl-2,2'-dithienyl

Sulfuric acid concn., %	Reaction temp., °C	Yield of nitro product, %	5'-Nitro/3'-nitro ratio
60,5	-30	—	—
	-20	—	—
	-10	—	—
	0	13	4.2:1
	+10	16	3.6:1
	+20	21	2.8:1
70,5	+30	32	2.2:1
	-30	25	9.2:1
	-20	30	7.9:1
	-10	36	6.6:1
	0	44	5.8:1
	+10	53	3.6:1
80,0	+20	62	2.6:1
	+30	60	2.4:1
	-30	25	13.7:1
	-20	28	12.5:1
	-10	32	9.8:1
	0	41	8.5:1
90,0	+10	50	7.8:1
	+20	53	7.5:1
	+30	54	7.3:1
	-30	18	20.3:1
	-20	20	18.6:1
	-10	26	17.5:1
95,0	0	37	15.4:1
	+10	46	14.6:1
	+20	49	13.9:1
	+30	47	11.6:1
	-30	20	20.1:1
	-20	21	18.9:1

TABLE 2. Quantitative Ratios of the 5'-Nitro and 3'-Nitro Isomers in the Nitration of 5-Acetyl-2,2'-dithienyl

Sulfuric acid concn. %	Reaction temp., °C	Yield of nitro product, %	5'-NO ₂ /3'-NO ₂ ratio
60,5	-30	—	—
	-20	—	—
	-10	—	—
	0	16	5.4:1
	+10	22	4.3:1
	+20	30	3.6:1
70,0	+30	39	2.8:1
	-30	15	7.5:1
	-20	20	6.8:1
	-10	40	6.0:1
	0	49	5.2:1
	+10	53	4.3:1
80,0	+20	60	3.3:1
	+30	55	2.9:1
	-30	16	9.7:1
	-20	20	9.3:1
	-10	38	8.8:1
	0	54	8.4:1
90,0	+10	62	8.2:1
	+20	66	7.8:1
	+30	59	7.1:1
	-30	23	14.6:1
	-20	35	12.5:1
	-10	40	11.3:1
95,0	0	44	9.9:1
	+10	48	9.3:1
	+20	59	9.1:1
	+30	56	7.8:1
	-30	25	14.5:1
	-20	40	12.5:1

It seemed of interest to us to follow the change in the ratio of the nitro isomers formed during the nitration of 5-formyl- and 5-acetyl-2,2'-dithienyls (I and II) under conditions of protonation of the carbonyl group. The nitration of dithienyls I and II was carried out with potassium nitrate in sulfuric acid solutions of varying concentration, and determined by potentiometry [2]. The experimental results are presented in Tables 1 and 2. It is apparent from the data in the tables that an increase in the sulfuric acid concentration from 70 to 90% at 20°C leads to a considerable increase in the relative percentage of the 5'-nitro isomers (from 2.6:1 to 13.9:1 in the case of dithienyl I, and from 3.3:1 to 9.1:1 in the case of dithienyl II).

In order to explain the results, we carried out the spectrophotometric determination of the ionization constants of I and II with the aid of the Hammett acidity function [7].

It is known that the electron-acceptor properties of substituents are intensified in the protonated form. However, since protonation is a reversible process, both the protonated and neutral forms of the I and II molecules may undergo nitration. The UV spectra of I and II dissolved in sulfuric acid solutions of varying concentration and in an inert solvent (1,2-dichloroethane) (Figs. 1 and 2) provide evidence that both compounds exist primarily in the protonated form even in 80% sulfuric acid. A mixture of protonated and unprotonated forms of I and II is formed when the sulfuric acid concentration is decreased. A similar effect has been observed [2] for 2-formylthiophene and 2-acetylthiophene. On the basis of the UV spectral data and the H_0 values of the sulfuric acid solutions we determined the ionization constants (pK_a) [8], which were found to be -4.8 for I and -4.5 for II. The ratios of the protonated and unprotonated forms in 80% sulfuric acid, calculated from the well-known equation [9], are 99.71/0.29 and 99.86/0.14, respectively. The fact that changing the sulfuric acid concentration from 90 to 95% does not affect the composition of the nitration products makes it possible to assume that, as in the case of 2-formylthiophene and 2-acetylthiophene, the protonated form of I and II is nitrated in these solutions. Protonation of the carbonyl group in 5-acetyl-2,2'-dithienyls leads to greater deactivation of the 3' position than of the 5' position due to weakening of the effect of the substituent during transmission along the conjugated chain, and the more remote (from the acyl group) 5' position proves to be the more active site for

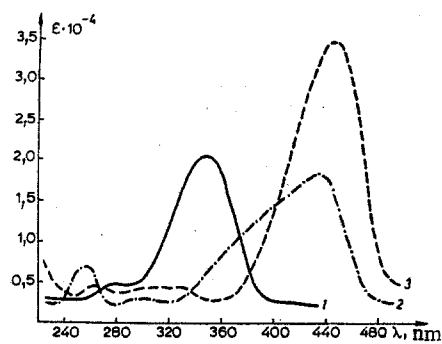


Fig. 1

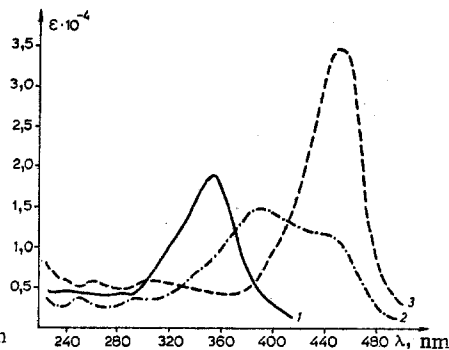


Fig. 2

Fig. 1. UV spectra of 5-formyl-2,2'-dithienyl: 1) in 1,2-dichloroethane (neutral molecule); 2) in 60% H_2SO_4 (mixture of neutral and protonated forms); 3) in 90% H_2SO_4 (protonated form).

Fig. 2. UV spectra of 5-acetyl-2,2'-dithienyl: 1) in 1,2-dichloroethane (neutral molecule); 2) in 60% H_2SO_4 (mixture of neutral and protonated forms); 3) in 90% H_2SO_4 (protonated form).

substitution. In addition, protonation of the carbonyl function in dithienyls I and II evidently promotes an increase in the planarity of the s-trans conformations of the I and II molecules, and this creates steric hindrance to incorporation of a nitro group in the 3' position.

A decrease in the reaction temperature from $+30$ to -30° during nitration in 80% sulfuric acid leads to an increase in the ratio of the 5'- NO_2 to 3'- NO_2 isomers from 7.3:1 to 13.7:1 for dithienyl I, and from 7.1:1 to 9.3:1 for dithienyl II. This change in the isomer ratio is evidently associated with the greater difficulty in overcoming steric hindrance during nitration in the 3' position; this hindrance is absent during attack on the 5' position. Thus an increase in the acidity of the medium and a decrease in the reaction temperature lead to an increase in the percentage of the 5'-nitro isomer in the mixtures of nitro compounds of dithienyls I and II.

EXPERIMENTAL

The UV spectra of $3.3 \cdot 10^{-5}$ M solutions of the carbonyl compounds in sulfuric acid and 1,2-dichloroethane were measured with an SF-16 spectrophotometer. Chromatographically pure mononitro isomers isolated from the products of nitration of I and II were used to construct the calibration graphs.

Nitration of 5-Formyl-2,2'-dithienyl (I) and 5-Acetyl-2,2'-dithienyl (II). A 1-g (5.6 mmole) sample of dithienyl I was dissolved in 15 ml of 70% sulfuric acid at 10° , the solution was heated to 20° , and 0.56 g (5.6 mmole) of powdered potassium nitrate was added in small portions with stirring at constant temperature. The mixture was then allowed to stand at 20° for 2 h, after which it was poured over ice. The resulting precipitate was removed by filtration, washed with water until the washings were neutral with respect to litmus, dried, and used for spectrophotometric analysis or isolation of the individual substances.

The nitration of dithienyls I and II was carried out similarly at -30 , -20 , -10 , 0 , $+10$, and 30°C with subsequent spectrophotometric determination of the resulting isomers. The experimental results are presented in Tables 1 and 2.

The isomers in the nitration products were separated by thin-layer chromatography (TLC) on activity II aluminum oxide in a hexane-ethyl acetate system (2:1) (R_f values: 0.86 for II, 0.71 for 5'-nitro-5-acetyl-2,2'-dithienyl, and 0.39 for 3'-nitro-5-acetyl-2,2'-dithienyl) and on SKT silica gel in a benzene-methanol system (1:1) (R_f values: 0.78 for I, 0.60 for 5'-nitro-5-formyl-2,2'-dithienyl, and 0.32 for 3'-nitro-5-formyl-2,2'-dithienyl).

The following substances were obtained as a result of chromatography: 5'-nitro-5-formyl-2,2'-dithienyl, with mp 196° [5]; 3'-nitro-5-formyl-2,2'-dithienyl, with mp 156° [5]; 5'-nitro-5-acetyl-2,2'-dithienyl, with mp 203° [6]; and 3'-nitro-5-acetyl-2,2'-dithienyl, with mp 141° [6].

For spectrophotometric analysis, an accurately weighed sample of the reaction mixture obtained by nitration of dithienyls I or II was chromatographed, the zones were collected quantitatively and eluted with methanol

into a calibrated flask, and the optical densities of the solutions at λ_{\max} were determined; the concentrations of the compounds were determined from the calibration graph.

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SYNTHESIS AND STEREOCHEMISTRY OF 3,4-DISUBSTITUTED SULFOLANES

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The stereochemistry of the reactions of 4-hydroxy-2-sulfolene, 4-hydroxy-3-chlorosulfolene, and 3,4-epoxysulfolene with nucleophilic reagents was studied. The optimum conditions for the preparation of sulfolanes with oxygen-containing substituents were worked out.

Little study has been devoted to the reactions of 4-hydroxy-2-sulfolene (I), 4-hydroxy-3-chlorosulfolene (II), and 3,4-epoxysulfolene (III) with nucleophilic reagents. A notable exception to this is an earlier study [1] in which it was shown that treatment of sulfolene I with sodium methoxide leads to a complex mixture of substances, the major portion of which remained unidentified.

We have previously developed methods for the preparation of cis- and trans-3,4-dihydroxysulfolanes (IV, V) by oxidation of 3-sulfolene [3]. In a continuation of our research on the synthesis of monomers from sulfolene (for example, see [4, 5]) we investigated the hydration and methanolysis of I-III.

The synthesis of 4-hydroxy-2-sulfolene (I) served as the subject of our special experiments, since we were unable to find convenient methods in the literature. We established that chlorohydrin II can be obtained in almost quantitative yield by hypochlorination of 3-sulfolene in aqueous solution. The dehydrochlorination of the chlorohydrin to give sulfolene I proceeds best (90% yield) in aqueous dioxane in the presence of an equivalent amount of KOH. The use of barium carbonate or pyridine gives I in 80 and 60% yields, respectively. The hydration of sulfolene I and the hydrolysis of chlorohydrin II in aqueous solution in the presence of KOH give mixtures of cis- and trans-diols in 65-95% yields, depending on the temperature (60-100°C) and reaction time (4-30 h). The ratio of IV to V ranges from 1:3 to 1:2. Thus the yields of diols are completely satisfactory under the described conditions. It should be noted that hydration is complicated by the formation of dimer VI, the yield of which may reach 80%. The tendency of sulfolene I to undergo dimerization is particularly high in solutions with concentrations above 0.04 M.

In the course of a study of the possibility of the use of dimer VI in the synthesis of diols we observed that it decomposes rapidly in aqueous alkaline solutions. The reaction has a distinct temperature barrier. Thus the dimer remains unchanged at 90° for 20 h, whereas after 1 h at 100°C it is converted to a mixture of

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