SYNTHESIS AND HYDROLYSIS OF 5-NITROFURANDICARBOXYLIC ACID ESTERS

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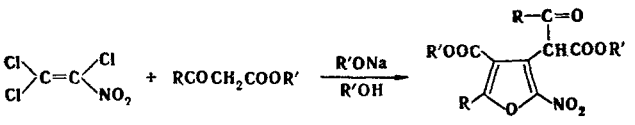
A method of the hydrolysis of 5-nitrofurandicarboxylic acid esters is proposed. The difference in the reactivities of the ester groups attached to the furan ring and in the side chain is explained by the effect of steric factors. It is shown that the direction of hydrolysis is determined by the structure of the alkyl substituent in the ester group. The mechanisms of the hydrolysis are discussed.

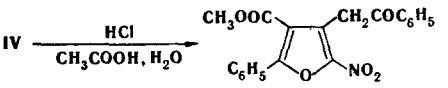
We have synthesized 5-nitrofurandicarboxylic acid esters I-IV from trichloronitroethylene and acetoacetic and benzoylacetic acid esters.



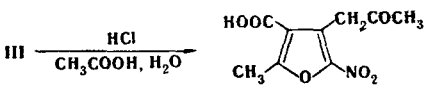
I-IV

I $R=CH_3$, $R'=CH_3$; II $R=CH_3$, $R'=C_2H_5$; III $R=CH_3$, $R'=C(CH_3)_3$; IV $R=C_6H_5$, $R'=CH_3$

The hydrolysis of esters I-IV opens up to a route to the preparation of the previously undescribed 4-nitrofurandicarboxylic acids and is the simplest method for the chemical proof of the structure of I-IV. However, both ester groups were found to be stable under the conditions recommended for the acid hydrolysis of α-alkylacetoacetic esters [3]. Prolonged (for many hours) heating with concentrated or dilute hydrochloric acid led to the isolation of the starting compounds. This sort of resistance of hydrolysis of substituted esters of acetoacetic acid has also been previously observed [4]. In our opinion, this is associated with the nonhomogeneity of the reaction medium. The use of acetic acid as the solvent, which, on the one hand, readily dissolves nitrofurandicarboxylic acid esters I-IV and, on the other, is miscible with concentrated hydrochloric acid, led, in the case of IV, to hydrolysis of the ester group only in the side chain. The reaction is accompanied by the decarboxylation characteristic for β-keto acid and gives ester V as the final product.



V



VI

The resistance of III and IV to hydrolysis on heating in acetic acid alone without the addition of hydrochloric acid indicates that in this reaction acetic acid acts only as the solvent. The increased resistance to hydrolysis of the ester group in the aromatic ring is

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probably associated with the effect of ortho, ortho'-substituents, which is well known in the benzene ring [5]. An attempt to saponify a 2,4-dimethyl-5-nitrofuran-3-carboxylic acid ester, in which the ester group is also located between two ortho substituents, was also unsuccessful, evidently for the same reason [6]. However, both ester groups in tert-butyl ester III are hydrolyzed under the same conditions, and acid VI is isolated as the final product. The difference in the behavior esters IV and III is associated with the hydrolysis mechanism. In the first case we are dealing with an $A_{ac}2$ mechanism, whereas in the second case we are dealing with an $A_{aL}1$ mechanism [5]. Moreover, the hydrolysis of ester III proceeds so readily that it can also be carried out at room temperature.

The IR spectrum of VI contains an absorption band at 3000 cm^{-1} due to the vibrations of the OH group of a carbonyl substituent; this band is absent in the spectrum of V. The ester and carboxyl groups have a maximum at 1730 cm^{-1}, whereas the keto group has a maximum at 1700 cm^{-1}. The bands at 1520 and 1360 cm^{-1} correspond to the nitro group, and the band at 1600 cm^{-1} probably should be assigned to the nitrofuran system.

The UV spectra of V and VI have the two high-intensity maxima at 220 and 300 nm that are characteristic for 5-nitrofuran derivatives [7]; the shift in the maxima to the long-wave region in the spectrum of ester V is associated with lengthening of conjugation chain through the phenyl ring in the 2 position of the furan ring.

EXPERIMENTAL

The IR spectra of chloroform solutions of the compounds were recorded with a UR-10 spectrometer. The UV spectra of methanol solutions were recorded with an SF-8 spectrophotometer. Esters I-IV were obtained from trichloronitroethylene and the appropriate acetoacetic acid esters.

Methyl 2-Methyl-4-(1-acetylcarbomethoxymethyl)-5-nitro-3-furancarboxylate (I). This compound, with mp 95-96°, (from methanol), was obtained in 50% yield. IR spectrum: 1720, 1655, 1620, 1518, 1440, 1410, 1345, 1270, 1240, 1150, 1090, 1000, 920, 860 cm^{-1}. UV spectrum, λ_{max}, nm (log ε): 224 (4.12), 252 (4.07), 311 (4.97). Found: C 48.3; H 4.6; N 4.8%. $C_{12}H_{13}NO_8$. Calculated: C 48.2; H 4.4; N 4.7%.

tert-Butyl 2-Methyl-4-(1-acetylcarbo-tert-butoxymethyl)-5-nitro-3-furancarboxylate (III). This compound, with mp 98-100° (from hexane), was obtained in 40%. IR spectrum: 1720, 1660, 1630, 1600, 1525, 1460, 1410, 1390, 1355, 1320, 1290, 1265, 1160, 1070, 970, 895, 860 cm^{-1}. UV spectrum, λ_{max}, (log ε): 228 (4.16), 252 (4.16), 314 (4.00). Found: C 56.4; H 6.6; N 3.6%. $C_{18}H_{25}NO_8$. Calculated: C 56.3; H 6.5; N 3.6%.

Methyl 2-Phenyl-4-(benzoylmethyl)-5-nitro-3-furancarboxylate (V). A 0.9-g sample of ester IV [2] was refluxed for 4 h with a mixture of 15 ml of acetic acid and 5 ml of concentrated hydrochloric acid, after which the mixture was concentrated in vacuo and worked up to give 0.5 g (64%) of ester V with mp 102° (successively from methanol and benzene–hexane). IR spectrum: 1724, 1700, 1608, 1521, 1500, 1450, 1420, 1360, 1340, 1297, 1260, 1120, 1020, 1000 cm^{-1}. UV spectrum, λ_{max}, nm (log ε): 249 (4.37), 338 (4.1). Found: C 65.6; H 4.2; N 3.7%. $C_{20}H_{15}NO_6$. Calculated C 65.8; H 4.1; N 3.8%.

2-Methyl-4-(2-oxopropyl)-5-nitrofuran-3-carboxylic acid (VI). A 2-ml sample of concentrated hydrochloric acid was added to a solution of 0.4 g of ester III in 10 ml of acetic acid, and the mixture was refluxed for 2 h (or allowed to stand at room temperature for 48 h). It was then cooled, and the acids were removed by vacuum distillation to dryness. The residue was recrystallized from aqueous methanol to give 0.2 g (70%) of VI with mp 150-151°. IR spectrum: 3040, 1730, 1605, 1509, 1455, 1359, 1322, 1300, 1268, 1167, 1075, 1038 cm^{-1}. UV spectrum, λ_{max}, nm (log ε): 218 (3.96), 318 (3.96). Found: C 47.7; H 3.9; N 5.7%. $C_9H_9NO_6$. Calculated: C 47.6; H 4.0; N 6.2%.

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NITRATION OF 2- AND 4-[2-(2-FURYL)VINYL]THIAZOLE DERIVATIVES

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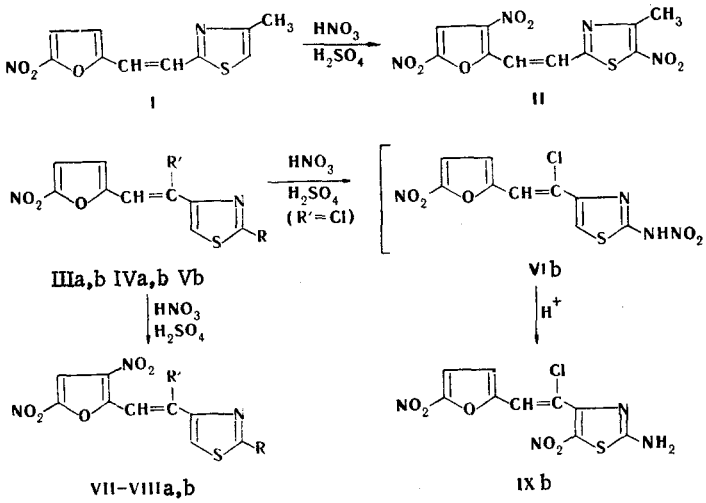
Nitration of 4-methyl-2-[2-(nitro-2-furyl)vinyl]thiazole with a mixture of concentrated nitric and sulfuric acids leads to 4-methyl-5-nitro-2-[2-(3,5-dinitro-2-furyl)vinyl]thiazole. Under the same conditions 2-methyl- and 2-acetamido-4-[1-R-2-(5-nitro-2-furyl)vinyl]thiazoles (R = CH_3, Cl) are nitrated in the 3 position of the furan ring, 2-amino-4-[1-chloro-2-(5-nitro-2-furyl)vinyl]thiazole is nitrated in the 5 position of the thiazole ring and 2-acetamido-5-nitro-4-[2-(2-furyl)vinyl]thiazole undergoes profound changes. Under the influence of a mixture of of nitric acid and acetic anhydride the latter compound is converted quantitatively to the 5-nitro derivative (with respect to the furan ring), whereas 4-[2-(5-nitro-2-furyl)vinyl]thiazole derivatives do not undergo reaction.

It is known that 4-methyl-2-[2-(2-furyl)vinyl]thiazole is converted to 4-methyl-2-[2-(5-nitro-2-furyl)vinyl]thiazole (I) by the action of a mixture of concentrated nitric acid and acetic anhydride [1]; this was proved by alternative synthesis from 5-nitrofurfural and 2,4-dimethylthiazole [2, 3].

We have established that another two nitro groups can be incorporated in I by the further action on I of a mixture of concentrated nitric and sulfuric acids. From a comparison of the PMR spectra of the starting compound and the final product (Table 1) it follows that 4-methyl-5-nitro[2-(3,5-dinitro-2-furyl)vinyl]thiazole (II) was obtained.



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