

DECARBOXYLATIVE NITRATION OF 3-(5-NITRO-2-FURYL)ACRYLIC ACID*

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Received July 2nd, 1976

Under the effect of a mixture of nitric acid and acetic anhydride on 3-(5-nitro-2-furyl)acrylic acid (*I*) an instable compound is formed at 20°C which decomposes in solvents to *I* and 1-nitro-2-(5-nitro-2-furyl)ethene (*II*). In the presence of boiling dilute nitric acid, or fuming nitric acid in acetic acid of 20°C, decarboxylative nitration takes place under formation of *II*. Nitration with a mixture of fuming nitric acid and concentrated sulfuric acid at 5–60°C gave *II* in addition to oxalic acid, 5-nitro-2-furylcarboxylic acid, 5-nitro-2-furaldehyde and 1-nitro-2-(3,5-dinitro-2-furyl)-ethene.

The introduction of the second nitro group into 3-(5-nitro-2-furyl)acrylic acid (*I*) during nitration has not yet been investigated although the finding of 1-nitro-2-(5-nitro-2-furyl)ethene (*II*) among the by-products of the nitration of 3-(2-furyl)acrylic acid¹ suggested such a reaction. In a preceding paper² we found that under the effect of nitrogen oxides on 3-(2-furyl)acrylic acid at lower temperatures decarboxylative nitration takes place preferentially, *i.e.* before the nitration of the furan nucleus. Decarboxylative nitration was studied directly on the furan ring by Sasaki³ who found that the substitution of the furan ring with a second nitro group is greatly impaired and that by nitration of 5-nitro-2-furancarboxylic acid 5,5'-dinitrofuryl is formed as the main product in preference to 2,5-dinitrofurane. Even during the nitration of 2-nitrofurane a more difficult entrance of the second substituent on the furan nucleus⁴ may be observed. Still greater problems are met during the substitution of the β -position of the furan ring with a second nitro group.

In the case of α -nitrofurane derivative the second nitro group could be introduced into the β -position of the furan ring⁵ when the second α -position has been substituted by an activating substituent. We concentrated on the study of the behaviour of 3-(5-nitro-2-furyl)acrylic acid during the reaction with various nitrating agents, with the aim of substituting a further hydrogen atom by a nitrogen group.

At temperatures up to 100°C compound *I* is stable in acid non-oxidizing medium, and it is possible to use strong nitrating agents for its nitration. The effect of a mixture

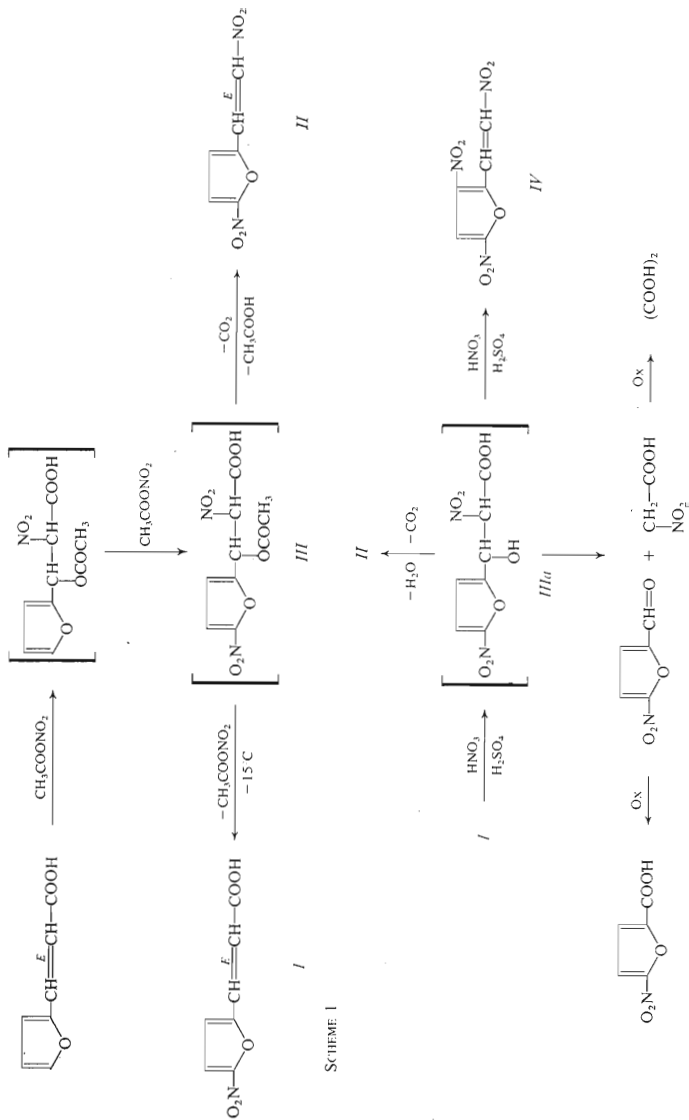
* Part CII in the series Furan Derivatives; Part CI: Chem. Zvesti, in press.

of nitric acid and acetic anhydride on *I* at temperatures below 0°C was not observable. The dissolution of a part of *I* could be observed above 0°C. At about 20°C the predominant part of *I* passed into solution, while at temperatures above 20°C decomposition began under formation of nitrogen oxides. The mixture obtained from the solution contained in addition to *I* also, mainly, compound *II* and product *III* identical with the intermediate from ref.¹. From the analogy with the nitration of cinnamic acid where such a nitration product (*i.e.* the intermediary addition product of nitration) was more stable and could be isolated and identified⁶, it may be assumed that the acetyl nitrate formed in the mixture of acetic anhydride and HNO₃ adds to the double bond of the acrylic group under formation of instable 2-nitro-3-acetoxy-3-(5-nitro-2-furyl)propanoic acid (*III*). The latter splits off CH₃COOH and CO₂ in non-polar medium under formation of *II*, or in aqueous medium it splits off acetyl nitrate under formation of *I*.

The results mentioned also give a partial answer to the question of how the by-products are formed during the nitration of 3-(2-furyl)acrylic acid. The formation of *III* is possible in two ways, *i.e.* by addition of acetyl nitrate to *II*, or by addition of acetyl nitrate to 3-(2-furyl)acrylic acid and subsequent nitration of the product formed. As *I* does not react at a measurable rate with acetyl nitrate at -5° to -25°C, the first path may be excluded as the source of by-products, formed at low temperatures, of nitration of 3-(2-furyl)acrylic acid. The main source of their formation is then the second path, during which *I* may be formed (Scheme 1) by decomposition of *III* in the nitrating mixture.

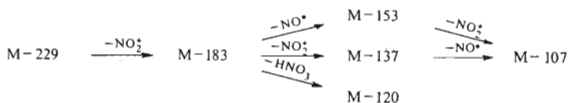
Under the effect of boiling dilute HNO₃ (10–30%) *I* is nitrated under decarboxylation and formation of *II* (yield about 80%; Scheme 2). As by-products of this reaction 5-nitro-2-furancarboxylic acid and 5-nitro-2-furaldehyde were obtained. With fuming nitric acid in glacial acetic acid at 20°C the decarboxylation nitration took place slowly. After 4 h 84.7% of unreacted *I* could be isolated from the reaction mixture, after 8 h the amount of *I* was 68.3% and after 24 h it was 52%. From the ethereal solution compound *II* was obtained. The use of fuming nitric acid alone under the mentioned conditions gave poorer results, due to the fact that the reaction was carried out in a heterogeneous two-phase system. The acidophilic character of *I* also enabled the nitration with a mixture of fuming HNO₃ and conc. H₂SO₄ at 5 to 60°C. In all instances *I* passed into solution completely under formation of nitrous fumes. From the reaction mixture in addition to compound *II* compound *IV* was also isolated.

In addition to this compound *I*, 5-nitro-2-furancarboxylic acid and oxalic acid were also obtained. In the aqueous solution which remained after the decomposition of the nitration mixture with water, 5-nitro-2-furaldehyde could be identified after precipitation with 2,4-dinitrophenylhydrazine.



SCHEME 1

Compound *IV* has mol. weight 229 and, according to elemental analysis, the composition $C_6H_3N_3O_7$, *i.e.* the molecule contains three nitro groups. When comparing the UV spectrum of *IV*, in which two distinct absorption bands at 242 nm and 340 nm appear, with that of *II*, containing bands at 245 nm and 350 nm and an inflexion at 290 nm, a hypsochromic shift becomes evident, due to a decrease in the mobility of the π -electron system, caused by the binding of another NO_2 group to the furyl-ethylene skeleton. In the IR spectrum the complex band with a maximum at 1533 cm^{-1} is conspicuous, which may be assigned to the asymmetric vibrations of the NO_2 group. The slightly stronger band at 1350 cm^{-1} belongs then to symmetric vibrations of this group. The intensity and the shape of the bands indicate the presence of several NO_2 groups in the molecule. The sharp absorption band at 1595 cm^{-1} may be assigned to the $C=C$ bond vibrations. In contrast to 2,5-disubstituted furan derivatives which show a characteristic band in the 1030 cm^{-1} region, this is shifted in the case of compound *IV* to the 1100 cm^{-1} frequency. In the mass spectrum a triple splitting off of the nitrogen radicals or cations may be observed in the sequences of the molecular radical-cation.



The branching of the splitting corresponds to relative intensities of the maxima of the fragments. The formation of the fragment $M-107$ and the intensive maximum $M-30$ indicate the presence of three NO_2 groups in the molecule, while the equal intensity of $M-153$ and $M-137$ supports the presence of two equal NO_2 groups in the molecule.

The 1H -NMR spectrum of *IV* shows that the compound contains three hydrogen atoms and that it is composed of one singlet $\delta = 8.25$ ppm and two doublets with $\delta = 8.20$ and 8.46 ppm and the coupling constant $J = 14$ Hz, belonging to vinylic hydrogens. The unsplit singlet belongs to a hydrogen atom, it is not affected by the double bond hydrogen atoms, *i.e.* it is located in the position 4 of the furan nucleus. On the basis of these facts it may be supposed that the compound *IV* is 1-nitro-2-(3,5-dinitro-2-furyl)ethene.

From the above data it may be inferred that on reaction of 3-(5-nitro-2-furyl)acrylic acid with nitric acid an addition takes place in the first step, followed by decarboxylative nitration (Scheme 2). Such a reaction course is supported by the fact that both in the starting compound *I* and in the resulting product of decarboxylative nitration, *II*, the *E* configuration is present, *i.e.* the reaction must take place through the inter-

mediary structure *III* in which such an orientation of substituents is possible, permitting the NO_2 group to come into the position *trans* with respect to the furan nucleus. If a substitution of the hydrogen atom on the acrylic group in the position 2 takes place in the first reaction stage, the so far unknown isomer *ZII* should result from such a reaction course. The unambiguity of the formation of the *E* isomer of *II* (m.p. 142°C) excludes such a reaction course.

EXPERIMENTAL

The melting points were determined on a Kofler block and they are not corrected. The IR spectra were measured on a UR-20 (Zeiss, Jena) spectrophotometer, in pellets prepared from 2 mg of substance and 1 g of KBr. The instrument was calibrated with a polystyrene foil. The UV spectra were measured on a Specord UV VIS Zeiss, Jena, spectrophotometer in a 1 cm cell. The concentrations were $10^{-5} \text{ mol l}^{-1}$ in methanol solution, the accuracy $\pm 1 \text{ nm}$. The $^1\text{H-NMR}$ spectra were recorded with a Tesla NMR BS 487C 80 MHz instrument, using tetramethylsilane as internal reference in predeuterated acetone. The mass spectra were measured with a MS 902 S (AEI) spectrometer. For nitration 3-(5-nitro-2-furyl)acrylic acid of m.p. $241-242^\circ\text{C}$ was used, prepared according to ref.⁶.

Nitration of 3-(5-Nitro-2-furyl)acrylic Acid (*I*)

a) *With a mixture of fuming HNO_3 and acetic anhydride:* Compound *I* (36.6 g; 0.2 mol) was added gradually to a mixture of acetic anhydride (102 g; 1 mol) and fuming HNO_3 (63 g; 1 mol) kept at 0°C . After 4 hours' stirring at 0°C the unreacted *I* was filtered off under suction, washed on the filter with ice-cold water and dried. The yield of the regenerated product *I* was 35.2 g, *i.e.* 96.2%. Using identical weight ratios and the same procedure compound *I* was added into the nitration mixture after the temperature has risen to 20°C . Compound *I* dissolved almost completely. The reaction mixture was then stirred at 20°C for 4 h, then cooled to -20°C , and the unreacted *I* was filtered off (4.7 g). The filtrate was poured onto 500 g of crushed ice and the precipitated product transferred into 200 ml of ether. The insoluble part was filtered off and again dissolved in 100 ml of ether. The insoluble part was filtered off under suction and dried. Yield 14.9 g of *I*. In the ethereal solution the presence of compounds *I*, *II* and *III* was proved by thin-layer chromatography on silica gel (containing 10% of gypsum) using tetrahydrofuran benzene 1 : 2 mixture for development. The ethereal solution was divided into two parts. One of them was allowed to evaporate freely, while the second was previously dried over Na_2SO_4 , then evaporated *in vacuo* at 0°C to a small volume, and the separated product filtered off and crystallized from CCl_4 . Yield 4.9 g of *II*. From the glassy material obtained by free evaporation of the moist ether 0.7 g of *II* were obtained after short boiling with CCl_4 and evaporation; the material which would not dissolve in CCl_4 was recrystallized from ethanol. Yield 5.1 g of *I*. Compound *II* obtained in this experiment and that in paper¹ are identical.

b) *With dilute nitric acid:* 630 g of 10% HNO_3 were brought to boiling and 36.6 g of *II* were then added to it in small portions. The mixture was refluxed for 4 h, cooled and the precipitated product was filtered off, dissolved in CCl_4 and allowed to crystallize. Yield 28.4 g (77.2%), m.p. 142°C .

c) *With fuming HNO_3 in acetic acid:* Compound *I* (36.6 g; 0.2 mol) was added at 20°C to a mixture of fuming HNO_3 (63 g; 1 mol) and acetic acid (200 g), and the mixture was kept at 20°C for 4, 8 and 24 h under stirring. After these intervals the mixture was poured onto 500 g of ice, the solid material was filtered off and extracted with 300 ml of ether. After the ether-insoluble

material had been dried the amount of unreacted *I* was determined. The recovered material weighed 31 g, 25 g and 19 g, *i.e.* the recovery was 84.7, 68.3 and 51.9% respectively.

d) *With a mixture of fuming HNO₃ and concentrated H₂SO₄*: Compound *I* (7.3 g; 0.04 mol) was added under stirring and at 5°C to a mixture of fuming nitric acid (21 g; 0.33 mol) and concentrated sulfuric acid (33 g; 0.33 mol), and the mixture was stirred at 5°C for one hour. It was then poured onto 200 g of ice and when the ice had dissolved the stirring was continued for another 30 minutes. The solution was extracted with 300 ml of ether and the extract washed with a solution of sodium carbonate and dried over sodium sulfate. Using thin-layer chromatography on Silufol (in tetrahydrofuran-benzene 1 : 3 mixture) the formation of a compound with $R_F = 0.91$ could be detected, when the starting compound *I* ($R_F = 0.66$) and compound *II* ($R_F = 0.79$) were employed as reference samples. The first mentioned substance in the ethereal solution contained only a small amount of *II* as impurity. Owing to thermal instability of *IV* this mixture could not be crystallized, and as a total vacuum evaporation of the solvent gave a poorly tractable syrupy material, the ethereal solution was evaporated in a vacuum to approximately 70 ml volume and then allowed to evaporate freely in darkness. The residue was gradually washed with ether, ethanol and water until chromatographically pure. Yield 1.2 g (13.2%) of 1-nitro-2-(3,5-dinitro-2-furyl)ethene, m.p. 121–123°C. For C₆H₃N₃O₇ (229) calculated: 31.44% C, 1.31% H, 18.34% N; found: 31.39% C, 1.33% H, 18.52% N. The aqueous solution obtained by the washing of the ethereal extract with sodium carbonate solution was acidified with HCl to pH 3, and the precipitated *I* was filtered off under suction. The filtrate was evaporated under reduced pressure to a small volume, acidified to pH 1 and the separated product was crystallized from ethanol and identified as 5-nitro-2-furancarboxylic acid. Oxalic acid was isolated from the concentrated mother liquors. From the aqueous solution which remained after the decomposition of the nitration mixture carbonyl-compounds were precipitated with 2,4-dinitrophenylhydrazine. The precipitate was dissolved in ethyl acetate and chromatographed analytically on Silufol plates in CCl₄-ethyl acetate 3 : 2. Comparison with standards demonstrated the presence of 2,4-dinitrophenylhydrazone of 5-nitro-2-furaldehyde. Concentration of the ethereal extract under reduced pressure gave a viscous liquid which decomposed gradually under liberation of nitrogen oxides and crystals of oxalic acid separated from the solution.

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Translated by Ž. Procházka.