

# Furan Derivatives. XXII.

## Identification of Some By-products from Nitration of 3-(2-Furyl)acrylic Acid

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By-products from nitration of *trans*-3-(2-furyl)acrylic acid were isolated from an ether extract and identified by chromatographic  $R_F$  values as being 1-nitro-2-(2-furyl)ethene, 1-nitro-2-(5-nitro-2-furyl)ethene and *cis*-3-(5-nitro-2-furyl)acrylic acid.

The nitration of furan derivatives was examined to ascertain mainly the reaction conditions for getting the appropriate 5-nitrofurans obtained hitherto in 20–70% yield. Also the nitration of 3-(2-furyl)acrylic acid (*I*) with nitric acid in acetic anhydride affords 3-(5-nitro-2-furyl)acrylic acid (*II*) in 40–70% yield [1–9] and there is no comment on the recovery of the unchanged starting material *I*. Recrystallization of the crude product *II* yields only 60–80% of pure substance *II* and at least 50% of compound *I* does not react or affords other reaction products.

The greatest part of furan derivatives behaves as a diene and adds acetyl nitrate in positions 2,5 when reacting with nitric acid and acetic anhydride. Some furan derivatives with an ethene group in position 2 (substance *I* belongs to them) are exceptions where addition of acetyl nitrate to the furan ring does not occur; instead, 5-substituted furan derivative is formed directly. The triene grouping of compounds thus obtained facilitates the substitution reaction at one end of the triene system, whereas addition reactions to the exocyclic double bond are favoured at the other end. Suchlike reaction affords 1-nitro-2-(2-furyl)ethene from compound *I* and nitrogen oxides [10] what can be classified as an addition-elimination reaction with simultaneous decarboxylation.

Taking the above-mentioned facts into consideration, we were curious to know whether similar side reactions do not occur upon nitration of substance *I* with nitric acid—acetic anhydride.

So far, the formation of by-products resulting from nitration of furan derivatives was studied with furaldehyde [11–14], 2-acetylfuran [15] and furancarboxylic acid [16], whereas that of compound *I* has not been reported. Aimed to throw some light on reactions taking place when reacting substance *I* with the mixture of nitric acid and acetic anhydride we attempted to isolate those products which can be — together with substance *II* — separated from the nitration mixture after its decomposition with water. The separation of the above-mentioned products from substance *II* was achieved by extraction with organic solvents among which diethyl ether was found to be the most effective.

## Experimental

Chromatographic reference substances were prepared as follows: *trans*-3-(5-nitro-2-furyl)acrylic acid (m.p. 241–242°C) from 5-nitrofuraldehyde diacetate according to [1], *cis*-3-(5-nitro-2-furyl)acrylic acid (m.p. 176°C) according to [9], 1-nitro-2-(2-furyl)ethene (m.p. 75°C) according to [17] and 1-nitro-2-(5-nitro-2-furyl)ethene (m.p. 143°C) according to [18].

Chromatographic separation was carried out on thin layer (0.275 mm) silica gel plates (with 10% plaster). Coated plates were activated at 105°C for 45 minutes and substances to be chromatographed were dissolved in tetrahydrofuran and developed in tetrahydrofuran–benzene 1 : 2 at 20°C. After developing, the chromatoplates were air-dried and visualized in iodine vapours and by spraying with 5% aqueous AgNO<sub>3</sub> in 10% ammonia followed by 5 minutes heating at 140°C [19].

Infrared spectra were measured with an UR-10 double-beam spectrophotometer (Zeiss, Jena) in the 3600–800 cm<sup>-1</sup> range in KBr cell of 0.427 mm width at 0.025 M concentration, chloroform being the solvent. Spectra of compounds *II* and *IIa* were recorded in nujol mull.

### Nitration of 3-(2-furyl)acrylic acid (*I*)

Acetic anhydride (153 g, 1.5 mole) was mixed with fuming nitric acid (63 g, 1 mole) and concentrated sulfuric acid (1 ml) at 0°C in a three-necked flask. After cooling to –30°C substance *I* (27.6 g, 0.2 mole) in acetic anhydride (102 g, 1 mole) was added so that the temperature would not rise above –25°C. Substance *I* being added, the reaction mixture was kept stirred at approximately –30°C for one hour. The products were isolated in two ways.

#### Method A

Ether (300 ml) was added to the reaction mixture, the precipitated 3-(5-nitro-2-furyl)acrylic acid (*II*) was filtered off, washed with ether (150 ml) and dried. The filtrate was poured onto crushed ice (1 kg) and while vigorously stirred the ice melted (approximately 20 minutes); the second crops of substance *II* which precipitated was filtered off, washed with ether and dried. The combined 3-(5-nitro-2-furyl)acrylic acids yielded 16.3 g (44.6%) of the calculated amount; m.p. 239–240°C.

The etheric layer was separated from the filtrate, washed with ice-cold water (100 ml) and dried with sodium sulfate. Ether was distilled off under reduced pressure at –10°C and the residue, a brown-red viscous oil (7.7 g – product A) explodes upon heating.

Found: 9.73% N.

#### Method B

The reaction mixture poured into a mixture consisting of 500 g ice and 500 ml water was vigorously stirred and the smeary brown-red material, separated after all the ice has been melted, was dissolved in ether (300 ml). Ether-insoluble substance was filtered off, washed with ether (100 ml) and dried, yielding 18.7 g of compound *II* (51% of calculated amount); m.p. 238–239°C.

Ether-soluble part was shaken with solid NaHCO<sub>3</sub> to remove traces of nitric acid, then washed twice with ice-cold water (100 ml each), dried with anhydrous sodium sulfate

and evaporated under reduced pressure at  $-10^{\circ}\text{C}$ . Yield 9.2 g of brown-red viscous compound (product B).

Found: 10.17% N.

Samples of products A and B were chromatographed immediately after the isolation was completed and once more after 48 hours. During this time one part of A and B was kept at room temperature, the other part in a refrigerator at  $0^{\circ}\text{C}$ . Cooled samples did not markedly change when compared with original ones.

According to chromatographic results both compounds A and B contain a small amount of unchanged 3-(2-furyl)acrylic acid ( $R_F = 0.62$ ). Moreover, product A revealed spots of  $R_F = 0.03$  and  $R_F = 0.21$  (unidentified substances), 0.32 [3-(5-nitro-2-furyl)acrylic acid (*II*)] and 0.55 [1-nitro-2-(2-furyl)ethene (*III*)]. After 48 hours' exposure at room temperature the spot of  $R_F = 0.21$  disappeared, that of  $R_F = 0.32$  grew greater and a new stain of  $R_F = 0.36$  [1-nitro-2-(5-nitro-2-furyl)ethene (*IV*)] appeared.

Product B was shown to consist of compound *I*, and others of  $R_F = 0.03$ , 0.21, 0.36 (*IV*) and 0.55 (*III*). The spot of  $R_F = 0.21$  disappeared, a new spot of  $R_F = 0.32$  (*II*) appeared and that of 0.36 (*IV*) became greater. No changes were observed with all others. After 48 hours products A and B differ from each other in content of substances *II* and *IV*, the first being present to greater extent in product A, the latter in product B.

#### *Isolation of by-products*

Attempts to isolate pure compounds from freshly prepared products A and B resulted in failure and for this reason the components were isolated after the self-decomposition of the unstable compounds. The viscous material A and B (10 g) was allowed to stand at room temperature for a fortnight. During this decomposition process nitrogen oxides and carbon dioxide (evidenced with  $\text{Ba}(\text{OH})_2$  solution) were released and the solidified material was extracted with light petroleum. The residue was pulverized and dissolved in boiling carbon tetrachloride. Light petroleum extract after evaporation and repeated crystallization from hexane afforded a compound (0.9 g, m.p.  $74-75^{\circ}\text{C}$ ) which was shown to be 1-nitro-2-(2-furyl)ethene (*III*). Mixed melting point with compound *III* of synthetic nature was  $74.5^{\circ}\text{C}$ , both spectra are superimposable.

For  $\text{C}_6\text{H}_5\text{NO}_3$  (139.1) calculated: 51.8% C, 3.59% H, 10.07% N; found: 51.43% C, 3.52% H, 10.11% N.

Yellow crystals which precipitated from the carbon tetrachloride solution after cooling were recrystallized from ether-carbon tetrachloride. Yield 2.4 g, m.p.  $142-143^{\circ}\text{C}$  was identified as being 1-nitro-2-(5-nitro-2-furyl)ethene (*IV*). Mixed melting point with synthetic *IV* was found to be  $142^{\circ}\text{C}$ , both substances have identical infrared spectra.

For  $\text{C}_6\text{H}_4\text{N}_2\text{O}_5$  (184.11) calculated: 39.13% C, 2.17% H, 15.22% N; found: 39.41% C, 2.12% H, 15.19% N.

The undissolved residue after carbon tetrachloride was hot-dissolved in such an amount of 10% sodium carbonate the solution to be neutral. The solution obtained was treated with charcoal, boiled, filtered and evaporated under diminished pressure to 1/5 of its original volume. Yellow-brown crystals which separated after cooling were recrystallized from water; to the sodium salt dissolved in water-diluted hydrochloric acid was added to pH 4.5, the liberated acid was filtered off and dried. Yield 2.1 g, m.p.  $240-241^{\circ}\text{C}$ . Mixed melting point with substance *II* did not reveal any depression. The infrared spectrum of the substance *II* was superimposable with that of the synthetic preparation.

To the filtrate after separation of substance *II* concentrated hydrochloric acid was added to pH 1 [20], the solution was cooled to  $0^{\circ}\text{C}$  and the precipitated red-brown com-

pound was recrystallized from ether. The isolated compound (m.p. 176°C) yielding 0.2 g was identified by means of mixed melting point and infrared absorption spectrum as being *cis*-3-(5-nitro-2-furyl)acrylic acid (*IIa*).

### Results and Discussion

We ascertained that the compound *II* is accompanied by unstable products which upon routine isolation process [2–9] undergo decomposition; we attempted to isolate and separate those substances from the reaction mixture in two ways. Properties of these compounds were shown to be similar to those prepared by nitration of substituted cinnamic acids [21, 22].

We did not succeed in isolation of the primarily originated nitration by-product in a pure state similarly as it was not with cinnamic acids and that is why it was characterized by means of thin layer chromatography. By this method it was found the  $R_F$  value of the unstable substance in tetrahydrofuran—benzene 2 : 1, to be 0.21; this compound undergoes decomposition within 48 hours at room temperature and it decomposes slowly when stored in a refrigerator.

The disappearance of the spot of  $R_F = 0.21$  in product A and B after 48 hours is associated with formation or expansion of spots belonging to compounds *II* and *IV* by self-decomposition.

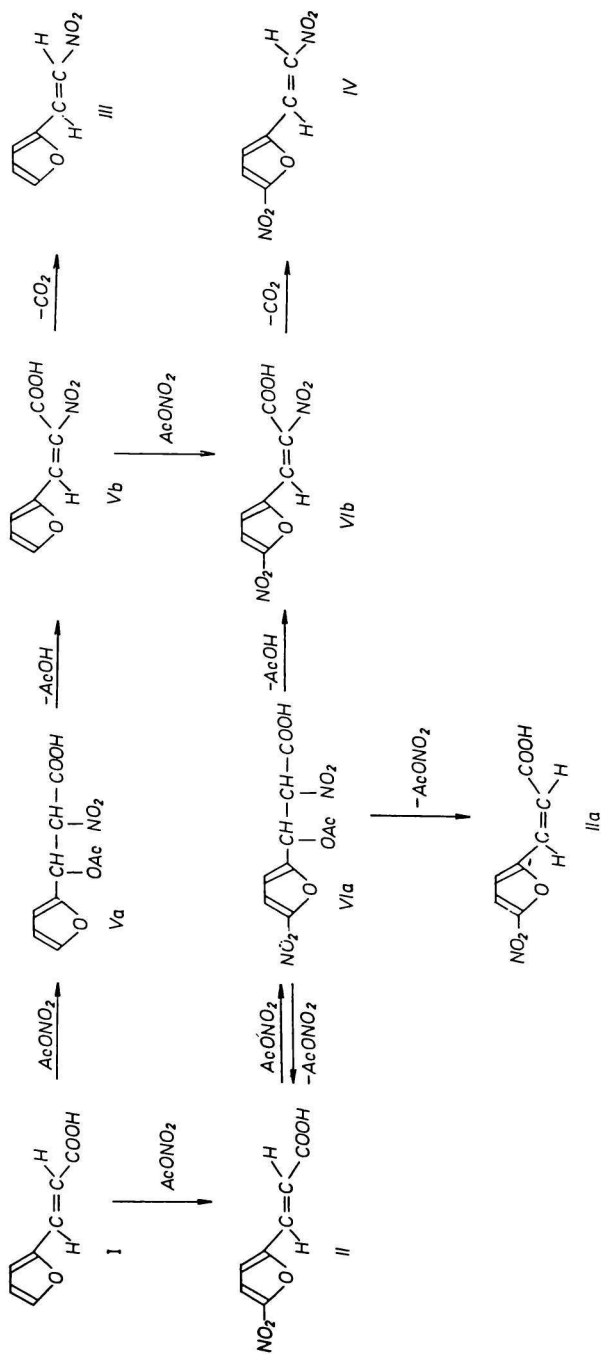
The composition of products A and B after 48 hours was found to be similar basing upon chromatographic separation and that is why they were worked up together. The unstable compound preventing the mixture from being separated was allowed to self-decompose to give the final products which were fractionated by crystallization into substances *II*, *IIa*, *III* and *IV*. A little amount of nitrogen oxides and carbon dioxide was liberated during the decomposition process.

The infrared spectra show geometric isomerism of the ethene bound in single compounds. Compound *I* displays a characteristic absorption band of the  $-\text{CH}=\text{CH}-$  bond  $\nu(\text{C}-\text{H})$  973  $\text{cm}^{-1}$  (out-of-plane), compound *II* at 980  $\text{cm}^{-1}$ , compounds *III* and *IV* at 965 and 975  $\text{cm}^{-1}$ , respectively. The above-mentioned derivatives are, therefore, *trans*-isomers [9]. Compound *IIa* has the absorption band  $\nu(\text{C}-\text{H})$  820  $\text{cm}^{-1}$  (out-of-plane) thereby being a *cis*-isomer.

The reaction, where the carboxylic group in *trans*-position is replaced by a nitro group in the same grouping is possible on condition that the exocyclic double bond disappears in the first stage after addition of the nitration agent, enabling thus free rotation about the C—C bond. In the second stage, acetic acid is eliminated and the bond having geometric arrangement of the reaction product is formed. Stereospecific course of the elimination, *i.e.* location of the nitro group in *trans*-position is subject to steric conditions because the nitro group in *cis*-position towards furan ring has to be non-coplanar [23]. Similarly, the formation of geometric isomers *II* and *IIa* is possible to rationalize by addition-elimination reaction.

From results observed both with nitration of alkenes with acetyl nitrate [24, 25] and those obtained during this work when nitrating substituted acrylic acid, it is possible to propose a probable reaction scheme 1.

Reactions leading to compound *III* are relatively unequivocal. Acetyl nitrate adds to substance *I* to form 2-nitro-3-aceoxy-3-(2-furyl)propanoic acid (*Va*) which splits off acetic acid affording 2-nitro-3-(2-furyl)acrylic acid (*Vb*); the latter decarboxylates to give compound *III*. Since decarboxylation has not been observed upon nitration of *I*, but only after decomposition of the reaction mixture with water, the possibility to nitrate substance *III* into substance *IV* is of little probability.



Scheme I

The simultaneous formation of substances *II*, *IIa* and *IV* by decomposition of the unstable material in product A and B indicates that this compound is 2-nitro-3-acetoxy-3-(5-nitro-2-furyl)propanoic acid (*VIa*) which splits off acetyl nitrate to give geometric isomers *II* and *IIa*, whilst the elimination of acetic acid leads to 2-nitro-3-(5-nitro-2-furyl)acrylic acid (*VIb*); the latter decarboxylates in turn to yield compound *IV*.

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