PECULIARITIES OF THE NITRATION OF 2-[α-CHLORO-β-(5-NITRO-2-FURYL)VINYLIMIDAZO[1,2-a]PYRIDINE

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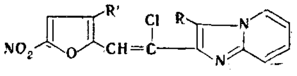
We have established that the reaction of nitric acid in a mixture of concentrated sulfuric and glacial acetic acids with 2-[α-chloro-β-(5-nitro-2-furyl)vinyl]imidazo[1,2-a]pyridine (I) gives 3,3'-dinitro- and 3-chloro-3'-nitro-substituted compounds (II, III) instead of the expected 3-nitro-substituted compound.



I-III

I R = R' = H; II R = R' = NO_2; III R = Cl, R' = NO_2

This is the first instance of the introduction of a nitro group in the β position of the ring in the series of 2-vinyl-5-nitrofuran derivatives.

The formation of chloro nitro derivative III is the result of the action of the chlorine formed during partial destructive oxidation.

The absence in the PMR spectrum of II of the singlet corresponding to 3-4 and the shift of the 5-H doublet (Δδ 1.1 ppm) to weak field as compared with the spectrum of the starting compound are due to the nitrogroup in the 3 position. A slight shift of the 5-H doublet (Δδ 0.09 ppm) to weak field is observed for the 3-chloro derivative (III). The singlets in the spectra of II and III, which are shifted by more than 1 ppm to weaker field as compared with the 4'-H signal in the spectrum of the starting compound, constitute evidence that the nitro group is in the adjacent 3' position.

A mixture of 2.5 ml (40 mole) of 70% HNO_3 in 10 ml of concentrated H_2SO_4 was added with ice-cooling to a solution of 2.5 g (8 mmole) of I in a mixture of 60 ml of concentrated H_2SO_4 and 30 ml of glacial acetic acid in the course of 40 min, after which the mixture was stirred for another 30 min. It was then poured over ice, and the aqueous mixture was filtered to give 0.72 g (24%) of yellow prisms (which darkened in the light) of 3-nitro-2-[α-chloro-β-(3,5-dinitro-2-furyl)vinyl]imidazo[1,2-a]pyridine (II). With mp 232-235° [from dimethylformamide (DMF)]. PMR spectra, δ: (in d_7-DMF, Brucker WH-90) m, 7.6-8.5 (6-H, 7-H, 8-H); s, 8.28 (β-H); s, 8.61 (4'-H); d, 9.66 (5-H); (in CF_3COOH, Perkin–Elmer R-12A, 60 MHz); m, 7.4-9.0 (6-H, 7-H, 8-H, β-H); s, 9.75 (4'-H); d, 9.74 ppm (5-H). IR spectrum: 3155 and 3105 (ring ν_{CH}), 3035 (β-CH); 1515 and 1355 cm^{-1} (NO_2). Found: C 41.3; H 1.6; N 18.0%; M 379 (mass spectrometrically). $C_{13}H_6ClN_5O_7$. Calculated: C 41.4; C 41.1; H 1.6; N 18.4%; M 379.

Extraction of the filtrate with ether gave 0.29 g (10%) of 3-chloro-2-[α-chloro-β-(3,5-dinitro-2-furyl)vinyl]imidazo[1,2-a]pyridine (III) as bright-red prisms with mp 225-226° (from DMF) that sublimed when they were heated. PMR spectrum in CF_3COOH, δ: m, 7.60-8.40 (6-H, 7-H, 8-H); s, 7.97 (β-H); s, 8.75 (4'-H); d, 8.74 ppm (5-H). IR spectrum: 3168 and 3110 (ring ν_{CH}), 3043 (β-CH), and 1520 and 1350 cm^{-1} (NO_2). Found: C 42.4; H 1.6; N 14.9%; M 369 (mass spectrometrically containing 2 atoms of Cl). $C_{13}H_6Cl_2N_4O_5$. Calculated: C 42.3; H 1.6; N 15.2%; M 369.

PMR spectrum of I in CF_3COOH, δ: m, 7.3-8.1 (6-H, 7-H, 8-H); d, 7.45 (4'-H); s, 7.56 (β-H); d, 8.04 (3'-H, $J_{3,4}$ = 3.9 Hz); s, 8.36 (3-H); d, 8.65 ppm (5-H).

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