SYNTHESIS OF FURAXANENITROLIC ACIDS

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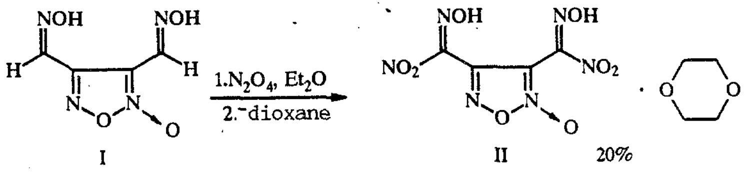
Previously unreported furoxanenitrolic acids have been synthesized.

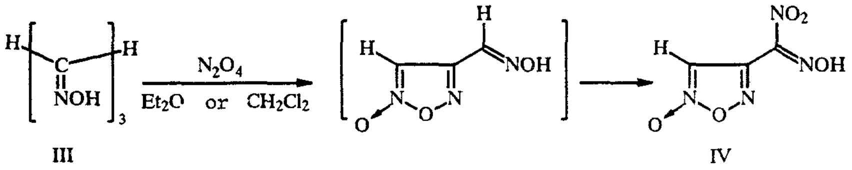
Nitrolic acids are frequently used in organic synthesis, for example, in the preparation of new derivatives of isoxazole [1], tetrazole [2], and furoxane [3, 4] as well as aliphatic acids [5, 6]. We should also note the use of these compounds as depolarizers [7, 8]. Heterocyclic nitrolic acids, including furoxanenitrolic acids, may be used for these purposes. However, the synthesis of these compounds and their reactions have virtually not been described.

In the present work, we synthesized furoxanenitrolic acids. Methods described for arylnitrolic acids may be used. The reaction of aldoximes with nitrogen tetroxide is the most common method for the synthesis of arylnitrolic acids [9, 10]. The only furoxane aldoximes reported are furoxanedialdoxime [11] and furoxane-3-aldoxime [12].

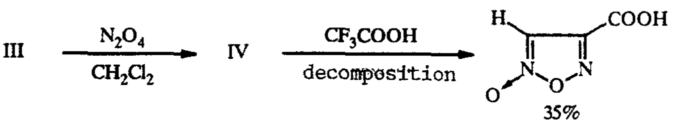
The reaction of furoxanedialdoxime (I) with N_2O_4 in CH_2Cl_2 or ether leads to furoxane-3,4-dinitrolic acid, which decomposes upon attempting to isolate it as a pure compound. However, this compound readily forms a rather strong, stable 1:1 complex with dioxane (II):



The synthesis of other furoxanenitrolic acids was carried out starting with trioximinopropane (III), since the method for preparing furoxane-3-aldoxime is laborious and involves multiple steps [12]. We assumed that the reaction of III with N_2O_4 would feature not only nitration of the oxime group but also oxidation of two oxime groups to give a furoxane ring. Indeed, furoxane-4-nitrolic acid (IV) was obtained 20 min after the reaction onset. This product is probably formed through furoxane-4-aldoxime:



Vigorous decomposition with the liberation of nitrogen oxides and the formation of furoxane-4-carboxylic acid occurred in several cases upon the isolation of IV.



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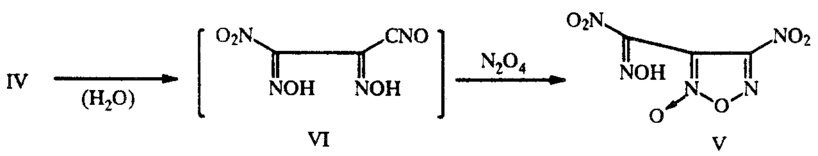
If this reaction is carried out in CH_2Cl_2 over 24 h, nitrolic acid IV is converted to 4-nitrofuroxane-3-nitrolic acid (V), probably through the corresponding nitrile oxide (VI):[*]



Thus, we are the first to report the synthesis of furoxanenitrolic acids II, IV, and V, whose structures were demonstrated using elemental analysis as well as IR and NMR spectroscopy.

EXPERIMENTAL

The IR spectra were taken for KBr pellets on a Specord spectrometer. The ^1H and ^{13}C NMR spectra were taken on a Bruker AM-300 spectrometer at 300 and 75.5 MHz, respectively, with TMS as the internal standard. The melting points were determined on a Boetius block with heating rate 4°C/min near the melting point.

The elemental analysis data for II, IV, and V corresponded to the calculated values.

Complex of Furoxane-3,4-dinitrolic Acid with Dioxane (II, $C_8H_{10}N_6O_{10}$). A solution of 0.64 ml (10 mmoles) N_2O_4 in 5 ml CH_2Cl_2 or ether was added dropwise with stirring to a suspension of 0.86 g (1 mmole) furoxanedialdoxime I in 15 ml CH_2Cl_2 or ether. The reaction mixture was maintained for 0.5 h and the solvent was then evaporated off. The residue was dissolved in 50 ml ether. The solution was washed with water, dried over $MgSO_4$, and filtered. Then, 5 ml dioxane was added and the solution was evaporated. The precipitate formed was filtered off, washed with CH_2Cl_2, and dried to give 0.35 g (20%) complex II, mp 81-82°C (dec.). IR spectrum: 3220-2600 (OH), 1630 (C=N), 1555 and 1340 (NO_2), 1450, 1380, 1260, 1100, 1050, 900, 865 cm^{-1} (dioxane). PMR spectrum in $(CD_3)_2CO$: 3.5 (dioxane), 13.7 ppm (OH). ^{13}C NMR spectrum: 67.15 (dioxane), 104.88 (C=N—O), 143.52, 146.62, 148.11 ppm (C—NO_2 and —C=N—O).

Furoxane-4-nitrolic Acid (IV, $C_3H_2N_4O_5$). A solution of 0.64 ml (10 mmoles) N_2O_4 in 5 ml CH_2Cl_2 was added dropwise with stirring to a suspension of 1.31 g (10 mmoles) trioxime III in 20 ml CH_2Cl_2 or ether at 5°C. The reaction mixture was maintained at 10-15°C for 20 min until III was fully dissolved. The solvent was distilled off and 50 ml ether was added to the residue. The solution was washed with water and dried over $MgSO_4$. The drying agent was filtered off and ether was evaporated from the filtrate. A sample of 4 ml CF_3CO_2H was added to the residue at 0°C. The crystalline product was filtered off, washed with cold CF_3CO_2H, and dried to give 0.7-0.82 g (40-47%) acid IV, mp 77°C (dec.). IR spectrum: 3350 (OH), 3150 (C—H), 1650 (C=N), 1550 and 1340 cm^{-1} (NO_2). PMR spectrum in $(CD_3)_2CO$: 11.44 (C—H), 13.5 ppm (OH). ^{13}C NMR spectrum: 134.77 (C—H), 149.35 (C=N), 161.62 ppm (C—NO_2).

4-Nitrofuroxane-3-nitrolic Acid (V, $C_3HN_5O_7$). A solution of 1.28 ml (20 mmoles) N_2O_4 in 4 ml CH_2Cl_2 was added dropwise to a solution of 1.31 g (10 mmoles) trioxime III in 20 ml CH_2Cl_2 at 5°C. The reaction mixture was maintained for 24 h at room temperature and then treated as in the synthesis of acid IV. The yield of acid V was 0.51 g (23%), mp 69°C. IR spectrum: 3340 (OH), 1645 (C=N), 1555 and 1330 cm^{-1} (NO_2). ^{13}C NMR spectrum in $(CD_3)_2CO$: 100.68 ($C=N\rightarrow O$), 144.64 (C=NOH), 156.96 (C—NO_2).

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[*] This transformation of acid IV will be described in greater detail in a subsequent communication.

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