SYNTHESIS OF 5-NITROFURAN-2-CARBOXYLIC ACID

G. D. Krapivin, L. A. Badovskaya,
and V. G. Kul'nevich

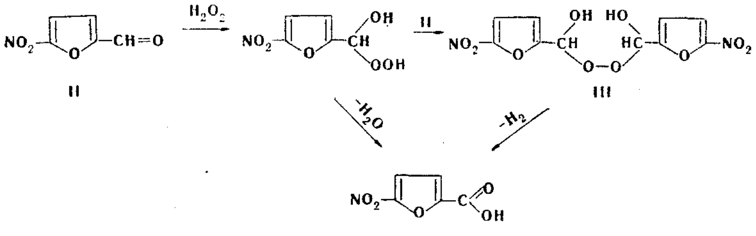
UDC 547.725.09

5-Nitrofuran-2-carboxylic acid was obtained in quantitative yield by oxidation of 5-nitrofurfural with hydrogen peroxide and decomposition of the intermediate 5-nitrofurfural α-hydroxyhydroperoxide. The mechanism of the reaction is discussed.

Several methods for the preparation of 5-nitrofuran-2-carboxylic acid (I) are known: by oxidation of 5-nitrofurfural diacetate with potassium dichromate [1, 2] and by nitration of pyromucic acid ester [3]. The most widely used method [2] has disadvantages – low yields of acid I (52%) and the time required to carry out the reaction.

The methods that we propose are simple to execute and give a high-purity product in quantitative yields. Acid I was obtained by oxidation of 5-nitrofurfural (II) with 25-35% H_2O_2 or by decomposition of 5-nitrofurfural α-hydroxyhydroperoxide (III) in water. Hydroxyhydroperoxide III was obtained by oxidation of II in dioxane with 70-75% hydrogen peroxide. The reaction times in both cases do not exceed 3 h, the products are obtained in 90-100% yields and do not contain any impurities, inasmuch as the oxidizing agent is decomposed to water, and the starting materials react completely.

The mechanism of the formation of I from II was studied kinetically and from the intermediates by chromatography [4]. The reaction proceeds through a step involving the formation of 5-nitrofurfural hydroxyperoxides (see the reaction scheme below), and the formation of acid I through both a dihydroxyperoxide and hydroxyhydroperoxide III is possible. The latter is confirmed by the synthesis of I from hydroxyhydroperoxide III.



The proposed methods can be used as preparative methods and can be realized in large volumes. Acid I obtained by this method has 99.9% purity and is stable on storage for more than a year.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-10 spectrometer. The UV spectra were recorded with a Spektromom-203 spectrophotometer (Hungary). Thin-layer chromatography (TLC) was carried out on Silufol plates (Czechoslovakian SSR) in toluene–ethanol (20:3), and paper chromatography was carried out with Filtrak No. 12 paper (German Democratic Republic) in butanol saturated with formic acid and water (9:1:14). The developers were solutions of 2,4-dinitrophenylhydrazine and Bromphenol Blue.

Krasnodar Polytechnic Institute. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1172-1173, September, 1975. Original article submitted July 16, 1974.

The nitrofurfural (II) used for the oxidation was obtained by the method in [3] and did not require prior purification. The syntheses of acid I were carried out until the starting furfural II was completely consumed: R_f 0.54 (TLC) and 0.86 [paper chromatography (PC].

5-Nitrofuran-2-carboxylic Acid (I) from 5-Nitrofurfural (II). A 10-g (0.071 mole) sample of II was dissolved by heating in 2-3 ml of dioxane, and 8.6 ml (0.071 mole) of 28% H_2O_2 was added to the resulting solution at 70° with stirring. After 1.5-2 h, the mixture was cooled, and the resulting precipitate was removed by filtration, washed with a small amount of water to remove traces of H_2O_2, and air dried to give 11 g (98%) of acid I as colorless crystals with mp 184°. UV spectrum (ethanol), λ_{max}, nm (log ε): 213 (4.04) and 310 (4.05). According to [3, 6], this compound has mp 184-185° and the following UV spectrum [λ_{max}, nm (log ε)] 213 (4.03) and 310 (4.04). The IR spectrum was identical to the spectrum of a reference spot [3]; R_f 0.16 (TLC) and 0.80 (PC).

5-Nitrofuran-2-carboxylic Acid (I) from 5-Nitrofurfural α-Hydroxyhydroperoxide (III). A 4.76-g sample of III in 10 ml of water was heated with stirring at 70° for 2-3 h, after which the precipitated crystals were worked up as in the preceding experiment to give 4.0 g (93%) of a product with mp 184°. The UV and IR spectra were identical to the spectra of a reference spot.

LITERATURE CITED

1. H. Gilman and J. Wright, J. Amer. Chem. Soc., 2500 (1930).
2. S. A. Giller, B. V. Kurgan, and N. O. Saldabol, Izv. Akad. Nauk SSSR, 140, 49 (1959).
3. A. A. Ponomarev, Syntheses and Reactions of Furan Compounds [in Russian], Saratov (1964).
4. G. D. Krapivin, L. A. Badovskaya, and V. G. Kul'nevich, Khim. i Khim. Tekhnol., Trudy KPI, Krasnodar, No. 63, 27 (1974).
5. Ya. É. Eidus, A. Ya. Ékame, K. K. Venter, and S. A. Giller, Atlas of Electronic Spectra of 5-Nitrofuran Compounds [in Russian], Riga (1968), p. 76.