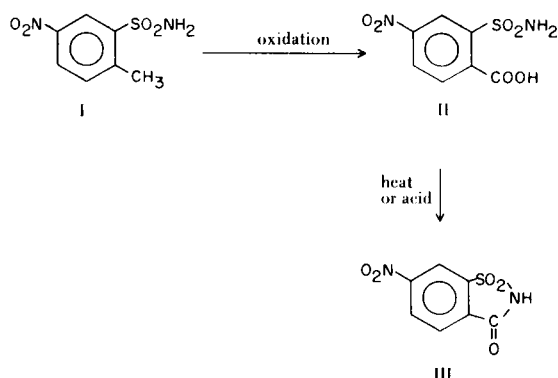


6-Nitrosaccharin

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The preparation of 6-nitrosaccharin was first reported by Noyes (1,2). Noyes oxidized 5-nitro-*o*-toluenesulfonamide (I) to 4-nitro-2-sulfamoylbenzoic acid (II) using potassium permanganate. 6-Nitrosaccharin (III) was obtained by maintaining II at a temperature above its melting point or by adding hydrochloric acid to a hot, concentrated solution of the potassium salt of II.



Other workers, in efforts to prepare artificial sweetening agents, have since employed Noyes' method (3,4). However, Loev and Kormendy state that in their hands the permanganate oxidation of I gave quite low yields of II (5). Attempts by these workers to improve the oxidation step by the use of manganese dioxide or ammonium persulfate as oxidizing agents were unsuccessful. Oxidation of I by permanganate in this laboratory also gave only very low yields of II under a variety of conditions and under a variety of modes of addition.

It was found that I could be oxidized and cyclized to form III in good yield in one step if a mixture of chromic trioxide and sulfuric acid were used as the oxidant. In this reaction it is essential that the oxidation be carried out at a temperature of 65° or higher because the oxidation does not seem to occur at lower temperatures. The

product was isolated by diluting the reaction mixture and filtering. That the desired product was produced was confirmed by reduction of the 6-nitrosaccharin to 6-aminosaccharin.

Starting material (I) was prepared by a procedure based upon that of Ullmann and Lehner for the chlorosulfonation of 4-nitrotoluene with chlorosulfonic acid (6). The organic material from the reaction was taken up in ether and stirred very vigorously with ammonium hydroxide. The desired amide precipitated as it is only slightly soluble in ether. Unreacted starting material remained in the ether and the sulfonamide thus produced was sufficiently pure for the oxidation step.

EXPERIMENTAL

5-Nitro-*o*-toluenesulfonamide (I).

A mixture of practical 4-nitrotoluene (10 g., 0.073 mole) and practical chlorosulfonic acid (30 g., 0.26 mole) was heated at 100° for 1 hour, cooled, and poured carefully onto ice. The brown, two phase mixture was extracted with 75 ml. of ether. Fifty ml. of concentrated ammonium hydroxide was added to the ether which was stirred very vigorously during the addition. Stirring was continued until the amide had formed. The 5-nitro-*o*-toluenesulfonamide was removed by filtration, washed with cold ether, dilute hydrochloric acid and water. The tan, crude product (8.6 g., 54% of the theoretical yield; m.p. 182-186°, lit. (1) 186-187°) was used in the next step.

6-Nitrosaccharin (III).

5-Nitro-*o*-toluenesulfonamide (4.3 g., 0.02 mole) and 25 ml. of concentrated sulfuric acid were heated to 65°. Technical chromium trioxide (6 g.) was added with stirring at a rate that kept the temperature between 65 and 70°. During the addition (20-30 minutes) a gas was evolved and the mixture became quite viscous. Stirring was continued for an additional 15 minutes while the temperature was kept between 65-70°. After being cooled, the mixture was poured into 100 ml. of water. The 6-nitrosaccharin (2.5 g., 55% of the theoretical yield) was removed by filtration and washed with water. Melting point, after recrystallization from water, was 208-209°, lit. (1) 209°. Infrared spectrum was consistent with the structure for 6-nitrosaccharin.

Reduction of a sample of 6-nitrosaccharin with ammonium sulfide (light, 20% solution) in an alkaline solution gave 6-aminosaccharin. After recrystallization from water, the product had a m.p. of 279-280°; lit. (3) 279°.

REFERENCES

- (1) W. A. Noyes, *Am. Chem. J.*, **8**, 167 (1886).
- (2) W. A. Noyes and W. B. Wiley, *ibid.*, **11**, 161 (1889).
- (3) C. Finzi and M. Colonna, *Gazz. Chim. Ital.*, **68**, 132 (1938).
- (4) L. Szabo, *Bull. Soc. Chim. France*, 771 (1953).
- (5) B. Loev and M. Kormendy, *J. Org. Chem.*, **27**, 2177 (1962).
- (6) F. Ullmann and A. Lehner, *Ber.*, **38**, 729 (1905).
- (7) The melting points are uncorrected. The IR spectra were determined as pressed potassium bromide discs with a Perkin-Elmer Model 137 spectrophotometer.

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