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The Preparation of 6-Nitro-3-acetamidotoluene

Aoi Ono

Chemical Laboratory, Takada Branch, Faculty of Education, Niigata University, Nishishiro-cho, Joetsu 943

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Synopsis. *m*-Acetamidotoluene was nitrated with fuming nitric acid in acetic acid or in a mixture of acetic and sulfuric acids at 20 °C, affording 6-nitro-3-acetamidotoluene in 38.6 and 53.7% yields respectively. The melting point of the product was found to be different from that reported in the literature.

In order to analyze mononitro acetamidotoluenes and toluidines by GLC, an authentic, pure sample of 6-nitro-3-acetamidotoluene was prepared by the simplest way. Noelting(1) reported that 6-nitro-3-aminotoluene could be obtained by the nitration of *m*-toluidine in a mixture of nitric and sulfuric acids. Coffey(2) nitrated *m*-acetamidotoluene with copper(II) nitrate. Cohen *et al.*(3) and Cook *et al.*,(4) nitrated *m*-acetamidotoluene with fuming nitric acid in acetic acid. Cohen *et al.*(5) and Morgan *et al.*(6) nitrated *m*-acetamidotoluene with a mixture of nitric and sulfuric acids. Morgan *et al.*,(7) Wibant,(8) and Cook *et al.*(4) compared the yields and ratios of 6- and 4-nitro-3-acetamidotoluenes formed under various conditions. However, the ratio of products (6- and 4-nitro-3-acetamidotoluenes) still remains ambiguous and the reported purification procedure seems unsatisfactory. The present author has, therefore, reinvestigated the procedure and found that an erroneous melting point of 6-nitro-3-acetamidotoluene was reported.

Experimental

The GLC analyses were performed on a 100 cm column (i.d. 3.0 mm) packed with C_{22} 60—80 mesh coated with 3% Silicone OV-17 or 20% Silicone KF-54 at 220 °C, using a Shimadzu GC-5A GC apparatus with FID. The IR and NMR spectra were recorded on a Hitachi EPI-S2 IR spectrophotometer and a Varian T-60 NMR spectrometer respectively. The measurement of the mp (corrected) and DTA were performed with a Yanagimoto Micro-Melting-Point Apparatus and a Rigaku Thermal TG-DTA M8075 respectively.

Reagent. The *m*-acetamidotoluene was prepared by refluxing a mixture of 70 g of *m*-toluidine (guaranteed grade, from the Nakarai Chemical Co.) and 300 ml of acetic acid (extra pure reagent, also from the Nakarai Chemical Co.) for 8 h. Fuming nitric acid (*d*, 1.50) and sulfuric acid (95%) of an extra pure reagent grade were purchased from the Nakarai Chemical Co.

Preparation. Part 1. Twenty grams of *m*-acetamidotoluene, suspended in 50 ml of acetic acid, were nitrated by adding 40 ml of fuming nitric acid (*d*, 1.50) over a period of 10 min with effective stirring below 20 °C. After the reaction, the contents were poured into 1 litre of ice water, and then the solid was filtered and dried. Pure 6-nitro-3-acetamidotoluene was obtained in a 38.6% yield after twice recrystallizations from 30% aqueous ethanol. Part 2. Twenty grams of *m*-acetamidotoluene were nitrated in a mixture of 30 ml of acetic and 30 ml of sulfuric acids with fuming nitric acid by the procedure described in Part 1. The yield was 53.7%. The melting point of the compound recrystallized from 30% aqueous ethanol or benzene was 117 °C, in contrast to the reported values of 101—102(9) and 103—104 °C.(3) Found: C, 50.98; H, 5.72; N, 13.49%. Calcd for $C_9H_{12}N_2O_4$: C, 50.94; H, 5.60; N, 13.20%. GLC retention time: 16.00 min on Silicone KF-54; 4.00 min on Silicone OV-17. TLC R_f; 0.50 on a silica gel plate; 0.80 on an alumina plate (solvent; carbon tetrachloride: ethyl acetate, 9: 1, v/v) at room temperature. IR; 3600—3200 (νNH_2), 1680 (νCO), 870 (δNO_2), and 750 cm^{-1} (δNH_2) NMR; δ (TMS, CD_3OD), 2.13 (s, 3H), 2.38 (s, 3H), 7.53—7.75 (m, 2H) and 7.90—8.11 (m, 1H).

6-Nitro-3-aminotoluene was obtained by the hydrolysis of 6-nitro-3-acetamidotoluene. Mp 136—138 °C (lit, 136—138,(5) 138—140 °C(7)); Found: C, 55.30; H, 5.29; N, 18.74%. Calcd for $C_7H_8N_2O_2$: C, 55.25; H, 5.30; N, 18.41%. GLC retention time; 6.00 min on Silicone KF-54; 1.00 min on Silicone OV-17. TLC R_f; 1.70 on a silica gel plate; 2.00 on an alumina plate (solvent: carbon tetrachloride: ethyl acetate, 9:1, v/v) at room temperature. IR; 3550, 3400 (νNH_2), 1620 ($\nu C{=}C$), 1300, 1250 (νNO_2), 850 (δNO_2), and 815 cm^{-1} (δNH_2). NMR; δ (TMS, CD_3OD), 2.61 (s, 3H), 6.56 (m, 2H), and 7.93—8.10 (m, 1H).

Results and Discussion

As has been mentioned in the Experimental section, when *m*-acetamidotoluene was nitrated in acetic acid or in a mixture of acetic and sulfuric acids (1: 1, v/v), 6-nitro-3-acetamidotoluene was obtained in a 38.6 or 53.7% yield respectively, after twice recrystallizations from 30% aqueous ethanol. The purity of the product was confirmed by GLC, TLC, IR, and NMR.

However, the melting point of the product was 117 °C, which is apparently different from that reported in the literature (lit, 101—102,(9) 103—104 °C(3)). Then DTA and elemental analyses were undertaken. The results of elemental analyses were reported in the Experimental section, the diagram of DTA had two peaks, at 117 and 102 °C, and the weight loss on DTA at 102 °C corresponded to the weight of one molecule of water. From these data, the prepared product was identified as 6-nitro-3-acetamidotoluene monohydrate. Details concerning the molecular structure of this prepared product will be reported elsewhere in the near future.

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