The Hofmann Rearrangement Using Household Bleach: Synthesis of 3-Nitroaniline

Keith A. Monk and Ram S. Mohan*
Department of Chemistry, Illinois Wesleyan University, Bloomington, IL 61702; **rmohan@titan.iwu.edu*

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The Hofmann rearrangement involves the conversion of an amide to an amine containing one fewer carbon atoms, by treatment with bromine (or chlorine) and alkali (*1*). The mechanism of this reaction is discussed in detail in most sophomore organic chemistry text books. Yet very few examples of this rearrangement are found in lab texts (*2*). With aromatic amides containing an electron-withdrawing group, hydrolysis to the corresponding carboxylic acid under the basic reaction conditions is often a serious competing side reaction. It has been reported that at elevated temperatures, the rearrangement is much more rapid than hydrolysis (*3*). We have successfully carried out the rearrangement of 3-nitrobenzamide at 80 °C using household bleach.[1] This procedure avoids the use of bromine and sodium hydroxide, which is typically used to effect the Hofmann rearrangement. The preparation of 3-nitrobenzamide from benzamide has been previously reported as a laboratory experiment (*4*). These two reactions can be completed in two-and-a-half hours, making this sequence a new and useful addition to the list of organic chemistry laboratory experiments.

Experimental Procedure

3-Nitrobenzamide was prepared by nitration of benzamide or purchased from Aldrich Chemical Co. The concentration of household bleach solution was determined to be 5.25% (wt/wt) by iodometric titration.

CAUTION: Nitro compounds are often toxic. Gloves should be worn throughout this experiment. Contact should be avoided with bleach solutions.

Finely powdered 3-nitrobenzamide (1.5 g, 9.03 mmol) was added to a 125-mL Erlenmeyer flask containing a magnetic stir bar, 18 mL of 1 M NaOH (18 mmol), and 13.3 mL (14.1 g) of household bleach (9.93 mmol).[2] The well-stirred mixture was heated at 80 °C in a water bath for 30 min. The mixture was cooled to 50 °C and then 10% aqueous $NaHSO_3$ (10 mL) was added, which resulted in the precipitation of a yellow solid. The flask was cooled in an ice bath and the solid was collected by suction filtration. Recrystallization from 95% ethanol gave 1.01 g (80%) of silky yellow crystals. The product was identical by TLC, mp, ^1H NMR, and ^{13}C NMR with an authentic sample of 3-nitroaniline. ^1H NMR (270 MHz) (DMSO): δ 5.82 (s, NH_2), 6.96 (doublet of triplets, 1 H), 7.28 (m, 2 H), 7.39 (t, 1 H). ^{13}C NMR (DMSO): δ 107.7, 111.4, 120.5, 130.3, 149.3, 150.6.[3]

Notes

1. It has been reported that 2-nitroaniline, the product of Hofmann rearrangement of 2-nitrobenzamide, reacts with NaOCl and alkali to give benzofuroxan (*5*). Under the same conditions 4-nitrobenzamide gives 50% 4-nitroaniline and 50% 4-nitrobenzoic acid (*3*).

2. The presence of excess bleach is checked using starch–iodide paper.

3. 3-Nitroaniline is not sufficiently soluble in $CDCl_3$. Hence spectra were recorded in d_6-DMSO.

Literature Cited

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