

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

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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 NaHSO₃ (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 ¹³C NMR with an authentic sample of 3-nitroaniline. ¹H NMR (270 MHz) (DMSO): δ 5.82 (s, NH₂), 6.96 (doublet of triplets, 1 H), 7.28 (m, 2 H), 7.39 (t, 1 H). ¹³C 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 CDCl₃. Hence spectra were recorded in *d*₆-DMSO.

Literature Cited

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