of water (250 ml.) and concentrated ammonium hydroxide (15 ml.) and the resulting deep red solution treated at room temperature and ordinary pressure with tank hydrogen in the presence of Raney nickel catalyst in an apparatus[15] designed for this purpose. The reduction, which proceeded rapidly in the beginning but gradually slowed down, appeared complete at the end of three hours, by which time 90% of the theoretical amount of hydrogen had been absorbed. The catalyst was removed by filtration and the light yellow filtrate acidified with 45 ml. of acetic acid solution (33%). The resulting precipitate was collected, redissolved in dilute aqueous ammonia and reprecipitated with dilute acetic acid and this sequence repeated once again. The yield was 3.6 g. (70%) of colorless, flaky crystals. This method of purification was used because the compound was insoluble in water and all the usual organic solvents. The substance, if heated rapidly, melted with decomposition at 210–212° and, if heated slowly, began to darken at around 200° and gradually carbonized without melting as the temperature was increased to 320° (limit of oil-bath).

Anal. Calcd. for $C_9H_9O_2N_3$: C, 56.51; H, 4.75; N, 21.99; neut. equiv., 191. Found: C, 56.22; H, 4.95; N, 21.2; neut. equiv., 192.

The compound was soluble in dilute ammonium hydroxide, insoluble in dilute acetic acid, soluble in dilute hydrochloric acid and did not reduce hot Fehling solution. Since the substance was very insoluble in water and alcohol, the neutralization equivalent was determined by solution in excess standard alkali and back titration with standard acid.

4-Acetaminohomophthalyl Cyclic Hydrazide.—4-Aminohomophthalyl cyclic hydrazide (1.5 g.) was refluxed in acetic anhydride (5 ml.) for a half hour. The precipitate obtained was insoluble in water and all the usual organic solvents, but was purified by solution in dilute aqueous ammonia and precipitation with dilute acetic acid. The yield was 1.3 g. (70%) of cream-colored crystals which did not melt at 320° (limit of oil-bath).

Anal. Calcd. for $C_{11}H_{11}O_3N_3$: C, 56.62; H, 4.75; N, 18.03; neut. equiv., 233. Found: C. 56.14; H. 5.02; N. 17.42; neut. equiv., 235.

The compound was soluble in dilute ammonium hydroxide. insoluble in dilute acetic acid and dilute hydrochloric acid and did not reduce hot Fehling solution. The neutralization value of this substance, like that of 4-aminohomophthalyl cyclic hydrazide, was determined by solution in excess standard alkali and back titration with standard acid.

Summary

1. The chromic acid oxidation of indene directly to homophthalic acid is by far the simplest and most economical of all the methods reported for the preparation of this acid.

2. The only method by which homophthalyl cyclic hydrazide could be prepared was by the interaction of homophthalic anhydride with hydrazine hydrate in either boiling ethyl alcohol or hot glacial acetic acid.

3. Homophthalyl cyclic hydrazide rearranged to N-aminohomophthalimide when refluxed in glacial acetic acid.

4. In the preparation of 4-aminohomophthalyl cyclic hydrazide, two other new compounds used as intermediates were formed, namely, 4-nitrohomophthalic anhydride and 4-nitrohomophthalyl cyclic hydrazide.

5. Substitution of the asymmetrical 7-membered cyclic hydrazide ring of the homophthalyl cyclic hydrazides for the symmetrical 6-membered cyclic hydrazide ring of the homologous phthalyl cyclic hydrazides caused a great decrease in the oxidative chemiluminescence.

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[15] Lieber and Smith, THIS JOURNAL, **57**, 2479 (1935).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE STATE UNIVERSITY OF IOWA]

2-(4-Nitrobenzoylamino)-phenol: a Correction on its Identity

BY L. CHARLES RAIFORD[1] AND NATHAN N. CROUNSE[2]

In studying certain molecular rearrangements, it was necessary to prepare 2-(4-nitrobenzoylamino)-phenol (I) previously prepared in low yield by Tingle and Williams,[3] who reported a melting point of 219° as well as a secondary product, 2-(4-nitrobenzoylamino)-phenyl 4-nitrobenzoate (III), m. p. 220°. Because of their low yield, we decided to prepare the phenol by another method for introducing the acyl group onto nitrogen and not oxygen in 2-aminophenols. We obtained a compound, m. p. 202–203°, which analyzed for 2-(4-nitrobenzoylamino)-phenol (I). Its phenolic character was shown by its solubility in alkali and its methylation to form an ether (II). Because of the discrepancy in melting points between the reported compound and ours, the earlier work was repeated. We isolated two fractions melting at 219° and 219–220° as reported. These were found by mixed melting point to be the same compound which on analysis, hydrolysis, and synthesis was identified as 2-(4-nitrobenzoylamino)-phenyl 4-nitrobenzoate (III). An examination of the alkaline filtrate, evidently not done in the earlier work, produced a compound, m. p. 202–203°, identical with our phenol.

Experimental

2-(4-Nitrobenzoylamino)-phenol (I).—A hot solution of 27.3 g. of 2-aminophenol in 125 ml. of dioxane and 35 ml. of dimethylaniline was cooled rapidly to give a slush of tiny crystals. A solution of 46.5 g. of 4-nitrobenzoyl chloride in 105 ml. of dioxane was added slowly with stirring and cooling with cold water. The resulting solution after standing overnight was poured into an excess of dilute hydrochloric acid. Filtration gave 61 g. of a yellow solid, m. p. 200–202°, which was dissolved in dilute potassium

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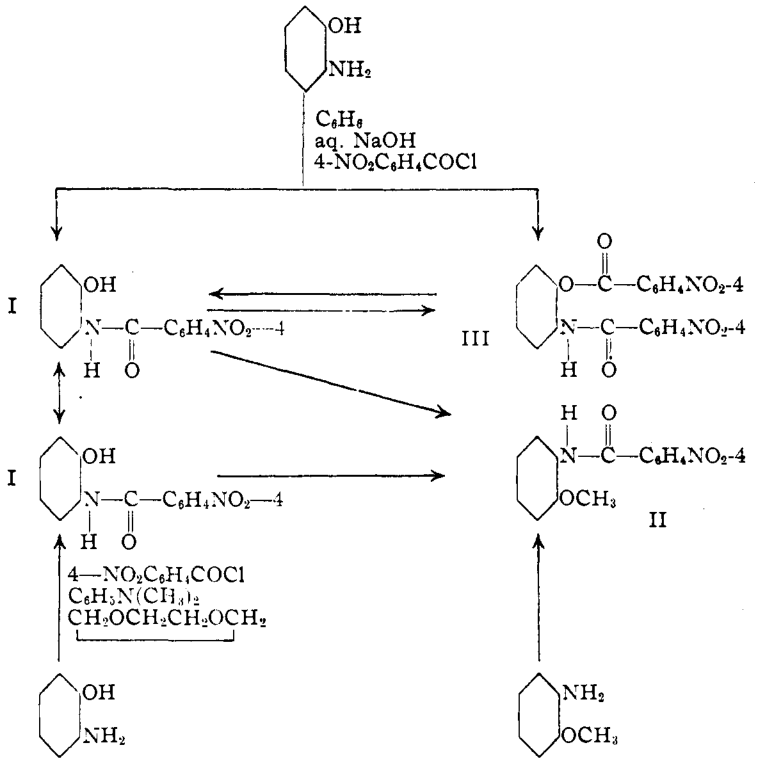
[1] Deceased January 8, 1944.

[2] This paper is a condensation of a portion of a thesis submitted by Nathan N. Crounse in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the State University of Iowa. Present address: The Hilton-Davis Chemical Co., Cincinnati, Ohio.

[3] Tingle and Williams, *Am. Chem. J.*, **37**, 59 (1907).



hydroxide, treated with charcoal, filtered, and recovered from the filtrate by addition of carbon dioxide. Crystallization from glacial acetic acid gave 50 g. (77%) of cream colored needles, m. p. 202–203°. Neither crystallization from *n*-butyl alcohol nor extraction of the solid with acetone in the Soxhlet extractor raised the melting point.

Anal. Calcd. for $C_{13}H_{10}O_4N_2$: N, 10.85. Found: N, 10.98.

2-(4-Nitrobenzoylamino)-anisidide (II). **(a) From 4-Nitrobenzyl Chloride and 2-Anisidine.**—A solution of 9.9 g. of 4-nitrobenzoyl chloride in 30 ml. of dioxane was added to a stirred water cooled solution of 6.3 g. of 2-anisidine in 11 ml. of pyridine. After standing for twenty-four hours at room temperature, yellow needles precipitated. The mixture was poured into dilute hydrochloric acid, and the resulting yellow solid was purified by repeated crystallization from ethanol, giving 11 g. (80%) of yellow needles, m. p. 145.5–146°.

Anal. Calcd. for $C_{14}H_{12}N_2O_4$: N, 10.27. Found: N, 10.32.

(b) **From Methyl Iodide and (I).**—To 2.58 g. of (I) dissolved in 20 ml. of methanol containing 0.3 g. of sodium as sodium methylate was added 11.5 g. of methyl iodide with a slight evolution of heat. After five minutes the solution was refluxed for forty-five minutes, water was added, and the excess methyl iodide boiled out. Filtration gave 2.5 g. of yellow needles, m. p. 137–139°. Two crystallizations from ethanol and one from 50% ethanol–chloroform mixture gave 1.5 g. (55%) of flat yellow rods, m. p. 144–145°. A mixed melting point with the compound prepared in (a) was 145–145.5°.

Anal. Calcd. for $C_{14}H_{12}N_2O_4$: N, 10.27. Found: N, 10.28.

2-(4-Nitrobenzoylamino)-phenyl 4-Nitrobenzoate (III).—A solution of 1.9 g. of 4-nitrobenzoyl chloride in 10 ml. of chloroform was added to a solution of 2.58 g. of (I) in 2 ml. of pyridine and 20 ml. of chloroform. Heat was evolved, and a precipitate formed. After twenty-four hours the chloroform was removed by steam distillation, and the mixture acidified to remove pyridine. The precipitate was crystallized by suspension in boiling ethyl acetate and addition of dioxane until solution was complete to give 2 g. (40%) of fluffy pale yellow needles, m. p. 219°.

Anal. Calcd. for $C_{20}H_{13}O_7N_3$: N, 10.32. Found: N, 10.32.

Repetition and Amplification of Tingle and Williams' Work.—In a carbon dioxide atmosphere, 12.7 g. of 4-nitrobenzoyl chloride in 40 ml. of benzene was added alternately with a solution of 8.8 g. of potassium hydroxide in 32 ml. of water to a stirred solution of 3.8 g. of 2-aminophenol in 50 ml. of 2.6% hydrochloric acid. The precipitated material was filtered from the water–benzene mixture (investigated below), and extracted in a Soxhlet thimble with acetone for one hour. Five grams of pale yellow needles, m. p. 219–220°, settled out of the acetone while 1.2 g. of needles, m. p. 220°, remained in the thimble. A mixed melting point of these two fractions came at 219–220°. Tingle and Williams did not report a mixed melting point.

Anal. Calcd. for $C_{20}H_{13}O_7N_3$: N, 10.32. Found: N, 10.36.

Proof that the compound in hand was 2-(4-nitrobenzoylamino)-phenyl 4-nitrobenzoate (III) was shown by a mixed melting point with (III). The mixed melting point was 219.5°. Also on hydrolysis 4-nitrobenzoic acid and 2-(4-nitrobenzoylamino)-phenol (I) were formed as shown below.

One and one-tenth grams of the questioned compound, m. p. 219–220°, was dissolved in 17 ml. of ethanol containing 3 g. of potassium hydroxide, and the resulting solution was heated for one minute on the steam-bath, poured into water, and acidified. The precipitate was extracted with sodium bicarbonate to separate the 4-nitrobenzoic acid which was identified by mixed melting point. On crystallization from dilute acetic acid, the residue gave needles, m. p. 203–204°, which gave a mixed melting point of 203–203.5° when mixed with (I).

The water–benzene mixture obtained above was not investigated by Tingle and Williams. It was separated, and the benzene layer was dried with sodium sulfate and evaporated to dryness. Only traces of solid remained. The aqueous layer was saturated with carbon dioxide. Three and one-half grams of brown solid, m. p. 196–197°, settled out. Crystallization from glacial acetic acid yielded tiny needles, m. p. 202–203°, which did not depress the melting point of (I). Acidification of the potassium carbonate filtrate gave 3 g. of 4-nitrobenzoic acid identified by mixed melting point.

Methylation of 1.2 g. of the phenol, isolated from the water layer, with 6.8 g. of methyl iodide in 10 ml. of methanol containing 0.015 g. of sodium as sodium methylate as in (II) (b) gave 57% yield of the ether, m. p. 144.5–145°. A mixed melting point with (II) was 145–145.5°.

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Summary

1. An improved synthesis and correction of the data in the literature for 2-(4-nitrobenzoylamino)-phenol have been given.

2. The synthesis of the methyl ether of 2-(4-nitrobenzoylamino)-phenol has been described.

3. The compound previously reported as 2-(4-nitrobenzoylamino)-phenol has been shown to be 2-(4-nitrobenzoylamino)-phenyl 4-nitrobenzoate.

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