reduction of 1,3:2,4-dimethylene-6-iodo-D-sorbitol. The yield was 0.75 g.

1,5-Diacetyl-3-acetoxymethyl-2,4-methylene-D-epirhamnitol (V) from 1,3:2,4-Dimethylene-D-epirhamnitol (IV).—Three grams of 1,3:2,4-dimethylene-D-epirhamnitol was dissolved in 15 cc. of an ice-cold acetylating mixture prepared by adding 1 cc. of concentrated sulfuric acid dropwise to an ice-cold mixture of 70 cc. of acetic anhydride and 30 cc. of glacial acetic acid. The solution was shaken in a bath at 0° and after about ten minutes it set to a magma of fine needles. The reaction mixture was diluted with 200 cc. of ice-water and, after, two hours, the precipitate (3.9 g.) was separated by filtration; the filtrate was extracted with chloroform and upon evaporation of the extract an additional 0.7 g. of product was recovered, the total yield of 4.6 g. being 87%. The compound was recrystallized from 8 parts of alcohol as long, fine needles which melted at 116–117° and rotated $[\alpha]^{20}D$ +5.3° in chloroform (*c*, 0.90). It is soluble in benzene, ethyl acetate, acetone and pyridine and practically insoluble in water, cold alcohol and ether.

Anal. Calcd. for $C_{14}H_{22}O_9$: C, 50.29; H, 6.63; saponification, 100 mg. substance requires 8.97 cc. 0.1 *N* alkali. Found: C, 50.30; H, 6.62; saponification, 100 mg. substance consumed 8.93 cc. 0.1 *N* alkali.

2,4-Methylene-D-epirhamnitol (VI) from 1,5-Diacetyl-3-acetoxymethyl-2,4-methylene-D-epirhamnitol (V).—An ice-cold solution of 2.0 g. of 1,5-diacetyl-3-acetoxymethyl-2,4-methylene-D-epirhamnitol in 10 cc. of chloroform was mixed with 2 cc. of 0.2 *N* sodium methylate and the reaction mixture was allowed to stand at 5° for two days; the crystalline precipitate of 2,4-methylene-D-epirhamnitol which had deposited was separated by filtration and upon recrystallization from 15 parts of alcohol it formed prismatic needles melting at 176–177° and rotating $[\alpha]^{20}D$ −20.2° in water (*c*, 0.90). The yield was 1.1 g. (quantitative). The acetal is soluble in cold water and hot methyl and ethyl alcohols, moderately soluble in pyridine and practically insoluble in cold alcohol, chloroform, dioxane and hot or cold benzene or ethyl acetate.

Anal. Calcd. for $C_7H_{14}O_5$: C, 47.18; H, 7.92. Found: C 47.35; H, 7.88.

Stability of 2,4-Methylene-D-epirhamnitol (VI) against Oxidation by Per-iodic Acid.—To a solution of 0.1016 g. of 2,4-methylene-D-epirhamnitol in 15 cc. of water at 25°, 2.50 cc. (3 molecular equivalents) of 0.675 *M* per-iodic acid was added and the volume was adjusted to 25 cc. with water. Analysis of 5-cc. subsamples at the expiration of two, five and seventy hours showed that none of the oxidant had been consumed. The methylene-D-epirhamnitol therefore does not contain a glycol grouping as a part of its structure. The only possible structure for a monoacetal of a 6-desoxy-hexitol which conforms with this limitation is that of a 2,4-acetal; methylene-D-epirhamnitol is therefore 2,4-methylene-D-epirhamnitol.

1,3,5-Triacetyl-2,4-methylene-D-epirhamnitol.—A solution of 0.6 g. of 2,4-methylene-D-epirhamnitol in a mixture of 5 cc. of pyridine and 6 cc. of acetic anhydride was allowed to stand at 25° for three days, during which time some precipitation of needles occurred. The reaction mixture was poured into 150 cc. of ice water and the precipitated triacetyl derivative (1.0 g.; quantitative) was collected and recrystallized from 10 parts of alcohol. It formed needles which melted at 149–150° and rotated $[\alpha]^{20}D$ −0.6° in chloroform (*c*, 1.24) and −1.8° in acetone (*c*, 0.96). The compound is also soluble in ether, benzene and ethyl acetate; it is practically insoluble in cold methyl and ethyl alcohols, petroleum ether and water.

Anal. Calcd. for $C_{13}H_{20}O_8$: C, 51.31; H, 6.62; CH_3CO, 42.4. Found: C, 51.29; H, 6.63; CH_3CO, 42.1.

Summary

The conversion of 1,3:2,4-dimethylene-D-sorbitol to 1,3:2,4-dimethylene-D-epirhamnitol has been described. The first named diacetal, upon treatment in pyridine solution with one molecular equivalent of *p*-toluenesulfonyl chloride, forms a monotosyl compound which can be converted to an iodo-1,3:2,4-dimethylene-D-sorbitol that is reduced by hydrogen and Raney nickel to a desoxy-1,3:2,4-dimethylene-D-sorbitol; the latter substance is identical with a diacetal that is obtained by the condensation of D-epirhamnitol and formaldehyde and hence it can be only 6-desoxy-1,3:2,4-dimethylene-D-sorbitol (*syn.*,1,3:2,4-dimethylene-D-epirhamnitol).

The 1,3:2,4-dimethylene-D-epirhamnitol has been subjected to limited acetolysis and the acetolysis product has been saponified to a monomethylene-D-epirhamnitol which is not oxidized by aqueous per-iodic acid, a fact which limits its structure to that of 2,4-methylene-D-epirhamnitol.

BETHESDA, MARYLAND RECEIVED APRIL 22, 1944

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF POLYTECHNIC INSTITUTE OF BROOKLYN]

The Preparation of Homophthalyl Cyclic Hydrazide and 4-Aminohomophthalyl Cyclic Hydrazide

BY WILLET F. WHITMORE AND ROBERT C. COONEY[1]

This paper describes the preparation of some homophthalyl cyclic hydrazides, homologous to the phthalyl cyclic hydrazides. The investigation was undertaken in order to study the effect of the substitution of the asymmetrical 7-membered cyclic hydrazide ring of the former type for the symmetrical 6-membered cyclic hydrazide ring of the latter type on the property of chemiluminescence.

Most of the conventional methods that could be used for the preparation of these new compounds would utilize homophthalic acid or one of its derivatives as the starting substance. Homophthalic acid was prepared by an extremely facile method,[2] which appears to have been overlooked by more recent investigators[3,4] studying homophthalic acid derivatives. In this method, a chromic acid oxidation of indene produces homophthalic acid directly in yields of 58%.

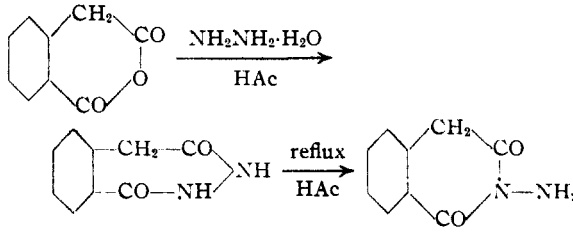
(1) An abstract of a dissertation presented in May, 1943, to the Graduate Faculty of Polytechnic Institute of Brooklyn by Robert C. Cooney in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Meyer and Vittenet, *Ann. Chim.*, [10] **17**, 271 (1932).

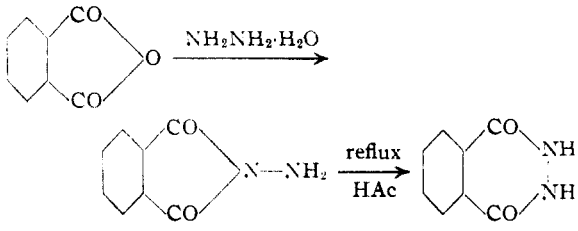
(3) Price, Lewis and Meister, THIS JOURNAL, **61**, 2762 (1939).

(4) Price, *Org. Syn.*, **22**, 30, 61 (1942).

Only one of the conventional methods used for the preparation of cyclic hydrazides produced homophthalyl cyclic hydrazide, parent member of the new series and homolog of phthalyl cyclic hydrazide. Attempts to dehydrate the hydrazine salt of homophthalic acid, or to hydrazinolyze dimethyl homophthalate and homophthalimide failed to yield any homophthalyl cyclic hydrazide. Homophthalyl chloride cannot be prepared by the usual methods,[5] and, therefore, was not available for hydrazinolysis. However, homophthalyl cyclic hydrazide was obtained, when homophthalic anhydride was treated with hydrazine hydrate, preferably in boiling ethyl alcohol. When the reaction was carried out in glacial acetic acid, the precipitate of homophthalyl cyclic hydrazide, that was initially obtained, rearranged, upon refluxing the mixture, to form N-aminohomophthalimide. This is precisely the



reverse of the change occurring when phthalic anhydride reacts with hydrazine hydrate.[6]

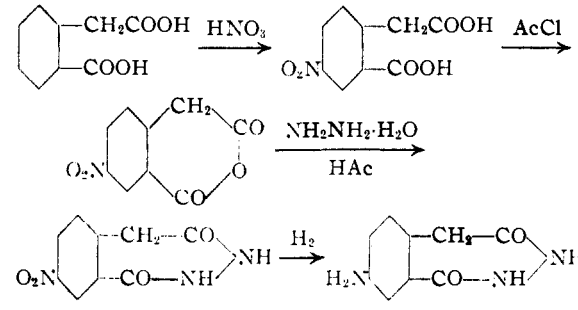


The changes indicated in the first set of formulas are predicated upon a consideration of the properties, analyses, constants and reactions of these new compounds. Homophthalyl cyclic hydrazide has physical and chemical properties typical of cyclic hydrazides, and its neutralization value and elementary analyses agree with the theoretical values. Attempts to prepare its monoacetyl derivative by the method of Huntress and Hearon[7] and its diacetyl derivative by the method of Drew and Hatt[6] were unsuccessful, but the refluxing of homophthalyl cyclic hydrazide in glacial acetic acid produced, by rearrangement, N-aminohomophthalimide. The latter has the physical and chemical properties manifested by aminoimides, and its neutralization value and elementary analyses agree with theory. In addition, it readily forms a monoacetyl derivative, whose neutralization value and elementary analyses agree with the calculated values.

(5) Davies and Poole, *J. Chem. Soc.*, 1617 (1928).
(6) Drew and Hatt, *ibid.*, 16 (1937).
(7) Huntress and Hearon, THIS JOURNAL, **64**, 88 (1942).

The formulas of the cyclic hydrazides are written in the keto form, but actually this form is in equilibrium with the monoenol form which acts as a monobasic acid and is titratable in the usual manner for a determination of the neutralization equivalent.

After a satisfactory method for the preparation of the parent compound, homophthalyl cyclic hydrazide, had been found, the authors desired to prepare 3-aminohomophthalyl cyclic hydrazide, the true homolog of "Luminol," but since homophthalic acid may be nitrated only in the 4-position, and reduction of the nitro group seemed to be the only practical method of introducing the amino group, 4-aminohomophthalyl cyclic hydrazide was synthesized.



The nitration of homophthalic acid by the use of potassium nitrate and concentrated sulfuric acid[8] gave a better yield and was found to be more reliable than nitration by the use of fuming nitric acid.[9] Dehydration of 4-nitrohomophthalic acid by the action of acetyl chloride gave a better yield than dehydration by the action of acetic anhydride. Treatment of 4-nitrohomophthalic anhydride in glacial acetic acid with hydrazine hydrate yielded 4-nitrohomophthalyl cyclic hydrazide, which had the physical and chemical properties anticipated. However, this compound could not be purified completely for analysis either by recrystallization, because it was insoluble in all of the usual organic solvents, or by repeated solution in dilute aqueous ammonia and subsequent precipitation with dilute acetic acid. Incidentally, earlier work[7] on the nitro cyclic hydrazides has indicated that their purification and analyses are sometimes difficult. Catalytic reduction of 4-nitrohomophthalyl cyclic hydrazide in ammoniacal solution by hydrogen and Raney nickel proved to be greatly superior to either reduction in an ammoniacal solution by ferrous sulfate or reduction in a hydrochloric acid solution by stannous chloride. The reduction product, 4-aminohomophthalyl cyclic hydrazide, also could not be recrystallized from any of the usual organic solvents, but it was readily purified by solution in dilute aqueous ammonia and precipitation with dilute acetic acid. This product had the physical and chemical properties typical of amino cyclic

(8) Borsch, Diacont and Hanau, *Ber.*, **67B**, 678 (1934).
(9) Ingold and Piggott, *J. Chem. Soc.*, **123**, 1497 (1923).

hydrazides, and it was further identified by elementary analyses and neutralization value. In addition, it formed a monoacetyl derivative whose elementary analyses agreed with the theoretical values.

Each of the compounds, phthalyl cyclic hydrazide, homophthalyl cyclic hydrazide, 4-nitrophthalyl cyclic hydrazide, 4-nitrohomophthalyl cyclic hydrazide, 4-aminophthalyl cyclic hydrazide and 4-aminohomophthalyl cyclic hydrazide was oxidized in sodium hydroxide solution with hydrogen peroxide under identical conditions, and the chemiluminescence of each homologous pair observed and compared qualitatively. In every case, the phthalyl cyclic hydrazide gave decidedly greater luminescence than the homologous homophthalyl cyclic hydrazide.

Experimental

All melting point values given are uncorrected.

Homophthalic Acid.—Potassium dichromate (240 g.) was dissolved in a solution of concentrated sulfuric acid (720 ml.) and water (3600 ml.), and this solution was heated to boiling in a 5-liter three-necked flask fitted with two 10-bulb Allihn condensers and a mechanical stirrer. Then 72 g. of indene[10] (87%) was added all at once through one of the condensers to the boiling, agitated solution. Immediately, such a vigorous oxidation occurred that for three minutes an active reflux was maintained without the use of agitation or heat. At the end of this time, the stirrer was started and heat applied to maintain the reflux for an additional seven minutes. Then the contents of the flask were chilled to 10° and the precipitate of homophthalic acid collected by filtration. To purify the product, the crude acid was dissolved in 250 ml. of dilute sodium hydroxide solution (10%), and the insoluble material extracted with 50 ml. of ether. The alkaline solution was acidified with 78 ml. of sulfuric acid solution (33%), and heated to boiling to dissolve the precipitated homophthalic acid. Decolorizing carbon (Norite) was added, and, after digestion for several minutes, the solution was filtered hot. Cooling the filtrate resulted in the deposition of 57 g. (58%) of colorless, crystalline homophthalic acid, m. p. 179–180° (recorded m. p. 180°),[11] neut. equiv. 180, (calcd. 180), solubility 1.6 g./100 ml. H_2O at 20°.

Homophthalyl Cyclic Hydrazide.—Homophthalic anhydride (5 g. = 0.031 mole), prepared by the action of acetyl chloride[12] or preferably acetic anhydride[13] on homophthalic acid, was added to ethyl alcohol (40 ml.) containing hydrazine hydrate (85%) (1.8 ml. = 0.031 mole) and the mixture refluxed for six hours. The precipitate formed was collected, washed with dilute acetic acid and recrystallized from boiling ethyl alcohol. The yield was 4.3 g. (80%) of colorless, flaky crystals with a pearly luster, m. p. 298–300°.

Anal. Calcd. for $C_9H_8O_2N_2$: C, 61.34; H, 4.58; N, 15.91; neut. equiv., 176. Found: C, 61.18; H, 4.65; N, 15.57; neut. equiv., 175.5.

The product, which could be recrystallized also from boiling water (0.44 g./l.), was soluble in dilute ammonium hydroxide, insoluble in dilute acetic acid and dilute hydrochloric acid, and did not reduce hot Fehling solution.

The neutralization equivalent of this compound and those of the ones described below, unless otherwise noted, were determined by dissolving the substance in hot alcohol and titrating the resulting solution with standard (0.1 *N*) sodium hydroxide solution using phenolphthalein as the indicator.

(10) The indene used in this study was generously supplied by the United Gas Improvement Company of Philadelphia.

(11) Dieckmann and Meiser, *Ber.*, **41**, 3258 (1908).

(12) Wislicenus, *Ann.*, **233**, 108 (1886).

(13) Dieckmann, *Ber.*, **47**, 1432 (1914).

N-Aminohomophthalimide.—Homophthalic anhydride (8.1 g. = 0.05 mole) was dissolved in hot (100°) glacial acetic acid (40 ml.) and hydrazine hydrate (85%) (3 ml. = 0.05 mole) added gradually with agitation. A precipitate of homophthalyl cyclic hydrazide formed immediately, but this gradually dissolved upon refluxing the reaction mixture for a half hour. Since, at the end of this time, no precipitate was obtained by chilling the homogeneous reaction mixture, the solvent, glacial acetic acid, was evaporated by a vacuum distillation. The resulting residue was a mass of yellow, sandy appearing crystals, which, when washed with cold water and recrystallized twice from boiling ethyl alcohol, yielded 6.5 g. (75%) of light yellow needles, m. p. 147–148°.

Anal. Calcd. for $C_9H_8O_2N_2$: C, 61.34; H, 4.58; N, 15.91; neut. equiv., 176. Found: C, 61.28; H, 4.63; N, 15.6; neut. equiv., 176.

This compound also could be purified by recrystallization from boiling water, in which it was more soluble than homophthalyl cyclic hydrazide. Like the latter, it was soluble in dilute ammonium hydroxide and insoluble in dilute acetic acid, but, unlike the latter, it was soluble in dilute hydrochloric acid and readily reduced hot Fehling solution. Alkaline solutions of this substance had the yellow color which is characteristic of alkaline solutions of homophthalic anhydride and homophthalimide.

N-Acetaminohomophthalimide.—N-Aminohomophthalimide (2 g.) was added to acetic anhydride (5.5 ml.) at room temperature and the mixture shaken for several minutes. The N-aminohomophthalimide dissolved rapidly, but soon thereafter a precipitate was deposited from the solution. This material, after recrystallization from boiling water, yielded 2 g. (80%) of colorless crystals, m. p. 239–240°.

Anal. Calcd. for $C_{11}H_{10}O_3N_2$: C, 60.52; H, 4.62; N, 12.85; neut. equiv., 218. Found: C, 60.28; H, 4.48; N, 12.7; neut. equiv., 219.

The product was soluble in dilute ammonium hydroxide and insoluble in dilute acetic and dilute hydrochloric acid.

4-Nitrohomophthalic Anhydride.—4-Nitrohomophthalic acid (10 g.), prepared by the nitration of homophthalic acid with fuming nitric acid[9] or preferably with potassium nitrate and concentrated sulfuric acid,[8] was refluxed with acetyl chloride (27 ml.) for one and one-half hours. The precipitate obtained was filtered from the dark red menstruum, and, after recrystallization from glacial acetic acid containing a little acetic anhydride, yielded 6.5 g. (70%) of yellow needles, m. p. 154–155°.

Anal. Calcd. for $C_9H_5O_5N$: C, 52.16; H, 2.43; N, 6.77. Found: C, 52.01; H, 2.50; N, 6.82.

The product could be recrystallized also from boiling benzene in which it was sparingly soluble. Alkaline solutions of this substance had a deep red color.

4-Nitrohomophthalyl Cyclic Hydrazide.—4-Nitrohomophthalic anhydride (5.2 g. = 0.025 mole) was dissolved in hot (100°) glacial acetic acid, and hydrazine hydrate (85%) (1.5 ml. = 0.025 mole) was added gradually with agitation. The precipitate formed was collected, washed with dilute acetic acid and water, and dried. The product (3.5 g. = 70%) was a white, amorphous material that gradually turned red on exposure to air and melted at 248–250°, forming a dark red liquid which decomposed. The substance was soluble in dilute ammonium hydroxide producing a red colored solution, insoluble in dilute acetic acid and dilute hydrochloric acid and did not reduce hot Fehling solution. Attempts to purify this material for analysis by recrystallization were unsuccessful, because it was insoluble in water and all the usual organic solvents. Attempts to purify it by repeated solution in dilute aqueous ammonia and subsequent precipitation with dilute acetic acid were also unsuccessful, because the resulting precipitate was always contaminated. The solubility behavior of this compound is similar to that of 3-nitrophthalyl cyclic hydrazide.[14]

4-Aminohomophthalyl Cyclic Hydrazide.—4-Nitrohomophthalyl cyclic hydrazide (6 g.) was dissolved in a solution

(14) Drew and Pearson, *J. Chem. Soc.*, 26 (1937).

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.

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

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.

BROOKLYN, NEW YORK RECEIVED APRIL 21, 1944

[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.

(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).

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