

The author wishes at this time to express his thanks to Professor Victor Lenher for valuable suggestions in this work, and to H. S. Miner, of the Welsbach Light Company, for a large part of the material.

UNIVERSITY OF WISCONSIN,  
MADISON, WIS.

### NOTE.

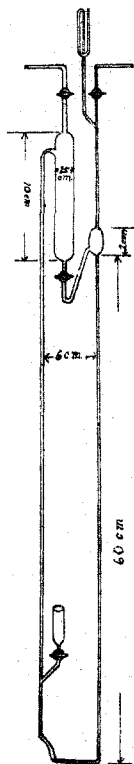
*A Modified Boltwood Pump.*—The modification of the Boltwood pump, which is represented by the accompanying diagram, may be of interest to those engaged in work which requires a high vacuum.

The original pump as stipulated by Boltwood<sup>1</sup> consists of a large bulb, 6 cm. diameter, which acts as the reservoir for the mercury and a smaller bulb of two to three centimeters diameter. The whole apparatus is about 120 cm. long, and 30 cm. wide, using from 700 to 1000 grams of mercury. The apparatus shown in the diagram is at present in use in this laboratory, and gives just as efficient service as the larger forms—sparks being obtained in Pflücker tubes after three minutes' operation, and within a quarter of an hour the pressure cannot be measured on an ordinary manometer—occupies only one-third the space, and requires 100 g. Hg for successful operation.

It might be added in this connection, that there is considerable deviation from the prescribed internal diameter of the dropping tube (2.5 mm.) in the manufactured forms; and it has been observed by the author, that a slightly larger tube refuses to give low vacuums—obviously while a tube smaller than 2 mm. works so slowly as to be comparable to the older hand-lift varieties.

ALLAN F. ODELL.

LOUISIANA STATE UNIVERSITY,  
BATON ROUGE, LA.



[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

### SOME DERIVATIVES OF PARA-AMINO BENZOHYDROL.<sup>2</sup>

By HENRY A. TORREY AND C. W. PORTER.

Received November 11, 1910.

This paper is a report of the beginning of the work in an extensive research on derivatives of para-aminobenzophenone which is being con-

<sup>1</sup> *Am. Chem. J.*, 19, 76 (1897).

<sup>2</sup> This research was suggested by the late Professor Henry A. Torrey and most of the experimental work was done under his direction, but the writing of the paper was deprived of the benefit of his supervision by his too early death.—C. L. JACKSON.

tinued in this laboratory. Para-aminobenzophenone was prepared in large quantities from aniline and benzoyl chloride according to the method of Döbner<sup>1</sup> and the ketone was reduced to the corresponding secondary alcohol called by Kippenberg "*p*-amidobenzhydrol".<sup>2</sup> The alcohol crystallizes from hot water in long, slender, colorless needles melting at 121°. A number of new derivatives of this compound were prepared as follows:

#### Azo Dyes.

*Benzohydrol-4-azo-β-naphthol*.—A beautiful red dye was prepared by diazotizing para-aminobenzohydrol and coupling it with β-naphthol. To accomplish this four grams of the secondary alcohol were dissolved in cold,<sup>3</sup> dilute hydrochloric acid and diazotized at zero with a solution of potassium nitrite. A solution of three grams of β-naphthol in sodium hydroxide was then added and a bright red dye was precipitated. The precipitate was washed with caustic soda solution to dissolve out the excess of β-naphthol, then with dilute hydrochloric acid to remove the last trace of free para-aminobenzohydrol. The residue was then dissolved in acetone and reprecipitated by adding a little water or dissolved in benzene and precipitated by the addition of gasoline. The product was insoluble in acids or bases and melted at 169.5°. The formula is  $C_6H_5CHOH-C_6H_4-N:N-C_{10}H_8OH$ .

Found: N, 8.00. Calculated, 7.91.

Para-aminobenzophenone when diazotized and treated with β-naphthol yielded a dye of a much lighter red color. It was easily purified by crystallization from hot alcohol. It separated on cooling as a light feathery substance resembling cotton wool, except in color. It melted at 185°–186.5°. The sample analyzed contained 8.17 per cent. N. The calculated value for  $C_6H_5-CO-C_6H_4N_2C_{10}H_8OH$  is 7.96.

*Benzohydrol-4-azodimethylaniline*.—Para-aminobenzohydrol diazotized and coupled with dimethylaniline yielded a fine dye crystallizing from hot alcohol in red sparkling flakes, melting sharply at 145°. The compound was readily soluble in glacial acetic and hydrochloric acids, acetone, chloroform, ether or benzene. It was precipitated from the latter by gasoline and crystallized from a hot alcoholic solution on cooling. Its formula is  $C_6H_5-CHOH-C_6H_4-N:N-C_6H_4N(CH_2)_2(p)$ .

Found: N, 12.90. Calculated, 12.70.

Since para-aminobenzohydrol readily yields an anhydride with cold concentrated hydrochloric acid or when warmed with dilute hydrochloric acid, it was thought advisable to determine whether or not the hydroxyl

<sup>1</sup> *Ann.*, 210, 260.

<sup>2</sup> *Ber.*, 30, 1136.

<sup>3</sup> When hot hydrochloric acid is used the anhydride of aminobenzohydrol,  $C_6H_5-CHC_6H_5-NH$ , is precipitated.

group remained unaltered in the molecule when subjected to the action of the cold dilute hydrochloric acid in which it was always diazotized. The dimethylaniline derivative furnished a good compound to work with in settling this question for in it there is no possibility of the existence of a hydroxyl group except the one originally present in the secondary alcohol.

From this dye an acetyl derivative was prepared by treatment with sodium acetate and acetic anhydride, the nitrogen content of which was 11.31 per cent. This is in close agreement with the theoretical value 11.27 per cent. and proves the presence of the hydroxyl group. The compound responded also to the Schotten-Baumann test (benzoyl chloride and sodium hydroxide), giving a well crystallized benzoyl derivative.

Condensed molecules of the diazo compounds would give practically the same analyses for nitrogen as would single molecules. The presence of the hydroxyl group in the dimethylaniline dye made it fairly certain that there had been no condensation, for condensation could hardly be expected to take place except by the elimination of one molecule of water from two molecules of the dye, leaving a compound with an ether formula and containing no hydroxyl group. The question was more definitely settled, however, by a determination of the molecular weight. The boiling-point method was used and benzene employed as a solvent. The average of four determinations for the dimethylaniline derivative of para-aminobenzohydrol was 345. The calculated value for the formula given above is 331.

#### Aldehyde Condensations.

*Salicylal-para-aminobenzohydrol.* — Equimolecular quantities of para-aminobenzohydrol and salicylaldehyde were dissolved in alcohol and heated on a steam bath for two hours. Upon cooling and diluting with a little water a yellow precipitate was produced. This condensation product was readily soluble in benzene, chloroform, acetone, alcohol or ether, and practically insoluble in water. It was, however, rapidly hydrolyzed by water, even at ordinary temperatures, and on that account was purified with difficulty. The addition of a little water was necessary to throw the compound out of solution and unless the temperature of the alcohol solution was reduced to zero or below before water was added, a distinct odor of salicylaldehyde was produced. At the temperature of boiling water the compound was quickly and completely hydrolyzed.

The sample analyzed was recrystallized several times from alcohol at zero and melted at 76°–79°. The formula is  $C_6H_5-CHOH-C_6H_4-N:CH-C_6H_5OH(o)$ .

Found: N, 4.70. Calculated, 4.62.

Para-aminobenzophenone formed a similar condensation product with salicylaldehyde, but unlike the hydrol derivative, it crystallized

from alcohol on cooling and was therefore more easily purified. It was a yellow solid soluble in benzene, acetone, or chloroform, insoluble in sodium hydroxide and sparingly soluble in cold alcohol. Formula,  $C_6H_5-CO-C_6H_4N:CH-C_6H_4OH$ .

Found: N, 4.84. Calculated, 4.65.

*β-Naphthol-α-methylol-para-aminobenzohydrol*.—Equivalent quantities of para-aminobenzohydrol and β-naphthol aldehyde were dissolved in a small quantity of 95 per cent. alcohol and boiled for one hour. On cooling, a yellow crystallin substance separated out which was readily soluble in alcohol, acetone, alkalis, or hot benzene, but crystallized from the latter on cooling in a fair state of purity. Its melting point was found to be 167.5°. Formula,  $C_6H_5-CHOH-C_6H_4N:CH-C_{10}H_6OH$ .

Found: N, 3.98. Calculated, 3.98.

The corresponding ketone, prepared in a similar way with para-aminobenzophenone, was a fine yellow crystallin substance melting at 152°. It was insoluble in alkalis, in this respect differing from the hydrol derivative.

It was easily purified by crystallizing from hot methyl alcohol. Formula,  $C_6H_5CO-C_6H_4N = CH-C_{10}H_6OH$ .

Found: N, 3.90. Calculated, 3.99.

The insolubility of this last compound in alkalis would be expected as it fulfils both the conditions found necessary<sup>1</sup> to produce this phenomenon in other cases—the free hydroxyl group is ortho to a large side chain, and another substituting group is present on the benzene ring to which the hydroxyl is attached—in this case the  $C_4H_4$  of naphthalene which has been found to be specially effective; but the addition compound of salicylaldehyde and para-aminobenzophenone does not conform to the second of these conditions and its insolubility in alkalis is therefore not in harmony with the general rule. Only two or three other exceptions to the above rule have been found. This substance therefore will be studied further in this laboratory.

---

[CONTRIBUTION FROM THE RESEARCH LABORATORY, ROOSEVELT HOSPITAL, NEW YORK.]

## PHENOLPHTHALEIN AND ITS COLORLESS SALTS.

(Potassium Salt of Phenolphthalic Acid.)

BY P. A. KOBER AND J. THEODORE MARSHALL.

Received November 17, 1910.

CONTENTS.—(1) Introduction. (2) The Study of Speed of Reaction: (a) Colorimetrically; (b) Electrolytically. (3) The Study of Concentrations at Equilib-

<sup>1</sup> Torrey and Kipper, THIS JOURNAL, 30, 841 (1908).