for studying the nature of the metabolic and undigested products which cannot be done with any degree of satisfaction upon the air-dried materials.

URBANA, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

SOME AZO DYES FROM *p*-AMINOACETOPHENONE.

BY HENRY A. TORREY AND WARREN MACPHERSON.

Received March 30, 1909.

So far as we have been able to discover, very few azo dyes derived from *p*-aminoacetophenone have been described. Klingel[1] prepared *p*-acetophenoneazo β-naphthol, but states that it is soluble in dilute alkalies, while we have found it to be entirely insoluble in aqueous alkalies, as would be expected from analogy with benzeneazo β-naphthol. Fr. Baeyer & Co.,[2] under D. R. P. 81152, patented the preparation of azo dyes by coupling $\alpha_1\alpha_4$dihydroxynaphthalene mono- and disulphonic acids with diazotized aromatic amino ketones, or the diazo compounds of the esters, amides, and anilides of aromatic amino carboxylic acids. Pröscher[3] prepared a colored compound by the action of bilirubin on diazotized *p*-aminoacetophenone.

We have prepared both hydroxyazo and aminoazo compounds and oximes of some of these bodies. The aminoazo compounds in general turn from yellow to red on the addition of acids. The sensitiveness of the phenyl-, dimethyl-, and diethylamino derivatives and the oxime of the latter toward hydrogen ions was determined by a method similar to that described by Salm,[4] which was called to our attention by Dr. L. J. Henderson of this Laboratory and the Harvard Medical School, who had used a modification of Salm's method in studying the ionization constants of β-hydroxybutyric acid and acetoacetic acid.[5] To 5 cc. of a 0.27 *N* sodium acetate solution containing a few drops of an alcoholic solution of the dye, 0.851 *N* hydrochloric acid was added until a pure pink color was obtained. The hydrogen-ion concentration at which this change in color took place was calculated from the following approximately accurate formula:

$$(\mathrm{H})^{+} = 2 \times 10^{-5}\,\frac{\mathrm{HCl}}{\mathrm{CH_3COONa{-}HCl}}$$

and was found to be for *p*-acetophenoneazodiethylaniline about 5×10^{-5}. The other three are less sensitive, the *p*-acetophenoneazophenylaniline being the least sensitive of all.

In the preparation of *p*-acetophenoneazophenylaniline a modification

---

[1] *Ber.*, **18**, 2695.

[2] *Ibid.*, **28**, R. 701.

[3] *Z. physiol. Chem.*, **29**, 411.

[4] *Z. physik. Chem.*, **57**, 471.

[5] Henderson and Spiro, *Biochemische Zeit.*, **15**, 105.

of the ordinary method of forming azo dyes was found to be highly advantageous, which consisted in the solution of the diphenylamine in a large quantity of glacial acetic acid and the addition of the diazotized solution to this. After several hours the *p*-acetophenoneazophenylaniline separated in good quantity in the form of its salt, probably the hydrochloride. This method should be generally applicable to the coupling with diazonium salts of weak bases, which do not dissolve readily in aqueous acids. Witt,[1] who first prepared phenylaminoazobenzene, dissolved the diphenylamine in alcoholic hydrochloric acid, but obtained the dye in such an impure condition that he found it necessary to convert it into the nitroso derivative in order to purify it. We found that excellent results could be obtained by using glacial acetic acid as a solvent for the diphenylamine. The details of the method are given in the experimental part of this paper.

Experimental Part.

p-Acetophenoneazoresorcin, $CH_3COC_6H_4N:NC_6H_3(OH)_2$. — Five grams *p*-aminoacetophenone were diazotized by dissolving in dilute hydrochloric acid (about 15 cc. conc. HCl in 150–200 cc. water) and adding slowly, while the solution was kept cool, a solution of sodium nitrite until starch-iodide paper showed the presence of free nitrous acid. It is best to dissolve the *p*-aminoacetophenone in concentrated acid diluted about three times, and then to add water to the required dilution. To this diazotized solution was added slightly more than one molecule of resorcin dissolved in sodium hydroxide. On acidification a copious bright yellow precipitate fell, which was at once collected on a filter and then crystallized from alcohol.

Calculated for $CH_3COC_6H_4N_2C_6H_3(OH)_2$: N, 10.94. Found, 11.00.

Properties of p-Acetophenoneazoresorcin.—It crystallizes in beautiful deep orange-red needles which melt with decomposition between 215° and 220°. It is soluble in acetone, ether, ethyl acetate, slightly soluble in cold alcohol, toluene, glacial acetic acid, but more soluble in these solvents when hot; it is insoluble in ligroin, chloroform, and carbon disulphide; it is only slightly soluble in water, giving it a yellow color. It dissolves easily in dilute alkalies forming a deep red solution which imparts to silk a very bright yellow color, after the dyed fabric has been thoroughly washed. It will also dye mordanted cotton.

p-Acetophenoneazodimethylaniline, $CH_3COC_6H_4N:NC_6H_4N(CH_3)_2$.—On adding a solution of dimethylaniline in dilute hydrochloric acid to a solution of diazotized *p*-aminoacetophenone and allowing it to stand, the color of the liquid changes from a light yellow to a purple-red, due to the formation of the hydrochloride of *p*-acetophenone azodimethylaniline. On adding

---

[1] *Ber.*, **12**, 259.

a slight excess of alkali to a solution of the salt in hydrochloric acid, the red free base is precipitated, and even water alone hydrolyzes the salt considerably. In order to obtain a satisfactory preparation of this dye, it is important to precipitate the free base by the addition of alkali, immediately after the diazotized solution and the dimethylaniline have been mixed. After several crystallizations from alcohol the constant melting point of 203°–4° was obtained.

Calculated for $CH_3COC_6H_4N_2C_6H_4N(CH_3)_2$: N, 15.73. Found, 15.94.

Properties of p-Acetophenoneazodimethylaniline.—It is easily soluble in chloroform, hot alcohol and acetone, less soluble in cold acetone and only slightly soluble in cold alcohol, and insoluble in water. It may be crystallized advantageously by dissolving it in chloroform and adding to the solution hot ethyl alcohol. It dissolves with a rich red color in dilute hydrochloric acid. The hydrochloride was formed by passing hydrochloric acid gas into a chloroform solution of the base, which on standing deposited purplish crystals. After drying in air they gave the following analysis:

Calculated for $CH_3COC_6H_4N_2C_6H_4N(CH_3)_2HCl$: Cl, 11.67. Found, 11.35.

The hydrochloride is considerably hydrolyzed by water. *p*-Acetophenone azodimethylaniline gives an *oxime* when heated for several hours with hydroxylamine hydrochloride and sodium acetate. After filtering off the sodium chloride formed in the reaction, the bright orange-red oxime crystallized out. It was recrystallized from alcohol and gave a constant melting point 242°–3°. The color of the oxime is lighter than that of the original substance, the crystals of the latter having a bluish reflex.

Calculated for $CH_3C:NOHC_6H_4N_2C_6H_4N(CH_3)_2$: N, 19.86. Found, 19.85.

The oxime may be converted into the original ketone by boiling with hydrochloric acid. After cooling, diluting and adding sodium hydroxide in slight excess to the solution a red precipitate fell, which after crystallization from chloroform and alcohol melted at 203°.

p-Acetophenoneazodiethylaniline, $CH_3COC_6H_4N:NC_6H_4N(C_2H_5)_2$.—This compound was made in exactly the same manner as the corresponding dimethylaniline derivative. It was purified by crystallization from alcohol.

Calculated for $CH_3COC_6H_4N_2C_6H_4N(C_2H_5)_2$: N, 14.23. Found, 14.65.

Properties.—Its properties are similar to those of the dimethyl derivative. It is insoluble in water, but dissolves in dilute acids, forming a fine crimson solution, which dyes silk a deep orange red. It is soluble in glacial acetic acid, acetone, toluene, carbon disulphide, ethyl acetate, hot alcohol and hot ligroin; slightly soluble in cold alcohol or ligroin. Its melting point is 162°–3°. Stannous chloride rapidly decolorizes its hydrochloric acid solution even without heating. The *oxime*, m. p. 199°–200°, is readily formed by heating in alcoholic solution with hydroxylamine hydrochloride and sodium acetate for five hours.

p-Acetophenoneazophenylaniline, $CH_3COC_6H_4N:NC_6H_4NHC_6H_5$.—Owing to the slight solubility of diphenylamine in hydrochloric acid, it was not found convenient in this case to use the method employed with dimethyl- and diethylaniline, but excellent results were obtained by using glacial acetic acid as a solvent for the diphenylamine. Two grams of *p*-aminoacetophenone, dissolved in 6 cc. conc. hydrochloric acid diluted with 18 cc. of water, and after solution diluted further to 80 cc., were diazotized with 1.2 grams sodium nitrite, dissolved in 10 cc. water. After standing some time, this solution was added to 2.5 grams diphenylamine, dissolved in 100 cc. glacial acetic acid. A beautiful deep purple solution was at once formed, which after standing about three hours deposited a heavy purple precipitate, the salt of the acetophenoneazophenylaniline. After collecting on a filter, the salt was hydrolyzed by heating with water, and treatment with alkali, which gave the red free base. It was purified by crystallization from alcohol.

Calculated for $CH_3COC_6H_4N_2C_6H_4NHC_6H_5$: N, 13.33. Found, 13.65, 13.59.

Properties.—It gives a bright purple solution when treated with rather concentrated acids. The salts thus formed are easily hydrolyzed and silk and wool treated with such an acid solution of the dye wash out to a poor shade of orange-yellow. It is soluble in ether, acetone, benzene and hot ethyl alcohol, difficultly soluble in cold alcohol and insoluble in water. It crystallizes in elongated red prisms, which under the microscope are seen to be twinned, frequently in the form of T-squares or in more complex figures. Its melting point is 184°–5°.

The corresponding phenylaminoazobenzene[1] was made by adding to 6.2 grams diphenylamine dissolved in 150 cc. glacial acetic acid, 5 grams aniline dissolved in 15 cc. hydrochloric acid (1.18), diluted with water to 42 cc. and diazotized, cold, with a concentrated solution of sodium nitrite. After standing several hours a considerable quantity of a black crystalline substance was deposited, the salt of the azo compound. This salt was collected in a filter and after washing with glacial acetic acid, the base was set free in the form of yellow crystals by treatment with alcohol and sodium hydroxide. After only one crystallization from gasoline, the phenylaminoazobenzene was obtained in the form of golden yellow leaflets, which melted at 80.5°, only a little below the melting point (82°) of the pure substance as given by Witt.

Before the base is crystallized, it turns dark quite rapidly, but after one crystallization it is permanent in the air.

---

[1] Witt, *Loc. cit.*

p-Acetophenone-azo-β-naphthol, $CH_3COC_6H_4N : NC_{10}H_6OH$.—Two grams of *p*-aminoacetophenone, dissolved in 12 cc. 5 *N* hydrochloric acid, diazotized and added to 2.5 grams *β*-naphthol dissolved in 12 cc. 5 *N* sodium hydroxide, gave a bright red precipitate, insoluble in both acid and alkalies. It can be purified by crystallization from glacial acetic acid or acetone, the former being preferable. M. p., 181°–3°.

Calculated for $CH_3COC_6H_4N_2C_{10}H_7O$: N, 9.69. Found, 9.32.

Properties.—This compound crystallizes in small red prisms with a yellowish green reflex. It is soluble in alcohol, chloroform, toluene, carbon disulphide, and in hot glacial acetic acid, acetone, ligroin and ethyl acetate. Like benzeneazo-*β*-naphthol it is *insoluble* in aqueous alkalies. It is insoluble in dilute acids, but dissolves in concentrated sulphuric acid with a deep purple color and somewhat less readily in concentrated hydrochloric acid with a crimson color. It dissolves in alcoholic potash. It gives an *oxime* when heated with hydroxylamine hydrochloride and sodium acetate in alcohol for several hours.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

VANILLIDENE- AND PIPERONYLENEBENZIDINES.

BY HENRY A. TORREY AND E. D. CLARKE.

Received March 30, 1909.

The observation that benzidine gives with vanillin a very abundant precipitate of vanillidene benzidine led us to study this reaction more closely in the hope that possibly it might be used in a quantitative determination of vanillin. The fact, however, that both a mono- and a divanillidene derivative can be obtained according to the amount of benzidine added and certain other disadvantages led us to abandon this idea in our work and to turn our attention to the study of other similar derivatives. The other benzidine derivatives described by us are all condensation products in which two molecules of the aldehyde have condensed with one molecule of benzidine. Unfortunately the work had to be discontinued before definite information regarding the existence of the corresponding mono-aldehyde derivatives had been obtained.

Action of Benzidine on Vanillin, 3-Methoxy-4-hydroxybenzalbenzidine, $C_6H_3(OH)(OCH_3)CH : NC_6H_4.C_6H_4NH_2$ and *Bis-3-methoxy-4-hydroxybenzalbenzidine,* $C_6H_3(OH)(OCH_3)CH : NC_6H_4.C_6H_4N : HCC_6H_3.(OH).(OCH_3)$.—When two grams of vanillin, dissolved in a hot mixture of 25 cc. alcohol and 50 cc. water, were mixed with one molecule of benzidine dissolved in hot 58 per cent. alcohol, a bright yellow precipitate came down immediately, but the mixture was allowed to stand some time in order that the precipitation might become quite complete, after which the substance was washed, dried and purified by crystallization from hot benzene. The