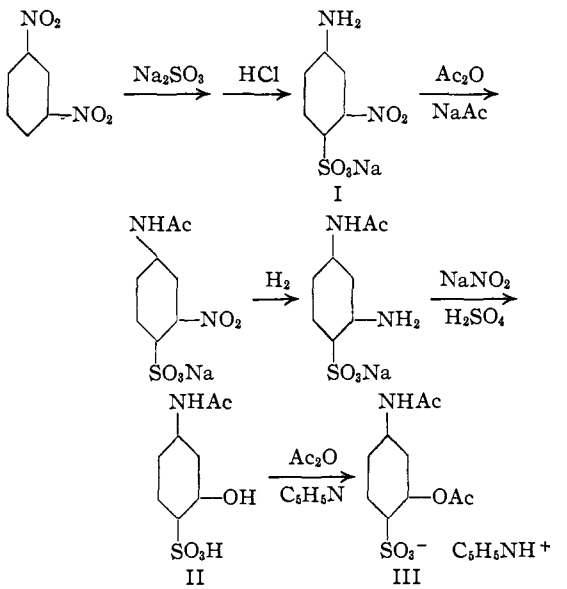
cedure have reported this latter structure for the product. To the best of our knowledge no structure proof for the product from the sulfonation of *m*-aminophenol has been reported.

In connection with some of our work in the field of synthetic drugs we have determined the structure of this amino-hydroxybenzenesulfonic acid by synthesis through another route as indicated in the series of reactions given. The structure of the intermediate 4-amino-2-nitrobenzenesulfonic acid (I) has been previously established beyond reasonable doubt.[8] Since neither 4-



amino-2-hydroxybenzenesulfonic acid nor the acetyl derivative (II) have definite melting points, comparison was made of the pyridinium-4-acetylamino-2-acetoxybenzenesulfonate (III) derivatives. The products made by the above method and that obtained from the sulfonation of *m*-aminophenol followed by the action of acetic anhydride and pyridine were shown to be identical by a mixed melting point study. This clearly indicates that the structure reported in the Oehler patent is in error and that the stable sulfonation product of *m*-aminophenol is 4-amino-2-hydroxybenzenesulfonic acid as assumed in the other reports.[5,6,7]

Experimental

The Sulfonation of *m*-Aminophenol.—The Oehler procedure[4] consists in heating a solution of one part of *m*-aminophenol in three parts of concentrated sulfuric acid on the water-bath for one hour. The product is obtained by dilution with water. It was converted into the pyridinium acetylaminoacetoxybenzenesulfonate (III) by the method of Thorpe and Williams.[7] After recrystallization from absolute ethanol and ether, it melted at 164–166°.

4-Amino-2-nitrobenzenesulfonic Acid.—A slurry of 86 g. of *m*-dinitrobenzene in 800 ml. of a saturated sodium sulfite solution was prepared and heated until solution was complete. To the hot solution, 250 ml. of concentrated hydrochloric acid was added and the resulting mixture heated at boiling for thirty minutes. The precipitate that formed on cooling was purified by solution and reprecipitation; yellow powder, 50 g.[8,9]

Sodium 4-Acetylamino-2-nitrobenzenesulfonate.—To a slurry of 10.5 g. of 4-amino-2-nitrobenzenesulfonic acid in 30 ml. of glacial acetic acid, sufficient sodium acetate was added to effect solution. After the addition of 30 ml. of acetic anhydride, the acetylation mixture was heated at reflux overnight. One-half of the acetic acid was evaporated and sufficient ether added to cause precipitation. The product was recrystallized from absolute ethanol; 14 g.

Sodium 4-Acetylamino-2-aminobenzenesulfonate.—A solution of 14 g. of sodium 4-acetylamino-2-nitrobenzenesulfonate in 300 ml. of absolute ethanol was shaken with hydrogen in the presence of Adams catalyst at three atmospheres pressure. The reduction was not complete. The precipitate which formed was filtered and purified, 2.5 g. It gave a positive test for an aromatic amine.

4-Acetylamino-2-hydroxybenzenesulfonic Acid.—A solution of 3.5 g. of sodium 4-acetylamino-2-aminobenzenesulfonate in 50 ml. of 3% sulfuric acid was prepared and cooled to 3°. Upon completion of the slow addition of a sodium nitrite solution (1.2 g. of sodium nitrite in 15 ml. of water), 100 ml. of a 1% copper sulfate solution was added and the resulting solution refluxed for one hour. After cooling for several days at 0°, approximately 1 g. of a light brown solid was isolated which gave a negative test for a free amine group and which had no definite melting point.

Pyridinium-4-acetylamino-2-acetoxybenzenesulfonate.—To a pyridine solution of the 1 g. of crude 4-acetylamino-2-hydroxybenzenesulfonic acid was added 1 ml. of acetic anhydride and the resulting precipitate was recrystallized from absolute ethanol and ether, m. p. 164–166°. A mixed melting point with the previously prepared pyridinium salt gave no depression.

We gratefully acknowledge the financial assistance of Parke, Davis and Company in this work.

(8) Nietzke and Helbach, *Ber.*, **29**, 2449 (1896).

(9) Hunter and Sprung, THIS JOURNAL, **53**, 1440 (1931).

SCHOOL OF CHEMISTRY AND PHYSICS
THE PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PENNSYLVANIA RECEIVED MAY 5, 1949

The Willgerodt Reaction with Acetylphenylacetylene and Benzalacetone

BY DOROTHY NIGHTINGALE AND RICHARD A. CARPENTER[1,2]

The Willgerodt reaction with acetylphenylacetylene and benzalacetone appeared to offer a method for the synthesis of γ-phenylethynylacetic acid and γ-phenylvinylacetic acid. Initial experiments with acetylphenylacetylene and ammonium polysulfide at 190°[3] yielded a product, m. p. 54–56°, containing nitrogen and sulfur which decomposed on standing and was too unstable for consistent analyses. When the reaction was repeated by the procedure of Schwenk and Bloch[4] using morpholine and sulfur, the γ-phenylethynylthioacetomorpholide (I) was obtained in 51% yield. Ozonolysis of (I) followed by oxidative cleavage yielded benzoic acid. All efforts to hydrolyze the thioacetomorpholide to γ-phenylethynylacetic acid were fruitless. Propionylphenylacetylene, morpholine and sulfur yielded an intractable tar.

(1) From the Master's thesis of Richard A. Carpenter.

(2) Present address: Wood River Refinery, Shell Oil Company, Wood River, Illinois.

(3) Wadsworth, Ph.D. Dissertation, University of Missouri (1948).

(4) Schwenk and Bloch, THIS JOURNAL, **64**, 3051 (1942).

Benzalacetone reacted with morpholine and sulfur under the same conditions to form γ-phenylvinylthioacetomorpholide (II) in 35% yield. Ozonolysis of (II) followed by reductive cleavage yielded benzaldehyde which was identified by its dimethone derivative. Hydrolysis of (II) with alcoholic potassium hydroxide yielded only unchanged starting material, but long refluxing with hydrochloric acid and acetic acid yielded a product (III) melting at 112–114°, soluble in base and containing neither nitrogen halogen nor sulfur. Analyses of (III) approximated an empirical formula of $C_7H_7O_2$, but a neutral equivalent of 189–195 and a mixed melting point indicated that the product was not benzoic acid.

Experimental[5]

γ-Phenylethynylthioacetomorpholide.—Acetylphenylacetylene (29 g., 0.2 mole), 26 g. (0.3 mole) of morpholine and 9.6 g. of sulfur were heated gently for one hour and then refluxed vigorously for three hours more. The reaction mixture was cooled, taken up in 200 cc. of benzene, washed with dilute hydrochloric acid and finally with water. The benzene solution was dried, the benzene removed and the residue recrystallized first from aqueous alcohol and finally from Skellysolve A. The thioacetomorpholide (I) crystallized in pale yellow amorphous knobs, m. p. 79–80°; yield 25 g. (51%).

Anal. Calcd. for $C_{14}H_{15}ONS$: C, 68.53, H, 6.16. Found: C, 68.34; H, 6.52.

Ozonolysis of 0.1 g. of (I) in carbon tetrachloride at 0° followed by oxidative cleavage yielded benzoic acid, melting point and mixed melting point, 121°.

When 2 g. of (I) was refluxed for ten hours with 20% alcoholic potassium hydroxide or with a solution of 2 cc. of concentrated hydrochloric acid in 15 cc. of glacial acetic acid, only starting material was recovered.

γ-Phenylvinylthioacetomorpholide (II).—Benzalacetone (30 g., 0.2 mole), 26 g. (0.3 mole) of morpholine and 9.6 g. (0.3 mole) of sulfur were heated gently for one hour and then refluxed vigorously for four hours. The product was worked up as described above except that the tarry residue was recrystallized from aqueous alcohol and finally treated with boneblack to remove the color. The thioacetomorpholide (II) crystallized in white plates, m. p. 133–134°; yield, 17 g. (35%).

Anal. Calcd. for $C_{14}H_{17}ONS$: C, 67.98; H, 6.93; N, 5.67. Found: C, 67.93; H, 6.57; N, 5.85.

The thioacetomorpholide (II) (80 mg.) dissolved in ethyl bromide was ozonized at 0°. The solvent was removed and the solid ozonide was decomposed reductively in the usual manner. The benzaldehyde was isolated as the dimethone derivative, melting point and mixed melting point 194–195°.

Hydrolysis of (II).—The thioacetomorpholide (II) (2 g.), 2 cc. of hydrochloric acid and 15 cc. of acetic acid were refluxed vigorously for ten hours. The reaction mixture was poured into water and after standing overnight the solution and suspended solid were extracted with ether. The ether extract was dried, the ether removed and the gummy residue was sublimed. A white solid (III) was obtained which melted at 112–114°[6] and contained no nitrogen or sulfur. The product was soluble in base but the melting point of the recovered acid was unchanged. A mixture of benzoic acid and (III) melted at 100–105°.

Anal. Calcd. for γ-phenylvinylacetic acid, $C_{10}H_{10}O_2$: C, 74.04; H, 6.21; neut. equiv., 162. Found: C, 67.10; H, 5.95; neut. equiv., 189, 195.

(5) The semimicro carbon-hydrogen analyses were done by R. A. Carpenter.

(6) The recorded melting point of γ-phenylvinylacetic acid is 86°. Fittig and Jayne, *Ann.*, **216**, 98 (1883).

When (II) was refluxed with 20% alcoholic potassium hydroxide for ten hours, only unchanged starting material was isolated.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MISSOURI
COLUMBIA, MISSOURI

RECEIVED MAY 20, 1949

N-(*p*-Chlorophenyl)-diamidophosphoric Acid

BY KURT RORIG

A compound considered to be N-(*p*-chlorophenyl)-amidophosphoric acid, *p*-$ClC_6H_4NHPO(OH)_2$, on the basis of an elemental analysis for carbon and hydrogen was first prepared by Otto[1] in 1895. Recently it has been prepared by Otto's method for use as an enzymatic substrate in histochemical experiments.[2]

This compound was also prepared according to Otto in our laboratory and was found to have the melting point reported by him. A complete elemental analysis, however, showed it to be N-(*p*-chlorophenyl)-diamidophosphoric acid, *p*-$ClC_6H_4NHPO(OH)(NH_2)$, rather than the monoamidophosphoric acid postulated by Otto. In accordance with the diamidophosphoric acid structure, the titration curve of our compound showed only the one break characteristic of a monobasic acid. A mixed melting point determination has shown that Gomori's compound[2] is the same as ours. However, our N-(*p*-chlorophenyl)-diamidophosphoric acid, melting at 156–157°, is insoluble both in hot water and in hot ethanol; whereas Otto reported that his compound, melting at 155°, was soluble in these solvents. Since Otto has also reported the existence of a di-silver salt of his compound, it is prudent to say only that by following his somewhat incomplete instructions as closely as possible, N-(*p*-chlorophenyl)-diamidophosphoric acid was obtained by Gomori and ourselves.

Furthermore, the formation of the diamidophosphoric acid is in harmony with the experience of Caven,[3] who found that anilidophosphoryl-dichloride, when dissolved in aqueous ammonia, formed N-phenyl-diamidophosphoric acid rather than the monoamidophosphoric acid as surmised by Michaelis and Schulze.[4]

Experimental

A mixture of 163.5 g. (1 mole) of *p*-chloroaniline hydrochloride and 307 g. (2 moles) of phosphorus oxychloride was refluxed for two and one-half hours. The cooled, solidified reaction mixture was filtered and washed with petroleum ether (b. p. 60–71°) to give 202 g. of crude *p*-chloroanilidophosphoryl-dichloride, *p*-$ClC_6H_4NHPOCl_2$, melting at 97–104°. A small sample melted at 105–107° when recrystallized from benzene.

Thirty grams of crude *p*-chloroanilidophosphoryl dichloride was added slowly to 60 ml. of aqueous ammonium hydroxide (28%) while keeping the temperature below 10°. The turbid solution was immediately filtered and acidified with a slight excess of hydrochloric acid to precipitate the

(1) Otto, *Ber.*, **28**, 617 (1895).

(2) Gomori, *Proc. Soc. Exp. Biol. Med.*, **69**, 407 (1948); *ibid.*, **70**, 7 (1949).

(3) Caven, *J. Chem. Soc.*, **81**, 1367 (1902).

(4) Michaelis and Schulze, *Ber.*, **26**, 2939 (1893).