minutes, and poured into about 500 cc. of water. Glittering, colorless crystals separated which were filtered and washed with water. The yield is almost quantitative. The crystals melt at 230–235°, becoming yellow at 200° and brown shortly before melting. The acid is obtained in small needles by recrystallization from dilute acetic acid, which melt at 235–236° with disintegration. The acridarsinic acid is almost insoluble in cold and also in boiling water; in warm glacial acetic acid, it is easily soluble.

Anal. Subs., 0.2026: $Mg_2As_2O_7$, 0.1164. Calcd. for $C_{13}H_{11}O_2As$: As, 27.5. Found: As, 27.7.

10-Chloro-9,10-dihydroacridarsine.—Ten grams of acridarsinic acid was finely pulverized and suspended in 100 cc. of hydrochloric acid; 100 cc. of chloroform was added to the suspension. By means of a wide tube which was submerged below the surface of the chloroform, sulfur dioxide and hydrogen chloride were passed through. After five minutes, a little potassium iodide was added and the reduction was completed on the steam-bath under refluxing.

The chloroform solution was separated from the aqueous liquor and the chloroform was distilled off on the steam-bath. The 10-chloro-9,10-dihydroacridarsine (9 g.) remained in large crystals of brownish color. The substance was obtained in beautiful, yellow prisms by recrystallization from benzene. The 10-chloro-9,10-dihydroacridarsine is soluble in the common organic solvents and melts at 114–115°.

Anal. Subs., 0.1411: $Mg_2As_2O_7$, 0.0778. Subs., 0.2318: AgCl, 0.1200. Calcd. for $C_{13}H_{10}ClAs$: As, 27.1; Cl, 12.83. Found: As, 26.7; Cl, 12.81.

Summary

Starting with *o*-aminodiphenylmethane, the diphenylmethane-*o*-arsonic acid and derivatives of the arsenic analog of 9,10-dihydroacridine, such as acridarsinic acid and 10-chloro-9,10-dihydroacridarsine have been synthesized.

BINGHAMTON, NEW YORK

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

THE PIRIA REACTION. I. THE OVER-ALL REACTION[1]

BY W. H. HUNTER AND MURRAY M. SPRUNG

RECEIVED NOVEMBER 28, 1930 PUBLISHED APRIL 6, 1931

Aminosulfonic acids can be obtained directly from aromatic nitro compounds by heating the latter with metal sulfites and then boiling with mineral acids. This reaction was discovered by Piria[2] in 1851, and will therefore be referred to in the following pages as "the Piria reaction." Piria, at that time, subjected α-nitronaphthalene to the action of ammonium sulfite in dilute alcoholic solution, and isolated two reduction products: the ammonium salts of naphthionic acid and of α-naphthylsulfaminic acid, respectively.

[1] The work described in this paper formed part of a thesis submitted to the Graduate Faculty of the University of Minnesota by Murray M. Sprung in partial fulfilment of the requirements for the degree of Doctor of Philosophy, September, 1928. Presented before the Division of Organic Chemistry of the American Chemical Society at the Minneapolis Meeting, September 9–16, 1929.

[2] Piria, *Ann.*, **78**, 31 (1851).

It would naturally be expected that this reaction would be of importance in the manufacture of intermediates for azo dyes and some such hope undoubtedly has inspired many workers, for in the eighty years which have intervened since its discovery, the Piria reaction has been studied by a large number of investigators.[3]

However, the information which has been obtained has been of a decidedly general nature. No systematic investigation, from a theoretical point of view, of a series of nitro compounds has been carried out; no two investigators have used identical procedures for carrying out the reduction, or for isolating the products. The original ammonium sulfite has in many cases been replaced by sodium or potassium sulfite of various concentrations, or by equally varied concentrations of bisulfite. Also, much of the information is in the usual none too clear specifications of an organic chemical patent of the early days.

Further, with the exception of Raschig,[4] no one has given any particular consideration to the mechanism of the changes involved.

Now the Piria reaction is carried out in two distinct stages: a reduction stage, in which the nitro group is known to be transformed into an amino group, a sulfaminic acid group, or both; and an acid treatment stage, in which an amine or an aminosulfonic acid appears. It is entirely fair, it would seem, to say that neither of these stages is understood, though many opinions have been expressed about both of them taken singly and together.

This situation is due primarily to the fact that most previous investigators other than Raschig, and perhaps Weil,[5] have been primarily interested in finding the best reagent and the best conditions for the production of a single desired compound, usually an aminosulfonic acid.

Aside from its value, or lack of it, as a source of intermediates, the

[3] The most important published articles and a number of the more significant patent citations are as follows: Hilkenkamp, *Ann.*, **95**, 86 (1855); Carius, *Z. Chem. Pharm.*, 632 (1861); Smit, *Ber.*, **8**, 1442 (1875); Nietzki, *ibid.*, **29**, 2448 (1896); German Patent 86,097, *Friedländer*, **4**, 90 (1895); Walter, German Patent 109,487, *ibid.*, **5**, 70 (1899); Turner, German Patent 123,115, *ibid.*, **6**, 171 (1900); Weil, German Patents 147,552 and 151,134, *ibid.*, **7**, 58 and 61 (1902); Weil and Moser, *Ber.*, **55**, 732 (1922); Weil and Wassermann, *ibid.*, **55**, 2533 (1922); E. and H. Erdmann, German Patent 65,240, *Friedländer*, **3**, 41 (1891); Willgerodt, *J. prakt. Chem.*, **32**, 117 (1885); Meister, Lucius and Brüning, German Patents, 92,082 and 215,338, *Friedländer*, **4**, 528 (1895), and **10**, 182 (1910); Alfred Fischesser and Company, German Patent 79,577, *ibid.*, **4**, 565 (1894); Bayer and Company, German Patent 113,944, *ibid.*, **6**, 184 (1900); Bucherer and Borsch, *J. prakt. Chem.*, [2] **111**, 329 (1925); Meister, Lucius and Brüning, German Patents 78,772 and 126,804, *Friedländer*, **4**, 305 (1894) and **6**, 384 (1901); Bayer and Company, German Patent 103,395, *ibid.*, **5**, 252 (1897); Raschig, "Stickstoff and Schwefel Studien," Verlag Chemie G. m. b. H., Leipzig, **1924.**

[4] Raschig, "Stickstoff and Schwefel Studien," Verlag Chemie G. m. b. H., Leipzig, **1924**, pp. 254–272.

[5] Weil and Wassermann, *Ber.*, **55**, 2533 (1922), and earlier references cited therein.

reaction presents interesting problems, as a study in oxidation–reduction, and as a problem in the effect of hydrogen-ion concentration.

However, the methods of carrying out the reaction have been so various that it was impossible to gain a viewpoint on previous work. It therefore seemed wise to set up certain standard conditions, into which any nitro compound would be forcibly fitted, both for the reduction stage and the acid-treatment stage, in order to arrive at some uniformity of treatment. This was done, and a series of eight somewhat coherently related nitro compounds was studied, under these standard conditions, as well as with some deliberate variation, in certain cases. In the discussion of this treatment it is convenient to use the terms "standard reduction," "standard acid treatment," and in addition, the term "over-all reaction," the latter referring to the use of both operations in sequence.[6]

The results of this preliminary survey of the reaction are set forth in the table. It will be noted that the standard procedure is not indicated for two of the nitro compounds. In these cases the standard procedure was used, but it failed to give satisfactory reduction, and the actual procedures are included, to illustrate the possibilities of variation, and as examples of the types of variation to be found in existing literature.

Discussion of the Results

It will be noted that in every case the over-all reaction produced an aminosulfonic acid, and in every case but one (*p*-nitrophenol)[7] an amine

[6] STANDARD REDUCTION.—To a weighed quantity of the nitro compound was added enough of a 5.2 *N* (2.6 *M*) solution of sodium bisulfite to constitute approximately 75% excess over that calculated on the basis of 3 moles of bisulfite per mole of nitro compound. Enough 5 normal sodium hydroxide was then added to neutralize one-fourth of the bisulfite, and to the whole was added water in the ratio of 1250 cc. for each mole of nitro compound. This mixture, contained in a round-bottomed flask, was heated to boiling under a reflux condenser (with continual mechanical stirring) until homogeneous. (At this time the odor of nitro compound should be no longer noticeable.)

STANDARD ACID TREATMENT.—The mixture was evaporated on the steam-bath to about half the original volume, and treated while hot with 250 cc. of concentrated (12 *N*) hydrochloric acid for each mole of original nitro compound. It was boiled for one-half to two hours, and then allowed to cool.

ISOLATION.—In all cases where the amine produced was volatile with steam, excess alkali was added at this point, and the amine distilled out in a current of steam. The sodium salt of the aminosulfonic acid usually crystallized from the cooled residue, since such sodium salts are quite insoluble in an alkaline salt solution of the concentration here produced. This method of isolating the products was varied whenever it was necessary or more convenient to use other means. The procedure was especially different in case of those reactions which gave rise to amines which are not volatile with steam. These reactions are described separately, as a general statement cannot be made about them.

[7] For reasons stated in the experimental part of the paper, we believe that very little, if any, amine was produced in this case.

TABLE I

NATURE AND QUANTITY OF PRODUCTS OBTAINED IN THE "OVER-ALL" PIRIA REACTION

Nitro compound	Experimental condition	Time for reduction phase, hours	Amine isolated	Av., %	Aminosulfonic acid isolated	Av., %	Other product isolated	Av., %
Nitrobenzene	St. proc.	1.25	Aniline	26	Sulfanilic	27	.....	..
α-Nitronaphthalene	St. proc.	5	α-Naphthyl-	2	Naphthionic	25	1-Naphthylamine-2,4-disulfonic acid	66
o-Nitrotoluene	Same	12	*o*-Toluidine	40	2-Toluidine-5-sulfonic	34	Sodium *o*-tolylsulfaminate	12
p-Nitrotoluene	Same	5	*p*-Toluidine	72	4-Toluidine-3-sulfonic	11	.....	..
Nitro-*p*-xylene	3 Times[a] usual amt. water	17	*p*-Xylidine	60	3-Amino-1,4-xylene-6-sulfonic	16	.....	..
m-Dinitrobenzene	*A* 10% excess Na_2SO_3(HCl used[c])	2	*m*-Nitroaniline	Tr.	*A* *m*-Nitraniline *p*-sulfonic	64	.....	..
	B 110% excess $NaHSO_3$(H_2SO_4 used)	8.5[b]	.....	..	*B* *m*-Nitraniline *p*-sulfonic	1	*m*-Phenylenediamine-*p*-sulfonic acid	10
p-Nitrobenzoic acid	St. proc.	4.5	*p*-Aminobenzoic acid	21[d]	*p*-Amino-*m*-sulfobenzoic	61[e]	.....	..
p-Nitrophenol	St. proc.	11[f]	.....	..	*p*-Aminophenol-*m*-sulfonic	14	.....	..

[a] When the normal amount of water was used, the reaction was found to be incomplete even after twenty or twenty-five hours of boiling. [b] The reaction was not complete at this time. [c] The standard reduction gave an abnormal reaction. [d] Isolated partly as such, and partly as the *p*-amino-*m*-sulfobenzoic acid salt of *p*-aminobenzoic acid. [e] Isolated partly as such and partly as the *p*-amino-*m*-sulfobenzoic acid salt of *p*-aminobenzoic acid. [f] The reduction was probably complete, in this case, in a much shorter time than is here indicated. Since there was no external evidence indicating just when the reduction phase was ended (as there was in all other cases) the heating was continued until we were sure that no unreacted nitro compound remained.

could be obtained. However, the relative amounts of these products varied widely, indicating that their formation is very probably largely governed by constitution factors. This is probably the most striking result of the present work. Without presuming to be arbitrary, since the evidence available at present is still not very extensive, we may recognize several definite influences. Thus it is apparent that a ring methyl group favors the formation of amines, while the presence of a carboxyl group, a second nitro group, or a condensed ring favors the formation of amino-sulfonic acids. In the few cases studied, the position of the second substituent seems to be of comparatively small influence.

In most cases, the combined yields of the two chief products (amine and mono-sulfonated amine) was slightly in excess of 80%. Only in two cases was it less. In the case of α-nitronaphthalene, the chief product was found to be an amino-disulfonic acid (isolated in 66% yield), and the total yield of this plus those of the two normal products was close to 95%. In the second case, that of nitrobenzene, we have not as yet succeeded in isolating a disulfonic acid. It is possible that the production of a very soluble disulfonic acid (extremely difficult to separate from the admixed inorganic salts) may account for the low total yield. We also believe it highly probably that in most of the other cases (that of *p*-nitrophenol is an exception, due to the inadequacy, in this case, of the methods used to isolate the product) the difference between the combined yields of the two chief products and 100% may be largely due to the occurrence of other very soluble amino-disulfonic acids, which we have not as yet attempted to isolate.

Another significant observation should be mentioned. It was noted that the speed of the first phase of the reaction (reduction) increased with dilution. This effect was particularly noted in experiments with nitrobenzene and with 2-nitro-1,4-xylene.[8] This led us to suspect that one of the early stages of the reaction is an *ionic* reduction, a suspicion which was lent further support by other observations. Thus it was noticed, in the case of α-nitronaphthalene, that the use of alcoholic aqueous media appreciably slowed down the reaction, contrary to expectation. It was also noted that neutral sodium sulfite was able to reduce dinitrobenzene in two hours, whereas bisulfite required over eight and one-half hours. All these observations can be reconciled with the view that for these reductions, the activity of the sulfite ion is of great importance.

On the contrary, however, it has been determined that partially neutralized sodium bisulfite is more effective in these reactions than normal

[8] It should be mentioned that the velocity of the first phase of the reaction (usually a heterogeneous reaction) depended upon the efficiency of agitation. However, it was attempted to keep this factor as constant as possible, and the results recorded are therefore comparable.

sodium sulfite. At present we can harmonize this with the above observation relative to dinitrobenzene only by the assumption that another stage in the reduction is favored by higher hydrogen-ion concentration than is furnished by neutral sulfite, and that this factor, in the case of dinitrobenzene, is of secondary importance, for some reason which is not as yet clear. In this connection it should also be stated that the addition of alkali had little or no effect upon the speed of reduction of α-nitronaphthalene. Completely neutralized bisulfite and un-neutralized bisulfite, in this case, were about equally effective. We hope to throw more light upon these problems by virtue of further investigations now being carried out in this Laboratory.

Experimental Part

Experiments with α-Nitronaphthalene

(A) **With Bisulfite and Aqueous Alcohol.**—Twenty-five grams of α-nitronaphthalene (m. p. 57–57.5°), 76 cc. of 5.2 *N* sodium bisulfite (15% excess), 100 cc. of 95% alcohol, and 200 cc. of water were heated under a reflux condenser. At the boiling point of the solution the reduction was incomplete at the end of thirteen hours. By working up the mixture there was obtained 9.5 g. of naphthionic acid, 7 g. of α-nitronaphthalene (unchanged), and 0.8 g. of α-naphthylamine; yields (on the basis of the nitro compound used): amine, 10%; aminosulfonic acid, 58%.

(B) **With Aqueous Bisulfite.**—A typical run is given. Thirty-five grams (0.2 mole) of α-nitronaphthalene, 200 cc. of 5.2 *N* sodium bisulfite (75% excess) and 250 cc. of water were heated under a return condenser until the mixture was completely homogeneous. The contents of the flask, evaporated to 300 cc. and treated with 50 cc. of 12 *N* hydrochloric acid, gave a heavy white precipitate, which was filtered from the cooled solution. This mixture was warmed with 300 cc. of water, which dissolved the salts present, leaving the naphthionic acid (soly., 0.024 g. in 100 cc. of water); 13.5 g. (29%) of the aminosulfonic acid was thus obtained.

The combined filtrates were saturated with sodium chloride, and the precipitate produced was filtered off. It was nearly free from inorganic salts. When dry it weighed 31 g., which, on the basis of a monosodium salt of a naphthylamine disulfonic acid is equivalent to a yield of 66%.

(C) **With Aqueous Bisulfite and Alkali.**—Thirty-five grams was reduced according to the standard procedure. The reduction required five hours. Acidification with 50 cc. of 12 *N* hydrochloric acid gave 10 g. (22%) of naphthionic acid. Seventy-five grams of stick sodium hydroxide was added to the combined filtrates and steam passed through, giving 0.5 g. or 2% of α-naphthylamine (m. p. 48–48.5°). The residue was made acid and was again distilled with steam, but no volatile substance was present, and therefore no naphthol was produced during the reaction.

Identification of the Products.—α-Naphthylamine was identified by melting point and mixed melting point with a sample of known purity. Naphthionic acid was identified by conversion to the diazonium salt, according to the method of Erdmann.[9] The diazonium salt thus obtained decomposed instantaneously at 140.5°. It gave characteristic azo dyes with alkaline β-naphthol and with phenol.

A sample of the monosodium salt of the naphthylamine disulfonic acid was crystallized four times from 70% alcohol. It still retained a slight pinkish tint, but was completely free from inorganic salts. It was dried at 140° and analyzed.

[9] Erdmann, *Ann.*, **24**, 330 (1888).

Anal. Calcd. for $C_{10}H_8S_2O_6Na$: S, 19.68; Na, 7.07. Found: S, 19.28; Na, 6.94, 7.00.

It is almost certain from these analyses and the method of synthesis that this compound is the monosodium salt of 1-aminonaphthalene-2,4-disulfonic acid, described in an early German patent.[10] No further time was spent on its orientation at this time, as we were interested only in the groups introduced by the reagent and not in their positions.

Experiments with Nitrobenzene

(A) **The Standard Procedure.**—Fifty grams was reduced in one and one-half hours. The contents of the flask were evaporated to 500 cc., decomposed with 100 cc. of concentrated hydrochloric acid, and re-evaporated to 500 cc. One hundred and twenty grams of solid sodium hydroxide was then immediately added, and the mixture steam distilled. The distillate, on extraction with ether, drying of the ethereal extracts, and distillation, gave 7 g. of aniline, boiling at 181–183° (16%, on the basis of the nitro compound used). The residue from the distillation was filtered, while still hot, from precipitated inorganic salts (sodium chloride and sodium sulfate). On cooling the filtrate to room temperature, crystals were obtained which were rendered almost colorless by repeated washing on the filter with methyl alcohol. These were nearly pure sodium sulfanilate, and when dry, weighed 38 g. (35%).

(B) **Bisulfite Followed by Sulfuric Acid.**—The standard procedure was followed, using 50 g. of the nitro compound. The reduction stage again required one and one-half hours.[11] One hundred cc. of concentrated sulfuric acid was used to decompose the solution. There were obtained 16 g. (20%) of sulfanilic acid and 12 g. (32%) of pure aniline.

Identification of Sodium Sulfanilate.—Bromination with liquid bromine gave tribromoaniline, identified by melting point and mixed melting point with a reliable specimen. The phosphorus pentachloride reaction product[12] was prepared by heating the sodium salt with phosphorus pentachloride in dry benzene. It melted at 154–155°, whereas the "trichloro compound" of Laar, when very pure, melts at 158°. Oxidation of the sodium salt with chromic acid and sulfuric acid in a current of steam gave benzoquinone, m. p., 113°; mixed m. p. with known sample of quinone, 113°. A purified sample of the sodium salt was analyzed, after drying at 140°.

Anal. Calcd. for $C_6H_6NSO_3Na$: Na, 11.53. Found: Na, 11.77.

Experiments with *p*-Nitrotoluene

Fifty grams was reduced, according to the standard procedure, in five hours. The mixture was evaporated to 500 cc., and decomposed with 100 cc. of 12 *N* hydrochloric acid. After re-evaporating to 500 cc., the solution was cooled, 100 g. of sodium hydroxide dissolved in 100 cc. of water was added, and this mixture was distilled with steam. From the distillate, 30.5 g. (72%) of nearly pure *p*-toluidine was obtained (m. p., 44.5°; b. p., 198–199°; acetyl derivative, m. p., 147–147.5°). The residue from the steam distillation deposited, on cooling, a white organic salt mixed with sodium chloride and sodium sulfate. This was dissolved in water, filtered hot, and the cooled filtrate acidified with hydrochloric acid. Eight grams (11%) of 4-toluidine-3-sulfonic acid was obtained.

---

[10] Meister, Lucius and Brüning, German Patent 92,082, *Friedländer*, **4**, 528 (1895).

[11] In one run the standard procedure was varied by diluting with 2000 cc. rather than the usual 500 cc. of water. At this dilution the reduction stage required only forty minutes. A 25% yield of sulfanilic acid was obtained.

[12] Laar, *J. prakt. Chem.*, [2] **20**, 250 (1879).

Identification of the Aminosulfonic Acid.—Bromination gave 3,5-dibromo-4-toluidine, m. p., 70–71°. A sample prepared by bromination of *p*-toluidine melted at 74–75°. A mixture of the two melted at 72–73°. The sodium salt (from the aminosulfonic acid and excess dilute sodium hydroxide) lost no weight when heated at 150°. It was analyzed for sodium.

Anal. Calcd. for $C_7H_8SO_3NNa$: Na, 10.99. Found: Na, 10.80, 10.92.

Experiments with *o*-Nitrotoluene

Using the standard procedure, the reduction required twelve hours. After treatment with 100 cc. of 12 *N* hydrochloric acid, the mixture was allowed to cool. Large, white, silky plates separated, which were filtered. When dry, they weighed 11 g., and proved to be sodium *o*-toluene-sulfaminate. That this salt should precipitate from a solution which was both hot and quite strongly acid was rather unexpected. The filtrate was now boiled on the steam-bath for an hour, cooled again, treated with 100 g. of solid sodium hydroxide, and steam distilled. By extracting the distillate with ether, and evaporating the ether, there was obtained 17 g. (40%) of *o*-toluidine, boiling at 196–197°; acetyl derivative, m. p., 106–106.4°. The distillation residue was filtered, while hot, from inorganic salts. On cooling, white, lustrous, scaly crystals of sodium 2-toluidine-5-sulfonate were deposited. After drying at 90°, they weighed 27.5 g., or 34% of the calculated yield.

Identification of the Sodium Sulfaminate.—This salt, when heated at 140–150°, decomposed, losing 23–24% of its weight, and giving a strong toluidine odor. A sample, purified until free from sulfate, was boiled with hydrochloric acid, after which it gave a heavy precipitate of barium sulfate when treated with barium chloride, and when made alkaline, it gave a positive carbylamine test, indicating the presence of a primary amine. A diazotized sample gave dyes of the same shade as a known solution of diazotized sodium *o*-tolyl-sulfaminate.

Anal. Calcd. for $C_7H_8NSO_3Na \cdot H_2O$: Na, 10.13. Found: Na, 10.04, 10.15.

Identification of the Sodium Salt of the Amine Sulfonic Acid.—*Anal.* Calcd. for $C_7H_8NSO_3Na$: Na, 11.01. Found: Na, 11.10, 11.13. Oxidation with chromic acid in sulfuric acid gave toluquinone, m. p. 67.5°; m. p. of known sample of toluquinone, 66.5°; mixed m. p., 66.5°. Acidification of a concentrated water solution yielded the free sulfonic acid, which gave reactions characteristic of a substance of its type. Toluquinone was obtained from it, by oxidation as above.

Experiments with 2-Nitro-1,4-xylene

Preparation of 2-Nitro-1,4-xylene.—*p*-Xylene was nitrated according to Willstätter's chloroform method.[13] Ten grams of the hydrocarbon was nitrated at one time. Fractional distillation of the oil resulting from ten nitrations gave 73 g. of 2-nitro-1,4-xylene, boiling at 238–242° (740 mm.).

Reduction of 2-Nitro-1,4-xylene.—Thirty and seven-tenths g. (0.2 mole) was reduced, using the standard procedure except that 1000 cc. of water was added instead of the usual 300 cc. The products were as follows: 14.8 g. (60%) of 1,4-xylidine (b. p. 218.5°, corr.; acetyl derivative, m. p. 139.7–140°); and 6.2 g. (15.5%) of 2-amino-1,4-xylene-5-sulfonic acid.

Identification of the Aminosulfonic Acid.—The diazotized acid gave the usual coupling reactions. 1,4-Xyloquinone was obtained by oxidation with chromium trioxide and dilute sulfuric acid, and identified by the method of mixed melting points. The sodium salt was obtained from the free acid and excess sodium hydroxide as white

[13] Willstätter, *Ber.*, **42**, 4151 (1909).

scale-like crystals, containing two molecules of water of crystallization. Heated at 50–60° it loses one molecule of crystal water, and at 140–150° it loses the second molecule of water. Although Nolting, Witt and Forel[14] and also Nolting and Kohn[15] reported that the salt crystallized water-free, our results indicate that this is not the case.

Anal. (air-dried salt). Calcd. for $C_8H_{10}NSO_3Na \cdot 2H_2O$: Na, 8.87. Found: Na, 8.80, 8.66, 8.77, 8.91, 8.75. (50° dried salt.) Calcd. for $C_8H_{10}NSO_3Na \cdot H_2O$: H_2O, 7.47. Found (by heating at 150° to constant weight): H_2O, 7.51, 7.46. (150° dried salt.) Calcd. for $C_8H_{10}NSO_3Na$: Na, 10.33. Found: Na, 10.46, 10.48.

Experiments with *m*-Dinitrobenzene

(A) **Reduction with Neutral Sulfite.**—The procedure approximated to that used previously by Nietzki.[16] Forty-three grams of *m*-dinitrobenzene and 400 cc. of a solution (5.2 *N*) of sodium bisulfite (10% excess on the basis of the reduction of one nitro group) was heated just above the melting point of the solid until, upon cooling, no dinitrobenzene precipitated (two hours). One hundred and twenty-five cc. of 12 *N* hydrochloric acid was then added and the mixture boiled for thirty minutes. Yellow needles of *m*-nitraniline sulfonic acid separated, which weighed, when dry, 35 g. or 64% of the calculated quantity. They were purified by repeated reprecipitation, with hydrochloric acid, from a sodium hydroxide solution; followed by two recrystallizations from water, and thorough washing on the filter with methyl alcohol. They were dried at 140° and analyzed.

Anal. Calcd. for $C_6H_6O_5N_2S$: S, 14.62. Found: S, 14.16, 14.14.

The filtrate from which the *m*-nitraniline sulfonic acid separated was made alkaline with sodium hydroxide, the Glauber's salt was filtered off, and the filtrate was extracted with ether. Evaporation of the ether left a small amount of long needles, m. p. 110–112°; m. p. of *m*-nitraniline, 114°.

(B) **Reduction with Bisulfite.**—Seventy-two grams of the dinitro compound was heated for eight and one-half hours with 500 cc. of 5.2 *N* sodium bisulfite (110% excess for the reduction of one nitro group), and 500 cc. of water. One hundred cc. of concentrated sulfuric acid was then added. The cooled solution, after evaporation to 500 cc., contained a black cake of solid. This was extracted, first with hot 95% alcohol, and then with hot water. The part insoluble in water was discarded. From the alcohol solution was obtained 5 g. of unchanged dinitrobenzene. From the water solution was obtained about a gram of a substance, which, from its properties and a sulfur analysis on the crude material, was found to be the *m*-nitraniline-*p*-sulfonic acid. The filtrate from which this precipitated, on standing in a total volume of 400 cc. for several days, deposited purplish colored crystals, weighing 20 g. They were purified from admixed sodium sulfate by extraction with cold water, leaving 8 g. of an organic substance, which proved to be 1,3-diaminobenzene-4-sulfonic acid. It was identified by its amphoteric nature, the readiness with which it could be diazotized, and its crystalline habits. It crystallized in two distinct modifications—large monoclinic plates and elongated prisms.[17]

Anal. Calcd. for $C_6H_8N_2SO_3$: S, 17.00. Found: S, 16.66, 16.40.

Experiments with *p*-Nitrophenol

The standard procedure was used, except that solid sodium hydroxide was added, equivalent to the phenol used, and in addition to the alkali added normally. From 55.6

[14] Nolting, Witt and Forel, *Ber.*, **18**, 2667 (1885).

[15] Nolting and Kohn, *ibid.*, **19**, 141 (1886).

[16] Nietzki, *Ber.*, **29**, 2448 (1896).

[17] *Cf.* Post, *Ann.*, **205**, 105 (1880).

g. of *p*-nitrophenol, 10.5 g., or 14% of the theoretical weight of *p*-aminophenol-*m*-sulfonic acid, was obtained, by extracting the mixture of salts obtained after the acid treatment with water at 30°, and filtering the insoluble portion. It was impossible to isolate any other product, or to increase the yield of the aminosulfonic acid. It is probable, however, that the aminosulfonic acid is the chief product of the reaction, but it is impossible to isolate more of it without resorting to a laborious series of fractional crystallizations of the mixture obtained after the usual acid treatment. (The aminosulfonic acid is soluble in water to the extent of about 3 parts per 100.) Evidence was obtained which indicated the presence of considerable quantities of the aminophenol sulfonic acid in later crystalline fractions and mother liquors. Thus, the pure aminophenolsulfonic acid shows an interesting and characteristic fluorescence—violet in pure water, and bluish-purple in alkaline solution. The acidified solutions do not fluoresce. Now, in an attempt to separate more of the product from the inorganic salts produced in the reaction, after acid treatment, by a process of fractional crystallization, it was noted that all succeeding crystalline fractions, mother liquors, and filtrates showed this same fluorescence. Furthermore, other typical color reactions of this compound persisted throughout these later fractions. Moreover, solutions of *p*-aminophenol (the other expected product) in aqua ammonia are lavender and do not fluoresce. This affords evidence that very little, if any, of this amine is produced, and that the amount of aminosulfonic acid isolated constitutes but a minimum yield.

Identification of the Aminophenol Sulfonic Acid.—This substance, when heated with 25% sulfuric acid in a sealed tube for six hours at 165–170°, gave *p*-aminophenol, m. p., 183–183.5° (decomp.); m. p. of a sample of *p*-aminophenol of known origin, 183.4–183.8° (decomp.); mixed m. p. 182.8–183.2° (dec.). The aminophenol sulfonic acid gave a diazonium sulfate which did not decompose upon boiling with water. This is in accord with the observation of Schultz and Stable,[18] who state that the diazo compound of this aminophenol sulfonic acid is stable toward boiling water. Our diazo salt melted at 171°, after two crystallizations from water. Schultz and Stable report a melting point of 189°. The diazo compound, when heated with 25% sulfuric acid in a sealed tube at 180° for two hours, gave hydroquinone, identified by the method of mixed melting points.

Experiments with *p*-Nitrobenzoic Acid

Twenty-five grams was reduced according to the standard procedure, except that sodium hydroxide was again added in quantity sufficient to convert the acid to its sodium salt. The reduction stage required four and one-half hours. Fifty cc. of 12 *N* hydrochloric acid was then added and the mixture boiled again for two and one-half hours. Upon cooling, a fluffy, white solid separated, weighing 11 g., when dry. This was shown to be the *p*-aminobenzoic acid salt of *p*-amino-*m*-sulfobenzoic acid. The filtrate was evaporated to 250 cc. and allowed to stand. A second solid substance separated, weighing, when dry, 6 g.[19] This was shown to be *p*-aminobenzoic acid sulfate. On further evaporation of the filtrate to 150 cc. and cooling to −10°, a precipitate of 37 g. of Glauber's salt was obtained, and 40 g. more was thrown out by the addition of 250 cc. of 95% alcohol. The Glauber's salt was extracted with hot methyl alcohol. Evaporation of the alcohol left 1.5 g. of *p*-aminobenzoic acid sulfate. Three grams more was obtained by evaporating the aqueous ethyl alcoholic filtrate to 50 cc., extracting the resulting

[18] Schultz and Stable, *J. prakt. Chem.*, [2] 69, 336 (1904).

[19] In another run, the filtrate was divided into two parts at this point. One part was extracted with ether as it was, but gave no appreciable ether-soluble material. The other part was made feebly alkaline, and then extracted with ether. Three grams of *p*-aminobenzoic acid was obtained.

precipitate of impure sodium chloride with hot methyl alcohol, and expelling the alcohol. The filtrate was now evaporated to dryness, the residue extracted with hot 95% ethyl alcohol, the alcohol evaporated to a volume of 25 cc. and cooled. A precipitate of 0.5 g. of *p*-aminobenzoic acid, melting, without purification, at 183–185°, was obtained.

Properties of the *p*-Aminobenzoic Acid Salt of *p*-Amino-*m*-sulfobenzoic Acid.—This is an acidic salt, which burns completely without melting. It is soluble in dilute alkali, and is reprecipitated unchanged by dilute acids. It is insoluble in acids, dilute or concentrated, and in ordinary organic solvents. It is practically insoluble in cold water, but appreciably soluble in hot water. Qualitative tests showed that it is neither an amine sulfate nor an amine hydrochloride. It crystallized from water in needles, showing a silky, fibrous nature under the microscope. A sample was purified for analysis by repeated reprecipitation from an alkaline solution (both ammonium and potassium hydroxides were used) with dilute hydrochloric acid, and then by repeated crystallization from water. It was then washed repeatedly on the filter with methyl alcohol and dried at 140°. The analytical results agree most closely with those calculated for a salt consisting of one molecule of *p*-aminobenzoic acid and one molecule of *p*-amino-*m*-sulfobenzoic acid.

Anal. Subs., 0.2747, 0.2982, 0.3005, 0.2627, 0.3865: $BaSO_4$, 0.1704, 0.1831, 0.1826, 0.1607, 0.2407. Subs., 0.1391, 0.1159: CO_2, 0.2378, 0.1988; H_2O, 0.0543, 0.0422. Calcd. for $C_{14}H_{14}O_7N_2S$: C, 47.5; H, 4.2; S, 9.04. Found: C, 46.7, 46.9; H, 4.0, 4.3; S, 8.53, 8.45, 8.35, 8.37, 8.55. *Titration equivalent.* Subs., 0.4376, 0.4355: 0.2230 *N* NaOH (phenolphthalein), 16.79, 16.60 cc. Calcd. for $C_{14}H_{14}O_7N_2S$ (tribasic): 16.61, 16.53 cc.

This insoluble salt was split into its components as follows. To 1.1664 g. of an analytically pure sample was added 29.54 cc. of 0.2230 *N* sodium hydroxide, the exact amount calculated to neutralize two mono-acidic groups of a molecule of molecular weight 354. A slight insoluble portion was brought into solution by adding a little water. The solution showed an acid reaction toward litmus. It was extracted thirteen times with ether. The thirteenth extract, evaporated separately, gave 0.003 g. of the ether-soluble material. In all 0.401 g. of this material (*p*-aminobenzoic acid, m. p. 184–185°) was obtained.

Titration equivalent. 0.2301 g. required 7.63 cc. of 0.2230 *N* NaOH. Calcd. for $C_7H_7O_2N$ (monobasic), 7.54 cc.

To the water solution was added hydrochloric acid until a precipitate formed. This weighed 0.1152 g., after drying at 80° and required 4.36 cc. of 0.2230 *N* NaOH. Calcd. for $C_{14}H_{14}O_7N_2S$: 4.37 cc. Thus it appears that thirteen extractions with ether did not remove quite all of the *p*-aminobenzoic acid. When acid was added, this precipitated as the *least soluble salt* of the ions present in the solution, namely, as the amino-sulfobenzoic acid salt. Since 0.115 g. of this salt is equivalent to 0.044 g. of *p*-aminobenzoic acid, the total yield of the latter was 0.401 + 0.044 = 0.445 g.; calculated for 1.1664 g. of the salt, 0.451 g.[20] The filtrate, after separation of the salt, was evaporated to a small volume. This gave 0.51 g. of a white substance (dried at 115°). This was a sulfur-containing acid which crystallized from water in small plates characteristic of *p*-amino-*m*-sulfobenzoic acid.[21]

Titration equivalent. 0.2659 g. required 10.90 cc. of 0.2230 *N* NaOH. Calcd. for $C_7H_7O_5NS$ (dibasic): 11.00 cc.

[20] In a previous run, in which only three extractions with ether were made, 0.27 g. of aminobenzoic acid as such, and 0.155 g. as the reprecipitated salt, or a total of 0.425 g., was obtained from 1.116 g. of the substance; calculated, 0.432 g.

[21] *Cf.* Van Dorssen, *Rec. trav. chim.*, **29**, 373 (1910); Scott and Cohen, *J. Chem. Soc.*, **123**, 3180 (1923).

Identification of *p*-Aminobenzoic Acid Sulfate.—A sample was dissolved in the least possible *N* potassium hydroxide, and carefully acidified with 2 *N* hydrochloric acid. At the neutral point, a substance precipitated which was identified as *p*-aminobenzoic acid by mixed melting points. With bromine water it gave tribromoaniline and an ammonia soluble substance. The latter, after reprecipitation with acid, showed a decomposition range of 266–286°. (Reported by Sudborough for dibromo-*p*-aminobenzoic acid, 260–270°.)

Summary

1. A number of aromatic nitro compounds have been reduced with sodium bisulfite, and the solutions thus obtained have been boiled with mineral acids.

2. The quantities of amines and aminosulfonic acids which are produced in this manner have been determined.

3. Several other reduction products have been isolated and identified.

4. A standard procedure for studying the Piria reaction has been adopted, and comparable results thereby obtained.

5. Factors have been pointed out which affect the reaction and require further investigation.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

THE PIRIA REACTION. II. THE ROLE OF THE SULFAMINIC ACIDS[1,2]

BY W. H. HUNTER AND MURRAY M. SPRUNG

RECEIVED NOVEMBER 28, 1930 PUBLISHED APRIL 6, 1931

When the acid treatment which follows the reduction of a nitro compound in the "over-all" Piria reaction[3] is omitted, the principal product which can be isolated is a sulfaminic acid salt, of the general formula $RNHSO_3M$. The isolation of an N-sulfonated compound of this type was included among the original findings of Piria,[4] and thereafter similar products were mentioned by other early investigators.[5] However, that these sulfaminic salts were the *chief* products of the reaction when acid treatment was avoided was first emphasized by Weil,[6] who investigated a variety of aromatic nitro compounds, including alkyl nitrobenzenes,

[1] The work described in this paper formed part of a thesis submitted to the Graduate Faculty of the University of Minnesota by Murray M. Sprung in partial fulfilment of the requirements for the degree of Doctor of Philosophy, September 1928.

[2] Presented before the Division of Organic Chemistry of the American Chemical Society at the Minneapolis Meeting, September 9–16, 1929.

[3] Hunter and Sprung, THIS JOURNAL, **53**, 1432 (1931).

[4] Piria, *Ann.*, **78**, 31 (1851).

[5] Hilkenkamp, *ibid.*, **95**, 86 (1885); Smit, *Ber.*, **8**, 1442 (1875).

[6] (a) Weil, German Patents 147,552 and 151,134, *Friedländer*, **7**, 58, (b) 61 (1902); (c) Weil and Moser, *Ber.*, **55**, 732 (1922); (d) Weil and Wassermann, *ibid.*, **55**, 2533 (1922).