tion. This was especially marked in the case of the barium salt; tests for methyl alcohol and for dimethylamine gave negative results.

2. The solubility of pure helianthine in water is 0.02 g. per liter; the solubilities of all of its salts are greater than this. This can indicate that its salts are not completely hydrolyzed. Since solutions of its salts are partially or largely hydrolyzed, as shown in previous studies,[1] and these colors are not parallel to these solubilities, it may be concluded that the chromoisomerizations of helianthine are largely dependent upon the stabilities of the salts toward water.

3. No obvious conclusion can as yet be drawn from studies of the melting points of helianthine salts.

The formation of salts by other indicators will be studied.

SEATTLE, WASH.

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH.]

ON NITRO- AND AMINOARYL ARSONIC ACIDS.

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Received July 9, 1918.

In the course of studies on the synthesis of organic arsenic compounds for therapeutic purposes it was found necessary to prepare a number of aminoaryl arsonic acids. It was therefore of importance to find methods which would furnish these substances in amounts sufficient for synthetic work. Of the methods available the application of the Béchamp synthesis, first used for the preparation of arsanilic acid, has rendered directly accessible only a limited number, mainly *p*-aminoaryl arsonic acids. In order to obtain *o*- and *m*-amino arsonic acids it has usually been necessary to employ indirect methods.

The most useful of these involves the preparation of the corresponding nitro compound, which is then reduced to the desired amino acid. In case the nitro acid is synthesized by direct nitration of an aryl arsonic acid, only the *m*-nitro compound can be obtained. More general, however, is Bart's excellent method[2] in which a diazo or isodiazo group is replaced by the arsonic acid residue. This reaction has greatly increased the availability of aromatic arsonic acids, many of which have been unobtainable by other means. Among the wide variety of examples given by Bart are enough to demonstrate the value of the method for the preparation of the nitro arsonic acids and his procedure was, in fact, used later in a few instances by others[3] for the same purpose.

In the present work we have found the method to be of exceptional

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[1] THIS JOURNAL, **39**, 1373 (1917). See especially the potassium salt.

[2] Bart, D. R. P. 250,264.

[3] D. R. P. 266,944, 267,307; Bauer, *Ber.*, **48**, 1582 (1915).

service, particularly when *o*- and *p*-nitro amines were used as starting material. The reaction gave excellent yields and permitted the preparation of fairly large amounts of the *o*- and *p*-nitroaryl arsonic acids.

In the case of the *m*-nitro amines, however, the reaction between the alkaline diazo solution and sodium arsenite was far from being a smooth one, side reactions apparently disturbing its course. Under the conditions employed *m*-nitraniline, for instance, was found to yield but a trace of *m*-nitrophenylarsonic acid. The results were better in the case of the *m*-nitrotolylamines, particularly *p*-nitro-*o*-toluidine, but in no case was the yield as good as those obtained in the *o*- and *p*-series.

Once in possession of the nitro acid the next step is the reduction of the nitro to the amino group without affecting the arsonic acid residue. The principal reagents which have been employed for the selective reduction of the nitro group in these compounds are ammonium sulfide, sodium hydrosulfite, sodium amalgam, and ferrous hydroxide. Ammonium sulfide has the disadvantage of attacking the arsenic residue, requiring subsequent removal of combined sulfur. Sodium hydrosulfite, although frequently used, requires careful control and it has often been found difficult to avoid simultaneous reduction of the arsonic acid group. Sodium amalgam has also given good results, but it is scarcely the most convenient reagent for preparative purposes if a better substitute is available.

On the other hand, ferrous hydroxide in an alkaline medium, first employed by Benda[1] for the preparation of *p*-phenylenediamine arsonic acid and later for other reductions,[2] has proven a very reliable selective reducing agent. We believe that this fact should be emphasized more than has been done in the past, since we have found it to give most excellent results in the reduction of all the nitro arsonic acids which we have prepared. In our study of the method, the remarkable specificity of this reagent for the nitro group was demonstrated by the fact that even if an excess of ferrous salt was employed the yield of amino compound in practically every case was 80% of the theory or better. In view of these facts the method seems directly indicated for the reduction of all nitroaryl arsonic acids which do not contain groups incompatible with strong alkali.

Experimental Part.

Since the reduction of the nitro arsonic acids with ferrous sulfate was carried out under identical conditions in each case, the procedure used by us is given here to avoid its frequent repetition.

Seven molecular equivalents (based on the amount of nitro arsonic acid) of ordinary ferrous sulfate are dissolved in about 3 parts of warm water,

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[1] *Ber.*, **44**, 3302 (1911).

[2] *Ibid.*, **47**, 1006, 1316 (1914).

chilled well, and transferred to a wide-mouthed bottle fitted with a rubber stopper; 25% sodium hydroxide solution is then added until the ferrous hydroxide mud reacts strongly alkaline to litmus paper on vigorous shaking. The use of a weak base, such as ammonia,[1] results in poor yields of the amino acid since ammonia is too weakly alkaline to decompose the insoluble iron salt formed by the arsonic acid during the reduction. A solution of the nitro acid in dil. sodium hydroxide is then poured in at once and the mixture vigorously shaken for 5 minutes. The pale blue hydroxide immediately changes in color to the dark brown of ferric hydroxide. Warming the mixture is unnecessary and diminishes the yield. The mud is poured on to a large Büchner funnel, the residue being finally washed with water. As this filtration is slow it is necessary to use a large funnel to avoid a troublesome delay. The isolation of the amino acid from the filtrate depended on the properties of the compound and is described separately for each case.

Arsenic was determined in each substance by decomposing 0.25 to 0.3 g. by the Kjeldahl method, using 25 cc. of sulfuric acid, 10 g. of potassium sulfate, and a very small crystal of copper sulfate. After destruction of the organic matter and dilution with water the arsenic was precipitated by hydrogen sulfide and determined gravimetrically in the usual way as magnesium pyroarsenate.

***o*-Nitrophenylarsonic Acid**, *o*-$O_2NC_6H_4AsO_3H_2$.—The preparation of this substance has been described by Bart,[2] but we believe the method used below to be more convenient. Moreover, the description of the substance in the patent is incomplete and inaccurate.

One hundred grams of *o*-nitraniline (prepared by the excellent method of Witt and Utermann[3]) was ground under 500 cc. of 1 : 1 hydrochloric acid, the mixture chilled to 10°, and diazotized with a solution of 55 g. of sodium nitrite. After 10 to 15 minutes' stirring the solution was filtered from traces of undissolved nitraniline and poured slowly, with shaking, into 550 cc. of 25% sodium hydroxide solution, keeping the temperature below 0°. The alkaline solution was then added to 135 g. of sodium arsenite dissolved in 1250 cc. of water and the mixture heated to 60–70° for 1.5 to 2 hours, during which a slow but steady nitrogen evolution occurred. Overheating is particularly to be avoided. After acidification with a slight excess of acetic acid the dark-colored solution was boneblacked and hydrochloric acid added to the deep yellow filtrate until strongly acid to congo red. On thorough chilling the nitrophenylarsonic acid crystallized as a heavy, pale yellow powder. The yield was 110 grams.

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[1] THIS JOURNAL, **39**, 1435 (1917).

[2] *Loc. cit.*

[3] *Ber.*, **39**, 3901 (1906).

Recrystallized from water the nitro acid separates as pale yellow, glistening, hexagonal plates which contain one molecule of water of crystallization. The anhydrous acid melts and decomposes at 235–40° with preliminary softening, and does not merely intumesce as stated by Bart. The anhydrous acid is difficultly soluble in cold alcohol but dissolves on warming and is very sparingly soluble in chloroform or acetone. The hydrate is sparingly soluble in cold water but dissolves easily on warming. It is partly soluble in acetic acid but again crystallizes out and is then practically insoluble, presumably due to dehydration.

Subst., air dry, 0.6741 g. *in vacuo* at 100° over H_2SO_4; loss, 0.0469 g.

Calc. for $C_6H_6O_5NAs.H_2O$: H_2O, 6.80. Found: 6.96.

Anhydrous: 0.1384 g. subst.; 7.0 cc. N (24.5°, 757 mm.); 0.3197 g. subst.; 0.1972 g. $Mg_2As_2O_7$.

Calc. for $C_6H_6O_5NAs$: N, 5.67; As, 30.32%. Found: N, 5.78; As, 29.77.

***o*-Aminophenylarsonic Acid (*o*-Arsanilic Acid),** *o*-$H_2NC_6H_4AsO_3H_2$.—Forty grams of *o*-nitrophenylarsonic acid were reduced with 300 g. of ferrous sulfate by the standard method given above. The alkaline filtrate was acidified with hydrochloric acid, warmed, and treated with concentrated barium chloride solution until the sulfuric acid was completely removed, avoiding at the same time an undue excess of barium chloride. The filtrate was rendered slightly alkaline and concentrated to small bulk *in vacuo*. The precipitate of sodium chloride was filtered off and washed with a small amount of saturated sodium chloride solution. On treating the filtrate, the volume of which was about 200 cc., with hydrochloric acid until congo red paper just began to turn, the *o*-arsanilic acid rapidly crystallized, forming a thick mass of needles. After thorough chilling the acid was filtered off and washed with ice water. The yield was 27 g., or 80% of the theory. By using ferrous chloride instead of ferrous sulfate the treatment with barium chloride would of course become unnecessary.

The substance is quite soluble in water and melts at 153° with slight preliminary softening. The diazotized solution couples with R-salt to form a not very intense reddish orange dye, the *m*- and *p*-isomers giving deeper shades. In other properties it corresponded to those given by Benda,[1] who obtained the acid by a more involved method.

Subst., 0.1456 g.; 8.3 cc. N (23.0°, 758 mm.).

Calc. for $C_6H_8O_3NAs$: N, 6.45. Found: 6.56.

***m*-Aminophenylarsonic Acid (*m*-Arsanilic Acid).**—Sixty-three grams of *m*-nitrophenylarsonic acid (prepared without difficulty by nitrating phenylarsonic acid according to Michaelis[2]), was reduced with 500 g. of ferrous sulfate as previously described. Owing to the sparing solubility of *m*-arsanilic acid in water it sufficed to acidify the filtrate strongly with acetic acid,

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[1] *Ber.*, 44, 3304 (1911).

[2] *Ann.*, **320**, 294 (1902).

whereupon the amino acid separated rapidly as a yellow, crystalline powder. The yield was 47.5 grams. It was recrystallized by dissolving in dilute ammonia, boneblacking, and reprecipitating with acetic acid, separating as practically colorless, stout, rhombic prisms which melt at 213–5° with gas evolution. We have nothing to add to the description given by Bertheim.[1]

Subst., 0.1304 g.; 7.4 cc. N (22.5°, 766 mm.).
Calc. for $C_6H_8O_3NAs$: N, 6.45. Found: 6.61.

***p*-Nitrophenylarsonic Acid.**—This substance is mentioned by Bart in D. R. P. 250,264, but no description is given. The following procedure was used by us for its preparation:

27.6 g. of *p*-nitraniline was dissolved in 400 cc. of hot, 10% hydrochloric acid, chilled to 10°, and diazotized with a solution of 14.4 g. of sodium nitrite. After 15 minutes the solution was poured into 460 cc. of 10% sodium hydroxide, keeping the temperature at 0°. After the addition of 40 g. of sodium arsenite dissolved in water the mixture was heated to 55–65° until evolution of nitrogen ceased. After acidification with acetic acid and boneblacking, the filtrate was concentrated to small bulk *in vacuo* and acidified to congo red with hydrochloric acid. The nitro acid separated quickly as a light yellow precipitate and was washed with ice-water. The yield was 18 grams. Recrystallized from water, the nitro acid separates as pale yellow aggregates of minute leaflets which do not melt below 275°. It is sparingly soluble in hot methyl alcohol or acetic acid and also difficultly soluble in the cold in water, alcohol, or 50% alcohol, but dissolves readily in these solvents on heating.

Subst., 0.1422 g.; 7.4 cc. N (25.0°, 757 mm.).
Calc. for $C_6H_6O_5NAs$: N, 5.67. Found: 5.94.

***p*-Aminophenylarsonic Acid (*p*-Arsanilic Acid).**—This important substance is most easily obtained by the direct arsenation of aniline, but as the reduction with ferrous hydroxide was carried out as a test of the method it is given here. Fifteen grams of *p*-nitrophenylarsonic acid was reduced with 125 g. of ferrous sulfate. Since arsanilic acid is only incompletely precipitated from large volumes the sulfate ion was replaced by the chloride ion with barium chloride as in the case of *o*-arsanilic acid. The filtrate from the barium sulfate was made slightly alkaline and concentrated to small bulk *in vacuo*. On careful treatment with hydrochloric acid the filtrate from the sodium chloride deposited arsanilic acid in 80% of the theory. Recrystallized from water it separated in characteristic form.

Subst., 0.2215 g. (Kjeldahl); 9.85 cc. 0.1 *N* HCl.
Calc. for $C_6H_8O_3NAs$: N, 6.45. Found: 6.23.

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[1] Bertheim, *Ber.*, 41, 1657 (1908); Bertheim and Benda, *Ber.*, 44, 3297 (1911).

2-Nitro-4-methylphenylarsonic Acid (4-Methyl-6-nitrophenylarsonic Acid).—Twenty-two grams of 3-nitro-4-toluidine, 3,4-$(O_2N)(H_2N)C_6H_3CH_3$, was pulverized under 100 cc. of 20% hydrochloric acid and diazotized at 10° with 11 g. of sodium nitrite. When solution was practically complete the diazo mixture was poured into 355 g. of 10% aqueous sodium hydroxide kept at 0°. A concentrated solution of 27 g. of sodium arsenite was added at once and the mixture heated at 60–70° for about 1.5 to 2 hours. After acidifying with acetic acid and boneblacking, the filtrate was acidified to congo red with hydrochloric acid and deposited the arsonic acid at once as a light yellow, crystalline powder. The yield was 22 grams. On dissolving in hot sodium acetate solution and acidifying again to congo red the nitro acid separates rapidly as faintly yellow, minute rods melting and decomposing at about 255–60°. It is very sparingly soluble in cold water, alcohol or acetic acid, but is appreciably soluble in these solvents on boiling.

Subst., 0.1172 g.; 5.6 cc. N (26.0°, 763 mm.); subst., 0.3116 g.; 0.1858 g. $Mg_2As_2O_7$

Calc. for $C_7H_8O_5NAs$: N, 5.36; As, 28.70. Found: N, 5.48; As, 28.79.

2-Amino-4-methylphenylarsonic Acid (4-Methyl-6-aminophenylarsonic Acid).—14.5 g. of 2-nitro-4-methylphenylarsonic acid was reduced with 120 g. of ferrous sulfate. The acidified filtrate was treated with barium chloride as in the case of *o*-arsanilic acid and the filtrate made slightly alkaline and concentrated to small bulk *in vacuo*. The insoluble sodium chloride was filtered off and the amino acid precipitated by the careful addition of hydrochloric acid. The yield was 10 grams. Recrystallized from a small volume of hot water the amino acid forms colorless needles which melt at 180° with preliminary sintering and darkening. It is easily soluble in methyl or ethyl alcohol or glacial acetic acid and but sparingly in acetone or ether, and is appreciably soluble in water at room temperature. Its solution in dil. hydrochloric acid diazotizes smoothly and couples with R-salt to form a weak, orange-red dye as in the case of *o*-arsanilic acid.

Subst., 0.2382 g.; Kjeldahl, 10.25 cc. 0.1 *N* HCl; subst., 0.2803 g.; 0.1870 g. $Mg_2As_2O_7$.

Calc. for $C_7H_{10}O_3NAs$: N, 6.06; As, 32.44. Found: N, 6.03; As, 32.20.

2-Nitro-6-methylphenylarsonic Acid (2-Methyl-6-nitrophenylarsonic Acid).—Twenty-two grams of 3-nitro-*o*-toluidine, 2,3-$(H_2N)(O_2N)C_6H_3CH_3$, was diazotized and treated with sodium arsenite exactly as in the case of 3-nitro-4-toluidine. The yield of the resulting nitroarsonic acid was 19 grams. Recrystallized from hot water it separates slowly as star-shaped aggregates of pale yellow, delicate needles which decompose at 228–30° with preliminary softening and darkening. It is sparingly soluble in hot water and practically insoluble in the cold, but is somewhat more soluble in boiling acetic acid and readily in hot alcohol. It dissolves in methyl alcohol at room temperature.

Subst., 0.1603 g.; 7.6 cc. N (25.0°, 761 mm.); subst., 0.3110 g.; 0.1837 g. $Mg_2As_2O_7$.
Calc. for $C_7H_8O_5NAs$: N, 5.36; As, 28.70. Found: N, 5.44; As, 28.50.

2-Amino-6-methylphenylarsonic Acid (2-Methyl-6-aminophenylarsonic Acid).—8.5 g. of 2-nitro-6-methylphenylarsonic acid was reduced with 70 g. of ferrous sulfate and the resulting amino acid isolated exactly as in the case of *o*-arsanilic acid. The yield was 5 grams. Recrystallized from a small volume of hot water the aminotolylarsonic acid separates slowly as rosets or plates which decompose at 175–80°. It is soluble in methyl or ethyl alcohol or glacial acetic acid, less so in acetone or water at room temperature. A solution in hydrochloric acid is readily diazotized but the diazo solution does not give a strong color with R-salt.

Subst., 0.1658 g.; Kjeldahl, 7.3 cc. 0.1 *N* HCl.
Calc. for $C_7H_{10}O_3NAs$: N, 6.06. Found: 6.16.

3-Nitro-4-methylphenylarsonic Acid (4-Methyl-5-nitrophenylarsonic Acid).—This substance was prepared by Michaelis[1] by the nitration of *p*-tolylarsonic acid. As in the case of other *m*-nitro amines, the application of the Bart reaction to 2-nitro-4-toluidine, 2,4-$(O_2N)(H_2N)C_6H_3CH_3$, did not give as good results as in the *o*- and *p*-series. Many modifications of the method were tried but the best that could be obtained was unsatisfactory from the standpoint of yield.

Sixty grams of 2-nitro-4-toluidine was dissolved in 400 cc. of hot 1 : 1 hydrochloric acid, poured into one liter of cold water, chilled to 10° and the mixture then treated with a concentrated solution of 30 g. of sodium nitrite. After complete diazotization the solution was poured into 600 cc. of 25% aqueous sodium hydroxide, keeping the temperature at 0°. A solution of 100 g. of sodium arsenite was then added and the mixture allowed to stand overnight at room temperature. A steady evolution of nitrogen occurred, but a large amount of insoluble tar was formed which consisted largely of nitrotoluene. After acidifying the mixture with acetic acid and boneblacking, the filtrate was concentrated to small bulk *in vacuo* and acidified to congo red with hydrochloric acid. The nitro acid separated rapidly as lustrous crystals which were purified by dissolving in dilute sodium acetate solution and acidifying the filtrate with hydrochloric acid. The yield was only 16 grams. Recrystallized from a small volume of hot water the nitro acid separates as cream-colored needles which do not melt below 285°. It is sparingly soluble in cold water or acetic acid, easily on boiling. It dissolves readily in methyl or ethyl alcohol and very sparingly in acetone or chloroform.

Subst., 0.1422 g.; 6.8 cc. N (25.0°, 764 mm.); subst., 0.3361 g.; 0.2015 g. $Mg_2As_2O_7$.
Calc. for $C_7H_8O_5NAs$: N, 5.36; As, 28.70. Found: N, 5.51; As, 28.93.

3-Amino-4-methylphenylarsonic Acid (4-Methyl-5-aminophenylarsonic Acid).—Ten grams of 3-nitro-4-methylphenylarsonic acid was reduced as

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[1] *Ann.*, 320, 321 (1902).

usual with 80 g. of ferrous sulfate. Owing to the solubility of the amino acid the method used for the isolation of *o*-arsanilic acid was found necessary. The concentrated filtrate from the barium sulfate yielded 7 g. of the aminotolyl arsonic acid on careful acidification with hydrochloric acid. Recrystallized from a small volume of hot water it separates very slowly as woolly masses of delicate, microscopic needles which soften and melt at 172–5° to a liquid filled with bubbles. It is somewhat soluble in water, methyl or ethyl alcohol, or acetic acid at room temperature, and dissolves readily in these on warming. The hydrochloric acid solution is smoothly diazotizable, giving a cherry-red color with R-salt.

Subst., 0.2127 g.; Kjeldahl, 9.3 cc. 0.1 *N* HCl; subst., 0.3057 g.; 0.2027 g. $Mg_2As_2O_7$.
Calc. for $C_7H_{10}O_3NAs$: N, 6.06; As, 32.44. Found: N, 6.12; As, 32.00.

3-Nitro-6-methylphenylarsonic Acid (2-Methyl-5-nitrophenylarsonic Acid).—This substance has recently been described by Karrer,[1] who obtained it by the direct nitration of *o*-tolylarsonic acid. By the Bart reaction 4-nitro-*o*-toluidine (2,4-$(H_2N)(O_2N)C_6H_3CH_3$), was found to yield the same product more conveniently. Being a *m*-nitro compound 4-nitro-*o*-toluidine did not react as smoothly as the *o*- and *p*-nitro amines, but the reaction proceeded more normally than in the case of 2-nitro-4-toluidine, described above.

Sixty-six grams of 4-nitro-*o*-toluidine was dissolved in 440 cc. of hot 1 : 1 hydrochloric acid and poured into 1100 cc. of water. The mixture was diazotized at 10° with a solution of 33 g. of sodium nitrite and the diazo-solution then poured into 660 cc. of 25% sodium hydroxide solution, keeping the temperature below 0°. After adding a concentrated solution of 110 g. of sodium arsenite and letting stand overnight at room temperature the mixture was acidified with acetic acid and the tar collected with boneblack. The filtrate was concentrated to small bulk *in vacuo* and acidified to congo red with hydrochloric acid. Forty grams of the nitro acid separated as light yellow, glistening plates. As so obtained the substance was contaminated with some amorphous material which depressed the melting point but did not interfere with the reduction to the amino acid. For analysis the nitro acid was dissolved in dil. sodium acetate solution and reprecipitated with hydrochloric acid after boneblacking in the cold. When rapidly heated it often melts completely at about 225°, evolves gas, and resolidifies, finally melting with decomposition at 261–3°. The same behavior was observed on plunging the substance into a bath heated to 230°, but if the acid is heated slowly it sinters and changes its appearance at about 220°, but does not melt until 261–3° is reached. As Karrer described the acid as darkening at 230° and melting at 261° some of the substance was synthesized by his method and was found to behave in the same way as our preparation. It is probable that at the melting

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[1] *Ber.*, **48**, 311 (1915).

point of the nitro acid, *i. e.*, about 225°, water is liberated with the formation of the anhydride, which then melts at 261–3°. The acid is very sparingly soluble in cold water, alcohol, or acetic acid, but dissolves in these on heating. It is soluble in methyl alcohol and practically insoluble in acetone or chloroform. Whereas the substance prepared by Karrer's method is colorless, a yellow color persists in the compound as obtained by the Bart method.

Subst., 0.1468 g.; 6.9 cc. N (23.0°, 756 mm.); subst., 0.2244 g.; 0.1346 g. $Mg_2As_2O_7$.
Calc. for $C_7H_8O_5NAs$: N, 5.36; As, 28.70. Found: N, 5.39; As, 28.93.

3-Amino-6-methylphenylarsonic Acid (2-Methyl-5-aminophenylarsonic Acid).—Thirty-seven grams of the above nitrotolylarsonic acid was reduced with 300 g. of ferrous sulfate. On acidification of the filtrate with acetic acid the amino acid separated on scratching. The crude product was purified by dissolving in dilute hydrochloric acid and reprecipitating with sodium acetate solution, the yield being 80% of the theory. Recrystallized from hot water it separates as cream-colored prisms which decompose at about 235–45° with preliminary darkening. It is rather difficultly soluble in boiling water and still less so in boiling alcohol, methyl alcohol, or acetic acid. It is smoothly diazotized in acid solution, giving a deep cherry-red color with R-salt.

Subst., 0.1425 g.; 7.6 cc. N (24.0°, 755 mm.).
Calc. for $C_7H_{10}O_3NAs$: N, 6.06. Found: 6.09.

4-Nitro-6-methylphenylarsonic Acid (2-Methyl-4-nitrophenylarsonic Acid).—Fifteen grams of 5-nitro-*o*-toluidine, 2,5-$(H_2N)(O_2N)C_6H_3CH_3$, was boiled with 80 cc. of 1 : 1 hydrochloric acid and then poured, with turbining, into 200 cc. of cold water. The solution was diazotized at 10° with 7.2 g. of sodium nitrite and the mixture poured into 100 g. of 25% aqueous sodium hydroxide, keeping the temperature below 0°. A solution of 20 g. of sodium arsenite was then added and the mixture warmed gently until the evolution of nitrogen ceased. It is important not to allow the temperature to exceed 70°, as the resulting nitrotolylarsonic acid will then be contaminated with by-products. After acidification with acetic acid and boneblacking, the filtrate was treated with hydrochloric acid, the nitro compound quickly separating as minute, almost colorless needles which melt and decompose at about 235–40°. The yield was 14 grams. The compound is sparingly soluble in cold water, alcohol or acetic acid, but dissolves in these on boiling. It is practically insoluble in acetone or chloroform.

Subst., 0.1341 g.; 6.4 cc. N (25.0°, 757 mm.); subst., 0.3049 g.; 0.1795 g. $Mg_2As_2O_7$.
Calc. for $C_7H_8O_5NAs$: N, 5.36; As, 28.70. Found: N, 5.45; As, 28.41.

4-Amino-6-methylphenylarsonic Acid (2-Methyl-4-aminophenylarsonic Acid, *m*-Toluidine Arsonic Acid).—Fifteen grams of the nitro acid was reduced with 120 g. of ferrous sulfate. On treating the filtrate with hydrochloric acid until congo red just began to turn, 11 g. of the amino acid quickly separated. As the volume of the liquid is quite large it is essential to add neither too much nor too little hydrochloric acid. This difficulty is obviated, however, by isolating the acid by the method used in the case of *o*-arsanilic acid. Recrystallized from hot water, the acid separates as flat, microscopic needles and pointed prisms which darken and decompose at 222–4°. Since this melting point did not correspond with that given by Benda and Kahn[1] (180°) for the substance as obtained by the direct arsenation of *m*-toluidine, we prepared the compound by this method. The amino acid as so obtained also melted at 222–4°, as did a mixture of the two. The substance is easily diazotized, coupling with R-salt to give an orange-red solution.

Subst., 0.1345 g.; 7.0 cc. N (22.0°, 768 mm.).
Calc. for $C_7H_{10}O_3NAs$: N, 6.06. Found: 6.09.

4-Nitro-2,5-dimethylphenylarsonic Acid (2,5-Dimethyl-4-nitrophenylarsonic Acid).—8.2 g. of *p*-nitro-*p*-xylidine (2,5-dimethyl-4-nitraniline) was ground up in a mortar with 25 cc. of concd. hydrochloric acid. The mixture was washed into a beaker with about 40 cc. of water and diazotized at 10° with 3.5 g. of sodium nitrite. The mixture was allowed to reach 15°, stirring continuously, and although a precipitate of apparently unchanged material remained, the whole was nevertheless poured into 180 cc. of 10% sodium hydroxide solution, keeping the temperature below 0°. 9 g. of sodium arsenite in a little water were then added, after which the mixture was heated to 50°. When the resulting gentle evolution of nitrogen had almost ceased the temperature was raised to 60–70° for one and one-half hours longer. After acidifying with acetic acid and boneblacking, the filtrate was acidified to congo red with hydrochloric acid, causing immediate separation of the nitro arsonic acid. This was allowed to stand in the ice box, filtered off, washed with water, and dried. The yield was 4.8 g. A portion was recrystallized from 50% acetic acid, separating as pale yellow, spindle-shaped prisms, wedge-shaped platelets, and long, flat plates which melt and decompose at about 290°, with preliminary softening and darkening. It is therefore not identical with the nitro-*p*-xylenearsonic acid obtained by Michaelis[2] by nitrating *p*-xylenearsonic acid. This substance forms needles melting at 205° and from its mode of formation would seem to be the 3-nitro isomer of the acid here described. The 4-nitro acid is sparingly soluble in boiling water or cold 50%, or glacial, acetic acid, but dissolves readily in the last two on heating. It is also soluble in boiling alcohol.

Subst., 0.1409 g.; 6.4 cc. N_2 at 30.0° and 757 mm.
Subst., 0.2943 g.; 0.1648 g. $Mg_2As_2O_7$.
Calc. for $C_8H_{10}O_5NAs$: N, 5.09; As, 27.24. Found: N, 5.10; As, 27.03.

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[1] *Ber.*, 41, 1675 (1908).

[2] *Ann.*, **320**, 339 (1902).

4-Amino-2,5-dimethylphenylarsonic Acid (2,5-Dimethyl-4-aminophenylarsonic Acid).—4.1 g. of the crude nitro acid was reduced in the usual way with 30 g. of ferrous sulfate in 90 cc. of water. The filtrate from the ferrous hydroxide was acidified with hydrochloric acid until congo red just began to change color and on rubbing the acid separated quickly as glistening scales. After filtering off and washing with ice water the yield was 3.0 g. A portion was recrystallized from water, forming thin, nacreous, serrated, almost colorless platelets containing one molecule of water of crystallization as described by Benda and Kahn,[1] who prepared the acid by the direct arsenation of *p*-xylidine. The amino acid is readily diazotizable and is sparingly soluble in cold water or alcohol, quite easily on boiling. When rapidly heated to 210°, then slowly, the anhydrous substance melts at 213–4° with decomposition.

Anhydrous subst. (Kjeldahl), 0.1526 g; 6.35 cc. 0.1 *N* HCl.
Calcd. for $C_8H_{12}O_3NAs$: N, 5.72. Found: 5.83.

3-Amino-4-hydroxyphenylarsonic Acid.—This substance, previously obtained by the reduction of 3-nitro-4-hydroxyphenylarsonic acid by the use of sodium hydrosulfite or sodium amalgam,[2] is also most conveniently prepared by the use of ferrous sulfate.

58.4 g. of 3-nitro-4-hydroxyphenylarsonic acid was reduced in the usual manner with 440 g. of ferrous sulfate. On acidifying the dark-colored filtrate with acetic acid and rubbing, the aminohydroxyphenylarsonic acid separated in characteristic form. The yield was 42 g., or 80% of the theory. The recrystallized acid darkens and softens at about 220° and finally decomposes at about 290°.

Subst., 0.1525; Kjeldahl, 6.9 cc. 0.1 *N* HCl.
Calc. for $C_6H_8O_4NAs$: N, 6.01. Found: 6.34.

NEW YORK CITY.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MOUNT HOLYOKE COLLEGE.]

THE ABSORPTION SPECTRA OF SOME DERIVATIVES OF CYCLOPROPANE.

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Received July 15, 1918.

A comparison of the ultraviolet absorption spectra of certain derivatives of cylopropane and their isomeric ethylenic derivatives with the spectra of the corresponding saturated derivatives of propane has shown distinct differences in the absorptive power of the 3 types of compounds and has given results of interest with regard to the effect of ring formation on absorption spectra.

The substances used in this investigation were made available through

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[1] Benda and Kahn, *Ber.*, 41, 1676 (1908).

[2] D. R. P. 224,953; Ehrlich and Bertheim, *Ber.*, 45, 757 (1911).