

atmosphere as 4 atmospheres, and the temperature as 5500° absolute, the partial pressure of calcium ion or of electron gas comes out 0.07 atmospheres corresponding to 1.7% ionization. This means that the sun's atmosphere has a very considerable electrical conductivity which can be calculated by making proper estimates of the ionic mobilities.

FIXED NITROGEN RESEARCH LABORATORY,
WASHINGTON, D. C.
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RICHARD C. TOLMAN.

Addendum.—In connection with my recent article on "The Ionization of Aqueous Solutions of Ammonia in the Presence of Urea," published in the December, 1920, number of THIS JOURNAL the following addendum should be made.

"This paper embodies the subject matter of a thesis presented to the Faculty of Clark University in partial fulfilment of the requirements for the Degree of Master of Arts. I wish to acknowledge my indebtedness to the Chemical Laboratory of Clark University for the use of the facilities of this Laboratory in connection with this investigation, and to Dr. Kraus for his interest and coöperation which made this investigation possible."

TOOBLER, UTAH.
Received January 11, 1921.

WINTHROP M. BURKE.

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

AROMATIC ARSENIC COMPOUNDS. IX. DIAZO-AMINO COMPOUNDS OF ARSANILIC ACID AND ITS DERIVATIVES.

BY WALTER A. JACOBS AND MICHAEL HEIDELBERGER.

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In a former communication¹ there was outlined a plan for the synthesis of aromatic arsenic compounds for chemotherapeutic study in which, among other series of substances which have since been published, were mentioned the two groups of diazo-amino and azo derivatives obtained from arsanilic acid. These substances with the first which we prepared for these investigations, and although interesting results were obtained with individual compounds in the treatment of experimental trypanosomiasis, we were soon led to discontinue the study of these types because of disadvantages which seemed inherent in them, such as the general instability of the diazo-amino compounds and certain harmful toxic effects induced by both groups. We believe, however, that a presentation of our chemical studies with these compounds should not be devoid of interest.

¹ THIS JOURNAL, 41, 1581 (1919).

In their determination of the constitution of arsanilic acid Ehrlich and Bertheim² found that the amino group could be readily diazotized and that the resulting diazo compound coupled without difficulty, yielding azo dyes. We have found that this reaction could be extended to the preparation of well-defined diazo-amino compounds containing the arsonic acid residue. We have prepared several groups of such substances, using as couplers dialkylamines, simple arylamines, aminobenzoic acids, arylglycines, and amino-phenoxyacetic acids.

The coupling of the secondary aliphatic amines and the simpler primary aromatic amines with diazotized arsanilic acid offered as a rule but little difficulty, the procedure being that adopted in the past for analogous substances. The reaction mixture was kept neutral or acid only with a weak acid such as acetic acid. The isolation of the individual compounds was accomplished either as the salt or as the acid, depending upon manipulative convenience. In certain cases it was found preferable, however, to diazotize the amino compound first and then to add arsanilic acid as the coupler. In the case of the aromatic amino acids, although coupling usually proceeded smoothly, it required considerable experimentation to determine in what form and under what conditions the product could best be isolated, since there were available the free acid, the monosodium salt, and the disodium salt from which to choose. The simpler aminobenzoic acids yielded diazo compounds under carefully controlled conditions by using the amino acid itself as coupler and isolating the products as the monosodium salts. In the first experiments in which *p*-amino-phenoxyacetic acid and its homologs were employed, however, it developed that the reaction either did not proceed entirely in the desired sense, or that the diazo-amino compounds possessed properties which rendered difficult their isolation from the reaction mixture. In such cases it was found that the amino acid esters coupled smoothly, giving the diazo-amino esters in excellent yield. Owing to the stability of the diazo-amino group on the alkaline side it then proved relatively simple to saponify the esters to the diazo-amino acids themselves. This method was consequently employed as a more certain means of obtaining these acids in satisfactory form and yield from the more complex amino-aryl acids, although in some instances the direct method might have been employed. This device also proved necessary in the preparation of the diazo-amino compound from *p*-aminophenol. Here *p*-aminophenyl benzoate was diazotized and coupled with arsanilic acid, yielding the diazo-amino benzoate, which was subsequently saponified.

The diazo-amino compounds derived from the secondary aliphatic amines and from most of the aromatic amino compounds formed both crystalline acids and sodium salts, the former possessing definite decompo-

² Ehrlich and Bertheim, *Ber.*, **40**, 3292 (1907).

sition points and being as a rule difficultly soluble in the usual solvents, while the salts formed more or less yellow solutions in water. The acids were unstable in acid solution, readily dissociating into the component amino and diazo compounds and evolving nitrogen on warming. In the case of several of the diazo-amino compounds derived from the arylglycines and the methyl derivatives of *p*-amino-phenoxyacetic acid, it was found impossible to isolate the free acids owing to their slight tendency to crystallize and to the ease with which they dissociated in acid solution. On the other hand, the esters of these substances, with few exceptions, proved to be more stable and easy to isolate. Practically all of the diazo-amino sodium salts were readily soluble in water, the solutions giving immediate precipitates with the heavy metal ions.

On the whole the work with this class of substances proved difficult, since in each case the conditions best suited for the preparation and isolation of the particular compound had to be carefully studied. It was also found essential to work as rapidly as possible throughout, and at low temperatures in order to avoid the decomposition which otherwise readily occurred.

Owing to the mass of detail the work is presented practically in abstract form, in order not to use undue space.

Experimental.

The values given for water of crystallization were obtained with substances which had been dried to constant weight in the air. Water was determined as a rule by drying *in vacuo* at room temperature over sulfuric acid, since higher temperatures caused decomposition.

In order to avoid repetition, it will be understood that the diazotization of arsanilic acid was carried out as follows. Arsanilic acid was dissolved in 2 molecular equivalents of *N* hydrochloric acid, chilled to about 5° and diazotized with one equivalent of 5 *N* sodium nitrite solution. The reaction proceeded smoothly and completely and toward the end there was a pronounced color change from orange to pale yellow. The solution was then neutralized before coupling according to the method given under each compound to be described. The expression A→B indicates that the diazotized arsanilic acid solution was added to the coupler; B→A, that the coupler was added to the diazotized arsanilic acid.

In cases in which no acid group was present in addition to the arsonic acid residue, acetic acid was in all cases sufficient to liberate the diazo-amino arsonic acid from solutions of the sodium salt. It was also found advantageous to work at rather high dilutions, except in the case of the aliphatic amines. When an additional carboxy group was present it was found necessary to add to the chilled solutions of the salt sufficient hydrochloric acid to render the reaction just acid to congo red.

(A) Diazo-amino Compounds of Arsanilic Acid and Aliphatic Amines.

Diazobenzene - (4-arsonic acid) - dimethylamine.—B→ neutralized A, coupling being complete in about 15 minutes. After adding acetic acid the product was recrystallized from alcohol, forming orange spears which intumesced at 182°. It is very difficultly soluble in cold alcohol, more readily in methyl alcohol, and decomposes in boiling water with nitrogen evolution.

Analyses. Calc. for $C_8H_{12}O_3N_3As$: N, 15.38; As, 27.44. Found: N, 15.52; As, 27.13.

On treating an alcoholic suspension with 1 mol. of 25% sodium hydroxide solution, heating, and carefully adding water until clear, the sodium salt crystallized on cooling, separating from 85% alcohol as glistening, salmon-colored platelets which dissolve easily in water.

Analyses. Calc. for $C_8H_{11}O_3N_3AsNa \cdot 3.5H_2O$: H_2O , 17.60. Found: 17.89.

Calc. for $C_8H_{11}O_3N_3AsNa$: N, 14.24. Found: 14.42.

Diazobenzene - (4-arsonic acid) - diethylamine.—The crude acid was reprecipitated from dil. sodium carbonate, dissolved in warm 50% alcohol, and cautiously diluted with an equal volume of water, separating as delicate, flat, cream-colored needles, which, when anhydrous, gradually soften and darken above 120°, decompose at about 195–200°, and dissolve readily in methyl alcohol and acetic acid.

Analyses. Calc. for $C_{10}H_{16}O_3N_3As \cdot H_2O$: H_2O , 5.65. Found: 6.51.

Calc. for $C_{10}H_{16}O_3N_3As$: N, 13.96; As, 24.88. Found: N, 13.59; As, 25.12.

A neutral aqueous solution of the sodium salt was prepared, evaporated to dryness *in vacuo*, and the residue dissolved in a little hot 85% alcohol, the salt slowly crystallizing in the cold as rosetts of somewhat deliquescent cream-colored needles.

Analyses. Calc. for $C_{10}H_{15}O_3N_3AsNa$: N, 13.00; As, 23.21. Found: N, 13.02; As, 23.82.

Diazobenzene - (4-arsonic acid) - piperidine.—The free acid, obtained from its salt, formed pale drab spherules and rosetts of narrow, microscopic platelets which melt and effervesce at 162–3°, and are appreciably soluble in methyl and ethyl alcohol.

Analyses. Calc. for $C_{11}H_{16}O_3N_3As$: N, 13.42; As, 23.93. Found: N, 13.53; As, 23.69.

Separation of the sodium salt from the initial reaction mixture was facilitated by the addition of sodium acetate. It forms drab-colored, minute platelets from 85% alcohol.

Analyses. Calc. for $C_{11}H_{15}O_3N_3AsNa \cdot 3.5H_2O$: H_2O , 15.83. Found: 15.35.

Calc. for $C_{11}H_{15}O_3N_3AsNa$: N, 12.53. Found: 12.57.

Bis-diazobenzene - (4-arsonic acid) - pentamethylene-tetramine.—8.7 g. of arsanilic acid were diazotized with 40 cc. of *N* sodium nitrite solution, diluted with an equal volume of saturated sodium acetate solution, and then treated with 3 g. of hexamethylene-tetramine.³ Coupling occurred rapidly with cleavage of formaldehyde, and 8 g. of the sodium salt quickly crystallized. Rapid recrystallization from water yielded lustrous, colorless platelets soluble in about 20 parts of water at ordinary temperatures.

Analyses. Calc. for $C_{17}H_{20}O_6N_8As_2Na_2 \cdot 6H_2O$: H_2O , 14.68. Found: 14.31.

Calc. for $C_{17}H_{20}O_6N_8As_2Na_2$: N, 17.83. Found: 17.65.

On slowly treating a very dilute solution in warm water with acetic acid the free acid separates as narrow, minute, colorless, microscopic platelets which are practically insoluble in neutral solvents. It puffs up at 210–12°, and dissolves very slowly in boiling water with nitrogen evolution, decomposition occurring rapidly on addition of a drop of acid, when the odor of formaldehyde becomes quite noticeable.

Analyses. Calc. for $C_{17}H_{22}O_6N_8As_2$: N, 19.18; As, 25.66. Found: N, 19.15; As, 25.40.

³ Cf. Duden and Scharf, *Ann.*, **288**, 218 (1895).

(B) Diazo-amino Compounds of Arsanilic Acid and the Simpler Aromatic Amines.

Diazobenzene - 4-(arsonic acid) - aniline.—Alcoholic B \rightarrow neutralized A. The yellow sodium salt gradually crystallized on adding sodium acetate, separating from 85% alcohol as minute, orange platelets and flat needles which dissolve readily in water.

Analyses. Calc. for $C_{12}H_{11}O_3N_3AsNa \cdot 4H_2O$: H_2O , 17.35. Found: 17.02.

Calc. for $C_{12}H_{11}O_3N_3AsNa$: N, 12.24. Found: 12.21.

The free acid forms bundles of minute, yellow, microscopic needles which melt and then decompose at 112–13°. It is difficultly soluble in cold methyl and ethyl alcohols but quite readily on boiling, and decomposes in boiling water.

Analyses. Calc. for $C_{12}H_{12}O_3N_3As$: N, 13.08; As, 23.33. Found: N, 12.77; As, 23.55.

Diazobenzene - (4-arsonic acid) - methylaniline.—Alcoholic B \rightarrow A + sodium acetate yielded a brown, gummy precipitate which crystallized on rubbing. On dissolving in very dilute aqueous ammonia, adding an equal volume of alcohol, cooling, and acidifying with acetic acid, the pure acid separated as orange-brown aggregates of minute radiating needles, effervescing at 160–2° with preliminary reddening. It dissolves in dil. acid with an orange-red color appearing a faint purple in thin layers, apparently due to partial dye formation, although the solution still evolves nitrogen on heating.

Analyses. Calc. for $C_{13}H_{14}O_3N_3As$: N, 12.54. Found: 12.58.

When the diazo solution was neutralized with sodium hydroxide and then coupled with methylaniline, a deep brown-orange solution resulted from which the sodium salt separated on adding sodium acetate, as a thick paste of lustrous, orange platelets which were recrystallized from water.

Analyses. Calc. for $C_{12}H_{13}O_3N_3AsNa \cdot 5.5H_2O$: H_2O , 21.70. Found: 21.53.

Calc. for $C_{13}H_{13}O_3N_3AsNa$: N, 11.76; As, 21.00. Found: N, 11.83; As, 21.30.

Diazobenzene - (4-arsonic acid) - *p* - toluidine.—The sparingly soluble sodium salt separated in almost quantitative yield, forming yellow, glistening leaflets from water containing a few drops of dil. sodium carbonate.

Analyses. Calc. for $C_{13}H_{13}O_3N_3AsNa \cdot 6H_2O$: H_2O , 23.23. Found: 22.79.

Calc. for $C_{13}H_{13}O_3N_3AsNa$: N, 11.76; As, 20.99. Found: N, 11.78; As, 20.79.

The free acid is precipitated from a 50% alcoholic solution of the salt as thin, pale yellow, microscopic needles which intumescence at 130–2° and dissolve in hot alcohol.

Analysis. Calc. for $C_{13}H_{14}O_3N_3As$: N, 12.53. Found: 12.63.

Diazobenzene - (4-arsonic acid) - 4' - chloro-aniline.—B + dil. hydrochloric acid \rightarrow A + sodium acetate. The acid immediately precipitated in quantitative yield and gradually crystallized. Dissolved in much 50% alcohol with the aid of sodium hydroxide and re-acidified it forms an emulsion which rapidly changes on rubbing to hexagonal platelets which intumescence at 177° with preliminary darkening and are practically insoluble in neutral solvents.

Analysis. Calc. for $C_{12}H_{11}O_3N_3ClAs$: N, 11.82. Found: 12.08.

Dissolved in 1 mol. of dil. sodium hydroxide solution it yielded the sodium salt on addition of alcohol, forming almost colorless platelets from 50% alcohol.

Analyses. Calc. for $C_{12}H_{10}O_3N_3ClAsNa \cdot 2H_2O$: H_2O , 8.71. Found: 8.37.

Calc. for $C_{12}H_{10}O_3N_3ClAsNa$: N, 11.12; As, 19.86. Found: N, 11.20; As, 20.01.

Diazobenzene - (4-arsonic acid) - *o* - anisidine.—Although Jacobson and Hönigsberger⁴ obtained a dye in using *o*-anisidine as a coupler, the method used in the above cases yielded the diazo-amino derivative. A certain amount of dye formation was, however, evident from the deep color. The sodium salt was salted out with sodium

⁴ Jacobson and Hönigsberger, *Ber.*, **36**, 4096 (1903).

acetate and washed with alcohol. It separates from 85% alcohol as aggregates of brown, rectangular platelets dissolving readily in water.

Analyses. Calc. for $C_{13}H_{13}O_4N_3AsNa \cdot 5H_2O$: H_2O , 19.44. Found: 20.02.

Calc. for $C_{13}H_{13}O_4N_3AsNa$: N, 11.26. Found: 11.19.

The free acid was precipitated from a chilled solution of the salt in 50% alcohol as sheaves of flat, microscopic needles which, when anhydrous, sinter, then darken, and finally intumesce at 95–9°.

Analyses. Calc. for $C_{13}H_{14}O_4N_3As \cdot 2.5H_2O$: H_2O , 11.37. Found: 10.58.

Calc. for $C_{13}H_{14}O_4N_3As$: N, 11.97. Found: 12.10.

Diazobenzene - (4-arsonic acid) - *p* - anisidine.—The sodium salt separates from 50% alcohol as rosets of pale brown leaflets.

Analyses. Calc. for $C_{13}H_{13}O_4N_3AsNa \cdot 5H_2O$: H_2O , 19.44. Found: 19.55.

Calc. for $C_{13}H_{13}O_4N_3AsNa$: N, 11.26; As, 20.08. Found: N, 11.39; As, 20.01.

The free acid was precipitated from a 33% alcoholic solution of the salt as pale brown aggregates of microscopic leaflets which sinter and begin to decompose at about 110° and intumesce slowly at 116–9° when anhydrous, and are quite soluble in methyl alcohol.

Analyses. Calc. for $C_{13}H_{14}O_4N_3As \cdot 0.5H_2O$: H_2O , 2.50. Found: 2.36.

Calc. for $C_{13}H_{14}O_4N_3As$: N, 11.97. Found: 11.88.

Diazobenzene - (4-arsonic acid) - 4' - amino-acetanilide.—The sodium salt separated from 50% alcohol as plumes of tan, microscopic leaflets.

Analyses. Calc. for $C_{14}H_{14}O_4N_4AsNa \cdot 5H_2O$: H_2O , 18.36. Found: 17.38.

Calc. for $C_{14}H_{14}O_4N_4AsNa$: N, 14.00; As, 18.74; Found: N, 13.88; As, 18.49.

The free acid liberated from the salt in 50% alcohol forms long, drab, lustrous hexagonal, microscopic platelets, which decompose at 165–70° when anhydrous.

Analyses. Calc. for $C_{14}H_{15}O_4N_4As \cdot H_2O$: H_2O , 4.54. Found: 4.80.

Calc. for $C_{14}H_{15}O_4N_4As$: N, 14.81. Found: 14.79.

Diazobenzene - (4-arsonic acid) - 4' - aminophenyl benzoate.—6.4 g. of well powdered *p*-aminophenyl benzoate⁵ suspended in 60 cc. of *N* hydrochloric acid were slowly diazotized at 10° with 2.2 g. of sodium nitrite. After 15 minutes' additional turbinizing the solution was filtered from a small amount of undissolved material and then treated, with stirring, with 6.6 g. of arsanilic acid in 30 cc. of *N* sodium hydroxide solution. The light yellow, pasty diazo-amino compound solidified completely on standing overnight in the ice-box. The yield was 12 g. A portion, dissolved in a large volume of warm methyl alcohol and cautiously treated with water until crystallization began on rubbing, formed thin, yellow, microscopic leaflets which decompose at 155–8° and are practically insoluble in neutral solvents except hot methyl and ethyl alcohols.

Analysis. Calc. for $C_{19}H_{16}O_5N_3As$: N, 9.52. Found: 9.65.

Diazobenzene - (4-arsonic acid) - 4' - aminophenol.—The crude benzoate was dissolved in 4 equivalents of 2 *N* sodium hydroxide solution, allowed to stand for 15 minutes at room temperature, saturated with sodium acetate, and then chilled and neutralized with acetic acid. On rubbing the sodium salt slowly crystallized, separating from 85% alcohol as rosets of yellow microscopic needles. Under carefully controlled conditions acetic acid precipitated the microcrystalline acid which, however, was too unstable to isolate.

Analyses. Calc. for $C_{12}H_{11}O_4N_3AsNa \cdot 4H_2O$: H_2O , 16.69. Found: 16.38.

Calc. for $C_{12}H_{11}O_4N_3AsNa$: N, 11.69; As, 20.87. Found: N, 11.34; As, 20.76.

Diazobenzene - (4-arsonic acid) - 4' - amino-acetophenone.—A + 1 mol. alkali → diazotized B + sodium acetate. The resulting sodium salt, recrystallized from 85% alcohol, formed brownish-yellow rosets of minute, flat needles.

Analyses. Calc. for $C_{14}H_{13}O_4N_3AsNa \cdot 6H_2O$: H_2O , 21.91. Found: 21.51.

⁵ Cf. Wohl, *Ber.*, **36**, 4143 (1903).

Calc. for $C_{14}H_{13}O_4N_3AsNa$: N, 10.91. Found: 10.94.

The **free acid** consists of sheaves of bright yellow, microscopic needles which intumesce to a reddish mass at 177–8° after preliminary darkening and sintering, and dissolve in boiling methyl alcohol.

Analyses. Calc. for $C_{14}H_{14}O_4N_3As$: N, 11.57; As, 20.63. Found: N, 11.40; As, 20.91.

(C) **Diazo-amino Compounds of Arsanilic Acid and the Aminobenzoic Acids.**

Diazobenzene - (4-arsonic acid) - 2' - aminobenzoic acid.—Only the following conditions were found to yield this substance and its salts in pure form. 8.7 g. of arsanilic acid diazotized in 80 cc. of *N* hydrochloric acid were treated with 80 cc. of saturated sodium acetate solution and then with 5.5 g. of anthranilic acid dissolved in 80 cc. of *N* sodium hydroxide solution. The **monosodium salt** soon separated in almost quantitative yield as a brownish-yellow powder. On dissolving in dil. sodium hydroxide solution, adding sodium acetate and then a slight excess of acetic acid, a gelatinous mass formed which rapidly changed to radiating masses of flat, yellow microscopic needles of the **monosodium salt**. The substance is difficultly soluble in cold water.

Analyses. Calc. for $C_{13}H_{11}O_6N_3AsNa \cdot 4.5H_2O$: H_2O , 17.31. Found: 16.74.

Calc. for $C_{13}H_{11}O_6N_3AsNa$: N, 10.85. Found: 11.06.

A concentrated solution prepared with an additional mol. of sodium hydroxide yielded with sodium acetate the **yellow disodium salt** which crystallized from 85% alcohol as long, flat, yellow needles, dissolving easily in water with a yellow color.

Analyses. Calc. for $C_{13}H_{10}O_6N_3AsNa_2 \cdot 8H_2O$: H_2O , 26.05. Found: 26.37.

Calc. for $C_{13}H_{10}O_6N_3AsNa_2$: N, 10.26; As, 18.32. Found: N, 10.14; As, 17.94.

With a large excess of acetic acid, it immediately gives the **free acid** as thin, yellow microscopic needles which intumesce at 160°, and dissolve in hot methyl or ethyl alcohol.

Analysis. Calc. for $C_{13}H_{12}O_6N_3As$: N, 11.51. Found: 11.51.

Diazobenzene - (4-arsonic acid) - 3' - aminobenzoic acid.—The same conditions were used, except that the addition of 12 cc. of 50% acetic acid was necessary to cause the precipitation of the **monosodium salt**. Recrystallized as in the preceding preparation it forms a cream-colored, microcrystalline, anhydrous salt.

Analysis. Calc. for $C_{13}H_{11}O_6N_2AsNa$: N, 10.85. Found: 10.71.

An aqueous suspension was dissolved with just sufficient sodium hydroxide and treated with absolute alcohol to incipient turbidity. The resulting **disodium salt** separated from 70% alcohol as long, thin, pale yellow, microscopic needles.

Analyses. Calc. for $C_{13}H_{10}O_6N_2AsNa_2 \cdot 6.5H_2O$: H_2O , 22.24. Found: 21.68.

Calc. for $C_{13}H_{10}O_6N_2AsNa_2$: N, 10.26. Found: 10.32.

A well chilled solution in 50 parts of 50% alcohol was made just acid to congo red, the **arsonic acid** then separating as buff-colored microcrystalline rosettes which intumesce at 141° and dissolve in hot methyl and ethyl alcohols.

Analyses. Calc. for $C_{13}H_{12}O_6N_2As$: N, 11.51; As, 20.52. Found: N, 11.29; As, 20.54.

Diazobenzene - (4-arsonic acid) - 4' - aminobenzoic acid.—The special conditions necessary were treatment of the well chilled diazotate from 4.4 g. of arsanilic acid in 40 cc. of *N* hydrochloric acid with 60 cc. of alcohol and then rapidly with a solution of 2.8 g. of *p*-aminobenzoic acid in 10 cc. of 2 *N* sodium hydroxide solution. The deep brown solution deposited the yellow, amorphous **monosodium salt** almost at once and this changed to aggregates of microscopic needles under 50% alcohol. It was dissolved in 50% alcohol with a little sodium hydroxide and again acidified with acetic acid in slight excess, crystallizing in anhydrous form on rubbing. It is very sparingly soluble in cold water. The **free acid** formed flat, microscopic needles, but was not obtained pure.

Analyses. Calc. for $C_{13}H_{11}O_2N_3AsNa$: N, 10.85; As, 19.36. Found: N, 11.07; As, 19.23.

Diazobenzene - (4-arsonic acid) - 3' - amino-6'-methoxybenzoic methyl ester.—B hydrochloride \rightarrow A + sodium acetate. The resulting thick, gelatinous mass crystallized after adding one-half volume of alcohol and stirring and chilling. Dissolved in much cold alcohol and treated with an equal volume of water the ester acid crystallized as buff-colored aggregates of narrow platelets with notched ends, melting and evolving gas at 90–95° and dissolving readily in methyl or ethyl alcohol, especially on warming.

Analyses. Calc. for $C_{16}H_{13}O_6N_3As \cdot 3H_2O$: H_2O , 11.31. Found: 11.08.

Calc. for $C_{16}H_{13}O_6N_3As$: N, 9.93. Found: 10.18.

Diazobenzene - (4-arsonic acid) - 3' - amino-6'-methoxybenzoic acid.—The ester, warmed for one hour in 50% alcohol containing 3 mols. of sodium hydroxide, neutralizing with 1 mol. of acetic acid, and adding alcohol to incipient turbidity, gave the **disodium salt**, which separated from 70% alcohol as rosetts of pale, brownish-yellow, hygroscopic needles.

Analyses. Calc. for $C_{14}H_{12}O_6N_3AsNa_2$: N, 9.57. Found: 9.67.

The **arsonic acid** was precipitated in 50% alcohol as rosetts of yellow microscopic needles which decompose at 140° when anhydrous.

Analyses. Calc. for $C_{14}H_{14}O_6N_3As \cdot 1.5H_2O$: H_2O , 6.40. Found: 6.47.

Calc. for $C_{14}H_{14}O_6N_3As$: N, 10.63. Found: 10.64.

Diazobenzene - (4-arsonic acid) - 3' - amino-anisic methyl ester.—Alcoholic B \rightarrow A + sodium acetate. The ester acid, recrystallized from much 50% alcohol, forms glistening yellow needles which decompose at about 150° with preliminary darkening, and dissolve readily in methyl alcohol.

Analyses. Calc. for $C_{16}H_{13}O_6N_3As \cdot 2.5H_2O$: H_2O , 9.91. Found: 9.20.

Calc. for $C_{16}H_{13}O_6N_3As$: N, 10.26. Found: 10.37.

Diazobenzene - (4-arsonic acid) - 3' - amino-anisic acid.—I. Best prepared by saponification of the ester as described for the isomeric *o*-methoxy derivative. From 70% alcohol the **disodium salt** forms balls of fine yellow needles. II. The salt was also obtained directly, although in poorer yield, by the reaction of sodium 3-amino-anisate with the neutralized diazo solution and the addition of an equal volume of absolute alcohol.

Analyses. Calc. for $C_{14}H_{12}O_6N_3AsNa_2 \cdot 10H_2O$: H_2O , 29.08. Found: I, 30.13; II, 30.36.

Calc. for $C_{14}H_{12}O_6N_3AsNa_2$: N, 9.57; As, 17.08. Found: N, I, 9.68; II, 9.69; As, 17.23, 16.92.

The **free acid** was precipitated from 50% alcohol as aggregates of minute, yellow, microscopic needles which intumesce at 150–5° with preliminary darkening when anhydrous and are difficultly soluble in hot methyl alcohol.

Analyses. Calc. for $C_{14}H_{14}O_6N_3As \cdot 1.5H_2O$: H_2O , 6.40. Found: 6.30.

Calc. for $C_{14}H_{14}O_6N_3As$: N, 10.63. Found: 10.63.

Diazobenzene - (4-arsonic acid) - 6' - aminopiperonylic methyl ester.—B hydrochloride \rightarrow A, followed by sodium acetate. Reprecipitated from very dilute aqueous ammonia the ester acid forms minute aggregates of short, flat, almost colorless needles which do not decompose below 280° and are practically insoluble in the neutral solvents.

Analyses. Calc. for $C_{15}H_{14}O_7N_3As$: N, 9.92. Found: 9.91.

On saponification, a sodium salt was easily obtained, which, however, gave poor analytical figures, as did also the acid obtained from it. An attempt to prepare the diazo-amino acid directly from 6-aminopiperonylic acid yielded a dye which was not investigated further.

Diazobenzene - (4-arsonic acid) - 4' - aminocinnamic ethyl ester.—3.8 g. of amino ester were diazotized in 60 cc. of *N* hydrochloric acid with chilling and treated with 20 cc.

of *N* sodium hydroxide solution. Without filtering from the yellow precipitate which formed, 4.4 g. of arsanilic acid in 20 cc. of *N* sodium hydroxide solution were added and finally 50 cc. of saturated sodium acetate solution. The initial amorphous precipitate changed to flat, yellow, microscopic needles of the sodium salt, which separates from 70% alcohol as bright yellow microscopic needles which are sparingly soluble in cold water.

Analyses. Calc. for $C_{17}H_{17}O_6N_3AsNa \cdot 6H_2O$: H_2O , 19.67. Found: 19.69.

Calc. for $C_{17}H_{17}O_6N_3AsNa$: N, 9.52. Found: 10.08.

The arsonic acid forms aggregates of fine, yellow, microscopic needles which decompose at 155–60°.

Analysis. Calc. for $C_{17}H_{15}O_6N_3As$: N, 10.02; As, 17.89. Found: N, 10.32; As, 17.88.

Diazobenzene - (4-arsonic acid) - 4' - aminocinnamic acid.—The ester salt was saponified in 50% alcohol containing 2 mols. of sodium hydroxide, followed by 1 mol. of acetic acid, and then alcohol. Recrystallized from 70% alcohol the disodium salt formed yellow microscopic needles which dissolved readily in water.

Analyses. Calc. for $C_{15}H_{12}O_6N_3AsNa_2 \cdot 6H_2O$: H_2O , 19.89. Found: 19.96.

Calc. for $C_{15}H_{12}O_6N_3AsNa_2$: N, 9.66; As, 17.23. Found: N, 9.43; As, 16.83.

The acid is precipitated from 50% alcohol as a gelatinous mass which changes to yellow, microscopic needles which decompose at 155–60° with preliminary darkening and sintering when anhydrous, and are appreciably soluble in boiling methyl alcohol.

Analyses. Calc. for $C_{15}H_{14}O_6N_3As \cdot 0.5 H_2O$: H_2O , 2.25. Found: 2.11.

Calc. for $C_{15}H_{14}O_6N_3As$: N, 10.74. Found: 10.83.

Diazobenzene - (4-arsonic acid) - 4' - amino-phenylarsonic acid.—The diazo solution from 4.4 g. of arsanilic acid was treated with 4.4 g. of arsanilic acid in 40 cc. of *N* sodium hydroxide solution. The monosodium salt crystallized on rubbing. From 50% alcohol it forms thin, yellow, lustrous platelets which dissolve appreciably in water.

Analyses. Calc. for $C_{12}H_{12}O_6N_3As_2Na \cdot 2.5H_2O$: H_2O , 8.79. Found: 9.47.

Calc. for $C_{12}H_{12}O_6N_3As_2Na$: N, 8.99. Found: 9.01.

In 1 mol. of normal sodium hydroxide it yields the disodium salt on addition of sodium acetate, separating from 50% alcohol as woolly masses of delicate yellow needles which dissolve quite readily in water.

Analyses. Calc. for $C_{12}H_{11}O_6N_3As_2Na_2 \cdot 7H_2O$: H_2O , 20.49. Found: 20.18.

Calc. for $C_{12}H_{11}O_6N_3As_2Na_2$: N, 8.59. Found: 8.61.

The arsonic acid, precipitated from dilute aqueous solution, separates from 95% alcohol as pale yellow aggregates of microscopic needles which intumesce at 154° with preliminary darkening and sintering.

Analyses. Calc. for $C_{12}H_{13}O_6N_3As_2$: N, 9.44; As, 33.68. Found: N, 9.17; As, 33.84.

(D) Diazo-amino Compounds of Arsanilic Acid with Aryl Glycines.

Diazobenzene - (4-arsonic acid) - phenylglycine.—Alcoholic B \rightarrow neutralized A gave a thick slurry of the red-brown monosodium salt. The collected salt was dissolved in 10 parts of 50% alcohol with sodium hydroxide and the filtrate treated with a slight excess of acetic acid, slowly separating as flat, brown-yellow microscopic needles which are sparingly soluble in cold water. The free acid could not be obtained crystalline. The properties of the substance show that it is a true diazo-amino compound, but its color and that of its solutions indicate that it is contaminated with the corresponding azo dye, especially as Mai⁶ obtained dyes on using phenylglycine as a coupler in mineral acid solution.

⁶ Mai, *Ber.*, **35**, 580 (1902).

Analyses. Calc. for $C_{14}H_{13}O_6N_3AsNa \cdot 2H_2O$: H_2O , 8.24. Found: 7.21.

Calc. for $C_{14}H_{13}O_6N_3AsNa$: N, 10.47; As, 18.70. Found: N, 10.22; As, 18.90.

Diazobenzene - (4-arsonic acid) - *p*-tolylglycine.— $B + 1$ mol. alkali $\rightarrow A +$ sodium acetate, gave the **monosodium salt**, which was dissolved in dil. sodium hydroxide solution, treated with saturated sodium acetate solution, and then with an excess of acetic acid. The pure salt crystallized as radiating masses of tan, microscopic needles which are difficultly soluble in cold water.

Analyses. Calc. for $C_{15}H_{15}O_6N_3AsNa \cdot 1.5H_2O$: H_2O , 6.11. Found: 6.83.

Calc. for $C_{15}H_{15}O_6N_3AsNa$: N, 10.12; As, 18.06. Found: N, 10.07; As, 17.68.

When liberated in 50% alcohol the acid separates as radiating masses of flat, pale terra-cotta-colored microscopic needles which intumesce at $148-9^\circ$ with preliminary softening and reddening, and are appreciably soluble in alcohol.

Analysis. Calc. for $C_{16}H_{16}O_6N_3As$: N, 10.69. Found: 10.77.

Diazobenzene - (4-arsonic acid) - benzylglycine.— $B +$ mol. alkali \rightarrow neutralized A followed by hydrochloric acid. The precipitate was dissolved in warm alcohol and water added to incipient turbidity, the arsonic acid separating as an almost colorless, glistening mass of branched and curved microscopic needles and prisms which intumesce at $155-60^\circ$. It is readily soluble in methyl alcohol.

Analyses. Calc. for $C_{15}H_{15}O_6N_3As$: N, 10.68; As, 19.07. Found: N, 10.68; As, 19.05.

Diazobenzene - (4-arsonic acid) - 4'-methoxy-phenylglycine ethyl ester.—Alcoholic B \rightarrow neutralized A + equal volume of alcohol, followed by sodium acetate, gave the **sodium salt** which separates from 85% alcohol as yellow-brown leaflets and flat needles which are easily soluble in water. The acid could not be obtained crystalline.

Analyses. Calc. for $C_{17}H_{19}O_6N_3AsNa \cdot 4H_2O$: H_2O , 13.55. Found: 13.79.

Calc. for $C_7H_{19}O_6N_3AsNa$: N, 9.15. Found: 9.05.

Diazobenzene - (4-arsonic acid) - 4'-methoxy-phenylglycine.— $B + 1$ mol. alkali \rightarrow neutralized A, on chilling in a freezing mixture, treating with an excess of acetic acid, and rubbing, gave the **monosodium salt** as a highly colored powder. Redissolved in dil. sodium hydroxide solution and acidified with acetic acid, it separated as yellow, microscopic platelets which are sparingly soluble in cold water, but dissolve on gentle warming, forming reddish solutions. The acid could not be made to crystallize. The salt was also obtained by saponification of the ethyl ester described above.

Analyses. Calc. for $C_{15}H_{16}O_6N_3AsNa \cdot 2H_2O$: H_2O , 7.71. Found: 6.98.

Calc. for $C_{15}H_{16}O_6N_3AsNa$: N, 9.74; As, 17.39. Found: N, 9.79; As, 17.16.

Diazobenzene - (4-arsonic acid) - 4'-ethoxy-phenylglycine ethyl ester.—Obtained as in the preceding case, the **sodium salt** separates from 70% alcohol as lustrous, cream-colored leaflets.

Analyses. Calc. for $C_{18}H_{21}O_6N_3AsNa \cdot 2.5H_2O$: H_2O , 8.69. Found: 8.78.

Calc. for $C_{18}H_{21}O_6N_3AsNa$: N, 8.88. Found: 9.05.

Liberated from 25% alcoholic solution, the acid forms almost colorless microscopic rhombohedra.

Diazobenzene - (4-arsonic acid) - 4'-ethoxy-phenylglycine.—On saponifying the ester in 2 mols. of *N* sodium hydroxide solution at room temperature, adding a little sodium acetate, and then an excess of acetic acid with chilling, the **monosodium salt** of the glycine arsonic acid crystallized as aggregates of thin, yellow, microscopic needles which are sparingly soluble in water. The free acid could not be obtained crystalline.

Analyses. Calc. for $C_{16}H_{17}O_6N_3AsNa \cdot 2H_2O$: H_2O , 7.48. Found: 6.49.

Calc. for $C_{16}H_{17}O_6N_3AsNa$: N, 9.44; As, 16.85. Found: N, 9.54; As, 16.63.

This salt was also obtained directly from the diazo solution and *p*-ethoxy-phenylglycine, as in the case of the *p*-methoxy compound.

(E) Diazo-amino Compounds of the Amino-phenoxyacetic Acids.

Diazobenzene - (4-arsonic acid) - 4'- amino-phenoxyacetic ethyl ester.—B hydrochloride \rightarrow neutralized A, half saturated with sodium acetate, gave the sodium salt which forms brownish aggregates of microscopic needles from 85% alcohol.

Analyses. Calc. for $C_{16}H_{17}O_6N_3AsNa \cdot 5H_2O$: H_2O , 16.83. Found: 17.04.

Calc. for $C_{16}H_{17}O_6N_3AsNa$: N, 9.44; As, 16.83. Found: N, 9.84; As, 16.99.

Liberated in 50% alcoholic solution, the ester acid forms salmon-colored, minute, glistening leaflets which melt and decompose at $132-3^\circ$ with preliminary softening and dissolve readily in warm methyl and ethyl alcohols.

Analysis. Calc. for $C_{16}H_{15}O_6N_3As$: N, 9.93. Found: 9.76.

Diazobenzene - (4-arsonic acid) - 4'- amino-phenoxyacetic acid.—Although this substance was prepared directly from *p*-amino-phenoxyacetic acid⁷ it was found preferable to saponify the above ester. The ester salt was warmed gently for one hour with 2 mols. of *N* sodium hydroxide solution and an equal volume of alcohol, chilled, neutralized with acetic acid, and the crude disodium salt precipitated with alcohol. It forms brown needles from 85% alcohol which gradually darken and decompose on standing.

Analyses. Calc. for $C_{14}H_{12}O_6N_3AsNa_2 \cdot 6.5H_2O$: H_2O , 21.05. Found: 21.35.

Calc. for $C_{14}H_{12}O_6N_3AsNa_2$: N, 9.56. As, 17.07. Found: N, 9.58; As, 17.06.

A well chilled solution in 100 parts of water was strongly acidified with acetic acid, causing the sudden incomplete separation of the free arsonic acid as aggregates of microscopic crystals. The cold mixture was just acidified to congo red and filtered cold, for if allowed to warm the acid rapidly dissociates and dissolves. It melts and intumesces at 132° .

Analysis. Calc. for $C_{14}H_{14}O_6N_3As$: N, 10.64. Found: 10.41.

Diazobenzene - (4-arsonic acid) - *p* - amino-phenoxyacetamide.—Aqueous *p*-amino-phenoxyacetamide⁸ \rightarrow neutralized A, half saturated with sodium acetate, gave the sodium salt in excellent yield. It separates from 50% alcohol as rosetts and sheaves of delicate, drab-colored needles which dissolve fairly readily in water.

Analyses. Calc. for $C_{14}H_{14}O_5N_4AsNa \cdot 6H_2O$: H_2O , 20.62. Found: 19.88.

Calc. for $C_{14}H_{14}O_5N_4AsNa$: N, 13.46; As, 18.02. Found: N, 13.72; As, 17.56.

The arsonic acid, obtained from the salt in 50% alcohol, formed branched aggregates of cream-colored, microscopic needles and hairs which melt and effervesce at about 162° with preliminary browning.

Analysis. Calc. for $C_{14}H_{15}O_5N_4As$: N, 14.22. Found: 14.09.

Diazobenzene - (4-arsonic acid) - *p* - amino-phenoxyacet-methylamide.—The amorphous salt from *p*-amino-phenoxyacet-methylamide⁹ soon crystallized, separating from water as pale yellow aggregates of hair-like needles.

Analyses. Calc. for $C_{15}H_{16}O_5N_4AsNa \cdot 4H_2O$: H_2O , 14.34. Found: 14.60.

Calc. for $C_{15}H_{16}O_5N_4AsNa$: N, 13.02; As, 17.43. Found: N, 12.94; As, 17.77.

The free arsonic acid from a dilute, 50% alcoholic solution of the salt, forms minute, flat, glistening cream-colored needles which melt with decomposition at 170° with preliminary darkening.

Analyses. Calc. for $C_{16}H_{17}O_5N_4As \cdot H_2O$: H_2O , 4.23. Found: 3.66.

Calc. for $C_{15}H_{17}O_5N_4As$: N, 13.73. Found: 13.33.

Diazobenzene - (4-arsonic acid) - 4'- methylamino-phenoxyacetic acid.—Coupled in neutral solution and then acidified strongly with acetic acid, *p*-*N*-methylamino-phenoxyacetic acid¹⁰ gave the diazo-amino acid which, on redissolving in dil. alkali and

⁷ THIS JOURNAL, 39, 2196 (1917).

⁸ *Ibid.*, 39, 2423 (1917).

⁹ *Loc. cit.*, p. 2424.

¹⁰ *Ibid.*, 39, 2197 (1917).

reprecipitating with acetic acid in excess, forms greenish-yellow aggregates of microscopic spindles which decompose at 155–60°.

Analyses. Calc. for $C_{15}H_{16}O_6N_3As$: N, 10.26; As, 18.32. Found: N, 10.47; As, 18.50.

Diazobenzene - (4-arsonic acid)-3'-methyl-4'-amino-phenoxyacetic methyl ester.—In neutral solution, in the presence of sodium acetate, the amino ester hydrochloride¹¹ gave the sodium salt as a thick mass of reddish-brown, microscopic needles. In 50% alcohol, acetic acid precipitates the acid as rosetts of minute needles, melting and decomposing at 105–7°.

Analysis. Calc. for $C_{16}H_{18}O_6N_3As$: N, 9.93. Found: 9.83.

Diazobenzene - (4-arsonic acid) - 3'-methyl-4'-amino-phenoxyacetic acid.—The ester was saponified and the disodium salt isolated as in previous examples. Dissolved in a small volume of water and treated with alcohol it crystallized as light brown, glistening plates containing water of crystallization which was not determined. The free acid proved too unstable for isolation.

Analyses. Calc. for $C_{15}H_{14}O_6N_3AsNa_2$: N, 9.27; As, 16.55. Found: N, 9.04; As, 16.32.

Diazobenzene - (4-arsonic acid) - 2'-methyl-4'-amino-phenoxyacetic methyl ester.—The sodium salt, obtained from the amino ester hydrochloride,¹² gave with acetic acid in 50% alcohol the acid as aggregates of round, purple-brown, microscopic leaflets which decompose at 143–4° and dissolve in hot methyl and ethyl alcohols.

Analysis. Calc. for $C_{15}H_{18}O_6N_3As$: N, 9.93. Found: 9.81.

Diazobenzene-(4-arsonic acid) - 2' - methyl-4'-amino-phenoxyacetic acid.—The disodium salt obtained from the ester crystallized from dil. alcohol as easily soluble, long, flat, pinkish-yellow, microscopic needles which gradually decomposed on exposure. The acid proved to be too unstable for isolation.

Analyses. Calc. for $C_{15}H_{14}O_6N_3AsNa_2 \cdot 4.5H_2O$: H_2O , 15.16. Found: 15.42.

Calc. for $C_{15}H_{14}O_6N_3AsNa_2$: N, 9.27; As, 16.55. Found: N, 9.50; As, 16.81.

Diazobenzene - (4-arsonic acid) -2',5'-dimethyl-4'-amino-phenoxyacetic methyl ester.—Amino ester hydrochloride¹³ in 50% alcohol \rightarrow A, followed by sodium acetate. Addition of an equal volume of alcohol to the thick amorphous slurry gave the microcrystalline ester acid which was dissolved in warm 50% alcohol with ammonia, diluted with several volumes of alcohol, chilled, and acidified with acetic acid, crystallizing as gray-yellow aggregates of short, flat, pointed microscopic needles. It decomposes at about 120° and is quite soluble in hot methyl alcohol.

Analyses. Calc. for $C_{17}H_{20}O_6N_3As \cdot 1.5 H_2O$: H_2O , 5.82. Found: 5.89.

Calc. for $C_{17}H_{20}O_6N_3As$: N, 9.61; As, 17.15. Found: N, 9.69; As, 17.35.

On saponifying the ester what was presumably the disodium salt of the acid was obtained as pale yellow needles, but all attempts to obtain an analytically pure sample of the salt as well as of the free acid proved futile.

Diazobenzene-(4-arsonic acid)-2'-methyl-5'-isopropyl-4'-amino-phenoxyacetic methyl ester.—Amino ester hydrochloride¹⁴ A \rightarrow + sodium acetate, followed by alcohol gave the ester acid, which, reprecipitated from ammoniacal 50% alcoholic solution, formed microscopic needles which decompose at 145° and are appreciably soluble in hot alcohol.

Analysis. Calc. for $C_{19}H_{24}O_6N_3As$: N, 9.03. Found: 9.16.

Diazobenzene-(4-arsonic acid)-2'-methyl-5'-isopropyl-4'-amino-phenoxyacetic acid.

¹¹ *Loc. cit.*, p. 2201.

¹² *Ibid.*, p. 2199.

¹³ *Ibid.*, p. 2205.

¹⁴ *Ibid.*, p. 2206.

—The ester was saponified as usual, yielding the **disodium salt**. Dissolved in a small volume of water and treated with alcohol it formed minute, flat, pale brown needles.

Analyses. Calc. for $C_{18}H_{20}O_6N_2AsNa_2 \cdot 9.5H_2O$: H_2O , 25.68. Found: 25.39.

Calc. for $C_{18}H_{20}O_6N_2AsNa_2$: N, 8.49; As, 15.14. Found: N, 8.24; As, 15.05. All attempts to obtain the free acid failed.

Diazobenzene - (4-arsonic acid) - 3'-methyl-6'-isopropyl-4'-amino-phenoxyacetic methyl ester.—Prepared from the ester hydrochloride¹⁵ as in the case of the 2,5-dimethyl analog. Recrystallized from 85% alcohol the acid formed rosetts of yellow microscopic leaflets. When rapidly heated it intumesces to an orange mass at about 130°, but if slowly heated it turns orange above 120°, then gradually darkens, but does not melt below 275°.

Analyses. Calc. for $C_{19}H_{24}O_6N_2As \cdot 1.5H_2O$: H_2O , 5.49. Found: 4.56.

Calc. for $C_{19}H_{24}O_6N_2As$: N, 9.03. Found: 8.92.

Diazobenzene - (4-arsonic acid) - 3'-methyl-6'-isopropyl-4'-amino-phenoxyacetic acid.—The crude **disodium salt** from the ester was reprecipitated from a little water by alcohol, separating as lustrous yellow microscopic leaflets.

Analyses. Calc. for $C_{18}H_{20}O_6N_2AsNa_2 \cdot 4H_2O$: H_2O , 12.69. Found: 12.26.

Calc. for $C_{18}H_{20}O_6N_2AsNa_2$: N, 8.49; As, 15.14. Found: N, 8.36; As, 14.67. The acid could not be isolated.

Diazobenzene-(4-arsonic acid) -2'-bromo-4'-amino-phenoxyacetic methyl ester.—

The ester acid from 2-bromo-4-amino-phenoxyacetic methyl ester hydrochloride¹⁶ was reprecipitated from very dilute aqueous ammonia, forming a jelly which changed to long, curved, cream-colored, microscopic needles which decompose at 154–5°.

Analysis. Calc. for $C_{11}H_{11}O_4N_2BrAs$: N, 8.61. Found: 8.71.

Diazobenzene -(4-arsonic acid) -2'-bromo-4'-amino-phenoxyacetic acid.—The **disodium salt** obtained from the ester was recrystallized as usual, forming flat, lustrous, pale brownish-yellow needles.

Analyses. Calc. for $C_{11}H_{11}O_4N_2BrAsNa_2 \cdot 4H_2O$: H_2O , 12.20. Found: 12.44.

Calc. for $C_{11}H_{11}O_4N_2BrAsNa_2$: N, 8.11; As, 14.47. Found: N, 8.26; As, 14.71.

On acidifying an aqueous solution of the salt to congo red, a thick jelly formed, which, on addition of alcohol changed to delicate, pale yellow, microscopic needles which decompose at about 120° when anhydrous.

Analyses. Calc. for $C_{14}H_{13}O_4N_2BrAs \cdot 3H_2O$: H_2O , 10.22. Found: 9.41.

Calc. for $C_{14}H_{13}O_4N_2BrAs$: N, 8.86. Found: 9.03.

Diazobenzene - (4-arsonic acid) - 2 - methyl-4-amino-6-bromo-phenoxyacetic methyl ester.—Amino ester hydrochloride¹⁷ in 50% alcohol neutralized \rightarrow A + sodium acetate. The yellow diazo-amino sodium salt, in ammoniacal dil. alcoholic solution, was acidified with acetic acid, yielding the free ester arsonic acid as bundles of delicate, pinkish, microscopic needles which intumesce at 188°.

Analyses. Calc. for $C_{16}H_{17}O_4N_2BrAs$: N, 8.37; As, 14.92. Found: N, 8.36; As, 15.15.

Diazobenzene-(4-arsonic acid)-2-methyl-4-amino-6-bromo-phenoxyacetic acid.

—The **disodium salt** was obtained as an indefinitely crystalline product and was dried *in vacuo*. It dissolves easily in water with a deep orange color.

Analyses. Calc. for $C_{16}H_{17}O_4N_2BrAsNa_2$: N, 7.90; As, 14.08. Found: N, 7.75; As, 13.42.

In dilute 50% alcoholic solution the salt yielded the free acid as grayish, micro-

¹⁵ *Loc. cit.*, p. 2207.

¹⁶ *Ibid.*, p. 2209.

¹⁷ *Ibid.*, 39, 2211 (1917).

crystalline aggregates which decompose at about 155°, with preliminary darkening and softening.

Diazobenzene - (4-arsonic acid) -4'- amino-6'-aceto-phenoxyacetic methyl ester.—The methyl ester hydrochloride¹⁸ \rightarrow A + 1 mol. sodium hydroxide, followed by sodium acetate. The free acid, obtained from a dilute 50% alcoholic solution of the salt, was dissolved in 50% alcohol with a little aqueous ammonia and precipitated with a large excess of acetic acid, separating as rosetts and sheaves of microscopic, often hair-like needles. It effervesces and reddens at about 155°, with preliminary darkening.

Analysis. Calc. for $C_{17}H_{13}N_3O_3As$: N, 9.31. Found: 9.64.

Diazobenzene - (4-arsonic acid) -4'- amino-6'-aceto-phenoxyacetic acid.—The disodium salt separated on adding alcohol to its aqueous solution as pale brown, microscopic leaflets. The free acid was not obtained pure.

Analysis. Calc. for $C_{16}H_{14}O_7N_3AsNa_2 \cdot 5H_2O$, 15.77. Found: 16.36.

Calc. for $C_{16}H_{14}O_7N_3AsNa_2$: N, 8.73; As, 15.58. Found: N, 8.88; As, 15.50.

Diazo-2-methylbenzene-(4-arsonic acid) - p - amino-phenoxyacetic methyl ester.—*o*-Methylarsanilic acid was diazotized in the same way as arsanilic acid and the solution treated first with a large excess of saturated sodium acetate solution and then with an equivalent of *p*-amino-phenoxyacetic methyl ester hydrochloride¹⁹ dissolved in water. The initially amorphous diazo-amino sodium salt crystallized on letting stand in the cold as spherules of drab, microscopic needles. The free ester acid forms sheaves, rosetts, and plumes of minute, flat needles which decompose at 130-2°.

Analysis. Calc. for $C_{16}H_{15}O_6N_3As$: N, 9.93. Found: 10.02.

Diazo - 2 - methylbenzene - (4-arsonic acid) - p - amino-phenoxyacetic acid.—The ester, saponified as usual, yielded the disodium salt which separated from aqueous solution on adding alcohol as radiating masses of minute, brownish leaflets. The free acid was not obtained crystalline.

Analysis. Calc. for $C_{15}H_{14}O_6N_3AsNa_2 \cdot 6.5H_2O$: H_2O , 20.53. Found: 20.80.

Calc. for $C_{15}H_{14}O_6N_3AsNa_2$: N, 9.27; As, 16.55. Found: N, 9.02; As, 16.64.

Diazo - 2 - bromobenzene - (4-arsonic acid) - p - amino-phenoxyacetic methyl ester.—4.5 g. of 3-bromo-arsanilic acid²⁰ were suspended in 30 cc. of 2 *N* hydrochloric acid, diazotized with 1.1 g. of sodium nitrite, and the solution chilled and treated with 22.5 cc. of 2 *N* sodium hydroxide, then with an equal volume of saturated sodium acetate solution and finally with a solution of 3.3 g. of the amino ester hydrochloride. The diazo-amino ester salt separated immediately as aggregates of pinkish, hair-like, microscopic needles. The ester acid forms spherules of brownish, microscopic needles which intumescence at 123-5°.

Analysis. Calc. for $C_{15}H_{13}O_6N_3BrAs$: N, 8.61. Found: 8.49.

Diazo - 2 - bromobenzene - (4-arsonic acid) - p - amino-phenoxyacetic acid.—The recrystallized disodium salt of the acid separates as drab-colored spherules of minute crystals.

Analysis. Calc. for $C_{14}H_{11}O_6N_3BrAsNa_2 \cdot 4H_2O$: H_2O , 13.19. Found: 13.77.

Calc. for $C_{14}H_{11}O_6N_3BrAsNa_2$: N, 8.11; As, 14.47. Found: N, 7.88; As, 14.28.

The free arsonic acid is precipitated from 50% alcohol as drab microscopic crystals which intumescence slowly at about 130° with preliminary browning.

Analysis. Calc. for $C_{14}H_{13}O_6N_3BrAs$: N, 8.87; As, 15.80. Found: N, 8.89; As, 15.77.

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¹⁸ *Loc. cit.*, p. 2215.

¹⁹ *Ibid.*, p. 2196.

²⁰ Bertheim, *Ber.*, 43, 532 (1910).