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AROMATIC ARSENIC COMPOUNDS. X. AZO DYES DERIVED FROM ARSANILIC ACID.

BY WALTER A. JACOBS AND MICHAEL HEIDELBERGER.

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As stated in the previous paper, azo dyes containing arsenic were first described by Ehrlich and Bertheim¹ and later by Barrowcliff, Pyman, and Remfry,² and others. In our work with diazo-amino derivatives it was found that certain classes of aromatic amino compounds yielded amino-azo dyes at once when used as couplers with diazotized arsanilic acid, or gave diazo-amino compounds which rapidly rearranged into the dyes. This occurred with *N*-alkyl anthranilic acids, *m*-amino-phenoxyacetic acid and its substitution products, the amino-veratric acids, and the *o*-methyl and *o*-alkoxy derivatives of *N*-phenylglycine.

As far as we can find, no mention has been made of the use of *N*-alkyl-anthranilic acids for the synthesis of azo dyes. The addition of *N*-methyl anthranilic acid to the neutralized diazo solution results in the rapid formation first of the diazo-amino compound, which slowly rearranges to the dye on standing or changes over rapidly on acidification with acetic acid. A similar behavior was noted with *N*-ethyl- and *N*-*iso*-amyl-anthranilic acids.

Under the usual conditions of coupling in neutral or slightly acid solution, *m*-amino-phenoxyacetic acid yielded at once a dye in which we assume the azo group to enter the position *para* to the amino group. We believe that *m*-amino-phenoxyacetic acid functions here as a *m*-anisidine derivative as we have since noted the analogous experience of Reverdin, Rilliet and Vernei,³ in which *p*-amino-azo dyes were prepared from *m*-phenetidine. Azo derivatives were also obtained by us from two groups of substitution products of *m*-anisidine and *m*-amino-phenoxyacetic acid, in one of which the position *para* to the amino group was free, and in the other of which this position was occupied by a substituent. In the former group were 4-methyl-5-amino-phenoxyacetic acid and 2-amino-3,4-dimethoxy-benzoic acid, and in these cases the azo group presumably entered the free *para* position. In the second group were 2-methyl-5-amino-phenoxyacetic acid, 3-amino-6-methoxy-phenoxyacetic acid, 6-amino-*o*-veratric acid, 4-amino-6-methoxy-phenoxyacetic acid, and amino-*o*-phenylene-di (oxyacetic acid); and in this group it is probable that the azo group enters the position *ortho* to the amino group. Thus German patent 230,592 describes the formation of *o*-amino-azo dyes

¹ Ehrlich and Bertheim, *Ber.*, **40**, 3292 (1907).

² Barrowcliff, Pyman and Remfry, *J. Chem. Soc.*, **93**, 1893 (1908).

³ *C. A.*, **13**, 312 (1919).

from 2-methyl-5-amino-phenoxyacetic acid and from the analogous 2-methyl-5-amino-anisole, and our experience has confirmed the ready formation of azo dyes from such substances.

Finally, although phenylglycine yields principally a diazo-amino compound under the conditions described in the preceding paper, the *o*-methyl, *o*-methoxy, and *o*-ethoxyphenyl glycines at once form dyes. According to Mai,⁴ however, when phenylglycine was coupled in a solution acid to congo red it yielded dyes with diazotized aniline and sulfanilic acid.

In most cases the reaction between the diazotized arsanilic acid and the coupler proceeded smoothly, with very little gas evolution. The isolation and purification of the resulting dyes often presented considerable difficulty, and much experimentation was necessary in order to discover the best conditions for the coupling and whether any dye were best isolated as the free acid, the monosodium salt, or the disodium salt. Hence the manipulative details are quite voluminous, and in order to save space it is deemed best to present the work in abstract form.

The monosodium salts of the dyes were generally very sparingly soluble in water, while the disodium salts dissolved easily. Even very dilute solutions of the latter gave immediate amorphous precipitates with salts of the heavier metals, while their behavior varied toward salts of the alkaline earths.

Experimental.

To avoid constant repetition it may be stated here that the diazotization of arsanilic acid was carried out under the conditions given in the preceding paper in 2 mols. of normal hydrochloric acid with 5 *N* sodium nitrite. Since most of the amino acids were coupled under the conditions necessary for the formation of the monosodium salts of the resulting dyes, it will be understood unless otherwise stated that the diazo solution was first treated with one mol. of *N* sodium hydroxide solution, the solution thus containing diazobenzene arsonic acid and no free mineral acid. This solution was then slowly treated, with continued turbinizing and chilling, with a solution of the amino acid dissolved in one mol. of *N* sodium hydroxide solution, or treated with an additional mol. of alkali and then with a solution of the coupler hydrochloride in the case of basic couplers. Such a procedure will be indicated by the expression **B**→**A**. Cases in which the diazo solution was added to the coupler are designated by **A**→**B**. Variations from this procedure will be described as they occur.

The values given for water of crystallization were determined on the substances after they had come to equilibrium in the air.

⁴ Mai, *Ber.*, **35**, 580 (1902).

(A) Dyes Derived from Arsanilic Acid and Methoxy-naphthylamines.

1-Amino-2-methoxy-naphthalene-4'-azobenzene-4'-arsonic acid.—**B** \rightarrow **A**, using β -methoxy- α -naphthylamine hydrochloride. The neamorphous acid was converted into the salt with just enough dil. sodium hydroxide solution. After salting out, dissolving in 50% alcohol, heating, and making just acid to congo red with hydrochloric acid, the arsonic acid slowly separated on rubbing and cooling as radiating aggregates of narrow, bluish-black, glistening, microscopic platelets, which did not melt below 285°. It dissolves in conc. sulfuric acid with a deep purple color and in dil. sodium hydroxide solution with a deep cherry-red tint.

Analyses. Calc. for $C_{17}H_{16}O_4N_3As \cdot 1.5H_2O$: H_2O , 6.3. Found: 5.9.

Calc. for $C_{17}H_{16}O_4N_3As$: N, 10.48; As, 18.68. Found: N, 10.42; As, 18.50.

1-Amino-4-methoxy-naphthalene-2-azobenzene-4'-arsonic acid.—Obtained like the preceding compound, the arsonic acid separated rapidly as dark brown, microcrystalline aggregates with a bronzy luster. It sintered and darkened when heated, softening to a tar at about 195° and intumescing at about 225°. It dissolves in conc. sulfuric acid with a purplish-red color, changing to brown-red, and becoming purplish again on dilution. In dil. sodium hydroxide solution the color is a deep cherry-red. It is soluble in acetic acid and alcohol.

Analyses. Calc. for $C_{17}H_{16}O_4N_3As \cdot 1.5 H_2O$: H_2O , 6.3. Found: 6.0.

Calc. for $C_{17}H_{16}O_4N_3As$: N, 10.48; As, 18.68. Found: N, 10.31; As, 18.83.

(B) Dyes Obtained from Arsanilic Acid and Substituted Amino-benzoic Acids.

4 - Methylamino - 5 - carboxy-phenylazo-benzene-4'-arsonic acid.—**B** (methylanthranilic acid) \rightarrow **A** + equal volume saturated sodium acetate solution. The orange colored solution, which presumably contained the diazo-amino compound, deepened in color on standing, gradually depositing the orange monosodium salt in good yield. Recrystallized from boiling water containing a little sodium acetate, it forms radiating masses of short, brownish-yellow, microscopic needles which dissolve with difficulty in hot or cold water with an intense orange-yellow color.

Analyses. Calc. for $C_{14}H_{13}O_5N_3AsNa \cdot 2.5H_2O$: H_2O , 10.08. Found: 10.49.

Calc. for $C_{14}H_{13}O_5N_3AsNa$: N, 10.47. Found: 10.53.

Treated in a little water with one mol. of sodium hydroxide, then with alcohol to initial turbidity, the disodium salt separated in the cold. It forms bundles of flat, red, microscopic needles from 70% alcohol and dissolves readily in water with a deep orange color.

Analyses. Calc. for $C_{14}H_{12}O_5N_3AsNa_2 \cdot 8.5H_2O$: H_2O , 26.57. Found: 26.63.

Calc. for $C_{14}H_{12}O_5N_3AsNa_2$: N, 9.93. Found: N, 9.83.

The monosodium salt, suspended in hot water, dissolved with a little sodium hydroxide, and treated with hydrochloric acid until just acid to congo red, gave the free acid, which when recrystallized from 50% alcohol forms brick-red, thin, glistening microscopic needles and plates. It does not melt below 280° dissolves in conc. sulfuric acid with a deep orange color and gives a red solution in hot 10% hydrochloric acid, from which the hydrochloride separates on cooling as rosetts of narrow, purplish-red plates with a steel-blue reflex. In dil. hydrochloric acid the dye reacts with sodium nitrite, giving a precipitate of pale salmon-colored, microscopic needles, presumably the nitroso compound.

Analyses. Calc. for $C_{14}H_{14}O_5N_3As$: N, 11.08; As, 19.78. Found: N, 11.24; As, 19.68.

4 - Ethylamino - 5 - carboxy-phenylazo-benzene-4'-arsonic acid.—**B** \rightarrow **A**.—The crude monosodium salt was dissolved in hot water with a little sodium hydroxide and

the solution just acidified to congo red, yielding the bright yellow arsonic acid. It separates from 85% alcohol as deep orange, glistening rectangular platelets which do not melt below 275°. It is more soluble in methyl alcohol or boiling amyl alcohol than in the other usual neutral solvents, and in its color reactions and chemical properties resembles the methylamino compound.

Analyses. Calc. for $C_{15}H_{16}O_5N_3As$: N, 10.69; As, 19.06. Found: N, 10.72; As, 19.11.

4 - Iso-amyl-amino - 5 - carboxy-phenylazo-benzene-4'-arsonic acid.—B → A.—The crude monosodium salt when recrystallized from much water containing a little sodium acetate forms orange-colored, microscopic leaflets which are very difficultly soluble in boiling water.

Analyses. Calc. for $C_{18}H_{21}O_5N_3AsNa \cdot 2H_2O$: H_2O , 7.31. Found: 6.59.

Calc. for $C_{18}H_{21}O_5N_3AsNa$: N, 9.19. Found: 9.18.

Recrystallized from acetic acid, the free acid forms orange-red, glistening, striated platelets which do not melt below 275°. It dissolves in boiling alcohol and gives a deep red-orange color with conc. sulfuric acid; in conc. hydrochloric acid it dissolves with a deep red color, the hydrochloride separating on rubbing as dark colored microscopic needles.

Analyses. Calc. for $C_{18}H_{22}O_5N_3As$: N, 9.66; As, 17.22. Found: N, 9.48; As, 17.32.

4 - Amino - 2,3 - dimethoxy-5-carboxy-phenylazo-benzene-4'-arsonic acid.—B → A.—Using vicinal aminoveratric acid, the monosodium salt was obtained, separating as flat, brown-orange, microscopic needles from hot water containing a little sodium acetate.

Analyses. Calc. for $C_{18}H_{16}O_7N_3AsNa \cdot 2.5H_2O$: H_2O , 9.15. Found: 9.79.

Calc. for $C_{18}H_{16}O_7N_3AsNa$: N, 9.40; As, 16.77. Found: N, 9.76; As, 16.54.

The free acid separates from 85% alcohol as long, narrow, glistening, orange-red platelets which turn a deeper red when anhydrous, but do not melt below 275°. It is quite easily soluble in cold methyl alcohol and gives a deep orange-colored solution in conc. sulfuric acid, dissolving in boiling 10% hydrochloric acid with a dark red color, depositing the hydrochloride on cooling as brown platelets and flat needles.

Analyses. Calc. for $C_{18}H_{16}O_7N_3As \cdot 1.5H_2O$: H_2O , 5.98. Found: 6.43.

Calc. for $C_{18}H_{16}O_7N_3As$: As, 17.62. Found: As, 17.78.

2 - Amino - 4,5 - dimethoxy-3-carboxy-phenylazo-benzene-4'-arsonic acid.—(B → A.—Alkalinity sufficient for formation of the disodium salt.) 6-Amino-*o*-veratric acid⁵ was used. After 24 hours about 20% of solid sodium acetate was added and then an excess of acetic acid, precipitating the monosodium salt. Recrystallized from water containing sodium acetate, cautiously adding acetic acid after cooling, the salt forms spherules of orange-red microcrystals which change to chocolate-brown when air-dry. It is very difficultly soluble in boiling water and dissolves on adding alkali with an orange color.

Analyses. Calc. for $C_{18}H_{16}O_7N_3AsNa \cdot 1.5H_2O$: H_2O , 5.70. Found: 6.37.

Calc. for $C_{18}H_{16}O_7N_3AsNa$: N, 9.40; As, 16.77. Found: N, 9.21; As, 16.65.

The free acid separates from an alkaline solution of the salt in 50% alcohol on acidifying to congo red as glistening brown leaflets and microcrystallizing aggregates with a purplish luster, containing about 1.5 molecules of water of crystallization and turning darker brown when dehydrated. It decomposes somewhat on heating, but does not melt up to 290°. It is difficultly soluble in the usual solvents, and unlike the monosodium salt, dissolves in dil. alkalis with a red color, only changing to orange at high dilution. It gives an intense red color in conc. sulfuric acid, and dissolves partially in conc. hydro-

⁵ This acid was prepared by the following series of reactions, which will be dealt with in a later communication: *o*-vanillin → *o*-veratric aldehyde → 6-nitro-*o*-veratric aldehyde → 6-nitro-*o*-veratric acid → 6-amino-*o*-veratric acid.

chloric acid, the hydrochloride soon separating as dark orange-red microcrystalline spherules.

Analyses. Calc. for $C_{15}H_{15}O_7N_2As \cdot 1.5H_2O$: H_2O , 5.98. Found: 5.29.

Calc. for $C_{15}H_{15}O_7N_2As$: N, 9.89. Found: 9.69.

(C) **Dyes Derived from Arsanilic Acid and Aromatic Glycines.**

4-[Phenyl - (4'-arsonic acid) azo] - phenylglycine.—Although phenylglycine yielded the diazo-amino compound under the conditions given in the preceding paper, the dye was formed in the presence of an excess of mineral acid. The diazo solution from 4.4 g. of arsanilic acid was added, with stirring and chilling, to a solution of 3.1 g. of phenylglycine in 40 cc. of *N* hydrochloric acid diluted to 100 cc. with 0.5 *N* hydrochloric acid. The dye, which crystallized soon after deposition commenced, was filtered off, washed first with cold and then with hot water, and was finally cooled and washed with acetone. The yield was 5.3 g. A dilute solution in 50% alcohol was obtained with the aid of a little ammonia and acidified hot to congo red, the arsonic acid soon separating as orange-red aggregates of minute, lenticular platelets with a golden luster. It sinters, melts, and decomposes slowly at 170–5°, and dissolves in dil. alkali with a reddish-orange color. It dissolves in conc. sulfuric acid or 1 : 1 hydrochloric acid with a deep red color, the hydrochloride separating from the latter on rubbing as red microscopic needles with a purplish luster.

Analyses. Calc. for $C_{14}H_{14}O_6N_2As \cdot 0.5H_2O$: H_2O , 2.32. Found: 2.86.

Calc. for $C_{14}H_{14}O_6N_2As$: N, 11.07. Found: 11.43.

2 - Methyl - 4 - [phenyl - (4'-arsonic acid) azo] phenylglycine.—(A unneutralized → B in 2 mols. of alkali.) The dye salt separated on rubbing and was dissolved in 50% alcohol with the aid of sodium hydroxide and the red-orange solution then made just acid to congo red, the arsonic acid separating as red-brown needles, leaflets, and rhombic platelets. When rapidly heated to 155°, then slowly, the acid reddens and intumesces at 157°. It is quite soluble in the cold in methyl alcohol, and dissolves in conc. sulfuric acid with a deep red color. A solution in 1 : 1 hydrochloric acid deposits the hydrochloride on rubbing as minute, dark brown platelets with a purple luster.

Analyses. Calc. for $C_{15}H_{16}O_6N_2As \cdot H_2O$: H_2O , 4.38. Found: 3.49.

Calc. for $C_{15}H_{16}O_6N_2As$: N, 10.69; As, 19.06. Found: N, 10.70; As, 19.08.

2 - Methoxy - 4 - [phenyl - (4'-arsonic acid) azo] phenylglycine.—(B in 1 mol. of alkali → A treated with one mol. of alkali and saturated with salt.) The monosodium salt gradually crystallized. It separates from dil. aqueous alcoholic alkali on adding acetic acid as very thin, nacreous, orange-red platelets containing about 2.5 molecules of water of crystallization when air-dry and dissolving in water with a deep red color, changing to brown and depositing microcrystalline spherules of what appears to be a different hydrate; on adding sodium acetate or sodium hydroxide a clear, deep orange solution results.

Analyses. Calc. for $C_{15}H_{16}O_6N_2AsNa \cdot 2.5H_2O$: H_2O , 9.46. Found: 8.93.

Calc. for $C_{15}H_{16}O_6N_2AsNa$: As, 17.39. Found: 17.28.

The acid was obtained in the usual way as minute, glistening, steel-blue aggregates of platelets. When rapidly heated the air-dry acid melts and effervesces at about 160°, but if dried first it gradually reddens on heating and intumesces at 167° to a blood-red mass. It is quite soluble in the cold in methyl alcohol, easily in hot ethyl alcohol, and dissolves in conc. sulfuric acid with a deep purple color, in 1 : 1 hydrochloric acid with a deep red color, and in dil. solutions of carbonates or alkalies with an orange color.

Analyses. Calc. for $C_{15}H_{16}O_6N_2As \cdot 1.5H_2O$: H_2O , 6.19. Found: 6.11.

Calc. for $C_{15}H_{16}O_6N_2As$: N, 10.27. Found: N, 10.30.

2 - Ethoxy - 4 - [phenyl - (4'-arsonic acid) azo] phenylglycine.—On adding an equal volume of saturated sodium chloride solution to the turbid reaction mixture

the **monosodium salt** separated as a paste, but crystallized on rubbing. From 50% alcohol it forms rosetts of orange-brown, glistening platelets which dissolve in water with a brown-red color.

Analyses. Calc. for $C_{16}H_{17}O_6N_3AsNa \cdot 2.5H_2O$: H_2O , 9.19. Found: 8.68.

Calc. for $C_{16}H_{17}O_6N_3AsNa$: N, 9.44. Found: 9.63.

The **free acid** separates very incompletely as rosetts and sheaves of flat, purplish-brown, microscopic needles which decompose at 245–50° and are freely soluble in 50% alcohol and 50% acetic acid, especially on warming. The solution in conc. sulfuric acid is deep red, appearing purple in thin layers.

Analysis. Calc. for $C_{16}H_{18}O_6N_3As$: N, 9.93. Found: 10.12.

α' - [Phenyl - (4-**arsonic acid**) azo] - α - **naphthylglycine**.—The **monosodium salt** was precipitated from the reaction mixture with an equal volume of alcohol, converted into the **disodium salt** by dissolving in one molecular equivalent of sodium hydroxide and adding alcohol until precipitation began, purifying by redissolving in warm 50% alcohol and treating with alcohol until the concentration of solvent was about 85%, whereupon the salt crystallized. It dissolves readily in water with a purple color.

Analyses. Calc. for $C_{18}H_{14}O_6N_3AsNa_2$: N, 8.88; As, 15.85. Found: N, 9.00; As, 15.36.

The salt was dissolved in 25% alcohol, made just acid to congo red, and filtered at once from a trace of amorphous matter, after which the **free acid** soon crystallized. It melts and decomposes at about 275° with preliminary darkening and softening and dissolves in conc. sulfuric acid with a deep red color, appearing purple in thin layers.

Analyses. Calc. for $C_{18}H_{16}O_6N_3As \cdot 0.5H_2O$: H_2O , 2.1. Found: 3.0.

Calc. for $C_{18}H_{16}O_6N_3As$: N, 9.79. Found: 9.48.

(D) Dyes Derived from Arsanilic Acid and Aromatic *N*-Methyl Sulfonic Acids.

4 - [Phenyl - (4'-**arsonic acid**) azo] - **phenyl-aminomethyl sulfonic acid**, $H_2O_2AsC_6H_4N:NC_6H_4NHCH_2SO_3H$.—Methylene-aniline sodium bisulfite solution was added to neutralized A saturated with salt. The **disodium salt** of the dye soon began to crystallize on keeping in the cold, and the process was hastened by the addition of two-thirds of a volume of saturated sodium acetate solution. Recrystallized from 50% alcohol, the salt separates as delicate, orange-colored needles which dissolve readily in water.

Analyses. Calc. for $C_{13}H_{12}O_6N_3SAsNa_2 \cdot 4.5H_2O$: H_2O , 15.01. Found: 15.09.

Calc. for $C_{13}H_{12}O_6N_3SAsNa_2$: N, 9.15; As, 16.32. Found: N, 9.63; As, 16.78.

The salt was dissolved in 25% alcohol and the solution acidified to congo red. The acid soon separated as sheaves of minute, flat, red needles with a purplish reflex. It dissolves with difficulty in cold water, readily on boiling, with a red color. When rapidly heated to 185°, then slowly, the anhydrous acid turns bright red, then sinters, and finally swells and melts partially at 187–9°. It dissolves in conc. sulfuric acid with a transient, deep orange color, quickly fading to yellow.

Analyses. Calc. for $C_{13}H_{14}O_6N_3SAs \cdot 2H_2O$: H_2O , 7.99. Found: 8.23.

Calc. for $C_{13}H_{14}O_6N_3SAs$: N, 10.12; As, 18.05. Found: N, 10.30; As, 18.25.

2 - **Methoxy - 4** - [phenyl - (4'-**arsonic acid**) azo] - **phenyl-aminomethyl sulfonic acid**.—As in the preceding case, methylene-*o*-anisidine sodium bisulfite yielded a **disodium salt** which was dissolved in a small volume of water and treated cautiously with somewhat more than an equal volume of alcohol. On standing in the cold, the salt separated as orange-red, microscopic needles dissolving readily in water with a deep orange-red color.

Analyses. Calc. for $C_{14}H_{14}O_7N_3SAsNa_2 \cdot 3H_2O$: H_2O , 9.95. Found: 9.96.

Calc. for $C_{14}H_{14}O_7N_3SAsNa_2$: As, 15.32. Found: 15.52.

In 50% alcohol, mineral acid causes the free arsenic acid to separate as lustrous, flat, violet needles. The anhydrous acid reddens and softens above 155°, and melts with slow gas evolution at 158–60°, dissolving in conc. sulfuric acid with a deep purple color which changes to deep red on standing.

Analyses. Calc. for $C_{14}H_{16}O_7N_2SAs \cdot 1.5H_2O$: H_2O , 5.72. Found: 4.95.

Calc. for $C_{14}H_{16}O_7N_2SAs$: N, 9.44. Found: 9.28.

(E) Dyes Derived from Arsanilic Acid and Substituted Phenoxyacetic Acids.

3 - Amino - 6 - [phenyl - (4'-arsenic acid) azo] - phenoxyacetic acid, $H_2O_2AsC_6H_4N:NC_6H_4(NH_2)OCH_2CO_2H$.—*m*-Amino-phenoxyacetic acid⁶ yielded a deep red solution which was gently warmed and treated with alcohol, depositing the orange microcrystalline monosodium salt, which was converted into the acid by dissolving in a considerable volume of dilute alcohol with the aid of sodium hydroxide and making the solution just acid to congo red. The acid separated as red, glistening needles. When anhydrous it blackens, but does not melt below 285°, dissolving in conc. sulfuric acid with an orange-red color, in dil. alkalis with an orange color, and gives an orange-red color in 1:1 hydrochloric acid, the hydrochloride separating on rubbing as orange-brown microscopic crystals.

Analyses. Calc. for $C_{14}H_{14}O_6N_2As \cdot 1.5H_2O$: H_2O , 6.40. Found: 6.99.

Calc. for $C_{14}H_{14}O_6N_2As$: N, 10.63; As, 18.96. Found: N, 10.74; As, 18.75.

4 - Methyl - 3 - amino - 6 - [phenyl - (4'-arsenic acid) azo] - phenoxyacetic acid.—4-Methyl-5-amino phenoxyacetic acid⁷ gave the monosodium salt of the dye as a red, crystalline mass which was converted as usual into the acid, this separating as dark red aggregates of flat needles with a purple reflex. When rapidly heated to 240°, then slowly, the dye intumesces at 242–3°, with preliminary blackening. It gives an orange color in conc. sulfuric acid or dil. alkalis, and is difficultly soluble in conc. hydrochloric acid, changing on rubbing to an orange-red, microcrystalline hydrochloride.

Analyses. Calc. for $C_{15}H_{16}O_6N_2As \cdot H_2O$: H_2O , 4.22. Found: 3.47.

Calc. for $C_{15}H_{16}O_6N_2As$: N, 10.27; As, 18.31. Found: N, 10.06; As, 18.51.

2 - Methyl - 5 - amino - 4 - [phenyl - (4'-arsenic acid) azo] - phenoxyacetic acid.—In the case of 2-methyl-5-amino-phenoxyacetic acid,⁷ the deep red-brown solution of the monosodium salt was filtered, concentrated partially *in vacuo*, and allowed to stand in the cold. The resulting crystals were dissolved in boiling 85% alcohol containing acetic acid, and on cooling the free acid separated. Reprecipitated in 33% alcohol it forms flat, glistening, purplish-brown needles which dissolve readily in methyl alcohol, less easily in ethyl alcohol. When rapidly heated to 185°, then slowly, it intumesces at 187–8°. It dissolves in conc. sulfuric acid with a deep orange color and partially in conc. hydrochloric acid with a red shade, soon depositing the hydrochloride as dull red microcrystals.

Analyses. Calc. for $C_{15}H_{16}O_6N_2As \cdot 2H_2O$: H_2O , 8.09. Found: 7.07.

Calc. for $C_{15}H_{16}O_6N_2As$: N, 10.27. Found: 10.38.

3 - Amino - 6 - methoxy - 4 - [phenyl - (4'-arsenic acid) azo] - phenoxyacetic acid.—Precipitation of the dye acid obtained from 3-amino-6-methoxy-phenoxyacetic acid⁸ was facilitated by the addition of acetic acid and the collected product was dissolved in dil. sodium hydroxide, filtered, and reprecipitated with an excess of acetic acid. Re-precipitated in 50% alcohol, the acid separates as flat, glistening, bronze needles and platelets. The air dry acid sinters, softens, and swells at 175–85°, while the anhydrous substance intumesces at 208–13° with preliminary sintering and softening. It dissolves

⁶ THIS JOURNAL, 39, 2912 (1917).

⁷ *Ibid.*, 39, 2193 (1917).

⁸ *Loc. cit.*, p. 2194.

appreciably in the cold in methyl or ethyl alcohol, readily on warming, and dissolves in dil. alkalis or carbonates with an orange-red color. It gives a bright red color in conc. sulfuric acid and yields a deep purplish-red solution in 1 : 1 hydrochloric acid, almost immediately depositing the hydrochloride as dark brown, microscopic platelets.

Analyses. Calc. for $C_{15}H_{16}O_7N_3As \cdot 4.5H_2O$: H_2O , 16.02. Found: 15.47.

Calc. for $C_{15}H_{16}O_7N_3As$: N, 9.88. As, 17.64. Found: N, 9.89; As, 17.62.

4 - Amino - 6 - methoxy - 3 - [phenyl - (4' - arsonic acid) azo] - phenoxyacetic acid.—

Using 4-amino-6-methoxy-phenoxyacetic acid,⁹ the monosodium salt of the dye gradually separated, best on concentrating to smaller bulk *in vacuo* and allowing to stand in the ice box. Recrystallized from dil. sodium acetate solution, it separates as chocolate colored, microscopic needles which are very sparingly soluble in water, but dissolve on adding carbonate or alkali with a dark red color.

Analyses. Calc. for $C_{15}H_{15}O_7N_3AsNa \cdot 6.5H_2O$: H_2O , 20.75. Found: 21.03.

Calc. for $C_{15}H_{15}O_7N_3AsNa$: As, 16.77. Found: 16.31.

The free acid can be precipitated in 50% alcohol as minute, glistening, maroon platelets. It does not melt below 280°, and dissolves in conc. sulfuric acid with a bright red color. A solution in hot 1 : 1 hydrochloric acid deposits the hydrochloride on cooling as dark red, flat needles.

Analyses. Calc. for $C_{15}H_{16}O_7N_3As \cdot 2H_2O$: H_2O , 7.81. Found: 7.89.

Calc. for $C_{15}H_{16}O_7N_3As$: N, 9.89. Found: 9.97.

4 - Amino - 5 - [phenyl - (4' - arsonic acid) azo] - 1,2-bis-phenoxyacetic acid.—A → B, using 4-amino-1,2-bis-phenoxyacetic acid.¹⁰ After acidifying with acetic acid the monosodium salt of the dye separated as dark purplish-brown, microcrystalline spherules. It is very sparingly soluble in water, but dissolves with an orange-red color on adding carbonate or alkali.

Analyses. Calc. for $C_{16}H_{15}O_9N_3AsNa \cdot 4.5 H_2O$: H_2O , 14.17. Found: 14.40.

Calc. for $C_{16}H_{15}O_9N_3AsNa$: N, 8.56. Found: 8.61.

When precipitated in much warm 50% alcohol, deposition of amorphous material is prevented and the free acid separates as dark purplish-brown microcrystals. Its repetition of this process was necessary before the acid was analytically pure. A dissolves in conc. sulfuric acid with an orange-red color, and when anhydrous, softens and sinters when heated, but does not melt below 280°.

Analyses. Calc. for $C_{16}H_{16}O_9N_3As \cdot 3H_2O$: H_2O , 10.33. Found: 10.58.

Calc. for $C_{16}H_{16}O_9N_3As$: N, 8.96. As, 15.97. Found: N, 9.07; As, 15.8.

α - Amino - β - [phenyl - (4 - arsonic acid)] azo - α' - naphthoxyacetic acid.— α -Amino- α' -naphthoxyacetic acid¹¹ gave a deep purple, amorphous precipitate which was dissolved by adding 1 mol. of sodium hydroxide and the solution treated with several volumes of alcohol, causing deposition of the disodium salt. Recrystallized from 50% alcohol, it separates as dark brown, felted microscopic needles which dissolve readily in water with a dark purplish-red color.

Analyses. Calc. for $C_{18}H_{14}O_6N_3AsNa_2 \cdot 9H_2O$: H_2O , 24.89. Found: 25.25.

Calc. for $C_{18}H_{14}O_6N_3AsNa_2$: N, 8.59; As, 15.33. Found: N, 8.46; As, 15.71.

The free acid may be precipitated in much warm 50% alcohol as flat, dark red needles with a golden luster. It decomposes at about 285°, with preliminary darkening and softening. It dissolves in conc. sulfuric acid with a deep purplish-red color.

Analyses. Calc. for $C_{18}H_{15}O_6N_3As$: N, 9.44. Found: 9.47.

α - Amino - α' - [phenyl - (4 - arsonic acid)] azo - β - naphthoxyacetic acid.—Sodium salt of α -amino- β -naphthoxyacetic acid → neutralized A. The deep purple solution was concentrated to small bulk *in vacuo* and treated with several volumes of alcohol.

⁹ *Loc. cit.*, p. 2212.

¹⁰ *Ibid.*, p. 2216.

¹¹ *Ibid.*, p. 2217.

the disodium salt separating in the cold. Recrystallized from 50% alcohol it forms almost black aggregates of microscopic hairs with a greenish reflex and dissolving in water with a deep red color.

Analyses. Calc. for $C_{18}H_{14}O_6N_3AsNa_2 \cdot 8.5H_2O$: H_2O , 23.84. Found: 23.64.

Calc. for $C_{18}H_{14}O_6N_3AsNa_2$: N, 8.59; As, 15.33. Found: N, 8.56; As, 15.81.

The free acid, when liberated in much 50% alcohol slowly separates as red-brown microcrystalline aggregates which do not melt below 285°.

Analyses. Calc. for $C_{18}H_{16}O_6N_3As \cdot H_2O$: H_2O , 3.89. Found: 3.96.

Calc. for $C_{18}H_{16}O_6N_3As$: N, 9.44. Found: 9.49.

2 - Hydroxy - 5 - [phenyl - (4'-arsonic acid) azo] - phenoxyacetic acid.—Neutral A \rightarrow alkaline *o*-hydroxy-phenoxyacetic acid solution. The neutralized solution was concentrated to small bulk *in vacuo*, and the dye precipitated by adding strong sodium hydroxide solution. Dissolved in hot 50% alcohol and treated with an excess of acetic acid, the monosodium salt separated as yellow, indefinitely crystalline, microscopic globules.

Analyses. Calc. for $C_{14}H_{12}O_7N_2AsNa$: N, 6.70; As, 17.93. Found: N, 6.42; As, 18.33.

The free arsonic acid separated from a solution in dil. sodium hydroxide as an emulsion which soon crystallized. Dissolved in boiling 85% alcohol, and the filtrate diluted with water, the acid separated as brown, microscopic platelets which do not melt below 280°. It dissolves in boiling alcohol, and gives a bright orange solution in dil. sodium hydroxide. The color in conc. sulfuric acid is a deep red-orange.

Analyses. Calc. for $C_{14}H_{12}O_7N_2As \cdot 0.5H_2O$: H_2O , 2.2. Found: 2.4.

Calc. for $C_{14}H_{12}O_7N_2As$: N, 7.07; As, 18.92. Found: N, 6.99; As, 18.61.

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CHROMO-ISOMERIC SILVER SALTS OF PENTABROMOPHENOL AND A THEORY OF CHROMO-ISOMERISM OF SOLID COMPOUNDS.

BY HOWARD J. LUCAS AND ARCHIE R. KEMP.

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1. Previous Investigations.

Two silver salts of pentabromophenol have been described. Bodroux¹ obtained a rose-colored amorphous precipitate upon adding silver nitrate to a solution of the potassium salt. Hantzsch and Scholtze² also obtained a reddish amorphous precipitate in the same manner, ascribing the color to an impurity present in the pentabromophenol; but they also described a colorless, amorphous form, which precipitates when alcoholic silver nitrate is added to an alcoholic solution of the ammonium salt, and they apparently regard it as a purer lot of the same salt, which they describe as colorless, and existing in only one form. Isomeric silver salts of other

¹ Bodroux, *Compt. rend.*, **126**, 1282-85 (1898).

² Hantzsch and Scholtze, *Ber.*, **40**, 4882 (1907).