Summary

1. Dibenzoyl ethylene has been prepared by the action of fumaryl chloride on benzene in the presence of aluminum chloride. Derivatives of dibenzoyl ethylene have been prepared by the use of toluene, chlorobenzene, mesitylene and anisole.

2. The product of the reaction is the colored *trans* isomer which is converted to the colorless *cis* isomer by the action of sunlight; the reverse transformation is caused by acid or a trace of iodine. With the exception of dibenzoyl ethylene, the *trans* isomer has the higher melting point and the lower solubility.

3. Both the *cis* and *trans* isomers of each compound are easily reduced to the corresponding saturated 1,4 diketone by sodium hydrosulfite.

CAMBRIDGE 38, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

ARSENATED DERIVATIVES OF PHENYLDIKETO-PYRROLIDINE[1]

BY JOHN R. JOHNSON[2] WITH ROGER ADAMS

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Trypanocidal compounds of practical importance containing an arsonic acid grouping and not containing other unstable groupings have been sought by many investigators, but none has been discovered which combines the properties found in the arsphenamines. Previous observations have shown that the most valuable arsenic-containing trypanocidal substances must contain nitrogen in some form. Since numerous drugs of various types and pharmacological properties have been discovered which contain nitrogen in a heterocyclic ring, this research was undertaken with the preparation of substances containing the arsonic acid group and a nitrogen atom in a heterocyclic ring as its object. Of the many arsenicals which have been described since the first work of Ehrlich and Bertheim, very few compounds of this type have been made.

Direct arsenation of indole and certain of its derivatives[3] introduces the arsonic acid group into the 2-position of the pyrrole ring. An unsuccessful attempt to arsenate quinoline and tetrahydroquinoline in a similar way, is reported by Fränkel and Löwy.[4]

A substance described as quinaldine-6-arsonic acid was obtained by Fränkel and Löwy[4] in poor yields, by the condensation of acetaldehyde with arsanilic acid in the presence of hydrobromic acid, but no evidence was presented to prove the quinaldine structure in this compound.

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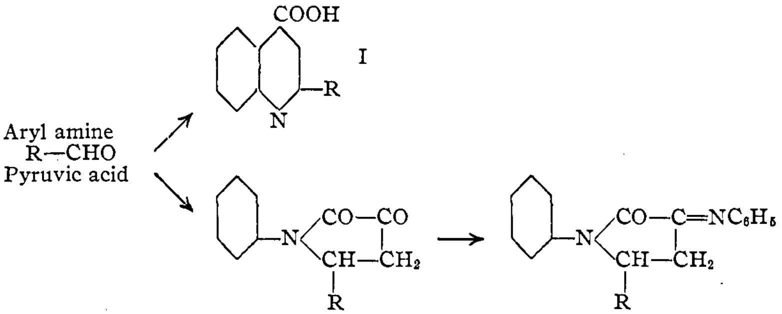
[2] This communication is an abstract of a thesis submitted by John R. Johnson in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[3] Ger. pat., 240,793; *Friedländer*, **10**, 1252 (1910–12).

[4] Fränkel and Löwy, *Ber.*, **46**, 2546 (1913).

More recently a German patent[5] has appeared in which is described the preparation of arsenic compounds of the pyrazolone series. Diazo-arsanilic acid was reduced with stannous chloride and arsenated phenylhydrazine obtained in solution, which was then condensed with aceto-acetic ester to produce an arsenated phenyl-methyl-pyrazolone. Various derivatives were made.

Since many compounds of therapeutic value contain nitrogen in pyrrolidine and quinoline rings the synthesis of arsenated derivatives of these substances was first undertaken. Several general reactions for these preparations have been tried but thus far promising results have been obtained only in the use of arsenated aryl amines in Döbner's cinchoninic acid synthesis.[6] This synthesis consists in the reaction of pyruvic acid, aldehydes and aromatic amines. Three types of compounds may be produced; (I) cinchoninic acids, (II) aryldiketo-pyrrolidines, and (III) anils of the latter.



I

II

III

With most aromatic amines, compounds of Types I and III are isolated, since the intermediate compound II reacts very readily with unchanged amine to produce the anil. In only one exception, namely with *p*-nitroaniline, Compound II was readily obtained. In contrast with *p*-nitroaniline, from which no cinchoninic acid could be obtained, is β-naphthylamine, which did not give the diketo-pyrrolidine derivatives under any conditions.[7]

By the action of pyruvic acid upon arsanilic acid and benzaldehyde in hot absolute alcohol, a condensation product was obtained which was considered to be 2-phenylquinoline-4-carboxylic-acid-6-arsonic acid, and the compound was described thus in a preliminary notice.[8] The composition of this substance corresponded either to that of a cinchoninic acid (IV), or to that of a simple diketo-pyrrolidine derivative (V).

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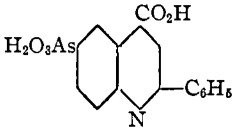
[5] Ger. pat., 313,320; *Chem. Zentr.*, **1921**, IV, 263.

[6] Döbner, *Ann.*, **242**, 265 (1887); **249**, 98 (1888); **281**, 1 (1894).

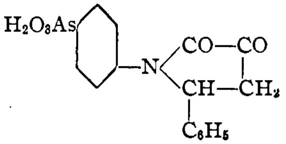
[7] Borsche, *Ber.*, **41**, 3884 (1908); **47**, 354 (1914).

[8] Johnson and Adams, THIS JOURNAL, **43**, 2255 (1921).



IV

$C_{16}H_{12}O_5NAs$



V

$C_{16}H_{14}O_5NAs$

The usual separation of these two types of substances by solution of the cinchoninic acid in dil. sodium carbonate could not be applied, since an acidic group was already present in the molecule. Further, the condensation product is unstable toward hot mineral acids, and therefore the usual replacement of the arsonic acid group by iodine and identification of the resulting iodo compound could not be accomplished.

The fact that the substance evolved approximately 1 molecular equivalent of carbon dioxide upon heating to its decomposition point, was considered good evidence for the cinchoninic acid structure, since it is well known that these acids lose 1 molecular equivalent of carbon dioxide when heated above their melting points. On the other hand, the similarity of the arsonic acid and nitro groups would lead to the conclusion that the use of arsanilic acid should result in the formation of the same type of substance as the use of *p*-nitro-aniline, namely, diketo-pyrrolidine. If the compound were a cinchoninic acid derivative, 2-phenyl-quinoline or 2-phenyl-6-hydroxy-quinoline should form upon fusion of the substance with sodium hydroxide. Actually, the chief nitrogenous product of alkaline fusion was aniline, the result of a behavior which could hardly be explained on the basis of the cinchoninic acid formula.

The loss of carbon dioxide upon heating was the only reaction which did not agree with a diketo-pyrrolidine structure. To clear up this point, the behavior of 1-(4′-nitrophenyl)-2-phenyl-4,5-diketo-pyrrolidine (the analogous diketo-pyrrolidine with nitro in place of the arsonic acid group) was investigated. This substance, when boiled with ethyl benzoate for 15 minutes, gave off 63% of 1 molecular equivalent of carbon dioxide and in the presence of an equal quantity of *o*-nitrophenyl-arsonic acid under the same conditions, liberated 95% of 1 molecular equivalent of carbon dioxide. This last experiment was made in order to have present an arsonic acid grouping such as is present in the compound made from arsanilic acid, since this group (as has actually been shown to be the case) might have an influence on the ease of decomposition.

These results, together with the behavior on alkaline fusion, indicate clearly that the condensation product previously described as 2-phenyl-quinoline-4-carboxylic-acid-6-arsonic acid (IV) should be designated as 1-(4′-arsonophenyl)-2-phenyl-4,5-diketo-pyrrolidine (V). This conclusion is supported further by the fact that the same condensation product is obtained when the reaction is carried out in ethereal suspension, and also when ethyl pyruvate is substituted for the acid. In both of these cases, the diketo-pyrrolidine derivative would be expected, and the product actually formed proved to be identical with the original condensation product.

With the idea of studying the limitations of this reaction and of preparing a series of derivatives, a number of amino-aryl arsonic acids and aromatic aldehydes were condensed with pyruvic acid in the manner described.

(1) It was found that arsanilic acid and pyruvic acid yielded condensation products with all of the aromatic aldehydes tried. These included *o*- and *p*-methoxy-, *p*-chloro-, and *p*-dimethylamino-benzaldehyde. No condensation products were obtained from paraldehyde and *n*-butyraldehyde.

(2) Amino-aryl arsonic acids containing substituents *ortho* to the amino group condensed with the aldehyde to give a benzylidene derivative of the amine, but the latter did not react further with pyruvic acid, even on long heating. The amino-aryl arsonic acids used for these experiments were *o*-arsanilic acid, 3-methyl-4-aminophenyl-arsonic acid, and 3-bromo-4-aminophenyl-arsonic acid. These results are in accord with those of Borsche, who was unable to obtain condensation products from *o*-chloro-aniline and *o*-nitro-aniline.

(3) Amino-aryl arsonic acids containing no substituent *ortho* to the amino but substituents *meta* or *para* to the amino condensed in the usual manner and good yields of the condensation products were obtained. The particular acids used for these experiments were 2-methyl-4-aminophenyl-arsonic acid, and 2-methoxy-4-aminophenyl-arsonic acid.

These observations indicate the following generalizations concerning the reaction between pyruvic acid, aldehydes and amino-aryl arsonic acids to form diketo-pyrrolidines under the conditions studied: (1) the reaction is general for aromatic aldehydes, but not for the simple aliphatic aldehydes, (2) the reaction occurs when substituents are present in the *meta* and *para* positions to the amino group in the amino-aryl arsonic acids, but does not occur when *ortho* substituents are present. In the latter instance, benzylidene-amino derivatives were obtained.

Preliminary pharmacological experiments have been carried out with 1-(4′-arsonophenyl)-2-phenyl-4,5-diketo-pyrrolidine dissolved in 2 molecular equivalents of sodium hydroxide. These have shown the toxicity to be much less than that of arsphenamine. On the other hand, the trypanocidal action is also much less so that the therapeutic index is considerably lower than that of arsphenamine. For the pharmacological data, the authors are indebted to Dr. G. W. Raiziss, Director of the Dermatological Research Laboratories of Philadelphia.

Experimental Part

The amino-aryl arsonic acids used in this investigation were produced by various methods. *o*-Arsanilic acid, 2-methyl-6-aminophenyl-arsonic acid, 2-methyl-4-aminophenyl-arsonic acid, and 2-methoxy-4-aminophenyl-arsonic acid were made by the reduction of the corresponding nitro compounds. On the other hand, 3-methyl-4-aminophenyl-arsonic acid was produced by the direct action of arsenic acid upon *o*-toluidine, and 3-bromo-4-aminophenyl-arsonic acid by the action of bromine upon arsanilic acid.

Preparation of Nitrophenyl-arsonic Acids.—These substances were produced in each case by the diazotization of the corresponding amine and treatment of the diazo solution with sodium arsenite solution. The general directions given below which involve a slight modification of those which appear in the literature, gave excellent results.

One molecular equivalent of the amine was dissolved or suspended in 600 cc. of 5 *N* hydrochloric acid (3 molecular equivalents). The mixture was cooled with ice and diazotized in the usual way, using mechanical stirring. The diazo solution thus produced was filtered, and transferred to a 12-liter flask. It was then thoroughly cooled and treated, with stirring, with 200 cc. of 5 *N* sodium hydroxide (1 molecular equivalent) which was followed at once by a mixture of 750 cc. of 2 *N* disodium monohydrogen arsenite solution,[9] 60 cc. of 5 *N* hydrochloric acid, 650 cc. of water, 650 g. of ice, and 200 cc. of 20% copper sulfate solution. Vigorous evolution of nitrogen took place, which caused excessive foaming. This could be lessened by the occasional addition of a few cubic centimeters of ethyl acetate. The mixture was allowed to stand for an hour, then warmed to 40–50° and filtered. The clear filtrate was acidified to litmus paper with acetic acid, concentrated on a steam-bath, and filtered hot to remove a yellow by-product which was generally produced in small quantities. Upon acidification of the clear filtrate with hydrochloric acid until acid to congo red paper, the arsonic acid separated. The crude product thus obtained is generally satisfactory for reduction to the amino-arsonic acid without further purification.

By this method *o*-nitro-aniline, *p*-nitro-aniline, 2-methyl-4-nitro-aniline,[10] 2-methyl-6-nitro-aniline, and 2-methoxy-4-nitro-aniline gave very good results. Although the addition of copper sulfate is not advised by a number of those who have worked with these arsonic acids, the experience in this Laboratory has indicated that it is decidedly desirable.

The directions for the nitro-aniline derivatives were used for the preparation of 2-methoxyphenyl-arsonic acid, and 4-methoxyphenylarsonic acid from the corresponding *o*- and *p*-anisidines.

2-Methoxyphenyl-arsonic Acid.—From 12.3 g. of pure *o*-anisidine, 13.5 g. of the corresponding arsonic acid was obtained. The crude *o*-methoxyphenyl-arsonic acid was

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[9] Prepared according to the method of Schmidt, *Ann.*, **421**, 168 (1921), by dissolving 198 g. of arsenious oxide in 800 cc. of 5 *N* sodium hydroxide, and making up to 1 liter.

[10] Produced by the nitration of *o*-acetotoluide and separation of the isomeric nitro compounds by the Witt-Utermann method. Compare Franzen and Engle, *J. prakt. Chem.*, [2] **102**, 156 (1921).

purified by crystallization from alcohol, from which it formed white needles melting at 193–194°.

Analyses. Subs., 0.2000, 0.1995: 21.50, 21.46 cc. of 0.0808 *N* I_2 soln. Calc. for $C_7H_9O_4As$: As, 32.31. Found: 32.57, 32.59.

4-Methoxyphenyl-arsonic Acid.—This acid has been previously made by the hydrolysis of *p*-anisyl-arsenic chloride[11] and also by the methylation of phenol-*p*-arsonic acid.[12] By the diazotization of *p*-anisidine and treatment with sodium arsenite, the product was readily formed. After purification by crystallization from water, it was found to melt at 176–177°.

2-Methoxy-4-nitrophenyl-arsonic Acid.—2-Methoxy-4-nitro-aniline was made by the nitration of *o*-acetaniside and separation of the resulting mixture of isomers. The method used was different from that in the literature. A solution of 123 g. of pure *o*-anisidine in 105 g. of acetic anhydride and 32 cc. of glacial acetic acid was heated to boiling. It was then placed in a 1.5-liter flask provided with a good mechanical stirrer and rapidly cooled by immersion in a freezing mixture. A solution of 65 cc. of fuming nitric acid (d., 1.52) in 90 cc. of cold acetic anhydride was added gradually to the cold reaction mixture during the course of 4 hours, and at all times the temperature was kept below 0°. After the addition of the nitric acid the mixture was allowed to warm slowly to room temperature and then to stand for 36 hours. When the resulting red-brown solution was poured into a mixture of 1200 g. of ice and water, a yellow precipitate of the mixed nitro-acetanisides was produced. The precipitate was filtered with suction, washed thoroughly with water and dried; yield, 208 g.

The product was hydrolyzed by warming on a water-bath with a mixture of 350 cc. of conc. sulfuric acid and 650 cc. of water. The acetyl derivatives dissolved gradually and after 1 to 1.5 hours the solution was poured into a beaker to cool. The solution was then chilled, resulting in the formation of a paste of 2-methoxy-4-nitro-aniline sulfate. This was filtered with suction, pressed as dry as possible, and transferred to a large beaker, in which it was thoroughly mixed with cold water. This caused the hydrolysis of the gray sulfate and the formation of the bright yellow base. The latter was filtered, washed and dried, after which it melted at 136–139° (previously reported, m. p., 140°). The product weighed 102 g. (60%, based on the anisidine used) and was sufficiently pure for ordinary purposes.

On neutralization of the sulfuric acid filtrate from the above preparation with ammonia, 55 g. of impure 2-methoxy-5-nitro-aniline was obtained (32%, based on the anisidine).

By diazotization of the 2-methoxy-4-nitro-aniline and treatment with sodium arsenite, 2-methoxy-4-nitro-phenyl-arsonic acid was produced. When crystallized from 90% alcohol it formed pale yellow needles, which did not melt up to 250°. The weight of product was about equal to that of the 2-methoxy-4-nitro-aniline used.

Analyses. Subs., 0.1987, 0.2060: 17.56, 18.27 cc. of 0.0808 *N* I_2 soln. Calc. for $C_7H_8O_6NAs$: As, 27.08. Found: 26.78, 26.86.

Reduction of the Nitro-aryl Arsonic Acids.—The method employed was a slight modification of that described by Benda[13] and by Jacobs, Heidelberger and Rolf.[14] It was found a distinct advantage to use ferrous chloride rather than ferrous sulfate. Ferrous chloride was conveniently produced by treating an excess of powdered iron with a known quantity

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[11] Michaelis, *Ber.*, **20**, 51 (1887); *Ann.*, **320**, 298 (1902).

[12] Bertheim, *Ber.*, **47**, 276 (1914).

[13] Benda, *ibid.*, **44**, 3302 (1911); **47**, 1006, 1316 (1914).

[14] Jacobs, Heidelberger and Rolf, THIS JOURNAL, **40**, 1580 (1918).

of hydrochloric acid and heating on a hot plate until no more gas was evolved. The solution was then kept over iron filings until just before using, when it was filtered and the ferrous chloride content determined by potassium permanganate titration.

By this method *o*-arsanilic acid, 2-methyl-6-aminophenyl-arsonic acid, 2-methyl-4-aminophenyl-arsonic acid and 2-methoxy-4-aminophenyl-arsonic acid were prepared. The last has not previously been described.

2-Methoxy-4-aminophenyl-arsonic Acid.—This substance was obtained in 60% yields by the reduction of the corresponding nitro-arsonic acid. It crystallized from water in white needles, and melted with decomposition at 203–204° if heated slowly, or 208–209° if heated rapidly.

Analyses. Subs., 0.1503, 0.2000: 15.07, 20.23 cc. of 0.0808 N I_2 soln. Calc. for $C_7H_{10}O_4NAs$: As, 30.36. Found: 30.38, 30.65.

Condensation of Amino-aryl Arsonic Acids with Pyruvic Acid and Aldehydes. General Procedure.—One molecular equivalent of the amino-aryl arsonic acid, dissolved or suspended in 10 to 12 times its weight of absolute alcohol, and 1 molecular equivalent of aldehyde were heated to boiling under a reflux condenser on a steam-bath. After a short time most of the arsonic acid passed into solution and 1 molecular equivalent of pyruvic acid was added. The reaction mixture was then heated for 3 to 4 hours, filtered hot to remove any slight insoluble material and allowed to cool. In some cases the product separated directly; in other cases it was necessary to concentrate the alcohol solution in a vacuum to about $^1/_2$ its original volume, after which the product crystallized upon standing. In each case the crude material was purified by recrystallization from alcohol.

The yields of products obtained by the general procedure described above varied from 50 to 70% of the calculated amounts.

1-(4′-Arsonophenyl)-2-phenyl-4,5-diketo-pyrrolidine (V).— This substance has already been described under the name of 2-phenylquinoline-4-carboxylic-acid-6-arsonic acid.[3] When pure it melted at 186–187° with decomposition. It may also be formed by substituting ethyl pyruvate for pyruvic acid in the general procedure.

Benzylidene-*p*-arsanilic Acid.—When the above preparation was carried out by the usual method, a small amount of a less soluble impurity was removed during crystallization. This impurity proved upon further purification and analysis, to be benzylidene-arsanilic acid. From alcohol it forms heavy, white, granular crystals, melting with decomposition at 225°.

Analyses. Subs., 0.2078, 0.2100: 15.27, 15.42 cc. of 0.0893 N I_2 soln. Calc. for $C_{13}H_{12}O_3NAs$: As, 24.58. Found: 24.62, 24.60.

1-(4′-Arsonophenyl)-2-(2′-methoxyphenyl)-4,5-diketo-pyrrolidine.—By using salicyl aldehyde methyl ether in place of benzaldehyde, the condensation product was obtained as a pale yellow powder; m. p., 173–176° with decomposition.

Analyses. Subs., 0.2025, 0.2022: 12.61, 12.25 cc. of 0.0808 N I_2 soln. Calc. for $C_{17}H_{16}O_6NAs$: As, 18.51. Found: 18.87, 18.36.

1-(4′-Arsonophenyl)-2-(4′-methoxyphenyl)-4,5-diketo-pyrrolidine.—This substance was made by using anisaldehyde with arsanilic acid and pyruvic acid. It formed almost white crystals which melted at 164–165° with decomposition.

Analyses. Subs., 0.2005, 0.2000: 10.51, 10.38 cc. of 0.0954 *N* I_2 soln. Calc. for $C_{17}H_{16}O_6NAs$: As, 18.51. Found: 18.71, 18.53.

1-(4′-Arsonophenyl)-2-(3′,4′-methylene-dioxyphenyl)-4,5-diketo-pyrrolidine.—This substance was obtained from arsanilic acid, piperonal, and pyruvic acid. It formed a light yellow powder; m. p., 176–178° with decomposition.

Analysis. Subs., 0.1474: 7.80 cc. of 0.0893 *N* I_2 soln. Calc. for $C_{17}H_{14}O_7NAs$: As, 17.90. Found: 17.73.

1-(4′-Arsonophenyl)-2-(4′-chlorophenyl)-4,5-diketo-pyrrolidine.—This substance was obtained by substituting *p*-chlorobenzaldehyde for benzaldehyde. It formed a white powder; m. p., 163–165° with decomposition.

Analysis. Subs., 0.2505: 14.90 cc. of 0.0808 *N* I_2 soln. Calc. for $C_{16}H_{13}O_5NClAs$: As, 18.29. Found: 18.00.

Condensation products were also formed when benzaldehyde was replaced by salicyl aldehyde, *p*-dimethylamino-benzaldehyde, and cinnamic aldehyde. The yields, however, were not so satisfactory as with the compounds just described and the purification was much more difficult.

When paraldehyde or *n*-butyraldehyde was used with arsanilic acid and pyruvic acid, no condensation product was obtained which could be purified.

1-(4′-Arsono-3′-methylphenyl)-2-phenyl-4,5-diketo-pyrrolidine.—This substance was made by the action of 2-methyl-4-aminophenyl-arsonic acid upon pyruvic acid and benzaldehyde by the general method already described. It formed a cream-colored powder; m. p., 180–186° with decomposition.

Analyses. Subs., 0.1981, 0.2008: 11.32, 11.55 cc. of 0.0893 *N* I_2 soln. Calc. for $C_{17}H_{16}O_5NAs$: As, 19.27. Found: 19.14, 19.27.

1-(4′-Arsono-3′-methoxyphenyl)-2-phenyl-4,5-diketo-pyrrolidine.—This compound was made from 2-methoxy-4-aminophenyl-arsonic acid, benzaldehyde and pyruvic acid. It formed a yellow powder which after purification from ethyl alcohol melted at 175–176° with decomposition.

Analyses. Subs., 0.2030, 0.2000: 9.80, 9.66 cc. of 0.1012 *N* I_2 soln. Calc. for $C_{17}H_{16}O_6NAs$: As, 18.51. Found: 18.32, 18.33.

Benzylidene-*o*-arsanilic Acid, $C_6H_5CH{=}NC_6H_4AsO_3H_2(o)$.—When *o*-arsanilic acid, benzaldehyde and pyruvic acid were condensed as described above, a crystalline precipitate formed in a short time and redissolved upon heating for 1 to 2 hours. After several hours the reaction mixture was cooled to room temperature, but no precipitate formed until the reaction mixture was cooled below 0°. The product thus formed was washed with cold alcohol, then ether, and dried. It melted at 227–229° with decomposition, and proved upon analysis to be benzylidene-*o*-arsanilic acid.

For comparison, a sample of benzylidene-*o*-arsanilic acid was prepared by heating *o*-arsanilic acid with 1 molecular equivalent of benzaldehyde in alcoholic solution. There was thus obtained a product which melted with decomposition at 228–230° and proved to be identical with a substance formed from pyruvic acid, benzaldehyde and *o*-arsanilic acid.

Analyses. Subs., 0.1997, 0.1985: 14.70, 14.86 cc. of 0.0893 *N* I_2 soln. Calc. for $C_{13}H_{12}O_3NAs$: As, 24.58. Found: 24.66, 24.74.

4-Benzalamino-3-methyl-phenyl-arsonic Acid.—When an attempt was made to condense pyruvic acid, benzaldehyde and 3-methyl-4-aminophenyl-arsonic acid, only the benzylidene derivative of the amine could be isolated. In order to obtain this substance from the reaction mixture, it was necessary to evaporate half of the alcohol used. The product formed a cream-colored solid from alcohol; m. p., 202–205° with decomposition.

Analyses. Subs., 0.2001, 0.2000: 13.80, 13.90 cc. of 0.0893 *N* I_2 soln. Calc. for $C_{14}H_{14}O_3NAs$: As, 23.51. Found: 23.10, 23.28.

4-(4′-Chlorobenzal)amino-3-methylphenyl-arsonic Acid.—This substance was obtained from *p*-chlorobenzaldehyde, 3-methyl-4-aminophenyl-arsonic acid and pyruvic acid. It formed a pale yellow powder from alcohol; m. p., 255–260° with decomposition.

Analysis. Subs., 0.2018: 13.74 cc. of 0.0808 *N* I_2 soln. Calc. for $C_{14}H_{13}O_3NClAs$: As, 21.20. Found: 20.63.

Summary

1. In the light of new experimental evidence, to the condensation product obtained from arsanilic acid, benzaldehyde and pyruvic acid, which was previously described as 2-phenylquinoline-4-carboxylic-acid-6-arsonic acid, has been assigned the constitution, 1-(4′-arsonophenyl)-2-phenyl-4,5-diketo-pyrrolidine.

2. A number of derivatives of this series have been prepared by the action of pyruvic acid upon substituted amino-aryl arsonic acids and aldehydes.

3. The following generalizations were made concerning the limitations of this reaction.

a. Amino-aryl arsonic acids with substituents in the *ortho* position to the amino group formed benzylidene derivatives which did not react further with pyruvic acid.

b. The usual condensation products were obtained from amino-aryl arsonic acids substituted in the *meta* and *para* positions to the amino group.

c. The reaction was applicable to substituted aromatic aldehydes but not to the simple aliphatic aldehydes.

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