dissolved in acetone by the addition of iodine and carbon tetrachloride. With 1.6 g. of the quaternary salt and 2 g. of iodine in 25 cc. of acetone, 2.2 g. of bronze plates, resembling completely those obtained in the above reaction, was obtained. These melted at 144–145° and were analyzed for free iodine as before.

Anal. Subs., 0.2760: thiosulfate, 18.90 cc. (1 cc. = 6.613 mg. of I_2). Calc. for $C_9H_{13}N_2O_2I_3$: I_2, 45.18. Found: 45.28.

Summary

1. Three new amine oxides formed from 4-bromo, and 3- and 4-nitrodimethylaniline have been studied and various salts prepared.
2. The iodides of these amine oxides are unstable. The iodide of 4-bromo-dimethylaniline oxide was isolated, but was found to decompose rapidly. The net result of this change is the liberation of iodine and the reduction of a part of the amine oxide to the corresponding tertiary amine.
3. These amine oxides do not add methyl iodide. During the reaction, iodine is liberated and the oxides are reduced to corresponding tertiary amines without the liberation of formaldehyde.
4. The various interpretations offered to explain the isomers discovered by Meisenheimer are discussed, especially those of Jones and of Michael, and the more recent explanations of Lewis and of Langmuir.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE LABORATORY OF THE HENRY PHIPPS INSTITUTE OF THE UNIVERSITY OF PENNSYLVANIA]

THE PREPARATION AND PROPERTIES OF 4,4-DIPHENYL-DIARSONIC ACID

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RECEIVED FEBRUARY 12, 1924 PUBLISHED AUGUST 5, 1924

Since the discovery by Boer[1] of the partially specific disinfectant action of certain dyes, attention has been more and more frequently directed toward the specific relationships of disinfectants generally. The synthetic dyes have been shown to be variously directed in this sense. Lewis[2] has shown that a certain group of dyes possesses the power of inhibiting the growth of *Bacillus tuberculosis* although few of them are active against *Bacillus typhosus* in a marked degree. Among these dyes the group of the azo, and particularly the so-called tetrazo dyes presents the most striking example of differential activity. The tetrazo dyes used for the most part in Lewis' published work and since in this Laboratory for the same purpose, have been derivatives of benzidine, and it has been a working hypothesis with us that in the so-called benzidine configuration there resides some specific property directed against the tubercle bacillus. This activity does not appear to extend to the point of killing the micro-organism

[1] Behring, "Gesammelte Abhandlungen," Leipzig, **1893**, p. 198.

[2] Lewis, *J. Exp. Med.*, **25**, 441 (1917).

and it has also failed to be exerted within the body of the infected animal in spite of the fact that many of the active dyes are capable of localization within the infected areas. It has therefore seemed desirable to attempt the combination of the benzidine configuration with other substances which have more definitely disinfectant properties or which are known to be therapeutically active in other directions. The present work concerns such an attempt with arsenic.

This paper describes the preparation and properties of 4,4-diphenyl-diarsonic acid, $AsO(OH)_2.C_6H_4.C_6H_4.AsO(OH)_2$, which is an arsenic-analog of the benzidine nucleus. As shown below the substance has proved to be very inert in the chemical sense and we have not succeeded in preparing analogs of the benzidine dyes with the arsenical as a nucleus.

The introduction of an arsonic acid group into a ring compound can be accomplished in several ways, but where the mother substance is a diazotizable amine, the method of Bart has been found in this Laboratory to be the easiest and the most satisfactory.[3] This method depends upon the decomposition of the diazonium compound in the presence of a concentrated solution of an arsenite. Specifically, we have proceeded as follows.

A solution of 184 g. of benzidine in 3 liters of water with the addition of 200 cc. of concd. hydrochloric acid was cooled with ice to 5°. An additional 300 cc. of hydrochloric acid was then added, and the solution tetrazotized in the usual manner, 144 g. of sodium nitrite being used for the purpose. The tetrazo solution was stirred for about an hour, and then poured into a solution of 900 g. of sodium arsenite in 1500 cc. of water, 300 cc. of alcohol and 300 cc. of 40% sodium hydroxide, care being taken to keep the reaction mixture alkaline. The resulting solution was slowly heated with a current of steam to 70°. During the heating a considerable evolution of nitrogen occurred, and the liquid frothed greatly. When this froth had largely subsided, acetic acid was added until no further precipitate of tarry substances could be obtained. This by-product was then collected on a filter, and the pale yellow liquid strongly acidified with hydrochloric acid. Diphenyl-diarsonic acid immediately separated as a white, crystalline precipitate.

The material was purified by repeated solution in sodium hydroxide, acidification with acetic acid, filtering, boiling with charcoal and acidification with hydrochloric acid.

Anal. Subs., 0.1015, 0.1030: CO_2, 0.1331, 0.1343; H_2O, 0.0310, 0.0278. Subs., 0.2591, 0.2822: As, 0.0969, 0.1055. Calc. for $C_{12}H_{12}O_6As_2$: C, 35.82; H, 3.01; As, 37.29. Found: C, 35.76, 35.56; H, 3.42, 3.02; As, 37.4, 37.38.

The material is a white, microcrystalline powder composed of masses of branching needles. Its most striking property is its insolubility. Boiling water dissolves it to the extent of 1 part per 1000. Hot sulfuric acid and hot glycerol also dissolve it, apparently without change. Diphenyl-diarsonic acid is neither dissolved nor acted upon by the other mineral acids, nor attacked by bromine or iodine. The substance is peculiarly inert. It is not soluble in any of the common organic solvents. Attempts have been made to sulfonate it, but without success. The material was dis-

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[3] Bart, Ger. pat. 250,264; Eng. pat. 568; U. S. pat. 1,061,587.

solved in hot sulfuric acid, in fuming sulfuric acid and also baked with sulfuric acid after the method of Griess and Duisberg.[4] In every case the original substance was recovered, and no trace of sulfonation was detected.

The material can be shown to be a tetrabasic acid in which all four of the hydrogen atoms are replaceable. By adding standard sodium hydroxide solution to a suspension of the material in water a titration can be made which, with properly selected indicators, shows the neutralization of the first one, then three, and finally (in the presence of salt to produce a common-ion effect) of four hydrogens.

This titration furnishes evidence that diphenyl-diarsonic acid is a tetrabasic acid and differs from the diphenyl-arsinic-*o*-arsonic acid described by Kalb.[5]

The tetrasodium salt can be prepared by adding to the free acid the theoretical amount of sodium hydroxide and concentrating the solution to the point of crystallization; 50 g. of diphenyl-diarsonic acid requires 20 g. of sodium hydroxide. The salt crystallizes from the very concentrated solution in white columnar crystals (probably hexagonal).

Anal. Subs. (dry), 0.3846: Na_2SO_4, 0.2218. Subs., 0.9978: As, 0.2997. Calc. for $C_{12}H_8O_6As_2Na_4$: Na, 18.78; As, 30.60. Found: Na, 18.67; As, 30.04.

The water of crystallization, found to be 34.26%, appears to correspond to 14 molecules, the calculated value for which is 33.96%.

Anal. Subs., 0.5850: H_2O, 0.2004 (dry 0.3846). Calc. for $C_{12}H_8O_6As_2Na_4.14H_2O$: H_2O, 33.96. Found: 34.26.

The by-product formed in large amounts in the preparation of 4,4-diphenyl-diarsonic acid, consists of a tarry mass, having approximately the same solubilities as the compound itself. The uncrystallizable mass was purified for analytical purposes by solution in aqueous sodium hydroxide, boiling with charcoal and acidification at the boiling point with acetic acid.

Anal. Subs., 0.1235, 0.1137: CO_2, 0.2120, 0.1967; H_2O, 0.0414, 0.0340. Subs., 1.8081: N, 0.0326. Subs., 0.3743: As, 0.0753. Found: C, 46.81, 47.18; H, 3.75, 3.35; N, 1.8; As, 20.12.

The constitution of this material was not investigated further.

The writer wishes to express her gratitude to Paul A. Lewis, who suggested the present investigation, and to acknowledge helpful suggestions and criticisms given by A. K. Balls.

Summary

A tetrabasic acid, 4,4-diphenyl-diarsonic acid, has been prepared from benzidine, together with one of its sodium salts, by means of Bart's reaction. The substance is characterized by its extreme inertness and stability.

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[4] Griess and Duisberg, *Ber.*, **22**, 2459 (1889).

[5] Kalb, *Ann.*, **423**, 39 (1921).