[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

DERIVATIVES OF DIBENZO-ARSENOLE

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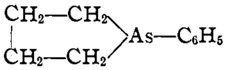
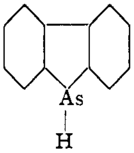
In most of the known organic arsenic compounds, in which arsenic appears as a ring member, this atom occurs as a part of a six-membered ring. Among such series of compounds the methylcyclopentamethylene-arsines[1] are saturated; the other series (phenarsazine and naphtharsazine,[2] phenoxarsine,[3] arsanthrene,[4] 10-chlorophenthiarsine)[5] are unsaturated.

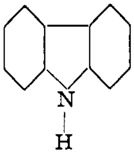
Only one series, phenylcyclotetramethylene-arsine and its derivatives,



is known, in which the arsenic is contained as a hetero atom in a five-membered, saturated ring.[6] The present paper treats of a series of organic arsenic compounds which contain the arsenic atom as a member of an unsaturated, five-membered ring. The type substance I of this series is called dibenzo-arsenole; it is analogous to carbazole (II).



I



II

The dibenzo-arsenole itself was prepared in solution but not isolated by Aeschlimann and his co-workers,[7] who called it *o,o'*-diphenylene-arsine. In this paper the nomenclature of A. M. Patterson is used. Aeschlimann's preparation of the dibenzo-arsenole system from diphenylyl-*o*-arsinic acid differs from the synthesis described below.

The Formation of Dimethoxydibenzo-arsenole Chloride and Its Derivatives

3,3'-Dimethoxydiphenyl[8] served as the starting material for the prepa-

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[1] Grüttner and Wiernik, *Ber.*, **48**, 1479 (1915). Zappi, *Bull. soc. chim.*, [4] **19**, 291 (1916).

[2] Baeyer and Co., Ger. pat. 281,049 (1913); *Friedländer*, **12**, 843 (1913). Wieland and Rheinheimer, *Ann.*, **423**, 1 (1921). Lewis and Hamilton, THIS JOURNAL, **43**, 2222 (1921).

[3] Lewis, Lowry and Bergeim, *ibid.*, **43**, 892 (1921).

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

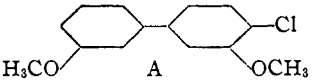
[5] Roberts and Turner, *J. Chem. Soc.*, **129**, 1207 (1926).

[6] Grüttner and Krause, *Ber.*, **49**, 440 (1916).

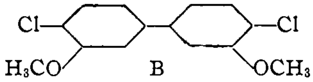
[7] Aeschlimann and co-workers, *J. Chem. Soc.*, **127**, 66 (1925).

[8] Brunner and Witt, *Ber.*, **20**, 1024 (1881). Starke, *J. prakt. Chem.*, [II] **59**, 226 (1899).

ration of the dibenzo-arsenole derivatives. The method of preparing this substance has been so much improved that it is possible to obtain it in yields of 60% from pure dianisidine. Previous yields were only 12%, based on the amount of dianisidine sulfate used. As by-products in this preparation, two new diphenyl derivatives, *p*-chlorodimethoxydiphenyl (A) and di-*p*-chlorodimethoxydiphenyl (B) were isolated.

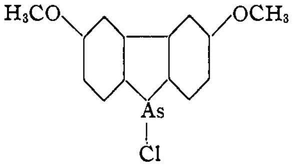


A

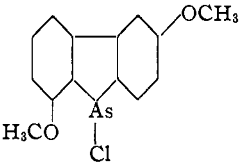


B

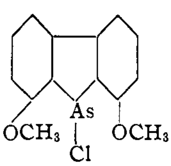
3,3′-Dimethoxydiphenyl was treated with arsenic trichloride and the reaction product recrystallized from xylene. The product corresponds to Formula III, IV or V. Formula III is the more likely structure because of the ready formation of a tetranitro derivative, presumably VII, but a method of definitely deciding among the three possibilities has not yet been found.



III



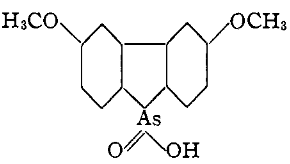
IV



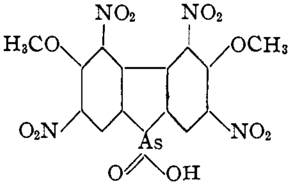
V

It is assumed in the further discussion that III is the correct formula, but it must be understood that the same uncertainty which exists in regard to the structure of this substance exists in regard to the structure of its derivatives.

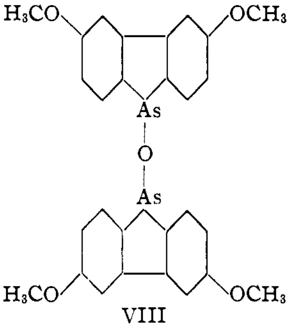
The oxidation of 2,8-dimethoxydibenzo-arsenole chloride (III) in pyridine with hydrogen peroxide yields the 2,8-dimethoxydibenzo-arsenolic acid (VI). Pyridine is a more suitable medium for this oxidation than glacial acetic acid, in which the dimethoxydibenzo-arsenole chloride is only slightly soluble. The nitration of 2,8-dimethoxydibenzo-arsenolic acid in sulfuric acid yields a tetranitro derivative (VII). A peculiar amorphous compound was formed by the action of sodium hydroxide on the 2,8-dimethoxydibenzo-arsenole chloride in a sealed tube at 150°. This substance has the same percentage of carbon and hydrogen as the arsenic oxide (VIII), but does not have the properties to be expected of such a compound. It becomes soft and plastic below 100°.



VI



VII



VIII

Experimental Part

3,3'-Dimethoxydiphenyl Derivatives

I. E. Muskat[9] aided in this work.

3,3'-Dimethoxydiphenyl.—One-half mole (122.2 g.) of purified *o*-dianisidine and 240 cc. of concd. hydrochloric acid (d., 1.18) are used to make a saturated solution of tetra-azo-dianisidine hydrochloride in ice water. This tetra-azo solution, 600 cc., is slowly added to 3 liters of absolute alcohol, kept boiling under a reflux condenser. Two hours is required for the addition. Then the acetaldehyde formed by the reaction is distilled off, together with the alcohol. An aqueous acid solution and a heavy oil remain in the distilling flask. The oil is extracted with ether and the ethereal solution shaken with sodium hydroxide to remove alkali-soluble impurities, washed with water and dried over calcium chloride. The ether is distilled off and the residual oil is heated for two hours on the water-bath. The oil is then distilled twice in a vacuum. If pure it boils at 198° (14 mm.). It solidifies at 35.5°, forming very large crystals; yield, 56 g. or 51.5% (based on dianisidine sulfate used). This yield was improved to 60% by adding 1 g. of copper powder to the alcohol, previous to the addition of the tetra-azo solution.

When copper is used, the reaction product must be subjected to fractional distillation because of the simultaneous formation of mono- and di-*p*-chlorodimethoxydiphenyl. The distillation was performed at 15 mm. and the distillate cut into the three following fractions: (A) 70.5 g. of 3,3'-dimethoxydiphenyl, b. p. 211–220°; (B) 17.0 g. of 4-chloro-3,3'-dimethoxydiphenyl, b. p. 220–225°; (C) 3.7 g. of 4,4'-dichloro-3,3'-dimethoxydiphenyl, b. p. 225–231°. A residue of 4.5 g. of the latter compound remained in the flask. All three fractions solidified when cooled overnight at 0°.

4-Chloro-3,3'-dimethoxydiphenyl.—The 3,3'-dimethoxydiphenyl was removed from the middle fraction B by washing the solidified fraction with cold ether. Small crystals were thus obtained; m. p., 74°. This compound was shown by analysis to be 4-chloro-3,3'-dimethoxydiphenyl. It is not very soluble in cold ether, acetone, ligroin (high-boiling) or absolute alcohol; it is very soluble in these solvents when warmed. It is soluble also in benzene, chloroform and glacial acetic acid.

Mol. wt. (Ebullioscopic method). Subs., 0.2872, 0.3407: Δt, 0.048, 0.057°. Calcd. for $C_{14}H_{13}O_2Cl$: mol. wt., 248.5. Found: 247.2, 247.5; av., 247.3.

Anal. Subs., 0.2784, 0.2392: CO_2, 0.6845, 0.5947; H_2O, 0.1329, 0.1156. Subs., 0.3007, 0.3006: AgI, 0.5451, 0.5354. Subs., 0.1372, 0.1238: AgCl, 0.0760, 0.0696. Calcd. for $C_{14}H_{13}O_2Cl$: C, 67.6; H, 5.2; OCH_3, 24.9; Cl, 14.2. Found: C, 67.1, 67.8; H, 5.3, 5.4; OCH_3 (Zeisel), 23.9, 23.5; Cl, 13.74, 13.90.

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[9] Muskat, *Master's Dissertation*, University of Chicago, June, 1925.

4,4'-Dichloro-3,3'-dimethoxydiphenyl.—The solidified, high-boiling fraction C of the distillate was recrystallized several times from absolute alcohol. A substance was finally obtained which had a constant melting point of 130°. This compound was shown by analysis to be 4,4'-dichloro-3,3'-dimethoxydiphenyl. It also may be recrystallized from ligroin or glacial acetic acid. It is fairly soluble in cold ether, chloroform and acetone, and very soluble in benzene.

Anal. Subs., 0.1863, 0.2320: CO_2, 0.4035, 0.5027; H_2O, 0.0720, 0.0907. Subs., 0.0839, 0.2431, 0.0919: AgCl, 0.0834, 0.2401, 0.0907. Calcd. for $C_{14}H_{12}O_2Cl_2$: C, 59.36; H, 4.2; Cl, 25.1. Found: C, 59.10, 59.10; H, 4.3, 4,3; Cl, 24.6, 24.4, 24.4.

Derivatives of Dibenzo-arsenole

2,8-Dimethoxydibenzo-arsenole Chloride (III).—Forty-three g. of 3,3'-dimethoxydiphenyl and 39 g. of arsenic trichloride were placed in a flask which was fitted by a ground-glass joint to a condenser. The mixture was then refluxed for about six hours. The reaction product was poured into 80 cc. of hot xylene. The xylene solution was boiled with Norite and filtered. When the filtrate was cooled, a yellowish, crystalline precipitate appeared, but the separation was not complete until the mixture had been allowed to stand for two days. The precipitate was removed by filtration and recrystallized from xylene. Sixteen g. of very pure 2,8-dimethoxydibenzo-arsenole chloride was obtained as a yellowish, crystalline product; m. p., 198–199°. It is soluble in nitrobenzene and pyridine, and insoluble in all other organic solvents, as well as in concd. sulfuric acid.

The chlorine in 2,8-dimethoxydibenzo-arsenole chloride is very firmly bound. A portion of this substance was heated with molecular silver in xylene at 100° and shaken for 12 hours, but the original material was recovered unchanged.

The qualitative test for arsenic is positive.

Anal. Subs., 0.4389, 0.2490: CO_2, 0.8388, 0.4755; H_2O, 0.1551, 0.0880. Subs., 0.2184, 0.3476, 0.7191: AgCl, 0.0940, 0.1469, 0.3110. Calcd. for $C_{14}H_{12}O_2ClAs$: C, 52.09; H, 3.75; Cl, 10.99. Found: C, 52.12, 52.07; H, 3.95, 3.95; Cl, 10.70, 10.50, 10.70.

2,8-Dimethoxydibenzo-arsenolic Acid (VI).—Nine g. of 2,8-dimethoxydibenzo-arsenole chloride was dissolved in 75 cc. of pyridine, and 4.5 cc. of Perhydrol (Merck 30%) was added at 45°. The temperature was not allowed to rise above 65°. After a quarter of an hour, during which the mixture was stirred, the solution was diluted with water to four times its original volume and then acidified with hydrochloric acid. The 2,8-dimethoxydibenzo-arsenolic acid separated first in a colloidal state, but soon became crystalline. It was redissolved several times in alcohol and reprecipitated with acid in order to purify it. When pure it is a white powder; decomp. point, 220°.

Anal. Subs., 0.1145, 0.2796: CO_2, 0.2212, 0.5403; H_2O, 0.0453, 0.1106. Calcd. for $C_{14}H_{13}O_4As$: C, 52.49; H, 4.09. Found: C, 52.68, 52.69; H, 4.43, 4.43.

Titration. Subs., 0.6400, 0.6400: moles of NaOH, 0.00193, 0.00194. Calcd. for $C_{14}H_{12}O_2Cl_2$: 0.00200 mole.

1,3,7,9-Tetranitro-2,8-dimethoxydibenzo-arsenolic Acid (VII).—Four and two tenths g. of arsenolic acid (VI) was dissolved in 40 cc. of concd. sulfuric acid (98%). Fuming nitric acid (7 cc.; d., 1.6) was added during 20 minutes at 25–30° and the mixture allowed to stand for 18 hours. When water was added a copious precipitate was formed. This was collected on a suction funnel. Recrystallized from glacial acetic acid, it yielded 1.2 g. of the pure product—a yellow powder. The product is highly insoluble in hot ether, hot benzene or hot, chloroform. For analysis it must be dried at 115° because it seems to retain acetic acid of cystallization. It is very sensitive to light, turning reddish when illuminated; decomp. point, 265°.

Anal. Subs., 0.2367, 0.2634: CO_2, 0.2890, 0.3226; H_2O, 0.0406, 0.0457. Subs., 0.2649, 0.2892: N_2, 26.6, 28.6 cc. (23°, 731 mm.; 24°, 738 mm.). Calcd. for $C_{14}H_9O_{12}N_4As$: C, 33.6; H, 1.81; N, 11.2. Found: C, 33.3, 33.4; H, 1.92, 1.94; N, 11.13, 11.05.

Product Formed from the 2,8-Dimethoxydibenzo-arsenole Chloride in Alkaline Medium.—Five g. of 2,8-dimethoxydibenzo-arsenole chloride was heated with 20 cc. of 10% sodium hydroxide solution for six hours in a sealed tube at 150–160°. After opening the tube, the plastic residue was extracted thrice with hot water. It was then dissolved in pyridine and reprecipitated with water in order to purify it. This process was repeated four times. An amorphous substance was obtained, softening at about 85°.

The carbon and hydrogen content corresponded to Formula VIII. However, such a substance should have a very high melting point, thus it is not probable that the material described is really the oxide. This substance is exceedingly insoluble and could not be obtained in crystalline form.

Anal. Subs., 0.2111, 0.3024: CO_2, 0.4423, 0.6343; H_2O, 0.0822, 0.1186. Calcd. for $C_{28}H_{24}O_5As_2$: C, 56.94; H, 4.1. Found: C, 57.13, 57.20; H, 4.36, 4.39.

I wish to express my thanks and appreciation to the International Education Board in New York for the financial aid which made this work possible.

Summary

The following derivatives of dibenzo-arsenole have been prepared: (1) 2,8-dimethoxydibenzo-arsenole chloride, (2) 2,8-dimethoxydibenzo-arsenolic acid, (3) 1,3,7,9-tetranitro-2,8-dimethoxydibenzo-arsenolic acid. They contain arsenic as a member of an unsaturated five-membered ring.

CHICAGO, ILLINOIS

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

POLYHYDROXY-ANTHRAQUINONES. VII. STRUCTURE AND SYNTHESIS OF HYDROXY-ANTHRARUFIN AND OF RUFIOPIN

BY S. V. PUNTAMBEKER[1] WITH ROGER ADAMS

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In recent papers[2] from this Laboratory, a method of condensing opianic acid with *p*-bromophenols to give phthalides was described in which the union has taken place in a position *ortho* to the hydroxyl. Upon reduction of these phthalides, benzylbenzoic acids were produced and at the same time the halogen was removed. These were dehydrated to anthrones, the latter oxidized to methylated anthraquinones, and then the anthraquinones demethylated. The method has now been applied to the syn-

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[1] This communication is an abstract of a thesis submitted by S. V. Puntambeker in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] (a) Jacobson with Adams, THIS JOURNAL, **46**, 2788 (1924). (b) Graves with Adams, *ibid.*, **45**, 2439 (1923). (c) Gardner with Adams, *ibid.*, **45**, 2455 (1923). (d) Jacobson with Adams, *ibid.*, **46**, 1312 (1924); (e) **47**, 283, 2011 (1925).