an hour. The action was very vigorous at first and the solution became a dark-colored, viscous mass. This was dissolved in water and treated with nitrous gases, when much heat was evolved with the formation of a dark, oily product. This oil was separated and allowed to stand until the change into a yellow product was complete. On recrystallization from acetic acid the substance melted at 83°, and was identified as *p*-nitrobenzylcyanide.

Anthraquinone. Preparation of β-Nitro-anthraquinone.

A mixture of 10 g. of anthraquinone and 10 cc. of fuming sulfuric acid was heated on a paraffin bath for about 2 hours, and the product dissolved in water and treated with nitrous gases. When reaction was complete, the solution was evaporated and a yellow solid obtained. It was soluble in chloroform and acetone, from which on crystallization a product melting at 180° was obtained, which was identified as β-nitro-anthraquinone.

Additional investigations along similar lines are being made.

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TETRAPHENYLDIARSINE.

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The earliest attempt to prepare tetraphenyldiarsine was made by LaCoste and Michaelis[1] who heated diphenylchloroarsine, $(C_6H_5)_2AsCl$, with zinc in a sealed tube at 100°. The crystalline body they obtained melted at 154°, and analyses showed 53.01% carbon instead of 62.88%, the theoretical value. Lack of material prevented them from making further examination of this body.

Two years later Michaelis and C. Schulte[2] reported the preparation of tetraphenyldiarsine by heating tetraphenyldiarsine oxide, $(C_6H_5)_4As_2O$, in absolute ethyl alcohol with phosphorous acid. It was found to be a crystalline body, melting at 135°. The substance oxidized readily in the air forming the anhydride of diphenyl arsenic acid, $(C_6H_5)_4As_2O_3$.

Later, Michaelis[3] reported its preparation by heating an alcoholic solution of diphenylarsenic acid, $(C_6H_5)_2AsOOH$, for 10 hours with a large excess of phosphorous acid. It was described as a crystalline body spontaneously combustible in air. The oxidation product of the substance in a stream of carbon dioxide containing some oxygen was identified as tetraphenyldiarsine oxide.

More important work was done by Schlenk[4] who determined the

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[1] *Ann.*, **201**, 222 (1880).

[2] *Ber.*, **15**, 1952 (1882).

[3] *Ann.*, **321**, 148 (1902).

[4] *Ibid.*, **394**, 216 (1912).

molecular weight of tetraphenyldiarsine. On the basis of one measurement he concluded that the body does not dissociate at the boiling point of benzene.

In view of the fact that some aromatic derivatives of ethane[1] and of hydrazine[2] dissociate with the production of free radicals capable of independent existence, it was considered worth while to redetermine the molecular weight of tetraphenyldiarsine and to measure its iodine and oxygen absorption with the hope of securing evidence of dissociation into radicals of the type $(C_6H_5)_2As^-$.

The tetraphenyldiarsine was prepared by means of the following reactions: triphenyl arsine was made from phenylmagnesium bromide and arsenic trichloride.[3] This application of the Grignard reaction was found to be very much more successful than the use of sodium on a mixture of arsenic trichloride and chlorobenzene.[4]

Triphenyl arsine (0.2 mol) and arsenic trichloride (0.1 mol), were heated in sealed tubes to 200° for 4 hours.[5] The mixture of diphenylchloroarsine (b. p. 333°) and monophenyldichloroarsine (b. p. 252°) formed was separated into two components by fractional distillation. The monophenyl derivative was then converted into diphenylchloroarsine by the use of mercury biphenyl.[6]

After complete purification of the substance according to the method of Michaelis[7] it was converted into tetraphenylarsine oxide by boiling with a solution of sodium hydroxide.[7] The oxide was extracted from the solution by ether and recrystallized.

Five g. of the oxide was added to 75 cc. of absolute alcohol. 7.5 g. of solid phosphorous acid was added to 75 cc. of absolute alcohol. Both solutions were saturated with dry nitrogen purified from oxygen according to the method of C. Van Brunt.[8] The solutions were mixed in the apparatus shown in drawing (Fig. 1) after it had been filled with nitrogen and thoroughly dried. The solution was boiled for 3 hours. On cool-

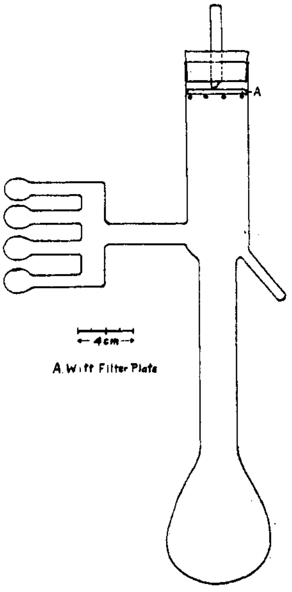

Fig. 1.

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[1] Gomberg, THIS JOURNAL, **22**, 757 (1900), and many later papers.

[2] Weiland, *Ann.*, **381**, 200 (1911); **392**, 127 (1912).

[3] Pfeiffer, *Ber.*, **37**, 4620 (1904).

[4] Phillips, *Ibid.*, **19**, 1031 (1886).

[5] Michaelis and Paetow, *Ann.*, **233**, 64 (1886).

[6] Michaelis and Link, *Ibid.*, **207**, 195 (1881).

[7] Michaelis, *Ibid.*, **321**, 141 (1902).

[8] THIS JOURNAL, **36**, 1448 (1914).

ing, the tetraphenyldiarsine separated as white leaflets. After the mother liquor had been decanted off the crystals were washed by decantation with absolute alcohol and then with dry ether. During the whole process dry nitrogen was passed through the apparatus. The crystals were dried by a stream of warm dry nitrogen and then deposited in the small side tubes by shaking. These were then sealed off without coming in contact with the air.

Pure, dry tetraphenyldiarsine, when exposed to the air, absorbed oxygen. If the crystals were scattered they oxidized in the air without melting, but if in large groups they melted. But the material never became spontaneously inflammable as reported by Michaelis.[1] From the solid oxidation products diphenylarsenic acid, $(C_6H_5)_2AsOOH$ (m. p. 170°) and tetraphenyldiarsine oxide, $(C_6H_5)_4As_2O$ (m. p. 91°) were isolated.

In solution in xylene it showed no color even when heated to 155° in a sealed tube. It was not very soluble in benzene, and at 20° the greatest concentration that could be obtained was about 1%.

Tetraphenyldiarsine reacted with hot alcohol. Fine, needle-shaped crystals were precipitated and the solution became yellowish in color. On evaporation, a yellow oil, with an intense and disagreeable odor, separated. This yellow oil reacted with iodine rapidly and at the same time the solution became acid. On addition of a solution of silver nitrate a yellow precipitate formed which darkened in the light. The compound was identified as diphenylarsine $(C_6H_5)_2AsH$. It had the properties described by Dehn and Wilcox.[2] When oxidized by the air tetraphenyldiarsine was dissolved in dry benzene and allowed to stand with oxygen over it, the absorption of the oxygen slowly approached the quantity necessary for the formation of tetraphenyldiarsine oxide.

A small tube containing tetraphenyldiarsine was broken in absolute benzene which was thoroughly saturated with nitrogen, and at all times there was nitrogen over the solution. The solution absorbed iodine readily and acquired a faint yellow color. This point was noted in each run, but it was not a fixed point. When the solution was older the color appeared with less iodine. The titration with iodine was carried beyond the end-point and the solution allowed to stand. After about 24 hours a crystalline body began to separate from solution. In one run there was a separation of a red oil, but this on standing gradually crystallized. The crude crystals, probably diphenyliodoarsine were brown in color and melted at about 30°.

A tube of tetraphenyldiarsine was broken in an evacuated vessel of one liter capacity. On heating to 200° in an oil bath the vapor pressure developed was about 1 mm. On cooling there was no sign of decomposi-

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[1] *Loc. cit.*

[2] *Am. Chem. J.*, 35, 45 (1906).

tion, and tetraphenyldiarsine crystallized again. On heating to about 300° there was decomposition, and metallic arsenic was deposited on the sides of the container. The container was opened, the contents extracted and recrystallized. The product melted at 59°, corresponding to triphenylarsine. The decomposition may be represented as follows:

$$3(C_6H_5)_4As_2 = 4(C_6H_5)_3As + 2As.$$

It was impossible, therefore, to determine the molecular weight of the compound in the vapor phase.

The molecular weight was determined in naphthalene as a solvent. (K = 6900.)

			M. W.	
Wt. of substance. G.	Wt. of solvent. G.	Δt.	Found.	Calc. for $(C_6H_5)_4As_2$.
0.4088	41.6	0.090°	755	458
0.6389	45.5	0.126°	765	...

Evidently the tetraphenyldiarsine in naphthalene at the freezing point was not dissociated but rather associated.

Conclusion.

Tetraphenyldiarsine, when exposed to air, oxidized to tetraphenyldiarsine oxide and diphenylarsenic acid. In benzene solution it gradually absorbs oxygen sufficient for the formation of tetraphenyldiarsine oxide. The tetraphenyldiarsine absorbs iodine rapidly, and from the solution a crystalline iodide slowly precipitates. It decomposes in hot alcohol, forming diphenylarsine.

Its vapor pressure at 200° is about 1 mm. At 300° it decomposes in a vacuum with the deposition of arsenic and formation of triphenylarsine.

The molecular weight cannot be determined in the vapor phase due to decomposition. In naphthalene it is apparently associated.

The bond between the arsenic atoms is easily broken, oxygen and iodine being rapidly absorbed; but these experiments furnish no evidence of the independent existence of a bivalent arsenic radical.

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