CLXIX.—*Diphenylamine*-p-*arsinic Acid.*

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LIEB and WINTERSTEINER (*Ber.*, 1928, **61**, 107) state that diphenylamine-*p*-arsinic acid has no melting point but decomposes somewhat sharply at 286° with foaming and blackening, and comment on the decomposition point, 265°, recorded by Burton and Gibson (J., 1926, 461).

No specimen of our original preparation being available, we have again prepared the acid and, using a somewhat different method of purification, now find that the melting or decomposition point previously recorded is too low. Diphenylamine-*p*-arsinic acid, about the purity of which there can be little doubt, begins to darken slightly at 287° and decomposes with foaming and blackening at 295—297°. The sodium salt is very sparingly soluble in 25% sodium hydroxide solution and can be obtained crystalline from an even more dilute solution of the alkali. We confirm the description of the magnesium salt and find that the easily prepared *hydrochloride* (m. p. 153—155° with decomp.) is convenient for identification purposes.

Incidentally we have characterised N-*acetyl*-p-*aminodiphenylamine* (p-*acetophenylamidoaniline*), which should have been described as a new compound in the former paper.

EXPERIMENTAL.

N-*Acetyl*-p-*aminodiphenylamine* (p-*Acetophenylamidoaniline*), $C_6H_5{\cdot}N(CO{\cdot}CH_3){\cdot}C_6H_4{\cdot}NH_2$.—To a mixture of *p*-nitroacetyldiphenylamine (22 g.), alcohol (55 c.c.), water (55 c.c.), and acetic acid (5·5 c.c.), iron filings (22 g.) were cautiously added and the whole was gently heated under reflux. After the first vigorous reaction (during which external cooling with water is necessary) was over, the mixture was boiled for

4 hours. The product was mixed with a large volume of alcohol and the solution was filtered without pressure, evaporated to small volume, and diluted with water. The *base*, which was partly precipitated, was removed by repeated extractions with ether, recovered from the extracts by means of dilute hydrochloric acid, and precipitated by concentrated aqueous ammonia as an oil which quickly solidified; after cooling in the ice-chest, it was collected and recrystallised from alcohol or ligroin, separating in colourless, flat, elongated needles, m. p. 127—128° [Found: N, 12·3 (Gibson and Johnson), 12·7 (Burton and Gibson). $C_{14}H_{14}ON_2$ requires N, 12·4%]. On hydrolysis with boiling dilute hydrochloric acid it gave *p*-aminodiphenylamine, m. p. 73° after recrystallisation from ligroin (b. p. 60—80°) (compare Fischer and Wacker, *Ber.*, 1888, **21**, 2614).

Diphenylamine-p-*arsinic Acid.*—The conversion of *N*-acetyl-*p*-aminodiphenylamine (31·3 g.) into crude *N*-acetyldiphenylamine-*p*-arsinic acid by means of the Bart reaction was carried out as previously described (Burton and Gibson, *loc. cit.*). The crude acid was dissolved in warm 25% sodium hydroxide solution (60 c.c.), and the sodium salt obtained on cooling was filtered off as completely as possible, dried on porous earthenware, and dissolved in warm water. Acidification of the cooled solution precipitated a slightly discoloured solid, the m. p. of which, 260—271° (decomp.), showed that some hydrolysis of the *N*-acetyldiphenylamine-*p*-arsinic acid had taken place. Hydrolysis was completed by boiling the crude acid (10·5 g.) with alcohol (21 c.c.) and hydrochloric acid (21 c.c.) for 1 hour and pouring the product into water. The precipitated acid was dissolved in a boiling dilute solution of ammonia and the solution was decolorised with charcoal and filtered while hot. The filtrate was again heated to boiling, acidified with dilute hydrochloric acid, treated with charcoal, and filtered. Long, fine, colourless needles of diphenylamine-*p*-arsinic acid separated from the hot solution and were dried over potassium hydroxide in a vacuum desiccator. On being heated, the acid melted at 295—297° with frothing and blackening after slight darkening at 287° (compare Lieb and Wintersteiner, *loc. cit.*) (Found: N, 4·8; As, 25·8. Calc.: N, 4·8; As, 25·6%).

When a solution of diphenylamine-*p*-arsinic acid (0·95 g.) in hot alcohol (5·0 c.c.) and hydrochloric acid (20 c.c.) cools, the *hydrochloride* is deposited in small, colourless needles, m. p. 153—155° (decomp.). It turns somewhat green during the decomposition, which is preceded by slight darkening and shrinking at about 148° (Found: Cl, 10·8. $C_{12}H_{12}O_3NAs,HCl$ requires Cl, 10·75%). The sodium salt of diphenylamine-*p*-arsinic acid separates from its solution in warm 25% sodium hydroxide on cooling in fine colourless needles. The solution has a marked tendency to remain supersaturated at the ordinary temperature.

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