

103. *Conversion of 3-Nitro-4-methylphenylarsonic Acid into 3-Amino-4-carboxyphenylarsonic Acid by Intramolecular Dismutation, and the Action of Hydrobromic Acid on m-Arsanilic Acid and 3-Amino-4-carboxyphenylarsonic Acid.*

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PREUSS and BINZ (*Z. angew. Chem.*, 1900, **16**, 385) state that anthranilic acid is formed in 20% yield when *o*-nitrotoluene (2 parts) and sodium hydroxide (2 parts) in water (1 part) are refluxed for five hours (cf. also D.R.-P. 114839), and D.R.-P. 138188 claims that 2-nitro-*p*-toluenesulphonic acid (I; R = SO₃H) yields 3-amino-4-carboxybenzenesulphonic acid (II; R = SO₃H) in good yield by treatment with 30% sodium hydroxide solution. It appeared of interest to ascertain with what yield, if any, the dismutation takes place in the case of 3-nitro-4-methylphenylarsonic acid and -stibonic acid (I; R = AsO₃H₂ and SbO₃H₂ respectively). The latter acid, when treated with aqueous caustic soda of various concentrations, gave none of the desired 3-amino-4-carboxyphenylstibonic acid, but from



3-nitro-4-methylphenylarsonic acid a yield of 10—15% of 3-amino-4-carboxyphenylarsonic acid (II; R = AsO₃H₂) was obtained by refluxing with 30% aqueous sodium hydroxide for 8 hours. The product was identical (isoelectric point, crystalline appearance, fluorescence and spectra of derived azo-dyes) with 3-amino-4-carboxyphenylarsonic acid prepared by the method of Cohen, King, and Strangeways (J., 1931, 3250), the chief difference being in the colour, which, however, showed considerable variation, due to traces of impurity, even when the same method was used. In the absence of any m. p. below 400° identification by means of mixed m. p.'s could not be effected. Both specimens, when heated with hydrobromic acid (*d* 1.58) (cf. Phillips, J., 1930, 2400; Schuster, *Compt. rend.*, 1932, **195**, 611) in a sealed tube at 160° for 8 hours, were converted into *p*-bromoaniline, identified as its acetyl derivative.

In order to obtain information as to the mechanism of this unexpected reaction, similar treatment with fuming hydrobromic acid at 160° was applied to aniline, *m*-bromoaniline, anthranilic acid, and *m*-arsanilic acid. The first two substances were recovered unchanged, the third yielded aniline, and from *m*-arsanilic acid an oil was obtained which gave *p*-bromoacetanilide on acetylation. Since under the above conditions decarboxylation of anthranilic acid takes place, it presumably occurs also with 3-amino-4-carboxyphenylarsonic acid. The mechanism of the replacement of the arsono-group by bromine has been discussed by Prat (*Compt. rend.*, 1934, **198**, 583).

The above results are most easily explained on the assumption that the hydrobromic acid causes fission of the arsono-group as arsenic acid, and that the aniline thus produced is brominated by bromine set free by the conversion of the arsenic from the quinque- to the ter-valent condition. In accordance with this view, after aniline hydrobromide had been heated with hydrobromic acid and arsenic acid in a sealed tube at 160°, *p*-bromo-

aniline hydrobromide (identified as *p*-bromoacetanilide) separated on cooling, but none was obtained when the arsenic acid was omitted or replaced by arsenious oxide. Presumably the bromination occurs on those molecules of aniline temporarily existing as free base, as the aniline ions would be expected to undergo *m*-bromination.

The replacement of the arsono-group by bromine has been advocated by Phillips and by Schuster (*loc. cit.*) as a useful method for identifying arsonic acids. Though our conditions are more drastic than theirs, the abnormal results obtained with *m*-arsanilic acid and 3-amino-4-carboxyphenylarsonic acid indicate the need for caution in the application of the method.

EXPERIMENTAL.

Dismutation of 3-Nitro-4-methylphenylarsonic Acid.—The acid (26 g.) was refluxed for 9 hours with 130 c.c. of 30% aqueous sodium hydroxide and the dark brown solution was then diluted to 200 c.c., filtered, and treated with hydrochloric acid until it was acid to litmus but still alkaline to Congo-red; a white gelatinous precipitate (mainly unchanged acid) separated in small quantity. The filtrate was further acidified until it gave a bluish-purple colour with Congo-red; a light brown, tarry precipitate was formed and filtered off. The filtrate was evaporated to 50 c.c., cooled, and, after removal of sodium chloride, boiled with charcoal and filtered. The solution still gave a bluish-purple colour with Congo-red, and sodium carbonate solution was added until the colour was reddish-purple; on standing over-night, a buff precipitate separated. This was purified by the method of Cohen, King, and Strangeways (*loc. cit.*). Yield, 3.1 g. (Found: As, 29.0. Calc. for $C_7H_8O_5NAs$: As, 28.7%).

Treatment of 3-Amino-4-carboxyphenylarsonic Acid with Hydrobromic Acid.—The arsonic acid (0.5 g., prepared by the above method) was heated in a sealed tube for 8 hours at 160° with hydrobromic acid (5 c.c., *d* 1.58). The crystals of hydrobromide which separated on cooling were collected and the base was liberated with sodium hydroxide and extracted and dried in ether; a further quantity was obtained from the hydrobromic acid mother-liquor. The oily base was heated with acetic anhydride on the water-bath for 30 minutes. The acetyl derivative obtained (0.19 g.) crystallised from ligroin in white needles, m. p. 164—165° alone or mixed with authentic *p*-bromoacetanilide (m. p. 167°). Mixed m. p.'s with *m*-bromoacetanilide (m. p. 84°) and 2:5-dibromoacetanilide (m. p. 172°) gave quite definite depressions.

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