CXXVII.—*Piperonal*-6-*arsonic Acid.*

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AROMATIC arsonic acids containing an aldehyde group have as yet received little attention. Margulies (B.P. 199023) has prepared benzaldehyde-*p*-arsonic acid and salicylaldehyde-4-arsonic acid and Scott and Hamilton (*J. Amer. Chem. Soc.*, 1930, **52**, 4122) have recorded the isolation of benzaldehyde-*m*-arsonic acid in the form of its *p*-nitrophenylhydrazone.

The author's attempts to prepare benzaldehyde-*m*-arsonic acid from *m*-nitrobenzaldehyde after reduction to the amino-compound were unsuccessful. When 6-aminopiperonal was submitted to the Bart–Schmidt reaction, however, *piperonal*-6-*arsonic acid* was obtained. This formed a *semicarbazone* in the normal way, but on treatment with hydroxylamine in neutral solution it gave 3 : 4-*methylenedioxy*-6-*benzarsonic acid* identical with the product obtained from it by oxidation with potassium permanganate.

The Reimer–Tiemann reaction for the preparation of aldehydes has been applied to 2- and 4-hydroxyphenylarsonic acids, but without success.

EXPERIMENTAL.

Piperonal-6-*arsonic Acid.*—16·5 G. of 6-aminopiperonal (Bogert and Elder, *J. Amer. Chem. Soc.*, 1929, **51**, 532), 17 c.c. of water, and 16·8 c.c. of concentrated hydrochloric acid were cooled to 0° and treated with sodium nitrite (3·5 g.) in water (35 c.c.). After 15 minutes, sodium arsenite (6·0 g. of arsenious oxide, 7·0 g. of sodium hydroxide, 80 c.c. of water, and 4 c.c. of copper acetate solution) was added, and the mixture heated for 30 minutes on the water-bath. The filtered solution was treated with concentrated hydrochloric acid, and whilst faintly alkaline filtered from amorphous material. The *arsonic acid* separated when the solution was acid to Congo-paper (yield, 12·0 g.; 43·8%). Recrystallised from dilute hydrochloric acid, it formed clusters of anhydrous, colourless, rectangular prisms, m. p. 268° (decomp.) with previous darkening (Found for material dried at 120° : As, 27·0, 27·2. $C_8H_7O_6As$

requires As, 27·4%). It was sparingly soluble in water and alcohol, crystallising from the latter in small prisms, and very sparingly soluble in glacial acetic acid. The magnesium and calcium salts were amorphous.

The acid was very stable towards boiling 16% hydrochloric acid, 70% of it being recovered after 1 hour; the mother-liquor gave a green coloration with ferric chloride.

After 1 hour's boiling with 25% sodium hydroxide solution, 60% of the acid was recovered. The mother-liquor yielded (*a*) a small amount of solid, obtained from a magnesium salt, which gave an intense blue colour with ferric chloride, and (*b*) a mother-liquor giving the catechol-green colour with ferric chloride solution. As in the case of 3 : 4-methylenedioxyphenylarsonic acid (Balaban, J., 1929, 1088), it has not been found possible to open the methylenedioxy-ring.

The *semicarbazone* crystallised from 2*N*-acetic acid or water in colourless needles, m. p. 213° (efferv.), which contained $2H_2O$ (Found for air-dried material : loss at 100°, 3·65. $C_9H_{10}O_6N_3As,2H_2O$ requires H_2O, 4·9%. Found for material dried at 100° : As, 21·05; N, 12·5. $C_9H_{10}O_6N_3As,H_2O$ requires As, 21·5; N, 12·0%).

3 : 4-*Methylenedioxy*-6-*benzarsonic acid* crystallised from water in pale yellow, boat-shaped plates, which did not melt at 300° and retained $1H_2O$ after being dried at 100° (Found for air-dried material : loss at 100°, 3·6. $C_8H_7O_7As,1{\cdot}75H_2O$ requires for loss of 0·75 H_2O, 4·2%. Found for material dried at 100° : As, 24·4. $C_8H_7O_7As,H_2O$ requires As, 24·3%). The barium salt crystallised in rosettes of needles. The arseno-compound obtained on reduction of the above acid was soluble in sodium bicarbonate, the presence of a carboxyl group thus being confirmed.

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