

95. *Derivatives of Benzaldehyde-p-arsonic Acid.*

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BENZALDEHYDE-*p*-ARSONIC acid and a number of its derivatives have already been described (J., 1931, 2388). This acid also undergoes condensation with such acids as malonic acid and cyanoacetic acid: *p*-arsonobenzylidenemalonic acid, $\text{H}_2\text{O}_3\text{As}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{C}(\text{CO}_2\text{H})_2$, results in the former case and *cinnamionitrile-p*-arsonic acid, $\text{H}_2\text{O}_3\text{As}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CN}$, in the latter. These examples indicate the reactivity of the aldehydo-group in benzaldehyde-*p*-arsonic acid and indicate that this compound may be a useful starting material for the preparation of unsaturated compounds containing the arsonic acid group. In view of the results previously described (*loc. cit.*), such compounds may have chemotherapeutic properties.

The *dichloroarsine*, *arsenious oxide* and the *arseno*-compounds derived from benzaldehyde-*p*-arsonic acid are also described.

p-Arsonobenzylidenemalonic Acid.—Benzaldehyde-*p*-arsonic acid (2.75 g.) and malonic acid (1.25 g.), dissolved in AcOH (12 c.c.), are heated on the water-bath for 1 hr. and the ppt. which separates on cooling is recrystallised from aq. AcOH (60%), forming colourless acicular needles, unmelted at 300° (Found: As 23.9; equiv., 82.5. $\text{C}_{10}\text{H}_8\text{O}_7\text{As}$ requires As, 23.7%; equiv., 79). The acid is readily sol. in H_2O and less sol. in AcOH.

Attempts to condense benzaldehyde-*p*-arsonic acid under similar conditions with ethyl malonate and malonamide were unsuccessful.

Cinnamionitrile-p-arsonic Acid.—Under similar conditions benzaldehyde-*p*-arsonic acid (2.3 g.) and cyanoacetic acid (0.85 g.) are condensed in AcOH (5 c.c.). The *product*, which separates when the mixture is kept for some hours at a low temp., crystallises from AcOH, in which it is readily sol., in colourless crystals, unmelted at 300°. It is sol. in H_2O and EtOH and insol. in Et_2O and C_6H_6 (Found: N, 5.1; As, 30.1. $\text{C}_9\text{H}_8\text{O}_3\text{NAs}$ requires N, 5.5; As, 29.7%).

So far it has not been found possible to obtain *p*-arsonocinnamic acid from *p*-aminocinnamic acid by the Bart-Schmidt reaction.

Benzaldehyde-p-dichloroarsine, $\text{AsCl}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, was prepared by reducing a solution of the arsonic acid in EtOH-HCl aq., containing a trace of I, with SO_2 . The oil rapidly solidified and then crystallised from C_6H_6 -ligroin (b. p. 60–80°) in pale yellow needles, m. p. 105° (Found: Cl, 27.5. $\text{C}_7\text{H}_5\text{OCl}_2\text{As}$ requires Cl, 28.3%).

Benzaldehyde-p-arsenious oxide, $\text{AsO}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, is obtained by passing CO_2 into a solution of the dichloroarsine in warm NaOH aq. The pptd. gum rapidly solidifies and is washed with H_2O . The *compound* cannot be recrystallised and has m. p. 232° (previous softening) (Found in specimen dried at 110°: As, 37.7. $\text{C}_7\text{H}_5\text{O}_2\text{As}$ requires As, 38.2%).

4 : 4'-Dialdehydroarsenobenzene, $(\text{CHO}\cdot\text{C}_6\text{H}_4\cdot\text{As})_2$, is obtained by boiling a solution of benzaldehyde-*p*-arsonic acid (2 g.) in hot H_2O (10 c.c.) for a few mins. after addition of hypophosphorous acid (*d* 1.14; 10 c.c.) and then keeping it for a few mins. on the water-bath. The pale yellow solid is washed with H_2O . It cannot be recrystallised and decomposes at 240° (Found: As, 40.6. $\text{C}_{14}\text{H}_{10}\text{O}_2\text{As}_2$ requires As, 41.6%).

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