NOTE.

The Preparation of 4-Acetamido-2-hydroxyphenylarsenoxide. By MONTAGUE A. PHILLIPS.

4-ACETAMIDO-2-HYDROXYPHENYLARSENOXIDE has hitherto been obtained from the corresponding arsonic acid by reduction with sulphurous acid (Cohen, King, and Strangeways, J., 1932, 2509), but the yield recorded by these authors could not be obtained in these laboratories and never exceeded 10%. The product was difficult to purify and considerable amounts of inorganic arsenic compounds were found in mother-liquors. This oxide has now been obtained in good yield by the following convenient method.

p-*Benzarsenious Acid* (compare Mann, J., 1932, 966).—*p*-Benzarsonic acid (50 g.) was dissolved in concentrated hydrochloric acid (500 c.c.) by boiling. To the solution, cooled to 40°, was added 10% potassium iodide solution (10 c.c.) and sulphur dioxide was passed for 2 hours. The *p*-carboxyphenyldichloroarsine so formed was collected, washed with concentrated hydrochloric acid, and drained on a porous tile. Solution in water (600 c.c.) by means of the requisite amount of 25% sodium hydroxide solution and precipitation by 2N-sulphuric acid after filtration (just acid to Congo-red) gave *p*-benzarsenious acid (39 g., 83% of the theoretical amount) (Found: As, 32·5. Calc.: As, 32·6%).

Biscarboxymethyl 4-Acetamido-2-hydroxyphenylthioarsinite.—Barium thiolacetate (crude, 105 g., corresponding to 35 g. of thiolacetic acid) was dissolved in water (240 c.c.) by means of concentrated hydrochloric acid (140 c.c.). Sufficient 2N-sulphuric acid was added completely to remove the metal as sulphate, and after addition of charcoal (5 g.) the liquid was filtered. The solids were washed with water (twice with 50 c.c.), and the filtrate neutralised with cooling with 25% sodium hydroxide solution. To the solution of sodium thiolacetate so obtained was added 4-acetamido-2-hydroxyphenylarsonic acid (24·5 g.), and the solution again adjusted to litmus with caustic soda solution. On stirring, solution ensued; the filtered solution (charcoal) was acidified to Congo-red with hydrochloric acid, the thioarsinite being precipitated as an oil which soon crystallised. Purified by reprecipitation of its solution in 2N-sodium hydroxide with hydrochloric acid, the pure *thioarsinite* was obtained in 90% yield, m. p. 160—161° (Found: As, 18·4. $C_{12}H_{14}O_6NS_2As$ requires As, 18·4%). This aryl thioarsinite (120 g.) was suspended in water (600 c.c.) and dissolved by means of sufficient 10% sodium hydroxide solution to give a solution neutral to litmus. A neutral solution of *p*-benzarsenious acid (65 g.) in water (600 c.c.) and 10% sodium hydroxide was similarly prepared and the solutions were mixed at 35°. After a few seconds delay, a crystalline precipitate of the arsenoxide was formed; this was collected, washed with water, and dried in a vacuum over sulphuric acid. It weighed 57 g. (73% of the theoretical amount) and had all the properties ascribed to it by Cohen, King, and Strangeways (*loc. cit.*) (Found: As, 29·9; N, 5·6. Calc. for hemihydrate: As, 30·0; N, 5·6%).

From the filtrate by acidification with hydrochloric acid was obtained crude biscarboxymethyl 4-carboxyphenylthioarsinite. Purified by reprecipitation of its solution in caustic alkali with mineral acid, it weighed 80 g. and melted at 176° alone or mixed with a preparation obtained from *p*-benzarsonic acid and thiolacetic acid by Barber's method (J., 1929, 1020). The above arsenoxide can also be obtained in the same yield by substituting the equivalent amount of bis-*o*-carboxyphenyl 4-acetamido-2-hydroxyphenylthioarsinite for the other arylthioarsinite in the above preparation. In neither case was any inorganic arsenic compound detected.

5-Acetamido-2-hydroxyphenylarsenoxide could not be obtained under the same conditions, no insoluble precipitate being formed.—RESEARCH LABORATORIES, MESSRS. MAY AND BAKER, LTD., DAGENHAM. [*Received, February 3rd*, 1941.]