224. *A Method for the Synthesis of Tertiary Aromatic Arsines.*

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Aryl diazonium chlorides, or their zinc double salts, $(ArN_2)_2ZnCl_4$, when decomposed, in acetone suspension, by zinc dust in the presence of arsenious chloride, or of a chloroarsine, give good yields of tertiary arsines, *e.g.* :

$$3PhN_2Cl + AsCl_3 + 3Zn = Ph_3As + 3N_2 + 3ZnCl_2$$

The optimum conditions for the synthesis of triphenylarsine from aniline are described, and two examples are given of extensions of the reaction to the synthesis of tertiary arsines which cannot be made so easily by other, previously described, methods.

In 1938 it was shown by one of us (Waters, *Nature*, 1938, **142**, 1077; *J.*, 1939, 867) that aromatic arsenic compounds could be obtained by the direct action of aryl diazonium chlorides on arsenic powder in the presence of acetone. The reaction, however, is not as vigorous as that between aryl diazonium chlorides and antimony (Makin and Waters, *J.*, 1938, 843), and the yield of organo-metallic product is very poor. To obviate this, it was decided to adopt the procedure of Nesmejanov (*Ber.*, 1929, **62**, 1010, 1018; 1935, **68**, 1877) for the preparation of organometallic compounds, and prepare the elementary arsenic *in situ* by the action of zinc dust on arsenious chloride. This method proved to be highly successful: aniline can be converted into triphenylarsine in 65% yield by a single stage process by adding zinc dust to a stirred suspension of zinc benzenediazonium chloride, $(PhN_2)_2ZnCl_4$, in anhydrous acetone containing arsenious chloride. Optimum yields are obtained when the diazonium salt and arsenious chloride are used in equivalent amounts, according to the equation (p. 1029).

If a larger proportion of arsenious chloride is used, the reaction product is a mixture of triphenylarsine with diphenylchloroarsine and phenyldichloroarsine, but though the reaction evidently occurs in stages it does not seem to be practicable to control it to obtain high yields of either of the last two products. Both phenyldichloroarsine and diphenylchloroarsine react, in acetone, with benzenediazonium chloride and zinc dust to give triphenylarsine. Mixed tertiary arsines can be prepared in this way, as illustrated in the experimental section of this paper by the preparation of *diphenyl-β-chlorovinylarsine* from β-chlorovinyldichloroarsine (lewisite-I).

The diazo synthesis of tertiary arsines has not the same limitations as the alternative methods of synthesis involving the use of metallic sodium, or of Grignard reagents, *e.g.*:

$$3PhCl + AsCl_3 + 6Na = Ph_3As + 6NaCl$$

$$Ph_2AsCl + MgEtBr = Ph_2AsEt + MgClBr$$

and, in view of the accessibility of aromatic amines, may prove to be of considerable practical value in synthetic work. The preparation of *tri*-p-*chlorophenylarsine* from *p*-chloroaniline illustrates one such application of the reaction.

Modification of the process by using other metals, or solvents, may of course be possible, but in view of their cheapness and availability it is improbable that zinc dust and acetone can be replaced by more convenient substances. Though the reaction can be effected by using iron filings in place of zinc dust, the yield of triphenylarsine is much less. Again, the reaction will proceed, though not so well, in ethyl acetate. It does not occur in alcohol.

Experimental.

Preparation of Triphenylarsine.—Aniline (300 g., technical quality) in hydrochloric acid (1 l. of concentrated acid + 400 c.c. of water) is diazotised (with 220 g. of sodium nitrite in 250 c.c. of water) and the zinc chloride double salt is precipitated (yield 90%) by adding slowly to the stirred solution at 0° a concentrated solution of zinc chloride (280 g., technical) in dilute hydrochloric acid (120 c.c.). This is filtered off at the pump, pressed free from water, and washed with dry acetone (500 c.c.) until powdery. The retention of even a little moisture at this stage leads to the production of considerable quantities of phenol and tarry by-products, and greatly lowers the final yield.

The dry zinc diazonium chloride (600 g.) is transferred to a large flask, surrounded with a freezing mixture, and stirred vigorously with *dry* acetone (1·5 l.; technical product treated with calcium chloride and decanted is satisfactory) and arsenious chloride (180 g.). Zinc dust (220 g. of 90%) is added in small portions during 2 hours, the temperature being kept below 5°. After being left overnight (or refluxed for 15 minutes) the mixture is filtered, and the filtrate evaporated on a water-bath. The last of the acetone is removed by steam, and the remaining oil is poured into a beaker and stirred with dilute hydrochloric acid (200 c.c.) so that the crude product (300 g.) solidifies in small lumps. This is triphenylarsine of about 68% purity. Pure triphenylarsine can be obtained from this crude solid by melting it under an equal weight of methanol; on cooling the pure product crystallises, leaving all tarry by-products in solution.

Optimum Conditions of Reaction.—The effect of varying the relative quantities of the reagents is shown below:

Yields of arsenicals from 75 g. of aniline.

Quantities of reagents.			Yields of products.		
$AsCl_3$ (g.).	Zn dust (g.).	Acetone (c.c.).	Ph_3As (g.).	% on $PhNH_2$.	% on $AsCl_3$.
27	40	500	34	41	74
36	30	500	39	47	64
45	50	300	52	63	69
45	60	350	56	68	74
49	50	300	52	63	63
72	60	500	Ph_3As, 23·5 g.	Ph_2AsCl, 21 g.	$PhAsCl_2$, 11 g.
100	60	500	,, 8 g	,, 26 g.	,, 20 g.

Tri-p-*chlorophenylarsine.*—This was obtained, by following the same procedure, from *p*-chloroaniline (20 g.), arsenious chloride (9 g.), and zinc dust (10 g.). The *compound* crystallised from light petroleum in needles, m. p. 75°. Yield, 4 g. (Found: C, 52·9; H, 2·95. $C_{18}H_{12}Cl_3As$ requires C, 52·8; H, 2·93%). Its *mercurichloride* crystallised from slightly diluted acetone in white needles, m.p. 235° [Found: C, 31·5; H, 1·72. $(C_6H_4Cl)_3As,HgCl_2$ requires C, 31·7; H, 1·76%].

Diphenyl-β-chlorovinylarsine was prepared in a similar manner from lewisite-I (1 mol.), zinc benzenediazonium chloride (2 mols.), and zinc dust in acetone at 0°. After the removal of the solvent, the product was washed with cold dilute sodium hydroxide solution to decompose any unchanged lewisite, and then was dried and distilled in a vacuum. Fractionation yielded an oil, b. p. 169—170°/3 mm., 161°/2 mm., which was not vesicant (Found: Cl, 12·4; equiv. wt. by iodine titration, 146. $C_{14}H_{12}ClAs$ requires Cl, 12·2%; equiv. wt., 145·3). On being boiled with sodium hydroxide solution it decomposed, evolving acetylene and leaving diphenylarsenoxide.

Note on the Analysis of Aromatic Arsenic Compounds.—The analysis of tervalent aromatic arsenic compounds by titration with iodine in the presence of sodium bicarbonate tends to give trouble, as the oxidation is often slow, but direct titration, in hydrochloric acid, with standard potassium iodate is both rapid and accurate. Individual tertiary arsines are best estimated gravimetrically as their insoluble mercurichlorides, $R_3As,HgCl_2$.

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