

LXXXIV.—*Diphenylarsenious Chloride and Cyanide.* (*Diphenylchloroarsine and Diphenylcyanoarsine.*)

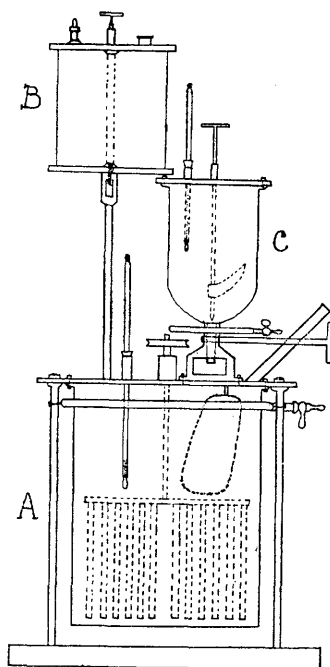
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THE employment of diphenylarsenious chloride as a military poison has led in recent years to many experiments on the preparation of this compound and its intermediates.

In one of these processes, triphenylarsine is the starting point, and this intermediate is produced by Michaelis's modification of the Fittig reaction, in which arsenious chloride, chlorobenzene, and sodium interact in an inert medium (La Coste and Michaelis, *Ber.*, 1878, 11, 1881; *Annalen*, 1880, 201, 215; 1881, 207, 195; 1902, 321, 160; Philips, *Ber.*, 1886, 19, 1031). As practised by these investigators, the process is unsuitable for large-scale operations. The introduction of the whole of the sodium at the commencement of the process renders the operation hard to regulate, and unless great care is taken, the condition of the metal as regards superficial oxidation is likely to vary considerably from one batch to another, so that the onset and course of the reaction are not easily controlled. Moreover, the sludgy form in which the sodium chloride is left at the end of the condensation when carried out under the earlier laboratory conditions leads to further difficulties in the separation of triphenylarsine. The sodium present in large excess at the commencement of the operation certainly sets up side reactions, leading to the formation of diphenyl and ill-defined arsenical products. In the small-scale plant illustrated in Fig. 1, these difficulties were obviated, and the whole operation could be completed without the addition of water, another factor which makes for safety.

The cylindrical, steel reaction vessel (3 litres capacity), fitted

FIG. 1.



with a steel cover rendered gas-tight with an asbestos washer, was supported by four upright steel rods fixed in a trough with a waste-pipe leading to the sink. Round the outside of the reaction vessel, and near the top, a perforated water-pipe was carried concentrically, and attached to the steel supports. By this means, a stream of cold water could be distributed over the outer surface of the reaction vessel, which could also be heated by a rose burner.

The cover of the reaction vessel, *A*, which was perforated to admit a thermometer, carried the following fittings:

(1) A central steel comb stirrer provided with a pulley for mechanical stirring.

(2) A water-cooled steel reflux condenser.

(3) A baffle plate projecting into the vessel to assist in the mixing of the contents and to prevent the rotating liquid from splashing up in the condenser.

(4) A sodium dropping apparatus, *C*, consisting of a cylindrical steel container (1 litre capacity) with a curved bottom perforated at its lowest point with an outlet hole (0.6 cm. in diameter). A steel tap and a sight-feed with transparent silica windows attached to the base of the container enabled the operator to regulate the flow of molten sodium.

A ring burner placed under the base of the sodium container just above the outlet tap was used to keep the metal in a molten condition. The steel cover of the container, made air-tight with an asbestos washer, carried a thermometer and a hand stirrer, shaped to scour the bottom of the container and provided with a sharp prong to dislodge any obstacle in the outlet tap.

(5) A cylindrical glass reservoir, *B*, for liquid (capacity, 800 c.c.) with steel ends, fitted with vertical outlet tube to reaction vessel, a needle valve regulated by a spindle, and a sight-feed with glass window. The steel cover of this reservoir was fitted with a screw-stoppered inlet and with a valve for introducing compressed air, so that the contained liquid was expelled under slight pressure.

Procedure.—Arsenious chloride (276 grams), chlorobenzene (510 grams), and xylene (400 c.c.) were mixed; half the liquid was placed in the reservoir and half in the reaction vessel, where it was diluted with 800 c.c. of xylene. Sodium (210 grams) was introduced into the sodium container and covered with xylene. The reaction vessel was heated to 70° and the sodium container to 110°. Stirring was commenced (speed of rotation, 250–300 revs. per minute), the sight-feed of the sodium apparatus warmed with a Bunsen burner, and molten sodium dropped into the reaction vessel, the rate being regulated by the lower thermometer, the

temperature of which was not allowed to rise above 70° . External cooling was applied when necessary.

After fifteen minutes, the solution from the liquid reservoir was allowed to flow in concurrently with the molten sodium. When all the reagents had been introduced, stirring was continued until the temperature began to fall without external cooling by water. The reaction vessel was then heated to 90° and allowed to cool. At 60° the mixture was filtered through a Bornett press, the granular precipitate of sodium chloride was washed with warm xylene, and afterwards exposed to the atmosphere until any traces of unaltered sodium had been oxidised. The filtrate was distilled up to 220° to remove solvent and chlorobenzene. The liquid residue, on cooling, changed to a pale yellow, crystalline mass of triphenylarsine (m. p. $58-59^{\circ}$). Yield, 383 grams=82 per cent.

The outstanding advantages of this process are as follows:

(1) As sodium is never in excess during the reaction, the process is readily controlled.

(2) Water is excluded from all stages of the preparation, thus eliminating danger from the explosive interaction of sodium and this liquid.

(3) The salt residue is granular and easily filtered.

(4) The product is obtained directly in a state of purity without further treatment.

(5) Other coal-tar hydrocarbons, such as benzene or toluene, can be substituted for xylene as the working fluid in this plant without any material change in the procedure.

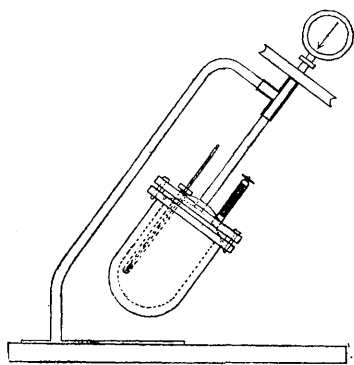
(6) The foregoing apparatus can be employed with advantage for other applications of the Fittig reaction, the gradual addition of clean, unoxidised sodium being a useful improvement on the older processes.

Very favourable results were obtained in the preparation of triphenylstibine. Freshly distilled antimony trichloride (344 grams), chlorobenzene (510 grams), and xylene (400 c.c.) were mixed, and the solution was divided equally between reservoir and reaction vessel. In the latter case, 600 c.c. of xylene were added as diluent. Sodium (210 grams) covered with 500 c.c. of xylene was placed in the sodium container, and the process effected at 70° in the manner already described. After filtering off in the Bornett press the dark grey, granular sodium chloride, the filtrate, on distilling up to 220° , left a residue of triphenylstibine (m. p. $48-50^{\circ}$).

*The Rotating Autoclave.**I. Conversion of Triphenylarsine into Diphenylarsenious Chloride.*

This conversion was carried out in the rotating autoclave, a vessel formed by boring out the steel core of a 6-inch high-explosive shell until the thickness of the wall was about 1.9 cm. The steel cover, which was of similar thickness, was fastened down with twelve bolts and rendered gas-tight with a lead washer. The cover carried a powerful adjustable spring safety valve, a steel thermometer tube projecting into the cavity of the autoclave, and a hollow steel tube carrying an all-steel pressure gauge, which communicated with the interior of the vessel by means of a narrow, bored steel tube dipping into and protected by a concentric steel case partly filled with heavy oil, and having a small aperture at

FIG. 2.



its upper end for admitting the compressed gases from the autoclave. The pressure-gauge tube was fixed in the centre of the cover and fitted with a pulley, so that it also served as the axle of rotation for the autoclave, which was supported and spun in an inclined position. Rotating autoclaves have been made on these lines by Mr. H. Edenborough, of the Technical College, Finsbury, with capacities ranging from 500 c.c. to 9 litres.

The vessel used in the following experiments had a working capacity of 1 litre. A glass lining blown to fit into the cavity of the autoclave was employed in lieu of an enamelled lining.

Procedure.—Triphenylarsine (250 grams) was heated for three hours with 75 grams of arsenious chloride at 250–280°, the pressure attained being about 4.2–7 kilos. per sq. cm. The contents of the autoclave were then distilled in a current of carbon dioxide under a pressure of 20–30 mm., the following fractions being collected:

(a) 150–190°: 68 grams, consisting of phenylarsenious dichloride with 32 per cent. of diphenylarsenious chloride.

(b) 190–220°: 180 grams of diphenylarsenious chloride, 93 per cent.

(c) 220–250°: 7 grams of triphenylarsine with 30 per cent. of diphenylarsenious chloride.

(d) Residue in still when extracted with chloroform yielded 27 grams of unchanged triphenylarsine.

Fraction (b) was cooled and drained, when it yielded 155 grams of colourless, crystalline diphenylarsenious chloride (m. p. 39—40°). The total yield of diphenylarsenious chloride was 66 per cent., of which 53 per cent. was isolated in a state of purity.

Fractions (a) and (c) and the triphenylarsine extracted from (d) were heated to 150° to remove volatile impurities, and returned to the autoclave for a subsequent operation, when 60 per cent. of this material was converted into crystalline diphenylarsenious chloride.

The residues from the second operation were available for further treatment, and the total yield of diphenylarsenious chloride was correspondingly increased. It was also found that 25 per cent. of this product could be frozen out from the contents of the autoclave without distillation.

By the foregoing dry processes, chlorobenzene and arsenious chloride can be converted into crystalline diphenylarsenious chloride without the intervention of water or the use of any aqueous reagent, the overall yield of this product being upwards of 60 per cent.

II. *Diphenylarsenious Chloride from Phenylarsenious Dichloride.*

The foregoing operations showed that the rotating autoclave can also be used with advantage in producing diphenylarsenious chloride from triphenylarsine obtained by the dry process, and phenylarsenious dichloride prepared by Bart's diazo-process (D.R.-P. 250264; Chem. Fabrik. von Heyden, D.R.-P. 264924).

These two reagents when heated for three hours at 250—280° gave a 60 per cent. yield of diphenylarsenious chloride, separated by the above-described fractional distillation.

III. *Diphenylstibine Chloride.*

Triphenylstibine, when heated with redistilled antimony trichloride for three hours at 250—280° in this autoclave, was converted into a mixture of diphenylstibine chloride (m. p. 68—70°) and phenylstibine dichloride (Morgan and Micklethwait, T., 1911, 99, 2295).

IV. *Diphenylarsenious Cyanide.*

(1) *From Diphenylarsenious Oxide.*—Diphenylarsenious oxide immersed in pure anhydrous hydrogen cyanide and left in contact with excess of this reagent for twenty-four hours yielded a yellow

oil which, on seeding with crystals of diphenylarsenious cyanide, solidified to a crystalline solid melting at 28—30° (Sturniolo and Bellinzoni, *Boll. chim. farm.*, 1919, **58**, 409, give m. p. 35°); this product contained 84 per cent. of diphenylarsenious cyanide and 12 per cent. of diphenylarsenious oxide. A similar experiment carried out with 90 per cent. hydrogen cyanide gave a product melting at 29—30°, and containing 87·5 per cent. of diphenylarsenious cyanide.

It was next found that it was quite unnecessary to work with anhydrous hydrogen cyanide in order to obtain diphenylarsenious cyanide. The following three methods, which are based on the use of cyanides of the heavy metals, rendered it possible to dispense entirely with concentrated aqueous solutions of hydrogen cyanide or its alkali salts.

(2) *From Diphenylcacodyl*.—Diphenylarsenious chloride (53 grams) was stirred at 100° with 30 c.c. of commercial hypophosphorous acid (30 per cent.). Diphenylcacodyl (tetraphenyldiarsine) separated in a yield of 83 per cent. This product was heated at 250° with mercuric cyanide in the rotating autoclave in the proportions demanded by the following equation:



The organic product was extracted with benzene, and the yield of diphenylarsenious cyanide was 94 per cent. of the calculated amount.

A similar experiment was carried out with silver cyanide, according to the equation



The result obtained was not so satisfactory.

(3) *From Diphenylarsenious Sulphide*.—Diphenylarsenious chloride was dissolved in benzene and shaken for fifteen minutes with a saturated aqueous solution of sodium sulphide (1½ mols.). The benzene solution, washed with water, dried with anhydrous calcium chloride, and concentrated, yielded a mass of colourless needles of diphenylarsenious sulphide; yield, 93 per cent. After one recrystallisation, the substance melted at 64°.

The foregoing sulphide was mixed with mercuric cyanide in the following proportions and heated for two hours at 160—200°:



The organic product was separated from mercuric sulphide with dry benzene, the yield of diphenylarsenious cyanide being 71 per cent.

Experiments were also carried out, using silver cyanide, according to the equation



The temperature was kept at 160° and the product extracted with dry benzene as before, the yield of diphenylarsenious cyanide being 69 per cent.

(4) *From Diphenylarsenious Chloride.*—After preliminary experiments, the following method was adopted in the preparation of $7\frac{1}{2}$ kilos. of dry, alkali-free diphenylarsenious cyanide. Silver cyanide was prepared quantitatively from silver nitrate by precipitation with a dilute aqueous solution of hydrogen cyanide and dried at 120° .

Diphenylarsenious chloride was heated with a 10 per cent. excess of dry silver cyanide in the glass-lined rotating autoclave for three hours at 150 — 160° . The contents of the autoclave were allowed to cool to 40° , and filtered through a heated filtering apparatus. When the liquid had been thoroughly drained from the silver chloride, the latter was extracted with warm, dry benzene, and the clear solution distilled. The total yield of diphenylarsenious cyanide was about 92 per cent. of the calculated amount. The product, without further purification, melted at 28° , and contained 90 per cent. of the cyanide, the remaining 10 per cent. consisting of diphenylarsenious oxide and chloride.

In this operation, 5 kilos. of silver cyanide were employed, and, after washing with hot benzene until free from organic arsenicals, the residual silver chloride was reduced to silver by fusion with sodium carbonate. Even with an improvised smelting apparatus, the total loss of this metal was less than 2 per cent.

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