XIV.—*Some Analogous Organic Compounds of Phosphorus and Arsenic.*

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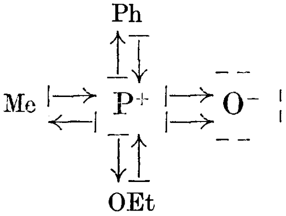
PHENYLMETHYLPHOSPHINIC acid reacts normally with thionyl chloride and *phenylmethylphosphinyl chloride* is easily isolated. The behaviour of this compound is that of a typical acid chloride. It yields an *anilide* and reacts with benzoic acid, giving benzoyl chloride; its reaction with the carboxyl group probably explains the non-production of the *o*-carboxyphenylethylamide of phenylmethylphosphinic acid when it is allowed to react with *o*-ethylaminobenzoic acid. The acid chloride reacts very readily with water and attempts to prepare the amide and anhydride have been unsuccessful. The *methyl* and *ethyl* esters are readily obtained from the acid chloride and the corresponding alcohol. They are both colourless liquids, very readily hydrolysed, and the boiling point of each is below that of the acid chloride.

The parachor (Sugden, J., 1924, **125**, 1177; 1925, **127**, 1868 and succeeding papers) of the ethyl ester has been determined by Dr. Sugden, who finds $[P] = 420{\cdot}5$, compared with $[P] = 417{\cdot}3$ calculated for the presence of a semipolar double bond, whereas, calculated for the presence of a non-polar double bond, $[P] = 442{\cdot}1$. The constitution of the ethyl ester of phenylmethylphosphinic acid may be conveniently represented by the annexed formula.



It will be seen that the outer octet of the phosphorus atom is complete without the oxygen atom, whose octet can only be completed by sharing the two lone electrons with the phosphorus atom, leaving the latter positively and the oxygen atom negatively charged. It is clear that the methyl and ethyl esters should be capable of existing in *lævo-* and *dextro*-optically active forms, whether their constitutions are regarded from the point of view of the electronic hypothesis or because their molecules are asymmetric. In this connexion, Dr. Sugden writes, " I might mention that, in my view, this compound (the ethyl ester), unlike Phillips' sulphinic ester (J., 1925, **127**, 2552), would be asymmetric even if the double bond were non-polar. That, however, is forbidden by the octet rule and the data for this compound give further evidence for the truth of the octet theory." * The fact that these esters are readily hydrolysed explains the reason why the preparation of the amide by the action of ammonia on the esters and of the esters by the action of the alkyl iodides on the silver salt of the acid have so far been unsuccessful. From this work, it is clear that a compound containing the $\colon PO_2H$ grouping reacts very similarly to one containing the $-CO_2H$ grouping.

Phenylmethylarsinic acid was first prepared by Bertheim (*Ber.*,

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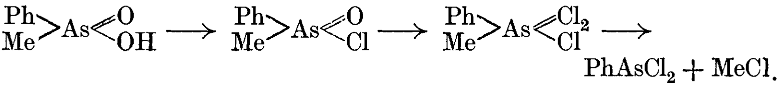
* It is hoped to carry out experiments on the resolution of one or both of the above esters, the supply of which unfortunately is very limited (compare Pope and Gibson, J., 1912, **101**, 735, 740).

1915, **48**, 350). We have prepared it more conveniently from phenylmethylchloroarsine (Burrows and Turner, J., 1920, **117**, 1377; 1921, **119**, 429) by oxidation with chloramine-T (Burton and Gibson, J., 1924, **125**, 2276). It is known that this acid, unlike the corresponding phosphorus acid, is distinctly amphoteric in character. Bertheim (*loc. cit.*) showed that it can be titrated with alkali, with litmus as indicator, and he described the barium, lead and mercury salts as well as the crystalline hydrochloride and nitrate. Diphenylarsinic acid also is amphoteric and forms, for example, barium and copper salts (La Coste and Michaelis, *Ber.*, 1878, **11**, 1886; *Annalen*, 1880, **201**, 231) and also two hydrochlorides and two hydrobromides (Grignard and Rivat, *Compt. rend.*, 1919, **169**, 126); a nitrate also is referred to in the literature ("Organic Arsenical Compounds," Raiziss and Gavron, 1923, p. 366).

Attempts to prepare the ethyl ester of phenylmethylarsinic acid by the action of ethyl iodide on the silver salt have been unsuccessful. Likewise, attempts to isolate the acid chloride from the action of thionyl chloride on the acid have been unavailing and consequently it has been impossible to prepare the esters of this acid by the method used for the preparation of the analogous phosphorus compounds.

The products of the reaction of thionyl chloride on phenylmethylarsinic acid were phenyldichloroarsine and probably methyl chloride, and it is highly probable from the work which is described below that the following series of reactions takes place :



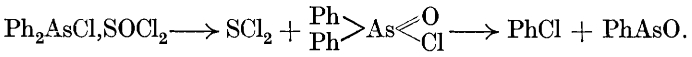
$$\begin{matrix}\mathrm{Ph}\\\mathrm{Me}\end{matrix}\!>\!\mathrm{As}\!<\!\begin{matrix}\mathrm{O}\\\mathrm{OH}\end{matrix} \longrightarrow \begin{matrix}\mathrm{Ph}\\\mathrm{Me}\end{matrix}\!>\!\mathrm{As}\!<\!\begin{matrix}\mathrm{O}\\\mathrm{Cl}\end{matrix} \longrightarrow \begin{matrix}\mathrm{Ph}\\\mathrm{Me}\end{matrix}\!>\!\mathrm{As}\!<\!\begin{matrix}\mathrm{Cl_2}\\\mathrm{Cl}\end{matrix} \longrightarrow \mathrm{PhAsCl_2} + \mathrm{MeCl}.$$

The same products were obtained when phenylmethylchloroarsine was substituted for the phenylmethylarsinic acid. Since, however, the methyl chloride was difficult to isolate, the reaction of thionyl chloride with diphenylchloroarsine and with diphenylarsinic acid was studied. In the case of diphenylchloroarsine, when the reaction was carried to completion, the products identified were phenyldichloroarsine, chlorobenzene and sulphur chloride. When, however, the decomposition was not carried to completion, strong evidence of the presence of diphenylarsinyl chloride was obtained, which later decomposed under the conditions of the experiment.

It is now shown that when thionyl chloride reacts with diphenylchloroarsine a definite colourless crystalline compound is formed. This has the composition $(C_6H_5)_2AsCl,SOCl_2$, and a similar compound is formed when thionyl chloride reacts with diphenylarsinic acid. When the compound $(C_6H_5)_2AsCl,SOCl_2$ is heated under the conditions described later, it decomposes, yielding the volatile products mentioned above, and when the decomposition is carried as far as possible, the residue which remains is, in all probability, phenylarsenious oxide. The results of carrying out as nearly as possible quantitative experiments indicate that the reaction of thionyl chloride with diphenylchloroarsine may be represented by the following equations :

(1) $Ph_2AsCl + SOCl_2 \longrightarrow Ph_2AsCl,SOCl_2$.

(2) $3Ph_2AsCl,SOCl_2 \longrightarrow 2PhAsCl_2 + PhAsO + 3PhCl + SO_2 + S_2Cl_2$.

(3) 

$$Ph_2AsCl,SOCl_2 \longrightarrow SCl_2 + {}^{Ph}_{Ph}{>}As{<}^{O}_{Cl} \longrightarrow PhCl + PhAsO.$$

According to equation (2), 29·15 g. of diphenylchloroarsine should yield 9·8 g. of phenylarsenious oxide and 12·4 g. of chlorobenzene. The amounts obtained were 11·35 and 10·63 g., respectively. If decomposition is going on at the same time according to equation (3), the amount of chlorobenzene produced relative to the amount of diphenylchloroarsine will not vary, but the amount of phenylarsenious oxide will increase considerably. If the decomposition proceeded wholly according to equation (3), 29·15 g. of diphenylchloroarsine would yield 18·5 g. of phenylarsenious oxide. The results obtained, therefore, indicate that the decomposition proceeds largely according to equation (2) and that some diphenylarsinyl chloride is formed which subsequently decomposes as indicated by equation (3).

The work furnished a case of thionyl chloride acting as an oxidising agent and indicates why it is impossible, under the experimental conditions described, to obtain the acid chlorides of phenylmethylarsinic acid and diphenylarsinic acid, the possibility of the preparation of the corresponding esters through these compounds being thereby precluded.

EXPERIMENTAL.

Through the kind co-operation of Sir William Pope, the phosphenyl chloride used for this investigation was the remainder of the preparation made for the original investigations (J., 1912, **101**, 735, 740). This compound was converted into phenylmethylphosphinic acid in the manner already described (*loc. cit.*, p. 741).

Phenylmethylphosphinyl chloride, PPhMeOCl, was obtained in 94% yield by heating phenylmethylphosphinic acid (15 g.) with thionyl chloride (25 c.c.) under reflux for 30 minutes on the water-bath. The excess of thionyl chloride was removed under reduced pressure and the residue was then distilled under the same conditions. The product was obtained as a colourless liquid,

b. p. 155°/11 mm., 167°/22 mm. For analysis, the chloride was decomposed with excess of sodium hydroxide solution, and the chlorine estimated in the usual way (Found : Cl, 20·1, 20·9. C_7H_8OClP requires Cl, 20·3%).

Phenylmethylphosphinyl chloride fumes in air and has an odour reminiscent of thiocarbonyl chloride. It reacts vigorously with water and the above acid, m. p. 134°, is readily obtained. Although a dry ethereal solution of the acid chloride reacts vigorously with dry ammonia, attempts to isolate phenylmethylphosphinamide were unsuccessful.

Phenylmethylphosphinanilide was obtained by carefully adding aniline (2·5 g.) to a solution of the acid chloride (2·5 g.) in dry ether (35 c.c.), allowing the mixture to stand for 15 minutes and then adding water. The pasty solid became granular on grinding with the water. It crystallised from ethyl acetate–ligroin (b. p. 60—80°) in colourless needles, m. p. 142° (Found : N, 6·1. $C_{13}H_{14}ONP$ requires N, 6·1%).

The acid chloride (3·0 g.) reacted vigorously with the sodium salt of the acid (3·5 g., dried at 130°) and the characteristic odour of the former substance rapidly disappeared. Nothing distilled on heating to 210°/20 mm. The product was extracted with benzene, and the solvent removed under diminished pressure; the gummy residue then crystallised and was shown to be phenylmethylphosphinic acid. The anhydride, if formed under the conditions of this experiment, must be very easily hydrolysed to the acid.

When benzoic acid (3 g.) was heated with phenylmethylphosphinyl chloride (3 g.) for 10 minutes on the water-bath, and the product distilled, a liquid (2·0 g.) distilling at 200° was obtained. This was proved to be benzoyl chloride by conversion into benzamide (m. p. 124°) and benzanilide (m. p. 161°). Attempts to prepare the *o*-carboxyphenylethylamide of phenylmethylphosphinic acid were unsuccessful. When equimolecular quantities of the acid chloride and *o*-ethylaminobenzoic acid reacted under the usual conditions, a small quantity of a substance, m. p. 186°, was obtained which contained nitrogen and phosphorus. In another experiment, a substance, m. p. 168°, was isolated, but after standing in air for some time it melted at 134° (m. p. of the acid).

Ethyl phenylmethylphosphinate, PPhMeO·OEt, was prepared by warming the acid chloride (3·9 g.) together with absolute ethyl alcohol (20 c.c.) for a short time on the water-bath, removing the excess of alcohol under diminished pressure, and distilling the residue under similar conditions. The ester is a colourless, highly refractive liquid, b. p. 143°/11 mm. (Found : C, 58·3; H, 7·0; *M*, by saponification, 179·7. $C_9H_{13}O_2P$ requires C, 58·7; H, 7·1%; *M*, 184).

We are very greatly indebted to Dr. S. Sugden for carrying out the following measurements leading to the determination of the parachor, [*P*]: $D^{20^\circ}_{4^\circ}$ 1·107, $D^{36\cdot5^\circ}_{4^\circ}$ 1·093, $D^{64^\circ}_{4^\circ}$ 1·068, whence $D^{t^\circ}_{4^\circ} = 1\cdot125 - 0\cdot00088t$.

App.	*t*.	*P*.	*D*.	ϕ.	γ.	Parachor.
4d	18°	5164	1·109	1·0202	40·92	420·3
4d	42	4772	1·088	1·0215	37·86	420·0
4d	62	4514	1·070	1·0223	35·84	421·2
					Mean [*P*] obsd.	420·5

($r_2 = 0\cdot139$ cm., $A = 0\cdot007767$)

[*P*] calc.: 417·3 (for semipolar double bond), 442·1 (for non-polar double bond).

The ester is readily hydrolysed; on boiling it for a few minutes with 20% aqueous sodium hydroxide and cooling and acidifying the solution, phenylmethylphosphinic acid was obtained. The *methyl* ester, prepared in a similar manner to the ethyl ester, is a colourless, highly refractive liquid, b. p. 137°/11 mm. (Found: C, 56·6; H, 6·7. $C_8H_{11}O_2P$ requires C, 56·5; H, 6·5%). Both esters have an odour like that of the mustard oils and when heated with ammonia in alcoholic solution do not appear to yield the amide.

Phenylmethylarsinic acid was originally prepared from phenyldichloroarsine through the arsine oxide (Bertheim, *loc. cit.*). The following method, which avoids the use of silver salts, does not take so long and gives a better yield. Phenylmethyliodoarsine, prepared from phenyldichloroarsine (Burrows and Turner, *loc. cit.*), was converted through the arsine oxide into phenylmethylchloroarsine (yield 80%, based on the phenyldichloroarsine). The phenylmethylchloroarsine (8·55 g.) in acetone (170 c.c.) was boiled under reflux with a solution of chloramine-T (23·4 g.) in water (230 c.c.) for 1 hour (see Burton and Gibson, *loc. cit.*). The acetone was distilled off, the precipitated *p*-toluenesulphonamide removed from the cooled aqueous solution, the filtrate evaporated to dryness, the residue extracted twice with hot alcohol, and the extracts evaporated to dryness. The residue was extracted twice with warm acetone to remove traces of *p*-toluenesulphonamide, leaving phenylmethylarsinic acid, m. p. 176—177° (yield, 96·5%). The acid may be prepared from phenylmethyliodoarsine by oxidation with chloramine-T or hydrogen peroxide, but the iodine liberated renders its separation somewhat difficult.

In an attempt to prepare ethyl phenylmethylarsinate by means of ethyl iodide (4·0 g.) and the silver salt (7·8 g.), suspended in dry ether, the product decomposed at about 90° when distilled under reduced pressure.

Action of Thionyl Chloride on Phenylmethylarsinic Acid.—When the acid (8·6 g.) and thionyl chloride (24 c.c.) were heated together on the water-bath a vigorous reaction took place, a gas (? methyl chloride) being evolved. After 30 minutes' heating, the excess of thionyl chloride was removed and the residue distilled under reduced pressure. The distillate, a colourless, highly refractive liquid, b. p. 127°/12 mm., was proved to be phenyldichloroarsine by analysis (Found : Cl, 32·6. Calc. : Cl, 32·5%) and by reduction to arsenobenzene (m. p. 201°).

Action of Thionyl Chloride on Phenylmethylchloroarsine.—The chloroarsine (8 g.) was treated with thionyl chloride (12 c.c.) as in the previous experiment, heat being evolved on mixing, although no evolution of gas was noticed until the mixture was heated on the water-bath. After 30 minutes' heating, the thionyl chloride was removed as before. At a higher temperature the product began to decompose. The first fraction of the distillate had the characteristic odour of sulphur chloride and gave a precipitate of sulphur on addition of water. More marked decomposition set in at a slightly higher temperature and a liquid (7·8 g.) distilled at 128°/16 mm. This was proved to be phenyldichloroarsine by its giving arsenobenzene on reduction. The residue in the flask (0·5 g.) was not identified.

Action of Thionyl Chloride on Diphenylchloroarsine.—The following are descriptions of typical experiments.

(*a*) When diphenylchloroarsine (m. p. 37·5° ; 10·55 g.) and thionyl chloride were heated on the water-bath, no reaction appeared to take place until after about 10 minutes' heating. Precipitation of a distinctly crystalline, colourless substance then began and was complete in about 30 minutes. The thionyl chloride was removed as before, leaving the crystalline solid dry and uncontaminated with tarry matter. Under diminished pressure, this melted at 188—192° (bath) and began to decompose at 195° ; the distillate, b. p. 120—125°, had the characteristic odour of chlorobenzene (but a more pungent odour also was noticed) and gave 2 : 4 : 6-trinitrochlorobenzene on nitration. In another experiment, carried out under similar conditions, sulphur chloride, S_2Cl_2, was identified in the distillate.

(*b*) Diphenylchloroarsine (11·44 g.) and thionyl chloride (16 c.c.) were treated as in (*a*), and the excess of thionyl chloride removed by heating the product at 75°/30 mm. for a short time. The distillate had no odour of sulphur chloride and no precipitate of sulphur was obtained when it was mixed with water. The solid residue in the flask had a characteristic odour different from that of thionyl chloride and weighed 16·02 g. [Calc. for $(C_6H_5)_2AsCl,SOCl_2$, 16·59 g.]. It was decomposed by heating to 200—215°/25—30 mm., decomposition not being allowed to proceed too far, and, after cooling, the product was extracted with warm aqueous ammonia; an oil remaining undissolved was removed in ether. From the aqueous solution, on acidification, diphenylarsinic acid was obtained, m. p. 171° after repeated crystallisation from dilute alcohol (Found: As, 28·5. Calc.: As, 28·6%).

(*c*) The preceding experiment was repeated with diphenylchloroarsine (29·15 g.) and thionyl chloride (42 c.c.), but after removal of the excess of the latter substance, the residue was heated at 200—215°/30 mm. until no more distillate was obtained. The final residue (11·35 g.) was shown not to contain diphenylarsinic acid. From the distillate, after extraction with dilute sodium hydroxide solution, 10·63 g. of chlorobenzene were obtained; this may have contained some small quantity of more highly chlorinated benzene derivatives. On acidification with hydrochloric acid, the sodium hydroxide solution gave phenyldichloroarsine, which yielded arsenobenzene on reduction.

Action of Thionyl Chloride on Diphenylarsinic Acid.—From diphenylarsinic acid (15 g.) and thionyl chloride (25 c.c.), by the treatment described in (*a*) above, a solid was obtained which melted at 188—192° and decomposed at about 195°/25 mm., the distillate passing over at 120—135°.* Sulphur chloride, chlorobenzene and phenyldichloroarsine were recognised in the distillate as before.

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