CCCVIII.—*The Formation of Phosphinic Acids from Triarylmethoxyphosphorus Dichlorides.*

By David Runciman Boyd and Frederick James Smith.

The tendency of tervalent phosphorus to acquire a higher valency is strikingly exhibited in the conversion of triphenylmethoxyphosphorus dichloride into triphenylmethylphosphinic acid (Boyd and Smith, J., 1924, **125**, 1477):

$$CPh_3{\cdot}O{\cdot}P^{III}Cl_2 \xrightarrow{\text{alc. KOH}} CPh_3{\cdot}P^{V}O(OEt)(OK).$$

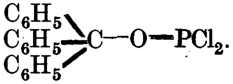
Hydrolysis of the phosphorus chloride is in this case accompanied by a molecular rearrangement involving the transference of the triphenylmethyl radical from oxygen to phosphorus. The hydrolytic decomposition of alkyloxyphosphorus dichlorides usually proceeds, however, on quite different lines, no migration of the alkyl group taking place:

$$RO{\cdot}P^{V}HO(OH) \xleftarrow{H_2O} RO{\cdot}P^{III}Cl_2 \xrightarrow{H_2O} ROH + HP^{V}O(OH)_2$$

In view of the unusual behaviour of the phosphorus chloride derived from triphenylcarbinol it has been thought desirable to investigate the action of hydrolysing agents upon a variety of triarylmethoxyphosphorus dichlorides. The interesting observations of Olivier (*Rec. trav. chim.*, 1922, **41**, 301) and of Lapworth and Shoesmith (J., 1922, **121**, 1391) have shown how greatly the ease of hydrolysis of benzyl halides is affected both by the chemical nature and by the orientation of substituents, and it seemed probable that similar phenomena would be met with in the behaviour of substituted triphenylmethoxyphosphorus chlorides towards hydrolysing agents. The present communication deals with the following compounds:

(I.) (*p*) $X{\cdot}C_6H_4{\cdot}CPh_2{\cdot}O{\cdot}PCl_2(X = NO_2$, Cl, Br, Me, or OMe)
(II.) (*m*) $OMe{\cdot}C_6H_4{\cdot}CPh_2{\cdot}O{\cdot}PCl_2$
(III.) (α and β) $C_{10}H_7{\cdot}CPh_2{\cdot}O{\cdot}PCl_2$.

The parent substance of this group, triphenylmethoxyphosphorus dichloride, is characterised by two peculiarities: (i) its extraordinary stability towards water and aqueous alkalis, (ii) the smoothness with which it undergoes rearrangement to a phosphinic acid under the influence of hot alcoholic potash. In a previous paper, it was suggested that the first step in the hydrolysis of a substance of the type $RO{\cdot}PCl_2$ is the formation of the compound $RO{\cdot}PHCl_2{\cdot}OH$ by addition of the elements of water. On this view the stability towards aqueous alkalis which is shown by the $-PCl_2$ group in triphenylmethoxyphosphorus dichloride may be attributed to a diminution in the free affinity of the phosphorus atom resulting from the enhanced valency demand of the oxygen :



$$(C_6H_5)_3C{-}O{-}PCl_2.$$

On the other hand, the ability of the substance to undergo molecular rearrangement under the influence of alcoholic potash is—it can scarcely be doubted—connected with the capacity for independent existence which is possessed by the radicals $-CAr_3$, and which is exhibited in greater or less degree in the dissociation of the hexa-arylethanes.

Intimately related to this capacity for independent existence on the part of the radicals $-CAr_3$ is the basic character which distinguishes the triarylcarbinols. Measurements of the " basicities " of the different carbinols have therefore been carried out by the method of Baeyer and Villiger (*Ber.*, 1902, **35**, 3020) and the figures obtained are included in the following table, in which the most important properties of the triarylmethoxyphosphorus dichlorides are summarised.

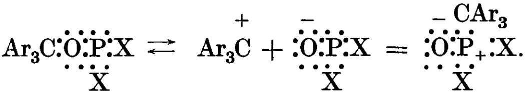
			Properties of $R{\cdot}O{\cdot}PCl_2$.	
Radical.	Basicity of carbinol.	% Yield of phosphinic acid as by-product in preparation of $R{\cdot}O{\cdot}PCl_2$.	Behaviour towards hot aqueous ammonia.	% Yield of phosphinic acid on treatment with alc. KOH.
p-Nitrotriphenylmethyl	0·76		Stable.	*
p-Chlorotriphenylmethyl	0·79	4·7	,,	93
p-Bromotriphenylmethyl	0·89	4·9	,,	90
Triphenylmethyl	1	5	,,	91
m-Anisyldiphenylmethyl	1·28	4·1	,,	80
β-Naphthyldiphenylmethyl	2·04	5·3	,,	77
p-Tolyldiphenylmethyl...	2·56 (2·55)*B*	6·7	,,	75
p-Anisyldiphenylmethyl	6·5 (6·99)*B* (6·3)*A*	9·5	Slowly hydrolysed to carbinol.	Nil.
α-Naphthyldiphenyl methyl	8·0 (8·83)*B*	10·75	Stable.	,,

A, Baeyer and Villiger, *Ber.*, 1902, 35, 3020. *B*, Skraup and Freundlich, *Ber.*, 1922, **55**, 1073.

* Reduction of the nitro-group caused difficulty in this case. An organic acid containing phosphorus was formed, but it was not possible to isolate it in a pure state.

Discussion of Results.

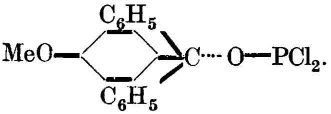
(1) The figures in the last column of the table can only be regarded as approximate values, but they point to the conclusion that a close relationship exists between the " basicities " of the carbinols and the capacities of their phosphorus chlorides to give rise to phosphinic acids under the influence of alcoholic potash. It would appear that there is an optimum position corresponding with a basicity of about 0·75, and that increase of basicity above this figure tends to diminish the yield of phosphinic acid produced by the action of alcoholic potassium hydroxide. If the basicity figures be taken as giving a measure of the dissociating tendencies of the radicals $-\mathrm{CAr_3}$, it may be concluded that, whilst a certain degree of dissociating power on the part of the radical is necessary if a molecular rearrangement of this nature is to take place at all, any increase above this minimum value militates against a simple migration of the $-\mathrm{CAr_3}$ group from oxygen to phosphorus. Greater dissociating power implies greater stability on the part of the free radical, and this will tend to increase its chances of passing out of the sphere of influence of the phosphorus atom. The molecular rearrangement is conveniently represented by the electronic equation :



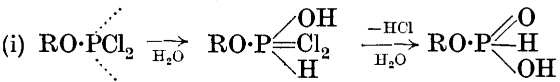
$$\mathrm{Ar_3C{:}\overset{..}{\underset{..}{O}}{:}\overset{..}{\underset{X}{P}}{:}X} \rightleftarrows \overset{+}{\mathrm{Ar_3C}} + \overset{-}{\mathrm{{:}\overset{..}{\underset{..}{O}}{:}\overset{..}{\underset{X}{P}}{:}X}} = \mathrm{{:}\overset{..}{\underset{..}{O}}{:}\overset{-\,CAr_3}{\underset{X}{P_+}}{:}X}.$$

At present there is no evidence to show whether the migration occurs before or after the exchange of Cl for OEt.

(2) Of the phosphorus chlorides investigated, the only one which does not resist prolonged treatment with hot aqueous ammonia is that derived from *p*-anisyldiphenylcarbinol. This fact appears, at first sight, to contradict the view previously developed with regard to the hydrolysis of compounds of the type $\mathrm{R{\cdot}O{\cdot}PCl_2}$, according to which the stability of the $\mathrm{PCl_2}$ group in the *p*-anisyl derivative should be greater than that of the same group in the parent substance :



In a molecule of this type, however, there are two points at which hydrolytic attack may occur :



$$\text{(i)}\quad \mathrm{RO{\cdot}PCl_2} \xrightarrow[H_2O]{} \mathrm{RO{\cdot}P}\begin{cases}\mathrm{OH}\\ \mathrm{Cl_2}\\ \mathrm{H}\end{cases} \xrightarrow[H_2O]{-HCl} \mathrm{RO{\cdot}P}\begin{cases}\mathrm{O}\\ \mathrm{H}\\ \mathrm{OH}\end{cases}$$

$$\text{(ii)}\quad \mathrm{R{\vdots}O{\cdot}PCl_2} \xrightarrow[H_2O]{} \mathrm{R{\cdot}OH + HO{\cdot}PCl_2} \longrightarrow \mathrm{R{\cdot}OH + HO{\cdot}P}\begin{cases}\mathrm{O}\\ \mathrm{H}\\ \mathrm{OH}\end{cases};$$

and since the products obtained by the action of hot aqueous ammonia upon *p*-anisyldiphenylmethoxyphosphorus dichloride are the carbinol and phosphorous acid, it is not illegitimate to conclude that hydrolysis occurs according to scheme (ii). That a *para*-placed methoxyl group should increase the ease of hydrolytic fission at the linking R—O is in agreement with general experience (compare Lapworth and Shoesmith, *loc. cit.*).

The absence of instability in the parallel case of the phosphorus dichloride derived from α-naphthyldiphenylcarbinol may be attributed to the steric hindrance which the naphthyl group will offer to the process of hydrolysis.

(3) It has already been suggested (*loc. cit.*) that the reaction between phosphorus trichloride and an alcohol usually proceeds according to the following scheme :

$$\text{(i) } \mathrm{RO|H + PCl_3 = RO{\cdot}PHCl_3 = RO{\cdot}PCl_2 + HCl};$$

but that in cases where the alcohol has pronounced basic properties and, therefore, some tendency to dissociate into R and OH, reaction may also take place as follows :

$$\text{(ii) } \mathrm{R|OH + PCl_3 = R{\cdot}P(OH)Cl_3 = R{\cdot}POCl_2 + HCl}.$$

This assumption makes it possible to account in a simple fashion for the presence of $\mathrm{Ph_3C{\cdot}PO(OH)_2}$ amongst the by-products of the reaction between $\mathrm{PCl_3}$ and $\mathrm{Ph_3C{\cdot}OH}$. From this hypothesis it may be deduced that the yield of phosphinic acid obtainable as a by-product in the reaction between $\mathrm{R{\cdot}OH}$ and $\mathrm{PCl_3}$ will be the larger the greater the " basicity " of the alcohol employed. The figures recorded in column 2 (p. 2324) show that the yields of phosphinic acid obtained from the different triarylcarbinols in the course of this investigation are in substantial agreement with this deduction.

EXPERIMENTAL.

In the preparation of the triarylmethoxyphosphorus dichlorides, the carbinol (1 mol.) was slowly added to phosphorus trichloride (about 2 mols.) cooled in ice, and the reaction mixture kept at least 48 hours at room temperature. The resulting solid was treated with ice and water, digested in the cold, during several days, first with ammonia and afterwards with sodium carbonate solution, washed free from alkali, dried in a vacuum, and crystallised from a suitable solvent. On acidification of the alkaline filtrate, a small quantity of triarylmethylphosphinic acid was precipitated; but in order to obtain the maximum yield of phosphinic acid, formed as a by-product in the preparation of a triarylmethoxyphosphorus dichloride, it was usually necessary to carry out the digestion with ammonia on the steam-bath.

The triarylmethoxyphosphorus dichlorides all dissolve in cold concentrated sulphuric acid with evolution of hydrogen chloride, and from the strongly coloured solutions the carbinols are precipitated on addition of water.

For the conversion of a triarylmethoxyphosphorus dichloride into a triarylmethylphosphinic acid, the chloride (1 mol.) was heated in a water-bath with potassium hydroxide (4·5—5 mols.) and ethyl alcohol (about 99% Et·OH). Heating was continued for a short time after potassium chloride had separated and then water was added and the alcohol evaporated on the steam-bath. The aqueous solution was boiled for some time and, when cold, was filtered from undissolved material and strongly acidified with hydrochloric acid. The precipitated mono-ethyl ester of the triarylmethylphosphinic acid was refluxed for an hour with glacial acetic acid–concentrated hydriodic acid. From this solution the phosphinic acid separated on cooling: the crystals were washed, and weighed after drying at 110°. A further small quantity of acid was obtained on addition of water to the filtrate. This was collected and included in the yield. From 5 g. of triphenylmethoxyphosphorus dichloride, 3·8 g. of potassium hydroxide, and 38 c.c. of alcohol, the yield of triphenylmethylphosphinic acid was 4·079 g. or 91% of the theoretical.

The acids obtained by this molecular rearrangement are all dibasic, in agreement with the constitutional formula which has been assigned, $CAr_3{\cdot}PO(OH)_2$. The basicity was established by the preparation of the corresponding dipotassium salts and by electrometric titration.

p-*Chlorotriphenylmethoxyphosphorus Dichloride* (I; X = Cl).—The carbinol required was prepared by the Grignard reaction from ethyl *p*-chlorobenzoate. The crude product (after steam distillation to remove unchanged ester, etc.) was kept for some days; the main portion then became crystalline. The crystals were finely powdered, washed with cold light petroleum, and crystallised from petroleum (b. p. 80—100°); they then melted at 85°, in agreement with the figure given by Gomberg and Cone (*Ber.*, 1906, **39**, 3278), who prepared the compound from *p*-chlorobenzophenone dichloride. The yield was about 35% of the theoretical.

The pure p-*chlorotriphenylmethoxyphosphorus dichloride* was obtained from the crude chloride by dissolution in chloroform and addition of an equal volume of acetone. It formed minute, colourless crystals, m. p. 161·5° (Found: P, 7·8; Cl, 26·9. $C_{19}H_{14}OCl_3P$ requires P, 7·85; Cl, 26·9%).

The dichloride was moderately easily soluble in boiling ethyl alcohol, but on refluxing for an hour it decomposed with formation of the carbinol and a trace of oil which was not identified. Heating with an alcoholic solution of potassium hydroxide brought about an almost quantitative conversion into *p*-chlorotriphenylmethylphosphinic acid ; from 4·6 g. of the phosphorus dichloride, 3·5 g. of potassium hydroxide, and 48 c.c. of alcohol, the yield of phosphinic acid was 3·9 g. or 93% of the theoretical. The sticky by-product (0·14 g.), insoluble in alkali, separated from benzene and light petroleum in colourless crystals, m. p. 146° ; it was not identified.

p-*Chlorotriphenylmethylphosphinic acid*, $C_6H_4Cl{\cdot}CPh_2{\cdot}PO(OH)_2$, crystallises from acetic acid or benzene in minute crystals, m. p. 273° (Found in material kept in a vacuum desiccator for some days : P, 8·8; Cl, 9·85. $C_{19}H_{16}O_3ClP$ requires P, 8·7; Cl, 9·9%).

The *dipotassium* salt, prepared by dissolving the acid in boiling concentrated potassium hydroxide solution, separated in small, lustrous plates. These were washed with absolute alcohol and air-dried (Found: K, 13·6; H_2O, 24·75. $C_{19}H_{14}O_3ClPK_2,8H_2O$ requires K, 13·5; H_2O, 24·8%).

p-*Bromotriphenylmethoxyphosphorus Dichloride* (I; X = Br).—The carbinol was prepared from ethyl *p*-bromobenzoate, and purified by the method of Gomberg and Blicke (*J. Amer. Chem. Soc.*, 1923, **45**, 1770), *viz.*, conversion into the chloride by hydrogen chloride in dry ethereal solution, followed by hydrolysis with aqueous acetone in presence of dimethylaniline. The product melted at 82°, even after repeated crystallisation from benzene and light petroleum (Gomberg and Blicke give m. p. 130°). A specimen of the carbinol purified by recrystallisation of the crude substance melted at 78°, as recorded by Gomberg and Cone (*Ber.*, 1906, **39**, 3279).

p-*Bromotriphenylmethoxyphosphorus dichloride* crystallises from benzene or chloroform–acetone in small, colourless crystals, m. p. 163° (Found: P, 7·3; Cl, 16·1. $C_{19}H_{14}OCl_2BrP$ requires P, 7·05; Cl, 16·1%). In properties it closely resembles the corresponding *p*-chloro-compound.

p-*Bromotriphenylmethylphosphinic Acid*, $C_6H_4Br{\cdot}CPh_2{\cdot}PO(OH)_2$.—From 5 g. of the phosphorus dichloride, with 3·18 g. of potassium hydroxide and 32 c.c. of alcohol, the yield of phosphinic acid was 4·15 g. (90%). The acid dissolves readily in boiling benzene, alcohol, or glacial acetic acid. From acetic acid, it separates in small, colourless crystals, m. p. 297°, containing a molecule of acetic acid, which is retained after prolonged keeping in a vacuum, but may be driven off by heating for several hours at 100° (Found: $CH_3{\cdot}CO_2H$, 13·0. $C_{19}H_{16}O_3BrP,CH_3{\cdot}CO_2H$ requires $CH_3{\cdot}CO_2H$, 13·0%. Found in material heated at 100°: P, 7·9; Br, 19·8. $C_{19}H_{16}O_3BrP$ requires P, 7·7; Br, 19·85%).

The *dipotassium* salt forms glistening plates (Found: K, 12·6; P, 5·2; H_2O, 20·25. $C_{19}H_{14}O_3BrPK_2,7H_2O$ requires K, 12·9;

P, 5·1; H_2O, 20·8%). The *barium* salt was obtained as a heavy, white precipitate from barium chloride and the potassium salt in aqueous solution (Found: Ba, 21·9; H_2O, 14·8. $C_{19}H_{14}O_3BrPBa,5H_2O$ requires Ba, 21·8; H_2O, 14·3%).

Diphenyl-p-*anisylmethoxyphosphorus Dichloride* (I; X = OMe).—The carbinol was prepared from ethyl *p*-anisate. Crystallisation from ether–ligroin as recommended by Baeyer and Villiger (*Ber.*, 1902, **35**, 3027) was not found satisfactory. A fair yield of pure subtance was obtained by submitting the oily carbinol, left after steam distillation, to distillation under reduced pressure (b. p. 247°/18 mm.). The glassy solid so obtained was dissolved in ether–light petroleum, the solvent removed in a vacuum, and the yellow, crystalline residue ground with light petroleum, which removed a small quantity of oily impurity leaving a white, crystalline product, m. p. 84° (yield 30%).

The carbinol reacts readily with phosphorus trichloride giving an orange-coloured solid. The crude diphenyl-*p*-anisylmethoxyphosphorus dichloride, after treatment with water and alkalis, was digested with cold ether for some hours, and then repeatedly crystallised from much benzene–light petroleum, which was heated as little as possible. It was finally obtained in minute, white crystals, m. p. 180° (Found: P, 7·8; Cl, 17·9. $C_{20}H_{17}O_2Cl_2P$ requires P, 7·9; Cl, 18·2%).

In one experiment 13 g. of the carbinol gave 11 g. of crude chloride, and from the alkaline filtrates, on acidification, 1·5 g. of *diphenyl*-p-*anisylmethylphosphinic acid* were precipitated, m. p. 210° after crystallisation from acetic acid. This acid is not decomposed on boiling with concentrated potassium hydroxide solution. Diphenyl-*p*-anisylmethoxyphosphorus dichloride shows a high degree of stability towards cold aqueous alkalis, but on digestion on the water-bath for 6 hours with aqueous ammonia it is decomposed to the carbinol and phosphorous acid. Treatment with hot alcoholic potassium hydroxide, carried out in the usual way, yielded, not the phosphinic acid, but a sticky solid which became brittle on keeping for some weeks. On crystallisation from petroleum (b. p. 60—80°), it yielded (along with a small quantity of yellow oil) colourless crystals, m. p. 82°. These were identified as diphenyl-*p*-anisylcarbinol by a mixed melting point determination, and by conversion into the carbinol chloride, m. p. 124°.

Diphenyl-m-*anisylmethoxyphosphorus Dichloride* (II).—The carbinol, prepared from ethyl *m*-anisate (Baeyer, von Bentheim, and Diehl, *Annalen*, 1907, **354**, 152), formed transparent prisms, m. p. 90·5°. The crude phosphorus dichloride is readily soluble in ether.

Separation from unchanged carbinol or carbinol chloride is conveniently effected by crystallisation from acetone–chloroform. The pure substance forms minute, snow-white crystals, m. p. 122—124° (Found: P, 7·85; Cl, 18·15. Calc. for $C_{20}H_{17}O_2Cl_2P$: P, 7·9; Cl, 18·2%).

The chloride dissolved slowly in boiling absolute alcohol. The crystals which separated on evaporation of the alcoholic solution were identified as the carbinol by a mixed melting point.

The dichloride (38 g.), heated with 28 g. of potassium hydroxide and 250 c.c. of alcohol, gave 30 g. of crude monoethyl phosphinic ester (P, 8·0%) (yield 80%). It was not possible to isolate the diphenyl-*m*-anisylmethylphosphinic acid. Boiling the ethyl ester with acetic acid–hydriodic acid converted it into m-*hydroxytriphenylmethylphosphinic acid*, $HO{\cdot}C_6H_4{\cdot}CPh_2{\cdot}PO(OH)_2$, fine, white needles which shrink at 239° and melt at 248°. The hydroxy-acid is very soluble in acetic acid and in cold alcohol. Even after crystallisation from glacial acetic acid and drying in a vacuum the substance was associated with 2 mols. of water, which were lost on drying at 100° (Found: H_2O, 9·3. $C_{19}H_{17}O_4P,2H_2O$ requires H_2O, 9·6%. Found for the anhydrous acid: C, 67·1; H, 5·35; P, 9·3, 9·1. $C_{19}H_{17}O_4P$ requires C, 67·05; H, 5·0; P, 9·1%).

The *disodium* salt, $HO{\cdot}C_6H_4{\cdot}CPh_2{\cdot}PO(ONa)_2$, formed lustrous plates which were dried at 100° (Found: P, 8·2; Na, 11·4. $C_{19}H_{15}O_4PNa_2$ requires P, 8·1; Na, 11·3%).

On benzoylating the hydroxy-acid by the Schotten-Baumann method the sodium salt of the *benzoyl* derivative separated as a white powder. The acid, prepared from this salt, crystallised from alcohol on addition of light petroleum in minute, white crystals, m. p. 237·5°, which were dried at 100° (Found: C, 70·05; H, 5·0; P, 7·0. $C_{26}H_{21}O_5P$ requires C, 70·3; H, 4·8; P, 7·0%). The *disilver* salt of the benzoylated acid was obtained as a white precipitate on adding silver nitrate to a solution of the acid in ammonia (Found, in material dried in a vacuum: H_2O, 5·65; Ag, 31·2. $C_{26}H_{19}O_5PAg_2,2H_2O$ requires H_2O, 5·2; Ag, 31·1%).

m-Hydroxytriphenylmethylphosphinic acid, on methylation with methyl sulphate, gave an *acid* which, after recrystallisation from glacial acetic acid, melted at 197°, and behaved as a dibasic acid on titration (Found: C, 67·5; H, 5·7; P, 8·65. $C_{20}H_{19}O_4P$ requires C, 67·8; H, 5·5; P, 8·8%).

Diphenyl-α-naphthylmethoxyphosphorus Dichloride (III).—The carbinol, prepared by the method of Acree (*Ber.*, 1904, **37**, 627), after repeated crystallisation from benzene–ligroin, formed almost colourless crystals, m. p. 136·5°. The crude *phosphorus dichloride* was digested with ether, triturated with cold acetone, and recrystallised from benzene–ligroin. It formed white, microscopic crystals, m. p. 171—172° (Found: P, 7·65, 7·4; Cl, 17·2. $C_{23}H_{17}OCl_2P$ requires P, 7·5; Cl, 17·3%).

The pure chloride is insoluble in cold ether, acetone, or light petroleum, but dissolves readily in warm benzene. It dissolves slowly in boiling absolute alcohol, and the solution, on cooling, deposits crystals of the ethyl ether of diphenyl-α-naphthylcarbinol, m. p. 134° (Found: C, 88·5; H, 6·6. Calc. for $C_{25}H_{22}O$: C, 88·8; H, 6·5%).

On treatment with potassium hydroxide and alcohol according to the usual method the phosphorus dichloride was converted into the carbinol (identified by the mixed melting point method and by reduction to diphenyl-α-naphthylmethane), and no phosphinic acid was produced.

Diphenyl-α-naphthylmethylphosphinic acid, $C_{10}H_7·CPh_2·PO(OH)_2$, was obtained as a by-product in the preparation of diphenyl-α-naphthylmethoxyphosphorus dichloride. In one experiment using 10 g. of carbinol, the yield of phosphinic acid obtained on acidifying the alkaline filtrates was 1·3 g. (10·8%). After recrystallisation from alcohol it formed fine needles, m. p. 256°, which were dried at 100° (Found: P, 8·1; C, 73·6; H, 5·2. $C_{23}H_{19}O_3P$ requires P, 8·3; C, 73·8; H, 5·1%).

Dipotassium diphenyl-α-naphthylmethylphosphinate separates in lustrous plates on cooling a solution of the acid in hot concentrated potash (Found: H_2O, 16·1; K, 14·3. $C_{23}H_{17}O_3PK_2,5H_2O$ requires H_2O, 16·7; K, 14·4%).

Diphenyl-β-naphthylmethoxyphosphorus Dichloride (III).—The carbinol, m. p. 118°, was obtained in excellent yield from β-naphthoic ester by the method of Gomberg and Sullivan (*J. Amer. Chem. Soc.*, 1922, **44**, 1810). The crude phosphorus dichloride was digested with ether and crystallised from chloroform–acetone, small, white crystals, m. p. 194°, being obtained (Found: P, 7·65; Cl, 17·4. $C_{23}H_{17}OCl_2P$ requires P, 7·5; Cl, 17·3%).

Boiling with absolute alcohol converts it into the ethyl ether of diphenyl-β-naphthylcarbinol, m. p. 116°. On treating 5 g. of diphenyl-β-naphthylmethoxyphosphorus dichloride with 3·41 g. of potassium hydroxide and 34 c.c. of alcohol, the yield of *diphenyl-β-naphthylmethylphosphinic acid*, $C_{10}H_7·CPh_2·PO(OH)_2$, was 3·5 g. (77%). After recrystallisation the acid formed colourless needles, m. p. 247·5°. The crystals from acetic acid contain one molecule of solvent. The sample analysed had been kept for a week in a vacuum over lime (Found: $CH_3·CO_2H$, 13·8; P, 8·3; C, 73·45; H, 5·1. $C_{23}H_{19}O_3P,CH_3·CO_2H$ requires $CH_3·CO_2H$, 13·8; P, 8·3; C, 73·8; H, 5·1%).

From the acid, a *dipotassium* salt was prepared (Found: H_2O, 17·0; P, 5·8; K, 14·3. $C_{23}H_{17}O_3PK_2,5H_2O$ requires H_2O, 16·7; P, 5·7; K, 14·4%).

The oily by-product formed in the treatment of the phosphorus dichloride with alcoholic potash was crystallised from ether–light petroleum and identified as the ethyl ether of diphenyl-β-naphthylcarbinol.

p-*Nitrotriphenylmethoxyphosphorus Dichloride* (I; X = NO_2).—The carbinol, m. p. 98°, was prepared by a Friedel-Crafts reaction from *p*-nitrobenzophenone dichloride (Baeyer and Villiger, *Ber.*, 1904, **37**, 606). The yield was poor, much of the nitroketone being recovered.

The crude *phosphorus dichloride* was dissolved in warm benzene, and a small quantity of light petroleum added; a red solid was then thrown down. The filtered solution deposited clear yellow crystals. By dissolving these in the least possible volume of chloroform and adding about twice the bulk of acetone, colourless crystals were finally obtained, m. p. 188·5° (Found: P, 7·7; Cl, 17·55. $C_{19}H_{14}O_3NCl_2P$ requires P, 7·65; Cl, 17·5%).

The chloride is difficultly soluble in boiling absolute alcohol and crystallises unchanged even after refluxing for an hour. On treatment with alcoholic potassium hydroxide an acid containing phosphorus and nitrogen was obtained. It was very dark in colour and attempts to crystallise it failed.

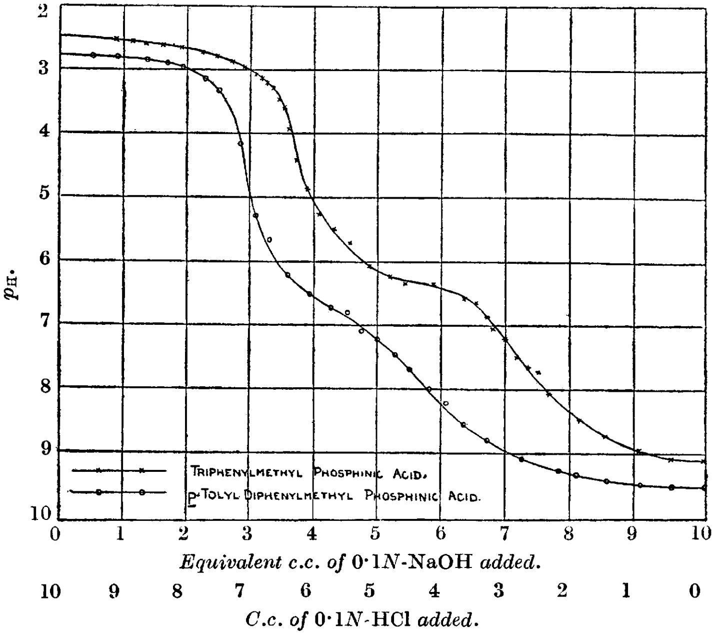
Diphenyl-p-*tolylmethoxyphosphorus Dichloride* (I; X = Me).—[With Mr. J. D. TULLY.] The carbinol was prepared by the Grignard reaction from benzophenone (Acree, *Ber.*, 1904, **37**, 992). Crystallised from ligroin, the substance melted at 78° (Acree gives 74°); but the crystals obtained from benzene melted at 73—74°.

The carbinol and phosphorus trichloride were mixed in the cold as in previous cases, but the reaction was completed by heating for 2 hours at 40—50°. The crude chloride, after being extracted twice with ether, crystallised from benzene in minute, colourless crystals, m. p. 193° (decomposition) (Found: P, 8·4; Cl, 18·65. $C_{20}H_{17}OCl_2P$ requires P, 8·3; Cl,18·9%).

The phosphorus dichloride dissolves in boiling absolute alcohol, and the solution, on cooling, deposits crystals of the carbinol (Found: C, 87·4; H, 6·7. Calc. for $C_{20}H_{18}O$: C, 87·5; H, 6·6%).

Diphenyl-p-*tolylmethylphosphinic Acid*, $C_6H_4Me{\cdot}CPh_2{\cdot}PO(OH)_2$.—From 5 g. of the phosphorus dichloride, with 3·74 g. of potassium hydroxide and 37·4 c.c. of alcohol, the yield of phosphinic acid was 3·4 g. (75%). After treatment with acetic acid–hydriodic acid and crystallisation from benzene, the phosphinic acid melted at 254°. The crystals contained one molecule of water, which was removed on heating at 100° for some hours (Found : H_2O, 5·6 ; C, 67·4, 67·7 ; H, 6·0, 5·9 ; P, 8·9, 8·4. $C_{20}H_{19}O_3P,H_2O$ requires H_2O, 5·1 ; C, 67·4 ; H, 5·9 ; P, 8·7%). On recrystallisation from glacial acetic acid the water molecule is replaced by a molecule of acetic acid (Found : $CH_3{\cdot}CO_2H$, 15·5. $C_{20}H_{19}O_3P,CH_3{\cdot}CO_2H$ requires $CH_3{\cdot}CO_2H$, 15·1%. Found in material heated for some hours at 100° : C, 70·7 ; H, 5·85 ; P, 9·4, 9·1. $C_{20}H_{19}O_3P$ requires C, 71·0 ; H, 5·6 ; P, 9·2%).

FIG. 1.



The *dipotassium* salt forms pearly leaflets (Found : H_2O, 20·6 ; K, 14·8 ; P, 5·9. $C_{20}H_{17}O_3PK_2,6H_2O$ requires H_2O, 20·7 ; K, 14·9 ; P, 5·9%).

Electrometric Titration of the Phosphinic Acids.

Owing to the low solubility of the acids in water, it was not practicable to titrate an aqueous solution of the acid with caustic soda. The plan adopted was to dissolve a weighed quantity of acid in excess of standard sodium hydroxide, and back-titrate with standard hydrochloric acid. For the titrations a Rideal hydrogen electrode and a Rideal *N*/10-calomel half-cell were used, the temperature being maintained at 18° throughout the series. Carbonate-free sodium hydroxide was prepared by the method of Cornog (*J. Amer. Chem. Soc.*, 1921, **43**, 2573) and standardised with acid potassium phthalate.

The titration curves for triphenylmethylphosphinic acid and for diphenyl-*p*-tolylmethylphosphinic acid are given in illustration of the results obtained.

The authors desire to thank the Research Fund Committee of the Chemical Society for a grant towards the cost of this investigation.

UNIVERSITY COLLEGE, SOUTHAMPTON. [*Received, June* 10*th*, 1926.]