Tetrahedron, 1967, Vol. 23, pp. 283 to 290. Pergamon Press Ltd. Printed in Northern Ireland

CYCLIC ORGANOPHOSPHORUS COMPOUNDS—IV[1]

CLEAVAGE OF 1,3,2-DIOXAPHOSPHOLANE AND 1,3,2-DIOXAPHOSPHORINANE RINGS BY GRIGNARD REAGENTS

R. S. EDMUNDSON and J. O. L. WRIGLEY
Department of Chemical Technology, Bradford Institute of Technology, England

(*Received* 7 *April* 1966; *accepted for publication* 14 *June* 1966)

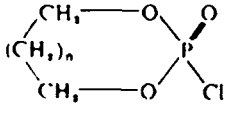
Abstract—Cyclic phosphorochloridates and phenylphosphonates based on the 1,3,2-dioxaphospholane and 1,3,2-dioxaphosphorinane ring systems, undergo ring cleavage when treated with phenylmagnesium halides, to yield ω-hydroxyalkyl diphenylphosphinic esters, and ultimately, triphenylphosphine oxide. In the case of the smaller ring, diphenylphosphinic acid is a major product of the reaction. Possible mechanisms for these reactions are discussed.

NUCLEOPHILIC displacements at phosphorus of halogen or alkoxy (aryloxy) groups by Grignard reagents is a well-established procedure for the formation of bonds between phosphorus and carbon.[2] The great difference in reactivity of five- and six-membered ring esters of phosphorus acids towards nucleophilic reagents[3] and the lack of information on the behaviour of such esters to organometallic reagents prompted our investigations. Our original concern was with the conversion of the cyclic phosphorochloridates (I) to the corresponding phenyl phosphonates (II). This reaction was chosen since the phosphonates are already authenticated,[4] and very convenient preparations of the phosphorochloridates have also been described.[5] We here report our preliminary results.

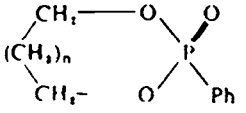
The results of our initial experiments rendered it necessary to make a re-investigation of the reactions between phenyl Grignard reagents and diethyl phosphorochloridate and the corresponding phosphorofluoridate. Diethyl phosphorochloridate and phenylmagnesium bromide react to yield diethyl phenylphosphonate and triphenylphosphine oxide, the relative amounts of these depending on the ratio of reactants. The formation of one or the other product is independent of the manner of addition, i.e. normal or inverse. According to Saunders and Simpson,[6] dialkyl (Et, i-Pr, cyclo-C_6H_{11}) phosphorofluoridates and phenylmagnesium bromide give only dialkyl phenylphosphonate, even upon normal addition of acid fluoride to Grignard reagent. We have now found that both diethyl phosphorochloridate and phosphorofluoridate give large amounts of triphenylphosphine oxide when treated with phenylmagnesium bromide under conditions comparable to those used by Saunders and Simpson. We have also observed differences in the reactivity of phenylmagnesium chloride and phenylmagnesium bromide towards diethyl phosphorochloridate,

[1] Part III: R. S. Edmundson, *Tetrahedron* **21**, 2379 (1965).
[2] K. D. Berlin, T. H. Austin, M. Peterson and M. Nagabhushanam, *Topics in Phosphorus Chemistry* Vol. 1; p. 17. Interscience, N.Y. (1964).
[3] For reviews see R. S. Edmundson, *Chem. & Ind.* 1770 (1962); Cox, J. R. jn., and O. B. Ramsey, *Chem. Rev.* **64**, 317 (1964).
[4] A. D. F. Toy, U.S. 2,382,622 *Chem. Abstr.* **40**, 604 (1946).
[5] R. S. Edmundson, *Chem. & Ind.* 1828 (1962).
[6] B. C. Saunders and P. Simpson, *J. Chem. Soc.* 3351, 3464 (1963).

although it is appreciated that in some experiments these differences may be due to differences in temperature of reaction. Addition of 3 M of phenylmagnesium chloride in tetrahydrofuran (THF) to diethyl phosphorochloridate gave diethyl phenylphosphonate (51%) and triphenylphosphine oxide (22%) as compared to yields of 28% and 19% respectively of the same products when an identical molar ratio of phenylmagnesium bromide in ether was used.



I



II

$HO{\cdot}(CH_2)_nOP(:O){\cdot}Ph_2$
III

$HO{\cdot}CH_2CH_2OP(:O)(OH){\cdot}Ph$
IV

These results suggested to us that a chloro Grignard reagent might be preferable to the bromide for the conversion I → II. It is evident however that this simple displacement is complicated by a further, fast, ring-opening reaction.

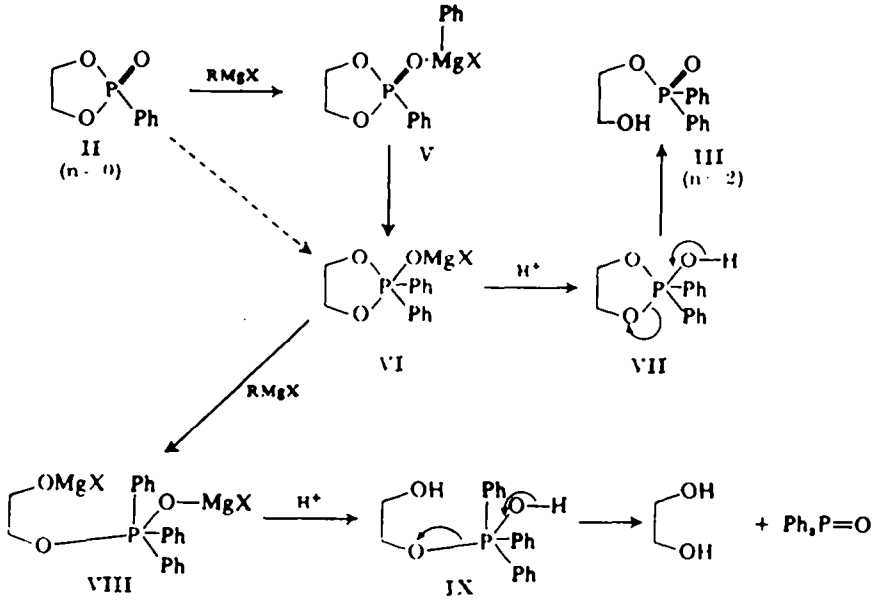
Addition of 2-chloro-2-oxo-1,3,2-dioxaphospholane (I; n = 0) to either 3 M of phenylmagnesium chloride in THF, or 2 M or 3 M of phenylmagnesium bromide in THF at below room temperature, gives a mixture of products from which 2-hydroxyethyl diphenylphosphinate[7] (III; n = 2) may be isolated. Some formation of triphenylphosphine oxide was also noted, but 2-oxo-2-phenyl-1,3,2-dioxaphospholane (II; n = 0) could not be isolated. This was not unexpected since the latter ester readily hydrolyses under aqueous conditions at room temperature to the acid (IV) characterized as its cyclohexylammonium salt. Attempts to obtain the phosphonate (II; n = 0) by anhydrous work—up procedures have so far been unsuccessful. In contrast, 2-chloro-2-oxo-1,3,2-dioxaphosphorinane (I; n = 1) yielded 38% of the corresponding phenylphosphonate (II; n = 1) accompanied by some 3-hydroxypropyl diphenylphosphinate[7] (III; n = 3) when 2 M of Grignard reagent and an aqueous work-up procedure were employed.

Table 1 summarizes the results of experiments in which the two phenylphosphonates were employed as co-reactants with Grignard reagents. 2-Oxo-2-phenyl-1,3,2-dioxaphospholane reacts with low ratios of either phenylmagnesium chloride or bromide to give primarily 2-hydroxyethyl diphenylphosphinate and diphenylphosphinic acid. When higher ratios of reagent to ester are used, diphenylphosphinic acid becomes noticeably absent, and the formation of triphenylphosphine oxide is observed at the expense of either (or both) of diphenylphosphinic acid and 2-hydroxyethyl diphenylphosphinate. For both phenylphosphonates, the yield of ω-hydroxyalkyl diphenylphosphinate is greatest with the ratio of reagent to ester at between 1 and 2 to 1.

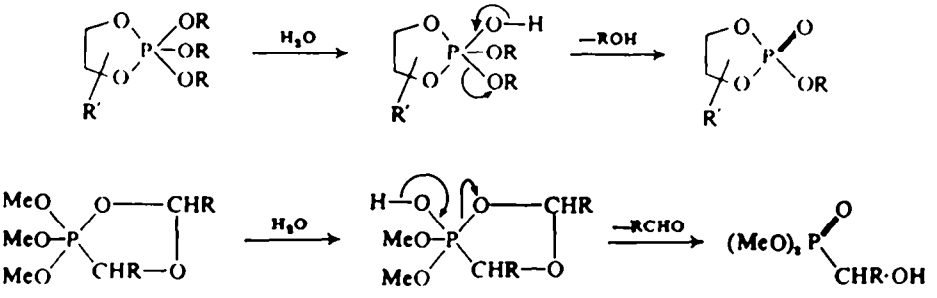
We tentatively suggest that the conversion of 2-oxo-2-phenyl-1,3,2-dioxaphospholane to the various isolated products takes place via the pathways indicated in the chart.

The highly polarized phosphoryl bond (in the sense $P^+–O^-$) is rendered even more polarized upon complexing with Grignard reagent. While no reports of the isolation

[7] Structure confirmed by independent synthesis. For details, see Exptl.



of such complexes involving Grignard reagents have been found in the literature, nevertheless the powerful complexing ability of the phosphoryl group in phosphates, pyrophosphates, phosphonates and phosphine oxides is well known.[8] The complex (V) then gives the phosphorane-type (VI). Alternatively, the latter could be produced by addition of the Grignard reagent across the phosphoryl bond. Under aqueous conditions, i.e. upon work-up, the hydroxy phosphorane (VII) would then undergo the indicated transformation to 2-hydroxyethyl diphenylphosphinate. Ramirez *et al.*[9,10] have postulated similar mechanisms to account for the formation of cyclic phosphates



on treatment of 2,2,2-trialkoxy-1,3,2-dioxaphospholanes with water, and for the ring opening observed in other reactions. It is unlikely that triphenylphosphine oxide is formed by a concerted attack of two molecules of Grignard reagent RMgX upon one

[8] The literature on tributyl phosphate as a solvent for metal ions is far too extensive to quote. Of more relevance here is the complexing power of phosphonates, see e.g. M. J. Frazer, W. Gerrard, R. Twaits, *J. inorg. nuclear Chem.* **25**, 637 (1963); T. H. Siddall, *J. inorg. nuclear Chem.* **25**, 883 (1963), and of phosphine oxides, see e.g. J. R. Parker and C. V. Banks, *J. inorg. nuclear Chem.* **27**, 883 (1965) and papers immediately following.

[9] F. Ramirez, *Pure and Appl. Chem.* **9**, 337 (1964).

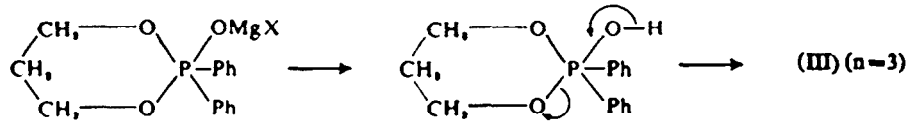
[10] F. Ramirez, O. P. Madan, C. P. Smith, *J. Amer. Chem. Soc.* **87**, 670 (1965).

of the cyclic phenylphosphonate, nor, as was demonstrated, is it formed from the hydroxyethyl diphenylphosphinate. It would therefore appear that further nucleophilic attack by Grignard reagent upon the intermediate (VI) must lead to ring opening and the formation of the pentacovalent state (VIII), which in aqueous medium, proceeds to ethylene glycol and triphenylphosphine oxide via the intermediate (IX).

A mechanism for the formation of 2-hydroxyethyl diphenylphosphinate by a S_N2 type of reaction cannot at this stage be excluded, and would presumably proceed via a bipyramidal transition state, but the same mechanism cannot be applied to the formation of triphenylphosphine oxide.

An interesting feature of the second series of experiments involving 2-oxo-2-phenyl-1-,3,2-dioxaphosphorinane, is that diphenylphosphinic acid was never detected among the reaction products. Diphenylphosphinic acid was shown not to arise from 2-hydroxyethyl- or 3-hydroxypropyl diphenylphosphinates under the conditions employed in the work-up procedure. When 3-hydroxypropyl diphenylphosphinate was treated with excess phenylmagnesium bromide in THF under conditions identical to those used for the cyclic esters, some 10% of diphenylphosphinic acid was isolated, and the balance of unreacted ester was recovered. Triphenylphosphine oxide was not detected in this experiment, nor was it when 2-hydroxyethyl diphenylphosphinate was similarly treated. Some ester was here also recovered, but diphenylphosphinic acid was obtained in much greater yield (49%). Evidently, the spatial relationship between OH and P=O groups would appear to be of some consequence. Mechanisms involving cyclic transitions states may be formulated for this reaction which is receiving further attention.

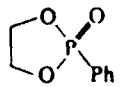
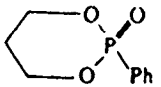
A number of observations still remain to be explained. Thus it is not at present apparent how diphenylphosphinic acid is so readily produced from 2-oxo-2-phenyl-1,3,2-dioxaphospholane, but not from the corresponding 1,3,2-dioxaphosphorinane. In spite of the ready formation of the acid from its 2-hydroxyethyl ester on treatment of the latter with a Grignard reagent, 2-hydroxyethyl diphenylphosphinate is presumed not to be present until the reaction mixture is hydrolysed, and we can therefore only assume a further reaction probably involving the intermediate (VI). 1,3,2-Dioxaphosphorinane rings are normally considerably more stable than 1,3,2-dioxaphospholane systems. Evidently, if our postulated mechanism is correct, the transformation of the complex (X) into 3-hydroxypropyl diphenylphosphinate is not prevented by the enhanced stability of the six-membered ring.



(X)

2-Hydroxyethyl diphenylphosphinate is easily hydrolysed by alkali to diphenylphosphinic acid. We are exploring the overall reaction sequence with a view to the synthesis of mixed diarylphosphinic acids.

TABLE 1

Phenyl phosphonate	Grignard reagent	Molar Ratio[a] Grignard reagent ester	Ester (moles)	Products (moles) $PhCO_2H$	Ph_3PO	$Ph_2P(O)OH$	$Ph_2P(O)O(CH_2)_nOH$
							n − 2
	PhMgCl	1	0·100	Absent	Absent	Present[a]	Present[a]
		2	0·075	Absent	0·0038	0·0142	0·0090
		3	0·100	0·184	0·0012[d]	Absent	0·0061
	PhMgBr	1	0·100	Absent	Absent	0·0165	0·0117
		3	0·100	0·0041	0·00109	Absent	0·0042
							n − 3
	PhMgCl	1[b,c]	0·075	Absent	Absent	Absent	0·0150
		2	0·075	0·021	Absent	Absent	0·0188
		3	0·100	0·053	0·059	Absent	0·0109
		4	0·075	0·037	0·068	Absent	Absent
	PhMgBr	3	0·100	0·062	0·048	Absent	0·0020

[a] "Inverse" addition unless otherwise stated
[b] "Direct" addition
[c] Some unreacted phosphonate isolated
[d] Estimated
[e] Detected by TLC

EXPERIMENTAL

All solns. of Grignard reagents were prepared and transferred under N. Reactions were subsequently carried out under the same atmosphere. All evaporations were carried out *in vacuo* at 55°. THF was dried by refluxing over Na, distillation from fresh Na, followed by storage over, and distillation from K as required. Other solvents were dried by conventional means. Organic extracts were dried over Na_2SO_4. M.ps are uncorrected. Pet. ether had b.p. 60–80°.

TLC employed diiso-Pr ether–AcOH (3:2) as solvent using Keiselgel PT 245/366 as support. Spots were indicated by a combination of UV light (indicating triphenylphosphine oxide) and a spray of I in EtOH[11] followed by fluorescein in EtOH. The brown spots produced by hydroxyalkyl diphenylphosphinic esters are less intense in colour, develop more slowly and fade more rapidly than that produced by triphenylphosphine oxide.

Reaction between diethyl phosphorochloridate and phenyl Grignard reagents

(a) *Using phenylmagnesium bromide.* Normal addition of diethyl phosphorochloridate (9·0 g) in ether (25 ml) to the Grignard reagent from Mg (3·75 g, 3M) and bromobenzene (24·6 g, 3M) in ether (60 ml) during 15 min, followed by refluxing for 3 hr, yielded diethyl phenylphosphonate (2·4 g) and triphenylphosphine oxide (2·8 g).

Inverse addition of 1 equiv of PhMgBr to diethyl phosphorochloridate under otherwise identical conditions yielded diethyl phenylphosphonate (2·7 g) only.

(b) *Using phenylmagnesium chloride.* Normal addition of diethyl phosphorochloridate (21·6 g) in THF (40 ml) to the Grignard reagent from Mg (5·2 g) and chlorobenzene (22·8 g, 1M) in THF (60 ml) during 15 min, followed by refluxing for 15 min, and working up in the usual way gave diethyl phenylphosphonate (6·6 g) and triphenylphosphine oxide (1·0 g). Inverse addition in the same ratio to diethyl phosphorochloridate (23·0 g) gave diethyl phenylphosphonate (12·7 g) and triphenylphosphine oxide (2·3 g).

Inverse addition of PhMgBr (2M) to diethyl phosphorochloridate (35·0 g) in THF gave diethyl phenylphosphonate (23·7 g–26·8 g) and triphenylphosphine oxide (2·0 g). When the molar ratio of reagent to substrate was 3:1, inverse reaction on diethyl phosphorochloridate (22·0 g) gave diethyl phenylphosphonate (7·6 g) and triphenylphosphine oxide (3·3 g).

Reaction between diethyl phosphorofluoridate and phenyl Grignard reagents

Addition of diethyl phosphorofluoridate (7·5 g) in ether (25 ml) to the Grignard reagent from Mg (3·6 g) and bromobenzene (24·0 g, 3M) in ether (60 ml) at room temp, followed by refluxing for 30 min, gave triphenylphosphine oxide (7·0 g).

Using the same quantities, but inverse order of addition, the products were diethyl phenylphosphonate (1·5 g) and triphenylphosphine oxide (3·2 g).

2-*Chloro*-2-*oxo*-1,3,2-*dioxaphospholane*, b.p. 84–88°/0·3 mm, was prepared in 63% yield as described previously.[6]

2-*Chloro*-2-*oxo*-1,3,2-*dioxaphosphorinane*, b.p. 138°/0·5 mm, was obtained in 70% yield by the same method.[6]

Reactions between cyclic phosphorochloridates and Grignard reagents

(a) *Using* 2-*chloro*-2-*oxo*-1,3,2-*dioxaphospholane*. The Grignard reagent from Mg (5·2 g) and bromobenzene (31·4 g, 2M) in THF (130 ml) was added dropwise to the acid chloride (14·25 g, 1M) in THF (50 ml) stirred at $< -15°$ during 15 min. The Grignard reagent soln. was washed into the reaction flask with more THF so that the final volume of solvent was 200 ml. The mixture was allowed to come to room temp (ca. 1·5 hr) and then poured on to powdered CO_2 under ether and the whole allowed to come to room temp. The solvent was removed, and the residue taken up in $CHCl_3$ (100 ml), washed with 0·5N HCl, then with sat $KHCO_3$ aq, finally with water, and then dried. Evaporation of the organic phase left a residue (7·45 g) which was crystallized from benzene to give a solid m.p. ca. 60° (5·0 g). On repeated recrystallization of this from benzene–pet. ether, the m.p. was raised to 103–104°, and the product was identical (m.p., mixed m.p., IR spectrum) with authentic

[11] C. W. Stanley, *J. Chromat.* **16**, 467 (1964).

2-hydroxyethyl diphenylphosphinate. The $KHCO_3$ soln was acidified to yield benzoic acid (yield of crude acid, 13·4 g).

In a similar experiment using 3M of PhMgBr in THF (100 ml) with a total, final solvent volume of 280 ml, the yield of 2-hydroxyethyl diphenylphosphinate was 10·3 g (40%). Recovery of 2M of benzoic acid was practically quantitative. In neither experiment was triphenylphosphine oxide detected by TLC.

In a second series of experiments, PhMgCl was used under essentially the same experimental conditions. When 1M of Grignard reagent was added, and the CO_2-treated reaction product taken up in $CHCl_3$ (300 ml). The soln was washed with water, dried and evaporated. A gummy residue was obtained which on treatment with cyclohexylamine yielded the cyclohexylammonium salt of 2-hydroxyethyl phenylphosphonic acid, m.p. 222° (from EtOH), identical with an authentic sample. Traces of triphenylphosphine oxide were detected by TLC.

Inverse addition of 3M of PhMgCl in a total final volume of 200 ml gave, after the same work-up procedure, a pale yellow liquid (12·6 g) which partially crystallized. The components of the mixture could not satisfactorily be separated by filtration, and hence the whole was recrystallized from benzene giving 2-hydroxyethyl diphenylphosphinate (6·9 g) shown to be pure by TLC. Evaporation of the mother liquors yielded an oil which was shown by TLC to contain triphenylphosphine oxide.

(b) 2-*Chloro*-2-*oxo*-1,3,2-*dioxaphosphorinane*. The inverse addition of the Grignard reagent from Mg (2·6 g) and chlorobenzene (11·25, 1M) in THF (70 ml) to the phosphorochloridate (15·6 g) in THF (40 ml) during 20 min at between −20° and −10°, was carried out. The final soln was poured on to CO_2 under ether. Evaporation of the mixture, acidification, extraction with $CHCl_3$ was followed by extraction of the $CHCl_3$ soln with $KHCO_3$ aq, and drying of the organic layer. Evaporation of this gave a liquid (3 g) which on distillation gave 2-oxo-2-phenyl-1,3,2-dioxaphosphorinane, b.p. 172°/0·6 mm, (1·3 g, 7%). Traces of 3-hydroxypropyl diphenylphosphinate were detected by TLC of the residues, but diphenylphosphinic acid was absent.

When the amount of Grignard reagent was doubled under otherwise identical conditions, 5·9 (30%) of the cyclic phenylphosphonate were obtained. The residue from the distillation contained diphenylphosphinic acid and 3-hydroxypropyl diphenylphosphinate in approximately equal (trace) amounts.

2-*Hydroxyethyl diphenylphosphinate*. Diphenylphosphinic chloride (15·8 g) in THF (50 ml) was added dropwise to ethylene glycol (4·15 g) and pyridine (5·3 g) in THF (50 ml). The mixture was refluxed 1·5 hr, cooled, filtered, the filtrate evaporated, and the residue (23 g) crystallized from benzene–pet. ether to yield hygroscopic, 2-hydroxyethyl diphenylphosphinate m.p. 91–95°. Repeated recrystallization of the ester from the same solvent, followed by drying *in vacuo* over P_2O_5 raised the m.p. to 103·5–104·5°. (Found: C, 64·3; H, 5·5; P, 12·05. $C_{14}H_{15}O_3P$ requires: C, 64·4; H, 5·4; P, 11·85%. ν_{max} 3395 (OH), 1205 (P—O) cm^{-1}.)

Hydrolysis of 2-*oxo*-2-*phenyl*-1,3,2-*dioxaphospholane*. The solid ester dissolved rapidly when placed in water at room temp to give an acid soln. Neutralization with cyclohexylamine and evaporation gave the cyclohexylammonium salt of 2-hydroxyethyl phenylphosphonic acid, m.p. 222° (from EtOH). (Found: C, 55·8; H, 8·1; P, 10·2. $C_{14}H_{24}NO_5P$ requires: C, 55·8; H, 8·0; P, 10·3%.)

3-*Hydroxypropyl diphenylphosphinate*. The crude compound, prepared as in the case of the hydroxyethyl ester, was taken up in benzene, and the soln washed with water and dried. Distillation gave the desired ester, (13·0 g) b.p. 203–210°/0·1–0·7 mm, m.p. 82–84° (from benzene). (Found: C, 65·0; H, 6·3. $C_{15}H_{17}O_3P$ requires: C, 65·1; H, 6·2% ν_{max} 3420 (OH), 1203 (P—O) cm^{-1}.)

2-*Oxo*-2-*phenyl*-1,3,2-*dioxaphospholane*. Addition of ethylene glycol with pyridine (2 equivs) to phenylphosphonic dichloride in benzene at room temp, followed by filtration and distillation gave 47–49% of the desired ester. Slightly lower yields were obtained when the pyridine was omitted, irrespective of the presence or absence of solvent. The pure ester had b.p. 182–185°/0·3 mm, n_D^{20} 1·5358 (lit.[4] b.p. 210°/6–7 mm), ν_{max} 1273 (P—O), 1077, 1043 (P—O—C) cm^{-1}.

2-*Oxo*-2-*phenyl*-1,3,2-*dioxaphosphorinane*. This was prepared in essentially the same way as the corresponding dioxaphospholane. In the presence of pyridine, the yield of ester, b.p. 170–174°/0·1 mm, m.p. 33°, n_D^{21} 1·5369, was 30%. In the absence of pyridine, and using benzene as solvent, addition of trimethylene glycol to phenylphosphonic dichloride gave 50–58% of the cyclic ester. ν_{max} 1260 (br) (P—O), 1032, 1060 (br) (P—O—C) cm^{-1}.

Reaction between cyclic phenylphosphonates and phenylmagnesium halides

The general procedure finally adopted was as follows: The Grignard soln prepared from either bromobenzene or chlorobenzene and Mg in THF (140–170 ml, including washings of the residual metal) was added dropwise with stirring during 15–20 min, to a soln of the phosphonate (0·1000 or 0·075M) in THF (75 ml) at −30 to −15°, the final reaction volume being 230–280 ml. The reaction flask and contents were allowed to come to room temp during 1 hr, and the mixture then refluxed for 0·75 hr, cooled and poured on to CO_2 under ether. The solvent was removed by evaporation *in vacuo*, and the residue taken up in $CHCl_3$ (200 ml), washed with 0·5N HCl (2 × 100 ml), sat $KHCO_3$ aq (2 × 100 ml), water, and then dried.

The filtered $CHCl_3$ extract was evaporated to give an oil which slowly crystallized, and which was recrystallized from benzene to yield 2-hydroxyethyl diphenylphosphinate or 3-hydroxypropyl diphenylphosphinate, and triphenylphosphine oxide.

The $KHCO_3$ washings were acidified to give impure benzoic acid, estimated after further recrystallization from water, or diphenylphosphinic acid. The latter was characterized as the cyclohexylammonium salt, m.p. 235–237° (from benzene–pet. ether). (Found: N, 4·4. $C_{18}H_{24}NO_2P$ requires: N, 4·45%.)

The results obtained in this series of experiments are summarized in Table 1.

Reaction between 2-hydroxyethyl diphenylphosphinate and phenylmagnesium bromide

To the Grignard reagent prepared from bromobenzene (1·0 g) and Mg (0·25 g) in THF (30 ml) was added 2-hydroxyethyl diphenylphosphinate (2·3 g) in THF (30 ml) and the mixture refluxed for 1·5 hr, cooled and poured on to solid CO_2 under ether. Working up the product in the usual way gave diphenylphosphinic acid (0·95 g, 44%) and 1·2 g of the original ester was recovered.

TLC indicated the absence of triphenylphosphine oxide in the crude product.

Reaction between 3-hydroxypropyl diphenylphosphinate and phenylmagnesium bromide

To the Grignard reagent prepared as in the previous experiment, was added 3-hydroxypropyl diphenylphosphinate (2·4 g) in THF and the mixture was refluxed for 1·5 hr, when a white ppt gradually formed. A further equivalent of the same Grignard reagent was added and the mixture again refluxed. During 0·5 hr, the ppt gradually disappeared. Working up the final soln gave diphenylphosphinic acid (0·2 g). Unattacked ester was recovered quantitatively. TLC indicated the absence of triphenylphosphine oxide.

Action of acid and alkali on the ω-hydroxyalkyl diphenylphosphinates

Each ester (1·0 g) in $CHCl_3$ (50 ml) was washed with 0·5N HCl (2 × 50 ml), sat $KHCO_3$ aq (2 × 50 ml) and water. The $CHCl_3$ was dried and evaporated. In each case, the ester was recovered quantitatively.

Hydrolysis of 2-hydroxyethyl diphenylphosphinate. The ester (0·45 g) was warmed with 2N NaOH until dissolved. The cooled solution was acidified, and the precipitated solid recrystallized from aqueous EtOH. The yield of diphenylphosphinic acid m.p. 190–191°, was 0·25 g (67%).