aldinic acids the change in pK is the difference between two pK values involving the dissociation of doubly charged anions. Hence the comparison is uncomplicated by charge variation. In the 4-hydroxyquinaldinic acid case, however, the pK_3 of the ligand involves the dissociation of a singly charged anion whereas that of the chelate corresponds to the dissociation of a neutral species. From a comparison of the pK values of 8-quinolinol, salicylic acid, and the corresponding sulfonates, the charge effect on the change in pK can be estimated to be about 1.0 log unit. This has been subtracted from the ΔpK for the 4-hydroxy compound and the resulting values are given in Table IV.

Table IV

ΔpK Values for the 4-Hydroxy Groups in the Metal Chelates

Metal ion	ΔpK 2,6-Dicarboxy-4-hydroxypyridine	4-Hydroxyquinaldinic acid[a]	4,8-Dihydroxyquinaldinic acid
Mn(II)	...	...	3.8
Co(II)	5.9	5.6	4.6
Ni(II)	5.7	5.7	4.5
Cu(II)	6.4	6.7	5.0
Zn(II)	5.7	5.9	4.8

[a] Corrected for the charge effect.

The ΔpK values in Table IV show that in the chelates of the three compounds considered here, Cu(II) exerts a significantly greater effect than the other metal ions, although this difference seems to be almost absent in the 4,8-dihydroxy compound. Furthermore, a comparison of the corrected ΔpK values (Table IV) reveals a great similarity in the effect of metal chelation on the pK_{OH} of 2,6-dicarboxy-4-hydroxypyridine and that of 4-hydroxyquinaldinic acid, both of which have the same chelate ring in the same position relative to the 4-hydroxy group. In the case of the 4,8-dihydroxy compound the effect is uniformly smaller. Although it is likely that the greater part of the change in the order of magnitude of the acid strengthening effect is due to the change in the nature of the chelate ring, the role played by the change in the location of the dissociating hydroxy group relative to the chelate ring as well as possible differences in the tautomeric equilibrium constants of the ligands must not be overlooked. Further work is underway to evaluate these separate effects.

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Preparation of Linear Phosphonitrilic Derivatives

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Reaction of diphenylphosphinyl azide with diphenylchlorophosphine afforded the compound $(C_6H_5)_2P(O)-[N{=}P(C_6H_5)_2]_3Cl$ (VIII) as the main product. Various mechanisms are considered for this process. Azido, triphenylphosphine, phenoxy, and phosphinyl terminated chains were prepared from compound VIII. Infrared and ultraviolet spectra of several of these phosphonitrilic derivatives were determined and are discussed.

Syntheses and Mechanism Discussion

Trivalent phosphorus compounds are readily oxidized by azides such as diphenylphosphinyl azide,[1] triphenylsilyl azide,[2] or phenyl azide,[3] forming phosphonitrilic linkages. Mono-, bis-, and trishalogenophosphines are also reported to give phosphonitriles[4] when treated with alkali metal azides. This reaction proceeds most probably *via* the trivalent phosphorus azide intermediate, inasmuch as bis(trifluoromethyl)azidophosphine (prepared from bis(trifluoromethyl)chlorophosphine and lithium azide) decomposed thermally into polymeric bis(trifluoromethyl)phosphonitrile.[5] Based on the facts outlined above a stepwise synthesis of linear phosphonitrilic derivatives, initiated by an oxidative attack of pentavalent phosphorus azide upon a trivalent phosphorus halide, appeared feasible. Accordingly, the reaction of diphenylphosphinyl azide[6] with an equimolar quantity of diphenylchlorophosphine should afford $(C_6H_5)_2P(O){-}N{=}P(C_6H_5)_2Cl$, wherein chlorine is attached to a pentavalent phosphorus atom, allowing chain extension *via* an exchange with an azido group (supplied by an alkali metal azide), followed by treatment with a trivalent phosphorus compound. Since the interaction products do not contain trivalent phos-

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(1) R. A. Baldwin and R. M. Washburn, *J. Am. Chem. Soc.*, **83**, 4466 (1961).

(2) N. Wiberg, F. Raschig, and R. Sustmann, *Angew. Chem. Intern. Ed. Engl.*, **1**, 551 (1962).

(3) H. Staudinger and E. Hauser, *Helv. Chim. Acta*, **4**, 61 (1921).

(4) D. L. Herring, *Chem. Ind.* (London), 717 (1960).

(5) G. Tesi, C. P. Haber, and C. M. Douglas, *Proc. Chem. Soc.*, 219 (1960).

(6) Diphenylphosphinyl azide was first prepared by Baldwin and Washburn[1] from diphenylphosphinyl chloride and sodium azide in boiling pyridine. Interestingly, treatment of diphenylphosphinyl chloride with lithium azide in acetonitrile at room temperature resulted in the formation of a 1:1 complex of diphenylphosphinyl azide and lithium chloride, which when heated above 73°, the melting point of the complex, decomposed into its constituents. The assignment of structure $(C_6H_5)_2P(O)N_3 \cdot LiCl$ to the complex is based on its infrared spectrum, which is almost identical with that of diphenylphosphinyl azide and differs from that exhibited by diphenylphosphinyl chloride. The failure of Baldwin and Washburn[1] to isolate the sodium analog of the complex can be ascribed to the relatively high temperatures employed in their reaction.

phorus, the sites for oxidative attack by an azide moiety are eliminated. Thus, the formation of cyclic materials is excluded. Cyclics were found under conditions where trivalent phosphorus azides were presumably the reaction intermediates,[4] or more clearly, where one end of the growing phosphonitrile "chain" consisted of a trivalent phosphorus atom.

Surprisingly, however, interaction of equimolar quantities of diphenylchlorophosphine (II) and diphenylphosphinyl azide (I) in refluxing ether gave as the main product (60% yield) $(C_6H_5)_2P(O)-[N-P(C_6H_5)_2]_3Cl$ (VIII) (insoluble in the reaction medium), together with 7.3% of $(C_6H_5)_2P(O)-N=P(C_6H_5)_2X$ and 3.1% of $(C_6H_5)_2P(O)-[N=P(C_6H_5)_2]_2X$ (present in solution) where X may be either Cl (compounds III and VI) or N_3 (compounds V and VII). Neither $(C_6H_5)_2P(O)-N=P(C_6H_5)_2Cl$ (III) and $(C_6H_5)_2P(O)-N=P(C_6H_5)_2N_3$ (V), nor $(C_6H_5)_2P(O)-[N=P(C_6H_5)_2]_2Cl$ (VI) and $(C_6H_5)_2P(O)-[N=P(C_6H_5)_2]_2N_3$ (VII) have been isolated as such to date, just in the form of their hydrolysis products, $(C_6H_5)_2P(O)-NH-P(O)(C_6H_5)_2$ (derived from III and V) and $(C_6H_5)_2P(O)-N=P(C_6H_5)_2-NH-P(O)(C_6H_5)_2$ (derived from VI and VII).

The main product, "tetramer" $(C_6H_5)_2P(O)-[N=P(C_6H_5)_2]_3Cl$, was found to be only slightly soluble in acetonitrile and almost completely insoluble in benzene and heptane. Due to the insolubility the molecular weight could not be determined; however, hydrolysis in aqueous acetonitrile afforded $(C_6H_5)_2P(O)-[N=P(C_6H_5)_2]_2-NH-P(O)(C_6H_5)_2$ (prepared previously by a different route[7]) in quantitative yield

$$(C_6H_5)_2P(O)-[N=P(C_6H_5)_2]_2-N=P(C_6H_5)_2Cl + H_2O \xrightarrow{CH_3CN} \underset{\text{IX}}{(C_6H_5)_2P(O)-[N=P(C_6H_5)_2]_2-NH-P(O)(C_6H_5)_2} + HCl$$

In contrast to $(C_6H_5)_2P(O)-[N=P(C_6H_5)_2]_3Cl$ (VIII), the azido derivative obtained on treatment of VIII with lithium azide

$$\underset{\text{VIII}}{(C_6H_5)_2P(O)-[N=P(C_6H_5)_2]_3Cl} + LiN_3 \longrightarrow \underset{\text{X}}{(C_6H_5)_2P(O)-[N=P(C_6H_5)_2]_3N_3} + LiCl$$

showed high solubility in acetonitrile. This material exhibited in its infrared spectrum a strong band at 4.7 μ proving that the $-N=P(C_6H_5)_2N_3$ grouping absorbs in the same region as the $O=P(C_6H_5)_2N_3$ arrangement. The azide X was recovered unchanged after 2 hr. heating at 100° (*in vacuo*), demonstrating amply the stability associated with the pentavalent oxidation state of phosphorus, since diphenylphosphinyl azide undergoes only a slight decomposition above 160°.[1] Treatment of $(C_6H_5)_2P(O)-[N=P(C_6H_5)_2]_3N_3$ with triphenylphosphine gave the phenyl-terminated derivative XI

$$\underset{\text{X}}{(C_6H_5)_2P(O)-[N=P(C_6H_5)_2]_3N_3} + (C_6H_5)_3P \longrightarrow \underset{\text{XI}}{(C_6H_5)_2P(O)-[N=P(C_6H_5)_2]_4C_6H_5}$$

whereas the chloride VIII and sodium phenoxide in boiling xylene yielded the phenoxy-terminated compound XII

$$\underset{\text{VIII}}{(C_6H_5)_2P(O)-[N=P(C_6H_5)_2]_3Cl} + C_6H_5ONa \longrightarrow \underset{\text{XII}}{(C_6H_5)_2P(O)-[N=P(C_6H_5)_2]_3OC_6H_5} + NaCl$$

The formation of $(C_6H_5)_2P(O)-[N=P(C_6H_5)_2]_3Cl$ (VIII) and the isolation of $(C_6H_5)_2P(O)-N=P(C_6H_5)_2-NH-P(O)(C_6H_5)_2$ (XVIII) (from the hydrolyzed mother liquors) can be interpreted only by an azide group exchange which proceeds at least as readily as the oxidizing attack of diphenylphosphinyl azide (I) upon diphenylchlorophosphine (II). Theoretically this azide exchange can occur both with II and the pentavalent chloro derivatives, assuming I to provide the azido moiety. Sequence A is based on the initial formation of $(C_6H_5)_2P(O)-N=P(C_6H_5)_2Cl$ (III) and subsequent exchanges of the azido and chloro groups between diphenylphosphinyl azide and the pentavalent chloro intermediates followed by a reaction with diphenylchlorophosphine.

SEQUENCE A

$$\underset{\text{I}}{(C_6H_5)_2P(O)N_3} + \underset{\text{II}}{(C_6H_5)_2PCl} \longrightarrow$$

$$\underset{\text{III}}{(C_6H_5)_2P(O)-N=P(C_6H_5)_2Cl} \xrightarrow{\text{I}}$$

$$\underset{\text{V}}{(C_6H_5)_2P(O)-N=P(C_6H_5)_2N_3} + \underset{\text{IV}}{(C_6H_5)_2P(O)Cl} \xrightarrow{\text{II}}$$

$$\underset{\text{VI}}{(C_6H_5)_2P(O)-[N=P(C_6H_5)_2]_2Cl} \xrightarrow{\text{I}}$$

$$(C_6H_5)_2P(O)Cl + \underset{\text{VII}}{(C_6H_5)_2P(O)-[N=P(C_6H_5)_2]_2N_3} \xrightarrow{\text{I}}$$

$$\underset{\text{VIII}}{(C_6H_5)_2P(O)-[N=P(C_6H_5)_2]_3Cl}$$

If Sequence A represents the true mechanism of chain propagation it can be inferred that the arrangement $N=P-N_3$, existing in $(C_6H_5)_2P(O)-N=P(C_6H_5)_2N_3$ and $(C_6H_5)_2P(O)-[N=P(C_6H_5)_2]_2N_3$, is less prone to an azide exchange with a chloro derivative than the $O=P-N_3$ entity. It can be further deduced that the $N=P-N_3$ terminated compounds, under the conditions employed, have a stronger tendency than diphenylphosphinyl azide to oxidize diphenylchlorophosphine.

In an alternate sequence (B) the exchange of the azido group between diphenylphosphinyl azide and diphenylchlorophosphine, resulting in the formation of diphenylazidophosphine, is assumed to be the initiating step.

An important stipulation of sequence B is an attack of diphenylphosphinyl azide (I) upon trivalent phosphorus terminated intermediates, thus postulating that I attacks diphenylazidophosphine and such products as $(C_6H_5)_2P-N=P(C_6H_5)_2N_3$ and $(C_6H_5)_2P-N=P(C_6H_5)_2Cl$ in preference to diphenylchlorophosphine. The exchange between pentavalent chlorides (compounds $(C_6H_5)_2P(O)-N=P(C_6H_5)_2Cl$, $(C_6H_5)_2P(O)-[N=P(C_6H_5)_2]_2Cl$, and $(C_6H_5)_2P-N=P(C_6H_5)_2$-

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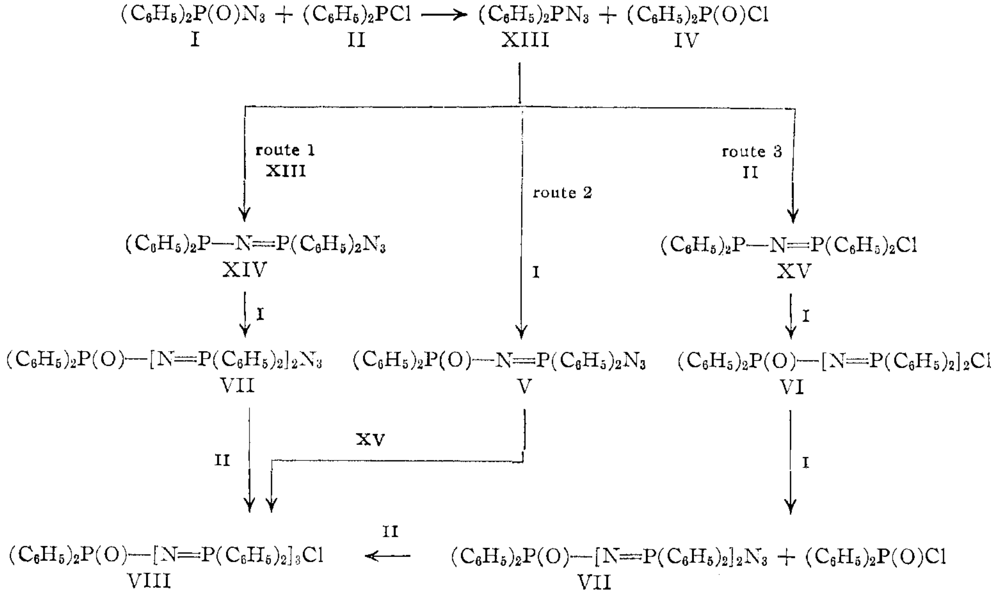
(7) V. V. Korshak, I. A. Gribova, T. V. Artamonova, and A. N. Bushmarina, *Vysokomol. Soedineniya*, **2**, 377 (1960).

SEQUENCE B



Cl) and diphenylazidophosphine was not considered here, because at 36° the latter decomposes rapidly.[8]

The absence of cyclic phosphonitriles, which would result from the attack by diphenylazidophosphine upon compounds such as $(C_6H_5)_2P—N{=}P(C_6H_5)_2N_3$ (followed by cyclization), indicates that the concentration of diphenylazidophosphine is relatively low at any given time. This consideration tends to eliminate route 1, where a higher concentration of trivalent phosphorus azide is required.

Inasmuch as the product $(C_6H_5)_2P(O)—[N{=}P(C_6H_5)_2]_3Cl$ (VIII) is insoluble in ether, it cannot react further. Thus, it is not very probable that under the conditions employed here homologs higher than VIII can be formed. Since the formation of VIII is believed to be a stepwise process, by selecting suitable reaction conditions, in particular the solvent, either higher or lower homologs of VIII could be conveniently synthesized.

The hydrolysis of unreacted starting materials and the products depicted in schemes A and B can give only four compounds, namely, $(C_6H_5)_2P(O)OH$ (XVI), $(C_6H_5)_2P(O)—NH—P(O)(C_6H_5)_2$ (XVII), $(C_6H_5)_2P(O)—N{=}P(C_6H_5)_2—NH—P(O)(C_6H_5)_2$ (XVIII), and $(C_6H_5)_2P(O)—[N—P(C_6H_5)_2]_2—NH—P(O)(C_6H_5)_2$(IX), providing that oxidation of the materials such as $(C_6H_5)_2P—N{=}P(C_6H_5)_2N_3$ and $(C_6H_5)_2P—N{=}P(C_6H_5)_2Cl$ takes place during the hydrolysis. Diphenylphosphinic acid (XVI) is a well-known compound, whereas compounds XVII and IX have been reported.[7]

It is noteworthy that for each mole of $(C_6H_5)_2P(O)$-$[N{=}P(C_6H_5)_2]_3Cl$ and $(C_6H_5)_2P(O)—[N{=}P(C_6H_5)_2]_2—NH—P(O)(C_6H_5)_2$ (IX) three moles of diphenylphosphinyl azide (I) are needed, one mole remaining in the product formed, the other two moles being used for azide exchange and consequently resulting in diphenylphosphinyl chloride. Two moles of I are used for $(C_6H_5)_2P(O)—N{=}P(C_6H_5)_2—NH—P(O)(C_6H_5)_2$ (XVIII) whereas $(C_6H_5)_2P(O)—NH—P(O)(C_6H_5)_2$ (XVII) requires only one mole of diphenylphosphinyl azide, no diphenylphosphinyl chloride being produced.

The hydrolysis of the ether-soluble materials and the residues recovered from the mother liquors of $(C_6H_5)_2P(O)—[N{=}P(C_6H_5)_2]_3Cl$ gave 79% of diphenylphosphinic acid (based on diphenylphosphinyl azide used), 7.3% of "dimer" XVII, and 3.1% of "trimer" XVIII, as well as 0.86 g. of unresolved mixture, presumably composed of "trimer" XVIII and "tetramer" IX. The 79% yield of diphenylphosphinic acid (39.3% based on total phosphorus used) is partly derived from the unreacted diphenylchlorophosphine and diphenylphosphinyl azide; however, in view of the high yield of tetramer and trimer (63.1%) and the 0.86 g. of unresolved mixture, diphenylphosphinyl chloride, the by-product of the azide exchange, must be the main source of diphenylphosphinic acid. Based on the information available at present both Sequence A and routes 2 and 3 of Sequence B appear equally plausible.

Spectral Investigations

In several publications concerning phosphonitriles[9-11] absorptions in the region 7.4–8.3 μ have been ascribed to vibrations associated with –P=N— systems. The published data pertain mainly to cyclic compounds. The results of infrared spectral examinations of the compounds discussed in the first part of the paper are compiled in Table I, whereas the ultraviolet data are compiled in Table II.

It is clear from the tabulated values that the infrared absorptions of the —P=N— moiety in the linear phosphonitrilic derivatives are well within the limits found for the cyclic compounds. The weak absorption exhibited by compound XVII at 7.50 and 7.62 μ suggests that the material exists predominantly as $(C_6H_5)_2P(O)—$

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(8) K. L. Paciorek and R. Kratzer, unpublished results.

(9) L. W. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951).

(10) L. W. Daasch, *J. Am. Chem. Soc.*, **76**, 3403 (1954).

(11) L. G. Lund, N. L. Paddock, J. E. Proctor, and H. T. Searle, *J. Chem. Soc.*, 2542 (1960).

TABLE I

INFRARED ABSORPTION SPECTRA OF PHOSPHONITRILIC DERIVATIVES AND RELATED COMPOUNDS IN THE 7.4–9.0 AND 10–11 μ REGIONS

Compound	Infrared bands
$(C_6H_5)_2POOH$	7.65 w, 8.40 s, 8.50 s, 8.68 w, 8.86 s, 8.94 s, 10.42 vs
$(C_6H_5)_2P(O)\text{—}NH\text{—}P(O)(C_6H_5)_2$	7.50 w, 7.62 w, 8.42 m, 8.90 s, 9.00 s, 10.80 m
$(C_6H_5)_2P(O)\text{—}N{=}P(C_6H_5)_3$[1]	7.70 vs, 8.58 vs, 9.00 s
$(C_6H_5)_2P(O)\text{—}N{=}P(C_6H_5)_2\text{—}NH\text{—}P(O)(C_6H_5)_2$	7.60 vw, 8.15 s, 8.50 m, 8.90 s, 10.80 vs
$(C_6H_5)_2P(O)\text{—}[N{=}P(C_6H_5)_2]_2NH\text{—}P(O)(C_6H_5)_2$	7.78 s, 7.90 s, 8.25 s, 8.50 m, 8.95 s, 10.80 vw
$(C_6H_5)_2P(O)\text{—}[N{=}P(C_6H_5)_2]_3Cl$	7.50 vw, 8.00 s, 8.25 s, 8.40 s, 8.52 s, 8.92 s
$(C_6H_5)_2P(O)\text{—}[N{=}P(C_6H_5)_2]_4C_6H_5$	7.78 s, 7.95 s, 8.15 s, 8.50 m, 8.72 m, 8.97 s

TABLE II

ULTRAVIOLET ABSORPTION SPECTRA OF PHOSPHONITRILIC DERIVATIVES AND RELATED COMPOUNDS

	Wave length, mμ			
	247	260	266	273
	ε			
$(C_6H_5)_2P(O)OH$[a]	956	1142	1392	1179
$(C_6H_5)_2P(O)\text{—}NH\text{—}P(O)(C_6H_5)_2$		1982	2479	1982
$(C_6H_5)_2P(O)\text{—}N{=}P(C_6H_5)_3$[1]		2370	2140	1850
$(C_6H_5)_2P(O)\text{—}N{=}P(C_6H_5)_2\text{—}NH\text{—}P(O)(C_6H_5)_2$		2820	2996	2239
$(C_6H_5)_2P(O)\text{—}[N{=}P(C_6H_5)_2]_2NH\text{—}P(O)(C_6H_5)_2$		4362	4117	2597
$(C_6H_5)_2P(O)\text{—}[N{=}P(C_6H_5)_2]_4C_6H_5$[b]			6337	3885
$[(C_6H_5)_2PN]_3$[c]			1239	769

[a] This and other spectra in ethanol. [b] In acetonitrile. [c] In hexane.

$NH\text{—}P(O)(C_6H_5)_2$ and not as the $(C_6H_5)_2P(O)\text{—}N{=}P(OH)(C_6H_5)_2$ arrangement. This is further confirmed by the presence of a medium band at 10.80 μ indicative of -P–NH–P- linkage.[12] Similar reasoning can be applied to compounds $(C_6H_5)_2P(O)\text{—}[N{=}P(C_6H_5)_2]_2\text{—}NH\text{—}P(O)(C_6H_5)_2$ and $(C_6H_5)_2P(O)\text{—}N{=}P(C_6H_5)_2\text{—}NH\text{—}P(O)(C_6H_5)_2$.

Ultraviolet electronic spectra of cyclic phosphonitriles have been discussed by several authors.[11,13–16] The maxima for $(PNX_2)_n$ rings are found at very short wave lengths; their positions vary with the halogen substituent. On this basis, Lund[11] assigned them tentatively to an excitation of the unshared electrons on the exocyclic halogens. This theory was supported by Lakatos.[17]

According to Dewar[15] the π-electrons of the phosphonitrilic system are localized in definite three-center π-bonds. This is an entirely different situation from that holding in organic aromatic systems where no transformation into localized equivalent orbitals is possible. Craig and Paddock[18] in their consideration of the aromaticity of phosphonitriles emphasize the participation of d-orbitals in π-bonds, although neither the three center "islands" of conjugation around the ring nor the cyclic conjugation has been positively established.

The maxima observed for the phenyl-substituted phosphonitrilic derivatives (see Table II) cannot be attributed to a conjugated —P=N— system, since with chain lengthening the absorption should shift toward the visible region, and the increase in $\epsilon_{\max}$ should be much more pronounced. Thus these absorptions are most likely due to vibrational components of the electronic spectrum of phosphorus-substituted benzenes. It is noteworthy that the spectral pattern of diphenylphosphinic acid, where no —N=P— conjugation is possible, tends to confirm this hypothesis.

Experimental

Reagents.—Reagent grade chemicals were used after additional purification. Acetonitrile was refluxed over and then distilled from phosphorus pentoxide. Benzene was distilled from lithium aluminum hydride. Xylene was distilled from sodium. Diphenylchlorophosphine, obtained from Victor Chemical Works, was purified by fractional distillation, b.p. 106–108° (10^{-3} mm.). Diphenylphosphinyl chloride, b.p. 155–156° (0.5 mm.), was prepared from diphenylchlorophosphine. Triphenylphoshine, obtained from Metal and Thermit Corporation, was recrystallized from ethanol and dried *in vacuo*, m.p. 79–80°. All reactions except the hydrolysis were conducted in a nitrogen atmosphere with rigid exclusion of moisture. For the spectral analyses spectrograde solvents were employed. The elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Diphenylphosphinyl Azide (I).—To a vigorously stirred solution of diphenylphosphinyl chloride (37.62 g., 0.159 mole) in acetonitrile (150 ml.) was added lithium azide (9.0 g., 0.184 mole) over a period of 4.5 hr. at such a rate that the temperature did not rise above 34°. The mixture was subsequently stirred overnight at room temperature and then filtered. The clear slightly yellow filtrate exhibited in its infrared spectrum a strong band at 4.70 μ. The solvent was removed *in vacuo*, and a solid admixed with an oil remained. A small quantity of this material was washed with acetonitrile on a filtration funnel and dried overnight *in vacuo*, and the complex $(C_6H_5)_2P(O)N_3 \cdot LiCl$, m.p. 71–72° dec. was isolated.

Anal. Calcd. for $C_{12}H_{10}PON_3LiCl$: C, 50.45; H, 3.52; P, 10.85; Cl, 12.41; Li, 2.43; O, 5.60. Found: C, 49.16; H, 3.78; P, 10.85; Cl, 11.69; Li, 2.42; O, 4.14.

The bulk of the product described above when distilled at reduced pressure yielded diphenylphosphinyl azide, 26.4 g. (68% yield), b.p. 137–144° (0.05 mm.).

Reaction of Diphenylphosphinyl Azide with Diphenylchlorophosphine.—Diphenylphosphinyl azide (5.00 g., 0.021 mole) and diphenylchlorophosphine (4.54 g., 0.021 mole) were refluxed

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(16) R. Foster, L. Mayor, P. Warsop, and A. D. Walsh, *Chem. Ind.* (London), 1445 (1960).

(17) B. Lakatos, A. Hess, S. Holly, and S. Horvath, *Naturwiss.*, **49**, 493 (1962).

(18) D. P. Craig and N. L. Paddock, *J. Chem. Soc.*, 4118 (1962).

for 7 days in ether (40 ml.). During this period a white precipitate was formed on the walls of the flask. The solution was filtered and the residue refluxed with acetonitrile. On filtration a 3.5-g. (60% yield) of $(C_6H_5)_2P(O)\text{—}[N{=}P(C_6H_5)_2]_3Cl$ was obtained, m.p. 338–345° (softening at 335°).

Anal. Calcd. for $C_{48}H_{40}P_4N_3ClO$: C, 69.11; H, 4.83; P, 14.85; N, 5.04; Cl, 4.25. Found: C, 69.05; H, 4.85; P, 14.82; N, 5.35; Cl, 4.35.

The acetonitrile and ether filtrates were combined and the solvents removed *in vacuo*. The residue, 5.70 g., was refluxed with aqueous acetonitrile and a crystalline precipitate was obtained on cooling. This material was then boiled three times with 10-ml. portions of benzene. The insoluble product (0.64 g., 7.3% yield) was found to be pure $(C_6H_5)_2P(O)\text{—}NH\text{—}P(O)(C_6H_5)_2$, m.p. 269–271° (lit.[7] 270–272°).

Anal. Calcd. for $C_{24}H_{21}P_2NO_2$: C, 69.06; H, 5.06; P, 14.84; N, 3.36. Found: C, 69.06; H, 5.41; P, 14.90; N, 3.59.

The benzene-soluble material (2.40 g., m.p. 191–192°) was found to be diphenylphosphinic acid (XVI). The acetonitrile solution on concentration afforded an additional 1.2 g. of diphenylphosphinic acid; thus the yield of XVI, based on total phosphorus employed, was 39.3%. The material that remained after evaporation of the mother liquors was crystallized from ethanol giving $(C_6H_5)_2P(O)\text{—}N{=}P(C_6H_5)_2\text{—}NH\text{—}P(O)(C_6H_5)_2$, 0.2 g. (3.1% yield), m.p. 145–146°.

Anal. Calcd. for $C_{36}H_{31}P_3N_2O_2$: C, 70.12; H, 5.07; P, 15.10; N, 4.54; mol. wt., 616. Found: C, 70.24; H, 5.03; P, 14.48; N, 4.83; mol. wt., 601 (in benzene, using a Mechrolab osmometer).

The 0.86-g. residue, which failed to crystallize, was assumed to be a mixture of $(C_6H_5)_2P(O)\text{—}N{=}P(C_6H_5)_2\text{—}NH\text{—}P(O)(C_6H_5)_2$ and $(C_6H_5)_2P(O)\text{—}[N{=}P(C_6H_5)_2]_2\text{—}NH\text{—}P(O)(C_6H_5)_2$ on the basis of infrared spectral analysis. The combined yield of P=N compounds was higher than 70.3% based on diphenylphosphinyl azide.

Hydrolysis of $(C_6H_5)_2P(O)\text{—}[N{=}P(C_6H_5)_2]_3Cl$ (VIII).—A 1.5-g. (0.00180 mole) sample of VIII was refluxed with aqueous acetonitrile; on cooling, $(C_6H_5)_2P(O)\text{—}[N{=}P(C_6H_5)_2]_2\text{—}NH\text{—}P(O)(C_6H_5)_2$ (1.30 g., 95% yield,) m.p. 171–172°, (lit.[7] 171–171.5°) was obtained.

Anal. Calcd. for $C_{48}H_{41}P_4N_3O_2$: C, 70.67; H, 5.03; P, 15.21; N, 5.12; mol. wt., 815. Found: C, 70.04; H, 5.32; P, 15.18; N, 5.22; mol. wt., 810 (in benzene using a Mechrolab osmometer).

Preparation of $(C_6H_5)_2P(O)\text{—}[N{=}P(C_6H_5)_2]_4C_6H_5$ (XI).—To a rapidly stirred suspension of $(C_6H_5)_2P(O)\text{—}[N{=}P(C_6H_5)_2]_3Cl$ (1.2 g.) in acetonitrile (40 ml.) was added lithium azide (0.2 g., 0.00408 mole). No rise in temperature was observed; however, almost all the precipitate appeared to dissolve and the solution acquired a pink discoloration. Only a very small quantity of insoluble material remained. An amorphous solid was left on removal of the solvent. Its infrared spectrum exhibited a strong band at 4.70 μ, which indicated the presence of an azide group. The spectrum was different from that of the starting material. Heating under vacuum at 100° for 2 hr. did not result in the decomposition of the azide $(C_6H_5)_2P(O)\text{—}[N{=}P(C_6H_5)_2]_3N_3$ (X).

To 1.05 g. of the azide X (0.00125 mole) in benzene (20 ml.) was added triphenylphosphine (0.85 g., 0.00324 mole), and the resulting solution was refluxed overnight. The solvent and excess triphenylphosphine were removed by distillation and vacuum sublimation at 80°. Crystallization of the residue that remained after sublimation of the reaction mixture from acetonitrile–ethanol gave $(C_6H_5)_2P(O)\text{—}[N{=}P(C_6H_5)_2]_4C_6H_5$, m.p. 157–160°.

Anal. Calcd. for $C_{66}H_{55}P_5N_4O$: C, 73.72; H, 5.16; P, 14.41; N, 5.21; O, 1.49; mol. wt., 1075. Found: C, 73.85; H, 5.36; P, 14.43; N, 5.39; O, 1.42; mol. wt., 1052 (in chloroform using a Mechrolab osmometer).

Preparation of $(C_6H_5)_2P(O)\text{—}[N{=}P(C_6H_5)_2]_3OC_6H_5$.—To xylene (30 ml.) was added finely divided sodium (0.060 g., 0.00261 g.-atom) followed by phenol (0.6 g., 0.00638 mole) and $(C_6H_5)_2P(O)\text{—}[N{=}P(C_6H_5)_2]_3Cl$ (2.10 g., 0.00252 mole). After refluxing the mixture overnight the precipitate, sodium chloride, was filtered. The filtrate, on removal of solvent and excess phenol by distillation and vacuum sublimation at 120°, yielded $(C_6H_5)_2P(O)\text{—}[N{=}P(C_6H_5)_2]_3OC_6H_5$, which, after recrystallization from an ether–heptane mixture, melted at 65–70°.

Anal. Calcd. for $C_{54}H_{45}P_4N_3O_2$: C, 72.72; H, 5.09; P, 13.89; N, 4.71. Found: C, 71.67; H, 5.32; P, 13.23; N, 4.50.

The infrared spectrum of XII exhibited a band at 10.85 μ, which indicated the presence of a phenoxy group attached to phosphorus.

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