1-Chloromercurinaphthalene.—To the Grignard reagent of 1-bromonaphthalene (10 g.) prepared in the usual way in THF was added a solution of mercuric chloride (7 g.) in THF. Yellowish solid formed and the reaction was left to stir for 1 hr. The solid was filtered, dissolved in acetone, and reprecipitated by adding water. This was recrystallized from an acetone–water mixture to give a white crystalline solid of 1-chloromercurinaphthalene (9 g., 55.6% yield), m.p. 190–192 (lit.[21] m.p. 190–191).

1-Bromo-8-chloromercurinaphthalene.—An ethereal solution of 1-bromo-8-iodonaphthalene (2.3 g.) was added dropwise to a solution of *n*-butyllithium in hexane (4 ml., 15% soln.). The reaction was stirred for 5 hr. at room temperature. A solution of mercuric chloride (1.8 g.) in THF was then added and the solution stirred for another 0.5 hr. The reaction mixture was hydrolyzed and extracted with ether. The ether layer was separated, dried, decolorized, and evaporated to give a white solid. The solid was recrystallized from benzene to give white needles of 1-bromo-8-chloromercurinaphthalene (0.9 g., 30% yield), m.p. 219–220.

Anal. Calcd.: mol. wt., 442.1. Found: mol. wt., 447.

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Organometallic Azides. I. Preparation and Reactions of Diarylphosphinic Azides[1a]

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A series of new diarylphosphinic azides, $Ar_2P(O)N_3$, having surprising thermal stability, has been prepared in high yield. Reaction of these phosphinic azides with tertiary phosphines provides a new series of compounds, the N-(diarylphosphinyl)iminophosphoranes, $Ar_2P(O)N{=}PR_3$, some of which have exceptional thermal and chemical stabilities. The synthesis of several bis tertiary phosphines is also described.

Prior to the initial communication[2] on the synthesis of diarylphosphinic azides and their reactions, only a few reports concerning group IV (noncarbon), V, and VI azides had been published. The arylsulfonyl azides,[3,4] triphenyllead azide,[5] and dimesitylboron azide[6] were reported to be relatively stable. Less stable were silicon tetraazide[7] and the trivalent phosphorus azides.[8,9] Since then a number of papers describing thermally stable organosilyl,[10] organotin,[11] organoarsenic,[12] and phosphonyl azides[13] has appeared.

Diarylphosphinic Azides.—As part of a program to study reactions leading to thermally stable materials, it was found that diarylphosphinic chlorides would react with sodium azide in pyridine or acetonitrile under anhydrous conditions to give high yields of the corresponding diarylphosphinic azides (I). Although pyridine solutions of the diarylphosphinic azides were readily hydrolyzed, pure samples of the azides were only slowly hydrolyzed in 0.5 *N* sodium hydroxide. This hydrolytic sensitivity is similar to that reported for the organosilyl azides[10a] but in contrast to that of the organotin,[11] lead,[5] and arylsulfonyl azides[3,4] which may be readily prepared *via* aqueous sodium azide. Although the phosphinic azides were initially prepared by refluxing the reactants in pyridine for 18–24 hr., further investigation has shown that these azides may be prepared in 75–100% yield by stirring the reactants at room temperature for 6–8 hr. In contrast to the

$$Ar_2P(O)Cl + NaN_3 \xrightarrow{\text{pyridine}} Ar_2P(O)N_3 + NaCl \qquad (1)$$

$$\begin{aligned} &\text{Ia, Ar} = C_6H_5 \\ &\text{b, Ar} = p\text{-}CH_3C_6H_4 \\ &\text{c, Ar} = p\text{-}ClC_6H_4 \end{aligned}$$

recently reported isolation of a diphenylphosphinic azide–lithium chloride complex from acetonitrile,[14] no analogous complex with sodium chloride was observed in any of these preparations. Analytical samples were obtained by distillation at low pressures in a simple bulb-to-bulb apparatus. Larger quantities of diphenylphosphinic azide were distilled with some decomposition through a short Vigreux column or without decomposition through a molecular still apparatus to give a water-white product. In a similar manner, sodium azide reacted with diphenylthiophosphinic chloride to yield diphenylthiophosphinic azide (II), $(C_6H_5)_2P(S)N_3$. Attempts to purify crude yellow II by distillation at 10^{-4} mm. resulted in dark red products which gave erratic azide analytical values. Table I reports the pertinent data for the phosphinic azides prepared. None of these diarylphosphinic azides exhibited any shock sensitivity and burned only sluggishly when placed in a bunsen flame.

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[1] (a) Presented in part at the 1961 Pacific Southwest Regional Meeting of the American Chemical Society, San Diego, Calif., Dec. 1961. (b) This investigation was supported by the Materials Laboratory, Wright Air Development Command, Wright-Patterson Air Force Base, Ohio, under Contracts AF 33(616)-6913, -7810, and 33(657)-11129.

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TABLE I

DIARYLPHOSPHINIC AZIDES

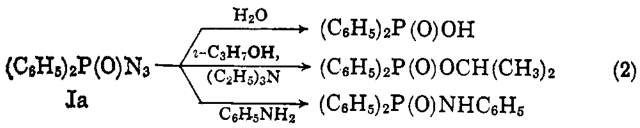
$Ar_2P(O)N_3$

Ar	B.p. C. (mm.)	Formula	Chlorine, % Calcd.	Chlorine, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Phosphorus, % Calcd.	Phosphorus, % Found	Mol. wt. Calcd.	Mol. wt. Found
C_6H_5[a]	137–140 (0.05)	$C_{12}H_{10}N_3OP$	0.00	Nil	17.28	17.2	12.74	12.88	243.2	247.2
p-$CH_3C_6H_4$	190–195 (0.5)	$C_{14}H_{14}N_3OP$	0.00	Nil	15.48	15.49	11.42	11.5	271.2	272
p-ClC_6H_4[b]	160–165 (0.005)	$C_{12}H_8Cl_2N_3OP$	22.72	22.65	13.46	13.90	9.93	9.75	312.1	324.7
C_6H_5[c]	...	$C_{12}H_{10}N_3PS$	0.00	0.0–0.3	16.21	14.1–17.5	11.95	11.90	259.3	264.4

[a] $n^{20}D$ 1.6077. [b] $n^{20}D$ 1.6246. [c] Diphenylthiophosphinic azide: *Anal.* Calcd.: S, 12.37. Found: S, 12.24.

The use of other solvents for the preparation of the phosphinic azides was investigated by allowing equal molar quantities of diphenylphosphinic chloride and sodium azide to react at ambient temperature with stirring in the test solvent. The extent of phosphinic azide formation was monitored by following the development of azide absorption at about 2150 cm.$^{-1}$. In benzene no azide absorption was observed, while after 48 hr. in p-dioxane the azide absorption was only very weak; in tetrahydrofuran after 48 hr. there was a strong azide absorption. Under similar conditions in pyridine, the displacement of chloride by azide is complete in approximately 6–8 hr. Qualitatively, the rate of azide formation in various solvents is in the order benzene $\ll$ p-dioxane $<$ tetrahydrofuran $\ll$ pyridine. Interestingly, the addition of only 2 equiv. of pyridine to a benzene solution of the phosphinic chloride and sodium azide resulted in immediate and rapid formation of azide. This result is under further investigation. When dimethylformamide was used as the solvent, an unknown reaction occurred which resulted in the liberation of nitrogen.

Diphenylphosphinic azide (Ia) undergoes solvolytic reactions such as hydrolysis, alcoholysis, and aminolysis (eq. 2). The alcoholysis reaction must be per-



$$(C_6H_5)_2P(O)N_3 \begin{cases} \xrightarrow{H_2O} (C_6H_5)_2P(O)OH \\ \xrightarrow[(C_2H_5)_3N]{i\text{-}C_3H_7OH,} (C_6H_5)_2P(O)OCH(CH_3)_2 \\ \xrightarrow[C_6H_5NH_2]{} (C_6H_5)_2P(O)NHC_6H_5 \end{cases} \qquad (2)$$

Ia

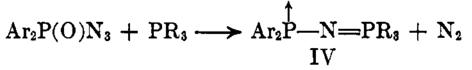
formed under anhydrous conditions to prevent the preferential hydrolytic formation of diphenylphosphinic acid. Furthermore, the alcoholysis reaction was more facile in the presence of a tertiary amine.

Arylsulfonyl azides have been reported to undergo reaction at 105–120° with aromatic compounds to yield arylsulfonanilides.[3,15] Under similar conditions and also in the presence of azobisisobutyronitrile, Ia failed to yield any of the expected diphenylphosphinanilides. A further comparison of the difference in the reactivity of the phosphinic and sulfonyl azides

$$(C_6H_5)_2P(O)N_3 + ArH \xrightarrow[\Delta]{R\cdot} \!\!\!\!\!\!\!\!/\;\; (C_6H_5)_2P(O)NHAr \qquad (3)$$

is afforded by the fact that the sulfonyl azides react with pyridine,[3,16] while the phosphinic azides can be prepared in pyridine without any evidence of reaction. As further evidence of the stability of these phosphinic azides, the attempted Schmidt-type rearrangement of Ia under the influence of boron trifluoride in ether at reflux for 48 hr. was unsuccessful. Infrared examination of the reaction mixture indicated little or no reaction had taken place as evidenced by the strong azide absorption at 2150 cm.$^{-1}$ and the lack of any NH absorption. There was also no evidence for reaction when diphenylphosphinic azide was stored under oxygen in a sealed vial for several weeks.

N-(Diarylphosphinyl)iminophosphoranes.—Of particular interest have been the reactions of the diarylphosphinic azides with a variety of tertiary phosphines (eq. 4) to yield a series of thermally and generally



$$Ar_2P(O)N_3 + PR_3 \longrightarrow \underset{IV}{Ar_2\overset{\displaystyle O \atop \uparrow}{P}{-}N{=}PR_3} + N_2 \qquad (4)$$

hydrolytically stable compounds, the N-(diarylphosphinyl)iminophosphoranes (IV).[17] Ia reacts rapidly with triphenylphosphine in ether to yield N-(diphenylphosphinyl)-P,P,P-triphenyliminophosphorane (V), $(C_6H_5)_2P(O)N{=}P(C_6H_5)_3$, with the concurrent liberation of an equal molar quantity of nitrogen. However, pyridine or toluene appear to be more useful solvents for the preparation of the phosphoranes. Toluene has the advantage that many of the phosphoranes will precipitate from it directly as white solids of high purity. At the reflux temperature in either of these solvents, reactions can be completed as rapidly as the nitrogen can be safely handled. Phosphorane V was recovered unchanged from boiling water, ammonium hydroxide, dilute sulfuric acid, and alcoholic sodium hydroxide. After 16 hr. at about 250° and then 5 hr. at 280° in an evacuated, sealed tube, V was recovered unchanged. After extended periods at 280–300°, a rearrangement appeared to have taken place and is under further study.

As would be expected, the nucleophilic character of the tertiary phosphine influences the rate of reaction illustrated in eq. 4. In comparison with triphenylphosphine, more nucleophilic phosphines such as tri-n-butylphosphine or phenyldimethylphosphine react so vigorously and exothermally that the reaction is best carried out at 0°. The data for the phosphoranes prepared according to eq. 4 are given in Table II.

The combination of excellent hydrolytic, oxidative, and thermal stabilities of the N-(diarylphosphinyl)-P,P,P-triphenyliminophosphoranes appears to be much better than that for the most closely related materials containing similar phosphorus–nitrogen bonds. For example, benziminotriphenylphosphorane, $C_6H_5CON{=}P(C_6H_5)_3$, has been reported to undergo rearrangement at 150° to benzonitrile and triphenylphosphine oxide,[18] and phenyliminotriphenylphosphorane, $C_6H_5N{=}P(C_6H_5)_3$, is cleaved by hydrochloric

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TABLE II

N-(DIARYLPHOSPHINYL)IMINOPHOSPHORANES

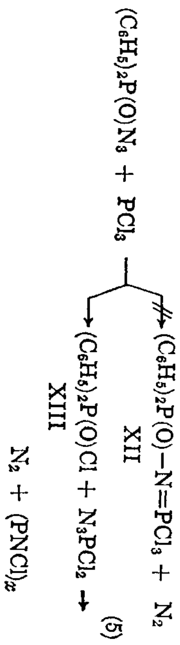
$Ar_2P(O)N{=}PR_3$

Diarylphosphinic azide	Tertiary phosphine	Yield, %	M.p. °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Phosphorus, % Calcd.	Phosphorus, % Found	Mol. wt. Calcd.	Mol. wt. Found
$(C_6H_5)_2P(O)N_3$	$(C_6H_5)_3P$	75–100	170–171	$C_{30}H_{25}NOP_2$	75.46	75.63	5.28	5.47	2.93	2.92	12.98	13.0	477.5	480
$(p\text{-}CH_3C_6H_4)_2P(O)N_3$	$(C_6H_5)_3P$	84	176–178	$C_{32}H_{29}NOP_2$	76.12	76.44	5.77	5.87	2.77	2.79	12.26	12.41	505.5	504
$(p\text{-}ClC_6H_4)_2P(O)N_3$[a]	$(C_6H_5)_3P$	74.5	205–206	$C_{30}H_{23}NOP_2$	65.94	65.89	4.24	4.30	2.56	2.40	11.34	10.8	546.4	552
$(C_6H_5)_2P(S)N_3$[b]	$(C_6H_5)_3P$	91	179–179.5	$C_{30}H_{25}NP_2S$	73.00	73.10	5.11	5.14	2.84	2.82	12.54	12.5	493.5	498
$(C_6H_5)_2P(O)N_3$	$C_6H_5P(CH_3)_2$	91	159.5–161	$C_{20}H_{21}NOP_2$	67.99	67.83	5.99	6.23	3.96	3.91	17.53	17.2	353.3	378
$(C_6H_5)_2P(O)N_3$	$(C_6H_5O)_3P$	98	c	$C_{30}H_{25}NO_4P_2$	...	...	...	...	2.67	2.69	11.79	11.94	525.5	532
$(C_6H_5)_2P(O)N_3$	$(C_4H_9)_3P$	87	66–67	$C_{24}H_{37}NOP_2$	69.04	69.07	8.93	8.60	3.36	3.22	14.84	14.7	417.5	411
$(C_6H_5)_2P(O)N_3$	$(NCC_2H_4)_3P$	91	193–194	$C_{21}H_{22}N_4OP_2$	61.76	61.50	5.43	5.21	13.72	13.45	15.17	15.06	...	d
$2(C_6H_5)_2P(O)N_3$	$1,4\text{-}[(C_6H_5)_2P]_2C_6H_4$	84	232–234	$C_{54}H_{44}N_2O_2P_4$	73.96	73.33	5.06	5.38	3.20	...	14.13	13.70	...	d
$2(C_6H_5)_2P(O)N_3$	$[(C_6H_5)_2PC_6H_4]_2$	100	241–243	$C_{60}H_{48}N_2O_2P_4$	75.62	75.91	5.08	5.35	2.94	2.94	13.00	12.9	...	d
$2(C_6H_5)_2P(O)N_3$	$[(C_6H_5)_2PCH_2]_2$	90	262–264	$C_{50}H_{44}N_2O_2P_4$	72.45	72.44	5.35	5.00	3.38	3.34	14.95	14.8	...	d
$2(C_6H_5)_2P(S)N_3$[e]	$[(C_6H_5)_2PCH_2]_2$	70	292–294	$C_{50}H_{44}N_2P_4S_2$	69.75	70.27	5.15	5.01	3.25	3.16	14.39	14.3	...	d
$(C_6H_5)_2P(O)N_3$	$(C_6H_5)_2POC_6H_5$	57	169.5–171	$C_{30}H_{25}NO_2P_2$	73.02	73.12	5.11	5.38	2.84	2.67	12.55	12.6	493.5	490
$(C_6H_5)_2P(S)N_3$[f]	$(C_6H_5)_2POC_6H_5$	53	164–165.5	$C_{30}H_{25}NOP_2S$	70.71	70.25	4.94	4.95	2.75	2.60	12.16	12.5	509.5	520

[a] *Anal.* Calcd.: Cl, 12.98. Found: Cl, 12.8. [b] *Anal.* Calcd.: S, 6.50. Found: S, 6.34. [c] A viscous oil. [d] Insoluble in benzene which was used for molecular weight determinations. [e] *Anal.* Calcd.: S, 7.45. Found: S, 7.51. [f] *Anal.* Calcd.: S, 6.29. Found: S, 6.35.

acid.[18] However, as anticipated, as the groups attached to the phosphorane phosphorus atom are changed from phenyl to other groups, so are changed the properties of the resulting phosphorane. Thus, N-(diphenylphosphinyl-P,P,P-tris(β-cyanoethyl)iminophosphorane is completely hydrolyzed by aqueous sodium hydroxide and the corresponding tri(*n*-butyl)-phosphorane decomposes slowly in the atmosphere.

In an effort to extend the phosphorane reaction to less nucleophilic phosphines, Ia was allowed to react with phosphorus trichloride in refluxing pyridine. The reaction was vigorous and the nitrogen evolved was nearly quantitative. However, instead of the expected phosphorane XII, only diphenylphosphinic chloride (XIII) contaminated with some azide was recovered. This suggests then that there was an extremely rapid exchange of azide and chloride to give XIII and phosphorus azidodichloride which would be expected to decompose to phosphonitrilic chloride.

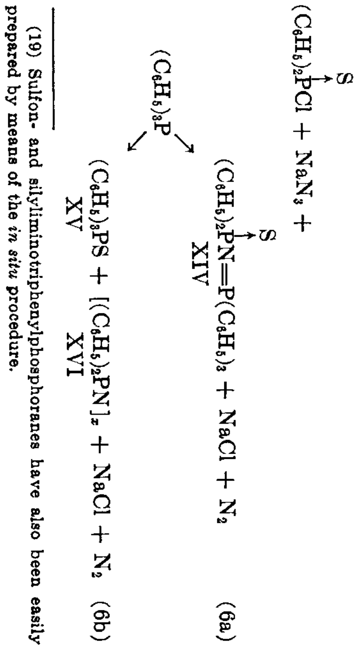


$$(C_6H_5)_2P(O)N_3 + PCl_3 \longrightarrow \begin{cases} \not\rightarrow \underset{\text{XII}}{(C_6H_5)_2P(O){-}N{=}PCl_3} + N_2 \\ \rightarrow \underset{\text{XIII}}{(C_6H_5)_2P(O)Cl} + N_3PCl_2 \rightarrow N_2 + (PNCl)_x \end{cases} \qquad (5)$$

A similar exchange between diphenylphosphinic azide and diphenylchlorophosphine has been described recently in an excellent paper by Paciorek.[14]

In Situ **Formation of Phosphoranes.**—An *in situ* procedure for the preparation of IV has been developed which does not require isolation of phosphinic azide.[19] In the *in situ* procedure, a mixture of sodium azide and triphenylphosphine in pyridine is warmed to gentle reflux under an inert atmosphere and then a pyridine solution of the phosphinic chloride is slowly added. The *in situ* procedure offers some advantages in choice of solvent. For example, when diphenylphosphinic chloride and sodium azide are allowed to react in dimethylformamide, there is an immediate evolution of nitrogen indicating decomposition of the azide. However, when diphenylphosphinic chloride was added to a hot solution of sodium azide and triphenylphosphine in dimethylformamide, a quantitative yield of V was obtained.

When an attempt was made to use the *in situ* method for the preparation of N-(diphenylthiophosphinyl)-P,P,P-triphenyliminophosphorane (XIV) (eq. 6a), none of the desired product was obtained. Instead, an 87% yield of triphenylphosphine sulfide (XV) and a yellow, gummy material which was insoluble in benzene was obtained (eq. 6b). After heat-



$$(C_6H_5)_2\overset{S\uparrow}{P}Cl + NaN_3 + (C_6H_5)_3P \rightarrow \underset{\text{XIV}}{(C_6H_5)_2\overset{S\uparrow}{P}N{=}P(C_6H_5)_3} + NaCl + N_2 \qquad (6a)$$

$$\rightarrow \underset{\text{XV}}{(C_6H_5)_3PS} + \underset{\text{XVI}}{[(C_6H_5)_2PN]_x} + NaCl + N_2 \qquad (6b)$$

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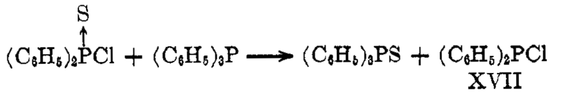
[19] Sulfon- and silyliminotriphenylphosphoranes have also been easily prepared by means of the *in situ* procedure.

ing a portion of the yellow material at 275–280° for 3 hr. under a high vacuum and extraction with benzene, a quantity of diphenylphosphinic nitride tetramer (XVI, $x = 4$) was isolated. The tetramer was characterized by comparison of its melting point and infrared spectrum with those of an authentic sample.[20]

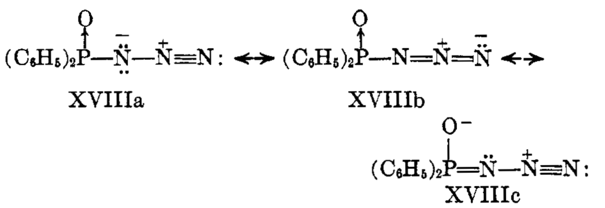
In an attempt to understand this anomalous *in situ* reaction better, it was determined that XIV, prepared in 87% yield from diphenylthiophosphinic azide and triphenylphosphine, did not react with triphenylphosphine *via* sulfur exchange to yield triphenylphosphine sulfide. The successful synthesis of XIV from preformed diphenylthiophosphinic azide and triphenylphosphine indicates that desulfurization of the thiophosphinic azide by the phosphine does not occur and hence does not represent the first step in the anomalous reaction (eq. 6b). However, it was found that triphenylphosphine reacted with diphenylthiophosphinic chloride to give triphenylphosphine sulfide and diphenylchlorophosphine (XVII) (eq. 7) which was



$$(C_6H_5)_2\overset{S}{\overset{\uparrow}{P}}Cl + (C_6H_5)_3P \longrightarrow (C_6H_5)_3PS + \underset{\text{XVII}}{(C_6H_5)_2PCl} \quad (7)$$

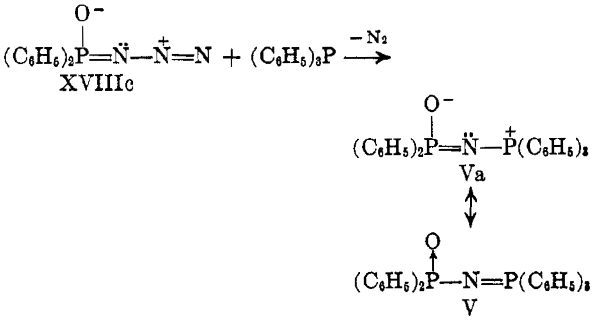
identified by conversion to diphenylphosphinic acid. Since unstable diphenylphosphinous azide has been successfully prepared from lithium azide and XVII in acetonitrile at low temperature[21] and from the chloride and sodium azide in pyridine in our laboratory, it seems likely, then, that eq. 7 represents the first step in the anomalous reaction of eq. 6b. The resulting XVII (eq. 7) then reacted with sodium azide to give the unstable diphenylphosphinous azide which decomposed to the observed XVI. Therefore, in the anomalous reaction, the desulfurization of diphenylthiophosphinic chloride occurs at the expense of the *in situ* formation of diphenylthiophosphinic azide and subsequent formation of the phosphorane XIV of eq. 6a.

The unusual properties of the diarylphosphinic azides and N-(diarylphosphinyl)iminophosphoranes can be rationalized by considering some of the resonance forms which do contribute to their total structures. Delocalization of the electrons *via* such canonial forms would be expected to contribute to increased thermal stabilities. All of the diarylphosphinic azides in this study contain characteristic strong infrared absorptions at about 2150 cm.$^{-1}$ due to the azide asymmetric



$$\underset{\text{XVIIIa}}{(C_6H_5)_2\overset{O}{\overset{\uparrow}{P}}-\overset{-}{\underset{\cdot\cdot}{N}}-\overset{+}{N}\equiv N:} \longleftrightarrow \underset{\text{XVIIIb}}{(C_6H_5)_2\overset{O}{\overset{\uparrow}{P}}-N=\overset{+}{N}=\overset{-}{\underset{\cdot\cdot}{N}}} \longleftrightarrow \underset{\text{XVIIIc}}{(C_6H_5)_2\overset{O^-}{\overset{|}{P}}=\overset{\cdot\cdot}{N}-\overset{+}{N}\equiv N:} \quad (8)$$

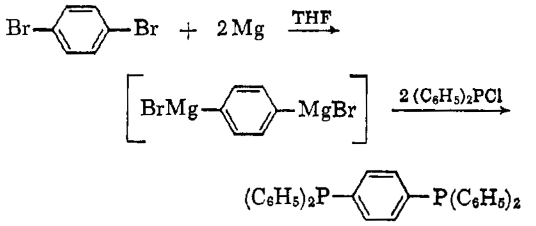
stretching frequency, at about 1260 cm.$^{-1}$ due to the azide symmetric stretching, and at about 1229 cm.$^{-1}$ due to the P→O stretching absorption. However, it is noteworthy that absorption in the 1260-cm.$^{-1}$ region is also that for the P=N stretching band.[17,22,23] Since this latter azide symmetric absorption is reported to be weak,[22] this would suggest that there is a significant contribution of the charge-separated structure XVIIIc. This structure, XVIIIc, can also be envoked to describe the reaction of the azides with trivalent phosphorus compounds to yield the phosphoranes (eq. 9). It would be expected that both XVIIIb



$$\underset{\text{XVIIIc}}{(C_6H_5)_2\overset{O^-}{\overset{|}{P}}=\overset{\cdot\cdot}{N}-\overset{+}{N}=N} + (C_6H_5)_3P \xrightarrow{-N_2} \underset{\text{Va}}{(C_6H_5)_2\overset{O^-}{\overset{|}{P}}=\overset{\cdot\cdot}{N}-\overset{+}{P}(C_6H_5)_3} \updownarrow \underset{\text{V}}{(C_6H_5)_2\overset{O}{\overset{\uparrow}{P}}-N=P(C_6H_5)_3} \quad (9)$$

and c would accommodate the tertiary phosphine and its pair of electrons more readily than XVIIIa during the displacement of the nitrogen. Structure XVIIIa in analogous to those structures used by Thayer and West to describe the Lewis-base properties of group IV-A azides.[24] Structure XVIIIc involves $d\pi-p\pi$ electron delocalization and accounts for the reactivity and unexpected thermal stability of the phosphinic azides.

Bis Tertiary Phosphines.—A number of bis tertiary phosphines were needed for the synthesis and investigation of bisphosphoranes (Table II). The synthesis of 1,4-bis(diphenylphosphino)benzene (XIX) was most conveniently accomplished in 55–60% yields *via* the diGrignard compound prepared from *p*-dibromobenzene in tetrahydrofuran (eq. 10). Repeated attempts to utilize the Grignard reagent from



(10)

XIX

4,4′-dibromobiphenyl and 4,4′-dibromodiphenyl ether were unsuccessful. None of the desired bis tertiary phosphines were obtained from the attempted reaction of lithium diphenylphosphide[25] and these same dibromides. However, 4,4′-bis(diphenylphosphino)biphenyl was successfully prepared from diphenylchlorophosphine and 4,4′-dilithiobiphenyl in 40–60% yields.

The ultraviolet spectra of the phosphinic azides and phosphoranes have been determined using ethanol or acetonitrile as the solvent. The phosphoranes show greatly enhanced aromatic absorptions at 264–265 and 266–267 mμ (log ϵ 3.2 and 3.5) and at 224–225 mμ (log ϵ >4.5). N-(Diphenylthiophosphinyl)-P,P,P-tri-

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[20] We wish to thank Mr. D. L. Herring, U. S. Naval Ordnance Laboratory, Corona, Calif., for the sample of diphenylphosphinic nitride tetramer and its infrared spectrum.

[21] K. L. Paciorek and R. Kratzer, *Inorg. Chem.*, **3**, 594 (1964).

[22] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 323.

[23] L. W. Daasch, *J. Am. Chem. Soc.*, **76**, 3403 (1954).

[24] J. S. Thayer and R. West, *Inorg. Chem.*, **4**, 114 (1965).

[25] A. M. Aguiar, H. J. Greenberg, and K. E. Rubenstein, *J. Org. Chem.*, **28**, 2091 (1963).

phenyliminophosphorane exhibits enhanced aromatic absorptions (log ϵ 3.7 and 3.85) at the same wave lengths as the oxygen analog. Similarly, triphenylphosphine sulfide also exhibits an enhancement of the aromatic absorptions compared to triphenylphosphine oxide at these wave lengths. Diphenylphosphinic azide has an ultraviolet spectrum similar to that of the phosphoranes.

Experimental Section

The infrared spectra were determined on a Perkin-Elmer Model 21 spectrophotometer. The ultraviolet spectra were determined on a Cary recording spectrophotometer, Model 14. The melting and boiling points are uncorrected. *CAUTION!* Although no difficulties have been experienced in the preparation or use of the azides of this study, adequate safety precautions should be observed at all times.

Intermediates.—The diarylphosphinic acids required as starting materials were synthesized by the reaction of the appropriate Grignard reagent with either phosphorus oxychloride or N,N-diethylaminophosphonyl dichloride in yields of 20–50%.

Bis(*p*-chlorophenyl)phosphinic Chloride.—A 78.6-g. (0.274-mole) quantity of bis(*p*-chlorophenyl)phosphinic acid was allowed to stand with excess thionyl chloride for 24 hr. before being refluxed for 2.5 hr. The excess thionyl chloride was removed at reduced pressure and the residue was distilled, b.p. 183–187° (0.2 mm.) [lit.[26] b.p. 280° (25 mm.)], to give 71.8 g. (0.235 mole, 86%) of a pale yellow oil which solidified on standing. A sample was sublimed at 100° and 10^{-4} mm. to give a white solid which melted at 69–70°.

Anal. Calcd. for $C_{12}H_8Cl_3OP$: Cl, 34.82; mol. wt., 305.5. Found: Cl, 34.6; mol. wt., 306.8.

Bis(*p*-tolyl)phosphinic Chloride.—In a similar manner, 72 g. (0.293 mole) of bis(*p*-tolyl)phosphinic acid was treated with excess thionyl chloride to give 61.1 g. (0.231 mole, 79%) of viscous oil, b.p. 164–167° (0.05 mm.) [lit.[26] b.p. 270–280° (25 mm.)]. On standing, the oil solidified to a white solid which softened at 45° and melted at 56–58°.

Anal. Calcd. for $C_{14}H_{14}ClOP$: Cl, 13.39; P, 11.70; mol. wt., 264.7. Found: Cl, 13.26; P, 11.76; mol. wt., 263.5.

Diphenylthiophosphinic Chloride.—A mixture of 750 ml. of benzene and 32.1 g. (1 mole) of sulfur was warmed to reflux before 220.5 g. (1 mole) of diphenylchlorophosphine was slowly added. After distillation, b.p. 155–157° (0.3 mm.) [lit.[27] b.p. 155–160° (0.3 mm.)], $n^{20}D$ 1.6588, the pale yellow diphenylthiophosphinic chloride weighed 246.1 g. (0.974 mole, 97%).

Anal. Calcd. for $C_{12}H_{10}ClPS$: Cl, 14.03; P, 12.26; S, 12.69; mol. wt., 252.7. Found: Cl, 14.20; P, 12.4; S, 12.8; mol. wt., 251.6.

The anilide, m.p. 157–158.5°, was obtained in 95% yield on refluxing aniline and diphenylthiophosphinic chloride in ether for 24 hr.

Anal. Calcd. for $C_{18}H_{16}NPS$: N, 4.53; P, 10.01; S, 10.37. Found: N, 4.36; P, 10.2; S, 10.2.

Diphenylphosphinic Chloride.—Large quantities (to 3000 g.) were prepared by bubbling dry oxygen through neat diphenylchlorophosphine at approximately 135° and monitoring the oxidation by the decrease in the index of refraction at 20° to approximately 1.6100. The resulting yellow-to-orange colored diphenylphosphinic chloride distilled at 0.1 mm. and 140° to give consistently yields of 95% or better.

1,4-Bis(diphenylphosphino)benzene.—To the yellow-green suspension of the diGrignard compound prepared by refluxing 36.7 g. (0.155 mole) of *p*-dibromobenzene with 7.5 g. (0.31 g.-atom) of magnesium turnings in 250 ml. of tetrahydrofuran for 8 hr. was slowly added 68.4 g. (0.31 mole) of diphenylchlorophosphine in 250 ml. of tetrahydrofuran. The mixture was refluxed an additional hour before saturated ammonium chloride was added to the cooled solution. The organic layer was decanted from the solids which were further extracted with two 50-ml. portions of tetrahydrofuran. The combined organic extracts were dried briefly over anhydrous sodium sulfate before the solvent was removed at reduced pressure to yield a yellow-white tacky residue which was digested with isopropyl alcohol to give 40.7 g. (0.091 mole, 59%) of a white powder which melted over the range 167–172°. The bis tertiary phosphine was purified by recrystallization from benzene–methanol or by sublimation at 160–180° and 10^{-4} mm. to give a white powder, m.p. 166–168.5° (lit.[28] m.p. 166–167°) which no longer contained any appreciable infrared absorption due to P–O at 1190 cm.$^{-1}$.

Anal. Calcd. for $C_{30}H_{24}P_2$: P, 13.82; mol. wt., 446.5. Found: P, 13.7; mol. wt., 436.6.

From the isopropyl alcohol extract was recovered a yellow-brown tacky residue which had an infrared spectrum very similar to that of diphenyl-4-hydroxybutylphosphine oxide isolated by Garner and Tedeschi.[29]

The corresponding bisoxide was prepared in 40% yield by this same method using diphenylphosphinic chloride. Recrystallization from dimethylformamide gave a white powder which melted at 297–302°. The infrared spectrum contained a strong P–O absorption at about 1190 cm.$^{-1}$.

Anal. Calcd. for $C_{30}H_{24}O_2P_2$: P, 12.16. Found: P, 12.2.

4,4′-Bis(diphenylphosphino)biphenyl.—To a 263.6-g. quantity of a benzene slurry of 4,4′-dilithiobiphenyl (Lithium Corporation of American), assumed to contain 0.17 mole of 4,4′-dilithiobiphenyl, was added 75 g. (0.34 mole) of diphenylchlorophosphine dissolved in 50 ml. of benzene. The reaction was held at 25–28° by means of an ice bath during the addition.

After stirring for 64 hr. under argon, the solvent was removed at reduced pressure to give a brown tacky residue. After digestion with methanol and with ethyl acetate, 70.7 g. (0.135 mole, 79%) of pale yellow bis tertiary phosphine, melting over the range 175–185°, was isolated. A mixture melting point with diphenylphosphinic acid was 178–190° showing that this material was not impure acid obtained from the oxidative hydrolysis of the diphenylchlorophosphine. Crystallization of analytical samples from tetrahydrofuran–methanol or ethylene glycol dimethyl ether and activated charcoal resulted in crystalline 4,4′-bis(diphenylphosphino)biphenyl, m.p. 192.5–194°.

Anal. Calcd. for $C_{36}H_{28}P_2$: C, 82.74; H, 5.40; P, 11.85. Found: C, 82.27; H, 5.58; P, 11.4.

Care must be taken when using the ethylene glycol dimethyl ether as the recrystallization solvent to insure that it is peroxide free. The peroxide-containing solvent oxidized the bis tertiary phosphine to a white powder, m.p. 290°, which was no longer soluble in the hot solvent and which contained a strong P–O absorption at 1176 cm.$^{-1}$. Identification of the suspected bisoxide was carried out by oxidizing a small quantity of 4,4′-bis(diphenylphosphino)biphenyl with 3% hydrogen peroxide in acetone. The resulting white crystalline bisoxide was recrystallized from ethanol and melted at 299–301.5°. The infrared spectra of the two oxides were identical.

Anal. Calcd. for $C_{36}H_{28}O_2P_2$: C, 77.97; H, 5.09; P, 11.17. Found: C, 77.6; H, 5.08; P, 10.9.

For the purification of grossly impure fractions containing considerable oxide contamination, it was found that it was beneficial to carry out the following purification. The crude material was dissolved in concentrated hydrochloric acid and filtered through glass wool on a medium-porosity sintered-glass funnel. The resulting clear filtrate was poured into ice and water to precipitate a white solid. After careful washing with water and ethanol and drying, the bisphosphine had a melting point of 185–190° or better.

1,2-Bis(diphenylphosphino)ethane.—Following the method described by Aguiar,[27] lithium diphenylphosphide was prepared in tetrahydrofuran and treated with 1,2-dichloroethane to give quantitative crude yields of 1,2-bis(diphenylphosphino)ethane. Careful purification by sublimation and recrystallization from cyclohexane resulted in the recovery of white crystals, m.p. 137–139° (sealed tube, nitrogen) (lit. m.p. 140–142,[30a] 161–163°[30b]).

Anal. Calcd. for $C_{26}H_{24}P_2$: C, 78.38; H, 6.07; mol. wt., 398.4. Found: C, 78.53; H, 5.93; mol. wt., 400.

Diarylphosphinic Azides.—In a typical run, 69.9 g. (0.297 mole) of diphenylphosphinic chloride and 20.9 g. (0.32 mole) of sodium azide were allowed to stir in 200 ml. of pyridine

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[26] V. M. Plets in "Organophosphorus Compounds," G. M. Kosolapoff, Ed., John Wiley and Sons, Inc., New York, N. Y., 1950, p. 75.

[27] W. Higgins, P. W. Vogel, and W. G. Craig, *J. Am. Chem., Soc.* **77**, 1864 (1955).

[28] D. L. Herring, *J. Org. Chem.*, **26**, 3998 (1961).

[29] A. Y. Garner and A. A. Tedeschi, *J. Am. Chem. Soc.*, **84**, 4734 (1962). We wish to thank Dr. Garner for the infrared spectrum of this material.

[30] (a) J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1378 (1960); (b) K. Issleib, K. Krech, and K. Gruber, *Ber.*, **96**, 2186 (1963).

(distilled from calcium hydride) overnight (18 hr.). The solids were removed by filtration. The solvent was removed from the filtrate at reduced pressure to give a quantitative yield of crude phosphinic azide Ia which was distilled at 0.05 mm. to yield 63.1 g. (87%) of colorless azide boiling at 137–140°, n^{20}_{D} 1.6077.

Anal. Calcd. for $C_{12}H_{10}N_3OP$: N, 17.28. Found: Cl, 0.19; N, 17.2.

Larger quantities (100–300 g.) were more conveniently distilled using a wiping-blade molecular still with a jacket temperature of 92–100° and a pressure of less than 0.01 mm. None of the distilled samples, the pyridine solutions, crude products, or stored samples showed any shock sensitivity in an Olin-Mathieson drop-test meter. Similarly the azide content remained constant on storage through at least 18 months.

The diphenylphosphinic azide was further characterized by means of the following reactions.

Under an atmosphere of argon, 5.0 ml. (0.055 mole) of aniline was added dropwise to 4.8 g. (0.20 mole) of Ia to yield 4.0 g. (0.014 mole, 70%) of diphenylphosphinanilide, m.p. 241–243° (lit.[31] m.p. 242–244°), after recrystallization from ethanol (Norit).

The reaction of 3.5 ml. of water with 0.5572 g. (0.00237 mole) of Ia yielded 0.5166 g. (0.00236 mole, 99.9%) of diphenylphosphinic acid, m.p. 194–196°; mixture melting point with an authentic sample was 194–196°.

A mixture of 2.85 g. (0.0117 mole) of Ia, 3.93 g. (5.0 ml., 0.0654 mole) of isopropyl alcohol (dried by distillation from calcium hydride), and 3.61 g. (5 ml., 0.0357 mole) of triethylamine was heated on a steam bath for 1 hr. and then allowed to stand overnight. After removal of the solvent at reduced pressure, the pale yellow solid was recrystallized from ethanol–water to give 2.65 g. (0.0101 mole, 86.6%) of isopropyl diphenylphosphinate, m.p. 97.5–98.5° (lit.[32] m.p. 95–96°), having a molecular weight of 261.4 (calcd. 260.3).

A catalytic quantity of azobisisobutyronitrile was placed in 20 ml. of benzene. The mixture was brought to reflux and then 3.4 g. (0.14 mole) of Ia dissolved in 15 ml. of benzene was added. Since only 30 cc. of gas was liberated, a second small quantity of catalyst was added. After 24 hr. at reflux, no further gas evolution was observed and the experiment was discontinued. The azide absorption was still strong at this point.

In a similar experiment, 2.43 g. (0.01 mole) of Ia was heated under reflux in 25 ml. of *p*-xylene with a small quantity of azobisisobutyronitrile for 24 hr. without the liberation of nitrogen. After removal of the solvent, an infrared examination of the residual liquid showed a strong azide absorption at 2150 $cm.^{-1}$ and no evidence of N–H absorption.

A 5.0-g. (0.0205-mole) quantity of diphenylphosphinic azide in 10 ml. of ether and 2.5 g. (0.037 mole) of boron trifluoride dissolved in 10 ml. of ether were allowed to reflux in a system arranged for the collection of nitrogen. No nitrogen was observed after 48 hr. and the heating was discontinued. Infrared analysis of the reaction mixture indicated that no reaction had occurred.

The qualitative evaluation of other potential solvents for use in preparing phosphinic azides was carried out by stirring 2.4 g. (0.01 mole) of diphenylphosphinic chloride and 0.8 g. (0.012 mole) of sodium azide in 35 ml. of the solvent. The extent of reaction was followed by observing the increase of the azide absorption at about 2150 $cm.^{-1}$.

N-(Diarylphosphinyl)iminophosphoranes.—In a typical example, 2.4 g. (0.01 mole) of diphenylphosphinic azide dissolved in 25 ml. of dry pyridine was added, so as to maintain a steady flow of nitrogen, to 2.6 g. (0.01 mole) of triphenylphosphine dissolved in 25 ml. of pyridine. The nitrogen evolved was 220 cc. (corrected, 98%). The pyridine was removed at reduced pressure to yield a white powder which was recrystallized from isopropyl alcohol and water to give 4.6 g. (0.00964 mole, 96%) of white needles of N-(diphenylphosphinyl)-P,P,P-triphenyliminophosphorane (V), m.p. 170–171°.

Anal. Calcd. for $C_{30}H_{25}NOP_2$: N, 2.93; P, 12.98. Found: N, 2.90; P, 13.0.

Alternatively, the phosphinic chloride and sodium azide in pyridine can be stirred overnight at ambient temperature and subsequently reacted without isolation of the azide or removal of the sodium chloride. Yields by this modification are as good as the preceding method.

***In Situ* Procedure.**—An *in situ* procedure was also developed which allows some choice in reaction solvent; for example, dimethylformamide can be used in contrast to the previously described decomposition of the azide during the attempted preparation in this solvent. The following is representative of this technique.

A 1.0-g. (0.015-mole) quantity of sodium azide and 2.6 g. (0.01 mole) of triphenylphosphine were mixed in 20 ml. of dry dimethylformamide and warmed almost to reflux before the addition of 2.4 g. (0.01 mole) of diphenylphosphinic chloride was begun. The addition was completed in 15 min. with a quantitative evolution of nitrogen and the formation of a precipitate. After removal of the solvent at reduced pressure (<1 mm.), the resulting cream-colored solid was washed with two 25-ml. portions of ether and 25 ml. of dilute ammonium hydroxide solution, and dried at reduced pressure for 8 hr. to give 3.8 g. (79.5%, 0.00795 mole) of V, m.p. 169–170°, having a molecular weight of 480 (calcd. 477.5).

Anomalous *in Situ* Reaction. Formation of Diphenylphosphinic Nitride.—The addition of a 25-ml. portion of a 253-g. (1.00-mole, 205-ml.) quantity of diphenythiophosphinic chloride to a hot mixture of 65 g. (1.0 mole) of sodium azide and 262 g. (1.00 mole) of triphenylphosphine (recrystallized from isopropyl alcohol and Norit) in pyridine resulted in little nitrogen evolution until the mixture was heated under reflux. After all of the diphenylthiophosphinic chloride had been added (6 hr.), the reaction mixture was heated and stirred for an additional 36 hr. while nitrogen slowly evolved. The resulting mixture was filtered through a sintered-glass funnel (under argon) to yield a yellow-white solid and an orange filtrate.

The yellow-white solid was washed with ether and then with water to yield 255 g. of a very pale yellow solid which, after recrystallization from *n*-butyl acetate, had a melting point of 160–162°. Comparison of the infrared spectrum of the unknown with the infrared spectra of N-(diphenylthiophosphinyl)-P,P,P-triphenyliminophosphorane, m.p. 179–179.5°, and triphenylphosphine sulfide, m.p. 161°,[33] indicated that the unknown product was triphenylphosphine sulfide and not the expected phosphorane.

Anal. Calcd. for $C_{30}H_{25}NP_2S$ [N-(diphenylthiophosphinyl)-P,P,P-triphenyliminophosphorane]: N, 2.84; P, 12.54; S, 12.54. Calcd. for $C_{18}H_{15}PS$ (triphenylphosphine sulfide): P, 10.52; S, 10.89. Found: N, 0.00; P, 10.8; S, 10.9. The yield of triphenylphosphine sulfide was 86.7%.

The orange pyridine filtrate was concentrated at reduced pressure to yield a tacky yellow residue which remained gummy after digestion with isopropyl alcohol. When the gum was dried under high vacuum, a yellow friable, benzene-soluble solid was obtained. Attempted recrystallization from benzene, ethanol, and butyl acetate was unsuccessful. When about half of the yellow solid was heated at 275–280° under high vacuum, the material refluxed gently. On cooling, a yellow glass formed which was dissolved in a minimum amount of hot benzene. A white solid slowly precipitated from the benzene solution on standing, m.p. 318–320° (softens 315°). The infrared spectrum was identical with that of diphenylphosphinic nitride tetramer.[20,34] Approximately 16 g. of tetramer was isolated from the viscous yellow gum. This represents a yield of approximately 16% based on diphenylthiophosphinic chloride.

Attempted Reaction of N-(Diphenylthiophosphinyl)-P,P,P-triphenyliminophosphorane (XIV) and Triphenylphosphine.—Under an atmosphere of argon, 1.0 g. (0.002 mole) of XIV and 0.52 g. (0.002 mole) of triphenylphosphine dissolved in 10 ml. of dry pyridine were heated on a steam bath for 6 hr. and allowed to stand overnight. After removal of the solvent, 0.95 g. (95% recovery) of thiophosphorane XIV, m.p. 174–178°, was obtained.

In a similar experiment, the reactants were refluxed for 24 hr. Again, only thiophosphorane XIV, 0.94 g. (94% recovery), m.p. 173–176°, and triphenylphosphine, 0.45 g. (83% recovery), m.p. 78–80°, were obtained. The small losses were attributed to mechanical losses.

Reaction of Triphenylphosphine and Diphenylthiophosphinic Chloride.—To 7.9 g. (0.03 mole) of triphenylphosphine dissolved in 20 ml. of refluxing pyridine was added 7.6 g. (0.03 mole) of

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[31] B. B. Hunt and B. C. Saunders, *J. Chem. Soc.*, 2413 (1957).

[32] A. E. Arbuzov, *J. Russ. Phys. Chem. Soc.*, **42**, 395 (1910).

[33] N. Strecker and C. Grossman, *Ber.*, **49**, 63 (1916); *Chem. Abstr.*, **10**, 897 (1916).

[34] C. P. Haber, D. L. Herring, and E. A. Lawton, *J. Am. Chem. Soc.*, **80**, 2116 (1958).

diphenylthiophosphinic chloride. After heating under reflux in an argon atmosphere for 18 hr., the solvent was removed at reduced pressure, yielding a semisolid. After washing with dilute ammonium hydroxide and digestion with isopropyl alcohol, 8.0 g. (0.027 mole, 91% yield) of triphenylphosphine sulfide, m.p. 158–160°, was obtained. Acidification of the basic extract with concentrated hydrochloric acid yielded 6.5 g. of impure diphenylphosphonic acid, m.p. 185–190°, as confirmed by the infrared spectrum of the solid.

Acknowledgments.—We wish to thank Messrs. Karl Sterner and William Birch for the elemental analyses and Mrs. Nancy Naumann for the infrared spectra.

Organometallic Azides. II. Preparation and Reactions of Phenylphosphonic Mono- and Diazides[1]

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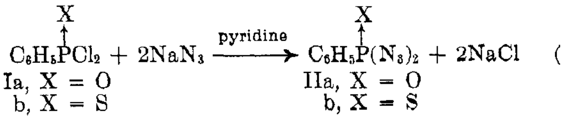
The synthesis and reactions of thermally unstable phenylphosphonic and phenylthiophosphonic diazide are described. These diazides react stepwise with triphenylphosphine to yield intermediate azidophosphoranes, $C_6H_5\underset{\underset{N_3}{|}}{P}(X)N{=}P(C_6H_5)_3$, which further react to yield bisphosphoranes, $C_6H_5P(X)[N{=}P(C_6H_5)_3]_2$. The chemistry of several mixed phosphonic azides, $C_6H_5\underset{\underset{Z}{|}}{P}(O)N_3$ [Z = Cl, N(CH$_3$)$_2$] is also described.

The syntheses of the stable diarylphosphinic azides from phosphinic chlorides and sodium azide in pyridine and their reaction to yield N-(diarylphosphinyl)-iminophosphoranes[2] as well as the addition of bromine to the N-(diarylphosphinyl)iminophosphoranes[3] have been recently described.

As a result of the thermal and chemical stability of N-diphenylphosphinyl-P,P,P-triphenyliminophosphorane,[2] it was of interest to synthesize and evaluate polyphosphorane polymers for use as thermally stable materials. One of the necessary intermediates required for the preparation of polyphosphoranes are aromatic phosphonic diazides such as II. Phenylphosphonic and phenylthiophosphonic dichlorides (Ia and b, respectively) were found to react smoothly with sodium azide in pyridine to yield the diazides IIa and b.



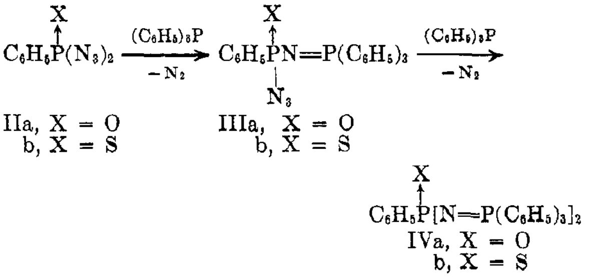
$$C_6H_5\overset{\overset{X}{\uparrow}}{P}Cl_2 + 2NaN_3 \xrightarrow{\text{pyridine}} C_6H_5\overset{\overset{X}{\uparrow}}{P}(N_3)_2 + 2NaCl \qquad (1)$$

Ia, X = O
b, X = S

IIa, X = O
b, X = S

In marked contrast to the thermal and shock stability of the previously prepared diarylphosphinic azides,[2] $Ar_2P(O)N_3$, IIa was found to be extremely shock sensitive and it "verpufft" when placed in a bunsen flame. Furthermore, during the attempted distillation of the thiophosphonic diazide IIb at 0.1 mm., the sample detonated, completely demolishing the distillation apparatus. Pyridine solutions of these phosphonic diazides did not show any shock or thermal sensitivity. However, as a matter of safe practice, all solutions of these and other azides were frequently tested for shock sensitivity.

In preparing the bisphosphoranes IVa and b which were to serve as reference compounds and prototypes for the polyphosphoranes, it was discovered that phenylphosphonic diazide (IIa) in pyridine solution reacted in a clearly defined stepwise manner with 2 equiv. of triphenylphosphine (eq. 2). The first mole of triphenylphosphine at ambient temperature reacted exothermally and then the reaction essentially stopped even in the presence of a second mole of triphenylphosphine. A strong azide absorption was still present at 2138 cm.$^{-1}$ at this halfway point. The nitrogen evolution to this point was 51.35% of the total nitrogen or 102.7% of the nitrogen expected by reaction of only one of the azide groups. The azide function of IIIa subsequently reacted with triphenylphosphine only slowly at reflux in pyridine. The resulting bisphosphorane IVa was isolated as a powder which was difficult to obtain in a crystalline form. Like the N-(diarylphosphinyl)-P,P,P-triphenyliminophosphoranes,[2] IVa was found also to be stable toward attack by aqueous acid and base.



$$C_6H_5\overset{\overset{X}{\uparrow}}{P}(N_3)_2 \xrightarrow[-N_2]{(C_6H_5)_3P} C_6H_5\underset{\underset{N_3}{|}}{\overset{\overset{X}{\uparrow}}{P}}N{=}P(C_6H_5)_3 \xrightarrow[-N_2]{(C_6H_5)_3P} C_6H_5\overset{\overset{X}{\uparrow}}{P}[N{=}P(C_6H_5)_3]_2 \qquad (2)$$

IIa, X = O
b, X = S

IIIa, X = O
b, X = S

IVa, X = O
b, X = S

Similarly, the reaction of phenylphosphonyl diazide (IIb) with triphenylphosphine was found to be stepwise. Isolation of the intermediate azidophosphorane IIIb in a pure solid state was not accomplished although there was not any evidence of hydrolysis products (by infrared examination) in the tacky IIIb which was recovered after removal of the pyridine. The azidophosphorane IIIb was, however, characterized by conversion to its methyl ester V and to the bisphosphorane

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[1] (a) This investigation was supported by the Materials Laboratory, Research and Technology Division, Wright-Patterson Air Force Base, Ohio, under Contract AF 33(657)-11129. (b) Presented before the Division of Organic Chemistry at the 146th National Meeting of the American Chemical Society, Denver, Colo., Jan. 1964.

[2] (a) R. A. Baldwin and R. M. Washburn, *J. Am. Chem. Soc.*, **83**, 4466 (1961); (b) R. A. Baldwin and R. M. Washburn, *J. Org. Chem.*, **30**, 3860 (1965).

[3] R. A. Baldwin and R. M. Washburn, *ibid.*, **30**, 2093 (1965).