is changed from dichloromethane to acetone to acetonitrile which is the order of increasing coordinating ability. This may mean either that the solvent is intimately involved in the electron transfer act or that the initial oxidation of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ gives a short-lived intermediate such as I or II which is rapidly attacked by solvent (in an EC step) to give $(\pi\text{-}C_5H_5)Fe(CO)_2S^+$ (S = solvent).

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Synthesis and Transformations of Phosphorus Imidazolidines (1,3-Diaza-2-phospholidines)

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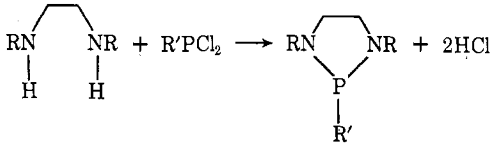
Four new derivatives of the phosphorus imidazolidine ring system have been prepared by amination of dichlorophosphines with variously *N,N'*-disubstituted ethylenediamines. The nmr spectra of the *N*-CH_3 substituted rings show a sharp doublet for these protons and a multiplet for the methylene bridge protons, while the *N*-phenyl derivatives show a sharp doublet for the methylene bridge protons at 60 and 100 MHz contrary to expectations on the basis of the pyramidal stereochemistry of phosphorus(III). These observations are interpreted in terms of the stereochemistry and dynamics of the diazaphospholidine heterocycles. The phosphorus imidazolidines are transformed to their boron analogs in an exothermic reaction with phenylboron dichloride with the release of dichlorophosphine, but the reaction is not reversible. Treatment of the phosphorus ring with arsenic trichloride yields a solid whose mass spectrum shows a peak at the highest mass corresponding to the ten-membered ring dimer of the known arsenic imidazolidine.

We have extended the previous studies in this laboratory on silicon[2] and germanium[2a,c-f,h-i] imidazolidines to phosphorus and boron.[3] This paper describes the synthesis and transformation reactions of phosphorus(III) imidazolidines.

Results and Discussion

Syntheses and Spectra.—Amination is the only method of synthesis extensively used to prepare phosphorus imidazolidines.[4] Lewis bases such as triethylamine facilitate the reactions, which are exothermic and rapid when the N substituent is small. We have prepared five simple derivatives by this route



(1)

I, R = CH_3, R' = CH_3
II,[5] R = CH_3, R' = C_6H_5
III, R = C_6H_5, R' = C_6H_5
IV, R = *p*-$CH_3C_6H_5$, R' = C_6H_5
V, R = *p*-$CH_3OC_6H_5$, R' = C_6H_5

Where R = CH_3, the reactions were carried out at room temperature in dilute media with slow addition. With larger groups, refluxing for 4–6 hr served to drive the reactions to completion. Yields were essentially quantitative. The *N*-alkyl derivatives are thermally stable liquids which hydrolyze rapidly in air; the solid aryl analogs are much more stable to atmospheric moisture. Hydrolysis regenerates the starting diamine and releases $R'P(OH)_2$.

The nmr spectra of I–V were measured at 60 and 100 MHz, and the data are gathered in Table I. The resonances in I assigned to the *N*-CH_3 and *P*-CH_3 protons appear as sharp doublets arising from ^{31}P coupling, but it was noted that $J(^{31}P\text{–N–C–}^1H) > J(^{31}P\text{–C–}^1H)$ in this compound (14.7 *vs.* 6.7 Hz). The methylene bridge protons in I and II appear as multiplets, while in III they give a sharp doublet signal both at 60 and at

TABLE I
NMR DATA (Hz)[a]

	N–C*H*$_3$			N–C*H*$_2$–			P–*R'*			N–C_6H_4–*R''*
	τ	*J*(P–H)	M[b]	τ	*J*(P–H)	M[b]	τ	*J*(P–H)	M[b]	τ
I	7.45	14.7[c]	d	6.95	...	m	9.25	6.7[c]	d	...
II	7.50	14.3[c,d]	d	7.15	...	m	2.77	...	m	...
III	...	...	...	6.11	7.3[c]	d	*e*	...	...	*e*
IV	...	...	...	6.35	5.0[c]	d	*e*	...	...	7.76
V	...	...	...	6.11	7.5[f]	d	*e*	...	...	6.33

[a] Measured at 60 MHz as neat liquids for I and II and as saturated solutions in $CDCl_3$ for the rest *vs.* tetramethylsilane as the internal standard at ambient temperature. [b] Multiplicity: d, doublet; m, multiplet. [c] Coupling constants verified at 100 MHz. [d] Reported as 14.5 Hz in ref 5. [e] P–R resonances of the compounds with three phenyl groups are not included here because of the complex nature of the overlapped *P*-phenyl and *N*-phenyl signals. [f] Multiplet at 100 MHz.

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(1) To whom all inquiries should be addressed.

(2) (a) C. H. Yoder and J. J. Zuckerman, *Inorg. Chem.*, **3**, 1329 (1964); (b) *ibid.*, **4**, 116 (1965); (c) *J. Amer. Chem. Soc.*, **88**, 2170 (1966); (d) *ibid.*, **88**, 4831 (1966); (e) *Inorg. Chem.*, **5**, 2055 (1966); (f) *ibid.*, **6**, 103 (1967); (g) *Chem. Commun.*, 694 (1966); (h) *Prep. Inorg. React.*, in press; (i) E. W. Randall, C. H. Yoder, and J. J. Zuckerman, *Inorg. Chem.*, **6**, 744 (1967).

(3) M. K. Das, P. G. Harrison, and J. J. Zuckerman, *ibid.*, **10**, 1092 (1971).

(4) Tetrahydroimidazoles or imidazolidines where the 2 carbon is replaced by phosphorus are named as 1,3-diaza-2-phospholidines or 1,3-diaza-2-phosphacyclopentanes or simply as phosphorus imidazolidines.

(5) L. Siekmann, H. O. Hoppen, and R. Appel, *Z. Naturforsch. B*, **23**, 1156 (1968).

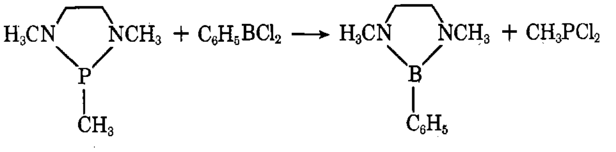
100 MHz. Multiplet methylene bridge patterns have been observed in compounds like I where R′ is a methyl derivative of the fourth or fifth groups,[6] and two methyl resonances were observed in 2-chloro-4,4,5,5-tetramethyl-1,3-dioxa-2-phospholane, presumably due to the pyramidal stereochemistry at phosphorus.[7] However, the phosphorus imidazolidine where R = C_2H_5 and R′ = C_6H_5 is reported to show a doublet in the methylene bridge region at 60 MHz.[8] The ^{31}P–N–CH coupling in III (7.3 Hz) is much less than in I or II. Analogs IV and V were synthesized to test these observations further, and both gave sharp doublet patterns for the methylene bridge protons at 60 MHz (J = 5.0 and 7.5 Hz, respectively), but V showed a multiplet signal at 100 MHz.

Assuming a pyramidal phosphorus atom, the sharp doublets observed for the N-CH_3 protons in I and II exclude the possibility that these groups are either (a) in a fixed trans position, (b) trans and inverting in less than *ca.* 0.01 sec, or (c) moving in a slow and unconcerted manner. The N-CH_3 groups must then be either (a) cis oriented to the ring, (b) coplanar with a planar ring (*i.e.*, attached to trigonal nitrogen atoms), or (c) trans and inverting rapidly with respect to *ca.* 0.01 sec. Since $J(^{31}P\text{–}N\text{–}C\text{–}^1H_3)$ is greater than the spread of the multiplet resonance of the methylene bridge protons, the mutual coupling of the latter must be an ABA′B′X situation arising from the destruction of the plane of symmetry of the ring by the pyramidal phosphorus and not from any conformational effect of the N-CH_3 group.

The sharp doublet for the methylene bridge protons in III and IV, on the other hand, can be interpreted alternatively in terms of ring planarity or oscillation about nitrogen and phosphorus (inversion) rapid with respect to the nmr time scale. The multiplet revealed at 100 MHz for V may arise from the mutual coupling of an A_2B_2X situation brought about by slow rotation of the bent methoxy groups about the para O-phenyl or N-phenyl bonds.[9]

Transformation Reactions.—We have replaced phosphorus in 1,3-diaza-2-phospholidines with other elements in analogy to the findings with the silicon and germanium systems.[2c,8]

Phenylboron dichloride acts on I at 0° in a strongly exothermic reaction to yield



I VI (2)

Methyldichlorophosphine[10] which distils first, followed by 1,3-dimethyl-2-phenyl-1,3-diaza-2-borocyclopentane[11] (VI), whose structure was verified by independent synthesis *via* the transamination of bis(diethylamino)phenylborane[11,12] with N,N'-dimethylethylenediamine.

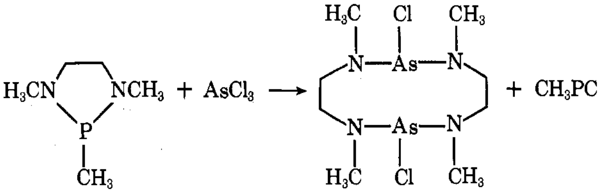
Attempted reversal of the transformation using phenyldichlorophosphine with VI did not proceed. The phosphorus(III) to boron conversion is strongly exothermic as are those of silicon and germanium to phosphorus(V).[2c] Excluding large heats of mixing, this enthalpy change could arise from a change in bond energies or the relief of ring strain. The available data suggest that $\{[E(\text{B–N}) + E(\text{P–Cl})] - [E(\text{B–Cl}) + E(\text{P–N})]\} > 0$.[13–15] Boron is smaller than phosphorus(III), and its incorporation may result in a less strained ring. The strikingly simple nmr spectrum of VI is consistent with a planar ring or one in which rapid inversion about tetrahedral nitrogen atoms is taking place.

Treatment of I with arsenic trichloride gives the white solid VII in a highly exothermic reaction. The hydrolytically sensitive solid, mp 118–120°, decomposed on attempted distillation. Microanalytical data fit the formulation $C_4H_{10}N_2AsCl$. Both the previously reported monomeric arsenic imidazolidines, the 1,3-dimethyl- (mp 19–21°; bp 103–105° (14 Torr))[16] and the 1,3-diethyl-2-chloro-1,3-diaza-2-arsacyclopentanes (bp 86° (0.7 Torr)),[8] have significantly different physical properties. The mass spectral features of VII, listed along with their assignments in Table II, are consistent with the formation of a dimeric product

TABLE II
MASS SPECTRAL DATA FOR COMPOUND VII[a]

Assignment	Mass no.	Intens, %	Assignment	Mass no.	Intens, %
P	393	100	$^1/_2$P − Cl	161	44
P − (2Cl + $2CH_3$)	292	48	$^1/_2$P − (Cl + CH_3)	146	36
$^1/_2$P[b]	196.5	12	$^1/_2$P − (Cl + $2CH_3$)	131	32
$^1/_2$P − CH_3	181.5	44			

[a] Recorded at 70 eV. [b] May also be due to P/2e.



I (3)

or an oligomer which neither passage through the inlet system of the mass spectrometer held at 150° nor attempted distillation apparently serves to convert to the monomer. The nmr spectrum of VII is complex, presumably due to the puckered nature of the ten-membered ring, unlike the monomeric arsenic imidazolidine where the methylene bridge protons are reported to give rise to a singlet resonance.[8]

Experimental Section

Melting points were recorded on a Townson and Mercer Type

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(6) O. J. Scherer and J. Wokulat, *Z. Anorg. Allg. Chem.*, **361**, 296 (1968).

(7) H. Goldwhite, *Chem. Ind.* (*London*), 494 (1964).

(8) E. W. Abel and R. P. Bush, *J. Organometal. Chem.*, **3**, 245 (1965).

(9) We have synthesized phenylphosphorus imidazolidines from unsymmetrically substituted N,N'-diphenylethylenediamines, and we observe multiplet patterns which must arise at least in part from the A_2B_2X nature of the methylene bridge protons in these compounds.

(10) I. P. Komkov, S. Z. Irin, and K. V. Karavanon, *Zh. Obshch. Khim.*, **28**, 2963 (1958).

(11) K. Niedenzu, H. Beyer, and J. W. Dawson, *Inorg. Chem.*, **1**, 738 (1962).

(12) B. M. Mikhailov and P. M. Aronovich, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1146 (1957).

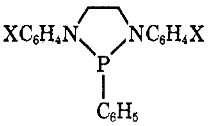
(13) E. L. Muetterties in "The Chemistry of Boron and Its Compounds," E. L. Muetterties, Ed., Wiley, New York, N. Y., 1967, p 13.

(14) J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. 1, Interscience, New York, N. Y., 1958, p 887.

(15) T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworths, London, 1954.

(16) O. J. Scherer and M. Schmidt, *Angew. Chem., Int. Ed. Engl.*, **3**, 702 (1964).

TABLE III
TRIARYL PHOSPHORUS(III) IMIDAZOLIDINES



	X	Yield, %	Mp, °C	Color	Anal., % C Calcd	C Found	H Calcd	H Found
III	*p*-H	35	236–238	White	75.46	74.88	5.97	5.81
IV	*p*-CH_3	45	175–176	White	76.30	76.02	6.64	6.70
V	*p*-OCH_3	42	211–212	Light pink	69.85	68.98	6.08	6.02

5 melting point block and like the boiling points are reported uncorrected. Mass spectra were recorded using an AEI MS-902 mass spectrometer. Nmr measurements were made using Varian Associates A60-A and HA-100 spectrometers using deuteriochloroform as the solvent and tetramethylsilane as the internal standard. Infrared measurements were carried out on a Beckman IR-10 spectrometer and were calibrated with polystyrene. Microanalyses were performed by Instranal Laboratory, Inc., Rensselaer, N. Y. All operations were carried out under nitrogen.

1,2,3-Trimethyl-1,3-diaza-2-phospholidine(I).—*N,N'*-Dimethylethylenediamine (8.82 g, 0.1 mol) was mixed with benzene (*ca.* 200 ml) in a three-necked flask fitted with a condenser and a dropping funnel. Triethylamine (22.2 g, 0.22 mol) was then added. Methylphosphorus dichloride (11.8 g, 0.1 mol) dissolved in benzene (25 ml) was added very slowly dropwise. Triethylamine hydrochloride precipitated in an exothermic reaction. When the addition was complete, stirring was continued for a further 12 hr. The mixture was then filtered, the precipitate was washed with the same solvent, and the solvent was evaporated under vacuum. Care was taken to remove the solvent, because the compound has a tendency to be carried over by the solvent when benzene was used. On the other hand, the yield was lower when ether was used as solvent. The residue was distilled (149–150° (760 Torr)) and collected as a colorless liquid (60% yield). *Anal.* Calcd for $C_5H_{13}N_2P$: C, 45.45; H, 9.85; N, 21.21. Found: C, 45.96; H, 10.33; N, 21.12.

1,3-Dimethyl-2-phenyl-1,3-diazaphospholidine(II).—*N,N'*-Dimethylethylenediamine (8.82 g, 0.1 mol) was added to benzene or ether (*ca.* 200 ml) in a 500-ml three-necked flask fitted with a condenser and a dropping funnel. Triethylamine (22.2 g, 0.22 mol) was then added with stirring. Dichlorophenylphosphine (17.9 g, 0.1 mol) dissolved in the same solvent (25 ml) was added slowly dropwise with magnetic stirring. The mixture became warm. When the addition of dichlorophenylphosphine was complete, the entire mass was stirred for another 12 hr (usually overnight). The solution was filtered and the precipitate of triethylamine hydrochloride was washed with the same solvent. The solvent was removed by a rotary evaporator and the residue was then distilled at reduced pressure. The diazaphospholidine distilled at 95° (0.7 Torr) as a colorless liquid (yield 70%). The yield was lower when ether was used as solvent. *Anal.* Calcd for $C_{10}H_{15}N_2P$: C, 61.86; H, 7.73; N, 14.43. Found: C, 59.74; H, 7.62; N, 14.40.

1,2,3-Triaryl-1,3-diaza-2-phospholidines (III–V).—The *N,N'*-diarylethylenediamine (0.02 mol) was dissolved in 50 ml of xylene, and triethylamine (4.45 g, 0.044 mol) was added. Dichlorophenylphosphine (3.5 g, 0.02 mol) was added dropwise with magnetic stirring, and the mixture was allowed to reflux for 4–6 hr. After cooling, the solid material was filtered and washed with xylene. The solid residue was then recrystallized from benzene, washed with benzene–petroleum ether (bp 40–60°) (40:60), and dried in a vacuum desiccator. The results are given in Table III.

Transformation Reactions. 1,3-Dimethyl-2-phenyl-1,3-diaza-2-borolidine. Transformation of Phosphorus(III) Imidazolidine to Boron Imidazolidine.—Phenylboron dichloride (6.7 g, 0.042 mol) was added dropwise to I (5.54 g, 0.042 mol) at 0°. The reaction was exothermic. After standing 0.5 hr with occasional stirring, methylphosphonous dichloride was distilled at 77–79° (1 atm) (lit. 81–82° (1 atm)[10]) and identified by its nmr spectrum. The boron imidazolidine was distilled at 55–57° (0.4 Torr) and was identified by nmr and ir spectra as well as by independent synthesis.[11,12]

Reaction of 1,2,3-Trimethyl-1,3,2-diazaphospholidine with Arsenic Trichloride.—Arsenic trichloride (5.4 g, 0.03 mol) dissolved in benzene (10 ml) was added to a solution of I (3.95 g, 0.03 mol) at 0° very slowly dropwise with stirring. The reaction was very exothermic. A white solid precipitated. After removal of the solvent, attempted distillation resulted in decomposition. In a separate run the mother liquor was removed by decantation and the solid was washed repeatedly with solvent and then dried under reduced pressure. The solid VII contains chlorine and is assumed to have the formula $C_8H_{20}N_4As_2Cl_2$, a dimer of the corresponding arsenic imidazolidine; yield 98–99%; mp 118–120°. *Anal.* Calcd for $C_8H_{20}N_4As_2Cl_2$: C, 24.42; H, 5.09. Found: C, 23.33; H, 5.32.

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