

When the crystalline compound  $P_4O_6[Ni(CO)_3]_4$  is allowed to react with various amounts of  $P_4O_6$  in chloroform, it is found that the initial steps of the reaction consist of the successive stripping of tricarbonylnickel groups from the  $P_4O_6$  molecule until only one is left. This is due to the fact that the rate of exchange of tricarbonylnickel groups between  $P_4O_6$  molecules is considerably faster than the rate of substituting more than one  $P_4O_6$  per nickel atom. This is consistent not only with the nmr data but with the rate of evolution of carbon monoxide from nickel tetracarbonyl. The reaction sequence shown on the composition diagram (Scheme I) by the dashed arrows corresponds to adding *ca.* 7 moles of  $P_4O_6$  per mole of  $P_4O_6[Ni(CO)_3]_4$ . In a matter of a few minutes for this mixture, the tricarbonylnickel groups are stripped from the  $P_4O_6[Ni(CO)_3]_4$  so as to give primarily  $P_4O_6Ni(CO)_3$  and  $P_4O_6$ . The  $P_4O_6Ni(CO)_3$  and its neighboring compound along the top of the diagram then start to lose carbon monoxide at a much slower rate. Thus, the reaction is kinetically controlled, following a path which avoids the region of polymeric structures beyond the gel point, although the most direct path should give network polymers in the intermediate region.

The rigid glasses corresponding to compositions be-

yond the gel point are quite stable. They remain clear and transparent upon being stored for several months (and presumably longer) in dry nitrogen and upon heating for several hours at  $100^\circ$  in dry nitrogen. At  $200^\circ$ , they finally give a Ni mirror on the walls of the tube in which the sample was heated. Unlike the crystalline compound  $P_4O_6[Ni(CO)_3]_4$ , these cross-linked glasses are very reactive with water, giving a black precipitate with rapid evolution of carbon monoxide.  $P^{31}$  nmr of the resulting solution, after filtration through a fine sintered-glass disk, indicates that the phosphorus is not oxidized during this hydrolysis.

**Reaction with Iron Carbonyls.** When  $P_4O_6$  is refluxed with an excess of  $Fe(CO)_5$ , the evolution of the first mole of carbon monoxide per  $P_4O_6$  occurs in about 1 day at  $103^\circ$ . Again the first nmr pattern to appear is of the  $AB_3$  type, corresponding to the molecule  $P_4O_6Fe(CO)_4$ . Continued refluxing leads to evolution of more CO, with the rate decreasing with time. When either  $Fe(CO)_5$  or  $Fe_2(CO)_9$  is reacted with an excess of  $P_4O_6$ , the same  $AB_3$  nmr pattern, ascribed to  $P_4O_6Fe(CO)_4$ , is the first to appear in addition to the line corresponding to unreacted  $P_4O_6$ . The reaction between  $Fe_2(CO)_9$  and excess  $P_4O_6$  is relatively fast with about 1 mole of CO being evolved in 0.5 hr at  $50-60^\circ$ .

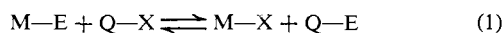
## Transformations of Heterocycles. The Conversion of Silicon and Germanium Imidazolidines into Their Phosphorus(V) Analog in One Step<sup>1</sup>

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**Abstract:** The generality of the sequence  $M-E + Q-X \rightleftharpoons Q-E + M-X$  for organometallic transformation reactions, where X is a halide, M and Q are metals or metalloids, and E is RO,  $R_2N$ , etc., has been tested by extending M to include germanium, and Q to include phosphorus(V). Imidazolidines with silicon and germanium replacing carbon in the 2 position are transformed to their phosphorus(V) analog by reaction with phenyldichlorophosphine oxide and release of dimethyldichlorosilane or -germane. The resulting diamide hydrolyzes in two stages through the phenylphosphonic amide of N,N'-dimethylethylenediamine to N,N'-dimethylethylenediamine itself and phenylphosphonic acid.

Recent reports in the literature on the formation of amino derivatives of various elements from the action of halides of these elements on silylamines have made it increasingly apparent that such reactions belong to a general class of organometallic transformations represented by the equation



where M and Q are metals or metalloids, X is a halogen, and E is an organic grouping RO,  $R_2N$ , etc. Such processes are of interest not only because of the chemical relationships they illustrate, but because they can be utilized as new avenues to various chemical systems. The range of these transformations in terms of M, E,

Q, and X is summarized in Table I along with leading references. In this publication we report our results in expanding the scope of such reactions to the  $M = Si$  and Ge cases where  $Q = P(V)$ .

### Discussion of Results

We have examined the reaction between silicon<sup>2</sup> and germanium imidazolidines and phenyldichlorophosphine oxide which produces the novel phosphorus(V) imidazolidine, 2-phenyl-1,3-dimethyldiazaphosphole oxide, with the release of dimethyldichlorosilane or -germane

(1) Work described in part at the Second International Symposium on Organometallic Chemistry, Madison, Wis., Sept 1965.

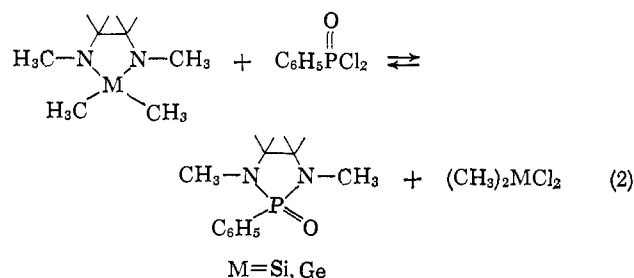
(2) C. H. Yoder and J. J. Zuckerman, *Inorg. Chem.*, **4**, 116 (1965).

**Table I.** Schematic Summary of Group IV Organometallic Transformation Reactions

M	E	Q	X	Ref <sup>a</sup>
Si	N	B	F, Cl	<i>b, c, d</i>
		C, C=O, N=O	Cl, I	<i>e</i>
		Al, P(III), As, Sb, Bi	Cl, Br	<i>c, f</i>
		P(V)	F, Cl	This work, <i>f, g</i>
		S	F, Cl	<i>h</i>
	O	Si	Cl, Br	<i>i</i>
		B, Al	F, Cl	<i>j, k</i>
		P(III), P(V)	F, Cl	<i>l, m</i>
		Si, Ge	Cl	<i>l, n</i>
		S	Cl, Br, I	<i>e, o</i>
S	C, C=OC, S	Cl, Br	<i>p</i>	
	P(III), P(V)	Cl, Br	<i>s</i>	
	Ge, Sn	Cl, Br	<i>s</i>	
	B	Cl	<i>t</i>	
	CN	F, Cl, Br	<i>q</i>	
Ge	N	P(V)	Cl	This work
	O	B	F	<i>r</i>
Pb	S	Si, Sn	Cl	<i>s</i>

<sup>a</sup> This listing is designed only as a guide to recent pertinent articles.

<sup>b</sup> H. Jenne and K. Niedenzu, *Inorg. Chem.*, **3**, 68 (1964); C. R. Russ and A. G. MacDiarmid, *Angew. Chem. Intern. Ed. Engl.*, **3**, 509 (1964). <sup>c</sup> M. Becke-Goehring and H. Krill, *Ber.*, **94**, 1059 (1961). <sup>d</sup> E. A. V. Ebsworth, "Volatile Silicon Compounds," Pergamon Press, New York, N. Y., 1963, pp 113, 114. <sup>e</sup> E. W. Abel and D. A. Armitage, *J. Chem. Soc.*, 5975 (1964). <sup>f</sup> E. W. Abel, D. A. Armitage, and G. R. Willey, *ibid.*, 57 (1965). <sup>g</sup> R. Schmutzler, *Z. Naturforsch.*, **19b**, 1101 (1964); *Angew. Chem. Intern. Ed. Engl.*, **3**, 753 (1964); *Chem. Commun. (London)*, 19 (1965). <sup>h</sup> E. W. Abel and D. A. Armitage, *J. Chem. Soc.*, 3122 (1964); G. C. Demitras, R. A. Kent, and A. G. MacDiarmid, *Chem. Ind. (London)*, 1712 (1964). <sup>i</sup> R. Fessenden and J. S. Fessenden, *Chem. Rev.*, **61**, 361 (1961); C. Eaborn, "Organosilicon Compounds," Butterworth, Inc., Washington, D. C., 1960, p 347. <sup>j</sup> H. J. Emeléus and M. Onyszchuk, *J. Chem. Soc.*, 604 (1958). <sup>k</sup> M. Onyszchuk, *Can. J. Chem.*, **39**, 808 (1961). <sup>l</sup> C. M. Silcox and J. J. Zuckerman, *J. Am. Chem. Soc.*, **88**, 168 (1966). <sup>m</sup> R. Schmutzler, *J. Chem. Soc.*, 4551 (1964); *Inorg. Chem.*, **3**, 410 (1964). <sup>n</sup> Note also that certain telomerization reactions are interesting examples of such transformations; see K. A. Andrianov and V. V. Severnyi, *J. Organometal. Chem.*, **1**, 268 (1964). <sup>o</sup> E. W. Abel, D. A. Armitage, and R. P. Bush, *J. Chem. Soc.*, 2455 (1964). <sup>p</sup> E. W. Abel, D. A. Armitage, and R. P. Bush, *ibid.*, 5584 (1964). <sup>q</sup> E. C. Evers, W. D. Freitag, W. A. Kriner, A. G. MacDiarmid, and S. Sujishi, *J. Inorg. Nucl. Chem.*, **13**, 239 (1960). <sup>r</sup> J. E. Griffiths and M. Onyszchuk, *Can. J. Chem.*, **39**, 339 (1961). <sup>s</sup> E. W. Abel, D. A. Armitage, and D. B. Brady, *J. Organometal. Chem.*, **5**, 130 (1966). <sup>t</sup> E. W. Abel, D. A. Armitage, and R. P. Bush, *J. Chem. Soc.*, 3045 (1965).

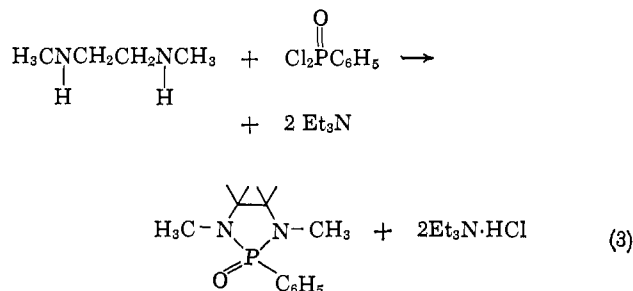


The success of such processes indicates that the transformations are not limited to silicon-nitrogen systems. Another investigation in this laboratory has extended these reactions to include silicon-oxygen systems.<sup>3</sup>

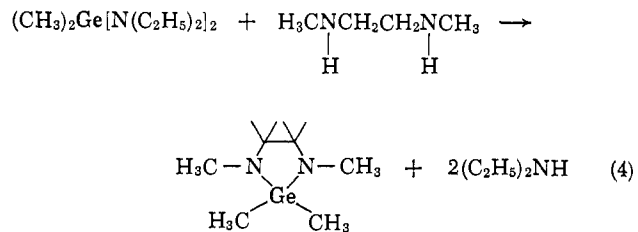
This transformation also offers a novel route to the phosphonic diamide systems, which as analogs of naturally occurring purines have been receiving attention as potential antimetabolites. Syntheses of the benzo- and pyrimidine derivatives have previously been

(3) See footnote 1, Table I; C. M. Silcox, C. H. Yoder, and J. J. Zuckerman, Abstracts, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

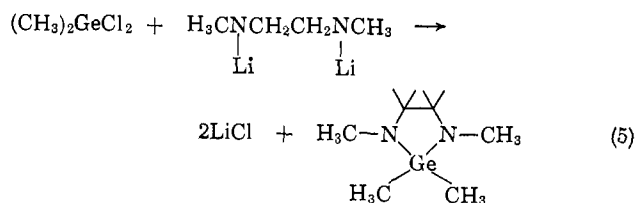
approached by transamination<sup>4,5</sup> and condensation<sup>6</sup> routes, and Abel has recently demonstrated that silyl imidazolidines react with phenylboron dichloride, arsenic trichloride, phenyldichlorophosphine, and thionyl chloride in a similar fashion.<sup>7</sup> We have confirmed the structure of the new phosphorus(V) imidazolidine by independent synthesis through the direct reaction of N,N'-dimethylethylenediamine and phenyldichlorophosphine oxide



The precursor germanium imidazolidine was obtained by two routes: (a) transamination of bis(diethylamino)dimethylgermane with N,N'-dimethylethylenediamine to form the heterocycle with release of diethylamine



and (b) the action of dimethyldichlorogermane on the dilithio salt of N,N'-dimethylethylenediamine



The rule that the imidazolidines take the physical form of the organic diamine is apparently a general one for the silicon<sup>2</sup> and germanium monocyclic as well as spiro compounds.<sup>8</sup> Structure assignment is based upon infrared and nmr spectra, molecular weight, and carbon, hydrogen, nitrogen, and germanium analytical data. The nmr spectrum of the germanium imidazolidine shows a single sharp resonance for the methylene bridge protons indicating either planarity of the ring or rapid inversion of tetrahedral nitrogen.<sup>9</sup>

The phosphorus(V) imidazolidine is a white crystalline solid (bp 187° (7–8 mm); mp 43°) whose structural assignment is based upon carbon, hydrogen, nitrogen, and phosphorus analytical data, molecular weight determinations, and infrared and nmr spectra.

(4) V. Gutmann, D. E. Hagen, and K. Utvary, *Monatsh.*, **93**, 627 (1962).

(5) J. H. Lister and G. M. Timmis, *Chem. Ind. (London)*, 819 (1963).

(6) R. L. Dannley and P. L. Wagner, *J. Org. Chem.*, **26**, 3995 (1961).

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

(8) C. H. Yoder and J. J. Zuckerman, *Inorg. Chem.*, **3**, 1329 (1964).

(9) D. Kummer and J. D. Baldeschwieler, *J. Phys. Chem.*, **67**, 98 (1963).

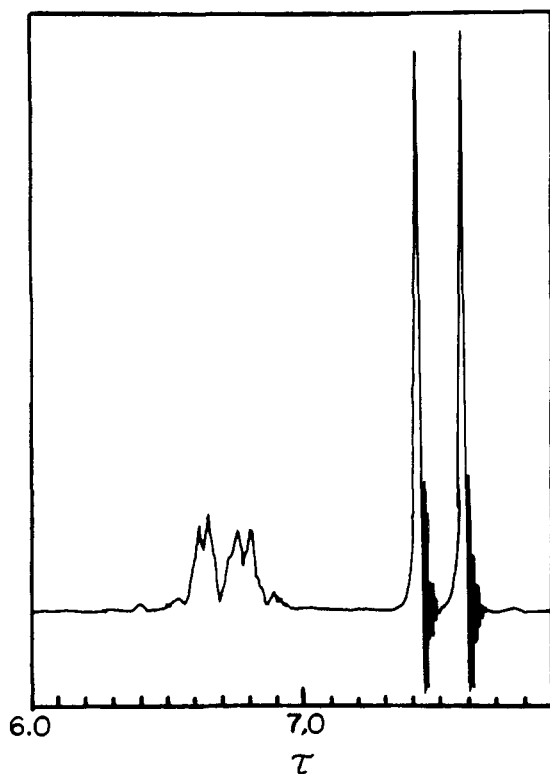


Figure 1.

The nmr spectrum of the phosphorus heterocycle in chloroform is shown in Figure 1 (excluding the phenyl proton resonance). We have recorded spectra in water and various organic solvents at 60 and 100 Mc. We conclude that the pair of doublet resonances in the methylene bridge region is a fortuitous result, and that the 60-Mc spectrum of this compound is deceptively simple. Protons labeled a and b in Figure 2 must be magnetically inequivalent with protons c and d no matter what processes of inversion are in progress about the ring nitrogen atoms. Thus mutual coupling between the two sets of methylene protons as well as  $P^{31}-N-C-H^1$  coupling which we observe for the N-methyl protons (or even four-bond  $P^{31}-N-C-C-H^1$  coupling through the other side of the ring) is to be expected. We interpret the doublet centered at  $\tau$  7.47 as produced by  $P^{31}$  coupling with the N-methyl protons. The separation between these peaks is independent of solvent and field strength and has a value of 10 cps consistent with other three-bond  $P^{31}-N-C-H^1$  couplings.<sup>10</sup>

This sharp doublet we observe for the N-methyl protons excludes the possibility that the N-methyl groups are (a) in a fixed *trans* position, or are (b) *trans* and inverting in less than approximately 0.01 sec, or are (c) moving slowly and in an unconcerted manner. We can then conclude that the N-methyl groups are either (a) *cis*-oriented to the ring, or (b) coplanar with a planar ring (*i.e.*, attached to trigonal nitrogen atoms), or (c) *trans* and inverting rapidly with respect to approximately 0.01 sec. Rapid inversion is not ruled out in (a) above.

2-Phenyl-1,3-dimethyldiazaphosphole oxide hydrolyzes only very slowly in distilled water and is stable for weeks in a dilute solution of potassium carbonate.

(10) A. H. Crowley and R. P. Pinnell, *J. Am. Chem. Soc.*, **87**, 4454 (1965).

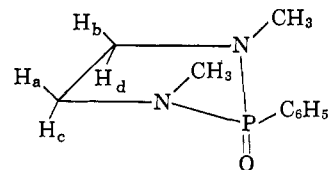
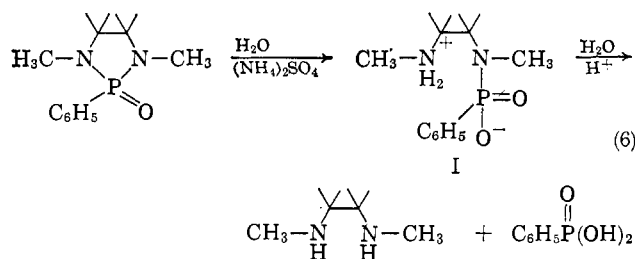


Figure 2.

Hydrolysis takes place within 2 days in a dilute solution of ammonium sulfate to give compound I below. Addition of strong acid is necessary to complete the two-stage hydrolysis to phenylphosphonic acid and the free diamine



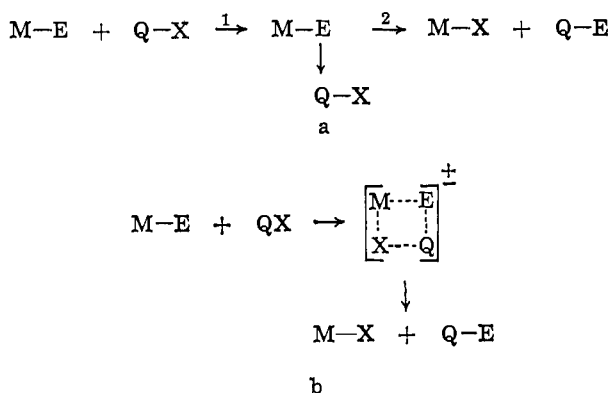
The intermediate zwitterion N-methyl-N'-(phenylphosphonate)ethylenediamine (I) is a white crystalline solid (mp 163–167°), very soluble in water and alcohols, but insoluble in common organic solvents. The two-step hydrolysis process can be followed by nmr and the nmr spectrum of I shows the expected complex pattern for the now inequivalent methylene bridge protons, as well as three lines in the N-methyl region which arise because now only one of the N-methyl groups is coupled to phosphorus. The proposed zwitterionic structure in solution is supported by the solubility of the material in water. The infrared spectrum of the solid contains peaks in the 2700–2300-cm<sup>-1</sup> region (P–OH absorbs in this region also, but the intensity is usually low) and only a small absorption in the 3400-cm<sup>-1</sup> region.

For the transamination routes to silicon- and germanium-nitrogen heterocycles *via* the bis(dialkylamino)silanes and -germanes, where the initial and final amines and element-nitrogen bonds are similar (such as eq 5), we have proposed that there is negligible enthalpy difference between the initial and final states of the reaction and the transaminations are thus volatility-controlled equilibrium processes.<sup>11</sup> In the silicon-oxygen transformation to P(III) and P(IV) seven-membered ring heterocycles, only slightly endothermic changes occur on mixing the reactants and only slight reaction occurs even after long periods without heating.<sup>3</sup> The reactions discussed above, however, are strongly exothermic. Excluding a large heat of mixing, a large enthalpy change in such a reaction can arise from three considerations: (a) the change in bond energy in going from silicon- and germanium-nitrogen bonds to the P(=O)N system, or (b) the relief of strain in the five-membered ring in going from the group IV to the group V member, or (c) the change in bond energy from fifth group halide to fourth group halide. Alternately the >P=O system might find some special stabilization which would tend to fix the ring in the conformation drawn in Figure 2. Our nmr studies do not rule out

(11) C. H. Yoder and J. J. Zuckerman, Proceedings of the 2nd International Symposium on Organometallic Chemistry, Madison, Wis., Sept 1965.

this possibility. Bond energy data for the amino derivatives of silicon are confined to three values and are nonexistent for germanium.<sup>12</sup> Accepted values for the covalent radius of P(V) are in all cases smaller than those for silicon and germanium,<sup>13</sup> and the smaller phosphorus atom might result in a less-strained ring system than is the case for either silicon or germanium.

Mechanisms which have been proposed for this reaction (2) involve a nucleophilic attack of E on Q. Elimination of M-X could occur as a second step as in Figure 3a or the whole mechanism of attack and elimination might be a four-center concerted process as in Figure 3b. It would be hazardous to predict how Figure 3.



varying M and Q would effect the rate of these reactions. Because of the sparsity of reliable bond energy data, it also is difficult to evaluate the change in  $\Delta G^\circ$  for a series of transformations in which M and Q are being varied.

It is interesting in this connection that several attempts by the present authors to transform imidazolidines from M = Si (E = N) to Q = Ge or Sn (X = Cl) have been unsuccessful. Abel found that reaction of *N,N*-diethylaminotrimethylsilane with trimethyltin bromide produced a very stable complex which did not decompose on heating, but that the secondary silylamine (*N*-ethylaminotrimethylsilane) underwent transformation to the stannylamine by heating the complex formed.<sup>14</sup> Possibly, the Q-N bond energies down group IV (Si  $\rightarrow$  Sn) decrease more rapidly than the Q-Cl energies (at least in certain systems). These bond energy differences affect the activation energies for these processes as well and this hypothesis is supported by trends in group IV amination reactions.<sup>11</sup> It is also instructive to recall that when M = C [and E's ordinary valence is saturated by organic groups, e.g.,  $\text{H}_3\text{C}-\text{N}(\text{CH}_3)_2$ ], reaction with Q-X does not produce elimination of M as it does in organometallic processes.

## Experimental Section

All commercial starting materials were redistilled before use. *N,N'*-Dimethylethylenediamine and diethylamine were stored over Molecular Sieves (Linde Type 4A), while ether was dried over sodium wire. Dimethyldichlorogermane (bp 119–123°) was obtained by direct reaction of methyl chloride with 20% copper-germanium metal.<sup>15</sup> The infrared and nmr spectra and properties

of this material were consistent with those reported. All operations were carried out under nitrogen.

**Dimethylbis(diethylamino)germane.** Butyllithium, 100 ml of a 1.6 *M* solution in hexane (Foote Mineral), was added dropwise to a stirred solution of diethylamine (12 g, 0.16 mole) in about 80 ml of ether. The exothermic reaction was cooled by an ice bath. Upon completion of the addition, the mixture was allowed to warm to room temperature and then dimethyldichlorogermane (14.5 g, 0.08 mole), diluted with 30 ml of ether, was added dropwise to the lithium salt. This addition was accompanied by mild evolution of heat and formation of a white precipitate of lithium chloride. The mixture was then refluxed gently for several hours and allowed to stand overnight. Since filtration through a glass frit funnel (C porosity) under vacuum was unsuccessful in removing lithium chloride, the mother liquor was decanted from the lithium chloride. After removal of the solvent *in vacuo*, the liquid residue was distilled at 87° (15 mm) to give ca. 14 g of product (70% yield). *Anal.* Calcd for  $\text{C}_{10}\text{H}_{26}\text{N}_2\text{Ge}$ : C, 48.64; H, 10.62; N, 11.35; Ge, 29.40; mol wt, 247. Found: C, 48.59; H, 10.23; N, 11.69; Ge, 29.26; mol wt, 227.

**1,2,2,3-Tetramethylgermylimidazolidine. A. By Transamination.** In the following procedure ammonium sulfate is used as a catalyst, but reaction occurs in its absence even at 100°. Bis-(diethylamino)dimethylgermane (18 g, 0.073 mole) was heated to 150° with *N,N'*-dimethylethylenediamine (6.5 g, 0.074 mole) in the presence of a small amount (<0.1 g) of ammonium sulfate for ca. 5 hr, and the released amine (5.6 g, 0.077 mole) was collected by distillation. The imidazolidine distilled at 152–153° (742 mm) to give 8 g (58%). *Anal.* Calcd for  $\text{C}_8\text{H}_{18}\text{N}_2\text{Ge}$ : C, 38.17; H, 8.54; N, 14.84; Ge, 38.45; mol wt, 189. Found: C, 37.88; H, 8.65; N, 14.79; Ge, 37.82; mol wt, 195.

**B. From the Dithio Derivative of *N,N'*-Dimethylethylenediamine.** Butyllithium (120 ml of a 1.6 *M* solution in hexane) was added to *N,N'*-dimethylethylenediamine (8.8 g, 0.1 mole) in about 300 ml of ether at 0°. After half the butyllithium had been added, a precipitate (insoluble in excess ether) formed in the solution. The mixture, after addition, was warmed to room temperature, and then, again at 0°, dimethyldichlorogermane (17 g, 0.1 mole) in ether was added with stirring. After standing overnight at room temperature, the solution was decanted from the precipitate which had formed during addition of the dichlorogermane. The precipitate was washed with ether and, by decantation, added to the mother liquor. The solvent was removed from the solution by distillation at atmospheric pressure to leave 8.5 g of a liquid residue which distilled at 152° (739 mm) (45% yield).

**1,3-Dimethyl-2-phenyldiazaphosphole Oxide. A. Transformation from Germanium Imidazolidine.** Phenyldichlorophosphine oxide (5.8 g, 0.03 mole) was added dropwise to 1,2,2,3-tetramethylgermylimidazolidine (5.6 g, 0.03 mole) with stirring. The reaction was very exothermic. After the addition the reaction mixture was heated to 150° for 3 hr and the product was then distilled at 20 mm to obtain a small forerun of dimethyldichlorogermane and 4 g (62% yield) of the diamide at 171°. The liquid solidifies at room temperature (mp ca. 43°) to a white solid which is insoluble in most common aprotic solvents, but rather soluble in chloroform, alcohols, and water, and slightly soluble in pyridine and triethylamine. *Anal.* Calcd for  $\text{C}_{10}\text{H}_{18}\text{N}_2\text{P}$ : C, 57.14; H, 7.19; N, 13.33; P, 14.73; mol wt, 210. Found: C, 57.41; H, 7.47; N, 13.47; P, 14.66; mol wt, 254.

**B. Transformation from Silicon Imidazolidine.** A similar reaction utilizing the silyl imidazolidine also produced the diamide. The immediate precipitation of a solid during this reaction and also the presence of peaks in the 4- $\mu$  region of the infrared spectrum of the product probably indicates cleavage of the heterocycle and formation of amine hydrochloride. This could be caused by HCl present in the phosphine.

**C. From *N,N'*-Dimethylethylenediamine.** To *N,N'*-dimethylethylenediamine (13 g, 0.15 mole) in 200 ml of 50:50 triethylamine-chloroform was added dichlorophenylphosphine oxide (29 g, 0.15 mole) dropwise at 0°. Formation of a white precipitate and a purple solution (near the end of the addition) accompanied the addition. After warming to room temperature and standing overnight, the mixture was filtered and solvent removed *in vacuo*. After a second filtration (additional precipitate came out during solvent removal) the product was distilled under reduced pressure to give 20 g (63% yield) of the diamide.

(12) See footnote *d*, Table I, p 105; U. Wannagat, *Advan. Inorg. Radiochem.*, **6**, 225 (1964).

(13) L. Pauling, "Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, Chapter 7.

(14) E. W. Abel, D. Brady, and B. R. Lerwill, *Chem. Ind. (London)*, 1333 (1962).

(15) E. G. Rochow, *J. Am. Chem. Soc.*, **69**, 1729 (1947); **70**, 436 (1948); M. Schmidt and I. Rudisch, *Z. Anorg. Allgem. Chem.*, **311**, 331 (1961); J. J. Zuckerman, *Advan. Inorg. Radiochem.*, **6**, 383 (1964).

**Hydrolysis of the Diamide.** An aqueous solution of the diamide and a small amount of ammonium sulfate was allowed to stand for 4 days at room temperature, during which time the water evaporated leaving a white solid which was recrystallized twice from hot water and after drying was washed with chloroform. This material (mp 163–167°) was very soluble in water and alcohols, but virtually insoluble in most organic solvents. *Anal.* Calcd for  $C_{10}H_{17}N_2O_2P$ : C, 52.63; H, 7.51; N, 12.27; P, 13.57; mol wt, 228. Found: C, 50.02; H, 7.74; N, 11.75; P, 13.14; mol wt, 218.

**Acknowledgments.** This investigation was supported by Public Health Service Research Grant CA-07064-02 from the National Cancer Institute. We are indebted to the National Science Foundation for a Predoctoral Fellowship to C. H. Y. The authors are grateful to Texas Instruments, Inc., for a supply of germanium metal and to Mr. Ross Pitcher of Varian Associates for obtaining the 100-Mc nmr spectrum.

## Organometallic Exchange Reactions. I. Lithium-7 and Proton Nuclear Magnetic Resonance Spectra of Methylithium and Ethyllithium in Ether<sup>1</sup>

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**Abstract:** The  $^7\text{Li}$  and  $^1\text{H}$  nmr spectra of ether solutions of methylithium and ethyllithium have been observed in the temperature range from 30 to  $-80^\circ$ . The data at lower temperatures provide evidence of association and can best be interpreted in terms of tetramer formation. The exchange process which causes collapse of the multiplet structure appears to be of the form  $\text{Li}_4\text{R}_4 \rightarrow 2\text{Li}_2\text{R}_2$ . It has also been established that lithium ethoxide, when present in concentrations which are low relative to the alkylithium, is incorporated into the tetrameric structure to give a species of the form  $\text{Li}_4\text{R}_3\text{OR}$ .

The extents of association of several organolithium compounds in ether have been measured by ebulliometry. Wittig, *et al.*, report benzyl- and phenyllithium as being approximately dimeric, *n*-butyllithium pentameric, and methylithium trimeric in boiling ether.<sup>3</sup> Talalaeva, *et al.*,<sup>4</sup> found phenyllithium and  $\alpha$ -naphthyllithium to be dimeric, and *n*-butyllithium to be approximately hexameric in ether. The latter authors also report the association of lithium halides and mixtures of organolithium compounds with lithium halides; *e.g.*, methylithium with lithium iodide is nearly tetrameric. However, ebulliometrically determined association numbers must be accepted with reservations since it is likely that there is some reaction with solvent, especially in the case of *n*-butyllithium and to a lesser extent phenyllithium. There is also danger of contamination from oxygen and water vapor in this type of experiment. In this respect, methylithium should be the most favorable for the ebulliometric method.

In this paper we report the results of a study of the  $^7\text{Li}$  and  $^1\text{H}$  magnetic resonance spectra at low temperatures for ethereal solutions of methyl- and ethyllithium. The data have an important bearing on the question of the constitution of alkylithium compounds and the mechanism of their reaction, in donor solvents.

### Experimental Section

**Materials and Procedures.** All operations, except manipulations involving dimethylmercury, were performed in a glove box under

argon atmosphere. Removal of traces of oxygen and water was effected by continuous circulation of the atmosphere through molecular sieve and manganese(II) oxide columns as described previously.<sup>5</sup> The concentrations of methyl- and ethyllithium solutions were determined by decomposing aliquot samples with water and titrating to a phenolphthalein end point with standard 0.1 *N* hydrochloric acid. Ethyllithium was obtained from Lithium Corp. of America, and dimethylmercury from Eastman Organic Chemicals. Mallinckrodt analytical reagent grade anhydrous ether was dried over sodium wire and used without further purification. Lithium-6 (96% isotopic purity) was purchased from Union Carbide Nuclear Co., Oak Ridge, Tenn.

Solutions of methylithium in ether were prepared by adding dimethylmercury to a cooled lithium metal-ether mixture. Excess lithium was used to ensure complete reaction. The lithium-mercury amalgam and excess lithium were removed by filtration to produce a clear methylithium solution. This method was chosen to eliminate contamination by lithium halides.

Ethyllithium was purified by sublimation under vacuum at  $80$ – $85^\circ$  and then dissolved in cold ether ( $-10$  to  $-15^\circ$ ) to give a clear, colorless solution. Low temperature is important to avoid reaction with ether, forming lithium ethoxide.

After the concentrations (usually about 1 *M*) of the separate methyl- and ethyllithium solutions were determined, the solutions were mixed in the appropriate volume proportions to form the methylithium-ethyllithium mixtures. The solutions were degassed, sealed under vacuum in standard size nmr tubes, and stored in Dry Ice.

Samples containing lithium ethoxide were prepared by using an ethyllithium-ether solution containing lithium ethoxide (prepared by dissolving ethyllithium in ether at room temperature).

**Nuclear Magnetic Resonance Spectra.** Lithium-7 spectra were obtained at 23.3 Mc in a field of 14,092 gauss using a Varian Associates Model DP60 spectrometer. Aqueous lithium bromide solution (7 g of commercial grade LiBr/10 ml of solution) was employed as an external standard for the room temperature chemical shift measurements. A Varian Associates A-60 spectrometer was used to obtain the proton spectra.

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