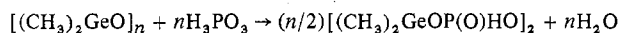


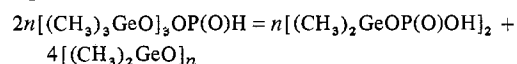
From the oxidation of $(\text{CH}_3)_3\text{GePH}_2$, we were able to isolate a small quantity of material whose highest mass envelope occurred at m/e 183, characteristic of $(\text{CH}_3)_3\text{GePO}_2\text{H}_2$. This compound may be an intermediate of type V or VI and bears further study.

In order to obtain large amounts of II, an alternate synthesis which involved the reaction of $[(\text{CH}_3)_2\text{GeO}]_n$ ^{13,25,26} (where $n = 3$ or 4) with a tenfold excess of anhydrous H_3PO_3 in ethanol solvent was studied. Compound II forms, apparently according to



in yields of about 70%. A small amount of material whose mass spectrum indicated the presence of three germanium atoms (parent ion centered at m/e 420) was isolated. The spectral envelope can be assigned tentatively as $[(\text{CH}_3)_2\text{GeO}]_3\text{OP(O)H}^+$, the parent molecular ion of the cyclic $[(\text{CH}_3)_2\text{GeO}]_3\text{OP(O)H}$ (IX).

The IX forms also along with other inseparable materials in reactions of II with H_2O and in reactions of $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)_2$ with moist ambient air. The failure to isolate pure cyclic products such as IX may be the result of rapid redistribution reactions of Ge-O-Ge bonds in the products in equilibrium reactions such as



Similar processes have been reported in the redistribution of $(\text{CH}_3)_2\text{GeO}$ linkages between $[(\text{CH}_3)_2\text{GeO}]_3$ and $[(\text{CH}_3)_2\text{GeO}]_4$.^{13,25,26} Since II contains no Ge-O-Ge linkages, it cannot undergo similar redistribution reactions.

Acknowledgment. Appreciation is gratefully expressed to Mr. David Fox for assistance in the calculation of isotopic distribution patterns.

Registry No. $(\text{CH}_3)_3\text{GePH}_2$, 20519-92-0; $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)_2$, 20519-93-1; $[(\text{CH}_3)_3\text{GeO}]_2\text{P(O)H}$, 54062-87-2; $[(\text{CH}_3)_2\text{GeO} \cdot \text{P(O)HO}]_2$, 54062-88-3; $[(\text{CH}_3)_2\text{GeO}]_n$, 54062-89-4; H_3PO_3 , 13598-36-2.

References and Notes

- (1) Supported by National Science Foundation Grant GP-23575.
- (2) Alfred P. Sloan Fellow, 1973-1975.
- (3) A. R. Dahl and A. D. Norman, *J. Amer. Chem. Soc.*, **92**, 5525 (1970).
- (4) A. R. Dahl, A. D. Norman, H. Shenav, and R. Schaeffer, submitted for publication.
- (5) H. Schumann, *Angew. Chem. Int. Ed. Engl.*, **8**, 937 (1969).
- (6) H. Schumann and M. Schmidt, *Angew. Chem.*, **77**, 159 (1964).
- (7) H. Schumann, P. Jutzi, A. Roth, P. Schwabe, and E. Shauer, *J. Organometal. Chem.*, **10**, 71 (1967).
- (8) D. F. Shriver, "The Manipulation of Air Sensitive Compounds," McGraw-Hill, New York, N.Y., 1969.
- (9) F. Glockling, "The Chemistry of Germanium," Academic Press, New York, N.Y., 1969.
- (10) B. D. Dombek, J. Lowther, and E. Carberry, *J. Chem. Educ.*, **48**, 729 (1971).
- (11) A. D. Norman, *Inorg. Chem.*, **9**, 870 (1970).
- (12) P. A. Tierney, D. W. Lewis, and D. Berg, *J. Inorg. Nucl. Chem.*, **24**, 1165 (1962).
- (13) M. P. Brown and E. G. Rochow, *J. Amer. Chem. Soc.*, **82**, 4166 (1960).
- (14) A. R. Dahl, C. A. Heil, and A. D. Norman, submitted for publication.
- (15) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, Wiley, New York, N.Y., 1963.
- (16) C. I. Meyrick and H. W. Thompson, *J. Chem. Soc.*, 225 (1950).
- (17) E. D. Bergman, U. Z. Littauer, and S. Pinchas, *J. Chem. Soc.*, 847 (1952).
- (18) R. S. Tobias and S. Hutcheson, *J. Organometal. Chem.*, **6**, 535 (1965).
- (19) J. E. Griffiths, *Spectrochim. Acta*, **20**, 1335 (1964).
- (20) K. R. Moedritzer and J. R. Van Wazer, *Inorg. Chem.*, **4**, 1753 (1965), and references cited therein.
- (21) H. Schmidbaur and H. Hussek, *J. Organometal. Chem.*, **1**, 235 (1964).
- (22) M. R. Crutchfield, C. H. Dugan, J. H. Letcher, V. Mark, and J. R. Van Wazer, *Top. Phosphorus Chem.*, **5**, (1967).
- (23) J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. I, Interscience, New York, N.Y., 1958, p 190, and references cited therein.
- (24) J. E. Drake and C. Riddle, *Quart. Rev., Chem. Soc.*, 263 (1970), and references cited therein.
- (25) E. G. Rochow, *J. Amer. Chem. Soc.*, **70**, 1801 (1948).
- (26) K. Moedritzer, *J. Organometal. Chem.*, **5**, 254 (1966).

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Thermal Redistribution of Hydrido and Phosphino Groups in Phosphinohydridogermanes¹

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The rapid redistribution of phosphino groups ($-\text{PH}_2$) and hydrogen atoms on germanium in phosphinohydridogermanes has been studied. The course of the redistribution reactions has been followed by ^1H nmr spectroscopy and verified by product characterization studies. Spectral evidence for the new compounds $\text{GeH}_2(\text{PH}_2)_2$ and $\text{GeH}(\text{PH}_2)_3$ as redistribution products of GeH_3PH_2 , in addition to GeH_4 , has been obtained. The $\text{CH}_3\text{Ge}(\text{PH}_2)_2\text{H}$ and $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)\text{H}$ redistribution reactions yield (1) CH_3GeH_3 , $\text{CH}_3\text{Ge}(\text{PH}_2)\text{H}_2$, and $\text{CH}_3\text{Ge}(\text{PH}_2)_3$ and (2) $(\text{CH}_3)_2\text{GeH}_2$ and $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)_2$, respectively. The $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)_x\text{H}_{2-x}$ system at equilibrium contains the respective redistribution species in a ratio which is in close agreement with that expected as a result of the statistical sorting of H atoms and PH_2 groups on germanium. The new compounds $\text{CH}_3\text{Ge}(\text{PH}_2)_2\text{H}$ and $\text{CH}_3\text{Ge}(\text{PH}_2)_3$ have been prepared by reaction of CH_3GeCl_3 with $\text{LiAl}(\text{PH}_2)_4$ in glyme solvents. Characterization data for the new compounds are given.

Introduction

Dialkyl(phosphino)germanes readily undergo redistribution reactions to form molecules which contain extended germanium-phosphorus bonding systems. For example, the redistribution of $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)_2$ yields PH_3 , $[(\text{CH}_3)_2\text{GePH}_2]_2\text{PH}$, $[(\text{CH}_3)_2\text{GePH}_2]_3\text{P}$,³ and ultimately the cage molecule $[(\text{CH}_3)_2\text{Ge}]_6\text{P}_4$.⁴ These reactions apparently involve the redistribution of hydrogen atoms and $(\text{CH}_3)_2\text{Ge}$ moieties on phosphorus atom centers. Recently, while attempting to extend our studies of germanium-phosphorus molecules to the preparation of new compounds containing hydrogen atoms

bonded to germanium, we have found that in these systems the facile redistribution of hydrido and phosphino groups on germanium centers also occurs. Although not well characterized, an indication of this is seen in studies of $(\text{GeH}_3)_3\text{P}$,⁵ GeH_3PH_2 ,⁶ and $\text{CH}_3\text{Ge}(\text{PH}_2)\text{H}_2$ ⁷ reported previously. Our studies of the redistribution reactions which occur in $\text{GeH}_x(\text{PH}_2)_{4-x}$, $\text{CH}_3\text{Ge}(\text{PH}_2)_x\text{H}_{3-x}$, and $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)_x\text{H}_{2-x}$ systems are described below.

Experimental Section

Apparatus. All manipulations were carried out in standard vacuum lines or N_2 -flushed glove bags.⁸ Mass spectra were obtained on Varian

Table I. Nuclear Magnetic Resonance Data^{a,b}

Measurement	CH ₃ Ge(PH ₂) ₂ H ^c	CH ₃ Ge(PH ₂) ₃ ^c
δ(CH)	-0.73 (3)	-0.90 (3)
δ(GeH)	-4.57 (1)	
δ(PH ₂)	-1.70 (4)	-1.94 (6)
³ J(HCGeH) ^c	2.5 ± 0.05	
³ J(HCGeP) ^c	2.5 ± 0.05	
¹ J(PH)	177 ± 1 ^d	185 ± 1 ^d
² J(HGeP)	20 ± 1	
³ J(HPGeH)	<i>e</i>	

^a Chemical shifts are given to ±0.02 ppm relative to internal (CH₃)₄Si; a minus δ value is downfield from (CH₃)₄Si. Coupling constants are in Hz. ^b Data were obtained at a probe temperature of -35° on samples, 40% by volume, in (CH₃)₄Si. ^c Relative peak areas are given in parentheses. ^d Distance between the two most intense peaks in the complex PH₂ multiplets. ^e A 16-line multiplet with coupling constants such that a first-order interpretation was not feasible.

MAT CH-5 and CH-7 spectrometers at an ionizing voltage of 70 eV. Infrared spectra were recorded with a Perkin-Elmer Model 337 spectrometer on gaseous samples in a 10-cm cell equipped with KBr windows. Proton nmr spectra were obtained at 60.0 MHz on a Varian A-60A spectrometer. Proton chemical shifts are reported relative to internal (CH₃)₄Si.

Materials. Germylphosphine⁹ and (CH₃)₂Ge(PH₂)H¹⁰ were prepared according to previously published techniques. CH₃Ge(PH₂)₂H and CH₃Ge(PH₂)₃ were prepared as described below. CH₃GeCl₃ (Alfa Inorganic) and HCl (Matheson Co.) were purified by routine fractional condensation techniques. In every case, compound purity was established by comparison of physical and spectral properties with literature values.

Preparation of CH₃Ge(PH₂)₂H and CH₃Ge(PH₂)₃. CH₃GeCl₃ (8.0 mmol) was allowed to react at -23° for 20 min with *ca.* 10 mmol of LiAl(PH₂)₄^{10,11} in 8 ml of triglyme. Slight gas evolution during the reaction was evident. Separation of volatile reaction materials by fractional condensation techniques yielded a CH₃Ge(PH₂)₃-C-H₃Ge(PH₂)₂H mixture, PH₃ (confirmed by ir spectrum),¹² and P₂H₄ (confirmed by ¹H nmr spectrum).¹³ The CH₃Ge(PH₂)₂H-CH₃Ge(PH₂)₃ mixtures decomposed slowly at room temperature. Separation of the mixture was achieved by its repeated passage through a -23° trap into a -45° trap. Pure CH₃Ge(PH₂)₂H collected in the -45° trap.

Characterization of CH₃Ge(PH₂)₂H and CH₃Ge(PH₂)₃. Samples for ¹H nmr measurements were prepared by pumping the sample into a U tube at -78° which had an nmr tube attached to the bottom. The ¹H nmr spectral parameters of CH₃Ge(PH₂)₂H and CH₃Ge(PH₂)₃ are given in Table I.

The mass spectrum of CH₃Ge(PH₂)₂H exhibits peak envelopes from *m/e* 12 to *m/e* 156. The highest mass peak, at *m/e* 156 (⁷⁴GeP₂CH₃⁺), is 3% as intense as the most intense spectral peak at *m/e* 89 (⁷⁴GeCH₃⁺). The spectrum of CH₃Ge(PH₂)₃ shows peak envelopes ranging from *m/e* 12 to *m/e* 188. The highest mass peak occurs at *m/e* 188 (⁷⁴GeP₃CH₃⁺) and is 7% the intensity of the most intense peak at *m/e* 89 (⁷⁴GeCH₃⁺).

Table II. Typical Redistribution on Germanium Data

Reactant	Time, hr	Products and amt, mmol				
		GeH ₄	GeH ₃ PH ₂	GeH ₂ (PH ₂) ₂	GeH(PH ₂) ₃	Other
GeH ₃ PH ₂ ^{a,c}	0	0	1.00	0	0	
	<i>a</i>	<i>d</i>	0.96	0.03	<0.01	<i>e</i>
CH ₃ Ge(PH ₂) ₂ H ^{b,f}	0	CH ₃ GeH ₃	CH ₃ Ge(PH ₂) ₂ H ₂	CH ₃ Ge(PH ₂) ₂ H	CH ₃ Ge(PH ₂) ₃	PH ₃
	1.0	0	0	0.55	0	0
	2.0	0.028	0.088	0.29	0.15	0
(CH ₃) ₂ Ge(PH ₂)H ^{b,g}	0	0.066	0.10	0.21	0.17	Trace
	0	(CH ₃) ₂ GeH ₂	(CH ₃) ₂ Ge(PH ₂)H	(CH ₃) ₂ Ge(PH ₂) ₂		Other
	24	0	0.50	0		
	50	0.050	0.40	0.052		<i>h</i>
		0.13	0.25	0.12		<i>h</i>

^a Sample warmed to -63° for 14 hr, -45° for 9 hr, -31° for 3 hr, and -23° for 3 hr. ^b Redistribution reactions occurring at room temperature (23-25°). ^c All spectral data obtained on samples maintained at -70°. ^d Most of the GeH₄ and PH₃ was removed by maintaining the sample at -130°, prior to sealing off the nmr tube. ^e A trace of PH₃, (GeH₃)₂PH, and (GeH₃)₃P could be seen in the spectrum. ^f Spectral data measured at -30°. ^g Spectral data measured at probe temperature (*ca.* 38°). ^h A broadening of the CH₃ resonances of both (CH₃)₂Ge(PH₂)₂ and (CH₃)₂Ge(PH₂)H and a trace amount of PH₃ could be seen in the spectrum.

Elemental analysis of CH₃Ge(PH₂)₂H was accomplished by the quantitative HCl cleavage of weighed samples according to



The CH₃Ge(PH₂)₂H:CH₃GeCl₂H:PH₃ ratio according to the equation is as follows: calcd, 1.00:1.00:2.00; found, 1.00:0.99:2.00. Since CH₃Ge(PH₂)₃ could not be obtained completely free of CH₃Ge(PH₂)₂H, HCl cleavage was not carried out.

Infrared spectra, melting points, and vapor tension vs. temperature characterization data were not obtained on either CH₃Ge(PH₂)₂H or CH₃Ge(PH₂)₃ because of their low volatilities and thermal instabilities.

Redistribution Reactions in Nmr Tubes. Samples in heavy-walled nmr tubes were warmed to room temperature for measured periods of time, between which the ¹H nmr spectra were obtained. Typical redistribution data are shown in Tables II and III. Relative quantities of species in the GeH₃PH₂ experiment were determined by integration of the following resonances: for GeH₄¹⁴ at δ -3.20 ppm, for PH₃⁶ at δ -3.32 ppm (low-field half of doublet), for GeH₃PH₂,¹⁵ GeH₂(PH₂)₂, and GeH(PH₂)₃ the high-field half of the PH₂ resonances at δ +0.11, -0.39, and -0.85 ppm, respectively, and for (GeH₃)₂PH₂⁶ and (GeH₃)₃P⁵ the low-field halves of the GeH₃ resonances at δ -3.99 and -4.15 ppm, respectively (Figure 1A). In GeH₃PH₂ experiments of the type shown in Table III, both relative quantities and absolute quantities of species were established by comparison with the CH₃ resonance of a known amount of internal toluene. Relative quantities of CH₃Ge(PH₂)₃, CH₃Ge(PH₂)₂H, and CH₃Ge(PH₂)₂H₂ in the CH₃Ge(PH₂)₂H redistribution experiments were determined by integration of the low-field half of the PH₂ resonances at δ -3.44, -3.19, and -2.86 ppm, respectively. The CH₃GeH₃ quantity was determined by difference based on a knowledge of total Ge in the reaction system. Quantities in the (CH₃)₂Ge(PH₂)H reactions were determined by integration of the following resonances: (CH₃)₂GeH₂¹⁶ at δ -3.74 ppm (GeH₂ resonance), (CH₃)₂Ge(PH₂)H¹⁰ at δ -2.85 ppm and (CH₃)₂Ge(PH₂)₂¹⁰ at δ -3.14 ppm (low-field resonance of PH₂ doublets), and PH₃⁶ (low-field half of doublet) at δ -3.35 ppm.

In one experiment a sample of (CH₃)₃GePH₂ was allowed to stand in an nmr tube for 30 days with periodic examination of the ¹H nmr spectrum. No evidence of any reaction could be seen after this time.

In a separate series of reactions, samples of GeH₃PH₂, CH₃Ge(PH₂)₂H, and (CH₃)₂Ge(PH₂)H in nmr tubes were exposed to trace quantities of air or an air-H₂O mixture and allowed to warm to room temperature for 20-30 min before being sealed off. In each case redistribution on germanium occurred as above, with no reproducible indication of rate enhancement. However, redistribution on phosphorus occurred at a much enhanced rate, as indicated by the rapid liberation of PH₃.

Redistribution Reactions in Bulbs. Reactions were carried out in Pyrex bulbs equipped with either Fischer-Porter O-ring valves or break-seals. Volatile materials from the reactions were characterized by comparison of their ir spectra with literature values: GeH₄,¹⁷ Ge₂H₆,¹⁸ Ge₃H₈,¹⁹ (CH₃)₂GeH₂,²⁰ PH₃,¹² GeH₃PH₂,²¹ (CH₃)₂Ge(PH₂)₂,¹⁰ (CH₃)₂Ge(PH₂)H,¹⁰ GeH₂Cl₂,²² and GeH₃Cl.²³

(A) GeH₃PH₂. Liquid GeH₃PH₂ (1.71 mmol) in a sealed bulb

Table III. Ambient Temperature Redistribution of GeH_3PH_2

Time, hr	Amt of redistribution materials, mmol ^a				
	GeH_3PH_2	GeH_4 ^b	PH_3 ^b	$(\text{GeH}_3)_2\text{PH}$	$(\text{GeH}_3)_3\text{P}$
0	1.30	0	0	0	0
3 ^c	1.20	0.003	0	0	0
24	1.25	0.018	0.016	0.016	0
48	1.15	0.024	0.016	0.016	(<0.001)
144	0.98	0.048	0.064	0.040	0.006
228 ^d	0.62	0.056	0.12	0.075	0.028

^a Quantities determined to $\pm 5\%$ by integration of ^1H nmr spectra at -30° . ^b Quantities of PH_3 and GeH_4 are likely low since some of these are in the vapor phase at -30° . ^c A trace of what may be $\text{GeH}_2(\text{PH}_2)_2$ was seen in this spectrum and all subsequent spectra. ^d Considerable yellow solid had formed making spectral resolution of low quality.

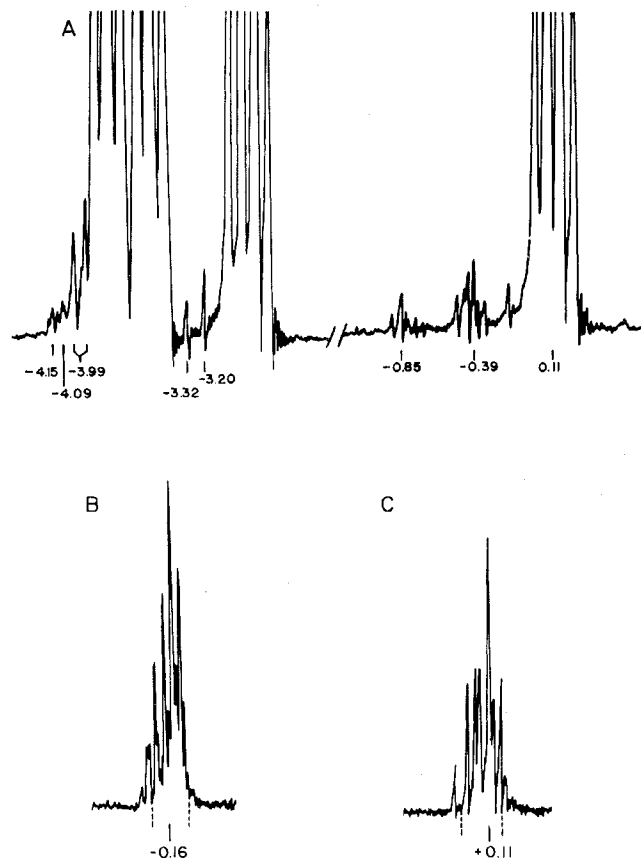


Figure 1. Proton nmr spectra: A, low-temperature redistribution products of GeH_3PH_2 ; B, upfield half of PH_2 resonance of $\text{SiH}(\text{PH}_2)_3$; C, upfield half of PH_2 resonance of $\text{SiH}_2(\text{PH}_2)_2$.

was allowed to stand at room temperature for 120 days to ensure essentially complete reaction. Volatile reaction products were separated by fractional condensation into a GeH_4 - PH_3 mixture (1.85 mmol), GeH_3PH_2 (0.15 mmol), Ge_2H_6 (0.030 mmol), and Ge_3H_8 (<0.001 mmol). The GeH_4 - PH_3 mixture (1.85 mmol), condensed at -196° , was allowed to react with BCl_3 at -112° in order to complex the PH_3 . Germane (0.75 mmol) was removed. The yellow-brown solid in the tube was allowed to react with excess HCl . The volatile products were found qualitatively to be a mixture of PH_3 , GeH_2Cl_2 , and GeH_3Cl . Some solid remained in the reaction vessel after treatment with HCl . It was not analyzed further.

(B) $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)\text{H}$. A sample of $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)\text{H}$ (0.94 mmol) was condensed into a bulb and heated at 31° for 26 hr. Upon completion, the reaction materials were found to consist of $(\text{C}-\text{H}_3)_2\text{Ge}(\text{PH}_2)_2$ (0.07 mmol), $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)\text{H}$ (0.44 mmol), $(\text{CH}_3)_2\text{GeH}_2$ (0.18 mmol), PH_3 (0.23 mmol), and a low-volatility solid (19.3 mg). Under more vigorous conditions of heating at 84° for 17 days, 0.86 mmol of $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)\text{H}$ decomposed to $(\text{CH}_3)_2\text{GeH}_2$ (0.46 mmol), PH_3 (0.69 mmol), and 41 mg of low-volatility solid. Analyses of HCl cleavage products and mass spectra of the solid showed them to consist only of the high molecular weight

products expected due to $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)_2$ condensation.^{3,4} Separation of products was achieved by repeated fractional condensation of the reaction mixture.

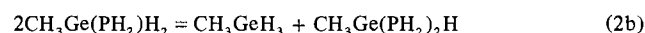
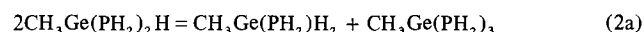
In another experiment, ca. 1 mmol of $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)\text{H}$ in a reaction bulb which had an attached nmr tube was pretreated with a small quantity of air. After 30 min at room temperature, the sample was cooled to -196° , unreacted air pumped out, and the bulb again warmed to room temperature for 2 days. At the end of this time high-volatility materials were pumped out and a low-volatility liquid remained in the tube. Infrared spectral analysis of the high-volatility material showed it to consist of $(\text{CH}_3)_2\text{GeH}_2$, $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)\text{H}$, $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)_2$, and PH_3 . No condensation products containing $\text{Ge}-\text{H}$ bonds were found. The ^1H nmr spectrum of the low-volatility liquid showed a broad featureless resonance at $\delta -0.67$ ppm, typical of the mixture of $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)_2$ condensation products.^{3,4}

Results and Discussion

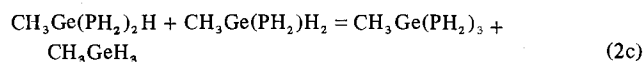
Redistribution Reactions. Typical redistribution data for $\text{GeH}_x(\text{PH}_2)_{4-x}$, $\text{CH}_3\text{Ge}(\text{PH}_2)_x\text{H}_{3-x}$, and $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)_x\text{H}_{2-x}$ systems are shown in Tables II and III. For these systems, the starting materials used were GeH_3PH_2 , $\text{CH}_3\text{Ge}(\text{PH}_2)_2\text{H}$, and $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)\text{H}$, respectively.

A sample of $\text{CH}_3\text{Ge}(\text{PH}_2)_2\text{H}$ at room temperature shows, within minutes, evidence of reaction by the disappearance of $\text{CH}_3\text{Ge}(\text{PH}_2)_2\text{H}$ resonances and the appearance of peaks due to $\text{CH}_3\text{Ge}(\text{PH}_2)_2\text{H}_2$ and $\text{CH}_3\text{Ge}(\text{PH}_2)_3$. After 2 hr the spectral changes cease, an apparent equilibrium is reached, and the only change noted is the appearance of a trace of PH_3 . At equilibrium, the $\text{CH}_3\text{Ge}(\text{PH}_2)_3$: $\text{CH}_3\text{Ge}(\text{PH}_2)_2\text{H}_2$: $\text{CH}_3\text{Ge}(\text{PH}_2)_2\text{H}$: CH_3GeH_3 ratio is 0.17:0.19:0.10:0.082. The $(\text{C}-\text{H}_3)_2\text{Ge}(\text{PH}_2)\text{H}$ at room temperature undergoes redistribution more slowly. After about 50 hr, the system reaches equilibrium and remains unchanged except for the slow formation of PH_3 and the broadening of the CH_3 resonances of the phosphinogermane products. At equilibrium, the ratios of $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)_2$: $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)\text{H}$: $(\text{CH}_3)_2\text{GeH}_2$ typically are 0.13:0.25:0.13.

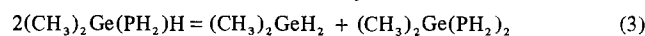
The redistribution of H and PH_2 groups on germanium in $\text{CH}_3\text{Ge}(\text{PH}_2)_2\text{H}$ can be represented by



which when combined yield



For the $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)_x\text{H}_{2-x}$ system, the reaction



can be written. For the reactions in eq 2c and 3, the equilibrium quotient expressions are of the forms

$$Q_1 = \frac{[\text{CH}_3\text{GeH}_3][\text{CH}_3\text{Ge}(\text{PH}_2)_3]}{[\text{CH}_3\text{Ge}(\text{PH}_2)_2\text{H}][\text{CH}_3\text{Ge}(\text{PH}_2)_2\text{H}_2]}$$

$$Q_2 = \frac{[(\text{CH}_3)_2\text{GeH}_2][(\text{CH}_3)_2\text{Ge}(\text{PH}_2)_2]}{[(\text{CH}_3)_2\text{Ge}(\text{PH}_2)\text{H}]^2}$$

If a statistical sorting of H and PH_2 groups on germanium occurs in the two systems, $Q_1(\text{stat})$ and $Q_2(\text{stat})$ values of 0.11 and 0.25, respectively, would be expected. The experimentally observed value of $Q_2(\text{exptl}) = 0.27$ is, within experimental error, equal to the statistical value. In the $\text{CH}_3\text{Ge}(\text{PH}_2)_x\text{H}_{3-x}$ system, the value for $Q_1(\text{exptl})$ of 0.74 is not in close agreement with $Q_1(\text{stat})$. However, because of the difficulties in obtaining equilibrium mixtures without some decomposition occurring, the difference between $Q_1(\text{stat})$ and $Q_1(\text{exptl})$ cannot be considered significant.

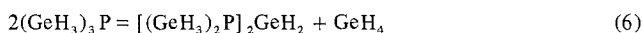
Evidence for the redistribution of H and PH_2 groups on germanium in GeH_3PH_2 is clearly present both in nmr spectral and sealed-bulb experiments. Direct evidence for $\text{GeH}_x(\text{PH}_2)_{4-x}$ redistribution materials other than GeH_4 is obtained

from the ^1H nmr spectral studies of GeH_3PH_2 at low temperatures. Samples of GeH_3PH_2 were allowed to decompose at temperatures up to -23° while the ^1H nmr spectrum was being continually observed. Small resonances at $\delta -0.39$ and -0.85 ppm appear and slowly increase in size until they are as shown in Figure 1A. Resonances due to GeH_4 , $(\text{GeH}_3)_2\text{PH}$, $(\text{GeH}_3)_3\text{P}$, and PH_3 , as reported previously by Drake,⁶ also appeared later. Unambiguous characterization of the species which yield the $\delta -0.39$ and -0.85 ppm multiplets was not possible because of the thermal instability of the samples. However, the silicon analogs of the species expected in this system, $\text{SiH}_2(\text{PH}_2)_2$ and $\text{SiH}(\text{PH}_2)_3$, have been prepared.⁹ Comparison of the upfield halves of their PH_2 resonances (Figure 1B and 1C) with the spectra of the germanium redistribution products in Figure 1A shows that the multiplets closely resemble one another. These comparisons and the early presence of GeH_4 in the reaction systems lead us to conclude that the multiplets of $\delta -0.39$ and -0.85 ppm may be attributed to $\text{GeH}_2(\text{PH}_2)_2$ and $\text{GeH}(\text{PH}_2)_3$, respectively. The downfield shift for resonances of the germanium species is expected, since, in general, PH_2 protons on germanium occur at a lower field than the PH_2 protons in analogous silicon systems. Thus, at low temperature, redistribution processes of the type such as



apparently occur.

In another series of experiments, GeH_3PH_2 was allowed to decompose at room temperature in nmr tubes (Table III). A similar but less quantitatively reported experiment was reported earlier by Drake.⁶ Reaction occurs slowly as evidenced first by the appearance of a singlet at $\delta -3.20$ ppm due to GeH_4 . This indicates that the initial reaction involves the redistribution of groups on germanium, although unambiguous spectral evidence for $\text{GeH}_2(\text{PH}_2)_2$ and $\text{GeH}(\text{PH}_2)_3$ could not be obtained. Beyond 12 hr, the formation of PH_3 , $(\text{GeH}_3)_2\text{PH}$, $(\text{GeH}_3)_3\text{P}$, and ultimately solid reaction products occurs. From bulk pyrolyses of GeH_3PH_2 , the composition of the final solid was established to be $\text{Ge}_{3.0}\text{P}_{1.9}\text{H}_{5.3}$. These observed products undoubtedly arise through a complex series of redistribution reactions. The extent to which redistribution on germanium involves GeH_3PH_2 (eq 4 and 5) or $(\text{GeH}_3)_2\text{PH}$ or $(\text{GeH}_3)_3\text{P}$ in processes such as



as anticipated by Ebsworth,⁵ cannot be established. However, the presence of GeH_4 as a reaction product requires that redistribution on germanium by one or all of these processes occurs.

It has been reported that $(\text{GeH}_3)_3\text{P}$ decomposes to GeH_4 and possibly $[(\text{GeH}_3)_2\text{P}]_2\text{GeH}_2$ and $[(\text{GeH}_3)_2\text{P}]_3\text{GeH}$;⁵ $(\text{GeH}_3)_2\text{Se}$ decomposes to GeH_4 and $[(\text{GeH}_3)\text{Se}]_2\text{GeH}_2$;²⁴ and GeH_3F at ambient conditions reacts to form GeH_4 and GeH_2F_2 .²⁵ These thermal decomposition reactions can be classed also as reactions in which hydrogen and the group V, VI, or VII moieties redistribute on germanium, suggesting that redistributions involving hydrogen and other groups on germanium may be a common phenomenon.

Our data indicate that in $\text{GeH}_x(\text{PH}_2)_{4-x}$, $\text{CH}_3\text{Ge}(\text{PH}_2)_x\text{H}_{3-x}$, and $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)_x\text{H}_x$ systems in the absence of catalyst materials the redistribution of groups on germanium occurs more rapidly than does the redistribution of groups on phosphorus. No evidence was obtained for condensed products containing germanium-hydrogen bonds, such as $[(\text{CH}_3)_2\text{GeH}]_2\text{PH}$ from the pyrolysis of $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)\text{H}$. Even in the presence of catalyst materials (*i.e.*, phosphinogermane oxidation products³) where the rate of redistribution of groups on phosphorus relative to germanium is increased, no products other than $(\text{CH}_3)_2\text{GeH}_2$ which contain germanium-hydrogen bonds were found. These results suggest that the synthesis of Ge-H bond containing condensed phosphinogermanes by methods based on the redistribution of groups on phosphorus will be difficult unless a method to increase significantly the rate of redistribution on phosphorus relative to that on germanium can be established.

Registry No. GeH_3PH_2 , 13573-06-3; GeH_4 , 7782-65-2; $\text{GeH}_2(\text{PH}_2)_2$, 54062-90-7; $\text{GeH}(\text{PH}_2)_3$, 54062-91-8; $\text{CH}_3\text{Ge}(\text{PH}_2)_2\text{H}$, 54062-92-9; CH_3GeH_3 , 1449-65-6; $\text{CH}_3\text{Ge}(\text{PH}_2)\text{H}_2$, 24570-69-2; $\text{CH}_3\text{Ge}(\text{PH}_2)_3$, 54062-93-0; PH_3 , 7803-51-2; $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)\text{H}$, 26465-28-1; $(\text{CH}_3)_2\text{GeH}_2$, 1449-64-5; $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)_2$, 20519-93-1; $(\text{GeH}_3)_2\text{PH}$, 21847-04-1; $(\text{GeH}_3)_3\text{P}$, 15587-38-9; CH_3GeCl_3 , 993-10-2; $\text{LiAl}(\text{PH}_2)_4$, 25248-80-0.

References and Notes

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- (2) Alfred P. Sloan Fellow, 1973-1975.
- (3) A. R. Dahl and A. D. Norman, *Inorg. Chem.*, preceding paper.
- (4) A. R. Dahl and A. D. Norman, *J. Amer. Chem. Soc.*, **92**, 5525 (1970); A. R. Dahl, A. D. Norman, H. Shenav, and R. Schaeffer, submitted for publication.
- (5) S. Cradock, E. A. V. Ebsworth, G. Davidson, and L. A. Woodward, *J. Chem. Soc. A*, 1229 (1967).
- (6) J. E. Drake and C. Riddle, *J. Chem. Soc. A*, 2709 (1968).
- (7) J. E. Drake, N. Goddard, and C. Riddle, *J. Chem. Soc. A*, 2704 (1969).
- (8) D. F. Shriver, "The Manipulation of Air Sensitive Compounds," McGraw-Hill, New York, N.Y., 1969.
- (9) A. D. Norman and D. C. Wingeleth, *Inorg. Chem.*, **9**, 98 (1970); A. D. Norman, D. C. Wingeleth, and C. A. Heil, *Inorg. Syn.*, **15**, 17 (1974).
- (10) A. D. Norman, *Inorg. Chem.*, **9**, 870 (1970).
- (11) A. E. Finholt, C. Helling, V. Imhof, L. Nielsen, and E. Jacobson, *Inorg. Chem.*, **2**, 504 (1963).
- (12) P. A. Tierney, D. W. Lewis, and D. Berg, *J. Inorg. Nucl. Chem.*, **24**, 1165 (1962).
- (13) R. M. Lynden-Bell, *Trans. Faraday Soc.*, **57**, 888 (1961).
- (14) E. A. V. Ebsworth, S. G. Frankiss, and A. G. Robiette, *J. Mol. Spectrosc.*, **12**, 299 (1964).
- (15) J. E. Drake and W. L. Jolly, *J. Chem. Phys.*, **38**, 1033 (1963).
- (16) G. P. Van der Kelen, L. Verdonck, and D. Van de Vondel, *Bull. Soc. Chim. Belg.*, **73**, 733 (1964).
- (17) J. W. Straley, C. H. Tindal, and H. H. Nielsen, *Phys. Rev.*, **62**, 161 (1942).
- (18) V. A. Crawford, K. H. Rhee, and M. K. Wilson, *J. Chem. Phys.*, **37**, 2377 (1962).
- (19) J. E. Drake and W. L. Jolly, *J. Chem. Soc.*, 2807 (1962).
- (20) D. F. Van de Vondel and G. P. Van der Kelen, *Bull. Soc. Chim. Belg.*, **74**, 467 (1965).
- (21) K. M. Mackay, J. K. Sutton, S. R. Stobart, J. E. Drake, and C. Riddle, *Spectrochim. Acta, Part A*, **25**, 925 (1969).
- (22) T. N. Strivastava, J. E. Griffiths, and M. Onyszchuk, *Can. J. Chem.*, **41**, 2101 (1963).
- (23) D. E. Freeman, K. H. Rhee, and M. K. Wilson, *J. Chem. Phys.*, **39**, 2908 (1963).
- (24) J. E. Drake and C. Riddle, *J. Chem. Soc. A*, 1573 (1969).
- (25) T. N. Strivastava and M. Onyszchuk, *Proc. Chem. Soc., London*, 205 (1961).