Registry No. BF_3, 7637-07-2; HBF_2, 13709-83-6; H_2, 1333-74-0; D_2, 7782-39-0.

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Oxidation of Trimethylgermylphosphine and Bis(phosphino)dimethylgermane[1]

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The phosphinogermanes $(CH_3)_3GePH_2$ and $(CH_3)_2Ge(PH_2)_2$ react rapidly with gaseous O_2 to yield a mixture of oxidation products. From these reactions, the new phosphonoxygermoxane compounds $[(CH_3)_3GeO]_2P(O)H$ and $[(CH_3)_2GeOP(O)HO]_2$ have been isolated. Spectral data allow the compounds to be characterized as phosphonates. An alternate synthesis of $[(CH_3)_2GeOP(O)HO]_2$ from the reaction of H_3PO_3 and $(CH_3)_2Ge(PH_2)_2$ is reported.

Introduction

Redistribution reactions on the phosphorus atoms of bis(phosphino)dialkylgermanes result in the formation of novel germanium–phosphorus condensed products.[3,4] These redistribution reactions were observed to be catalyzed by trace quantities of oxidation products of the bis(phosphino)dialkylgermanes. Since catalyzed redistribution reactions might have application to the syntheses of a wide variety of new compounds, characterization of the oxidation products becomes of paramount importance. Although the oxidation products of tertiary phosphines containing covalently bonded silicon, germanium, tin, and lead have been studied,[5-7] the O_2 oxidation of primary or secondary group IV moiety substituted phosphines has not been examined. We report the first study of this type.

Experimental Section

Apparatus, Materials, and Techniques. All work was carried out in a standard high-vacuum system.[8] Melting points were obtained in sealed capillaries. Infrared spectra were obtained in the range 4000–400 cm^{-1} on a Perkin-Elmer Model 337G spectrometer on neat samples or samples pressed between KBr plates. Proton nmr spectra were obtained at 60.0 and 100.0 MHz using Varian A-60A and HA-100 spectrometers. Phosphorus-31 nmr spectra were obtained at 40.5 MHz using a Varian HA-100 equipped with standard probe and radiofrequency unit accessories. Mass spectra were obtained using Varian MAT CH-5 and CH-7 spectrometers operating at an ionizing voltage of 70 eV. Mass spectral envelopes for polygermanium-containing molecular species[9] were calculated essentially as described previously.[10] The isotopic distribution patterns centered at *m/e* 146 and 218 are diagnostic for Ge_2- and Ge_3-containing species, respectively.

The $(CH_3)_3GePH_2$ and $(CH_3)_2Ge(PH_2)_2$ were prepared and purified as described previously.[11] Reagent grade anhydrous phosphorous acid (Baker Chemical Co.), 95% ethanol, and chloroform were used without further purification. Oxygen (Matheson Co.) was passed through a −196° trap prior to use.

Reactions with O_2. (A) $(CH_3)_3GePH_2$. Typically, 3.5 mmol of $(CH_3)_3GePH_2$ and 10 ml of chloroform were condensed into a 500-ml round-bottom flask. The flask was connected to the vacuum line at a side-arm U tube on the flask. The reaction bulb was warmed to −45° and 5–10 Torr of gaseous oxygen was admitted. After *ca.* 1 hr, additional oxygen was bled slowly into the reactor. Bursts of flame occurred as the oxygen pressure reached *ca.* 20 Torr. *Caution! Care should be taken to add the oxygen slowly, since an excessive burning rate could cause overheating and a subsequent explosion.* Oxygen was added in intervals of 5–10 min until bursts of flame no longer occurred. During the reaction yellow-orange solid deposited on the walls of the reactor. The reactor was heated to 150° and reaction materials were removed through the side-arm U trap maintained at −30°. Chloroform and a trace of PH_3 (confirmed by ir spectrum)[12] passed the −30° trap. The side arm was reattached to a double U-tube sublimation tube. The material in the side arm was heated to 100–110° and allowed to distil into the two traps, maintained at −30° (fraction I) and 0° (fraction II). Repeated distillation of fraction II resulted in a 10% yield of pure $[(CH_3)_3GeO]_2P(O)H$. *Anal.* Calcd for $C_6H_{19}Ge_2O_3P$: C, 19.09; H, 5.07. Found: C, 19.31; H, 5.01.

Table I. Nuclear Magnetic Resonance Spectral Data

Measurement	$[(CH_3)_3GeO]_2$-P(O)H	$[(CH_3)_2GeOP(O)$-$HO]_2$
	^1H Nmr Data[a]	
$\delta(CH_3)^b$	-0.52 ± 0.03	-1.02 ± 0.03
$\delta(PH)^b$	-6.75 ± 0.03	-6.80 ± 0.03
$^1J(PH)^c$	681 ± 2	708 ± 3
	^{31}P Nmr Data[a]	
$\delta(P)^d$	-1 ± 2	7 ± 2

[a] Obtained on 10–20% (by volume) solutions in $CHCl_3$. [b] Chemical shifts in ppm relative to internal $(CH_3)_4Si$. [c] Coupling constants in Hz. [d] Chemical shift in ppm relative to external 85% H_3PO_4.

$[(CH_3)_3GeO]_2P(O)H$ shows infrared absorptions at 3390 (m), 2963 (m), 2899 (m), 2778 (vw), 2331 (s), 1639 (w), 1412 (m), 1227 (vs), 1149 (s), 1094 (m, sh), 1010 (vs), 830 (vs), 769 (w, sh), 671 (w), 627 (s), 577 (m), and 478 (m) cm^{-1}. The most intense peaks in the ten most intense mass spectral envelopes occur at *m/e* (relative intensities in parentheses) 316 (8.9), 301 (29.0), 183 (13.1), 167 (5.6), 137 (7.9), 119 (100.0), 105 (12.6), and 89 (18.2). The parent envelope centered at *m/e* 316 is, within experimental error, superimposable with that expected for a molecule containing two Ge atoms. Proton and ^{31}P nuclear magnetic resonance data are given in Table I.

Fraction I, upon repeated distillation, could not be separated completely. Mass spectral analyses showed it to consist predominantly of a material whose parent molecular ion mass spectral envelope occurred at *m/e* 183, along with a small quantity of $[(CH_3)_3GeO]_2P(O)H$. The most intense peak in each of the eight most intense envelopes for this material occurred at *m/e* (relative intensity in parentheses) 75 (13.0), 89 (48.8), 105 (100), 119 (65.2), 137 (22.6), 169 (84.1), and 183 (10.4). The envelope centered at *m/e* 183 was clearly attributable to a monogermanium species. Owing to the small amounts of material available and the difficulties encountered in purifying it, no further characterization data were obtained.

The involatile brown-orange material, when analyzed mass spectrometrically, showed only traces of $[(CH_3)_3GeO]_2P(O)H$. The ^{31}P nmr spectra of concentrated CH_3OH or H_2O extracts of the solid showed weak resonances due to H_3PO_3 and H_3PO_2 along with several small unassigned peaks. No attempts were made to examine the solid mixture further.

(B) $(CH_3)_2Ge(PH_2)_2$. Typically, 0.50 mmol of $(CH_3)_2Ge(PH_2)_2$ and 5 ml of chloroform were condensed into a bulb and reaction with O_2 was effected in a manner analogous to that described above. The reaction bulb was connected to the vacuum line by a 50-cm horizontal sublimation tube (12-mm o.d). High-volatility materials, $CHCl_3$ and PH_3, were removed from the reactor at room temperature. Then the reactor was heated to *ca.* 300° in order to distil the viscous product oil to the end of the sublimation tube. The reactor was removed from the sublimation tube at a constriction. A resistance wire-wound brass pipe was placed around the sublimation tube and the tube was heated (*ca.* 200°), at which temperature white solid material sublimed slowly along the tube.

The solid was removed and repeatedly resublimed to yield 6 mg (3% yield) of pure $[(CH_3)_2GeOP(O)HO]_2$ (mp 113.0–113.5°). *Anal.* Calcd for $C_4H_{14}Ge_2O_6P_2$: C, 13.15; H, 3.86. Found: C, 13.00; H, 3.66.

High-quality infrared spectral data for $[(CH_3)_2GeOP(O)HO]_2$ were difficult to obtain since it is an extremely hygroscopic solid. Samples dissolved in Nujol showed absorptions at 2338 (s), 1233 (vs), 1142 (s), 1018 (vs), 832 (vs), and 668 (w) cm^{-1}. The mass spectrum exhibits a series of peak envelopes, the most intense peak in each of the ten largest envelopes occurring at *m/e* (relative intensities in parentheses) 365 (38.8), 351 (65.7), 303 (100.0), 287 (74.0), 271 (71.0), 241 (37.4), 167 (35.8), 119 (81.2), 105 (29.8), and 89 (66.5). The parent envelope (centered at *m/e* 365) was essentially superimposable with that expected for a molecule which contains two Ge atoms. Proton and ^{31}P nmr data are given in Table I.

In a second type experiment, neat $(CH_3)_2Ge(PH_2)_2$ was treated with O_2 at 300 Torr. Vigorous reaction occurred, forming a dark red solid and a viscous yellow liquid. Distillation of the liquid yielded a trace of clear liquid whose mass spectrum exhibited a near-continuous array of peaks from *m/e* 70 to *m/e* 500. Some spectral envelopes appeared to arise from fragments containing three or more germanium atoms while many others arose from species containing only hydrogen, oxygen, and phosphorus. The small amount of material available and its complexity precluded further study and analyses.

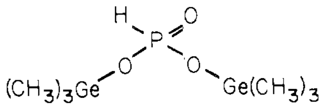
In a third series of experiments, 0.5 mmol of $(CH_3)_2Ge(PH_2)_2$ was allowed to react with ambient air in an open container at room temperature for periods of 10–12 hr. Separation of the product mixture by sublimation yielded a trace of material of volatility higher than that of pure $[(CH_3)_2GeOP(O)HO]_2$, which remained contaminated with $[(CH_3)_2GeOP(O)HO]_2$. The two highest mass envelopes, centered at *m/e* 405 and 420, clearly arise from species containing three Ge atoms.

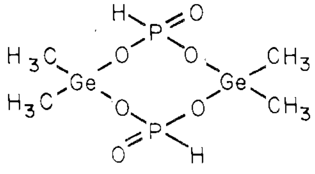
Reaction of $[(CH_3)_2GeO]_n$ with H_3PO_3. A 0.43-mmol sample of $[(CH_3)_2GeO]_n$,[13] prepared from the hydrolysis of $(CH_3)_2Ge(PH_2)_2$,[14] was dissolved in 20 ml of 95% ethanol and treated with excess anhydrous H_3PO_3. After 1 hr, the ethanol was removed *in vacuo*. Mass spectral analysis of the residue showed it to be a mixture of $[(CH_3)_2GeOP(O)HO]_2$ and the compound above whose parent ion envelope occurred at *m/e* 420. Sublimation of the residue yielded 40 mg (22% yield) of pure $[(CH_3)_2GeOP(O)HO]_2$.

Results and Discussion

$(CH_3)_3GePH_2$ and $(CH_3)_2Ge(PH_2)_2$ are rapidly oxidized by O_2 in complex reactions which result in the production of phosphine (or phosphine oxidation products), voluminous amounts of intractable solid, and trace amounts of previously uncharacterized phosphonoxygermoxane compounds. Under carefully controlled conditions, in which reaction with O_2 is allowed to proceed in $CHCl_3$ solution, low yields of the two new compounds $[(CH_3)_3GeO]_2P(O)H$ (I) and $[(CH_3)_2GeOP(O)HO]_2$ (II) have been obtained and characterized.

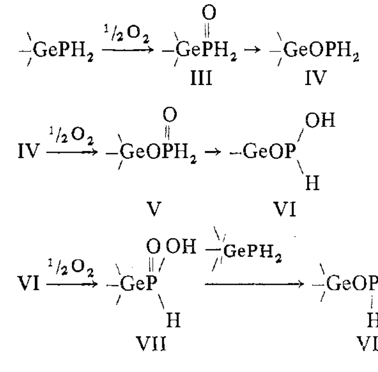
The structures shown for I and II are consistent with the ir, nmr, and mass spectral data.


I


II

The mass spectra yield highest mass envelopes centered at *m/e* 316 and 365 for I and II, respectively. By analysis of the peak distributions within the envelopes, the latter are readily identified as molecules containing two germanium atoms. The envelope at *m/e* 316 can be assigned to the parent ion $[(CH_3)_3GeO]_2P(O)H^+$. The *m/e* 365 envelope for II is attributable to the parent ion minus one hydrogen atom. The infrared spectrum of $[(CH_3)_3GeO]_2P(O)H$ shows absorptions at 2331, 1227, 1010, and 671 cm^{-1} which are characteristic of P—H stretching,[15,16] P=O stretching,[15,16] O—P(=O)—O stretching,[17] and O—Ge—O stretching modes,[15,18] respectively. For $[(CH_3)_2GeOP(O)HO]_2$, the peaks at 2338, 1018, and 668 cm^{-1} can tentatively be assigned to P—H, O—P(=O)—O, and O—Ge—O modes also; however, the quality of spectral data precludes unambiguous assignments. The absence of a P—OH absorption expected to be in the 2560–2700-cm^{-1} region[15] for either I or II supports their formulation as phosphonates rather than phosphites. For both I and II, the absorptions expected as a result of CH_3–Ge moieties present[15,19] are evident. The large singlet resonances observed in the ^1H nmr spectra of I and II at δ −0.52 ppm (area 18) and δ −1.02 (area 12), respectively, are in the region expected for CH_3 groups of methylgermoxane species.[20,21] The widely spaced doublets at δ −6.75 (J = 681 Hz, area 1) and δ −6.80 (J = 708 Hz, area 2) for I and II in the ^1H nmr spectra and at δ −1 ppm (J = 700 Hz) and δ 7 ppm for I and II in the ^{31}P nmr spectra are consistent with that expected for a hydrogen atom directly bonded to a pentavalent phosphorus. The ^{31}P nmr spectral resonances are in the region expected, based on earlier observations of organophosphonates of the type $(RO)_2P(O)H$.[22]

The O_2 oxidation of $(CH_3)_3GePH_2$ and $(CH_3)_2Ge(PH_2)_2$ may occur in stepwise reactions shown in general form as



$$-GePH_2 \xrightarrow{1/2\,O_2} -Ge\overset{O}{\overset{\|}{P}}H_2 \rightarrow -GeOPH_2 \qquad \text{III} \quad \text{IV}$$

$$\text{IV} \xrightarrow{1/2\,O_2} -GeO\overset{O}{\overset{\|}{P}}H_2 \rightarrow -GeOP(OH)(H) \qquad \text{V} \quad \text{VI}$$

$$\text{VI} \xrightarrow{1/2\,O_2} -Ge\overset{O\ OH}{\overset{\|\,/}{P}}\underset{H}{} \xrightarrow{-GePH_2} -GeO\underset{H}{P}OGe- \qquad \text{VII} \quad \text{VIII}$$

Phosphine is formed as an intermediate in the oxidation reactions, as judged from the intermittent bursts of flame[23] that occur during the reaction and the fact that traces of PH_3 are isolatable from some reactions. Also the presence of H_3PO_3, H_3PO_2, and phosphoric acid materials is consistent with PH_3 oxidation having occurred. Intermediates of the types III–VII have not been isolated. Formation of VII-type species has been suggested previously by Schumann for the O_2 oxidation of $R_3MPR'_2$ and $(R_3M)_2PR'$ (where M = Si, Ge, or Sn) compounds.[3] Species of type VIII would arise through the expected cleavage of Ge–P bonds by Bronsted acids, as demonstrated in our studies with H_3PO_3 and by others.[24] Phosphine oxide rearrangements by reverse Arbuzov reactions would result in the III → IV and V → VI interconversions.

From the oxidation of $(CH_3)_3GePH_2$, we were able to isolate a small quantity of material whose highest mass envelope occurred at m/e 183, characteristic of $(CH_3)_3GePO_2H_2$. 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 $[(CH_3)_2GeO]_n$[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

$$[(CH_3)_2GeO]_n + nH_3PO_3 \rightarrow (n/2)[(CH_3)_2GeOP(O)HO]_2 + nH_2O$$

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 $[(CH_3)_2GeO]_3OP(O)H^+$, the parent molecular ion of the cyclic $[(CH_3)_2GeO]_3OP(O)H$ (IX).

The IX forms also along with other inseparable materials in reactions of II with H_2O and in reactions of $(CH_3)_2Ge(PH_2)_2$ 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

$$2n[(CH_3)_3GeO]_3OP(O)H = n[(CH_3)_2GeOP(O)OH]_2 + 4[(CH_3)_2GeO]_n$$

Similar processes have been reported in the redistribution of $(CH_3)_2GeO$ linkages between $[(CH_3)_2GeO]_3$ and $[(CH_3)_2GeO]_4$.[13,25,26] Since II contains no Ge–O–Ge linkages, it cannot undergo similar redistribution reactions.

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Registry No. $(CH_3)_3GePH_2$, 20519-92-0; $(CH_3)_2Ge(PH_2)_2$, 20519-93-1; $[(CH_3)_3GeO]_2P(O)H$, 54062-87-2; $[(CH_3)_2GeOP(O)HO]_2$, 54062-88-3; $[(CH_3)_2GeO]_n$, 54062-89-4; H_3PO_3, 13598-36-2.

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Thermal Redistribution of Hydrido and Phosphino Groups in Phosphinohydridogermanes[1]

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The rapid redistribution of phosphino groups ($-PH_2$) 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 $GeH_2(PH_2)_2$ and $GeH(PH_2)_3$ as redistribution products of GeH_3PH_2, in addition to GeH_4, has been obtained. The $CH_3Ge(PH_2)_2H$ and $(CH_3)_2Ge(PH_2)H$ redistribution reactions yield (1) CH_3GeH_3, $CH_3Ge(PH_2)H_2$, and $CH_3Ge(PH_2)_3$ and (2) $(CH_3)_2GeH_2$ and $(CH_3)_2Ge(PH_2)_2$, respectively. The $(CH_3)_2Ge(PH_2)_xH_{2-x}$ 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 $CH_3Ge(PH_2)_2H$ and $CH_3Ge(PH_2)_3$ have been prepared by reaction of CH_3GeCl_3 with $LiAl(PH_2)_4$ 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 $(CH_3)_2Ge(PH_2)_2$ yields PH_3, $[(CH_3)_2GePH_2]_2PH$, $[(CH_3)_2GePH_2]_3P$,[3] and ultimately the cage molecule $[(CH_3)_2Ge]_6P_4$.[4] These reactions apparently involve the redistribution of hydrogen atoms and $(CH_3)_2Ge$ 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 $(GeH_3)_3P$,[5] GeH_3PH_2,[6] and $CH_3Ge(PH_2)H_2$[7] reported previously. Our studies of the redistribution reactions which occur in $GeH_x(PH_2)_{4-x}$, $CH_3Ge(PH_2)_xH_{3-x}$, and $(CH_3)_2Ge(PH_2)_xH_{2-x}$ 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