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Oligogermanes

Photodecompostion of the Oligogermanes $n\mathrm{Bu}_3\mathrm{GeGePh}_2\mathrm{Ge}n\mathrm{Bu}_3$ and $n\mathrm{Bu}_3\mathrm{GeGePh}_3$: Identification of the Photoproducts by Spectroscopic and Spectrometric Methods

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Abstract: The oligogermane $n\mathrm{Bu}_3\mathrm{GeGePh}_2\mathrm{Ge}n\mathrm{Bu}_3$ was photolyzed using UV-C light in the presence of acetic acid as a trapping agent and the photoproducts were identified using ^{1}H NMR spectroscopy, gas chromatography/electron-impact mass spectrometry, and high resolution accurate mass mass spectrometry. The products identified were the germanes $n\mathrm{Bu}_3\mathrm{GeH}$, $n\mathrm{Bu}_3\mathrm{GeOAc}$, and $\mathrm{Ph}_2\mathrm{Ge(H)OAc}$ (OAc = $\mathrm{C}_2\mathrm{H}_3\mathrm{O}_2$) and the digermane $n\mathrm{Bu}_6\mathrm{Ge}_2$. This indicates that both germanium–germanium single bonds are cleaved homolytically upon irradiation to generate two $n\mathrm{Bu}_3\mathrm{Ge}^{\cdot}$ radicals and the germylene $\mathrm{Ph}_2\mathrm{Ge}$**:**. The digermane $n\mathrm{Bu}_3\mathrm{GeGePh}_3$ was also photolyzed under identical conditions, and in this case the photoproducts were identified as $n\mathrm{Bu}_3\mathrm{GeH}$, $n\mathrm{Bu}_3\mathrm{GeOAc}$, $\mathrm{Ph}_3\mathrm{GeH}$, $\mathrm{Ph}_3\mathrm{GeOAc}$ and the digermanes $n\mathrm{Bu}_6\mathrm{Ge}_2$ and $\mathrm{Ph}_6\mathrm{Ge}_2$.

Introduction

The photochemistry of catenated group 14 compounds is of interest since this method can be used to convert one type of catenate to another and also can be used for the generation of reactive intermediates including silylenes, germylenes, stannylenes, and group 14 element centered radical species that can be trapped and characterized.[1–33] In the case of germanium, the photochemistry of the cyclotrigermane $(\mathrm{Mes}_2\mathrm{Ge})_3$[34] has been the most extensively studied and it has been shown that this compound is photochemically converted to a germylene $\mathrm{Mes}_2\mathrm{Ge}$**:** and a digermene $\mathrm{Mes}_2\mathrm{Ge{=}GeMes}_2$. The chemistry of both of these photoproducts has been thoroughly investigated.[1,2,4,13,14,35–42] However, only a few investigations into the photochemistry of linear oligogermanes have been described. These include the photolysis of the permethylated oligogermanes $\mathrm{Me(GeMe}_2)_n\mathrm{Me}$ (n = 3–6)[7,9] and the polygermanes $(\mathrm{R}_2\mathrm{Ge})_n$ (R_2 = Et_2, $n\mathrm{Bu}_2$, Hex_2, PhMe).[8,14]

It has been shown that linear oligogermanes decompose via both the homolytic scission of the Ge–Ge bonds to yield germyl radicals, by germylene extrusion with concomitant chain contraction, or by a combination of both processes. The photochemistry of heteroleptic oligogermanes, where the substituent pattern is different at different germanium atoms, has yet to be explored. In this regard, we have prepared the trigermane $n\mathrm{Bu}_3\mathrm{GeGePh}_2\mathrm{Ge}n\mathrm{Bu}_3$ (**1**) and have photolyzed this compound in the presence of acetic acid.

It was expected that photolysis of **1** would yield several photoproducts that would be the trapping products of both radicals and germylenes generated during the reaction, including $n\mathrm{Bu}_3\mathrm{GeH}$, $n\mathrm{Bu}_3\mathrm{GeOAc}$ from generation of the tributylgermyl radical, and also $\mathrm{Ph}_2\mathrm{Ge(H)OAc}$ and also possibly $n\mathrm{Bu}_2\mathrm{Ge(H)OAc}$ from extrusion of the germylenes $\mathrm{Ph}_2\mathrm{Ge}$**:** and $n\mathrm{Bu}_2\mathrm{Ge}$**:**, respectively. If any trapped $\mathrm{Ph}_2\mathrm{Ge}$**:** were identified as $\mathrm{Ph}_2\mathrm{Ge(H)OAc}$, the presence of different substituents at the germanium atoms of **1** would indicate that the source of this germylene would be the central germanium atom of **1**. Similarly, if $n\mathrm{Bu}_2\mathrm{Ge(H)OAc}$ were obtained then the germylene $n\mathrm{Bu}_2\mathrm{Ge}$**:** would be generated from the terminal germanium atoms of **1**. Ligand scrambling processes also might be expected to occur, and any resulting mixed-ligand radicals or germylenes that were produced also could be trapped and identified. The photoproducts from **1** have been characterized by ^{1}H NMR spectroscopy, gas chromatography/electron impact mass spectrometry (GC/MS), and high resolution accurate mass mass spectrometry (HRAM-MS). The photochemistry of the related digermane $n\mathrm{Bu}_3\mathrm{GeGePh}_3$ (**2**) has also been studied. We have found that HRAM-MS is a highly useful tool for the study of these photoproduct mixtures and is used here for the first time in this regard.

Results and Discussion

Synthesis and Characterization of Materials

The trigermane **1** and the digermane **2**[43] were synthesized using the hydrogermolysis reaction as shown in Scheme 1, where the starting germanium amide reagent is converted in situ to an α-germyl nitrile that is the active species in the ger-

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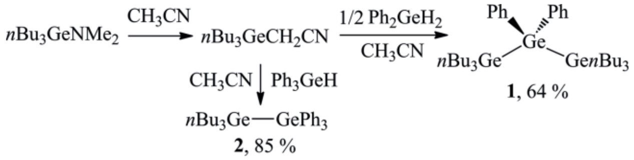
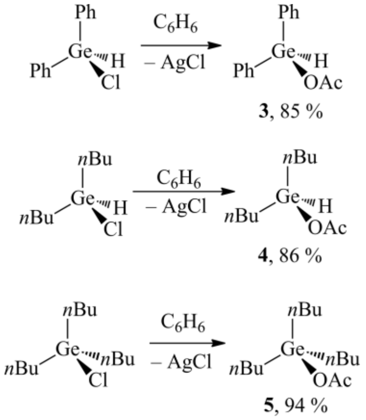
manium–germanium bond forming process.[43–46] The possible germylene trapping products $Ph_2Ge(H)OAc$ (**3**) and $n$$Bu_2Ge(H)OAc$ (**4**) were prepared from the corresponding germanium hydrochlorides R_2GeHCl[47] and silver acetate, while $n$$Bu_3GeOAc$ (**5**) was prepared from $n$$Bu_3GeCl$ and silver acetate (Scheme 2). The acetate-containing compounds exhibit characteristic resonances of the acetate methyl group hydrogen atoms in their ^1H NMR spectra at δ = 1.86 (**3**), 1.86 (**4**), and 1.90 ppm (**5**). The germanium-bound hydrogen atom in **3** results in the observation of a singlet at δ = 6.72 ppm in the ^1H NMR spectrum of **3**, while that for **4** appears as a pentet at δ = 5.71 ppm.



Scheme 1.



Scheme 2.

Investigation of the Photochemistry of 1 by ^1H NMR Spectroscopy

The trigermane **1** was dissolved in [D_{12}]cyclohexane in a quartz NMR tube in the presence of 2 equiv. of AcOH and was irradiated at regular intervals with UV-C light after which the ^1H NMR spectrum of the sample was recorded. The ^1H NMR spectra recorded at four different exposure times are shown in Figure 1. After irradiation of the sample for 3 min a noticeable decrease in the intensity of the signals for AcOH at δ = 12.00 and 1.93 ppm and the appearance of a multiplet at δ = 3.79 and a singlet at δ = 1.88 ppm was observed, and these two resonances continued to increase in intensity as the photolysis was continued. After a total irradiation time of 15 min two additional singlets at δ = 6.52 and 1.99 ppm had appeared and these are assigned to the germanium-bound hydrogen and the acetate methyl group of $Ph_2Ge(H)OAc$ (**3**), respectively.[5] The four signals at δ = 6.52, 3.79, 1.99, and 1.88 ppm continued to increase in intensity as the photolysis experiment was continued until a total irradiation time of 120 min, after which no further change in the ^1H NMR spectrum was observed. The singlet at δ = 1.93 ppm persisted indicating that AcOH was still present in the reaction mixture although the singlet at δ = 12.00 ppm had broadened into the baseline. Irradiation for a further 3 h did not result in any additional observable changes in the spectrum.

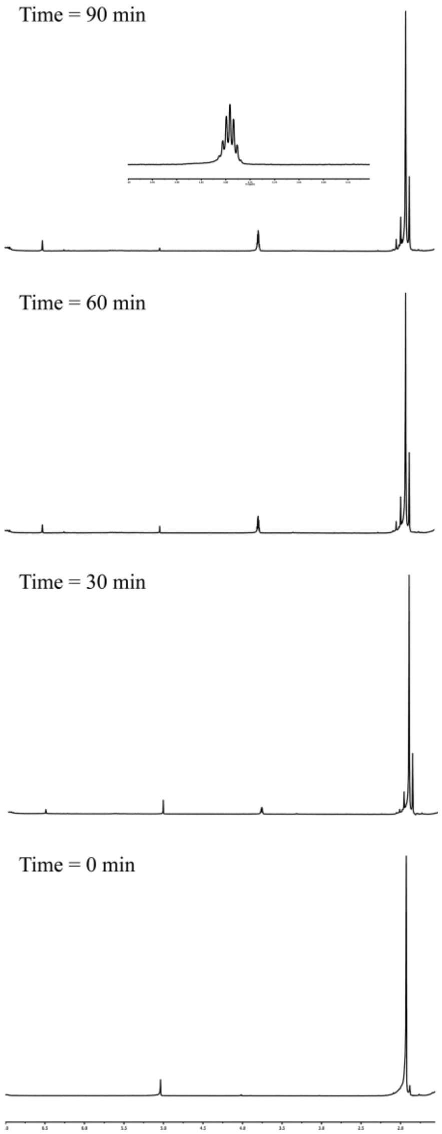


Figure 1. ^1H NMR spectra for the phtolysis of $n$$Bu_3GeGePh_2Ge$$n$$Bu_3$ (**1**) in the presence of AcOH in [D_{12}]cylcohexane at various time intervals.

The trigermane **1** was also irradiated for 18 h with UV-C light in THF solution in the presence of 10 equiv. of acetic acid (AcOH). After workup to remove the excess AcOH the ^1H NMR spectrum in [D_6]benzene contained a complex pattern of peaks in the alkyl and aryl region of the spectrum indicting the presence of multiple photoproducts. However, there were two clearly visible singlets at δ = 6.72 and 1.78 ppm indicating the presence of **3**, as well as an additional singlet at δ = 1.90 ppm and a multiplet at δ = 4.02 ppm (J = 3.0 Hz). Given these results and those from the NMR scale experiment described above, it was postulated that the singlet at δ = 1.90 ppm and the multiplet at δ = 4.02 ppm might be attributed to either the germylene trapping product $n$$Bu_2Ge(H)OAc$ (**4**) that could be generated by extrusion of $n$$Bu_2Ge$**:** from the terminal $n$$Bu_3Ge$-groups of **1**, or the multiplet alone could be due to the presence of the germane $n\mathrm{Bu_3GeH}$ (**6**) while the singlet results from a separate species containing an acetate group. The multiplet is identical to that observed in the ^{1}H NMR spectrum of a commercial sample of **6**, and thus the singlet $\delta = 1.90$ ppm must be due to the presence of another acetate-containing species. The acetate **5** exhibits an identical singlet at $\delta = 1.90$ ppm for the methyl group protons and so **5** also appears to be present in the photolysis product mixture of **1**.

Investigation of the Photochemistry of 1 by Mass Spectrometry

The photolysis product mixture for **1** was analyzed using electron impact GC/MS. The GC trace for the product mixture exhibited five peaks with retention times of 10.9, 16.4, 23.7, 29.9, and 44.9 min and the GC/MS data are collected in Table 1. Although phenyl-substituted germanes were also present in the product mixture, any of these species that are present decompose under the thermal conditions of the GC column. The mass spectrum of the first compound eluted had three main peaks at $m/z = 189$, 133, and 75. These are assigned to the $n\mathrm{Bu_2GeH^+}$, $n\mathrm{BuGeH_2}^+$, and $\mathrm{GeH^+}$ ions, while the two peaks at $m/z = 132$ and 75 are assigned to the $n\mathrm{BuGeH^+}$ and $\mathrm{GeH^+}$ ions resulting from fragmentation of the $n\mathrm{Bu_2GeH^+}$ ion. The retention time and mass spectrum are identical to that of a pure sample of $n\mathrm{Bu_3GeH}$ run under identical conditions, and so the first compound eluted is **6**.

Table 1. EI-GC/MS data for photolyzed $n\mathrm{Bu_3GeGePh_2Ge}n\mathrm{Bu_3}$ (**1**).

	Area %	m/z	Assignment
$n\mathrm{Bu_3GeH}$ (**6**)	85.6	189	$n\mathrm{Bu_2GeH^+}$
(t_r = 10.9 min)		133	$n\mathrm{BuGeH_2}^+$
		75	$\mathrm{GeH^+}$
$n\mathrm{Bu_3GeOGe}n\mathrm{Bu_3}$	1.8	223	$n\mathrm{Bu_2GeO(H_3O)^+}$
(t_r = 16.4 min)		167	$n\mathrm{BuHGeO(H_3O)^+}$
		131	$n\mathrm{BuGe^+}$
$n\mathrm{Bu_3GeOAc}$ (**5**)	2.5	265	$n\mathrm{Bu_2Ge(C_2H_3O_2)(H_2O)^+}$
(t_r = 23.7 min)		209	$n\mathrm{BuGe(C_2H_3O_2)(H_2O)H^+}$
		153	$\mathrm{Ge(C_2H_3O_2)(H_2O)H_2}^+$
$n\mathrm{Bu_3GeGe}n\mathrm{Bu_3}$ (**7**)	7.6	431	$\mathrm{Ge_2}n\mathrm{Bu_5}^+$
(t_r = 29.9 min)		375	$\mathrm{Ge_2}n\mathrm{Bu_4H^+}$
		319	$\mathrm{Ge_2}n\mathrm{Bu_3H_2}^+$
		263	$\mathrm{Ge_2}n\mathrm{Bu_2H_3}^+$
		207	$\mathrm{Ge_2}n\mathrm{BuH_4}^+$
1	2.5	394	$n\mathrm{Bu_3GeGePh^+}$
(t_r = 44.9 min)		338	$n\mathrm{Bu_2HGeGePh^+}$
		282	$n\mathrm{BuH_2GeGePh^+}$
		225	$\mathrm{HGeGePh^+}$

The mass spectrum of the second compound eluted (t_r = 16.4 min) exhibited significant peaks at $m/z = 223$, 167, and 131 that correspond to the $n\mathrm{Bu_2GeO(H_3O)^+}$, $n\mathrm{BuHGeO(H_3O)^+}$, and $n\mathrm{BuGe^+}$ ions that are likely generated by the fragmentation of $n\mathrm{Bu_3GeOGe}n\mathrm{Bu_3}$, which is formed from the insertion of oxygen into the Ge–Ge bond of $n\mathrm{Bu_6Ge_2}$ (**7**) under the experimental conditions. The mass spectrum of the third compound eluted (t_r = 23.6 min) exhibited peaks at $m/z = 265$, 209, and 153 that are assigned to the $n\mathrm{Bu_2Ge(C_2H_3O_2)(H_2O)^+}$, $n\mathrm{BuGe(C_2H_3O_2)(H_2O)H^+}$, and $\mathrm{Ge(C_2H_3O_2)(H_2O)H_2}^+$ ions indicating that the third compound eluted is $n\mathrm{Bu_3GeOAc}$ (**5**).

The mass spectrum of fourth compound eluted (t_r = 29.9 min) exhibits a peak at $m/z = 431$ that is assigned to the $n\mathrm{Bu_5Ge_2}^+$ ion, and four additional peaks were observed that correspond to the successive fragmentation of four butyl groups from this ion. This indicates that the digermane $n\mathrm{Bu_6Ge_2}$ (**7**) is present in the photolysis product mixture. The GC/MS of a synthetically prepared sample of **7**[48] exhibited the same retention time and mass spectrum confirming that **7** is present in the photolysis product mixture. The mass spectrum of the fifth species eluted (t_r = 44.9 min) contained a peak at $m/z = 394$ that is assigned to the $n\mathrm{Bu_3GeGePh^+}$ ion, as well as peaks at $m/z = 338$, 282, and 225 resulting from fragmentation of this ion via the successive loss of all three butyl groups. This material is unreacted **1** that remained in the photolysis product mixture. The two most abundant species in the GC trace of the photolysis product mixture of **1** are **6** and the digermane **7**.

Analysis of the photolysis product mixture of **1** by High Resolution Accurate Mass Mass Spectrometry (HRAM-MS) resulted in the observation of six intense peaks at $m/z = 230.0964$, 245.1325, 270.0337, 286.1588, 305.0385, and 346.0652 (Figure 2, Table 2). These are assigned to the $n\mathrm{Bu_2GeH(CH_3CN)^+}$, $n\mathrm{Bu_3Ge^+}$, $\mathrm{Ph_2GeH(CH_3CN)^+}$, $n\mathrm{Bu_3Ge(CH_3CN)^+}$, $\mathrm{Ph_3Ge^+}$, and $\mathrm{Ph_3Ge(CH_3CN)^+}$ ions, respectively. A less intense signal at $m/z = 565.1749$ was also observed that corresponds to the $n\mathrm{Bu_3GeOGe}n\mathrm{Bu_3H^+}$ ion that is generated by insertion of oxygen into the germanium–germanium bond of **7** under the experimental MS conditions. A weak signal at $m/z = 731.2704$ due to the $n\mathrm{Bu_3GeGePh_2Ge}n\mathrm{Bu_3H_3O^+}$ ion indicates the presence of unphotolyzed **1**.

The HRAM-MS of unphotolyzed **1** contains a signal at $m/z = 368.2119$ corresponding to the $n\mathrm{Bu_3Ge(CH_3CN)_3}^+$ ion, as well as a less intense signal at $m/z = 594.2128$ due to the presence of the $n\mathrm{Bu_3GeGePh_2(CH_3CN)_3}^+$ ion (Table 2). This indicates that the oligogermanes do not remain intact under the experimental MS conditions. However, the $n\mathrm{Bu_3Ge^+}$ fragment was observed in the HRAM-MS of both photolyzed and unphtopholyzed **1**, indicating that this species could be produced from unreacted **1** or the germanes $n\mathrm{Bu_3GeOAc}$ (**5**) and/or $n\mathrm{Bu_3GeH}$ (**6**).

Synthetically prepared **5** and a commercial sample of **6** were also analyzed by HRAM-MS. The most intense peak in the HRAM-MS of **5** was at $m/z = 327.1342$ that is assigned to the $n\mathrm{Bu_3Ge(CH_3CN)_2}^+$ ion, and a weak but observable signal at $m/z = 428.2320$ corresponds to the $n\mathrm{Bu_3GeOAc(CH_3CN)_3H^+}$ ion. The MS/MS of the $n\mathrm{Bu_3GeOAc(CH_3CN)_3H^+}$ ion contains two signals at $m/z = 368.2113$ and 327.1847 resulting from fragmentation to the $n\mathrm{Bu_3Ge(CH_3CN)_3}^+$ and $n\mathrm{Bu_3Ge(CH_3CN)_2}^+$ ions, respectively. Therefore, although no solvated **5** was observed in the HRAM-MS of the photolysis product mixture of **1**, the non-solvated and mono-solvated $n\mathrm{Bu_3Ge^+}$ ion that was detected could also be generated from **5**. The HRAM-MS of a commercial sample of **6** contains signals at $m/z = 286.1582$ and 505.2684 corresponding to the $n\mathrm{Bu_3Ge(CH_3CN)^+}$ and $n\mathrm{Bu_3GeOGe}n\mathrm{Bu_3H^+}$ ions, respectively, indicating that both of these species that were detected in the photolysis product mixture of **1** could arise from the presence of **6**.

The HRAM-MS of $\mathrm{Ph_2Ge(H)OAc}$ **3** contained a signal at $m/z = 270.0239$ due to the $\mathrm{Ph_2Ge(CH_3CN)H^+}$ ion that is identical to

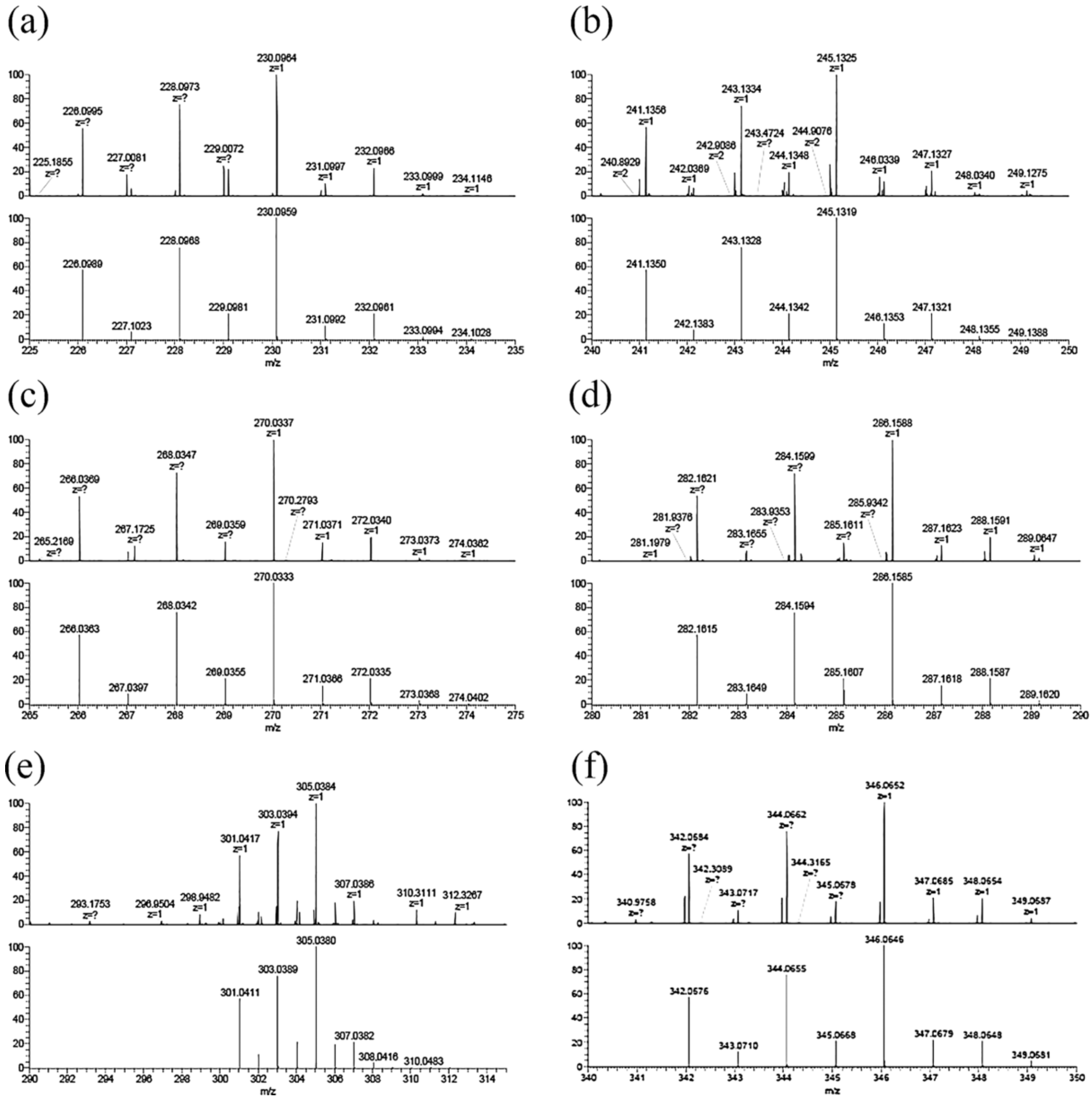


Figure 2. High resolution accurate mass mass spectra (HRAM-MS) of six components of the photolysis product mixture of *n*$Bu_3GeGePh_2Ge$*n*Bu_3 (**1**): *n*$Bu_2Ge(CH_3CN)H^+$ (**a**), *n*Bu_3Ge^+ (**b**), $Ph_2Ge(CH_3CN)H^+$ (**c**), *n*$Bu_3Ge(CH_3CN)H^+$ (**d**), Ph_3Ge^+ (**e**), $Ph_3Ge(CH_3CN)H^+$ (**f**).

the signal observed in the HRAM-MS of the photolysis product mixture of **1**. However, the most intense peak in the HRAM-MS of **3** was at *m/z* = 473.0180 that is assigned to the ion $Ph_3Ge_2(CH_3CN)(H_2O)_3H^+$. This ion is generated under the experimental MS conditions, and analysis of this ion by MS/MS shows that it fragments into Ph_3Ge^+ at *m/z* = 305.0374, as well as the daughter ions $Ph_2Ge(OH)^+$ at *m/z* = 245.0012 and Ph_2GeH^+ at *m/z* = 270.0239. Therefore, the ion observed at *m/z* = 305.0385 in the photolysis product mixture of **1** is most likely generated under the conditions of the mass spectrometer and is not due to the presence of a photoproduct. Rather, this ion is observed as a result of the presence of **3** in the photolysis product mixture.

The HRAM-MS of the other possible germylene trapping product *n*$Bu_2Ge(H)OAc$ (**4**) was also obtained and the two most intense signals for **4** were observed at *m/z* = 230.0968 and 393.1447. These correspond to the *n*$Bu_2Ge(CH_3CN)H^+$ and *n*$Bu_4Ge_2(H_2O)H^+$ ions, respectively. The signal at 230.0968 was also observed in the photolysis product mixture of **1**, but in this case it is likely that this species is generated from the fragmentation of the free and solvated *n*Bu_3Ge^+ that is present. The MS/MS of the *n*$Bu_3Ge(CH_3CN)_3{}^+$ ion generates free *n*Bu_3Ge^+ and also *n*$Bu_2Ge(CH_3CN)H^+$ even under the lowest energy MS/MS conditions. Given these observations and the fact that the pentet for the germanium-bound hydrogen in **4** was not observed in the photolysis product mixture of **1**, the germylene *n*Bu_2Ge**:** is not being photolytically produced from **1**.

Photolysis of the Digermane *n*$Bu_3GeGePh_3$ (2)

The photolysis of the digermane *n*$Bu_3GeGePh_3$ (**2**) was also investigated. A sample of **2** was irradiated in THF solution for 18 h in the presence of 10 equiv. AcOH. After workup of the reaction mixture in the same manner as for **1** the ^1H NMR spectrum

Table 2. HRAM-MS data for photolyzed *n*Bu$_3$GeGePh$_2$Ge*n*Bu$_3$ (**1**).

	Observed	Calculated	Δ_{mass} (ppm)	Assignment
1 (photolyzed with 10 equiv. AcOH)	230.0964	230.0959	2.173	*n*Bu$_2$Ge(CH$_3$CN)H$^+$
	286.1588	286.1585	1.048	*n*Bu$_3$Ge(CH$_3$CN)$^+$
	270.0337	270.0333	1.481	Ph$_2$Ge(CH$_3$CN)H$^+$
	305.0385	305.0380	1.639	Ph$_3$Ge$^+$
	346.0652	346.0646	1.733	Ph$_3$Ge(CH$_3$CN)$^+$
	565.1749	565.1741	1.415	*n*Bu$_3$GeOGe*n*Bu$_3$H$^+$
	731.2704	731.2861	21.47	**1**H$_3$O$^+$
1 (unphotolyzed)	368.2110	368.2116	1.629	*n*Bu$_3$Ge(CH$_3$CN)$_3{}^+$
	594.2128	594.2119	1.514	*n*Bu$_3$GeGePh$_2$(CH$_3$CN)$_3{}^+$
	999.4687	999.4536	15.11	**1**(CH$_3$CN)$_7{}^+$
Ph$_2$Ge(H)OAc (**3**)	229.0065	229.0067	0.8733	Ph$_2$GeH$^+$
	270.0329	270.0333	1.481	Ph$_2$Ge(CH$_3$CN)H$^+$
	473.0180	473.0261	17.12	Ph$_3$Ge$_2$(CH$_3$CN)(H$_2$O)$_3$H$^+$
*n*Bu$_2$Ge(H)OAc (**4**)	230.0968	230.0959	3.911	*n*Bu$_2$Ge(CH$_3$CN)H$^+$
	393.1447	393.1428	4.832	*n*Bu$_4$Ge$_2$(H$_2$O)H$^+$
*n*Bu$_3$GeOAc (**5**)	428.2320	428.2327	6.134	*n*Bu$_3$GeOAc(CH$_3$CN)$_3$H$^+$
	327.1342	327.1850	155.2	*n*Bu$_3$Ge(CH$_3$CN)$_2{}^+$
*n*Bu$_3$GeH (**6**)	286.1582	286.1585	1.048	*n*Bu$_3$Ge(CH$_3$CN)$^+$
	505.2684	505.2683	0.1979	*n*Bu$_3$GeOGe*n*Bu$_3$H$^+$

Table 3. EI-GC/MS data for photolyzed *n*Bu$_3$GeGePh$_3$ (**2**).

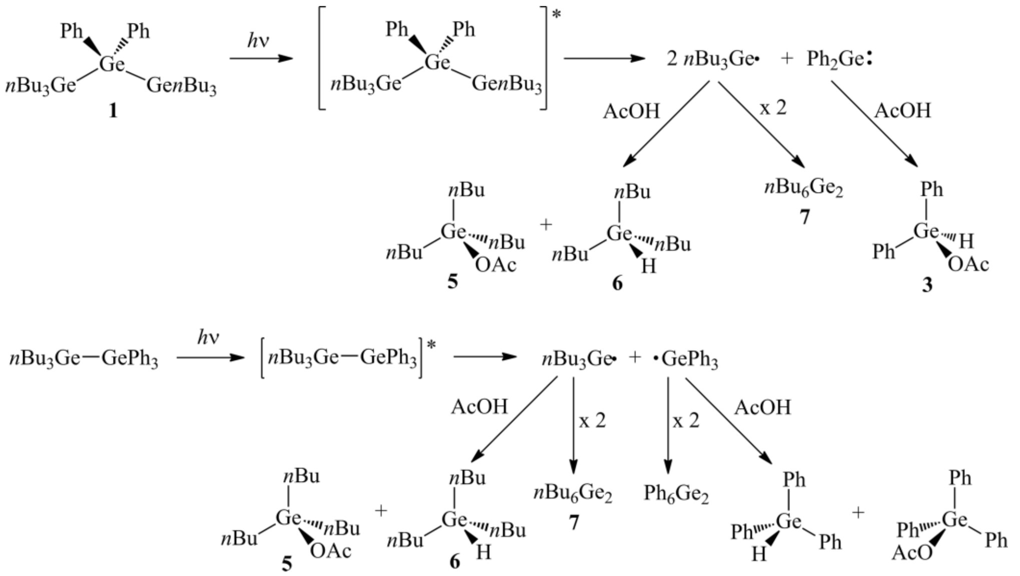
	Area %	*m/z*	Assignment
*n*Bu$_3$GeH (**6**) (t_r = 10.9 min)	70.1	189	*n*Bu$_2$GeH$^+$
		133	*n*BuGeH$_2{}^+$
		75	GeH$^+$
*n*Bu$_3$GeOGe*n*Bu$_3$ (t_r = 16.4 min)	11.3	223	*n*Bu$_2$GeO(H$_3$O)$^+$
		167	*n*BuHGeO(H$_3$O)$^+$
		131	*n*BuGe$^+$
*n*Bu$_3$GeOAc (**5**) (t_r = 23.7 min)	11.7	265	*n*Bu$_2$Ge(C$_2$H$_3$O$_2$)(H$_2$O)$^+$
		209	*n*BuGe(C$_2$H$_3$O$_2$)(H$_2$O)H$^+$
		153	Ge(C$_2$H$_3$O$_2$)(H$_2$O)H$_2{}^+$
*n*Bu$_3$GeGe*n*Bu$_3$ (**7**) (t_r = 29.9 min)	1.7	431	Ge$_2$*n*Bu$_5{}^+$
		375	Ge$_2$*n*Bu$_4$H$^+$
		319	Ge$_2$*n*Bu$_3$H$_2{}^+$
		263	Ge$_2$*n*Bu$_2$H$_3{}^+$
		207	Ge$_2$*n*BuH$_4{}^+$
Ph$_6$Ge$_2$ (t_r = 40.2 min)	0.9	305	Ph$_3$Ge$^+$
		228	Ph$_2$Ge$^+$
		151	PhGe$^+$
2 (t_r = 42.7 min)	0.5	379	Ph$_3$Ge$_2$H$_2{}^+$
		305	Ph$_3$Ge$^+$
		189	*n*Bu$_2$GeH$^+$
		151	PhGe$^+$
		133	*n*BuGeH$_2{}^+$
Trace components	3.8		

was recorded in [D$_6$]benzene. The aryl and alkyl regions of the spectrum were again complex, but diagnostic resonances were present at δ = 5.85 (s), 4.02 (sept, J = 3.0 Hz), 1.90 (s), and 1.81 ppm. These data indicate the presence of the four germanes Ph$_3$GeH, *n*Bu$_3$GeH (**6**), *n*Bu$_3$GeOAc (**5**), and Ph$_3$GeOAc, where the peak at δ = 1.81 ppm matches that of a commercial sample of Ph$_3$GeOAc.

The GC/MS of the photolysis product mixture of **2** indicated the presence of both *n*Bu$_3$GeH (**6**) and *n*Bu$_6$Ge$_2$ (**7**) that had identical retention times and mass spectra as found in the photolysis product mixture of **1** (Table 3). In addition, two other significant peaks with retention times of 13.4 and 23.6 min corresponding to *n*Bu$_3$GeOGe*n*Bu$_3$ and *n*Bu$_3$GeOAc (**5**) were observed that had identical mass spectra for these components present in the photolysis product mixture of **1**. However, the three most abundant components in the GC trace for **2** are **6**, *n*Bu$_3$GeOGe*n*Bu$_3$ and *n*Bu$_3$GeOAc (**5**).

The GC also contained six trace components with longer retention times, and we have identified two of these species. The component with t_r = 40.2 min contains the Ph$_3$Ge$^+$ ion (m/z = 305) and daughter ions resulting from the fragmentation of the phenyl groups. This species is due to the presence of Ph$_6$Ge$_2$ in the product mixture that is formed by the coupling of two Ph$_3$Ge$^\cdot$ radicals, which was confirmed by the analysis of a commercial sample of Ph$_6$Ge$_2$ that exhibited the same retention time and mass spectrum. The mass spectrum of the component with t_r = 42.7 min contained the Ph$_3$Ge$_2$H$_2{}^+$ ion (m/z = 379) and this is due to the presence of unreacted **2** in the product mixture, which was confirmed by analysis of a sample of pure **2**. The mass spectrum also contains signals for the *n*Bu$_2$GeH$^+$ and *n*BuGeH$_2{}^+$ ions.

The HRAM-MS of the photolysis product mixture of **2** contained signals at m/z = 305.0383 and 286.1588 for the Ph$_3$Ge$^+$ and *n*Bu$_3$Ge(CH$_3$CN)$^+$ ions, respectively. The latter ion results from the presence of **5**, **6**, **7**, and unreacted **2** in the product mixture, while the Ph$_3$Ge$^+$ ion is formed from Ph$_3$GeH, Ph$_6$Ge$_2$, and Ph$_3$GeOAc and unreacted **2**. A third significant signal at m/z = 452.9151 corresponds to the *n*BuPh$_3$Ge$_2$(H$_3$O)$^+$ ion that is



Scheme 3.

also attributable to the presence of unreacted **2** in the product mixture.

Conclusions

Based on the ^1H NMR and mass spectrometric data, the trigermane **1** decomposes by the homolytic scission of both Ge–Ge single bonds to generate two $nBu_3Ge^•$ radicals as well as the germylene Ph_2Ge**:** (Scheme 3). The tributylgermyl radicals are trapped by acetic acid to form the germane nBu_3GeH (**6**) as the major product as well as nBu_3GeOAc (**5**). The $nBu_3Ge^•$ radicals also combine to generate the digermane nBu_6Ge_2 (**7**), while diphenylgermylene is trapped by acetic acid to provide the germane $Ph_2Ge(H)OAc$ (**3**). No evidence was found for the generation of the germylene nBu_2Ge**:** that would be trapped by acetic acid to provide the germane $nBu_2Ge(H)OAc$ (**4**).

The digermane **2** also decomposes by homolytic scission of the Ge–Ge single bond to provide the radicals $nBu_3Ge^•$ and $Ph_3Ge^•$. In this case, both of these radical species react with acetic acid to provide the corresponding germanes **6** and Ph_3GeH as well as the acetate species **5** and Ph_3GeOAc. Two $nBu_3Ge^•$ radicals also combine to yield the digermane **7** and also two $Ph_3Ge^•$ radicals also combine to provide the digermane Ph_6Ge_2.

Experimental Section

General Considerations: All reagents were handled under an inert atmosphere of N_2 using standard Schlenk, syringe, and glovebox techniques unless otherwise specified. Solvents were dried using a Glass Contour solvent purification system. The compounds nBu_3GeNMe_2 and $nBu_3GeGePh_3$ (**2**) were prepared according to the literature procedures[43] and Ph_2GeH_2, nBu_2GeH_2, Ph_6Ge_2, nBu_3GeCl, and nBu_3GeH were purchased from Gelest, Inc. Glacial acetic acid was purchased from Aldrich and was used without further purification. ^1H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, using a Varian UNITY INOVA 400 spectrometer. Photolysis experiments were conducted using a Luzchem photolysis panel equipped with five UV-C lamps. GC/MS data were acquired using a Shimadzu QP2010 GC/MS and HRAM-MS data were collected using a Thermo Fisher Q Exactive™ Hybrid Quadruple-Orbitrap™ Mass Spectrometer. Elemental analyses were conducted by Galbraith Laboratories.

$nBu_3GeGePh_2GenBu_3$ (1): To a solution of nBu_3GeNMe_2 (1.385 g, 4.810 mmol) in acetonitrile (15 mL) was added a solution of Ph_2GeH_2 (0.500 g, 2.18 mmol) in acetonitrile (10 mL). The reaction mixture was sealed in a Schlenk tube fitted with a Teflon® stopper and was stirred under nitrogen for 48 h at 85 °C. The acetonitrile was removed in vacuo and the resulting oil was vacuum distilled in a Kugelrohr oven (125 °C, 0.10 Torr) to yield **1** (0.992 g, 64 %) as a colorless oil. ^1H NMR (C_6D_6, 23 °C): δ = 7.73 (d, J = 8.4 Hz, 6 H, *o*-H), 7.22 (m, 6 H, *m*-H), 7.14 (d, J = 7.8 Hz, 3 H, *p*-H), 1.49 (m, 6 H, $-CH_2CH_2CH_2CH_3$), 1.34 (q, J = 7.2 Hz, 6 H, $-CH_2CH_2CH_2CH_3$), 1.19 (m, 6 H, $-CH_2CH_2CH_2CH_3$), 0.90 (t, J = 7.2 Hz, 9 H, $-CH_2CH_2CH_2CH_3$) ppm. ^{13}C NMR (C_6D_6, 23 °C): δ = 140.7 (*ipso*-C), 136.1 (*o*-C), 128.3 (*p*-C), 128.1 (*m*-C), 28.8 ($-CH_2CH_2CH_2CH_3$), 27.1 ($-CH_2CH_2CH_2CH_3$), 15.0 ($-CH_2CH_2CH_2CH_3$), 13.9 ($-CH_2CH_2CH_2CH_3$) ppm. $C_{36}H_{64}Ge_3$ (714.67): calcd. C 60.47, H 9.03; found C 60.35, H 9.11.

$Ph_2Ge(H)OAc$ (3): A Schlenk flask covered with aluminum foil was charged with Ph_2GeHCl[47] (0.27 g, 1.0 mmol) in 5 mL on benzene. To this solution was added AgOAc (0.22 g, 1.3 mmol) in the dark as a suspension in 10 mL of benzene. The reaction mixture was stirred in the dark for 12 h and then was filtered through Celite. The solvent was evaporated from the filtrate in vacuo to yield **3** (0.25 g, 85 %) as a colorless oil. ^1H NMR (C_6D_6, 25 °C): δ = 7.65 (t, J = 7.9 Hz, 4 H, *o*-C_6H_5), 7.16–7.11 (m, 6 H, *m*-C_6H_5 and *p*-C_6H_5), 6.72 (s, 1 H, Ge-*H*), 1.86 [s, 3 H, $-OC(O)CH_3$] ppm. ^{13}C NMR (C_6D_6, 25 °C): δ = 173.3 [$-OC(O)CH_3$], 135.0 (*ipso*-C_6H_5), 134.6 (*o*-C_6H_5), 130.3 (*m*-C_6H_5), 128.3 (*p*-C_6H_5), 21.1 [$-OC(O)CH_3$] ppm. $C_{14}H_{14}GeO_2$ (286.85): calcd. C 58.61, H 4.92; found C 58.39, H 4.85.

$nBu_2Ge(H)OAc$ (4): A Schlenk flask was charged with nBu_2GeHCl[47] (0.40 g, 1.8 mmol) in 10 mL of benzene. The flask was wrapped with aluminum foil and AgOAc (0.36 g, 2.2 mmol) was added to the solution in the dark. The reaction mixture was stirred in the dark for 48 h and then was filtered though Celite. The solvent was removed in vacuo from the filtrate to yield **4** (0.38 g, 86 %) as a colorless oil. ^{1}H NMR (C$_6$D$_6$, 25 °C): δ = 5.71 (pent, J = 3.9 Hz, 1 H, Ge-H), 1.86 [s, 3 H, -OC(O)CH_3], 1.44–1.38 (m, 4 H, -CH$_2$CH_2CH$_2$CH$_3$), 1.24 (sext, J = 8.0 Hz, 4 H, -CH$_2$CH$_2$CH_2CH$_3$), 0.81 (t, J = 7.8 Hz, 4 H, -CH_2CH$_2$CH$_2$CH$_3$), 0.78 (t, J = 7.8 Hz, 6 H, -CH$_2$CH$_2$CH$_2$CH_3) ppm. ^{13}C NMR (C$_6$D$_6$, 25 °C): δ = 173.2 [-OC(O)CH$_3$], 26.5 [-OC(O)CH$_3$], 24.9 (-CH$_2$CH$_2$CH$_2$CH$_3$), 15.8 (-CH$_2$CH$_2$CH$_2$CH$_3$), 13.5 (-CH$_2$CH$_2$CH$_2$CH$_3$), 1.0 (-CH$_2$CH$_2$CH$_2$CH$_3$) ppm. $C_{10}H_{22}GeO_2$ (246.87): calcd. C 48.64, H 8.98; found C 48.55, H 8.87.

Bu$_3$GeOAc (5): A Schlenk flask covered with aluminum foil was charged with *n*Bu$_3$GeCl (0.40 g, 1.4 mmol) in 5 mL on benzene. To this solution was added AgOAc (0.29 g, 1.7 mmol) in the dark as a suspension in 10 mL of benzene. The reaction mixture was stirred in the dark for 12 h and then was filtered through Celite. The solvent was evaporated from the filtrate in vacuo to yield **6** (0.41 g, 94 %) as a colorless oil. ^{1}H NMR (C$_6$D$_6$, 25 °C): δ = 1.90 [s, 3 H, -OC(O)CH_3], 1.49–1.43 (m, 6 H, -CH$_2$CH_2CH$_2$CH$_3$), 1.30 (sext, J = 8.0 Hz, 6 H, -CH$_2$CH$_2$CH_2CH$_3$), 1.14 (t, J = 8.0 Hz, 6 H, -CH_2CH$_2$CH$_2$CH$_3$), 0.88 (t, J = 8.0 Hz, 9 H, -CH$_2$CH$_2$CH$_2$CH_3) ppm. ^{13}C NMR (C$_6$D$_6$, 25 °C): δ = 173.0 [-OC(O)CH$_3$], 26.1 [-OC(O)CH$_3$], 21.7 (-CH$_2$CH$_2$CH$_2$CH$_3$), 16.0 (-CH$_2$CH$_2$CH$_2$CH$_3$), 13.5 (-CH$_2$CH$_2$CH$_2$CH$_3$), 1.0 (-CH$_2$CH$_2$CH$_2$CH$_3$) ppm. $C_{14}H_{30}GeO_2$ (302.98): calcd. C 55.49, H 9.98; found C 55.31; H, 9.86.

Photolysis of *n*Bu$_3$GeGePh$_2$Ge*n*Bu$_3$ (1) in THF Solution: A 100 mL quartz reaction flask was charged with a solution of **1** (0.300 mg, 0.420 mmol) in THF (15 mL). Glacial acetic acid (0.75 mL, 0.79 g, 13.1 mmol) was added to the reaction mixture via syringe and the resulting solution was irradiated with UV-C light for 18 h under an atmosphere of nitrogen. The volatiles were removed in vacuo, the resulting colorless oil was dissolved in benzene (15 mL), and the solution was washed with water (2 × 10 mL) to remove excess acetic acid. The benzene layer was dried with anhydrous MgSO$_4$, filtered, and the solvent was removed in vacuo to yield a thick oil.

Photolysis of *n*Bu$_3$GeGePh$_2$Ge*n*Bu$_3$ (1) in C$_6$D$_{12}$ Solution: A quartz NMR tube was charged with **1** (0.035 g, 0.049 mmol) in [D$_{12}$]cyclohexane (0.5 mL) and glacial acetic acid (5.6 µL, 0.0059 g, 0.098 mmol) was added. The reaction mixture was irradiated with UV-C light for 1 min intervals and the ^{1}H NMR spectrum was recorded for the first ten minutes. Intervals of 2 min were then used until a total exposure time of 30 min was reached, after which time the sample was irradiated for 15 min intervals.

Photolysis of *n*Bu$_3$GeGePh$_3$ (2) in THF Solution: A 100 mL quartz reaction flask was charged with a solution of **2** (0.375 mg, 0.684 mmol) in THF (20 mL). Glacial acetic acid (0.59 mL, 0.615 g, 6.55 mmol) was added to the reaction mixture via syringe and the resulting solution was irradiated with UV-C light for 18 h under an atmosphere of nitrogen. The volatiles were removed in vacuo, the resulting colorless oil was dissolved in benzene (15 mL), and the solution was washed with water (2 × 10 mL) to remove excess acetic acid. The benzene layer was dried with anhydrous MgSO$_4$, filtered, and the solvent was removed in vacuo to yield a thick oil.

Supporting Information (see footnote on the first page of this article): ^{1}H NMR spectra for the photolysis of **1** and **2**, GC/EI-MS spectra for the photolysis product mixtures of **1** and **2**, and HRAM-MS spectra for compounds **1**–**6** and the photolysis product mixtures of **1** and **2**.

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Keywords: Germanium · Photochemistry · Mass spectrometry

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Oligogermanes

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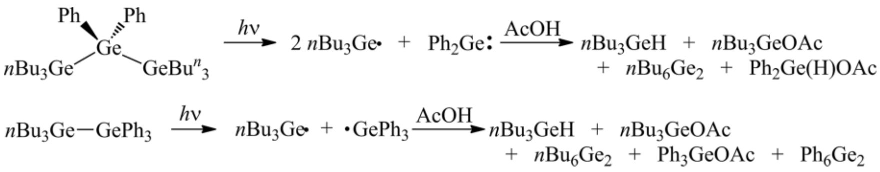
Photodecompostion of the Oligogermanes $n\mathrm{Bu}_3\mathrm{GeGePh}_2\mathrm{Ge}n\mathrm{Bu}_3$ and $n\mathrm{Bu}_3\mathrm{GeGePh}_3$: Identification of the Photoproducts by Spectroscopic and Spectrometric Methods



Photolysis of a trigermane and digermane results in homolytic scission of the germanium–germanium bonds in these molecules to yield germanium radicals and germylenes.

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