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Photochemistry of a Matrix-Isolated Geminal Diazide. Dimethylgermylene

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UV irradiation of matrix-isolated dimethyldiazidogermane [$Me_2Ge(N_3)_2$] permits identification of dimethylgermylene (Me_2Ge) by its IR and UV–visible spectra. IR of the annealed matrix shows peaks attributable to the known dimer $Me_2Ge{=}GeMe_2$. Chemical trapping experiments in room-temperature solutions are compatible with the possibility that here, too, free Me_2Ge is generated by the irradiation of $Me_2Ge(N_3)_2$.

Introduction

Divalent compounds of elements of group 14 have been the subject of considerable experimental and theoretical scrutiny.[2,3] Quite a few reports on the direct observation of organosilylenes have appeared since the initial observation of dimethylsilylene,[4] but spectroscopic data on simple organogermylenes remain rather limited. A few dialkylgermylenes and diarylgermylenes have been characterized by UV,[5-9] NMR,[10,11] and EXAFS[12] spectroscopy, but, to our knowledge, there is no precedent for IR observation. We report herein the IR and UV spectroscopic characterization of matrix-isolated dimethylgermylene, Me_2Ge (1), which has been frequently postulated as intermediate in thermal and photochemical processes.[13,14]

Results and Discussion

The geminal diazide $Me_2Ge(N_3)_2$ (2) was chosen as a photochemical precursor to 1. This selection was inspired by the known photochemical conversion of certain geminal diazides in the carbon and silicon series, which yield carbenes[15] and silylenes,[16,17] respectively.

Scheme I. Chemical Trapping Experiments

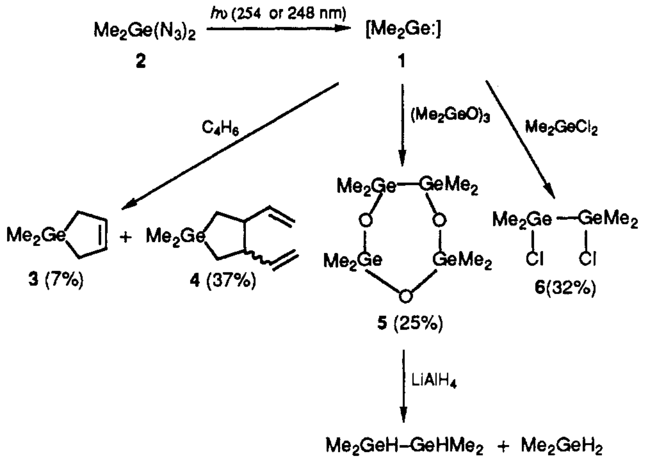

Table I. Dimethylgermylene (1) Vibrations

no.	freq, cm^{-1}	intensity (relative)	assignt
1	2987	w	C–H stretch
2	2974	s	C–H stretch
3	2957	s	C–H stretch
4	2897	w	C–H stretch
5	1234	m	CH_3 deformation
6	1217	w	CH_3 deformation
7	1205	m	CH_3 deformation
8	1195	w	CH_3 deformation
9	882	m	in-plane CH_3 rock
10	817	m	in-plane CH_3 rock
11	541	w	Ge–C stretch
12	527	vs	Ge–C stretch

Chemical Trapping Experiments. Preliminary experiments demonstrated that 1 might indeed be formed from 2. Thus 2 was irradiated at 254 or 248 nm in hydrocarbon solution at room temperature or glass at 77 K in the presence of excess germylene-trapping agents. Significant yields of the trapping adducts expected from 1 were isolated (Scheme I), suggesting but not proving the intermediacy of 1.

With 1,3-butadiene in benzene solution, we isolated a small yield of the formal 1:1 1,4-cycloadduct 3 and a fair yield of the mixed cis and trans germacyclopentanes 4

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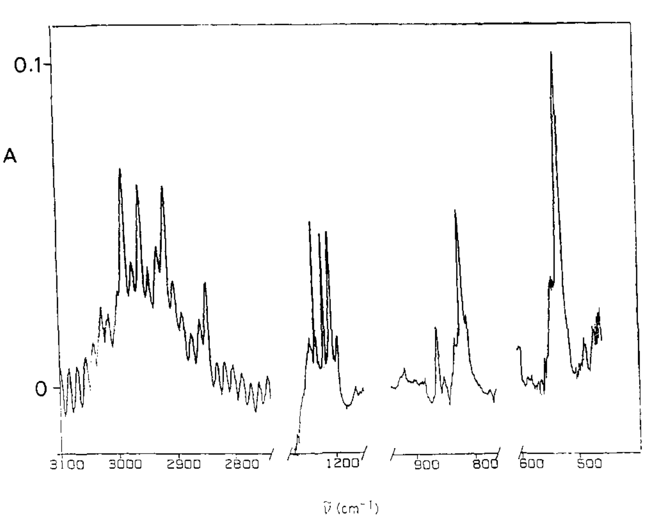

Figure 1. The IR spectrum of 1. The sinusoidal background in the high-frequency region is due to interference fringes.

expected from a 1,2-addition followed by insertion of a second molecule of butadiene into the germacyclopropane intermediate.[18]

Trapping with a $(Me_2GeO)_n$ mixture (n = 3, >75%; n = 4, 5, <25%) in cyclohexane solution yielded the product **5** expected from insertion into a Ge–O bond of hexamethylcyclotrigermoxane. This could not be separated from octamethylcyclotetragermoxane by distillation but was characterized by GC-MS and by reductive conversion to the known[19] 1,1,2,2-tetramethyldigermane.

Dichlorotetramethyldigermane[14] (**6**), expected from the insertion of **1** into a Ge–Cl bond, was isolated after the irradiation of **2** in a 3-methylpentane (3-MP) glass at 77 K in the presence of dichlorodimethylgermane. When **2** is irradiated in this glass, a yellow color develops. The UV–visible spectrum is similar to that described below for the argon matrix-isolation experiment.

Matrix Isolation. A highly dilute mixture of the vapor of the diazide **2** and argon obtained by leading argon over crystalline **2** held at −25 °C was deposited on a CsI window at 26 K. Because **2** is relatively polar, it tends to aggregate, and special care was necessary to prevent this, including use of ultrasound for vapor mixing.[20] The matrix was cooled to 12–18 K for irradiation and spectroscopy. The relatively high deposition temperature was chosen to optimize the optical quality of the matrix, permitting UV–visible and IR spectra to be measured reliably in the same matrix at various levels of photoconversion. This permitted us to establish that the UV–visible band and all of the IR peaks listed in Table I are due to the same photoproduct.

Upon irradiation at 254 nm, the IR and UV spectra of the diazide **2** diminish in intensity and a new set of peaks appears. The disappearance of **2** is most conveniently monitored by following the very strong NNN antisymmetric stretching bands that appear as a doublet at 2105 and 2126 cm^{-1}. These are gradually replaced by a singlet at 2113 cm^{-1}, presumably due to an intermediate monoazide. Finally, all absorption intensity in this region vanishes, indicating complete destruction of **2** and any intermediate azides. At this point, the matrix is yellow and shows a very broad absorption band centered near 405 nm as well as a series of IR bands (Figure 1, Table I).

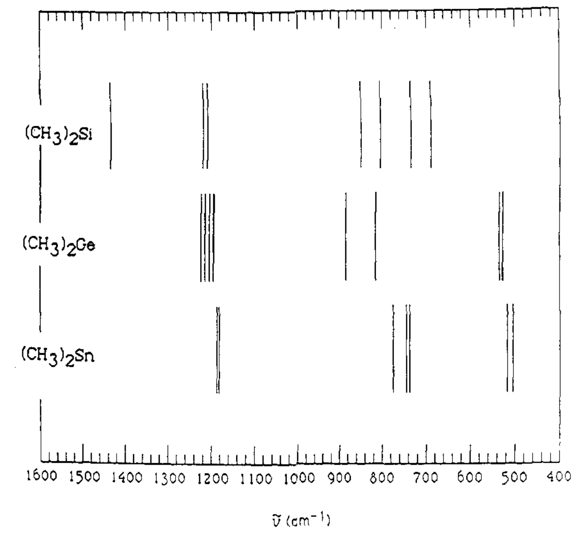

Figure 2. A comparison of the observed vibrational frequencies.

The UV–visible spectrum of this photoproduct corresponds closely to the UV spectra of dimethylgermylene obtained recently by irradiation of 7-germanorbornadienes[6] or bis(benzeneselenyl)dimethylgermane[9] at 77 K in 3-MP glass (λ_{max} = 420–430 nm). The difference in the positions of the maxima of these broad bands can be attributed to a different solvent environment (a value of λ_{max} = 370 nm has been reported[7] for room-temperature solution in heptane). The spectrum is quite similar to that of dimethylsilylene, which has a broad band peaking at 445 nm.[4,21,22] It agrees fairly well with the value of 560 nm predicted for the 0–0 transition by a pseudopotential ab initio calculation.[23]

In addition to the expected CH_3 vibrations, the IR spectrum shows clearly only the two skeletal modes expected for **1**, namely, the Ge–C stretches at 527 and 541 cm^{-1} (Figure 1, Table I), close to the values predicted by pseudopotential ab initio calculations,[23] 497 and 560 cm^{-1}. The observed IR frequencies of the photoproduct are intermediate between those of dimethylsilylene[21,22] and dimethylstannylene[24] (Figure 2). The relatively low frequency of the symmetric deformation vibrations of the methyl groups is similar to those observed for other members of this class of divalent compounds (Table I). Significantly, Ge–N stretching vibrations are absent.

The identity of the UV–visible spectrum with those obtained from other precursors, the chemical trapping experiments, and the similarity to the IR spectra of Me_2Si and Me_2Sn leave little if any doubt that the photoproduct is dimethylgermylene (**1**). Since the attribution of the observed methyl vibrations was quite clear, we saw no need to synthesize the CD_3 derivative.

The behavior of the photoproduct upon annealing provides additional evidence for the dimethylgermylene structure. No changes are observed up to 31 K, but between 32 and 36 K, the IR bands of the photoproduct gradually disappear and new bands appear, particularly at 828, 797, 793, 594, and 569 cm^{-1}, corresponding to the strongest IR frequencies observed for the expected self-trapping dimerization product, tetramethyldigermene.[25]

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The optical quality of the annealed matrix was not sufficient to record a reliable UV absorption spectrum.

Extended irradiation of matrix-isolated 1 with UV or visible light for up to 33 h induced no changes in the UV–visible and IR spectra. This contrasts with the behavior of dimethylsilylene, which undergoes a photorearrangement to 1-methylsilene,[4,21,22,26] and is in keeping with the expected significantly higher stability of the divalent over the isomeric π-bonded form of germanium compared with silicon.[27]

As described in the supplementary material, matrix-isolated $[(CH_3)_3Si]_2Ge(CH_3)_2$ was found to be photochemically inert. Even in room-temperature solution, it is not an efficient photochemical source of dimethylgermylene, in contrast to the diaryl analogues.[6,8]

Experimental Section

Chemical Trapping. The experiments were performed under an atmosphere of dry argon by using standard Schlenk and high-vacuum-line techniques. Solvents were dried by distillation from sodium and degassed prior to use. Irradiations were done with the aid of a quartz photochemical reactor with a low-pressure mercury lamp (254 nm) or with a Lambda Physik EMG 50 excimer laser (248 nm). The ^1H NMR spectra were recorded on a Varian EM 390 instrument. Mass spectra were measured on a Model 5995 Hewlett-Packard GC–MS instrument. In all cases the complex envelope of peaks obtained for monogermanes or polygermanes agreed with the isotopic distribution characteristic of germanium.[28]

Butadiene. **2**[29] (35 mg) and butadiene (6.5 mL) were dissolved in benzene (70 mL), and the resulting solution was irradiated at 248 nm in a quartz tube for 30 m. After concentration, ^1H NMR and GC–MS analyses of the remaining solution revealed the formation of the known compounds **3**[18,30] and **4**[18] in 7% and 37% yield, respectively. **3** was characterized by GC (coinjection with authentic sample), MS (70 eV, $M^+ = 158$), and ^1H NMR. **4** was characterized by MS (70 eV, $M^+ = 212$) and ^1H NMR [(CCl_4) δ 0.29 s (*cis*-GeMe), 0.31 s (*trans*-GeMe), 0.69–2.82 m (CH_2, CH), 4.56–5.12 m (=CH_2), 5.28–6.1 m (=CH_2)].

Hexamethyltrigermoxane. **2** (250 mg) and a mixture of $(Me_2GeO)_n$[31] (2.00 g, n = 3–5, n = 3 over 75%) were irradiated at 254 nm in cyclohexane (100 mL) in a quartz flask for 2.5 h. After evaporation of most of the solvent, GC–MS analysis of the remainder showed formation of a product whose structure was attributed to **5** (MS 445 [$M^+ - 15$]). This remainder dissolved in Et_2O (10 mL) was added dropwise to a suspension in Et_2O (100 mL) of $LiAlH_4$ (1.50 g) in a flask connected to a vacuum line via a −78 °C trap. The reaction mixture was then heated at 35 °C for 1.5 h. ^1H NMR analysis of the gases trapped at −78 °C showed the formation of the known Me_2GeH_2 (spectral properties consistent with those reported[32]). After hydrolysis (saturated aqueous NH_4Cl) and extraction, the organic phase was dried over Na_2SO_4 and concentrated under reduced pressure (130 mmHg). GC (coinjection with authentic sample) and ^1H NMR of the concentrate revealed the formation of the known $Me_2HGeGeHMe_2$ (spectral properties consistent with those reported[19]).

Dimethyldichlorogermane. A 3-methylpentane glass of **2** doped with dimethyldichlorogermane (300 mg of **2** and 1 mL of Me_2GeCl_2 in 15 mL of 3-MP) was irradiated at 77 K for 3.5 h. After warmup and removal of the solvent and Me_2GeCl_2 under reduced pressure (10 mmHg), ^1H NMR analysis revealed the formation of the known **6**[14] in 32% yield ($\delta_{Me} = 0.60$ ppm in C_6H_6; mp 49 °C).

Matrix Isolation. The matrices were prepared by using standard vacuum-line techniques and a Displex 202E cryostat (Air Products Co.). Complete destruction of the dimethyldiazidogermane and production of dimethylgermylene took 1–3 h of irradiation with unfiltered light of a low-pressure mercury lamp (Ultraviolet Products, Inc.) through a quartz window, depending on the thickness of the matrix. IR spectra were recorded on a Nicolet 6000 series FT-IR spectrometer with 1 cm^{-1} resolution (1000 scans). UV spectra were taken on a Cary 17-D UV spectrometer.

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Registry No. 1, 74963-95-4; 2, 20588-37-8; 3, 1731-10-8; 4, 122623-98-7; 5, 122623-99-8; 6, 22702-77-8; $(Me_2GeO)_3$, 16090-53-2; $Me_2GeHGeHMe_2$, 59409-81-3; Me_2GeH_2, 1449-64-5; Me_2GeCl_2, 1529-48-2; butadiene, 106-99-0.

Supplementary Material Available: Synthesis of 7 and ^1H NMR and MS data for 7 and 8 and MS data for 9 (3 pages). Ordering information is given on any current masthead page.

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