Photochemical Reactions of Aryltriethylgermanes and Diethyldiphenylgermane

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Aryltriethylgermanes and diethyldiphenylgermane were found to split easily to generate germyl radicals by irradiation with a medium-pressure mercury lamp in hexane or cyclohexane. The germyl free radicals produced reacted with hydrocarbon radicals generated from the solvent by hydrogen abstraction either by recombination or by disproportionation.

There have been only a few studies[1)] of the photochemical reaction of organogermanium compounds. We have investigated the photochemical behavior of several alkylarylgermanes and found that germanium-carbon bonds are cleaved readily by irradiation to generate germyl free radicals and the results will be described in this paper.

Results and Discussion

Photochemical reactions of three aryltriethylgermanes, Et_3GeAr (**1a**, Ar=Ph; **1b**, Ar=p-$CH_3C_6H_4$; **1c**, Ar=p-$NO_2C_6H_4$) and diethyldiphenylgermane Et_2GePh_2 (**1d**) were examined.

When a solution of **1a** (or **1b**) in hexane was irradiated under an argon atmosphere with a 450 W medium-pressure mercury lamp through a Vycor filter for 20—30 min, about 40% of the substrate was photolyzed. Hexyltriethylgermanes, Et_3GeR (**2a**, R=n-C_6H_{13}; **2b**, R=$CH(CH_3)C_4H_9$; **2c**, R=$CH(C_2H_5)$-$C_3H_7(n\text{-})$, hexaethyldigermane (**3**), benzene (or toluene in the case of **1b**) and dodecanes (**5**) were identified as products. Structure assignment was performed by GC-MS, IR, ^1H NMR, and ^{13}C NMR. The yields were estimated by GLC and HPLC. The results are summarized in Table 1.

$$\underset{\mathbf{1}}{Et_3GeAr} \xrightarrow[\text{hexane}]{250\,\text{nm}} \underset{\mathbf{2}}{Et_3GeR} + \underset{\mathbf{3}}{(Et_3Ge)_2} + \underset{\mathbf{4}}{ArH} + \underset{\mathbf{5}}{C_{12}H_{26}}$$

a: Ar=Ph
b: Ar=p-Tol

In the case of **1a**, some polymers were also formed. The relative yields of **2b** and **2c** could not be determined, since these two products have almost the same GLC retention time.

Formation of hexaethyldigermane (**3**), hexyltriethylgermanes (**2a—c**) and large amounts of benzene (or toluene) indicates that the aryl-germanium bond, not the alkyl-germanium bond, splits in the photolysis as is shown in the following reaction sequences.

$$Et_3GeAr \longrightarrow Et_3Ge\cdot + Ar\cdot$$
$$RH + Ar\cdot \longrightarrow R\cdot + ArH$$
$$Et_3Ge\cdot + R\cdot \longrightarrow Et_3GeR$$
$$2Et_3Ge\cdot \longrightarrow (Et_3Ge)_2$$

RH=hexane

In the first step, the aryl-Ge bond is cleaved. Since the germyl free radical is known[1,2)] to possess little ability to abstract hydrogen atom from alkanes, the aryl radical must play a major role to abstract a hydrogen atom from the solvent (hexane or cyclohexane). Hexyl radicals may recombine with a germyl radical to give triethylhexylgermanes or with other hexyl radicals to form a dodecane mixture. The germyl radical can also dimerize to hexaethyldigermane.

The ratio **2a**/(**2b**+**2c**) after statistical correction (10/18 with **1a**; 4/15 with **1b**) evaluates the relative reactivity for primary to secondary C-H toward hydrogen abstraction from a hexane by a phenyl radical. Relative selectivities of hydrogen abstraction from primary, secondary, and tertiary C-H by a phenyl radical generated thermally from phenylazotriphenylmethane was reported as 1 : 9.3 : 44 at 60 °C.[3)] Compared with the latter figures, the selectivities of the aryl radical from **1a** or **1b** are about 1/2 to 1/4.

The reason for the preferential cleavage of the aryl-Ge bond instead of the alkyl-Ge bond may be explained as follows. The UV absorption maximum of aryltriethylgermane (**1a**, **1b**) lies near the 257 nm region, which corresponds to a ^1L_a transition of the

Table 1. Photolysis of Aryltriethylgermanes

Ar	Irr. time min	Products (yield/%)[a)]					Recovered **1**/%
		2a	**2b 2c**	**3**	**4**	**5**	
Ph (**1a**)	20	5	6	13	78	Trace	49
p-$CH_3C_6H_4$ (**1b**)	30	12	30	57	97	Trace	65

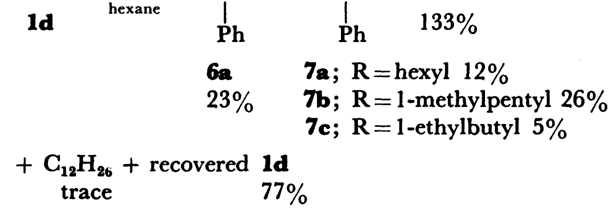
a) Yields were based on the starting materials consumed.

benzene pi orbital. Since in the present photochemical experiments, a medium pressure mercury lamp was used as the light source, 253.7 nm radiation with highest intensity is considered to excite the aryl pi electron of the arylgermanes, accompanied by a weakening of the aryl–Ge bond, thus subsequently resulting,in its splitting before the energy transfer to an ethyl–Ge bond occurred effectively.

The effects of the triplet sensitizer was examined using acetophenone. When **1b** was irradiated in hexane for 30 min in the presence of acetophenone (0.1 mol/mol of **1b**), the extent of the photolysis of **1b** was found to be about 7%, much lower than that in the absence of acetophenone. This finding suggests that the photolysis proceeds via a singlet excited state. The decrease of the extent of the photolysis may be attributed to the quenching effects of acetophenone.

The photochemical behavior of *p*-nitrophenyltriethylgermane (**1c**) was different from those of **1a** and **1b**. Irradiation of **1c** in cyclohexane for 15 min (or in benzene for 5 h) with a 450 W medium-pressure mercury lamp through a Vycor filter under an argon atmosphere resulted in the formation of a complex mixture. Small amounts of phenyltriethylgermane (**1a**) (3%), *p*-hydroxyphenyltriethylgermane (14%) and cyclohexanone (11%) were detected among the products. (the yields in parenthesis are conversion yields. 78% of **1c** was recovered). No cyclohexyltriethylgermane was detected. These findings suggest that the nitro group of **1c** suffers photolysis more readily than the carbon–germanium bond.

When diethyldiphenylgermane (**1d**) was irradiated in hexane for 30 min under argon with radiation of wavelength >250 nm, the main products were diethylphenylgermane (**6a**), diethylphenylgermylhexanes (**7a**—**c**), benzene, and dodecanes (**5**).



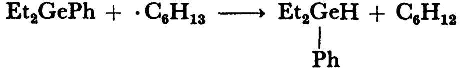
$$\underset{\mathbf{1d}}{Et_2GePh_2} \xrightarrow[\text{hexane}]{} \underset{\substack{|\\ Ph \\ \mathbf{6a} \\ 23\%}}{Et_2GeH} + \underset{\substack{|\\ Ph}}{Et_2GeR} + \underset{133\%}{PhH}$$

7a; R = hexyl 12%
7b; R = 1-methylpentyl 26%
7c; R = 1-ethylbutyl 5%

$+ \underset{\text{trace}}{C_{12}H_{26}}$ + recovered **1d** 77%

(yields are conversion yields)

The remarkable difference of the photochemical behavior of **1d** from those of **1a** or **1b** is the production of hydrogermane (**6a**) and no formation of digermane $(Et_2GePh)_2$. In order to confirm that the hydrogen atom of hydrogermane **6a** originated from the solvent hexane, **1d** was irradiated in cyclohexane-d_{12}. Formation of deuteriogermane, Et_2GePhD (**6b**) was confirmed by GC-MS. As mentioned before, the germyl free radical is believed to lack ability to abstract a hydrogen atom from alkanes.[1,2] The only known examples of hydrogen abstraction by a germyl radical are the cases of the reaction in toluene or 2-propanol as solvent.[2] Formation of **6a** may be explained by a disproportionation reaction between a diethylphenylgermyl radical and hexyl radicals (hexyl, 1-methylpentyl and 1-ethylbutyl radical), as shown in the following equation:

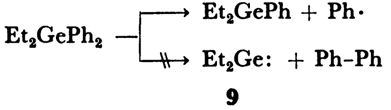


$$Et_2\dot{G}ePh + \cdot C_6H_{13} \longrightarrow \underset{\substack{|\\ Ph}}{Et_2GeH} + C_6H_{12}$$

6a

Formation of a saturated and an unsaturated compound by a disproportionation reaction between two free radicals is well known among aliphatic hydrocarbon radicals. To confirm the formation of hexenes required in the disproportionation, bromine was added to the solvent recovered by distillation. After being kept for a few h in the dark, the mixture was concentrated and the residue subjected to GC-MS analysis. Formation of 6% of a dibromohexane mixture (1,2-, 2,3-, and 3,4-) was observed, thus verifying the formation of hexenes in the photoreaction of diethyldiphenylgermane in hexane. When the photolysis of **1d** was carried out in cyclohexane, formation of hydrogermane **6a** (23%) and cyclohexene (10% as dibromocyclohexane) was detected. The absence of digermane among the products in the photolysis of **1d** may be attributed to the steric hindrance toward recombination of the diethylphenylgermyl radical.

The possibility of the photochemical generation of germylene (**9**) from **1d** was also examined. If two geminal phenyl groups of **1d** split off from germanium atom simultaneously, diethylgermylene and biphenyl would be formed. When **1d** was photolyzed in the presence of 2,3-dimethyl-1,3-butadiene, (which is known as a good scavenger for germylene,[4]) in cyclohexane as solvent, only a trace of 1,1-diethyl-3,4-dimethyl-3-germacyclopentene and 0.5—1.0% of biphenyl were detected by GC-MS. This finding indicates that the Ph–Ge bond splitting occurs stepwise in the photolysis of **1d**.



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In this reaction, no products which should arise from the addition of diethylphenylgermyl radical to diene were detected by GC-MS. The main products in this experiment were those from the recombination of a cyclohexyl radical and a germyl radical as in the absence of 2,3-dimethyl-1,3-butadiene.

Experimental

GLC and HPLC were performed on a Hitachi 163 Gas Chromatograph with SE-30 10% coated column (2 m) and a Hitachi 655 Liquid Chromatograph with Hitachi 638-

41 UV monitor. IR and UV spectra were recorded on a Hitachi 260-10 IR spectrophotometer and Hitachi 220 A UV spectrophotometer respectively. The proton NMR spectra were recorded at 60 MHz using a JNM-PMX-60 spectrometer with TMS as an internal standard in $CDCl_3$ or C_6D_6. Mass spectra were measured with a JMS-DX300 high resolution mass spectrometer.

Materials. *p*-Tolyltriethylgermane (**1b**),[5] *p*-nitrophenyltriethylgermane (**1c**),[6] diethyldiphenylgermane (**1d**)[7] and hexaethyldigermane (**3**)[8] were prepared according to the literature.

Phenyltriethylgermane (1a): Bromotriethylgermane (5.00 g; 20.9 mmol) in benzene (20 cm^3) was added to the phenylmagnesium bromide prepared from bromobenzene (4.00 g; 25.0 mmol) and magnesium (0.60 g ; 25.0 m gatom) in ether (30 cm^3). The mixture was refluxed for 3.5 h, then hydrolyzed with ice and dilute hydrochloric acid. After the usual work-up and purification by silica-gel column chromatography with hexane as an eluent and fractional distillation, **1a** was obtained in 94% yield. Bp 77—78 °C/1 mmHg (1 mmHg=133.322 Pa)(lit,[5] 117—118 °C/13.5 mmHg). UV; λ_{max}=257 nm, ε=230. ^{1}H NMR δ=0.97—1.03 (m, 15H), 7.34—7.37 (m, 5H). MS; *m/z* 238 (M$^+$).

Hexyltriethylgermane (2a): Bromotriethylgermane (2.00 g; 8.34 mmol) in tetrahydrofuran (50 cm^3) was added to hexylmagnesium bromide prepared from 1-bromohexane (2.75 g; 16.7 mmol) and magnesium (0.41 g; 16.7 m gatom) in THF (50 cm^3). The reaction mixture was refluxed for 17 h. After the usual work-up, the product was purified by silica-gel column chromatography and fractional distillation. Yield 97%. Bp 60 °C/0.7 mmHg (lit, [9] 117 °C/20 mmHg). ^{1}H NMR δ=0.45—1.53 (m, 28H). MS; *m/z* 246 (M$^+$).

1-Methylpentyltriethylgermane (2b): This compound was synthesized from bromotriethylgermane (4.00 g; 16.7 mmol) and 1-methylpentylmagnesium bromide, prepared from 2-bromohexane (5.15 g; 33.4 mmol), in a similar way as **2a**. Yield 43%. Bp 56—57 °C/0.5 mmHg. MS; *m/z* 246 (M$^+$): Exact MS; Found, 217.0995, Calcd for $C_{10}H_{23}Ge$ ($M^+-C_2H_5$) 217.1011. ^{1}H NMR; δ=0.40—1.67 (m, 28H).

1-Ethylbutyltriethylgermane (2c) was synthesized from bromotriethylgermane and 3-bromohexane in a similar way as **2b**. Yield 59%. Bp 62—64 °C/1.05 mmHg. MS; *m/z* 246 (M$^+$): Exact MS; Found, 217.1004, Calcd for $C_{10}H_{23}Ge$ ($M^+-C_2H_5$) 217.1011. ^{1}H NMR; δ=0.43—1.67 (m, 28H).

Bromodiethylphenylgermane (8): Bromine (5.61 g; 35.1 mmol) in 1,2-dibromoethane (10 cm^3) was added to diethyldiphenylgermane (10.0 g; 35.1 mmol) in 1,2-dibromoethane (100 cm^3) at 80—85 °C. The mixture was refluxed for 2 h, then the solvent was distilled off under reduced pressure. The residue was purified by fractional distillation. Yield 80%. Bp 110—112 °C/4 mmHg (lit,[10] 141 °C/18 mmHg). MS; *m/z* 288 (M$^+$). ^{1}H NMR; δ=0.85—1.90 (m, 10H), 7.17—7.70 (m, 5H).

Diethylphenylgermane (6a): **8** (2.00 g; 6.95 mmol) in dry ether (10 cm^3) was slowly added to lithium aluminum hydride (0.26 g; 6.95 mmol) in ether (20 cm^3) with stirring and refluxing. The reaction mixture was refluxed for 2 h. The reaction was quenched by slow addition of water with cooling and followed by 3 M sulfuric acid. The organic layer was separated within 10 min and dried over sodium sulfate. After expelling the solvent, the residue was purified by fractional distillation. Yield 83%. Bp 100—102 °C/21 mmHg. MS; *m/z* 210 (M$^+$). ^{1}H NMR; δ=0.75—1.28 (m, 10H), 4.40—4.63 (m, 1H), 7.03—7.60 (m, 5H). IR (neat); 2007 cm^{-1} (ν_{Ge-H}). Exact MS; *m/z* Found, 210.0548, Calcd for $C_{10}H_{16}{}^{74}Ge$ 210.0462.

1-(Diethylphenylgermyl)hexane (7a): **8** (3.01 g; 10.5 mmol) in THF (50 cm^3) was added to hexylmagnesium bromide prepared from 1-bromohexane (3.44 g; 20.9 mmol) and magnesium (0.51 g; 20.9 m gatom) in THF (100 cm^3). The reaction mixture was refluxed for one night and hydrolyzed with ice and water. The THF layer was separated and the aqueous layer extracted with ether. After the solvent was evaporated, the residue was purified by silica-gel column chromatography and fractional distillation. Yield 48%. Bp 100 °C/0.6 mmHg. MS; *m/z* 265 ($M^+-C_2H_5$): Exact MS; Found, 265.1043, Calcd for $C_{14}H_{23}Ge$ ($M^+-C_2H_5$) 265.1011. ^{1}H NMR; δ=0.63—1.70 (m, 23H), 7.07—7.57 (m, 5H).

2-(Diethylphenylgermyl)hexane (7b): This compound was synthesized from **8** (2.94 g; 10.2 mmol) and 1-methylpentylmagnesium bromide prepared from 2-bromohexane (3.44 g; 20.9 mmol) in a similar way to **7a**. Yield 45%. Bp 95—96 °C/0.55 mmHg. MS; *m/z* 294 (M$^+$): Exact MS; Found, 265.0978, Calcd for $C_{14}H_{23}Ge$ ($M^+-C_2H_5$) 265.1011. ^{1}H NMR δ=0.67—1.63 (m, 23H), 7.07—7.55 (m, 5H).

3-(Diethylphenylgermyl)hexane (7c) was prepared from **8** (1.60 g; 5.56 mmol) and 1-ethylbutylmagnesium bromide in a similar way to **7a**. Yield 43%. Bp 101 °C/0.85 mmHg. MS; *m/z* 294 (M$^+$): Exact MS; Found, 265.0964, Calcd for $C_{14}H_{23}Ge$ ($M^+-C_2H_5$), 265.1011. ^{1}H NMR; δ=0.60—1.77 (m, 23H), 7.07—7.57 (m, 5H).

Photolysis: A typical example of the photolysis is described in the case of **1a**. A solution containing 210.7 mg (0.89 mmol) of **1a** in 230 cm^3 hexane was irradiated under an argon atmosphere with a 450 W medium-pressure mercury lamp (Hanovia) through a Vycor filter for 20 min. After the removal of the solvent by distillation, the products were analyzed by GC-MS. Products **2**, **3**, and **5** were identified by comparison of their GLC retention time and mass fragment pattern with those of authentic samples.

Photolysis of 1d in cyclohexane-*d*$_{12}$: A solution containing 4.14 mg of **1d** in 0.7 cm^3 of cyclohexane-d_{12} was externally irradiated with a 450 W medium-pressure mercury lamp through a Vycor filter for 30 min. The photolysate was analyzed by GC-MS. Although a parent peak of deuterated germane (**6b**) was not observed, its fragment peaks, *m/z* 182 (**6b**$-C_2H_5$) and 153 (**6b**$-2C_2H_5$) (base peak) were observed with high intensity.

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