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Photochemical Addition of Benzyltriethylgermane and Dibenzyldiethylgermane to Olefins

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A novel photochemical addition of a germyl radical to the olefinic double bond was discovered when benzyltriethylgermane or dibenzyldiethylgermane was irradiated with a medium-pressure mercury lamp in the presence of olefins.

There have been only scattered reports on the photochemical behavior of organogermanium compounds.[1] We have reported previously that the photolysis of aryltrialkylgermanes and diaryldialkyl-germanes generated germyl and aryl free radicals.[2] In order to widen the scope of this photochemical reaction, the photolysis of benzyltrialkylgermane and dibenzyldialkylgermane were investigated. Contrary to the arylalkylgermanes, which show no tendency to add to the olefinic double bond but to abstract a hydrogen atom from solvent hydrocarbon upon irradiation, the photolysis of benzylsubstituted germanes in the presence of olefins were found to readily form 1,2-adducts. Even in the absence of olefins, the photolysis of the Ge–benzyl bond of these benzylgermanes proceeded rapidly. The high photoreactivity of alkylbenzylgermanes makes a good contrast to the very low rate of conversion of analogous trimethylbenzylsilanes that have recently been reported.[3]

Results and Discussion

Photolysis of Benzyltriethylgermane and Diethyldibenzylgermane. The photolysis of benzyltriethylgermane (**1**) in hexane with a medium-pressure mercury lamp through a Vycor filter for 10 min resulted in the facile decomposition of **1** to give hexaethyldigermane (**2**)[5] and bibenzyl (**3**) as shown below:

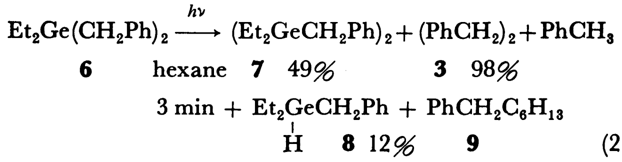
$$\begin{array}{ccccccc} \mathrm{Et_3GeCH_2Ph} & \xrightarrow{h\nu} & (\mathrm{Et_3Ge})_2 & + & (\mathrm{PhCH_2})_2 & + & \mathbf{1} \\ \mathbf{1} & \text{10min} & \mathbf{2} & & \mathbf{3} & & \text{(recovered)} \\ & \text{hexane} & 75\% & & 86\% & & 9\% \end{array}$$

The formation of the above two products can be explained by assuming the photochemical dissociation of the benzyl–germanium bond (Eq. 1) and a subsequent dimerization of triethylgermyl and benzyl radicals. Both the germyl radical (**4**) and the benzyl radical are known to be relatively inactive and to possess little ability to abstract hydrogen atoms from saturated aliphatic hydrocarbons such as hexane.[1]

$$\mathrm{Et_3GeCH_2Ph} \xrightarrow{h\nu} \underset{\mathbf{4}}{\mathrm{Et_3Ge\cdot}} + \mathrm{PhCH_2\cdot} \qquad (1)$$

When **1** was irradiated in benzene under similar conditions, a small amount of triethyl-*p*-tolylgermane (**5**) was detected among the products in addition to bibenzyl and digermane (**2**). The formation of **5** suggests an intramolecular rearrangement of the triethylgermyl group from the benzyl carbon to the benzene ring by recombination in a solvent cage of the benzyl radical and the triethylgermyl radical pair once generated by the homolysis of Ge–benzyl bond. A similar rearrangement was observed in the photolysis of trimethylbenzylsilane.[3] An intramolecular photorearrangement of the germyl group has also been observed in cinnamylgermanes.[4]

When dibenzyldiethylgermane (**6**) was irradiated in hexane under similar conditions for 3 min, about 40% of **6** was photolyzed to form bibenzyl (**3**) and 1,2-dibenzyl-1,1,2,2-tetraethyldigermane (**7**) as major products. However, in this case, small amounts of germane (**8**), toluene and heptylbenzene (**9**) were also detected.



$$\begin{array}{lllll} \mathrm{Et_2Ge(CH_2Ph)_2} \xrightarrow{h\nu} & (\mathrm{Et_2GeCH_2Ph})_2 + & (\mathrm{PhCH_2})_2 + \mathrm{PhCH_3} & & \\ \quad \mathbf{6} \quad\quad \text{hexane} & \mathbf{7} \;\; 49\% & \mathbf{3} \;\; 98\% & & \\ \quad\quad\quad\quad \text{3 min} + & \underset{\displaystyle \mathrm{H}}{\mathrm{Et_2GeCH_2Ph}} + & \mathrm{PhCH_2C_6H_{13}} & & \\ & \quad\; \mathbf{8} \;\; 12\% & \quad \mathbf{9} & & (2) \end{array}$$

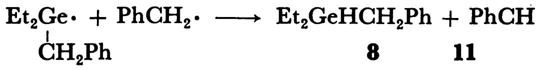
The formation of bibenzyl and digermane (**7**) suggests the splitting of the Ge–benzyl bond under irradiation to give a diethylbenzylgermyl radical (**10**) and a benzyl radical, and a subsequent dimerization of each radical.

$$\mathbf{6} \longrightarrow \underset{\mathbf{10}}{\mathrm{Et_2\dot{G}eCH_2Ph}} + \mathrm{PhCH_2\cdot} \qquad (3)$$

$$\mathbf{10} + \mathbf{10} \longrightarrow (\mathrm{Et_2GeCH_2Ph})_2 \qquad (4)$$

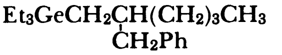
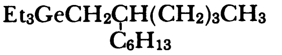
$$2\,\mathrm{PhCH_2\cdot} \longrightarrow (\mathrm{PhCH_2})_2 \qquad (5)$$

Since neither the germyl radical nor the benzyl radical can abstract hydrogen atom from a saturated hydrocarbon (as stated before), it is unreasonable to explain the formation of germane (**8**), toluene and **9** by the simple hydrogen abstraction of a germyl radical from hexane and a subsequent recombination of the hexyl and benzyl radicals. The formation of these products can be tentatively explained by the following reaction sequence:



$$\underset{\displaystyle \mathrm{CH_2Ph}}{\mathrm{Et_2Ge\cdot}} + \mathrm{PhCH_2\cdot} \longrightarrow \underset{\mathbf{8}}{\mathrm{Et_2GeHCH_2Ph}} + \underset{\mathbf{11}}{\mathrm{PhC\dot{H}:}} \qquad (6)$$

Table 1. Photochemical Addition of **1** to 1-Hexene

Product		Yield/%[a]
 $Et_3GeCH_2\underset{\displaystyle CH_2Ph}{\underset{\mid}{C}}H(CH_2)_3CH_3$	(**12**)	50
$Et_3Ge(CH_2)_5CH_3$	(**13**)	35
$Et_3GeCH{=}CH(CH_2)_3CH_3$	(**14**)	
$Et_3GeCH_2CH{=}CH(CH_2)_2CH_3$	(**15**)	
 $Et_3GeCH_2\underset{\displaystyle C_6H_{13}}{\underset{\mid}{C}}H(CH_2)_3CH_3$	(**17**)	15
$(PhCH_2)_2$	(**3**)	35

a) Yields were determined by GLC.

and

$$PhCH: + C_6H_{14} \longrightarrow \underset{\mathbf{9}}{PhCH_2C_6H_{13}} \quad (7)$$

By a metathesis between **10** and benzyl radical or by a direct alpha elimination from **6**, phenylcarbene (**11**) which undergoes insertion into the C–H bond of the solvent (hexane) to give heptylbenzene (**9**).

Photolysis in the Presence of Olefins. When benzyltriethylgermane **1** was irradiated with a medium-pressure mercury lamp in the presence of 1-hexene for 1.5 h, **1** was completely consumed to give the following products (yields are shown in Table 1):

$$Et_3GeCH_2Ph + CH_3(CH_2)_3CH{=}CH_2 \xrightarrow{h\nu}$$

$$\underset{\mathbf{12}}{CH_3(CH_2)_3CH(CH_2Ph)CH_2GeEt_3} + \underset{\mathbf{13}}{CH_3(CH_2)_5GeEt_3} +$$

$$\underset{\mathbf{14}}{CH_3(CH_2)_3CH{=}CHGeEt_3} + \underset{\mathbf{15}}{CH_3(CH_2)_2CH{=}CHCH_2GeEt_3}$$

$$+ \mathbf{3} + C_{12}H_{26} \quad (8)$$

This reaction can also be understood by assuming a splitting of the Ge–benzyl bond to give a triethylgermyl radical (**4**) and a benzyl radical (Eq. 1). **4** would add (Eq. 9) to 1-hexene to give a 1-(triethylgermylmethyl)-pentyl radical (**16**), which may recombine (Eq. 10) with a benzyl radical to form 1,2-adduct (**12**) or may disproportionate[2,5] (Eq. 11) to give 1-triethylgermylhexane (**13**) and 1-triethylgermyl-1-hexene (**14**) or 1-triethyl-germyl-2-hexene (**15**), accompanying the dimerization of excess benzyl radicals to bibenzyl.

$$\underset{\mathbf{4}}{Et_3Ge\cdot} + C_4H_9CH{=}CH_2 \longrightarrow \underset{\mathbf{16}}{Et_3GeCH_2\dot{C}HC_4H_9} \quad (9)$$

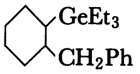
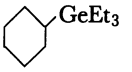
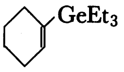
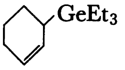
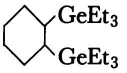
$$\mathbf{16} + PhCH_2\cdot \longrightarrow \mathbf{12} \quad (10)$$

$$\mathbf{16} + \mathbf{16} \longrightarrow \mathbf{13} + \mathbf{14} + \mathbf{15} \quad (11)$$

The formation of adduct **12** indicates the attack of a germyl radical to a terminal carbon atom of the olefinic double bond during the first step of the addition (Eq. 9), thus showing the higher addition ability of a germyl radical than that of a benzyl radical.

When **1** was photolyzed in the presence of cyclohexene under similar conditions for 1 h, the starting germane **1** was completely consumed. Products are summarized in Table 2.

Table 2. Photochemical Addition of **1** to Cyclohexene

Product		Yield/%[a]
	(**19**)	35 (cis: trans=1:4.4)
	(**20**)	22
	(**21**)	
	(**22**)	
	(**23**)	21 (cis and trans)
$(Et_3Ge)_2$	(**2**)	21
$(PhCH_2)_2$	(**3**)	45

a) Yields were determined by GLC.

The first step in this reaction was the cleavage of the Ge–benzyl bond (Eq. 1). The triethylgermyl radical (**4**) added to cyclohexene to form a 2-(triethylgermyl)cyclohexyl radical (**18**), which reacted either by recombination with a benzyl radical resulting in the formation of the 1,2-adduct (**19**), or by disproportionation to give triethylgermylcyclohexane (**20**), 1-(triethylgermyl)cyclohexene (**21**) and 3-(triethylgermyl)cyclohexene (**22**). Part of the triethylgermyl radical combined with **18** to form 1,2-bis(triethylgermy)cyclohexane (**23**) or dimerized to hexaethyldigermane (**2**).[5] About half of the benzyl radical dimerized to bibenzyl. The formation of digermane **2** and 1,2-digermyl compound **23** suggest that the triethylgermyl radical is rather stable and can diffuse out of the solvent cage to seek combinations with other free radicals.

1,2-Adduct **19** is a mixture of cis and trans isomers. The ratio of cis:trans is 1:4.4, indicating that the addition is mainly trans, but not strictly stereospecific. The formation of both cis and trans isomers indicates that addition is not concerted but proceeds by a two-step mechanism.

In order to survey the effects of substituents, the photolysis of **1** in the presence of di-, tri-, and tetra-substituted olefins were also investigated.

Products of the photolysis of **1** in the presence of 2-hexene are shown in Table 3. Starting germane **1** was completely consumed in 1.5 h. Three types of 1,2-adducts (**24A**, **24B**, **24C**) were detected with GLC and GC-Mass but could not be separated from each other. Most probably, they are the 2- and 3-germyl isomers and their threo–erythro isomers.

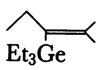
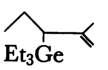
Results of the photolysis of **1** in 2-methyl-2-pentene

Table 3. Photochemical Addition of **1** to 2-Hexene

Product[a]	Yield/%[b]
1,2-Adducts of **1** with 2-hexene (**24A**, **24B**, **24C**)	22
$(Et_3Ge)_2$ (**2**)	Trace
$(PhCH_2)_2$ (**3**)	40
$(Et_3Ge)_2O$	21

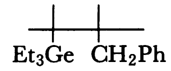
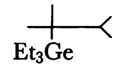
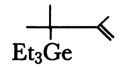
a) Germylhexanes, germylhexenes (total yield 21%), and germyldodecane (3%) were also detected by GC-MS.
b) Yields were determined by GLC.

Table 4. Photochemical Addition of **1** to 2-Methyl-2-pentene

Product		Yield/%[a]
	(**25**)	5
	(**27**)	22
	(**28**)	
	(**29**)	
$(Et_3Ge)_2$	(**2**)	Trace
$(Et_3Ge)_2O$		17
$(PhCH_2)_2$	(**3**)	40

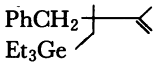
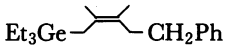
a) Yields were determined by GLC.

Table 5. Photochemical Addition of **1** to 2,3-Dimethyl-2-butene

Product		Yield/%[a]
	(**30**)	3
	(**31**)	7
	(**32**)	
$(Et_3Ge)_2$	(**2**)	45
$(Et_3Ge)_2O$		4
$(PhCH_2)_2$	(**3**)	71

a) Yields were determined by GLC.

Table 6. Photochemical Addition of **1** to 2,3-Dimethyl-1,3-butadiene

Product		Yield/%[a]
	(**34**)	22
	(**35**)	29
$(PhCH_2)_2$	(**3**)	17

a) Yields were determined by GLC based on the consumed **1**. 5% of **1** was recovered.

are summarized in Table 4. The structure of 1,2-adduct **25** indicates that the attack of triethylgermyl radical (**4**) occurred at a less-hindered olefinic carbon to give a more stable tertiary carbon radical **26**. The low yield of the 1,2-adduct **25** suggests a steric inhibition toward the recombination between **26** and the benzyl radical. A larger part of radical **26** disproportionated to afford germylhexane (**27**) and germylhexenes (**28** and **29**).

In the case of the photolysis of **1** in the presence of 2,3-dimethyl-2-butene, the yield of 1,2-adduct, 2-benzyl-2,3-dimethyl-3-(triethylgermyl)butane (**30**) was only 3%. The major products were hexaethyldigermane (**2**) and bibenzyl. Small amounts of 2,3-dimethyl-2-(triethylgermyl)butane (**31**) and 2,3-dimethyl-3-(triethylgermyl)-1-butene (**32**) were also detected. The formation of these germylbutane and germylbutene derivatives can be explained by a disproportionation of the adduct radical **33**.

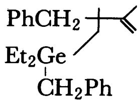
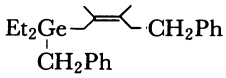
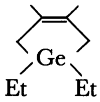
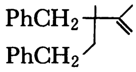
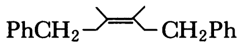
In the reaction of **1** with a series of the substituted olefins, the yields of the 1,2-adduct greatly decreased with an increase in the number of the substituents on the olefinic carbon; this indicates the important role played by steric hindrance.

Photolysis in the Presence of 1,3-Dienes. The reaction of benzylgermane **1** with 1,3-diene is also interesting. When **1** was photolyzed in the presence of 2,3-dimethyl-1,3-butadiene, 1,2-adduct (**34**) and 1,4-adduct (**35**), both having triethylgermyl group on terminal carbon atom, were obtained in a 2:3 molar ratio (see Table 6). The orientation of the germyl group in the adducts again indicated a more preferential addition of the germyl free radical to diene than benzyl radical to.

Photochemical Reaction of Diethyldibenzylgermane with 1,3-Dienes. When diethyldibenzylgermane **6** was irradiated in the presence of 2,3-dimethyl-1,3-butadiene for 2 h under similar conditions as in the case of **1**, the major products were 1,2-adduct (**36**) and 1,4-adduct (**37**) in almost the same molar ratio (Table 7). However, in this reaction (although in low yield), the formation of 1,1-diethyl-3,4-dimethylgerma-3-cyclopentene (**38**)[7] was confirmed by GC-MS. The formation of **38** clearly indicated the generation of diethylgermylene (**39**) by the photolysis of **6**. Dimethylgermylene, thermally generated from 7-dimethylgerma-2,5-norbornadiene, is known to add to styrenes or dienes to give germacyclohexane or germacyclopentene derivatives respectively.[8]

The formation of 1,2- and 1,4-dibenzyl adducts (**40** and **41**) shows that benzyl radical can add to 1,3-diene, which was not observed in the reaction with simple olefins.

Table 7. Photochemical Addition of **6** to 2,3-Dimethyl-1,3-butadiene

Product		Yield/%[a)]
	(**36**)	29
	(**37**)	30
	(**38**)	2
	(**40**)	11
	(**41**)	
$(PhCH_2)_2$	(**3**)	17

a) Yields were determined by GLC based on the consumed **6**. 3% of **6** was recovered.

Experimental

IR and UV spectra were recorded on a Hitachi 260-10 IR spectrometer and Hitachi 220A UV spectrometer, respectively. The proton and ^{13}C NMR spectra were recorded with TMS as an internal standard in $CDCl_3$ or benzene-d_6 at 60 MHz by JNM-PMX-60 and Jeol FX-60, respectively. Mass spectra were measured with a Jeol-DX300 high-resolution mass spectrometer with a JMA-5000 Mass Data System. 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 a Hitachi 638-41 UV monitor.

Materials. Benzyltriethylgermane (1): Bromotriethylgermane (5.00 g; 20.9 mmol) in ether (50 cm^3) was added to benzylmagnesium bromide prepared from 5.35 g (31.3 mmol) of benzyl bromide and magnesium (0.76 g; 31.3 mg atm) in ether (100 cm^3). The reaction mixture was refluxed for one night, then hydrolyzed with ice and dilute hydrochloric acid. After the usual work-up and purification by silica-gel column chromatography with hexane as an eluant and fractional distillation, **1** was obtained in 97% yield. Bp 71—73 °C/0.45 mmHg (1 mmHg=133.322 Pa). UV; 270 nm (ε 420). ^{1}H NMR ($CDCl_3$) δ=0.43—1.43 (m, 15H), 2.17 (s, 2H), 6.76—7.33 (m, 5H). ^{13}C NMR ($CDCl_3$) δ=3.9, 8.8, 21.1, 123.6, 127.7, 128.1, 141.7. MS m/z 252 (M$^+$). Exact MS; Found: m/z 252.0872. Calcd for $C_{13}H_{22}{}^{74}Ge$: 252.0933.

Dibenzyldiethylgermane (6): Dibromodiethylgermane[9)] (11.03 g; 0.038 mol) in ether (30 cm^3) was added to benzylmagnesium bromide prepared from benzyl bromide (19.5 g; 0.114 mol) and magnesium (2.77 g; 0.114 g atom) in ether (90 cm^3). The reaction mixture was refluxed for one night and hydrolyzed with ice water. The product was purified by silica-gel column chromatography with hexane–ether (50:1 mixture) as an eluant and fractional distillation. Yield 96%. Bp 120—122 °C/0.12 mmHg. ^{1}H NMR ($CDCl_3$) δ=0.37—1.40 (m, 10H), 2.19 (s, 4H), 6.76—7.47 (m, 10H). ^{13}C NMR ($CDCl_3$) δ=4.2, 8.6, 21.2, 123.8, 127.9, 128.2, 141.0. MS m/z 314 (M$^+$). Exact MS; Found: m/z 314.1032. Calcd for $C_{18}H_{24}{}^{74}Ge$: 314.1089. UV; 267 nm (ε 840).

Photolysis. A solution of 0.93 mmol of **6** in 230 cm^3 of hexane was irradiated with a medium-pressure mercury lamp through a Vycor filter for 3 min under an argon atmosphere. The products were separated by preparative GLC and identified by GC-Mass, ^{1}H NMR, ^{13}C NMR and IR spectroscopy. Yields were determined by GLC.

Photochemical Addition. General procedure is shown in the case of benzyltriethylgermane in the presence of 1-hexene.

A solution of 2.4 mmol of **1** and 14.3 mmol of 1-hexene in 140 cm^3 of hexane was irradiated with a medium-pressure mercury lamp through a Vycor filter for 1.5 h under an argon atmosphere. The starting material was completely disappeared at this point. Products were isolated by GPC, preparative GLC and silica-gel column chromatography, and identified by ^{1}H NMR, ^{13}C NMR, IR, and GC-MS. Yields were determined by GLC using nonane, dodecane or tetradecane as an internal standard.

Physical Properties of the Product. 1,2-Dibenzyl-1,1,2,2-tetraethyldigermane (7): Colorless liquid; ^{1}H NMR ($CDCl_3$) δ=0.67—1.47 (m, 20H), 2.27 (s, 4H), 6.77—7.37 (m, 10H). ^{13}C NMR ($CDCl_3$) δ=6.7, 10.3, 22.8, 124.3, 128.2, 128.6, 142.3. MS m/z 355 (M$^+$−$PhCH_2$). Ex MS Found: m/z 353.0583. Calcd for $C_{15}H_{27}{}^{74}Ge^{72}Ge$: 353.0546.

1-Triethylgermyl-2-benzylhexane (12): Colorless liquid; ^{1}H NMR ($CDCl_3$) δ=0.43—1.13 (m, 18H), 1.13—2.17 (m, 9H), 2.52 (d, J=7.2 Hz, 2H), 6.97—7.43 (m, 5H). ^{13}C NMR ($CDCl_3$) δ=4.7, 8.9, 14.2, 17.1, 23.0, 28.8, 35.8, 37.1, 43.5, 125.5, 128.0, 129.2, 141.8. MS m/z 307 (M$^+$−C_2H_5). EX MS Found: m/z 307.1435. Calcd for $C_{17}H_{29}{}^{74}Ge$: 307.1481.

Diethylbenzylgermane (8): Colorless liquid; ^{1}H NMR (benzene-d_6) δ=0.72—1.17 (m, 10H), 2.20 (d, J=3 Hz, 2H), 3.90—4.20 (m, 1H), 6.87—7.14 (m, 5H). IR (neat) 2001 cm^{-1} (ν_{Ge-H}). MS m/z 224 (M$^+$). EX MS Found: m/z 224.0679. Calcd for $C_{11}H_{18}{}^{74}Ge$: 224.0620.

1-(Triethylgermyl)-2-benzylcyclohexane (19) (cis: trans=1:4 mixture): Colorless liquid; ^{1}H NMR ($CDCl_3$) δ=0.57—2.03 (m, 25H), 2.49 (m, 2H), 6.92—7.48 (m, 5H). ^{13}C NMR ($CDCl_3$) δ=4.6, 9.4, 22.0, 25.6, 26.4, 28.3, 29.1, 29.8, 32.1, 33.4, 37.4, 39.0, 42.0, 43.6, 125.7, 128.2, 129.2, 141.7. MS m/z 305 (M$^+$−C_2H_5). EX MS Found: m/z 305.1284. Calcd for $C_{17}H_{27}{}^{74}Ge$: 305.1325.

1,2-Bis(triethylgermyl)cyclohexane (23) (cis-trans mixture): Colorless liquid; ^{1}H NMR ($CDCl_3$) δ=0.50—1.33 (m, 32H), 1.33—1.87 (m, 8H). ^{13}C NMR ($CDCl_3$) δ=5.1, 9.2, 25.3, 26.5, 27.2, 27.6, 30.1, 30.5. MS m/z 404 (M$^+$). EX MS; Found: m/z 243.1125. Calcd for $C_{12}H_{25}{}^{74}Ge$ (M$^+$−Et_3Ge): 243.1082.

1,2-Adduct of 1 with 2-Hexene (24A, 24B, 24C) (mixture of 3 isomer): Colorless liquid; ^{1}H NMR ($CDCl_3$) δ=0.50—1.77 (m, 27H), 2.30—2.93 (m, 2H), 6.80—7.30 (m, 5H). MS m/z 307 (M$^+$−C_2H_5). EX MS: Found Isomer **A**; m/z 307.1443. Isomer **B**; m/z 307.1504. Isomer **C**, m/z 307.1418. Calcd for $C_{17}H_{29}{}^{74}Ge$; (M$^+$−C_2H_5): 307.1481.

2-Methyl-2-benzyl-3-trimethylgermylhexane (25): Colorless liquid; ^{1}H NMR ($CDCl_3$) δ=0.65—1.14 (m, 27H), 2.54 (s, 2H), 6.97—7.30 (m, 5H). ^{13}C NMR ($CDCl_3$) δ=6.1, 8.9, 14.7, 17.4, 26.0, 27.5, 37.4, 44.2, 49.0, 125.6, 127.5, 130.7, 139.7. MS m/z 307 (M$^+$−C_2H_5). EX MS Found m/z 307.1394. Calcd for $C_{17}H_{29}{}^{74}Ge$ (M$^+$−C_2H_5): 307.1481.

2,3,3-Trimethyl-4-phenyl-2-(triethylgermyl)butane (30): Colorless liquid; ^{1}H NMR ($CDCl_3$) δ=0.76—1.23 (m, 27H), 2.58 (s, 2H), 7.07—7.28 (m, 5H). MS *m/z* 307 ($M^+-C_2H_5$). EX MS Found: *m/z* 307.1481. Calcd for $C_{17}H_{29}{}^{74}Ge$ ($M^+-C_2H_5$); 307.1481.

2,3-Dimethyl-3-benzyl-4-triethylgermyl-1-butene (34): Colorless liquid; ^1H NMR ($CDCl_3$) δ=0.52—1.32 (m, 20H), 1.83 (s, 3H), 2.54, 2.78 (AB q, *J*=13.8 Hz, 2H), 4.51 (s, 1H), 4.73 (m, 1H), 6.93—7.37 (m, 5H). ^{13}C NMR ($CDCl_3$) δ=5.7, 9.0, 20.4, 25.6, 26.1, 42.9, 50.1, 111.4, 125.8, 127.4, 130.5, 139.2, 150.8. MS *m/z* 334 (M^+). EX MS Found: *m/z* 334.1699. Calcd for $C_{19}H_{32}{}^{74}Ge$: 334.1716.

2,3-Dimethyl-5-phenyl-1-triethylgermyl-2-pentene (35): Colorless liquid; ^1H NMR ($CDCl_3$) δ=0.43—1.30 (m, 17H), 1.65 (s, 6H), 2.47 (m, 4H), 6.93—7.47 (m, 5H). ^{13}C NMR ($CDCl_3$) δ=5.0, 8.9, 18.8, 20.3, 20.6, 34.9, 37.0, 123.9, 125.6, 127.5, 128.2, 128.4, 142.9. MS *m/z* 334 (M^+). EX MS Found: *m/z* 334.1781. Calcd for $C_{19}H_{32}{}^{74}Ge$: 334.1716.

2,3-Dimethyl-3-benzyl-4-diethylbenzylgermyl-1-butene (36): Colorless liquid; ^1H NMR ($CDCl_3$) δ=0.43—1.24 (m, 12H), 1.57 (s, 3H), 1.66 (s, 3H), 2.20 (s, 2H), 2.33, 2.51 (AB q, *J*=9 Hz, 2H), 4.48 (s, 1H), 4.72 (m, 1H), 6.77—7.43 (m, 10H). MS *m/z* 396 (M^+). EX MS Found: *m/z* 396.1837. Calcd for $C_{24}H_{34}{}^{74}Ge$: 396.1872.

2,3-Dimethyl-5-phenyl-1-diethylbenzylgermyl-2-pentene (37): Colorless liquid; ^1H NMR ($CDCl_3$) δ=0.38—1.33 (m, 12H), 1.56 (s, 6H), 2.33 (s, 2H), 2.49 (m, 4H), 6.96—7.32 (m, 10H). MS *m/z* 396 (M^+). EX MS Found: *m/z* 396.1846. Calcd for $C_{24}H_{34}{}^{74}Ge$: 396.1872.

5-(Triethylgermylmethyl)undecane (17): Colorless liquid; ^1H NMR ($CDCl_3$) δ=0.43—1.80 (m, 40H), ^{13}C NMR ($CDCl_3$) δ=4.8, 9.0, 11.7, 14.0, 14.2, 23.2, 23.3, 30.2, 30.5, 32.7, 33.8, 36.9, 38.5. MS *m/z* 301 ($M^+-C_2H_5$). EX MS Found: *m/z* 245.1331. Calcd for $C_{12}H_{27}{}^{74}Ge$ ($M^+-C_6H_{13}$): 245.1324.

1,1-Diethylgermacyclo-3,4-dimethyl-3-pentene (38): Due to the low yield this product could not be isolated in pure state in the photoreaction of diethyldibenzylgermane and 3,4-dimethyl-1,3-butadiene. Its mass fragmentation pattern [*m/z* 214 (M^+), 185 ($M^+-C_2H_5$, base peak), 157 ($M^+-2\,C_2H_5$), 132 (Et_2Ge), 115, and 103 (EtGe)] is identical with that of the authentic sample prepared as described below.

Synthesis of 38: To a solution of trichlorogermane (0.025 mol) in ether (20 ml) was added 2,3-dimethyl-1,3-butadiene (0.027 mol) in ether (10 ml) with stirring at room temperature. Stirring was continued for 1 h, and a precipitated white solid was filtered off. A filtrate containing 1,1-dichloro-3,4-dimethyl-1-germacyclo-3-pentene was added dropwise to a solution of ethylmagnesium bromide, prepared from ethyl bromide (0.25 mol) and magnesium (0.25 mol) in ether (200 ml), under reflux. After refluxing for 3 h, excess Grignard reagent was hydrolyzed with a saturated ammonium chloride solution. The solvent was expelled at room temperature and the residue was purified by silica-gel chromatography (eluant: hexane) and GPC to give **38**. Yield 22%. Bp 60 °C/7 mmHg (lit,7) 102 °C/26 mmHg (1 mm Hg=133.322 Pa)). ^1H NMR δ=0.54—1.30 (m, 10H, C_2H_5), 1.47 (s, 4H, CH_2), 1.68 (s, 6H, CH_3). ^{13}C NMR δ=5.8, 9.2, 19.5, 22.9, 131.0. Mass: *m/z* 214 (M^+), 185, 157, 132 (Et_2Ge), 115, 103, 83, 75.

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