Experimental Section

Compounds and the Reactions. The cyclohex-2-enylstannanes were prepared and characterized as described previously.[6,9,13] Reactions with sulfur dioxide in chloroform or methanol were conducted (at 0 °C), normally in NMR tubes, and examined directly by ^{1}H and ^{13}C spectroscopy. The solvent was then removed, and the viscous gel or white solid remaining represented essentially pure insertion product (the cyclohex-2-enylsulfinate). IR spectroscopy established *O*-sulfinato products.[3,4] The key ^{13}C and ^{1}H NMR spectra are located in Tables IV and V.

NMR Spectra. These were acquired by utilizing the conditions and solvents described fully in the preceding paper.

Registry No. 1, 113353-45-0; **2**, 113353-46-1; **3**, 113353-47-2; **4**, 113378-70-4; **5**, 113353-48-3; **6**, 113353-49-4; **7**, 113353-50-7; **8**, 113353-51-8; **9**, 113353-52-9; **10**, 113353-53-0; **11**, 89633-90-9; **12**, 89633-91-0; **13**, 113353-54-1; **14**, 113353-55-2; **15**, 89633-99-8; **16**, 89633-98-7; **17**, 89633-97-6; **18**, 89633-96-5; SO_2, 7446-09-5; (*cis*-5-methylcyclohex-2enyl)trimethylstannane, 74089-88-6; (*trans*-5-methylcyclohex-2-enyl)trimethylstannane, 74089-89-7; (*cis*-5-methylcyclohex-2-enyl)triphenylstannane, 83269-35-6; (*trans*-5-methylcyclohex-2-enyl)triphenylstannane, 83269-36-7; (*cis*-3,5-dimethylcyclohex-2-enyl)trimethylstannane, 83269-39-0; (*trans*-3,5-dimethylcyclohex-2-enyl)trimethylstannane, 83269-40-3; (*cis*-5-(1,1-dimethylethyl)cyclohex-2-enyl)trimethylstannane, 84537-09-7; (*trans*-5-(1,1-dimethylethyl)cyclohex-2-enyl)trimethylstannane, 84537-11-1; (*cis*-4-(1,1-dimethylethyl)cyclohex-2-enyl)trimethylstannane, 89633-88-5; (*trans*-4-(1,1-dimethylethyl)cyclohex-2-enyl)trimethylstannane, 89633-89-6; (*cis*-4-(1,1-dimethylethyl)cyclohex-2-enyl)triphenylstannane, 89634-12-8; (*trans*-4-(1,1-dimethylethyl)cyclohex-2-enyl)triphenylstannane, 89634-11-7.

Chemistry of Heavy Carbene Analogues R_2M (M = Si, Ge, Sn). 12.[1] Concerted and Nonconcerted Insertion Reactions of the Germylene Me_2Ge into the Carbon–Halogen Bond

Jürgen Köcher,[2] Manfred Lehnig,* and Wilhelm P. Neumann

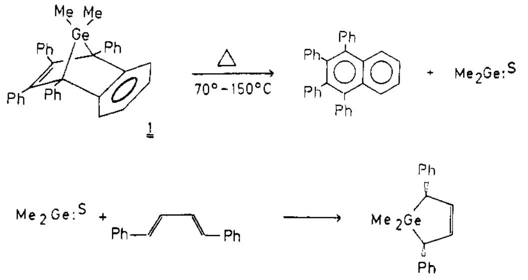
Lehrstuhl für Organische Chemie I, University of Dortmund, D-4600 Dortmund 50, Germany

Received October 22, 1986; Revised Manuscript Received December 17, 1987

During the reaction of Me_2Ge with CCl_3X (X = Cl, Br), $PhCH_2X$ (X = Br, I), and Ph_2CHCl, ^{1}H CIDNP is observed in the products of net insertion of Me_2Ge into the carbon–halogen bond and in Me_2GeX_2 (X = Cl, Br). It is concluded that a two-step radical reaction takes place by an abstraction–recombination mechanism. No reaction takes place with alkyl halides that have a C–X bond dissociation energy of more than about 70 kcal/mol. Me_2Ge is generated thermally at 70–95 °C or photochemically from the 7-germabenzonorbornadiene 1 and reacts in both cases in the singlet state. The activation energy for forming Me_2Ge from 1 is 19 kcal/mol for the reaction with CCl_4. Insertion products are also formed with the alkenyl halides $CH_2{=}CHCH_2X$, $PhCH{=}CHX$ (X = Cl, Br), and 2-bromobut-2-ene, but without showing CIDNP effects. Since Me_2GeX_2 was not found either, Me_2Ge reacts in these cases in a nonradical manner. It does not react with 1-chlorocyclohexene, but it does react with Me_2GeX_2 under formation of digermanes and/or oligogermanes without CIDNP.

Introduction

Carbenes, R_2C:, play an important role as intermediates in organic chemistry. Similarly, the chemistry of the heavy carbene analogues, the silylenes R_2Si,[3] the germylenes R_2Ge,[4] and the stannylenes R_2Sn,[5] has received much attention in recent years. In principle, the heavy carbene analogues undergo the same types of reactions as the carbenes—addition and insertion—but there are characteristic differences that are still in need of investigation. A question that is still of great interest is the spin state of the reacting intermediate (singlet or triplet). For example, dimethylgermylenes generated by thermolysis from the 7-germabenzonorbornadiene 1[6] or pentamethyldigermane[7] have been shown to undergo concerted 1,4-additions to 1,3-dienes (eq 1), indicating a singlet state for the reacting species.



(1)

Carbenes are known to undergo insertion into the carbon–hydrogen bond. From the beginning of carbene chemistry, two different reaction mechanisms were discussed. The first is a concerted one, meaning that the insertion occurs in a single step without further reaction intermediates via a three-center-type transition state (eq

---

[1] Part 11: Appler, H.; Neumann, W. P. *J. Organomet. Chem.* **1986**, *314*, 261.

[2] Köcher, J. Dr. rer. nat. Thesis, University of Dortmund, 1985.

[3] Gaspar, P. P. *React. Intermed.* (Wiley) **1978**, *1*, 228; **1981**, *2*, 335; **1985**, *3*, 333.

[4] Rivière, P.; Castel, A.; Satgé, J. *J. Am. Chem. Soc.* **1980**, *102*, 5413.

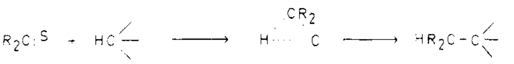
[5] Neumann, W. P. *The Stannylenes R_2Sn in Organometallic and Coordination Chemistry of Ge, Sn, and Pb*; Gielen, M., Harrison, P. G., Eds.; Freund: Tel Aviv, 1978.

[6] Schriewer, M.; Neumann, W. P. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1019; *J. Am. Chem. Soc.* **1983**, *105*, 897.

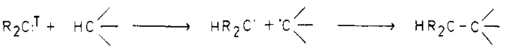
[7] Ma, E. C.-L.; Kobayashi, K.; Barzilai, M. W.; Gaspar, P. P. *J. Organomet. Chem.* **1982**, *224*, C 13.

0276-7333/88/2307-1201$01.50/0

2). The second is a two-step reaction via a radical pair

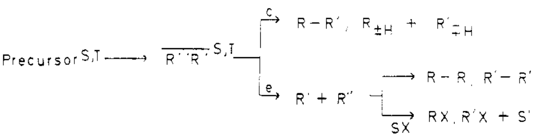

(2)

formed by hydrogen abstraction that collapses to the recombination product, the formal net insertion product (eq 3). It has been found that carbenes in the singlet (S) state


(3)

react with C–H bonds in a concerted manner while from the triplet (T) state they react via an abstraction–recombination mechanism with radicals as intermediates.[8]

These two mechanisms can be distinguished by studying the minor reaction products; the abstraction–recombination reaction should give products typical for radical reactions such as abstraction, recombination, and disproportionation; the concerted reaction should not. However, the product analysis does not allow a distinction in every case and is not capable of differentiating between S and T states. A method that allows this is CIDNP[9] (chemically induced dynamic nuclear polarization) through the observance of emission (E) and enhanced absorption (A) signals in the NMR spectra of the reaction products of radical pairs taken during or immediately after reaction (eq 4).[10,11] It has been shown by CIDNP that S carbenes


(4)

do not react with halides in a concerted manner but are capable of abstracting halogen and reacting via radical pairs (eq 5).[13]

$$R_2C\colon^{S} + R'Hal \longrightarrow \overline{HalR_2C^{\cdot}\ {}^{\cdot}R'}^{\,S} \longrightarrow HalR_2C-R' \qquad (5)$$

Germylenes do not react with the carbon–hydrogen bond but react with the carbon–halogen,[14] metal–halogen,[15] metal–carbon,[16] metal–metal,[17] and metal–hydrogen bonds,[18] although thorough mechanistic studies have not been performed. The only mechanistic study concerns the insertion of Me_2Ge into the Sn–Cl bond of Me_3SnCl, giving $Me_2ClGeSnMe_3$ in greater than 90% yield.[6] As radical reaction products such as Me_6Sn_2 or $Me_2ClGeGeMe_2Cl$ are not present as byproducts, the occurrence of a one-step reaction has been assumed. In a preliminary communication we have shown by CIDNP that Me_2Ge generated thermally from the 7-germabenzonorbornadiene 1 reacts with $PhCH_2Br$ via an abstraction–recombination mechanism from its singlet state.[19] In this paper CIDNP investigations of the reactions of photochemically generated germylenes Me_2Ge with $PhCH_2Br$ will be described as well as reactions of Me_2Ge generated by thermolysis of 1 with other organic halides and with Me_2GeCl_2 and Me_2GeBr_2.

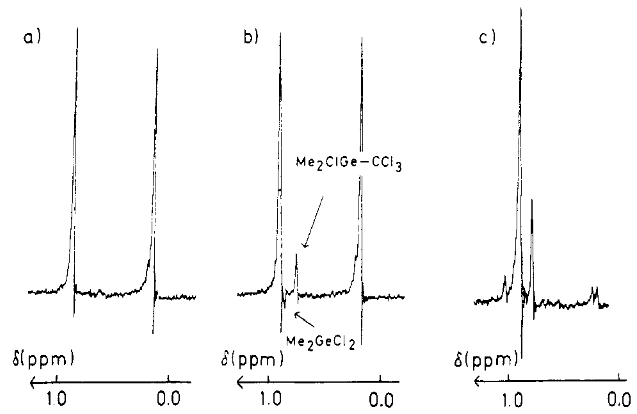


Figure 1. ^1H CIDNP during thermal decomposition of 1 in the presence of CCl_4: (a) before reaction; (b) during reaction at 80 °C taken ca. 1 min after beginning; (c) after reaction.

Table I. ^1H CIDNP during Thermal Decomposition of 1 with Organic Halides[a] (See Figures 1-4)[b]

δ	assignt	Figures	CIDNP
0.20	GeMe (1)	1–4	N
0.95 (0.98)	GeMe (1)	1–3 (4)	N
0.58	$PhCH_2Ge\underline{Me_2}Br$	3	E
0.63	$Ph_2CHGe\underline{Me_2}Cl$	4	E
0.80	$Me_2ClGeCCl_3$	1	A[c]
0.90 (0.93)	Me_2GeCl_2	1 (4)	E (A)[c]
1.03	$Me_2BrGeCCl_3$	2	E
1.15	Me_2GeBr_2	2, 3	A[c]
2.57	$Ph\underline{CH_2}GeMe_2Br$	3	E
3.95	$Ph_2\underline{CH}GeMe_2Cl$	4	E
0.52–0.56	oligogermanes	3	N
0.55–0.62	(GeGeMe$_2$Ge)	4	N
0.80	oligogermanes (GeMe$_2$Cl)	4	N
0.90–0.93	oligogermanes (GeMe$_2$Br)	3	N
2.22	$PhCH_3$	3	N
2.84	$PhCH_2CH_2Ph$	3	N
3.75	Ph_2CH_2	4	N
4.69	$Ph_2CHCHPh_2$	4	N

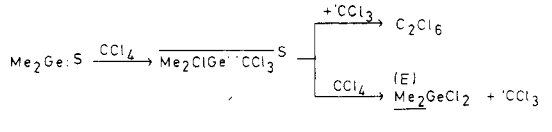
[a] E = emission; A = enhanced absorption: N = no effect. [b] The signals not listed are due to impurities or not identified products. [c] The signal shows 30% intensity after the reaction stopped.

Results and Discussion

(A) Thermal and Photochemical Decomposition of 1. Thermal Decomposition in the Presence of CCl_4 and Me_2GeCl_2. Thermal and photochemical decomposition of 1 in toluene quantitatively gives tetraphenylnaphthalene and poly(dimethylgermylene) (eq 1 and 6).

$$n\ Me_2Ge\colon \longrightarrow (Me_2Ge)_n \qquad (6)$$

CIDNP effects are not observed. Thermal decomposition of 1 in the presence of CCl_4 at 70 °C results in the formation of C_2Cl_6, Me_2GeCl_2 and $Me_2ClGeCCl_3$ as the main products (eq 7).[20] The formation of these products sug-


(7)

---

[8] Jones, M., Jr.; Moss, R. A. *Carbenes*; Wiley: New York, 1973, 1975; Vols. 1, 2.

[9] Closs, G. L.; Trifunac, A. D. *J. Am. Chem. Soc.* **1969**, *91*, 4554; Closs, G. L. In ref 8, Vol. 2, pp 159–184.

[10] Bargon, J.; Fischer, H.; Johnsen, U. *Z. Naturforsch., A: Astrophys., Phys. Phys. Chem.* **1967**, *22A*, 1551. Ward, H. R.; Lawler, R. G. *J. Am. Chem. Soc.* **1967**, *89*, 5518. Muus, L. T., Atkins, P. W., McLauchlan, K. A., Pedersen, J. B., Eds. *Chemically Induced Magnetic Polarisation*; D. Reidel: Dordrecht, Boston, 1977.

[11] For determining the phase of the nuclear polarization, the following rule has been given by Kaptein:[12] $\Gamma_n = \mu\epsilon\Delta g a$ (Γ_n = +, A; Γ_n = −, E). μ = + for T and − for S precursor; ϵ = + for cage (c) products and − for escape (e) products; g = g values of the radicals involved; a = sign of the splitting parameter of the nucleus in the radical that leads to the product.

[12] Kaptein, R. *J. Chem. Soc. D* **1971**, 732.

[13] Roth, H. D. *J. Am. Chem. Soc.* **1971**, *93*, 1527. Roth, H. D. *Acc. Chem. Res.* **1977**, *10*, 85.

[14] Massol, M.; Barrau, J.; Rivière, P.; Satgé, J. *J. Organomet. Chem.* **1971**, *30*, 27. Joffe, A. I.; Nefedov, O. M. *Zh. Vses. Khim. Ova. im. D.I. Mendeleeva* **1979**, *24*, 475.

[15] Bulten, E. J.; Noltes, J. G. *J. Organomet. Chem.* **1969**, *16*, P8.

[16] Barrau, J.; Satgé, J. *J. Organomet. Chem.* **1978**, *148*, C9.

[17] Castel, A.; Escudié, J.; Rivière, P.; Satgé, J. *J. Organomet. Chem.* **1981**, *210*, 37.

[18] Ma, E. C.-L.,; Paquin, D. P.; Gaspar, P. P. *J. Chem. Soc., Chem. Commun.* **1980**, 381.

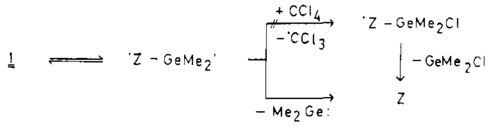
[19] Köcher, J.; Lehnig, M. *Organometallics* **1984**, *3*, 937.

Table II. Kinetic Data of the Thermal Decomposition of 1

solv	T, °C	$t_{1/2}$, min	ref
benzene	70	47	20
CCl_4	70	40	20
CCl_4	80	20	this work
CCl_4	85	16.5	this work
CCl_4	90	9	this work

gests radical reactions involving free germylenes (eq 3–5). CIDNP experiments confirm this presumption (see Figure 1 and Table I). When a solution of 1 and CCl_4 in toluene is warmed to 80 °C in the probe of a ^1H NMR spectrometer, the methyl resonance of Me_2GeCl_2 shows emission. When the reaction is finished, the Me_2GeCl_2 proton signal appears with absorption, as expected. Additionally, an enhanced absorption signal appears during the reaction due to the protons of a minor product that might be $Me_2ClGeCCl_3$.[20] For determining the spin state of the germylene, the sign of the g value difference of the two radicals forming the radical pair has to be used.[11] The g value of $Me_2ClGe^\bullet$ is not known, but it is expected that it is very similar to the g value of $Cl_3C^\bullet$ ($g = 2.0091$[21]). From the known g values of $Me_3Ge^\bullet$ ($g = 2.0104$[22]) and $Cl_3Ge^\bullet$ ($g = 2.0070$[23]), a g value of 2.008 might be estimated for $Me_2ClGe^\bullet$, meaning $g(Me_2ClGe^\bullet) < g(Cl_3C^\bullet)$. This gives the observed emission for Me_2GeCl_2 if Me_2Ge reacts from singlet states[6,19] ($\mu < 0$, $\epsilon < 0$, $\Delta g < 0$, $a > 0$;[24] $\Gamma_n = -$) and enhanced absorption for $Me_2ClGeCCl_3$ ($\mu < 0$, $\epsilon > 0$, $\Delta g < 0$, $a > 0$;[24] $\Gamma_n = +$).

In a preliminary communication,[20] a two-step decomposition mechanism of 1 has been proposed, in which a biradical is generated by Ge–C bond scission in a first step, which is in turn scavenged by CCl_4 or leads to the germylene in a second step (eq 8). The CIDNP results



(8)

suggest the existence of free germylenes as reaction intermediates rather than of radicals $^\bullet Z{-}GeMe_2Cl$ (eq 8). Furthermore, it has been shown that it is not a biradical but instead a free germylene that is the reacting intermediate during reaction of 1 with dienes (eq 1).[6] To provide support that this is in fact the case during the thermal decomposition of 1 with CCl_4, decomposition rates of 1 have been determined. Table II gives the results of the kinetic experiments. Data for the decomposition in benzene without scavenger are added.

The thermal decomposition of 1 follows a first-order rate law, in benzene with $\tau_{1/2} = 47$ min and in CCl_4 with $\tau_{1/2} = 40$ min at 70 °C. This indicates the absence of or only a small scavenger effect. The activation energy for the decomposition of 1 in CCl_4 is 19 kcal/mol. As there is no indication of the formation of a biradical such as $^\bullet Z{-}GeMe_2{}^\bullet$ as an intermediate, it might be suggested that a

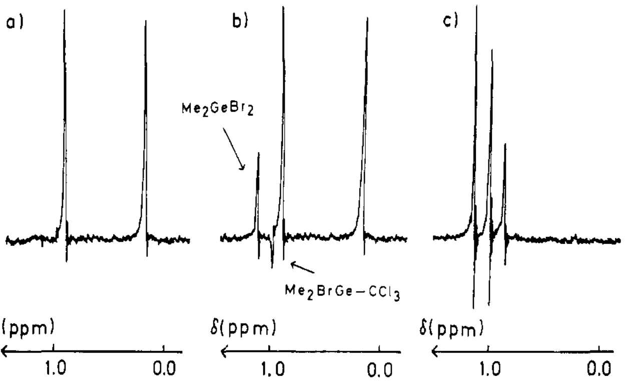
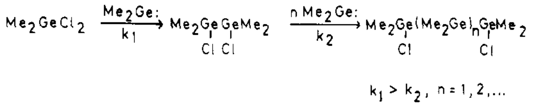


Figure 2. ^1H CIDNP during thermal decomposition of 1 in the presence of CCl_3Br: (a) before reaction; (b) during reaction at 90 °C taken ca. 1 min after beginning; (c) after reaction.

synchronous decomposition reaction takes place. This, however, is unlikely following Dewar's arguments[28] and can neither be proved nor disproved here. It has been shown that 7-phospha- and 7-silanorbornadienes decompose in an analogous manner.[29,30]

Me_2Ge does not react with $CHCl_3$,[27] CH_2Cl_2,[27] CH_3Cl, and the higher alkyl chlorides $C_nH_{2n+1}Cl$ but instead polymerizes (eq 6). It does, however, react with Me_2GeCl_2 (eq 9).[27] The main reaction product is $Me_2ClGeGeMe_2Cl$;



$$\mathrm{Me_2GeCl_2 \xrightarrow[k_1]{Me_2Ge:} Me_2\underset{Cl}{Ge}\,\underset{Cl}{Ge}Me_2 \xrightarrow[k_2]{n\,Me_2Ge:} Me_2\underset{Cl}{Ge}(Me_2Ge)_n\underset{Cl}{Ge}Me_2} \tag{9}$$

$$k_1 > k_2,\ n = 1, 2, \ldots$$

a minor product is $Me_2ClGeGeMe_2GeMe_2Cl$. Higher oligogermanes are also present. CIDNP effects are not observed.

The decomposition rate of 1 in the presence of Me_2GeCl_2 is comparable to that in the presence of CCl_4. This can also be interpreted as favoring the existence of free germylenes as intermediates as well. Because of the absence of CIDNP effects, a one-step, nonradical reaction of Me_2Ge with Me_2GeCl_2 is likely, in analogy to the reaction path formulated with Me_2SnCl_2.[6] However, the two-step pathway cannot be excluded unambiguously, as the radicals which might appear are identical or nearly so and the products of the radical and the nonradical reactions are identical.

(B) Thermal Decomposition of 1 in the Presence of CCl_3Br and Me_2GeBr_2. Me_2GeBr_2 is the main product of the reaction of Me_2Ge with CCl_3Br.[20] A mechanism analogous to that of the reaction of Me_2Ge with CCl_4 is given in eq 10. Enhanced absorption is observed in the

$$\mathrm{Me_2Ge{:}^{S} \xrightarrow{CCl_3Br} \overline{Me_2BrGe^{\bullet}\ {}^{\bullet}CCl_3}^{\,S} \xrightarrow{CCl_3Br} \overset{(A)}{\underline{Me_2}GeBr_2} + {}^{\bullet}CCl_3} \tag{10}$$

Me_2GeBr_2 proton signals (Figure 2; Table I). The emission line observed might be due to the $Me_2BrGeCCl_3$ protons. A more detailed analysis was not performed, as the g value of the dimethylbromogermyl radical $Me_2BrGe^\bullet$ is not known and cannot be estimated from similar radicals. If Me_2Ge reacts from singlet states, it follows from the enhanced absorption observed in Me_2GeBr_2 that $g(Me_2BrGe^\bullet) > g(Cl_3C^\bullet) = 2.0091$ ($\mu < 0$, $\epsilon < 0$, $\Delta g > 0$, $a > 0$;[24] $\Gamma_n = +$); $Me_2BrGeCCl_3$ would show emission ($\mu <$

---

(20) Neumann, W. P.; Schriewer, M. *Tetrahedron Lett.* **1980**, *21*, 3273. Schriewer, M. Dr. rer. nat. Thesis, University of Dortmund, 1981. Maslov, S., unpublished work from this laboratory.

(21) Hudson, A.; Hussain, H. A. *Mol. Phys.* **1969**, *16*, 199.

(22) Bennett, S. W.; Eaborn, C.; Hudson, A.; Hussain, H. A.; Jackson, R. A. *J. Organomet. Chem.* **1969**, *16*, P36.

(23) Lloyd, R. V.; Rogers, M. T. *J. Am. Chem. Soc.* **1973**, *95*, 2459.

(24) A positive sign for $a_H^{CH_3}(Me_2ClGe^\bullet)$ and $a_H^{CH_3}(Me_2BrGe^\bullet)$ is assumed in accordance with the signs of $a_H^{CH_3}(Me_3C^\bullet)$[25] and $a_H^{CH_3}(Me_3Sn^\bullet)$.[26]

(25) Scheffler, K.; Stegmann, H. B. *Elektronenspinresonanz*; Springer: Berlin, Heidelberg, New York, 1970.

(26) Lehnig, M. *Chem. Phys.* **1975**, *8*, 419.

(27) Walczak, R. F. Staatsexamensarbeit, University of Dortmund, 1982.

(28) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 209. Dewar, M. J. S.; Chantranupong, L. *J. Am. Chem. Soc.* **1983**, *105*, 7161.

(29) Marinetti, A.; Charrier, C.; Mathey, F.; Fischer, J. *Organometallics* **1985**, *4*, 2134. Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 275.

(30) Barton, T. J.; Goure, W. F.; Witiak, J. L.; Wulff, W. D. *J. Organomet. Chem.* **1982**, *225*, 87.

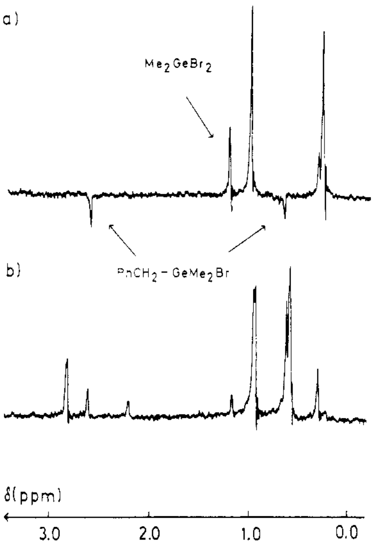
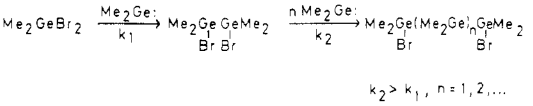


Figure 3. ^{1}H CIDNP during thermal decomposition of 1 in the presence of PhCH$_2$Br: (a) during reaction at 85 °C taken 1–3 min after beginning; (b) after 1-h reaction.

0, $\epsilon > 0$, $\Delta g > 0$, $a > 0$;[24] $\Gamma_n = -$).

Alkyl bromides $C_nH_{2n+1}Br$ do not react with Me$_2$Ge. Me$_2$GeBr$_2$ shows reactivity similar to that of Me$_2$GeCl$_2$ (eq 11) without CIDNP. The insertion product

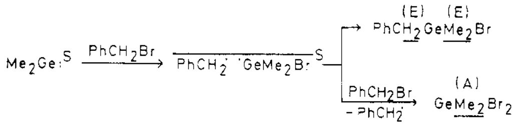


$$\mathrm{Me_2GeBr_2} \xrightarrow[k_1]{\mathrm{Me_2Ge:}} \mathrm{Me_2\underset{Br}{Ge}\underset{Br}{Ge}Me_2} \xrightarrow[k_2]{n\,\mathrm{Me_2Ge:}} \mathrm{Me_2\underset{Br}{Ge}(Me_2Ge)_n\underset{Br}{Ge}Me_2} \quad (11)$$

$$k_2 > k_1,\ n = 1, 2, \ldots$$

Me$_2$BrGeGeMe$_2$Br is not observed, and the main products are Me$_2$BrGeGeMe$_2$GeMe$_2$Br and Me$_2$BrGe(GeMe$_2$)$_2$GeMe$_2$Br. It is assumed that the reaction of Me$_2$Ge with Me$_2$GeBr$_2$ is a one-step reaction, analogous to the Me$_2$Ge reactions with Me$_2$GeCl$_2$ and Me$_3$SnCl.

(C) Thermal and Photochemical Decomposition of 1 in the Presence of PhCH$_2$Br and Thermal Decomposition of 1 in the Presence of PhCH$_2$I and Ph$_2$CHCl. ^{1}H NMR spectra taken during and after the thermal decomposition of 1 in the presence of PhCH$_2$Br in chlorobenzene are shown in Figure 3. The assignment of the signals is given in Table I. The methyl as well as the methylene proton signals of PhCH$_2$GeMe$_2$Br show emission; the Me$_2$GeBr$_2$ proton signals enhanced absorption. The scheme shown in eq 12 explains the effects. With



(12)

g(PhCH$_2^{\cdot}$) = 2.0026[31] and g(Me$_2$BrGe$^{\cdot}$) > 2.009 and with the assumption of singlet states of the reacting germylene, Kaptein's rule[11] gives emission for the methyl protons ($\mu < 0$, $\epsilon > 0$, $\Delta g > 0$, $a > 0$;[25] $\Gamma_n = -$) as well as for the methylene protons ($\mu < 0$, $\epsilon > 0$, $\Delta g < 0$, $a < 0$;[25] $\Gamma_n = -$) of PhCH$_2$GeMe$_2$Br and enhanced absorption for Me$_2$GeBr$_2$ ($\mu < 0$, $\epsilon < 0$, $\Delta g > 0$, $a > 0$;[25] $\Gamma_n = +$), as observed. PhCH$_2$GeMe$_2$Br, toluene, and PhCH$_2$CH$_2$Ph are only side products of the reaction because Me$_2$Ge reacts more efficiently with Me$_2$GeBr$_2$ than with PhCH$_2$Br. This is shown independently by adding Me$_2$GeBr$_2$ to the reaction mixture, from the beginning. In this case, only traces of the benzylic products are formed.

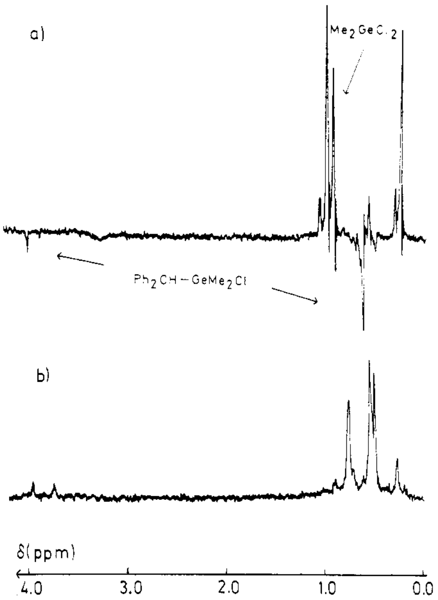
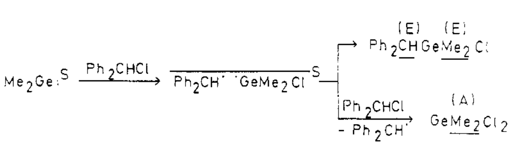


Figure 4. ^{1}H CIDNP during thermal decomposition of 1 in the presence of Ph$_2$CHCl: (a) during reaction at 95 °C taken 1–3 min after beginning; (b) after reaction.

Photochemical decomposition of 1 in the presence of PhCH$_2$Br in the probe of a ^{1}H NMR spectrometer leads to the same product distribution and CIDNP pattern as during thermal decomposition of 1. This indicates the occurrence of a singlet germylene Me$_2$Ge during the photochemical decomposition of 1.

The thermal decomposition of 1 in the presence of PhCH$_2$I leads to PhCH$_2$GeMe$_2$I and to Me$_2$GeI$_2$ as the main products. The methylene proton signal of PhCH$_2$GeMe$_2$I shows emission; further CIDNP effects are not observed. The explanation for the emission signal is analogous to that with PhCH$_2$Br as the germylene trap. With PhCH$_2$Cl, no reaction is observed.

The thermal decomposition of 1 in the presence of Ph$_2$CHCl leads to the CIDNP spectrum shown in Figure 4 and described in Table I. In analogy to the reaction with PhCH$_2$Br, the methine and the methyl proton signals of the net insertion product Ph$_2$CHGeMe$_2$Cl and the abstraction product Me$_2$GeCl$_2$ show CIDNP as explained by the scheme shown in eq 13.



(13)

g(Ph$_2$CH$^{\cdot}$) is not known. It should be similar to g(PhCH$_2^{\cdot}$) = 2.0026[31] and g(Ph$_3$C$^{\cdot}$) = 2.0026,[32] leading to an analogous interpretation of the CIDNP effects as in the PhCH$_2$Br case. Some minor emission and enhanced absorption signals are due to side products and are not analyzed here. Me$_2$GeCl$_2$ formed during the reaction reacts with Me$_2$Ge to give oligogermanes as described in section A.

During the thermal decomposition of 1 in the presence of Ph$_3$CCl, ESR signals of the trityl radical can be observed.

Table III covers the results of the thermal decomposition of 1 with organic alkyl halides. Additionally, carbon–halogen bond energies of the investigated halides are

---

(31) Paul, H.; Fischer, H. *Helv. Chim. Acta* **1973**, *56*, 1575.

(32) Möbius, K.; Plato, M. *Z. Naturforsch., A: Astrophys., Phys. Phys. Chem.* **1969**, *24A*, 1078.

Table III. Reactions of Me_2Ge with the Carbon–Halogen (C–X) Bond of Some Organic Halides at 70–95 °C[31]

compd	C–X bond energy, kcal/mol	reactn	CIDNP
CCl_4	73	×	×
$CHCl_3$	78		
CH_2CCl_2	81		
CH_3Cl	84		
CCl_3Br	55	×	×
C_nH_{2n+1}–Cl	80–84		
C_nH_{2n+1}–Br	66–70		
$PhCH_2Cl$	70		
$PhCH_2Br$	55	×	×
$PhCH_2I$	40	×	×
Ph_2CHCl	60[a]	×	×
Ph_3CCl	50[a]	×	[b]
allyl–Cl	68	×	
allyl–Br	57	×	
vinyl–Cl	89	(×)[c]	
vinyl–Br	76	×[d]	

[a] The bond dissociation energies of Ph_2CHCl and Ph_3CCl are estimated from the values given for CH_3Cl and $PhCH_2Cl$. [b] $Ph_3C^{\bullet}$ is observed by ESR, and CIDNP cannot be observed under these conditions. [c] The reaction occurs with PhCH=CHCl, but not with 1-chlorocyclohexene. [d] The reaction occurs with PhCH=CHBr as well as with 2-bromobut-2-ene.

given.[33] A comparison of the values shows that a bond energy of about 70 kcal/mol is the upper limit allowed for the halogen abstraction reaction of Me_2Ge from organic alkyl halides to take place. Germyl radicals behave differently; they are known to react with alkyl chlorides and bromides in processes that are independent of the carbon–halogen bond energies.[34,35]

(D) Thermal Decomposition of 1 in the Presence of Allyl and Vinyl Halides. The thermal decomposition of 1 in the presence of allyl chloride and allyl bromide leads to the insertion product of Me_2Ge into the C–X bond in high yields (80%) (eq 14). Neither the formation of

$$Me_2Ge{:} + CH_2{=}CHCH_2X \longrightarrow CH_2{=}CHCH_2GeMe_2X \quad X = Cl, Br \tag{14}$$

Me_2GeCl_2 or Me_2GeBr_2 nor CIDNP has been observed. This indicates a one-step, nonradical reaction. A competition experiment between $PhCH_2Br$ and $CH_2{=}CHCH_2Br$ with Me_2Ge gave only $CH_2{=}CHCH_2GeMe_2Br$ (eq 14), indicating a higher activation energy of the two-step reaction of Me_2Ge with $PhCH_2Br$ compared with the nonradical one with $CH_2{=}CHCH_2Br$.

The decomposition of 1 in the presence of β-chlorostyrene gives the insertion product of Me_2Ge into the C–Cl bond, $PhCH{=}CHGeMe_2Cl$, as well as higher oligomers. With β-bromostyrene as the Me_2Ge trap, $PhCH{=}CHGeMe_2Br$ is the exclusive product. As in the case of the allyl halides, neither Me_2GeCl_2 or Me_2GeBr_2 are formed nor are CIDNP effects observed in the reaction products, indicating the occurrence of a nonradical reaction. 1-Chlorocyclohexene does not trap Me_2Ge generated by thermolysis of 1. 2-Bromobut-2-ene as substrate gives the expected insertion product, bromine-containing oligogermanes, and polygermanes. No Me_2GeBr_2 is obtained, and CIDNP effects do not appear. A nonradical reaction is indicated here as well.

The results of the reactions of Me_2Ge with allyl and vinyl halides are collected in Table III; C–X bond dissociation energies are given as well. An upper limit of the bond dissociation energy might exist above which no reaction takes place. The restricted number of data does not allow its determination, but it should be ≥89 kcal/mol.

It may be that the π-system of the allyl and vinyl halides is involved in the first reaction steps by formation of a π-complex,[36] followed by a different reaction path than in the case of alkyl halides. Germylenes are known to undergo smooth reactions with unsaturated systems such as styrenes,[36] 1,3-dienes,[6,37] vinyl ketones,[38] α-diketones,[38] and alkynes.[39]

Conclusion

The 7-germabenzonorbornadiene 1 decomposes thermally in the presence of alkyl and alkenyl halides with formation of insertion products if the bond dissociation energy does not exceed an upper limit. Free germylenes, Me_2Ge, are the reacting intermediates. However, the mechanism of the reactions is different for various halides. Whereas alkyl halides give side products and show CIDNP effects indicating a two-step radical reaction, alkenyl halides do not. Me_2GeCl_2 and Me_2GeBr_2 give insertion products, too, but show no CIDNP effects.

MNDO calculations have been performed for the similar reactions of Me_2Sn with Me_2SnCl_2 and Me_3SnCl that are one-step insertions and with MeI that is a two-step abstraction–recombination process.[40] In these cases, the differences of the activation energies between the concerted and the nonconcerted mechanism are about 10 kcal/mol. Similar calculations would be valuable in the germylene case in order to better understand the different behavior of Me_2Ge toward alkyl halides and Me_2GeX_2 (X = Cl, Br).

Experimental Section

General Comments. The solvents were dried and distilled under argon. ^1H NMR spectra were taken on a 60-MHz Varian EM-360A spectrometer and GC–MS spectra with a CH 7 (Varian) in connection with a Varian Aerograph 1740-1. For further details see the foregoing communications.[1] The ESR spectrum was taken with a Varian E-109 E spectrometer.

CIDNP Experiments. 1 (50 mg, 0.09 mmol) and a threefold excess of the halide were added to 0.5 mL of solvent, PhCl, or, if D lock was used, PhCl with C_6D_6 (3:1), filled under argon into an NMR tube, and transferred to the probe of the ^1H NMR spectrometer (Bruker HFX 90, pulsed, or Perkin-Elmer R 32, CW) which was preheated to the reaction temperature (80–95 °C). In the CW case, the spectrum was scanned at a rate of 2 ppm/min. The pulsed spectra were taken with 32 scans meaning 2 min. The photochemical experiments were performed with a suitably modified spectrometer (HFX 90) allowing irradiation during the taking of a spectrum.[26] The unfiltered light of an Hg-Xe high-pressure lamp (Hanovia 977-B1, 1000 W) was used. The light was focussed with quartz lenses to a quartz light pipe leading to the sensitive part of the spectrometer. Quartz NMR tubes were used. Emission lines could be detected directly in the spectra. For distinguishing between enhanced absorption and the absence of a CIDNP effect, the reaction was interrupted, and the ^1H NMR spectrum was compared with the ^1H NMR spectrum taken during the reaction.

Kinetic Experiments. The kinetic experiments were performed by observing the disappearance of the GeMe ^1H NMR signals of 1. At 80–90 °C, they were carried out in the heated probe of the ^1H NMR spectrometer as described under "CIDNP Experiments". At 70 °C, 30 mg of 1 (0.056 mmol) was added to 0.5 mL of CCl_4 or benzene with traces of toluene, filled under argon into the NMR tube, and heated in a thermostat ("Unistat", Firma

---

(33) Egger, K. W.; Cocks, A. T. *Helv. Chim. Acta* **1973**, *56*, 1516.
(34) Carlsson, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1968**, *90*, 7047.
(35) Lehnig, M.; Werner, F.; Neumann, W. P. *J. Organomet. Chem.* **1975**, *97*, 375.
(36) Köcher, J.; Neumann, W. P. *Organometallics* **1985**, *4*, 400.
(37) Köcher, J.; Neumann, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 3861.
(38) Michels, E.; Neumann, W. P. *Tetrahedron Lett.* **1986**, *27*, 2455.
(39) Krebs. A.; Berndt, J. *Tetrahedron Lett.* **1983**, *24*, 4083.
(40) Dewar, M. J. S.; Friedheim, J. E.; Grady, G. L. *Organometallics* **1985**, *4*, 1784.

Huber). The methyl proton signal of toluene was used as an internal standard. The following values of the relative concentrations c/c_0 were found at 70 °C:

t (min)	0	19	36	58	78
$c/c_o(CCl_4)$	1	0.70	0.54	0.35	0.27
$c/c_o(C_6H_6)$	1	0.75	0.59	0.43	0.32

Determination of Products and Product Yields. The products and product yields were determined from the ^{1}H NMR spectra after completing the reactions (see Figures 1–4). The chemical shifts were measured against Me_4Si and determined by adding authentic samples of Me_2GeCl_2, Me_2GeBr_2, $PhCH_3$, Ph_2CH_2, $PhCH_2CH_2Ph$, and $Ph_2CHCHPh_2$. In order to identify the further reaction products, the reactions were repeated under dry argon at 70–80 °C and analyzed by GC or GC–MS. A methylation or ethylation of the reaction mixture proved to be necessary before analysis, since otherwise only molecular fragments could be detected.

For methylation or ethylation of the compounds containing C–Br bonds, about 8 mmol of MeMgBr or EtMgBr in Et_2O was added to the reaction mixture at 0 °C and the solution stirred at 0 °C for $^1/_2$ h and at room temperature for 1 h. After H_2O and NH_4Cl were added at 0 °C, the phases were separated and the aqueous phase was extracted twice with 50 mL of Et_2O. The combined organic phases were washed with H_2O and dried with Na_2SO_4. The solvent was removed, and the tetraphenylnaphthalene precipitated with *n*-pentane. The crude product was either investigated directly by GC–MS or after distillation by GC–MS, as described below.

Thermal and Photochemical Decomposition of 1.[20] 1 (0.3 g, 0.56 mmol) was heated at 70 °C for 3 h in 3 mL of benzene. The formation of poly(dimethylgermylene) (δ 0.4) was demonstrated by treatment of the reaction mixture with I_2 leading to Me_2GeI_2 in quantitative yield (δ 0.90). Evaporation of the solvent and recrystallization from CH_2Cl_2/EtOH quantivatively gave tetraphenylnaphthalene (mp 250 °C; δ 6.9–7.3 (br signals)). The photochemical decomposition of 1 without a scavenger in the probe of the ^{1}H NMR spectrometer also lead to poly(dimethylgermylene) and tetraphenylnaphthalene (see also "CIDNP Experiments").

Thermal Decomposition of 1 in CCl_4.[6,20] 1 (0.2 g, 0.4 mmol) was heated at 70 °C for 3 h in 3 mL of CCl_4. GC analysis (column 4m OV17) demonstrated the presence of C_2Cl_6 and Me_2GeCl_2 in yields of 100% and 95%, respectively. The ^{1}H NMR spectrum showed that further products were present, probably $Me_2ClGeCCl_3$ (δ 0.80), which is expected to decompose thermally,[14] and tetraphenylnaphthalene, which was precipitated with EtOH in quantitative yield.

Thermal Decomposition of 1 in the Presence of Me_2GeCl_2.[27] 1 (0.53 g, 1.0 mmol) was heated at 70 °C for 2 h in 2 mL of benzene with 35 mg of Me_2GeCl_2 (0.2 mmol). GC analysis demonstrated the formation of a major and two minor products. GC–MS analysis (column 4m OV17) showed $Me_2ClGeGeMe_2Cl$ as the major product and $Me_2ClGeGeMe_2GeMe_2Cl$ as one of the minor products (6:1). $Me_2ClGeGeMe_2Cl$: MS (70 eV), *m/e* (relative intensity) 241 ($m^+ - Cl$, 19), 205 ($m^+ - 2Cl$, 10), 157 ($m^+ - Me_3Ge$, 3), 139 (Me_2GeCl^+, 8), 89 ($MeGe^+$, 33). $Me_2ClGeGeMe_2GeMe_2Cl$: MS (70 eV), *m/e* (relative intensity) 343 ($m^+ - Cl$, 23), 221 ($m^+ - MeGeCl$, 31), 205 ($m^+ - Me_2GeCl_2$, 7), 189 ($m^+ - Me_3GeCl_2$, 9), 139 (Me_2GeCl^+, 8), 119 (Me_3Ge^+, 100), 104 (Me_2Ge^+, 7), 89 ($MeGe^+$, 40). The ^{1}H NMR spectrum showed two signals at δ 0.52 and 0.56 ($GeGeMe_2Ge$) and at δ 0.76 ppm (Me_2ClGe).

Thermal Decomposition of 1 in the Presence of Me_2GeBr_2. 1 (1.0 g, 1.9 mmol) and 0.6 g of Me_2GeBr_2 (0.3 mL, 2.4 mmol) were heated at 75 °C for 4 h in 10 mL of benzene. The reaction mixture was methylated with MeMgBr.[41] GC–MS analysis demonstrated the formation of Me_8Ge_3 and $Me_{10}Ge_4$ as the methylation products (1:1). Me_8Ge_3: MS (70 eV), *m/e* (relative intensity) 338 (m^+, 4), 323 ($m^+ - Me$, 7), 221 ($m^+ - Me_3Ge$, 32), 206 ($m^+ - Me_4Ge$, 13), 191 ($Me_3Ge_2^+$, 2), 119 (Me_3Ge^+, 100), 104 (Me_2Ge^+, 6), 89 ($MeGe^+$, 25). $Me_{10}Ge_4$: MS (70 eV), *m/e* (relative intensity) 440 (m^+, 7), 425 ($m^+ - Me$, 4), 323 ($m^+ - Me_3Ge$, 26), 308 ($m^+ - Me_4Ge$, 3), 221 ($m^+ - Me_5Ge_2$, 52), 206 ($m^+ - Me_6Ge_2$, 13), 176 ($Me_2Ge_2^+$, 2), 119 (Me_3Ge^+, 100), 104 (Me_2Ge^+, 5), 89 ($MeGe^+$, 19). Me_6Ge_2 was not found.

Thermal Decomposition of 1 in the Presence of $PhCH_2Br$. 1 (0.5 g, 0.95 mmol) and 0.5 g of $PhCH_2Br$ (0.35 mL, 2.9 mmol) were heated at 80 °C for 4 h in 5 mL of benzene. GC–MS analysis demonstrated the formation of $PhCH_2GeMe_2Br$. The presence of Me_2GeBr_2 (yield 5%: δ 1.15), $PhCH_3$ (yield ca. 5%: δ 2.22), and $PhCH_2CH_2Ph$ (yield ca. 15%: δ 2.84) was demonstrated by adding authentic material to the reaction mixture. After methylation, the formation of $PhCH_2GeMe_3$[42] was shown by ^{1}H NMR and GC–MS by using authentic material which was prepared from Me_3GeCl and $PhCH_2MgBr$.[41] Me_8Ge_3, $Me_{10}Ge_4$, and $Me_{12}Ge_5$ were detected by GC–MS as well. After ethylation of the reaction mixture with EtMgBr,[41] $PhCH_2GeMe_2Et$ and $Et_2Me_6Ge_3$ were detected by GC–MS. $PhCH_2GeMe_2Br$: MS (70 eV), *m/e* (relative intensity) 274 (m^+, 12), 259 ($m^+ - Me$, 11), 195 ($m^+ - Br$, 7), 183 ($GeMe_2Br^+$, 7), 153 ($GeBr^+$, 10), 139 ($GeC_5H_5^+$, 17), 91 ($PhCH_2^+$, 100), 65 ($C_5H_5^+$, 55). $PhCH_2GeMe_3$: MS (70 eV), *m/e* (relative intensity) 210 (m^+, 10), 195 ($m^+ - Me$, 18), 165 ($PhCH_2Ge^+$, 3), 119 ($GeMe_3^+$, 100), 105 (Me_2GeH^+, 12), 91 ($PhCH_2^+$, 72), 65 ($C_5H_5^+$, 26); ^{1}H NMR (CCl_4) δ 0.12 (s, 6 H, GeMe), 2.18 (s, 2 H, $PhCH_2$), 6.9–7.2 (m, 5 H, Ph). $Me_{12}Ge_5$: MS (70 eV), *m/e* (relative intensity) 544 (m^+, 6), 529 ($m^+ - Me$, 3), 425 ($m^+ - Me_3Ge$, 14), 323 ($Me_7Ge_3^+$, 30), 308 ($Me_6Ge_3^+$, 9), 221 ($Me_5Ge_2^+$, 45), 206 ($Me_4Ge_2^+$, 12), 529 ($m^+ - Me$, 3), 425 ($m^+ - Me_3Ge$, 14), 323 ($m^+ - Me_5Ge_2$, 30), 308 ($m^+ - Me_6Ge_2$, 9), 221 ($m^+ - Me_7Ge_3$, 45), 206 ($Me_4Ge_2^+$, 12), 191 ($Me_3Ge_2^+$, 9), 176 ($Me_2Ge_2^+$, 3), 119 (Me_3Ge^+, 100), 104 (Me_2Ge, 4) 89 ($MeGe^+$, 16). $PhCH_2GeMe_2Et$: MS (70 eV), *m/e* (relative intensity) 224 (m^+, 4), 209 ($m^+ - Me$, 5), 195 ($m^+ - Et$, 100), 179 ($PhCH_2GeCH_2^+$, 24), 165 ($PhCH_2Ge^+$, 19), 151 ($PhGe^+$, 9), 139 ($GeC_5H_5^+$, 10), 89 ($MeGe^+$, 37), 65 ($C_5H_5^+$, 44). $Et_2Me_6Ge_3$: MS (70 eV), *m/e* (relative intensity) 366 (m^+, 5), 351 ($m^+ - Me$, 2), 337 ($m^+ - Et$, 7), 309 ($Me_6Ge_3H^+$, 10, 220 ($Me_3Ge_2Et^+$, 11), 205 ($Me_3Ge_2CH_2^+$, 18), 191 ($Me_3Ge_2^+$, 11), 133 (Me_2GeEt^+, 53), 119 (Me_3Ge^+, 35), 105 (Me_2GeH^+, 100), 89 ($MeGe^+$, 49).

Thermal Decomposition of 1 in the Presence of Me_2GeBr_2 and $PhCH_2Br$. 1 (162 mg, 0.30 mmol), 143 mg of $PhCH_2Br$ (0.1 mL, 0.84 mmol), and 42 mg of Me_2GeBr_2 (0.02 mL, 0.16 mmol) were heated at 80 °C for 4 h in 4 mL of benzene. As shown by ^{1}H NMR, benzylic products were only formed in traces (<5%).

Photochemical Decomposition of 1 in the Presence of $PhCH_2Br$. 1 (0.29 mg, 0.05 mmol) and 29 mg of $PhCH_2Br$ (0.02 mL, 0.17 mmol) in 0.2 mL of $PhCl/C_6D_6$ were irradiated in a quartz tube in the probe of the ^{1}H NMR spectrometer for 20 min. The products formed are identical with those formed during the thermal decomposition of 1 with $PhCH_2Br$ (^{1}H NMR). The product yields were identical as well.

Thermal Decomposition of 1 in the Presence of $PhCH_2I$. 1 (1.0 g, 1.9 mmol) and 1.2 g of $PhCH_2I$ (0.7 mL, 5.6 mmol) were heated at 75 °C in 10 mL of benzene. $PhCH_3$ (yield ca. 10%; δ 2.10) and $PhCH_2CH_2Ph$ (yield ca. 20%, δ 2.74) were present as products which was demonstrated by adding authentic material to the reaction mixture. After methylation, the presence of $PhCH_2GeMe_3$ and $GeMe_4$ was demonstrated by ^{1}H NMR and GC–MS using authentic material and of Me_8Ge_3, $Me_{10}Ge_4$, and $Me_{12}Ge_5$ by GC–MS (yield ca. 70%). A singlet (δ 2.53) which shows emission during the reaction was assigned to the methylene protons of $PhCH_2GeMe_2I$ (yield 10–20%), a further singlet (δ 1.26 ppm) to the methyl protons of Me_2GeI_2 (yield 10–20%).

Thermal Decomposition of 1 in the Presence of Ph_2CHCl. 1 (1.0 g, 1.9 mmol) and 1.1 g of Ph_2CHCl (1.0 mL, 5.6 mmol) were heated at 75 °C for 4 h in 10 mL of benzene. $Ph_2CHCHPh_2$ was identified by ^{1}H NMR (yield 5–10%, δ 4.69) using authentic material. After methylation, $Ph_2CHGeMe_3$[43] was detected by ^{1}H NMR and GC–MS using authentic material which was prepared from Me_3GeCl and *n*-BuLi/Ph_2CH_2[44] (yield ca. 5%). Me_8Ge_3, $Me_{10}Ge_4$, and $Me_{12}Ge_5$ were identified by GC–MS (yield ca. 5%). $Ph_2CHGeMe_3$: MS (70 eV), *m/e* (relative intensity) 286 (m^+, 4),

---

(41) Lesbre, M.; Mazerolles, P.; Satgé, J. *The Organic Compounds of Germanium*; Wiley: London, 1971.

(42) Mironov, V. F.; Dzhurinskaya, N. G.; Gar, T. K.; Petrov, A. D. *Izv. Akad. Nauk SSSR, Khim. Nauki* **1962**, 460.

(43) Bott, R. W.; Eaborn, C.; Swaddle, T. W. *J. Chem. Soc.* **1963**, 2342.

(44) Brook, A. G.; Warren, C. M.; McGriskin, M. E. *J. Am. Chem. Soc.* **1959**, *81*, 981.

271 (m^+ − Me, 3), 167 (Ph_2CH^+, 39), 119 (Me_3Ge^+, 100), 89 ($MeGe^+$, 8), 77 (Ph^+, 31); ^1H NMR (CCl_4) δ 0.15 (s, 6 H, GeMe), 3.68 (s, 1 H, Ph_2CH), 7.10 (s, 10 H, Ph).

Thermal Decomposition of 1 in the Presence of Ph_3CCl. 1 (30 mg, 0.06 mmol) and 30 mg of Ph_3CCl (0.11 mmol) in 0.5 mL of PhCl were filled into an ESR tube, and the tube was heated up to 75 °C in the cavity of the ESR spectrometer. After some minutes, the trityl radical was observed (a_o = 2.53 G, a_m = 1.14 G, a_p = 2.76 G).

Thermal Decomposition of 1 in the Presence of $CH_2=CHCH_2Cl$. 1 (1.0 g, 1.9 mmol) and 4.7 g of $CH_2=CHCH_2Cl$ (5.0 mL, 61 mmol) were heated at 70 °C for 4 h in 10 mL of benzene. After the benzene was removed and the mixture methylated all volatile compounds including $CH_2=CHCH_2GeMe_3$ were separated from the reaction mixture by distilling in vacuo at room temperature and collecting in a trap cooled with dry ice. The mixture contained ether, $CH_2=CHCH_2GeMe_3$, and traces of benzene. Most of the ether was removed from the mixture by using a microcolumn. The residue was $CH_2=CHCH_2GeMe_3$ with traces of benzene and ether. $CH_2=CHCH_2GeMe_3$[45] was detected by ^1H NMR and GC–MS by using authentic material that was prepared from Me_3GeCl and $CH_2=CHCH_2MgBr$.[41] Yield of $CH_2=CHCH_2GeMe_2Cl$: ca. 80% (^1H NMR). $CH_2=CHCH_2GeMe_3$: MS (70 eV), *m/e* (relative intensity) 160 (m^+, 2), 145 (m^+ − Me, 19), 119 (Me_3Ge^+, 100), 105 (Me_2GeH^+, 16), 89 ($MeGe^+$, 34); ^1H NMR (Et_2O) δ 0.17 (s, 6 H, GeMe), 1.62 (d, 2 H, CH_2), 4.51–4.95 (m, 2 H, $=CH_2$), 5.35–6.10 (m, 1 H, =CH).

Thermal Decomposition of 1 in the Presence of $CH_2=CHCH_2Br$. 1 (1.5 g, 2.8 mmol) and 2.8 g of $CH_2=CHCH_2Br$ (2 mL, 23 mmol) were heated at 25 °C for 4 h in 25 mL of benzene. The volatiles were distilled off at room temperature under reduced pressure, and the residue was stirred in 10 mL of *n*-pentane at room temperature for 1.5 h. The tetraphenylnaphthalene was precipitated, and $CH_2=CHCH_2GeMe_2Br$ was obtained as crude product: ^1H NMR (CCl_4) δ 0.80 (s, 6 H, GeMe), 2.17 (d, 2 H, CH_2), 4.62–5.20 (m, 2 H, $=CH_2$), 5.42–6.27 (m, 1 H, =CH). After methylation and following the same procedure as described in the case of allylic chloride, $CH_2=CHCH_2GeMe_3$ was detected by GC–MS analysis.

Thermal Decomposition of 1 in the Presence of $PhCH_2Br$ and $CH_2=CHCH_2Br$. 1 (200 mg, 0.37 mmol), 172 mg of $PhCH_2Br$ (0.12 mL, 1.00 mmol), and 1.13 mg of $CH_2=CHCH_2Br$ (0.08 mL, 0.93 mmol) were heated at 70 °C in 10 mL of benzene for 4 h. The ^1H NMR spectrum after reaction is identical with that after decomposition of 1 with $CH_2=CHCH_2Br$ alone; benzylic products were not found.

Thermal Decomposition of 1 in the Presence of PhCH=CHCl. 1 (1.0 g, 1.9 mmol) and 0.8 g of PhCH=CHCl (5.8 mmol) were heated at 75 °C for 4 h in 10 mL of benzene. After methylation, the crude product was divided into two fractions by distillation. The first fraction (bp 60 °C at 1 Torr) contained PhCH=CHCl and $PhCH=CHGeMe_3$; the second fraction (bp 180 °C at 0.5 Torr) contained $PhCH=CHGeMe_2GeMe_3$ and $PhCH=CHGeMe_2GeMe_2GeMe_3$. All the products were detected by GC–MS analysis; $PhCH=CHGeMe_3$[46] was detected additionally via ^1H NMR of authentic material prepared from Me_3GeCl and PhCH=CHMgBr.[41] $PhCH=CHGeMe_3$ (*Z* and *E*): MS (70 eV), *m/e* (relative intensity) 222 (m^+, 23), 207 (m^+ − Me, 100), 191 (m^+ − 2 Me − H, 15), 177 (m^+ − 3 Me − H, 9), 151 ($GePh^+$, 23), 119 (Me_3Ge^+, 17), 105 (Me_2GeH^+, 78), 89 ($MeGe^+$, 39), 77 (Ph^+, 24). $PhCH=CHGeMe_2GeMe_3$: MS (70 eV), *m/e* (relative intensity) 324 (m^+, 1), 309 (m^+ − Me, 5), 221 ($Me_5Ge_2^+$, 3), 207 ($Me_2GeC_2H_2Ph^+$, 100), 191 ($MeGeC_2HPh^+$, 8), 151 ($GePh^+$, 11), 119 (Me_3Ge^+, 38), 105 (Me_2GeH^+, 60), 89 ($MeGe^+$, 26). $PhCH=CHGeMe_2GeMe_2GeMe_3$: MS (70 eV), *m/e* (relative intensity) 309 ($Me_2GeMe_2GeC_2H_2Ph^+$, 24), 221 ($Me_5Ge_2^+$, 8), 207 ($Me_2GeC_2H_2Ph^+$, 83), 151 ($GePh^+$, 15), 119 (Me_3Ge^+, 100), 105 (Me_2GeH^+, 54), 89 ($MeGe^+$, 24).

Thermal Decomposition of 1 in the Presence of PhCH=CHBr. 1 (1.5 g, 2.8 mmol) and 0.5 g of PhCH=CHBr (0.4 mL, 3.1 mmol) were heated at 75 °C for 4 h in 20 mL of benzene. After methylation, 300 mg of a clear liquid were obtained by distillation (bp 60 °C at 0.2 Torr) containing a mixture of PhCH=CHBr and $PhCH=CHGeMe_3$ (data, see above). Further insertion products, such as $PhCH=CHGeMe_2GeMe_3$, were not found.

Thermal Decomposition of 1 in the Presence of MeCH=CMeBr. 1 (1.0 g, 1.9 mmol) and 0.8 g of MeCH=CMeBr (0.6 mL, 5.9 mmol) were heated at 75 °C for 4 h in 10 mL of benzene. After methylation, the crude reaction mixture was distilled (bp 100 °C at 15 Torr), and $MeCH=CMeGeMe_2GeMe_3$ and $MeCH=CMeGeMe_2GeMe_2GeMe_3$ were detected by GC–MS. Poly(dimethylgermylene) was identified by ^1H NMR. $MeCH=CMeGeMe_2GeMe_3$: MS (70 eV), *m/e* (relative intensity) 276 (m^+, 4), 261 (m^+ − Me, 11), 221 ($Me_5Ge_2^+$, 2), 207 ($Me_4Ge_2H^+$, 8), 159 ($Me_2GeC_4H_7^+$, 100), 144 ($MeGeC_4H_7^+$, 2), 129 ($GeC_4H_7^+$, 4), 119 (Me_3Ge^+, 50), 105 (Me_2GeH^+, 50), 89 ($MeGe^+$, 25). $MeCH=CMeGeMe_2GeMe_2GeMe_3$: MS (70 eV), *m/e* (relative intensity) 378 (m^+, 5), 363 (m^+ − Me, 6), 261 ($Me_4Ge_2C_4H_7^+$, 27), 206 ($Me_4Ge_2^+$, 21), 191 ($Me_3Ge_2^+$, 6), 159 ($Me_2GeC_4H_7^+$, 75), 129 ($GeC_4H_7^+$, 6), 119 (Me_3Ge^+, 100), 105 (Me_2GeH^+, 100), 89 ($MeGe^+$, 21).

Thermal decomposition of 1 in the presence of CH_2Cl_2, alkyl chlorides $C_nH_{2n+1}Cl$, 1-chlorocyclohexene, and alkyl bromides $C_nH_{2n+1}Br$. 1 (1.0 g, 1.9 mmol) and an approximately threefold excess of the halide were heated at 75 °C for 4 h in 10 mL of benzene. The poly(dimethylgermylene) formed was detected by ^1H NMR (δ 0.4); see "Decomposition of 1 without Scavenger".

Acknowledgment. We thank the Fonds der Chemischen Industrie and the Minister für Wissenschaft und Forschung, Düsseldorf, for support of this work.

Registry No. 1, 76054-64-3; $(Me_2Ge)_n$, 74963-95-4; Me_2GeI_2, 1184-77-6; CCl_4, 56-23-5; C_2Cl_6, 67-72-1; Me_2GeCl_2, 1529-48-2; $Me_2ClGeCCl_3$, 84174-04-9; $Me_2ClGeGeMe_2Cl$, 22702-77-8; $Me_2ClGeGeMe_2GeMe_2Cl$, 22702-79-0; Me_2GeBr_2, 1730-66-1; Me_8Ge_3, 1066-63-3; $Me_{10}Ge_4$, 14938-41-1; $PhCH_2Br$, 100-39-0; $PhCH_2GeMe_2Br$, 90030-12-9; $PhCH_3$, 108-88-3; $PhCH_2CH_2Ph$, 103-29-7; $PhCH_2GeMe_3$, 2848-62-6; $Me_{12}Ge_5$, 13189-68-9; $PhCH_2GeMe_2Et$, 113352-21-9; $Et_2Me_6Ge_3$, 94845-52-0; $PhCH_2I$, 620-05-3; $GeMe_4$, 865-52-1; $PhCH_2GeMe_2I$, 113352-22-0; Ph_2CHCl, 90-99-3; $Ph_2CHCHPh_2$, 632-50-8; $Ph_2CHGeMe_3$, 2848-62-6; Ph_3CCl, 76-83-5; $CH_2=CHCH_2Cl$, 107-05-1; $CH_2=CHCH_2GeMe_3$, 762-66-3; $CH_2=CHCH_2Br$, 106-95-6; $CH_2=CHCH_2GeMe_2Br$, 113352-23-1; PhCH=CHCl, 622-25-3; $PhCH=CHGeMe_3$, 14629-97-1; $PhCH=CHGeMe_2GeMe_3$, 113352-24-2; $PhCH=CHGeMe_2GeMe_2GeMe_3$, 113352-25-3; PhCH=CHBr, 103-64-0; MeCH=CMeBr, 13294-71-8; $MeCH=CMeGeMe_2GeMe_3$, 113352-26-4; $MeCH=CMeGeMe_2GeMe_2GeMe_3$, 113352-27-5; $CHCl_3$, 67-66-3; CH_2Cl_2, 75-09-2; CH_3Cl, 74-87-3; CCl_3Br, 75-62-7; $PhCH_2Cl$, 100-44-7; $CH_2=CHCl$, 75-01-4; $CH_2=CHBr$, 593-60-2; $PhCHGeMe_2Cl$, 113352-28-6; $Me_2BrGeCCl_3$, 113352-29-7; Ph_2CH_2, 101-81-5; tetraphenylnaphthalene, 751-38-2; 1-chlorocyclohexene, 930-66-5.

---

(45) Petrov, A. D.; Mironov, V. F.; Dolgii, I. E. *Isv. Akad. Nauk SSSR, Khim. Nauki* **1956**, 1146.

(46) Nametkin, N. S.; Durgar'yan, S. G.; Tikhonova, L. I. *Dokl. Akad. Nauk SSSR* **1967**, *172*, 867.