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Addition Reactions of Tris(trimethylsilyl)germyl Radicals to Unsaturated Compounds. An EPR and Product Study

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Tris(trimethylsilyl)germyl radicals, $(TMS)_3Ge^•$, thermally or photochemically generated by means of suitable radical initiators, were reacted with a number of unsaturated compounds. The preparative scale reaction of $(TMS)_3GeH$ with a variety of alkynes proceeded stereo- and regioselectively affording exclusively 2-alkenylgermanes in excellent chemical yields. In the analogous reactions with alkenes, no addition products were obtained except in the case of 4-vinylpyridine. This behavior is explained in terms of the reversibility of germyl radical addition to olefines. The reaction with arylalkenes, ketones, quinones, azines, and nitroalkanes was instead carried out in the cavity of an EPR spectrometer. In most cases the corresponding radical adducts were observed; however, quite often the intensity of the spectra was lower than expected and with azines no EPR signals could be detected. These results have been interpreted as an indication that the addition reaction of tris(trimethylsilyl)germyl radicals to multiple bonds is less exothermic than that of trialkylgermyl radicals. With some of the investigated compounds, the addition of $(TMS)_3Ge^•$ is thermoneutral or even endothermic and is therefore readily reversible.

Introduction

The reactions of tris(trimethylsilyl)germane with a variety of organic derivatives such as chlorides, bromides, iodides, thiono esters, isocyanides, selenides, and nitroalkanes in the presence of α,α′-azoisobutyronitrile have recently been described.[2] These compounds were all reduced by the organometallic hydride via a free radical chain mechanism involving the intermediacy of tris(trimethylsilyl)germyl radicals (eqs 1 and 2), as suggested

$$R^• + (TMS)_3GeH \longrightarrow RH + (TMS)_3Ge^• \qquad (1)$$

$$RX + (TMS)_3Ge^• \longrightarrow R^• + (TMS)_3GeX \qquad (2)$$

by the fact that the reactions did not proceed in the absence of radical initiators and were retarded by the free radical scavengers 2,6-di-*tert*-butyl-4-methylphenol and 2,6-tetramethylpiperidinyl-1-oxyl (TEMPO).[3]

Furthermore, the rate constant of step 1 was found to be 3.1×10^6 M^{-1} s^{-1} at 25 °C.[2] This result indicates that $(TMS)_3GeH$ is one of the most efficient hydrogen atom donors toward alkyl radicals among the group 14 hydrides.[4,5] To have a more general picture of the homolytic reactivity of tris(trimethylsilyl)germane, we performed additional product studies on its reactions with alkynes and alkenes and carried out an EPR investigation on the reaction of $(TMS)_3Ge^•$ radicals and unsaturated organic compounds such as aromatic olefins, ketones, quinones, azines, and nitroalkanes, which, when reacted with the analogous trialkylgermyl and triphenylgermyl radicals, give rise to paramagnetic adducts easily detectable by EPR spectroscopy.[6]

Results

Adducts of Alkenes, Carbonyl Compounds, and Azines. Tris(trimethylsilyl)germyl radicals were generated inside the EPR cavity, in the temperature range 292−350 K, either by photolytic cleavage of $(TMS)_3GeGe(TMS)_3$ or by hydrogen abstraction from the corresponding germanium hydride by *tert*-butoxy radicals produced by photolysis of di-*tert*-butyl peroxide or by thermal decomposition of di-*tert*-butyl hyponitrite in benzene solutions.

The reaction of $(TMS)_3Ge^•$ radicals with 1,1-diphenylethylene and with 9-methylenanthrone gave rise to detectable EPR spectra of the expected adducts interpretable in terms of hyperfine splitting constants similar to those previously reported for the analogous adducts of triphenylgermyl radicals.[7,8]

In the case of 9-methylenanthrone, where attack may in principle occur at either of the two reaction sites, i.e., the exocyclic C═C and C═O double bonds, the reaction with $(TMS)_3Ge^•$ radicals exclusively afforded the adduct

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(1) Deleted in proof.

(2) Chatgilialoglu, C.; Ballestri, M. *Organometallics* **1995**, *14*, 5017.

(3) The most popular group 14 organometallic hydrides as radical-based reducing agents are Bu_3SnH and $(TMS)_3SiH$. For reviews regarding Bu_3SnH, see: (a) Neumann, W. P. *Synthesis* **1987**, 665. (b) Curran, D. P. *Synthesis* **1988**, 417, 489. For reviews regarding $(TMS)_3SiH$, see: (a) Chatgilialoglu, C. *Acc. Chem. Res* **1992**, *25*, 188. (b) Chatgilialoglu, C.; Ferreri, C.; Gimisis, T. In: *The Chemistry of Organic Silicon Compounds, Part 3*; Rappoport, Z., Apeloig, Y., Eds; Wiley: Chichester, 1997.

(4) Newcomb, M. *Tetrahedron* **1993**, *49*, 1151.

(5) Chatgilialoglu, C. *Chem. Rev.* **1995**, *95*, 1229.

(6) (a) Krusic, P. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1969**, *91*, 6161. (b) Krusic, P. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1971**, *93*, 846. (c) Kawamura, T.; Kochi, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 648. (d) Kawamuta, T.; Meakin, P.; Kochi, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 972. (d) Cooper, J.; Hudson, A.; Jackson, R. A. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1933. (f) Schroeder, B; Neumann, W. P.; Hillgartner, H. *Chem. Ber.* **1974**, *107*, 3494. (g) Alberti, A.; Pedulli, G. F. *Tetrahedron Lett.* **1978**, 3283. (h) Ingold, K. U.; Lusztyk, J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 343.

(7) Leardini, R.; Tundo, A.; Zanardi, G.; Pedulli, G. F. *J. Chem. Soc., Perkin Trans. 2* **1983**, 285.

(8) Alberti, A.; Pedulli, G. F.; Leardini, R.; Tundo, A.; Zanardi, G. *Tetrahedron* **1986**, 2533.

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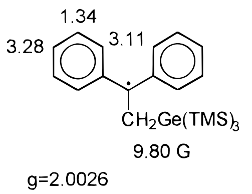
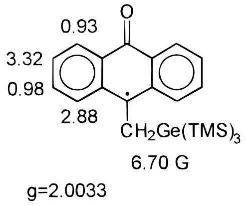
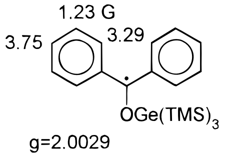
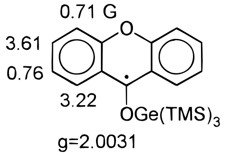
arising from addition to the methylene carbon, similar to what has been observed with silyl and triphenylgermyl radicals.[8] The preferential formation of the adduct to carbon rather than to oxygen, which is expected to be thermodynamically more stable, indicates that the addition of $(TMS)_3Ge^{\bullet}$ to 9-methylenanthrone undergoes kinetic control.[9]

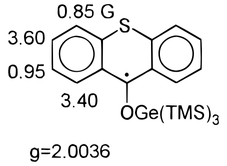


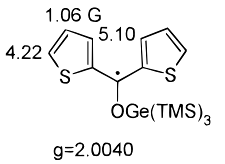


The reaction of $(TMS)_3Ge^{\bullet}$ with diaryl ketones gave rise to EPR spectra of moderate intensity, indicative of steady-state concentrations of radical adducts lower than those observed when adding $(TMS)_3Si^{\bullet}$ or $Et_3Si^{\bullet}$ radicals to the same compounds.[10,11] The hyperfine splitting constants of these radicals are close to those reported for the related adducts of other germyl and silyl radicals and have been assigned on a similar basis.[11]

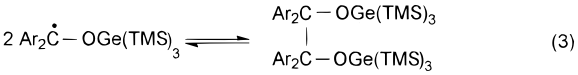








When tris(trimethylsilyl)germane was the source of germyl radicals, the EPR spectra of the adducts became weaker with increasing temperature. This behavior is in contrast with that shown by the analogous Et_3Si or Ph_3Si adducts, which instead gave stronger signals at high temperatures where the equilibrium between the monomeric radicals and their diamagnetic dimers (eq 3) is more shifted to the left.



$$2\,Ar_2\dot{C}-OGe(TMS)_3 \rightleftharpoons \begin{array}{c} Ar_2C-OGe(TMS)_3 \\ | \\ Ar_2C-OGe(TMS)_3 \end{array} \qquad (3)$$

The low concentration of the $R_2C(^{\bullet})-OGe(TMS)_3$ adducts observed at high temperature can be attributed to their short lifetime, presumably due to the fast reduction of the adduct by the germanium hydride via hydrogen transfer. Actually the room-temperature rate constant for hydrogen abstraction from $(TMS)_3GeH$ by primary alkyl radicals is quite large (3.1×10^6 M^{-1} s^{-1})[2] when compared with that from triethylsilane (6.3×10^2 M^{-1} s^{-1}), for example.[12]

Strong EPR signals were observed however when $(TMS)_3Ge^{\bullet}$ radicals were reacted with 2,6-di-*tert*-butyl-*p*-benzoquinone and duroquinone; in the latter case (see Figure 1), we could also measure the hyperfine coupling at the three equivalent silicon atoms in the γ position (^{29}Si, n.a. 4.7%, $a_{Si} = 1.10$ G). Weaker spectra were observed for the adducts of 1,4-benzoquinone and 1,4-naphthoquinone.

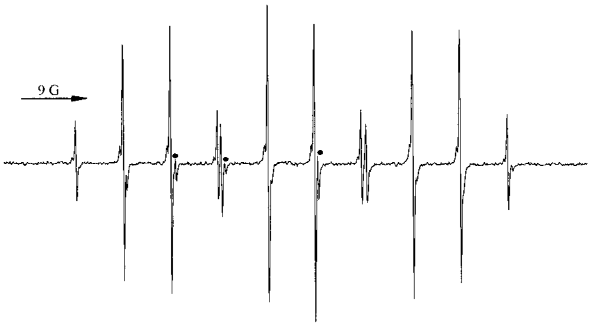
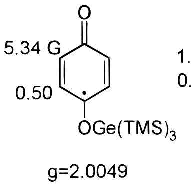
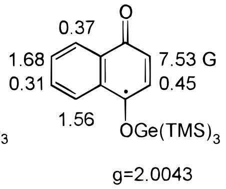
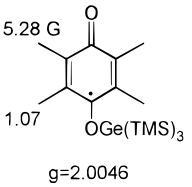
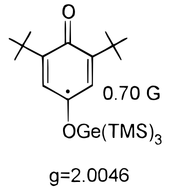


Figure 1. EPR spectrum of the germiloxy nitroxide **1a** obtained by photolysis of *tert*-butylbenzene solutions of di-*tert*-butyl peroxide, $(TMS)_3GeH$, and $MeNO_2$ at room temperature. Marks (●) indicate some of the signals due to the secondary nitroxide **2a**.









An attempt was made to react tris(trimethylsilyl)-germyl radicals with pyrazine, 2,6-dimethylpyrazine, and tetramethylpyrazine, but in no case could the EPR spectra of the resulting adducts be detected. This behavior is in contrast with that of the related triphenylgermyl radicals, which were readily trapped by pyrazine and 2,6-dimethylpyrazine at room temperature to give stable adducts.[13]

Adducts to Nitroalkanes. The photochemical reactions between tris(trimethylsilyl)germane (0.01 M) and the various nitroalkanes (0.01 M), i.e., nitromethane, nitroethane, 1-nitrohexane, 2-nitropropane, and 2-methyl-2-nitropropane, were carried out in *tert*-butylbenzene or in toluene in the presence of di-*tert*-butyl peroxide (ca. 1 M). In all cases the observed EPR spectra contained signals from two or more paramagnetic species with relative concentrations which depend on temperature, light intensity, and amount of the radical initiator present in solution (Table 1).

A similar behavior was observed when reacting tris-(trimethylsilyl)silane with nitroalkanes under similar experimental conditions;[14] also in this case two nitroxides were detected, one being identified as the adduct of $(TMS)_3Si^{\bullet}$ to the nitroalkane, $RN(O^{\bullet})OSi(TMS)_3$, and the other having structure $RN(O^{\bullet})OSi(TMS)_2OTMS$. This

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(9) Alberti, A.; Chatgilialoglu, C.; Pedulli, G. F.; Zanirato, P. *J. Am. Chem. Soc.* **1986**, *108*, 4993.

(10) Alberti, A.; Chatgilialoglu, C. *Tetrahedron* **1990**, *46*, 3963.

(11) Alberti, A.; Pedulli, G. F. *Rev. Chem. Intermed.* **1987**, *8*, 207 and references therein.

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Table 1. EPR Spectral Parameters (hfs constants in gauss = 10^{-4} T) of the Germyloxy Nitroxides $RN(O^•)OGe(TMS)_3$ (1a–e) and $RN(O^•)OGe(TMS)_2OTMS$ (2a–e)

R	radical	a_N	$a_{(R)}$	a_{other}	g-factor
CH_3	**1a**	28.28	9.14 (3H)	1.10 ($3^{29}Si$)	2.0057
	2a	28.02	9.70 (3H)		2.0055
CH_2CH_3	**1b**	28.25	8.51 (2H), 0.34 (3H)		2.0056
	2b	27.90	9.20 (3H), 0.28 (3H)		2.0054
$(CH_2)_5CH_3$	**1c**	28.41	8.53 (2H)		2.0055
	2c	28.00	9.30 (2H)		2.0053
$CH(CH_3)_2$	**1d**	28.33	5.21 (1H), 0.25 (6H)		2.0055
	2d	28.04	6.50 (1H), 0.25 (6H)		2.0053
$C(CH_3)_3$	**1e**	28.48			2.0054
	2e	28.21			2.0053

arises from fragmentation at the N–O bond of the primarily formed nitroxide, rearrangment of the resulting $(TMS)_3SiO^•$ radical to $(TMS)_2Si(^•)OTMS$, and addition of the latter to RNO_2. The rearrangment of the $(TMS)_3GeO^•$ (eq 7) is an example of a 1,2-shift of a silyl group from germanium to oxygen analogous to the well-documented 1,2-shifts from silicon to oxygen and from silicon to sulfur.[5]

In the present case the two species were identified by analogy as $RN(O^•)OGe(TMS)_3$ (**1**) and $RN(O^•)OGe(TMS)_2$-OTMS (**2**).

$$Me_3CO^• + (TMS)_3Ge\text{-}H \longrightarrow Me_3COH + (TMS)_3Ge^• \tag{4}$$

$$(TMS)_3Ge^• + RNO_2 \longrightarrow \underset{\mathbf{1}}{RN(O^•)OGe(TMS)_3} \tag{5}$$

$$RN(O^•)OGe(TMS)_3 \longrightarrow RN{=}O + (TMS)_3GeO^• \tag{6}$$

$$(TMS)_3GeO^• \longrightarrow (TMS)_2\dot{G}eOTMS \tag{7}$$

$$(TMS)_2\dot{G}eOTMS + RNO_2 \longrightarrow \underset{\mathbf{2}}{RN(O^•)OGe(TMS)_2OTMS} \tag{8}$$

Other radical species observed under photolysis include the *tert*-butoxy alkyl nitroxide (**3**) formed by addition of $Me_3CO^•$ to the nitrosoalkane (eq 9) resulting from reaction 6, as well as the dialkyl nitroxide (**4**) arising from addition to the nitrosoalkane (eq 11) of the alkyl radical formed in the photofragmentation of RN=O (eq 10).

$$Me_3CO^• + RN{=}O \longrightarrow \underset{\mathbf{3}}{RN(O^•)OCMe_3} \tag{9}$$

$$RN{=}O \xrightarrow{h\nu} R^• + NO \tag{10}$$

$$R^• + RN{=}O \longrightarrow \underset{\mathbf{4}}{R_2NO^•} \tag{11}$$

The alkyl radical $R^•$, and thus the adduct **4**, could also arise from the fragmentation of nitroxide **1** or **2** at the carbon–nitrogen bond; this process, although unfavored, may be of some importance with resonance-stabilized alkyl radicals (vide infra).

The more thoroughly studied nitroalkane was nitromethane, since it gave the simplest and most readily interpretable EPR spectra (see Figure 1), even in the presence of several radical species. When photolyzing deoxygenated *tert*-butylbenzene solutions of di-*tert*-butyl peroxide, $(TMS)_3GeH$, and $MeNO_2$ at room temperature, the resulting EPR spectrum contained signals of **1a** (see Table 1) with strong satellite lines corresponding to the coupling of the unpaired electron with three equivalent ^{29}Si atoms (a_{Si} = 1.10 G) and those of the secondary nitroxide **2a**. The concentration of the latter increased reversibly by increasing the temperature. The same species were also present when the thermal initiator *tert*-butyl hyponitrite was used instead of $Me_3COOCMe_3$ and light was used as the source of *tert*-butoxy radicals. The relative amount of **2a** also increased upon increasing the concentration of the initiator or the light intensity. At ca. 60 °C a third species, identified on the basis of its spectral parameters[14] as the methyl *tert*-butoxy nitroxide, $MeN(O^•)OCMe_3$ (**3a**), became visible. Adduct **1a** decayed at 298 K following first-order kinetics with a measured rate constant $k_4 = 4.7 \times 10^{-2}\ s^{-1}$ (see Figure 2).

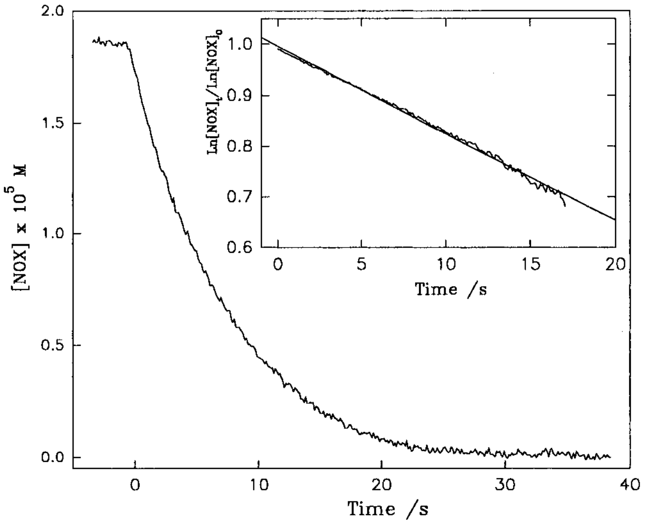

Figure 2. Decay of the germiloxy nitroxide **1a** produced by reaction of $MeNO_2$ with $(TMS)_3Ge^•$ radicals at 298 K. Insert: plot of $\ln[\mathbf{1a}]_0/\ln[\mathbf{1a}]_t$ vs time.

The photolytic reaction of the germane with nitroethane or nitrohexane in the presence of $(Me_3CO)_2$ led to the formation of both primary (**1b** or **1c**) and secondary (**2b** or **2c**) nitroxide adducts (see Table 1). At room temperature the decay of **1b** and of **1c** followed mixed first and second-order kinetics, thus suggesting that the disproportionation reaction of the nitroxides is competitive with their fragmentation.[15] However, at higher temperature first-order decay was observed with rate constants k_4 of $8.3 \times 10^{-2}\ s^{-1}$ for **1b** and $7.8 \times 10^{-2}\ s^{-1}$ for **1c** at 313 K.

With 2-nitropropane and 2-methyl-2-nitropropane, the primary and secondary germyloxy nitroxides were visible, but overlap of the lines from the two species prevented any attempt to follow the decay of **1d** and **1e**. It was possible, however, to measure the rate constant for the first-order decay of the signal resulting from the sum of those from **1e** and **2e** as $k_{EPR} = 1.1 \times 10^{-3}\ s^{-1}$ at 298 K. It is worth pointing out that weak EPR lines due to the alkyl nitroxides **4d** and **4e**, which increased with the irradiation time, were also detected.

Hydrogermylation of Alkenes and the Role of the Reversible Addition. The hydrogermylation of a variety of alkenes was attempted by using tris(trimethylsilyl)germane and AIBN (α,α′-azoisobutyronitrile) as radical initiator in toluene at 80–85 °C under argon atmosphere. The following alkenes were used: vinylcyclohexane, 4,4-dimethylpent-1-ene, vinyltrimethylsilane, vinylsilatrane, 2,3-dihydrofuran, 3,4-dihydrofuran, and 4-vinylpyridine (**5**). The last one afforded the addition product with a good yield (Table 2), but all the other

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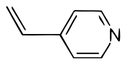
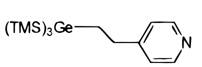
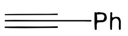
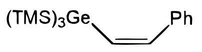
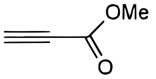
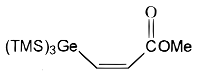
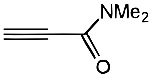
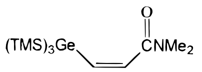
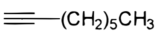
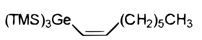
(15) Adamic, K.; Bowman, D. F.; Gillan, T.; Ingold, K. U. *J. Am. Chem. Soc.* **1971**, *93*, 902.

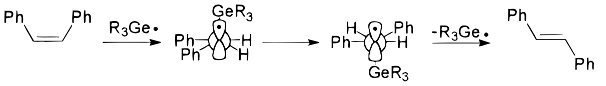
Table 2. Hydrogermylation of Some Unsaturated Compounds by Tris(trimethylsilyl)germane Hydride

No	Substrate[a]	Reaction Conditions T, °C / t, h	Product	Yield[c] %
5		82[b] / 2		99
6		25 / 0.5		98
7		25 / 0.5		98
8		25 / 1		88
9		82[b] / 1		95

[a] [substrate]:[hydride] = 2:1. [b] In the presence of AIBN (10 mol %). [c] Yield based on hydride after isolation of pure compounds.

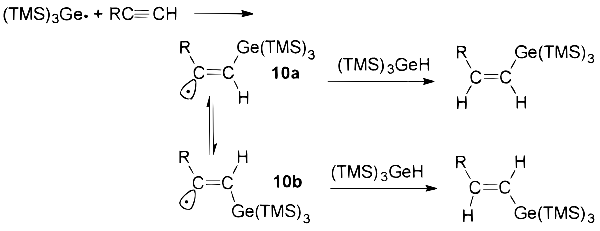
alkenes did not react with $(TMS)_3GeH$ even under 12 h heating at 82 °C. We attribute this behavior to the reversibility of the attack of the $(TMS)_3Ge^•$ radicals to the olefinic double bond; only with 4-vinylpyridine is the intermediate adduct, being resonance stabilized, long-lived enough to undergo the subsequent hydrogen transfer from the germane.

To provide unambiguous evidence of the reversibility of the attack of $(TMS)_3Ge^•$ radicals to alkenes, the following experiment was performed. *cis*-Stilbene (1 M) was dissolved in *tert*-butyl benzene, where this isomer is highly soluble, and was then photolyzed either in the presence or in the absence of a small amount of $(TMS)_3GeGe(TMS)_3$. Irradiation for ca. 1 h of the sample containing the digermane produced a precipitate of *trans*-stilbene, which is slightly soluble in *tert*-butylbenzene, while the other solution remained transparent during the irradiation. This indicates that the *cis*–*trans* photoisomerization of stilbene, which is also known to occur,[16] is much slower than the isomerization induced by $(TMS)_3Ge^•$ radicals. The latter takes place by initial addition of germyl radicals to the olefinic double bond (eq 12) followed by fast isomerization of the resulting adduct to the more stable conformer having the phenyl rings almost *trans* and by elimination of the germyl radicals to give *trans*-stilbene.[17]



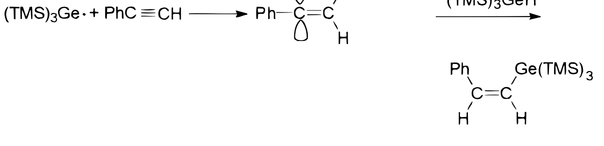
(12)

Hydrogermylation of Alkynes. Carefully degassed solutions of acetylenic derivatives in toluene were mixed with $(TMS)_3GeH$ at room temperature. With phenylacetylene (**6**), methyl propiolate (**7**), and *N*,*N*-dimethylpropiolamide (**8**) the reactions proceeded smoothly in less than 1 h without the addition of radical initiators. We believe that the "adventurous radicals" present in the reaction mixture are sufficient to initiate these processes which probably have very long chains.[18] However, for 1-octyne (**9**) heating at 82 °C in the presence of AIBN was necessary. With all alkynes **6**–**9** the reaction afforded hydrogermylation products in high yields, the addition of the germyl radical taking place at the less crowded end of the triple bond (Table 2). A remarkable feature of this reaction is its stereospecificity, as only the thermodynamically less stable *Z*-isomeric alkene (eq 13) was obtained in all cases. This behavior was however predictable on the basis of the results reported in the literature[19,20] regarding the homolytic addition of hydrides and hydrocarbons to triple bonds. In fact, this reaction is known to occur with increasing stereoselectivity by increasing the size of the entering radical. This is because the hydrogen transfer reaction from the hydride to the two equilibrating σ vinyl radicals **10a** and **10b** obtained from **7**, **8**, and **9** occurs preferentially to **10a** rather than to **10b** due to the presence of the bulky $(TMS)_3Ge$ group syn to the radical center in the **10b**.



(13)

Similarly, in the phenyl-substituted vinyl radical from phenylacetylene (**6**) (eq 14), which is known to have π



(14)

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(18) The "adventurous radicals" may be generated by sunlight or traces of molecular oxygen.

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symmetry,[21] the approach of the hydride to afford the alkene takes place anti to the bulky organometallic group for steric reasons.

Discussion

The experimental results obtained in the course of the present study indicate that the addition of tris(trimethylsilyl)germyl radicals to unsaturated compounds is reversible with several of the investigated derivatives. Thus, while the hydrogermylation reaction takes place readily with alkynes, no hydrogermylation products were obtained from alkenes except with 4-vinylpyridine, which gives a resonance stabilized intermediate adduct by radical addition. It is worth pointing out that $(TMS)_3GeH$, like Bu_3SnH,[22] Ph_3GeH,[23] and $(TMS)_3SiH$[20] add to C−C triple bonds to give mainly the corresponding (*Z*)-alkenyl derivatives (kinetic control). However, both $Bu_3Sn^\bullet$ and $Ph_3Ge^\bullet$ radicals are effective to isomerize their adducts into thermodynamically more stable (*E*)-isomer, whereas $(TMS)_3Ge^\bullet$ like $(TMS)_3Si^\bullet$ were found to be unreactive toward their (*Z*)-vinyl adducts.[24] This behavior is probably due to steric hindrance.

Furthermore, when the reactions were performed inside the EPR cavity, no radical adducts were detected with some of the substrates which are instead known to afford adducts of moderately long life by attack of other group 14 centered radicals. The effect is especially manifest in azine derivatives, none of which afforded radical adducts; we attribute the failure to observe stable adducts to the weakness of the N−Ge bond formed by $(TMS)_3Ge^\bullet$ radicals.

The reversible addition of tris(trimethylsilyl)germyl radicals to unsaturated compounds is not unexpected in view of the fact that the bond between germanium and the organic moiety is usually weaker in germanium derivatives than those involving the lighter elements of the same group. In fact, it is known that the addition of trialkylgermyl radicals to some of the investigated compounds is nearly thermoneutral.[25] The reversibility of the radical attack should be even more important for $(TMS)_3Ge^\bullet$ radicals than for trialkylgermyl radicals, since the replacement of an alkyl with a Me_3Si groups in $R_3Ge^\bullet$ radicals is expected to produce a weakening of the bond between germanium and the substrate in the intermediate adducts, similarly to what has been reported for the Ge−H bond in the related germanium hydrides.[2] Actually, the rate constant for hydrogen abstraction from germanes by primary alkyl radicals undergoes a 33-fold increase on passing from Bu_3GeH to $(TMS)_3GeH$.[2] By assuming that the value of log *A* remains constant in the two reactions, this change corresponds to a reduction in the activation energy of 2.1 kcal mol^{-1}. When considering that in the corresponding silanes, i.e., Et_3SiH and $(TMS)_3SiH$, which are characterized by Si−H bond dissociation energy values differing by 11 kcal mol^{-1},[5] the difference in activation energy for hydrogen abstraction is 3.5 kcal mol^{-1}, we can roughly estimate the strength of the $(TMS)_3Ge$−H bond to be lower than that of the Bu_3Ge−H bond by ca. 6 kcal mol^{-1}. Since the BDE value reported[26] for the latter compound is equal to 82.6 kcal mol^{-1}, the strength of the germanium hydrogen bond in tris(trimethylsilyl)germaniun hydride should be about 77 kcal mol^{-1}.

Since a similar reduction of BDE is also expected for the Ge−C and Ge−N bonds on passing from trialkylgermyl to tris(trimethylsilyl)germyl radicals, it is reasonable that those addition reactions which are slightly exothermic when the attacking species is $R_3Ge^\bullet$ become thermoneutral or even exothermic with $(TMS)_3Ge^\bullet$ radicals.

As far as the fragmentation of the $(TMS)_3Ge^\bullet$ adducts to nitroalkanes is concerned, the present results indicate that the cleavage of the oxygen−nitrogen bond in the $MeN(O^\bullet)OGe(TMS)_3$ nitroxide takes place more slowly than in the corresponding $(TMS)_3Si^\bullet$ adducts. On the other hand, product studies have shown that resonance-stabilized nitroalkanes can be reduced by using $(TMS)_3Ge$−H,[2] while no reduction is observed with $(TMS)_3SiH$.[14] These two experimental results are consistent in light of the following considerations. The possibility to reduce nitroalkanes with metal hydrides to the corresponding hydrocarbons is related to the ease by which the nitroxide intermediates fragment either at the carbon−nitrogen or at the nitrogen−oxygen bond. Under the assumption that the rate of cleavage at the C−N bond does not depend on the nature of the organometallic group, it is reasonable to admit that the faster the fragmentation of the N−O bond is, the lower the yield of the hydrodenitration reaction will be.

Experimental Section

Materials. Di-*tert*-butyl hyponitrite,[27] 9-methylenanthrone[9] hexakis(trimethylsilyl) digermane,[28] and *N*,*N*-dimethylpropiolamide[29] were prepared according to literature. All other materials were commercially available (Aldrich Co.).

EPR Measurements. The EPR spectra were recorded on a Bruker ESP 300 spectrometer equipped with an NMR gaussmeter for field calibration and a Hewlett-Packard 5350B microwave frequency counter for the determination of the *g*-factors, which were corrected with respect to that of perylene radical cation in concentrated H_2SO_4 ($g = 2.00258$).

Photolysis was carried out by focusing the unfiltered light from a 500 W high-pressure mercury lamp on the EPR cavity. Digitized EPR spectra were transferred to an AT-486 (33 MHz) personal computer, to analyze complex spectra by means of numerical techniques. The temperature was controlled with a standard variable temperature accessory and was monitored before and after each run with a copper−constantan thermocouple.

General Procedure for Hydrogermylation of Alkanes and Alkynes (Table 2). To a solution of substrate (1 mmol) in dry toluene (1 mL), stirred in a Wheaton microreactor under an argon atmosphere, was added $(TMS)_3GeH$ (0.5 mmol) in one portion through a microsyringe. Heating of the solution at 82 °C with 10% AIBN was in some cases required (see Table 2). The reaction was monitored by GC, and after completion, the solvent was evaporated in vacuo; the crude reaction mixture was then flash chromatographed on silica gel giving 95−99% yield of the products.

(*Z*)-1-[Tris(trimethylsilyl)germyl]styrene. GC/MS *m*/*z* 396 (M^+), 220. ^1H NMR (200 MHz, $CDCl_3$): δ 7.41 (d, 1H, $J = 13.6$ Hz), 7.15−7.35 (m, 5H), 6.12 (d, 1H, $J = 13.6$ Hz), 0.25 (s, 27H). IR (neat), cm^{-1}: 1592, 1570, 1490. Anal. Calcd for $C_{17}H_{34}GeSi_3$: C, 51.65; H, 8.67. Found: C, 51.91; H, 8.81.

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(*Z*)-1-[Tris(trimethylsilyl)germyl]octene. GC/MS *m*/*z* 404 (M^+), 73 (TMS). ^1H NMR (200 MHz, $CDCl_3$): δ 6.33 (dt, 1H, $J = 12.0$ Hz, $J = 6.8$ Hz), 5.67 (dt, 1H, $J = 12.0$ Hz, 1.4 Hz), 2.01 (m, 2H), 1.28 (m, 8H), 0.88 (m, 2H), 0.21 (s, 27H). IR (neat), cm^{-1}: 1600. Anal. Calcd for $C_{17}H_{42}GeSi_3$: C, 50.62; H, 10.49. Found: C, 50.85; H, 10.57.

Methyl (*Z*)-3-[Tris(trimethylsilyl)germyl]propenoate. GC/MS *m*/*z* 378 (M^+), 363 ($M^+ - 15$), 73 (TMS). ^1H NMR (200 MHz, $CDCl_3$): δ 7.02 (d, 1H, $J = 12.8$ Hz), 6.63 (d, 1H, $J = 12.8$ Hz), 3.69 (s, 3H), 0.22 (s, 27H). IR (neat), cm^{-1}: 1720 ($\nu_{C=O}$), 1638, 1532. Anal. Calcd for $C_{13}H_{32}GeO_2Si_3$: C, 41.39; H, 8.55. Found: C, 41.76; H, 8.67.

***N*,*N*-Dimethyl (*Z*)-3-[Tris(trimethylsilyl)germyl]propenamide**. GC/MS *m*/*z* 391 (M^+), 376 ($M^+ - 15$), 73 (TMS). ^1H NMR (200 MHz, $CDCl_3$): δ 6.92 (d, 1H, $J = 13.4$ Hz), 6.54 (d, 1H, $J = 13.4$ Hz), 3.01 (s, 3H), 2.91 (s, 3H), 0.20 (s, 27H). IR (neat), cm^{-1}: 1645 ($\nu_{C=O}$), 1598, 1580. Anal. Calcd for $C_{14}H_{35}GeNOSi_3$: C, 43.08; H, 9.04. Found: C, 43.31; H, 9.16.

4-[2′-[Tris(trimethylsilyl)germyl]ethyl]pyridine. GC/MS *m*/*z* 399 (M^+), 73 (TMS). ^1H NMR (200 MHz, $CDCl_3$): δ 8.49 (m, 2H), 7.11 (m, 2H) 2.71 (m, 2H), 1.24 (m, 2H), 0.24 (s, 27H). IR (neat), cm^{-1}: 1600 ($\nu_{C=N}$), 1560 (Py), 1495 (Py). Anal. Calcd for $C_{16}H_{35}GeNSi_3$: C, 48.25; H, 8.86; N, 3.52. Found: C, 48.83; H, 8.93; N, 4.16. Due to the low stability of this compound, we were unable to obtain satisfactory analytical data.

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