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Generation and reactions of metal-free trialkylgermyl anions from silylgermane and digermane ☆

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Abstract

Metal-free trimethylgermyl anions were prepared by cleavage of the Ge–Si bond of (trimethylsilyl)trimethylgermane and the Ge–Ge bond of hexamethyldigermane with tetrabutylammonium fluoride (TBAF) in hexamethylphosphoric triamide (HMPA). The reactions of metal-free germyl anions produced by a catalytic or one-equivalent amount of TBAF with organic halides carbonyl compounds, and α,β-unsaturated ketones were examined.

Keywords: Silicon; Germanium; Germyl anions; Tetrabutylammonium fluoride; Organic halides; Group 14

1. Introduction

Triorganogermyl anions, the heavy analogs of carbanions, have recently been recognized as useful synthetic nucleophiles, and are effective for the introduction of triorganogermyl group into organic halides, metal halides, carbonyl compounds, etc. [1–4]. Generation of triorganogermyl anions hitherto studied was limited to reduction of Ge–X or Ge–Ge bond with alkali metals or other metals. The reactivity of germyl anions thus prepared should be understood in association with the counter ion. We describe here the first generation of metal-free trialkylgermyl anions by cleavage of Ge–Si bond of silylgermane or Ge–Ge bond of digermane with tetrabutylammonium fluoride (TBAF) in hexamethylphosphoric triamide (HMPA), and reactions of the metal-free germyl anions thus produced by a catalytic or one equivalent amount of TBAF with organic halides, carbonyl compounds, and α,β-unsaturated ketones.

2. Results and discussion

2.1. Preparation and spectroscopically identification

(Trimethylsilyl)trimethylgermane ($Me_3SiGeMe_3$) and TBAF were dissolved in HMPA at room temperature for 5 min to give a yellow solution of metal-free trimethylgermyl anion ($[Bu_4N]^+[GeMe_3]^-$, **1**) (λ_{max} 325 nm). ^1H NMR analysis (HMPA as a standard) of **1** gave a singlet at δ −0.38 with Bu_4N^+.

$$Me_3Ge{-}EMe_3 + [Bu_4N]^+[F]^- \longrightarrow \underset{\mathbf{1}}{[Me_3Ge]^-[NBu_4]^+} + Me_3EF$$

E = Si, Ge

In this way, a metal-free germyl anion **1** was formed quantitatively. This was proved by decomposition of the yellow solution with water and subsequent GLC determination.

The absorption maximum of **1** implies that the germyl anion has a highly ionic character in comparison with $Me_3SiGeMe_3$ ($\lambda_{max} > 200$ nm). Hence, in a qualitative way, the absorption band observed may be stated to arise from the nonbonding orbital of the germyl anion (HOMO) to the lowest antibonding orbital of germa-

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☆ Dedicated to Professor Hideki Sakurai upon his retirement from Tohoku University and in honor of his contribution to organometallic chemistry and silicon chemistry.

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TABLE 1. Reactions of metal-free trimethylgermyl anion with organic halides [a]

Halide RX	Products (Yield/%) [b]	
	R-GeMe$_3$	R-H
^{n}BuCl	^{n}BuGeMe$_3$ (3.7)	^{n}BuH [c]
^{n}BuBr	^{n}BuGeMe$_3$ (34.3)	^{n}BuH [c]
^{n}BuI	^{n}BuGeMe$_3$ (36.7)	^{n}BuH [c]
C_6H_5F	$C_6H_5GeMe_3$ (trace)	C_6H_6 (0)
C_6H_5Cl	$C_6H_5GeMe_3$ (5.4)	C_6H_6 (1.6)
C_6H_5Br	$C_6H_5GeMe_3$ (45.3)	C_6H_6 (5.3)
C_6H_5I	$C_6H_5GeMe_3$ (46.2)	C_6H_6 (5.8)
o-MeC_6H_4Cl	*o*-$MeC_6H_4GeMe_3$ (5.2)	C_6H_5Me (1.2)
m-MeC_6H_4Cl	*m*-$MeC_6H_4GeMe_3$ (4.9)	C_6H_5Me (trace)
p-MeC_6H_4Cl	*p*-$MeC_6H_4GeMe_3$ (5.0)	C_6H_5Me (trace)
o-MeC_6H_4Br	*o*-$MeC_6H_4GeMe_3$ (42.5)	C_6H_5Me (6.9)
m-MeC_6H_4Br	*m*-$MeC_6H_4GeMe_3$ (38.2)	C_6H_5Me (5.8)
p-MeC_6H_4Br	*p*-$MeC_6H_4GeMe_3$ (36.5)	C_6H_5Me (6.5)

[a] At room temperature for 24 h. [b] The yield of products was determined by GC. [c] The yield of products could not be determined by GC.

nium–carbon bonds (LUMO). The upfield chemical shift of **1** compared with that of $Me_3SiGeMe_3$ (δ 0.04) may be caused by a localized negative charge on the germanium center. Similar bathochromic shifts of UV absorption maxima and upfield chemical shifts of the ^{1}H NMR signals have been reported for the spectra of germylalkali metals and related compounds [5–7].

Hexamethyldigermane ($Me_3GeGeMe_3$) is also cleaved by TBAF in HMPA, but the reaction is much slower than for the silylgermane.

2.2. *Reactions of metal-free germyl anion 1 with organic halides*

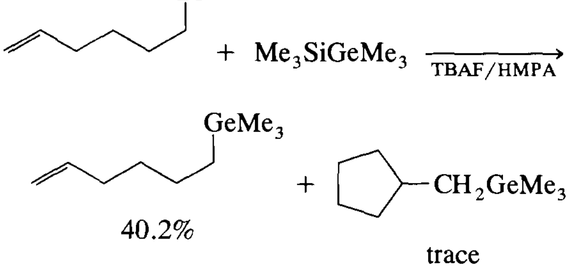
The germyl anion **1**, prepared by cleavage of Si–Ge bond of silylgermane with one equivalent of TBAF, reacted slowly with organic halides (RX) at room temperature for 24 h to give, after hydrolysis, trimethylgermyl-substituted products (Me_3GeR), reduction products (R–H), and hexamethyldisiloxane. All products were identified by comparing their NMR and GC–MS spectra and retention times on GLC with those of authentic samples. The results are summarized in Table 1.

$$\underset{\mathbf{1}}{[Me_3Ge]^-[NBu_4]^+} + RX \xrightarrow{H_2O} Me_3GeR + RH + \text{other products}$$

R = alkyl, aryl; X = F, Cl, Br, I

Reaction of **1** with phenyl halides yielded phenyltrimethylgermane together with a small amount of benzene. No formation of biphenyl was observed. The yields of phenyltrimethylgermane increased in the order PhF ≪ PhCl < PhBr, PhI. The relative ratio of benzene to phenyltrimethylgermane increased in the order PhCl < PhBr < PhI. These sequences are consistent with the recognized reactivities of alkali metal derivatives of organometal anions and with the bond strengths between the carbon and the halogen in reactions proceeding by way of an initial electron-transfer step [8]. The germyl anion **1** reacted with halotoluenes to give regiospecific substitution products. The reactions of germylalkali metals with halotoluenes have been reported to afford cine substitution products as results of an aryne process [9,10]. With butyl halides the germyl anion **1** afforded trimethylbutylgermane in the order BuCl ≪ BuBr < BuI with a trace amount of butane. Unreacted trimethylgermyl anion **1** was converted to trimethylgermane by hydrolysis with water. The results given in Table 1 suggest that the reactions of **1** with organic halides in HMPA may be involve a free radical process rather than a simple bimolecular nucleophilic reaction and halogen–metal exchange.

To investigate free radical pathways via electron-transfer process, the reaction of **1** with 6-bromo-1-hexene was examined. 6-Hexenyl radicals are known to be cyclized rapidly to yield cyclopentylmethyl products [11,12].



6-Bromo-1-hexene reacted with **1** to afford (cyclopentylmethyl)trimethylgermane (trace) and 1-hexenyltrimethylgermane (40.2%). The formation of the cyclized product implies that electron-transfer processes are important in this reaction.

2.3. *Reactions of metal-free germyl anion 1 with carbonyl compounds*

Me_3GeEMe_3 (E = Si or Ge) reacted with a variety of aliphatic and aromatic ketones at room temperature for 4 h to give, after hydrolysis, the expected trimethylgermylcarbinols together with reduction products of ketones with a catalytic amount of TBAF (5 mol%). The products were analyzed by GLC, NMR and GC–MS.

$$\underset{\mathbf{1}}{[Me_3Ge]^-[NBu_4]^+} + RR'C{=}O \xrightarrow{H_2O} RR'(Me_3Ge)COH + RR'CHOH$$

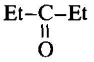
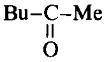
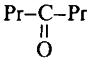
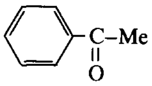
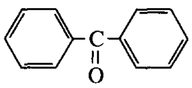
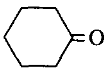
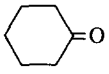
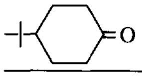
Addition of $Me_3GeSiMe_3$ with a catalytic amount of TBAF to 2-butanone resulted in the formation of 2-trimethylgermyl-2-trimethylsiloxybutane. Quenching 2-trimethylgermyl-2-trimethylsiloxybutane formed with water and work-up yielded 2-trimethylgermyl-2-methylpropanol quantitatively. With other alkylketones such as 2-hexanone and 3-heptanone $Me_3SiGeMe_3$/TBAF (5 mol%) afforded, after hydrolysis, quantitative yields the corresponding α-hydroxytrimethylgermanes. With acetophenone and benzophenone the yellow color of the solution of **1** changed to a clear deep blue and then to red, probably due to the presence of ketyl radicals. The red solution was hydrolyzed to give 1-trimethylgermyl-1-phenylethanol and (trimethylgermyl)diphenylmethanol were obtained in 74.8% and 12.3% yield, respectively. Diphenylmethanol was obtained in 17.8% yield in the reaction of $Me_3SiGeMe_3$/TBAF with benzophenone. The reaction with arylketones to give ketyl radicals and germyl radicals initially suggests that electron transfer may be involved from the germyl anion to the ketone. Gilman and Gerow [13] and Gladyshev et al. [14] have reported on the germylation of acetophenone by use of organogermyllithium, but Vyazankin et al. [15] and Noltes and Bulten [16] could not obtain α-triemthylgermylcarbinols and triethylgermane was formed as the exclusive products. The formation of α-hydroxygermanes depends largely upon the counter ions and solvents used

With cyclic ketones $Me_3SiGeMe_3$/TBAF (5 mol%) underwent very smooth reactions to give, after hydrolysis, the germylated cyclic alcohols in good yield. The stereochemistry of the germylated alcohols (*cis* : *trans* = 0 : 100) produced from 4-tert-butylcyclohexanone is assumed to be that which would result from the less hindered equatorial attack by a trimethylgermyl anion **1**. This result is in sharp contrast with that of other organometallics, which exhibits little preference for axial or equatorial attack on 4-tert-butylcyclohexanone [18]. $Me_3GeGeMe_3$ also reacted with a variety of ketones to give the corresponding α-hydroxyltrimethylgermanes in poor yield. These reactions did not occur in the absence of one equivalent of TBAF. These results are summarized in Table 2.

2.4. Reactions of metal-free germyl anion 1 with α,β-unsaturated ketones

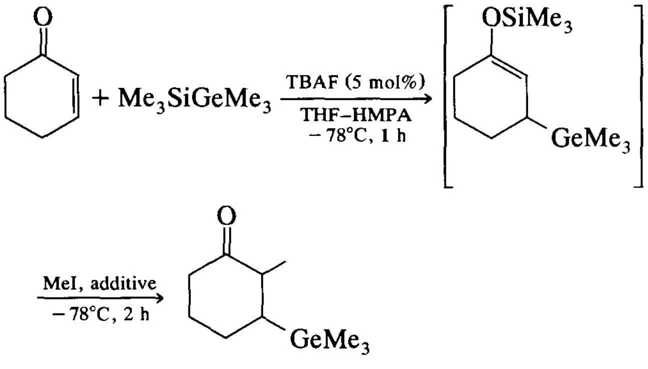
It is well known that addition reactions of organometallics such as Grignard reagents, to α,β-unsaturated compounds take place both in the 1,2 and 1,4 senses

Table 2
Reactions of Me_3EGeMe_3TBAF with carbonyl compounds [a]

Ketone	Me_3EGeMe_3TBAF	Products (Yield/%) [b]	
		α-Germyl-substituted product	Reduction product
 $Et-C(=O)-Et$	$Me_3SiGeMe_3$/TBAF [c] $Me_3GeGeMe_3$/TBAF [d]	(98.2) (28.8)	(trace) (0)
 $Bu-C(=O)-Me$	$Me_3SiGeMe_3$/TBAF [c]	(97.8)	(trace)
 $Pr-C(=O)-Pr$	$Me_3SiGeMe_3$/TBAF [c]	(79.5)	(0)
	$Me_3SiGeMe_3$/TBAF [c]	(74.8)	(0)
	$Me_3SiGeMe_3$/TBAF [c] $Me_3GeGeMe_3$/TBAF [d]	(12.3) (trace)	(17.8) (14.0)
	$Me_3SiGeMe_3$/TBAF [c] $Me_3GeGeMe_3$/TBAF [d]	(81.5) (27.7)	(0) (0)
	$Me_3SiGeMe_3$/TBAF [c]	(78.2)	(0)
	$Me_3SiGeMe_3$/TBAF [c]	(90.5, 100% *trans*)	(0)

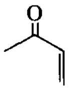
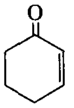
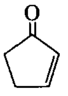
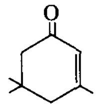
[a] At room temperature for 4 h.
[b] Isolated yields.
[c] TBAF (5.0 mol%).
[d] TBAF (equivalent mol).

[19,20]. Addition of $Me_3SiGeMe_3$ to 3-butene-2-one with a catalytic amount of TBAF in HMPA–THF at −78°C for 1 h resulted, after hydrolysis, in the formation of 4-trimethylgermylbutane-2-one as the only product in 52.3% yield. With 2-cyclohexene-1-one at −78°C addition of $Me_3SiGeMe_3$/TBAF (5 mol%) afforded the intermediate enolate. Quenching the enolate with methanol followed by work-up yielded 3-(trimethylgermyl)cyclohexanone as the only product in 82.3% yield. Alternatively, quenching the enolate with methyl iodide produced 2-methyl-3-(trimethylgermyl)cyclohexanone and 3-(trimethylgermyl)cyclohexanone in 11.1% and 52.3% yield, respectively. HPLC and NMR data of 2-methyl-3-(trimethylgermyl)cyclohexanone indicate this compound to be present as a single isomer (*trans*). Quenching the enolate from 2-cyclohexanone with methyl iodide in the presence of $TiCl_4$ (10 mol%) followed by work-up yielded 2-methyl-3-(trimethylgermyl)cyclohexanone and 3-(trimethylgermyl)cyclohexanone in 19.2% and 50.4% yield, respectively.



$Me_3SiGeMe_3$/TBAF also performs addition reactions with 2-cyclopentene-1-one at −78°C. Quenching of the enolate with methanol yielded 3-(trimethylgermyl)cyclopentanone in 72.7% yield. These results, together with those for other enones produced from reactions of silyl and stannyl anions indicate that Group

Table 3
Reactions of $Me_3SiGeMe_3$/TBAF with α,β-unsaturated ketones

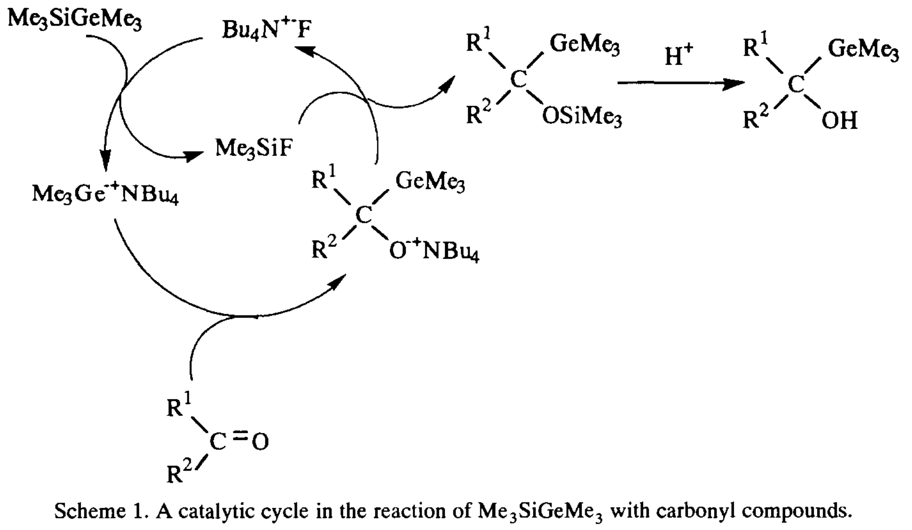
Ketone	Conditions	Product (Yield/%) [a]	
		1,4-addition	1,2-addition
	−78°C, 1 h	52.3 (100:0)	
	−78°C, 1 h	82.3 (100:0)	
	−78°C, 1 h	72.7 (100:0)	
	0°C, 1 h	16.2 (100:0)	

[a] Isolated yields.

14 element-centered anions have a strong preference for 1,4 axial addition to α,β-unsaturated compounds [17,21–26]. $Me_3SiGeMe_3$/TBAF is less reactive in addition to isophorone to give, after hydrolysis, 3,5,5-trimethyl-3-(trimethylgermyl)cyclohexanone in 16.2% yield. Still reported no addition of trimethylsilyllithium to isophorone under similar conditions as a result of steric hindrance [21]. A loose 1,3-diaxial methyl-trimethylgermyl interaction would be more favorable than that of 1,3-diaxial methyl-trimethylsilyl to the formation of a transition state for axial addition to isophorone. The results are summarized in Table 3.

A catalytic amount of TBAF is sufficient to drive the reaction of $Me_3SiGeMe_3$ with carbonyl compounds. These results are rationalized as illustrated in Scheme 1.

Nucleophilic attack of a fluoride ion on the silicon atom of $Me_3SiGeMe_3$ results in the formation of



Scheme 1. A catalytic cycle in the reaction of $Me_3SiGeMe_3$ with carbonyl compounds.

$[Me_3Ge]^-[NBu_4]^+$ (**1**) and trimethylfluorosilane. Reaction of **1** with a carbonyl compound forms a trimethylgermylated alkoxide which reacts with trimethylfluorosilane to afford a trimethylgermylated silylether. The fluoride ion is thereby regenerated to complete the catalytic cycle. Indeed, even without methanolysis of the reaction mixture, trimethylgermylated silylether can be detected by NMR. A similar mechanism has been proposed for allysilane or disilane–carbonyl compounds with TBAF [27,28].

3. Experimental details

All reactions and manipulations were performed under nitrogen. Solvents were freshly distilled under nitrogen from the appropriate drying agents immediately before use. The ^1H NMR spectra were recorded on a JEOL GX270 using tetramethylsilane as the internal standard. GC–MS spectra were obtained with a JEOL JMS-DX 303 mass spectrometer. IR spectra were recorded on a Shimadzu FT IR 4200 spectrometer. UV and UV–Vis spectra were recorded on a Shimadzu 2200 UV spectrometer. Gas and liquid chromatographies were performed on a Shimadzu GC-14A with 20 m 20% SE30 and Shimadzu LC-10 AS with finepak SIL, respectively.

3.1. Materials

Tetrabutylammonium fluoride, organic halides, carbonyl compounds, Me_3SiF, and $Me_3SiOSiMe_3$ were obtained commercially. Me_3GeH [29], $Me_3SiGeMe_3$ [30], $Me_3GeGeMe_3$ [31], $Me_3GeOGeMe_3$ [32], $C_4H_9GeMe_3$ [33] $C_6H_5GeMe_3$ [34] *o*-, *m*-, *p*-$CH_3C_6H_4GeMe_3$ [35], (cyclopentylmethyl)trimethylgermane [12], 1-hexenyltrimethylgermane [12], 3-(trimethylgermyl)cyclohexanone [17], 3-methyl-3-(trimethylgermy)cyclohexanone [17] 3-(trimethylgermyl)cyclopentanone [17] and 3,5,5-trimethyl-3-(trimethylgermyl)-cyclohexanone [17] were prepared described in the literature.

3.2. Reactions of metal-free germyl anion with organic halides

A typical example for the reaction of metal-free germyl anion with bromobenzene is described as follows. Metal-free trimethylgermyl anion was prepared from (trimethylsilyl)trimethylgermane (0.052 ml, 0.26 mmol) and tetrabutylammonium fluoride (0.068 g, 0.26 mmol) in HMPA (1 ml) at room temperature for 5 min. To a yellow solution of metal-free trimethylgermyl anion, bromobenzene (0.027 ml, 0.26 mmol) was added by a syringe, and the reaction mixtute was stirred at room temperature for 24 h. After hydrolysis, the organic layer was extracted with ether, dried, and concentrated in vacuo. The reaction products were separated by preparative GLC and TLC and their structures were identified by GC, NMR and GC–MS analyses. Phenyltrimethylgermane (0.023 g, 0.12 mmol, 45.3%) and benzene (0.008 g, 0.01 mmol, 5.3%) were obtained.

3.3. Reaction of $Me_3SiGeMe_3$ / TBAF (5 mol%) with carbonyl compounds

A typical example for the reaction of $Me_3SiGeMe_3$/TBAF (5 mol%) with acetophenone is described as follows. To a solution of $Me_3SiGeMe_3$ (0.10 ml, 0.50 mmol), TBAF (0.012 g, 0.047 mmol) and HMPA (1.5 ml) acetophenone (0.062 ml, 0.50 mmol) was added by a syringe. The reaction mixture was stirred at room temperature for 5 h. After hydrolysis, the organic layer was extracted, dried, and concentrated in vacuo. The reaction mixture was separated by preparative TLC and the products were characterized by GC, NMR, IR and GC–MS analyses. 1-Trimethylgermyl-1-phenylethanol (0.089 g, 0.37 mmol) was obtained in 74.8% yield.

3.4. Reaction of $Me_3SiGeMe_3$ / TBAF (5 mol%) with α,β-unsaturated ketones

A typical example for the reaction of $Me_3SiGeMe_3$/TBAF (5 mol%) with 2-cyclohexene-1-one is described as follows. A solution of $Me_3SiGeMe_3$ (0.10 ml, 0.50 mmol) and TBAF (0.012 g, 0.047 mmol) in HMPA (1.5 ml)–THF (1.6 ml) was cooled to −78°C. To this solution, 2-cyclohexene-1-one (0.048 ml, 0.50 mmol) was added at −78°C with stirring for 1 h. After methanolysis of the reaction mixture with MeOH, the solution was taken to dryness and the residue was purified by TLC affording 0.089 g (0.41 mmol) of 3-(trimethylgermyl)cyclohexanone. The enolate was quenched with methyl iodide (0.062 ml, 0.50 mmol) and $TiCl_4$ (0.006 ml, 0.055 mmol) and a similar work-up yielded 2-methyl-3-(trimethylgermyl)cyclohexanone (0.022 g, 0.095 mmol) and 3-(trimethylgermyl)cyclohexanone (0.054 g, 0.25 mmol).

Reaction of $Me_3SiGeMe_3$/TBAF 3-buten-2-one afforded a product characterized, MS *m/z*: 190 (10), 175 (60), 119 (100), 105 (40), 89 (40); NMR (δ in CCl_4) 0.06 (s, 9H), 1.24 m, 2H), 1.68 (m, 2H), 2.07 (s, 3H); IR (neat, cm^{-1}) 1720 ν(C=O), 1234 (Ge–C).

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