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The effect of substituents on the structure and reactivity of organogermanium anions

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Abstract

The replacement of the ethyl group in Et_3GeH by a phenyl group was shown by equilibrium metallation to halve the pK_a value compared with analogous CH acids. NMR showed that the decreased acceptor effect of the phenyl group in the $PhEt_2Ge^-$ anion is caused by a considerably reduced contribution of the mesomeric effect to anion stabilization compared with what happens in the corresponding carbanions. At the same time, the stabilization of the organogermanium anion increases the role of π-polarization of the aromatic substituent and this contribution is comparable with the mesomeric effect value.

A stabilizing effect of organosilicon and organogermanium substituents due to a high degree of polarizability has been shown by concurrent methanolysis of Et_3GeLi and REt_2GeLi ($R = Me_3Si$, Et_3Si, Me_3Ge, Et_3Ge, t-Bu, Ph).

An unexpected reaction of the trimethylsilyl anion with the $Me_3SiGeEt_2^-$ anion leading to diethylgermane dianion, Et_2Ge^{2-} has been revealed. The existence of this process supports the suggested absence of $(d\text{–}p)\pi$ interaction in germanium anions with organo-silicon and -germanium substituents.

Introduction

In recent years a number of original studies dedicated to donor conjugation in phenyl-substituted silicon and germanium anions has been carried out. Thus, while studying the metallation of CH acids with $Ph_nMe_{3-n}SiLi$ Evans et al. found the reaction rate to be nearly independent of the number of phenyl substituents in the silicon anion. The rate of metallation with carbanions, however, is reduced by several orders as the number of phenyl substituents is increased [1,2]. Study of the equilibrium metallation of phenyl germanes, Ph_nGeH_{4-n}, has revealed a considerable decrease in acidity as n is increased whereas with CH acids the opposite effect

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of phenyl substituents on the pK_a value is common [3,4]. No signs of the effect of the number of phenyl substituents in $Ph_nMe_{3-n}SiLi$ on λ_{max} have been observed in the UV spectra of these compounds. For their carbon analogues, $Ph_nMe_{3-n}CLi$, a characteristic bathochromic shift was detected upon the introduction of each phenyl group, which is caused by the classic $(p-p)\pi$ conjugation [1]. In the ^1H NMR spectra of phenyl substituted germanium anions the *ortho*-proton resonance is shifted downfield with respect to benzene [5] whereas the benzyl anion is characterized by an upfield shift of these protons [6]. The ^{13}C NMR data for these compounds also provide evidence for differences in the electron density distribution around the aromatic substituents of organo-silicon, -germanium anions and carbanions [7–9]. The study reported by Eaborn and Singh [10] is one of the few which support the hypothetis of $(p-p)\pi$ conjugation having a considerable effect in aryl-substituted germanium anions. The authors draw this conclusion from study of the exchange reactions of tritium for hydrogen in compounds $(XC_6H_4)_3GeT$ where $X = p\text{-}NO_2$, p-CN, m-Cl, p-F. The rate constants of these compounds correlate well with the σ^- value of substituents.

Gilman [11] and Eaborn [12] assumed the abnormally low reactivity of silyl substituted silicon and carbon anions to be accounted for by the $(d-p)\pi$ effect. However, some subsequent data on the structure of $(Me_3Si)_3CH$ [13] and the corresponding lithium derivative [14] provide evidence that steric factors determine the structure and reactivity of the above compounds. X-ray diffraction of the $(Me_3Si)_3SiLi \cdot 3$ THF complex [15] has shown the anion electron pair to be localized at the central silicon atom and this contradicts the model [11] suggesting a partial transition of the electron density onto trimethylsilyl substituents via $(d-p)\pi$ interactions.

Thus, the nature of the electron effects stabilizing the organo-silicon and -germanium anions and their relation to the contribution of classic mesomeric interaction remain uncertain.

Results and discussion

Metallation of germanium hydrides with organic substituents

Earlier it has been found that triethylgermyl potassium does not react with toluene in HMTA [16]. We have established that triethylgermylcesium metallates toluene if the latter is taken as a solvent. The solution concentration is 0.6 M.

$$\begin{tikzcd}
Et_3GeCs + PhCH_3 \arrow[r, phantom, "\rightleftarrows"] \arrow[d, "Me_3SiCl"] & PhCH_2Cs + Et_3GeH \arrow[d, "Me_3SiCl"] \\
Et_3GeSiMe_3 & PhCH_2SiMe_3
\end{tikzcd} \tag{1}$$

The equilibrium concentration of tolylcesium and triethylgermanium were determined according to the amount of their products obtained in the reaction with trimethylchlorosilane. The equilibrium acidity of germanes was defined using a conventional procedure which is as shown in eq. 2 for triethylgermane:

$$pK_a(Et_3GeH) = pK_a(PhCH_3) - \frac{[Et_3GeCs]}{[Et_3GeH]} + \frac{[PhCH_2Cs]}{[PhCH_3]} \tag{2}$$

The pK_a value 39.7 for triethylgermane was obtained from equation 2 taking into consideration that according to the Streitwieser's ion-pair scale the pK_a value for toluene is 40.9 [17]. If the MSAD* scale is used [4] the $pK_a(Et_3GeH) = 33.3$.

The reactions of t-butyldiethylgermane and phenyldiethylgermane in hexamethylphosphoramide (HMPA) with triethylgermylcesium in benzene are also reversible. However, whereas equilibrium in HMPA is established within a few hours, it takes several days in benzene. This significant influence of medium on the reaction equilibrium may be explained by the fact that triethylgermyllithium in HMPA is present as free ions whereas Et_3GeCs in benzene is a contact ion pair [18].

We have found that the acidity of t-butyldiethylgermane does not differ much from that of triethylgermane ($pK_a = -0.2$) whereas with phenyldiethylgermane the pK_a value is 2.8 lower, which is determined by the corresponding expressions analogous to equation 2.

Since the enhanced acidity of phenyldiethylgermane points to the increase in stabilization of the corresponding phenyl-substituted germanium anion, the nature of the stabilizing effect of the phenyl group is to be examined.

The nature of the stabilizing effect of the phenyl group in $PhEt_2GeLi$

Essential information concerning the nature of electron interaction of the aromatic substituent with the germanium atom in $PhEt_2GeLi$ can be derived from the internal chemical shift ($\Delta\delta = \delta(CH_3) - \delta(CH_2)$) of the ethyl group protons in ^1H NMR spectra.

A linear dependence of δ upon the inverse radius of the cation M^+ in benzene Et_3GeM solutions with M = Li, Na, K, Rb, Cs, and a high sensitivity of the $\Delta\delta$ parameter to the solvation of these compounds with donor ligands have been reported [19].

We have shown that in compounds of type REt_2GeLi with R = Et, Ph, t-Bu the internal chemical shift value is dependent on the nature of substituent R and of the solvent.

The decreased $\Delta\delta$ value for $PhEt_2GeLi$ compared with that of compounds with the substituent Et or t-Bu indicates again the electron-acceptor character of the Ph substituent and agrees with the acidity of germanium hydrides with analogous substituents. The $\Delta\delta$ value does not answer the question of how electron density is distributed between the phenyl substituent and the germanium atom.

Table 1

$\Delta\delta$ Values for REt_2GeLi and pK_a for the corresponding germanium hydrides

Solvent	R		
	Et	t-Bu	Ph
DME	0.66	0.69	0.42
HMPA	0.81	0.91	0.57
pK_a	39.7	+0.2	−2.8

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* MSAD = McEwen–Streitwieser–Applequist–Dessy scale.

Table 2

^{13}C NMR chemical shifts of compounds PhR_2EX (X = Li, Na, H)

PhR_2EX	Chemical shifts of ^{13}C (ppm)						
	α-C	*ipso*	*ortho*	*meta*	*para*	CH_3	CH_2
$PhEt_2GeLi$ [a]		173.09	134.96	124.83	120.71	16.04	13.88
		(163.94)	(134.25)	(125.37)	(122.12)	(12.15)	(12.15)
$PhMe_2SiLi$ [b]		166.1	134.0	126.8	123.1	8.1	
PhH_2CLi [b]	36.9	161.5	117.0	128.6	104.7		
PhH_2GeNa [c]		163.28	139.61	127.69	124.11		
$PhEt_2GeH$		137.65	132.95	128.17	128.55	4.90	9.96
$PhMe_2SiH$ [b]		137.3	134.0	127.9	129.2		
$PhCH_3$ [b]	21.5	138.5	129.0	129.7	126.1		
$PhGeH_3$ [c]		131.60	136.06	129.04	129.70		

[a] Solution HMPA and (DME). [b] Ref. 7. [c] Ref. 8.

In order to elucidate the phenyl group electronic effects we have carried out a ^{13}C NMR study of phenyldiethylgermyllithium and phenyldiethylgermane. The ^{13}C chemical shifts for compounds $PhEt_2GeX$ (X = Li, H) along with those for related silicon, germanium and carbon compounds, taken from ref. 7 and 8, are presented in Table 2.

Application of the method described previously [9] to the observed difference in chemical shifts of the corresponding atoms of aromatic substituents of the germanium anion and the conjugated germane in HMPA (Fig. 1d) indicates the absence of any mesomeric effect in the $PhEt_2Ge^-$ anion.

This approach is based on the assumption that the presence of mesomeric interaction should lead to an alternation of charges on the carbon atoms of the phenyl substituent. The authors [9] refer to the Ph_3CK/Ph_3CCl system (Fig. 1a) as

(a) Δδ ^{13}C ($Ph_3CK—Ph_3CCl$) [9]

(b) Δδ ^{13}C ($PhH_2CLi—PhCH_3$) [7]

conjugation

(c) Δδ ^{13}C ($PhMe_2SiLi—PhMe_2SiH$) [7]

(d) Δδ ^{13}C ($PhEt_2GeLi—PhEt_2GeH$)

π-polarization

Fig. 1.

Table 3

δ (C4) − δ (C3) values in PhR_2EM and $\Delta\delta$ (*para*-^{13}C) ($PhR_2EM - PhR_2EH$)

PhR_2EM	Solvent	δ (C4) − δ (C3)	$\Delta\delta$ (*para*)
PhH_2CLi [a]	THF	−23.9	−21.4
Ph_2HCLi [a]	THF	−21.2	−19.7
Ph_2MeCLi [a]	THF	−21.0	−20.4
$Ph_2MeSiLi$ [b]	THF	−2.8	−5.6
$PhMe_2SiLi$ [b]	THF	−3.8	−6.5
PhH_2GeNa [c]	NH_3	−3.58	−5.6
Ph_2HGeNa [c]	NH_3	−3.36	−6.3
$PhEt_2GeLi$	HMPA	−4.1	−7.8

[a] δ (^{13}C) chemical shifts are taken from ref. 7. [b] From ref. 9. [c] From ref. 8.

an example. Such an alternation does occur in this system for $\Delta\delta(^{13}C)$ values. However, there is no alternation of this kind in the tolyllithium/toluene system [7], although a considerable contribution from mesomeric effect is beyond doubt, since a significant increase in the shielding effect of the carbon atom is observed in both *ortho*- and *para*-positions (Fig. 1b).

The observed absence of charge alternation on the carbon atoms of the phenyl substituents of germyl and silyl anions (Fig. 1c,d) provides evidence for the decreased role of the mesomeric effect in stabilizing these anions compared with what happens in their carbon analogs. At the same time, the increased significance of the π-polarization of the aromatic substituent is quite evident.

It is reasonable to assume from Ref. 8, that the change in the charge density on the *para*-carbon reflects the total contribution from the two effects and is 7.8 ppm for $PhEt_2GeLi$ (Fig. 1d). The contribution from the mesomeric effect may be estimated by the difference in the chemical shifts of the *para*- and *meta*-carbon atoms. In the present case this effect is equal to 4.1 ppm and comparable with the polarization effect (cf. Table 3).

Therefore, when the mesomeric effect on the stabilization of the phenyl-substituted carbanions is compared with that of the corresponding anions of silicon and germanium, it is found to be 7–9 times as high for the former as for the latter, although the total influence of mesomeric and field effects is 3–4 times greater. This seems to indicate a different influence of phenyl groups on the acidity of hydrocarbons, and on organo-silicon and -germanium hydrides bearing phenyl substituents. By the MSAD scale [4] in going from methane to toluene, the acidity is increased by 5 points, the pK_a value ($Et_3GeH \rightarrow PhEt_2GeH$) being as low as 2.8, i.e., the influence of the Ph group in the germanium anion, $PhEt_2Ge^-$ is half as great as in the carbanion $PhCH_2^-$. Naturally, the differences in substituents and solvents for these species accounts for some inconsistency in comparative analysis.

Metallation of germanium hydrides with organometallic substituents

The replacement of an alkyl or phenyl substituent by an organo-silicon or -germanium one leads to considerable changes in the properties of germanium hydride. This is observed in the reaction of metallation with alkalitriethylgermyl derivatives.

The reactions of element-substituted germanes, R_3EGeEt_2H with Et_3GeM are irreversible since metallation involves cleavage of the element–germanium bond, the triethylgermyl anion being attacked at both the germanium atom and the element atom in the substituent. Pentaethyldigermane is the major product of the reaction of trimethylsilyldiethylgermane with triethylgermylcesium. Route 3b is observed only in HMPA.

$$\mathrm{Me_3SiGeEt_2H + Et_3GeM} \left\{ \begin{array}{l} \xrightarrow[\mathrm{M=Cs}]{\text{(a) benzene}} \mathrm{Me_3SiCs + Et_3GeGeEt_2H} \\ \xrightarrow[\mathrm{M=Li}]{\text{(b) HMPA}} \mathrm{Me_3SiGeEt_3 + LiGeEt_2H} \\ \qquad\qquad \mathrm{Me_3SiGeEt_2H} \downarrow \\ \qquad \mathrm{Me_3SiLi + HEt_2GeGeEt_2H} \end{array} \right. \qquad (3)$$

The pentaethyldigermane/tetraethyldigermane ratio is 2/1. In this case there is some analogy with the reaction with diethylchlorogermane. If pentaethyldigermane is the major reaction product from the reaction of Et_3GeLi with Et_2GeHCl in hexane, the yield of this product decreases when the reaction is carried out in HMPA and the formation of tetraethyldigermane is observed (Scheme 4).

$$\mathrm{Et_2GeHCl + Et_3GeLi} \left\{ \begin{array}{l} \xrightarrow[\mathrm{H_2O}]{\text{hexane}} \mathrm{Et_3GeGeEt_2H + Et_3GeH + Et_3GeGeEt_3} \\ \qquad\qquad (82\%) \qquad\quad (10.7\%) \qquad (7.3\%) \\ \xrightarrow[\mathrm{H_2O}]{\text{HMPA}} \mathrm{Et_3GeGeEt_2H + Et_3GeH + (Et_3Ge)_2 + (HEt_2Ge)_2} \\ \qquad\qquad (15.5\%) \qquad (27.4\%) \qquad (50.0\%) \qquad (7.1\%) \end{array} \right.$$

Synthesis of dilithiumdiethylgermane

We have found by special tests that the products testifying to cleavage of the element–element bond in the reactions of type 3 can be prepared by two other routes. So, the reaction of trimethylsilyldiethylgermyllithium with trimethylsilyldiethylgermane in HMPA gives a mixture of products among which bis(trimethylsilyl)diethylgermane, trimethylsilyltetraethyldigermane, hexamethyldisilane, tetraethyldigermane and hexaethyldigermane determined after hydrolysis. Unexpectedly we have found that silyl-substituted germyllithium reacts readily with triethylgermyllithium in HMPA, also with cleavage of the Si–Ge bond.

$$\begin{array}{l} \mathrm{Me_3SiGeEt_2Li + Et_3GeLi \rightarrow Me_3SiGeEt_3 + Et_5Ge_2Li + Li_2GeEt_2} \\ \qquad\qquad\qquad\qquad\qquad\quad (31\%) \qquad\quad (35\%) \qquad\quad (34\%) \end{array} \qquad (5)$$

In this reaction the formation of dilithiumdiethylgermane has been detected. Earlier studies have produced some precedents for the formation of the germanium dianion in analogous yields [20–22]. We have found, however, that the use of trimethylsilyllithium facilitates greatly the synthesis of the germanium anion [23]:

$$\mathrm{Me_3SiGeEt_2Li + Me_3SiLi \rightleftarrows (Me_3Si)_2 + Li_2GeEt_2} \qquad (6)$$

This is due to the fact that the equilibrium achieved in the reaction can readily be shifted towards the formation of the dianion by a low pressure removal of the hexamethyldisilane formed from the reaction mixture. The use of trimethylsilyllithium made it possible to obtain dilithiumdiethylgermane in a yield up to 70%

which was determined by the products of its reaction with ethyl bromide, triethylbromogermane and water.

$$Et_2GeLi_2 \begin{cases} \xrightarrow{+H_2O} Et_2GeH_2 \quad (68\%) \\ \xrightarrow{+EtBr} Et_4Ge \quad (69\%) \\ \xrightarrow{+Et_3GeBr} (Et_3Ge)_2GeEt_2 \quad (71\%) \end{cases} \qquad (7)$$

Recently the reaction of diarylgermanes with alkali metals in a mixture HMPA + THF has successfully been used [24]. The yields of diarylgermane derivatives bearing two alkali atoms attain 84–96%.

Our attempt to employ this method for preparing the germane anion from diethylgermane was a failure. Like that in the reaction with excess triethylgermyllithium in HMPA, diethylgermane reacts with excess alkali metal to form the monoanion Et_2GeH^- only.

Competing reactions of REt_2GeLi and Et_3GeLi with methanol

It is evident that equilibrium metallation is not suitable for the investigation of the acidity of organometallic substituted germanium hydrides, since it leads to an undesirable process, i.e. cleavage of the E–Ge bond. All disadvantages of this process can be eliminated by use of a method of competing reactions.

A study of the competing reactions of Et_3GeLi and REt_2GeLi with methanol was carried out by us in THF at −78 °C with the use of trimethylchlorosilane for a fast removal of nucleophiles from the reaction mixture.

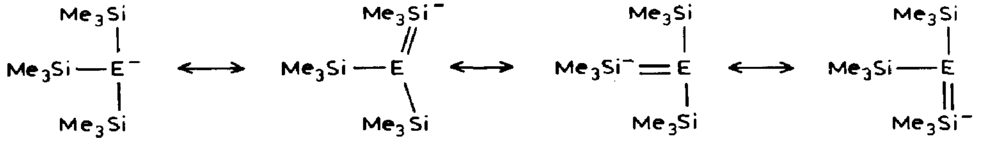
As seen from Table 4, the relative rate of the methanolysis of REt_2GeLi with $R = Me_3Si$, Et_3Si, Me_3Ge is lower than that of their analog with $R = Me_3C$ possessing a similar screening ability. The internal chemical shift value, $\Delta\delta$, in the ^1H NMR spectrum of $Me_3SiGeEt_2Li$ is, likewise, lower than in compounds Et_3GeLi and $t\text{-}BuEt_2GeLi$. This provides evidence for an electron-withdrawing character of the Me_3Si group in $Me_3SiGeEt_2Li$. This feature of substituents R_3E ($E = Si$, Ge) seems to be responsible for the decrease in the rate of R_3EGeEt_2Li methanolysis.

Table 4 shows that $PhEt_2GeLi$ undergoes methanolysis more slowly. The lower reactivity of this compound is due to mesomeric and field inductive effects arising from electron interaction of the phenyl substituent with the anion centre.

What is the reason for the acceptor effect of organo-silicon and -germanium substituents?

The nature of electron-acceptor effect of an organometallic substituent in the $R_3EGeEt_2^-$ anion

The stabilizing effect of trimethylsilyl substituent on silicon and carbon anions has been observed long ago and explained in terms of traditional $(d\text{–}p)\pi$ interaction, which is demonstrated by resonance structures:



(8)

(E = Si [11] , C [12])

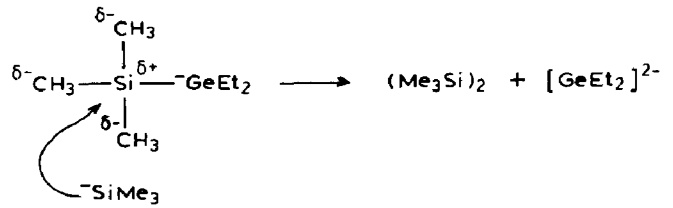
Table 4

The relative rates of methanolysis ($K_{rel.}$), internal chemical shift ($\Delta\delta$ (^{1}H)) of REt_2GeLi and pK_a of corresponding hydrides

REt_2GeLi	$K_{rel.}$	Internal CS ($\Delta\delta$ (^{1}H) (ppm)		pK_a (ΔpK_a)
		HMPA	DME	
Et_3GeLi	1.00	0.81	0.66	39.7
t-$BuEt_2GeLi$	1.04	0.91	0.69	(+0.2)
$PhEt_2GeLi$	0.59	0.57	0.42	(−2.8)
$Me_3SiGeEt_2Li$	0.74	0.41	0.40	–
$Me_3GeGeEt_2Li$	0.75	–	–	–
$Et_3SiGeEt_2Li$	0.76	–	–	–
$Et_3GeGeEt_2Li$	0.91	–	–	–

If this stabilization mechanism is extended to organogermanium anions bearing organoelement substituents, the observed reaction of trimethylsilyllithium with trimethylsilyldiethylgermyllithium does not take place. In the presence of $(d\text{–}p)\pi$-conjugation the Me_3Si^- nucleophile should attack the $Me_3SiGeEt_2^-$ anion at the silicon atom bearing an excess negative charge. In discussing this reaction it should be admitted that the silicon atom in the substituent bears a partially positive charge. This arises from inductive polarization of the organometallic substituent induced by the negative charge concentrated on the anion centre. A marked localization of the positive charge on the silicon atom in silyl-substituted carbanions is supported by calculations [25,26]. Calculations of the $H_3SiCH_2^-$ anion structure have been carried out by Schleyer et al. [25]. They have suggested that the contribution from $(d\text{–}p)\pi$-interaction is negligible, the main contribution to the stabilization of this anion being made by inductive polarization and negative hyperconjugation. Pitt's calculations [27] confirm that the H_3SiCH_2 group may exhibit acceptor properties with respect to anion centres. The H_3ECH_2 groups also seem to acquire acceptor properties due to polarization and negative conjugation since there is no $(d\text{–}p)\pi$-interaction in the $H_3ECH_2CH_2^-$ anion [28].

All this suggests that polarization plays the main part in stabilization of R_3E-substituted germanium anions. This explains the possibility for the trimethylsilyl anion attack to take place at the positively charged silicon atom in the trimethylsilyldiethylgermyl anion. It is most likely, that the attacking nucleophile field strengthens considerably the initial polarization of the anion-substrate:



(9)

Our suggestion that the substituent polarization effect makes the major contribution to the stabilization of R_3E-substituted germanium anions is confirmed by a study of competing reactions of $Me_3SiGeEt_3$ and $Me_3SiGeEt_2Li$ with trimethylsilyllithium in HMPA. It has been found that the rate of the Si–Ge bond cleavage in neutral compound $Me_3SiGeEt_3$ is only 40% that in the $Me_3SiGeEt_2^-$ anion. This is in agreement with the assumption of a higher electrophilicity of the silicon atom in an anion than in a neutral molecule.

Experimental

All operations with alkali and mercury organo-silicon and -germanium derivatives were carried out in dry argon or in evacuated sealed systems by a technique described previously [29].

NMR spectra were run on a JEOL FX-90Q spectrometer. TMS was used as an internal standard. IR spectra were recorded on a UR-20 instrument. GLC was performed on a Chrom-5 instrument, detector, catharometer; carrier: gas, helium; stainless steel columns, 2 m × 1.5 mm, packed with 5% SE-30 on N-AW Chromaton. Mass spectra were taken on a Varian MAT-212 mass spectrometer.

Synthesis of germanium hydrides

Pentaethyldigermane. To a solution of Et_3GeLi (16.2 g) in hexane 15.8 g of diethylchlorogermane was added at room temperature. The mixture was stirred for 1 h. After hydrolysis three products were detected in the reaction mixture by GLC: triethylgermane (10.7%), pentaethyldigermane (82.0%), and hexaethyldigermane (7.3%). After fractionation 20.5 g (74%) of pentaethyldigermane were isolated. B.p. 62–63 °C/3 mm Hg, n_D^{20} 1.4933. Found: C, 40.89; H, 8.73; Ge, 49.14. $C_{10}H_{26}Ge_2$ calcd.: C, 41.20; H, 8.99; Ge, 49.80%. IR spectrum (ν, cm^{-1}) 1990 (Ge–H).

$Me_3SiGeEt_2H$ was obtained in an analogous manner in 72% yield. B.p. 75–76 °C/40 mm Hg, n_D^{20} 1.4581. Found: C, 40.86; H, 9.61, Ge, 35.30; Si, 13.59. $C_7H_{20}GeSi$ calcd.: C, 41.03; H, 9.84; Ge, 35,43; Si, 13.71%. IR spectrum (ν, cm^{-1}) 1985 (Ge–H).

$Et_3SiGeEt_2H$ (yield 66%). B.p. 81–82 °C/5 mmHg, n_D^{20} 1.4771. Found: C, 47.91, H, 10.50; Ge, 28.84; Si, 11.00. $C_{10}H_{26}GeSi$ calcd.: C, 48.63; H, 10.61; Ge, 29.39; Si, 11.37%.

$Me_3GeGeEt_2H$ (yield 68%). B.p. 82–83 °C/35 mmHg, n_D^{20} 1.4767. Found: C, 33.66; H, 8.07; Ge, 57.89. $C_7H_{20}Ge_2$ calcd.: C, 33.71; H, 8.08; Ge, 58.21%.

t-$BuEt_2GeH$ (yield 60%). B.p. 126–127 °C/723 mmHg, n_D^{20} 1.4442. Found: C, 50.71; H, 10.50; Ge, 38.83. $C_8H_{20}Ge$ calcd.: C, 50.88; H, 10.67; Ge, 38.44%.

Metallation of germanium hydride of the REt_2GeH series

Reaction of triethylgermylcesium with toluene. A 0.60 *M* solution (30 ml) of triethylgermylcesium in toluene (prepared as described previously [30]) was stirred for 120 h at 25 °C, after which Me_3SiCl (1.1 g) was added. As shown by GLC (benzene as an internal standard), the concentrations of $Et_3GeSiMe_3$, $PhCH_2SiMe_3$ and Et_3GeH were 0.24, 0.36 and 0.36 mol/l, respectively. The concentration of toluene was 8.10 mol/l. Analogous tests carried out for 160 and 200 h led to the same results. Introducing the equilibrium concentration obtained into equation 2 shows that with toluene $pK_a = 40.9$ [17] the pK_a value for Et_3GeH is 39.7 ± 0.1.

Metallation of t-butyldiethylgermane. An equimolar mixture of triethylgermyllithium (0.46 g) and t-butyldiethylgermane (0.53 g) in 5 ml of HMPA was stirred for

72 h at 25°C, then Me_3SiCl (1.5 g) was added. The concentration of Et_3GeH, $Et_3GeSiMe_3$, t-$BuEt_2GeH$ and t-$BuEt_2GeSiMe_3$, were determined by GLC to be 0.28, 0.17, 0.29 and 0.26 mol/l, respectively. Increasing the reaction time to 150 h did not affect the reaction mixture composition. By equation 2 the pK_a difference between two hydrides was determined to be + 0.2.

Metallation of phenyldiethylgermane. When metallation of phenyldiethylgermane with triethylgermyllithium in HMPA was followed by the addition of excess Me_3SiCl the concentrations of Et_3GeH, $PhEt_2GeH$, $Et_3GeSiMe_3$ and $PhEt_2GeSiMe_3$ were 0.37, 0.02, 0.01 and 0.37 mol/l, respectively. Introducing these values into equation 2 we obtained the difference between these two hydrides of − 2.8.

Reaction of trimethylsilyldiethylgermane with triethylgermylcesium. An equimolar mixture of silylgermane (0.57 g) and Et_3GeCs (0.82 g) in benzene (4 ml) was stirred for 72 h at 25°C. After hydrolysis GLC and GC/MS spectroscopy showed the reaction mixture to contain $Et_3GeGeEt_2H$ (53.2%), Et_3GeH (18.9%), $Me_3SiGeEt_2H$ (12.8%), Me_3SiH (7.7%), $Et_3GeGeEt_3$ (4.4%), $Me_3SiGeEt_3$ (3.0%).

Under analogous conditions, the reaction of trimethylsilyldiethylgermane with triethylgermyllithium in HMPA gave: $Et_3GeGeEt_2H$ (36.7%), $HEt_2GeGeEt_2H$ (17.8%), Et_3GeH (25.2%), $Me_3SiGeEt_2H$ (0.5%), Me_3SiH (15.8%), $Et_3GeGeEt_3$ (3.4%), $Me_3SiGeEt_3$ (0.7%).

Metallation of diethylgermane. A mixture of Et_3GeLi (0.83 g) and diethylgermane (0.22 g) in a ratio of 3/1 in HMPA (8 ml) was stirred for 10 h at 25°C. The reaction mixture was divided into two portions each of 4 ml. To one portion 0.5 g of EtBr was added and stirred for 30 min, following which water (2 ml) and hexane (4 ml) were added. GLC showed the organic layer to contain Et_3GeH (49.0%) and Et_4Ge (51.0%). The remaining portion of the reaction mixture was treated with trimethylchlorosilane (0.5 g). After stirring for 1 h 2 ml of water and 4 ml of hexane were added. In the organic layer Et_3GeH (24.6%), $Et_3GeSiMe_3$ (52.1%) and $Me_3SiGeEt_2H$ (23.3%) were found.

1.8 g of sodium cut into small pieces was placed in an ampoule containing 7.5 ml of HMPA and 11 ml of THF; to this, after stirring for 30 min, 0.66 g of Et_2GeH_2 dissolved in 1 ml of THF was gradually added. The blue reaction mixture turned yellow after the addition of diethylgermane and then became blue again. When the entire amount of diethylgermane had been added, the reaction mixture was stirred for 24 h. Then 3.0 g of EtBr and, 30 min later, 5 ml of water and 10 ml of hexane were added. Et_2GeH_2 (57%), Et_3GeH (35%) and Et_4Ge (8%) were found in the organic layer.

The same products Et_2GeH_2 (46%), Et_3GeH (42%) and Et_4Ge (12%) were observed upon potassium metallation under similar conditions and analogous treatment of the reaction mixture.

Synthesis of mercury and lithium organogermanium derivatives

Compounds $(REt_2Ge)_2Hg$ with R = t-Bu, Ph were obtained by a technique proposed for the synthesis of bis(triethylgermyl)mercury [31]. $(PhEt_2Ge)_2Hg$ (yield to 60%, b.p. 158–160°C/0.04 mm Hg) and (t-$BuEt_2Ge)_2Hg$ (yield to 82%, b.p. 100–102°C/0.04 mm Hg) were isolated by fractionation. The structures of the germanium mercury derivatives were revealed by their reactions with mercury salts HgX_2 (X = Cl, Br) as described in ref. 32.

Bis(pentaethyldigermyl)mercury. Diethylmercury (10.3 g)and pentaethyldi-

Table 5

Amounts of ethane (%) formed in reactions of $HgEt_2$ with REt_2GeH (1 h at 25 °C)

R	Et	t-Bu	Ph	Et_3Ge	Et_3Si	Me_3Si	Me_3Ge	Cl
Ethane (%)	1	1	2.4	17.3	20.0	40.8	55.5	70.0

germane (24.5 g) were placed in a 50 ml ampoule (equipped with a magnetic stirrer) in a flow of argon. The argon feed was stopped and the ampoule was kept at a water bath at 40 °C until completion of the synthesis. The synthesis was considered complete when the amount of the gas liberated during the reaction reached a calculated value (1880 ml in this case). The heating was stopped and the reaction mixture was vacuum distilled. The fraction (b.p. 147–148 °C/0.02 mmHg) contained 31.2 g of $(Et_3GeGeEt_2)_2Hg$, yield 73%.

$(Me_3GeGeEt_2)_2Hg$ (74%, b.p. 114–115 °C/0.02 mmHg), $(Et_3SiGeEt_2)_2Hg$ (84%, b.p. 136–137 °C/0.02 mm Hg) and $(Me_3SiGeEt_2)_2Hg$ (81%, b.p. 105–106 °C/0.02 mm Hg) were synthesized in a similar manner.

We have found that the reaction of diethylmercury with organogermanium hydrides containing organo-silicon or -germanium substituents is over within 3 or 4 h whereas triethylgermane is known to react with the above reagent at 80–120 °C [31].

As can be seen from Table 5, hydrides with R = Et, t-Bu and Ph are less reactive than analogous hydrides with organometallic substituents. Evidently, in the former, the energy of the Ge–H bond dissociation is lower. It is known that the energy of the Si–H bond dissociation in polysilanes is smaller than that in triethylsilane [33].

The germylmercury derivatives obtained react readily with metallic lithium in hexane, benzene as well as in Et_2O, THF, HMPA. However, in compounds with R = Ph, t-Bu the complete replacement of mercury by lithium in hydrocarbons does not occur because strong mercury-lithium complexes are formed, whose analogs have been described [34,35].

Reactions of R_3ELi with trimethylsilyldiethylgermyllithium

Reaction of triethylgermyllithium with trimethylsilyldiethylgermyllithium. An equimolar mixture of Et_3GeLi (0.35 g) and $Me_3SiGeEt_2Li$ (0.44 g) in 4 ml of HMPA was stirred for 94 h at 25 °C. Then the mixture was divided into two portions. To one portion 1.1 g of Me_3SiCl and 4 ml of water was added. The ether extract of this portion contained: $Me_3SiGeEt_3$ (30.8%), $(Me_3Si)_2GeEt_2$ (35.3%) and $Et_3GeGeEt_2SiMe_3$ (33.9%). The other portion was hydrolyzed and ether was added. The ether extract contained: Et_2GeH_2 (25.8%), Et_3GeH (28.4%), $Me_3SiGeEt_2H$ (1.8%), $Et_3GeSiMe_3$ (14.6%), $Et_3GeGeEt_2H$ (27.1%) and $(Me_3Si)_2GeEt_2$ (2.3%).

Reaction of trimethylsilyllithium with trimethylsilyldiethylgermyllithium. A mixture of $Me_3SiGeEt_2Li$ (4.2 g) and Me_3SiLi (1.6 g) in 30 ml of HMPA was stirred for 2 h at 25 °C; after adding Et_3GeBr (8.7 g) the mixture was stirred for another hour. After hydrolysis the ether extract was dried over $MgSO_4$. Fractionation enabled 6.4 g (71%) of octaethyltrigermane, b.p. 122–123 °C/0.08 mmHg, n_D^{20} 1.5315 to be isolated. Found: C, 43.40; H, 9.46; Ge, 47.20. $C_{16}H_{40}Ge_3$ calcd.: C, 42.48, H, 8.95, Ge, 48.36%. Following analogous procedures, tetraethylgermane (69%), diethylgermane (68%), and bis(trimethylsilyl)diethylgermane (73%) were isolated. B.p. of the latter is 110-111°C/20 mmHg, n_D^{20} 1.4861. Found: C, 43.55; H, 10.12; Ge, 26.19; Si, 20.27. $C_{10}H_{28}GeSi_2$ calcd.: C, 43.45; H, 10.19; Ge, 26.20; Si, 20.27%.

Competing reactions of trimethylsilyllithium with trimethylsilyltriethylgermane and trimethylsilyldiethylgermyllithium. $Me_3SiGeEt_3$ (0.93 g), $Me_3SiGeEt_2Li$ (0.84 g) and Me_3SiLi (0.16 g) were allowed to react in 10 ml of HMPA at 25°C for 30 min. Then the reaction mixture was divided into two portions. To one portion Me_3SiCl was added, and another portion was hydrolyzed. The ratio of the Si–Ge bond cleavage rates was determined by a change in the ratio of the starting $Me_3SiGeEt_3$ and $Me_3SiGeEt_2Li$ concentrations (the latter reagent being in the $(Me_3Si)_2GeEt_2$ or $Me_3SiGeEt_2H$ form) using GLC with benzene as the internal standard. In this way the rate of the Si–Ge bond cleavage in $Me_3SiGeEt_2Li$ was found to be 2.5 as high as that in $Me_3SiGeEt_3$.

Competing reactions of Et_3GeLi and REt_2GeLi with methanol

Reactions of triethylgermyllithium and pentaethyldigermyllithium with methanol. To an equimolar mixture of Et_3GeLi (0.50 g) and Et_5Ge_2Li (0.89 g) in 10 ml of THF at −78°C a solution of MeOH (0.05 g) in 2.5 ml of THF with a certain amount of benzene was added. The reagent ratio was 2/2/1, respectively. Five minutes later Me_3SiCl (1.0 g) was added and the reaction mixture was heated to room temperature and stirred for 1 h. Then 2 ml of water and 3 ml of hexane were added to the reaction mixture. The organic layer was separated and dried over $MgSO_4$. The ratio of methanolysis rates was determined by the ratio of methanolysis products (Et_3GeH and Et_5Ge_2H). The $K_{rel.}$ value was also found by a change in the ratio of starting reagents after treatment with Me_3SiCl ($Me_3SiGeEt_3$ and $Me_3SiGeEt_2GeEt_3$). As shown by GLC, after methanolysis the initial ratio of molar concentration ($Et_3GeLi/Et_5Ge_2Li = 1$) changes to 0.91. Some other competing methanolyses of Et_3GeLi and REt_2GeLi were carried out in an analogous manner.

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