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THE MECHANISM OF CLEAVAGE OF Si—Ge BONDS BY BASE *

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Summary

The compounds $R_3SiGePh_3$ with R = Me or Et have been shown to undergo cleavage in NaOMe-MeOH to give Ph_3GeH. From rate measurements and solvent isotope effect studies it is concluded that the Ph_3Ge^- anion separates in the rate-determining transition state. There is an unusually large steric effect, $Me_3SiGePh_3$ being roughly 1300 times as reactive as $Et_3SiGePh_3$.

Introduction

A recent study revealed that tritiated triphenylgermane, Ph_3Ge^3H, undergoes hydrogen exchange in NaOMe-MeOH about 5 times as rapidly as 9-tritiofluorene [1]. This means that the anion Ph_3Ge^- is formed rather more readily from Ph_3GeH than is the fluoren-9-yl anion from fluorene. Since cleavage of Me_3Si—R bonds by base is, in the absence of special factors, much faster than that of corresponding Me_3Ge—R bonds [2,3], and since the ease of base cleavage of Me_3SiR species where R is an aryl or an alkyl group normally parallels the acidity of the acid RH, it could be predicted that the compound $Me_3SiGePh_3$ would be readily cleaved in NaOMe-MeOH by attack of the methoxide ion at silicon and separation of the anion Ph_3Ge^-, which would give Ph_3GeH, and that this reaction would be even faster than the cleavage of 9-trimethylsilylfluorene. The results presented below show that these predictions were correct.

Results and discussion

The compounds $Me_3SiGePh_3$ and $Et_3SiGePh_3$ were both found to be cleaved by 1 *M* MeONa-MeOH to give Ph_3GeH. The progress of the reaction could be monitored by UV spectrophotometry and rates were measured at 30°C for the trimethyl and at 50°C for the less reactive triethyl compound. The observed

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TABLE 1

RATE CONSTANTS FOR CLEAVAGE OF $R_3SiGePh_3$ COMPOUNDS BY METHANOLIC SODIUM METHOXIDE

R	Temp. (°C)	Solvent	10^3[NaOMe] (M)	10^3k (s^{-1})	10^3k_S (l mol^{-1} s^{-1})	RIE [a]
Me	30.0	MeOH	0.43	3.2	7400	0.54
Me	30.0	MeOD	0.39	5.3	13600	
Et	50.0	MeOH	111	0.73	6.6	0.59
Et	50.0	MeOD	111	1.23	11.1	

[a] Given by k_S(MeOH)/k_S(MeOD).

first order rate constants k are shown in Table 1, along with the specific rate constants k_s, given by k/[NaOMe]. Measurements were also made in MeONa-MeOD, as shown in Table 1.

The cleavage of 9-trimethylsilylfluorene in MeONa-MeOH has a specific rate constant, k_s, of 0.16 l mol^{-1} s^{-1} at 30°C [4], and so $Me_3SiGePh_3$ is cleaved about 50 times as rapidly. There is a further point of resemblance between the $R_3SiGePh_3$ and 9-R_3Si-fluorene systems in that the change from Me to Et causes a large rate decrease in both cases; the decrease is by a factor of roughly 1300 for the $R_3SiGePh_3$ compounds (a factor of 4 being assumed for the rate increase between 30°C and 50°C for these compounds) and by a factor of 950 for the fluorene derivatives as determined in 5 : 1 MeOH-H_2O [3]. The large steric effect for the $R_3SiGePh_3$ compounds, like that for the fluorene compounds, is in line with the earlier proposal for $R_3Si—R'$ cleavage that the steric effects are largest for the fastest reactions, in which the rate-determining transition state is not far removed from the (possibly hypothetical) 5-coordinate silicon species $[MeOSiR_3R']^-$, where the steric crowding will be at a maximum [5—7].

To confirm the mechanism of the cleavage of the $R_3SiGeMe_3$ compounds, we also examined the solvent isotope effects. The values of the rate isotope effect, RIE, given by the ratio of k_s in MeOH to that in MeOD, are shown in Table 1. (It should be noted that because of the difficulty of determining accurately the low concentration of NaOMe involved, the value for $Me_3SiGePh_3$ is subject to a larger than usual uncertainty.) The value of 0.54 and 0.59 for the Me_3Si and Et_3Si compounds, respectively, are in keeping with a mechanism in which in the transition state the MeO^- anion is fully or almost fully attached to the silicon atom and the Ph_3Ge group is separating as the anion Ph_3Ge^-, with no simultaneous proton transfer (electrophilic asistance) from the solvent [4,5,8,9].

Only a rough value, of ca. 2.7, was obtained for the product isotope effect, PIE, given by the product ratio Ph_3GeH/Ph_3GeD obtained on cleavage of $Me_3SiGePh_3$ in 1 : 1 MeOH-MeOD, but there is no doubt that while the value is sustantially larger than unity it is markedly smaller than values observed for 9-trimethylsilylfluorene [viz. 9] and other Me_3SiR' species of comparably high reactivity [4,9]. On the simplest reasoning, similar PIE values would be expected for anions R'^- derived from acids R'H of similar acidities [10], and thus comparable PIE values for $Me_3SiGePh_3$ and 9-Me_3Sifluorene. However, it has recently been shown that the relationship between the PIE for R'^- and the acidity of R'H cannot be carried over from one class of compound to another [10], and in particular that for comparable pK_a values of R'H, highly delocalized anions may give rise to larger PIE's than do localized anions [11]. The lower PIE for Ph_3Ge^- than for the fluorenyl anion is consistent with the probability that the conjugative delocalization of charge in the anion Ph_3Ge^-, while significant [1], is probably markedly smaller than that in the 9-fluorenyl anion.

It is noteworthy that if there were proton transfer to the separating Ph_3Ge^- anion in the rate-determining step of the cleavage of the $R_3SiGePh_3$ compounds, the PIE values would imply RIE values in the region of 1.5, rather than the observed 0.54 and 0.59 [4,9,12].

While, as we have shown, the rate-determining step involves separation of the Ph_3Ge^- anion, we cannot decide between the stepwise mechanism (1) shown in Scheme 1, involving prior formation of an Si^V intermediate, and the synchronous mechanism (2) involving separation of the Ph_3Ge^- as the MeO^- attacks at Si. From the RIE values we do know, however, that the MeO^- must be fully or almost fully freed from the solvent molecules which initially solvated it, and thus the structure of the transition state would be much the same irrespective of whether route 1 or route 2 were followed.

It is of interest to consider briefly why the overall course of base cleavage of R_3SiSiR_3' compounds (which in MeOH gives R_3SiOMe and $R_3'SiOMe$) is different from that for $R_3SiGePh_3$ (and no doubt for R_3SiGeR_3' compounds in general). The explanation is that any R_3SiH generated in a process analogous to that for the $R_3SiGePh_3$ compounds, would be very rapidly converted into R_3SiOMe with evolution of hydrogen at the base concentrations involved, whereas R_3GeH species are not decomposed in this way [15]. The difference in behaviour is associated with (a) the normally greater ease of nucleophilic attack by alkoxide ion at silicon than at germanium, and (b) the much greater ease of formation of R'_3Ge^- than of $R_3'Si^-$ anions from corresponding precursors. It is possible to envisage $Me_3SiSiR'_3$ compounds which might cleave to give Me_3SiOMe and R'_3SiH; what would be required would be very bulky R' groups which would sterically inhibit the solvolysis of the R'_3SiH species, preferably coupled with an enhanced stability of the R'_3Si^- anion arising from electron withdrawal by the R' groups.

The tin-germanium compounds $R_3SnGePh_3$ can be expected also to be cleaved very readily by base to give Ph_3GeH.

SCHEME 1
POSSIBLE MECHANISMS OF CLEAVAGE OF $Me_3SiGePh_3$ BY NaOMe — MeOH.

$$\begin{array}{lll}
(1) & MeO^- + Me_3SiGePh_3 \rightleftharpoons [(MeO)Me_3SiGePh_3]^- & \text{(fast)} \\
 & [(MeO)Me_3SiGePh_3]^- \rightarrow MeOSiMe_3 + Ph_3Ge^- & \text{(slow)} \\
 & Ph_3Ge^- + MeOH \rightarrow Ph_3GeH + MeO^- & \text{(fast)} \\
(2) & MeO^- + Me_3SiGePh_3 \rightarrow [MeO\text{—}Me_3Si \cdots GePh_3]^- & \\
 & \quad \rightarrow MeOSiMe_3 + Ph_3Ge^- & \text{(slow)} \\
 & Ph_3Ge^- + MeOH \rightarrow Ph_3GeH + MeO^- & \text{(fast)}
\end{array}$$

Experimental

Preparation of $R_3SiGePh_3$ compounds

A solution of Ph_3GeH in ether was treated with n-BuLi in ether, and the resulting solution of Ph_3GeLi was treated with Me_3SiCl or Et_3SiCl. The mixture was kept at room temperature for 3 h, then water was added. Extraction with ether, followed by washing, drying (Na_2SO_4), and evaporation of the extract left a solid which was recrystallized from ethanol to give $Me_3SiGePh_3$ (55%), m.p. 113—114°C (lit. [13], 114—115°C) or $Et_3SiGePh_3$ (48%), m.p. 95—96°C (lit. [14], 95—98°C).

Confirmation of cleavage product

A solution of $Me_3SiGePh_3$ (0.14 g, 0.38 mmol) in 0.1 *M* NaOMe-MeOH (5 cm^3) was kept at room temperature for 1 h. Hexane was added, followed by an excess of water. The hexane layer was separated, washed, dried ($MgSO_4$), and evaporated to leave Ph_3GeH (0.097 g, 83%), which gave ^1H NMR and IR spectra identical with those of an authentic sample. When MeOD was used the product was Ph_3GeD (IR spectrum). Similar results were obtained with $Et_3SiGePh_3$.

Rate measurements

The rates were determined spectrophotometrically as previously described for cleavages of Me_3SiR compounds [5], a wave-length of 244 (R = Me) or 242 nm (R = Et) being used.

Product isotope effects

These were determined by the method previously described [4,5]. This involved determination of the H/D rates in the Ph_3GeH/Ph_3GeD product mixtures obtained from cleavage of $Me_3SiGePh_3$ in 1 : 1 and 1 : 2 MeOH-MeOD containing 0.1 *M* NaOMe. For this the Applied Research Laboratories MPD 850 Organic Analyzer was used. When calibration was carried out with 9-^2H-fluorene, the product Ph_3GeD obtained from cleavage in 100% MeOD gave a H/D ratio of 17.55 compared with the theoretical 15. Thus the Ph_3GeD was used for calibration, and this led to H/D ratios of 65.11 and 46.06 for cleavage in 1 : 1 and 1 : 2 MeOH-MeOD, respectively, corresponding with PIE values of 2.5 and 3.0. Because of the relatively poor result for the H/D ratio of the product obtained from 100% MeOD as based on the calibration with 9-^2H-fluorene, the mean PIE value of 2.7 must be regarded as approximate, but it is unlikely that this value is in error by as much as ±0.7.

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