

Carbanion mechanisms

XVIII *. Generation of silyl anions by nucleophilic cleavage of disilanes **

Erwin Buncel ^a, T. Krishnan Venkatachalam ^a and U. Edlund ^b

^a *Department of Chemistry, Queen's University, Kingston, K7L 3N6 (Canada)*

^b *Department of Organic Chemistry, Umeå University, S-901 87 Umeå (Sweden)*

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Abstract

Organosilyl potassium compounds are conveniently generated by cleavage of hexaorganodisilanes with potassium *t*-butoxide in common solvents other than HMPA (*i.e.* in THF or DME). Nucleophilic attack on unsymmetrical disilanes results in formation of the more stable silyl anion, *i.e.* the one with the most phenyl groups bonded to silicon.

The utility of organosilyl-alkali metal compounds as synthetic reagents [1–3] has led to the development of a number of methods for their preparation. The commonly used methods have involved the reaction of alkali metals with the corresponding silyl halides, silanes, bis(trialkylsilyl)mercury compounds, or hexaorganodisilanes, in solvents such as tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME) [4–8]. More recent methods have entailed cleavage of the disilanes with powerful nucleophilic reagents in aprotic, strongly coordinating solvents, especially hexamethylphosphoramide (HMPA). The nucleophile/solvent systems most often used in disilane cleavage have been: MeONa/HMPT [9], ^tBuOK/HMPA [10], MeLi/HMPA [11], KH/DME-HMPA [12] and NaH/THF/18-crown-6 [12].

We wish to report the ready cleavage of disilanes of various structural types, in solvents other than HMPA, under homogeneous conditions and in the absence of alkali-metal complexing agents such as 18-crown-6. The recently discovered toxic properties of HMPA have rendered its use somewhat problematic, despite the superior coordinating properties of this solvent. Moreover, it has been noted that

Correspondence to: Dr. E. Buncel.

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Table 1

Generation of silyl potassium compounds by nucleophilic cleavage of disilanes with potassium t-butoxide

$R_3SiSiR'_3$	Solvent	Temperature (°C)	Time (h)	R_3SiK	Yield (%)
$Ph_3SiSiPh_3$	THF	25	24	Ph_3SiK	20
	THF	40	24	Ph_3SiK	30
	DME	25	18	Ph_3SiK	15
	DMPU	25	24	—	—
$Ph_2MeSiSiMePh_2$	THF	0	0.5	Ph_2MeSiK	65
	THF	0	1	Ph_2MeSiK	80
	DME	0	0.5	Ph_2MeSiK	90
	DME	0	1	Ph_2MeSiK	95
	DMPU	0	0.5	—	—
$Ph_3SiSiMePh_2$	THF	25	3	Ph_3SiK	10
	THF	25	5	Ph_3SiK	20
	THF	40	24	Ph_3SiK	40
	THF	0	0.5	Ph_3SiK	90
$Ph_3SiSiMe_2Ph$	DME	0	0.5	Ph_3SiK	85
	THF	0	24	Ph_3SiK	95
$Ph_3SiSiMe_3$	DME	0	0.5	Ph_3SiK	80
	DME	0	1	Ph_3SiK	90
	DME	0	1	—	—
$Me_3SiSiMe_3$	DMPU	0	1	Me_3SiK	60
	DMPU	0	2	Me_3SiK	70

nucleophilic reactions of the silyl anions in HMPA are often accompanied by electron transfer processes, leading to formation of side products [12].

We have found that hexaorganodisilanes containing methyl or phenyl groups, or both, bonded to silicon, are conveniently cleaved by the reaction of potassium tert-butoxide in tetrahydrofuran, 1,2-dimethoxyethane or *N,N'*-dimethylpropyleneurea (DMPU).

The reactions investigated in this work are shown in eqs. 1–6:



Reaction conditions and yields of the silyl anions are given in Table 1. The silyl anions were characterized by their 1H and ^{13}C NMR spectra [13]. A representative ^{13}C NMR spectrum of a reaction mixture, for the case of $Ph_3SiSiMe_2Ph$, is presented in Fig. 1. The chemical shifts for the silyl anions were in good agreement with our earlier work [13]. Assignment of the ^{13}C chemical shifts for the silyl ethers, $R'_3SiOCMe_3$, obtained in the reactions of the disilanes, $R_3SiSiR'_3$, with potassium t-butoxide, is given in Table 2.

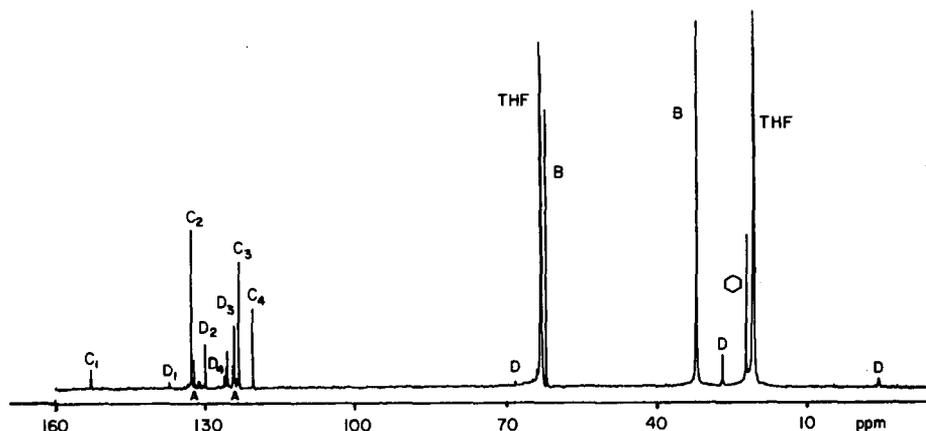


Fig. 1. ^{13}C NMR spectrum of products of reaction between $\text{Ph}_3\text{SiSiMe}_2\text{Ph}$ and potassium *t*-butoxide in THF at 0°C after 30 min. The peaks are designated as: (A) $\text{Ph}_3\text{SiSiMe}_2\text{Ph}$; (B) $(\text{CH}_3)_3\text{COK}$; (C) Ph_3SiK ; (D) $\text{PhMe}_2\text{SiOCMe}_3$. The suffices 1, 2, 3 and 4 refer to *ipso*, *ortho*, *meta* and *para* carbons, respectively. Cyclohexane was used as internal reference (27.7 ppm).

The results in Table 1 show that the reaction of disilanes with $^t\text{BuOK}$ provides reasonable yields of R_3SiK derivatives in THF and DME when one or more of the R groups is a phenyl moiety, but use of DMPU as solvent did not give detectable yields of silyl anions in these cases. It appears that DMPU reacts with these silyl anions since the ^{13}C NMR spectra showed the presence of unidentified products. On the other hand, formation of Me_3SiK can be accomplished in DMPU as solvent but not in DME.

Our earlier studies [13,14] have shown that triphenylsilylpotassium in THF and DME exists largely as contact ion pairs (CIP). In addition, our previous attempts to generate Ph_3SiK in DMPU by various methods also failed, only products of decomposition being detected [14a]. Possibly, the highly polar DMPU solvent may not be able to stabilize the CIP species and the solvent separated ion pairs (SSIP)

Table 2

^{13}C chemical shifts of silyl *t*-butyl ethers, $\text{R}'_3\text{SiOCMe}_3$, obtained in reactions of the disilanes, $\text{R}_3\text{SiSiR}'_3$, with potassium *tert*-butoxide (δ , ppm, with cyclohexane as internal reference at 27.7 ppm)

$\text{R}'_3\text{SiOCMe}_3$ ($\text{R}'_3\text{Si}$)	Solvent	<i>ipso</i>	<i>ortho</i>	<i>meta</i>	<i>para</i>	Me_3	C-O	Me-Si
Ph_3Si	THF	147.3	135.8	127.9	127.8	32.3	74.4	
	DME	146.5	136.3	128.3	127.9	32.5	74.7	
Ph_2MeSi	THF ^a	139.5	134.9	128.1	129.8	32.4	72.0	0.23
	DME ^a	139.5	135.3	128.5	130.2	32.5	73.9	0.35
	THF ^b	139.5	134.9	128.2	129.9	32.4	73.9	0.20
PhMe_2Si	THF	141.1	134.0	128.3	128.6	32.4	72.4	1.5
	DME	146.6	134.1	128.3	128.6	32.4	73.8	1.6
Me_3Si	THF ^c					32.4	72.6	2.7
	DME ^c					32.4	73.3	2.8
	DMPU ^d					32.7	72.6	2.6

^a From reaction of $\text{Ph}_2\text{MeSiSiMePh}_2$. ^b From reaction of $\text{Ph}_3\text{SiSiMePh}_2$. ^c From reaction of $\text{Ph}_3\text{SiSiMe}_3$. ^d From reaction of $\text{Me}_3\text{SiSiMe}_3$.

may react with DMPU. In contrast, the lack of formation of Me_3SiK in solvents THF and DME in the present work, suggests that this anion is not stabilized in these less polar solvents compared to DMPU.

The regiochemistry of nucleophilic attack of unsymmetrical disilanes has been examined in several cases. It is interesting that cleavage of unsymmetrical disilanes results in the formation of the more stable silyl anion, i.e. the anion with the most phenyl groups bonded to silicon. However, a steric factor may contribute to this result since the bulky *t*-butoxide nucleophile would tend to attack the sterically least hindered silicon atom. The importance of a steric factor is evident in the much greater reactivity of $\text{Ph}_3\text{SiSiMe}_3$ compared to $\text{Ph}_3\text{SiSiPh}_3$ (Table 1).

In conclusion, we have described a simple method for the preparation of silylpotassium derivatives by reaction of $^t\text{BuOK}$ with disilanes. The reaction provides reasonable yields of R_3SiK derivatives in THF or DME when one or more R group is a phenyl moiety, but DMPU is the solvent of choice in the case of Me_3SiK . The generally ready accessibility of disilanes renders this method of preparation of silyl potassium compounds an attractive alternative to other currently available methods.

Experimental section

Materials and procedures

Tetrahydrofuran (THF), 1,2-dimethoxyethane (DME), 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidone (*N,N'*-dimethylpropyleneurea, DMPU) and cyclohexane were purchased from Fluka, and potassium *t*-butoxide was procured from Alfa. The disilanes were prepared by literature procedures [15] except for 1,2-dimethyl-1,1,2,2-tetraphenyldisilane which was purchased from Petrarch Inc. The THF, DME and cyclohexane were treated with sodium wire overnight, then distilled under argon into a vessel containing freshly cut shiny potassium metal and distilled again under argon. The distillation from potassium metal was repeated once more and the final distillate was kept over sodium wire in a septum sealed flask from which solvent was transferred by syringe under argon. The DMPU was allowed to stand over molecular sieves (4A grade) overnight and filtered in an argon flushed glove box. This treatment was repeated three times and the resulting solvent was stored under argon over molecular sieves. Potassium *t*-butoxide was purified by sublimation under vacuum at 150–160°C. Solutions of $^t\text{BuOK}$ in the organic solvents prepared under argon, when kept in the refrigerator, remained colorless for several days after which they were not used in the preparations.

The apparatus used in the work has been described previously [13,14,16]. In a typical preparation, the sublimed $^t\text{BuOK}$ (1.8 g) was introduced into a 50 mL round bottom flask under argon in a glove box, solvent (20 ml) was added, the flask was septum capped, removed from the glove box and stirred magnetically to yield a clear solution. The $^t\text{BuOK}$ solution (5 ml) was added by means of a syringe to a septum capped 20 ml tube containing 0.1 g of substrate and the reaction was allowed to occur at various temperatures and reaction times. The extent of the reaction was followed by transferring an aliquot of the reaction solution by syringe under argon into a septum capped NMR tube, adding cyclohexane as internal reference, and recording the NMR spectrum.

NMR spectra were recorded on a Bruker 400 MHz multinuclear spectrometer with selective decoupling. The spectrometer was standardized by means of ethylbenzene. The methods used were as described in our previous work [13,14].

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