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Efficient formation and cleavage of disilanes by potassium-graphite. Silylation with silyl metal reagents

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Abstract

Potassium-graphite laminate (C_8K) very rapidly forms disilanes from chlorosilanes and then rapidly cleaves the disilanes to give silyl potassium reagents which can be converted into potassium silyl cuprates, -manganates, and -vanadates that are useful for various nucleophilic substitution and addition reactions.

Introduction

Nucleophilic silylation of alkynes [1], allenes [2], allylic and propargylic substrates [3] or α,β-unsaturated carbonyl compounds [4], including nitriles, by lithium silyl cuprates [5] have made available numerous kinds of organosilicon compounds that are valuable intermediates in organic synthesis [6]. While the formation of the more or less complex cuprates is rapid, and their reactions with electrophiles are readily performed, the generation of the precursor silyl-lithium reagents is generally slow [4a,7], and this limits the over-all efficiency of the reaction sequences. All the procedures for their preparation hitherto described are limited to a greater or lesser extent by specific shortcomings, as follows:

1. The two-step reactions of chlorosilanes with intermediate formation of bissilylmercury compounds followed by treatment with an excess of lithium are extremely slow and too complicated [8].
2. The cleavage of disilanes by sodium or potassium ethoxide needs aprotic dipolar solvents or crown ether in oxolane [9], which are difficult to remove and are known to hamper certain subsequent reactions [10,11].
3. Proton abstraction from monohydric silanes by an excess of potassium hydride is quite slow and requires dimethoxyethane (DME) or hexamethyl phosphoramide (HMPA) as solvents [11]. Both, sodium and lithium hydrides are ineffective.
4. The fission of silicon–silicon bonds by butyl- or methyllithium, although very efficient, can only be performed in the presence of HMPA [12], and the resulting products show a distinct propensity for side reactions in nucleophilic additions [13].

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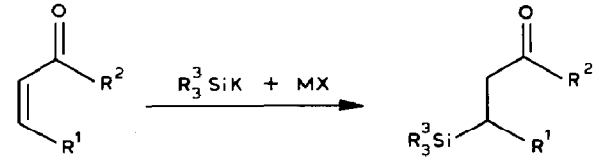
5. Reactions of chlorosilanes or disilanes in oxolane with lithium carried out at room temperature in order to minimize solvent cleavage [14] are very slow [4a,7], and require a large excess of high purity metal [15].
6. The reactions of disilanes with potassium [16], sodium-potassium alloy [16] or sodium naphthalide [16,17], all require elevated temperatures and lead to substantial cleavage of the ether solvents generally used, and furthermore work-up is rather complicated [16].
7. The fluoride-induced cleavage of disilanes is best effected by a complex reagent [18] and the products cannot be directly converted into silyl cuprates.

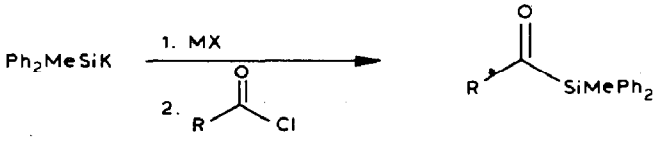
Results and Discussion

The important field of metal-induced reductions in organic chemistry has recently gained a new dimension by the introduction of graphite-supported metals of very high reactivity [19]. Among others [19], the Reformatsky- [20], Grignard- [21], and McMurry-reactions [22] could be extended in their scope and/or improved, generally applicable magnesium-graphite and low-valent titanium-based pinacol reductions [22,23] were found, and the synthesis of glycals was substantially improved by use of zinc/silver-graphite [24] or C_8K [25]. The great efficiency and selectivity under very mild conditions of reductions of even polyfunctional compounds such as glycosyl halides by C_8K [25] suggested to us that this would be a promising reducing agent for chlorosilanes and disilanes. As can be seen from Table 1, various chlorosilanes containing at least one phenyl group in the presence of



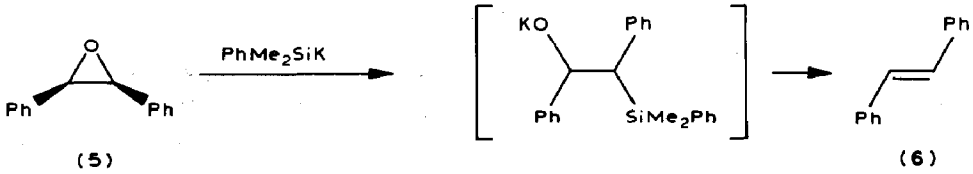
(1)

(1) $R^1 / R^2 = -(CH_2)_3-$
(2) R^1 = Phenyl, R^2 = OEt



(2)

(3) R = Phenyl
(4) R = Cyclohexyl



(3)

(5) (6)

Table 1

Disilanes by C_8K-reduction of chlorosilanes in oxolane

R^1	R^2	R^3	Temperature (°C)	Reaction time (min)	Yield (%)
Ph	Ph	Ph	0	5	90
Ph	Ph	Me	0	5	94
Ph	Ph	t-Bu	0	5	96
Ph	Me	Me	0	5	95
Me	Me	Me	25	60	88
Me	Me	t-Bu	25	60	92

equimolar amounts of C_8K immediately give the corresponding symmetrical disilanes [26] in excellent yields. Under the same conditions trialkylchlorosilanes react somewhat more slowly.

All phenyl-containing disilanes are cleaved very rapidly by a second equivalent of C_8K, with formation of the corresponding silyl potassium, which can also be directly obtained in reactions of the respective silyl chlorides with two moles of C_8K. This again demonstrates the extremely high reactivity of this reducing agent, which is superior to any of the methods listed above.

Like the silyllithium reagents almost always previously used [1–6] the silylpotassiums can be transformed in complex silyl metalates by addition of transition metal salts. Their reactions with an array of electrophiles such as chlorosilanes, alkyl- and acyl halides (eq. 2) [27], epoxides (eq. 3) [28], and α,β-unsaturated carbonyl compounds (eq. 1) lead to the corresponding organosilyl derivatives, as shown in Table 2. The utility of complex silyl manganates [29] and vanadates in these reactions demonstrates the transferability of carbanion [30,31] to silyl anion chemistry.

While the various reactions of the silyl-potassium reagents were found to be of equal synthetic value as of their lithium counterparts, the formation of the former is extremely rapid, they do not react with the oxolane solvent, and work-up is very conveniently carried out simply by filtering off the insoluble material. The reaction sequences are easily monitored by using the colour changes from that of the bronze-coloured C_8K to the brownish-green of the silylpotassium, to the reddish-brown after addition of transition metal salts, and the immediate change to the black colour of the graphite on admixture with electrophiles.

It is evident that nucleophilic reactions of silyl metalates are not restricted to those of cuprates.

Experimental

General

Reactions were performed in oxolane (Merck puriss. p.a.) distilled over $LiAlH_4$ before use. For all C_8K preparations Lonza HSAG 9 graphite was used, but any other type of graphite was found to be suitable. TLC was performed on precoated silica gel plates (Merck 60 F 254) and column chromatography on silica gel (Merck 230–400 mesh). ^1H NMR spectra were recorded with a Hitachi Perkin–Elmer R24B spectrometer, and ^{13}C and ^{29}Si NMR spectra on a Bruker MSL 300 instrument; deuterochloroform (Aldrich, containing 5% tetramethylsilane as internal standard),

Table 2

Nucleophilic substitution and addition reactions of silyl metalates

Educt	Electrophile	Product	Additive [a]	Reaction time (min) [b]	Temperature (°C) [c]	Yield (%)
t-BuPh$_2$SiSiPh$_2$-t-Bu	t-BuMe$_2$SiCl	t-BuPh$_2$SiSiMe$_2$-t-Bu	–	5/5	0	97
t-BuMe$_2$SiSiMe$_2$-t-Bu	t-BuPh$_2$SiCl	t-BuPh$_2$SiSiMe$_2$-t-Bu	–	120/10	25	12 [d]
Ph$_3$SiCl	Me$_3$SiCl	Ph$_3$SiSiMe$_3$	–	5/5	0	98
MePh$_2$SiCl	benzyl bromide	PhCH$_2$SiPh$_2$Me	–	5/60	0	90
MePh$_2$SiSiPh$_2$Me	cyclohex-2-enone	**1**	CuI (0.5)	5/120	−70	60
		1	CuCN (0.5) [e]	5/120	−70	70
		1	MnI$_2$ (1.0)	5/120	0	68
MePh$_2$SiSiPh$_2$Me	ethyl cinnamate	**2**	CuCN (0.5)	5/150	−70	74
MePh$_2$SiSiPh$_2$Me	benzoyl chloride	**3**	–	5/80	−70	– [f]
		3	CuCN (0.5) [g]	5/80	−70	54
		3	MnI$_2$ (1.0)	5/80	−10	74
		3	VCl$_3$ (0.3)	5/80	−70	67
MePh$_2$SiSiPh$_2$Me	cyclohexanecarboxyl chloride	**4**	MnI$_2$ (1.0)	5/100	−10	79
		4	VCl$_3$ (0.3)	5/80	−70	80
Me$_2$PhSiCl	*cis*-stilbeneoxide	*trans*-stilbene (**6**)	–	5/30	20	90

[a] (1.0), (0.5) or (0.3) refers to molar ratio additive to silyl potassium reagent. [b] The first figure is the time of reaction of the disilane or chlorosilane with the C_8K and the second that of the formed reagent. [c] With the transition metal salt and the subsequent reaction with the electrophile. [d] 1,2-Di-t-butyl-1,1,2,2-tetraphenyldisilane formed as major product because of the slow cleavage reaction 1,2-di-t-butyl-1,1,2,2-tetramethyldisilane. [e] The higher order silyl potassium cuprates obtained with CuCN permit cleaner 1,4-additions and higher yields (cf. ref. 5) [f] Complex mixture (c.f. ref. 32) [g] With CuI this reaction is reported to fail (cf. ref. 27).

was used as solvent unless otherwise stated. IR spectra were recorded on a Beckman IR 33 instrument from films of the corresponding product on a NaCl plate. The chlorosilanes, CuCN, and MnI_2 were purchased from Fluka AG, Switzerland, VCl_3 by Aldrich, FRG. Toluene or toluene/ethyl acetate (5/1) were used as solvents for chromatography.

Preparation of disilanes. General procedure

A mixture of graphite (3.0 g, 250 mmol), degassed at 150 °C for 20 min, and potassium (1.2 g, 31 mmol) is heated for 15 min at 150 °C with mechanical stirring under a stream of argon. After rapid addition of a solution of chlorosilane (30 mmol) in oxolane (30 ml) to the bronze-coloured suspension of C_8K in oxolane (25 ml) at 0 °C with stirring under argon, the mixture is filtered, the filtrate evaporated, and the residues recrystallized from ethanol or in the case of liquids, distilled.

Organosilanes from silyl metalates. General procedure

(A) From disilanes. A solution of disilane (14 mmol) in oxolane (25 ml) is added to a stirred suspension of C_8K (31 mmol) in oxolane (25 ml) at 0 °C. After 5 min the appropriate amount (cf. Table 2) of the transition metal salt is added in one portion at the temperature given in the table, and this is followed by dropwise addition of a solution of the corresponding electrophile (15 mmol) in oxolane (25 ml). The mixture is stirred until the reaction is complete (TLC; cf. Table 2), then filtered, the solvent evaporated, and the residue subjected to column chromatography.

(B) From chlorosilanes. This was carried out as described above but with replacement of the disilane by the relevant chlorosilane and reduction of the amount of this reagent and of the electrophile to 7 mmoles each.

Hexamethyl disilane: b.p. 112–113 °C (lit. 112–113 °C [33]); $n_D^{20} = 1.4226$ (lit.: 1.4229 [33]); ^{29}Si NMR: −19.82.

1,2-Di-t-butyl-1,1,2,2-tetramethyl disilane: b.p. 60 °C (70 torr, Kugelrohr); ^{1}H NMR: 0.06(s,12H); 0.95(s,18H); ^{29}Si NMR: −8.61.

1,2-Di-t-butyl-1,1-dimethyl-2,2-diphenyl disilane: syrup; ^{1}H NMR: 0.15(s,6H); 0.68(s,9H; -$SiPh_2$-t-Bu); 1.0(s,9H; -$SiMe_2$-t-Bu); 7.1–7.7(m,10 H); ^{29}Si NMR: −9.17(-$SiMe_2$t-Bu); −11.48(-$SiPh_2$-t-Bu).

1,1,1-Trimethyl-2,2,2-triphenyl disilane: m.p. 107–108 °C (lit.: 107–108 °C [33]); ^{1}H NMR: 0.08(s,9H); 7.1–7.65(m, 15H); ^{29}Si NMR: −18.43(-$SiMe_3$); −20.20 (-$SiPh_3$) [36].

1,1,2,2-Tetramethyl-1,2-diphenyl disilane: m.p. 33–35 °C (lit.: 34–35 °C [15]); ^{1}H NMR: 0.25(s,12H); 7.25(bs,10 H); ^{29}Si NMR: −21.70.

1,2-Di-t-butyl-1,1,2,2-tetraphenyl disilane: m.p. 203–204 °C; ^{1}H NMR: 0.8(s,18H); 7.05–7.7(m,20 H); ^{29}Si NMR: −13.36.

1,2-Dimethyl-1,1,2,2-tetraphenyl disilane: m.p. 139–141 °C (lit.: 141–143 °C [35]); ^{1}H NMR: 0.42(s,6H); 7.2(s,20 H); ^{29}Si NMR: −23.21.

Hexaphenyl disilane: m.p. 350–355 °C (lit.: 352, 355, 365–366 °C; [33]); ^{1}H NMR(DMSO-d_6): 7.1–7.4(m); ^{29}Si NMR: −26.54 [34].

Benzylmethyldiphenyl silane: m.p. 66–69 °C (lit.: 68–69 °C [37]); ^{1}H NMR: 0.4(s,3H); 2.6(s,2H,-CH_2-); 7.15–7.85(m,15H); ^{29}Si NMR: −8.51.

3-(Methyldiphenylsilyl)cyclohexanone (1): oil; IR: 1685cm^{-1}; ^{1}H NMR: 0.6(s,3H), 1.87–2.5(m,9H); 7.4(bs,10H); ^{29}Si NMR: −6.73.

Ethyl (dimethylphenylsilyl) 3-phenyl propanoate (2) [4a]: oil; IR: 1720 cm^{-1}; ^1H NMR: 0.35 and 0.4(s,6H); 1.2(t,3H,CH_3-); 2.6–3.0(m,3H, -CH,CH_2-); 4.0(q,2H,-OCH_2-); 7.0–7.5(m,5H,Ph-).

Benzoyl methyl diphenyl silane (3): yellow oil; IR: 1600 cm^{-1}; ^1H NMR: 0.65(s,3H); 7.25–7.9(m,15H); ^{13}C NMR: −3.13(MeSi-); 127.99, 128.28, 129.12, 130.13, 132.91, 133.99, 135.24 (Ph); 231.80 (=CO); ^{29}Si NMR: −20.29.

Cyclohexanecarboxyl diphenyl methyl silane (4): yellow oil; IR: 1615 cm^{-1}; ^1H-NMR: 0.6(s,3H,MeSi-); 0.65–1.5(m,10H); 2.7(m,1H,=CH-CO-); 7.05–7.8(m,Ph, 10H); ^{13}C-NMR: −4.52(MeSi-); 25.71, 26.08, 27.01 (ring carbon atoms); 56.19(=*C*H-CO); 127.65, 128.22, 130.04, 134.12, 135.09 (Ph); 246.37(=CO); ^{29}Si NMR: −24.87.

(E)-Stilbene (6) m.p. 124–125 °C (lit.: 124–125 °C, [33]); ^1H NMR: 7.1(s,2H); 7.2–7.6(m,10 H); identified by comparison with an authentic sample.

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