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Potassium *tert*-Butoxide-Catalyzed Dehydrogenative Si–O Coupling: Reactivity Pattern and Mechanism of an Underappreciated Alcohol Protection

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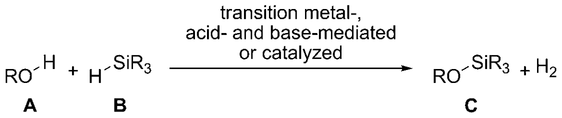
Abstract: A remarkable *tert*-butoxide-catalyzed coupling of alcohols and silanes is reported. Dihydrogen and not hydrochloric acid (generated in the prevalent, related coupling of alcohols and chlorosilanes) is formed as the sole by-product. A comprehensive survey of common silanes provides a reliable tool for the predictability of their reactivity under defined reaction conditions. The debated mechanism of this transformation is investigated monitoring the stereochemical course at the silicon atom by means of a silicon-stereogenic silane. On this basis, a transition state for the enantiospecific Si–O coupling step is suggested rationalizing the observed frontside attack and thus retention at the silicon atom.

Keywords: alcohols · nucleophilic substitution · protective groups · reaction mechanisms · silylation

Introduction

Elegant complex-molecule synthesis is rated highly if it only involves a minimal number or even no protective group manipulations.[1] Nevertheless, protective group chemistry will certainly hold its place as a pivotal tool in organic synthesis. The chemistry of protective groups itself as well as strategic synthetic planning was greatly influenced and enhanced by the Si–O linkage for temporary hydroxy group protection. Its extensive use stems from the convenient alteration of both the steric and the electronic environment at the silicon atom, which, in turn, oftentimes ensures orthogonality in the protection and deprotection steps.[2]

An impressive selection of Si–O bond forming reactions is available today, the prominent protocol being the treatment of an alcohol with a moisture-sensitive chlorosilane in the presence of a nucleophilic catalyst and a stoichiometric amount of a base as a hydrochloric acid scavenger.[3] While this setup, which eventually produces equimolar amounts of a hydrochloride salt by-product, is commonly employed without reconsidering alternatives, another powerful technique is only rarely used. The direct dehydrogenative Si–O coupling of alcohols **A** and readily available silanes **B**[4] liberates dihydrogen as the sole by-product (Scheme 1).[5] Remarkably, it is long known that this process is efficiently mediated or catalyzed by several late transition metal complexes[6] as well as Brønsted and Lewis acids/bases.[7]



Scheme 1. Dehydrogenative Si–O coupling.

In connection with a novel kinetic resolution strategy, we had recently developed diastereoselective, transition metal-catalyzed Si–O couplings of racemic mixtures of alcohols and enantioenriched silicon-stereogenic silanes.[8,9] The central step of these Cu–H[8] and Rh–H[9] catalyses is believed to be a racemization-free σ-bond metathesis of an intermediate transition metal alkoxide and the Si–H bond.[8c] The active catalyst is normally generated from the otherwise inert transition metal *tert*-butoxide through alkoxide exchange. Sodium or potassium *tert*-butoxide and a transition metal salt serve as viable precatalysts. It was in the course of these investigations that we discovered the catalytic activity of potassium *tert*-butoxide alone, as indicated by the vigorous evolution of dihydrogen. We are aware of the fact that such transition metal-free, alkoxide-catalyzed dehydrogenative Si–O couplings are not totally unprecedented,[5,7] but the present potassium *tert*-butoxide catalysis displays

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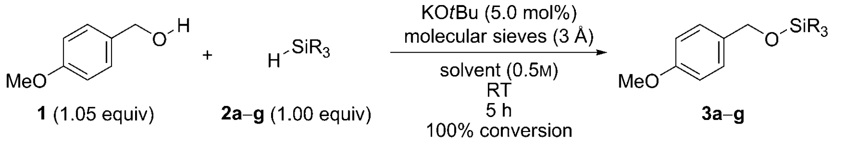
noteworthy generality and practicability. We therefore decided to elaborate on this reaction and wish to report a handy reactivity survey of several silane–solvent combinations and the corroboration of an unusual mechanism.

Table 1. Reactivity pattern in the potassium *tert*-butoxide-catalyzed Si–O coupling.



Entry	Silane 2[4]	Abbreviation	Yield of isolated product 3 [%]		
			THF	THF/DMF 4:1	DMF
1	Ph_3Si–H (**2a**)	TPS-H	99	92	98
2	$MePh_2Si$–H (**2b**)	MDPS-H	99	99	97
3	Me_2PhSi–H (**2c**)	DMPS-H	76[a]	94	94
4	*t*$BuPh_2Si$–H (**2d**)	TBDPS-H	–	92[a]	99
5	Et_3Si–H (**2e**)	TES-H	–	97	95
6	*t*$BuMe_2Si$–H (**2f**)	TBDMS-H	–	–	90[a]
7	*i*Pr_3Si–H (**2g**)	TIPS-H	–	–	68[b,c]

[a] The reaction required double the amount of KO*t*Bu (10 mol%) and extended reaction time (12 h). [b] The reaction required double the amount of KO*t*Bu (10 mol%), 18-crown-6 (10 mol%), and extended reaction time (14 h). [c] Reaction in DMSO yielded 69% conversion at extended reaction time (14 h).

Results and Discussion

Reactivity Pattern

The pivotal experimental observation was made in a systematic solvent screening. In the past, we had always used toluene as the solvent as well as a donor-functionalized alcohol and sterically encumbered triorganosilanes.[8,9] Under those reaction conditions, the transition metal was necessary to promote the Si–O coupling, likely to be assisted by a directing effect of the tethered donor. Conversely, performing the coupling of a simple primary alcohol, for example, **1**,[10] and an unhindered silane **2** in THF immediately liberated dihydrogen accompanied by silicon ether formation (**1**→**3**, column 4, Table 1). In detail, aryl-substituted silanes **2a–c** reacted cleanly in the presence of catalytic amounts of potassium *tert*-butoxide (Table 1, entries 1–3) whereas trialkylsilanes **2e–g** were completely inert (Table 1, entries 5–7); the apparent activation by aryl groups at the silicon atom was overridden by sterics, *tert*-butyldiphenylsilane (**2d**) showed no conversion at all (Table 1, entry 4).

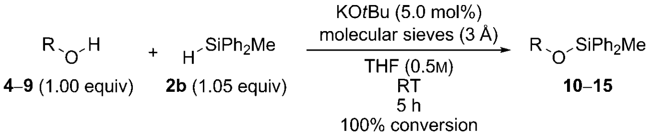
The substantial decrease in reactivity in the order Ph_3Si–H ≈ $MePh_2Si$–H > Me_2PhSi–H ≫ *t*$BuPh_2Si$–H ≈ $Alkyl_3Si$–H might be rationalized by the distinct Lewis acidities of these silanes. As C(sp^2) is more electronegative than C(sp^3), the Lewis acidity at the silicon atom will correlate with the number of electron-withdrawing sp^2-hybridized substituents attached to it. In order to render the less reactive silanes more Lewis acidic, a Lewis base might be added to generate a hypervalent and therefore more Lewis acidic silicon intermediate (Lewis base activation of Lewis acids).[11] The admixture of DMF (or DMSO) and the reaction mixture (column 5, Table 1) indeed facilitated the Si–O coupling of *tert*-butyldiphenylsilane (**2d**) as well as triethylsilane (**2e**) (Table 1, entries 4 and 5) but hindered silanes **2f** and **2g** remained, again, untouched under these reaction conditions (Table 1, entries 6 and 7). In DMF alone (column 6, Table 1), the former was finally brought to reaction albeit requiring double the amount of potassium *tert*-butoxide and prolonged reaction time (Table 1, entry 6); tri-*iso*-propylsilane (**2g**) was sterically too congested to participate in this reaction under conventional conditions.[12] Either addition of 18-crown-6[5a] or a solvent switch to pure, slightly more Lewis basic DMSO then facilitated turnover (Table 1, entry 7).

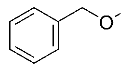
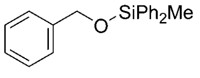
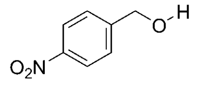
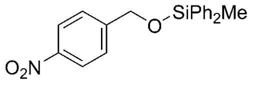
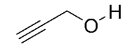
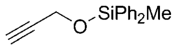
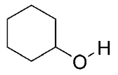
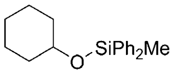
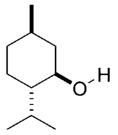
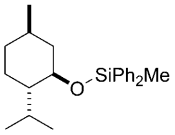
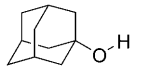
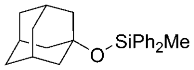
Abstract in German: Eine bemerkenswerte, *tert*-butanolat-katalysierte Kupplung von Alkoholen und Silanen wird vorgestellt. Diwasserstoff und nicht Chlorwasserstoffsäure (aus der weitverbreiteten, entsprechenden Kupplung von Alkohlen und Chlorsilanen) wird als einziges Abfallprodukt gebildet. Eine umfassende Untersuchung gebräuchlicher Silane stellt ein verlässliches Instrument zur Vorhersagbarkeit ihrer Reaktivität unter definierten Reaktionsbedingungen zur Verfügung. Der kontrovers diskutierte Mechanismus dieser Umsetzung wird über den stereochemischen Verlauf am Siliciumatom mit einem siliciumstereogenen Silan untersucht. Auf dieser Grundlage wird ein Übergangszustand für den enantiospezifischen Kupplungsschritt vorgeschlagen, der den beobachteten Vorderseitenangriff und damit die Retention am Siliciumatom erklärt.

Verification of the General Procedure

We made several noteworthy observations: 1) While potassium *tert*-butoxide (5.0 mol%) and **1** reacted cleanly with silanes in the above solvent systems, almost no conversion was detected neither with the potassium alkoxide of **1** alone nor with a 1:1 mixture of the potassium alkoxide of **1** and *tert*-butanol (5.0 mol%) and **1**. The former outcome indicates that a proton source (traces of water or the alcohol itself) is needed for turnover[13] but reasons for the latter outcome are less obvious. Solubility of the alkoxides involved appears to be a crucial parameter in this reaction; whereas potassium *tert*-butoxide (5.0 mol%) and **1** give a clear solution, the potassium alkoxide of **1**–*t*-butanol–**1** cocktail remained turbid in THF, THF/DMF 4:1, and DMF. 2) The reaction rate increased by at least one order of magnitude in the presence of 18-crown-6 likely owing to an increased nucleophilicity of the alkoxide. 3) We note that this reaction was also catalyzed by sodium *tert*-butoxide yet at markedly lower rate. 4) In all reactions, the formation of Si–OH and Si–O–Si by-products was almost suppressed by addition of molecular sieves although excessive amounts of it inhibited the reaction. 5) Using 5.0 mol% of potassium *tert*-butoxide turned out to be practicable, however, lower catalyst loadings were possible. The general procedure was then further verified for a few 1°, 2°, and even 3° alcohols (Table 2). The high-yielding etherification of 1-adamantanol in THF/DMF 4:1 or at a higher rate in THF/DMSO 4:1 is remarkable (**9**$\rightarrow$**15**, Table 2, entry 6) in that we had never observed silylated *tert*-butanol.

Table 2. Brief verification of the potassium *tert*-butoxide-catalyzed Si–O coupling.



Entry	Alcohol	Product	Yield of isolated product [%]
1	 **4**	 **10**	99
2	 **5**	 **11**	93
3	 **6**	 **12**	75
4	 **7**	 **13**	97
5	 **8**	 **14**	99
6	 **9**	 **15**	98[a,b]

[a] The reaction was performed in THF/DMF 4:1 and extended reaction time (14 h). [b] Quantitative conversion was seen in THF/DMSO 4:1 within 5 h.

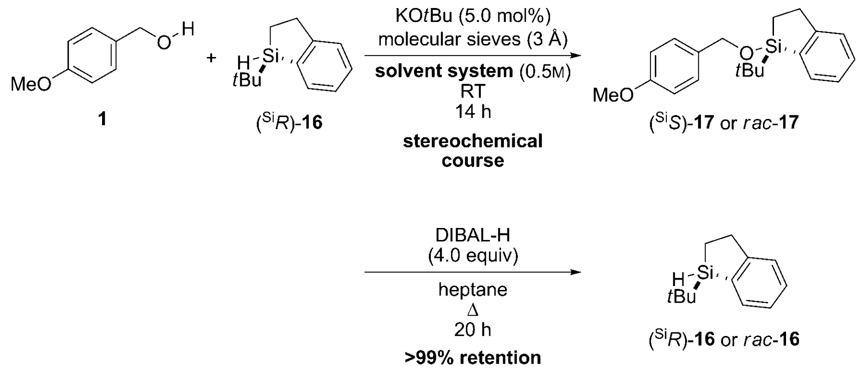
Reaction Mechanism

Over the last few years, we have been largely involved in the chemistry of silicon-stereogenic silanes,[14] which serve as stereochemical probes for a better understanding of reaction mechanisms.[15] The mechanism of alkoxide-mediated dehydrogenative couplings was the subject of several investigations in the past,[7,13,16,17] and Wilzbach et al.[16] as well as Sommer et al.[18] had already suggested reasonable mechanisms, which rationalized the observed predominant stereoretention at the silicon atom.[19] On the other hand, Le Bideau et al. recently suggested a mechanism for a hydroxide-catalyzed coupling, which would result in racemization.[5a] We therefore decided to also interrogate the stereochemical course of our related potassium *tert*-butoxide-catalyzed Si–O coupling. As expected, acyclic *tert*-butylmethylphenylsilane (99% *ee*) was too unreactive to undergo the coupling using THF as solvent, which is why we employed the strained silane (${}^{Si}R$)-**16** (84–89% *ee*) recently introduced by us.[8b,c] A dehydrogenative Si–O coupling–reductive Si–O cleavage sequence would then reveal the enantiospecificity of the coupling step (Table 3). When THF or THF/DMF 4:1 were used as solvents, the reaction proceeded with (almost) immaculate stereoretention at the silicon atom [(${}^{Si}R$)-**16**$\rightarrow$(${}^{Si}S$)-**17**$\rightarrow$(${}^{Si}R$)-**16**, entries 1 and 2, Table 3], whereas racemization was seen with DMF as solvent [(${}^{Si}R$)-**16**$\rightarrow$*rac*-**17**$\rightarrow$*rac*-**16**, entry 3, Table 3]; the acyclic chiral silane also racemized in the latter solvent. The Lewis basicity as well as the E_T parameter (that is the polarity) of these solvents might be important [E_T(THF) = 37.4 vs E_T(DMF) = 43.2 and E_T(DMSO) = 45.1].[20] DMF and DMSO might either increase the Lewis acidity of tetravalent silicon compounds through coordination and thus facilitate activation[11] or simply stabilize charged species.

To further understand this curious solvent effect,[21] namely the role of DMF,[22] in this catalysis, we conducted a series of racemization experiments of both silane (${}^{Si}R$)-**16** (Table 4) and silicon ether (${}^{Si}S$)-**17** (Table 5). All reactions were performed in DMF at room temperature; (${}^{Si}R$)-**16** and (${}^{Si}S$)-**17** were configurationally stable in THF. Silane (${}^{Si}R$)-**16** basically retained its stereochemical integrity in all cases (entries 1–4, Table 4); marginal loss of enantioenrichment was detected after prolonged treatment with potassium *tert*-butoxide (1.0 equiv), which cannot explain completely racemized *rac*-**17** in the presence of catalytic amounts of potassium *tert*-butoxide (5.0 mol%). It is particularly important to note that (${}^{Si}R$)-**16** is not racemized by pure DMF (vide infra). An almost similar situation is seen for silicon ether (${}^{Si}S$)-**17** (entries 1–4, Table 5) but this time, potassium *tert*-butoxide (1.0 equiv) brings about complete racemization with concomitant decomposition, which, in turn, might account for the loss of stereochemical information observed in the Si–O coupling through subsequent *tert*-butoxide-induced racemization.

As *tert*-butoxide is able to interact with (${}^{Si}S$)-**17** (entry 2, Table 5), the alkoxide of **1** (generated from KH and **1**) might do so even more. However, interaction of tetravalent silicon with an alkoxide results in (partial) racemization exclusively with sterically hindered systems (entry 2, Tables 4 and 5) while enantiospecific alkoxy–alkoxy exchange at silicon ethers is well-documented.[23,24] To understand this, front- and backside attack at the silicon atom must be juxtaposed: non-hindered alkoxides favor (concerted) frontside S_N2-type mechanisms;[23] conversely, hindered alkoxides favor S_N2-type backside attack because of sterical considera-

Table 3. Solvent dependence of the stereochemical course at the silicon atom.[a]



Entry	Si–O coupling Solvent system	Yield of **17** [%]	*ee* of (^{Si}R)-**16** [%]	Stereochemical course	Si–O cleavage Yield of **16** [%]	*ee* of **16** [%]
1	THF	97	89	retention	74	89
2	THF/DMF 4:1	70	85	retention	74	80
3	DMF	82	84	racemization	72	0

[a] Enantiomeric excesses determined by HPLC analysis using a Daicel Chiralcel OJ-RH column (MeOH/H_2O = 80:20 at 12 °C): 35.3 min for (^{Si}R)-**16** and 38.5 min for (^{Si}S)-**16**.

Table 4. Racemization experiments of silane (^{Si}R)-**16** in DMF.

Entry	Additive (1.0 equiv)	*t* [h]	Enantiomeric excess [%][a] before	 after
1	–	24	84	80
2	potassium *tert*-butoxide	24	84	60
3	potassium alkoxide of **1** (generated from KH and **1**)	24	89	89
4	alcohol **1**	14	89	89

[a] Determined by HPLC analysis using a Daicel Chiralcel OJ-RH column (MeOH/H_2O = 80:20 at 12 °C): 35.3 min for (^{Si}R)-**16** and 38.5 min for (^{Si}S)-**16**.

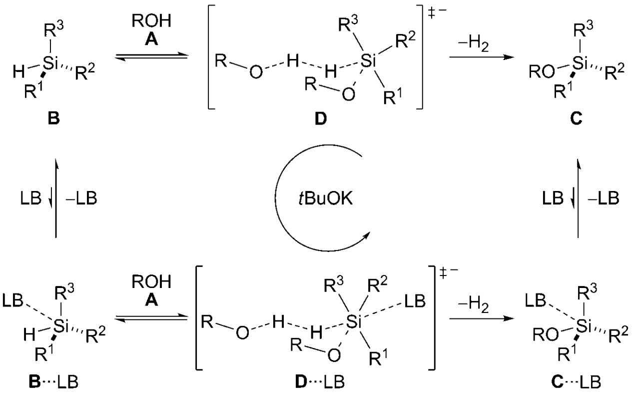
Table 5. Racemization experiments of silicon ether (^{Si}S)-**17** in DMF.

Entry	Additive (1.0 equiv)	*t* [h]	Enantiomeric excess [%][a] before	 after
1	–	14	89	89
2	potassium *tert*-butoxide	14	89	0
3	potassium alkoxide of **1** (generated from KH and **1**)	24	89	89
4	alcohol **1**	14	89	89

[a] Determined by racemization-free, reductive cleavage of the Si–O bond [(^{Si}S)-**17**→(^{Si}R)-**16**] followed by HPLC analysis using a Daicel Chiralcel OJ-RH column (MeOH/H_2O = 80:20 at 12 °C): 35.3 min for (^{Si}R)-**16** and 38.5 min for (^{Si}S)-**16**.

tions,[25] thereby forming a trigonal bipyramidal intermediate prone to pseudorotational processes.[26] In order to distinguish between racemization during or after the Si–O coupling step, we would have to prove post-coupling, *tert*-butoxide-catalyzed racemization [(^{Si}S)-**17**→*rac*-**17**]. For this, we repeated the Si–O coupling in DMF (entry 3, Table 3) and terminated the reaction after 1 h instead of 14 h. After reductive Si–O cleavage, silane (^{Si}R)-**16** was isolated in 70% *ee*, which is unambiguous evidence for a racemization-free coupling.

The alkoxide-catalyzed Si–O coupling is enantiospecific in all three solvent systems. In THF, the mechanism (1) agrees with the seminal postulate by Wilzbach et al.[16] and (2) is similar to the proposed cyclic transition state by Sommer et al.;[19] a sufficiently Lewis acidic silane **B**, strained (^{Si}R)-**16** or $Ph_nMe_{3-n}SiH$ (n = 3–1, **2a**–**c**), reacts directly with alcohol **A** through transition state **D** forming **C** (**B**→**D**→**C**, Scheme 2). The involvement of both the potassium alkoxide of **A** and *tert*-butanol or **A** itself in the concerted S_N2-type displacement in **D** is experimentally supported by a proton source (**A** or trace of water) as a key requirement.[13] We think that, in contrast to the Sommer mechanism,[19] the potassium cation is not an integral part of this process since the reaction is still enantiospecific (!) in the presence of 18-crown-6 (vide supra).[5a] In DMF, the situation is somewhat more complicated. The activation of otherwise unreactive silanes **2d**–**f** by this Lewis base (LB) is a generally accepted mode of action (Table 1); nevertheless, we do hesitate to propose a hypervalent silicon intermediate as DMF and related donors cannot racemize any of the silanes used in this study. We currently believe that a weak Lewis acid–base interaction as depicted in **B**···LB activates the silicon atom to enter the S_N2-type Si–O coupling



Scheme 2. Mechanistic picture of enantiospecific, dehydrogenative Si–O coupling with and without Lewis base-activation (LB = Lewis base).

(**B**⋅⋅⋅LB→**D**⋅⋅⋅LB, Scheme 2).[25] Liberation of **C** might proceed through an associative (**D**⋅⋅⋅LB→**C**⋅⋅⋅LB→**C**, Scheme 2) or a dissociative mechanism (**D**⋅⋅⋅LB→**D**→**C**, not shown).

Conclusions

We believe that the alkoxide-catalyzed, dehydrogenative Si–O coupling using silanes deserves its place amongst the important techniques for alcohol protection. It is a mild and reliable process with the predictability of orthogonality (Table 1) required in silicon-based protective group chemistry. The mechanistic part of the present investigation shows that the coupling itself is enantiospecific but base-induced racemization of the silicon ethers formed is problematic in very polar solvents.

Experimental Section

A flame-dried Schlenk tube was charged under an argon atmosphere with the indicated alcohol (Table 2, 0.525 mmol, 1.05 equiv), the silane (Tables 1 and 2, 0.500 mmol), molecular sieves (30 mg, 3 Å), and, according to Table 1, the appropriate solvent mixture (0.5 M). Then, potassium *tert*-butoxide (2.8 mg, 0.025 mmol, 5.0 mol%) was added. After full conversion (monitored by GLC) the reaction mixture was directly subjected to flash column chromatography on silica gel using cyclohexane-*t*-butylmethylether solvent mixtures. The silicon ethers are isolated as colourless oils or solids.

Acknowledgements

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[1] a) P. S. Baran, T. J. Maimone, J. M. Richter, *Nature* **2007**, *446*, 404–408; b) R. W. Hoffmann, *Synthesis* **2006**, 3531–3541.

[2] a) P. G. M. Wuts, T. W. Greene, *Greene's Protective Groups in Organic Synthesis* 4th ed., Wiley, New York, **2007**, pp. 165–221; b) P. J. Kocieński, *Protecting Groups*, 3rd ed., Thieme, Stuttgart, **2004**, pp. 188–230.

[3] E. J. Corey, A. Venkateswarlu, *J. Am. Chem. Soc.* **1972**, *94*, 6190–6191.

[4] A recent comparison of €/mmol prices of silanes and chlorosilanes reveals that, except $t\text{BuMe}_2\text{Si–X}$ (X = H or Cl), the former are usually cheaper than the latter.

[5] For recent examples of catalyzed dehydrogenative Si–O couplings, see: a) KOH–18-crown-6: F. Le Bideau, T. Coradin, J. Hénique, E. Samuel, *Chem. Commun.* **2001**, 1408–1409; b) NaH: M. J. Zacuto, S. J. O'Malley, J. L. Leighton, *J. Am. Chem. Soc.* **2002**, *124*, 7890–7891; c) *t*Bu-P4 (Schwesinger base): M. Ueno, M. Yonemoto, M. Hashimoto, A. E. H. Wheatley, H. Naka, Y. Kondo, *Chem. Commun.* **2007**, 2264–2266.

[6] J. Y. Corey in *Advances in Silicon Chemistry, Vol. 1* (Ed.: G. Larson), JAI Press, Greenwich, **1991**, pp. 327–387.

[7] For an authoritative review, see: E. Lukevics, M. Dzintara, *J. Organomet. Chem.* **1985**, *295*, 265–315.

[8] a) S. Rendler, G. Auer, M. Oestreich, *Angew. Chem.* **2005**, *117*, 7793–7797; *Angew. Chem. Int. Ed.* **2005**, *44*, 7620–7624; b) B. Karatas, S. Rendler, R. Fröhlich, M. Oestreich, *Org. Biomol. Chem.* **2008**, *6*, 1435–1440; c) S. Rendler, O. Plefka, B. Karatas, G. Auer, R. Fröhlich, C. Mück-Lichtenfeld, S. Grimme, M. Oestreich, *Chem. Eur. J.* **2008**, *14*, 11512–11528.

[9] H. F. T. Klare, M. Oestreich, *Angew. Chem.* **2007**, *119*, 9496–9499; *Angew. Chem. Int. Ed.* **2007**, *46*, 9335–9338.

[10] Since separation of silanes and silicon ethers by flash chromatography on silica gel was problematic with benzyl alcohol, we decided to use cognate **1** as standard.

[11] a) S. E. Denmark, G. L. Beutner, *Angew. Chem.* **2008**, *120*, 1584–1663; *Angew. Chem. Int. Ed.* **2008**, *47*, 1560–1638; b) S. Rendler, M. Oestreich, *Synthesis* **2005**, 1727–1747.

[12] Steric effects, namely *i*Bu and *t*Bu groups, were reported to hamper silane hydrolysis: O. W. Steward, O. R. Pierce, *J. Am. Chem. Soc.* **1961**, *83*, 1916–1921 and references cited therein.

[13] a) Mechanistic investigation including discussion of the role of water (or related proton sources): F. P. Price, *J. Am. Chem. Soc.* **1947**, *69*, 2600–2604; b) Necessity of proton transfer in the transition state: R. L. Schowen, R. Bacon, *Tetrahedron Lett.* **1970**, *11*, 4177–4180.

[14] M. Oestreich, *Synlett* **2007**, 1629–1643.

[15] a) S. Rendler, M. Oestreich, C. P. Butts, G. C. Lloyd-Jones, *J. Am. Chem. Soc.* **2007**, *129*, 502–503; b) S. Rendler, M. Oestreich, *Angew. Chem.* **2008**, *120*, 6086–6089; *Angew. Chem. Int. Ed.* **2008**, *47*, 5997–6000.

[16] Seminal mechanistic proposal: L. Kaplan, K. E. Wilzbach, *J. Am. Chem. Soc.* **1955**, *77*, 1297–1302.

[17] Important previous mechanistic work: a) K. O'Donnell, R. Bacon, K. L. Chellappa, R. L. Schowen, J. K. Lee, *J. Am. Chem. Soc.* **1972**, *94*, 2500–2505; b) C. R. Howie, J. K. Lee, R. L. Schowen, *J. Am. Chem. Soc.* **1973**, *95*, 5286–5288; c) C. Eaborn, I. D. Jenkins, *J. Organomet. Chem.* **1974**, *69*, 185–192.

[18] L. H. Sommer, *Stereochemistry, Mechanism and Silicon*, McGraw-Hill, New York, **1965**, pp. 104–106.

[19] Cyclic transition state with KO*t*Bu in *t*BuOH: L. H. Sommer, W. D. Korte, C. L. Frye, *J. Am. Chem. Soc.* **1972**, *94*, 3463–3469.

[20] C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, Wiley-VCH, Weinheim, **2003**, pp. 418–424.

[21] Influence of solvents: O. W. Steward, A. G. Lutkus, J. B. Geenshields, *J. Organomet. Chem.* **1978**, *144*, 147–154.

[22] Role of DMF in transition metal-catalyzed dehydrogenative Si–O couplings: J. J. Crusciel, *Can. J. Chem.* **2005**, *83*, 508–516.

[23] L. H. Sommer, *Stereochemistry, Mechanism, and Silicon*, McGraw-Hill, New York, **1965**, pp. 51–56.

[24] a) Stereochemical course of alkoxy-alkoxy exchange: L. H. Sommer, H. Fujimoto, *J. Am. Chem. Soc.* **1968**, *90*, 982–987; b) Racemization is reported to occur with methoxide: R. Baker, R. W. Bott, C. Eaborn, P. W. Jones, *J. Organomet. Chem.* **1963**, *1*, 37–42.

[25] A. P. Bento, M. F. Bickelhaupt, *Chem. Asian J.* **2008**, *3*, 1783–1792.

[26] a) E. P. A. Couzijn, M. Schakel, F. J. J. de Kanter, A. W. Ehlers, M. Lutz, A. L. Spek, K. Lammertsma, *Angew. Chem.* **2004**, *116*, 3522–3524; *Angew. Chem. Int. Ed.* **2004**, *43*, 3440–3442; b) E. P. A. Couzijn, A. W. Ehlers, M. Schakel, K. Lammertsma, *J. Am. Chem. Soc.* **2006**, *128*, 13634–13639.

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