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Silicon α-Effect: A Systematic Experimental and Computational Study of the Hydrolysis of C_α- and C_γ-Functionalized Alkoxytriorganylsilanes of the Formula Type $ROSiMe_2(CH_2)_nX$ (R = Me, Et; *n* = 1, 3; X = Functional Group)

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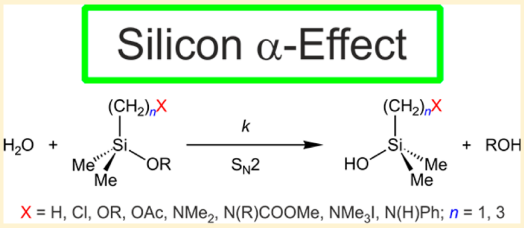
Supporting Information

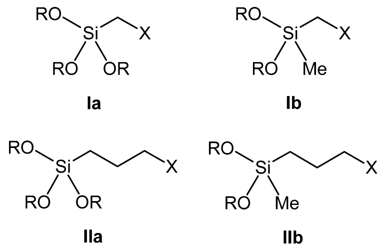
ABSTRACT: To understand the silicon α-effect in terms of an enhanced reactivity of the Si−OC bond of α-silanes of the formula type $ROSiMe_2CH_2X$ compared to analogous γ-silanes $ROSiMe_2(CH_2)_3X$ (R = Me, Et; X = functional group), a systematic experimental and computational study of the kinetics and mechanisms of hydrolysis of such compounds was performed. For this purpose, a series of suitable model compounds was synthesized and studied for their hydrolysis kinetics in CD_3CN/D_2O under basic and acidic conditions, using ^1H NMR spectroscopy as the analytical tool. To get more information about the reaction mechanisms, the experimental investigations were complemented by computational studies. These investigations demonstrated that the silicon α-effect cannot be rationalized in terms of a special single effect. The reactivities observed rather result from a summation of different components, such as electronic and steric effects, pD dependence, and hydrogen bonds between the functional group (or even protonated functional group) and the alkoxy leaving group. Therefore, the term "silicon α-effect" should not be used furthermore to explain the hydrolysis reactivity at the silicon atom of alkoxyorganylsilanes with functional groups in α- or γ-position of the organyl groups (so-called α- or γ-silanes).



■ INTRODUCTION

C_α-Functionalized trialkoxymethylsilanes and dialkoxydimethylsilanes of the formula types **Ia** and **Ib** (known as α-silanes, Scheme 1) constitute a very interesting class of compounds with unique properties that can be exploited in a wide range of cross-linking technologies for the preparation of a variety of polymers.[1−3] In particular, these α-silanes can be used to modify organic polymers (e.g., polyurethanes or polyethers) by introducing them via their functional group X into α-silane-terminated prepolymers that are highly reactive toward water. Hydrolysis of the Si−OMe or Si−OEt groups of these silylmethyl-end-capped prepolymers leads to the corresponding silanols, which then undergo condensation reactions to give a two- or three-dimensional polysiloxane network constructed from Si−O−Si moieties. As the reactivity of α-silane-terminated prepolymers against humidity and/or moisture is very high and tunable, such materials are predestinated for applications in sealants, adhesives, coatings, and spray foams.[1−3] In contact with moisture, certain α-silane-terminated prepolymers cross-link 10−1000 times faster than the corresponding prepolymers produced from conventional C_γ-functionalized trialkoxypropylsilanes and dialkoxymethylpropylsilanes of the formula types **IIa** and **IIb** (known as γ-silanes, Scheme 1). This reactivity

Scheme 1. α-Silanes Ia and Ib and γ-Silanes IIa and IIb[a]



[a]R = Me, Et; X = functional group.

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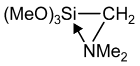
phenomenon has been termed "α-effect". Although α-silanes of the formula types **Ia** and **Ib** constitute the basis of a very important and economically successful technology platform in the silicone industry, the α-effect is not yet fully understood.

From an industrial point of view, the α-effect was first observed in the late 1960s by researchers at Bayer AG as an increase in reactivity at the silicon atom and was already used at that time for cross-linking of α-silane-terminated prepolymers.[4] Surprisingly, this initial work was interrupted after 1975 for almost 25 years, until this chemistry was reactivated by scientists at Wacker Chemie AG and then developed into a practical and commercial enterprise.[5]

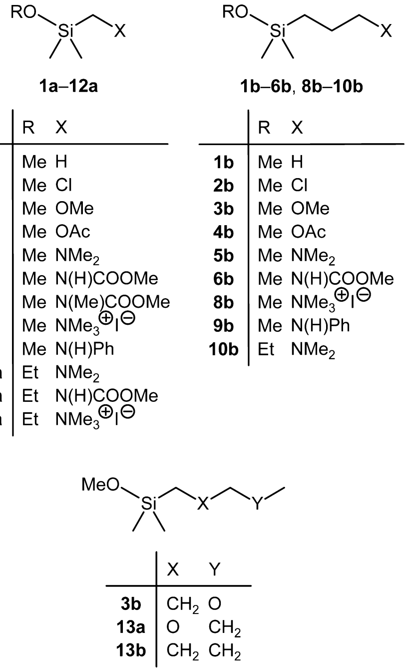
The term α-effect was introduced to describe the unique reactivity of α-silanes at both the silicon atom and the functional group X (mainly NR_2, OC(O)R, N(H)COOMe)[3−5] and to address some unusual physicochemical and spectroscopic properties of these compounds; that is, the α-effect is not sharply defined and its nature has been a matter of debate for many decades.[6,7] As shown exemplarily for the α-silane $(MeO)_3SiCH_2NMe_2$ in Scheme 2, for a long time the α-effect has been rationalized in terms of an intramolecular donor−acceptor interaction between the lone pair of the organofunctional group (in this case NMe_2) and the silicon atom. However, in a series of more recent experimental and computational studies (structure determination of some α-silanes and analysis of the binding situation in these compounds), Mitzel et al. have clearly demonstrated that this picture is incorrect and cannot be used to explain the α-effect.[8]

Scheme 2. Hypothetical Intramolecular Si···N Interaction in $(MeO)_3SiCH_2NMe_2$ as a Model to Explain the α-Effect



Although the kinetic cross-linking behavior of α-silanes is determined by both the hydrolysis and the condensation reactivity, the term "α-effect" is mainly used in relation to the hydrolysis reaction because this step is assumed to be much faster than the condensation. To understand the α-effect in terms of the enhanced hydrolysis reactivity of the Si−OC bond of α-silanes (**Ia**, **Ib**) compared to the analogous γ-silanes (**IIa**, **IIb**), we have performed a systematic experimental and computational study of the kinetics and the mechanisms of the hydrolysis of the model compounds **1a**−**13a**, **1b**−**6b**, **8b**−**10b**, and **13b** (Scheme 3). To simplify matters, only monoalkoxysilanes with one hydrolyzable Si−OR group were chosen for these studies.

Scheme 3. Model Compounds Studied for Their Hydrolysis Reactivity



	R	X
1a	Me	H
2a	Me	Cl
3a	Me	OMe
4a	Me	OAc
5a	Me	NMe_2
6a	Me	N(H)COOMe
7a	Me	N(Me)COOMe
8a	Me	$NMe_3^{\oplus}I^{\ominus}$
9a	Me	N(H)Ph
10a	Et	NMe_2
11a	Et	N(H)COOMe
12a	Et	$NMe_3^{\oplus}I^{\ominus}$

	R	X
1b	Me	H
2b	Me	Cl
3b	Me	OMe
4b	Me	OAc
5b	Me	NMe_2
6b	Me	N(H)COOMe
8b	Me	$NMe_3^{\oplus}I^{\ominus}$
9b	Me	N(H)Ph
10b	Et	NMe_2

	X	Y
3b	CH_2	O
13a	O	CH_2
13b	CH_2	CH_2

Depending on the pH value of the aqueous reaction medium, different reaction mechanisms for the hydrolysis of the model silanes **1a**−**13a**, **1b**−**6b**, **8b**−**10b**, and **13b** have to be considered. Generally, the hydrolysis of the alkoxysilanes studied can be described by eq 1:

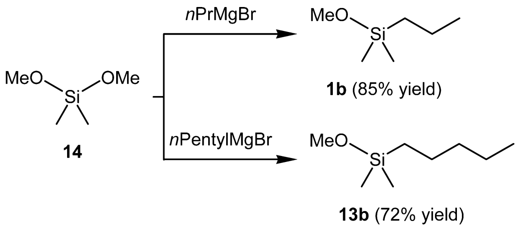
$$\text{Alkoxysilane} + \text{Nucleophile} \rightarrow \text{Silanol} + \text{Alkanol} \qquad (1)$$

The nucleophile in this reaction can be H_2O or OH^-, and the alkoxysilane (electrophile) is protonated or nonprotonated. Protonation can occur at the alkoxy group (OMe, OEt) and/or the functional group X (OMe, OAc, NMe_2, N(H)COOMe, N(Me)COOMe, N(H)Ph, OPr), depending on the different proton affinities of these groups and the pH value of the reaction medium. For the selection of the model compounds studied, we aimed to use compounds that demonstrate a broad variation of (i) the proton affinities of the functional groups X and the alkoxy groups (→ impact on the degree of protonation) and (ii) the electronegativities of the functional group X (→ impact on the electrophilicity of the silicon center). Furthermore, this selection also implies some variation of steric effects. This collection of model compounds was designed to allow the investigation of both the α/γ-effect (comparison of α- and γ-silanes with identical functional groups X) and the α/α′-effect (comparison of α-silanes with different functional groups X).

■ RESULTS AND DISCUSSION

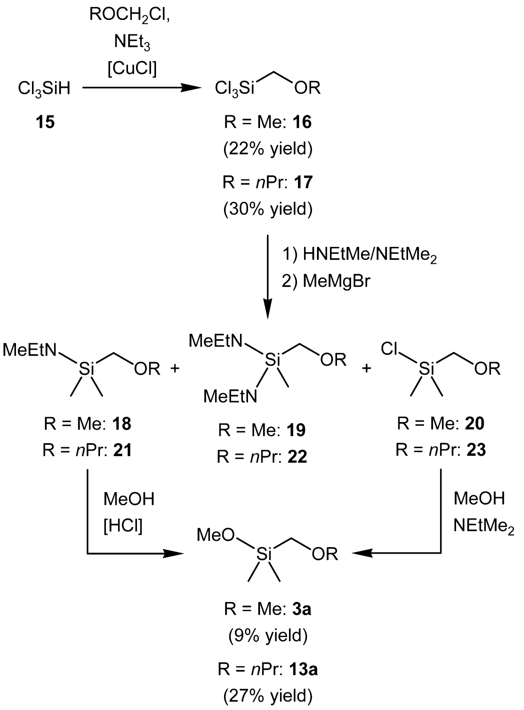
Syntheses. Compounds **1b** and **13b** were synthesized by treatment of dimethoxydimethylsilane (**14**) with *n*-propyl- or *n*-pentylmagnesium bromide in diethyl ether (yields: **1b**, 85%; **13b**, 72%; Scheme 4).

Scheme 4. Syntheses of Compounds 1b and 13b



Compounds **3a** and **13a** were prepared according to Scheme 5, starting from trichlorosilane (**15**). Thus, treatment of **15** with the corresponding alkyl chloromethyl ether ($MeOCH_2Cl$ or $nPrOCH_2Cl$) and triethylamine, in the presence of copper(I) chloride, furnished the (alkoxymethyl)trichlorosilanes **16** and **17**.[8b,9] Reaction of **16** with one molar equivalent of ethylmethylamine in tetrahydofuran (THF), in the presence of ethyldimethylamine as a hydrogen chloride acceptor, and subsequent treatment with an excess of methylmagnesium

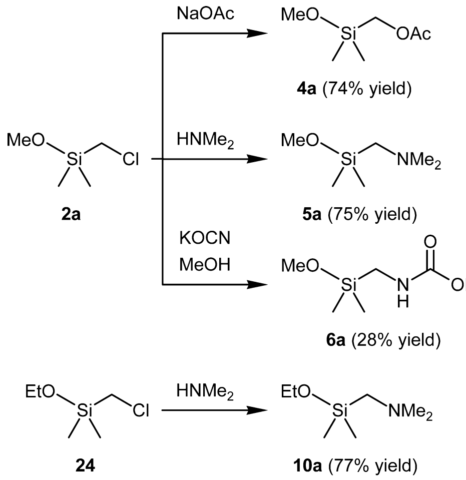
Scheme 5. Syntheses of Compounds 3a and 13a



bromide in diethyl ether afforded a mixture of MeEtNSiMe$_2$CH$_2$OMe (**18**), (MeEtN)$_2$SiMeCH$_2$OMe (**19**), and ClSiMe$_2$CH$_2$OMe (**20**). Compounds **18** and **20** were isolated by fractional distillation and then transformed into **3a** by treatment with methanol and catalytical amounts of hydrogen chloride (**18**) or by reaction with methanol and ethyldimethylamine (**20**). Both syntheses were performed in *n*-pentane, and **3a** was obtained with a total yield of 2% (relative to **15**). Compound **13** was synthesized analogously (**17** → **21**/**22**/**23** → **13a**) and isolated with a total yield of 8% (relative to **15**).

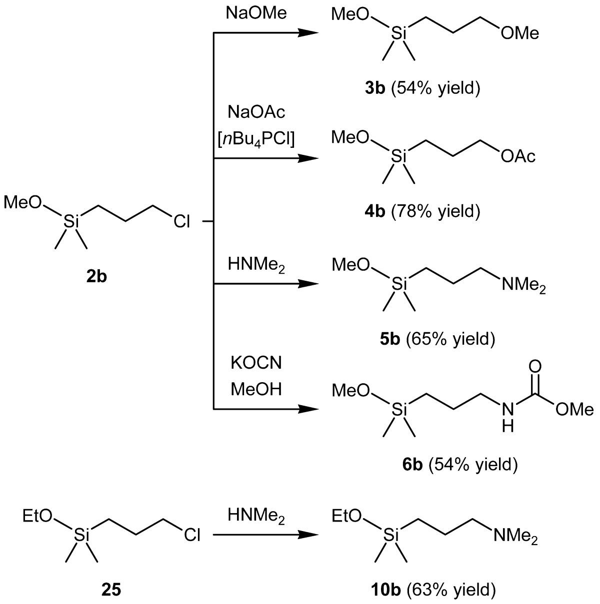
Compounds **4a**–**6a** and **10a** were synthesized according to Scheme 6, starting from (chloromethyl)methoxydimethylsilane (**2a**) or (chloromethyl)ethoxydimethylsilane (**24**). Thus, treatment of **2a** with sodium acetate in THF furnished MeOSiMe$_2$CH$_2$OAc[10] (**4a**). Reaction of **2a** with an excess of dimethylamine in an autoclave afforded MeOSiMe$_2$CH$_2$NMe$_2$ (**5a**),[11] and treatment of **2a** with potassium cyanate and methanol in *N*,*N*-dimethylformamide furnished MeOSiMe$_2$CH$_2$N(H)C(O)OMe[12] (**6a**). Compound **10a** was synthesized analogously to **5a**.

Scheme 6. Syntheses of Compounds 4a–6a and 10a



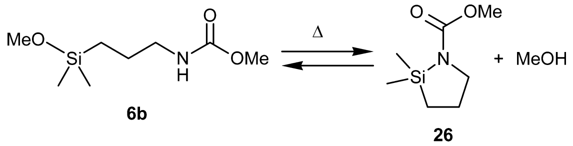
Compounds **3b**–**6b** and **10b** were synthesized according to Scheme 7, starting from (3-chloropropyl)methoxydimethylsilane (**2b**) or (3-chloropropyl)ethoxydimethylsilane (**25**). Thus, treatment of **2b** with sodium methoxide in methanol afforded MeOSiMe$_2$(CH$_2$)$_3$OMe[5a] (**3b**), and reaction of **2b** with sodium acetate in THF, in the presence of the phase transfer catalyst tetra-*n*-butylphosphonium chloride, furnished MeOSiMe$_2$(CH$_2$)$_3$OAc[10] (**4b**). Treatment of **2b** with an excess of dimethylamine in an autoclave afforded MeOSiMe$_2$(CH$_2$)$_3$NMe$_2$ (**5b**), and reaction of **2b** with potassium cyanate and methanol in *N*,*N*-dimethylformamide furnished MeOSiMe$_2$(CH$_2$)$_3$N(H)C(O)OMe[12] (**6b**). Compound **10b** was synthesized analogously to **5b**.

Scheme 7. Syntheses of Compounds 3b–6b and 10b



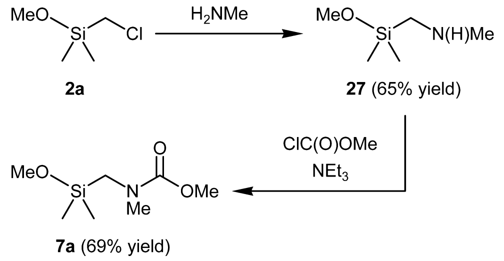
Purification of **6b** by distillation yielded a small amount (ca. 14 mol %) of the five-membered ring compound **26** (formed by intramolecular condensation of **6b**), which could be transformed back to **6b** by treatment with a stoichiometric amount of methanol at room temperature (Scheme 8). Compound **26** was enriched by distillation to validate its identity (for details, see the Supporting Information).

Scheme 8. Formation of Compound 26 and Its Transformation to 6b



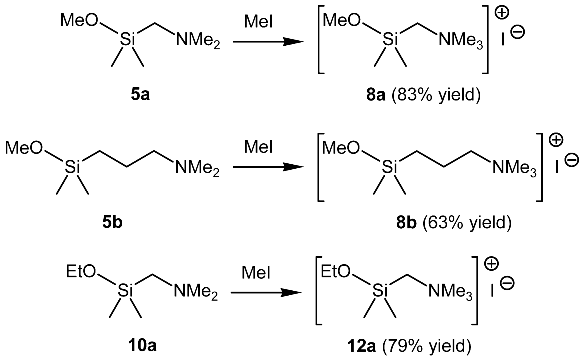
Compound **7a** was synthesized according to Scheme 9, staring from MeOSiMe$_2$CH$_2$Cl (**2a**). Thus, treatment of **2a** with an excess of methylamine in an autoclave afforded MeOSiMe$_2$CH$_2$N(H)Me[13] (**27**), which upon reaction with methyl chloroformate and triethylamine in *n*-pentane furnished **7a**.

Scheme 9. Synthesis of Compound 7a



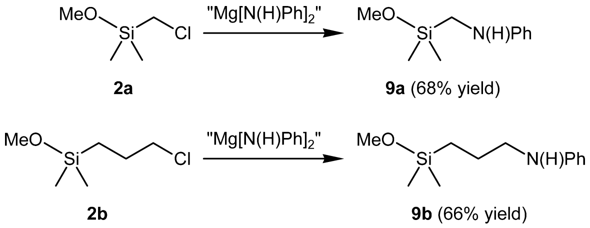
Compounds **8a**, **8b**, and **12a** were synthesized according to Scheme 10 by reaction of $MeOSiMe_2CH_2NMe_2$ (**5a**), $MeOSiMe_2(CH_2)_3NMe_2$ (**5b**), and $EtOSiMe_2CH_2NMe_2$ (**10a**), respectively, with an excess of iodomethane in acetonitrile.[14]

Scheme 10. Syntheses of Compounds 8a, 8b, and 12a



Compounds **9a** and **9b** were synthesized according to Scheme 11 by reaction of $MeOSiMe_2CH_2Cl$ (**2a**) and $MeOSiMe_2(CH_2)_3Cl$ (**2b**), respectively, with "$Mg[N(H)Ph]_2$"[15] in aniline.

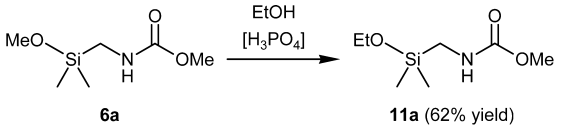
Scheme 11. Syntheses of Compounds 9a and 9b



Compound **11a** was synthesized according to Scheme 12 by treatment of $MeOSiMe_2CH_2N(H)C(O)OMe$ (**6a**) with an excess of ethanol, in the presence of catalytic amounts of orthophosphoric acid.

At first glance, some of the product yields obtained in the syntheses described in this section may appear somewhat unsatisfactory; however, it is important to note that we aimed at the preparation of analytically pure products (NMR and GC analysis), if necessary at the expense of the yield. The identities of all the compounds synthesized were established by elemental analyses (C, H, N) and NMR spectroscopic studies (^1H, ^{13}C, ^{29}Si).

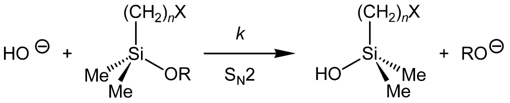
Scheme 12. Synthesis of Compound 11a



Kinetics of Hydrolysis. General Considerations. The kinetics of the hydrolysis of nonfunctional alkoxytriorganylsilanes have already been studied extensively, and it has been demonstrated that the reaction rates are influenced by acids, bases, solvents, temperature, and steric and electronic effects.[16] The pH-dependence (here pD-dependence; see below) of the hydrolysis kinetics shows two clearly separated different regimes for all silanes investigated in the present study: rate constants generally increase with increasing pD values above ca. pD 8.5, while at lower pD values (up to ca. pD 7) the rate constants decrease with increasing pD values. These findings clearly indicate the presence of different reaction mechanisms under basic (pD > 8.5) and acidic conditions (pD < 7) and are in good agreement with earlier studies.[16] Therefore, the hydrolysis kinetics of the compounds studied have to be discussed separately for the acidic and basic regime.

As shown in Scheme 13, under basic conditions OH^- is the nucleophile, and the nonprotonated silane $ROSiMe_2(CH_2)_nX$ is the electrophile. Assuming that a vast excess of water is present, the kinetics of this S_N2 reaction can be described in terms of pseudo-first-order kinetics by eq 2, which can be transformed into eq 3:

Scheme 13. Hydrolysis of α- and γ-Silanes of the Formula Type $ROSiMe_2(CH_2)_nX$ (R = Me, Et; *n* = 1, 3; X = Functional Group) under Basic Conditions



$$r = k[OH^-][ROSiMe_2(CH_2)_nX]$$
$$= k_{exp}[ROSiMe_2(CH_2)_nX] \quad (2)$$

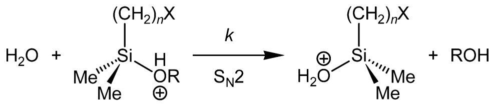
$$k_{exp} = k[OH^-] \text{ (consequence: } \log(k_{exp}) \approx +1\cdot pH) \quad (3)$$

where r = reaction rate, k = "microscopic" rate constant, and k_{exp} = experimental ("macroscopic") rate constant.

As can be seen from eq 3, the experimental ("macroscopic") rate constant k_{exp} depends on both the pH value and the "microscopic" rate constant k. At a given pH value, k depends only on the functional group X and n (length of the spacer between the silicon atom and X).

As shown in Scheme 14, under acidic conditions H_2O is the nucleophile, and the protonated silane $(ROH^+)SiMe_2(CH_2)_nX$ (protonation at the alkoxy leaving group) is the electrophile:

Scheme 14. Hydrolysis of α- and γ-Silanes of the Formula Type $ROSiMe_2(CH_2)_nX$ (R = Me, Et; *n* = 1, 3; X = Functional Group) under Acidic Conditions



Again assuming that a vast excess of water is present, the kinetics of this S_N2 reaction can be described in terms of pseudo-first-order kinetics according to eq 4:

$$r = k[H_2O][(ROH^+)SiMe_2(CH_2)_nX] = k_{exp}[ROSiMe_2(CH_2)_nX] \tag{4}$$

Combination of eq 4 with the acid constant K_A of the protonated α- or γ-silane $(ROH^+)SiMe_2(CH_2)_nX$ (eq 5) results in eq 6:

$$K_A = \frac{[H_3O^+]\cdot[ROSiMe_2(CH_2)_nX]}{[(ROH^+)SiMe_2(CH_2)_nX]} \tag{5}$$

$$k_{exp} = \frac{k[H_2O]}{K_A}[H_3O^+] \text{ (consequence: } \log(k_{exp}) \approx -1\cdot\text{pH)} \tag{6}$$

As can be seen from eq 6, the experimental ("macroscopic") rate constant k_{exp} depends on the pH value, the "microscopic" rate constant k (impact of the functional group X and n (length of the spacer between the silicon atom and X)), and the thermodynamic parameter K_A, which describes the degree of protonation of the alkoxy leaving group RO; that is, k_{exp} also depends on the functional group X, which may also act as proton acceptor (→ competition of RO and X as proton acceptors; impact of the different proton affinities of RO and X).

Provided that the proton affinity of X is significantly higher than that of RO (protonation at the functional group X instead of the alkoxy leaving group RO), the pseudo-first-order kinetics of hydrolysis can be described on the basis of eqs 7–9:

$$r = k[H_2O][ROSiMe_2(CH_2)_nXH^+] = k_{exp}[ROSiMe_2(CH_2)_nX] \tag{7}$$

$$K_{A'} = \frac{[H_3O^+][ROSiMe_2(CH_2)_nX]}{[ROSiMe_2(CH_2)_nXH^+]} \tag{8}$$

$$k_{exp} = \frac{k[H_2O]}{K_{A'}}[H_3O^+] \text{ (consequence: } \log(k_{exp}) \approx -1\cdot\text{pH)} \tag{9}$$

Kinetics of Hydrolysis. Experimental Method and Results. To investigate the dependence of the rate of hydrolysis on (i) the functional group X, (ii) the spacer between the silicon atom and the functional group X (CH_2 vs $(CH_2)_3$; α- vs γ-silane), and (iii) the pH value (acidic and basic conditions; here pD value; see below), a ^1H NMR spectroscopic study was carried out in order to monitor the hydrolysis of the model compounds studied. All measurements were performed in NMR tubes at 23 °C. To guarantee homogenic phases for all the reaction systems investigated, a mixture of CD_3CN and D_2O was used as the reaction medium. The molar ratio silane:D_2O:CD_3CN was 1:90:150 (D_2O in vast excess) to allow for an analysis in terms of pseudo-first-order kinetics and to prevent condensation of the resulting silanols to the corresponding disiloxanes.

Preliminary studies have shown that the rates of hydrolysis depend extremely strongly on both the structure of the silane and the pD value. Therefore, all kinetic measurements were performed as competition experiments with two (comparison of an α- and a γ-silane with identical functional groups X) or three different silanes (comparison of either α- or γ-silanes with different functional groups X). This experimental design allowed for an exact comparison of the hydrolysis rates of different silanes at a given pD value. In order to avoid overlapping of the mechanisms for the acidic and basic regime, no experiments were performed at neutral pD values. A series of test experiments have shown that buffer systems are not suitable for adjusting the pD values, because these buffer systems can interfere with the hydrolysis reactions. The rate of hydrolysis can be influenced by the type of acid or base used, but this effect is assumed to be negligible compared to the effect of the pD value.[17] Therefore, the acidic pD values (4.5–6.5) were adjusted by the addition of formic acid, and the basic pD values (9.0–12.5) were adjusted by the addition of triethylamine. In the case of the silanes **5a**, **5b**, **10a**, and **10b**, the basic pD values resulted from the basic amino groups of these compounds and were adjusted by the addition of DCl. To prevent any interference during the kinetic experiments, the pD values were measured outside the NMR tubes in separate reaction vessels that contained identical reaction mixtures as in the NMR tubes. The pD values were determined with a glass electrode. As the measurements were performed in CD_3CN/D_2O mixtures, the values obtained do not represent exact pD values but can be regarded as suitable approximate values to characterize the acidic or basic nature of the reaction mixture studied.[18,19] The hydrolysis reactions investigated were found to proceed with pseudo-first-order kinetics. Figure 1 shows a typical example of the results obtained in these kinetic competition experiments (for analogous figures for all the other experiments performed, see the Supporting Information).

The experimental kinetic data are summarized in Figures 2–5, in which the decadic logarithms of the rate constants (log

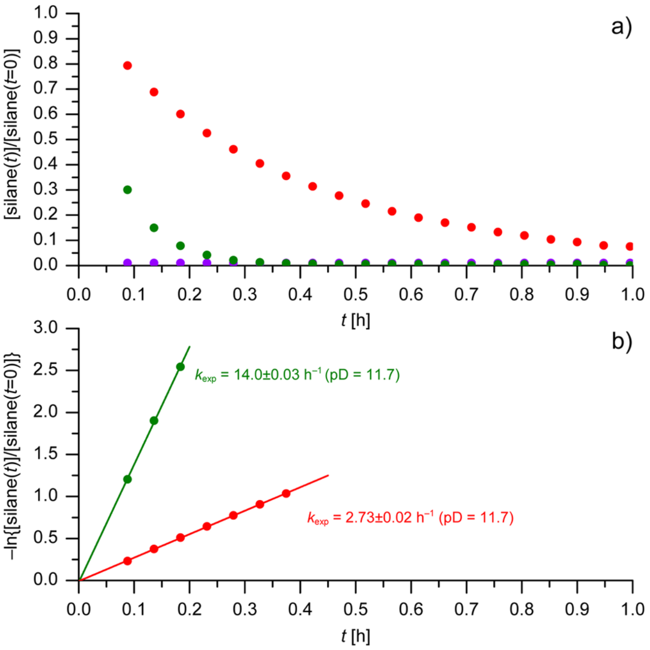


Figure 1. (a) Kinetics of the co-hydrolysis of compounds **3a** (α-OMe, red), **4a** (α-OAc, green), and **5a** (α-NMe_2, purple) in CD_3CN/D_2O [5:1 (v/v)] at 23 °C; [**3a**] = [**4a**] = [**5a**] = 0.1 mol L^{-1}, [DCl] = 1×10^{-5} mol L^{-1}; average pD value 11.7 ± 0.2. (b) Determination of the k_{exp} values as the gradient of the linear functions. Due to its very fast hydrolysis (complete hydrolysis at t < 2 min), the k_{exp} value of compound **5a** could not be determined.

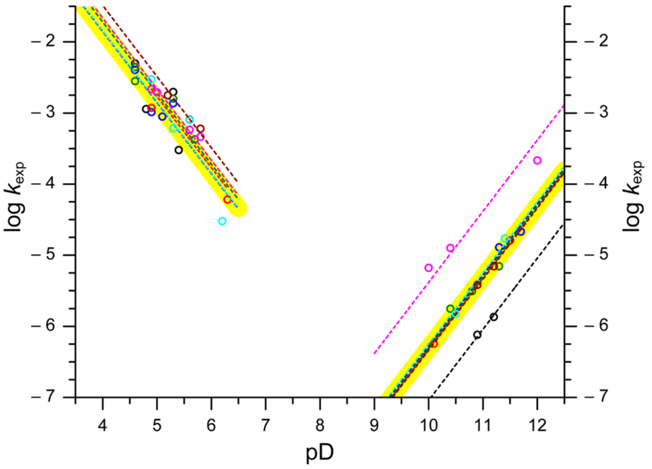


Figure 2. log k_{exp} values of the γ-silanes **1b** (γ-H, black), **2b** (γ-Cl, blue), **3b** (γ-OMe, red), **4b** (γ-OAc, green), **6b** (γ-N(H)COOMe, aqua), **8b** (γ-NMe$_3^+$, magenta), and **9b** (γ-N(H)Ph, brown) as a function of the pD values. Due to its very fast hydrolysis (complete hydrolysis at $t < 2$ min), the k_{exp} values of compound **5b** (γ-NMe$_2$) could not be determined at pD 4.5−6.5. The k_{exp} values of **5b** at pD 8.0−12.5 are given in Figure 4. The linear functions of the γ-silanes are shown as dashed lines. The yellow areas, which are also depicted in Figures 3−5, summarize the linear functions of the γ-silanes, except **1b** (pD 9.0−12.5), **8b** (pD 9.0−12.5), and **9b** (pD 4.5−6.5).

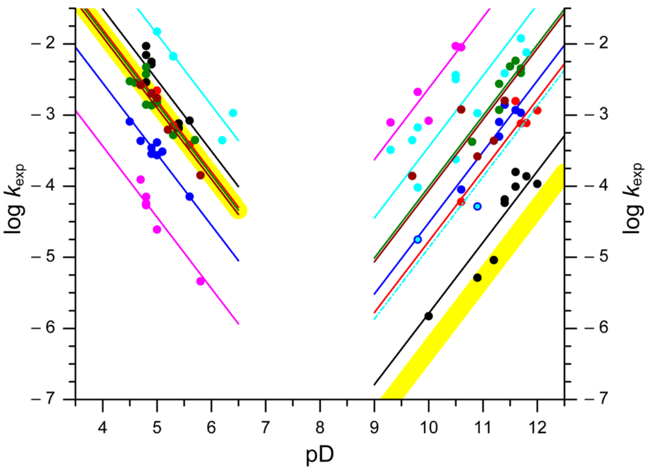


Figure 3. log k_{exp} values of the α-silanes **1a** (α-H, black), **2a** (α-Cl, blue), **3a** (α-OMe, red), **4a** (α-OAc, green), **6a** (α-N(H)COOMe, aqua), **7a** (α-N(Me)COOMe, blue with outline), **8a** (α-NMe$_3^+$, magenta), and **9a** (α-N(H)Ph, brown) and γ-silanes as a function of the pD values. For reasons of clarity, the linear functions of the γ-silanes (except **1b** (pD 9.0−12.5), **8b** (pD 9.0−12.5), and **9b** (pD 4.5−6.5); for log k_{exp} values of **1b** (pD 9.0−12.5), **8b** (pD 9.0−12.5), and **9b** (pD 4.5−6.5), see Figure 2) are summarized by the yellow areas taken from Figure 2. Due to their very fast hydrolysis (complete hydrolysis at $t < 2$ min), the k_{exp} values of compounds **5a** (α-NMe$_2$; pD 4.5−6.5 and 9.0−12.5) and **7a** (pD 4.5−6.5) could not be determined. The linear function of compound **7a** is shown as a dashed-dotted line. The linear functions of the γ-silanes are shown as dashed lines.

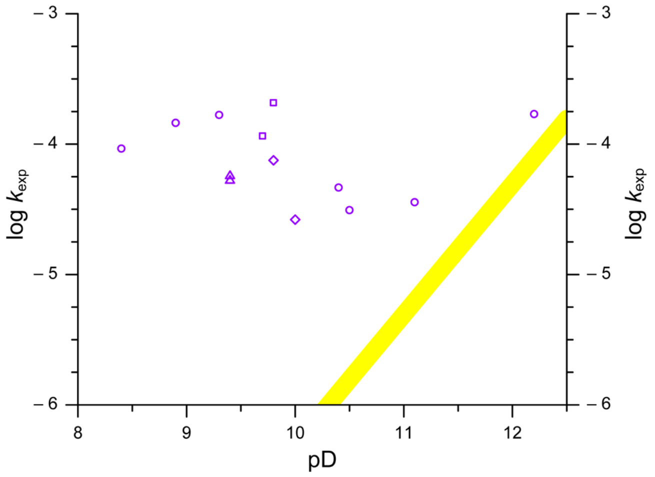


Figure 4. log k_{exp} values of the γ-silanes **5b** (γ-NMe$_2$, SiOMe) and **10b** (γ-NMe$_2$, SiOEt) in different CD_3CN/D_2O mixtures as a function of the pD values. (a) Co-hydrolysis of compounds **5a** (α-NMe$_2$, SiOMe) and **5b** (○) in CD_3CN/D_2O [5:1 (v/v)]; (b) co-hydrolysis of compounds **10a** (α-NMe$_2$, SiOEt) and **10b** (△) in CD_3CN/D_2O [5:1 (v/v)]; (c) co-hydrolysis of compounds **5a** and **5b** (□) in CD_3CN/D_2O [59:1 (v/v)]; (d) co-hydrolysis of compounds **10a** and **10b** (◇) in CD_3CN/D_2O [59:1 (v/v)]. For reasons of clarity, the linear functions of the γ-silanes (except **1b** (pD 9.0−12.5) and **8b** (pD 9.0−12.5); for log k_{exp} values of **1b** (pD 9.0−12.5) and **8b** (pD 9.0−12.5), see Figure 2) are summarized by the yellow area taken from Figure 2. Due to their very fast hydrolysis (complete hydrolysis at $t < 2$ min), the k_{exp} values of compounds **5a** and **10a** (pD 8.0−12.5) could not be determined.

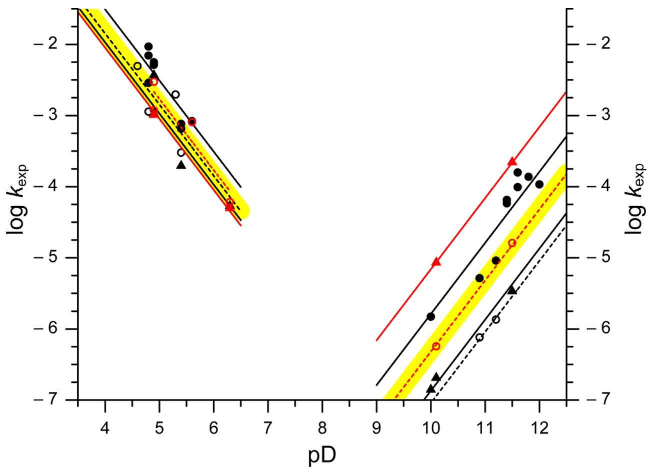


Figure 5. log k_{exp} values of the silanes **1a** (α-H, ●), **1b** (γ-H, ○), **3b** (γ-OMe, red ○), **13a** (α-O*n*Pr, red ▲), and **13b** (γ-Et, black ▲) as a function of the pD values. The linear functions of compound **1b** and **3b** are shown as dashed lines. For reasons of clarity, the linear functions of the γ-silanes (except **1b** (pD 9.0−12.5), **8b** (pD 9.0−12.5), and **9b** (pD 4.5−6.5); for log k_{exp} values of **1b** (pD 9.0−12.5), **8b** (pD 9.0−12.5), and **9b** (pD 4.5−6.5), see Figure 2) are summarized by the yellow areas taken from Figure 2.

k_{exp}; the k_{exp} values were transformed into [s^{-1}] before converting them to logarithms) are plotted as a function of the pD. Taking into account the direct proportionality between k_{exp} and [OD$^-$] (eq 3) or [D_3O^+] (eq 9), the gradient of the linear functions is set to +1 in the basic regime and to −1 in the acidic regime. This procedure allows for a clear documentation of the kinetic data.

Kinetics of Hydrolysis. Computational Methods and Results. All calculations were performed with the ADF[20] and QUILD[21] programs at the ZORA-OLYP/TZ2P level[22,23] of relativistic density functional theory (DFT), with technical settings as follows: CORE small; ACCINT 8.0 8.0; SCFCONV

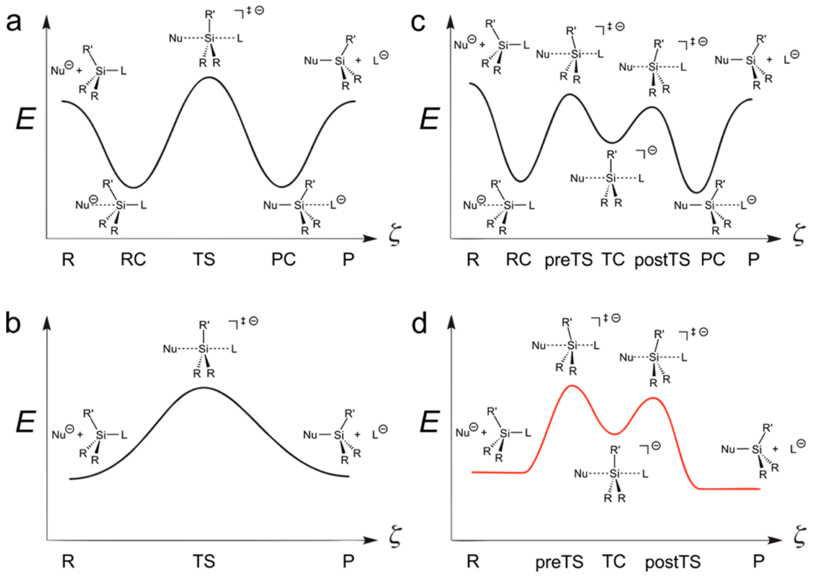


Figure 6. Shape of reaction profiles for S_N2 reactions of a nucleophile Nu^- with an electrophilic substrate $SiR_2R'L$ with leaving group L along the reaction coordinate ζ: (a) single-step double-well potential; (b) single-step unimodal profile; (c) two-step triple-well potential; (d) two-step bimodal profile occurring in our model reactions (see also text).

Table 1. k_{exp} Values at pD 11 and Calculated Reaction Barriers and Energies Relative to Reactants of Intermediate Transition Complexes (TC) for Hydroxide-Induced Hydrolysis of the Silanes 1a–9a, 1b–6b, 8b, 9b, 11a–13a, and 13b[a]

	k_{exp} [h^{-1}]	reaction barrier [kcal mol^{-1}]		TC [kcal mol^{-1}]	
compound	(pD = 11)	(in H_2O)	(in CH_3CN)	(in H_2O)	(in CH_3CN)
1a (α-H)	0.0582 ± 0.0144	14.1	14.1	6.8	6.9
1b (γ-H)	0.003 26 ± 0.0019	14.6	14.5	7.8	7.8
2a (α-Cl)	1.09 ± 0.18	12.6	12.0	3.7	3.8
2b (γ-Cl)	0.0189 ± 0.0043				
3a (α-OMe)	0.599 ± 0.149	12.7	13.7	5.6	5.6
3b (γ-OMe)	0.0172 ± 0.0011	14.5	14.4	7.5	7.8
4a (α-OAc)	3.50 ± 0.56	11.2	12.0	3.6	3.8
4b (γ-OAc)	0.0178 ± 0.0040	13.8	13.3	8.1	8.0
5a (α-NMe_2)		15.3	14.5	9.1	8.8
5a (α-NMe_2H^+)	>90			−7.0[d]	−8.7[d]
5b (γ-NMe_2)	0.129[b]				
6a (α-N(H)COOMe, SiOMe)	12.8 ± 5.2	6.3[c]	5.9[c]	2.6[c]	2.0[c]
6b (γ-N(H)COOMe)	0.0204 ± 0.0042				
7a (α-N(Me)COOMe)	0.486 ± 0.522				
8a (α-NMe_3^+, SiOMe)	84.7 ± 26.9			1.2	−0.2
8b (γ-NMe_3^+)	0.149 ± 0.060			2.1	1.5
9a (α-N(H)Ph)	3.10 ± 2.08	8.9[c]	8.4[c]	4.1[c]	3.4[c]
9b (γ-N(H)Ph)	0.0165 ± 0.0007				
11a (α-N(H)COOMe, SiOEt)	4.81 ± 0.17				
12a (α-NMe_3^+, SiOEt)	20.5 ± 4.0				
13a (α-O*n*Pr)	0.248 ± 0.004	12.8	14.5	5.5	6.9
13b (γ-Et)	0.004 84 ± 0.000 63	14.4	14.4	8.1	8.2

[a] Electronic energies computed at ZORA-OLYP/TZ2P using COSMO for solvation in H_2O and CH_3CN. [b] This k_{exp} value was obtained at pD 11.1 (for details, see Figure S57). [c] This reaction barrier was calculated considering hydrogen bonds between the functional group and the nucleophile. [d] The intermediate is not a thermodynamic trap: the correction $\Delta G - \Delta E$ is estimated to be 8–9 kcal mol^{-1}, leading to a relative Gibbs free energy of the TC around 0–2 kcal mol^{-1}.

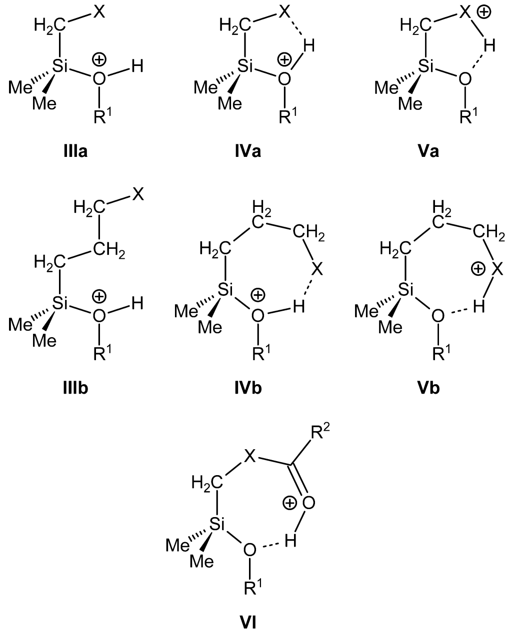
0.000001; GEOMCONV 0.0001. This approach was previously shown to agree satisfactorily with highly correlated *ab initio* benchmarks.[24] Stationary points were characterized as minima or transition states through vibrational analyses and intrinsic reaction coordinate (IRC) calculations.[25] In selected cases, enthalpies and entropies at 298.15 K and 1 atm (ΔH_{298} and ΔS_{298}) were calculated using standard thermodynamic relationships and the computed partition functions, assuming an ideal gas.[26] Solvent effects were taken into account in all condensed-phase calculations using the COSMO model.[27] This model describes bulk solvation as well as the average electrostatic effects of the first solvation shell, but it neglects covalent bonding with the solvent. Thus, the COSMO model is well suited for describing the average interaction of the reaction system with the dynamically fluctuating solvent environment, including the weakening of nucleophile−substrate and hydrogen-bonding interactions. Also, solvent molecules participating in the reaction cannot be treated with this approach and have been included explicitly in the quantum mechanical treatment. Preliminary explorations suggest that mechanisms involving multiple discrete water molecules are less likely, e.g., for entropic reasons. We wish to point out, however, that such mechanisms cannot be completely ruled out. At the same time, the qualitative agreement between the order of computed and measured relativities indicates that we catch the major features of the systems under investigation. For further details, see the Supporting Information.

Under basic conditions, the nucleophile in our computational model systems that induces silane hydrolysis is OH^-, whereas the leaving group is OMe^-. Based on our earlier work on S_N2 reactions at carbon,[28] silicon,[29] and phosphorus,[30] the expectation was that nucleophilic attack of OH^- at the silicon center in solution may proceed via a unimodal reaction profile,[29c] as shown in Figure 6b for the S_N2 reaction of Cl^- + SiH_3Cl. However, for the reactants (R) that are investigated herein, the reaction profile has a pretransition state (preTS), an intermediate transition complex (TC), and a post-transition state (postTS), as shown in Figure 6d. Note that the intermediate TC is the pentacoordinate species in this stepwise (A_N + D_N) substitution process and corresponds structurally and electronically with the saddle point or transition state (TS) in concerted (A_ND_N) substitution reactions ("A_N" = nucleophilic association; "+" = occurrence of intermediate; "D_N" = nucleofugic dissociation). The first elementary reaction, from R via preTS to TC, is in general the rate-determining step. In the gas phase and in poorly solvating media, reactants and products form, in general, reactant complexes (RC) and product complexes (PC), as illustrated for one- and two-step substitution processes in Figure 6a and c, respectively. However, extensive computational explorations of our model reactions reveal that, in water and acetonitrile solution, there are essentially no stable reactant complexes and product complexes. The computed reaction barriers associated with the first and rate-determining reaction step and the calculated energies relative to reactants of the intermediate transition complexes are listed in Table 1, together with the experimental rate constants of the hydrolysis under basic conditions.

For the hydrolysis under acidic conditions, the nucleophile in our computational model systems that induces silane hydrolysis is water, and the leaving species is methanol. The reaction barrier under acidic condition appears to be unimodal and has a remarkably broad and shallow maximum (see Figure 6b). This makes it very difficult to determine the precise position of the highest point along the potential energy surface (PES). In the range of about 1.0 Å around the transition state (TS) the energy varies by less than half a kcal mol^{-1}. We have carried out TS optimizations at various points on the PES plateau resulting from a linear transit, all of which return a transition vector with a positive frequency. The reaction barriers resulting from choosing the highest point of this PES scan are in a range of 6−7 kcal mol^{-1} (not contained in Table 1).

We have also computed the electronic proton affinity energies of most of the silanes studied, both for the alkoxy leaving group and the functional group. The different model structures used for these calculations are shown in Scheme 15. The calculations were performed at the ZORA-OLYP/TZ2P level of theory using COSMO for solvation in H_2O and CH_3CN. The results of these studies and the experimental rate constants of the hydrolysis under acidic conditions are summarized in Table 2.

Scheme 15. Model Structures for the Protonation of the α- and γ-Silanes at the Alkoxy Leaving Group (IIIa, IIIb, IVa, and IVb) or at the Functional Group X (Va, Vb, and VI)[a]



[a]Some of these species contain an intramolecular hydrogen bond between the protonated leaving group and the functional group or between the protonated functional group and the leaving group.

Kinetics of Hydrolysis under Basic Conditions. Discussion of Experimental and Theoretical Results. Trends in reactivity evolving from the hydrolysis experiments and those from the computations are qualitatively in nice agreement. Figure 7 shows the log k_{exp} values of all the model compounds studied at pD 11 (except for **11a** and **12a**), ranked in ascending order. The pD-dependence of the hydrolysis rate under basic conditions is positive for all silanes, which is in general agreement with OH^- being the nucleophile attacking the silicon atom (see Scheme 13). As the electron-withdrawing effect of the functional groups of the γ-silanes **2b**−**4b**, **6b**, and **9b** on the silicon center is similar, these compounds show almost identical rates of hydrolysis (k_{exp} = 1.65−2.04 × 10^{-2} h^{-1}). However, their rate is slower than that of the sterically less demanding silane **1a** (α-H, no functional group; k_{exp} = 5.82 × 10^{-2} h^{-1}) but somewhat faster than those of the long-chain alkylsilanes **1b** (k_{exp} = 3.26 × 10^{-3} h^{-1}) and **13b** (4.84 × 10^{-3} h^{-1}). Notable exceptions are the γ-silanes **5b** (k_{exp} = 1.29 × 10^{-1} h^{-1}; γ-NMe_2) and **8b** (k_{exp} = 1.49 × 10^{-1} h^{-1}; γ-NMe_3^+; positively charged, strongly electron-withdrawing functional group), which hydrolyze significantly faster, separating them from all the other γ-silanes studied. All α-silanes studied not only hydrolyze significantly faster than any γ-silane but also show a strong variation of their rate of hydrolysis compared to the γ-silanes, strongly depending on the functional group and spanning more than 3 orders of magnitude (k_{exp} = 5.82 × 10^{-2} to >90 h^{-1}). Interestingly, some exceptionally fast hydrolyses are observed for compounds **5a** (α-NMe_2; k_{exp} > 90 h^{-1}), **6a** (α-N(H)COOMe; k_{exp} = 12.8 h^{-1}), and **8a** (α-NMe_3^+; k_{exp} = 84.7 h^{-1}), whereas a significantly slower hydrolysis is observed

Table 2. k_{exp} Values at pD 5 and Calculated Proton Affinities of the Silanes **1a**–**9a**, **1b**–**6b**, **8b**, **9b**, **11a**–**13a**, and **13b**[a]

compound	k_{exp} [h^{-1}]	proton affinity[a] [kcal mol^{-1}]			
		alkoxy leaving group		functional group	
	(pD = 5)	(in H_2O)	(in CH_3CN)	(in H_2O)	(in CH_3CN)
1a (α-H)	11.2 ± 2.1	9.9[b]	12.1[b]		
1b (γ-H)	5.15 ± 2.61	10.0[c]	12.7[c]		
2a (α-Cl)	1.02 ± 0.09	6.7[d]	9.2[d]		
2b (γ-Cl)	5.08 ± 1.50	9.4[e]	12.0[e]		
3a (α-OMe)	5.76 ± 0.49	9.1[d]	11.6[d]	6.7[f]	11.3[f]
3b (γ-OMe)	6.16 ± 2.04	14.7[b]	17.4[b]		
4a (α-OAc)	5.23 ± 0.76	6.6[b]	9.1[b]	11.7[h]	13.7[h]
4b (γ-OAc)	6.88 ± 1.66	9.5[c]	12.0[c]	11.2[i]	13.9[i]
5a (α-NMe_2)	>90	8.3[d]	10.9[d]	39.9[f]	42.5[f]
5b (γ-NMe_2)	>90			39.3[g]	41.2[g]
6a (α-N(H)COOMe, SiOMe)	49.6 ± 11.8	5.0[b]	7.1[b]	16.6[h]	19.5[h]
6b (γ-N(H)COOMe)	5.20 ± 2.72			17.1[g]	19.9[g]
7a (α-N(Me)COOMe)	>90			20.2[h]	22.0[h]
8a (α-NMe_3^+, SiOMe)	0.132 ± 0.019	1.6[b]	2.0[b]		
8b (γ-NMe_3^+)	7.83 ± 0.95	8.2[c]	9.5[c]		
9a (α-N(H)Ph)	4.55 ± 0.63	7.3[d]	9.3[d]	27.5[f]	28.4[f]
9b (γ-N(H)Ph)	11.7 ± 1.9	9.7[e]	12.0[e]	29.7[g]	31.4[g]
11a (α-N(H)COOMe, SiOEt)	128[k]				
12a (α-NMe_3^+, SiOEt)	74.0[k]				
13a (α-O*n*Pr)	3.24 ± 0.34	9.7[d]	10.9[d]	10.5[f]	12.8[f]
13b (γ-Et)	3.85 ± 1.74	10.4[c]	13.5[c]		

[a] Electronic proton affinity energy ΔE_{PA} computed at ZORA-OLYP/TZ2P using COSMO for solvation in H_2O and CH_3CN. In this context, see also Scheme 15. [b] Calculated for model structure **IIIa**. [c] Calculated for model structure **IIIb**. [d] Calculated for model structure **IVa**. [e] Calculated for model structure **IVb**. [f] Calculated for model structure **Va**. [g] Calculated for model structure **Vb**. [h] Calculated for model structure **VI**. [i] Calculated for the protonation at the carbonyl oxygen atom without an intramolecular hydrogen bond. [k] This k_{exp} value was obtained by using one k_{exp} value at pD 6.1 (for details, see Figure S56).

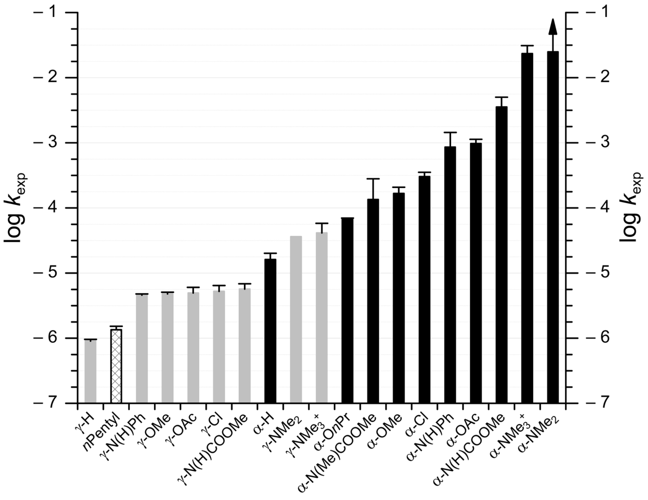


Figure 7. log k_{exp} values (including the error bars) of the silanes **1a**–**9a**, **1b**–**6b**, **8b**, **9b**, **13a**, and **13b** at pD 11 (■ α-silanes; gray □ γ-silanes). Due to its very fast hydrolysis (complete hydrolysis at $t < 2$ min; $k_{exp} > 90$ h^{-1}), the k_{exp} value of compounds **5a** (α-NMe_2) could not be determined (log $k_{exp} > -1.60$).

for compounds **7a** (α-N(Me)COOMe; $k_{exp} = 4.86 \times 10^{-1}$ h^{-1}) and **9a** (α-N(H)Ph; $k_{exp} = 3.10$ h^{-1}). The rate constants of the ethoxysilanes **11a** (α-N(H)COOMe; $k_{exp} = 4.81$ h^{-1}) and **12a** (α-NMe_3^+; $k_{exp} = 20.5$ h^{-1}) are lower than those of the corresponding methoxysilanes **6a** ($k_{exp} = 12.1$ h^{-1}) and **8a** ($k_{exp} = 84.7$ h^{-1}). As observed for the methoxysilane **5a** (α-NMe_2), the rate constant of the corresponding ethoxysilane **10a** (α-NMe_2) could not be determined ($k_{exp} > 90$ h^{-1}; complete hydrolysis at $t < 2$ min). Generally, sterically more demanding substituents of comparable functional groups, such as α-O*n*Pr (**13a**; $k_{exp} = 2.48 \times 10^{-1}$ h^{-1}) < α-OMe (**3a**; $k_{exp} = 5.99 \times 10^{-1}$ h^{-1}) or γ-Et (**13b**; $k_{exp} = 4.84 \times 10^{-3}$ h^{-1}) ≈ γ-H (**1b**; $k_{exp} = 3.26 \times 10^{-3}$ h^{-1}) < α-H (**1a**; $k_{exp} = 5.82 \times 10^{-2}$ h^{-1}), decrease the rate of hydrolysis.

The experimental results described above can be rationalized as follows: under basic conditions, the rate of hydrolysis is mainly controlled by the electrophilicity of the silicon center. Thus, the rate of the hydrolysis of the γ-silanes should be less influenced by the generally electronegative functional groups than that of their corresponding α-silanes. Indeed, most of the γ-silanes show very similar rates of hydrolysis, which is in agreement with the reaction barriers calculated for **3b** and **4b** (in H_2O: 13.8–14.5 kcal mol^{-1}; in CH_3CN: 13.3–14.4 kcal mol^{-1}). In contrast, the rate constants k_{exp} for the α-silanes **1a**–**4a** and **8a** are significantly higher by a factor of 18 (**1a**/**1b**), 58 (**2a**/**2b**), 35 (**3a**/**3b**), 211 (**4a**/**4b**), and 570 (**8a**/**8b**), respectively, than those for the corresponding γ-silanes **1b**–**4b** and **8b**. The strength of this effect correlates with the strength of the electron-withdrawing power of the functional group (NMe_3^+ > OAc > Cl > OMe > H), which is also reflected by the reaction barriers calculated for **1a**–**4a** (in H_2O: 11.2–14.1 kcal mol^{-1}; in CH_3CN: 12.0–14.1 kcal mol^{-1}) as well as by the energies relative to reactants of the intermediate transition complexes (TC) calculated for **1a**–**4a** and **8a** (in H_2O: 1.2–6.8 kcal mol^{-1}; in CH_3CN: −0.2–6.9 kcal mol^{-1}). Nevertheless, there are some experimental observations that need to be explained: (i) compounds **5b** (γ-NMe_2) and **8b** (γ-NMe_3^+) show a significantly faster hydrolysis than all the other γ-silanes studied; (ii) due to a very fast hydrolysis, the rate constant for the hydrolysis of **5a** (α-NMe$_2$) could not be determined ($k_{exp} > 90$ h^{-1}; complete hydrolysis at $t < 2$ min); (iii) the related (aminomethyl)silanes **5a** (α-NMe$_2$) and **9a** (α-N(H)Ph) differ significantly in their rate constants; and (iv) the NH/NMe analogues **6a** (α-N(H)COOMe) and **7a** (α-N(Me)COOMe) show very different k_{exp} values (**6a**: k_{exp} = 12.8 h^{-1}; **7a**: $k_{exp} = 4.86 \times 10^{-1}$ h^{-1}).

To understand the high reactivity of compound **8b** (γ-NMe$_3^+$), it is important to note that permanently positively charged cationic species exist as ion pairs in solution. Under basic conditions, both the original counteranion (I$^-$) and the hydroxide anion will be randomly mixed, so a significant fraction of all hydroxide anions present in solution will be concentrated as ion pairs close to the electrophilic silicon centers of **8b**. This high local concentration of hydroxide can explain the high rate of hydrolysis of the γ-silane **8b** ($k_{exp} = 1.49 \times 10^{-1}$ h^{-1}). The same holds true for the α-silane **8a** (α-NMe$_3^+$; k_{exp} = 84.7 h^{-1}), which is even more reactive due to its much higher electrophilicity compared with **8b**. This is also reflected by the relatively low energy of the intermediate transition complex for **8a** (in H_2O: 1.2 kcal mol^{-1}; in CH_3CN: −0.2 kcal mol^{-1}) as compared to those of other α-silanes, such as **4a** (α-OAc; in H_2O: 3.6 kcal mol^{-1}; in CH_3CN: 3.8 kcal mol^{-1}).

The α-silane **6a** contains an NH moiety in its functional group (N(H)COOMe), enabling the formation of hydrogen bonds to the entering nucleophile (see Figure 8), which results in a significantly increased reactivity (k_{exp} = 12.8 h^{-1}). This experimental result is in good agreement with the calculated low reaction barrier (in H_2O: 6.3 kcal mol^{-1}; in CH_3CN: 5.9 kcal mol^{-1}). Such kind of hydrogen bond assisted nucleophilic substitution is excluded by the exchange of the NH moiety of **6a** by an NMe moiety (→ **7a**), and indeed, compound **7a** (α-N(Me)COOMe; $k_{exp} = 4.86 \times 10^{-1}$ h^{-1}) is much less reactive than **6a**.

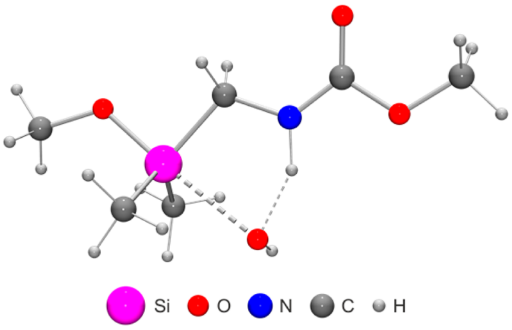


Figure 8. Calculated structure of the pretransition state in the S_N2@Si reaction of OH$^-$ + **6a** in acetonitrile, stabilized by an N−H···O hydrogen bond (for details, see the Supporting Informations).

The amines investigated in this study are characterized by a vastly different basicity (**5a**, α-NMe$_2$: pK_A 9.3; **5b**, γ-NMe$_2$: pK_A 9.0; **9a**, α-N(H)Ph: pK_A 3.2; **9b**, γ-N(H)Ph: pK_A 3.0).[31] According to their basicities, silanes **5a** and **5b** will be present in significant fractions (~50% even at pD 9) as protonated species, while **9a** and **9b** will be essentially unprotonated. This behavior is in agreement with the rate constants of the γ-silanes **5b** (γ-NMe$_2$, SiOMe) and **10b** (γ-NMe$_2$, SiOEt) under basic conditions (Figure 4), which show a changing dependency on the pD value in the range pD 8−12, clearly indicating a change in the dominating mechanism. At pD > 11, the rate constants of **5b** and **10b** are similar to the general range observed for the γ-silanes (yellow bar in Figure 4) and fit into the general explanation given for the basic hydrolysis of γ-silanes, with OH$^-$ being the nucleophile attacking a nonprotonated silane. The very high reactivity of the α-silane **5a** at pD > 11 is due to the high electrophilicity at the silicon atom combined with hydrogen-bond assistance toward the attacking hydroxide anion similar to that described for **6a** (see above). On the contrary, the hydrolysis of **5a**, **5b**, **10a**, and **10b** (X = NMe2) up to the pD of ~11 is obviously governed by a different mechanism (with water being the nucleophile attacking a protonated silane), which will be discussed below.

Due to their very high electrophilicity at the silicon center, the α-silanes generally show much higher rates of hydrolysis than the corresponding γ-silanes. Thus, the rate of hydrolysis of the essentially unprotonated compounds **9a** (α-N(H)Ph) and **9b** (γ-N(H)Ph) is controlled by the electrophilicity of the silicon center, which is much higher for the α-silane (k_{exp} = 3.10 h^{-1}) when compared with the corresponding γ-silane ($k_{exp} = 1.65 \times 10^{-2}$ h^{-1}). In addition, the NH moiety of the α-silane **9a** seems to assist the attacking hydroxide anion through hydrogen bonds similarly to the α-silane **6a**, which also results in a significantly lower reaction barrier (in H_2O: 8.9 kcal mol^{-1}; in CH_3CN: 8.4 kcal mol^{-1}), thus explaining the higher hydrolysis rate of **9a** (α-N(H)Ph; k_{exp} = 3.10 h^{-1}) compared to the more electronegatively substituted α-silane **2a** (α-Cl; k_{exp} = 1.09 h^{-1}). This is supported by the computed reaction barriers, which are lower for **9a** (in H_2O: 8.9 kcal mol^{-1}; in CH_3CN: 8.4 kcal mol^{-1}) than for **2a** (in H_2O: 12.6 kcal mol^{-1}; in CH_3CN: 12.0 kcal mol^{-1}).

Kinetics of Hydrolysis under Acidic Conditions. Discussion of Experimental and Theoretical Results. Figure 9 shows the log k_{exp} values of all the model compounds studied at pD 5 (except for **11a** and **12a**), ranked in ascending order. The pD-dependence of the hydrolysis rate under acidic conditions is negative for all silanes, which is in general agreement with H_2O being the nucleophile attacking the protonated silane (see Scheme 14). Generally, most γ-silanes

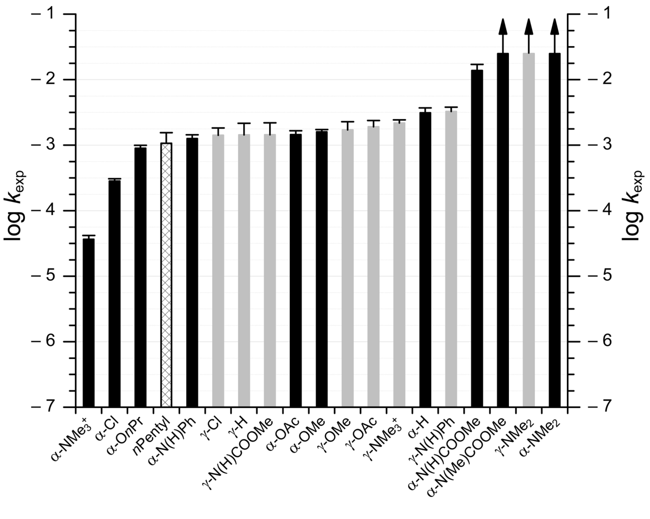


Figure 9. log k_{exp} values (including the error bars) of the silanes **1a**−**9a**, **1b**−**6b**, **8b**, **9b**, **13a**, and **13b** at pD 5 (■ α-silanes; gray □ γ-silanes). Due to their very fast hydrolysis (complete hydrolysis at $t < 2$ min; $k_{exp} > 90$ h^{-1}), the k_{exp} values of compounds **5a** (α-NMe$_2$), **5b** (γ-NMe$_2$), and **7a** (α-N(Me)COOMe) could not be determined (log k_{exp} > −1.60).

(**1b**–**4b**, **6b**, and **8b**) show almost identical rates of hydrolysis (k_{exp} = 5.08–7.83 h^{-1}). Their rate is consistently slower than that of methylsilane **1a** (α-H; k_{exp} = 11.2 h^{-1}) but somewhat faster than that of the long-chain alkylsilane **13b** (γ-Et; k_{exp} = 3.85 h^{-1}). Notable exceptions are compounds **9b** (γ-N(H)Ph; k_{exp} = 11.7 h^{-1}) and **5b** (γ-NMe$_2$; k_{exp} > 90 h^{-1}), which show a much faster hydrolysis than all the other γ-silanes. The α-silanes show a strong variation of their hydrolysis rate depending on the functional group and spanning more than 3 orders of magnitude (k_{exp} = 1.32 × 10^{-1} to >90 h^{-1}). Contrary to the basic regime, where all α-silanes hydrolyze faster than the corresponding γ-silanes, the rates of acidic hydrolysis of the α-silanes do not show such a general correlation; for example, α is slower than γ for X = NMe$_3^+$, α is similar to γ for X = OMe and OAc, and α is faster than γ for X = N(H)COOMe. In contrast to the behavior observed under basic conditions, the cationic α-silane **8a** (α-NMe$_3^+$; k_{exp} = 1.32 × 10^{-1} h^{-1}) is the least reactive silane under acidic conditions. Surprisingly, the related α-silane **5a** (α-NMe$_2$; k_{exp} > 90 h^{-1}), being completely protonated at the functional group and therefore being cationic as well, is the most reactive silane. The corresponding ethoxysilane **10a** (α-NMe$_2$; SiOEt) shows also a very fast hydrolysis (k_{exp} > 90 h^{-1}; for details, see Figure S56). These findings indicate that the proton at the functional group of **5a** (and of **5b** as well) is directly involved in the reaction mechanism, which is responsible for the extremely fast hydrolysis of compounds **5a** and **5b**. Interestingly, exceptionally fast hydrolyses are also observed for the α-silanes **6a** (α-N(H)COOMe; k_{exp} = 49.6 h^{-1}) and **7a** (α-N(Me)COOMe; k_{exp} > 90 h^{-1}), whereas a significantly slower hydrolysis is observed for **2a** (α-Cl; k_{exp} = 1.02 h^{-1}). Generally, sterically more demanding substituents of comparable functional groups, such as α-O*n*Pr (**13a**; k_{exp} = 3.24 h^{-1}) < α-OMe (**3a**; k_{exp} = 5.76 h^{-1}) or γ-Et (**13b**; k_{exp} = 3.85 h^{-1}) ≈ γ-H (**1b**; k_{exp} = 5.15 h^{-1}) < α-H (**1a**; k_{exp} = 11.2 h^{-1}), decrease the rate of hydrolysis, as also observed under basic conditions. As pointed out above, in previous theoretical analyses, the retarding effect of bulky groups has been traced to an earlier onset, along the reaction coordinate, of Pauli repulsion between closed-shell orbitals of nucleophile and substrate.[28a,29a]

The experimental results described above can be rationalized as follows: under acidic conditions, the rate of hydrolysis depends on both the electrophilicity of the silicon center (determining the molecular reactivity) and the concentration of the (protonated) reactive species (Scheme 14). Both, the electrophilicity of the silicon center and the proton affinity of the alkoxy leaving group depend on the strength of the electron-withdrawing effect of the functional group. These two inverse effects of the functional group may compensate each other. As the silane protonated at the leaving group is the reactive species, the electrophilicity of the protonated silane is dominated by the protonated leaving group, whereas the electronegativity of the functional group plays a minor role. Therefore, only little variation of the microscopic reactivity of the α-silanes compared with the corresponding γ-silanes is to be expected. The concentration of the reactive protonated silane will be strongly influenced by the basicity (proton affinity) of the leaving group, which is affected by the electron-withdrawing effect of the functional group (which can also be protonated in some cases). Indeed, both the experimental rate constants k_{exp} and the calculated proton affinities for the compounds studied support this assumption. Thus, in the case of the α-silanes **1a**–**4a** and **8a**, the differences in the rate constants (k_{exp} = 1.32 × 10^{-1} to 11.2 h^{-1}) and the calculated proton affinities of the methoxy leaving group (1.6–9.9 kcal mol^{-1} (H_2O); 2.0–12.1 kcal mol^{-1} (CH_3CN)) are significantly more pronounced than those for the corresponding γ-silanes **1b**–**4b** and **8b** (k_{exp} = 5.08–7.83 h^{-1}; proton affinity = 8.2–10.0 kcal mol^{-1} (H_2O) and 9.5–12.7 kcal mol^{-1} (CH_3CN)). The slow hydrolysis of the α-silanes **2a** (α-Cl; k_{exp} = 1.02 h^{-1}) and **8a** (α-NMe$_3^+$; k_{exp} = 1.32 × 10^{-1} h^{-1}), with their strong electron-withdrawing functional group, can be correlated with the proton affinities of the methoxy leaving group (**2a**: proton affinity = 6.7 (H_2O) or 9.2 (CH_3CN) kcal mol^{-1}; **8a**: proton affinity = 1.6 (H_2O) or 2.0 (CH_3CN) kcal mol^{-1}). Compared to the α-silane **8a**, the cationic functional group of the γ-silane **8b** seems to have only little influence on the protonation of the methoxy leaving group.

While the above-described mechanism applies for all silanes that are mainly protonated at the alkoxy leaving group (see eqs 3 and 4), it cannot explain the fast hydrolysis of the α-silanes **5a**–**7a** and **9a** and the γ-silanes **5b** and **9b**. For α-silanes with basic functional groups (NMe$_2$, N(H)Ph, N(H)COOMe, or N(Me)COOMe), an additional mechanism has to be considered. For these silanes, a small or minor (N(H)COOMe < N(Me)COOMe < N(H)Ph) or even complete (NMe$_2$) amount of the silane concentration is protonated at the functional group, which results in a cationic substituent bearing a hydrogen atom being available for hydrogen bonding to the leaving group. As hydrogen bonds preferably constitute an approximately linear bond between the heteroatoms involved, this gives rise to the formation of (i) distorted seven-membered rings for the γ-silanes **5b** and **9b** (see model structure **Vb**, Scheme 15) and for the α-silanes **6a** and **7a** (see model structure **VI**, Scheme 15) and (ii) a distorted (less favorable) five-membered ring for the α-silanes **5a** and **9a** (see model structure **Va**, Scheme 15). This hydrogen bond toward the leaving group, which in this case is not protonated (no doubly protonated species are expected), should strongly assist the release of the leaving group, preventing the generation of an anionic methoxy group.

When considering this particular mechanism, the rate of hydrolysis should depend on (i) the equilibrium concentration of the protonated substituent, (ii) the equilibrium concentration of the protonated silane forming a hydrogen bond toward the leaving group, and (iii) the electrophilicity at the silicon center, which is expected to be significantly higher for the α-silanes than for the corresponding γ-silanes.

Under acidic conditions, compounds **5a** (α-NMe$_2$; pK_A 9.3) and **5b** (γ-NMe$_2$; pK_A 9.0)[31] are completely protonated. Thus, compounds **5a** and **5b** show extremely high rates of hydrolysis (k_{exp} > 90 h^{-1}). The protonation leads to five- and seven-membered rings, respectively, with an intramolecular N–H···O hydrogen bond to the nonprotonated leaving group (model structures **Va** and **Vb**, Scheme 15). Although the distorted five-membered ring of the α-silane **5a** is disadvantageous compared with the seven-membered ring of the corresponding γ-silane **5b**, the proton affinities of **5a** (39.9 kcal mol^{-1} (H_2O); 42.5 kcal mol^{-1} (CH_3CN)) are slightly higher than those of **5b** (39.3 kcal mol^{-1} (H_2O); 41.2 kcal mol^{-1} (CH_3CN)). Together with the higher electrophilicity of **5a** this explains the higher reactivity of the α-silane **5a** compared to the γ-silane **5b**. It should be noted that this mechanism with water attacking the protonated silane also applies for basic pD values as even at pD well above pK_A a large fraction of **5a** and **5b** will be present as protonated silane.

Contrarily, compounds **9a** (α-N(H)Ph; pK_A 3.2) and **9b** (γ-N(H)Ph; pK_A 3.0)[31] are significantly less protonated, resulting in a significantly lower tendency to form a hydrogen bond toward the leaving group. Again, the five-membered ring of the protonated α-silane **9a** is disadvantageous compared to the more stable seven-membered ring of the γ-silane **9b**, but in this case the proton affinities of **9b** are significantly higher (29.7 kcal mol^{-1} (H_2O); 31.4 kcal mol^{-1} (CH_3CN)) than those of **9a** (27.5 kcal mol^{-1} (H_2O); 28.4 kcal mol^{-1} (CH_3CN)), resulting in an increase of the hydrolysis rate of the γ-silane **9b** compared to the corresponding α-silane (**9a**: k_{exp} = 4.55 h^{-1}; **9b**: k_{exp} = 11.7 h^{-1}). Similarly, the α-silanes **6a** (α-N(H)COOMe) and **7a** (α-N(Me)COOMe) are partially protonated at the carbonyl-oxygen atom (see model structure **VI**, Scheme 15), giving rise to the formation of a more favored seven-membered ring, combined with a more electrophilic silicon center, thus leading to very fast (**6a**: k_{exp} = 49.6 h^{-1}; **7a**: k_{exp} > 90 h^{-1}) rates of hydrolysis for these α-silanes contrary to the corresponding γ-silane **6b**. Substitution of the N(H)COOMe group (**6a**) by the more basic N(Me)COOMe moiety (**7a**) results in an increase of the rate of hydrolysis, which is in agreement with the different proton affinities of the functional groups (**6a**: proton affinity =16.6 (H_2O) or 19.5 (CH_3CN) kcal mol^{-1}; **7a**: proton affinity = 20.2 (H_2O) or 22.0 (CH_3CN) kcal mol^{-1}).

■ CONCLUSION

To understand the silicon α-effect in terms of an enhanced hydrolysis reactivity of the Si−OC bond of α-silanes of the formula type $ROSiMe_2CH_2X$ compared to analogous γ-silanes $ROSiMe_2(CH_2)_3X$ (R = Me, Et; X = functional group), a systematic experimental and computational study of the kinetics and mechanisms of hydrolysis of such compounds was performed. For this purpose, a series of suitable model compounds was synthesized and studied for their hydrolysis kinetics in CD_3CN/D_2O under basic and acidic conditions, using ^{1}H NMR spectroscopy as the analytical tool. To get more information about the impact of (i) the functional group X, (ii) the spacer between the silicon atom and the functional group (CH_2 vs $(CH_2)_3$), and (iii) the pD value on the mechanisms of hydrolysis, the experimental investigations were complemented by computational studies.

Generally, the trends in hydrolysis reactivity evolving from the kinetic experiments and those obtained from the computations agree well. The results of these studies clearly demonstrate that the silicon α-effect cannot be rationalized in terms of a special single effect. Instead, the different hydrolysis reactivities observed are the result of a number of components, such as electronic and steric effects, the strong impact of the pD value, and hydrogen bonds between the functional group (or even protonated functional group) and the alkoxy leaving group, which affect the hydrolysis reactivity of the α- and γ-silanes in an analogous or inverse manner. That is, the observed hydrolysis reactivity is the result of the summation of all these effects and cannot be correlated with one particular silicon α-effect. Therefore, the term "silicon α-effect" should not be used at all furthermore to explain the hydrolysis reactivity of α- or γ-silanes, and the many decades long lasting debate on this issue should be finished, at least as far as the hydrolysis reactivity at the silicon atom is concerned.

Not only is this finding important for basic research, it also has consequences for the silicone industry. It is interesting to note that the commercially relevant organofunctional α- and γ-silanes with amino, urea, and carbamato groups show the above-mentioned specific interactions of the functional group with the alkoxy leaving group or the attacking nucleophile, which gives them a significantly increased reactivity over a broad range of pH both for α- and (to a lesser extent) for γ-silanes. The insight gained from this work allows for a much clearer conceptual understanding of the reactivity of α- and γ-silanes in moisture-curing applications. Due to the broad variation of functional groups and resulting reactivity effects, our experimental and computational study of the mechanisms of hydrolysis of selected model compounds constitutes a general understanding of the rate of hydrolysis as a function of both type and position of the functional group and pH value. Therefore, this knowledge will be a valuable guidance for the further development of moisture-curing silane cross-linking and adhesion technology and their application, leading to tailor-made materials and properties.

■ EXPERIMENTAL SECTION

Syntheses and Characterization. General Procedures. All reactions involving chemicals sensitive to water and/or oxygen were carried out under a dry argon atmosphere. The organic solvents used were dried and purified according to standard procedures and stored under dry nitrogen. Starting materials, reagents, and solvents were purchased from Aldrich, ABCR, or Acros. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded at 23 °C using a Bruker DRX-300 (^{1}H, 300.1 MHz; ^{13}C, 75.5 MHz; ^{29}Si, 59.6 MHz) or Bruker Avance 500 NMR spectrometer (^{1}H, 500.1 MHz; ^{13}C, 125.8 MHz; ^{29}Si, 99.4 MHz). C_6D_6 or [D_6]DMSO served as the solvent. Chemical shifts (ppm) were determined relative to internal C_6HD_5 (^{1}H, δ 7.28), [D_5]DMSO (^{1}H, δ 2.49), C_6D_6 (^{13}C, δ 128.0), or [D_6]DMSO (^{13}C, δ 39.5), or external TMS (^{29}Si, δ 0.0). Analysis and assignment of the ^{1}H NMR spectroscopic data were supported by ^{1}H,^{1}H COSY, ^{13}C,^{1}H HMQC, ^{13}C,^{1}H HMBC, and ^{29}Si,^{1}H HMQC (optimized for $^2J_{SiH}$ = 7 Hz) experiments. The $AA'M_3XX'$, $A_3M_2X_2$, AA′FF′MM′X, and AA′MM′XX′ spin systems observed for the compounds synthesized were analyzed by using the WIN-DAISY 4.05 software package.[32] Assignment of the ^{13}C NMR spectroscopic data was supported by DEPT-135 and the aforementioned ^{13}C,^{1}H correlation experiments. Elemental analyses were performed using a VarioMicro apparatus (Elementar Analysensysteme GmbH). ESI-HRMS spectra were recorded on a Bruker MicrOTOF instrument using solutions in acetonitrile.

*Methoxytrimethylsilane (**1a**).* This compound was commercially available and was purified by distillation prior to use.

*Methoxydimethyl(n-propyl)silane (**1b**).* A 2.0 M solution of *n*-propylmagnesium bromide in diethyl ether (62.4 mL, 125 mmol of *n*-PrMgBr) was added dropwise at 0 °C within 2 h to a stirred solution of **14** (15.0 g, 125 mmol) in diethyl ether (250 mL). After the mixture had been stirred at 20 °C for 17 h, the solvent was removed by distillation at ambient pressure. Subsequently, *n*-pentane (300 mL) was added, the mixture was stirred for 30 min, and the solid was filtered off, washed with *n*-pentane (3 × 25 mL), and discarded. The solvent of the filtrate (including the wash solutions) was removed by distillation at ambient pressure, and the residue was purified by distillation at ambient pressure to furnish **1b** as a colorless liquid (14.0 g, 106 mmol; 85% yield). Bp: 98 °C. ^{1}H NMR (300.1 MHz, C_6D_6): δ 0.19 (s, 6 H; $SiCH_3$), 0.68 (δ_A), 1.09 (δ_M), and 1.50 (δ_X) ($AA'M_3XX'$ system, $^2J_{AA'}$ = 14.1 Hz, $^3J_{AX}$ = 11.1 Hz, $^3J_{AX'}$ = 5.4 Hz, $^2J_{XX'}$ = 15.2 Hz, $^3J_{MX}$ = $^3J_{MX'}$ = 7.3 Hz, 7 H; $SiCH_AH_{A'}CH_XH_{X'}C(H_M)_3$), 3.39 (s, 3 H; OCH_3). ^{13}C NMR (75.5 MHz, C_6D_6): δ −2.5 ($SiCH_3$), 17.1 (CH_2CH_3), 18.3 (CH_2CH_3), 18.9 ($SiCH_2$), 49.9 (OCH_3). ^{29}Si NMR (59.6 MHz, C_6D_6): δ 17.7. Anal. Calcd for $C_6H_{16}OSi$ (132.28): C, 54.48; H, 12.19. Found: C, 54.69; H, 12.13.

*(Chloromethyl)methoxydimethylsilane (**2a**).* This compound was commercially available and was purified by distillation prior to use.

*(3-Chloroprop-1-yl)methoxydimethylsilane (**2b**).* This compound was commercially available and was purified by distillation prior to use.

*Methoxydimethyl(methoxymethyl)silane (**3a**).* A solution of ethylmethylamine (9.95 g, 1.68 mmol) in THF (20 mL) was added dropwise at 0 °C within 2 h to a stirred solution of **16** (30.2 g, 168 mmol) and ethyldimethylamine (12.3 g, 168 mmol) in THF (200 mL). After the mixture had been stirred at 0 °C for 2 h and at 20 °C for 2 h, a 3.0 M solution of methylmagnesium bromide in diethyl ether (140 mL, 420 mmol of MeMgBr) was added dropwise at 0 °C within 1 h. The reaction mixture was stirred at 20 °C for 16 h and was then concentrated to a volume of ca. 50 mL by distillation at ambient pressure, *n*-pentane (250 mL) was added, and the mixture was stirred at 20 °C for 30 min. The resulting solid was filtered off, washed with *n*-pentane (3 × 25 mL), and discarded. The solvent of the filtrate (including the wash solutions) was removed by distillation at ambient pressure, and the residue was distilled at ambient pressure to give three fractions (**20**, 1.97 g, bp 93−105 °C; **18**, 4.47 g, bp 110−121 °C; **19**, 3.17 g, bp 140−147 °C (discarded)).

Transformation A: A 1.25 M solution of hydrogen chloride in methanol (1.14 mL, 1.43 mmol of HCl, 29.6 mmol methanol) was added dropwise at 20 °C within 15 min to a stirred solution of **18** (4.47 g, 27.7 mmol) in *n*-pentane (30 mL), and the resulting mixture was stirred at 20 °C for 30 min. The resulting solid was filtered off, washed with *n*-pentane (3 × 5 mL), and discarded. The solvent of the filtrate (including the wash solutions) was removed by distillation at ambient pressure, and the residue was distilled at ambient pressure to give 2.12 g of **3a** as a crude distillate (bp 87−91 °C).

Transformation B: Methanol (455 mg, 14.2 mmol) was added dropwise to a stirred solution of **20** (1.97 g, 14.2 mmol) and ethyldimethylamine (1.04 g, 14.2 mmol) in *n*-pentane (15 mL) at 20 °C within 15 min, and the mixture was stirred at 20 °C for 30 min. The resulting solid was filtered off, washed with *n*-pentane (3 × 3 mL), and discarded. The solvent of the filtrate (including the wash solutions) was removed by distillation at ambient pressure, and the residue was distilled at ambient pressure to give 1.18 g of **3a** as a crude distillate (bp 84−91 °C).

The product fractions obtained after the transformations A and B were combined and finally purified by distillation at ambient pressure to furnish **3a** as a colorless liquid (1.93 g, 14.4 mmol; 9% yield). Bp: 90 °C. ^{1}H NMR (500.1 MHz, C_6D_6): δ 0.28 (s, 6 H; SiCH_3), 3.14 (s, 2 H; SiCH_2), 3.29 (COCH_3), 3.47 (s, 3 H; SiOCH_3). ^{13}C NMR (125.8 MHz, C_6D_6): δ −3.7 (SiCH$_3$), 50.5 (SiOCH$_3$), 63.0 (COCH$_3$), 66.2 (SiCH$_2$). ^{29}Si NMR (99.4 MHz, C_6D_6): δ 12.1. Anal. Calcd for $C_5H_{14}O_2Si$ (134.25): C, 44.73; H, 10.51. Found: C, 45.12; H, 10.30.

*Methoxy(3-methoxyprop-1-yl)dimethylsilane (**3b**).* Methanol (4.10 g, 128 mmol) was added dropwise within 20 min to sodium (1.39 g, 60.5 mmol), and the resulting mixture was heated under reflux for 1 h and was then allowed to cool to 20 °C, followed by the addition of methanol (25 mL). Subsequently, compound **2b** (9.15 g, 54.9 mmol) was added dropwise under reflux within 20 min to the stirred MeONa/MeOH mixture, which was heated under reflux for a further 4 d and then allowed to cool to 20 °C. *n*-Pentane (100 mL) was added, and the resulting precipitate was filtered off, washed with *n*-pentane (3 × 15 mL), and discarded. The solvent of the filtrate (including the wash solutions) was removed by distillation at ambient pressure, and the residue was purified by distillation *in vacuo* to furnish **3b** as a colorless liquid (4.80 g, 29.6 mmol; 54% yield). Bp: 45 °C/4 mbar. ^{1}H NMR (500.1 MHz, C_6D_6): δ 0.18 (s, 6 H; SiCH_3), 0.74 (δ_A), 1.77 (δ_M), and 3.33 (δ_X) (AA′MM′XX′ system, $^2J_{AA'}$ = 15.4 Hz, $^3J_{AM}$ = 5.1 Hz, $^3J_{AM'}$ = 11.8 Hz, $^2J_{MM'}$ = 14.4 Hz, $^3J_{MX}$ = 6.6 Hz, $^3J_{MX'}$ = 6.6 Hz, $^2J_{XX'}$ = 11.9 Hz, 6 H; SiC$H_AH_{A'}$C$H_MH_{M'}$C$H_XH_{X'}$), 3.27 (s, 3 H; COCH_3), 3.38 (s, 3 H; SiOCH_3). ^{13}C NMR (125.8 MHz, C_6D_6): δ −2.6 (SiCH$_3$), 12.4 (SiCH$_2$), 23.8 (SiCH$_2$CH$_2$), 50.0 (SiOCH$_3$), 58.2 (COCH$_3$), 75.4 (CH$_2$O). ^{29}Si NMR (99.4 MHz, C_6D_6): δ 18.2. Anal. Calcd for $C_7H_{18}O_2Si$ (162.30): C, 51.80; H, 11.18. Found: C, 51.81; H, 11.30.

*(Acetoxymethyl)methoxydimethylsilane (**4a**).* Sodium acetate (17.7 g, 216 mmol) was added at 20 °C in a single portion to a stirred solution of **2a** (10.0 g, 72.1 mmol) in THF (200 mL). The reaction mixture was heated under reflux for 1 d and was then concentrated to a volume of ca. 50 mL by distillation at ambient pressure, *n*-pentane (250 mL) was added, and the mixture was stirred at 20 °C for 30 min. The resulting solid was filtered off, washed with *n*-pentane (3 × 20 mL), and discarded. The solvent of the filtrate (including the wash solutions) was removed by distillation at ambient pressure, and the residue was purified by distillation *in vacuo* to furnish **4a** as a colorless liquid (8.68 g, 53.5 mmol; 74% yield). Bp: 67 °C/20 mbar). ^{1}H NMR (300.1 MHz, C_6D_6): δ 0.19 (s, 6 H; SiCH_3), 1.81 (s, 3 H; C(O)CH_3), 3.36 (s, 3 H; OCH_3), 3.92 (s, 2 H; SiCH_2). ^{13}C NMR (75.5 MHz, C_6D_6): δ −3.7 (SiCH$_3$), 20.2 (C(O)CH$_3$), 50.3 (OCH$_3$), 56.2 (SiCH$_2$), 170.7 (C(O)CH$_3$). ^{29}Si NMR (59.6 MHz, C_6D_6): δ 12.5. Anal. Calcd for $C_6H_{14}O_3Si$ (162.26): C, 44.41; H, 8.70. Found: C, 44.53; H, 8.77.

*(3-Acetoxyprop-1-yl)methoxydimethylsilane (**4b**).* Sodium acetate (14.8 g, 180 mmol) was added at 20 °C in a single portion to a stirred solution of **2b** (10.0 g, 60.0 mmol) and tetra-*n*-butylphosphonium chloride (1.77 g, 6.00 mmol) in THF (200 mL). The reaction mixture was heated under reflux for 3 d and was then concentrated to a volume of ca. 50 mL by distillation at ambient pressure, *n*-pentane (250 mL) was added, and the mixture was stirred at 20 °C for 30 min. The resulting solid was filtered off, washed with *n*-pentane (3 × 20 mL), and discarded. The solvent of the filtrate (including the wash solutions) was removed by distillation at ambient pressure, and the residue was purified by distillation *in vacuo* to furnish **4a** as a colorless liquid (8.90 g, 46.8 mmol; 78% yield). Bp: 91 °C/12 mbar. ^{1}H NMR (500.1 MHz, C_6D_6): δ 0.12 (s, 6 H; SiCH_3), 0.55 (δ_A), 1.68 (δ_M), and 4.10 (δ_X) (AA′MM′XX′ system, $^2J_{AA'}$ = 14.7 Hz, $^3J_{AM}$ = 5.0 Hz, $^3J_{AM'}$ = 12.0 Hz, $^2J_{MM'}$ = 13.7 Hz, $^3J_{MX}$ = 6.4 Hz, $^3J_{MX'}$ = 7.5 Hz, $^2J_{XX'}$ = 10.8 Hz, 6 H; SiC$H_AH_{A'}$C$H_MH_{M'}$C$H_XH_{X'}$), 1.82 (s, 3 H; C(O)CH_3), 3.33 (s, 3 H; OCH_3). ^{13}C NMR (125.8 MHz, C_6D_6): δ −2.7 (SiCH$_3$), 12.1 (SiCH$_2$), 20.5 (C(O)CH$_3$), 22.9 (SiCH$_2$CH$_2$), 50.0 (SiOCH$_3$), 66.7 (CH$_2$O), 170.1 (C(O)CH$_3$). ^{29}Si NMR (99.4 MHz, C_6D_6): δ 17.8. Anal. Calcd for $C_8H_{18}O_3Si$ (190.31): C, 50.49; H, 9.53. Found: C, 50.15; H, 9.54.

*[(Dimethylamino)methyl]methoxydimethylsilane (**5a**).* This compound was synthesized according to ref 11, with slight modifications. A mixture of **2a** (19.2 g, 138 mmol) and dimethylamine (15.6 g, 346 mmol) was heated in an autoclave at 100 °C for 8 h. The reaction mixture was allowed to cool to 20 °C within 30 min, *n*-pentane (400 mL) was added, and the resulting precipitate was filtered off, washed with *n*-pentane (3 × 20 mL), and discarded. The solvent of the filtrate (including the wash solutions) was removed by distillation at ambient pressure, and the residue was purified by distillation at ambient pressure to furnish **5a** as a colorless liquid (15.3 g, 104 mmol; 75% yield). Bp: 125 °C. ^{1}H NMR (300.1 MHz, C_6D_6): δ 0.27 (s, 6 H; SiCH_3), 1.94 (s, 2 H; SiCH_2), 2.32 (s, 6 H; NCH_3), 3.41 (s, 3 H; OCH_3). ^{13}C NMR (75.5 MHz, C_6D_6): δ −2.6 (SiCH$_3$), 49.7 (NCH$_3$), 50.1 (OCH$_3$), 50.9 (SiCH$_2$). ^{29}Si NMR (59.6 MHz, C_6D_6): δ 14.6. Anal. Calcd for $C_6H_{17}NOSi$ (147.29): C, 48.93; H, 11.63; N, 9.51. Found: C, 48.65; H, 11.59; N, 9.30.

*[3-(Dimethylamino)prop-1-yl]methoxydimethylsilane (**5b**).* A mixture of **2b** (10.0 g, 60.0 mmol) and dimethylamine (13.5 g, 299 mmol) was heated in an autoclave at 100 °C for 8 h. The reaction mixture was allowed to cool to 20 °C within 30 min, *n*-pentane (500 mL) was added, and the resulting precipitate was filtered off, washed with *n*-pentane (3 × 30 mL), and discarded. The solvent of the filtrate (including the wash solutions) was removed by distillation at ambient pressure, and the residue was purified by distillation *in vacuo* to furnish **5b** as a colorless liquid (6.80 g, 38.8 mmol; 65% yield). Bp: 57 °C/5 mbar. ^{1}H NMR (500.1 MHz, C_6D_6): δ 0.20 (s, 6 H; SiCH_3), 0.74 (δ_A), 1.67 (δ_M), and 2.32 (δ_X) (AA′MM′XX′ system, $^2J_{AA'}$ = 14.7 Hz, $^3J_{AM}$ = 5.2 Hz, $^3J_{AM'}$ = 11.6 Hz, $^2J_{MM'}$ = 13.5 Hz, $^3J_{MX}$ = 8.5 Hz, $^3J_{MX'}$ = 5.9 Hz, $^2J_{XX'}$ = 11.7 Hz, 6 H; SiC$H_AH_{A'}$C$H_MH_{M'}$C$H_XH_{X'}$), 2.24 (s, 6 H; NCH_3), 3.40 (s, 3 H; OCH_3). ^{13}C NMR (125.8 MHz, C_6D_6): δ −2.5 (SiCH$_3$), 13.7 (SiCH$_2$), 21.8 (SiCH$_2$CH$_2$), 45.5 (NCH$_3$), 50.0 (OCH$_3$), 63.1 (CH$_2$N). ^{29}Si NMR (99.4 MHz, C_6D_6): δ 18.2. Anal. Calcd for $C_8H_{21}NOSi$ (175.35): C, 54.80; H, 12.07; N, 7.99. Found: C, 54.62; H, 12.19; N, 8.02.

*Methoxy{[(methoxycarbonyl)amino]methyl}dimethylsilane (**6a**).* A solution of **2a** (10.0 g, 72.1 mmol) and methanol (2.43 g, 75.8 mmol) in *N*,*N*-dimethylformamide (10 mL) was added dropwise to a boiling suspension of potassium cyanate (6.14 g, 75.7 mmol) in *N*,*N*-

dimethylformamide (20 mL) at 145 °C (±5 °C, temperature measurement within the flask) within 30 min. The reaction mixture was allowed to cool to 20 °C within 1 h and was then stirred at this temperature for 17 h, diethyl ether (150 mL) was added, and the mixture was stirred at 20 °C for 30 min. The resulting precipitate was filtered off, washed with diethyl ether (3 × 30 mL), and discarded. The solvent of the filtrate (including the wash solutions) was removed by distillation at ambient pressure, and the residue was purified by distillation *in vacuo* to furnish **6a** as a colorless liquid (3.60 g, 20.3 mmol; 28% yield). Bp: 52 °C/0.02 mbar. ^{1}H NMR (300.1 MHz, $\mathrm{C_6D_6}$): δ 0.12 (s, 6 H; $\mathrm{SiC}H_3$), 2.78 (d, $^3J_{\mathrm{HH}}$ = 5.3 Hz, 2 H; $\mathrm{SiC}H_2$), 3.27 (s, 3 H; $\mathrm{SiOC}H_3$), 3.60 (s, 3 H; $\mathrm{C(O)OC}H_3$), 4.65 (br s, 1 H; NH). ^{13}C NMR (75.5 MHz, $\mathrm{C_6D_6}$): δ −3.5 ($\mathrm{SiCH_3}$), 30.3 ($\mathrm{SiCH_2}$), 50.1 ($\mathrm{SiOCH_3}$), 51.8 ($\mathrm{C(O)OCH_3}$), 157.9 ($\mathrm{C(O)OCH_3}$). ^{29}Si NMR (59.6 MHz, $\mathrm{C_6D_6}$): δ 14.6. Anal. Calcd for $\mathrm{C_6H_{15}NO_3Si}$ (177.28): C, 40.65; H, 8.53; N, 7.90. Found: C, 40.41; H, 8.44; N, 8.00.

*Methoxy{3-[(methoxycarbonyl)amino]prop-1-yl}dimethylsilane (**6b**).* A solution of **2b** (10.0 g, 60.0 mmol) and methanol (3.46 g, 108 mmol) in *N*,*N*-dimethylformamide (10 mL) was added dropwise to a boiling suspension of potassium cyanate (5.11 g, 63.0 mmol) in *N*,*N*-dimethylformamide (20 mL) at 145 °C (±5 °C, temperature measurement within the flask) within 30 min. The reaction mixture was allowed to cool to 20 °C within 1 h and was then stirred at this temperature for 17 h, diethyl ether (100 mL) was added, and the mixture was stirred at 20 °C for 30 min. The resulting precipitate was filtered off, washed with diethyl ether (3 × 30 mL), and discarded. The solvent of the filtrate (including the wash solutions) was removed by distillation at ambient pressure, and the residue was purified by distillation *in vacuo*. The relevant fractions (GC analysis) were combined, methanol (200 mg, 6.24 mmol) was added, and the resulting mixture was stirred at 20 °C for 30 min to furnish **6b** as a colorless liquid (9.12 g, 44.4 mmol; 74% yield). Bp: 127 °C/5 mbar. ^{1}H NMR (500.1 MHz, $\mathrm{C_6D_6}$): δ 0.11 (s, 6 H; $\mathrm{SiC}H_3$), 0.45 (δ_{A}), 1.43 (δ_{F}), 3.11 (δ_{M}), and 4.48 (δ_{X}) (AA′FF′MM′X system, $^2J_{\mathrm{AA'}}$ = 11.1 Hz, $^3J_{\mathrm{AF}}$ = 11.7 Hz, $^3J_{\mathrm{AF'}}$ = 5.1 Hz, $^2J_{\mathrm{FF'}}$ = 9.9 Hz, $^3J_{\mathrm{FM}}$ = 6.4, $^3J_{\mathrm{F'M}}$ = 7.9 Hz, $^2J_{\mathrm{MM'}}$ = 14.6 Hz, $^3J_{\mathrm{MX}}$ = $^3J_{\mathrm{M'X}}$ = 6.3 Hz, 7 H; $\mathrm{SiC}H_{\mathrm{A}}H_{\mathrm{A'}}\mathrm{C}H_{\mathrm{F}}H_{\mathrm{F'}}\mathrm{C}H_{\mathrm{M}}H_{\mathrm{M'}}\mathrm{N}H_{\mathrm{X'}}$), 3.33 (s, 3 H; $\mathrm{SiOC}H_3$), 3.60 (s, 3 H; $\mathrm{C(O)OC}H_3$). ^{13}C NMR (125.8 MHz, $\mathrm{C_6D_6}$): δ −2.7 ($\mathrm{SiCH_3}$), 13.1 ($\mathrm{SiCH_2}$), 24.1 ($\mathrm{SiCH_2CH_2}$), 44.0 ($\mathrm{CH_2N}$), 50.0 ($\mathrm{SiOCH_3}$), 51.6 ($\mathrm{C(O)OCH_3}$), 156.9 ($\mathrm{C(O)OCH_3}$). ^{29}Si NMR (99.4 MHz, $\mathrm{C_6D_6}$): δ 18.1. Anal. Calcd for $\mathrm{C_8H_{19}NO_3Si}$ (205.33): C, 46.80; H, 9.33; N, 6.82. Found: C, 46.79; H, 9.24; N, 6.94.

*Methoxy{[(methoxycarbonyl)methylamino]methyl}dimethylsilane (**7a**).* Methyl chloroformate (5.53 g, 58.5 mmol) was added dropwise at 20 °C within 30 min to a stirred solution of **27** (7.79 g, 58.5 mmol) and triethylamine (5.92 g, 58.5 mmol) in *n*-pentane (300 mL), and the reaction mixture was stirred at 20 °C for 30 min. The resulting precipitate was filtered off, washed with *n*-pentane (3 × 50 mL), and discarded. The solvent of the filtrate (including the wash solutions) was removed by distillation at ambient pressure, and the residue was purified by distillation *in vacuo* to furnish **7a** as a colorless liquid (7.72 g, 40.4 mmol; 69% yield). Bp: 77 °C/4 mbar. ^{1}H NMR (500.1 MHz, $\mathrm{C_6D_6}$): data for two rotational isomers (molar ratio, 9:5); main isomer: δ 0.12 (s, 6 H; $\mathrm{SiC}H_3$), 2.76 (s, 3 H; $\mathrm{NC}H_3$), 2.83 (s, 2 H; $\mathrm{SiC}H_2$), 3.39 (s, 3 H; $\mathrm{SiOC}H_3$), 3.58 (s, 3 H; $\mathrm{C(O)OC}H_3$); minor isomer: δ 0.35 (s, 6 H; $\mathrm{SiC}H_3$), 2.72 (s, 2 H; $\mathrm{SiC}H_2$), 2.95 (s, 3 H; $\mathrm{NC}H_3$), 3.29 (s, 3 H; $\mathrm{SiOC}H_3$) 3.60 (s, 3 H; $\mathrm{C(O)OC}H_3$). ^{1}H NMR (500.1 MHz, $\mathrm{C_6D_6}$, 70 °C): δ 0.26 (s, 6 H; $\mathrm{SiC}H_3$), 2.81 (s, 2 H; $\mathrm{SiC}H_2$), 2.86 (s, 3 H; $\mathrm{NC}H_3$), 3.38 (s, 3 H; $\mathrm{SiOC}H_3$), 3.61 (s, 3 H; $\mathrm{C(O)OC}H_3$). ^{13}C NMR (75.5 MHz, $\mathrm{C_6D_6}$): data for two rotational isomers (molar ratio, 9:5); main isomer: δ −2.4 ($\mathrm{SiCH_3}$), 36.4 ($\mathrm{NCH_3}$), 40.3 ($\mathrm{SiCH_2}$), 50.0 ($\mathrm{SiOCH_3}$), 52.4 ($\mathrm{C(O)OCH_3}$), 157.0 ($\mathrm{C(O)OCH_3}$); minor isomer: δ −3.0 ($\mathrm{SiCH_3}$), 37.0 ($\mathrm{NCH_3}$), 39.0 ($\mathrm{SiCH_2}$), 50.0 ($\mathrm{SiOCH_3}$), 52.0 ($\mathrm{C(O)OCH_3}$), 156.5 ($\mathrm{C(O)OCH_3}$). ^{13}C NMR (75.5 MHz, $\mathrm{C_6D_6}$, 70 °C): δ −2.6 ($\mathrm{SiCH_3}$), 36.7 ($\mathrm{NCH_3}$), 40.2 ($\mathrm{SiCH_2}$), 50.0 ($\mathrm{SiOCH_3}$), 52.1 ($\mathrm{C(O)OCH_3}$), 157.0 ($\mathrm{C(O)OCH_3}$). ^{29}Si NMR (59.6 MHz, $\mathrm{C_6D_6}$): data for two rotational isomers (molar ratio, 9:5); main isomer: δ 13.2; minor isomer: δ 14.6. ^{29}Si NMR (59.6 MHz, $\mathrm{C_6D_6}$, 70 °C): δ 13.5. Anal. Calcd for $\mathrm{C_7H_{17}NO_3Si}$ (191.30): C, 43.95; H, 8.96; N, 7.32. Found: C, 43.82; H, 9.01; N, 7.50.

*[(Methoxydimethylsilyl)methyl]trimethylammonium Iodide (**8a**).* Freshly distilled iodomethane (14.5 g, 102 mmol) was added dropwise at 20 °C within 30 min under exclusion of light to a stirred solution of **5a** (3.00 g, 20.4 mmol) in acetonitrile (50 mL). The reaction mixture was heated under reflux for 2 h, cooled to 20 °C within 30 min, and then stirred at this temperature for 18 h. The solvent and the excess iodomethane were removed under reduced pressure, the residue was washed with *n*-pentane (4 × 15 mL), and the wash solutions were discarded. Acetonitrile (15 mL) was added to the residue, and the resulting suspension was heated under reflux until a clear solution was obtained, which was kept undisturbed at 20 °C for 3 h and then at −20 °C for a further 17 h. The product was isolated by filtration at −20 °C, washed with *n*-pentane (5 mL), and dried *in vacuo* (0.01 mbar, 40 °C, 4 h) to give **8a** as a colorless solid (4.89 g, 16.9 mmol; 83% yield). ^{1}H NMR (300.1 MHz, [$\mathrm{D_6}$]DMSO): δ 0.28 (s, 6 H; $\mathrm{SiC}H_3$), 3.17 (s, 9 H; $\mathrm{NC}H_3$), 3.21 (s, 2 H; $\mathrm{SiC}H_2$), 3.43 (s, 3 H; $\mathrm{OC}H_3$). ^{13}C NMR (75.5 MHz, [$\mathrm{D_6}$]DMSO): δ −1.7 ($\mathrm{SiCH_3}$), 50.4 ($\mathrm{OCH_3}$), 56.1 (t, $^1J_{\mathrm{NC}}$ = 3.6 Hz; $\mathrm{SiCH_2}$), 57.9 (t, $^1J_{\mathrm{NC}}$ = 2.3 Hz; $\mathrm{NCH_3}$). ^{29}Si NMR (59.6 MHz, [$\mathrm{D_6}$]DMSO): δ 12.0. Anal. Calcd for $\mathrm{C_7H_{20}INOSi}$ (289.23): C, 29.07; H, 6.97; N, 4.84. Found: C, 29.23; H, 7.08; N, 4.72.

*[3-(Methoxydimethylsilyl)prop-1-yl]trimethylammonium Iodide (**8b**).* Freshly distilled iodomethane (10.5 g, 74.0 mmol) was added dropwise at 20 °C within 30 min under exclusion of light to a stirred solution of **5b** (2.60 g, 14.8 mmol) in acetonitrile (40 mL). The reaction mixture was heated under reflux for 4 h, cooled to 20 °C within 30 min, and then stirred at this temperature for 18 h. The solvent and the excess iodomethane were removed under reduced pressure, the residue was washed with *n*-pentane (4 × 15 mL), and the wash solutions were discarded. Acetonitrile (15 mL) was added to the residue, and the resulting suspension was heated under reflux until a clear solution was obtained, which was kept undisturbed at 20 °C for 3 h and then at −20 °C for a further 17 h. The product was isolated by filtration at −20 °C, washed with *n*-pentane (5 mL), and dried *in vacuo* (0.01 mbar, 40 °C, 4 h) to give **8a** as a colorless solid (2.94 g, 9.27 mmol; 63% yield). ^{1}H NMR (300.1 MHz, [$\mathrm{D_6}$]DMSO): δ 0.10 (s, 6 H; $\mathrm{SiC}H_3$), 0.48 (δ_{A}), 1.66 (δ_{M}), and 2.35 (δ_{X}) (AA′MM′XX′ system, $^2J_{\mathrm{AA'}}$ = 11.5 Hz, $^3J_{\mathrm{AM}}$ = 4.9 Hz, $^3J_{\mathrm{AM'}}$ = 12.0 Hz, $^2J_{\mathrm{MM'}}$ = 13.0 Hz, $^3J_{\mathrm{MX}}$ = 4.7 Hz, $^3J_{\mathrm{MX'}}$ = 12.4 Hz, $^2J_{\mathrm{XX'}}$ = 12.7 Hz, 6 H; $\mathrm{SiC}H_{\mathrm{A}}H_{\mathrm{A'}}\mathrm{C}H_{\mathrm{M}}H_{\mathrm{M'}}\mathrm{C}H_{\mathrm{X}}H_{\mathrm{X'}}$), 3.05 (s, 9 H; $\mathrm{NC}H_3$), 3.33 (s, 3 H; $\mathrm{OC}H_3$). ^{13}C NMR (75.5 MHz, [$\mathrm{D_6}$]DMSO): δ −2.7 ($\mathrm{SiCH_3}$), 11.7 ($\mathrm{SiCH_2}$), 16.3 ($\mathrm{SiCH_2CH_2}$), 49.8 ($\mathrm{OCH_3}$), 52.1 (t, $^1J_{\mathrm{NC}}$ = 3.6 Hz; $\mathrm{NCH_3}$), 67.7 (t, $^1J_{\mathrm{NC}}$ = 1.9 Hz; $\mathrm{CH_2N}$). ^{29}Si NMR (59.6 MHz, [$\mathrm{D_6}$]DMSO): δ 18.5. Anal. Calcd for $\mathrm{C_9H_{24}INOSi}$ (317.29): C, 34.07; H, 7.62; N, 4.41. Found: C, 34.01; H, 7.62; N, 4.35.

*Methoxydimethyl[(phenylamino)methyl]silane (**9a**).* A stirred mixture of magnesium turnings (911 mg, 37.5 mmol) and aniline (60.4 g, 649 mmol) was heated under reflux for 2 h and was then concentrated to a volume of ca. 40 mL by distillation at ambient pressure and heated under reflux for a further 2 h. The resulting suspension was cooled to 125 °C within 15 min, and **2a** (10.0 g, 72.1 mmol) was added dropwise at this temperature within 30 min, followed by the addition of aniline (30.0 g, 32.2 mmol). The reaction mixture was stirred at 120 °C for 1 h and was then cooled to 20 °C within 30 min. The resulting precipitate was filtered off, washed with toluene (3 × 30 mL), and discarded. The solvent of the filtrate (including the wash solutions) and the excess aniline were removed by distillation under reduced pressure, and the residue was purified by distillation *in vacuo* to furnish **9a** as a colorless liquid (9.58 g, 49.0 mmol; 68% yield). Bp: 132 °C/12 mbar. ^{1}H NMR (300.1 MHz, $\mathrm{C_6D_6}$): δ 0.14 (s, 6 H; $\mathrm{SiC}H_3$), 2.49 (s, 2 H; $\mathrm{SiC}H_2$), 3.31 (s, 3 H; $\mathrm{OC}H_3$), 3.64 (br s, 1 H; NH), 6.68 (δ_{A}), 6.90 (δ_{M}), and 7.32 (δ_{X}) (AA′MXX′ system, $^3J_{\mathrm{AX}}$ = $^3J_{\mathrm{A'X'}}$ = 8.2 Hz, $^3J_{\mathrm{MX}}$ = $^3J_{\mathrm{MX'}}$ = 7.3 Hz, $^4J_{\mathrm{AA'}}$ = 2.6 Hz, $^4J_{\mathrm{AM}}$ = $^4J_{\mathrm{A'M}}$ = 1.1 Hz, $^4J_{\mathrm{XX'}}$ = 1.7 Hz, $^5J_{\mathrm{AX'}}$ = $^5J_{\mathrm{A'X}}$ = 0.5 Hz, 5 H; H-2$_{\mathrm{A}}$/H-6$_{\mathrm{A'}}$, H-3$_{\mathrm{X}}$/H-5$_{\mathrm{X'}}$, and H-4$_{\mathrm{M}}$, $\mathrm{C_6H_5}$). ^{13}C NMR (75.5 MHz, $\mathrm{C_6D_6}$): δ −3.5 ($\mathrm{SiCH_3}$), 32.5 ($\mathrm{SiCH_2}$), 50.2 ($\mathrm{OCH_3}$), 113.0 (C-2/C-6, $\mathrm{C_6H_5}$), 117.5 (C-4, $\mathrm{C_6H_5}$), 129.4 (C-3/C-5, $\mathrm{C_6H_5}$), 150.7 (C-1, $\mathrm{C_6H_5}$). ^{29}Si NMR (59.6 MHz, $\mathrm{C_6D_6}$): δ 15.3. Anal. Calcd for $\mathrm{C_{10}H_{17}NOSi}$

(195.34): C, 61.49; H, 8.77; N, 7.17. Found: C, 61.52; H, 8.92; N, 7.30.

*Methoxydimethyl[3-(phenylamino)prop-1-yl]silane (**9b**).* A stirred mixture of magnesium turnings (1.52 g, 62.5 mmol) and aniline (101 g, 1.08 mol) was heated under reflux for 2 h and was then concentrated to a volume of ca. 60 mL by distillation at ambient pressure and heated under reflux for a further 2 h. The resulting suspension was cooled to 125 °C within 15 min, and **2b** (20.0 g, 120 mmol) was added dropwise at this temperature within 30 min, followed by the addition of aniline (50.0 g, 53.7 mmol). The reaction mixture was stirred at 120 °C for 1 h and was then cooled to 20 °C within 30 min. The resulting precipitate was filtered off, washed with toluene (3 × 50 mL), and discarded. The solvent of the filtrate (including the wash solutions) and the excess of aniline were removed by distillation under reduced pressure, and the residue was purified by distillation *in vacuo* to furnish **9b** as a colorless liquid (17.6 g, 78.8 mmol; 66% yield). Bp: 145 °C/8 mbar. ^{1}H NMR (300.1 MHz, C_6D_6): δ 0.15 (s, 6 H; $\mathrm{SiC}H_3$), 0.57 (δ_A), 1.54 (δ_M), and 2.96 (δ_X) (AA′MM′XX′ system, $^2J_{AA'}$ = 15.9 Hz, $^3J_{AM}$ = 11.6 Hz, $^3J_{AM'}$ = 5.2 Hz, $^2J_{MM'}$ = 14.6 Hz, $^3J_{MX}$ = 6.1 Hz, $^3J_{MX'}$ = 8.1 Hz, $^2J_{XX'}$ = 13.3 Hz, 6 H; $\mathrm{SiC}H_AH_{A'}\mathrm{C}H_MH_{M'}\mathrm{C}H_XH_{X'}$), 3.32 (br s, 1 H; N$H$), 3.36 (s, 3 H; $\mathrm{OC}H_3$), 6.63 (δ_A), 6.88 (δ_M), and 7.32 (δ_X) (AA′MXX′ system, $^3J_{AX}$ = $^3J_{A'X'}$ = 8.2 Hz, $^3J_{MX}$ = $^3J_{MX'}$ = 7.3 Hz, $^4J_{AA'}$ = 1.7 Hz, $^4J_{AM}$ = $^4J_{A'M}$ = 1.1 Hz, $^5J_{AX'}$ = $^5J_{A'X}$ = 0.5 Hz, 5 H; H-2$_A$/H-6$_{A'}$, H-3$_X$/H-5$_{X'}$ and H-4$_M$, C_6H_5). ^{13}C NMR (75.5 MHz, C_6D_6): δ −2.6 ($SiCH_3$), 13.6 ($SiCH_2$), 23.4 ($SiCH_2CH_2$), 46.9 (CH_2N), 50.0 (OCH_3), 113.0 (C-2/C-6, C_6H_5), 117.3 (C-4, C_6H_5), 129.5 (C-3/C-5, C_6H_5), 148.9 (C-1, C_6H_5). ^{29}Si NMR (59.6 MHz, C_6D_6): δ 18.0. Anal. Calcd for $C_{12}H_{21}NOSi$ (223.39): C, 64.52; H, 9.48; N, 6.27. Found: C, 64.59; H, 9.51; N, 6.26.

*[(Dimethylamino)methyl]ethoxydimethylsilane (**10a**).* A mixture of **24** (45.1 g, 295 mmol) and dimethylamine (66.6 g, 1.48 mol) was heated in an autoclave at 100 °C for 16 h. The reaction mixture was allowed to cool to 20 °C within 30 min, *n*-pentane (600 mL) was added, and the resulting precipitate was filtered off, washed with *n*-pentane (3 × 100 mL), and discarded. The solvent of the filtrate (including the wash solutions) was removed by distillation at ambient pressure, and the residue was purified by distillation at ambient pressure to furnish **10a** as a colorless liquid (37.5 g, 232 mmol; 79% yield). Bp: 137 °C. ^{1}H NMR (300.1 MHz, C_6D_6): δ 0.29 (s, 6 H; $\mathrm{SiC}H_3$), 1.24 (t, $^3J_{HH}$ = 7.0 Hz, 3 H; $\mathrm{CH_2C}H_3$), 1.96 (s, 2 H; $\mathrm{SiC}H_2$), 2.33 (s, 6 H; $\mathrm{NC}H_3$), 3.68 (q, $^3J_{HH}$ = 7.0 Hz, 2 H; $\mathrm{OC}H_2$). ^{13}C NMR (75.5 MHz, C_6D_6): δ −2.0 ($SiCH_3$), 18.7 (CH_2CH_3), 49.8 (NCH_3), 51.4 ($SiCH_2$), 58.3 (OCH_2). ^{29}Si NMR (59.6 MHz, C_6D_6): δ 12.2. Anal. Calcd for $C_7H_{19}NOSi$ (161.32): C, 52.12; H, 11.87; N, 8.68. Found: C, 52.01; H, 11.98; N, 9.00.

*[3-(Dimethylamino)prop-1-yl]ethoxydimethylsilane (**10b**).* A mixture of **25** (19.9 g, 110 mmol) and 41.5 g (920 mmol) of dimethylamine was heated in an autoclave at 120 °C for 17 h. The reaction mixture was allowed to cool to 20 °C within 30 min, *n*-pentane (400 mL) was added, and the resulting precipitate was filtered off, washed with *n*-pentane (3 × 50 mL), and discarded. The solvent of the filtrate (including the wash solutions) was removed by distillation at ambient pressure, and the residue was purified by distillation *in vacuo* to furnish **10b** as a colorless liquid (13.1 g, 69.2 mmol; 63% yield). Bp: 65 °C/5 mbar. ^{1}H NMR (500.1 MHz, C_6D_6): δ 0.23 (s, 6 H; $\mathrm{SiC}H_3$), 0.77 (δ_A), 1.69 (δ_M), and 2.33 (δ_X) (AA′MM′XX′ system, $^2J_{AA'}$ = 14.8 Hz, $^3J_{AM}$ = 11.6 Hz, $^3J_{AM'}$ = 5.1 Hz, $^2J_{MM'}$ = 13.5 Hz, $^3J_{MX}$ = 8.5 Hz, $^3J_{MX'}$ = 5.9 Hz, $^2J_{XX'}$ = 11.7 Hz, 6 H; $\mathrm{SiC}H_AH_{A'}\mathrm{C}H_MH_{M'}\mathrm{C}H_XH_{X'}$), 1.24 (t, $^3J_{HH}$ = 7.0 Hz, 3 H; $\mathrm{CH_2C}H_3$), 2.25 (s, 6 H; $\mathrm{NC}H_3$), 3.66 (q, $^3J_{HH}$ = 7.0 Hz, 2 H; $\mathrm{OC}H_2$). ^{13}C NMR (125.8 MHz, C_6D_6): δ −1.9 ($SiCH_3$), 14.2 ($SiCH_2$), 18.8 (CH_2CH_3), 21.9 ($SiCH_2CH_2$), 45.6 (NCH_3), 58.2 (OCH_2), 63.2 (CH_2N). ^{29}Si NMR (99.4 MHz, C_6D_6): δ 15.7. Anal. Calcd for $C_9H_{23}NOSi$ (189.37): C, 57.08; H, 12.24; N, 7.40. Found: C, 56.75; H, 12.29; N, 7.75.

*Ethoxy{[(methoxycarbonyl)methylamino]methyl}dimethylsilane (**11a**).* A stirred mixture of **6a** (20.0 g, 113 mmol), ethanol (15.6 g, 339 mmol), and orthophosphoric acid (166 mg, 1.69 mmol) was heated under reflux for 1 h, and the resulting ethanol/methanol mixture was removed by distillation at ambient pressure. Ethanol (7.80 g, 169 mmol) was added to the residue, and the reaction mixture was heated under reflux for 30 min. The resulting ethanol/methanol mixture was removed by distillation at ambient pressure, and the residue was purified by distillation *in vacuo* to furnish **11a** as a colorless liquid (13.3 g, 69.5 mmol; 62% yield). Bp: 110 °C/12 mbar. ^{1}H NMR (300.1 MHz, C_6D_6): δ 0.14 (s, 6 H; $\mathrm{SiC}H_3$), 1.13 (t, $^3J_{HH}$ = 7.0 Hz, 3 H; $\mathrm{CH_2C}H_3$), 2.81 (d, $^3J_{HH}$ = 5.2 Hz, 2 H; $\mathrm{SiC}H_2$), 3.54 (q, $^3J_{HH}$ = 7.0 Hz, 2 H; $\mathrm{OC}H_2$), 3.61 (s, 3 H; $\mathrm{OC}H_3$), 4.69 (br s, 1 H; NH). ^{13}C NMR (75.5 MHz, C_6D_6): δ −3.0 ($SiCH_3$), 18.6 (CH_2CH_3), 30.7 ($SiCH_2$), 51.8 ($C(O)OCH_3$), 58.5 (OCH_2), 157.9 ($C(O)OCH_3$). ^{29}Si NMR (59.6 MHz, C_6D_6): δ 12.2. Anal. Calcd for $C_7H_{17}NO_3Si$ (191.30): C, 43.95; H, 8.96; N, 7.32. Found: C, 44.03; H, 9.03; N, 7.50.

*[(Ethoxydimethylsilyl)methyl]trimethylammonium Iodide (**12a**).* Freshly distilled iodomethane (15.5 g, 109 mmol) was added dropwise at 20 °C within 30 min under exclusion of light to a stirred solution of **10a** (4.41 g, 27.3 mmol) in acetonitrile (60 mL). The reaction mixture was heated under reflux for 4 h, cooled to 20 °C within 30 min, and then stirred at this temperature for 18 h. The solvent and the excess iodomethane were removed under reduced pressure, the residue was washed with *n*-pentane (4 × 15 mL), and the wash solutions were discarded. Acetonitrile (17 mL) was added to the residue, and the resulting suspension was heated under reflux until a clear solution was obtained, which was kept undisturbed at 20 °C for 3 h and then at −20 °C for a further 17 h. The product was isolated by filtration at −20 °C, washed with *n*-pentane (3 × 5 mL), and dried *in vacuo* (0.01 mbar, 40 °C, 4 h) to give **12a** as a colorless solid (6.70 g, 22.1 mmol; 81% yield). ^{1}H NMR (300.1 MHz, [D$_6$]DMSO): δ 0.27 (s, 6 H; $\mathrm{SiC}H_3$), 1.13 (t, $^3J_{HH}$ = 7.0 Hz, 3 H; $\mathrm{CH_2C}H_3$), 3.18 (s, 9 H; $\mathrm{NC}H_3$), 3.20 (s, 2 H; $\mathrm{SiC}H_2$), 3.71 (q, $^3J_{HH}$ = 7.0 Hz, 2 H; $\mathrm{OC}H_2$). ^{13}C NMR (75.5 MHz, [D$_6$]DMSO): δ −1.1 ($SiCH_3$), 18.1 (CH_2CH_3), 56.1 (t, $^1J_{NC}$ = 3.4 Hz; NCH_3), 58.1 (t, $^1J_{NC}$ = 1.9 Hz; $SiCH_2$), 58.4 (OCH_2). ^{29}Si NMR (59.6 MHz, [D$_6$]DMSO): δ 9.6. Anal. Calcd for $C_8H_{22}INOSi$ (303.26): C, 31.69; H, 7.31; N, 4.62. Found: C, 31.42; H, 7.28; N, 4.81.

*Methoxydimethyl(n-propoxymethyl)silane (**13a**).* A solution of ethylmethylamine (12.8 g, 217 mmol) in THF (30 mL) was added dropwise at 0 °C within 2 h to a stirred solution of **17** (45.0 g, 217 mmol) and ethyldimethylamine (17.4 g, 238 mmol) in THF (200 mL). After the mixture had been stirred at 0 °C for 2 h and at 20 °C for 2 h, a 3.0 M solution of methylmagnesium bromide in diethyl ether (181 mL, 543 mmol of MeMgBr) was added dropwise at 0 °C within 1 h. The reaction mixture was stirred at 20 °C for 16 h and was then concentrated to a volume of ca. 70 mL by distillation at ambient pressure, *n*-pentane (300 mL) was added, and the mixture was stirred at 20 °C for 30 min. The resulting solid was filtered off, washed with *n*-pentane (3 × 30 mL), and discarded. The solvent of the filtrate (including the wash solutions) was removed by distillation at ambient pressure, and the residue was distilled *in vacuo* to give three fractions (**23**, 5.87 g, bp 38−46 °C/9 mbar; **21**, 5.60 g, bp 63−72 °C/9 mbar; **22**, 9.07 g, bp 90−97 °C/9 mbar (discarded)).

Transformation A: A 1.25 M solution of hydrogen chloride in methanol (2.37 mL, 2.96 mmol of HCl, 29.6 mmol of methanol) was added dropwise at 20 °C within 15 min to a stirred solution of **21** (5.60 g, 29.6 mmol) in *n*-pentane (40 mL), and the mixture was stirred at 20 °C for 30 min. The resulting solid was filtered off, washed with *n*-pentane (3 × 5 mL), and discarded. The solvent of the filtrate (including the wash solutions) was removed by distillation at ambient pressure, and the residue was distilled *in vacuo* to give 5.37 g of **13a** as crude distillate (bp 108−115 °C/300 mbar).

Transformation B: Methanol (1.69 g, 52.7 mmol) was added dropwise to a stirred solution of **23** (5.87 g, 35.2 mmol) and ethyldimethylamine (2.58 g, 35.3 mmol) in *n*-pentane (40 mL) at 20 °C within 15 min, and the mixture was stirred at 20 °C for 30 min. The resulting solid was filtered off, washed with *n*-pentane (3 × 5 mL), and discarded. The solvent of the filtrate (including the wash solutions) was removed by distillation at ambient pressure, and the residue was distilled *in vacuo* to give 4.61 g of **13a** as crude distillate (bp 93−102 °C/200 mbar).

The product fractions obtained after the transformations A and B were combined and finally purified by distillation *in vacuo* to furnish **13a** as a colorless liquid (9.48 g, 58.4 mmol; 27% yield). Bp: 95 °C/200 mbar. ^{1}H NMR (300.1 MHz, C_6D_6): δ 0.30 (s, 6 H; SiCH_3), 1.00 (δ_A), 1.64 (δ_M), and 3.37 (δ_X) ($A_3M_2X_2$ system, $^3J_{AM}$ = 7.5 Hz, $^3J_{MX}$ = 6.5 Hz, 7 H; $OC(H_X)_2C(H_M)_2C(H_A)_3$), 3.21 (s, 2 H; Si$CH_2$), 3.50 (s, 3 H; O$CH_3$). ^{13}C NMR (125.8 MHz, C_6D_6): δ −3.6 ($SiCH_3$), 10.8 ($OCH_2CH_2CH_3$), 23.3 (OCH_2CH_2), 50.5 (OCH_3), 63.7 ($SiCH_2O$), 77.4 (OCH_2CH_2). ^{29}Si NMR (99.4 MHz, C_6D_6): δ 12.3. Anal. Calcd for $C_7H_{18}O_2Si$ (162.30): C, 51.80; H, 11.18. Found: C, 51.87; H, 11.30.

Methoxydimethyl(n-pentyl)silane (13b). A 2.0 M solution of *n*-pentylmagnesium bromide in diethyl ether (41.6 mL, 83.2 mmol of *n*-pentylMgBr) was added dropwise at 0 °C within 45 min to a stirred solution of **14** (10.0 g, 83.2 mmol) in diethyl ether (250 mL). After the mixture had been stirred at 20 °C for 17 h, the solvent was removed by distillation at ambient pressure. Subsequently, *n*-pentane (300 mL) was added, the mixture was stirred at 20 °C for 30 min, and the solid was filtered off, washed with *n*-pentane (3 × 25 mL), and discarded. The solvent of the filtrate (including the wash solutions) was removed by distillation at ambient pressure, and the residue was purified by distillation *in vacuo* to furnish **13b** as a colorless liquid (9.57 g, 59.7 mmol; 72% yield). Bp: 41 °C/5 mbar. ^{1}H NMR (500.1 MHz, C_6D_6): δ 0.18 (s, 6 H; SiCH_3), 0.68 (m, 2 H; SiCH_2), 1.00 (m, 3 H; $Si(CH_2)_4CH_3$), 1.40 (m, 4 H; $CH_2CH_2CH_3$), 1.46 (m, 2 H; $SiCH_2CH_2$), 3.40 (s, 3 H; OCH_3). ^{13}C NMR (125.8 MHz, C_6D_6): δ −2.5 ($SiCH_3$), 14.2 (CH_2CH_3), 16.3 ($SiCH_2$), 22.8 (CH_2CH_3), 23.3 ($SiCH_2CH_2$), 36.1 ($SiCH_2CH_2CH_2$), 49.9 (OCH_3). ^{29}Si NMR (59.6 MHz, C_6D_6): δ 18.0. Anal. Calcd for $C_8H_{20}OSi$ (160.33): C, 59.93; H, 12.57. Found: C, 59.78; H, 12.66.

Dimethoxydimethylsilane (14). This compound was commercially available and was purified by distillation prior to use.

Trichlorosilane (15). This compound was commercially available and was purified by distillation prior to use.

Trichloro(methoxymethyl)silane (16). This compound was synthesized according to ref 8b.

Trichloro(n-propoxymethyl)silane (17). A mixture of trichlorosilane (119 g, 879 mmol) and chloromethyl *n*-propyl ether[33,34] (85.8 g, 790 mmol) was added dropwise at 20 °C within 1 h to a mixture of triethylamine (80.0 g, 791 mmol) and copper(I) chloride (3.80 g, 38.4 mmol) in diethyl ether (450 mL). The reaction mixture was heated under reflux for 2 h and then cooled to 20 °C, and the resulting precipitate was filtered off, washed with diethyl ether (3 × 40 mL), and discarded. The solvent of the filtrate (including the wash solutions) was removed by distillation, and the residue was purified by distillation at ambient pressure to furnish **17** as a colorless liquid (49.0 g, 236 mmol; 30% yield). Bp: 148 °C. ^{1}H NMR (300.1 MHz, C_6D_6): δ 0.87 (δ_A), 1.45 (δ_M), and 3.13 (δ_X) ($A_3M_2X_2$ system, $^3J_{AM}$ = 7.5 Hz, $^3J_{MX}$ = 6.5 Hz, 7 H; $OC(H_X)_2C(H_M)_2C(H_A)_3$), 3.20 (s, 2 H; Si$CH_2$). ^{13}C NMR (75.5 MHz, C_6D_6): δ 10.4 ($OCH_2CH_2CH_3$), 22.7 (OCH_2CH_2), 65.2 ($SiCH_2$), 76.6 (OCH_2). ^{29}Si NMR (59.6 MHz, C_6D_6): δ 3.7. Anal. Calcd for $C_4H_9Cl_3OSi$ (207.56): C, 23.15; H, 4.37. Found: C, 23.31; H, 4.46.

(Chloromethyl)ethoxydimethylsilane (24). This compound was commercially available and was purified by distillation prior to use.

(3-Chloroprop-1-yl)ethoxydimethylsilane (25). This compound was commercially available and was purified by distillation prior to use.

1-Methoxycarbonyl-2,2-dimethyl-2-silapyrrolidine (26). Compound **26** was obtained as an impurity during the distillation of **6b**. ^{1}H NMR (500.1 MHz, C_6D_6): δ 0.25 (s, 6 H; SiCH_3), 0.58 (t, $^3J_{HH}$ = 7.3 Hz, 2 H; SiCH_2), 1.58 (tt, $^3J_{HH}$ = 7.3 Hz, $^3J_{HH}$ = 6.4 Hz, 2 H; $SiCH_2CH_2$), 3.45 (t, $^3J_{HH}$ = 6.4 Hz, 2 H; NCH_2), 3.59 (s, 3 H; $C(O)OCH_3$). ^{13}C NMR (125.8 MHz, C_6D_6): δ −1.5 ($SiCH_3$), 12.4 ($SiCH_2$), 23.0 ($SiCH_2CH_2$), 47.4 (CH_2N), 51.8 ($C(O)OCH_3$), 157.8 ($C(O)OCH_3$). ^{29}Si NMR (99.4 MHz, C_6D_6): δ 17.3; HRMS (ESI), *m/z* calcd for $[C_7H_{15}NO_2Si+Na]^+$: 196.0764 [M + Na^+]. Found: 196.0763.

Methoxy[(methylamino)methyl]dimethylsilane (27). A mixture of **2a** (19.0 g, 137 mmol) and methylamine (38.3 g, 1.23 mol) was heated in an autoclave at 100 °C for 16 h. The reaction mixture was allowed to cool to 20 °C within 30 min, diethyl ether (300 mL) was added, and the resulting precipitate was filtered off, washed with diethyl ether (3 × 30 mL), and discarded. The solvent of the filtrate (including the wash solutions) was removed by distillation at ambient pressure, and the residue was purified by distillation at ambient pressure to furnish **27** as a colorless liquid (11.8 g, 88.5 mmol; 65% yield). Bp: 127 °C. ^{1}H NMR (500.1 MHz, C_6D_6): δ 0.22 (s, 6 H; SiCH_3), 0.55 (br s, 1 H; NH), 2.14 (s, 2 H; SiCH_2), 2.46 (s, 3 H; NCH_3), 3.42 (s, 3 H; OCH_3). ^{13}C NMR (125.8 MHz, C_6D_6): δ −3.3 ($SiCH_3$), 41.3 (NCH_3), 42.3 ($SiCH_2$), 50.2 (OCH_3). ^{29}Si NMR (59.6 MHz, C_6D_6): δ 14.5. Anal. Calcd for $C_5H_{15}NOSi$ (133.27): C, 45.06; H, 11.35; N, 10.51. Found: C, 44.97; H, 11.47; N, 10.44.

Kinetic Studies. All ^{1}H NMR spectra for the kinetic studies were recorded at 23 °C using a Bruker DRX-300 NMR spectrometer (^{1}H, 300.1 MHz). The respective CD_3CN/D_2O mixture (1.0 mL) was added to **2a** (41.6 mg, 300 μmol) in a 5 mm screw-cap NMR tube (Wilmad). After tuning and matching the probe to this CD_3CN/D_2O mixture, the spectrometer was also shimmed with this standard sample. Subsequently, the NMR tube was replaced by a freshly prepared sample for a co-hydrolysis reaction, and the ^{1}H NMR measurement of the locked sample was started using an aquisition time of 10.0 s and a sweep width of 3004.8 Hz. At least four scans (in the case of slow hydrolysis reactions eight scans) per spectrum were recorded with a 30° pulse width and a delay D1 of 30 s. The starting points of acquisition were extracted automatically from the audit files and were used as the value on the time axis. For the preparation of the samples for the hydrolysis reactions, a mixture of two or three different silanes (500 mmol each; for the respective compositions, see Figures S1−S60) was added under a dry argon atmosphere to a Schlenk flask (25 mL). The CD_3CN/D_2O mixture including acid or base (5.0 mL; for the respective compositions, see Figures S1−S60) was added to the reaction vessel in a single portion, and the resulting solution was stirred for 20 s. Subsequently, 1.0 mL of the reaction mixture were removed with a syringe and then transferred into a clean screw-cap NMR tube. Further samples (0.5 mL each) were removed at regular intervals and were used for the measurement of the pD values. For the measurement of the pD values, a combination of a Mettler Toledo MP 220 pH meter and a Mettler Toledo InLab Science Pro was used. The glass electrode was conditioned for 7 days in D_2O prior to use. The pH meter was standardized with conventional buffer mixtures with a pD close to the range of the pD measurements.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Plots of $-\ln\{[\text{silane}(t)]/[\text{silane}(t=0)]\}$ vs t for the hydrolyses of compounds **1a−9a**, **1b−6b**, **10b**, **11a−13a**, and **13b** (Figures S1−S60), ^{1}H, ^{13}C, and ^{29}Si NMR spectra of compound **26** (Figures S61−63), and Cartesian coordinates of all stationary points occurring along the reaction coordinate of the model reactions of compounds **1a−6a**, **1b**, **3b**, **4b**, **9a**, **13a**, and **13b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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