ChemPubSoc Europe
DOI: 10.1002/chem.201303215
CHEMISTRY
A European Journal
Full Paper

Nucleophilicity

Electrophilic Alkylations of Vinylsilanes: A Comparison of α- and β-Silyl Effects

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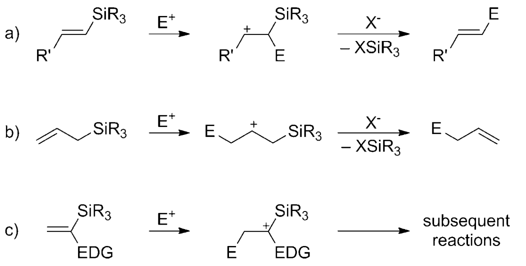
Dedicated to Professor Heinz Langhals on the occasion of his 65th birthday

Abstract: Kinetics of the reactions of benzhydrylium ions ($Aryl_2CH^+$) with the vinylsilanes $H_2C{=}C(CH_3)(SiR_3)$, $H_2C{=}C(Ph)(SiR_3)$, and (*E*)-$PhCH{=}CHSiMe_3$ have been measured photometrically in dichloromethane solution at 20 °C. All reactions follow second-order kinetics, and the second-order rate constants correlate linearly with the electrophilicity parameters *E* of the benzhydrylium ions, thus allowing us to include vinylsilanes in the benzhydrylium-based nucleophilicity scale. The vinylsilane $H_2C{=}C(CH_3)(SiMe_3)$, which is attacked by electrophiles at the CH_2 group, reacts one order of magnitude faster than propene, indicating that α-silyl-stabilization of the intermediate carbenium ion is significantly weaker than α-methyl stabilization because $H_2C{=}C(CH_3)_2$ is 10^3 times more reactive than propene. *trans*-β-(Trimethylsilyl)styrene, which is attacked by electrophiles at the silylated position, is even somewhat less reactive than styrene, showing that the hyperconjugative stabilization of the developing carbocation by the β-silyl effect is not yet effective in the transition state. As a result, replacement of vinylic hydrogen atoms by $SiMe_3$ groups affect the nucleophilic reactivities of the corresponding C=C bonds only slightly, and vinylsilanes are significantly less nucleophilic than structurally related allylsilanes.

Introduction

Vinylsilanes represent important reagents in organic synthesis and commonly undergo electrophilic substitution reactions with replacement of the silyl group.[1] It has been shown that they can be combined with a large variety of electrophiles, including carbonyl compounds, Michael acceptors, acyl derivatives, halogens, and stabilized carbocations.[1] Reactions involving reagents of low electrophilicity, like carbonyl compounds, commonly need activation of either the electrophile by Lewis acids or the vinylsilanes by nucleophiles, for example, fluoride ions. The vinylsilane functionality has also been utilized as an internal nucleophile for trapping intermediate carbocations.[2] Carbenes and peracids have been applied for the vinylsilane-based synthesis of silylated cyclopropanes[3] and epoxysilanes,[1c,i,4] respectively.

Electrophilic attack at vinylsilanes commonly occurs at the olefinic carbon atom α to the silicon moiety, eventually leading to the direct displacement of the silyl group (*ipso* substitution, Scheme 1 a). Electrophilic substitutions of allylsilanes usually follow an S_E2' mechanism, where the electrophilic attack occurs in the position γ to the silyl substituent, giving the product with allyl rearrangement (Scheme 1 b).[1i]



Scheme 1. Electrophilic substitution of vinyl- (a + c) and allylsilanes (b); E = electrophile, EDG = electron-donating group.

Although the reactions in Scheme 1 a,b proceed via intermediates with a carbocationic center in the position β to the silyl group, allylsilanes are known to react under milder conditions and with weaker electrophiles than the corresponding vinylsilanes,[1i] indicating that allylsilanes are more nucleophilic than vinylsilanes. The lower efficiency of the organosilicon moiety to enhance the nucleophilic reactivity of vinylsilanes can also be deduced from the fact that the introduction of electron-donating substituents, for example, alkoxy, alkyl, or aryl groups, in the position α to the silyl group of vinylsilanes directs the electrophilic attack to the β-position of the vinylsilanes, thus giving rise to the formation of α-silyl stabilized carbocations (Scheme 1c).[5]

Soderquist and Hassner[6] studied the rates of formation of such α-silyl stabilized carbocations through the deuterolyses of α-silylated methyl vinyl ethers. We now report on the magnitude of α- and β-silyl effects on the electrophilic alkylations of vinylsilanes by studying the kinetics of the reactions of the

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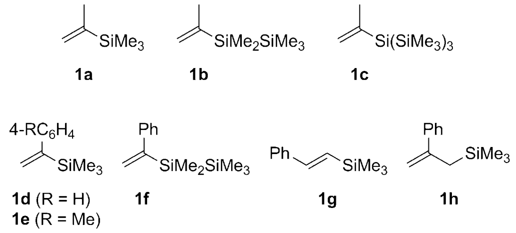
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201303215.



Scheme 2. Organosilanes studied for the quantification of the α- and β-silyl effects in vinylsilanes.

propene- (**1 a**–**c**) and styrene-derived organosilanes (**1 d**–**h**, Scheme 2) with carbenium ions.

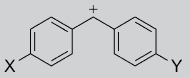
By utilizing the benzhydrylium method[7] for the quantification of the nucleophilic reactivities of **1 a**–**h**, it will be possible to compare their nucleophilicities with those of previously investigated compounds, including allylsilanes,[7a,f,8] silyl enol ethers,[7a,8b,9] and ordinary alkenes.[7a,b,f,g] All of these compounds are part of a comprehensive nucleophilicity scale, which has been derived by the method of overlapping correlation lines by using benzhydrylium ions with variable *para* and *meta* substituents as reference electrophiles.[7a] The correlations are based on Equation 1, where electrophiles are characterized by the electrophilicity parameter *E* and nucleophiles by the solvent-dependent parameters s_N (sensitivity) and *N* (nucleophilicity).

$$\lg k(20\,^\circ\mathrm{C}) = s_\mathrm{N}(N + E) \qquad (1)$$

Abstract in German: *Die Kinetik der Reaktionen von Benzhydrylium-Ionen (Aryl$_2$CH$^+$) mit den Vinylsilanen H$_2$C=C(CH$_3$)(SiR$_3$), H$_2$C=C(Ph)(SiR$_3$) und (E)-PhCH=CHSiMe$_3$ wurde in Dichlormethan bei 20°C photometrisch bestimmt. Alle Reaktionen verlaufen nach einer Kinetik 2. Ordnung, und die Geschwindigkeitskonstanten 2. Ordnung korrelieren linear mit der Elektrophilie E der Benzhydrylium-Ionen, wodurch es möglich wird, Vinylsilane in die auf Reaktivitäten gegenüber Benzhydrylium-Ionen aufgebaute Nucleophilieskala aufzunehmen. Das Vinylsilan H$_2$C=C(CH$_3$)(SiMe$_3$), das von Elektrophilen an der CH$_2$-Gruppe angegriffen wird, reagiert um eine Größenordnung schneller als Propen, was darauf hinweist, dass die Stabilisierung des intermediären Carbokations durch den α-Silyl-Effekt wesentlich schwächer ist als die Stabilisierung durch den α-Methyl-Effekt, da H$_2$C=C(CH$_3$)$_2$ 10^3 mal reaktiver ist als Propen.* trans*-β-(Trimethylsilyl)styrol, das von Elektrophilen an der silylierten Position angegriffen wird, ist sogar etwas weniger reaktiv als Styrol, was zeigt, dass die hyperkonjugative Stabilisierung des entstehenden carbokationischen Zentrums im Übergangszustand noch nicht wirksam ist. Somit beeinflusst der Austausch eines vinylischen Wasserstoffs durch eine SiMe$_3$-Gruppe die nucleophile Reaktivität der betrachteten C=C Doppelbindung nur marginal, und Vinylsilane sind beträchtlich weniger nucleophil als strukturell verwandte Allylsilane.*

For this study, benzhydrylium ions **2 a**–**j** with values of electrophilicity parameter *E* from −4.72 to +3.63 (Table 1) were used as reaction partners for organosilanes **1 a**–**h**.

Table 1. Reference electrophiles ArAr′CH$^+$ used for quantifying the nucleophilicities of **1 a**–**h**.



ArAr′CH$^+$[a]	X	Y	E[b]
(tol)$_2$CH$^+$ (**2 a**)	CH$_3$	CH$_3$	3.63
(Ph)(pop)CH$^+$ (**2 b**)	H	OPh	2.90
(tol)(pop)CH$^+$ (**2 c**)	CH$_3$	OPh	2.16
(Ph)(ani)CH$^+$ (**2 d**)	H	OMe	2.11
(tol)(ani)CH$^+$ (**2 e**)	CH$_3$	OMe	1.48
(ani)(pop)CH$^+$ (**2 f**)	OMe	OPh	0.61
(ani)$_2$CH$^+$ (**2 g**)	OMe	OMe	0.00
(pfa)$_2$CH$^+$ (**2 h**)	N(Ph)CH$_2$CF$_3$	N(Ph)CH$_2$CF$_3$	−3.14
(mfa)$_2$CH$^+$ (**2 i**)	N(Me)CH$_2$CF$_3$	N(Me)CH$_2$CF$_3$	−3.85
(dpa)$_2$CH$^+$ (**2 j**)	NPh$_2$	NPh$_2$	−4.72

[a] tol = *p-tol*yl; pop = *p*-*p*henoxyphenyl; ani = *p-ani*syl; pfa = 4-(*p*henyl(tri*f*luoroethyl)*a*mino)phenyl; mfa = 4-(*m*ethyl(tri*f*luoroethyl)*a*mino)phenyl; dpa = 4-(*d*i*p*henyl*a*mino)phenyl. [b] Empirical electrophilicities *E* from ref. [7a].

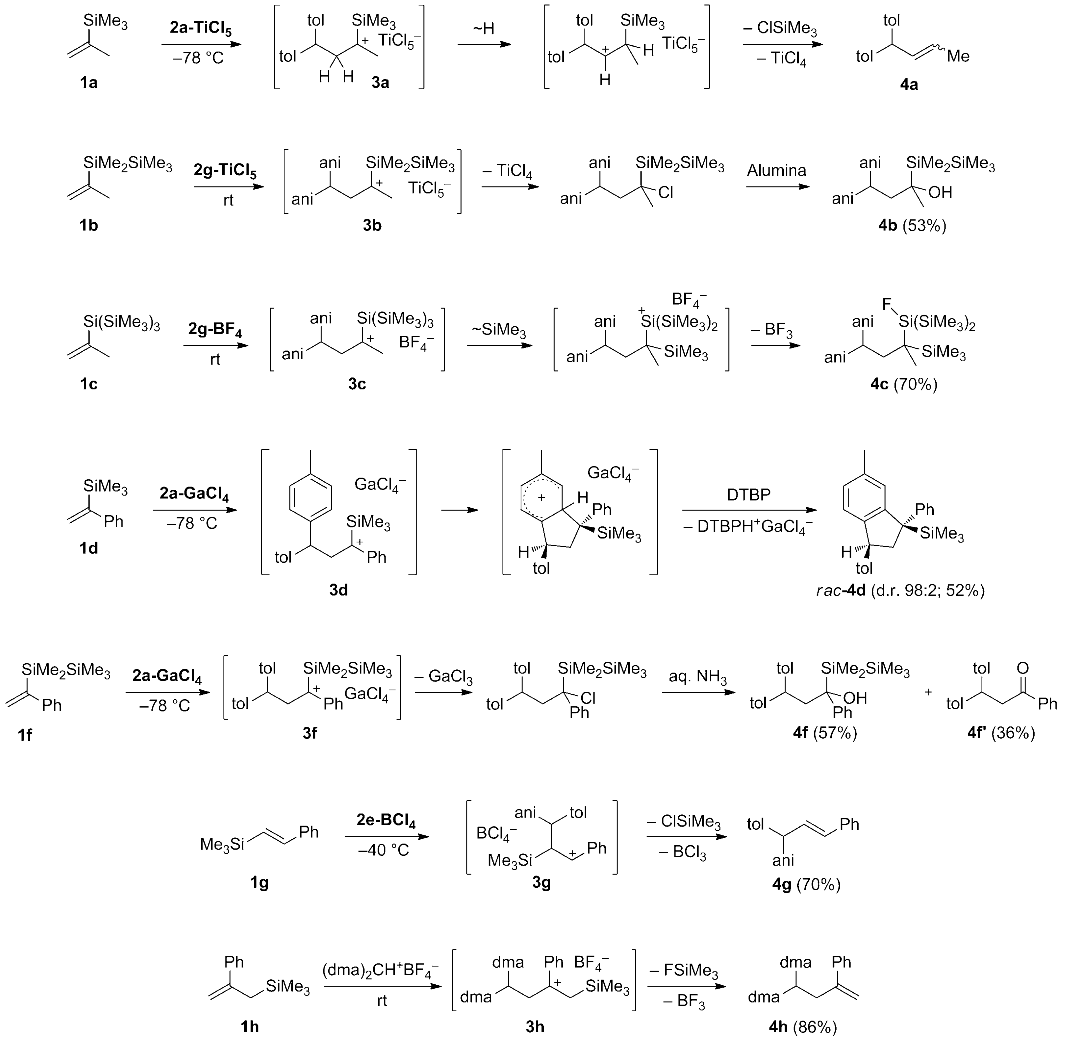
Results and Discussion

Product analysis

For the attack of electrophiles at vinylsilanes, two sites of attack are conceivable—in position α or β to silicon (Scheme 1 a,c). As shown in Scheme 3, vinylsilanes **1 a**–**f** with a terminal double bond are attacked at the β-position with formation of the α-silyl stabilized carbocations, which undergo different subsequent reactions.

While the formation of **4 a** can be explained by a 1,2-hydride shift in **3 a**, followed by a chloride-induced desilylation,[10a] carbocations **3 b** and **3 f** are probably intercepted by chloride ions to give α-chlorosilanes, which hydrolyze with formation of the alcohols **4 b** and **4 f** during workup. The formation of **4 f′** as a side product is probably due to the oxidation of **4 f** by atmospheric oxygen; an analogous conversion of α-silyl substituted benzyl alcohols by *t*BuONO into arylalkylketones has previously been reported.[11] 1,2-Silyl migration in **3 c** followed by fluoride trapping of the resulting silylium ion can explain the formation of the fluorosilane **4 c**. In analogy to previously reported reactions of benzhydrylium ions with ordinary alkenes,[12] the α-silyl substituted carbocation **3 d** cyclizes with formation of the indane **4 d** with high diastereoselectivity (d.r. 98:2, main diastereoisomer shown in Scheme 3).

In contrast to the vinylsilanes with terminal double bonds, *trans*-β-(trimethylsilyl)styrene **1 g** was attacked at the silyl-substituted vinylic carbon yielding the phenyl-stabilized carbocation **3 g**, which gives **4 g** by desilylation.[10b] For comparison, also the allylsilane **1 h** was investigated and found to give the common S$_E$2′ substitution product **4 h**.



Scheme 3. Reactions of silyl substituted propenes (**1a–c**) and styrenes **1d,f–h** with benzhydrylium salts (DTBP = 2,6-di-*tert*-butylpyridine; dma = 4-(dimethylamino)phenyl).

Kinetic measurements

Since the benzhydrylium ions **2a–j** possess absorption maxima in the visible spectrum, while the products arising from the nucleophilic attack are colorless, we were able to study the kinetics of these bimolecular reactions in CH_2Cl_2 spectrophotometrically. First-order conditions were obtained by employing at least 9 equivalents of the unsaturated organosilanes **1a–h** with respect to the benzhydrylium ions **2a–j**. From the resulting mono-exponential decays of the absorbances of the benzhydrylium ions, the corresponding first-order rate constants k_{obs} were derived.

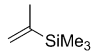
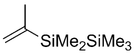
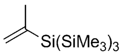
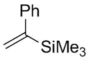
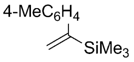
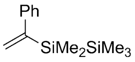
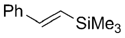
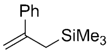
The second-order rate constants k_2 given in Table 2 and Table 3 were derived as the slopes of the linear correlations of the k_{obs} values against the corresponding nucleophile concentrations $[Nu]_0$ (Figure 1).

The reactions with the highly reactive benzhydrylium ions **2a,b** and the reaction of **1e** with **2d-GaCl$_4$** were studied in the temperature range between −70 °C and −20 °C. In these cases, the second-order rate constants k_2 were calculated by dividing the corresponding first-order rate constants k_{obs} by the corresponding mean nucleophile concentrations $[Nu]_{av} = [Nu]_0 - 0.5[\mathbf{2\text{-}MX}_{n+1}]_0$. Figure 2 shows exemplarily the linear Eyring plot for the reaction of **1d** with **2b-GaCl$_4$** between −69 °C and −30 °C. From analogous correlations, the activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ and the second-order rate constants k_2 at 20 °C given in Table 2 were calculated.

Table 2 shows that most reactions studied at variable temperature possess activation entropies between −112 and −138 $J\,mol^{-1}\,K^{-1}$, similar to those previously reported for the reactions of benzhydrylium ions with terminal alkenes[12b,13] and allylsilanes.[8a,13b] It is not clear, why the reaction of **1e** with **2d** proceeds with significantly more negative activation entropy.

Table 3 shows that the second-order rate constants for the reactions of the organosilanes **1b**, **1f**, and **1g** with the benzhydrylium ions **2d**, **2e**, and **2g** are only slightly affected by the counterions. Therefore, the second-order rate constants given in Table 2 can be assigned to the formation of the initial C–C bond, while the subsequent reactions of the intermediates **3b**,

Table 2. Second-order rate constants k_2 for the reactions of organosilanes **1 a–h** with benzhydrylium ions **2** (counterion $GaCl_4^-$) in dichloromethane and the nucleophilicity parameters for **1 a–h** derived thereof.

Nucleophile (N, s_N)[a]	**2**	k_2 (20 °C) [$M^{-1}\,s^{-1}$]	$\Delta H^{\ddagger}$ [$kJ\,mol^{-1}$]	$\Delta S^{\ddagger}$ [$J\,mol^{-1}\,K^{-1}$]
 **1a** (-1.46, 1.05)	**2a**	223[b]	25.9	−112
	2b	30.6[b]	27.1	−124
	2c	4.28	–	–
	2d	4.89	–	–
	2e	1.30	–	–
 **1b** (-0.26, 0.95)	**2d**	53.7	–	–
	2e	15.2	–	–
	2g	0.557	–	–
 **1c** (-0.31, 0.99)	**2d**	63.6	–	–
	2e	13.6	–	–
	2g	0.507	–	–
 **1d** (-1.13, 1.46)	**2a**	4.10×10^{3}[b]	16.1	−121
	2b	403[b]	16.8	−138
	2d	28.7	–	–
	2e	3.75	–	–
	2f	0.153	–	–
 **1e** (-0.65, 1.59)	**2d**	177[b]	13.3	−156
	2e	28.3	–	–
	2f	0.777	–	–
 **1f** (0.61, 1.01)	**2e**	137	–	–
	2f	14.8	–	–
	2g	4.49	–	–
 **1g** (-0.43, 1.06)	**2b**	407[b]	18.1	−133
	2d	66.1	–	–
	2e	13.3	–	–
	2f	1.32	–	–
	2g	0.387	–	–
 **1h** (5.38, 0.89)	**2h**	102	–	–
	2i	22.1	–	–
	2j	3.94	–	–

[a] For determination, see next section. [b] Calculated by using the Eyring activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ which were determined between −70 °C and −20 °C, see the Supporting Information for details.

Table 3. Counterion effects on the second-order rate constants for the reactions of vinylsilanes **1** with benzhydrylium salts **2-MX_{n+1}** in dichloromethane.

MX_{n+1}	k_2 (20 °C) [$M^{-1}\,s^{-1}$]				
	1b+2d	**1f+2e**	**1g+2d**	**1g+2e**	**1g+2g**[a]
$GaCl_4^-$	53.7	137	66.1	13.3	0.387
$SnCl_5^-$	45.9	–	–	–	0.468
$FeCl_4^-$	57.2	141	–	–	0.402
BCl_4^-	–	–	73.4[b]	15.0[c]	–

[a] With triflate as counterion the kinetics do not follow a first-order rate law. [b,c] Calculated by using the following Eyring activation parameters (for determination see the Supporting Information): [b] $\Delta H^{\ddagger} = 23.2\,kJ\,mol^{-1}$ and $\Delta S^{\ddagger} = -130\,J\,mol^{-1}\,K^{-1}$; [c] $\Delta H^{\ddagger} = 26.7\,kJ\,mol^{-1}$ and $\Delta S^{\ddagger} = -131\,J\,mol^{-1}\,K^{-1}$.

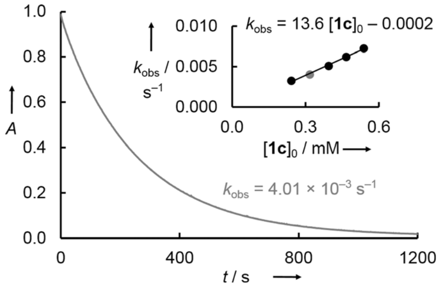


Figure 1. Exponential decay of the absorbance at 488 nm during the reaction of **1 c** ($c = 3.18\times10^{-4}$ M) with **2 e-GaCl$_4$** ($c = 2.43\times10^{-5}$ M) at 20 °C in CH_2Cl_2. Inset: $k_2 = 13.6\,M^{-1}\,s^{-1}$ is obtained as the slope of the linear correlation of the first-order rate constants k_{obs} against $[\mathbf{1c}]_0$.

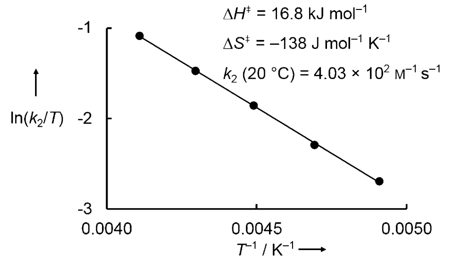


Figure 2. Eyring plot for the reaction of **1 d** with **2 b-GaCl$_4$** in CH_2Cl_2 between −69 °C and −30 °C.

3 f, and **3 g** with the halometallates MX_{n+1}^- have no or only little influence on the overall rate. As counterion independence of the rate constants has already been shown in previous studies of allylsilanes, we assume that the measured rate constants for the reactions of allylsilanes **1 h** with benzhydrylium ions also refer to the C–C bond-forming step.[8–9]

Linear free-energy relationships

Plots of $\lg k_2$ for the reactions of the benzhydrylium ions **2** with the propene derivatives **1 a–c** (Figure 3) and styrene derivatives **1 d–h** (Figure 4) against the electrophilicity parameters E

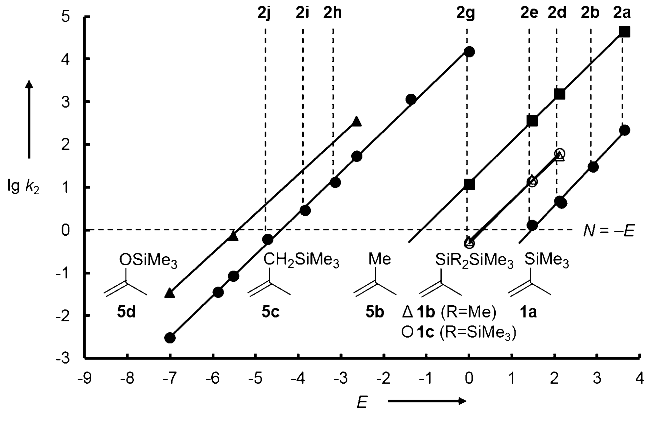


Figure 3. Plots of $\lg k_2$ for the reactions of the propene derivatives **1 a–c** and **5 b–d** (from ref. [7a]) with benzhydrylium ions in CH_2Cl_2 at 20 °C versus the electrophilicity parameters E of the benzhydrylium ions.

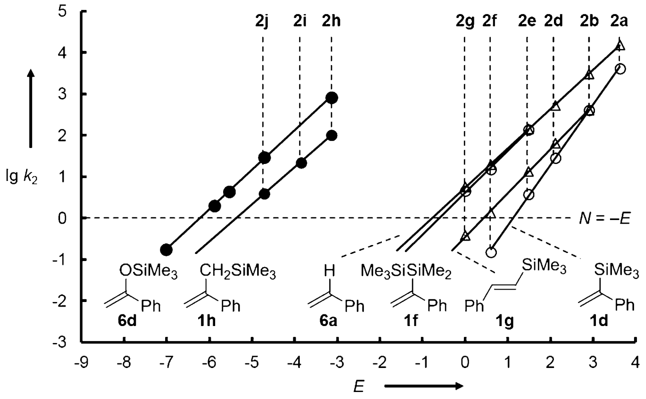


Figure 4. Plots of lg k_2 for the reactions of styrene derivatives **1 d**,**f**–**h** and **6 a**,**d** (from ref. [7a,b]) with benzhydrylium ions in CH_2Cl_2 at 20 °C versus the electrophilicity parameters E of the benzhydrylium ions.

of the reference electrophiles show linear correlations. Equation 1 allowed us to calculate the N and s_N parameters for the organosilanes **1 a**–**h**, which are given in Table 2.

These correlations do not only confirm the consistency of the rate constants determined in this work but also allow to extrapolate rate constants for reactions that cannot be directly measured. Such rate constants are needed for the structure-reactivity correlations in Table 4. Because the s_N parameters differ slightly for the various π-systems, the relative reactivities depend somewhat on the nature of the attacking electrophile. For that reason, small reactivity differences should only be discussed when systems with equal s_N are compared. In order to avoid ambiguity, the following discussion will focus on the reactivities toward the *p*-methoxy substituted benzhydrylium ion **2 d**, for which most directly measured rate constants are available.

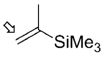
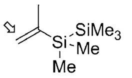
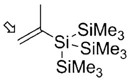
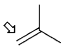
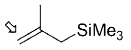
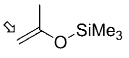
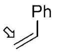
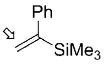
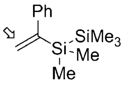
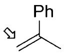
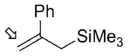
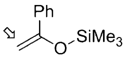
Table 4 shows that all vinylsilanes (**1 a**–**f**) investigated are significantly less nucleophilic than the allylsilanes **5 c** and **1 h** owing to the fact that the stabilization of the intermediate carbocation by a β-silyl substituent is much more effective than that by an α-silyl substituent. Comparison of propene (**5 a**) with **1 a** and of styrene (**6 a**) with **1 d** shows different silyl effects in both reaction series: while the trimethylsilyl group in α-position of the new carbenium center activates propene by a factor of 10 (**1 a**/**5 a**), it deactivates styrene by a factor of 18 (**1 d**/**6 a**). These opposing effects can be assigned to the perturbation of conjugation in α-substituted styrenes, in line with the observation that introduction of an α-methyl group activates propene by a factor of 3100 (**5 b**/**5 a**) and styrene by only 55 (**6 b**/**6 a**). Analogously, an α-CH_2SiMe_3 group activates propene by 3.5×10^6 (**5 c**/**5 a**) and styrene by only 8.7×10^3 (**1 h**/**6 a**); for the same reason, $OSiMe_3$ also activates propene 10^2 times more (**5 d**/**5 *a*** $= 1.4 \times 10^7$) than styrene (**6 d**/**6 a** $= 1.9 \times 10^5$).

Perturbation of π-conjugation in α-substituted styrenes also explains why $SiMe_2SiMe_3$ activates by a factor of 10^2 in the propene series (**1 b**/**5 a**), but has no effect in the styrene series (**1 f**/**6 a**). The perturbation of the conjugation between vinyl and phenyl group by $SiMe_3$, CH_3, CH_2SiMe_3, and $OSiMe_3$ in the α-position is also reflected by the UV spectra of the styrenes[14] listed in Table S1 of the Supporting Information.

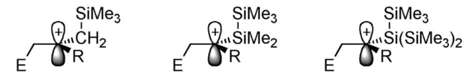
In the propene as in the styrene series, the $SiMe_2SiMe_3$ group activates one order of magnitude more than the $SiMe_3$ group (**1 b**/**1 a** and **1 f**/**1 d**), while the supersilyl group[15] ($Si(SiMe_3)_3$) activates by the same extent as $SiMe_2SiMe_3$ (**1 c**/**1 b**), because only one Si–Si σ-bond of the $Si(SiMe_3)_3$ group can be aligned coplanar with the empty p orbital of the developing carbenium center. The vinyl silanes **1 b**, **1 c**, and **1 f** may thus be considered as sila-allylsilanes as illustrated in Figure 5

While an allylic $SiMe_3$ group activates isobutylene by 3 orders of magnitude (**5 c**/**5 b**), the introduction of an analogously positioned $SiMe_3$ group in **1 a** accelerates only by one order of magnitude (**1 b**/**1 a**). Therefore, the hyperconjugative stabilization of a carbocation by a C–Si bond (Figure 5, left) is

Table 4. Comparison of absolute (in $M^{-1}s^{-1}$) and relative rate constants for the reactions of silyl substituted propenes (upper part) and styrenes (lower part) with the *p*-methoxy substituted benzhydrylium ion **2 d** in CH_2Cl_2 at 20 °C.

							
	5a	**1a**	**1b**	**1c**	**5b**	**5c**	**5d**
k_2 (**2d**)	0.51[a]	4.9	5.4×10^{1}	6.4×10^{1}	1.6×10^{3} [a]	1.8×10^{6} [b]	7.0×10^{6} [b]
k_{rel}	1	9.6	1.1×10^{2}	1.3×10^{2}	3.1×10^{3}	3.5×10^{6}	1.4×10^{7}
							
	6a	**1d**	**1f**		**6b**	**1h**	**6d**
k_2 (**2d**)	5.3×10^{2} [a]	2.9×10^{1}	5.6×10^{2} [c]		2.9×10^{4} [d]	4.6×10^{6} [c]	9.9×10^{7} [b]
k_{rel}	1	5.5×10^{-2}	1.1		5.5×10^{1}	8.7×10^{3}	1.9×10^{5}

[a] Taken from ref. [12b]. [b,c] Calculated by using Eq. 1, $E(\mathbf{2d}) = 2.11$ and the corresponding nucleophilicity parameters reported in: [b] ref. [7a]; [c] Table 2. [d] Calculated by using the Eyring equation, $k_2(-70\,^{\circ}C) = 1.45 \times 10^3\ M^{-1}s^{-1}$ reported in ref. [12b], and a value of $\Delta S^{\neq} = -110\ J\,mol^{-1}K^{-1}$ (estimated by taking activation parameters of structurally related compounds into account; ref. [7a,b]).



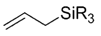
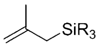
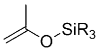
from **5c** and **1h** from **1b** and **1f** from **1c**

Figure 5. Comparison of β-silyl stabilization of the intermediate carbocations obtained by electrophilic attack at allylsilanes (left) and $SiMe_2SiMe_3$ (middle) as well as supersilyl (right) substituted vinylsilanes.

significantly larger than the hyperconjugative stabilization of a carbocation by a Si–Si bond (Figure 5, middle).

Nevertheless, replacement of the $SiMe_3$ group by the supersilyl group has an effect in the vinylsilane series, as **1c** is one order of magnitude more reactive than **1a**. In contrast, earlier work has shown that replacement of the $SiMe_3$ group by the supersilyl group $Si(SiMe_3)_3$ has almost no effect in allylsilanes and silylated enol ethers (Table 5) due to the fact that in these species the Si–Si bond is not in a suitable position for hyperconjugative interaction with the new carbenium center.[8b]

Table 5. Supersilyl effects in allylsilanes and silyl enol ethers (absolute and relative rate constants toward **2i** in CH_2Cl_2, 20 °C, from ref. [8b]).

Nucleophile	k_2 (R = $SiMe_3$) / M^{-1} s^{-1}	k_2 (R = Me) / M^{-1} s^{-1}	$\frac{k_2(Si(SiMe_3)_3)}{k_2(SiMe_3)}$
	84.9[a]	46.9[a]	1.81[a]
	3.54	2.97	1.19
	65.8	26.3[b]	2.50

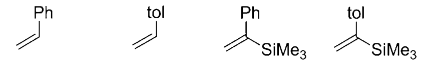
[a] Toward **2g**. [b] Calculated by using Eq. 1, N and s_N from ref. [7a] and $E(\mathbf{2i}) = -3.85$.

Soderquist and Hassner[6] reported that the silylated vinyl ether **7b** is deuterated only 1.8 times faster than the vinyl ether **7a**, while we found an activation by a factor of 9.6 when comparing the electrophilic alkylations of the analogous propene derivatives **1a** and **5a** with the benzhydrylium ion **2d** (Scheme 4). The diminished α-silyl effect observed for the vinyl ether **7b** may not only be due to the different electrophile considered but could also result from the smaller electron demand of the alkoxy-substituted carbenium ion, which is generated from vinyl ethers in the rate-determining step.

In contrast, Scheme 5 shows that the introduction of a 4-methyl substituent activates styrene for the reaction with benzhydrylium ion **2e** by a factor of 17 (**8**/**6a**), while a 4-methyl group activates the less reactive α-(trimethylsilyl)styrene by only 7.4 (**1e**/**1d**). This reduction of the electron-releasing effect of the 4-methyl substituent can again be rationalized by the perturbation of conjugation in α-substituted styrenes.

	7a	**7b**		**5a**	**1a**
k_{rel} (D^+)	1	1.8	k_{rel} (**2d**)	1	9.6

Scheme 4. Comparison of the relative rates for the deuterolyses of vinyl ethers **7a,b**[6] with the relative rates for the alkylation of the propene derivatives **5a** and **1a** with the benzhydrylium ion **2d**.



	6a	**8**	**1d**	**1e**
k_2 (**2e**)	1.5 × 10^2	2.6 × 10^3	3.8	28
k_{rel}	1	17	1	7.4

Scheme 5. Comparison of absolute (in $M^{-1}s^{-1}$) and relative rate constants for the reactions of 4-methyl substituted styrenes with the benzhydrylium ion **2e** in CH_2Cl_2 at 20 °C (tol = *p*-tolyl).[7a]

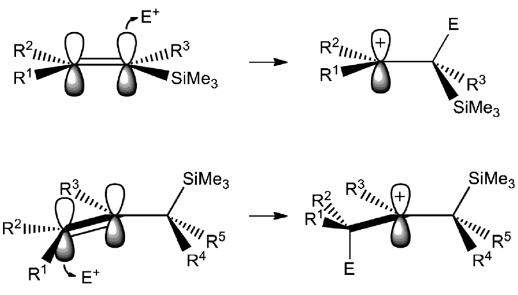
Vinylsilanes without electron-donating substituents at C_α or with electron donors at C_β are usually attacked at C_α by electrophiles to give β-silyl stabilized carbenium ions. Despite this stabilization, **1g** reacts almost one order of magnitude more slowly with the benzhydrylium ion **2d** than styrene (Scheme 6). This retardation of the electrophilic attack can be explained by the steric shielding of the *ipso* position and the fact that the hyperconjugative stabilization of the intermediate carbocation requires rotation around the former C=C bond and is obviously not yet effective in the transition state of electrophilic attack.

	6a	**1g**
k_2 (**2d**)	5.3 × 10^2	6.6 × 10^1
k_{rel}	1	0.12

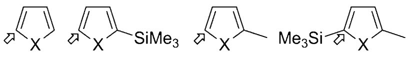
Scheme 6. Absolute (in $M^{-1}s^{-1}$) and relative rate constants for the reactions of styrene (**6a**) and trans-β-(trimethylsilyl)styrene (**1g**) toward the *p*-methoxy substituted benzhydrylium ion **2d** in CH_2Cl_2 at 20 °C (ref. [7a]).

As shown in Scheme 7, the situation in vinylsilanes differs from that in allylsilanes, where the hyperconjugative β-silyl stabilization can already become effective in the transition state.

Related silyl effects have previously been observed in the furan and thiophene series (Scheme 8).[16] Comparison of the first and third number column of Scheme 8 shows that a methyl group in 2-position increases the nucleophilicity by



Scheme 7. Differences of the stereoelectronic effects in reactions of electrophiles with vinylsilanes (top) and allylsilanes (bottom).



k_{rel} (X = O)[a]	1[b]	3.2×10^1	1.5×10^3	1.1×10^3
k_{rel} (X = S)[c]	1[b]	4.1	5.6×10^2	4.3×10^2

Scheme 8. Relative rate constants k_2 for the reactions of furan and thiophene derivatives toward benzhydrylium ions in CH_2Cl_2 at 20 °C ([a] towards the ferrocenylphenylcarbenium ion, [b] partial rate constant, [c] towards the bis(*p*-anisyl)carbenium ion **2g**; ref. [16]).

three orders of magnitude, similar to the isobutylene/propene (**5b**/**5a**) ratio (Table 4). From the almost equal reactivities of non-silylated and silylated compounds in columns 3 and 4 of Scheme 8, one can derive that in the heteroarene series the weak electronic activation of the silyl-substituted position is fully compensated by the steric retardation. The stereoelectronic arguments (Scheme 7, top) which explain the (even retarding) silyl effect in the comparison **1g**/**6a** (Scheme 6) apply analogously.

The weak activation of the 5-position in furan and thiophene by a 2-trimethylsilyl group (compare columns 1 and 2 in Scheme 8) is in the same order of magnitude as in the comparison **1a**/**5a** (Table 4), which also measures the effect of $SiMe_3$ in α-position of the resulting carbenium ion. As this activation is stronger than the *ipso* activation, 2-(trimethylsilyl)furan and 2-(trimethylsilyl)thiophene react with electrophiles in the 5-position and not in the 2-position, as indicated by the arrows in Scheme 8.[16] The substituent effects found in the vinylsilane series are, therefore, fully consistent with those previously observed in the furan and thiophene series.

Conclusion

The kinetic measurements reported in this article allow us to include vinylsilanes in our comprehensive nucleophilicity scale (Figure 6), which shows that vinylsilanes are significantly less reactive than structurally related allylsilanes.

Scheme 9 compares the effects on nucleophilicity when allylic and vinylic hydrogens (marked by shaded circles) are replaced by different groups. Replacement of the marked allylic hydrogen atom in isobutylene by the trimethylsilyl or the supersilyl group activates the π-bond for electrophilic attack by a factor of 10^3 (Scheme 9 A), which is explained by the well-known hyperconjugative stabilization of the intermediate carbenium ion by the C–Si σ-bond.[1,8a] The equal effects of $SiMe_3$ and $Si(SiMe_3)_3$ can be explained by the large separation of the developing carbenium center from the Si–Si bond. Replacement of the allylic hydrogen atom by an alkyl group has little effect on nucleophilicity owing to the similar magnitude of C–H and C–C hyperconjugation.[12b]

Replacement of the marked vinylic hydrogen atom in propene by $SiMe_3$ activates by one order of magnitude showing that the stabilizing effect of silicon in the α-position of the developing carbocation is significantly smaller than the effect of a methyl group (10^3, Scheme 9 B). The larger effect of a supersilyl group at the developing carbenium center (10^2) can be explained by stabilization of the intermediate carbenium ion by

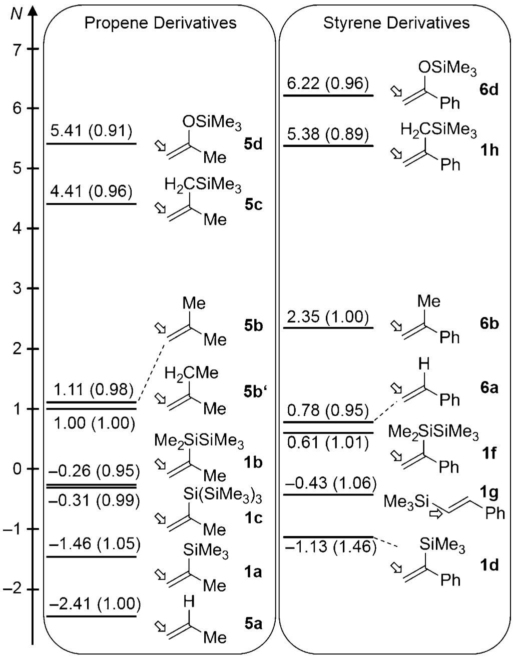
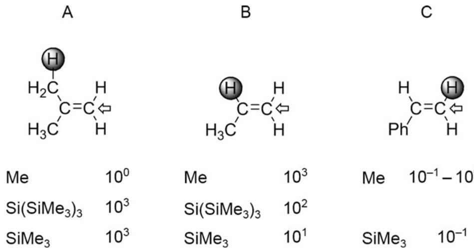


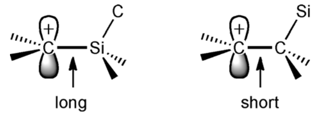
Figure 6. Nucleophilicities of propene (left) and styrene derivatives (right) compared to those of other π-nucleophiles (ref. [7b]); s_N values given in parentheses.



Scheme 9. Approximate changes of nucleophilicity due to replacement of the marked hydrogens by different groups.

Si–Si hyperconjugation, thus prompting us to consider vinylsilanes incorporating the supersilyl group (or the $SiMe_2SiMe_3$ group) as sila-allylsilanes.

From the comparison **5a** < **1a** < **1b** < **5b′** ≈ **5b** ⋘ **5c** in Figure 6 we can derive the following series of carbenium-stabilizing effects: H < Si–C < Si–Si < C–C ≈ C–H ⋘ C–Si. At first glance, it may be surprising that the hyperconjugative stabilization of a carbenium center through a Si–C bond is so much weaker than that through a C–Si bond. One reason is the smaller overlap between the empty *p*-orbital with the Si–C bond than with the C–Si bond because of the longer C^+–Si bond compared with the C^+–C bond (Scheme 10).[17] A second



Scheme 10. Comparison between hyperconjugative stabilization of a carbenium center by a Si–C (left) and a C–Si (right) bond.

reason is the polarization of the carbon–silicon bond which is reflected by the larger AO coefficient at the carbon atom in a σ_{C-Si} bond.

Whereas methyl groups in the β-position of styrene have a weak activating or deactivating effect on the reactivity towards electrophiles,[13b] β-trimethylsilyl groups deactivate slightly (Scheme 9C), indicating that the steric retardation overcompensates the weak electronic activation because the perpendicular orientation between developing carbenium center and the C–Si σ-bond inhibits significant hyperconjugative stabilization of the transition state of electrophilic attack. As a result, vinylsilanes are generally only slightly activated or deactivated compared to the corresponding alkenes, independent of the position of the silyl group in α- or β-position of the intermediate carbocation.

Experimental Section

Chemicals

CH_2Cl_2 (*p.a.* grade) used for kinetic experiments was purchased from Merck and successively treated with concentrated sulfuric acid, water, 10% $NaHCO_3$ solution, and water. After drying with $CaCl_2$, it was freshly distilled over CaH_2 under exclusion of moisture (N_2 atmosphere). $GaCl_3$, $TiCl_4$, $FeCl_3$, and BCl_3 were purchased and used as obtained. $SnCl_4$ was purchased and distilled prior to use. Ethereal $HBF_4 \cdot Et_2O$ was purchased from Aldrich. For the syntheses of nucleophiles and electrophiles as well as the product studies, see the Supporting Information.

Kinetics

All kinetics were followed using UV/Vis spectroscopy. The kinetic experiments conducted below 20 °C were carried out by using the method described previously.[13a] The rates of the reactions studied at 20 °C were determined by using a J&M TIDAS diode array spectrophotometer controlled by Labcontrol Spectacle Software and connected to a Hellma 661.502-QX quartz Suprasil immersion probe (5 mm light path) through fiber optic cables and standard SMA connectors.

Acknowledgements

The authors thank Dr. Mirjam Herrlich-Loos for studying the reactions of **1g** with **2d,e-BCl$_4$** and Dr. Gisela Hagen-Bartl for a product study (**1a**+**2a**). Helpful discussions with Dr. Armin Ofial are gratefully acknowledged. We thank the Deutsche Forschungsgemeinschaft (SFB 749, Project B1) for financial support.

Keywords: electrophilic substitution · hyperconjugation · kinetics · linear free-energy relationships · organosilanes

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Received: August 14, 2013