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Determination of the Nucleophilicities of Silyl and Alkyl Enol Ethers

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Abstract: The kinetics of the reactions of benzhydryl cations with 19 silyl enol ethers, four silyl ketene acetals, and two alkyl enol ethers have been determined photometrically in dichloromethane solution. All reactions reported in this investigation follow second-order rate laws, and the rates are independent of the nature of the complex counterion (BF_4^-, $F_3CSO_3^-$, or $ZnCl_3^-$) in accord with rate-determining C−C bond formation. The nucleophilic reactivities span over a range of 10^8 from the vinyl ethers **1a,x** as the least reactive compounds (comparable to allylsilanes) to the highly nucleophilic silyl ketene acetal **1u** (comparable to enamines). Linear free enthalpy relationships are used to compare the reactivities of these compounds with those of other aliphatic and aromatic π-nucleophiles.

Whereas alkyl enol ethers have frequently been used in organic syntheses since the late 1930s,[1a−d] the tremendous synthetic potential of silylated enol ethers has only become obvious during the last two decades.[1e−j] Their usefulness surpasses that of all other enol derivatives because of their ease of preparation and clean reactions with electrophiles.[1e] Due to the rapid desilylation of the siloxycarbenium ions generated by electrophilic attack at silyl enol ethers, their tendency to polymerization is considerably lower than that of comparable alkyl enol ethers.

Because of the +M effect of the alkoxy and siloxy groups, both classes of enol ethers are fairly nucleophilic and react even with relatively weak electrophiles as the tropylium ion,[2] iminium ions,[3] or many diazonium ions.[4] Weaker electrophiles that are unable to attack enol ethers can often be combined with the more nucleophilic enamines to synthesize the corresponding α-substituted carbonyl compounds.

We have recently shown that the rates of electrophile nucleophile combinations can be predicted by eq 1, where the strengths of electrophiles are characterized by the parameter *E* while the nucleophilicity parameter *N* and the nucleophile-specific slope parameter *s* are used to characterize nucleophiles.[5] Since *s* usually varies between 0.6 and 1.2, we have suggested the rule of thumb that electrophile−nucleophile reactions take place at room temperature if $N + E > -5$.

$$\log k_2\ (20\ °\mathrm{C}) = s(E + N) \qquad (1)$$

To explore the propensity of enol ethers to react with electrophiles, we set out to determine the nucleophilicity parameters *N* of enol ethers by measuring the rates of their reactions with reference electrophiles, employing the procedure described in refs 5 and 6. Previous kinetic investigations on the reactions of carbocations with enol ethers were restricted to relatively fast reactions of carbocations which were generated by laser flash photolysis.[7] Since many of the rate constants thus determined were close to the diffusion limit, leveling occurred and the range of validity of eq 1 was left. Therefore, nucleophilicity parameters *N* could only be determined for few enol ethers.

Preparative Investigations. The reactions of the silyl enol ethers and silyl ketene acetals **1a**−**w** with the benzhydryl salts (**2a**−**c**)MX_{n+1} produce aldehydes, ketones, or esters in high yield due to the fast desilylation of the intermediate siloxy substituted carbenium ions **3** (Scheme 1).

In contrast, the reactions of these carbenium salts with alkyl enol ethers often give rise to the formation of polymers since the reactions of the intermediate alkoxy carbenium ions **5** with the counterions are reversible, and the selective formation of the 1:1 product **6** is only observed in the presence of very weak Lewis acids, when the α-substituted ethers **6** do not undergo consecutive reactions with the alkyl enol ethers. While the reaction of $(p\text{-}Me_2NC_6H_4)_2CH^+BF_4^-$ (**2a**-BF_4) with the vinyl ethers **1x,y** gave rise to the formation of polymers, termination

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Scheme 1. Reactions of Enol Ethers with Electrophiles

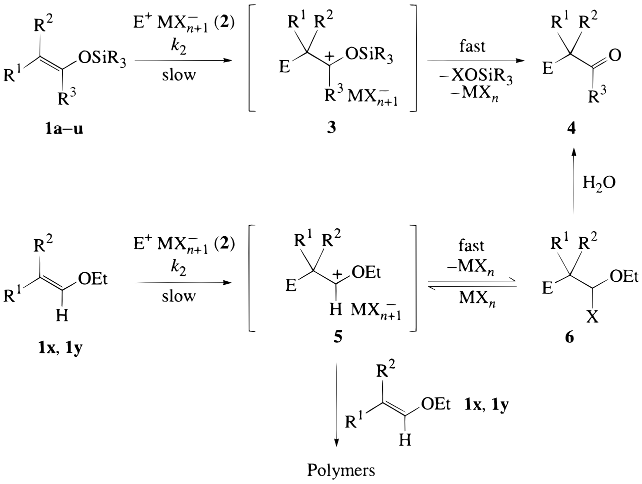
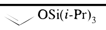
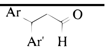
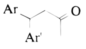
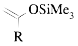
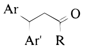
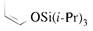
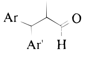
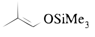
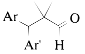
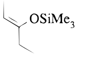
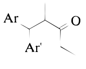
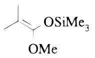
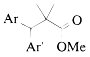
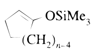
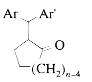
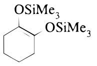
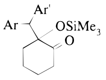
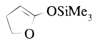
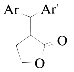
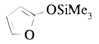
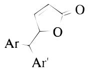
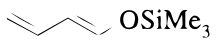
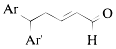
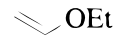
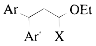
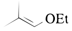
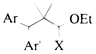


Table 1. Reference Carbenium Ions **2**

ArAr′CH⁺	Ar	Ar′	E[a]	λ_{obs}, nm
2a	p-Me$_2$NC$_6$H$_4$	p-Me$_2$NC$_6$H$_4$	−7.45	630
2b	fc[b]	Ph	−2.92	410
2c	An[c]	An	0.00	490
2d	p-MeC$_6$H$_4$	p-MeC$_6$H$_4$	3.51	464
2e	p-ClC$_6$H$_4$	p-ClC$_6$H$_4$	5.96	472

[a] From ref 5. [b] fc = ferrocenyl. [c] An = p-MeOC$_6$H$_4$.

Table 2. Second-Order Rate Constants, Eyring Parameters, and Products from the Reactions of Diaryl Carbenium Ions **2** with the Enol Ethers **1** (CH_2Cl_2)

enol ether			N	ArAr′CH⁺ [b]	k_2 (20 °C),[a] L mol^{-1} s^{-1}	$\Delta H^{\neq}$, kJ mol^{-1}	$\Delta S^{\neq}$, J K^{-1} mol^{-1}	product
		**1a**	3.81[c]	**2b**	5.72	33.4	−116	
				2c	1.76×10^{3}	23.9	−101	
	SiR$_3$							
	SiMe$_3$	**1b**	5.95[d]	**2a**	3.52×10^{-2}	50.7	−100	
				2b	3.49×10^{2} [e]	31.4[e]	−89[e]	
	Si(i-Pr)$_3$	**1c**	5.75[f]	**2a**	4.02×10^{-2} [g]	51.8	−95	
				2b	2.15×10^{2}	27.9	−105	
	SiMe$_2$(t-Bu)	**1d**	5.95[h]	**2a**	5.10×10^{-2}	56.4	−77	
	SiPh$_3$	**1e**	4.77[h]	**2a**	4.94×10^{-3}	56.5	−96	
	R							
	i-Pr	**1f**	5.77[h]	**2a**	3.56×10^{-2}	–	–	
				2e	2.1×10^{8} [i]	–	–	
	t-Bu	**1g**	4.47[h]	**2a**	2.76×10^{-3}	–	–	
				2c	(1.50×10^{2})[j]	–	–	
				2e	5.5×10^{7} [i]	–	–	
	Ph	**1h**	6.66[k]	**2a**	1.72×10^{-1}	47.5	−98	
	CH=CH$_2$	**1i**	5.16[h]	**2a**	1.08×10^{-2}	–	–	
	OPh	**1j**	8.58[h]	**2a**	9.45	37.9	−97	
	(E)-CH=CH–OMe	**1k**	9.02[h]	**2a**	2.25×10^{1}	–	–	
		**1l**	4.24[l]	**2b**	1.69×10^{1}	32.4	−111	
		**1m**	4.39[m]	**2a**	–	–	–	
				2b	2.30×10^{1}	30.7	−114	
				2c	7.12×10^{3}	17.2	−112	
				2d	4.2×10^{7} [i]	–	–	
				2e	1.5×10^{9} [i]	–	–	
		**1n**	5.90[h]	**2a**	3.65×10^{-2}	46.7	−113	
		**1o**	9.49[n]	**2a**	7.96×10^{1}	25.7	−121	
				2e	2.4×10^{9} [i]	–	–	
	n							
	5	**1p**	6.86[n]	**2a**	3.61×10^{-1}	40.8	−114	
				2b	3.31×10^{3} [e]	22.1[e]	−102[e]	
				2d	6.0×10^{8} [i]			
				2e	2.5×10^{9} [i]			
	6	**1q**	5.58[n]	**2a**	1.91×10^{-2}	47.5	−116	
				2b	3.70×10^{2} [e]	25.1[e]	−110[e]	
				2c	1.9×10^{5} [o]			
				2d	1.3×10^{8} [i]			
				2e	2.3×10^{9} [i]			
	7	**1r**	7.02[l]	**2a**	4.01×10^{-1}	39.6	−117	
	8	**1s**	7.18[l]	**2a**	5.66×10^{-1}	41.6	−108	
		**1t**	4.5[p]	**2a**	1.15×10^{-3}	44.2	−150	
		**1u**	11.7[l]	**2a**	9.40×10^{3}	13.8	−122	
		**1v**	7.66[l]	**2a**	1.58	40.1	−104	
		**1w**	4.92[h]	**2a**	6.67×10^{-3}	–	–	
		**1x**	3.9[q]	**2c**	(1.94×10^{1})[j]	–	–	
				2d	6.3×10^{6} [i]	–	–	
				2e	1.7×10^{8} [i]	–	–	
		**1y**	4.68[r]	**2b**	3.85×10^{1}	21.8	−140	
				2c	(1.23×10^{3})[j]	–	–	
				2d	2.2×10^{8} [i]	–	–	
				2e	2.2×10^{9} [i]	–	–	

[a] If k_2 has been measured at variable temperature, the entry in this column refers to the value derived from the Eyring equation. [b] Key to formula numbers see Table 1. [c] Derived from eq 1 (s = 0.85, Figure 1). [d] s = 0.90; ref 5. [e] Data from ref 9. [f] Derived from eq 1, s = 0.82. [g] Selected value, see text and Table 3. [h] Derived from eq 1 [assuming s = 0.86 as for the structurally analogous compounds **1a** (s = 0.85), **1b** (s = 0.90), and **1c** (s = 0.82)]. [i] Experiments carried out in acetonitrile; data from ref 7. [j] T = −70 °C. [k] s = 0.89; ref 5. [l] Derived from eq 1 [assuming s = 0.93 as for the structurally analogous compounds **1p,q** (ref 5)]. [m] Derived from eq 1 (s = 0.90, Figure 1). [n] s = 0.93; ref 5. [o] Extrapolated value (assuming $\Delta S^{\ddagger} = -113$ J mol^{-1} K^{-1}). [p] Estimated value assuming s = 1.0. [q] Derived from eq 1 [assuming k_2 (**1x** + **2d**, 20 °C, CH_2Cl_2) = 2.1×10^{6} L mol^{-1} s^{-1}, i.e., one-third of the value determined in CH_3CN and s = 0.86 (footnote h)]. [r] Derived from eq 1 from k_2 (**1y** + **2b**) assuming s = 0.90 as for the structurally analogous compound **1m**.

at the 1:1 product stage **6** was observed, when the reactions of fcCH(OAc)Ph (**2b**-OAc) or (p-MeOC$_6$H$_4$)$_2$CHCl (**2c**-Cl) with the alkyl enol ethers **1x** or **1y** were initiated with $ZnCl_2$ in a mixture of diethyl ether and dichloromethane.

Kinetics. For the determination of the reaction rates, solutions of the carbenium salts (**2a**−**c**)MX_{n+1} (Table 1) were combined with an excess of the enol ethers **1a**−**y** and the decay of the carbenium absorbance at λ = 410−640 nm was monitored as a function of time using the work station described previously.[8] All reactions reported in this article followed second-order kinetics, first-order with respect to carbocation and first-order with respect to enol ether (Table 2).

Attempts to measure the kinetics of the reactions of (p-Me$_2$NC$_6$H$_4$)$_2$CH$^+$ (**2a**-BF$_4$ or -OTf) with (trimethylsiloxy)ethene, (triisopropylsiloxy)ethene (**1a**), or 2-methyl-1-(trimethylsiloxy)propene (**1m**) were unsuccessful. Under the reaction conditions the decomposition of these silyl enol ethers was faster than the reaction under consideration. Nevertheless, the nucleophilicities of the compounds **1a,m** have been characterized by measuring the rates of their reactions with the more electrophilic carbenium ions fc(Ph)CH$^+$ (**2b**) and An$_2$CH$^+$ (**2c**). Side reactions (polymerization?) also interferred with the reaction of An$_2$CH$^+$ZnCl$_3^-$ (**2c**-ZnCl$_3$) with ethyl vinyl ether (**1x**), and a deviation of the second-order rate law was already observed after 50% of conversion.

As suggested in Scheme 1, the rate-determining step of these reactions corresponds to the formation of the carbenium ions **3** or **5**, respectively. In accord with this suggestion, the overall reaction rate is usually not affected by the nature and the concentration of the counterions MX_{n+1} (Tables S14, S20, S23, S28, S30, and S31). As shown by Table 3, an influence of the counterion has been observed, however, for the reaction of 2-(triisopropylsiloxy)propene (**1c**) with the highly stabilized carbenium ion (p-Me$_2$NC$_6$H$_4$)$_2$CH$^+$ (**2a**). According to Table 3, the rate constant decreases by approximately 30% when PF_6^- or $F_3CSO_3^-$ is replaced by BF_4^-. Probably the attack of **2a** at **1c** becomes reversible when the weakly nucleophilic counterion BF_4^- is employed, since the steric shielding of the bulky isopropyl groups retards the desilylation of **3**. The closely similar reactivities of compounds **1b**,**c**,**d**, where the steric

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(8) Mayr, H.; Schneider, R.; Schade, C.; Bartl, J.; Bederke, R. *J. Am. Chem. Soc.* **1990**, *112*, 4446−4454.

Table 3. Second-Order Rate Constants for the Reaction of (p-$Me_2NC_6H_4)_2CH^+$ (**2a**) with 2-(Triisopropylsiloxy)propene (**1c**) in the Presence of Different Counterions (20 °C, CH_2Cl_2)

anion	k_2, L mol^{-1} s^{-1}
BF_4^-	2.70×10^{-2}
PF_6^-	3.90×10^{-2}
$F_3CSO_3^-$	4.02×10^{-2}

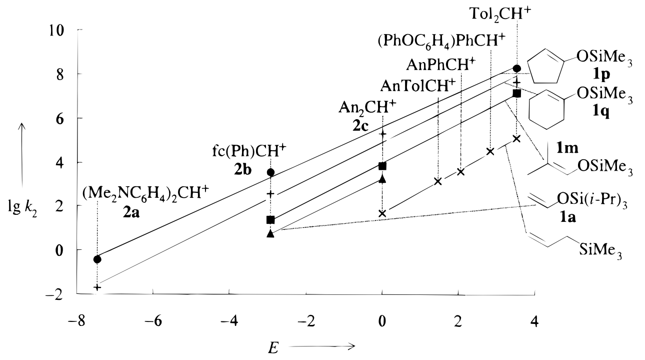
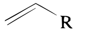
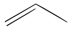
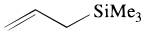
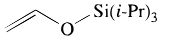
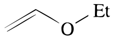
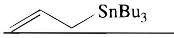


Figure 1. Correlation of the rate constants log k_2 (20 °C, CH_2Cl_2) of the reactions of the silyl enol ethers **1a**,**m**,**p**,**q** and allyltrimethylsilane with different electrophiles vs their E parameters (used for the determination of N and s values according to eq 1). An = p-$MeOC_6H_4$; Tol = p-MeC_6H_4.

Table 4. Relative Reactivities of Donor-Substituted Ethylenes

	k_{rel} (An_2CH^+, −70 °C)
	$5.0 \times 10^{-6\,a}$
	1.0^b
	56
	69
	1800^c

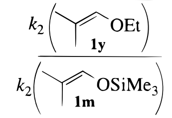
[a] From relative reactivities of propene (ref 13) and allyltrimethylsilane (ref 10) toward $AnPhCH^+$ (−70 °C). [b] k_2 (−70 °C) = 2.81×10^{-1} L mol^{-1} s^{-1}; ref 10. [c] Reference 11.

shielding of silicon differs strongly, clearly indicates however, that the desilylation step cannot be rate-determining.

When the rate constants (log k_2) determined for the reactions of enol ethers with different electrophiles are plotted against their E parameters (Figure 1), linear correlations are obtained, from which s and N can be determined (eq 1). Since the slopes s are almost constant ($0.85 < s < 0.93$) and resemble those of other noncharged nucleophiles,[5] estimated values of s (see footnotes to Table 2) could be used to derive N parameters also for those enol ethers which have only been studied with respect to a single electrophile. The (almost constant) selectivity relationship shown in Figure 1 indicates that structure–reactivity relationships of these enol ethers can be discussed without referring to a certain reaction partner.

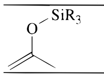
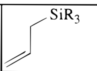
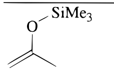
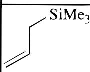
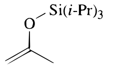
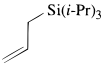
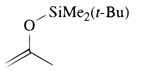
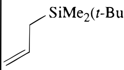
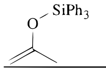
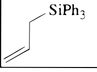
As indicated in Table 4, the triisopropylsilyl vinyl ether shows a reactivity similar to that of the ethyl vinyl ether. Their nucleophilicities are between those of allyltrimethylsilane and allyltributylstannane. Similar reactivities of structurally analogous ethyl and trimethylsilyl enol ethers have also been derived from a comparison of compounds **1m** and **1y** (Table 5). The ethyl enol ether **1y** was generally found to be five to eight times more reactive than the corresponding silyl enol ether **1m**, while the electrophilicity of the reference carbenium ion has been altered by 8 orders of magnitude.

Table 5. Relative Reactivities of the Alkyl and Trimethylsilyl Enol Ethers **1m** and **1y**

Electrophile (Conditions)	
2b (CH_2Cl_2, −70 °C)	8.5
2c (CH_2Cl_2, −70 °C)	5.6
2d (CH_3CN, 20 °C)	5.2^a

[a] Data from ref 7.

Table 6. Influence of the Substituents at Silicon on the Reactivities of Silyl Enol Ethers (Left Part) and Allylsilanes (Right Part)

	k_{rel} (**2a**, 20 °C)		k_{rel} ($AnPhCH^+$, −70 °C)^a
	1.0^b		1.0^c
	1.1^d		2.4
	1.4		1.1
	0.14		0.017

[a] Data from refs 10 and 11. [b] k_2 (20 °C) = 3.52×10^{-2} L mol^{-1} s^{-1} (Table 2). [c] k_2 (−70 °C) = 1.87×10^2 L mol^{-1} s^{-1}. [d] $F_3CSO_3^-$ employed as counterion; cf. Table 3.

Previous kinetic investigations of the acid-catalyzed hydrolysis of enol ethers[12] afforded comparable results: methyl vinyl ethers have been reported to be protonated on average 2.5 times faster than the corresponding *tert*-butyldimethylsilyl enol ethers.[12e]

Since the previous laser flash photolytic studies also revealed a system where the silyl enol ether is slightly more reactive than the corresponding alkyl enol ether [k_2(1-(trimethylsiloxy)-cyclopentene)/k_2(1-methoxycyclopentene) = 2.7 (**2d**, 20 °C)],[7] one has to conclude that alkyl and silyl enol ethers differ only very little in reactivity, but one cannot presently predict the exact ratios of reactivities of structurally analogous silyl and alkyl enol ethers.

The left part of Table 6 shows that variation of the trialkylsilyl groups in the upper three silyl enol ethers has only little influence on reactivity, corroborating C–C bond formation as the rate-determining step, which is followed by rapid desilylation. Only when the trialkylsilyl group was replaced by a triphenylsilyl group (bottom entry in Table 6), did the negative inductive effect of the phenyl groups cause the nucleophilicity to decrease.

An analogous ranking of reactivity has been observed for allyltrialkylsilanes (right part of Table 6),[10,11] where the nature of the alkyl group also exerts little influence on reactivity, while allyltriphenylsilane is noticeably less reactive.

Since the trimethylsiloxy compound **1b** and the triisopropylsiloxy compound **1c** possess similar reactivities (Table 2), the

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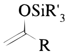
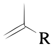
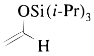
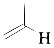
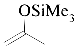
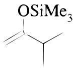
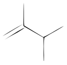
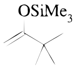
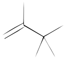
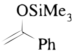
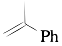
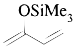
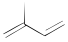
(9) Mayr, H.; Rau, D. *Chem. Ber.* **1994**, *127*, 2493–2498.

(10) Mayr, H.; Schneider, R.; Grabis, U. *J. Am. Chem. Soc.* **1990**, *112*, 4460–4467.

(11) Hagen, G.; Mayr, H. *J. Am. Chem. Soc.* **1991**, *113*, 4954–4961.

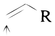
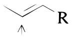
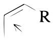
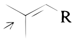
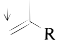
(12) (a) Okuyama, T.; Fueno, T.; Nakatsuji, H.; Furukawa, J. *J. Am. Chem. Soc.* **1967**, *89*, 5826–5831. (b) Fueno, T.; Matsumura, I.; Okuyama, T.; Furukawa, J. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 818–823. (c) Knittel, P.; Tidwell, T. T. *J. Am. Chem. Soc.* **1977**, *99*, 3408–3414. (d) Kresge, A. J.; Sagatys, D. S.; Chen, H. L. *J. Am. Chem. Soc.* **1977**, *99*, 7228–7233. (e) Novice, M. H.; Seikaly, H. R.; Seitz, A. D.; Tidwell, T. T. *J. Am. Chem. Soc.* **1980**, *102*, 5835–5838. (f) Kresge, A. J.; Leibovitch, M. *J. Org. Chem.* **1990**, *55*, 5234–5236. (g) Kresge, A. J.; Leibovitch, M. *J. Am. Chem. Soc.* **1992**, *114*, 3099–3102.

Table 7. Effects of Substituents at the Position of the Developing Carbenium Center in the Series of Silyl Enol Ethers (Left Part) and Propenes (Right Part)

		k_{rel} (**2a**, 20 °C)		k_{rel} (AnPhCH$^+$, −70 °C)[a]
	**1a**	0.023[b]		4.0×10^{-5}
	**1b**	1.0[c]		1.0[d]
	**1f**	1.0		0.26
	**1g**	0.078		0.052
	**1h**	4.9		62
	**1i**	0.31		0.67

[a] Data from ref 13. [b] k_2 (20 °C) $= 8.05 \times 10^{-4}$ L mol^{-1} s^{-1} (derived from eq 1; Figure 1). [c] k_2 (20 °C) $= 3.52 \times 10^{-2}$ L mol^{-1} s^{-1} (Table 2). [d] k_2 (−70 °C) $= 2.33 \times 10^{1}$ L mol^{-1} s^{-1}.

Table 8. Influence of Methyl Groups on the Reactivity of Several π-Nucleophiles[a]

R	k_{rel}					
CH_3	AnPhCH$^+$, −70 °C[b]	1.0[c]	1.3	1.1	–[d]	25000
CH_2SiMe_3	AnPhCH$^+$, −70 °C[e]	1.0[f]	22	8.9	8.1	1740[g]
$OSi(i\text{-}Pr)_3$	**2b**, 20 °C	1.0[h]		3.0	4.0[i]	38

[a] ↑ indicates the site of electrophilic attack. [b] Data from ref 13. [c] k_2 (−70 °C) $= 9.39 \times 10^{-4}$ L mol^{-1} s^{-1}. [d] Electrophilic attack occurs at the R-substituted carbon; therefore, the reactivity data cannot be compared with the other entries in this series. [e] Data from ref 11. [f] k_2 (−70 °C) $= 1.87 \times 10^{2}$ L mol^{-1} s^{-1}; ref 11. [g] Relative reactivity of (2-methylallyl)trimethylsilane and allyltrimethylsilane toward **2c** (−70 °C); ref 11. [h] k_2 (20 °C) $= 5.72$ L mol^{-1} s^{-1} (Table 2). [i] R = $OSiMe_3$.

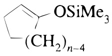
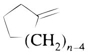
reactivity ratio $k_2(\mathbf{1b})/k_2(\mathbf{1a}) = 43$ can be attributed to the activating effect of the α-methyl group (left part of Table 7).

While replacement of methyl by isopropyl (compounds **1b,f**) does not affect the reactivity, the steric bulk of the *tert*-butyl group in **1g** reduces the nucleophilicity by a factor of 13. Replacement of the alkyl groups by CC-conjugating substituents as phenyl or vinyl has little influence on reactivity. The electron-donating effect of the trimethylsiloxy group reduces the electron demand of the developing carbenium center to such an amount that phenyl activates only five times better than methyl while vinyl is even deactivating compared to methyl.

The right part of Table 7 shows that related but more pronounced substituent effects are observed in the analogous series of 2-substituted propenes:[13] Because of the greater electron demand of the developing carbenium center, these compounds are more sensitive toward variation of the substituents.

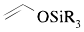
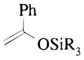
The effects of additional methyl groups on the nucleophilicity of various π-systems (alkenes, allyltrimethylsilanes, and silyl vinyl ethers) are collected in Table 8. The last column shows a significant effect of the methyl group located at the position of the developing carbenium center, which decreases from top to bottom with increasing electron-donating ability of R. Methyl groups at the position of electrophilic attack exert a considerably smaller activating effect (columns 4, 5, and 6), and it is not clear why this effect is largest in the allylsilane series.

Table 9. Relative Reactivities of Cyclic Silyl Enol Ethers and Methylenecycloalkanes

			
n		k_{rel} (**2a**, 20 °C)	k_{rel} (AnPhCH$^+$, −70 °C)[a]
5	**1p**	19	37
6	**1q**	1.0[b]	1.0[c]
7	**1r**	21	9.1
8	**1s**	30	108

[a] Data from ref 14a. [b] k_2 (20 °C) $= 1.91 \times 10^{-2}$ L mol^{-1} s^{-1} (Table 2). [c] k_2 (−70 °C) $= 4.69 \times 10^{1}$ L mol^{-1} s^{-1}.

Table 10. Comparison of the Relative Reactivities of Silyl Enol Ethers (Left Part) and Alkenes (Right Part) toward Diarylcarbenium Ions or Acid-Catalyzed Hydrolysis, Respectively

	k_{rel} (**2a**, 20 °C)	k_{rel} (H_3O^+, 25 °C)[a]		k_{rel} (AnPhCH$^+$, −70 °C)[b]	k_{rel} (H_3O^+, 25 °C)[c]
	1.0[d]	1.0		1.0	1.0
	214[e]	14		1.5×10^{6}	4.1×10^{4}
	44[e]	340		2.5×10^{4}	1.6×10^{5}

[a] Data from ref 12e [$k_{H^+}(H_2C{=}CHOSi(t\text{-}Bu)Me_2) = 6.35 \times 10^{-2}$ L mol^{-1} s^{-1}]; $R_3 = (t\text{-}Bu)Me_2$. [b] Data from ref 13 [k_2(propene) $= 9.39 \times 10^{-4}$ L mol^{-1} s^{-1}]. [c] Data from ref 17 [k_2(propene) $= 2.39 \times 10^{-9}$ L mol^{-1} s^{-1}]. [d] R = *i*-Pr; $k_2 = 8.05 \times 10^{-4}$ L mol^{-1} s^{-1} (derived from eq 1; Figure 1). [e] R = Me, Table 2.

As indicated in Table 9, cyclic silyl enol ethers follow a similar reactivity pattern as the corresponding methylenecycloalkanes.[14a] The six-membered rings show a minimum and the eight-membered ring compounds a maximum of nucleophilicity. An analogous reactivity ranking has previously been observed for the acid-catalyzed hydrolyses of 1-ethoxycycloalkenes[12d] and the solvolyses of 1-chloro-1-methylcycloalkanes.[14b] We have recently discussed[14a] that the classical interpretation of this reactivity series by strain effects is inconsistent, but we have not been able to offer an alternative interpretation.

Substitution of the vinylic α-hydrogen in silyl enol ethers by an *O*-alkyl or *O*-aryl group (cf. compounds **1a→j,m→o**) leads to the corresponding silyl ketene acetals and increases the nucleophilicity of the π-system by approximately 5 orders of magnitude (*N*, Table 2).[15] A comparable nucleophilicity is also observed for the vinylogous silyl ketene acetal **1k** (Danishefky's diene). Due to the loss of aromatic delocalization energy in the course of the electrophilic attack, the furan derivative **1v** is somewhat less reactive than other silyl ketene acetals, while the nucleophilicity of its 4,5-dihydrogenated analogue **1u** is extremely high, comparable to that of enamines.[16]

In the silyl enol ether series presented in the left part of Table 10, the phenyl-substituted compound exhibits a maximum of reactivity toward diarylcarbenium ions while the methyl-substituted silyl vinyl ether is most reactive toward hydronium ions. Comparable results have previously been obtained from kinetic studies of the corresponding reactions of the analogously substituted propenes,[13,17] as indicated in the right part of Table 10.

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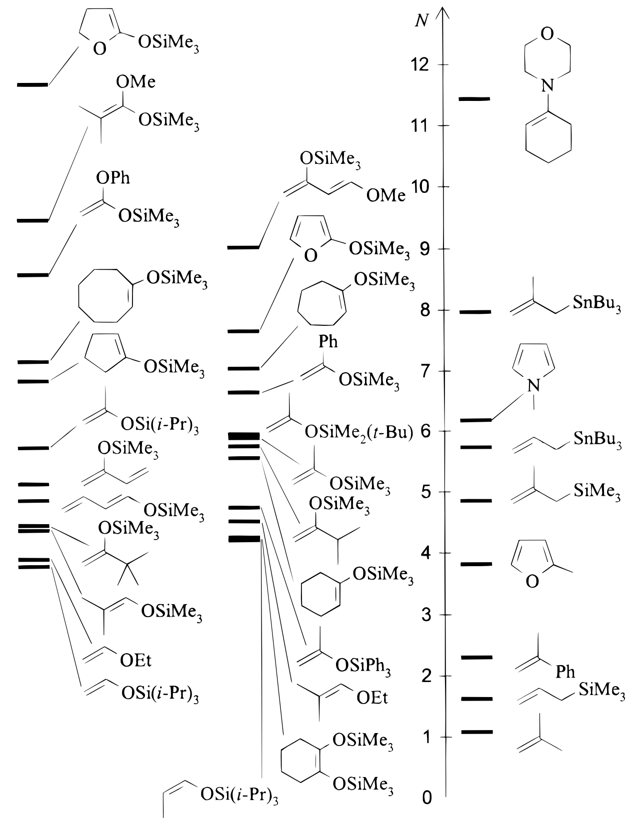

Figure 2. Nucleophilicities of enol ethers compared with other π-systems.

The nucleophilicity parameters listed in Table 2 allow the prediction of the rates of reactions with various electrophiles on the basis of eq 1. Because of the small variations in s, the N parameters can furthermore be used to roughly compare the nucleophilicities of enol ethers and ketene acetals with those of other nucleophiles. Figure 2 shows, for example, that ordinary alkyl or silyl enol ethers with N values from 3.8 to 7.2 are comparable to allylsilanes and allylstannanes. Ketene acetals ($7.7 < N < 11.7$) are considerably more nucleophilic and range between allylstannanes and enamines.

Enol ethers and ketene acetals thus cover a wide range of nucleophilic reactivity. Since most of the reactions of these compounds with carbenium salts follow clean second-order kinetics up to high degree of conversion, silyl enol ethers and silyl ketene acetals can be used as reference nucleophiles for determining reactivities of weak electrophiles. In forthcoming papers, we will show how to employ the kinetic data reported in this work for synthesis planning and for characterizing the electrophilicities of cationic transition metal π-complexes.

Experimental Section

Kinetics. The kinetic method has previously been described.[8]

Electrophiles. **2a**-OTf has been prepared as described in ref 6 by dropwise addition (5 min) of a solution of bis(*p*-(dimethylamino)phenyl)methanol (4.1 g, 15 mmol) in dry THF (50 mL) to a stirred solution of F_3CSO_3H (2.3 g, 15 mmol) in dry THF (50 mL) at room temperature. The precipitate was filtered, washed with dry THF (20 mL), and dried in vacuo to give 4.5 g (11 mmol, 74%) of dark-green lamella: mp 139−140 °C.

Compound **2a**-BF_4 has been obtained in a similar way by dropwise addition of a solution of bis(*p*-(dimethylamino)phenyl)methanol (12 g, 44 mmol) in dry THF (50 mL) to a stirred solution of HBF_4 (7.1 g [54% in Et_2O], 44 mmol) in dry THF (20 mL) at room temperature. The precipitate was filtered, washed with dry THF (20 mL), and dried in vacuo to afford 14 g (41 mmol, 93%) of deep-blue powder: mp 150−151 °C.

2a-PF_6 has been prepared by addition of HPF_6 (2.0 g [75% in H_2O], 10 mmol) to a solution of bis(*p*-(dimethylamino)phenyl)methanol (2.0 g, 7.4 mmol) in acetic anhydride (60 mL) at 0 °C. After stirring at room temperature for 15 min, the mixture was diluted with diethyl ether (100 mL) and chilled (0 °C) to precipitate **2a**-PF_6, which was filtered after 15 min, washed with dry ether (50 mL), and dried in vacuo to yield 2.3 g (5.8 mmol, 78%) of dark-green powder: mp 180−181 °C.

The diarylmethyl compounds **2b**-OAc and **2c**-Cl have been synthesized according to refs 9 and 18, respectively. For the in situ generation of the carbenium ions **2b,c**, trimethylsilyl triflate (TMSOTf) or the zinc chloride diethyl ether complex $ZnCl_2{\cdot}(OEt_2)_2$ (ref 19) have been added to solutions of the precursors **2b**-OAc and **2c**-Cl in CH_2Cl_2.

Nucleophiles. The compounds **1b**,**k**,**o**−**q**,**v**−**x** (Fluka, Aldrich) and **1i** (Merck-Schuchardt) are commercially available. The silyl enol ethers **1d**−**h** have been prepared by treatment of the corresponding ketones with $NEt_3/ClSiR_3$ as described in ref 20. For the preparation of the silyl ketene acetals **1j,u**, phenyl acetate or γ-butyrolactone, respectively, have been deprotonated with LDA and treated with $ClSiMe_3$ according to ref 21. **1n** has been obtained by silylation of 3-pentanone with Me_3SiCH_2COOEt in the presence of tetrabutylammonium fluoride.[22] Treatment of the corresponding carbonyl compounds with TMSOTf or TIPSOTf and NEt_3 according to ref 23 afforded the silyl enol ethers **1a**,**c**,**g**,**l**,**m**,**r**,**s**. The NMR spectra of compounds **1a**,**c**,**l** have not yet been reported. **1a**: ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 0.9-1.1$ (m, 21 H, CH(CH_3)$_2$), 3.99 (d, $J_Z = 6.0$ Hz, 1 H, $=CH_2$), 4.35 (d, $J_E = 13.6$ Hz, 1 H, $=CH_2$), 6.42 (dd, $J_Z = 5.7$ Hz, $J_E = 13.5$ Hz, 1 H, $=CHO$); ^{13}C NMR (75.5 MHz, $CDCl_3$) $\delta = 12.4$ (d, CH(CH$_3$)$_2$), 17.8 (q, CH$_3$), 94.1 (t, $=CH_2$), 147.0 (d, $=CHO$). **1c**: ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 1.0-1.1$ (m, 21 H, CH(CH_3)$_2$), 1.74 (s, 3 H, CH$_3$), 3.94 (s, 1 H, $=CH_2$), 3.98 (s, 1 H, $=CH_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$) $\delta = 12.4$ (d, CH), 18.1 (q, CH(CH$_3$)$_2$), 22.8 (q, CH$_3$), 90.6 (t, $=CH_2$), 156.4 (s, $=C$(CH$_3$)O). **1l**: ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 0.9-1.1$ (m, 21 H, CH(CH_3)$_2$), 1.52 (dd, $J_{2,3} = 6.6$ Hz, $J_{1,3} = 1.7$ Hz, 3 H, $=$CHCH_3), 4.37 (dq, $J_{1,2} \approx J_{2,3} \approx 6$ Hz, 1 H, $=$CHCH$_3$), 6.21 (dq, $J_{1,2} = 5.8$ Hz, $J_{1,3} = 1.7$ Hz, 1 H, $=CHO$); ^{13}C NMR (75.5 MHz, $CDCl_3$) $\delta = 8.96$ (q, $=$CHCH$_3$), 12.0 (d, CH(CH$_3$)$_2$), 17.8 (q, CH(CH$_3$)$_2$), 104.2 (d, $=C$HCH$_3$), 139.8 (d, $=CHO$). The alkyl enol ether **1y** has been obtained from the corresponding diethyl acetal[24] by elimination of ethanol as described in ref 25.

Products of the Reactions of Benzhydryl Salts with Silyl and Alkyl Enol Ethers. Procedure A. The enol ether **1** (1.5−250 equiv) is added to a stirred solution of the carbenium salt **2a**-MX_{n+1}^- (and benzyltriethylammonium chloride or 2,6-di-*tert*-butylpyridine, respectively) in dry CH_2Cl_2 at room temperature. After fading of the blue color, the reaction mixture is washed with aqueous ammonia and the aqueous layer is extracted with CH_2Cl_2. The organic layers are combined, washed with water, and dried over $MgSO_4$. The solvent is evaporated in vacuo to yield the crude product, which is purified by recrystallization or column chromatography to be characterized as described in the Supporting Information. Most reaction products have

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been characterized completely; some have been identified as crude material by ^{1}H NMR.

Procedure B. Compounds **2b**-OAc or **2c**-Cl are dissolved in dry CH_2Cl_2 at −78 to −40 °C and combined with $ZnCl_2 \cdot (OEt_2)_2$ or $ZnBr_2 \cdot (OEt_2)_2$ (in CH_2Cl_2, $c \approx 2$ mol L^{-1}) or TMSOTf, respectively, to give red solutions. The enol ether **1** (1.5−250 equiv) is added, and the reaction mixture is allowed to warm to room temperature. After fading of the red color, workup is performed as described in procedure A.

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Supporting Information Available: Experimental details for the reactions of silyl and alkyl enol ethers with diarylcarbenium ions, including characterization of the products listed in Table 2, and tables with concentrations and rate constants of the individual kinetic experiments at variable temperatures described in Tables 2 and 3 (24 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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