

# Quantitative Determination of the Nucleophilicity of Allylsilanes

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Kinetic investigations on the reactivity of allylsilanes (**1a—o**) towards the *p*-methoxy substituted diphenylcarbenium ion (**2**) are reported.

In spite of the wide use of allylsilanes in organic synthesis,<sup>1</sup> little quantitative information concerning the activation of C=C  $\pi$ -bonds by allylic silyl groups is available. Competition experiments have shown that the reactivity of the C=C double bond towards the diphenylmethyl cation increases by 30 700 when an allylic hydrogen of propene is replaced by a trimethylsilyl group.<sup>2</sup> We have now determined the rate constants for the reactions of the allylsilanes (**1a—o**) towards the *p*-anisylphenylcarbenium ion (**2**) using the kinetic method previously described.<sup>3</sup>

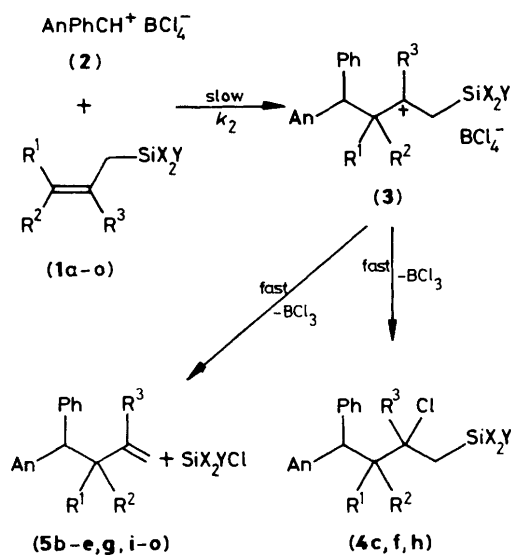
When allyltrimethylsilane (**1e**) was added to a solution of (**2**)- $\text{BCl}_4^-$  in dichloromethane at  $-70^\circ\text{C}$ , the decrease of the carbenium ion concentration, monitored photometrically and conductimetrically, followed a second order rate law [first order with respect to each (**1e**) and (**2**)].<sup>3</sup> Addition of a tetra-alkylammonium tetrachloroborate or replacement of  $\text{BCl}_4^-$  by  $\text{BCl}_3\text{OMe}^-$  or  $\text{SnCl}_5^-$  did not influence the rate of the overall reaction, indicating that the  $\beta$ -silyl substituted carbenium ion (**3**) is generated in the rate determining step.

Table 1 shows that the reactivity of allylsilanes strongly depends on the nature of the substituents X and Y. Replacement of methyl by larger alkyl groups (branched or unbranched) leads to a slight increase of reactivity, and exchange of the three methyl groups by phenyl reduces the reactivity by two orders of magnitude. A reduction of reactivity by three orders of magnitude is observed when one methyl group of (**1e**) is replaced by chlorine (**1b**). The inductively withdrawing effect of chlorine is cumulated in allyltrichlorosilane (**1a**). This compound, in contrast to propene, does not react with (**2**)- $\text{BCl}_4^-$  at  $-70^\circ\text{C}$ , indicating a deactivation of the double bond by the trichlorosilyl group.

As reported for alkenes,<sup>4</sup> an additional methyl group at the developing carbenium centre causes a strong reactivity increase, and the addition rate of (**1m**) is too high to be determined by our method. A quantitative value for the  $\alpha$ -methyl effect (5950) is derived from the comparison (**1c**/**1l**). In contrast to (**1a**), the trichlorosilyl derivative (**1k**) does react with (**2**), and the comparison (**1k**)/isobutene shows a deactivating effect of 360 for the trichlorosilyl group.

One methyl group at the initially attacked vinylic carbon increases the reactivity to a similar degree [(**1n**/**1e**) = 21] as reported for alkenes (trimethylethylene/isobutene = 30 to 50),<sup>4</sup> and the expected electronic acceleration by the second methyl group is overcompensated by steric retardation, resulting in a reduced reactivity of (**1o**) compared with (**1n**).

In summary, the rate effects caused by  $\alpha$ - and  $\beta$ -methyl groups in allylsilanes closely resemble those reported for the corresponding reactions of normal alkenes, an indication for similar transition state structures.<sup>5</sup> The reactivity scale in Table 1, which refers to the reference electrophile (**2**) will certainly experience changes when other electrophiles are considered.<sup>6</sup> We expect, however, only relatively small modifications for other carbon electrophiles if systems with strong steric interactions are excluded, so that the *k* values in Table 1 should be useful for designing C-C bond forming reactions *via* electrophilic attack at allylsilanes.



**Table 1.** Second order rate constants for the reactions of the allylsilanes (**1a—o**) with *p*-anisylphenylcarbenium tetrachloroborate (**2**)- $\text{BCl}_4^-$  ( $\text{CH}_2\text{Cl}_2$ ,  $-70^\circ\text{C}$ ,  $1 \text{ mol}^{-1} \text{ s}^{-1}$ ).

	<i>k</i>
	( <b>1a</b> ) No reaction
	( <b>1b</b> ) 0.276
	( <b>1c</b> ) <sup>a</sup> 3.21
	( <b>1d</b> ) 38.7
	( <b>1e</b> ) 197
	( <b>1f</b> ) 204
	( <b>1g</b> ) 313
	( <b>1h</b> ) 439
	( <b>1i</b> ) 507
	( <b>1j</b> ) 542
$\alpha$ -methylation	
	( <b>1k</b> ) 0.066
	( <b>1l</b> ) $1.91 \times 10^4$
	( <b>1m</b> ) $> 10^5$
$\beta$ -methylation	
	( <b>1n</b> ) $4.15 \times 10^3$
	( <b>1o</b> ) $1.56 \times 10^3$
	Reference compound <sup>3</sup> 23.8

<sup>a</sup> (**4c**):(**5c**) = 1 : 1.5.

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