

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,¹ little quantitative information concerning the activation of C=C π -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.² 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.³

When allyltrimethylsilane (**1e**) was added to a solution of (**2**)- BCl_4^- in dichloromethane at -70°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**)].³ Addition of a tetra-alkylammonium tetrachloroborate or replacement of BCl_4^- by BCl_3OMe^- or SnCl_5^- did not influence the rate of the overall reaction, indicating that the β -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**)- BCl_4^- at -70°C , indicating a deactivation of the double bond by the trichlorosilyl group.

As reported for alkenes,⁴ 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 α -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),⁴ 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 α - and β -methyl groups in allylsilanes closely resemble those reported for the corresponding reactions of normal alkenes, an indication for similar transition state structures.⁵ The reactivity scale in Table 1, which refers to the reference electrophile (**2**) will certainly experience changes when other electrophiles are considered.⁶ 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.

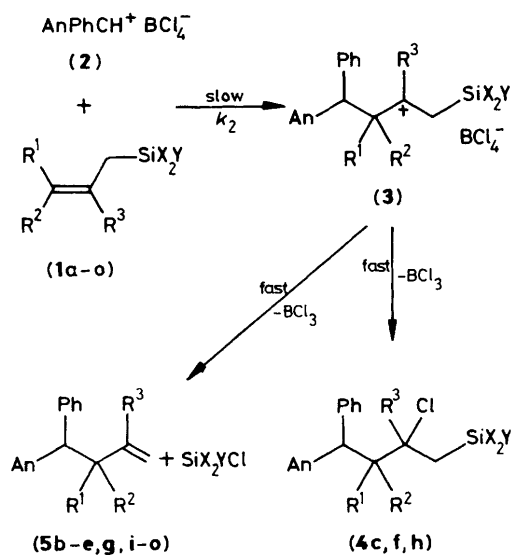


















Table 1. Second order rate constants for the reactions of the allylsilanes (**1a—o**) with *p*-anisylphenylcarbenium tetrachloroborate (**2**)- BCl_4^- (CH_2Cl_2 , -70°C , $1 \text{ mol}^{-1} \text{ s}^{-1}$).

	<i>k</i>
 SiCl_3	(1a) No reaction
 SiClMe_2	(1b) 0.276
 SiPh_3	(1c) ^a 3.21
 SiMe_2Ph	(1d) 38.7
 SiMe_3	(1e) 197
 SiMe_2Bu^t	(1f) 204
 SiEt_3	(1g) 313
 SiPr_3	(1h) 439
 SiBu^i_3	(1i) 507
 SiHex^i_3	(1j) 542
α -methylation	
 SiCl_3	(1k) 0.066
 SiPh_3	(1l) 1.91×10^4
 SiMe_3	(1m) $>10^5$
β -methylation	
 SiMe_3	(1n) 4.15×10^3
 SiMe_3	(1o) 1.56×10^3
	Reference compound ³ 23.8

^a (**4c**):(**5c**) = 1 : 1.5.

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