Quantitative Determination of the Nucleophilicity of Allylsilanes

Herbert Mayr* and Gisela Hagen

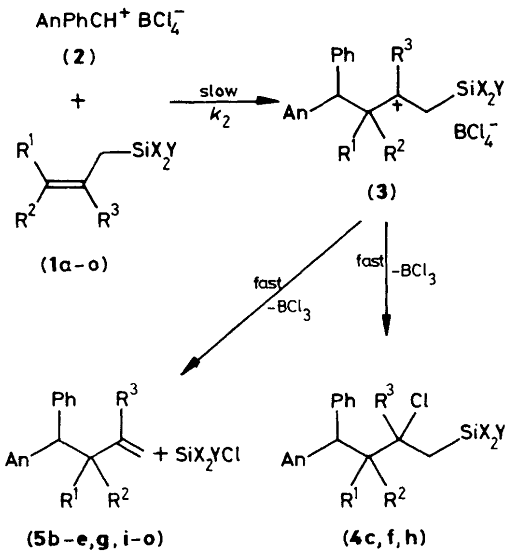
Institut für Chemie, Medizinische Universität zu Lübeck, Ratzeburger Allee 160, D-2400 Lübeck 1, Federal Republic of Germany

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.



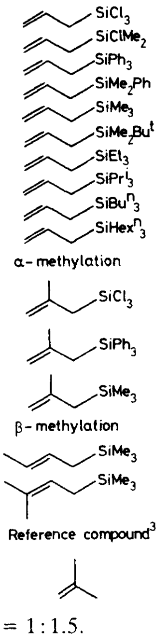
An = *p*-Anisyl

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, l mol^{-1} s^{-1}).



	k
(**1a**)	No reaction
(**1b**)	0.276
(**1c**)[a]	3.21
(**1d**)	38.7
(**1e**)	197
(**1f**)	204
(**1g**)	313
(**1h**)	439
(**1i**)	507
(**1j**)	542
(**1k**)	0.066
(**1l**)	1.91×10^4
(**1m**)	$>10^5$
(**1n**)	4.15×10^3
(**1o**)	1.56×10^3
	23.8

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

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