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ELECTROPHILIC ATTACK AT ALLYLSILANES: A QUANTITATIVE DETERMINATION OF THE β-SILYL EFFECT

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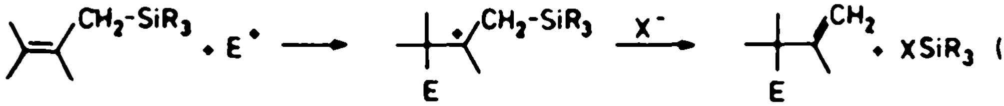
Abstract: The relative reactivities of allylsilanes and alkenes towards diarylmethyl cations have been determined by competition experiments. Introduction of a β-trimethylsilyl group increases the reactivity of propene towards the diphenylmethyl cation by a factor of 30700.

Allylsilanes are widely used as allyl anion equivalents in organic synthesis since their double bond is regioselectively attacked by electrophiles under mild reaction conditions (eq. 1).[1] This behaviour has been attributed to the β-silicon stabilization of the intermediate carbenium ions.

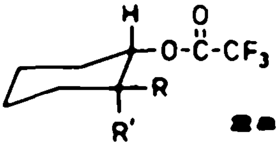


(1)

Solvolytic studies of appropriately substituted derivatives have been used to derive the magnitude of the β-silyl effects.[2] Sommer and Baughman reported that **1** solvolyzes via a carbenium ion mechanism (m = 1.02), 6.6 times more rapidly than tert. butyl chloride (80% aq. ethanol).[2a] This comparison shows that solvolysis is more enhanced by one β-trimethylsilyl group than by two α-methyl groups, and evidence for neighbouring group participation in such solvolysis has been reported.[2b,c]

$(CH_3)_3Si-CH_2-CH_2-Cl$

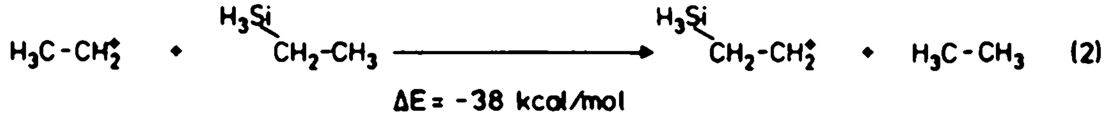
1



2

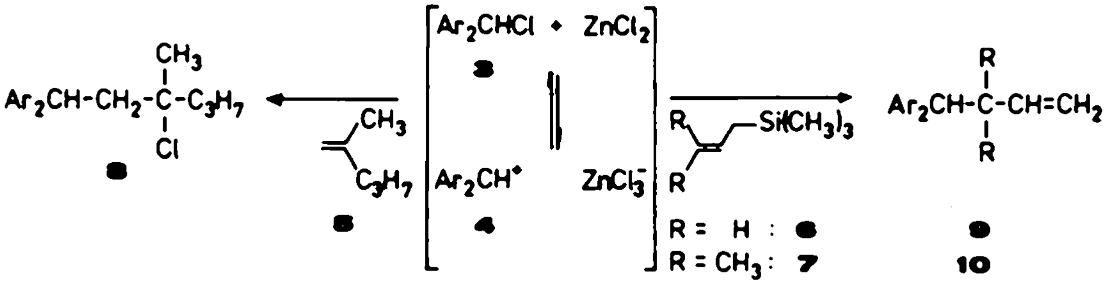
	R	R'	k_{rel}
2a	H	H	1.00
2b	H	$Si(CH_3)_3$	$3.35 \cdot 10^4$
2c	$Si(CH_3)_3$	H	$2.47 \cdot 10^6$

Lambert and Finzel found that cis and trans β-trimethylsilyl groups increase the solvolysis rates of cyclohexyl trifluoroacetates (**2**) considerably, though anchimeric assistance may only be effective in the trans isomer.[2d] The large β-silyl effect has also been employed for the solvolytic generation of phenyl cations.[3] On the contrary, the formation of α-silyl substituted carbenium ions via solvolysis is much less favored.[4]



$$H_3C\text{-}CH_2^+ \;+\; H_3Si\text{-}CH_2\text{-}CH_3 \xrightarrow[\Delta E = -38\ \text{kcal/mol}]{} H_3Si\text{-}CH_2\text{-}CH_2^+ \;+\; H_3C\text{-}CH_3 \qquad (2)$$

Ab initio MO calculations represent a second source for silicon effects in carbenium ions.[5] In the most comprehensive study, a β-silyl stabilization energy of 38 kcal/mol (MP3/6-31G*) has been calculated (eq. 2), which is mostly ascribed to Si-C hyperconjugative stabilization.[5a] Only a small fraction of this stabilization energy is effective in the transition states of the solvolysis reactions, and the question arises, which percentage of the gas phase stabilization effect is realised in the transition states of the synthetically important electrophilic reactions with allylsilanes. This paper describes the direct determination of the effect of β-trimethylsilyl groups on the reactivity of CC double bonds towards carbenium ions.



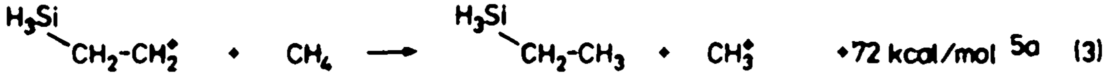
a : Ar = C_6H_5 , b : Ar = p-CH_3-C_6H_4

The diarylmethyl chlorides 3a and 3b react with 2-methyl-1-pentene (5) in the presence of $ZnCl_2$-Et_2O to give > 90% of the addition products 8a,b.[6] Under the same conditions, 3a,b react with the allyl silanes 6 and 7 to yield the substitution products 9a,b and 10a,b in 85 - 94% isolated yield. The relative reactivity of 5, 6 and 7 was derived from the ratios of 1:1 products, which were obtained when 3a or b was added to mixtures of 5 and 6 or 7 in the presence of $ZnCl_2$ (competition method).[7]

	5	6	7
k_{rel} ($Ph_2\overset{+}{C}H$)	1.00	4.45	89.9
k_{rel} (p-$Tol_2\overset{+}{C}H$)	1.00	5.56	81.7

If two methyl groups are appended to allyltrimethylsilane (6 —> 7), a twenty-fold reactivity increase towards 4a results. The corresponding structural change from isobutene to tetramethylethylene was reported to augment the reactivity by a factor of 27.[7] In both cases, the steric retardation is overcompensated by the electronic acceleration, which can be explained by the increasing HOMO energy.

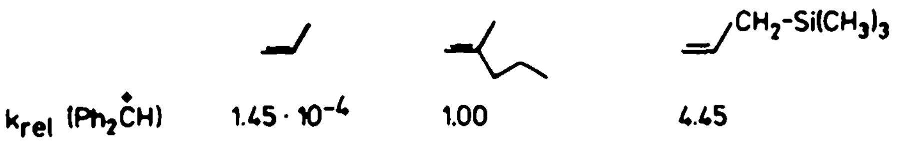
The comparison of 5 and 6 shows that a β-silyl group favours the electrophilic attack more than an α-alkyl group. This is in accord with the relative carbenium ion stabilities derived from ab initio MO (MP3/6-31G*) calculations (eqs 3, 4).



$$\mathrm{H_3Si{-}CH_2{-}CH_2^+ \;+\; CH_4 \;\longrightarrow\; H_3Si{-}CH_2{-}CH_3 \;+\; CH_3^+} \qquad +72\ \text{kcal/mol}\ ^{5a} \qquad (3)$$

$$\mathrm{CH_3{-}\overset{+}{C}H{-}CH_3 \;+\; CH_4 \;\longrightarrow\; CH_3{-}CH_2{-}CH_3 \;+\; CH_3^+} \qquad +63\ \text{kcal/mol}\ ^{8} \qquad (4)$$

If these data are combined with the rate ratio 5/propene , which has been determined under the same conditions at -78°C,[7] the magnitude of the β-silyl effect can be derived. The replacement of an allylic hydrogen in propene by the β-trimethylsilyl group increases the reactivity towards 4a by a factor of 30700, corresponding to ΔΔG* = 4.2 kcal/mol at -70°C, i.e., only a small fraction of the calculated gas phase stabilization energy is effective in the addition transition states.



The rate ratio of 30700 can directly be compared with the relative solvolysis rates of the cyclohexyl trifluoroacetates 2, which also reflect the β-silyl effect in reactions proceeding *via* secondary carbenium ions. Since 2b solvolyzes 3.35 · 10^4 faster, and 2c solvolyzes 2.47 · 10^6 faster than 2a, we conclude that solvolysis data give a good estimate for the β-silyl effect on the rate of C^+ attack at CC double bonds.

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EXPERIMENTAL SECTION

NMR spectra: JEOL JNM-C-60-HL. Mass spectra: Varian MAT CH 4. HPLC: Knauer HPLC pump 64; steel columns 250 mm length, 4.6 mm diameter; UV detector SF 769 Z, Kratos Analytical Instruments. Dichloromethane and diethyl ether were purified as described in lit.[6]

3,3-Dimethyl-4,4-diphenyl-1-butene (10a). A solution of 0.28 g $ZnCl_2$ in 0.33 mL of diethyl ether and 0.67 mL of CH_2Cl_2 was cooled to -78°C.[6] A solution of 7 (1.84 g, 13.0 mmol) in 50 mL CH_2Cl_2 was added at low temperature to give a colorless homogeneous liquid. Diphenylmethyl chloride (3a, 2.01 g, 9.90 mmol) dissolved in 10 mL of CH_2Cl_2 was added dropwise within 15 min. After 20 min stirring at -78°C the mixture was poured on a solution of conc. aqueous ammonia to destroy the catalyst. The organic layer was separated, washed with aqueous ammonia and dried with $CaCl_2$. The solvent was evaporated and the residue was distilled to give 10a (2.10 g, 90%), a colorless liquid with bp. 135 - 140°C (bath)/10^{-4} bar which solidifies in the refrigerator. - ^1H NMR (CCl_4) δ 1.07 (s, 6 H), 3.77 (s, 1 H), 4.77 - 5.20 (m, 2 H), 5.80 - 6.37 (m, 1 H), 6.97 - 7.47 (m, 10 H). - MS (70 eV) *m/e* 236 (37%, M^+), 221 (100), 167 (40), 165 (15), 143 (51).
An analogous method was used for the preparation of the following products.

4,4-Diphenyl-1-butene (9a). Yield: 85%. - B.p. 100 - 110°C (bath)/10^{-4} bar. - ^1H NMR (CCl_4) δ 2.77 (br. t, 2 H, J = 7 Hz), 3.95 (t, 1 H, J = 7.6 Hz), 4.73 - 5.17 (m, 2 H), 5.33 - 6.10 (m, 1 H), 7.18 (s, 10 H). - MS (70 eV) *m/e* 208 (0.45%, M^+), 182 (0.5), 167 (100), 165 (21), 152 (13), 138.4 (m^*, 167 → 152). - **Anal.** Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 91.69; H, 7.76.

4,4-Bis(4-methylphenyl)-1-butene (9b). Yield: 94%. - B.p. 105 - 110°C (bath)/10^{-4} bar. - ^1H NMR (CCl_4) δ 2.27 (s, 6 H), 2.73 (br. t, 2 H, *J* = 7 Hz), 3.88 (t, 1 H, *J* = 7.9 Hz), 4.77 - 5.20 (m, 2 H), 5.33 - 6.10 (m, 1 H), 7.03 (s, 8 H). - MS (70 eV) *m/e* 236 (0.8%, M^+), 195 (100), 180 (25), 179 (12), 178 (10), 166.1 (m^*, 195 → 180), 165 (27). - **Anal.** Calcd. for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.46; H, 8.50.

3,3-Dimethyl-4,4-bis(4-methylphenyl)-1-butene (10b). Yield: 89%. M.p. 64 - 65°C (from ethanol). - ^1H NMR (CCl_4) δ 1.07 (s, 6 H), 2.27 (s, 6 H), 3.63 (s, 1 H), 4.73 - 5.13 (m, 2 H), 5.77 - 6.27 (m, 1 H), 6.83 - 7.27 (m, 8 H). - MS (70 eV) *m/e* 264 (0.9%, M^+), 195 (100), 181 (9), 180 (14), 179 (8), 178 (6), 166.2 (m^*, 195 → 180), 165 (16). - **Anal.** Calcd. for $C_{20}H_{24}$: C, 90.85; H, 9.15.

Found: C, 90.67; H, 9.04.

Competition Experiments: Mixtures of 5 and 6 or 7 were dissolved in 50 mL of CH_2Cl_2 and cooled at - 70.0°C. A solution of 1.9 mmol $ZnCl_2$ in 0.31 mL diethyl ether and 0.62 mL CH_2Cl_2 was admixed. After addition of a small amount of 3a or 3b the reaction mixture was kept at -70.0°C for 1 h. The solution was poured into 50 mL of aqueous ammonia, and the product ratio was analyzed by HPLC (Nucleosil 5 C_{18}, CH_3OH/H_2O = 92/8). The rate ratios (Table 1) were calculated as described previously.[7]

Table 1: Determination of Reactivity Ratios by Competition Experiments

3 (mg)	6, 7 (mg)	5 (mg)	molar product ratio	$k_{6,7}$ / k_5	Average
3a (98)	6 (73)	(513)	9a : 8a = 0.426	4.48	4.45 ± 0.12
(96)	(74)	(997)	0.226	4.37	
(96)	(75)	(1507)	0.162	4.60	
(96)	(71)	(2255)	0.098	4.34	
3b (103)	6 (74)	(537)	9b : 8b = 0.496	5.42	5.56 ± 0.16
(104)	(70)	(1005)	0.265	5.53	
(105)	(80)	(1603)	0.201	5.73	
3a (94)	7 (96)	(1004)	10a : 8a = 3.58	90.4	89.9 ± 1.3
(90)	(96)	(3009)	1.37	91.1	
(105)	(116)	(4007)	1.23	88.2	
3b (106)	7 (94)	(479)	10b : 8b = 6.10	79.6	81.7 ± 2.1
(100)	(95)	(1005)	3.41	84.4	
(104)	(92)	(2023)	1.66	80.7	
(101)	(91)	(3004)	1.18	82.1	

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(8) ΔE for 1-propyl (+46.4 kcal/mol) from ref. 5a corrected by the isomerization energy 1-propyl cation —> isopropyl cation: -17.0 kcal/mol (6-31G*), -16 kcal/mol (exptl., gas phase).[9]

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