Relative Reactivities of Alkyl Chlorides under Friedel-Crafts Conditions

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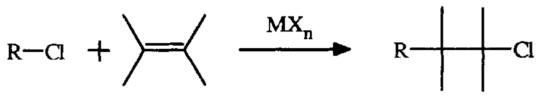
Competition experiments have been performed to determine the relative reactivities of 23 alkyl chlorides toward allyltrimethylsilane in the presence of catalytic amounts of $ZnCl_2$.The k_{rel} scale spans over 11 orders of magnitude from 1-adamantyl chloride (least reactive) to bis(*p*-methoxyphenyl)methyl chloride (most reactive compound). A fair correlation between the alkylating ability and the S_N1 reactivity in solvolysis reactions is found, thus providing a quantitative basis for our long-standing working hypothesis that Lewis acid-catalyzed additions of alkyl halides to CC multiple bonds only yield 1:1 products if the reactants ionize faster than the products. Trityl chlorides do not follow this correlation and are 10^5 times less reactive than predicted from their S_N1 reactivities.

Lewis acid-promoted alkylations of alkenes (eq. 1) yield products **3** which have electrophilic properties like the reactants **1**, and it depends on the relative electrophilicity of **1** and **3** whether the products **3** can be isolated or whether they will react further to give higher adducts or polymers. A high ratio [**3**]/[**1**] can only develop in the reaction mixture if product **3** is less reactive than reactant **1** under the reaction conditions.



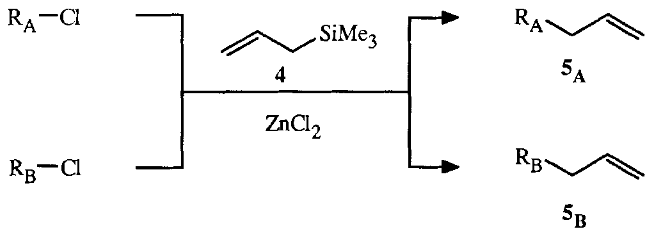
(1)

1 **2** **3**

Relative reactivities of diarylchloromethanes have been determined by competition experiments, and it has been shown that *in the presence of catalytic amounts of Lewis acids* the reactivity of Ar_2CHCl grows with increasing stabilization of the carbenium ion Ar_2CH^+ (the situation is opposite under conditions of complete ionization!)[1]. This result had been anticipated by the postulate that Lewis acid-catalyzed additions of alkyl halides to CC multiple bonds can only lead to 1:1 products (eq. 1) if the reactants **1** ionize faster than the products **3**[2].

We have now investigated the quantitative relationship between relative electrophilicities of alkyl chlorides and their ionization rates as expressed by their S_N1 reactivities. In contrast to the related study in ref.[1] which was restricted to benzhydryl chlorides, we now report on electrophilicities of alkyl chlorides of large structural variety. Since alkylations of allyltrimethylsilane (**4**) selectively yield the S_E2' products **5** which unlike **3** cannot undergo sequential electrophilic reactions, compound **4** has been selected as the reference nucleophile for determining relative electrophilicities of alkyl chlorides by competition experiments (Scheme 1).

Scheme 1



Reaction Products

Compounds **1a–y** (Table 1) react with allyltrimethylsilane (**4**) to give compounds **5**, i.e., the chlorine atom in **1a–y** becomes substituted by an allyl group. In general, the reactions proceed almost quantitatively, but in few cases the isolated yields of products are relatively low. This is mostly due to losses during workup, since repeated microdistillations are necessary to separate compounds with low boiling points (molecular formula $\leq C_9$) from hexamethyldisiloxane (b.p. 101°C), which is formed as a byproduct during workup. In order to avoid this problem, allyltrimethylsilane (**4**) has been replaced by allyltripropylsilane for the synthesis of compounds **5p**, **s**, and **v** (Table 1).

Compound **1p** is employed as a mixture containing 19% of an isomer (4-chloro-4-methyl-2-pentene) that ionizes with formation of the same allyl cation. When this mixture is combined with allyltripropylsilane in the presence of $ZnCl_2 \cdot OEt_2$, compound **5p** is formed as the major product, and only 5% of 4,4-dimethyl-1,5-heptadiene, its allylic isomer, is detected by GC-MS. Analogously, **5u** is produced along with 6% of its regioisomer [6-methyl-4-(trimethylsilyl)-1,4,5-heptatriene]. Due to decomposition during distillation the yield of **5s** is very low.

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When **1w**, **4**, and $TiCl_4$ were combined at 20°C as described in ref.[3], a viscous oil was formed, which solidified at 20°C to give a glassy material. Compound **5w** was obtained in 34% yield, however, when the reactants were combined with $ZnCl_2 \cdot OEt_2$ at −28°C for 6 days.

Table 1. Zinc chloride/ether-catalyzed reactions of allyltrimethylsilane (**4**) with compounds **1a−y**

	RCl	*T* / °C	Time / h	isolated yield / %
a	$(p\text{-MeOC}_6H_4)_2$ CH-Cl	-78	1	74
b	$(p\text{-MeOC}_6H_4)$ $(p\text{-MeC}_6H_4)$ CH-Cl	-78	1	95
c	$(p\text{-MeOC}_6H_4)$ (C_6H_5) CH-Cl	-78	1	87
d	$(p\text{-MeC}_6H_4)_2$ CH-Cl	-78	1	92
e	$(p\text{-MeC}_6H_4)$ (C_6H_5) CH-Cl	-78	1	91
f	$(C_6H_5)_2$ CH-Cl	-78	1	87
g	$(p\text{-ClC}_6H_4)_2$ CH-Cl	-78	3	89
h	$(C_6H_5)_3$ C-Cl	25	68	80[a]
i	$(p\text{-MeC}_6H_4)$ Me_2C-Cl	-78	2	92
j	(C_6H_5) Me_2C-Cl	-78	60	90
k	$(p\text{-MeOC}_6H_4)$ MeCH-Cl	-78	2	86
l	$(p\text{-MeC}_6H_4)$ MeCH-Cl	-78	24	86
m	(C_6H_5) MeCH-Cl	-28	65	79
n	$(p\text{-MeOC}_6H_4)$ CH_2-Cl	-78	1.5	85
o	(C_6H_5) (MeO) CH-Cl	-78	15	92
p	Me_2C=CH-CHMe-Cl	-78	2	58[b, c]
q	$\overline{(CH_2)_2\text{-CH=CH-CH}}$-Cl	-78	1	50
r	(*E*)-Me-CH=CH-CHMe-Cl	-78	3	37
s	(*E*)-H_2C=CH-CH=CH-CH_2-Cl	-40	67	7[b, d]
t	C_6H_5-C≡C-CMe_2-Cl	-78	2	91
u	Me_3Si-C≡C-CMe_2-Cl	-78	20	73[e]
v	Me-C≡C-CMe_2-Cl	-78	48	50[b]
w	1-Adamantyl-Cl	-28 / 0	144 / 48	34
x	Me_3C-Cl	0	48	40
y	MeO-CH_2-Cl	-78	10	24

[a] $SnCl_4$. − [b] Allyltripropylsilane instead of allyltrimethylsilane (**4**). − [c] Includes 5% of 4,4-dimethyl-1,5-heptadiene (GC), **1p** employed is a mixture with 19% allylic isomer. − [d] Includes 10% of impurities (GC). − [e] Includes 6% of 6-methyl-4-(trimethylsilyl)-1,4,5-heptatriene (GC).

Competition Experiments

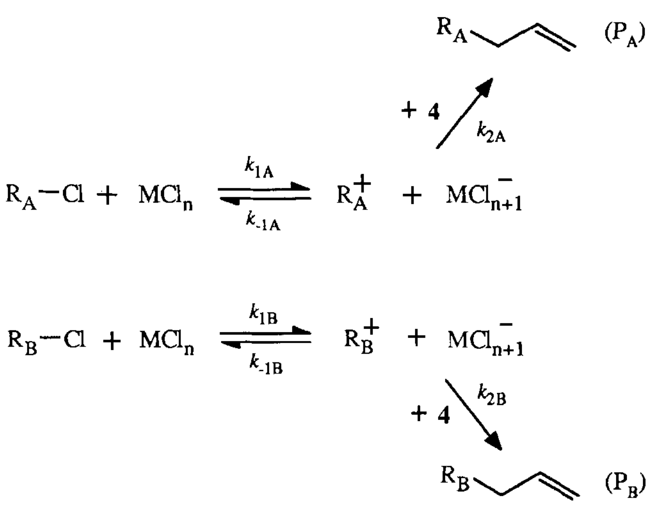
Formal Analysis: Previous work on the mechanism of these reactions suggests the kinetic formalism outlined in Scheme 2.

For the reactions of carbenium ions R^+ with allyltrimethylsilane (**4**) second-order kinetics (eq. 2) have been observed[4].

$$\frac{d[P_A]}{dt} = -\frac{d[R_A^+]}{dt} = k_{2A}[R_A^+][\mathbf{4}] \qquad (2)$$

If the Lewis acid MCl_n is used in catalytic amounts, a stationary carbenium ion concentration can be assumed, and $[R_A^+]$ is given by eq. (3).

Scheme 2



$$[R_A^+] = \frac{k_{1A}[R_ACl][MCl_n]}{k_{-1A}[MCl_{n+1}^-] + k_{2A}[\mathbf{4}]} \qquad (3)$$

Eq. (3) implies complete ion pair dissociation, i.e., $v_{-1A} = k_{-1A}[R_A^+][MCl_{n+1}^-]$. If the carbenium ions were partially paired, an additional, first-order ion-pair recombination term had to be considered. As this modification does not affect the general conclusions, it will be neglected in the following.

Substitution of eq. (3) into (2) and combination with analogous equations for P_B and R_B^+ yields eq. (4).

$$\frac{d[P_A]}{d[P_B]} = \frac{k_{1A}k_{2A}[R_ACl](k_{-1B}[MCl_{n+1}^-] + k_{2B}[\mathbf{4}])}{k_{1B}k_{2B}[R_BCl](k_{-1A}[MCl_{n+1}^-] + k_{2A}[\mathbf{4}])} \qquad (4)$$

Three different cases have to be considered:

Case 1: The ionization equilibria described in Scheme 2 are rapidly established, i.e. k_{-1A} $[MCl_{n+1}^-] \gg k_{2A}[\mathbf{4}]$ and $k_{-1B}[MCl_{n+1}^-] \gg k_{2B}[\mathbf{4}]$. Now the second terms of the sums in eq. (4) can be omitted, and the resulting quotients k_{1A}/k_{-1A} and k_{1B}/k_{-1B} can be replaced by the equilibrium constants K_{1A} and K_{1B}, respectively, to yield eq. (5) (Curtin-Hammett situation).

$$\frac{d[P_A]}{d[P_B]} = \frac{K_{1A}k_{2A}[R_ACl]}{K_{1B}k_{2B}[R_BCl]} \qquad (5)$$

The competition constant κ is then given by eq. (6)

$$\kappa = \frac{K_{1A}k_{2A}}{K_{1B}k_{2B}} \qquad (6)$$

Case 2: If the reaction of R^+ with the nucleophile **4** is much faster than ion recombination, i.e., $k_{-1A}[MCl_{n+1}^-] \ll k_{2A}[\mathbf{4}]$ and $k_{-1B}[MCl_{n+1}^-] \ll k_{2B}[\mathbf{4}]$, the first terms of the sums in eq. (4) can be omitted to give eq. (7), and the resulting competition constant reflects the ratio of the ionization rate constants (eq. 8).

$$\frac{d[P_A]}{d[P_B]} = \frac{k_{1A}[R_ACl]}{k_{1B}[R_BCl]} \tag{7}$$

$$\kappa = \frac{k_{1A}}{k_{1B}} \tag{8}$$

Case 3: If the ion combination ($R^+ + [MCl_{n+1}^-]$) and the reaction of R^+ with **4** have similar rates, a simplification of eq. (4) is not possible, and eq. (9) shows that κ, defined as above, is not constant but depends on the concentrations $[MCl_{n+1}^-]$ and [**4**]. Since, on the other hand, $[MCl_{n+1}^-]$ depends on the concentrations $[R_ACl]_0$ and $[R_BCl]_0$, the value of κ may depend on the concentrations of the reactants.

$$\kappa = \frac{k_{1A}k_{2A}(k_{-1B}[MCl_{n+1}^-] + k_{2B}[\mathbf{4}])}{k_{1B}k_{2B}(k_{-1A}[MCl_{n+1}^-] + k_{2A}[\mathbf{4}])} \tag{9}$$

An alternative reaction mechanism, attack of allyltrimethylsilane (**4**) at RCl · $ZnCl_2$ complexes was not taken into consideration, since in a case where ionization equilibria and the rate constants k_{2A} and k_{2B} could be independently determined, the observed competition constants were in accord with those calculated from eq. (6)[1]. It is conceivable, however, that this reaction mechanism is operative in cases, where the relative reactivities were found to depend on the reactants' ratio (see below).

Results

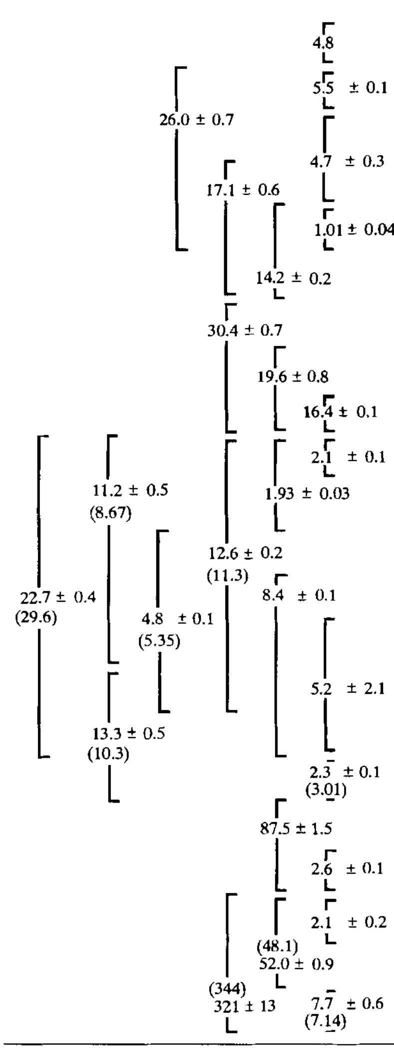
Determinations of the relative reactivities of **1e**/**1f** and of **1d**/**1e** with BCl_3 (15%) as the Lewis acid gave values between 7 and 12, depending on the reactant ratios[5]. Addition of $BnEt_3N^+$ BCl_4^- increased the **1e**/**1f** ratio to 16–19. Obviously, case 3 is realized under these conditions: BCl_4^- is a kinetically stable anion, and chloride transfer from BCl_4^- to Ph_2CH^+ and $TolPhCH^+$ is not much faster than the reaction of these carbenium ions with **4**. When these experiments were performed with the weaker Lewis acid $ZnCl_2 \cdot OEt_2$, the less stable counterion $ZnCl_3^-$ is produced, and v_{-1A} (or v_{-1B}) grows relative to v_{2A} (or v_{2B}) (Scheme 2). Consequently, case 1 becomes realized, and the κ values derived from eq. (6) are competition *constants*, independent of the reactant ratio. All competition experiments have, therefore, been carried out with $ZnCl_2 \cdot OEt_2$ as the Lewis acid.

Table 2 in the Experimental Section shows that the κ values determined in this way are independent of the reactant ratios. Exceptions are the chloro ethers **1o** and **1y**. While the κ values determined for **1o** were dependent on the reactant ratios, chloro ether **1y** and allyltrimethylsilane (**4**) gave only a very low yield of **5y** under the conditions of the competition experiments.

A poor reproducibility was also found for the relative reactivities of **1g** and **1h**. Since in this case no relationship between reactivity ratio and ratio of the reactants was observed, the averaged value given in Scheme 3 can be considered to represent the approximate reactivity of trityl chloride (**1h**).

The logarithms of the competition constants give an overdetermined set of linear equations which is solved by the method of least squares to yield the k_{rel} values shown in Scheme 3.

Scheme 3. Competition constants and relative reactivities of the alkyl chlorides **1a**–**x** towards allyltrimethylsilane (**4**) (CH_2Cl_2, −70°C)[a]



	k_{rel}	k_{EtOH}[b]
1a	1.45×10^{11}	57.54
1b	3.03×10^{10}	5.37
1c	5.50×10^{9}	0.50
1p	1.36×10^{9}	3.26×10^{-2}
1d	1.15×10^{9}	2.00×10^{-2}
1k	1.15×10^{9}	2.00×10^{-2}
1e	8.07×10^{7}	1.23×10^{-3}
1q	5.20×10^{7}	6.76×10^{-3}
1i	4.38×10^{7}	1.78×10^{-2}
1f	2.65×10^{6}	5.37×10^{-5}
1t	1.26×10^{6}	2.75×10^{-5}
1n	1.26×10^{6}	1.66×10^{-5}
1j	7.44×10^{5}	3.89×10^{-4}
1h	4.48×10^{5}	5.62
1r	3.08×10^{5}	4.57×10^{-5}
1l	2.35×10^{5}	9.12×10^{-6}
1g	8.97×10^{4}	8.13×10^{-6}
1v	2.99×10^{4}	7.59×10^{-6}
1m	8.93×10^{2}	1.66×10^{-7}
1u	3.44×10^{2}	1.95×10^{-7}
1s	1.64×10^{2}	1.58×10^{-7}
1x	7.1	8.51×10^{-8}
1w	1	2.51×0^{-11}

[a] Calculated competition constants that deviate from experimental ones by more than 4% are given in parentheses. – [b] Solvolysis rate constants in 100% ethanol at 25°C. Literature data converted to these conditions according to ref.[19]. See also ref.[5]

The range of relative reactivities shown in Figure 1 covers more than eleven orders of magnitude. It is easily recognized that those precursors which form the best stabilized carbenium ions are the most reactive electrophiles in presence of catalytic amounts of $ZnCl_2 \cdot OEt_2$.

A more detailed discussion of the relationship between structure and reactivity is superfluous since Figure 2 reveals a linear relationship between the k_{rel} values determined in this work and the ethanolysis rate constants of these substrates. The same arguments, which have been used to

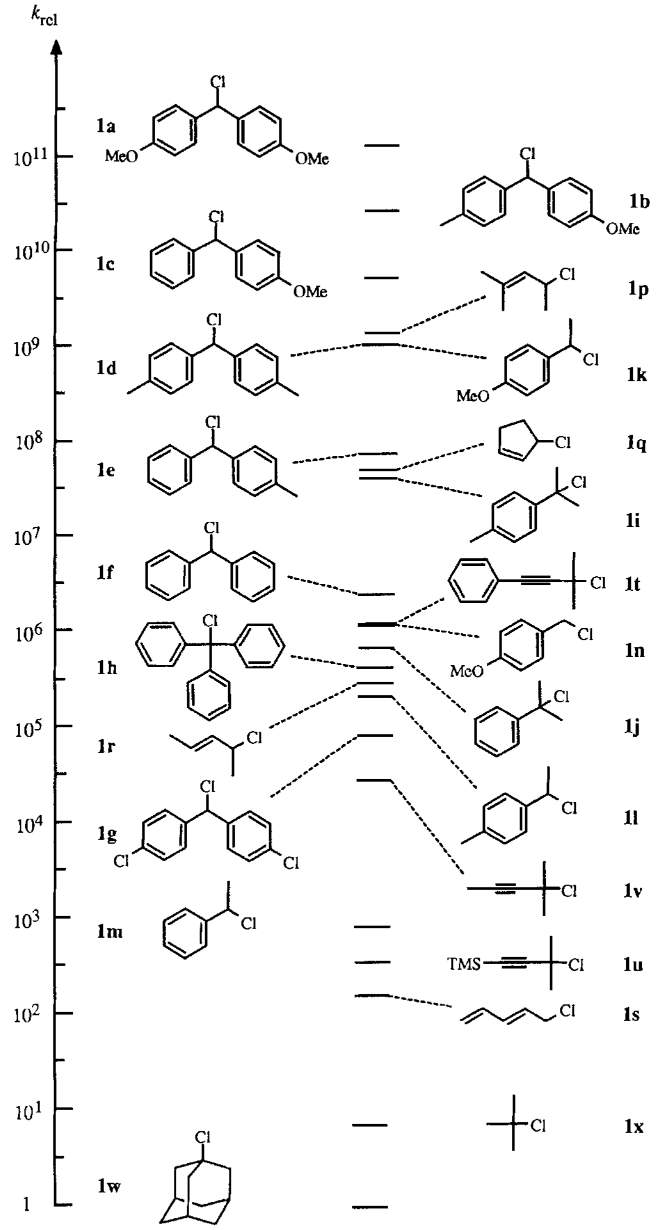


Figure 1. Relative electrophilicities of alkyl chlorides towards allyltrimethylsilane (**4**) (cat. Zn Cl_2, CH_2Cl_2, $-70°C$)

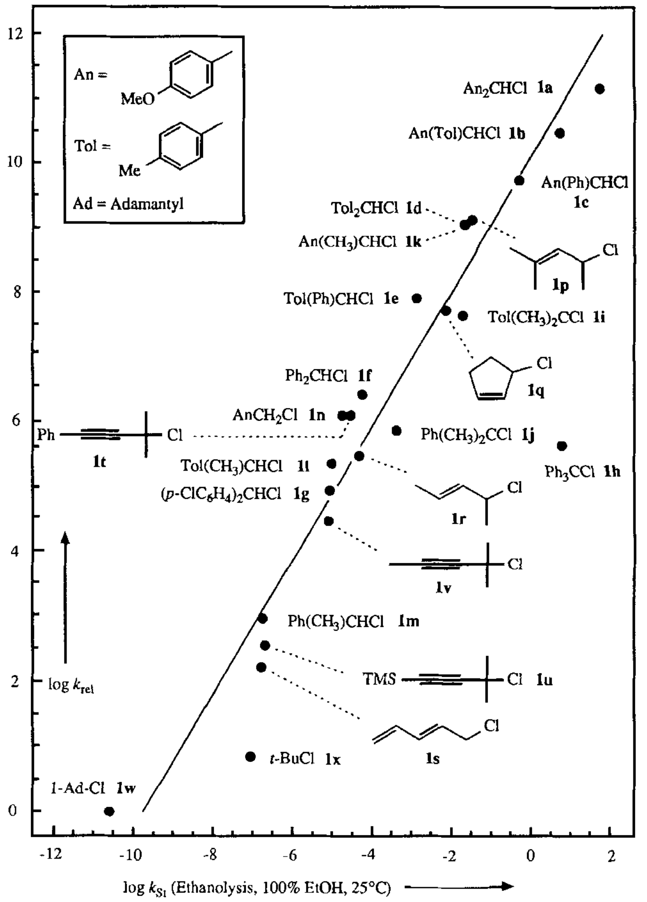


Figure 2. Correlation of the relative reactivities of alkyl chlorides **1a**–**x** towards allyltrimethylsilane (**4**) (CH_2Cl_2, $-70°C$) with their ethanolysis rate constants (25°C). – The value for Ph_3CCl has not been used for calculating the correlation equation log k_{rel} = 1.036 log k_{EtOH} + 10.1 (r = 0.971)

rationalize the relative S_N1 reactivities of alkyl chlorides[6] can, therefore, be employed to explain the reactivity order of Figure 1.

The slope of 1.036 calculated for the correlation in Figure 2 reduces to 0.7 when the different reference temperatures are taken into account (assumption: ΔS^0 and $\Delta S^{\neq}$ are equal for all reactions). One can conclude, therefore, that the carbenium character at the $\mathbf{1}^+$ fragment is more developed in the ethanolysis transition states of **1a**–**y** than in the transition states of the Lewis acid-catalyzed reactions of **1** with **4**.

Triphenylmethyl chloride (**1h**) spectacularly deviates from the correlation shown in Figure 2. Its alkylating ability is approximately 100000 times smaller than expected on the basis of its S_N1 reactivity. The steric strain which is built up during electrophilic attack of the trityl cation at **4** is obviously so great that **1h** shows an anomalously low electrophilicity. In accord with this finding, we have previously reported that the absolute rate constants for the attack of trityl cations at CC double bonds are 5000 times smaller than those of diarylcarbenium ions of the same pK_R^+ value[7]. Since other tertiary chlorides follow the same correlation as secondary and primary derivatives (Figure 2, *t*BuCl also deviates somewhat!), we have to conclude that trityl chlorides are exceptional in this respect. Steric effects are certainly not absent for the other compounds, but their magnitude appears to be small compared to the electronic effects which predominantly control the 10^{11} reactivity range, considered in Figure 2.

Conclusion

The formation of 1:1 products according to eq. (1) is possible, if the reactants **1** are more electrophilic than the products **3**. Figure 2 now corroborates our earlier working hypothesis[2a,8] that solvolysis rates of reactants **1** and products **3** (or suitable model compounds) can be used to predict relative electrophilicities of alkyl halides in the presence of catalytic amounts of Lewis acids. This simple relationship has long been masked by the fact that cationic tritylations are not easily performed, though trityl halides undergo S_N1 reactions very rapidly. Since trityl cations are among the most intensively investigated carbenium ions, their behavior was misleading. It is now clear that trityl chlorides are abnormally poor electrophiles, and there are probably only few other types of bulky electrophiles that show similar behavior. In general, S_N1 reactivities provide a reliable index for designing Lewis acid-catalyzed alkylations (eq. 1).

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Experimental

^1H NMR: EM 390 (Varian) and XL 200 (Varian). – ^{13}C NMR: XL 200 (Varian). – MS: 70–250E (VG Instruments). – HPLC: Knauer HPLC pump 64 with Rheodyne 7125 injection valve, LDC/Milton-Roy spectroMonitor D, and Hitachi-Merck D2000 integrator. 250 × 4.5-mm columns packed with Nucleosil RP_{18}, 3 or 5 μm particles. – GC: Carlo Erba GC 6000 Vega Series 2 with 50 m SE-30 column.

Reactants: Commercially available allyltrimethylsilane (**4**) was distilled over $LiAlH_4$ before use. *Allyltripropylsilane* was synthesized in analogy to a procedure described in ref.[4]: A solution of allyl chloride (19.1 ml, 17.9 g, 0.23 mol) in THF (200 ml) was added dropwise (2 h) to a mixture of magnesium (8.5 g, 0.35 mol), chlorotripropylsilane (25 g, 0.13 mol), and THF (100 ml) kept in an ultrasound bath at 0°C. The mixture was then stirred at 40°C (2 h) at ambient temp. (15 h). After addition of a saturated, solution of NH_4Cl in 2 M aqueous ammonia (150 ml), the layers were separated, and the aqueous layer was extracted with three 50-ml portions of ether. The combined organic layers were dried with Na_2SO_4 and distilled to give 20.8 g (81%) of allyltripropylsilane with b.p. 56–57°C/1.7 mbar (ref.[9] 216–217°C/748 Torr). – ^1H NMR (90 MHz, $CDCl_3$): δ = 0.38–0.68 (m, 6H, CH_2Si), 0.95 (t, J = 7 Hz, 9H, CH_3), 1.11–1.47 (m, 6H, $CH_2CH_2CH_3$), 1.53 (br. d, J = 8 Hz, 2H, $CH_2CH=$), 4.68–5.00 (m, 2H, $=CH_2$), 5.53–6.06 (m, 1H, $=CH-$).

Alkyl chlorides **1** are either commercially available or have been obtained by treatment of the corresponding alcohols or alkenes with HCl (conc. aqueous or gaseous). For details see ref.[5]

General Procedure for the Reactions of **1a–y** *with Allyltrimethylsilane* (**4**): Compounds **1** and **4** (1.5 equivalents) were dissolved in CH_2Cl_2 (20 ml per gram of **1**). The solutions were cooled at −78°C (N_2 protection), before the catalyst $ZnCl_2 \cdot (OEt_2)_{1.03}$[10] (0.2 equiv.) was added. After a certain period (see Table 1), the mixture was washed with an equal volume of conc. aqueous ammonia. The phases were separated, and the organic layer was dried with $CaCl_2$, filtered, and evaporated.

4,4-Bis(4-methoxyphenyl)-1-butene (**5a**): Chlorobis(4-methoxyphenyl)methane (**1a**) (2.00 g, 7.60 mmol) and **4** (1.30 g, 11.4 mmol) reacted within 1 h to give 1.50 g (74%) of **5a** with m.p. 38–39°C (from pentane) (ref.[4] 36.5–37.5°C). – ^1H NMR (90 MHz, $CDCl_3$): δ = 2.75 (br. t, J = 8 Hz, 2H, 3-H), 3.76 (s, 6H, OCH_3), 3.92 (t, J = 8 Hz, 1H, 4-H), 4.83–5.17 (m, 2H, $=CH_2$), 5.50–6.0 (m, 1H, $=CH-$), 6.82, 7.13 (AA'BB' system, J_{AB} = 9 Hz, 8H, aromatic H).

4-(4-Methoxyphenyl)-4-(4-methylphenyl)-1-butene (**5b**): Chloro(4-methoxyphenyl)(4-methylphenyl)methane (**1b**) (2.50 g, 10.1 mmol) and **4** (1.73 g, 15.1 mmol) reacted within 1 h to give 2.43 g (95%) of **5b** as a viscous oil[11]. – ^1H NMR (90 MHz, $CDCl_3$): δ = 2.32 (s, 3H, CH_3), 2.76 (br. t, J = 8 Hz, 2H, 3-H), 3.75 (s, 3H, OCH_3), 3.93 (t, J = 8 Hz, 1H, 4-H), 4.80–5.16 (m, 2H, $=CH_2$), 5.46–5.97 (m, 1H, $=CH-$), 6.78, 7.08 (AA'BB'-system, J_{AB} = 9 Hz, 4H, $C_6H_4OCH_3$), 7.05 (s, 4H, $C_6H_4CH_3$, superimposed by the AA'BB' system).

4-(4-Methoxyphenyl)-4-phenyl-1-butene (**5c**): Chloro(4-methoxyphenyl)phenylmethane (**1c**) (4.70 g, 20.2 mmol) and **4** (3.47 g, 30.4 mmol) reacted within 1 h to give 4.19 g (87%) of **5b**, colorless needles with m.p. 63.5–64°C (from pentane) (ref.[4] 62.5–63.5°C). – ^1H NMR (90 MHz, $CDCl_3$): δ = 2.78 (br. t, J = 8 Hz, 2H, 3-H), 3.76 (s, 3H, OCH_3), 3.97 (t, J = 8 Hz, 1H, 4-H), 4.83–5.17 (m, 2H, $=CH_2$), 5.50–6.0 (m, 1H, $=CH-$), 6.82, 7.12 (AA'BB' system, J_{AB} = 9 Hz, 4H, $C_6H_4OCH_3$), 7.26 (br. s, 5H, C_6H_5, superimposed by the AA'BB' system).

4,4-Bis(4-methylphenyl)-1-butene (**5d**) see ref.[12] For conditions used in this work, see Table 1.

4-(4-Methylphenyl)-4-phenyl-1-butene (**5e**)[13]: Chloro(4-methylphenyl)phenylmethane (**1c**) (2.20 g, 10.2 mmol) and **4** (1.71 g, 15.0 mmol) reacted within 1 h to give 2.05 g (91%) of **5e** with b.p. 120°C (bath)/4 · 10^{-5} mbar. – ^1H NMR (90 MHz, $CDCl_3$): δ = 2.27 (s, 3H, CH_3), 2.78 (br. t, J = 8 Hz, 2H, 3-H), 3.95 (t, J = 8 Hz, 1H, 4-H), 4.80–5.15 (m, 2H, $=CH_2$), 5.46–5.97 (m, 1H, $=CH-$), 7.10 (s, 4H, $C_6H_4CH_3$), 7.22 (mc, 5H, C_6H_5).

4,4-Diphenyl-1-butene (**5f**) see ref.[12] For conditions used in this work, see Table 1.

4,4-Bis(4-chlorophenyl)-1-butene (**5g**)[13]: Chlorobis(4-chlorophenyl)methane (**1g**) (2.00 g, 7.40 mmol) and **4** (1.27 g, 11.1 mmol) reacted within 3 h to give 1.84 g (90%) of **5g** as a viscous oil. – ^1H NMR (90 MHz, $CDCl_3$): δ = 2.73 (br. t, J = 8 Hz, 2H, 3-H), 3.95 (t, J = 8 Hz, 1H, 4-H), 4.82–5.15 (m, 2H, $=CH_2$), 5.42–5.92 (m, 1H, $=CH-$), 6.95–7.33 (m, 8H, aromatic H).

4,4,4-Triphenyl-1-butene (**5h**) see ref.[7] For conditions used in this work, see Table 1.

4-Methyl-4-(4-methylphenyl)-1-pentene (**5i**): 2-Chloro-2-(4-methylphenyl)propane (**1i**) (0.84 g, 5.0 mmol) and **4** (0.86 g, 7.5 mmol) were combined for 2 h to yield 800 mg (92%) of **5i** with b.p. 70°C (bath)/1 mbar. – ^1H NMR (200 MHz, $CDCl_3$): δ = 1.28 (s, 6H, CH_3), 2.32 (s, 3H, aryl-CH_3), 2.35 (br. d, J = 7.2 Hz, 2H, 3-H), 4.89–5.03 (m, 2H, $=CH_2$), 5.45–5.68 (m, 1H, $=CH-$), 7.11, 7.24 (AA'BB' system, J_{AB} = 8 Hz, 4H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 20.85 (q, aryl-CH_3), 28.59 (q, CH_3), 37.22 (s, C-4), 48.83 (t, C-3), 116.77 (t, C-1), 125.69 (d, C_o), 128.72 (d, C_m), 134.85 (s, C_p), 135.65 (d, C-2), 147.55 (s, C_i). – MS (70 eV), m/z (%): 174 (0.7) [M^+], 159 (0.6), 133 (100), 105 (32), 93 (10). – $C_{13}H_{18}$: calcd. 174.14085; found 174.13798 (MS).

4-Methyl-4-phenyl-1-pentene (**5j**)[14]: 2-Chloro-2-phenylpropane (**1j**) (3.10 g, 20.0 mmol) and **4** (3.42 g, 30.0 mmol) reacted for 60 h to yield 2.87 g (90%) of **5j** with b.p. 50°C (bath)/1.2 mbar (ref.[14] 38–39°C/0.7 mbar). – ^1H NMR (200 MHz, $CDCl_3$): δ = 1.30 (s, 6H, CH_3), 2.36 (br. d, J = 7 Hz, 2H, 3-H), 4.90–5.03 (m, 2H, $=CH_2$), 5.45–5.70 (m, 1H, $=CH-$), 7.12–7.42 (m, 5H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 28.50 (q, CH_3), 37.56 (s, C-4), 48.84 (t, C-3), 116.88 (t, C-1), 125.50 (d, C_p), 125.78 (d, C_o), 128.01 (d, C_m), 135.51 (d, C-2), 149.15 (s, C_i). – MS (70 eV), m/z (%): 160 (0.5) [M^+], 145 (0.7), 119 (100), 91 (48), 79 (8). (ref.[14] MS: 160 [M^+], 145, 119 (100)).

4-(4-Methoxyphenyl)-1-pentene (**5k**): 1-Chloro-1-(4-methoxyphenyl)ethane (**1k**) (0.80 g, 4.7 mmol) and **4** (0.80 g, 7.0 mmol) reacted for 2 h to yield 710 mg (86%) of **5k** with b.p. 40–45°C (bath)/0.15 mbar. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.22 (d, J = 7 Hz, 3H, CH_3), 2.16–2.45 (m, 2H, 3-H), 2.74 (sext, J = 7 Hz, 1H, 4-H), 3.77 (s, 3H, OCH_3), 4.91–5.04 (m, 2H, $=CH_2$), 5.60–5.83 (m, 1H, =CH–), 6.84, 7.11 (AA'BB' system, J_{AB} = 8.8 Hz, 4H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 21.71 (q, CH_3), 38.91 (d, C-4), 42.87 (t, C-3), 55.16 (q, OCH_3), 113.62 (d, C_m), 115.78 (t, C-1), 127.80 (d, C_o), 137.27 (d, C-2), 139.13 (s, C_i), 157.22 (s, C_p). – MS (70 eV), *m/z* (%): 176 (5.2) [M^+], 161 (0.3), 135 (100), 105 (11), 91 (5). – $C_{12}H_{16}O$: calcd. 176.12012; found 176.12152 (MS).

4-(4-Methylphenyl)-1-pentene (**5l**): 1-Chloro-1-(4-methylphenyl)-ethane (**1l**) (2.00 g, 13.0 mmol) and **4** (2.22 g, 19.3 mmol) reacted for 24 h to yield 1.79 g (86%) of **5l** with b.p. 43°C (bath)/1 mbar. – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 1.20 (d, J = 7 Hz, 3H, CH_3), 2.28 (s, 3H, aryl-CH_3), 2.04–2.45 (m, 2H, CH_2, superimposed by singlet of aryl-CH_3), 2.70 (sext, J = 7 Hz, 1H, 4-H), 4.76–5.06 (m, 2H, $=CH_2$), 5.40–5.9 (m, 1H, =CH–), 6.98 (s, 4H, aromatic H).

4-Phenyl-1-pentene (**5m**) see ref.[15] For conditions used in this work, see Table 1.

4-(4-Methoxyphenyl)-1-butene (**5n**): 4-Methoxybenzyl chloride (**1n**) (1.00 g, 6.40 mmol) and **4** (1.09 g, 9.53 mmol) reacted for 1.5 h to yield 880 mg (85%) of **5n** with b.p. 55–60°C (bath)/0.9 mbar. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.26–2.43 (m, 2H, 3-H), 2.61–2.74 (m, 2H, 4-H), 3.78 (s, 3H, OCH_3), 4.93–5.17 (m, 2H, $=CH_2$), 5.75–6.00 (m, 1H, =CH–), 6.83, 7.11 (AA'BB' system, J_{AB} = 8.8 Hz, 4H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 34.44, 35.76 (2 t, C-3, C-4), 55.21 (q, OCH_3), 113.66 (d, C_m), 114.82 (t, $=CH_2$), 129.27 (d, C_o), 133.93 (s, C_i), 138.17 (d, =CH–), 157.70 (s, C_p). – MS (70 eV), *m/z* (%): 162 (10.5) [M^+], 121 (100), 91 (6), 78 (16), 77 (12).

4-Methoxy-4-phenyl-1-butene (**5o**)[16]: α-Methoxybenzyl chloride (**1o**) (2.00 g, 12.8 mmol) and **4** (2.19 g, 19.2 mmol) reacted for 15 h to yield 1.91 g (92%) of **5o** with b.p. 38°C (bath)/1 mbar (ref.[16] 75°C/2.5 Torr). – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 2.18–2.78 (m, 2H, 3-H), 3.23 (s, 3H, OCH_3), 4.15 (t, J = 8 Hz, 1H, 4-H), 4.86–5.17 (m, 2H, $=CH_2$), 5.51–6.03 (m, 1H, =CH–), 7.31 (s, 5H, aromatic H).

4,6-Dimethyl-1,5-heptadiene (**5p**): 4-Chloro-2-methyl-2-pentene (**1p**) (2.00 g, 16.9 mmol, including 19% of 4-chloro-4-methyl-2-pentene) and allyltripropylsilane (4.36 g, 22.0 mmol) reacted for 2 h to yield 1.21 g (58%) of **5p** with b.p. 60°C (bath)/79 mbar. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.92 (d, J = 6.8 Hz, 3H, 4-CH_3), 1.61 (d, J = 1.4 Hz, 3H, *cis*-CH_3), 1.68 (d, J = 1.4 Hz, 3H, *trans*-CH_3), 1.96–2.04 (m, 2H, 3-H), 2.33–2.46 (m, 1H, 4-H), 4.89–5.04 (m, 3H, $=CH_2$, 5-H), 5.66–5.87 (m, 1H, 2-H). – ^{13}C NMR ($CDCl_3$): δ = 17.96 (q, *cis*-CH_3), 20.75 (q, 4-CH_3), 25.76 (q, *trans*-CH_3), 32.50 (d, C-4), 42.01 (t, C-3), 115.23 (t, C-1), 130.05 (s, C-6), 130.69 (d, C-5), 137.65 (d, C-2). – GC-MS (70 eV), *m/z* (%): 124 (1.3) [M^+], 109 (1), 83 (100), 67 (10), 55 (64), 41 (46). – The product contains 5% of the isomeric 4,4-dimethyl-1,5-heptadiene, detected by the following NMR signals: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.95 (s, CH_3), 5.35–5.40 (m, 5-H, 6-H). – ^{13}C-NMR ($CDCl_3$): δ = 27.06 (q, 4-CH_3). – GC-MS (70 eV), *m/z* (%): 109 (1.4), 83 (100), 67 (9), 55 (62), 41 (38). – C_9H_{16}: calcd. 124.12520; found 124.12535 (MS).

3-Allyl-1-cyclopentene (**5q**): 3-Chloro-1-cyclopentene (**1q**) (8.20 g, 80.0 mmol) and **4** (9.70 g, 85.0 mmol) reacted for 1 h to yield 4.34 g (50%) of **5q** with b.p. 88–89°C/400 mbar. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.35–1.54, 1.96–2.36 (m, 6H, 3 CH_2), 2.64–2.84 (m, 1H, 3-H), 4.95–5.09 (m, 2H, $=CH_2$), 5.65–5.89 (m, 3H, =CH–). – ^{13}C NMR ($CDCl_3$): δ = 29.18 (t, C-4), 31.98 (t, C-5), 40.21 (t, CH_2, allyl part), 45.10 (d, C-3), 115.27 (t, $=CH_2$), 130.60 (d, C-1), 134.62 (d, C-2), 137.55 (d, =CH–, allyl part). – MS (70 eV), *m/z* (%): 108 (1.6) [M^+], 77 (2), 67 (100), 66 (10), 41 (15).

4-Methyl-1,5-heptadiene (**5r**)[17]: (*E*)-4-Chloro-2-pentene (**1r**) (9.00 g, 86.1 mmol) and **4** (10.7 g, 93.6 mmol) reacted for 3 h to yield 3.49 g (37%) of **5r** with b.p. 66–72°C/397 mbar. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.96 (d, J = 6.4 Hz, 3H, 4-CH_3), 1.65 (d, J = 4.8 Hz, 3H, 7-H), 1.97–2.26 (m, 3H, 3-H, 4-H), 4.90–5.05 (m, 2H, $=CH_2$), 5.25–5.52 (m, 2H, 5-H, 6-H), 5.65–5.90 (m, 1H, 2-H). – ^{13}C NMR ($CDCl_3$): δ = 17.94 (q, C-7), 20.09 (q, 4-CH_3), 36.43 (d, C-4), 41.54 (t, C-3), 115.45 (t, C-1), 123.02 (d, C-6), 136.82, 137.47 (2 d, C-2, C-5). – MS (70 eV), *m/z* (%): 110 (1.2) [M^+], 95 (5), 69 (100), 53 (5), 41 (68).

1,3,7-Octatriene (**5s**): 2.00 g (19.5 mmol) of (*E*)-5-Chloro-1,3-pentadiene (**1s**) and allyltripropylsilane (5.02 g, 25.3 mmol) reacted for 67 h at –40°C to yield 140 mg (7%) of **5s** with b.p. 25°C (bath)/0.8 mbar. The product contains 10% of impurities (GC). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.14–2.25 (m, 4H, 5-H, 6-H), 4.94–5.16 (m, 4H, $=CH_2$), 5.46–6.42 (m, 4H, =CH–). – ^{13}C NMR ($CDCl_3$): δ = 31.93, 33.34 (2 t, C-5, C-6), 114.84, 115.00 (2 t, C-1, C-8), 131.29 (d, C-3), 134.43 (d, C-4), 137.18, 138.08 (2 d, C-2, C-7). – MS (70 eV), *m/z* (%): 108 (13.3) [M^+], 93 (14), 67 (100), 41 (57).

4,4-Dimethyl-6-phenyl-1-hexen-5-yne (**5t**): 3-Chloro-3-methyl-1-phenyl-1-butyne (**1t**) (2.00 g, 11.2 mmol) and **4** (1.92 g, 16.8 mmol) reacted for 2 h to yield 1.87 g (91%) of **5t** with b.p. 40°C (bath)/0.1 mbar. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.27 (s, 6H, 4-CH_3), 2.25 (dt, J_{32} = 7.2, J_{31} = 1.2 Hz, 2H, 3-H), 5.05–5.15 (m, 2H, $=CH_2$), 5.90–6.13 (m, 1H, =CH–), 7.23–7.38 (m, 5H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 28.87 (q, 4-CH_3), 31.45 (s, C-4), 47.7 (t, C-3), 80.63 (s, C-6), 96.87 (s, C-5), 117.37 (t, C-1), 123.95 (s, C_i), 127.45 (d,C_p), 128.11 (d, C_m), 131.56 (d, C_o), 135.29 (d, C-2). – MS (70 eV), *m/z* (%): 184 (5.9) [M^+], 169 (2), 143 (100), 128 (21), 115 (6). – $C_{14}H_{16}$: calcd. 184.12520; found 184.12568 (MS).

4,4-Dimethyl-6-(trimethylsilyl)-1-hexen-5-yne (**5u**): 3-Chloro-3-methyl-1-(trimethylsilyl)-1-butyne (**1u**) (2.00 g, 11.4 mmol) and **4** (1.90 g, 16.7 mmol) reacted for 20 h to yield 1.52 g (74%) of **5u** with b.p. 70–80°C (bath)/40 mbar. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.10 [s, 9H, $Si(CH_3)_3$], 1.14 (s, 6H, 4-CH_3), 2.12 (br. d, J = 7.3 Hz, 2H, 3-H), 4.93–5.08 (m, 2H, $=CH_2$), 5.78–6.02 (m, 1H, 2-H). – ^{13}C NMR ($CDCl_3$): δ = 0.32 (q, $SiCH_3$), 28.78 (q, 4-CH_3), 31.59 (s, C-4), 47.60 (t, C-3), 83.54 (s, C-6), 114.22 (s, C-5), 117.22 (t, C-1), 135.21 (d, C-2). – GC-MS (70 eV), *m/z* (%): 180 (0.8) [M^+], 165 (2), 139 (25), 123 (12), 97 (100), 73 (27). – The product contains 6% of the isomeric 6-methyl-4-(trimethylsilyl)-1,4,5-heptatriene (GC): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.62 (s, CH_3) terminal methyl groups. – GC-MS (70 eV), *m/z* (%): 180 (6.8) [M^+], 165 (4), 139 (4), 123 (9), 97 (42), 73 (100). – $C_{11}H_{20}Si$: calcd. 180.13343; found 180.13345 (MS).

4,4-Dimethyl-1-hepten-5-yne (**5v**): 4-Chloro-4-methyl-2-pentyne (**1v**) (2.20 g, 18.8 mmol) and allyltripropylsilane (4.84 g, 24.3 mmol) reacted for 48 h to yield 1.15 g (50%) of **5v** with b.p. 80°C (bath)/87 mbar. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.15 (s, 6H, 4-CH_3), 1.79 (s, 3H, 7-H), 2.13 (br. d, J = 7.2 Hz, 2H, 3-H), 4.98–5.11 (m, 2H, $=CH_2$), 5.83–6.07 (m, 1H, =CH–). – ^{13}C NMR ($CDCl_3$): δ = 3.48 (q, C-7), 29.14 (q, 4-CH_3), 30.80 (s, C-4), 47.88 (t, C-3), 75.35 (s, C-6), 86.29 (s, C-5), 116.97 (t, C-1), 135.62 (d, C-2). – MS (70 eV), *m/z* (%): 122 (1.1) [M^+], 107 (28), 81 (100), 79 (30), 53 (41), 41 (47).

1-Allyladamantane (**5w**): 1-Adamantyl chloride (**1w**) (2.00 g, 11.7 mmol) and **4** (2.00 g, 17.5 mmol) reacted for 6 d at –28°C and 48 h at 0°C. The product contained 7% of **1w** (GC) and was heated under reflux in acetone/water (1:1) for 60 h to hydrolyze **1w**. The resulting 1-adamantanol was removed by filtration through silica gel using pentane as the eluent. Distillation yields 700 mg (34%) of **5w** with b.p. 50–55°C (bath)/0.8 mbar. – ^{1}H NMR (200 MHz, CDCl$_3$): δ = 1.22–2.02 (m, 15H, adamantyl-H), 1.94 (br. s, 2H, CH$_2$, allyl part, superimposed by adamantyl-H), 4.85–5.05 (m, 2H, =CH$_2$), 5.69–5.91 (m, 1H, =CH–). – ^{13}C NMR (CDCl$_3$): δ = 28.75 (d, C-3), 32.66 (s, C-1), 37.14 (t, C-4), 42.40 (t, C-2), 49.06 (t, CH$_2$, allyl part), 116.47 (t, =CH$_2$), 134.94 (d, =CH–). – MS (70 eV), *m/z* (%): 176 (0.9) [M$^+$], 135 (100), 107 (5), 93 (13), 79 (15), 67 (7).

4,4-Dimethyl-1-pentene (**5x**): Unlike the other reactions, which were performed according to the general procedure, this reaction has been carried out without a solvent. *tert*-Butyl chloride (**1x**) (10.4 ml, 94.4 mmol) was dropped to a suspension of **4** (10.4 g, 91.0 mmol) and dry ZnCl$_2$ (7.00 g, 51.2 mmol) at 0°C within 3 h. The mixture was kept at this temp. for 48 h. After workup with 50 ml 5 N HCl, distillation yielded 3.56 g (40%) of **5x** with b.p. 73°C. – ^{1}H NMR (90 MHz, CDCl$_3$): δ = 0.90 (s, 9H, CH$_3$), 1.95 (br. d, J = 8 Hz, 2H, 3-H), 4.82–5.12 (m, 2H, =CH$_2$), 5.58–6.10 (m, 1H, =CH–).

4-Methoxy-1-butene (**5y**)[18]: Unlike the other reactions, which were performed according to the general procedure, this reaction has been carried out without a solvent. Chloromethyl methyl ether (**1y**) (11.0 ml, 145 mmol) was dropped to a suspension of **4** (14.3 g, 125 mmol) and dry ZnCl$_2$ (8.80 g, 64.3 mmol) at –78°C within 2 h. The mixture was kept at this temp. for 10 h. After washing with 50 ml of a half-saturated aqueous ammonium chloride solution, drying with CaCl$_2$, and filtration, distillation yielded 2.60 g (24%) of **5y** with b.p. 68°C (ref.[18] 68–69°C/760 Torr). – ^{1}H NMR (90 MHz, CDCl$_3$): δ = 2.26 (mc, 2H, 3-H), 3.26 (s, 3H, OCH$_3$), 3.35 (t, J = 7 Hz, 2H, CH$_2$O, superimposed by singlet of OCH$_3$), 4.87–5.18 (m, 2H, =CH$_2$), 5.50–6.03 (m, 1H, =CH–).

Competition Experiments: In order to determine the relative reactivity of two electrophiles, the competition constant κ, as defined by eqs. (6) and (8) is introduced into eqs. (5) and (7) to give (10)

Table 2. Determination of the competition constants in CH$_2$Cl$_2$ (10 ml) at –70°C

	R_ACl / mg		R_BCl / mg	**4** / mg	$[LA]/[R_ACl]_0$[a] (molar ratio)	$[P_A]/[P_B]$ (molar ratio)	Time	Standard[b]	$\kappa_{A/B}$[f]
1a	18.9	**1b**	35.5	574.6	0.20[c]	3.46	20 min	PPT	(7.4)
	19.2		72.0	574.6	0.20[c]	1.26	20 min	PPT	(6.0)
	18.6		105.8	574.6	0.20[c]	0.71	20 min	PPT	4.8
1b	25.1	**1c**	47.3	5.7	0.20	3.16	75 s	PD	(6.6)
	25.2		94.6	5.7	0.20	1.30	75 s	PD	5.4
	27.1		182.3	5.7	0.20	0.75	75 s	PD	5.6
1c	23.4	**1d**	46.8	5.7	0.20	2.43	3 min	PHX	5.3
	25.0		101.3	5.7	0.20	0.98	3 min	PHX	4.1
	26.4		157.6	5.7	0.20	0.76	3 min	PHX	4.8
1d	70.0	**1e**	293.8	17.1	0.30	2.73	5 min	PO	14.6
	70.5		472.8	17.1	0.30	1.69	5 min	PO	13.8
	71.1		570.0	17.1	0.30	1.58	5 min	PO	14.1
1e	70.9	**1f**	368.1	17.1	0.30	4.40	5 min	PHX	29.2
	70.3		557.7	17.1	0.30	2.96	5 min	PHX	30.3
	76.5		753.2	17.1	0.30	2.53	5 min	PHX	31.7
1f	69.8	**1g**	326.7	17.1	0.50	5.25	5 min	PHX	22.1
	60.9		574.2	17.1	0.50	2.77	5 min	PHX	22.6
	62.7		822.7	17.1	0.50	2.11	5 min	PHX	23.5
1h	27.5	**1g**	28.1	716	0.08[d]	1.94	34 d	PHP	2.06
	56.5		29.5	716	0.08[d]	7.87	34 d	PHP	4.34
	28.5		56.0	716	0.08[d]	4.73	34 d	PHP	9.21
1i	23.0	**1f**	81	5.7	0.50	4.94	3 min	HMB	16.5
	21.5		140	5.7	0.50	2.70	3 min	HMB	16.5
	25.8		207	5.7	0.50	2.18	3 min	HMB	16.3
1j	24.7	**1g**	112.3	5.7	0.50	3.00	12 min	PO	8.4
	25.6		170.8	5.7	0.50	2.13	12 min	PO	8.5
	24.5		249.5	5.7	0.50	1.33	12 min	PO	8.2
1b	15.9	**1k**	98.9	4.6	0.50	4.59	16 min	PHX	25.3
	14.1		174.8	4.6	0.50	1.24	16 min	PHX	26.7
	12.0		248.8	4.6	0.50	0.61	16 min	PHX	(20.5)
1d	23.8	**1k**	18.2	5.7	0.50	0.93	4 min	PPT	0.96
	23.5		38.9	5.7	0.50	0.48	4 min	PPT	1.08
	57.7		19.4	5.7	0.50	2.17	4 min	PPT	0.99
1f	22.2	**1n**	15.7	5.7	0.50	2.01	21 min	PPT	1.98
	21.1		49.4	5.7	0.50	0.60	21 min	PPT	1.87
	22.2		97.4	5.7	0.50	0.34	21 min	PPT	1.94
1f	25.5	**1l**	95.3	5.7	0.50	2.24	42 min	HMB	12.4
	26.1		145.9	5.7	0.50	1.61	42 min	HMB	12.9
	27.4		200.3	5.7	0.50	1.19	42 min	HMB	12.5
1n	18.0	**1l**	22.4	28.5	0.20	3.70	30 min	PPT	4.7
	16.1		53.5	28.5	0.20	1.28	30 min	PPT	4.7
	30.0		182.1	28.5	0.20	0.69	30 min	PPT	5.0
1p	23.7	**1e**	86.0	11.4	0.15[d]	7.05	1 min	PHX	17.1
	26.1		171.5	11.4	0.15[d]	4.47	1 min	PHX	18.2
	22.5		262.5	11.4	0.15[d]	2.12	1 min	PHX	16.0
1q	23.6	**1f**	82.8	20.5	0.20	6.97	1 min	PPT	18.2
	21.3		165.5	19.4	0.20	3.86	1 min	PPT	19.5
	24.6		272.4	21.7	0.20	2.81	1 min	PPT	21.1
1f	64.3	**1t**	19.5	5.7	0.17[e]	5.40	2 min	HMB	1.9
	136.3		20.0	5.7	0.08[e]	13.2	2 min	HMB	2.2
	192.7		20.2	5.7	0.06[e]	23.7	2 min	HMB	2.3
1f	26.4	**1r**	113.2	5.7	0.50	1.32	22 min	PHX	12.2
	22.5		110.2	5.7	0.50	0.93	22 min	PHX	10.0
	26.1		168.5	5.7	0.50	0.81	22 min	PHX	11.0
	27.9		234.2	5.7	0.50	0.67	22 min	PHX	11.6
1g	27.0	**1v**	45.8	358	0.88	0.45	16 min	PHP	2.2
	27.6		96.0	358	0.88	0.22	16 min	PHP	2.2
	28.1		147.4	358	0.88	0.15	16 min	PHP	2.4
1o	24.5	**1b**	154.8	5.7	0.50	7.40	25 min	PHX	33.8
	20.6		224.1	5.7	0.50	1.82	25 min	PHX	15.4
	24.8		305.9	5.7	0.50	0.59	25 min	PHX	5.1
1r	94.2	**1v**	107.9	358	0.10	11.6	8 min	E	14.2
	92.9		212.0	358	0.10	5.07	8 min	E	13.3
	94.3		418.9	358	0.10	2.83	8 min	E	12.4
1v	10.2	**1u**	127.8	716	4.00	7.35	10 min	IO	89.9
	9.6		261.9	716	4.00	3.45	10 min	IO	87.9
	9.7		409.9	716	4.00	2.34	10 min	IO	84.7
1m	15.5	**1u**	19.3	716	7.30	2.57	31 min	PPT	2.7
	9.9		14.6	716	7.30	1.20	31 min	PPT	2.5
	14.2		75.1	716	7.30	0.58	31 min	PPT	2.6
1u	17.9	**1s**	41.7	716	18.0	0.62	31 min	PPT	2.5
	20.1		83.7	716	18.0	0.30	31 min	PPT	2.1
	17.5		122.1	716	18.0	0.14	31 min	PPT	1.7
1u	18.3	**1x**	187.2	716	14.0	2.42	20 min	T	52.5
	21.1		374.4	716	14.0	1.58	20 min	T	53.3
	18.5		553.2	716	14.0	0.79	20 min	T	50.2
1u	18.7	**1w**	511.1	716	27.0	9.40	20 min	PPT	297
	17.5		1014.4	716	27.0	5.36	20 min	PPT	341
	18.6		1537.0	716	27.0	2.94	20 min	PPT	325
1x	28.7	**1w**	10.8	1432	18.0[d]	31.8	27 min	E	6.5
	28.7		51.8	1432	18.0[d]	8.52	27 min	E	8.4
	28.7		101.9	1432	18.0[d]	4.19	27 min	E	8.1

[a] Lewis acid (LA): ZnCl$_2$ · (OEt$_2$)$_{1.03}$. – [b] HPLC analysis for the first three quarters of competition experiments (including **1o**/**1b**); GC analysis for the last quarter (starting with **1r**/**1v**). Standards: IO = isooctane, T = toluene, E = ethylbenzene, PPT = 1-phenylpentane, PHX = 1-phenylhexane, PHP = 1-phenylheptane, PO = 1-phenyloctane, PD = 1-phenyldecane, HMB = hexamethylbenzene. – [c] 50 ml of CH$_2$Cl$_2$. – [d] 5 ml of CH$_2$Cl$_2$. – [e] ≅50% of R$_B$Cl. – [f] Because of inaccurate integration (unsymmetrical peaks) the values in parentheses are not used for the calculation of the averaged competition constants.

$$\frac{d[P_A]}{d[P_B]} = \kappa \frac{[R_ACl]}{[R_BCl]} = -\frac{d[R_ACl]}{d[R_BCl]} \quad (10)$$

which can be transformed and integrated to yield (11)

$$\kappa = \frac{\ln[R_ACl]_0 - \ln[R_ACl]_e}{\ln[R_BCl]_0 - \ln[R_BCl]_e} \quad (11)$$

Since $[RCl]_e = [RCl]_0 - [P]$, eq. (11) can be rewritten:

$$\kappa = \frac{\ln[R_ACl]_0 - \ln([R_ACl]_0 - [P_A])}{\ln[R_BCl]_0 - \ln([R_BCl]_0 - [P_B])} \quad (12)$$

According to eq. (12), the calculation of κ requires knowledge of the product concentrations $[P_A]$ and $[P_B]$ in addition to the initial concentration of the competing electrophiles. Their determination is described by the following:

Typical Procedure: Compounds **1f** (22.5 mg, 0.111 mmol), **1q** (100.2 mg, 1.05 mmol), and 1-phenylhexane (internal standard, 21.5 mg, 0.13 mmol) were placed into a 25-ml round-bottom flask (N_2 atmosphere) and dissolved in CH_2Cl_2 (10 ml, freshly distilled from P_2O_5). The flask was sealed with a septum and cooled at −70°C. After 10 min, 16 μl of a 3.52 M solution of $ZnCl_2 \cdot (OEt_2)_{1.03}$ in CH_2Cl_2 was injected and 1 ml of a 0.05 M solution of **4** in CH_2Cl_2 was added within 2 min. After 20 min, methanol (5 ml) and K_2CO_3 (ca. 0.1 g) was added, the solid was separated by centrifugation, and the solution was analyzed by HPLC. In cases, where the product analysis was performed by GC, the Lewis acid was removed from the reaction mixture by washing with an equal volume of half-concentrated aqueous NH_3. The organic solution was then dried with K_2CO_3, filtered and directly injected for GC analysis.

The chromatographic analysis was based on the relative peak areas of products (P_A, P_B) and internal standard (1-phenylpropane, -pentane, -hexane, -heptane, -octane, -decane, or hexamethylbenzene), which were determined by HPLC (detection of the absorbance at 254 nm or refractive index) or GC (FID). Calibration curves based on three of four artificial mixtures of **5** $\equiv P_A$, P_B and internal standard allowed the calculation of $[P_A]$ and $[P_B]$.

Each competition experiment has been performed at least three times with variable ratios $[R_ACl]_0/[R_BCl]_0$. Usually, the quantity of **4** was less than half of the quantity of each of the competitors in order to avoid almost complete consumption of the more reactive electrophile. In cases of very slow reactions, however, the nucleophile **4** and the Lewis acid have been used in excess to speed up the reaction, and the mixtures have been worked up prior to completion of the reactions.

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[1] H. Mayr, C. Schade, M. Rubow, R. Schneider, *Angew. Chem.* **1987**, *99*, 1059–1060; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1029–1030.

[2] [2a] H. Mayr, B. Seitz, I. K. Halberstadt-Kausch, *J. Org. Chem.* **1981**, *46*, 1041–1043. – [2b] H. Mayr, W. Striepe, *J. Org. Chem.* **1983**, *48*, 1159–1165.

[3] T. Sasaki, A. Usuki, M. Ohno, *J. Org. Chem.* **1980**, *45*, 3559–3564.

[4] G. Hagen, H. Mayr, *J. Am. Chem. Soc.* **1991**, *113*, 4954–4961.

[5] J.-P. Dau-Schmidt, Ph. D. Thesis, Medizinische Universität zu Lübeck, **1992**.

[6] P. Vogel, *Carbocation Chemistry*, Elsevier, Amsterdam, **1985**, chapter 7.

[7] C. Schade, H. Mayr, *Makromol. Chem., Rapid Commun.* **1988**, *9*, 477–482.

[8] [8a] H. Mayr, *Angew. Chem.* **1981**, *93*, 202–204; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 184–186. – [8b] H. Mayr, H. Klein, *Chem. Ber.* **1982**, *115*, 3528–3546. – [8c] H. Mayr, H. Klein, G. Kolberg, *Chem. Ber.* **1984**, *117*, 2555–2579.

[9] A. V. Topchiev, N. S. Nametkin, S. G. Durgar'yan, *Issled. v Obl. Kremniiorgan, Soedin., Sintez i Fiz-Khim. Svoistva, Akad. Nauk SSSR. Inst. Neftekhim Sinteza, Sb Statei* **1962**, 28–55; *Chem. Abstr.* **1963**, *59*, 1670g.

[10] H. Mayr, W. Striepe, *J. Org. Chem.* **1985**, *50*, 2995–2998.

[11] R. Schneider, Ph. D. Thesis, Universität Erlangen-Nürnberg, **1987**.

[12] H. Mayr, R. Pock, *Tetrahedron* **1986**, *42*, 4211–4214.

[13] C. Schade, Ph. D. Thesis, Medizinische Universität zu Lübeck, **1988**.

[14] B. Åkermark, A. Ljungqvist, *J. Organomet. Chem.* **1978**, *149*, 97–112.

[15] H. Lehmkuhl, W. Bergstein, D. Henneberg, E. Janssen, O. Olbrysch, D. Reinehr, G. Schomburg, *Liebigs Ann. Chem.* **1975**, 1176–1192.

[16] S. Torii, T. Inokuchi, S. Takagishi, H. Horike, H. Kuroda, K. Uneyama, *Bull. Chem. Soc. Jpn.* **1987**, *60*, 2173–2188.

[17] A. Hosomi, T. Imai, M. Endo, H. Sakurai, *J. Organomet. Chem.* **1985**, *285*, 95–107.

[18] P. E. Peterson, B. R. Bonazza, *J. Am. Chem. Soc.* **1972**, *94*, 5017–5023.

[19] T. W. Bentley, J.-P. Dau-Schmidt, G. Llewellyn, H. Mayr, *J. Org. Chem.* **1992**, *57*, 2387–2392.

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