Kinetics of the Reactions of Carboxonium Ions and Aldehyde Boron Trihalide Complexes with Alkenes and Allylsilanes[‡]

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Abstract: Second order rate constants for the reactions of carboxonium ions Ar(MeO)CH$^+$ and aldehyde−boron trihalide complexes ArCH=O→BX$_3$ with allylsilanes and alkenes have been determined in CH$_2$Cl$_2$ solution. The relative reactivities of these electrophiles are almost independent of the nature of the π-nucleophiles, and it is possible to give an averaged reactivity order. For the electrophiles PhCH=O→BF$_3$, PhCH=O→BCl$_3$, Ph(p-MeOC$_6$H$_4$)CH$^+$, and Ph(MeO)CH$^+$, i.e., for PhCHX$^+$ with X = F$_3$BO$^-$, Cl$_3$BO$^-$, p-MeOC$_6$H$_4$, MeO relative averaged reactivities of $1 : 5 \times 10^2 : 1 \times 10^4 : 4 \times 10^5$ (CH$_2$Cl$_2$, −70 °C) are determined indicating that the electrophilicities of aldehyde−BHal$_3$ complexes are only 3−6 orders of magnitude smaller than those of the corresponding carboxonium ions. The α-methoxy substituted benzyl cations Ar(MeO)CH$^+$ are 3−16 times more reactive (CH$_2$Cl$_2$, 20 °C) than their phenylogous benzhydryl analogues Ar(p-MeOC$_6$H$_4$)CH$^+$.

Lewis acid promoted reactions of aldehydes and acetals with nucleophilic π-systems are of eminent importance in organic synthesis.[1] The mechanisms of these reactions, including the determinations of relative electrophilicities,[2] have intensively been studied,[1c,3] but to our knowledge, rate constants for these reactions have not yet been reported.[4] We have now studied the kinetics of the reactions of carboxonium ions and aldehyde−Lewis acid complexes with alkenes and allylsilanes, and we will show that these data can be used for comparing the reactivities of these electrophiles with those of ordinary carbenium ions.

Generation of the Electrophiles. Alkoxycarbenium ions (carboxonium ions), which have previously been characterized by NMR spectroscopy,[5] have been generated by addition of the corresponding dimethyl acetals to solutions of BCl$_3$ in CH$_2$Cl$_2$ at low temperature. Complete ionization of the acetals was proven by the disappearance of the 246−273 nm absorptions of the acetals and the development of a new band at λ_{max} > 300 nm (Table 1).[6]

As previously described for the corresponding BF$_3$ complexes,[7] the investigated aldehydes give crystalline complexes with BCl$_3$. While the BF$_3$ complexes are stable at 20 °C, the BCl$_3$ complexes often decompose with formation of the corresponding dichloromethylarenes. This reaction takes place within several minutes for the p-chloro- and the unsubstituted benzaldehyde−BCl$_3$ complex, while the corresponding p-anisaldehyde complex can be stored for months at 20 °C. Table 2 shows an increase of the molar absorption coefficient of the B-band[9] in the series of Ar-CHO < Ar-CHO→BF$_3$ < Ar-CHO→BCl$_3$ which is associated with a shift of the absorption maxima. The

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[‡] Dedicated to Professor Rolf Huisgen on the occasion of his 75th birthday.

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Table 1. UV Absorption Maxima of Some Aromatic Dimethyl Acetals and the Corresponding Carboxonium Ions in CH_2Cl_2

Ar	λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})	
	$ArCH(OMe)_2$[a]	$ArCH(OMe)^+$[b]
Ph	246 (26 500)	308 (24 500)
p-MeC_6H_4	257 (24 900)	323 (28 300)
p-$MeOC_6H_4$	273 (30 200)	356 (37 000)

[a] At 20 °C. [b] Ionization of the acetals with BCl_3 at −70 °C.

Table 2. UV Absorption Maxima of Some Aromatic Aldehydes and Their Boron Trihalide Complexes

compound	λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})		
	uncomplexed[a] CH_2Cl_2	BF_3 complex[a] CCl_4	BCl_3 complex[b] CH_2Cl_2
p-ClC_6H_4CHO	257.8 (18 100)	298.5 (23 600)	319.8 (27 900)
Ph-CHO	246.5 (12 800)	281.6 (18 800)	299.0 (23 600)
p-MeC_6H_4CHO	251.2 (12 400)	285.7 (18 300)	316.5 (26 600)
p-$MeOC_6H_4CHO$	284.5 (17 000)	331.0 (34 900)	350.5 (35 000)
	276.0 (18 200)		

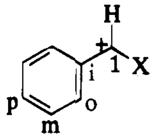
[a] From ref 7. [b] At −70 °C.

red-shift caused by BF_3 ($\Delta\lambda_{max}$ = 34−47 nm) is generally smaller than that induced by the stronger Lewis acid BCl_3 ($\Delta\lambda_{max}$ = 53−66 nm). The maxima of the UV spectra of structurally analogous BCl_3 complexes (Table 2) and carboxonium ions (Table 1) differ by only 6−9 nm, indicating the close similarity of these two types of electrophiles. The analogy between aldehyde−BX_3 complexes and carboxonium ions is also revealed by their NMR spectra (Tables 3 and 4). Nonequivalent ortho hydrogens or carbons, in one case also nonequivalent meta-carbons, indicate the partial double bond character of the C_i−C^+ bond. Increasing deshielding of the para carbon from top to bottom of Table 3 is in accord with the qualitative Lewis acidity order BF_3 < BCl_3 < CH_3^+ < H^+. It is interesting to note that another sequence is found for the chemical shifts of C-1, which are perturbed by anisotropy effects of the variable groups and do not reflect the electron deficiency at this center.[10]

Reaction Products. Lewis acid promoted reactions of acetals and aldehydes with allylsilanes have widely been used for the synthesis of homoallylic ethers and alcohols, respectively.[1d−g] Under the conditions of this work, the formation of a homoallylic ether was only observed when pregenerated $TolCH(MeO)^+BCl_4^-$ was combined with allyltrimethylsilane at 0 °C (Table 5, entry 6) or when less than equimolar amounts of BCl_3 were employed. In all other BCl_3 promoted reactions of acetals and aldehydes with allyltrimethylsilanes further halogenation by excess BCl_3 took place, and the 4-aryl-4-chloro-1-butenes **6** or consecutive products were isolated instead of the corresponding ethers or alcohols.

While the BCl_3 promoted reactions of the dimethyl acetals

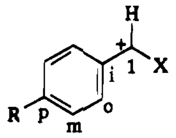
Table 3. ^{13}C NMR Spectra of Benzaldehyde (X = O^-), Protonated Benzaldehyde, Its BF_3 and BCl_3 Complexes and the α-Methoxybenzyl Cation in $CDCl_3$



X	C_o	C_m	C_p	C_i	C-1	others	T, °C	ref
O^-	129.5	128.9	134.2	136.4	192.0			*a*
OBF_3^-	135.50	130.38	141.82	130.57	200.83		28	this work[b]
$OBCl_3^-$	132.60	130.65	144.29	129.44	199.84		−30	this work[b]
	142.20	131.02						
OMe	*c*	130.95	145.67	128.32	207.52	53.48 (q),[e] 74.57 (q)	28	this work
OH	133.7	131.8	148.9	128.4	204.7		−(60−80)	*d*
	146.1							

[a] Reference 8. [b] Assignment by $^1H^{13}C$ correlation. [c] Not observed; probably broad signal due to coalescence. [d] Benzaldehyde and SbF_5/FSO_3H = 1:1 in SO_2ClF; ref 10. [e] $[BX_3OMe]^-$.

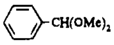
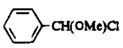
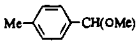
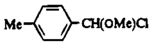
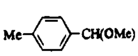
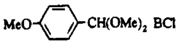
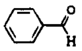
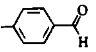
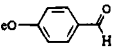
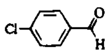
Table 4. ^1H NMR Spectra (300 MHz) of the Aromatic Aldehydes (X = O^-), Their BF_3 and BCl_3 Complexes and the Corresponding α-Methoxybenzyl Cations in $CDCl_3$



R	X	H_o	H_m	$J_{o,m}$, Hz	H_p	H-1	others	T, °C	ref
H	O^-	7.85	7.49		7.56	10.0			*a*
	OBF_3^-	8.24	7.72		8.01	9.63		28	this work
	$OBCl_3^-$	8.33, 8.48	7.82		8.16	9.90		−30	this work
	OMe	8.39	7.76[b]	8.2	8.15	9.80	3.70 (s, 3H),[h] 5.10 (s, 3H)	28	this work[c]
Cl	O^-	7.72				10.0		28	this work[d]
	$OBCl_3^-$	8.25	7.73	8.0		9.77[e]		28	this work[d]
Me	O^-	7.80	7.34	7.8		9.86	2.43	−50	this work
	OBF_3^-	8.04, 8.24	7.53	7.7		9.50	2.58	−50	this work
	$OBCl_3^-$	8.28	7.60	8.5		9.79	2.64 (s, 3H)	28	this work[d]
	OMe	8.17	7.51	8.3		9.47	2.54 (s, 3 H), 3.52 (s, 3 H),[h] 4.98 (s, 3 H)		*f*
OMe	O^-	7.84	6.99	8.4		9.86	3.88 (s, 3 H)	−50	this work
	OBF_3^-	8.18[g]	7.15	9.4		9.29	4.05 (s, 3 H)	28	this work
	$OBCl_3^-$	8.30	7.12	9.0		9.54	4.05 (s, 3 H)	28	this work[d]
	OMe	8.29	7.21	9.0		9.17	4.08 (s, 3 H), 3.61 (s, 3H),[h] 4.82 (s, 3 H)		*f*

[a] Reference 8. [b] Superimposed by $PhCHOBF_3$. [c] Reference 5e reports δ 3.56 (s, 3 H), 4.98 (s, 3 H), 7.61 (H_m), 8.18 (H_o), 9.56 (H-1). [d] 60 MHz. [e] Broad, ±0.1 ppm. [f] Reference 5e, 100 MHz. [g] Nonequivalent protons at −50 °C: δ 8.05 and 8.35. [h] $[BX_3OMe]^-$.

Table 5. Lewis Acid Promoted Reactions of Carboxonium Ions and Aldehyde Lewis Acid Complexes with Allylsilanes and Alkenes[a]

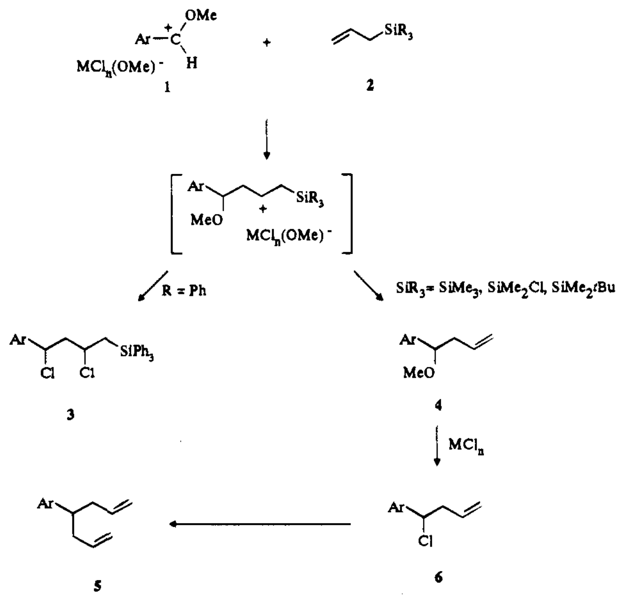
Entry	Electrophile	Lewis acid (equivalents)	Nucleophile (equivalents)	T, °C	Reaction time, min	Products (isolated yields, %)
1		BCl_3 (3.3)	$H_2C=CH-CH_2-SiMe_3$ (1.0)	0	15	Ph-CHCl-CH_2-CH=CH_2 **6a** (99)[b]
2		BCl_3 (2.2)	$H_2C=CH-CH_2-SiPh_3$ (1.2)	-78	10	Ph-CHCl-CH_2-CHCl-CH_2-$SiPh_3$ **3a** (64)[c], **6a** (8)
3		BCl_3 (1.2)	$H_2C=C(CH_3)-CH_2-CH_2-CH_3$ (1.5)	-78	20	Ph-CHCl-CH_2-CCl(CH_3)-CH_2-CH_2-CH_3 **7** (76)
4		BCl_3 (3.3)	$H_2C=CH-CH_2-SiMe_3$ (1.0)	-70	10	Tol-CHCl-CH_2-CH=CH_2 **6b** (99)[b]
5		BCl_3 (2.1)	$H_2C=CH-CH_2-SiPh_3$ (1.2)	-78	10	Tol-CHCl-CH_2-CHCl-CH_2-$SiPh_3$ **3b** (80)[d], **6b** (5)
6		BCl_3 (1.0)[e]	$H_2C=CH-CH_2-SiMe_3$ (1.2)	0	20	Tol-CHCl-CH_2-CH=CH_2 **6b** (66), Tol-CH(MeO)-CH_2-CH=CH_2 **4b** (24)
7		BCl_3 (1.0)[e]	$H_2C=CH-CH_2-SiPh_3$ (1.2)	0	10	Tol-CHCl-CH_2-CHCl-CH_2-$SiPh_3$ **3b** (41)
8		BCl_3 (1.0)	$H_2C=C(CH_3)-CH_2-CH_2-CH_3$ (1.7)	-78	15	Tol-CH(MeO)-CH_2-CCl(CH_3)-CH_2-CH_2-CH_3 **8** (86)
9		BCl_3 (0.3)	$H_2C=C(CH_3)-CH_2-SiPh_3$ (1.2)	-78	10	An-CH(MeO)-CH(CH_3)-CH=CH_2 **4c'** (25)[f]
10		$SnCl_4$ (1.0)	$H_2C=CH-CH_2-SiMe_3$ (2.2)	0	20	An-CH(CH_2-CH=CH_2)$_2$ **5c** (36)
11		BCl_3 (1.1)	$H_2C=CH-CH_2-SiMe_3$ (0.26)	-60	3	An-CHCl-CH_2-CH=CH_2 **6c** (64)
12		BCl_3 (0.3)	methylenecyclopentane (1.5)	-78	23 h	An-CH(OMe)$CH_2\overline{CCl-(CH_2)_3-CH_2}$ **9** (44)[f] An-CH(OMe)$CH_2-\overline{C=CH-(CH_2)_2-CH_2}$ **10** (16)
13		BF_3 (1.0)[g]	$H_2C=CH-CH_2-SiMe_3$ (2.5)	20	80	Ph-CH(CH_2-CH=CH_2)$_2$ **5a** (72)[h]
14		BF_3 (1.1)	$H_2C=CH-CH_2-SiMe_2Cl$ (1.2)	20	24 h	Ph-CH(CH_2-CH=CH_2)$_2$ **5a** (7)[f] Ph-CHCl-CH_2-CH=CH_2 **6a** (23)
15		BCl_3 (2.7)	$H_2C=CH-CH_2-SiMe_3$ (1.2)	0	30	Ph-CHCl-CH_2-CH=CH_2 **6a** (78)[i]
16		BCl_3 (3.7)	$H_2C=CH-CH_2-SiMe_2tBu$ (1.2)	0	2	Ph-CHCl-CH_2-CH=CH_2 **6a** (88)[i]
17		BCl_3 (3.0)	$H_2C=CH-CH_2-SiPh_3$ (1.2)	-40	60	Ph-CHCl-CH_2-CH=CH_2 **6a** (88)[k]
18		BCl_3 (3.6)	$H_2C=CH-CH_2-SiMe_2Cl$ (1.2)	-60	24 h	Ph-CHCl-CH_2-CH=CH_2 **6a** (92)
19		BF_3 (1.0)[g]	$H_2C=CH-CH_2-SiMe_3$ (2.5)	20	18 h	Tol-CH(CH_2-CH=CH_2)$_2$ **5b** (64)
20		BCl_3 (1.0)[g]	$H_2C=CH-CH_2-SiMe_3$ (1.0)	20	10	Tol-CHCl-CH_2-CH=CH_2 **6b** (66)
21		BF_3 (1.0)[g]	$H_2C=CH-CH_2-SiMe_3$ (2.7)	20	24 h	An-CH(CH_2-CH=CH_2)$_2$ **5c** (62)
22		BCl_3 (2.7)	$H_2C=CH-CH_2-SiMe_3$ (1.2)	0	90	(p-ClC_6H_4)-CHCl-CH_2-CH=CH_2 **6d** (76)
23		BCl_3 (3.2)	$H_2C=CH-CH_2-SiPh_3$ (1.2)	0	60	(p-ClC_6H_4)-CHCl-CH_2-CH=CH_2 **6d** (73)[k]

[a] The conditions are not optimized. [b] NMR analysis of crude product did not show contaminations. [c] 2:1 mixture of diastereomers, NMR analysis of crude product shows small amounts of **6a** (8%). [d] 5:1 mixture of diastereomers, NMR analysis of crude product shows small amounts of **6b** (5%). [e] The crystalline Tol-$CHOMe^+BCl_4^-$ was isolated and used for this reaction. [f] NMR analysis of the crude material showed complete consumption of the electrophile. [g] The crystalline BX_3 complexes have been isolated and used for these reactions. [h] The [1:1] product does not form, even when less than 1 equiv of allylsilane is used. [i] The [2:1] product does not form, when 2 equiv of allylsilane is used. [j] NMR analysis of crude material showed the presence of 12% of unreacted benzaldehyde. [k] NMR analysis of crude material, which was contaminated by $(Ph_3Si)_2O$.

of benzaldehyde and p-methylbenzaldehyde with allyltrimethylsilane give rise to the quantitative formation of the homoallylic chlorides **6** (entries 1 and 4), those are not the major products in the corresponding reactions with allyltriphenylsilane (entries 2 and 5). As shown in Scheme 1, the intermediate β-triphenylsilyl stabilized carbocations are not desilylated but accept a chloride ion to give addition products which are transformed into mixtures (2:1 to 5:1) of diastereomeric dichlorides **3** by BCl_3 (entries 2, 5, and 7). A similar behavior has been observed in Lewis acid promoted reactions of allyltriphenylsilane with benzhydryl chlorides.[11]

The ratio of [1:1] and [2:1] products generated by the reaction of p-anisaldehyde dimethyl acetal with allyltrimethylsilane depends on the ratio of the reactants. In the presence of Lewis acids the [1:1] product **6c** is only slightly less reactive toward allyltrimethylsilane than the anisaldehyde dimethyl acetal, and a fair yield of **6c** can only be obtained, when the acetal is employed in excess over allyltrimethylsilane (entry 11). A consecutive reaction of **6c** with allyltrimethylsilane and formation of the [2:1] product **5c** takes place, when 2 equiv of allylsilane per mol acetal are used (entry 10). While $BF_3 \cdot OEt_2$ induced reactions of aldehydes with allyltrimethylsilane have been reported to yield the [1:1] product **4** selectively,[12] only [2:1] products **5** could be isolated in the BF_3-promoted reactions

Scheme 1



a: Ar = Ph-
b: Ar = p-H$_3$C-C$_6$H$_4$-
c: Ar = p-H$_3$CO-C$_6$H$_4$-
d: Ar = p-Cl-C$_6$H$_4$-

of aldehydes with allyltrimethylsilane under the conditions of this work (entries 13, 19, and 21). NMR-spectroscopic monitoring of the course of these reactions did not allow the detection of any intermediate [1:1] products, indicating that the [1:1] products are consumed as fast as they are produced. In contrast, the [1:1] product **6a** was produced along with **5a** in the BF_3-promoted reaction of benzaldehyde with allylchlorodimethylsilane (entry 14). The analogous BCl_3 induced reactions of the benzaldehydes with equimolar amounts of allyltrimethylsilane selectively gave the [1:1] products **6a,b,d** (entries 15, 20, and 22). These products were also formed in the BCl_3 promoted reactions of the benzaldehydes with allyltriphenylsilane (entries 17 and 23) in contrast to the formation of the silylated products **3** in the corresponding reactions with acetals (entries 2, 5, and 7).

Ordinary Markovnikov addition products were obtained, when α-chloroethers or acetals were combined with 2-methyl-1-pentene in the presence of BCl_3 (entries 3 and 8), as previously reported for analogous reactions with readily ionizable alkyl chlorides.[13] The corresponding adduct **9** from *p*-anisaldehyde dimethyl acetal and methylenecyclopentane was accompanied by some cyclopentene derivative **10** (entry 12).

Kinetic Methods. Since nonionic products are formed by the reactions of the carboxonium salts with allylsilanes or alkenes, the rates of these reactions can either be followed conductometrically or by UV-spectrometry (fiber optics) using the work station described previously.[14] The disappearance of the carbonyl chromophor was monitored photometrically to determine the rates of reactions of the aldehyde−BCl_3 complexes, while NMR spectroscopy was used to measure the rates of the reactions of the aldehyde−BF_3 complexes. All reactions reported in this article follow second order kinetics, first order with respect to carboxonium ion or carbonyl−Lewis acid complex and first order with respect to allylsilane or olefin.

As shown in the supplementary material, in many cases UV and conductivity measurements were employed simultaneously to demonstrate that the reported rate constants do not depend on the method. Identical rate constants have also been obtained when the reaction of the benzaldehyde−BCl_3 complex with allylchlorodimethylsilane was followed by UV- or by NMR spectroscopy.

Scheme 2

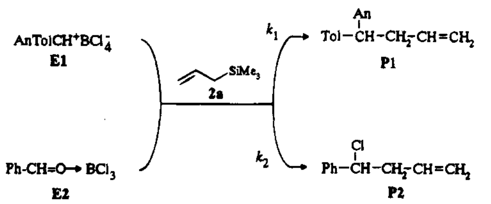
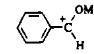
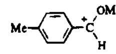
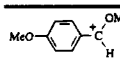
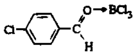
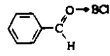
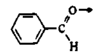
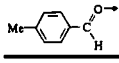


Table 6. Kinetics of the Reactions of Carboxonium Ions and Aldehyde Lewis Acid Complexes with Allylsilanes and Alkenes in CH_2Cl_2

Electrophile	Counterion	Nucleophile	$\Delta H^{\ddagger}$,	$\Delta S^{\ddagger}$,	k(-70 °C),	E[a]
			kJ mol^{-1}	J K^{-1} mol^{-1}	L mol^{-1} s^{-1}	
	$[BCl_4]^-$	$H_2C{=}CH(Me)CH_2CH_2CH_3$	8.7 ± 0.2	-138 ± 1	1.56×10^3	3.26
	$[BCl_3OMe]^-$	$H_2C{=}CH\text{-}CH_2\text{-}SiPh_3$	18.2 ± 0.6	-119 ± 3	5.53×10^1	
	$[BCl_3OMe]^-$	$H_2C{=}CH\text{-}CH_2\text{-}SiMe_3$			2.18×10^2	2.04
	$[BCl_4]^-$	$H_2C{=}CH(Me)CH_2CH_2CH_3$	18.0 ± 0.1	-133 ± 1	1.18×10^2	
	$[BCl_3OMe]^-$	$H_2C{=}CH\text{-}CH_2\text{-}SiPh_3$	22.8 ± 0.5	-127 ± 2	1.37	
	$[BCl_3OMe]^-$	$H_2C{=}C(Me)\text{-}CH_2\text{-}SiPh_3$			2.07×10^2	0.45
	$[BCl_3OMe]^-$	methylenecyclopentane			7.59	
	$]BCl_3OMe]^-$	$H_2C{=}CH\text{-}CH_2\text{-}SiMe_3$			3.19×10^{-1}	
	$[SnCl_4OMe]^-$	$H_2C{=}CH\text{-}CH_2\text{-}SiMe_3$			3.36×10^{-1}	
	-	$H_2C{=}CH\text{-}CH_2\text{-}SiMe_3$	13.1 ± 0.4	-146 ± 2	4.17×10^1	1.03
	-	$H_2C{=}CH\text{-}CH_2\text{-}SiPh_3$			3.14×10^{-1}	
	-	$H_2C{=}CH\text{-}CH_2\text{-}SiMe_2tBu$			1.61×10^1	0.69
	-	$H_2C{=}CH\text{-}CH_2\text{-}SiMe_3$	13.6 ± 0.1 22.5 ± 1.1	-152 ± 1 -126 ± 4	1.50×10^1 1.98[b]	
	-	$H_2C{=}CH\text{-}CH_2\text{-}SiPh_3$			1.20×10^{-1}	
	-	$H_2C{=}CH\text{-}CH_2\text{-}SiMe_2Cl$			6.84×10^{-3}	
	-	$H_2C{=}CH\text{-}CH_2\text{-}SiMe_3$			$\approx 1.4 \times 10^{-2}$	
	-	$H_2C{=}CH\text{-}CH_2\text{-}SiMe_2Cl$			$\approx 3.3 \times 10^{-5}$	
	-	$H_2C{=}CH\text{-}CH_2\text{-}SiMe_3$			2.29×10^{-3}	

[a] Definition of the electrophilicity parameter *E* see ref 15. [b] In chloroform, extrapolated value.

The consistency of the data given in Table 6 with those published previously has furthermore been proven by the competition experiment illustrated in Scheme 2. When a small quantity of allyltrimethylsilane was added to a mixture of $AnTolCH^+BCl_4^-$ and $PhCHO{\rightarrow}BCl_3$ in CH_2Cl_2, a product mixture was formed, from which a reactivity ratio $k_1/k_2 = 1.80 \pm 0.39$ (eight experiments) was derived. This ratio is almost identical to that calculated from the absolute rate constants for the reactions of $AnTolCH^+$ [11b] and $PhCHO{\rightarrow}BCl_3$ (Table 6) with allyltrimethylsilane ($k_1/k_2 = 1.75$).

Discussion. As in previously studied reactions of benzhydryl cations with π-nucleophiles,[11,13b,14] the rate determining carbon−carbon bond formation was proven by investigating the reactions

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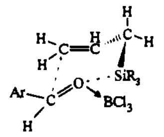
(10) Olah, G. A.; Westerman, P. W.; Forsyth, D. A. *J. Am. Chem. Soc.* **1975**, *97*, 3419−3427.

(11) (a) Mayr, H.; Hagen, G. *J. Chem. Soc., Chem. Commun.* **1989**, 91−92. (b) Hagen, G.; Mayr, H. *J. Am. Chem. Soc.* **1991**, *113*, 4954−4961.

Chart 1



of carboxonium ions with different counterions. Ionization of *p*-anisaldehyde dimethyl acetal with BCl_3 or $SnCl_4$, yielded different carboxonium salts which showed the same reactivity toward allyltrimethylsilane (Table 6). This experiment proves that the CC-bond-forming step must be rate-determining since variation of the rate of the following desilylation step does not affect the overall reaction rate.

In the case of the reactions of carbonyl–Lewis acid complexes with allylsilanes, rate determining carbon–carbon bond formation is derived from the almost identical reactivities of allyltrimethylsilane and allyl-*tert*-butyldimethylsilane toward the benzaldehyde–BCl_3 complex. If the rate determining step involved a coordination of the carbonyl–oxygen to silicon as shown in Chart 1 or if a reversible CC-bond forming step were followed by a rate-determining desilylation, the steric shielding of the silicon center should give rise to a lower reactivity of the *tert*-butyl substituted compound.

Table 6 shows that the activation entropies of the carboxonium ion additions are closely similar to those of the corresponding benzhydryl cation additions in accord with an analogous reaction mechanism.[11b,13b] Slightly more negative activation entropies were found for the reactions of the aldehyde Lewis acid complexes, which can be explained by the charge separation in the rate determining step.

Whereas the rates of the reactions of positively charged electrophiles with neutral π-nucleophiles have been found to be almost independent of the polarity of the solvent,[14,15] one expects the reactivities of the aldehyde–Lewis acid complexes to increase with solvent polarity. Accordingly, the benzaldehyde boron trichloride complex was found to react 4.9 times faster at -50 °C with allyltrimethylsilane in CH_2Cl_2 [$E_T(30) = 40.7$ kcal mol^{-1}][16] than in $CHCl_3$ [$E_T(30) = 39.1$ kcal mol^{-1}].[16] Surprisingly, $\Delta S^\ddagger$ was found to be 26 J mol^{-1} K^{-1} less negative in the less polar solvent $CHCl_3$, though usually activation entropies associated with charge separation are more negative in less polar solvents.[16] A more comprehensive study of solvent effects is limited by the fact that the solubility of the aldehyde–Lewis acid complexes is not sufficient for the kinetic experiments in less polar solvents. On the other hand, more polar solvents act as Lewis bases toward $BHal_3$ and do not allow the quantitative complexation of the substrate aldehydes.

In previous work, we have shown that the relative nucleophilicities of alkenes and allylsilanes with terminal double bonds toward benzhydryl cations are independent of the electrophilicities of the cations,[17] i.e., Ritchie type constant selectivity behavior has been observed.[18] Vice versa, the relative reactivities of the benzhydryl cations are independent of the nucleophilicities of the π-systems, and we have selected the reactivities of the benzhydryl cation toward 2-methyl-1-pentene as a measure of their electrophilicities (x-axis of Figure 1). After constructing the correlation lines of Figure 1 on the basis of the benzhydryl cation data,[11,17] the data in Table 6 have then been added by minimizing the squares of deviation from the correlation lines. The relatively good match of the data for carboxonium ions and aldehyde–BX_3 complexes indicates that the relative nucleophilicities of π-systems determined with respect to benzhydryl cations are also observed with respect to these types of electrophiles. From the position of the carboxonium ions and the aldehyde–BX_3 complexes on the x-axis one obtains their relative reactivities ($\log k$) at -70 °C (reference reaction: R^+ + 2-methyl-1-pentene[17]). Since charge separation occurs in the rate-determining step of the reactions of aldehyde–BX_3 complexes with neutral nucleophiles, their rates will increase with solvent polarity, and the electrophilicities listed in Table 6 refer to CH_2Cl_2 as a solvent.

Chart 2. Relative Electrophilicities (k_{rel}, CH_2Cl_2, 20 °C) of Methoxycarbenium Ions and Their Phenylogous *p*-Anisyl Analogues[15]

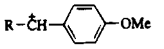
	$R\text{-}\overset{+}{C}H\text{-}OMe$	
$R = C_6H_5$	15.5	1
$R = p\text{-}MeC_6H_4$	3.9	1
$R = p\text{-}MeOC_6H_4$	2.8	1

Chart 3. Comparison of the Electrophilicities of $Ph{-}CH^+{-}OX$ Species in CH_2Cl_2 (-70 °C)

Electrophile	$Ph\text{-}\overset{+}{C}H\text{-}O\overset{-}{B}F_3$	$Ph\text{-}\overset{+}{C}H\text{-}O\overset{-}{B}Cl_3$	$Ph\text{-}\overset{+}{C}H\text{-}OMe$
k_{rel}	1.0	5.0×10^2	4.1×10^5

One now finds that the ionized benzaldehyde dimethyl acetal ($PhCHOMe^+$) has a similar reactivity as the ditolyl carbenium ion ($(p\text{-}MeC_6H_4)_2CH^+$. Chart 2 reveals that α-methoxybenzyl cations are somewhat more reactive than their phenylogs and that the reactivity difference decreases with increasing electron donating ability of R. As expected from spectroscopic and theoretical investigations,[19] the BCl_3 complexes are considerably more reactive than the corresponding BF_3 complexes; according to Chart 3, their electrophilicity is just median in between BF_3 complexes and the corresponding carboxonium ions, and one can derive decreasing electron donating effect in the series $OBF_3^- > OBCl_3^- > OMe$. From the activation parameters given in Table 6, k (20 °C) values are calculated, which are used to calculate the E-parameters (right column in Table 6) following the procedure described in ref 20. In cases where only k (-70 °C) is known, values k (20 °C) are calculated by estimating $\Delta S^\ddagger$ which is constant within certain classes of reactions.[15] Preliminary experiments on the temperature dependence of the reactions of the BF_3 complexes indicate, however, that $\Delta S^\ddagger$ may be different for these reactions.

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(12) (a) Reetz, M. T.; Kesseler, K.; Jung, A. *Tetrahedron Lett.* **1984**, *25*, 729–732. (b) Heathcock, C. H.; Kiyooka, S.; Blumenkopf, T. A. *J. Org. Chem.* **1984**, *49*, 4214–4223. (c) Danishefsky, S.; De Ninno, M. *Tetrahedron Lett.* **1985**, *26*, 823–824.

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(15) Mayr, H.; Patz, M. *Angew. Chem.* **1994**, *106*, 990–1010; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 938–957.

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(17) Mayr, H.; Scheider, R.; Grabis, U. *J. Am. Chem. Soc.* **1990**, *112*, 4460–4467.

(18) (a) Ritchie, C. D. *Acc. Chem. Res.* **1972**, *5*, 348–354. (b) Ritchie, C. D. *Can. J. Chem.* **1986**, *64*, 2239–2250.

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(20) Mayr, H.; Rau, D. *Chem. Ber.* **1994**, *127*, 2493–2498.

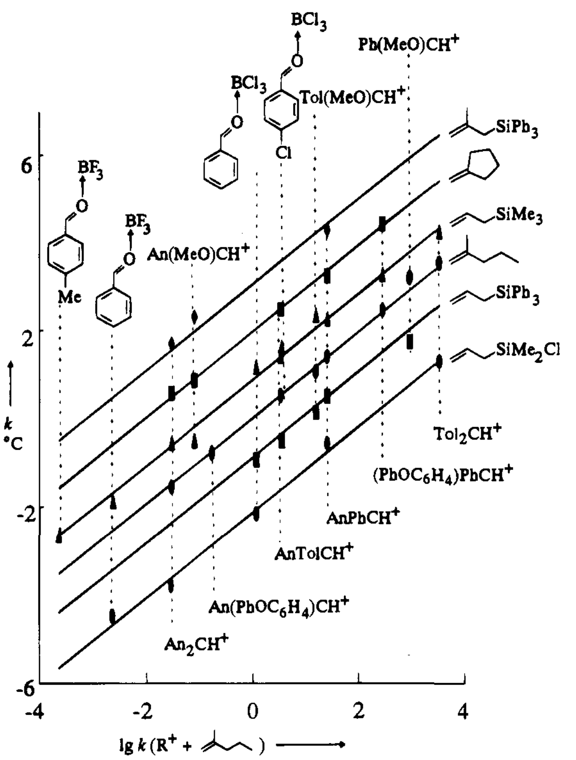

Figure 1. Rate constants for the reactions of diarylcarbenium ions,[14,17] carboxonium ions, and aldehyde−Lewis acid complexes toward π-nucleophiles with terminal double bonds vs rate constants of the reference reaction (CH_2Cl_2, −70 °C).

Therefore, it is not yet possible to calculate reliable *E*-parameters (20 °C) for these electrophiles.

Since correlations as shown in Figure 1 have been demonstrated to hold for a large variety of electrophile nucleophile combinations, one can now use the *E*-parameters given in Table 6 for predicting the rates of reactions of carboxonium ions and aldehyde−Lewis acid complexes with different types of alkenes, alkynes, allylelement compounds, and arenes using the reactivity scales presented in a recent review.[15]

Experimental Section

General Methods. NMR: WM 300, AC 300 (Bruker) and EM 360 L (Varian); chemical shifts versus tetramethylsilane ($\delta = 0.00$) as internal standard. Assignment of ^{13}C NMR signals by DEPT experiments; UV-spectra: spectral photometer MCS 220 (Zeiss) using single-beam fiber optics (d = 0.5 cm), submersible probe TS 5A, and the deuterium lamp CLD 300. Conductivity measurements were performed with the conductimeter CD 810 (Tacussel) using platinum electrodes. Gas chromatograph Sigma 3, SE 30 10% chrom WHP 80−100 mesh 2.5 m · 2 mm SS; temperature program 50 → 250 °C (15 °C/min). Integrator SP 4290.

The allylsilanes were either purchased or prepared as described in ref 11b, and the acetals were synthesized from the commercially available aldehydes and methyl orthoformate following the procedure by Davis et al. (ref 21).

Generation of the α-Methoxybenzyl Cations. α-Methoxy-*p*-methyl-benzyl cation [1b-BCl_3OMe^-]. *p*-Methylbenzaldehyde dimethyl acetal (0.68 g, 4.1 mmol) was placed into a 50-mL round-bottom flask and cooled at 0 °C. A solution of BCl_3 in CH_2Cl_2 (2.3 M, 2.0 mL) was added dropwise within 3 min to give a colorless precipitate, which was isolated by filtration with suction in a nitrogen atmosphere and washed with pentane. ^1H NMR spectrum see Table 4.

α-Methoxybenzyl cation [1a-BF_3OMe^-]. Gaseous boron trifluoride (4.0 mL, 160 μmol) was condensed into a solution of benzaldehyde dimethyl acetal (10 μL, 66 μmol) in 0.70 mL $CDCl_3$ at 0 °C. The NMR spectra determined in this solution are given in Tables 3 and 4.

The UV spectra of the carboxonium ion 1a−c were obtained by adding the dimethyl acetals (~1 μmol) to ~1 × 10^{-4} M solutions of BCl_3 in CH_2Cl_2 (25−100 mL).

Preparation of the Aldehyde−Boron Trichloride Complexes. Solutions of the aldehydes (1 mL) in CH_2Cl_2 (5 mL) were added slowly to solutions of BCl_3 (1 equiv) in CH_2Cl_2 (0 °C). Partial evaporation of the solvent in vacuo yield microcrystalline solids which were isolated by filtration with suction in a nitrogen atmosphere (return frit) and washed with pentane. Spectral data: Tables 2, 3, and 4.

Preparation of the Aldehyde−Boron Trifluoride Complexes. A solution of 2−10 mmol of the freshly distilled aldehydes in 2−5 mL of CH_2Cl_2 was placed in one compartment of a two-chamber-flask and cooled at 0 °C. An equimolar amount of $BF_3 \cdot OMe_2$ was added to this solution within 2 min. After filling the second chamber with *n*-hexane, the flask was plugged and left at 0−20 °C for several hours or days. The slow diffusion of hexane into the first chamber induced the slow growth of aldehyde−BF_3 crystals, which were isolated by filtration with suction in a nitrogen atmosphere.

Benzaldehyde−boron trifluoride adduct (crystallization at 20 °C), colorless needles; *p*-methylbenzaldehyde−boron trifluoride adduct (crystallization at 0 °C), colorless cubes; *p*-methoxybenzaldehyde−boron trifluoride adduct (crystallization at 20 °C), colorless needles; spectral data: Tables 2, 3, and 4.

Kinetic Investigations. (A) UV and Conductivity Measurements. The consumption of the α-methoxybenzyl cations **1** was determined photometrically by using fiber optics and the working station described in ref 14. Calibration curves, i.e., the correlations between absorbance and concentration of the cations or Lewis acid−aldehyde complexes were obtained by adding the acetals or aldehydes in portions to solutions of BCl_3 in CH_2Cl_2 and determination of the absorbance after completion of the ionization of the acetal or complexation of the aldehyde. As described in ref 14, the same working station can be used for following the ionization of the acetals (calibration) and the reactions of α-methoxybenzyl cations with nucleophiles conductometrically.

(B) NMR Kinetics. The NMR tube (Ø 5 mm) is heated, evacuated, and flushed with N_2 (3−4 times). It was then charged with 0.80−1.00 mL of dry CD_2Cl_2 or $CDCl_3$, 3.0 μL of aldehyde (25−28 μmol), and gaseous BF_3 (3−5 mL, 120−200 μmol). The tube was sealed by a septum and thermostated in the NMR spectrometer. After reaching the required temperature, the tube was removed from the spectrometer, and 5−25 equiv of the allylsilane was added. The solution was mixed and returned into the NMR spectrometer. Eight scans, which were taken within 27 s, were averaged to give one ^1H NMR spectrum. The [2:1] products **5** were the only products observable, and the kinetics of the reaction

$$\mathrm{ArCHO{\rightarrow}BF_3} + 2\ \mathbf{2} \rightarrow \mathbf{5}$$

were evaluated by plotting

$$\frac{1}{[\mathbf{2}]_o - 2[\mathrm{E}]_o} \ln \frac{[\mathrm{E}]_o([\mathbf{2}]_o - 2[\mathbf{5}]_t)}{[\mathbf{2}]_o([\mathrm{E}]_o - [\mathbf{5}]_t)}$$

vs *t* (second order reaction with E = $\mathrm{ArCHO{\rightarrow}BF_3}$).[22]

Determination of the Relative Reactivity of *p*-Anisyl-*p*-tolyl-methyl-Cation and PhCHO→BCl_3 by Competition Experiments. The relative reactivities of the two electrophiles E1 and E2 toward the nucleophile **2a** ([E1], [E2] ≫ [**2a**]) are calculated from eq 1[23] where

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the symbols defined in Scheme 2 are used.

$$\kappa = \frac{k_1}{k_2} = \frac{\ln [\mathrm{E1}]_o - \ln ([\mathrm{E1}]_o - [\mathrm{P1}])}{\ln [\mathrm{E2}]_o - \ln ([\mathrm{E2}]_o - [\mathrm{P2}])} \qquad (1)$$

Typical Procedure. Benzaldehyde (0.359 g, 3.38 mmol), *p*-anisyl-*p*-tolylmethyl chloride (0.292 g, 1.18 mmol), and phenyldecane (0.343 g, 1.57 mmol, internal standard) were dissolved in dry CH_2Cl_2 to give 10 mL of a solution. This solution (3.2 mL) was transferred into a 50-mL round-botton flask (N_2 atmosphere) and diluted with CH_2Cl_2 (10 mL). The solution was placed in a cryostat at −70 °C. After thermal equilibration, 2.5 mL (5.0 mmol) of a 2.0 M solution of BCl_3 in CH_2Cl_2 and finally 0.470 mL (0.300 mmol) of a 0.639 M solution of allyltrimethylsilane in CH_2Cl_2 were added. After 5 min the reaction mixture was poured into 20 mL of an aqueous solution of NH_3 (2.0 M). The layers were separated, the organic phase was dried over Na_2SO_4, concentrated, and filtered over silcia gel (1 g, eluant: diethyl ether) and the solvent was evaporated. For the gas chromatographic analysis (FID), 5 μL of the crude material was dissolved in 0.5 mL of CH_2Cl_2.

The chromatographic analysis was based on the relative peak areas of products (P1 and P2) and the internal standard phenyldecane. Calibration curves based on three mixtures of P1, P2, and internal standard allowed the calculation of [P1] and [P2]. Eight competition experiments with $[\mathrm{AnTolCHCl}]_o/[\mathrm{PhCHO}{\rightarrow}\mathrm{BCl_3}]_o$ varying from 1.1 to 0.59 gave $k_1/k_2 = 1.80 \pm 0.39$.

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Supporting Information Available: Experimental procedures for the reactions of acetals and aldehyde−Lewis acid complexes with allylsilanes and alkenes, including characterization of the products listed in Table 5, and tables with concentrations and rate constants of the kinetic experiments at variable temperatures (21 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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