Kinetics and Mechanism of the Reactions of Amine Boranes with Carbenium Ions

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Dedicated to Professor Wolfgang Beck on the occasion of his 65th birthday

Abstract: The kinetics of the reactions of trialkylamine boranes and pyridine boranes with benzhydryl cations have been determined photometrically. Second-order rate laws are obeyed, first-order with respect to amine borane concentration and first-order with respect to carbocation concentration. As for other reactions of carbocations with neutral nucleophiles, the rates of these reactions are only slightly affected by solvent polarity. The structure–reactivity relationships and kinetic isotope effects are in accord with a polar mechanism proceeding through a transition state where the migrating hydride is partly bound to the entering carbon and to the leaving boron atom. The rate constants correlate linearly with the electrophilicity parameters E of the carbenium ions. It is therefore possible to use the linear free enthalpy relationship $\log k_2 = s(E+N)$ for determining nucleophilicity parameters N for the amine boranes and to compare their hydride-donating abilities with those of other non-charged hydride donors (silanes, germanes, stannanes, and dihydropyridines).

Keywords
amine boranes · carbocations · kinetics · linear free enthalpy relationship · reductions

Introduction

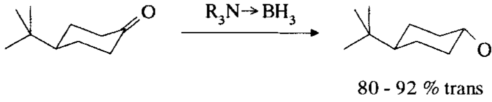
Amine boranes **1** are versatile reducing agents in organic and inorganic chemistry.[1] They are produced quantitatively by the reaction of amines with diborane (Scheme 1) and are stable coordination complexes.[2] A large number of amine boranes are commercially available.

$$2\,R_3N + B_2H_6 \longrightarrow 2\;\overset{\delta^+}{R_3N}\!\rightarrow\!\overset{\delta^-}{BH_3}$$

Scheme 1.

Because of their dipolar, non-ionic character, they are readily soluble in water as well as in many organic solvents (e.g., ethanol, ether, dichloromethane, toluene, or acetone).[1, 3, 4] While trialkylamine boranes are relatively stable in water or ethanol, they solvolyze under acidic conditions.[1, 3] Borane complexes of primary and secondary amines decompose with formation of hydrogen when heated above 70 °C,[1, 2b, 4] but in the presence of impurities (e.g., amines, proton donors, or heavy-metal cations) hydrogen evolution may occur even at room temperature.[2b, 5]

The reduction of aldehydes and ketones is usually performed in aprotic solvents between 50 and 100 °C,[6] whereas in water or alcohol solution the reaction of dialkylketones with various amine boranes proceeds at room temperature in good yields.[7] The reactivity toward 4-*tert*-butylcyclohexanone in aqueous methanol (Scheme 2) was reported to decrease according to the order $H_3N \rightarrow BH_3 > Me_2HN \rightarrow BH_3 >$ pyridine $\rightarrow BH_3 > Me_3N \rightarrow BH_3$ yielding *trans*-4-*tert*-butylcyclohexanol with high selectivity.[7]



Scheme 2.

Acyl chlorides are reduced with formation of alcohols,[5, 8] while alkyl and alkali carboxylates do not react with amine boranes.[5] Since hydroborations with trialkylamine boranes or pyridine boranes require elevated temperatures,[3, 9] carbonyl groups can be reduced selectively in the presence of C=C double bonds at room temperature.[5, 7] In contrast, hydroboration of alkenes (e.g., 1-hexene or styrene) and reduction of carbonyl compounds (e.g., aldehydes) with sterically hindered amine boranes (e.g., *N*-phenyl-*N*,*N*-diisopropylamine borane) at 20 °C takes place within 1–10 h in solvents such as THF or pentane.[10]

Despite their wide use in synthesis, little information on the mechanism of reductions with amine boranes is available.[11] During our efforts to quantify the reactivities of various classes of nucleophiles with respect to carbenium ions,[12] we have re-

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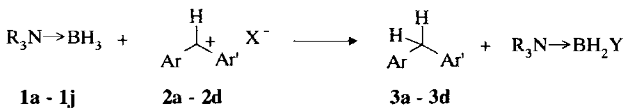
cently studied the kinetics of hydride abstractions from silanes, germanes, and stannanes by benzhydryl cations.[13] In order to add amine boranes **1** to this list of reactivities of non-ionic hydride donors, we have now studied the kinetics of their reactions with the intensely colored benzhydryl cations **2**, which yield the corresponding colorless diarylmethanes **3** quantitatively (Scheme 3).



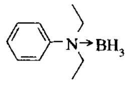
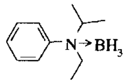
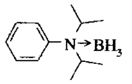
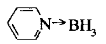
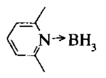
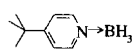
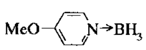
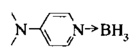
Scheme 3. Reaction of amine boranes with benzhydryl cations. For keys to the compounds, see Table 1 (**1a**–**j**) and Table 2 (**2a**–**d**).

Results

All reactions of the tertiary-amine boranes **1** with the carbenium ions **2** reported in this paper follow second-order kinetics, first-order with respect to carbenium ion concentration and first-order with respect to amine borane concentration (Tables 1 and 2). In contrast, simple rate laws were not observed for the reactions of carbenium ions **2** with borane adducts of secondary amines, and we have not pursued the preliminary investigations of these systems.

The rate constants of the reactions of **2a-BF$_4$**, **2a-OTf**, and **2a-PF$_6$** with various amine boranes were found to be independent of the counterions (Table 3) in analogy to related studies which have shown that the rate-determining step of the reactions of carbocations with non-charged nucleophiles (e.g., alkenes, allylsilanes, trialkylsilanes, or silyl enol ethers) is usually not affected by the nature of weakly nucleophilic counterions.[13,16]

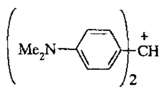
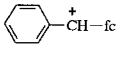
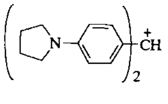
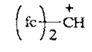
Table 1. Second-order rate constants k_2 (CH_2Cl_2, 20 °C) and Eyring parameters for the reactions of the amine boranes **1** with the benzhydryl cation **2a** [a].

	Amine borane	pK_a [b]	k_2 [c] / L mol^{-1} s^{-1}	k_{rel}	$\Delta H^{\neq}$ / kJ mol^{-1}	$\Delta S^{\neq}$ / J mol^{-1} K^{-1}
1a	$Et_3N \rightarrow BH_3$	10.6	27.9	≡ 1.0	46.6 ± 0.6	-57.9 ± 2.0
1a-D	$Et_3N \rightarrow BD_3$	10.6	15.6	0.6	50.0 ± 0.3	-51.3 ± 1.1
1a-Br	$Et_3N \rightarrow BH_2Br$	10.6	2.24	0.08	——	——
1b	$Me_3N \rightarrow BH_3$	10.9	5.20	0.2	53.0 ± 0.5	-50.2 ± 1.9
1c		6.6	13.6	0.5	52.7 ± 0.5	-43.0 ± 1.9
1d		—	37.4	1.3	46.2 ± 0.4	-56.8 ± 1.3
1e		—	23.3	0.8	——	——
1f		5.3	176	6.3	44.9 ± 0.4	-48.7 ± 1.6
1g		6.6	302	10.8	43.5 ± 0.5	-48.9 ± 2.1
1h		6.0	380	13.6	43.2 ± 0.3	-48.0 ± 1.1
1i		6.6	976	35.0	40.4 ± 0.5	-49.7 ± 1.9
1j		9.7	1.3×10^5 [d]	≈4700	——	——

[a] Counterion $X^- = BF_4^-$, PF_6^-, or OTf^-. [b] pK_a of the corresponding ammonium ion in water according to ref. [14]. [c] If temperature dependence was determined, k_2 listed in this column was calculated from the Eyring parameters. [d] Calculated from $k_2(-70\,°C) = 492$ L mol^{-1} s^{-1} assuming $\Delta S^{\neq} \approx -49$ J mol^{-1} K^{-1}.

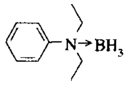
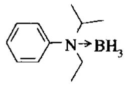
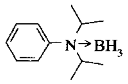
Abstract in German: *Die Kinetik der Reaktionen von Trialkylamin-Boranen und Pyridin-Boranen mit Benzhydrylkationen wurde photometrisch bestimmt. Die Reaktionen folgen Geschwindigkeitsgesetzen zweiter Ordnung, erster Ordnung bezüglich der Amin-Boran-Konzentration und erster Ordnung bezüglich der Benzhydrylkationen-Konzentration. Wie bei anderen Reaktionen von Carbokationen mit neutralen Nucleophilen werden die Geschwindigkeiten dieser Reaktionen durch die Lösungsmittelpolarität nur wenig beeinflußt. Die Struktur-Reaktivitäts-Beziehungen und die kinetischen Isotopeneffekte sind mit einem polaren Mechanismus im Einklang, bei dem im Übergangszustand das wandernde Hydridion partiell an das angreifende Kohlenstoffatom sowie an das austretende Boratom gebunden ist. Die Geschwindigkeitskonstanten korrelieren linear mit den Elektrophilie-Parametern der Carbeniumionen. Daher ist es möglich, die Lineare-Freie-Enthalpie-Beziehung* $\lg k_2 = s(E + N)$ *zur Bestimmung der Nucleophilie-Parameter N der Amin-Borane zu nutzen und deren Hydrid-Übertragungsfähigkeit mit der anderer ungeladener Hydrid-Donoren (Silane, Germane und Dihydropyridine) zu vergleichen.*

Table 2. Second-order rate constants k_2 (20 °C, CH_2Cl_2) and Eyring parameters for the reaction of **1a** with the carbocations **2** [a].

	carbocation	E [b]	k_2 [c] / L mol^{-1} s^{-1}	$\Delta H^{\neq}$ / kJ mol^{-1}	$\Delta S^{\neq}$ / J mol^{-1} K^{-1}
2a		-7.45	27.9	46.6 ± 0.6	-57.9 ± 2.0
2b [d]		-2.92	52800	31.7 ± 0.4	-46.1 ± 2.3
2c		-8.10	7.76	52.5 ± 0.3	-48.6 ± 1.1
2d [d]		-8.50	5.45	48.8 ± 0.6	-64.2 ± 2.1

[a] Counterion $X^- = BF_4^-$ or OTf^-. [b] Electrophilicity parameters E of the carbenium ions **2** from refs. [12,15]. [c] Calculated from Eyring parameters. [d] fc = ferrocenyl ($C_5H_5FeC_5H_4$).

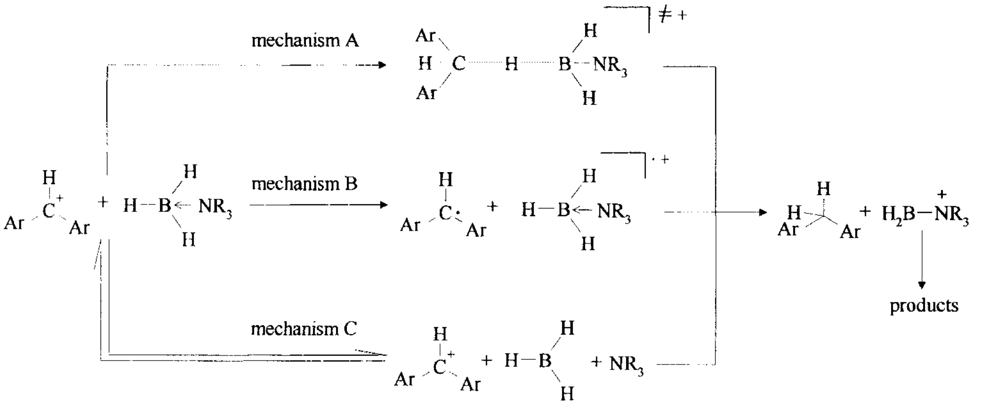
Table 3. Influence of the counterion X^- on the second-order rate constants k_2 (CH_2Cl_2, 20±1 °C) of the reactions of amine boranes **1** with **2a**.

	amine borane	counterion X^-	k_2 / L mol^{-1} s^{-1}
1a	$Et_3N \rightarrow BH_3$	**BF_4**	30.4 [a]
		OTf	28.8 [a]
1b	$Me_3N \rightarrow BH_3$	**BF_4**	5.48 [a]
		OTf	5.27 [a]
1c		**BF_4** **OTf**	14.7 14.4
1d		**BF_4** **PF_6**	38.0 [a] 37.5
1e		**BF_4** **PF_6**	23.3 [a] 23.4 [a]

[a] Average calculated from the values in Table 7.

Discussion

Rate-determining step: The hydride transfer from amine boranes to carbenium ions may proceed by one of the three mechanisms shown in Scheme 4.



Scheme 4. Possible mechanisms for hydride transfer from amine boranes to carbenium ions.

The polar mechanism A proceeds via a transition state in which the migrating hydride is partly bound to the entering carbon and to the leaving boron atom. In the SET mechanism B the initial rate-determining electron transfer step is followed by a fast hydrogen transfer. Mechanism C refers to a reaction sequence which is initiated by dissociation of the amine borane followed by hydride transfer analogous to that in mechanism A or B.

Rate-determining electron transfer (mechanism B) was excluded by the primary kinetic isotope effect of $k_H/k_D = 1.81$ observed for the reaction of triethylamine borane **1a** and deuterated triethylamine borane **1a-D** with **2a** at 20 °C (Table 1). For mechanism B a considerably smaller secondary kinetic isotope effect would be expected. Comparison of the ionization potentials of the pyridine boranes (**1f**, 9.72 eV; **1h**, 9.30 eV[17]) with the electron affinities of benzhydryl cations (Ph_2CH^+, 7.32 eV[18]) confirms that the SET mechanism B is energetically unfavorable.

The dissociative mechanism C is excluded by the finding that the reactivities of the borane adducts with sterically hindered amines **1d** and **1e** toward **2a** are similar to that of the less bulky analogue **1c**, in spite of the higher tendency of **1d** and **1e** to dissociate into amine and BH_3.[10] In addition, the reactivities of the pyridine boranes **1f–j** increase with the electron-donating ability of the substituents in pyridine, that is, in the opposite order to that expected for the dissociation constants in the series **1f**, **1h**, **1i**, and **1j** (Table 1). For the same reason this ranking also excludes the possibility that the monitored disappearance of the carbocation absorbance is due to coordination of the carbocation with the amines produced by dissociation of **1a–j**.

By excluding mechanisms B and C we are left with mechanism A, which is analogous to the mechanism suggested for the hydride abstractions from silanes, stannanes, germanes,[13] and *hydridic* CH groups.[19] Nucleophilic counterion assistance in this mechanism is also excluded by the independence of the observed rate constants of the nature of the counterions (Table 3).

Solvent effects: The rates of the reactions of carbocations with neutral nucleophiles have been observed to show little dependence on the solvent. Whereas reactions of benzhydryl cations with alkenes were found to be three times faster in nitromethane than in chloroform,[16a] an analogous change of solvent polarity did not have any effect on the rate of hydride abstraction from dimethylphenylsilane.[13a]

Table 4 and Figure 1 show that the rate of hydride abstraction from triethylamine borane is slightly reduced as the solvent polarity is increased. Variation of solvent polarity affects these rates in the opposite sense to the corresponding reactions with alkenes, and Reichardt's E_T(**30**) parameter[20] again proved to be most suitable for a quantitative correlation.

Table 4. Second-order rate constants k_2(20 °C) and Eyring parameters for the reaction of triethylamine borane (**1a**) with **2a** and **2d** in various solvents.

Cation	Solvent	E_T(**30**) [a]	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/J mol^{-1} K^{-1}	k_2(20 °C) [b]/ L mol^{-1} s^{-1}
2a	CH_2Cl_2	40.7	46.6±0.6	−57.9±2.0	27.9
	acetone	42.2	46.8±0.1	−62.0±0.6	15.7
	CH_3CN	45.6	46.9±0.3	−63.5±1.3	12.6
	CF_3CH_2OH	59.8		–	5.95
2d	CH_2Cl_2	40.7	48.8±0.6	−64.2±2.1	5.45
	liquid SO_2	≈68 [c]	49.1±0.7	−81.8±2.8	0.570

[a] Ref. [20]. [b] If temperature dependence was determined, k_2 listed in this column was calculated from the Eyring parameters. [c] Estimated value (ref. [21]).

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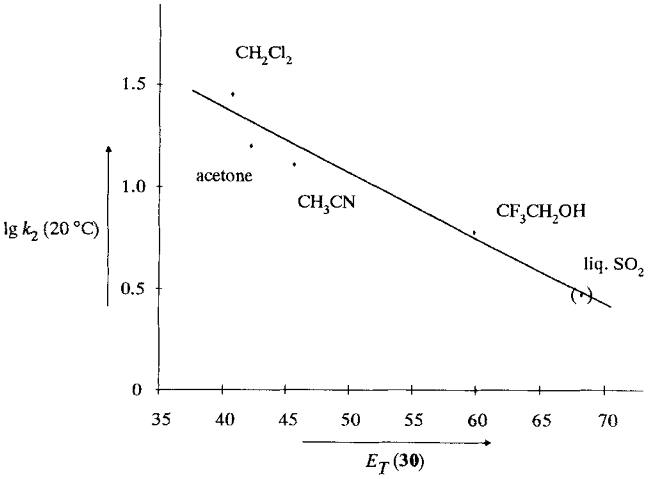


Figure 1. Plot of $\log k_2$ (20 °C) for the reaction of **1a** with **2a** versus Reichardt's $E_T(30)$ values [$\log k_2$ (20 °C) = $-3.082 \times 10^{-2} \times E_T(30) + 2.583$, $r = 0.976$). The rate constant for liquid SO_2 [k_2(20 °C) = 2.92 L mol^{-1} s^{-1}] was estimated from the relative rate of the reaction of **2d** with **1a** in SO_2 and dichloromethane.

Because of the low solubility of **2a-BF$_4$** and **2a-OTf** in ethers or hydrocarbons ($c < 5 \times 10^{-6}$ mol L^{-1}), kinetic investigations in solvents of low polarity (E_T(30) < 40) were not performed. Ordinary alcohols were also not used for studying solvent effects since ethanol, in contrast with the less nucleophilic trifluoroethanol, slowly reacts with **2a** at ambient temperature.

Kinetic studies in liquid SO_2 were only performed with the bis(ferrocenyl)methylium cation (**2d**) as reference electrophile, since the dimethylamino groups of **2a** undergo a coordination with the Lewis acid SO_2 resulting in the formation of a complex which is more electrophilic than **2a**. This coordination, which has also been observed upon treatment of **2a** with other Lewis acids (e.g., $ZnCl_2 \cdot OEt_2$ or BCl_3), is detected by a change from the intense blue color of **2a** to yellow.

Because of the small differences in k_2 in Table 4, it is difficult to assign the solvent effects to variations in either $\Delta H^{\ddagger}$ or $\Delta S^{\ddagger}$. The considerably smaller rate constant in liquid SO_2 is clearly due to a more negative value of $\Delta S^{\ddagger}$. An analogous change in $\Delta S^{\ddagger}$ has been observed for the reactions of benzhydryl cations with dimethylphenylsilane in either liquid SO_2 or dichloromethane.[21]

Variation of the amine borane: In the section "Rate-determining step" we have already discussed how electron donors in the 4-position of the pyridine ring increase the reactivities of those complexes. The activating electronic effect of two methyl groups in the 2- and 6-positions of the pyridine is partially compensated by the retarding steric effect, however, and **1g** is less reactive than the 4-(*tert*-butyl)pyridine complex **1h**.

Comparison of **1f** with the trialkylamine complexes **1a** and **1b** shows that the basicity of the amine is not the major factor determining the reactivities of these compounds. Despite the higher basicity of trimethylamine and triethylamine compared with pyridine, the trialkylamine complexes are weaker hydride donors than the pyridine complexes **1f**–**j**. The observation that the reactivity of the borane complex **1c** of the weak base *N*,*N*-diethylaniline is similar to those of the trialkylamine complexes **1a** and **1b** also argues against control of the reactivities by the basicity of the amines.

The rate constants for the reactions of the monosubstituted pyridine boranes with **2a** ($\log k_2$) do not correlate linearly with Hammett's σ_p parameters (Figure 2) or σ_p^+[22] parameters.

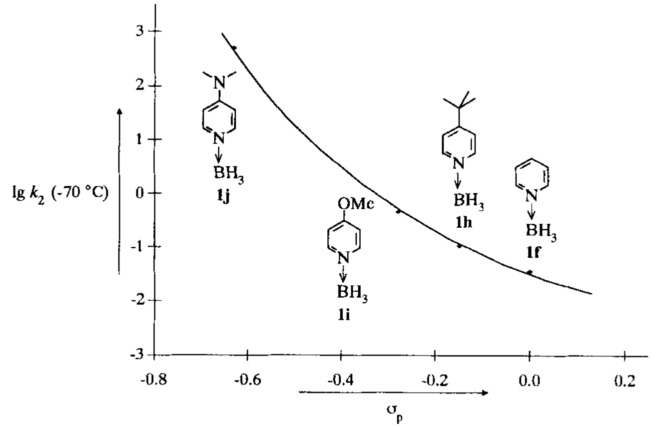
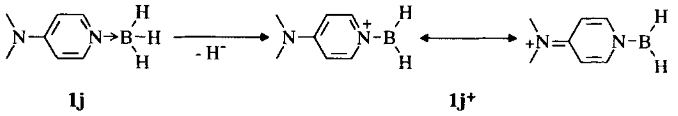


Figure 2. Plot of $\log k_2$ (−70 °C, CH_2Cl_2) for the reaction of pyridine boranes **1f**, **1h**, **1i**, and **1j** with **2a** versus σ_p.

The electron-donating effect of the *para* substituents can be explained by the quinoid structure of the resulting cations **1$^+$**, as depicted for the dimethylamino pyridine borane **1j** in Scheme 5.



1j **1j$^+$**

Scheme 5. Stabilization of **1j$^+$** by through the *para* substituent.

Complex **1a-Br** was the only amine borane investigated where one of the hydrogen atoms on boron was replaced by another atom. The fact that the reactivity of **1a-Br** is twelve times lower than that of **1a** is probably attributable to the electron-withdrawing effect of bromine, although steric effects cannot be excluded.

Assuming that the reactivities of the amine boranes are controlled by the thermodynamics of the hydride abstraction step, we performed semiempirical MO calculations (AM1) on the amine boranes **1** and the cations **1$^+$** resulting from hydride abstraction (Table 5). Figure 3 shows a linear correlation between the reactivities of the amine boranes **1** toward **2a** and

Table 5. Calculated heats of formation of the amine boranes **1** and the cations **1$^+$** (AM1; ref. [23]).

Amine borane	$\Delta H_f^\circ(\mathbf{1})$/ kcal mol^{-1}	$\Delta H_f^\circ(\mathbf{1}^+)$/ kcal mol^{-1}	$\Delta H_f^\circ(\mathbf{1}^+) - \Delta H_f^\circ(\mathbf{1})$/ kcal mol^{-1}
1a	−11.0	145.1	156.1
1a-Br	−35.7	127.2	162.9
1b	8.1	164.7	156.6
1f	34.7	187.2	152.5
1g	22.4	172.5	150.1
1h	15.2	164.1	148.9
1i	−4.2	142.8	147.0
1j	40.3	177.8	137.5

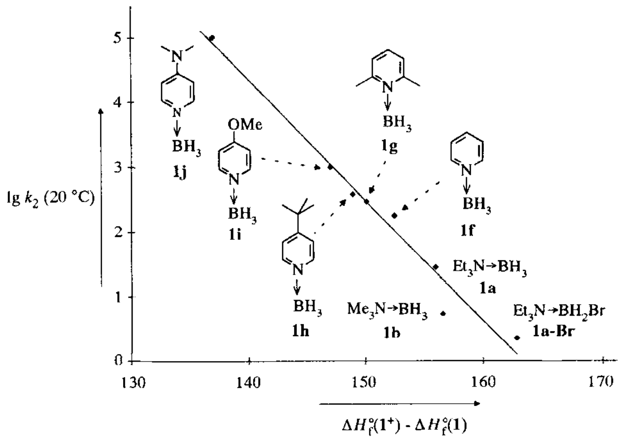


Figure 3. Correlation between the kinetics [$\log k_2(20\,^\circ C, CH_2Cl_2)$] and the thermodynamics [$\Delta H_f^\circ(1^+) - \Delta H_f^\circ(1)$] of the reaction of **1a–j** with **2a**; $\log k_2(20\,^\circ C) = -0.186(\Delta H_f^\circ(1^+) - \Delta H_f^\circ(1)) + 30.4$, $r = -0.987$.

$\Delta H_f^\circ(1^+) - \Delta H_f^\circ(1)$. The increase of the exothermicity of the hydride transfer step (Figure 3, from right to left) is associated with an increase of the corresponding rate constant. The small slope of this correlation (0.186) indicates that only 25% ($0.186 \times 2.303RT$) of the variation in ΔH_r° is detected in ΔG^{+}.

Variation of the carbocation: According to Figure 4, the rate constants of the reactions of the triethylamine borane complex

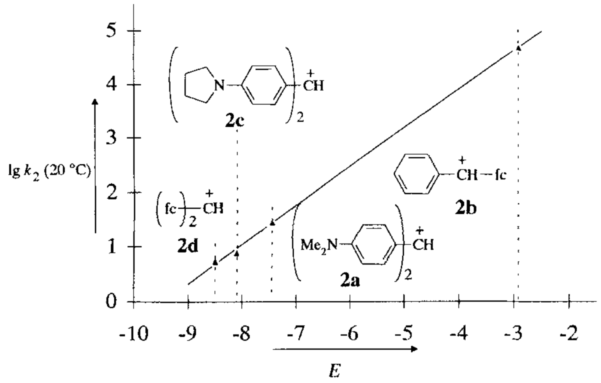


Figure 4. Correlation of the second-order rate constants ($\log k_2$, 20 °C, CH_2Cl_2) for the reactions of triethylamine borane (**1a**) with carbocations **2a–d**, with their electrophilicity parameters E.

1a ($\log k_2$, 20 °C, Table 2) correlate linearly with the electrophilicity parameters E of the carbenium ions **2a–d**, that is, they obey the linear free enthalpy relationship [Eq. (1)].[12] The

$$\log k_2(20\,^\circ C) = s(N + E) \qquad (1)$$

slope of this correlation ($s = 0.72$) is slightly larger than those of corresponding hydride abstractions from trialkylstannanes and trialkylgermanes (0.56–0.69)[12] and comparable with that for trialkylsilanes (0.64–0.76).[12] From the intersection of the graph in Figure 4 with the abscissa a nucleophilicity parameter of $N(\mathbf{1a}) = 9.44$ is obtained, that is, the nucleophilicity of triethylamine borane (**1a**) is similar to that of tributylstannane ($N = 9.29$).[12]

According to previous work,[12] structurally analogous hydride donors are characterized by similar values of s. One can assume, therefore, that the slope parameter $s = 0.72$ determined for **1a** will also hold approximately for the other amine boranes studied in this work, and one can calculate approximate N parameters from the rate constants given in Table 1 (Figure 5).

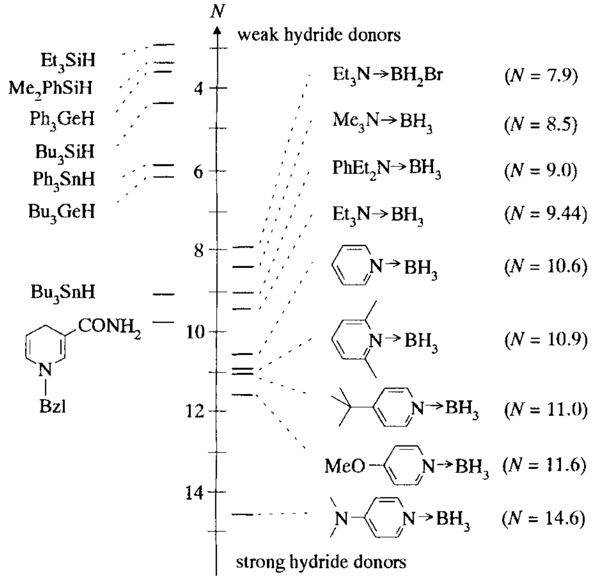


Figure 5. Nucleophilicity N of amine boranes **1** compared with other non-ionic hydride donors.

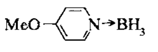
If s were exactly the same for all hydride donors shown in Figure 5, the N values would represent electrophile-independent relative reactivities of these compounds [as a consequence of Eq. (1)]. As discussed above, small variations in s occur, however, with the result that the order of the relative reactivities of hydride donors with comparable N parameters may be reversed when the electrophilic reaction partners are varied. The following discussion, therefore, concentrates on the comparison of compounds with large differences in N.

As shown in Figure 5, the trialkylamine boranes are more reactive hydride donors than trialkylsilanes ($s\Delta N \approx 4$) and trialkylgermanes ($s\Delta N \approx 2$). Their reactivity is comparable with that of trialkylstannanes and 1,4-dihydropyridines. Pyridine boranes are considerably stronger hydride donors, and the most reactive complex in this series (N,N-dimethylaminopyridine borane) exceeds the reactivity of N-benzyl-1,4-dihydronicotinamide by approximately four orders of magnitude.

With $s = 0.72$ and the N parameters listed in Figure 5, one can use Equation (1) to calculate the rate constants for the reactions of other carbocations with amine boranes. As shown in Figure 1, these rate constants depend little on solvent polarity, and it is possible to compare the reactivities of amine boranes directly with those of ionic boron hydrides toward the anisylferrocenylmethylium ion in water.

Table 6 shows that the reactivities of amine boranes are similar to that of cyanoborohydride, that is, somewhat lower than that of BH_4^- in water. It should be noted, however, that the comparison of the reactivities of neutral hydride donors with those of ionic hydride donors strongly depends on solvent polar-

Table 6. Second-order rate constants k_2 for the reaction of the anisylferrocenylmethylium ion with boron hydrides.

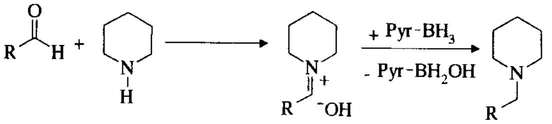
hydride donor		N	(s)	k_2 / L mol^{-1} s^{-1}
BH_3CN^-				7.4×10^3 [a]
$Et_3N \rightarrow BH_3$	(**1a**)	9.44	(0.72)	1.4×10^4 [b]
	(**1i**)	11.6	(0.72)	4.9×10^5 [b]
BH_4^-				1.5×10^6 [a]

[a] Rate constants at 25 °C in water (see ref. [24]). [b] Calculated values (from Eq. (1) with $E = -3.70$; refs. [12,27b] at 20 °C in dichloromethane).

ity, and the reactivities of the ionic hydride donors BH_3CN^- and BH_4^- can be expected to increase considerably as water is replaced by a less polar solvent.

Conclusions

Amine boranes are among the strongest non-ionic hydride donors which are valuable reducing agents because of their solubility in many organic solvents. In reactions with positively charged electrophiles, they are more reactive hydride donors than trialkylsilanes, and comparable with $NaBH_3CN$. As a consequence amine boranes may replace this expensive and toxic reagent in many applications (e.g., reductive amination of carbonyl groups). According to the linear free-enthalpy relationship [Eq. (1)] the reduction of iminium ions ($E \approx -7$)[25] is expected to proceed smoothly with all the amine boranes shown in Figure 5. In agreement with this analysis, Moormann has recently reported the reductive amination of aldehydes in protic and aprotic solvents with pyridine borane instead of BH_3CN^- as reducing agent (Scheme 6).[26]



Scheme 6. Example of application of pyridine borane as reducing agent [26].

Further applications of amine boranes as reducing agents can be deduced from the reactivity scales presented by Mayr and Patz.[12]

Experimental Section

General: Melting points are uncorrected. High-vacuum sublimations (0.01 mbar) were performed in a Büchi Kugelrohr apparatus. ^1H NMR spectra were recorded at 60 or 300 MHz and ^{13}C NMR spectra at 75.7 MHz in $CDCl_3$; chemical shifts are in ppm relative to TMS and coupling constants are in Hz.

Materials: The benzhydryl salts **2a-BF$_4$**, **2a-PF$_6$**, **2a-OTf**, **2c-BF$_4$**, and **2d-BF$_4$** were prepared as described previously.[15, 27a, 27c] The cation **2b** was generated from the acetate **2b**-OAc by ionization with TMSOTf.[27b] Commercially available amine boranes **1a**, **1b**, **1c**, **1f**, **1g**, and **1j** were used after either sublimation or recrystallization from pentane/CH_2Cl_2. The amine boranes **1h** and **1i** were prepared from the corresponding amines and diborane as described by Mooney and Qaseem.[2a] The haloborane **1a-Br** was prepared from **1a** and *N*-bromosuccinimide,[28] and **1a-D** was obtained by deuteration of **1a** with D_2O pretreated with $SOCl_2$.[29]

General procedure for the reduction of 2: At 20 °C the amine borane **1a** (3.50 mmol) was added in one portion to a stirred solution of **2a-BF$_4$** (2.70 mmol) in dry CH_2Cl_2 (50 mL). After disappearance of the blue color of the cation **2a** (< 1 h) the mixture was stirred for 1 h with 6 M hydrochloric acid (30 mL) to hydrolyze the boranes. The layers were separated, and NaOH (6 M, 40 mL) was added to the aqueous layer which was then extracted with diethyl ether (2 × 30 mL). The combined organic layers were dried (Na_2SO_4), filtered, and evaporated. The volatile compounds were removed at the Kugelrohr apparatus before sublimation or crystallization of the product **3a**.

Bis(4-*N*,*N*-dimethylaminophenyl)methane (**3a**) was obtained from **2a-BF$_4$** (0.92 g, 2.70 mmol) and **1a** (0.43 g, 3.74 mmol). Yield 77% (0.53 g, 2.08 mmol). The diarylmethane **3a** was also obtained from **2a-BF$_4$**, **2a-OTf**, or **2a-PF$_6$** with the other amine boranes **1** in good yield (75–90%); m.p. 90–91 °C (91 °C[30]); b.p. 140–150 °C (0.01 mbar); for NMR data see refs. [31, 32].

Bis(4-*N*,*N*-dimethylaminophenyl)-[D$_1$]methane (**3a-D**) was obtained from **2a-BF$_4$** (0.81 g, 2.38 mmol) and **1a-D** (0.41 g, 3.47 mmol). Yield 86% (0.52 g, 2.04 mmol); b.p. 140–150 °C (0.01 mbar); m.p. 84–85 °C (84–84.5 °C);[33] ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.12$ (d, $J = 8.5$ Hz, 4H, AA'BB' system), 6.76 (d, $J = 8.5$ Hz, 4H, AA'BB' system), 3.85 (brs, 1H, CHD), 2.96 (s, 12H, CH_3); ^{13}C NMR (75.7 MHz, $CDCl_3$): $\delta = 148.9$, 130.8, 129.8, 113.6, 41.3, 39.4.

Ferrocenylphenylmethane (**3b**) was obtained from **2b**-OAc (0.82 g, 2.45 mmol) and **1a** (0.65 g, 5.65 mmol) in the presence of TMSOTf (0.25 g, 1.12 mmol). Yield 87% (0.59 g, 2.14 mmol) after crystallization from ethanol at −20 °C; m.p. 73–73.5 °C (73.5–74.0 °C);[34] ^1H NMR (60 MHz; $CDCl_3$): $\delta = 7.35$ (m, 5H, Ph), 4.15 (s, 9H, Fc), 3.75 (s, 2H, CH_2).

Bis(4-pyrrolidinophenyl)methane (**3c**) was obtained from **2c-BF$_4$** (0.52 g, 1.33 mmol) and **1a** (0.22 g, 1.91 mmol). Yield 69% (0.28 g, 0.92 mmol) after crystallization from pentane/CH_2Cl_2 (1/1); m.p. 88–88.5 °C (88–89 °C[15]); for spectroscopic data see ref. [15].

Kinetic investigations: The consumption of the colored benzhydryl cations **2** by the amine borane was determined photometrically by using fiber optics and the workstation described previously.[16a] The results are summarized in Table 7.

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[1] a) R. O. Hutchins, K. Learn, B. Nazer, D. Pytiewski, *Org. Prep. Proced. Int.* **1984**, *16*, 335–372; b) A. M. Salunkhe, E. R. Burkhardt, *Tetrahedron Lett.* **1997**, *38*, 1519–1522 and references therein.

[2] a) E. F. Mooney, M. A. Qaseem, *J. Inorg. Nucl. Chem.* **1968**, *30*, 1439–1446; b) H. Nöth, H. Beyer, *Chem. Ber.* **1960**, *93*, 928–938; c) A. Burg, H. Schlesinger, *J. Am. Chem. Soc.* **1937**, *59*, 780.

[3] H. C. Brown, L. T. Murray, *Inorg. Chem.* **1984**, *23*, 2746–2753.

[4] L T. Murray, Ph.D. Thesis, Purdue University of West Lafayette, Indiana, USA, **1963** (cited in ref. [1]).

[5] Product information on amine boranes, Bayer AG, Leverkusen, Germany, **1993**.

[6] R. P. Barnes, J. H. Graham, M. D. Taylor, *J. Org. Chem.* **1958**, *23*, 1561–1562.

[7] G. C. Andrews, T. C. Crawford, *Tetrahedron Lett.* **1980**, *21*, 693-696.

[8] E. M. Fedneva, *J. Gen. Chem. USSR (Engl. Transl.)* **1960**, *30*, 2796–2798.

[9] H. C. Brown, J. Chandrasekharan, *Gazz. Chim. Ital.* **1987**, *117*, 517–523.

[10] M. Zaidlewicz, reported at IXth Imeboron (Lecture SB 11), Heidelberg, Germany, **1996**.

[11] a) H. C. Kelly, M. B. Giusto, F. R. Marchelli, *J. Am. Chem. Soc.* **1964**, *86*, 3882–3884; b) S. S. White Jr., H. C. Kelly, *ibid.* **1970**, *92*, 4203–4209; c) T. C. Wolfe, H. C. Kelly, *J. Chem. Soc. Perkin Trans. 2* **1973**, 1948–1950; d) W. M. Jones, *J. Am. Chem. Soc.* **1960**, *82*, 2528–2532.

Table 7. Kinetics of the reactions of carbenium ions **2** with amine boranes **1**.

Reaction of **2a** and **1a** in CH_2Cl_2.

T/°C	X^- [a]	[**2a**]$_0$/ 10^{-5} mol L^{-1}	[**1a**]$_0$/ mmol L^{-1}	Conv./ % [b]	k_2/ L mol^{-1} s^{-1}
21.1	BF_4	18.7	4.13	86	29.7
21.3	BF_4	9.32	2.74	74	31.0
20.4	OTf	8.29	3.30	86	29.0
20.4	OTf	8.70	2.30	98	28.5
12.3	BF_4	7.21	2.65	77	18.0
5.4	BF_4	7.21	2.82	93	9.90
−15.9	BF_4	8.22	2.70	96	1.63
−27.0	BF_4	5.31	2.71	57	0.633

Reaction of **2a** and **1a-D** in CH_2Cl_2.

T/°C	X^- [a]	[**2a**]$_0$/ 10^{-5} mol L^{-1}	[**1a-D**]$_0$/ mmol L^{-1}	Conv./ % [b]	k_2/ L mol^{-1} s^{-1}
20.0	BF_4	7.06	0.763	94	15.8
19.4	OTf	5.70	0.817	87	14.8
19.1	BF_4	7.98	1.68	97	14.6
19.0	OTf	4.91	1.79	97	14.5
7.6	BF_4	5.20	0.437	96	6.25
−4.0	BF_4	7.53	0.814	80	2.46
−18.0	BF_4	4.83	0.732	91	0.663
−40.1	BF_4	8.55	0.809	92	0.0614

Reaction of **2a** and **1a-Br** in CH_2Cl_2.

T/°C	X^- [a]	[**2a**]$_0$/ 10^{-5} mol L^{-1}	[**1a-Br**]$_0$/ mmol L^{-1}	Conv./ % [b]	k_2/ L mol^{-1} s^{-1}
20.0	BF_4	5.89	1.26	82	2.21
20.0	BF_4	5.32	2.27	94	2.23
20.0	OTf	3.27	0.926	79	2.23
20.0	OTf	4.79	2.58	63	2.30

Reaction of **2a** and **1b** in CH_2Cl_2.

T/°C	X^- [a]	[**2a**]/ 10^{-5} mol L^{-1}	[**1b**]/ mmol L^{-1}	Conv./ % [b]	k_2/ L mol^{-1} s^{-1}
20.4	BF_4	10.8	2.51	95	5.46
20.4	BF_4	9.18	1.17	99	5.50
20.4	OTf	8.40	0.931	98	5.23
20.3	OTf	9.18	0.566	97	5.31
10.8	BF_4	9.37	0.852	95	2.69
3.0	BF_4	5.64	0.878	93	1.33
−22.7	BF_4	5.79	0.902	94	0.109

Reaction of **2a** and **1c** in CH_2Cl_2.

T/°C	X^- [a]	[**2a**]$_0$/ 10^{-5} mol L^{-1}	[**1c**]$_0$/ mmol L^{-1}	Conv./ % [b]	k_2/ L mol^{-1} s^{-1}
20.0	BF_4	7.06	1.32	52	14.7
20.0	OTf	7.22	1.35	92	14.4
19.3	OTf	8.69	2.60	96	13.4
18.6	BF_4	6.43	0.563	76	12.1
5.4	BF_4	7.07	0.796	62	4.21
−6.4	BF_4	8.87	0.798	96	1.40
−15.1	BF_4	5.72	0.810	95	0.594
−45.2	BF_4	7.44	0.837	69	0.0235

Reaction of **2a** and **1d** in CH_2Cl_2.

T/°C	X^- [a]	[**2a**]$_0$/ 10^{-5} mol L^{-1}	[**1d**]$_0$/ mmol L^{-1}	Conv./ % [b]	k_2/ L mol^{-1} s^{-1}
20.0	BF_4	4.79	0.303	79	37.9
20.0	BF_4	7.34	0.510	62	38.0
20.0	BF_4	6.41	0.706	76	38.7
20.0	BF_4	7.19	2.08	96	37.2
20.0	PF_6	5.08	0.878	87	37.5
−7.7	BF_4	8.28	1.44	95	4.83
−18.0	BF_4	7.01	0.664	82	2.09
−33.8	PF_6	5.38	0.930	95	0.418

Reaction of **2a** and **1e** in CH_2Cl_2.

T/°C	X^- [a]	[**2a**]$_0$/ 10^{-5} mol L^{-1}	[**1e**]$_0$/ mmol L^{-1}	Conv./ % [b]	k_2/ L mol^{-1} s^{-1}
20.0	BF_4	8.59	0.370	78	23.2
20.0	BF_4	6.88	1.24	71	23.3
20.0	PF_6	4.91	0.682	70	23.0
20.0	PF_6	4.90	0.618	79	23.8
20.0	PF_6	5.20	3.01	74	23.3

Reaction of **2a** and **1f** in CH_2Cl_2.

T/°C	X^- [a]	[**2a**]$_0$/ 10^{-5} mol L^{-1}	[**1f**]$_0$/ mmol L^{-1}	Conv./ % [b]	k_2/ L mol^{-1} s^{-1}
5.3	BF_4	5.99	0.516	95	67.4
−7.5	BF_4	7.51	0.520	89	24.5
−10.5	OTf	8.76	5.07	83	18.5
−10.5	OTf	8.10	3.12	81	18.4
−29.4	BF_4	7.51	0.517	97	3.53
−29.1	BF_4	7.79	0.965	97	3.57
−50.0	BF_4	8.49	1.05	97	0.438

Reaction of **2a** and **1g** in CH_2Cl_2.

T/°C	X [a]	[**2a**]$_0$/ 10^{-5} mol L^{-1}	[**1g**]$_0$/ mmol L^{-1}	Conv./ % [b]	k_2/ L mol^{-1} s^{-1}
−20.3	OTf	6.26	0.765	66	14.6
−20.2	BF_4	6.36	0.688	99	15.4
−20.2	BF_4	7.48	0.405	98	15.8
−40.5	BF_4	7.70	0.833	97	2.63
−50.0	BF_4	8.95	0.967	98	0.906
−58.0	BF_4	7.70	0.934	95	0.333
−67.8	BF_4	8.26	0.446	90	0.103

Reaction of **2a** and **1h** in CH_2Cl_2.

T/°C	X^- [a]	[**2a**]$_0$/ 10^{-5} mol L^{-1}	[**1h**]$_0$/ mmol L^{-1}	Conv./ % [b]	k_2/ L mol^{-1} s^{-1}
6.5	BF_4	5.84	0.555	87	161
−4.0	BF_4	4.35	0.465	87	74.8
−4.4	OTf	9.65	0.567	93	70.1
−4.5	OTf	6.06	1.07	92	69.6
−17.9	OTf	6.28	1.48	89	23.7
−30.0	OTf	8.82	1.56	98	8.60
−42.2	OTf	6.13	1.62	96	2.57

Reaction of **2a** and **1i** in CH_2Cl_2.

T/°C	X^- [a]	[**2a**]$_0$/ 10^{-5} mol L^{-1}	[**1i**]$_0$/ mmol L^{-1}	Conv./ % [b]	k_2/ L mol^{-1} s^{-1}
−10.8	BF_4	5.83	0.310	92	127
−10.9	BF_4	7.82	0.208	95	131
−12.0	OTf	4.71	0.213	92	120
−27.0	BF_4	6.72	0.357	97	34.7
−41.0	BF_4	9.64	0.320	94	9.42
−50.8	BF_4	8.80	0.468	96	3.62
−70.9	BF_4	8.35	4.44	83	0.429

Reaction of **2a** and **1j** in CH_2Cl_2.

T/°C	X^- [a]	[**2a**]$_0$/ 10^{-5} mol L^{-1}	[**1j**]$_0$/ mmol L^{-1}	Conv./ % [b]	k_2/ L mol^{-1} s^{-1}
−70.2	BF_4	6.13	1.53	24	465
−70.1	OTf	2.65	0.745	41	507
−70.0	OTf	2.68	0.376	66	496
−70.1	OTf	3.10	0.566	71	500

Table 7. (continued)

Reaction of **2b** and **1a** in CH_2Cl_2.

T/ °C	X^- [a]	[**2b**]$_0$/ 10^{-5} mol L^{-1}	[**1a**]$_0$/ mmol L^{-1}	Conv./ % [b]	k_2/ L mol^{-1} s^{-1}
−44.8	OTf	7.75	0.257	71	1037
−54.7	OTf	12.2	0.381	71	479
−65.7	OTf	16.6	0.628	73	164
−75.3	OTf	18.1	0.855	79	69.3
−75.3	OTf	18.8	1.34	75	69.2
−74.4	OTf	16.2	0.580	71	75.5

Reaction of **2c** and **1a** in CH_2Cl_2.

T/ °C	X^- [a]	[**2c**]$_0$/ 10^{-5} mol L^{-1}	[**1a**]$_0$/ mmol L^{-1}	Conv./ % [b]	k_2/ L mol^{-1} s^{-1}
21.5	BF_4	7.32	3.00	98	8.93
21.5	BF_4	5.41	1.57	97	8.88
10.7	BF_4	5.53	1.33	96	3.67
0.8	BF_4	5.62	1.63	88	1.68
−10.6	BF_4	5.30	1.53	93	0.567
−28.4	BF_4	6.65	1.92	92	0.0938

Reaction of **2d** and **1a** in CH_2Cl_2.

T/ °C	X^- [a]	[**2d**]$_0$/ 10^{-5} mol L^{-1}	[**1a**]$_0$/ mmol L^{-1}	Conv./ % [b]	k_2/ L mol^{-1} s^{-1}
20.0	BF_4	12.2	1.78	39	5.60
20.0	BF_4	18.6	1.80	58	5.47
20.0	BF_4	17.5	3.04	77	5.56
6.2	BF_4	9.38	3.64	65	2.02
−8.9	BF_4	13.7	5.91	77	0.531
−18.5	BF_4	9.48	7.36	76	0.242

Reaction of **2a** and **1a** in acetone.

T/ °C	X^- [a]	[**2a**]$_0$/ 10^{-5} mol L^{-1}	[**1a**]$_0$/ mmol L^{-1}	Conv./ % [b]	k_2/ L mol^{-1} s^{-1}
20.0	BF_4	9.25	3.97	97	15.7
20.0	OTf	4.62	2.53	85	15.9
20.0	OTf	5.37	0.863	95	16.1
−3.1	OTf	6.96	0.932	88	2.88
−20.3	OTf	5.20	1.27	98	0.655
−39.0	OTf	6.06	1.30	97	0.0995

Reaction of **2a** and **1a** in acetonitrile.

T/ °C	X^- [a]	[**2a**]$_0$/ 10^{-5} mol L^{-1}	[**1a**]$_0$/ mmol L^{-1}	Conv./ % [b]	k_2/ L mol^{-1} s^{-1}
19.4	BF_4	9.00	0.529	97	12.5
19.2	BF_4	8.65	3.71	86	12.1
19.4	OTf	8.15	3.60	95	12.3
19.4	OTf	8.95	0.534	85	12.5
5.1	BF_4	7.59	2.48	90	4.27
−12.9	BF_4	8.95	0.846	88	0.976
−22.8	BF_4	8.48	0.641	89	0.434
−29.6	BF_4	9.25	0.874	86	0.205

Reaction of **2a** and **1a** in 2,2,2-trifluoroethanol.

T/ °C	X^- [a]	[**2a**]$_0$/ 10^{-5} mol L^{-1}	[**1a**]$_0$/ mmol L^{-1}	Conv./ % [b]	k_2/ L mol^{-1} s^{-1}
20.0	BF_4	9.10	10.6	79	5.92
20.0	BF_4	9.97	5.78	94	5.89
20.0	BF_4	8.26	7.18	95	5.99
20.0	BF_4	5.90	1.71	69	6.02

Reaction of **2d** and **1a** in liquid SO_2.

T/ °C	X^- [a]	[**2d**]$_0$/ 10^{-5} mol L^{-1}	[**1a**]$_0$/ mmol L^{-1}	Conv./ % [b]	k_2/ mL mol^{-1} s^{-1}
−20.0	BF_4	7.21	24.9	70	21.4
−24.9	BF_4	4.76	7.84	33	12.7
−33.5	BF_4	7.13	3.68	67	5.16
−47.8	BF_4	7.30	11.8	58	1.06

[a] Counterion. [b] Range evaluated for the determination of k_2.

[12] H. Mayr, M. Patz, *Angew. Chem.* **1994**, *106*, 990–1010; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 938–957.

[13] a) H. Mayr, N. Basso, G. Hagen, *J. Am. Chem. Soc.* **1992**, *114*, 3060–3066; b) H. Mayr, N. Basso, *Angew. Chem.* **1992**, *104*, 1103–1105; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1046–1048.

[14] D. D. Perrin, *Dissociation Constants of Organic Bases in Aqueous Solution*, Butterworths, London, **1965**.

[15] N. Hering, Diploma Thesis, Technische Hochschule Darmstadt, **1996**.

[16] a) H. Mayr, R. Schneider, C. Schade, J. Bartl, R. Bederke, *J. Am. Chem. Soc.* **1990**, *112*, 4446–4454; b) H. Mayr, R. Schneider, B. Irrgang, C. Schade, *ibid.* **1990**, *112*, 4454–4459; c) H. Mayr, R. Schneider, U. Grabis, *ibid.* **1990**, *112*, 4460–4467; d) G. Hagen, H. Mayr, *ibid.* **1991**, *113*, 4954–4961; e) H. Mayr, J. Bartl, G. Hagen, *Angew. Chem.* **1992**, *104*, 1689–1691; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1613–1615.

[17] M. A. Weiner, M. Lattmann, *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 723–728.

[18] L. J. Franklin in *Carbonium Ions, General Aspects and Methods of Investigation, Vol. 1* (Eds.: G. A. Olah, P. v. R. Schleyer), John Wiley, New York, **1968**, pp. 77–109.

[19] H. Mayr, M. Roth, G. Lang in *Cationic Polymerization: Fundamentals and Applications; ACS Symp. Ser. 665* (Eds.: R. Faust, T. Shaffer), ACS, Washington, DC, **1997**, pp. 25–40.

[20] C. Reichardt *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed., VCH, Weinheim, **1988**.

[21] H. Mayr, M.-A. Funke, Technische Hochschule Darmstadt, unpublished results.

[22] In the correlation of $\log k_2$ versus σ_p^+, compound **1j** was located above a relatively poor linear correlation line. For this reason neither the correlation with σ_p^+ nor a Yukawa/Tsuno treatment has been considered.

[23] a) M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, J. J. P. Stewart, *J. Am. Chem. Soc.* **1985**, *107*, 3902–3909; b) M. J. S. Dewar, C. Jie, E. G. Zoebisch, *Organometallics* **1988**, *7*, 513–521; c) F. J. Seiler, *MOPAC Program, Version 6.00*, Research Laboratory U. S. Air Force Academy, Colorado Springs, CO.

[24] C. A. Bunton, N. Carrasco, F. Davoudzadeh, W. E. Watts, *J. Chem. Soc. Perkin Trans. 2* **1980**, 1520–1528.

[25] H. Mayr, A. Ofial, *Tetrahedron Lett.* **1997**, *38*, 3503–3506.

[26] A. E. Moormann, *Synth. Commun.* **1993**, *23*, 789–795.

[27] a) M. Patz, H. Mayr, *Tetrahedron Lett.* **1993**, *34*, 3393–3396; b) H. Mayr, D. Rau, *Chem. Ber.* **1994**, *127*, 2493–2498; c) J. Burfeindt, Diploma Thesis, Technische Hochschule Darmstadt, **1996**.

[28] J. E. Douglas, *J. Org. Chem.* **1966**, *31*, 962–966.

[29] Z. Polivka, V. Kubelka, N. Holubová, M. Ferles, *Collect. Czech. Chem. Commun.* **1970**, *35*, 1131–1146.

[30] A. Mangini, R. Passerini, *J. Chem. Soc.* **1956**, 4954–4959.

[31] J. R. L. Smith, J. M. Linford, L. C. McKeer, P. M. Morris, *J. Chem. Soc. Perkin Trans. 2* **1984**, 1099–1105.

[32] T. Sakakibara, Y. Dogomori, Y. Tsuzuki, *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3592–3596.

[33] M. Sekiya, K. Suzuki, *Chem. Pharm. Bull.* **1974**, *22*, 1788–2746; N. Weliky, E. S. Gould, *J. Am. Chem. Soc.* **1957**, *79*, 2742–2746.

0947-6539/97/0308-1222 $ 17.50+.50/0