Reference Scales for the Characterization of Cationic Electrophiles and Neutral Nucleophiles[†,‡]

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Abstract: Twenty-three diarylcarbenium ions and 38 π-systems (arenes, alkenes, allyl silanes and stannanes, silyl enol ethers, silyl ketene acetals, and enamines) have been defined as basis sets for establishing general reactivity scales for electrophiles and nucleophiles. The rate constants of 209 combinations of these benzhydrylium ions and π-nucleophiles, 85 of which are first presented in this article, have been subjected to a correlation analysis to determine the electrophilicity parameters E and the nucleophilicity parameters N and s as defined by the equation $\log k(20\ °\mathrm{C}) = s(N + E)$ (Mayr, H.; Patz, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 938−957). Though the reactivity scales thus obtained cover more than 16 orders of magnitude, the individual rate constants are reproduced with a standard deviation of a factor of 1.19 (Table 1). It is shown that the reactivity parameters thus derived from the reactions of diarylcarbenium ions with π-nucleophiles (Figure 3) are also suitable for characterizing the nucleophilic reactivities of alkynes, metal-π-complexes, and hydride donors (Table 2) and for characterizing the electrophilic reactivities of heterosubstituted and metal-coordinated carbenium ions (Table 3). The reactivity parameters in Figure 3 are, therefore, recommended for the characterization of any new electrophiles and nucleophiles in the reactivity range covered. The linear correlation between the electrophilicity parameters E of benzhydryl cations and the corresponding substituent constants σ^+ provides Hammett σ^+ constants for 10 substituents from −1.19 to −2.11, i.e., in a range with only very few previous entries.

Introduction

Lapworth was the first to recognize that polar reagents fall into two categories which he termed “cationoid” and “anionoid” (1925).[1] Shortly after, Ingold suggested the alternative designations “electrophilic” and “nucleophilic” for these classes of compounds,[2] two terms that are now in general use for discussing organic reactivity.

Attempts to quantify these terms started in 1953, when Swain and Scott characterized nucleophiles by one parameter (n) and electrophiles by two parameters (s, $\log k_{\mathrm{H_2O}}$).[3] Succeeding investigations added more and more parameters,[4,5] and finally Bunnett listed 17 factors that have to be considered in a quantitative description of nucleophilicity.[6] On this background, Ritchie’s “constant selectivity relationship” attracted much attention because it calculates the rates of the reactions of carbocations or diazonium ions with nucleophiles from only a single parameter for electrophiles and a single parameter for nucleophiles.[7] Kane-Maguire and Sweigart reported analogous relationships for reactions of electrophilic metal−π-complexes with phosphines, amines, and arenes.[8,9] These results indicated that electrophile-nucleophile combinations that do not involve the cleavage of a C−X bond in the rate-determining step follow a much simpler reactivity pattern than the $\mathrm{S_N2}$ type reactions that were investigated earlier.

In view of the results of Ritchie, Kane-Maguire, and Sweigart it was not astonishing that many reactions of carbocations with olefins were also found to follow constant selectivity relationships.[10] To satisfactorily describe the reactivities of a larger variety of nucleophiles, however, the introduction of a second parameter for nucleophiles[11−13] was found to be necessary. In 1994, we subjected the rate constants of 327 reactions of carbocations, metal−π-complexes, and diazonium ions with π-, σ-, and n-nucleophiles to a correlation analysis on the basis of eq 1,

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[†] Dedicated to Prof. Jürgen Sauer on the occasion of his 70th birthday.

[‡] A comprehensive listing of nucleophilicity and electrophilicity parameters can be found from October 2001 at http://www.cup.uni-muenchen.de/oc/mayr/.

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10.1021/ja010890y CCC: $20.00

$$\log k(20\ °\mathrm{C}) = s\,(N + E) \qquad (1)$$

where E is the electrophilicity parameter, N is the nucleophilicity parameter, and s is the nucleophile-dependent slope parameter, and obtained N and s parameters of 56 nucleophiles and E parameters of 43 electrophiles.[11]

Despite the large structural variety of substrates and reactions considered, the rate constants k calculated by the three-parameter eq 1 were usually found to be accurate within a factor of 10−100, when reagents of obvious steric bulk (e.g., tritylium ions) were excluded. This precision is quite remarkable in view of the fact that each of the scales covered 18 orders of magnitude, resulting in an overall reactivity range of appoximately 36 orders of magnitude. Because solvent effects are small in ion molecule reactions,[11,14,15] their influence is already included in the aforementioned error-limits.

Since 1994, numerous other types of reactions have been found to follow eq 1. N and s parameters of further classes of nucleophiles, e.g., amine boranes,[15] metal−π-complexes,[16,17] heteroarenes,[18] silyl enol ethers,[19] and silyl ketene acetals,[19] have been determined by plotting the rate constants (log k) of their reactions with previously characterized electrophiles versus the published E parameters[11] of the electrophilic reaction partners.

Electrophilicity parameters E of dithiocarbenium ions,[20] iminium ions,[21,22] propargyl cations with cobalt carbonyl stabilization[23] or (arene)Cr(CO)$_3$ substituents,[24,25] cationic allyl palladium complexes,[26] and Fe(CO)$_3$-coordinated tropylium ions[27] have been derived from the rate constants of the reactions of these electrophiles with nucleophiles that were characterized by the reactivity parameters N and s in the 1994 paper.[11] Ideally, the electrophilicity parameter E_i of a certain electrophile i should not depend on the choice of nucleophile j used for its determination. In practice, the electrophilicity parameters obtained from reactions of the electrophile i with various nucleophiles differed slightly, and E_i was taken as the arithmetic mean of the values calculated with different reaction partners (eq 2)

$$E_i = \frac{1}{n}\sum_{j=1}^{n} E_{ij} = \frac{1}{n}\sum_{j=1}^{n}\left(\frac{\log k_{ij}}{s_j} - N_j\right) \qquad (2)$$

where n is the number of nucleophiles used for the characterization of the new electrophile; E_{ij} is the E parameter of electrophile i derived from the reaction with the nucleophile j; s_j and N_j are the slope and nucleophilicity parameters published in 1994 (ref 11).

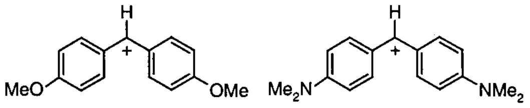
In both cases the originally published E, N, and s parameters[11] were kept unchanged. As a consequence, rate constants that had entered our data collection at an early stage (before 1994) received higher weight than data that were introduced later.

An alternative and more consequent way of handling the kinetic data would be a complete correlation analysis of all available rate constants after the addition of each new entry. This procedure is not practicable, however, because it would continuously alter all reactivity parameters and thus cause confusion.

The use of all available rate constants for the determination of E, N, and s by correlation analysis would cause an additional problem: Imagine the case that a reaction series, investigated for the elucidation of the reactivity parameters of a structurally unique reagent, matches eq 1 only moderately. One would then have to decide whether the benefit of obtaining the new reactivity parameter compensates for the deterioration of the quality of the overall correlation, which is associated with the incorporation of a poorly matching reaction series. An unambiguous decision would often be impossible!

We will now provide a solution for these problems by deriving E, N, and s parameters for a set of well-behaved reference electrophiles and nucleophiles. Because of the clearly defined origin of the reactivity parameters presented in this article, future reparametrizations are not intended, and it will be shown that the parameters determined in this way can be used for characterizing any further reagents in the reactivity range covered.

Electrophile Basis Set: Benzhydryl Cations. Previous work has shown perfect linear reactivity−reactivity correlations for reactions of benzhydryl cations with numerous classes of nucleophiles,[11,28] probably because the steric situation at the reaction centers is kept constant while the reactivities of the benzhydrylium ions are modified by variation of the para-substituents. For that reason the choice of benzhydryl cations as reference electrophiles appeared attractive. However, whereas we had characterized numerous benzhydrylium ions with 6 > E > 0, the 4,4′-bis(dimethylamino)benzhydrylium ion was the only diarylcarbenium ion with a negative E value studied so far. For the construction of benzhydryl cation based reactivity scales, the characterization of more benzhydryl cations with E < 0 was, therefore, necessary.



E	0.00	−7.02
pK_{R+}	−5.71	+5.61
σ_p^+	−0.78 (OMe)	−1.70 (NMe$_2$)

Since previous work showed a correlation between pK_{R+} values and the electrophilicity parameters E of carbocations,[13,23] we searched for benzhydrylium ions with pK_{R+} > −5.71. However, while dozens of benzhydrylium ions with pK_{R+} < −5.71 have been reported in the literature,[29,30] the 4,4′-bis-

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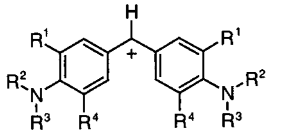
(dimethylamino)-substituted cation was the only one with a higher pK_{R+} value so far characterized. The surprising lack of compounds in this range mirrors the shortage of substituents with Hammett σ_p^+ parameters more negative than -0.78.[31,32]

We have not been successful in synthesizing benzhydrylium ions with a *p*-dimethylamino group on one phenyl ring and *p*-alkoxy on the other ring,[33] and problems were encountered when preparing bis(3-Me,4-NMe$_2$)-substituted benzhydrylium ions.[34] Probably because of electrophilic attack at nitrogen, the generation of such carbenium ions was not well reproducible, and for that reason we have not selected such species as reference electrophiles.

We have been able, however, to isolate and characterize ten Ar$_2$CH$^+$ analogues of Michler's Hydrol Blue, the syntheses of which are summarized in Schemes 1−3.



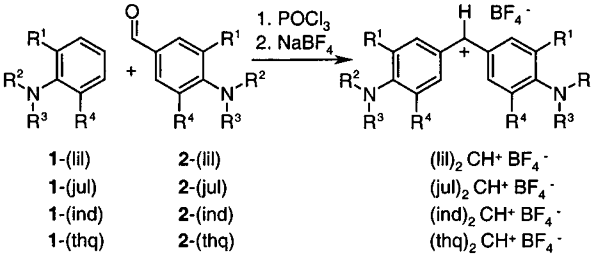
Ar_2CH^+ [a]	R^1	R^2	R^3	R^4
$(lil)_2CH^+$	$-(CH_2CH_2)-$		$-(CH_2CH_2CH_2)-$	
$(jul)_2CH^+$	$-(CH_2CH_2CH_2)-$		$-(CH_2CH_2CH_2)-$	
$(ind)_2CH^+$	$-(CH_2CH_2)-$		CH_3	H
$(thq)_2CH^+$	$-(CH_2CH_2CH_2)-$		CH_3	H
$(pyr)_2CH^+$	H	$-(CH_2CH_2CH_2CH_2)-$		H
$(dma)_2CH^+$ *b*	H	CH_3	CH_3	H
$(mpa)_2CH^+$	H	C_6H_5	CH_3	H
$(mor)_2CH^+$	H	$-(CH_2CH_2OCH_2CH_2)-$		H
$(dpa)_2CH^+$	H	C_6H_5	C_6H_5	H
$(mfa)_2CH^+$	H	CH_2CF_3	CH_3	H
$(pfa)_2CH^+$	H	CH_2CF_3	C_6H_5	H

[a] For abbreviations, see ref. 35. [b] Michler's Hydrol Blue.

The tetrafluoroborate salts of (lil)$_2$CH$^+$, (jul)$_2$CH$^+$,[36] (ind)$_2$CH$^+$, and (thq)$_2$CH$^+$ were generated by phosphorus oxychloride-promoted coupling of the arenes **1** with the corresponding carbaldehydes **2**[37] and successsive treatment with an aqueous solution of sodium tetrafluoroborate analogous to a procedure described by Jutz[38] (Scheme 1).

The 4,4′-diaminobenzophenones **4**-(pyr)$_2$ and **4**-(mor)$_2$ were obtained by heating sulfolane or dimethyl sulfoxide solutions of 4,4′-difluorobenzophenone **3** and excess pyrrolidine or morpholine, respectively, as described by Hepworth et al[39] (Scheme 2). The analogous formation of **4**-(mpa)$_2$ and **4**-(dpa)$_2$ was achieved in the presence of potassium *tert*-butoxide. Reduction of **4** with sodium borohydride[39] gave the 4,4′-diaminobenzhydrols **5**, which were treated with tetrafluoroboric acid to generate the corresponding tetrafluoroborates of (mpa)$_2$CH$^+$, (dpa)$_2$CH$^+$, and (pyr)$_2$CH$^+$.

Scheme 1



Since pure 4,4′-bis(morpholino)benzhydrylium tetrafluoroborate was not obtained by this procedure, the benzhydrol **5**-(mor)$_2$ was ionized with tritylium tetrafluoroborate according to eq 3.

$$\mathbf{5}\text{-(mor)}_2 + Ph_3C^+\ BF_4^- \xrightarrow[-Ph_3COH]{CH_2Cl_2} \text{(mor)}_2CH^+\ BF_4^- \qquad (3)$$

Oxidation of the trifluoroethylamino-substituted[40] diphenylmethanes **6**-(mfa)$_2$ and **6**-(pfa)$_2$ with DDQ in methanol and reduction of the resulting benzophenones with sodium borohydride gave the bis(diarylmethyl) ether **7** (R = Me) and the benzhydrol **5**-(pfa)$_2$ (R = Ph), respectively (Scheme 3). Treatment of these compounds with tetrafluoroboric acid yielded the corresponding benzhydrylium salts (mfa)$_2$CH$^+$ BF$_4^-$ and (pfa)$_2$CH$^+$ BF$_4^-$.

Since the synthetic procedures illustrated in Schemes 1−3 still require optimization, we will describe details of these syntheses later.

In contrast to the yellow or red alkyl- and alkoxy-substituted benzhydryl cations, which have absorption maxima between 435 and 510 nm,[41,42] the *p*-amino-substituted benzhydrylium ions are blue due to their absorption maxima between 590 and 680 nm.[36,39,43] Details of the UV−vis spectra are given in Table S19 of the Supporting Information.

Nucleophile Basis Set: π_{CC}-Systems. Previous work has shown that the reactions of benzhydrylium ions with many types of nucleophiles, including aliphatic and aromatic π-systems, metal π-complexes, hydride donors, and n-nucleophiles, follow linear reactivity−reactivity correlations of comparable quality.[11] For that reason, representatives of all of these classes of compounds may be considered as potential reference nucleophiles. Since carbon−carbon double-bonded systems, including substituted benzenes, heteroarenes, alkenes, allylsilanes, silyl enol ethers, and enamines, represent the largest group of structurally related nucleophiles—all these compounds share an sp^2-hybridized carbon atom as the center of nucleophilicity—representatives of these classes of compounds were selected as

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(35) The following abbreviations are used (in alphabetical order): ani: *p*-*ani*syl (= 4-methoxyphenyl); dpa: 4-(*di*phenyl*a*mino)phenyl; fc: ferrocenyl; fur: 2,3-dihydrobenzo*fur*an-5-yl; ind: *N*-methyl-2,3-dihydro-1*H*-*ind*ol-5-yl; jul: *jul*olidin-9-yl (= 2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinolin-9-yl); lil: *lil*olidin-8-yl (= 1,2,5,6-tetrahydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-8-yl); mfa: 4-(*m*ethyl(tri*f*luoroethyl)*a*mino)phenyl; mor: 4-(*N*-*mor*pholino)phenyl; mpa: 4-(*m*ethyl*p*henyl*a*mino)phenyl; pcp: *p*-*c*hloro*p*henyl; pfp: *p*-*f*luoro*p*henyl; pfa: 4-(*p*henyl(tri*f*luoroethyl)*a*mino)phenyl; pop: p-*p*henoxy*p*henyl; pyr: 4-(*N*-*pyr*rolidino)phenyl; thq: *N*-methyl-1,2,3,4-*t*etra*h*ydro*q*uinolin-6-yl; tol: p-*tol*yl (= 4-methylphenyl).

(36) For a synthesis of bis(julolidin-9-yl)methylium perchlorate, see: Mikhailenko, F. A.; Balina, L. V. *Khim. Geterotsikl. Soedin.* **1982**, 450−452.

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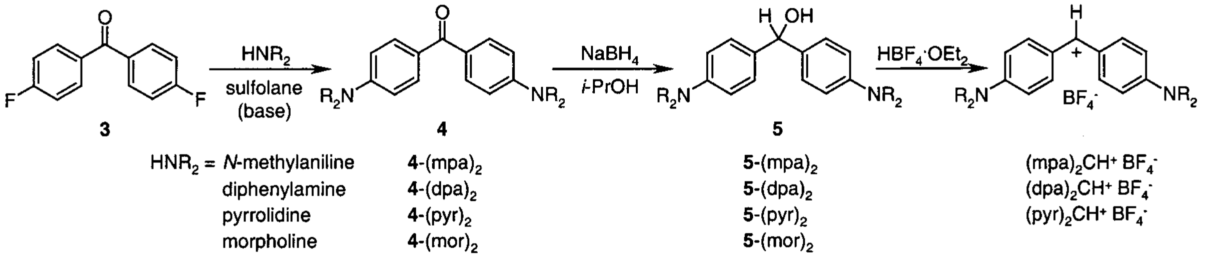
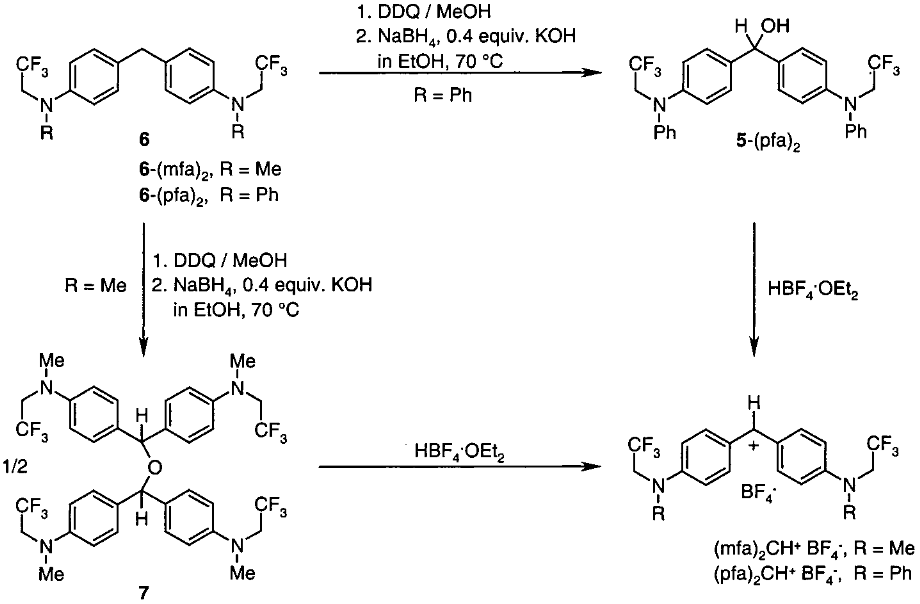
Scheme 2



Scheme 3



reference nucleophiles. Electrophilic attack at the π-bond yields cationic adducts, which usually undergo fast consecutive reactions (Scheme 4), as proven by the independence of the reaction rates of the nature and concentration of the counterion.[14,19,44]

The reaction products are generally analogous to those identified in previous investigations[18,19,44,45] (see Supporting Information). In some cases, diarylmethanes were isolated as side products which were presumably formed by hydride transfer from the reaction products to the benzhydrylium ions.

Kinetic Investigations. UV–visible kinetic measurements of rapid reactions ($\tau_{1/2}$ < 10 s) were performed on a Hi-Tech SF-61DX2 stopped-flow spectrophotometer system and controlled by using Hi-Tech KinetAsyst 2 software running on an IBM-compatible PC. The kinetic runs were initiated by mixing equal volumes of the nucleophile solution and the benzhydrylium salt solution. The temperature of the reactant solutions was controlled within ±0.1 °C using the circulating water bath F25-HD by Julabo and monitored via the Pt resistance thermometer of the SF-61DX2 mixing unit. Nucleophile concentrations $[\mathrm{Nuc}]_0$ at least 10 times higher than the benzhydryl cation concentrations were usually employed, resulting in pseudo-first-order kinetics with an exponential decay of the benzhydryl cation concentration. Observed first-order rate constants k_{obs} (s^{-1}) for the reactions of benzhydrylium ions with nucleophiles were obtained from at least five runs at each nucleophile concentration by least-squares fitting of the absorbance data to the single exponential $A = A_0 \exp(-k_{\mathrm{obs}}t) + C$. The second-order rate constants k_{exp} (M^{-1} s^{-1}) were then calculated from $k_{\mathrm{obs}} = k_{\mathrm{exp}}[\mathrm{Nuc}]_0$.

For slow reactions ($\tau_{1/2}$ > 10 s) the decrease of the absorptions of the benzhydrylium ions at or close to λ_{max} was followed photometrically as a function of time by using fiber optics and the working-station described in ref 14.

Details of the kinetic experiments can be found in Tables S1–S18 of the Supporting Information.

Correlation Analysis for the Basis Set Compounds. Table 1 lists 209 rate constants for the reactions of 23 benzhydrylium ions with 38 π-nucleophiles,[46–56] 87 of which have not been published previously. It is a complete collection of all presently available rate constants for reaction series consisting of a benzhydrylium ion with three or more π-nucleophiles. To avoid ambiguity, this listing does not include rate constants which cannot definitely be assigned to the relevant carbon–carbon bond-forming step. For that reason, the gross rate constants for the reactions of benzhydrylium ions with 2,3-dimethyl-2-butene[10] are omitted, though they match eq 1 very well.

Following our previous treatment,[11] the electrophilicity parameter of the dianisylcarbenium ion and the slope parameter of 2-methyl-1-pentene were selected as standard, i.e., $E[(\mathrm{ani})_2\mathrm{CH}^+] = 0$ and $s(\text{2-methyl-1-pentene}) = 1.00$. All other reactivity

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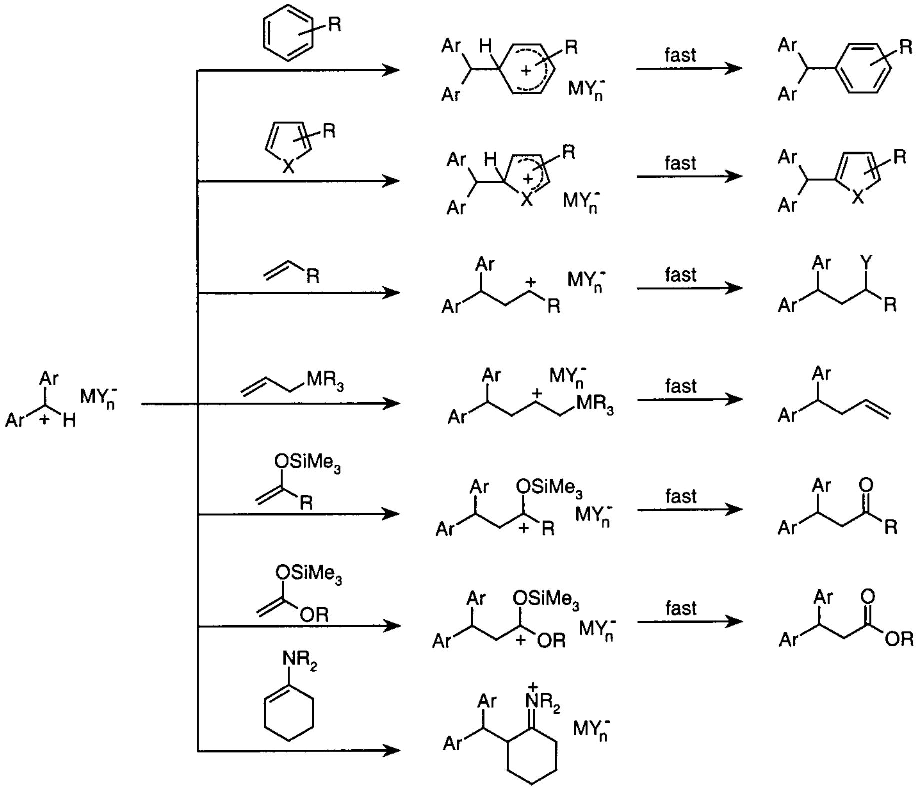
Scheme 4



parameters E, N, and s, as defined by eq 1, were then calculated by minimizing Δ^2 specified by eq 4 using the program "What'sBest! 4.0 Commercial" by Lindo Systems Inc.[57]

$$\Delta^2 = \Sigma(\log k_{\mathrm{exp}} - \log k_{\mathrm{calc}})^2 = \Sigma(\log k_{\mathrm{exp}} - s(E + N))^2 \quad (4)$$

Since charge is neither developed nor neutralized during the combination of the carbocations with the neutral nucleophiles, solvent effects are usually small (e.g., $k_{\mathrm{CH_3NO_2}}/k_{\mathrm{CH_2Cl_2}} = 4$),[11,14] and the few rate constants measured in solvents other than dichloromethane (footnotes in Table S20) have been used in the correlation analysis without correction. Comparison of calculated (eq 1) and experimentally obtained rate constants in Table 1 shows a standard deviation[58] of a factor of 1.19. Only for 4% of the reactions, predominantly those with rate constants $> 10^7$ $\mathrm{M^{-1}\ s^{-1}}$ or those for which k(20 °C) was extrapolated from measurements at lower temperature, the deviation is higher than a factor of 1.50. It should be noted, however, that in none of the eight entries with $5 \times 10^6 < k_{\mathrm{exp}} < 1 \times 10^8$ $\mathrm{M^{-1}\ s^{-1}}$ which have been determined by laser flash spectroscopy in acetonitrile[55] was the deviation between calculated and experimental rate constants greater than a factor of 1.7.

Comparison of the N and E parameters given in Table 1 with those published in 1994[11] shows that the parameters remained almost identical for systems with $E \geq 0$ or $N \leq 2$, because the data basis in these regions has only slightly been altered. More remarkably, however, though $(\mathrm{dma})_2\mathrm{CH}^+$ is the only electrophile with $E < -3$ which has been used in this and in the 1994 correlation, its E parameter and the N parameters of the nucleophiles linked to it ($3 < N < 13$) also have not changed by more than 0.5 units. 2-(Trimethylsiloxy)-4,5-dihydrofuran is the only compound for which N has to be corrected by as much as 0.9 units, because the original calculation[19] was based on an erroneously estimated value of s. Since the previous correlation[11] rested predominantly on reactions of electrophilic metal−π-complexes and heteroaromatic cations in this range, this agreement implies that the reactivity parameters presented in this work are transferable to other types of compounds as demonstrated in detail below.

A graphical representation of this correlation analysis is given in Figures 1 and 2. Figure 1, which plots log k versus the E parameters of the electrophiles shows correlation lines with slightly different slopes for different nucleophiles. Deviations from the linear correlations occur as the diffusion limit (5×10^9 $\mathrm{M^{-1}\ s^{-1}}$) is approached,[12,59] and for that reason rate constants $k_{\mathrm{exp}} > 10^8$ $\mathrm{M^{-1}\ s^{-1}}$ have not been considered for the correlations. For the sake of clarity, only 20 out of 38 correlation lines are shown in Figure 1, and we have omitted nucleophiles in regions with a high density of data points.

An important message can be taken from Figure 1. The similarities of the slopes and the narrow range accessible by second-order kinetics ($-6 < \log k < 9$) implies that crossing can only occur for correlation lines of nucleophiles with closely

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(52) Schneider, R. Dissertation, Friedrich-Alexander-Universität Erlangen-Nürnberg, 1987.

(53) Mayr, H.; Bartl, J.; Hagen, G. *Angew. Chem.* **1992**, *104*, 1689−1691; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1613−1615.

(54) Mayr, H.; Schneider, R.; Irrgang, B.; Schade, C. *J. Am. Chem. Soc.* **1990**, *112*, 4454−4459.

(55) (a) Bartl, J.; Steenken, S.; Mayr, H. *J. Am. Chem. Soc.* **1991**, *113*, 7710−7716. (b) Bartl, J. Inaugural Dissertation, Medizinische Universität zu Lübeck, 1990.

(56) Wang, Y.; Dorfman, L. M. *Macromolecules* **1980**, *13*, 63−65.

(57) The What'sBest!'s nonlinear solver employs both successive linear programming and generalized reduced gradient algorithms. The minimization procedure for Δ^2 was performed by solving the model several times with different initial values of E, N, and s.

(58) The standard deviation σ is defined as $\log \sigma = (\Delta^2/n)^{0.5}$ with Δ^2 from eq 4. This definition has been criticized by one referee. We did, however, not find a more straightforward way to characterize the reliability of the calculated rate constants which result from 23 correlation lines in Table 1 and from 15 correlation lines in Table 2.

(59) Roth, M.; Mayr, H. *Angew. Chem.* **1995**, *107*, 2428−2430; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2250−2252.

Table 1. Second-Order Rate Constants *k* ($M^{-1}\ s^{-1}$, 20 °C, CH_2Cl_2), Activation Parameters $\Delta H^{\ddagger}$ ($kJ\ mol^{-1}$), and $\Delta S^{\ddagger}$ ($J\ mol^{-1}\ K^{-1}$), and Reactivity Parameters (*E*, *N*, and *s*) Determined for the Reactions of Basis Set Benzhydrylium Ions with Basis Set π-Nucleophiles.[a] The Complete Content of Table 1 Is Found as Table S20 in the Supporting Information

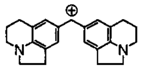
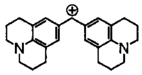
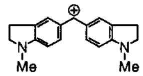
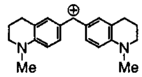
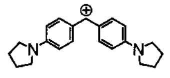
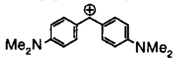
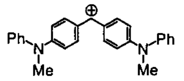
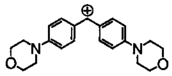
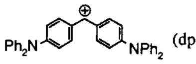
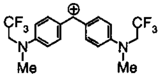
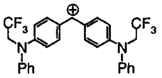
Reactants	N	s	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	k_{exp}	k_{calc}	Ref.
 $(lil)_2CH^+$, $E = -10.04$							
1-phenoxy-1-(trimethylsiloxy)ethene	8.23	0.81	—	—	3.60×10^{-2}	3.42×10^{-2}	[b]
Danishefsky's diene	8.57	0.84	—	—	5.84×10^{-2}	5.78×10^{-2}	[b]
2-(trimethylsiloxy)-5,6-dihydro-4H-pyran	10.61	0.86	—	—	2.84	3.08	[b]
1-(*N*-morpholino)cyclohexene	11.40	0.83	—	—	1.58×10^{1}	1.34×10^{1}	[b]
2-(trimethylsiloxy)-4,5-dihydrofuran	12.56	0.70	31.0	−107	4.86×10^{1}	5.91×10^{1}	[b]
1-(*N*-piperidino)cyclohexene	13.36	0.81	—	—	5.06×10^{2}	4.92×10^{2}	[b]
 $(jul)_2CH^+$, $E = -9.45$							
tributyl(2-methylallyl)stannane	7.48	0.89	—	—	1.55×10^{-2}	1.78×10^{-2}	[b]
1-phenoxy-1-(trimethylsiloxy)ethene	8.23	0.81	—	—	1.25×10^{-1}	1.02×10^{-1}	[b]
Danishefsky's diene	8.57	0.84	—	—	1.93×10^{-1}	1.80×10^{-1}	[b]
1-methoxy-2-methyl-1-(trimethylsiloxy)propene	9.00	0.98	—	—	3.16×10^{-1}	3.57×10^{-1}	[b]
2-(trimethylsiloxy)-5,6-dihydro-4H-pyran	10.61	0.86	—	—	1.11×10^{1}	9.82	[b]
1-(*N*-morpholino)cyclohexene	11.40	0.83	—	—	3.35×10^{1}	4.12×10^{1}	[b]
2-(trimethylsiloxy)-4,5-dihydrofuran	12.56	0.70	27.5	−108	1.81×10^{2}	1.52×10^{2}	[b]
1-(*N*-piperidino)cyclohexene	13.36	0.81	—	—	1.41×10^{3}	1.46×10^{3}	[b]
 $(ind)_2CH^+$, $E = -8.76$							
1-(trimethylsiloxy)cyclopentene	6.57	0.93	—	—	9.44×10^{-3}	8.96×10^{-3}	[b]
tributyl(2-methylallyl)stannane	7.48	0.89	—	—	8.21×10^{-2}	7.35×10^{-2}	[b]
Danishefsky's diene	8.57	0.84	—	—	6.58×10^{-1}	6.92×10^{-1}	[b]
2-(trimethylsiloxy)-5,6-dihydro-4H-pyran	10.61	0.86	—	—	3.53×10^{1}	3.88×10^{1}	[b]
1-(*N*-morpholino)cyclohexene	11.40	0.83	26.2	−114	1.51×10^{2}	1.55×10^{2}	[b]
 $(thq)_2CH^+$, $E = -8.22$							
1-(trimethylsiloxy)cyclopentene	6.57	0.93	—	—	2.68×10^{-2}	2.85×10^{-2}	[b]
tributyl(2-methylallyl)stannane	7.48	0.89	—	—	2.38×10^{-1}	2.21×10^{-1}	[b]
Danishefsky's diene	8.57	0.84	—	—	2.10	1.96	[b]
2-(trimethylsiloxy)-5,6-dihydro-4H-pyran	10.61	0.86	29.2	−106	1.13×10^{2}	1.12×10^{2}	[b]
1-(*N*-morpholino)cyclohexene	11.40	0.83	24.1	−112	3.97×10^{2}	4.34×10^{2}	[b]
 $(pyr)_2CH^+$, $E = -7.69$							
1-(trimethylsiloxy)cyclohexene	5.21	1.00	—	—	3.42×10^{-3}	3.35×10^{-3}	[b]
tributyl(2-methylallyl)stannane	7.48	0.89	44.4	−97	6.35×10^{-1}	6.53×10^{-1}	[b]
1-phenoxy-1-(trimethylsiloxy)ethene	8.23	0.81	44.9	−85	2.35	2.75	[b]
Danishefsky's diene	8.57	0.84	43.9	−83	4.41	5.50	[b]
1-methoxy-2-methyl-1-(trimethylsiloxy)propene	9.00	0.98	31.1	−112	2.32×10^{1}	1.89×10^{1}	[b]
1-(*N*-morpholino)cyclohexene	11.40	0.83	23.2	−105	1.36×10^{3}	1.20×10^{3}	[b]
1-(*N*-piperidino)cyclohexene	13.36	0.81	14.3	−108	3.95×10^{4}	3.91×10^{4}	[b]
 $(dma)_2CH^+$, $E = -7.02$							
allyltriphenylstannane	3.09	0.90	—	—	2.54×10^{-4}	2.80×10^{-4}	46
(2-methylallyl)trimethylsilane	4.41	0.96	53.2	−112	3.04×10^{-3}	3.10×10^{-3}	47
1-(trimethylsiloxy)cyclohexene	5.21	1.00	47.5	−116	1.91×10^{-2}	1.58×10^{-2}	19
2-(trimethylsiloxy)propene	5.41	0.91	50.7	−100	3.52×10^{-2}	3.40×10^{-2}	19
allyltributylstannane	5.46	0.89	47.0	−113	3.21×10^{-2}	4.15×10^{-2}	46
N-methylpyrrole	5.85	1.03	—	—	6.03×10^{-2}	6.22×10^{-2}	18
1-phenyl-1-(trimethylsiloxy)ethene	6.22	0.96	47.5	−98	1.72×10^{-1}	1.72×10^{-1}	19
1-(trimethylsiloxy)cyclopentene	6.57	0.93	40.8	−114	3.61×10^{-1}	3.82×10^{-1}	19
tributyl(2-methylallyl)stannane	7.48	0.89	40.9	−98	2.55	2.60	46
1-phenoxy-1-(trimethylsiloxy)ethene	8.23	0.81	37.9	−97	9.45	9.71	19
Danishefsky's diene	8.57	0.84	—	—	2.25×10^{1}	2.04×10^{1}	19
1-methoxy-2-methyl-1-(trimethylsiloxy)propene	9.00	0.98	25.7	−121	7.96×10^{1}	8.64×10^{1}	19
2-(trimethylsiloxy)-5,6-dihydro-4H-pyran	10.61	0.86	—	—	1.31×10^{3}	1.23×10^{3}	[b]
1-(*N*-morpholino)cyclohexene	11.40	0.83	20.5	−105	4.69×10^{3}	4.36×10^{3}	[b]
2-(trimethylsiloxy)-4,5-dihydrofuran	12.56	0.70	13.8	−122	9.40×10^{3}	7.90×10^{3}	19
 $(mpa)_2CH^+$, $E = -5.89$							
(2-methylallyl)trimethylsilane	4.41	0.96	—	—	3.64×10^{-2}	3.74×10^{-2}	[b]
1-(trimethylsiloxy)cyclohexene	5.21	1.00	—	—	2.14×10^{-1}	2.10×10^{-1}	[b]
1-phenyl-1-(trimethylsiloxy)ethene	6.22	0.96	—	—	2.00	2.04	[b]
1-(trimethylsiloxy)cyclopentene	6.57	0.93	—	—	4.52	4.28	[b]
tributyl(2-methylallyl)stannane	7.48	0.89	—	—	2.76×10^{1}	2.59×10^{1}	[b]
1-phenoxy-1-(trimethylsiloxy)ethene	8.23	0.81	—	—	7.49×10^{1}	7.93×10^{1}	[b]
2-(trimethylsiloxy)-5,6-dihydro-4H-pyran	10.61	0.86	—	—	1.20×10^{4}	1.14×10^{4}	[b]
2-(trimethylsiloxy)-4,5-dihydrofuran	12.56	0.70	—	—	4.32×10^{4}	4.87×10^{4}	[b]
 $(mor)_2CH^+$, $E = -5.53$							
(2-methylallyl)trimethylsilane	4.41	0.96	—	—	8.54×10^{-2}	8.45×10^{-2}	[b]
1-(trimethylsiloxy)cyclohexene	5.21	1.00	—	—	5.18×10^{-1}	4.87×10^{-1}	[b]
2-(trimethylsiloxy)propene	5.41	0.91	—	—	7.45×10^{-1}	7.85×10^{-1}	[b]
N-methylpyrrole	5.85	1.03	—	—	2.25[c]	2.14	[b]
1-phenyl-1-(trimethylsiloxy)ethene	6.22	0.96	38.6	−101	4.36	4.59	[b]
1-(trimethylsiloxy)cyclopentene	6.57	0.93	33.6	−111	1.05×10^{1}	9.43	[b]
tributyl(2-methylallyl)stannane	7.48	0.89	31.4	−104	5.53×10^{1}	5.49×10^{1}	[b]
1-phenoxy-1-(trimethylsiloxy)ethene	8.23	0.81	32.3	−94	1.38×10^{2}	1.57×10^{2}	[b]
Danishefsky's diene	8.57	0.84	31.6	−88	3.81×10^{2}	3.69×10^{2}	[b]
2-(trimethylsiloxy)-5,6-dihydro-4H-pyran	10.61	0.86	—	—	2.28×10^{4}	2.35×10^{4}	[b]
2-(trimethylsiloxy)-4,5-dihydrofuran	12.56	0.70	—	—	8.59×10^{4}	8.83×10^{4}	[b]
 $(dpa)_2CH^+$, $E = -4.72$							
(2-methylallyl)trimethylsilane	4.41	0.96	—	—	6.13×10^{-1}	5.03×10^{-1}	[b]
1-(trimethylsiloxy)cyclohexene	5.21	1.00	—	—	2.05	3.09	[b]
allyltributylstannane	5.46	0.89	—	—	6.40	4.53	[b]
1-phenyl-1-(trimethylsiloxy)ethene	6.22	0.96	—	—	3.01×10^{1}	2.70×10^{1}	[b]
1-(trimethylsiloxy)cyclopentene	6.57	0.93	24.3	−128	5.80×10^{1}	5.32×10^{1}	[b]
tributyl(2-methylallyl)stannane	7.48	0.89	24.3	−116	2.57×10^{2}	2.84×10^{2}	[b]
1-phenoxy-1-(trimethylsiloxy)ethene	8.23	0.81	22.5	−116	5.41×10^{2}	7.06×10^{2}	[b]
1-methoxy-2-methyl-1-(trimethylsiloxy)propene	9.00	0.98	—	—	1.66×10^{4}	1.51×10^{4}	[b]
2-(trimethylsiloxy)-5,6-dihydro-4H-pyran	10.61	0.86	—	—	1.12×10^{5}	1.15×10^{5}	[b]
1-(*N*-morpholino)cyclohexene	11.40	0.83	—	—	3.38×10^{5}	3.51×10^{5}	[b]
 $(mfa)_2CH^+$, $E = -3.85$							
allyltriphenylstannane	3.09	0.90	—	—	2.24×10^{-1}	2.04×10^{-1}	[b]
(2-methylallyl)trimethylsilane	4.41	0.96	—	—	2.97	3.48	[b]
1-(trimethylsiloxy)cyclohexene	5.21	1.00	—	—	2.17×10^{1}	2.30×10^{1}	[b]
allyltributylstannane	5.46	0.89	—	—	2.84×10^{1}	2.70×10^{1}	[b]
1-(trimethylsiloxy)cyclopentene	6.57	0.93	24.9	−112	3.20×10^{2}	3.47×10^{2}	[b]
tributyl(2-methylallyl)stannane	7.48	0.89	—	—	1.80×10^{3}	1.69×10^{3}	[b]
1-phenoxy-1-(trimethylsiloxy)ethene	8.23	0.81	—	—	4.16×10^{3}	3.61×10^{3}	[b]
2-(trimethylsiloxy)-5,6-dihydro-4H-pyran	10.61	0.86	—	—	6.40×10^{5}	6.49×10^{5}	[b]
 $(pfa)_2CH^+$, $E = -3.14$							
allyltriphenylstannane	3.09	0.90	—	—	1.07	8.86×10^{-1}	[b]
(2-methylallyl)trimethylsilane	4.41	0.96	—	—	1.35×10^{1}	1.66×10^{1}	[b]
allyltributylstannane	5.46	0.89	—	—	1.13×10^{2}	1.14×10^{2}	[b]
1-phenyl-1-(trimethylsiloxy)ethene	6.22	0.96	24.3	−106	8.39×10^{2}	8.72×10^{2}	[b]
tributyl(2-methylallyl)stannane	7.48	0.89	—	—	6.93×10^{3}	7.16×10^{3}	[b]
1-phenoxy-1-(trimethylsiloxy)ethene	8.23	0.81	—	—	1.72×10^{4}	1.35×10^{4}	[b]
1-methoxy-2-methyl-1-(trimethylsiloxy)propene	9.00	0.98	—	—	4.80×10^{5}	5.28×10^{5}	[b]

Table continued as Table S20 in the Supporting Information

[a] The values of k_{calc} were actually calculated by eq 1 with more decimals of *E*, *N*, and *s* than indicated in the table. The use of the *E*, *N*, and *s* parameters given in this table leads to slightly deviating results. [b] This work. [c] In the presence of 2,6-di-*tert*-butylpyridine.

similar *N* parameters. In other words, nucleophiles with sufficiently different *N* values will not invert relative reactivities in the experimentally relevant range. Since crossing above log $k > 9$ (diffusion control) or below log $k < -6$ (no reaction at room temperature) does not have any practical consequences, the definition of *N* as the intercepts of the correlation lines with the abscissa (log $k = 0$) provides a useful measure for nucleophilic reactivities.

It should be noted that eq 1 is mathematically equivalent to the conventional linear free energy relationship (eq 5), as eq 5

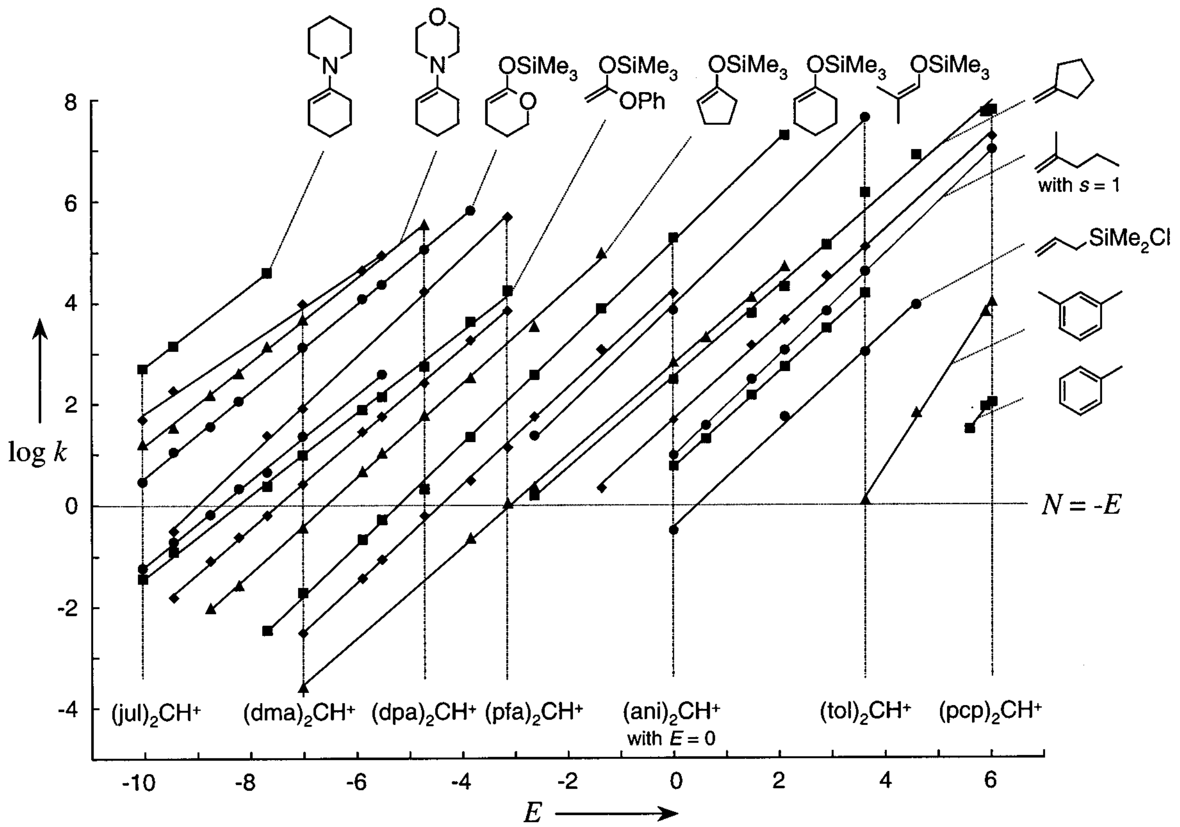


Figure 1. Plot of log k(20 °C) vs E for the reactions of benzhydryl cations with π-nucleophiles (for abbreviations, see ref 35).

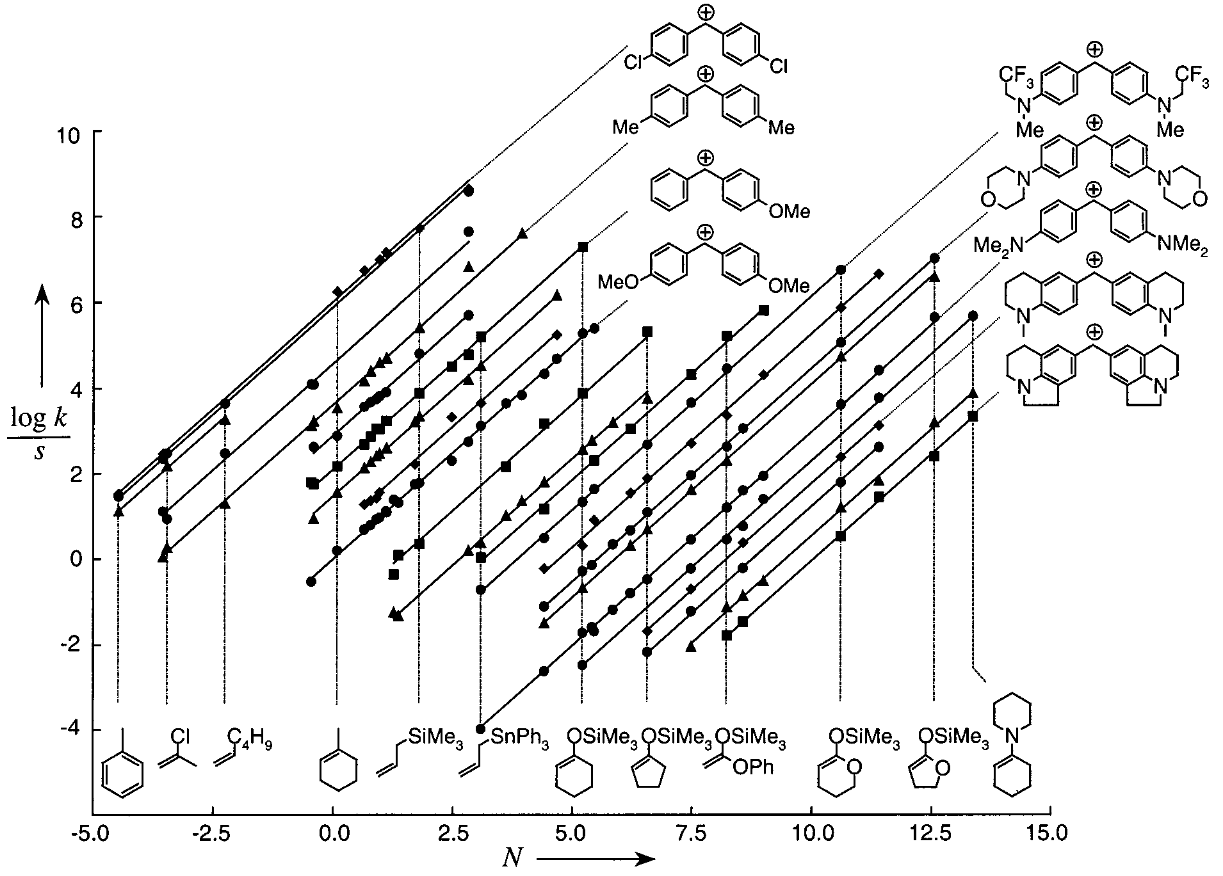


Figure 2. Plot of (log k)/s versus N for the reactions of benzhydryl cations with π-nucleophiles.

can be converted to eq 1 by replacement of Nu by sN.

$$\log k = \mathrm{Nu} + sE \qquad (5)$$

The only difference between eqs 1 and 5 is that the latter defines nucleophilicities Nu by the intercepts of the correlation lines with the ordinate (Nu = log k for E = 0) whereas the

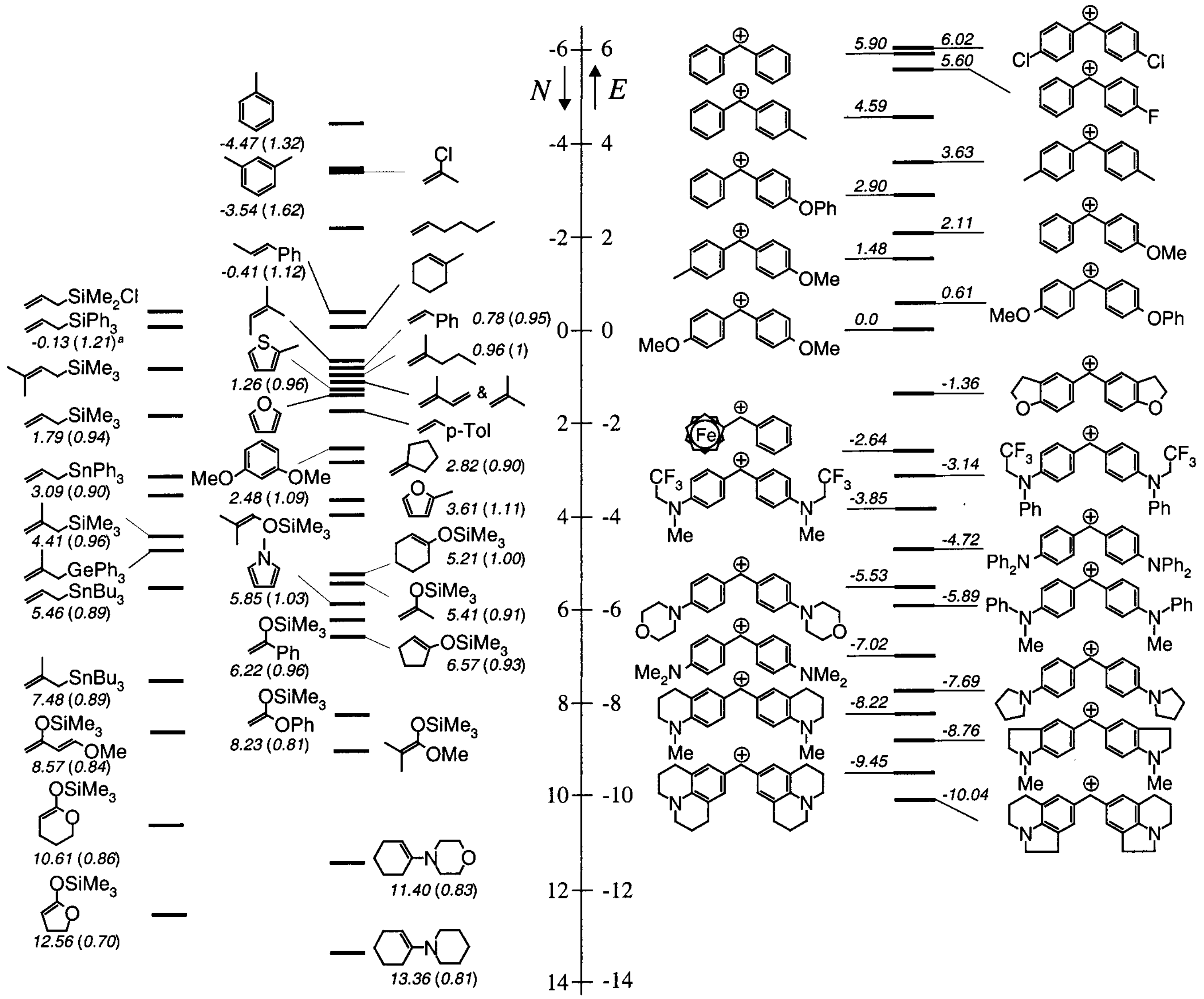


Figure 3. Compilation of all compounds used for the determination of *E*, *N*, and *s*. Reactivity parameters of the recommended reference compounds are explicitly listed (*s* in parentheses). [a]Reference compound, not used for the correlation analysis: see ref 60.

former defines nucleophilicities N by the intersections of correlation lines with the abscissa ($N = -E$ for $\log k = 0$).[11−13] Thus N, in contrast to Nu, is generally defined within the experimentally accessible range, and its use avoids long-range extrapolations as needed for the determination of Nu values for very strong (Nu > 8) as well as for very weak nucleophiles (Nu < −5) according to eq 5.

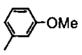
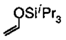
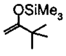
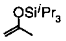
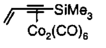
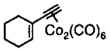
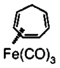
All 209 reactions of Table 1 are included in Figure 2, in which each correlation line corresponds to a benzhydryl cation. One can see that the benzhydryl cations characterized so far, continuously cover the range $-10 < E < 6$ and thus allow the straightforward quantification of nucleophiles with $-8 < N < 16$. Vice versa, the nucleophiles listed in Table 1 may be used to characterize electrophiles with $-15 < E < 7$.

All compounds used for the determination of *E*, *N*, and *s* in Table 1 are depicted in Figure 3 (basis set). However, not all of the basis set nucleophiles are recommended as reference compounds. Some of them are difficult to handle because of their volatility, others tend to undergo side reactions, and there are highly substituted π-systems which can be expected to highly differentiate reaction partners on the basis of steric strain. To facilitate the usage of these scales, numerical values for *E*, *N*, and *s* are only given for those compounds of the basis set in Figure 3, which are recommended as reference compounds for the characterization of further electrophiles and nucleophiles.

Reactivity Parameters for Electrophiles and Nucleophiles Outside the Basis Set. The definition of basis sets and fixation of the corresponding *E*, *N*, and *s* parameters as described above is only useful if these parameters can be employed for the characterization of other types of compounds. We demonstrate this by analyzing reaction series in which reference compounds are combined with electrophiles or nucleophiles that do not belong to the basis set.

Table 2 examines the applicability of the electrophilicity parameters of benzhydrylium ions listed in Figure 3 for reactions with alkynes, transition metal π-complexes, hydride donors, and CC-double-bonded systems not belonging to the basis set. The standard deviation[58] between experimentally obtained and calculated rate constants listed in Table 2 is a factor of 1.26, only slightly higher than for the compounds of the basis set, indicating the general applicability of the *E* parameters given in Figure 3. Correlations of comparable quality have also been obtained for the reactions of benzhydrylium ions with water and alcohols.[65,66] To limit the length of this article, reactions with n-nucleophiles have not been included in Table 2. In a forthcoming paper we will show that all n-nucleophiles,

Table 2. Second-Order Rate Constants k (M^{-1} s^{-1}, 20 °C, CH_2Cl_2) for the Reactions of Nucleophiles Not Belonging to the Basis Set with Electrophiles of the Basis Set[a]

Nucleophile	N	s	Electrophile	E	k_{exp}	k_{calc}	Ref.
– π-nucleophiles:							
	−2.44	(1.09)	ani(Ph)CH$^+$	2.11	4.36×10^{-1}	(4.36×10^{-1})	54
			tol(Ph)CH$^+$	4.59	2.28×10^{2}	(2.28×10^{2})	10
 [b]	−0.13	1.21	(fur)$_2$CH$^+$	−1.36	1.98×10^{-2}	1.55×10^{-2}	[c]
			(ani)$_2$CH$^+$	0.00	4.57×10^{-1}	6.93×10^{-1}	[c]
			ani(Ph)CH$^+$	2.11	2.90×10^{2} [e]	2.47×10^{2}	44
			(tol)$_2$CH$^+$	3.63	1.65×10^{4}	1.68×10^{4}	[c]
	0.13	1.27	(ani)$_2$CH$^+$	0.00	9.55×10^{-1}	1.46	53
			ani(Ph)CH$^+$	2.11	1.32×10^{3}	6.90×10^{2}	53
			(pcp)$_2$CH$^+$	6.02	5.20×10^{7} [d]	6.53×10^{7}	53
PhC≡CH	0.34	0.68	ani(Ph)CH$^+$	2.11	3.77×10^{1} [f]	4.46×10^{1}	61
			(tol)$_2$CH$^+$	3.63	6.30×10^{2}	4.76×10^{2}	61
			Ph$_2$CH$^+$	5.90	1.46×10^{4} [f]	1.63×10^{4}	61
	3.44	(0.94)	fc(Ph)CH$^+$	−2.64	5.72	(5.72)	19
			(ani)$_2$CH$^+$	0.00	1.76×10^{3}	(1.76×10^{3})	19
	3.78	(0.79)	(dma)$_2$CH$^+$	−7.02	2.76×10^{-3}	(2.76×10^{-3})	19
			(pcp)$_2$CH$^+$	6.02	5.53×10^{7} [e]	(5.53×10^{7})	55
	4.17	(0.83)	(ani)$_2$CH$^+$	0.00	3.02×10^{3} [g]	(3.02×10^{3})	44
			ani(Ph)CH$^+$	2.11	1.73×10^{5} [g]	(1.73×10^{5})	44
	5.38	(0.85)	(dma)$_2$CH$^+$	−7.02	4.02×10^{-2}	(4.02×10^{-2})	19
			fc(Ph)CH$^+$	−2.64	2.15×10^{2}	(2.15×10^{2})	19
– metal π-complexes:							
	−1.11	0.92	ani(Ph)CH$^+$	2.11	8.95	8.16	17
			(tol)$_2$CH$^+$	3.63	1.59×10^{2}	2.02×10^{2}	17
			tol(Ph)CH$^+$	4.59	1.78×10^{3}	1.54×10^{3}	17
	−0.44	1.06	ani(tol)CH$^+$	1.48	1.70×10^{1}	1.26×10^{1}	17
			ani(Ph)CH$^+$	2.11	3.81×10^{1}	5.78×10^{1}	17
			(tol)$_2$CH$^+$	3.63	2.65×10^{3}	2.34×10^{3}	17
	3.42	0.94	(dma)$_2$CH$^+$	−7.02	3.88×10^{-4}	4.29×10^{-4}	16
			fc(Ph)CH$^+$	−2.64	6.47	5.37	16
			(fur)$_2$CH$^+$	−1.36	9.80×10^{1}	8.42×10^{1}	16
			(ani)$_2$CH$^+$	0.00	1.25×10^{3}	1.58×10^{3}	16
– hydride donors:							
H_3SiPh	0.25	0.67	ani(Ph)CH$^+$	2.11	3.56×10^{1} [h]	3.71×10^{1}	62
			pop(Ph)CH$^+$	2.90	1.12×10^{2} [h]	1.26×10^{2}	62
			(tol)$_2$CH$^+$	3.63	5.24×10^{2} [h]	3.83×10^{2}	62
			tol(Ph)CH$^+$	4.59	1.44×10^{3} [h]	1.68×10^{3}	62
$HSiPh_3$	2.06	0.68	(fur)$_2$CH$^+$	−1.36	3.29	3.02	63
			(ani)$_2$CH$^+$	0.00	2.34×10^{1} [i]	2.57×10^{1}	62
			ani(tol)CH$^+$	1.48	2.70×10^{2} [i]	2.64×10^{2}	62
			ani(Ph)CH$^+$	2.11	6.72×10^{2}	7.05×10^{2}	62
			pop(Ph)CH$^+$	2.90	2.18×10^{3} [i]	2.46×10^{3}	62
			(tol)$_2$CH$^+$	3.63	8.96×10^{3} [i]	7.72×10^{3}	62
$HSiMe_2Ph$	3.27	0.73	fc(Ph)CH$^+$	−2.64	1.56	2.91	49
			(fur)$_2$CH$^+$	−1.36	4.07×10^{1}	2.51×10^{1}	63
			(ani)$_2$CH$^+$	0.00	3.86×10^{2}	2.49×10^{2}	62
			ani(tol)CH$^+$	1.48	3.31×10^{3} [j]	3.03×10^{3}	62
			ani(Ph)CH$^+$	2.11	8.05×10^{3}	8.68×10^{3}	62
			pop(Ph)CH$^+$	2.90	2.81×10^{4} [j]	3.32×10^{4}	62
			(tol)$_2$CH$^+$	3.63	9.86×10^{4} [j]	1.13×10^{5}	62
$HSiEt_3$	3.64	(0.65)	(fur)$_2$CH$^+$	−1.36	3.01×10^{1}	(3.01×10^{1})	63
			ani(Ph)CH$^+$	2.11	5.29×10^{3}	(5.29×10^{3})	62
$HGePh_3$	3.99	0.62	(ani)$_2$CH$^+$	0.00	3.10×10^{2} [h]	3.04×10^{2}	64
			ani(Ph)CH$^+$	2.11	5.99×10^{3} [h]	6.18×10^{3}	64
			pop(Ph)CH$^+$	2.90	1.86×10^{4} [h]	1.93×10^{4}	64
			(tol)$_2$CH$^+$	3.63	5.72×10^{4} [h]	5.46×10^{4}	64
$HSiBu_3$	4.45	0.64	(ani)$_2$CH$^+$	0.00	6.21×10^{2} [h]	6.85×10^{2}	62
			ani(pop)CH$^+$	0.61	1.89×10^{3} [h]	1.68×10^{3}	62
			ani(tol)CH$^+$	1.48	6.31×10^{3} [h]	6.00×10^{3}	62
			ani(Ph)CH$^+$	2.11	1.40×10^{4} [h]	1.50×10^{4}	62
$HSnPh_3$	5.64	0.59	(dma)$_2$CH$^+$	−7.02	1.53×10^{-1}	1.56×10^{-1}	64
			(ani)$_2$CH$^+$	0.00	2.37×10^{3} [k]	2.04×10^{3}	64
			ani(pop)CH$^+$	0.61	7.67×10^{3} [k]	4.67×10^{3}	64
			ani(tol)CH$^+$	1.48	4.17×10^{3} [k]	1.51×10^{4}	64
			ani(Ph)CH$^+$	2.11	3.26×10^{4} [k]	3.51×10^{4}	64
$HGeBu_3$	5.92	0.73	(dma)$_2$CH$^+$	−7.02	1.45×10^{-1}	1.61×10^{-1}	64
			(ani)$_2$CH$^+$	0.00	2.47×10^{4} [l]	1.99×10^{4}	64
			ani(pop)CH$^+$	0.61	9.13×10^{4} [l]	5.54×10^{4}	64
			ani(tol)CH$^+$	1.48	1.56×10^{5} [l]	2.36×10^{5}	64
			ani(Ph)CH$^+$	2.11	5.48×10^{5} [l]	6.69×10^{5}	64
$H_3B \leftarrow NEt_3$	8.90	0.75	(pyr)$_2$CH$^+$	−7.69	7.76	8.15	15
			(dma)$_2$CH$^+$	−7.02	2.79×10^{1}	2.64×10^{1}	15
			fc(Ph)CH$^+$	−2.64	5.28×10^{4}	5.32×10^{4}	15
$HSnBu_3$	9.96	0.55	(jul)$_2$CH$^+$	−9.45	1.78	1.91	[c]
			(pyr)$_2$CH$^+$	−7.69	1.68×10^{1}	1.80×10^{1}	[c]
			(dma)$_2$CH$^+$	−7.02	5.41×10^{1}	4.26×10^{1}	64
			(dpa)$_2$CH$^+$	−4.72	7.18×10^{2}	7.91×10^{2}	[c]

[a] For abbreviations, see ref 35. The values of k_{calc} were actually calculated by eq 1 with more decimals of E, N, and s than indicated in the table. The use of the E, N, and s parameters given in this table leads to somewhat deviating results. [b] See ref 60. [c] This work. [d] In acetonitrile. [e]–[l] From rate constants determined at different temperatures, assuming the same activation entropy as for the reactions of this nucleophile with other benzhydrylium ions: $\Delta S^{\ddagger} =$ [e] −120; [f] −104; [g] −110; [h] −105; [i] −115; [j] −97; [k] −130; [l] −86 J mol^{-1} K^{-1}.

including anions (Ritchie-type nucleophiles[7]), are characterized by similar s values and thus give rise to a set of constant selectivity relationships as a subset of our correlations.

It should be noted that a comparison of calculated with experimental rate constants is not possible in reaction series only comprising two electrophiles (k_{calc} and k_{exp} must then be identical!) and these entries have been omitted when calculating the standard deviation. In these cases the similarities of the slopes s with the slopes of structurally related nucleophiles indicate the applicability of eq 1.

Table 3 proves that the N parameters of π-nucleophiles listed in Figure 3 are also suitable for the characterization of other types of electrophiles. One can see that k_{exp} and k_{calc} show a standard deviation[58] of a factor of 2.05. This may be considered being high, but in view of the wide structural variety covered by the electrophiles in Table 3, the reliability of the predictions is remarkable, particularly when one considers that a large percentage of the standard deviation comes from the poorly matching reactions of the π-allyl palladium complex.[26]

Comparison of k_{exp} and k_{calc} for the reactions of the hexacarbonyldicobalt coordinated propargylium ions with nucleophiles (Table 3) illustrates the advantage of using reference compounds with fixed E, N, and s parameters. The deviations between calculated and experimentally obtained rate constants are rather large for some reactions of these cations, that one would not want to allow these data to affect the nucleophilicity parameters of allylsilanes and silyl enol ethers which have been derived from well-behaved linear free energy relationships. This would be the case, if all rate constants would uniformly be employed for the correlation analysis. On the other hand, these rate constants are presently the best source providing quantitative information on the electrophilicities of these cobalt complexes, and we have shown[23] that they allow the semiquantitative analysis of the reactions of these cationic complexes. The approach presented in this article, which uses fixed E, N, and s parameters derived from the basis set compounds serves both requirements.

A final test of the reliability of the approach to employ fixed reactivity parameters from basis set compounds is given in Table 4, which compares experimentally measured and calculated rate constants for electrophiles not belonging to the basis set (Table 3) with nucleophiles not belonging to the basis set (Table 2). The standard deviation[58] now is a factor of 6.26 which reflects the predictive power of this method in practice. It should be mentioned, however, that the maximum deviation for reactions with C-nucleophiles is a factor of 3.4, indicating that the reliability is higher for CC-bond-forming reactions.

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(60) By the criteria used for the selection of basis set compounds (Table 1), allyltriphenylsilane should be treated as basis set nucleophile. However, the rate constants for this compound had not been available at the time the correlation analysis for the data in Table 1 was performed. For that reason, the kinetic data for allyltriphenylsilane have only been used for determining its N and s values, and not for the parametrization of E of its electrophilic reaction partners.

(61) Mayr, H.; Gonzalez, J. L.; Lüdtke, K. *Chem. Ber.* **1994**, *127*, 525−531.

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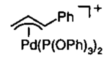
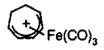
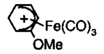
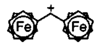
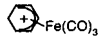
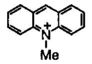
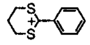
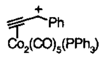
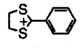
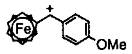
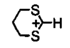
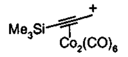
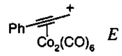
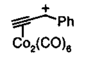
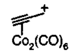
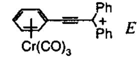
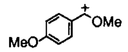
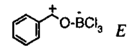
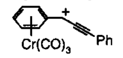
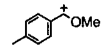
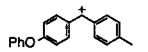
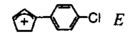
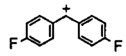
(64) Mayr, H.; Basso, N. *Angew. Chem.* **1992**, *104*, 1103−1105; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1046−1048.

(65) (a) McClelland, R. A.; Kanagasabapathy, V. M.; Steenken, S. *J. Am. Chem. Soc.* **1988**, *110*, 6913−6914. (b) McClelland, R. A.; Kanagasabapathy, V. M.; Banait, N. S.; Steenken, S. *J. Am. Chem. Soc.* **1989**, *111*, 3966−3972.

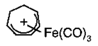
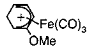
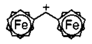
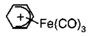
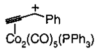
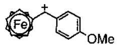
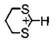
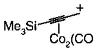
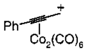
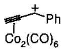
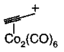
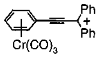
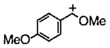
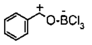
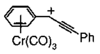
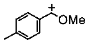
(66) (a) Kirmse, W.; Krzossa, B.; Steenken, S. *J. Am. Chem. Soc.* **1996**, *118*, 7473−7477. (b) Kirmse, W.; Guth, M.; Steenken, S. *J. Am. Chem. Soc.* **1996**, *118*, 10838−10849.

Table 3. Second-Order Rate Constants k (M^{-1} s^{-1}, 20 °C, CH_2Cl_2) for the Reactions of Electrophiles Not Belonging to the Basis Set with Nucleophiles of the Basis Set[a]

Reactants	N	s	k_{exp}	k_{calc}	Ref.
 $E = -10.33$					
1-methoxy-2-methyl-1-(trimethylsiloxy)propene	9.00	0.98	3.50×10^{-1}	4.95×10^{-2}	26
1-(N-morpholino)cyclohexene	11.40	0.83	1.75×10^{1}	7.69	26
2-(trimethylsiloxy)-4,5-dihydrofuran	12.56	0.70	4.49	3.68×10^{1}	26
 $E = -9.19$					
1-phenyl-1-(trimethylsiloxy)ethene	6.22	0.96	2.78×10^{-3}[b]	1.42×10^{-3}	67
tributyl(2-methylallyl)stannane	7.48	0.89	4.58×10^{-2}[b]	3.03×10^{-2}	67
1-methoxy-2-methyl-1-(trimethylsiloxy)propene	9.00	0.98	2.05×10^{-1}[b]	6.42×10^{-1}	67
 $E = -8.94$					
1-phenyl-1-(trimethylsiloxy)ethene	6.22	0.96	3.35×10^{-3}[b]	2.48×10^{-3}	67
tributyl(2-methylallyl)stannane	7.48	0.89	5.50×10^{-2}[b]	5.09×10^{-2}	67
1-methoxy-2-methyl-1-(trimethylsiloxy)propene	9.00	0.98	7.66×10^{-1}[b]	1.14	67
 $E = -8.54$					
1-(trimethylsiloxy)cyclohexene	5.21	1.00	1.21×10^{-3}	4.80×10^{-4}	49
1-(trimethylsiloxy)cyclopentene	6.57	0.93	3.05×10^{-2}	1.45×10^{-2}	49
1-methoxy-2-methyl-1-(trimethylsiloxy)propene	9.00	0.98	5.21×10^{-1}	2.81	49
 $E = -7.78$					
2-methylthiophene	1.26	0.96	7.09×10^{-7}[c]	5.92×10^{-7}	8
furan	1.36	1.31	4.78×10^{-7}[c,d]	3.69×10^{-9}	8
2-methylfuran	3.61	1.11	4.14×10^{-5}[c]	2.33×10^{-5}	8
1-(trimethylsiloxy)cyclohexene	5.21	1.00	9.16×10^{-3}[b]	2.75×10^{-3}	67
1-phenyl-1-(trimethylsiloxy)ethene	6.22	0.96	2.56×10^{-2}[b]	3.20×10^{-2}	67
1-(trimethylsiloxy)cyclopentene	6.57	0.93	8.56×10^{-2}[b]	7.42×10^{-2}	67
tributyl(2-methylallyl)stannane	7.48	0.89	2.36×10^{-1}[b]	5.48×10^{-1}	67
1-methoxy-2-methyl-1-(trimethylsiloxy)propene	9.00	0.98	6.59[b]	1.55×10^{1}	67
 $E = -7.14$					
1-(trimethylsiloxy)cyclohexene	5.21	1.00	1.29×10^{-2}	1.19×10^{-2}	46
allyltributylstannane	5.46	0.89	4.55×10^{-2}[e,f]	3.21×10^{-2}	68
1-(trimethylsiloxy)cyclopentene	6.57	0.93	2.19×10^{-1}	2.91×10^{-1}	46
1-methoxy-2-methyl-1-(trimethylsiloxy)propene	9.00	0.98	5.50×10^{1}[e,g]	6.50×10^{1}	69
 $E = -6.43$					
1-(trimethylsiloxy)cyclohexene	5.21	1.00	5.64×10^{-2}	6.08×10^{-2}	20
1-(trimethylsiloxy)cyclopentene	6.57	0.93	1.29	1.34	20
tributyl(2-methylallyl)stannane	7.48	0.89	9.58	8.62	20
 $E = -6.15$					
tributyl(2-methylallyl)stannane	7.48	0.89	3.75×10^{1}	1.53×10^{1}	23
1-methoxy-2-methyl-1-(trimethylsiloxy)propene	9.00	0.98	2.26×10^{2}	6.07×10^{2}	23
 $E = -5.88$					
1-(trimethylsiloxy)cyclohexene	5.21	1.00	1.31×10^{-1}	2.15×10^{-1}	20
allyltributylstannane	5.46	0.89	9.16×10^{-1}	4.22×10^{-1}	20
1-phenyl-1-(trimethylsiloxy)ethene	6.22	0.96	8.58×10^{-1}	2.09	20
1-(trimethylsiloxy)cyclopentene	6.57	0.93	3.11	4.38	20
tributyl(2-methylallyl)stannane	7.48	0.89	6.00×10^{1}	2.65×10^{1}	20
 $E = -3.72$					
(2-methylallyl)trimethylsilane	4.41	0.96	5.01	4.64	27
1-phenyl-1-(trimethylsiloxy)ethene	6.22	0.96	2.27×10^{2}	2.45×10^{2}	27
 $E = -3.50$					
(2-methylallyl)trimethylsilane	4.41	0.96	9.14	7.61	27
allyltributylstannane	5.46	0.89	7.54×10^{1}	5.55×10^{1}	27
tributyl(2-methylallyl)stannane	7.48	0.89	2.16×10^{3}	3.48×10^{3}	27
 $E = -2.90$					
(2-methylallyl)trimethylsilane	4.41	0.96	2.37×10^{1}	2.88×10^{1}	49
2-(trimethylsiloxy)propene	5.41	0.91	2.40×10^{2}	1.99×10^{2}	49
 $E = -2.14$					
allyltrimethylsilane	1.79	0.94	4.04×10^{-1}	4.75×10^{-1}	20
(2-methylallyl)trimethylsilane	4.41	0.96	1.82×10^{2}	1.54×10^{2}	20
 $E = -1.59$					
allyltrimethylsilane	1.79	0.94	3.26	1.55	23
(2-methylallyl)trimethylsilane	4.41	0.96	2.43×10^{2}	5.20×10^{2}	23
 $E = -1.55$					
allyltrimethylsilane	1.79	0.94	7.51	1.68	23
(2-methylallyl)trimethylsilane	4.41	0.96	6.21×10^{2}	5.65×10^{2}	23
1-(trimethylsiloxy)cyclohexene	5.21	1.00	8.29×10^{2}	4.49×10^{3}	23
 $E = -0.98$					
allyltrimethylsilane	1.79	0.94	4.94	5.87	23
(2-methylallyl)trimethylsilane	4.41	0.96	2.44×10^{3}	2.04×10^{3}	23
 $E = -0.83$					
allyltrimethylsilane	1.79	0.94	1.74×10^{1}	8.05	23
(2-methylallyl)trimethylsilane	4.41	0.96	1.28×10^{3}	2.82×10^{3}	23
 $E = -0.28$					
allyltrimethylsilane	1.79	0.94	1.76×10^{1}	2.64×10^{1}	24
1,3-dimethoxybenzene	2.48	1.09	4.77×10^{2}	2.45×10^{2}	24
allyltriphenylstannane	3.09	0.90	2.92×10^{2}	3.43×10^{2}	24
 $E = 0.14$					
allyltrimethylsilane	1.79	0.94	6.31×10^{1}[h]	6.51×10^{1}	70
methylenecyclopentane	2.82	0.90	4.71×10^{2}[i]	4.57×10^{2}	70
 $E = 0.93$					
allylchlorodimethylsilane	−0.45	0.96	4.08[j]	2.89	70
allyltrimethylsilane	1.79	0.94	2.58×10^{2}	3.61×10^{2}	70
 $E = 1.06$					
allylchlorodimethylsilane	−0.45	0.96	7.60	3.87	25
allyltrimethylsilane	1.79	0.94	2.50×10^{2}	4.82×10^{2}	25
 $E = 1.95$					
2-methyl-1-pentene	0.96	1.00	4.45×10^{2}	8.17×10^{2}	70
allyltrimethylsilane	1.79	0.94	5.81×10^{3}[h]	3.28×10^{3}	70
 $E = 2.16$					
styrene	0.78	0.95	5.65×10^{2}[k]	6.07×10^{2}	10
2-methyl-1-pentene	0.96	1.00	1.41×10^{3}[l]	1.31×10^{3}	14
 $E = 2.93$					
2-methyl-2-butene	0.65	1.17	5.56×10^{3}[m]	1.49×10^{4}	[n]
styrene	0.78	0.95	4.37×10^{3}[k]	3.25×10^{3}	[n]
2-methyl-1-pentene	0.96	1.00	6.65×10^{3}	7.69×10^{3}	[n]
isoprene	1.10	0.98	7.14×10^{3}	8.59×10^{3}	[n]
allyltrimethylsilane	1.79	0.94	6.09×10^{4}[h]	2.70×10^{4}	[n]
 $E = 3.25$					
2-methyl-2-butene	0.65	1.17	9.10×10^{3}[m]	3.57×10^{4}	[n]
styrene	0.78	0.95	9.89×10^{3}[k]	6.62×10^{3}	[n]
2-methyl-1-pentene	0.96	1.00	1.00×10^{4}	1.63×10^{4}	[n]
isoprene	1.10	0.98	1.60×10^{4}	1.79×10^{4}	[n]
allyltrimethylsilane	1.79	0.94	1.93×10^{5}[h]	5.45×10^{4}	[n]
 $(pfp)_2CH^+$, $E = 5.39$					
toluene	−4.47	1.32	1.43×10^{1}	1.64×10^{1}	55b
m-xylene	−3.54	1.62	1.20×10^{3}	1.01×10^{3}	55b

[a] The values of k_{calc} were actually calculated by eq 1 with more decimals of E, N, and s than indicated in the table. The use of the E, N, and s parameters given in this table leads to somewhat deviating results. [b] In acetone. [c] In nitromethane, the original rate constant (at 45 °C) was converted to k(20 °C) assuming $\Delta S^{\ddagger} = -100$ J mol^{-1} K^{-1}, see also ref 18. [d] This rate constant was not used for the determination of E. [e] In acetonitrile. [f,g] From rate constants determined at different temperature assuming the same activation entropy as for the reactions of this nucleophile with benzhydrylium ions: $\Delta S^{\ddagger} =$ [f] −110; [g] −120 J mol^{-1} K^{-1}. [h–m] From rate constants determined at −70 °C, assuming the same activation entropy as for the reactions of this nucleophile with benzhydrylium ions: $\Delta S^{\ddagger} =$ [h] −118; [i] −123; [j] −120; [k] −122; [l] −121; [m] −153 J mol^{-1} K^{-1}. [n] This work.

Table 4. Second-Order Rate Constants k (M^{-1} s^{-1}, 20 °C, CH_2Cl_2) for the Reactions of Nucleophiles Not Belonging to the Basis Set (from Table 2) with Electrophiles Not Belonging to the Basis Set (from Table 3)[a]

Electrophile	E	Nucleophile	N	s	k_{exp}	k_{calc}	Ref.
	–9.19	$HSnBu_3$	9.96	0.55	$5.98 \times 10^{-1\,b}$	2.66	67
	–8.94	$HSnBu_3$	9.96	0.55	$8.31 \times 10^{-1\,b}$	3.67	67
	–8.54	$H_3B{\leftarrow}NEt_3$	8.90	0.75	5.45	1.87	15
		$HSnBu_3$	9.96	0.55	3.50	6.14	49
	–7.78	$HSnBu_3$	9.96	0.55	4.87^{b}	1.61×10^{1}	67
	–6.15	$HSnBu_3$	9.96	0.55	1.10×10^{1}	1.28×10^{2}	23
	–3.72	$HSiMe_2Ph$	3.27	0.73	$3.04 \times 10^{-2\,c}$	4.70×10^{-1}	27
		$HSiEt_3$	3.64	(0.65)	$3.24 \times 10^{-2\,d}$	8.92×10^{-1}	71
		$HSnPh_3$	5.64	0.59	1.20×10^{1}	1.34×10^{1}	27
	–2.90	$HSiMe_2Ph$	3.27	0.73	8.99×10^{-1}	1.88	49
	–2.14	(2-methylallyl)-triphenylsilane	4.17	(0.83)	2.57×10^{1}	4.94×10^{1}	20
		$HSiMe_2Ph$	3.27	0.73	1.07	6.75	20
	–1.59	$HSiMe_2Ph$	3.27	0.73	1.13	1.70×10^{1}	23
	–1.55	$HSiMe_2Ph$	3.27	0.73	1.79	1.81×10^{1}	23
		$HSiBu_3$	4.45	0.64	7.09	7.02×10^{1}	23
	–0.98	$HSiMe_2Ph$	3.27	0.73	9.35	4.81×10^{1}	23
	–0.83	$HSiMe_2Ph$	3.27	0.73	3.95	6.14×10^{1}	23
		(2-methylallyl)-triphenylsilane	4.17	(0.83)	1.78×10^{2}	6.13×10^{2}	23
	–0.28	$HSiPh_3$	2.06	0.68	2.48	1.65×10^{1}	24
	0.14	(2-methylallyl)-triphenylsilane	4.17	(0.83)	$7.53 \times 10^{3\,e}$	3.93×10^{3}	70
	0.93	allyltriphenylsilane	–0.13	1.21	9.82^{f}	9.21	70
	1.06	$HSiMe_2Ph$	3.27	0.73	9.99×10^{1}	1.50×10^{3}	25
	1.95	allyltriphenylsilane	–0.13	1.21	1.24×10^{2}	1.58×10^{2}	70

[a] The values of k_{calc} were actually calculated by eq 1 with more decimals of E, N, and s than indicated in the table. The use of the E, N, and s parameters given in this table leads to somewhat deviating results. [b] In acetone. [c] A second-order rate constant of 3.46×10^{-2} M^{-1} s^{-1} (25 °C, CH_2Cl_2) has been reported in ref 71. [d–f] From rate constants determined at different temperature assuming the same activation entropy as for the reactions of this nucleophile with benzhydrylium ions: $\Delta S^{\ddagger} =$ [d] −100; [e] −110; [f] −150 J mol^{-1} K^{-1}.

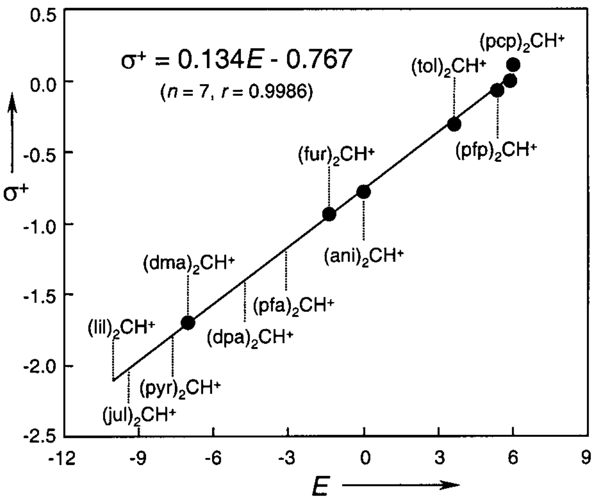


Figure 4. Correlation of Hammett's σ^+ constants[31] with the electrophilicity parameters E of the corresponding symmetrically substituted benzhydrylium ions (for abbreviations, see ref 35).

New Hammett Parameters. The Hammett equation is one of the oldest and the most developed empirical relationship which has been employed for correlating kinetic and thermodynamic as well as spectroscopic properties.[31,72–74] Most quantitative information about substituent effects have been derived from Hammett's σ constants and modifications thereof. However, as indicated above, the wealth of substituent constants for electron-withdrawing and weakly electron-donating groups is contrasted by a remarkable shortage of substituent constants for groups that are better electron donors than alkoxy.[75]

In agreement with earlier studies,[76] there is only a moderate correlation ($r = 0.9955$) between the electrophilicity parameters E of benzhydrylium ions with $\Sigma\sigma^+$, because in case of unsymmetrically substituted systems, the twisting angle of the two aryl rings is different.[73] If only symmetrically substituted benzhydryl cations are considered, the linear correlation (Figure 4) is of higher quality, however, and can be used to determine the σ^+ parameters of a series of new donor substituents (Table 5).

Conclusion

The linear free enthalpy relationships presented in Figures 1 and 2 represent the most extended reactivity−reactivity correlations presently known. Since the E parameters of the benzhydrylium cations and the N and s parameters of the π-nucleophiles derived therefrom were found to be a proper

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(70) Mayr, H.; Gorath, G. *J. Am. Chem. Soc.* **1995**, *117*, 7862−7868.

(71) Chojnowski, J.; Fortuniak, W.; Stańczyk, W. *J. Am. Chem. Soc.* **1987**, *109*, 7776−7781.

(72) (a) Hine, J. *Structural Effects on Equilibria in Organic Chemistry*; Robert E. Krieger Publishing Company: Huntington, NY, 1981. (b) *Advances in Linear Free Energy Relationships*; Chapman, N. B., Shorter, J., Eds.; Plenum Press: London, 1972.

(73) Tsuno, Y.; Fujio, M. *Adv. Phys. Org. Chem.* **1999**, *32*, 267−385.

(74) Tsuno, Y.; Fujio, M. *Chem. Soc. Rev.* **1996**, 129−139.

(75) For $\sigma_R°$ constants of amino substituents, see: Gawinecki, R.; Kolehmainen, E.; Kauppinen, R. *J. Chem. Soc., Perkin Trans. 2* **1998**, 25−29.

(76) Schade, C.; Mayr, H. *Tetrahedron* **1988**, *44*, 5761−5770.

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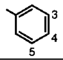
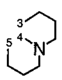
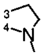
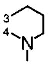
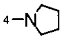
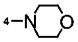
Table 5. Hammett σ^+ Constants of Donor Substituents

Ar_2CH^+ [a]	substituent at 	σ^+
$(lil)_2CH^+$		–2.11
$(jul)_2CH^+$		–2.03
$(ind)_2CH^+$		–1.94
$(thq)_2CH^+$		–1.87
$(pyr)_2CH^+$		–1.80
$(dma)_2CH^+$	4–NMe_2	–1.70[b]
$(mpa)_2CH^+$	4–N(Ph)Me	–1.56
$(mor)_2CH^+$		–1.51
$(dpa)_2CH^+$	4–NPh_2	–1.40
$(mfa)_2CH^+$	4–$N(Me)CH_2CF_3$	–1.28
$(pfa)_2CH^+$	4–$N(Ph)CH_2CF_3$	–1.19

[a] For abbreviations, see ref 35. [b] From ref 31.

basis for the characterization of numerous other nucleophiles and electrophiles (Tables 2 and 3), the reference compounds listed in Figure 3 are suggested as the basis for a systematic treatment of polar organic reactions.

As demonstrated for the electrophiles and nucleophiles treated in Tables 2–4, one can now easily compare the reactivities of structurally different electrophiles[77,78] and nucleophiles[79] including reaction media[80] and use these data for a rational design of organic transformations[81] and of carbocationic polymerizations.[82] The electrophilicity parameters E and the nucleophilicity parameters N can further be employed for elucidating reaction mechanisms[83] and for theoretical treatments of organic reactivity.[84] Though a moderate correlation between the electrophilicity parameters E and the corresponding reduction potentials has been reported,[12] outer sphere SET processes for the reactions of carbocations with π-nucleophiles have been excluded.[83b]

Though the reactivity scales presented in this work cover already 16 orders of magnitude, extensions of the scales in both directions are desirable. Laser flash experiments have already been employed to characterize more electrophilic carbocations,[41,66,85] and quinone methides have been reported to behave like highly stabilized carbocations which can be used for the investigation of stronger nucleophiles.[86,87] The integration of these data is in progress.

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measuring the UV−vis spectra as well as Dr. M.-A. Funke and Dr. M. Patz for experimental contributions.

Supporting Information Available: Details and tables with concentrations and rate constants of the kinetic experiments, synthetic procedures of the carbocation-nucleophile combinations with product characterization, UV−vis spectral data of Michler's Hydrol Blue and its analogues, and the complete version of Table 1 with second-order rate constants, activation and reactivity parameters for the reactions of basis set benzhydrylium ions with basis set π-nucleophiles (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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