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Reactivity

Nucleophilic Reactivities of Bis-Acceptor-Substituted Benzyl Anions

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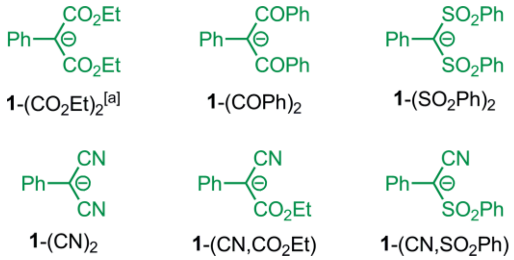
Abstract: The kinetics of the reactions of bis-acceptor-substituted benzyl anions ($PhCXY^-$, X,Y = CN, CO_2Et, COPh, SO_2Ph) with benzhydrylium ions and quinone methides (reference electrophiles) have been determined in dimethyl sulfoxide solution at 20 °C. The reactions follow second-order kinetics, first order with respect to the electrophile and first order with respect to the carbanion. The addition of 18-crown-6 ether, which efficiently coordinates to the anions' counter ions K^+, did not affect the kinetics, which indicates that the measured rate constants refer to the reactivities of the nonpaired carbanions. Comparison with the reactivities of the structurally analogous secondary carbanions $HCXY^-$ shows that replacement of H at the carbanionic center by Ph reduces the nucleophilic reactivities towards a reference benzhydrylium ion by factors in the range of only 1.2 (X,Y = SO_2Ph) to 6 (X,Y = CO_2Et). The plots of lg k_2 versus the electrophilicity parameters E of the reference electrophiles are linear, thereby indicating that the correlation lg $k_2(20\ °C) = s_N(E + N)$, which characterizes nucleophiles by the two solvent-dependent parameters s_N and N and electrophiles by the parameter E, is applicable. In this way, it becomes possible to integrate these carbanions into our comprehensive nucleophilicity scale, which provides a direct comparison of the nucleophilic reactivities of different families of compounds.

Introduction

Acceptor-substituted carbanions, commonly generated by the deprotonation of CH-acidic compounds, are important reagents in organic synthesis due to their ability to act as nucleophiles in numerous synthetic transformations.[1] Furthermore, relationships between the rate and equilibrium constants for their formation and for their reactions with electrophiles have contributed significantly to the development of our present understanding of organic reactivity.[2,3] In previous work, we have already quantified the nucleophilicities of several secondary anions bearing CN, CO_2Et, COPh, SO_2R, and NO_2 groups,[4,5c] and demonstrated that their additions to benzhydryl cations and structurally related quinone methides followed the linear free-energy relationship given in Equation (1), in which E is an electrophile-specific parameter and N and s_N are solvent-dependent nucleophile-specific parameters.[5]

$$\lg k_2\ (20\ °C) = s_N(N + E) \qquad (1)$$

Because only a few examples of tertiary carbanions[6] have previously been studied by our group, we have now investigated the nucleophilic reactivity of different bis-acceptor-substituted benzyl anions **1** (Scheme 1). These carbanions are ideal candidates for mechanistic studies, because the absence of protons at the α carbon enables equilibrium studies and systematic determinations of heterolysis kinetics without disturbing proton shifts.

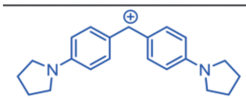
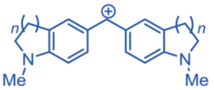
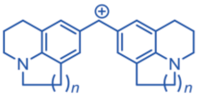
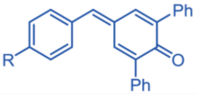


1-$(CO_2Et)_2$[a] **1**-$(COPh)_2$ **1**-$(SO_2Ph)_2$

1-$(CN)_2$ **1**-(CN,CO_2Et) **1**-(CN,SO_2Ph)

Scheme 1. Tertiary benzyl anions **1** studied in this work. [a] Previously reported in ref.[6c]

Table 1. Benzhydrylium ions **2a**–**e** and quinone methides **2f**–**h** employed as reference electrophiles in this study.

Electrophile[a]			E[b]	λ_{max}(in DMSO) [nm]
		**2a**	–7.69	620
	$n = 2$	**2b**	–8.22	618
	$n = 1$	**2c**	–8.76	627
	$n = 2$	**2d**	–9.45	635
	$n = 1$	**2e**	–10.04	630
	R = H	**2f**	–11.87	384
	R = OMe	**2g**	–12.18	422
	R = NMe_2	**2h**	–13.39	533

[a] Counter ions for **2a**–**e**: BF_4^-. [b] From refs.[5b,c,f,j]

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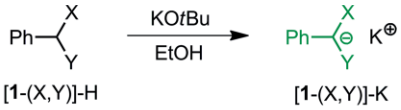
The colored reference electrophiles **2**, benzhydrylium ions and structurally related quinone methides, that served as reference electrophiles in this work are listed in Table 1.

Results

Synthesis of the Potassium Salts of the Carbanions 1

The CH acids [**1**-(COPh)$_2$]-H, [**1**-(CN)$_2$]-H, and [**1**-(CN,SO$_2$Ph)]-H were prepared by CuI-catalyzed reaction of iodobenzene with the corresponding bis-acceptor-substituted methane derivatives H$_2$C(Acc)$_2$ in DMSO following a literature procedure.[7] The bis(sulfone) [**1**-(SO$_2$Ph)$_2$]-H was obtained by oxidation of the corresponding dithioacetal.[8] Treatment of the corresponding CH acids [**1**]-H with an equimolar amount of potassium *tert*-butoxide (KO*t*Bu) in ethanol, subsequent concentration of the solutions, and washing of the precipitated salts with diethyl ether furnished good yields of the potassium salts [**1**]-K (Scheme 2), which were characterized by NMR techniques.



1-(X,Y)	Yield
1-(COPh)$_2$	41%
1-(SO$_2$Ph)$_2$	72%
1-(CN)$_2$	85%
1-(CN,CO$_2$Et)	93%
1-(CN,SO$_2$Ph)	91%

Scheme 2. Synthesis of the potassium salts [**1**]-K.

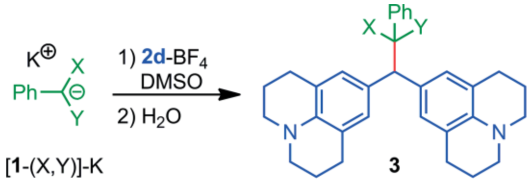
Quantitative deprotonation of the CH acids [**1**]-H with 1 equivalent of base was confirmed photometrically by adding solutions of the CH acids [**1**]-H in DMSO to solutions of potassium *tert*-butoxide in the same solvent. Addition of further equivalents of KO*t*Bu did not lead to a further increase in absorbance of the carbanions. The detected absorption maxima λ_{max} and molar absorption coefficients (lg ε_{max}) for the potassium methanides [**1**]-K are summarized in Table 2.

Table 2. Absorption maxima of the potassium methanides [**1**]-K generated by deprotonation of the corresponding CH acids [**1**]-H by KO*t*Bu in DMSO at 20 °C.

[**1**-(X,Y)]-K	λ_{max} [nm]	lg ε_{max}
[**1**-(COPh)$_2$]-K	258	3.84
[**1**-(SO$_2$Ph)$_2$]-K	268	3.39
[**1**-(CN)$_2$]-K	304	4.44
[**1**-(CN,CO$_2$Et)]-K	308	4.37
[**1**-(CN,SO$_2$Ph)]-K	292	4.22

Product Studies

Benzhydrylium ion **2d** was selected as a representative electrophile to examine the course of the kinetically studied reactions. For this purpose DMSO solutions of the potassium salts [**1**]-K were combined with the benzhydrylium tetrafluoroborate **2d** at room temperature. After the disappearance of the deep-blue color of the solution (commonly within 2 min at ambient temperature), water was added to precipitate adducts **3**. Recrystallization from ethyl acetate/pentane mixtures yielded of 61–70 % of the pure products **3**, which were characterized by NMR spectroscopy and mass spectrometry (Scheme 3).



1	3	Yield[a]
1-(CO$_2$Et)$_2$	**3**-(CO$_2$Et)$_2$	61%[b]
1-(CN)$_2$	**3**-(CN)$_2$	70%
1-(CN,CO$_2$Et)	**3**-(CN,CO$_2$Et)	69%
1-(CN,SO$_2$Ph)	**3**-(CN,SO$_2$Ph)	69%

Scheme 3. Reactions of the potassium methanides [**1**]-K with the benzhydrylium tetrafluoroborate **2d**-BF$_4$. [a] Yield of isolated products after crystallization. [b] From ref.[6c]

When the potassium salts [**1**-(COPh)$_2$]-K and [**1**-(SO$_2$Ph)$_2$]-K were combined with the benzhydrylium tetrafluoroborate **2d** in DMSO solution, the blue color of the electrophile disappeared within a few minutes. The corresponding adducts could not be isolated by aqueous work-up, however, because in the polar solvent water a fast retroaddition led to the regeneration of the starting compounds.

Kinetic Investigations

The kinetic investigations of the reactions of the anions **1** with the reference electrophiles **2** were performed in DMSO solutions at 20 °C and monitored by UV/Vis spectroscopy at the absorption maxima of the electrophiles (Table 1) using stopped-flow techniques. Owing to their stability, stock solutions of the potassium salts [**1**]-K in DMSO could be employed. As the nucleophiles **1** were employed in large excess (typically 10–100 equiv.) over the electrophiles **2**, their concentrations can be considered to be almost constant throughout the reactions, resulting in first-order kinetics with an exponential decay of the concentration of **2**. The first-order rate constants k_{obs} were derived by least-squares fitting of the exponential function $A_t = A_0 e^{-k_{obs}t} + C$ to the time-dependent absorbances A_t of the electrophiles. Second-order rate constants k_2 (Table 3) were obtained as the slopes of the linear correlations of k_{obs} versus typically five different concentrations of the nucleophiles (Figure 1).

The coordination of 1,3-dicarbonyl-substituted carbanions to potassium ions was previously reported to reduce their nucleophilic reactivities in DMSO by up to 60 %.[4h] However, because the first-order rate constants k_{obs} measured in this study in the presence or absence of 18-crown-6 ether are on the same k_{obs} versus [**1**] correlation line (see Figure 1b), one can conclude that the measured rate constants reflect the reactivities of the free carbanions.

All the reactions of the carbanions **1** (used in excess) with the benzhydrylium tetrafluoroborates **2a**–**e** proceeded with

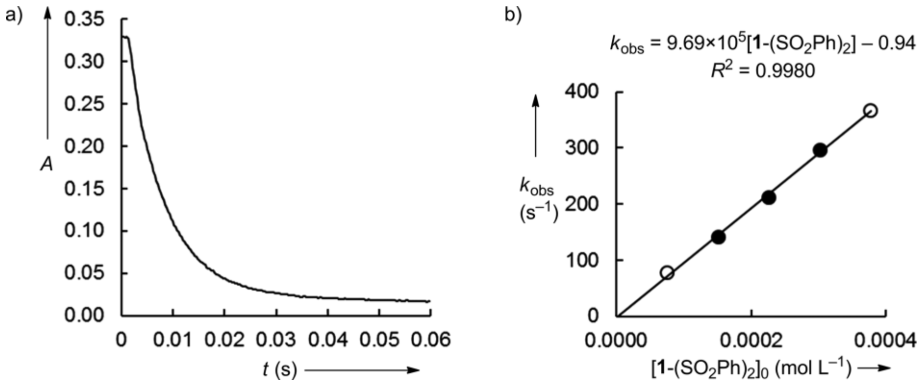
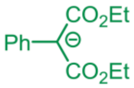
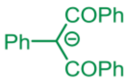
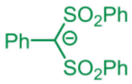
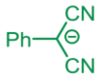
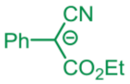
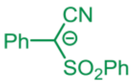


Figure 1. a) Decay of the absorbance *A* (at 620 nm) of the benzhydrylium ion **2a** during its reaction with **1**-(SO$_2$Ph)$_2$ {[**1**-(SO$_2$Ph)$_2$]$_0$ = 1.51 × 10^{-4} M, [**2a**]$_0$ = 7.65 × 10^{-6} M, k_{obs} = 1.42 × 10^2 s^{-1}} in DMSO at 20 °C. b) Determination of the second-order rate constant k_2 = 9.69 × 10^5 M^{-1} s^{-1} for this reaction by plotting k_{obs} against the concentration of **1**-(SO$_2$Ph)$_2$ {empty circles: in the presence of 1.05 equiv. of 18-crown-6 with respect to [**1**-(SO$_2$Ph)$_2$]-K}.

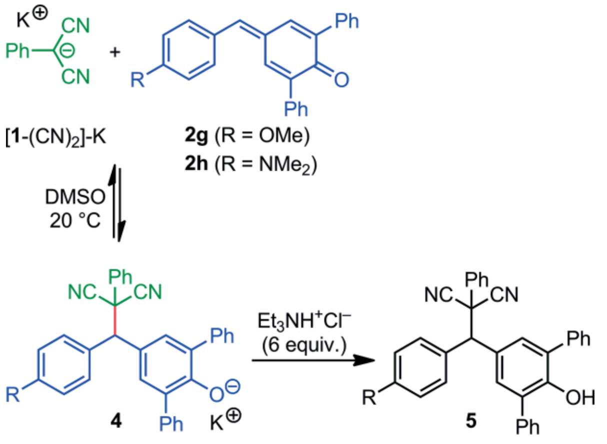
Table 3. Second-order rate constants for the reactions of the carbanions **1** (counter ion: K$^+$) with the reference electrophiles **2** in DMSO at 20 °C.

Carbanion	*N* (s_N)[a]	2	k_2[b] [M^{-1} s^{-1}]
 **1**-(CO$_2$Et)$_2$	15.93 (0.99)[c]	**2e**	6.47 × 10^5 [c]
		2f	1.04 × 10^4 [c]
		2g	4.33 × 10^3 [c]
		2h	3.33 × 10^2 [c]
 **1**-(COPh)$_2$	14.99 (0.83)	**2a**	1.38 × 10^6
		2b	3.75 × 10^5
		2c	1.14 × 10^5
		2d	3.48 × 10^4
		2e	1.55 × 10^4
 **1**-(SO$_2$Ph)$_2$	15.07 (0.79)	**2a**	9.69 × 10^5
		2b	2.47 × 10^5
		2c	7.18 × 10^4
		2d	2.77 × 10^4
		2e	1.23 × 10^4
 **1**-(CN)$_2$	15.58 (1.00)	**2d**	1.10 × 10^6
		2e	5.14 × 10^5
		2g	1.27 × 10^3 [d]
		2h	2.25 × 10^2 [d]
 **1**-(CN,CO$_2$Et)	15.85 (1.04)	**2e**	1.07 × 10^6
		2f	1.43 × 10^4
		2g	6.17 × 10^3
 **1**-(CN,SO$_2$Ph)	15.97 (0.72)	**2b**	4.93 × 10^5
		2c	1.21 × 10^5
		2d	5.31 × 10^4
		2e	2.09 × 10^4

[a] The nucleophile-specific parameters *N* and s_N were determined by correlation analysis using Equation (1) as described below. [b] The listed second-order rate constants (k_2) were obtained from typically five experiments with different anion concentrations (see the Supporting Information for details). [c] From ref.[6c] [d] Data obtained in the presence of 6 equiv. of triethylammonium chloride relative to the electrophiles.

complete decolorization of the solutions, that is, quantitative consumption of the benzhydrylium ions. Accordingly, the intercepts in the plots of the pseudo-first-order rate constants k_{obs} versus the concentration of the potassium salts [**1**]-K were negligible [exception **1**-(CN)$_2$ + **2d**], as shown in Figure 1 and the Supporting Information. Rate constants for the reactions of **1**-(CN)$_2$ with the more electrophilic benzhydrylium ions **2a**–**c** could not be measured, because these reactions proceeded too fast to be followed with our stopped-flow instruments.

We have also investigated the kinetics of the reactions of the carbanions **1**-(CO$_2$Et)$_2$[6c] and **1**-(CN,CO$_2$Et) with the less electrophilic quinone methides **2f**–**h**. The consumption of these electrophiles was almost complete and the final concentrations of the quinone methides **2f**–**h** were negligibly small, leading to small intercepts in the linear correlations of k_{obs} versus the concentration of **1** [except for **1**-(CN,CO$_2$Et) + **2g**]. In contrast, the degree of conversion was very small in the reactions of the phenylmalononitrile anion **1**-(CN)$_2$ with the quinone methides **2g** and **2h**, which impeded the measurement of the corresponding addition rate constants. Full conversion of **2g** and **2h** with **1**-(CN)$_2$ was achieved, however, when the reactions with **1**-(CN)$_2$ were carried out in the presence of triethylammonium chloride as proton source. The protonation of the initially formed phenolates **4** favored the consumption of **2g**,**h** (Scheme 4). The amount of Et$_3$NH$^+$Cl$^-$ with respect to the quinone methides was optimized to 6 equiv. (Figure 2) with a zero-order of reaction, which implies that the presence of Et$_3$NH$^+$Cl$^-$



Scheme 4. Reversible addition of phenylmalonitrile **1**-(CN)$_2$ to the quinone methides **2g**,**h**.

does not affect the rate of the addition of the anion **1**-$(CN)_2$ to **2g**,**h** (Figure 3). Under these conditions second-order kinetics with complete disappearance of the quinone methides occurred.

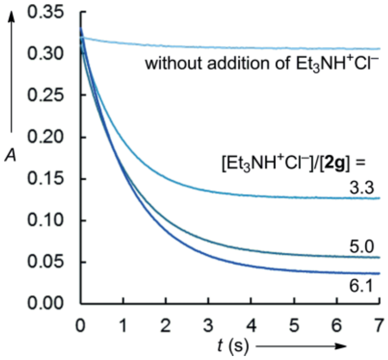


Figure 2. Decay of the absorbance A of the quinone methide **2g** at 422 nm during its reaction with $[$**1**-$(CN)_2]$-K in DMSO at 20 °C in the presence of variable concentrations of $Et_3NH^+Cl^-$ $\{[$**1**-$(CN)_2]_0 = 6.16 \times 10^{-4}$ м, $[$**2g**$]_0 = 1.51 \times 10^{-5}$ м$\}$.

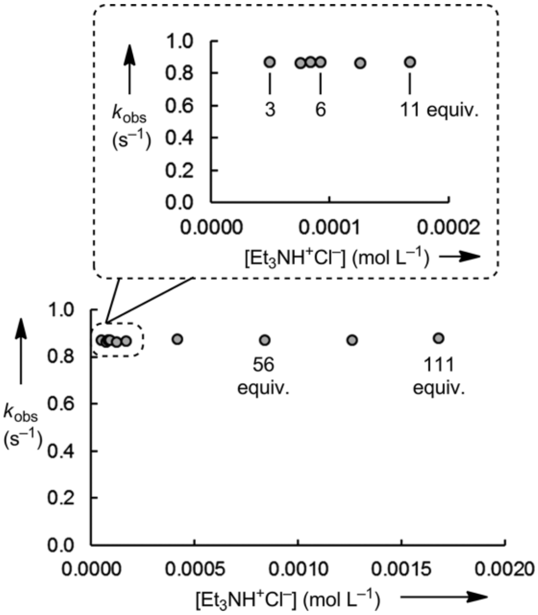


Figure 3. Dependence of the observed first-order rate constant k_{obs} on the concentration of added $Et_3NH^+Cl^-$ in the reaction of $[$**1**-$(CN)_2]$-K with **2g** $\{[$**1**-$(CN)_2]_0 = 6.16 \times 10^{-4}$ м, $[$**2g**$]_0 = 1.51 \times 10^{-5}$ м, $[Et_3NH^+Cl^-]_0/[$**2g**$]_0$ = 3–111$\}$.

Correlation Analysis and Discussion

To determine the nucleophilicity parameters N and s_N of the carbanions **1**, values of lg k_2 for their reactions with the reference electrophiles **2** were plotted against the corresponding electrophilicity parameters E. As shown for some representative examples in Figure 4, and for all the reactions in the Supporting Information, linear correlations of lg k_2 with E were found, which indicates that Equation (1) is applicable. From the slopes of these correlations, the nucleophile-specific parameters s_N were derived, and the negative intercepts on the abscissa (lg k_2 = 0) correspond to the nucleophilicity parameters N (Table 3). The similar values of s_N listed in Table 3 ($0.72 < s_N < 1.04$), reflected by the almost parallel correlation lines in Figure 4, imply that the relative reactivities of these anions depend only slightly on the nature of the electrophiles.

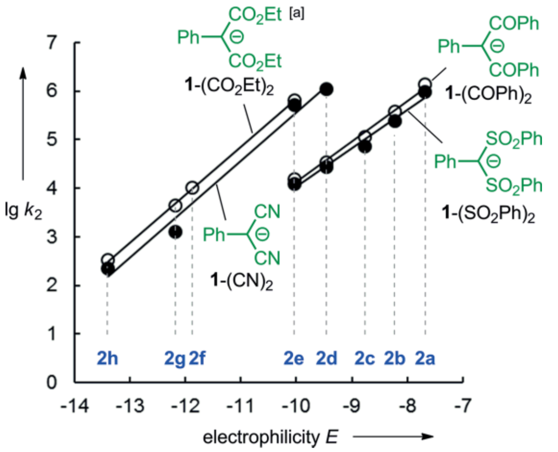


Figure 4. Correlation of the rate constants lg k_2 for the reactions of the benzylic anions **1** with the electrophiles **2** in DMSO at 20 °C with the corresponding electrophilicity parameters E. [a] With rate constants from ref.[6c]

Benzhydrylium ion **2e** is the electrophile for which most directly measured rate constants are available. For that reason, we selected this electrophile to compare the reactivities of the tertiary carbanions **1** $[PhC(Acc)_2^-]$ with those of the corresponding secondary carbanions **6** $[HC(Acc)_2^-]$. Figure 5 shows that the reactivities all lie within a narrow range, and the rate constants k_2 for the reactions with **2e** increase from the disulfonyl-substituted benzyl anion **1**-$(SO_2Ph)_2$ (least reactive) to the diethyl malonate anion **6**-$(CO_2Et)_2$ as the most reactive species by a factor of only 330. Replacement of the proton at the carbanionic center in **6**-(X,Y) by phenyl to give **1**-(X,Y) has an astonishingly small effect. Thus, the disulfonyl-substituted methyl anion **6**-$(SO_2Ph)_2$ and the corresponding benzyl anion **1**-$(SO_2Ph)_2$ have almost equal reactivities. Replacement of the proton at the carbanionic center by phenyl reduces the reactivities of the cyano-stabilized carbanions by factors of 1.3–3, and in the case of benzoyl- and ethoxycarbonyl-substituted carbanions by factors of 4–6. Although the phenyl effects are generally small, the largest effects are found for the carbonyl-substituted systems, which are stabilized by π conjugation, and the differences disappear for the pyramidal sulfonyl-stabilized carbanions, which are stabilized by polarization.

As previously discussed,[6c] the correlation between the nucleophilic reactivities of carbanions and the corresponding pK_{aH} values in DMSO is generally rather poor.[9] Figure 6 shows that the large difference in the pK_{aH} values of the malononitrile anions **1**-$(CN)_2$ and **6**-$(CN)_2$ ($\Delta pK_{aH} = 6.8$) is not reflected by the relative nucleophilic reactivities towards carbocation **2e**, which differ only by a factor 3.4. The comparison of the benzylic anions **1**-$(CN)_2$ and **1**-$(CO_2Et)_2$ is even more striking: They have almost the same reactivity towards **2e** but differ in pK_{aH} by 12 orders of magnitude. On the other hand, the diethyl malonate **6**-$(CO_2Et)_2$ and the phenyl-substituted diethyl malonate anion **1**-$(CO_2Et)_2$, which differ by a factor of 6 in nucleophilic reactivity towards **2e**, have equal pK_{aH} values.

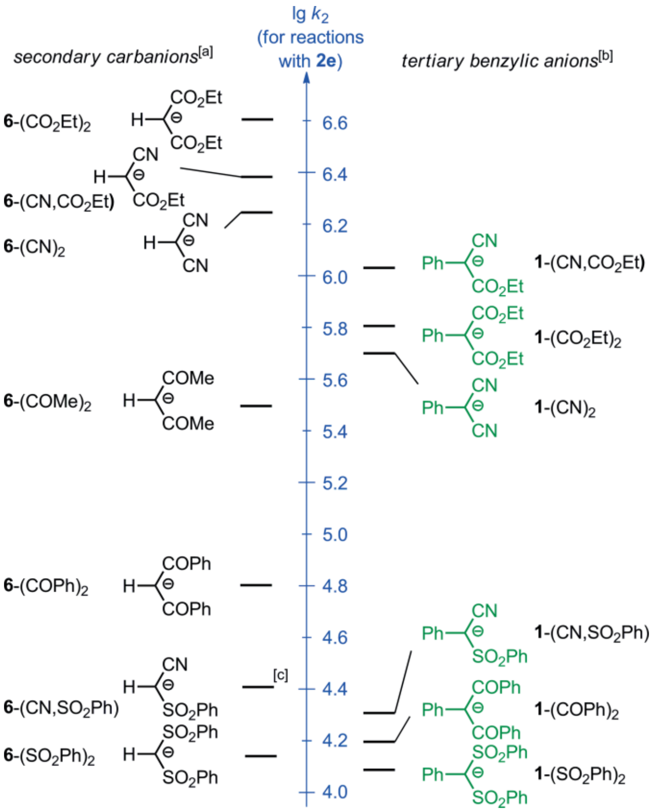


Figure 5. Second-order rate constants lg k_2 for the reactions of the tertiary benzyl anions **1** (right) and the structurally related secondary anions **6** (left) with the benzhydrylium ion **2e** in DMSO at 20 °C. [a] Rate constants from refs.[4h,5c,6d] [b] Rate constants from Table 3. [c] The kinetic data in ref.[4a] give N = 16.73 and s_N = 0.66 for **6**-(CN,SO$_2$Ph), which were used to calculate lg k_2 for the reaction with **2e** by using Equation (1).

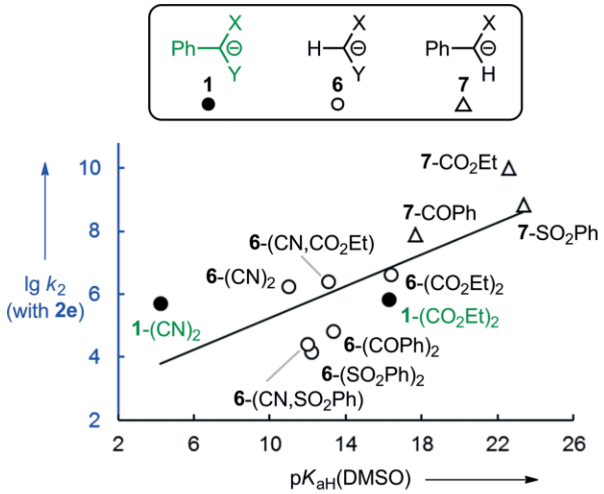


Figure 6. Brønsted correlation for the reactions of the acceptor-substituted carbanions **1**, **6**, and **7** with the benzhydrylium ion **2e** (DMSO, 20 °C, pK_{aH} from ref.[10]); for references and further details see the Supporting Information.

Conclusions

Phenyl groups are known to stabilize charge by the mesomeric effect. Thus, phenyl substitution at the reaction center generally reduces the electrophilic reactivities of carbocations as well as the nucleophilic reactivities of carbanions. We have now found, however, that the nucleophilicities of carbanions stabilized by two acceptor groups (CN, CO$_2$Et, COPh, SO$_2$Ph) are barely reduced by an additional phenyl group. Although steric effects can be expected to augment the electronic effect by also reducing the nucleophilic reactivities of the carbanions [PhC(Acc)$_2$]$^-$ (**1**) relative to their secondary analogues [HC(Acc)$_2$]$^-$ (**6**), we have now found that both classes of carbanions have almost the same nucleophilic reactivities. It should be noted, however, that this analysis refers to reactions with an electrophile of E = –10 and that the relative reactivities of two nucleophiles depend on the nature of the electrophile if they differ in s_N.

To compare nucleophiles of widely differing reactivity, we usually neglect s_N and consider the magnitudes of N, as shown in Figure 7. The nucleophilicity parameter N reflects relative reactivities towards an electrophile, which reacts with an average rate constant of 1 M^{-1} s^{-1} (lg k = 0) with the nucleophiles under consideration (floating scale of reference electrophiles).[11] In this way, a rough estimation of relative reactivities over a wide range of reactivity can be obtained.

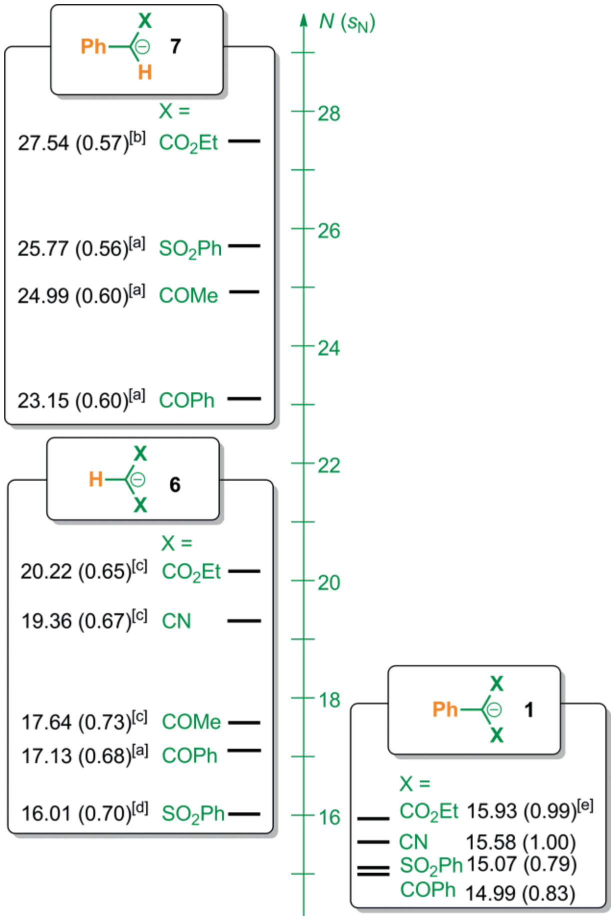


Figure 7. Structure–reactivity relationships for benzyl anions **7**, secondary anions **6**, and tertiary anions **1**, including their nucleophilicity parameters N (and s_N). [a] From ref.[4h] [b] From ref.[4g] [c] From ref.[5c] [d] From ref.[6d] [e] From ref.[6c]

Figure 7 illustrates the limitations of the neglect of s_N, however. Owing to the similar magnitude of their s_N values, carbanions **1**-(SO$_2$Ph)$_2$ and **6**-(SO$_2$Ph)$_2$, which differ by only one unit in N (Figure 7), also react with almost the same rates with electrophile **2e** (Figure 5). Carbanions **1**-$(CO_2Et)_2$ and **6**-$(CO_2Et)_2$, on the other hand, which differ by four units of N according to Figure 7, differ in the rates of their reactions with **2e** by only a factor of 6 because of the different magnitude of s_N. Despite these deviations, in light of the fact that the N scale presently covers almost 40 orders of magnitude,[5g–5i,12] inspection of the N scale gives valuable first information about the relative reactivities of different nucleophiles, which has to be refined by s_N if more accurate comparisons are needed.

Experimental Section

Materials: All solvents were of p.a. quality. Unless otherwise specified, materials were obtained from commercial sources and used without purification. The reference electrophiles (benzhydrylium tetrafluoroborates **2a**–**e** and quinone methides **2f**–**h**) used in this work were prepared as described before.[5c,5f] Bis(phenylsulfonyl)methane was prepared by oxidation of bis(phenylthio)methane with hydrogen peroxide.[8b] Procedures for the synthesis of the CH acids [**1**]-H that are not commercially available are given in the Supporting Information.

General Procedure for the Synthesis of Potassium Salts 1-K (GP A): In a dried round-bottomed Schlenk flask, the corresponding CH acid [**1**]-H (1.00 equiv.) was added to a solution of KO*t*Bu (0.95 equiv.) in ethanol (10 mL) under argon. The resulting solution was stirred at room temperature for 30 min and then concentrated under reduced pressure to give a solid residue, which was further washed with freshly distilled Et_2O (3 × 10 mL) under argon. The solid residue was dried under vacuum for an additional 2 h to afford the corresponding potassium salt [**1**]-K, which was stored in a glove box under argon.

Potassium 1,3-Dioxo-1,2,3-triphenylpropan-2-ide [1-$(COPh)_2$]-K: Obtained according to GP A from 1,2,3-triphenylpropane-1,3-dione [**1**-$(COPh)_2$]-H (500 mg, 1.66 mmol) and KO*t*Bu (180 mg, 1.60 mmol). Yield: 223 mg (41 %); white solid. ^{1}H NMR (400 MHz, [D_6]DMSO): δ = 8.06–8.04 (m, 2 H, Ar), 7.85–7.83 (m, 3 H, Ar), 7.66–7.62 (m, 1 H, Ar), 7.55–7.51 (m, 2 H, Ar), 7.42–7.31 (m, 2 H, Ar), 7.27–7.24 (m, 5 H, Ar) ppm. ^{13}C NMR (101 MHz, [D_6]DMSO): δ = 195.0 (CO), 168.4 (Ar), 135.5 (Ar), 133.7 (Ar), 130.0 (Ar), 129.0 (Ar), 128.9 (Ar), 128.5 (Ar), 127.0 (Ar), 61.3 (C^-) ppm.

Potassium Phenyl[bis(phenylsulfonyl)]methanide [1-$(SO_2Ph)_2$]-K: Obtained according to GP A from (phenylmethylenedisulfonyl)dibenzene [**1**-$(SO_2Ph)_2$]-H (550 mg, 1.48 mmol) and KO*t*Bu (157 mg, 1.40 mmol). Yield: 412 mg (72 %); white solid. ^{1}H NMR (400 MHz, [D_6]DMSO): δ = 7.81–7.80 (m, 4 H, Ar), 7.39 (br. s, 6 H, Ar), 7.05–7.04 (m, 4 H, Ar), 6.93 (br. s, 1 H, Ar) ppm. ^{13}C NMR (101 MHz, [D_6]DMSO): δ = 150.6 (Ar), 137.4 (Ar), 132.3 (Ar), 129.2 (Ar), 127.8 (Ar), 126.7 (Ar), 125.7 (Ar), 123.5 (Ar), 76.4 (C^-) ppm.

Potassium Dicyano(phenyl)methanide [1-$(CN)_2$]-K: Obtained according to GP A from 2-phenylmalononitrile [**1**-$(CN)_2$]-H (1.00 g, 7.03 mmol) and KO*t*Bu (750 mg, 6.68 mmol). Yield: 1.03 g (85 %); white solid. ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 7.03–6.97 (m, 2 H, Ar), 6.74–6.70 (m, 2 H, Ar), 6.52–6.47 (m, 1 H, Ar) ppm. ^{13}C NMR (75.5 MHz, [D_6]DMSO): δ = 141.4 (C, Ar), 128.1 (CH, Ar), 126.3 (C, CN), 118.0 (CH, Ar), 116.8 (CH, Ar), 27.2 (C, C^-) ppm. ^{13}C NMR spectroscopic data agree with those reported for [**1**-$(CN)_2$]-Na in DMSO.[13]

Potassium 1-Cyano-2-ethoxy-2-oxo-1-phenylethan-1-ide [1-(CN,CO_2Et)-K]: Obtained according to GP A from commercially available ethyl 2-cyano-2-phenylacetate [**1**-(CN,CO_2Et)]-H (1.0 mL, 5.8 mmol) and KO*t*Bu (628 mg, 5.60 mmol). Yield: 1.19 g (93 %); white solid. ^{1}H NMR (400 MHz, [D_6]DMSO): δ = 7.55 (d, J = 7.4 Hz, 2 H, Ar), 6.99–6.95 (m, 2 H, Ar), 6.55–6.51 (m, 1 H, Ar), 3.89 (q, J = 7.1 Hz, 2 H, OCH_2), 1.12 (t, J = 7.1 Hz, 3 H, CH_3) ppm. ^{13}C NMR (101 MHz, [D_6]DMSO): δ = 167.5 (C, CO_2), 141.8 (C, Ar), 127.6 (C, CN), 127.2 (CH, Ar), 120.9 (CH, Ar), 117.3 (CH, Ar), 55.8 (CH_2, OCH_2CH_3), 54.6 (C, C^-), 15.5 (CH_3, OCH_2CH_3) ppm.

Potassium Cyano(phenyl)(phenylsulfonyl)methanide [1-(CN,SO_2Ph)]-K: Obtained according to GP A from 2-phenyl-2-(phenylsulfonyl)acetonitrile [**1**-(CN,SO_2Ph)]-H (950 mg, 3.69 mmol) and KO*t*Bu (394 mg, 3.51 mmol). Yield: 944 mg (91 %); white solid. ^{1}H NMR (400 MHz, [D_6]DMSO): δ = 7.74–7.72 (m, 2 H, Ar), 7.44–7.39 (m, 3 H, Ar), 7.09–7.07 (m, 2 H, Ar), 6.98–6.94 (m, 2 H, Ar), 6.56–6.52 (m, 1 H, Ar) ppm. ^{13}C NMR (101 MHz, [D_6]DMSO): δ = 148.0 (C, Ar), 138.5 (C, Ar), 130.0 (CH, Ar), 128.3 (CH, Ar), 127.7 (CH, Ar), 125.2 (C, CN), 124.8 (CH, Ar), 119.5 (CH, Ar), 117.9 (CH, Ar), 59.9 (C, C^-) ppm. ^{13}C NMR spectroscopic data agree with those reported for [**1**-(CN,SO_2Ph)]-Na in DMSO.[13]

Reactions of Highly Stabilized Carbanions 1 with 2d: A solution of **2d**-BF_4 (1.00 equiv.) in DMSO (5 mL) was added to a solution of [**1**]-K (1.05 equiv.) in DMSO (5 mL). After the disappearance of the deep-blue color (usually within 2–5 min), H_2O (5 mL) was added and a precipitate formed. The mixture was filtered and the collected precipitate was redissolved in CH_2Cl_2. The solution was washed with water (2 × 10 mL), dried with $MgSO_4$, and evaporated under reduced pressure to afford a crude product, which was recrystallized in EtOAc/*n*-pentane mixtures. See the Supporting Information for details of the product characterizations of **3**-$(CN)_2$, **3**-(CN,CO_2Et), and **3**-(CN,SO_2Ph).

Determination of Rate Constants: The rates of all investigated reactions were determined photometrically. For the evaluation of the kinetics, stopped-flow spectrophotometer systems (Hi-Tech SF-61DX2 or Applied Photophysics SX.18MV-R) were used. All kinetic measurements were carried out in DMSO (Acros Organics, H_2O content <50 ppm) under exclusion of moisture. The temperature of the solutions during all kinetic studies was kept constant (20.0 ± 0.1 °C) by using a circulating bath thermostat. The nucleophiles were always employed as the major component (typically at least 10 equiv.) in the reactions with the electrophiles to ensure first-order conditions with $k_{obs} = k_2[\mathrm{Nu}]_0 + k_0$. In a few cases, plots of k_{obs} versus $[\mathrm{Nu}]_0$ showed negative intercepts, which were explained by the presence of unknown contaminations. Pseudo-first rate constants k_{obs} [s^{-1}] were obtained by fitting the monoexponential function $A_t = A_0\exp(-k_{obs}t) + C$ to the observed time-dependent absorbance (average from 10 kinetic runs for each nucleophile concentration). To obtain the second-order rate constants k_2 [$\mathrm{M}^{-1}\,s^{-1}$], each electrophile/nucleophile combination was measured at three to five different concentrations of the nucleophile. N and s_N parameters for benzylic carbanions **1** were determined from Equation (1).

Supporting Information (see footnote on the first page of this article): Synthetic procedures, product characterization, detailed kinetic data, and NMR spectra of new compounds.

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Keywords: Kinetics · Linear free energy relationships · Nucleophilicity · Carbanions

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