

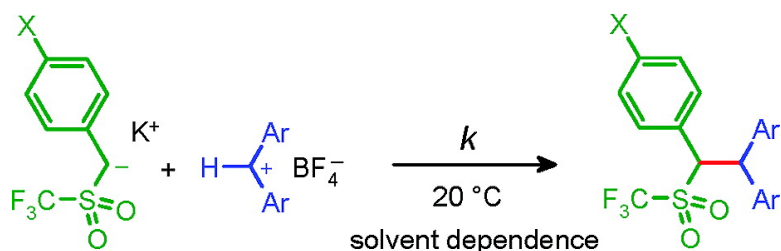
Article

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X = CH<sub>3</sub>, H, CF<sub>3</sub>, CN, NO<sub>2</sub>

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## Inverse Solvent Effects in Carbocation Carbanion Combination Reactions: The Unique Behavior of Trifluoromethylsulfonyl Stabilized Carbanions

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**Abstract:** Second-order rate constants for the reactions of the trifluoromethylsulfonyl substituted benzyl anions **1a–e** ( $\text{CF}_3\text{SO}_2\text{CH}^- - \text{C}_6\text{H}_4 - \text{X}$ ) with the benzhydrylium ions **2f–j** and structurally related quinone methides **2a–e** have been determined by UV–vis spectroscopy. The reactions proceed approximately 10–40 times faster in methanol than in DMSO leading to the unique situation that these carbocation carbanion combinations are faster in protic than in dipolar aprotic media. The  $\text{p}K_{\text{a}}$  values of some benzyl trifluoromethylsulfones were determined in methanol (**1c–H**, 17.1; **1d–H**, 16.0; **1e–H**, 15.0) and found to be 5 units larger than the corresponding values in DMSO. Rate and equilibrium measurements thus agree that the trifluoromethylsulfonyl substituted benzyl anions **1a–e** are more effectively solvated by ion–dipole interactions in DMSO than by hydrogen bonding in methanol. Brønsted correlations show that in DMSO the trifluoromethylsulfonyl substituted carbanions **1** are less nucleophilic than most other types of carbanions of similar basicity, indicating that in DMSO the intrinsic barriers for the reactions of the localized carbanions **1** are higher than those of delocalized carbanions, including nitroalkyl anions. The situation is reversed in methanol, where the reactions of the localized carbanions **1** possess lower intrinsic barriers than those of delocalized carbanions as commonly found for proton-transfer processes. As a consequence, the relative magnitudes of intrinsic barriers are strongly dependent on the solvent.

Relationships between nucleophilicity (i.e., relative rates of reactions of electron-pair donors with a given electrophile) and basicity (i.e., relative affinities for a proton in acid–base equilibria) play a central role for our understanding of organic reactivity.<sup>1–5</sup> While it is well-known that good correlations between nucleophilic reactivities and the  $\text{p}K_{\text{a}}$  values of the conjugate acids can only be obtained when the nature of the reaction center remains unchanged,<sup>6</sup> in some cases anomalous rate equilibrium relationships have been observed, even within families of closely related compounds.<sup>7</sup> The most prominent example for an untypical Brønsted correlation is the so-called “nitroalkane anomaly” which implies that the rates of protonation of nitronate anions decrease with increasing basicity.<sup>8</sup>

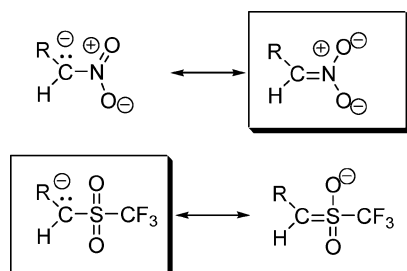
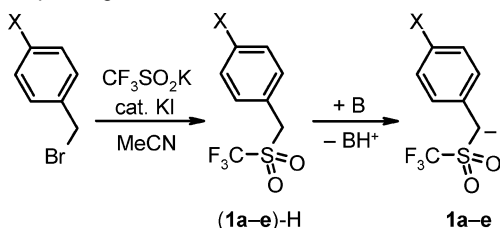
Transition state imbalances, due to the extensive  $\pi$ -delocalization of nitro stabilized carbanions, have been claimed to be responsible for the high intrinsic barriers of these reactions.<sup>9</sup>

There is ample evidence that nitro-stabilized carbanions are best described by the resonance structure with a CN double bond, as indicated in Scheme 1.<sup>9,10</sup>

A completely different type of anion stabilization is exerted by the  $\text{CF}_3\text{SO}_2$  group, which has been known to be one of the strongest electron acceptor groups in organic chemistry since the pioneering investigations by Sheppard<sup>11</sup> and Yagupol'skii.<sup>12</sup>

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**Scheme 1.** Nitro- and Triflate Stabilized Carbanions**Scheme 2.** Preparation of the 4-X-Benzyl Trifluoromethyl Sulfones (**1a–e**)–H According to the Hendrickson Method and Generation of the Corresponding  $\alpha$ -Triflate Stabilized Carbanions **1a–e**

1	1a	1b	1c	1d	1e
X	CH <sub>3</sub>	H	CF <sub>3</sub>	CN	NO <sub>2</sub>

The  $pK_a$  values of substituted benzoic acids indicate that the  $CF_3SO_2$  group ( $\sigma_p = 0.96$ )<sup>12,13</sup> is a stronger electron acceptor than the nitro group ( $\sigma_p = 0.81$ ).<sup>13</sup>

Comparison of the  $pK_a$  values of substituted anilinium ions and phenols also showed the greater electron-accepting power of  $CF_3SO_2$  ( $\sigma_p^- = 1.63$  or  $1.65$ )<sup>12,13</sup> compared to  $NO_2$  ( $\sigma_p^- = 1.24$ ).<sup>13,14</sup> NMR spectroscopic investigations of triflate substituted carbanions revealed that the carbanion center is  $sp^3$ -hybridized and that resonance stabilization is unimportant, resulting in the high weight of the resonance structure on the left side of Scheme 1.<sup>15</sup> In line with this interpretation is the unusual solvent dependence of the  $pK_a$  values of the benzyl trifluoromethyl sulfones. In contrast to the behavior of most CH acids, their acidities decrease with increasing water content of DMSO/H<sub>2</sub>O mixtures.<sup>8p,15</sup>

In this work we have studied the rates of the reactions of the  $\alpha$ - $CF_3SO_2$ -substituted 4-X-benzyl anions **1a–e** (Scheme 2) with a set of reference electrophiles (quinone methides **2a–e** and the structurally analogous benzhydrylium ions **2f–j**, Table 1)

**Table 1.** Quinone Methides **2a–e** and Benzhydrylium Ions **2f–j** Employed in This Work

	Electrophile	$E^a$	$\lambda_{max}$ (nm) <sup>b</sup>
<b>2a</b>		-17.90	521
<b>2b</b>		-17.29	486
<b>2c</b>		-16.11	393
<b>2d</b>		-15.83	371
<b>2e</b>		-13.39	533 <sup>c</sup>
<b>2f</b>		-10.04	640
<b>2g</b>		-9.45	643
<b>2h</b>		-8.76	624
<b>2i</b>		-8.22	628
<b>2j</b>		-7.69	621

<sup>a</sup> Electrophilicity parameters  $E$  for **2a–e** from ref 22a and for **2f–j** from from ref 16d. <sup>b</sup>In DMSO, from ref 23. <sup>c</sup>From ref 24.

in order to determine the nucleophilicity parameters  $N$  and  $s$  (eq 1)<sup>16</sup> of **1a–e** in DMSO and in methanol.

$$\log k_{20^\circ C} = s(N + E) \quad (1)$$

$E$  = electrophilicity parameter

$N$  = nucleophilicity parameter

$s$  = nucleophile-specific slope parameter

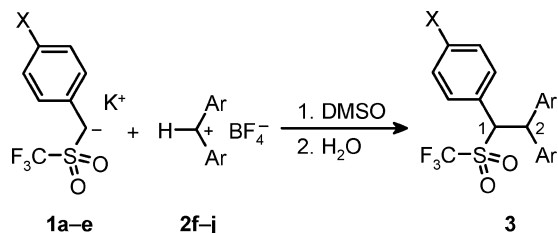
We will show that the comparison of the reactivities of nitro- and trifluoromethylsulfonyl substituted carbanions in DMSO and methanol provides significant new insights in the origin of intrinsic barriers.

**Preparation and Deprotonation of Benzyl Trifluoromethyl Sulfones.** A variety of methods have been developed for the

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**Scheme 3.** Reactions of the Potassium Salts of the Trifluoromethylsulfonyl Stabilized Carbanions **1a–e** with the Benzhydrylium Tetrafluoroborates **2f–j** in DMSO



**Table 2.**  $^1\text{H}$  NMR Chemical Shifts (in ppm) and Coupling Constants  $^3J$  (in Hz) for 1-H and 2-H of the Products **3**<sup>a</sup>

entry	nucleophile	Ar <sub>2</sub> CH <sup>+</sup>	product	$\delta(1\text{-H})$	$\delta(2\text{-H})$	$^3J$
1	<b>1a</b> (X = CH <sub>3</sub> )	<b>2f</b>	<b>3af</b>	5.15	4.74	10.2
2	<b>1b</b> (X = H)	<b>2f</b>	<b>3bf</b>	5.16	4.76	10.2
3	<b>1b</b> (X = H)	<b>2d</b>	<b>3bd</b>	5.17	4.86	9.8
4	<b>1c</b> (X = CF <sub>3</sub> )	<b>2g</b>	<b>3cg</b>	5.22	4.68	9.3
5	<b>1d</b> (X = CN)	<b>2f</b>	<b>3df</b>	5.21	4.71	10.1
6	<b>1d</b> (X = CN)	<b>2h</b>	<b>3dh</b>	5.21	4.77	10.2
7	<b>1d</b> (X = CN)	<b>2i</b>	<b>3di</b>	5.18	4.70	9.8
8	<b>1e</b> (X = NO <sub>2</sub> )	<b>2f</b>	<b>3ef</b>	5.27	4.74	10.1
9	<b>1e</b> (X = NO <sub>2</sub> )	<b>2g</b>	<b>3eg</b>	5.28	4.68	9.6
10	<b>1e</b> (X = NO <sub>2</sub> )	<b>2h</b>	<b>3eh</b>	5.27	4.81	10.2
11	<b>1e</b> (X = NO <sub>2</sub> )	<b>2i</b>	<b>3ei</b>	5.25	4.73	9.9

<sup>a</sup> Assignments not confirmed.

synthesis of the benzyl trifluoromethyl sulfones (**1a–e**)-H.<sup>17</sup> We used the procedure described by Hendrickson and co-workers,<sup>18</sup> which combines benzyl bromides with potassium triflate<sup>19</sup> in boiling acetonitrile in the presence of catalytic amounts of potassium iodide (Scheme 2).

Solutions of **1a–e** were obtained by treatment of the benzyl trifluoromethyl sulfones (**1a–e**)-H with 1.05 equiv of either Schwesinger's P<sub>2</sub>-*t*Bu phosphazene base [(Me<sub>2</sub>N)<sub>3</sub>P=N–P[NMe<sub>2</sub>]<sub>2</sub>N*t*Bu]<sup>20,21</sup> or KO*t*Bu in DMSO. The potassium salts (**1d–e**)-K precipitated when the benzyl trifluoromethyl sulfones (**1d–e**)-H were combined with 1 equiv of KO*t*Bu in dichloromethane under a nitrogen atmosphere. Only partial deprotonation was achieved when the sulfones (**1a–e**)-H were treated with 1 equiv of sodium methoxide in methanol.

**Reaction Products.** As shown in Scheme 3, the triflate stabilized benzyl anions **1a–e** react with the benzhydrylium ions **2f–j** to give the addition products **3**, several of which have been characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy (for details, see the Supporting Information).

Evidence for the formation of the compounds **3** comes from their  $^1\text{H}$  NMR spectra, which show doublets ( $J = 9.3$ – $10.2$  Hz) in the range of  $\delta = 5.15$ – $5.28$  ppm (1-H) and  $\delta = 4.65$ – $4.81$  ppm (2-H) as summarized in Table 2.

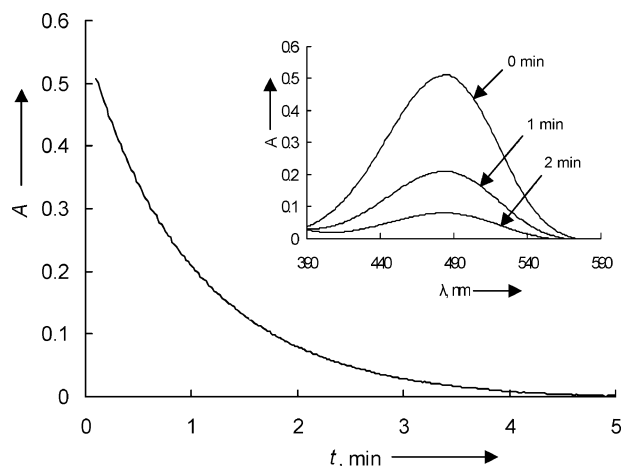
We also studied the reaction of the quinone methide **2d** with the triflate stabilized carbanion **1b** by  $^1\text{H}$  NMR spectroscopy (entry 3 in Table 2). In contrast to our expectation, only one pair of doublets was observed for 1-H and 2-H indicating the formation of only one diastereoisomer.

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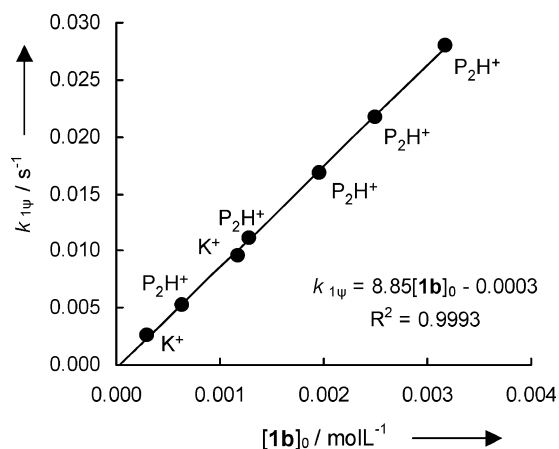
(19) Potassium triflate was obtained from commercially available CF<sub>3</sub>SO<sub>2</sub>Cl and potassium iodide in cold acetone (see ref 18 for details).

(20) P<sub>2</sub>-*t*Bu: 1-(*tert*-butylimino)-1,1,3,3,3-pentakis(dimethylamino)-1λ5,3λ5-diphosphazene,  $pK_{\text{BH}^+} = 21.4$  (in DMSO), CAS Registry No. 111324-03-9.

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**Figure 1.** UV-vis-spectroscopic monitoring of the reaction of benzyl triflate (**1b**,  $6.29 \times 10^{-4}$  mol L<sup>-1</sup>) with the quinone methide **2b** ( $3.16 \times 10^{-5}$  mol L<sup>-1</sup>) at 500 nm in DMSO at 20 °C.



**Figure 2.** Determination of the second-order rate constant  $k_2 = 8.85$  L mol<sup>-1</sup> s<sup>-1</sup> for the reaction of benzyl triflate (**1b**) with the quinone methide **2b** in DMSO at 20 °C from a plot of the first-order rate constants  $k_{1\psi}$  vs the triflate concentration. Counterions were K<sup>+</sup> or protonated Schwesinger's phosphazene base *t*Bu–P<sub>2</sub>H<sup>+</sup> (ref 20).

**Kinetic Investigations in DMSO.** The kinetic investigations in DMSO were performed at 20 °C. All reactions proceeded quantitatively, and the rates were determined photometrically by following the decrease of the absorbances of the electrophiles **2** at their absorption maxima (Table 1), as shown in Figure 1.

All reactions were studied under pseudo-first-order conditions using 10 to 100 equiv of the benzyl triflate ions **1**. The concentrations of **1** ( $10^{-3}$ – $10^{-4}$  mol L<sup>-1</sup>) were thus kept almost constant throughout the kinetic measurements, resulting in an exponential decay of the concentrations of the colored electrophiles (eq 2).

$$-d[\mathbf{2}]/dt = k_{1\psi}[\mathbf{2}] \quad (2)$$

The pseudo-first-order rate constants  $k_{1\psi}$  ( $= k_2[\mathbf{1}]_0$ ) were obtained by least-squares fitting of the single-exponential  $A_t = A_0 \exp(-k_{1\psi}t) + C$  to the time-dependent absorbance  $A$  of the electrophile. Plots of  $k_{1\psi}$  versus the nucleophile concentration  $[\mathbf{1}]_0$  give straight lines with the slope  $k_2$  (Table 3), as shown for one example in Figure 2 and for all other experiments in the Supporting Information.

In several  $k_{1\psi}$  vs  $[\mathbf{1}]_0$  plots,  $k_{1\psi}$  values obtained with the potassium and the phosphazanium salts of **1** were used side by

**Table 3.** Second-Order Rate Constants  $k_2$  for the Reactions of the Quinone Methides **2a–e** and Benzhydrylium Ions **2f–j** with the  $\alpha$ -Triflate Stabilized Carbanions **1a–e** (DMSO, 20 °C)

Nucleophile	$N^a$	$s^a$	Electrophile	Base	$k_2$ ( $M^{-1}s^{-1}$ )	Product
<b>1a</b> 	19.35	0.67	<b>2a</b>	P <sub>2</sub>	$1.02 \times 10^1$	-
			<b>2b</b>	P <sub>2</sub>	$2.23 \times 10^1$	-
			<b>2c</b>	P <sub>2</sub>	$1.51 \times 10^2$	-
			<b>2f</b>	P <sub>2</sub>	$1.87 \times 10^6$	<b>3af</b>
<b>1b</b> 	18.67	0.68	<b>2a</b>	P <sub>2</sub>	1.91	-
			<b>2b</b>	P <sub>2</sub> or KOtBu	8.85	-
			<b>2c</b>	P <sub>2</sub> or KOtBu	$7.78 \times 10^1$	-
			<b>2d</b>	P <sub>2</sub>	$1.34 \times 10^2$	<b>3bd<sup>b</sup></b>
			<b>2e</b>	P <sub>2</sub>	$4.26 \times 10^3$	-
			<b>2f</b>	P <sub>2</sub>	$6.51 \times 10^5$	<b>3bf</b>
<b>1c</b> 	17.33	0.74	<b>2e</b>	P <sub>2</sub>	$7.97 \times 10^2$	-
			<b>2f</b>	P <sub>2</sub>	$2.35 \times 10^5$	-
			<b>2g</b>	-	-	<b>3cg</b>
<b>1d</b> 	16.28	0.75	<b>2e</b>	P <sub>2</sub>	$1.20 \times 10^2$	-
			<b>2f</b>	P <sub>2</sub> or KOtBu	$6.82 \times 10^4$	<b>3df</b>
			<b>2f</b>	K <sup>+</sup> salt	$6.80 \times 10^4$	-
			<b>2g</b>	KOtBu	$2.02 \times 10^5$	-
			<b>2h</b>	P <sub>2</sub> or KOtBu	$3.71 \times 10^5$	<b>3dh</b>
<b>1e</b> 	14.49	0.86	<b>2f</b>	KOtBu	$6.73 \times 10^3$	<b>3ef</b>
			<b>2g</b>	KOtBu	$1.89 \times 10^4$	<b>3eg</b>
			<b>2h</b>	P <sub>2</sub>	$8.09 \times 10^4$	<b>3eh</b>
			<b>2i</b>	-	-	<b>3ei</b>
			<b>2j</b>	P <sub>2</sub>	$6.61 \times 10^5$	-

<sup>a</sup> Nucleophilicity parameters  $N$  and  $s$  derived by eq 1. <sup>b</sup>Characteristic product signals identified by proton NMR in CDCl<sub>3</sub>.

side. The fact that first-order rate constants obtained with different counterions are on the same correlation line (see Figure 2) demonstrates the independence of the rate constants of the nature of the counterion. In line with these observations, the same rate constants within experimental error were obtained, when the rate of the reaction of **1d** with **2f** was studied with a solution of the isolated potassium salt **1d-K** or with a solution of the corresponding sulfone **1d-H** and 1.05 equiv of KOtBu. When solutions of the triflates (**1c–e**-H) were combined with KOtBu in DMSO, limiting values of the absorbances of the colored carbanions **1c–e** were reached after the addition of 1 equiv of KOtBu indicating that 1 equiv of KOtBu is sufficient for a complete deprotonation of the benzyl trifluoromethyl sulfones.

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**Kinetic Investigations in Methanol.** The analysis of the kinetic experiments in methanol is more complicated because of the presence of different nucleophiles. Because most of the reference electrophiles **2** listed in Table 1 react readily with methanol, it was not possible to prepare solutions of these electrophiles in methanol and mix them with methanolic solutions of the triflates **1a–e** in order to determine the rate constants for the reactions of **1a–e** with **2** in pure methanol. However, we were able to measure the kinetics of the reactions of the CF<sub>3</sub>SO<sub>2</sub>-substituted benzyl anions **1c–e** with benzhydryl cations **2** in methanol/acetonitrile mixtures (91:9, v/v) in a stopped-flow instrument by mixing 10 volume parts of methanol with 9 volume parts of acetonitrile.

(23) Lucius, R. Dissertation, Ludwig-Maximilians-Universität, München, Germany, 2001.

(24) Remennikov, G. Y.; Mayr, H., unpublished results.

(25) In order to be consistent with the quoted literature, we also use the term  $K_{MeOH}$  to designate the ion product of methanol: Schaal, A. R.; Lamber, G. J. *Chim. Phys. Phys.-Chim. Biol.* **1962**, 1153–1163; (b) Rochester, C. H. *Acidity Functions*; Academic Press: London, 1970; p 246.



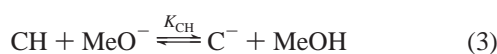
**Table 4.** Deprotonation of the Benzyl Trifluoromethyl Sulfones (**1c–e**)-H by Sodium Methoxide (20 °C, MeOH)

triflone	$\lambda_{\max}$ (nm) <sup>a</sup>	$K_{\text{CH}}$ (M <sup>-1</sup> )	p <i>K</i> <sub>a</sub>
<b>1c</b> -H (X = CF <sub>3</sub> )	305	0.600	17.1
<b>1d</b> -H (X = CN)	345	8.24	16.0
<b>1e</b> -H (X = NO <sub>2</sub> )	476	76.1	15.0

<sup>a</sup> Absorption maxima of the  $\alpha$ -triflate stabilized carbanions ( $\lambda_{\max}$  for **1c**, **1d**, and **1e** in DMSO reported in ref 15b: 316, 347, and 476 nm, respectively).

nolic solutions of the triflones **1**-H and methoxide with one part of a solution of Ar<sub>2</sub>CH<sup>+</sup> BF<sub>4</sub><sup>-</sup> (**2**) in acetonitrile.

As previously reported by Terrier,<sup>15</sup> the 4-X-benzyl trifluoromethyl sulfones (**1a–e**)-H are weaker acids in water than in DMSO. In line with this observation, even the acceptor substituted sulfones (**1c–e**)-H cannot completely be deprotonated by sodium methoxide in methanol, and the equilibrium (eq 3) has to be considered.



$$K_{\text{CH}} = [\text{C}^-]/([\text{CH}][\text{MeO}^-]) \quad (4)$$

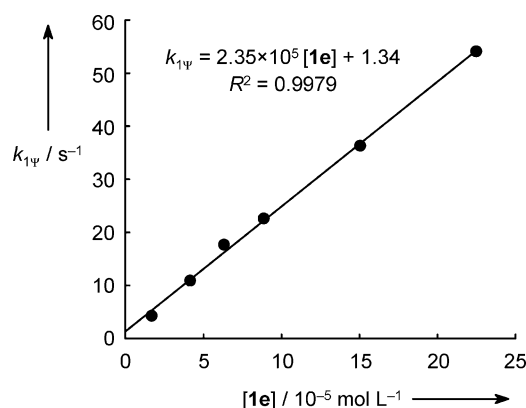
$$\text{p}K_{\text{MeOH}} = -\log\{[\text{MeO}^-][\text{H}^+]\} = 16.92 \text{ (at } 20^\circ\text{C)}^{25} \quad (5)$$

$$\text{p}K_{\text{a}} = -(\log K_{\text{CH}}) + \text{p}K_{\text{MeOH}} \quad (6)$$

For the trifluoromethyl sulfones (**1c–e**)-H neither the p*K*<sub>a</sub> nor the *K*<sub>CH</sub> values in methanol have been reported. The equilibrium constants *K*<sub>CH</sub> (eq 4) were, therefore, determined photometrically at the absorption maxima of the carbanions by titration of (**1c–e**)-H with sodium methoxide (Table 4). Because quantitative deprotonation of the triflones could not be achieved, the acid dissociation constants *K*<sub>CH</sub> (eq 4, Table 4) were obtained by least-squares fitting of calculated and experimental concentrations of C<sup>-</sup> (= **1c–e**) as described in the Supporting Information. The p*K*<sub>a</sub> values were then calculated according to eq 6.

Phan and Mayr have reported that the ionization constants of *p*-cyanophenylnitromethane in pure methanol and in MeOH/CH<sub>3</sub>CN (91:9, v/v) agree within experimental error.<sup>26</sup> The p*K*<sub>a</sub> values for (**1c–e**)-H in pure MeOH (Table 4) have, therefore, been used for the calculation of the carbanion concentrations during the kinetic experiments in MeOH/CH<sub>3</sub>CN (91:9, v/v). Because of the low acidities of **1a**-H and **1b**-H, we were not able to determine their equilibrium constants *K*<sub>CH</sub> in methanol, and therefore we have not performed kinetic investigations with these carbanions in methanol.

As a consequence of the incomplete deprotonation of the triflones (**1c–e**)-H in many of the kinetic experiments, it was often not possible to achieve a high excess of the carbanions **1** over the electrophiles **2**. However, even in the case [1] ≈ [2] pseudo-first-order conditions were warranted when [1-H] ≫ [2] because the proton transfer between the carbanions **1c–e** and methanol is much faster than the reaction of **1c–e** with the electrophiles used in these investigations. Fast proton transfer from **1**-H to methoxide, as expected for the formation of carbanions with little rehybridization, was proven by the observation that treatment of **1c**-H (2.24 × 10<sup>-4</sup> mol L<sup>-1</sup>), **1d**-H (2.36 × 10<sup>-4</sup> mol L<sup>-1</sup>), and **1e**-H (2.21 × 10<sup>-4</sup> mol L<sup>-1</sup>) with

**Figure 3.** Determination of the second-order rate constant  $k_{2,\text{C}} = 2.35 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$  for the reaction of **2f** with benzyl triflinate **1e** in MeOH/CH<sub>3</sub>CN (91:9, v/v) at 20 °C.**Table 5.** Second-Order Rate Constants  $k_{2,\text{MeO}}$  for the Reactions of Methoxide Anion and First-Order Rate Constants  $k_{1,\text{MeOH}}$  for the Reactions of Methanol with Benzhydrylium Ions **2f–k** in MeOH/CH<sub>3</sub>CN (91:9, v/v) at 20 °C (from ref 26)

electrophile	$k_{2,\text{MeO}}$ (M <sup>-1</sup> s <sup>-1</sup> )	$k_{1,\text{MeOH}}$ (s <sup>-1</sup> )
<b>2f</b>	$1.17 \times 10^3$	$6.14 \times 10^{-3}$
<b>2g</b>	$2.48 \times 10^3$	$3.16 \times 10^{-2}$ <sup>a</sup>
<b>2h</b>	$7.41 \times 10^3$	$2.13 \times 10^{-1}$ <sup>a</sup>
<b>2i</b>	$1.56 \times 10^4$	$2.17 \times 10^{-1}$
<b>2j</b>	$4.80 \times 10^4$	$9.32 \times 10^{-1}$

<sup>a</sup> Calculated according to eq 1.

sodium methoxide in methanol yielded the equilibrium concentrations of **1c–e** in less than 2 ms, the dead time of our stopped-flow instrument.

According to eq 7, the pseudo-first-order rate constants  $k_{\text{obsd}}$  determined in methanol reflect the sum of the reactions of the electrophile with the carbanion ( $k_{2,\text{C}}[\text{C}^-]$ ), with methoxide ( $k_{2,\text{MeO}}[\text{MeO}^-]$ ), and with methanol ( $k_{1,\text{MeOH}}$ ).

$$k_{\text{obsd}} = k_{2,\text{C}}[\text{C}^-] + k_{2,\text{MeO}}[\text{MeO}^-] + k_{1,\text{MeOH}} \quad (7)$$

The second-order rate constants  $k_{2,\text{MeO}}$  for the reactions of methoxide ion with benzhydrylium ions and the relevant first-order rate constants for the reactions of benzhydrylium ions with methanol, which have previously been reported,<sup>26</sup> are summarized in Table 5.

Rearrangement of eq 7 gives eq 8,

$$k_{1\psi} = k_{\text{obsd}} - k_{2,\text{MeO}}[\text{MeO}^-] = k_{2,\text{C}}[\text{C}^-] + k_{1,\text{MeOH}} \quad (8)$$

which implies that the second-order rate constants  $k_{2,\text{C}}$  can be derived from the slopes of plots of  $k_{1\psi}$  vs [C<sup>-</sup>] as shown in Figure 3 for the reaction of **2f** with benzyl triflinate **1e**. The intercepts of these correlations correspond to the reactions of the electrophiles **2** with the solvent MeOH. In agreement with the entries in the right column of Table 5, these intercepts are small and can be neglected.

In all kinetic experiments, the term  $k_{2,\text{C}}[\text{C}^-]$  was the major contribution to  $k_{\text{obsd}}$ , which excludes major errors in the determination of the carbanion reactivities. For the reaction of **1d** with **2i**, it was furthermore shown that almost the same rate constants  $k_{1\psi}$  were obtained when variable ratios of [1d-H]/[MeO<sup>-</sup>] were employed, as required by the suggested kinetic formalism (Supporting Information).

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**Table 6.** Second-Order Rate Constants  $k_{2,c}$  for the Reactions of the  $\alpha$ -Triflate Stabilized Carbanions **1c–e** with the Benzhydrylium Ions **2f–j** in MeOH/CH<sub>3</sub>CN (91:9, v/v) at 20 °C

nucleophile <sup>a</sup>	$N^b$	$s^b$	electrophile	$k_{2,c}$ (M <sup>-1</sup> s <sup>-1</sup> )
<b>1c</b> (X = CF <sub>3</sub> )	20.72	0.58	<b>2f</b>	$1.55 \times 10^6$
			<b>2g</b>	$4.09 \times 10^6$
			<b>2h</b>	$9.85 \times 10^6$
			<b>2i</b>	$2.20 \times 10^7$
			<b>2j</b>	$3.50 \times 10^7$
<b>1d</b> (X = CN)	19.49	0.63	<b>2f</b>	$8.52 \times 10^5$
			<b>2g</b>	$1.99 \times 10^6$
			<b>2h</b>	$5.44 \times 10^6$
			<b>2i</b>	$1.22 \times 10^7$
			<b>2j</b>	$2.50 \times 10^7$
<b>1e</b> (X = NO <sub>2</sub> )	18.24	0.66	<b>2f</b>	$2.35 \times 10^5$
			<b>2g</b>	$7.98 \times 10^5$
			<b>2h</b>	$1.31 \times 10^6$
			<b>2i</b>	$3.85 \times 10^6$
			<b>2j</b>	$9.83 \times 10^6$

<sup>a</sup> Generated from the corresponding triflates (**1c–e**)-H and NaOMe.  
<sup>b</sup> Nucleophilicity parameters  $N$  and  $s$  derived by eq 1.

## Discussion

As previously shown for many other nucleophile electrophile combinations,<sup>16,22,26–28</sup> the second-order rate constants given in Tables 3 and 6 correlate well with the electrophilicity parameters  $E$  of the benzhydrylium ions **2f–j** and quinone methides **2a–e** (Figures 4 and 5).

Figures 4 and 5 as well as the nucleophilicity parameters  $N$  in Table 7, which were determined by eq 1, show the expected substituent effects on the reactivities of the carbanions. Donors (methyl) increase the nucleophilicities of the triflate ions **1**, whereas acceptors (trifluoromethyl, cyano, nitro) decrease their reactivity. The similarities of the slopes of the linear correlations in Figures 4 and 5, which are numerically expressed by the parameters  $s$  in Table 7, imply that the relative nucleophilicities of the triflate stabilized benzyl anions depend only slightly on the electrophilicity of the reaction partner.

Comparison of the nucleophilicity parameters of  $\alpha$ -nitro<sup>28</sup> and  $\alpha$ -triflate substituted benzyl anions (Figure 6) shows that both classes of carbanions possess similar nucleophilicities in DMSO but that variation of the para-substituents has a much larger effect on the triflate than on the nitro substituted benzyl anions.

This effect, which can be explained by the localization of the negative charge on carbon in the triflate stabilized carbanions and the charge delocalization in the nitronate anions

(with most of the negative charge residing on the oxygen atoms, Scheme 1), can also be seen in the different slopes of the Hammett-type correlations in Figure 7. In contrast to the good correlation between  $N$  of the triflate anions **1a–e** with Hammett's  $\sigma_p^-$  the corresponding correlation with  $\sigma_p$  is of considerably lower quality ( $R^2 = 0.8919$ ).

Unusual solvent effects, as previously reported for the basicities of carbanions **1a–e**,<sup>15</sup> have now been found for their nucleophilicities. Because the stabilization of most carbanions occurs to a large extent through hydrogen bonding, the basicities as well as the nucleophilicities of carbanions are usually smaller in protic than in aprotic solvents. In line with the observation that the acidities of benzyl triflates are higher in DMSO than in DMSO/water mixtures,<sup>15</sup> Figure 8 shows that also the nucleophilic reactivities of the benzyl triflates **1c–e** are higher in methanol than in DMSO. The differences of  $s$  for the triflate anions **1** in methanol and DMSO imply that the relative nucleophilic reactivities in the two solvents depend on the electrophile. The direct comparison of the rate constants in Tables 3 and 6 shows that the triflate-stabilized carbanions studied in this work react 10 to 40 times faster (!) with benzhydrylium ions in methanol than in DMSO.

This unusual solvent dependence of the  $pK_{aH}$  values has been explained by the electronic structure of the triflates **1**. Terrier has shown that the negative charge of the triflates **1** is localized on the benzylic carbon atom and is highly polarizable.<sup>15</sup> For that reason, the carbanions **1** are better solvated in the highly polarizable and dielectric solvent DMSO ( $\epsilon = 47$ )<sup>30</sup> than in methanol ( $\epsilon = 33$ ).<sup>30</sup> The higher acidities of fluorenes in DMSO than in methanol have analogously been rationalized by the high polarizabilities of the resulting carbanions.<sup>31</sup> Because the CC-coupling step of Scheme 3 must be preceded by the destruction of the ion–dipole interactions which prevail in DMSO, the kinetic phenomena observed in this work can also be explained by the fact that the highly polarizable triflate stabilized carbanions **1a–e** are better solvated in DMSO.

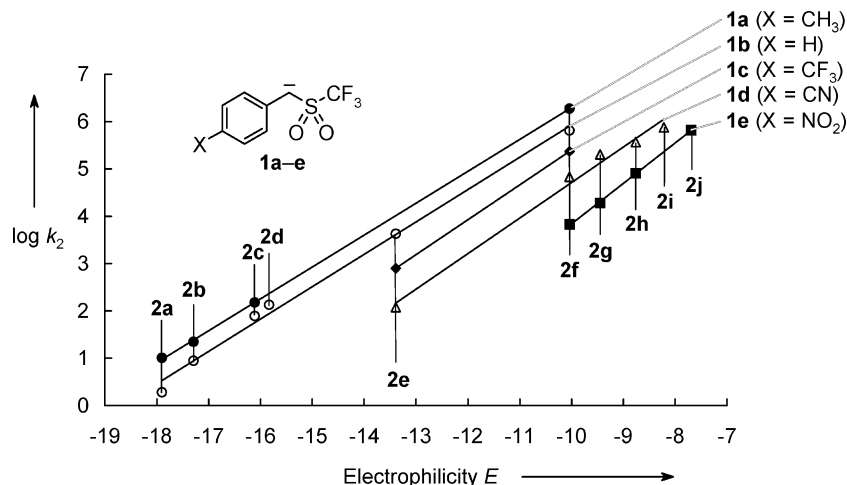
The dominant role of ion–dipole forces for the solvation of the trifluoromethylsulfonyl substituted carbanions **1** is further confirmed by the observation that the reactivity of **1e** (X = NO<sub>2</sub>) toward the carbocations **2f–j** (Table 8) is considerably higher in the less dipolar solvent acetonitrile ( $\epsilon = 38$ )<sup>30</sup> than in DMSO (Figure 9).

Figure 10 shows that the Brønsted plot for the reactions of the triflate stabilized carbanions **1a–e** with the benzhydrylium ion **2f** has a slope of 0.36, comparable to that for substituted  $\alpha$ -nitrobenzyl anions in DMSO.<sup>28</sup> Because only a small number of carbanions have been studied with respect to a single reference electrophile, more comprehensive nucleophilicity–basicity correlations shall be based on the nucleophilicity parameters  $N$ .

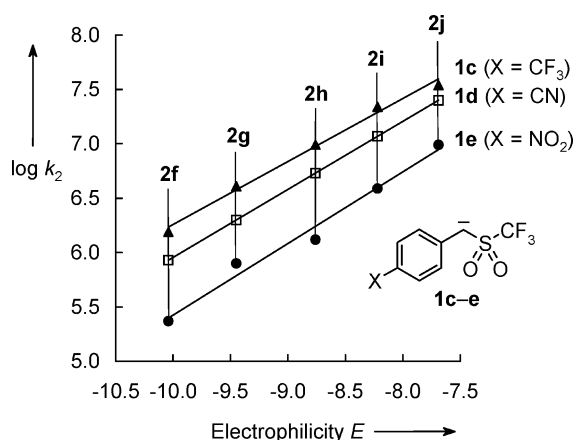
A correlation of low quality is obtained, when the nucleophilicities of carbanions of variable structure ( $N$  in DMSO) are plotted against their  $pK_{aH}$  values in DMSO (Figure 11). The most remarkable feature of this correlation is that the triflate substituted carbanions **1** are at the lower edge of this “correlation

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**Figure 4.** Plots of  $\log k_2$  for the reactions of the triflate stabilized anions **1a–e** (from Table 3) with the quinone methides **2a–e** and benzhydryl cations **2f–j** in DMSO at 20 °C versus their electrophilicity parameters  $E$ .



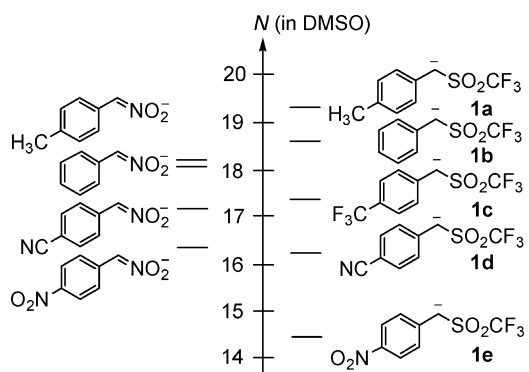
**Figure 5.** Plots of  $\log k_{2,C}$  for the reactions of the triflate stabilized anions **1c–e** (from Table 6) with the benzhydryl cations **2f–j** in MeOH at 20 °C versus their electrophilicity parameters  $E$ .

**Table 7.** Nucleophilicity Parameters  $N$  and  $s$  and  $pK_{aH}$  Values of the Triflate Stabilized Carbanions **1a–e** in DMSO and MeOH

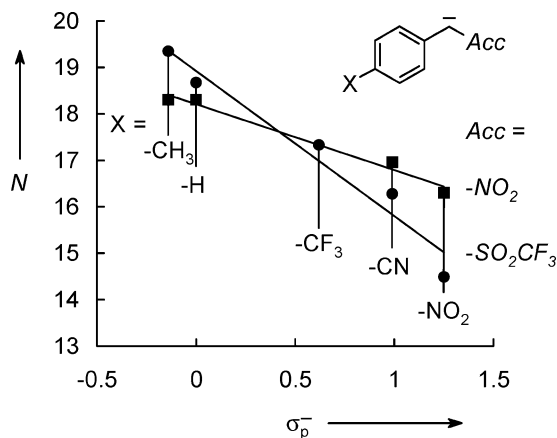
nucleophile	in DMSO			in MeOH		
	$pK_{aH}$	$N$	$s$	$pK_{aH}$	$N$	$s$
<b>1a</b> (X = CH <sub>3</sub> )	15.4 <sup>a</sup>	19.35	0.67	-	-	-
<b>1b</b> (X = H)	14.62 <sup>b</sup>	18.67	0.68	-	-	-
<b>1c</b> (X = CF <sub>3</sub> )	11.95 <sup>b</sup>	17.33	0.74	17.1	20.72	0.58
<b>1d</b> (X = CN)	10.7 <sup>a</sup>	16.28	0.75	16.0	19.49	0.63
<b>1e</b> (X = NO <sub>2</sub> )	9.46 <sup>b</sup>	14.49	0.86	15.0	18.24	0.66

<sup>a</sup> From ref 29. <sup>b</sup> From ref 15b.

corridor”, i.e., that their nucleophilic reactivities are lower than those of most other carbanions of comparable  $pK_{aH}$  values, indicating low intrinsic reactivities.<sup>9b,32,33</sup> On the other hand, the resonance-stabilized nitronates are in the center or on the upper edge of this correlation band, indicating high intrinsic reactivities of the anions **4**. These findings were in contrast to our expectation, because we had assumed that in analogy to the behavior of cyano substituted carbanions<sup>34–37</sup> the low



**Figure 6.** Comparison of the nucleophilicities  $N$  of triflate stabilized carbanions (**1a–e**) and nitronate anions in DMSO.



**Figure 7.** Correlations of the nucleophilicity parameters  $N$  (in DMSO) with the Hammett  $\sigma_p^-$  values for triflates (●:  $N = -3.12\sigma_p^- + 18.9$ ,  $R^2 = 0.9557$ ,  $n = 5$ ) and nitronates (■:  $N = -1.42\sigma_p^- + 18.2$ ,  $R^2 = 0.9792$ ,  $n = 4$ ).

reorganization energies of the localized triflate anions **1**, which had been derived from their fast proton-transfer reactions, and the high reorganization energies for the nitronate ions **4** which had been derived from their slow proton-transfer reactions<sup>38</sup> (Table 9) should also be reflected in the reactions with carbon

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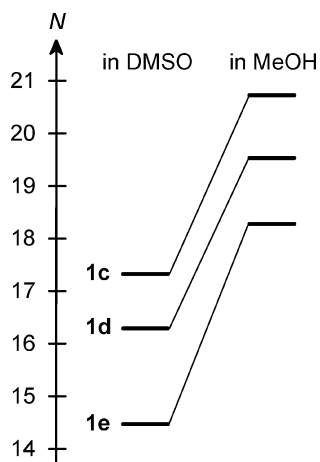
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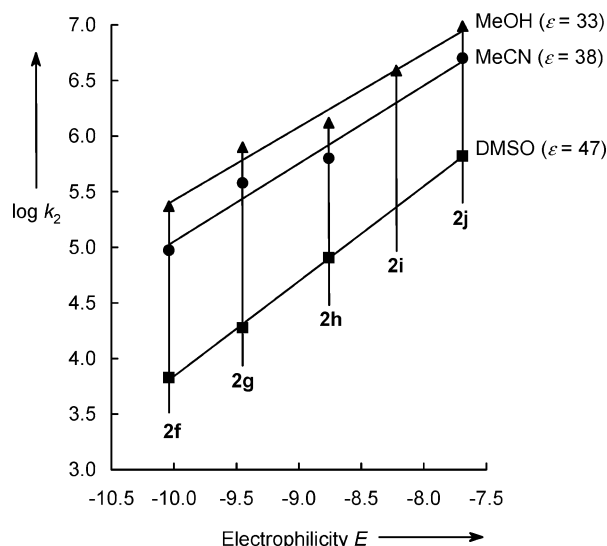


**Figure 8.** Comparison of the nucleophilicity parameters  $N$  of the benzyl triflates **1c–e** in DMSO and MeOH.

**Table 8.** Second-Order Rate Constants  $k_2$  for the Reactions of **1e** with the Electrophiles **2f–h** ( $\text{CH}_3\text{CN}$ ,  $20^\circ\text{C}$ )<sup>a</sup>

electrophile	$k_2$ ( $\text{M}^{-1}\text{s}^{-1}$ )
<b>2f</b>	$9.41 \times 10^4$ <sup>b</sup>
<b>2g</b>	$3.79 \times 10^5$
<b>2h</b>	$6.34 \times 10^5$
<b>2j</b>	$5.04 \times 10^6$

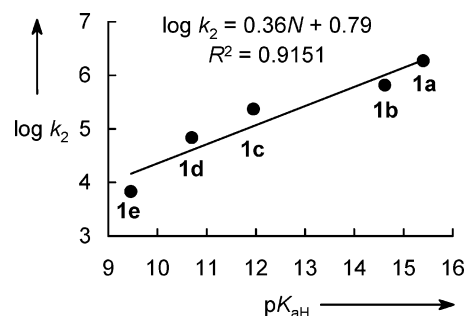
<sup>a</sup> Carbanion **1e** was generated by mixing **1e–H** with 1.0 equiv of Verkade's base (2,8,9-triisopropyl-2,5,8,9-tetraaza-1-phosphabicyclo[3.3.3]undecane). <sup>b</sup> A second-order rate constant of  $k_2 = 8.28 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  was obtained when **1e** was generated from **1e–H** by deprotonation with potassium *tert*-butoxide.



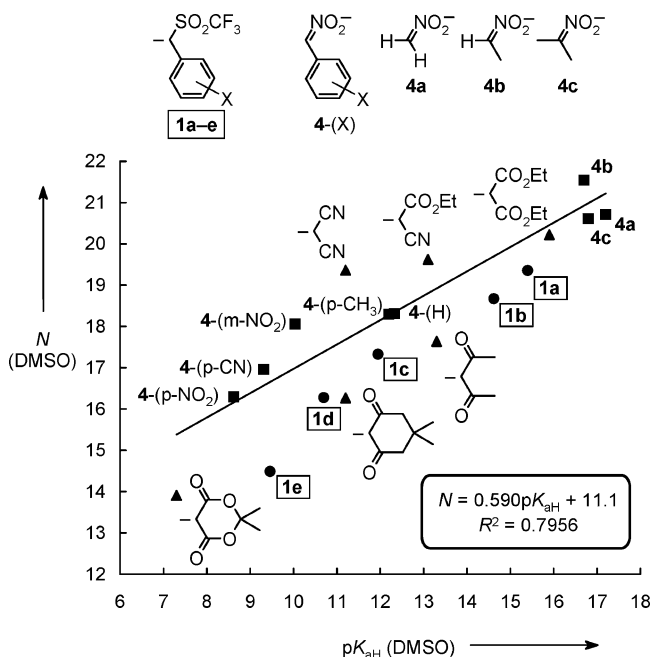
**Figure 9.** Comparison of the rate constants of the reactions of the carbocations **2f–j** with the carbanion **1e** in DMSO, acetonitrile, and methanol (cosolvent: 9 vol % acetonitrile).

electrophiles.<sup>39,40</sup> Why are carbanions **1** and **4** on the “wrong” edges of the “correlation corridor”?

A solution of this paradox came from consideration of the  $N$  vs  $\text{p}K_{\text{aH}}$  correlation in methanol (Figure 12). In methanol, the correlation between nucleophilicity<sup>42</sup> and basicity<sup>271,43</sup> is even worse than that in DMSO, but the triflate substituted carban-



**Figure 10.** Plot of  $\log k_2$  for the reactions of the triflate substituted carbanions **1a–e** with the benzhydrylium ion **2f** in DMSO at  $20^\circ\text{C}$  versus their  $\text{p}K_{\text{aH}}$  values.



**Figure 11.** Brønsted plot for the reactions of different carbanions with benzhydrylium ions and quinone methides in DMSO (nucleophilicity parameters  $N$  and  $\text{p}K_{\text{aH}}$  values used for this diagram are compiled in the Supporting Information)

**Table 9.** Intrinsic Rate Constants  $\log k_0$  for Deprotonation of Some Carbon Acids by Primary and Secondary Amines in DMSO/Water (50:50, v/v) at  $25^\circ\text{C}$  unless Indicated Otherwise

carbon acid	$\log k_0$
$\text{C}_6\text{H}_5\text{CH}_2\text{NO}_2$	$-0.25^b$
$\text{CH}_3\text{NO}_2$	$0.73^b$
acetylacetone	$2.75^b$
<b>1c–H</b> ( $\text{X} = \text{CF}_3$ )	$\geq 5^a$
<b>1d–H</b> ( $\text{X} = \text{CN}$ )	$\geq 5^a$
<b>1e–H</b> ( $\text{X} = \text{NO}_2$ )	$\geq 5^a$
$\text{NC–CH}_2\text{–CN}$	$\sim 7^c$

<sup>a</sup> Reference 15b. <sup>b</sup> At  $20^\circ\text{C}$ , from ref 41. <sup>c</sup> In water at  $20^\circ\text{C}$ , from ref 41.

ions **1** are now found on the upper rim of the correlation corridor, while the nitronate ions are found on the lower edge. In methanol, the intrinsic reactivities of the localized triflate substituted carbanions **1** are high and those of the delocalized

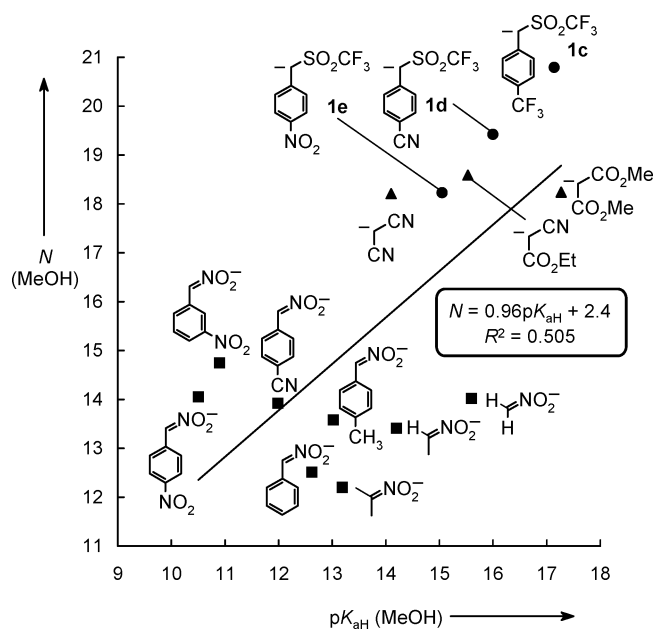
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(43) Acidity constants  $\text{p}K_{\text{aH}}$  in methanol: (a) Cox, J. P. L.; Crampton, M. R.; Paul, W. *J. Chem. Soc., Perkin. Trans. 2* **1988**, 25–29. (b) Belokon, Y. N.; Faleev, N. G.; Belikov, V. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1969**, 1039–1046; *Bull. Acad. Sci. USSR* **1969**, 949–955. (c) Gandler, J. R.; Saunders, O. L.; Barbosa, R. *J. Org. Chem.* **1997**, *62*, 4677–4682. (d) Crampton, M. R.; Stevens, J. A. *J. Chem. Soc., Perkin. Trans. 2* **1991**, 1715–1720.



**Figure 12.** Nucleophilicity parameters  $N$  (in methanol) for different types of carbanions versus their acidity constants  $pK_{\text{aH}}$  in methanol (data compilation in the Supporting Information).

nitronate anions are low as expected from earlier work, where the high reorganization energy of the resonance stabilized nitronate anions was accounted for by the high intrinsic barriers of the reactions of nitronate anions.<sup>9</sup>

Our observation that nitronate anions do not have low intrinsic reactivities in DMSO (Figure 11) is in agreement with earlier

conclusions that the nitroalkane anomaly<sup>8</sup> only shows up in protic solutions, and not in the gas phase<sup>8g</sup> or DMSO.<sup>8n</sup> While nitronate ions (resonance stabilized carbanions) show low intrinsic reactivities in protic solvents and high or normal intrinsic reactivities in DMSO, we have now found that the opposite holds for the highly polarizable carbanions **1**. Thus, nitro and triflate substituted carbanions represent two different extremes: while transition state imbalances for reactions of nitronate anions are found in protic solvents, where hydrogen bridging has to be abandoned prior to rehybridization, analogous imbalances for reactions of triflate substituted carbanions **1** are found in the highly polarizable, dipolar solvent DMSO, where ion–dipole interactions have to be removed prior to bond formation.

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**Supporting Information Available:** Details of the product characterization, kinetic experiments, and determination of equilibrium constants (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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