Nucleophilic reactivities of benzenesulfonyl-substituted carbanions†

Florian Seeliger and Herbert Mayr*

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Kinetics of the reactions of four benzenesulfonyl-stabilized carbanions (**1a–d**)$^-$ with reference electrophiles (quinone methides **2** and diarylcarbenium ions **3**) have been determined in dimethyl sulfoxide solution at 20 °C in order to derive the reactivity parameters N and s according to the linear free-energy relationship $\log k(20\ °\mathrm{C}) = s(N + E)$ (eqn (1)). The additions of (**1a–d**)$^-$ to ordinary Michael acceptors (*e.g.*, benzylidene Meldrum's acid **4a**, benzylidenebarbituric acids **5a–c**, and benzylidene-indan-1,3-diones **6a–d**) were also studied kinetically and found to be 5–24 times slower than predicted by eqn (1).

Introduction

The relative inertness of the sulfone group to nucleophilic attack and its ability to facilitate deprotonation in the α-position have elevated the sulfone moiety to a premier position amongst carbanion-stabilizing groups.[1–4] Sulfonyl-stabilized carbanions can efficiently be alkylated and acylated, and therefore are important reagents for the formation of C–C bonds.[5,6] Deprotonation of sulfones and subsequent reaction with carbonyl compounds yields β-hydroxysulfones,[7] which can easily be reduced to give C=C bonds (Julia olefination).[8–11] In the Julia–Kocienski olefination reaction, olefins are produced directly from sulfonyl-stabilized carbanions and carbonyl compounds *via* Smiles rearrangement.[10,11]

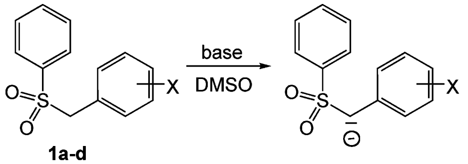
The pK_a values of sulfones have systematically been investigated by Bordwell, who also studied the rate constants for the S_N2 reactions of a family of sulfonyl-stabilized carbanions with *n*-butyl chloride and *n*-butyl bromide in DMSO solution.[12] In contrast to the predictions of the reactivity–selectivity principle, *n*-butyl bromide was found to be generally 300–400 times more reactive than *n*-butyl chloride, independent of the nucleophilicity of the carbanion. Because pK_a values are only a measure of relative nucleophilicities within classes of structurally related compounds,[13] we now set out to characterize the nucleophilicities of the title compounds by studying the kinetics of their reactions with reference electrophiles following the previously established methodology.[14]

The linear free-energy relationship (1), introduced in 1994,[15] is a versatile and powerful tool to organize polar organic reactivity. The reactions of carbocations with various types of nucleophiles as well as the reactions of carbanions with quinone methides and Michael acceptors are described by eqn (1).[16]

$$\log k_2(20\ °\mathrm{C}) = s(N + E) \qquad (1)$$

In this equation, electrophiles are characterized by the electrophilicity parameter E, and nucleophiles are characterized by a nucleophilicity parameter N and a nucleophile-specific slope-parameter s.

In order to investigate whether eqn (1) can also be used to describe the nucleophilic reactivities of sulfonyl-stabilized carbanions, we have now investigated the addition reactions of four sulfonyl-stabilized carbanions (**1a–d**)$^-$ (Scheme 1) with quinone methides (**2a–e**, Scheme 2), diarylcarbenium ions (**3a–b**, Scheme 2), and Michael acceptors (**4a–6d**, Scheme 2) in DMSO. The reactions of nucleophiles with the Michael acceptors **4** (benzylidene Meldrum's acids), **5** (benzylidenebarbituric acids), and **6** (2-benzylidene-indan-1,3-diones) have only recently been demonstrated to follow eqn (1),[18–20] though with lower precision.



1a-d

X	pK_a ^{a}
1a: *m*-Cl	21.6
1b: *p*-CF$_3$	20.2
1c: *p*-CN	18.5
1d: *p*-NO$_2$	15.8

Scheme 1 Sulfones **1a–d** studied in this work. ^{a} In DMSO, ref. 17.

Results

Product studies

The attack of the sulfonyl-stabilized carbanions **1**$^-$ at Michael acceptors has previously been described in the literature.[21,22] In order to examine the course of the kinetically studied reactions, the sulfones **1b** and **1c** were combined with 1.05 equivalents of potassium *tert*-butoxide in dry THF solution and then treated with equimolar amounts of **5b** or **6b** (Scheme 3). The resultant anionic adducts were then precipitated as potassium salts *via* slow addition of dry Et$_2$O. ^{1}H and ^{13}C NMR analyses in DMSO-d_6 showed that despite drying for 10 h at 10^{-2} mbar, the isolated crystalline products contain 0.2–0.5 equivalents of tetrahydrofuran.

The observation of two sets of signals in the ^{1}H-NMR spectra of the anionic adducts (**7–9**)$^-$ indicates the formation of two

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Department Chemie und Biochemie, Ludwig-Maximilians-Universität, Butenandtstr. 5–13 (Haus F), 81377 München, Germany. E-mail: herbert.mayr@cup.uni-muenchen.de; Fax: +49 89-2180-77717; Tel: +49 89-2180-77719

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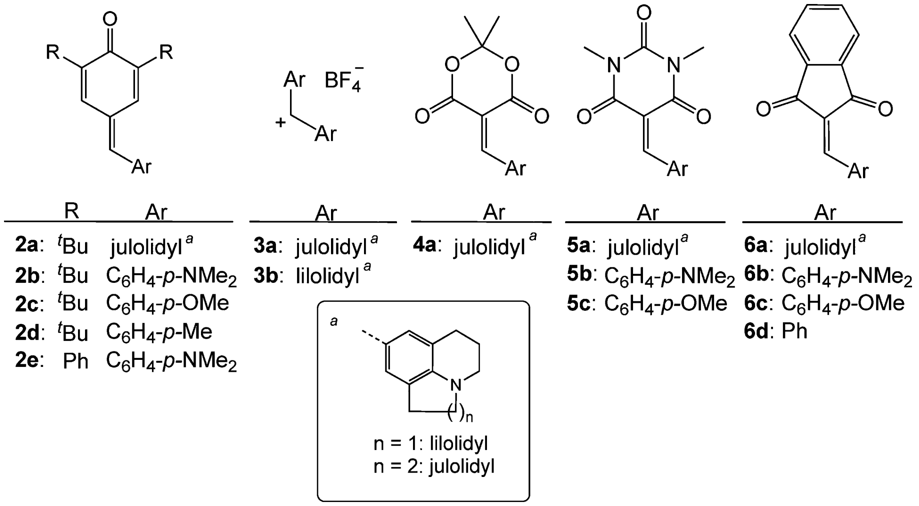
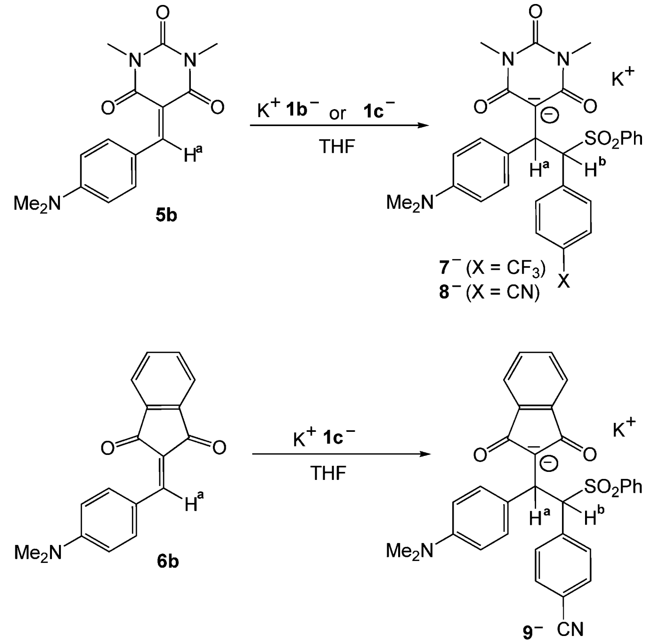
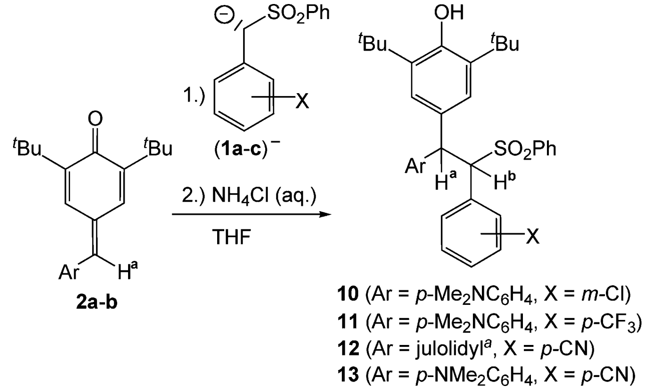


Scheme 2 Electrophiles **2–6** employed for the kinetic investigations with the sulfonyl-stabilized carbanions (**1a–d**)$^-$.



Scheme 3 Michael additions of the sulfonyl-stabilized carbanions **1b**$^-$ and **1c**$^-$ to the benzylidenebarbituric acid **5b** and the 2-benzylidene-indan-1,3-dione **6b**.



Scheme 4 Additions of the sulfonyl-stabilized carbanions (**1a–c**)$^-$ to the quinone methides **2a–b**. ^{a} See Scheme 2.

diastereomers (**7**$^-$: ratio 3 : 2; **8**$^-$: ratio 5 : 4; **9**$^-$: ratio 7 : 3). Protons H^a and H^b, which absorb as doublets between δ 4.51–5.08 ppm (H^a) and δ 5.95–6.57 ppm (H^b) with vicinal coupling constants of approximately 12 Hz, are characteristic for compounds (**7**–**9**)$^-$. The high upfield shifts of the ^{1}H-NMR signals of the vinylic protons H^a in compounds **5b** (δ 8.41 ppm)[23] and **6b** (δ 7.58 ppm)[24] to δ 4.51–5.08 ppm in products (**7–9**)$^-$ indicate the rehybridization of the β-carbon of the Michael acceptors during nucleophilic attack.[25]

The adducts of the carbanions (**1a–c**)$^-$ to the quinone methides **2a** and **2b** were synthesized analogously and treated with saturated aqueous ammonium chloride solution to yield diastereomeric mixtures of the corresponding phenols **10–13** (Scheme 4), from which one diastereomer was separated by column chromatography. In compounds **10–13**, protons H^a and H^b absorb as doublets between δ 4.56–4.82 ppm (H^a) and δ 4.86–4.96 ppm (H^b) with ^3J coupling constants of (10.4 ± 0.4) Hz.

Because analogous reaction products can be expected for other combinations of (**1a–d**)$^-$ with **2–6**, product studies have not been performed for all reactions which have been studied kinetically.

Kinetics

The electrophiles **2–6** show strong absorption bands in the UV-Vis spectra at $\lambda_{\max} = 375$–525 nm. By attack of the nucleophiles at the electrophilic double bond, the chromophore is interrupted, and the reaction can be followed by the decrease of the absorbances of the electrophiles. All reactions proceeded quantitatively, as indicated by the complete decolourisation of the solutions. The kinetic experiments were performed under first-order conditions using a high excess of the nucleophiles. From the exponential decays of the UV-Vis absorbances of the electrophiles, the first-order rate constants $k_{1\Psi}$ were obtained. Plots of $k_{1\Psi}$ *versus* [**1**$^-$] were linear, and their slopes yielded the second-order rate constants k_2 (Table 1).

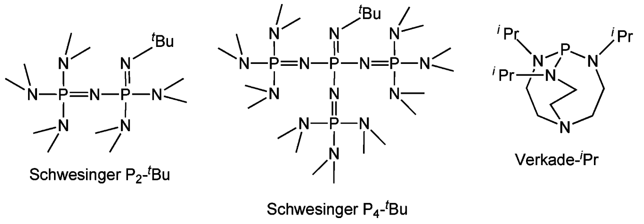
The carbanions were generated in DMSO solution by treatment of the sulfones **1a–d** with 1.05 equivalents of a strong, yet sterically hindered base, *e.g.*, potassium *tert*-butoxide, Schwesinger's

Table 1 Second-order rate constants k_2 (DMSO, 20 °C) for the reactions of sulfonyl-stabilized carbanions (**1a–d**)$^-$ with the reference electrophiles **2–3** and Michael acceptors **4–6**

No.	Sulfone	Base	Electrophile	E	k_2/M^{-1} s^{-1}
1	**1a**	KO^{t}Bu^a	**2a**	−17.90	9.74×10^3
2		P$_4$-^{t}Bu	**2a**	−17.90	9.89×10^3
3		P$_4$-^{t}Bu	**2b**	−17.29	2.30×10^4
4		KO^{t}Bu	**6a**	−14.68	6.25×10^4
5		KO^{t}Bu	**4a**	−13.97	6.75×10^4
6		KO^{t}Bu	**5a**	−13.84	1.54×10^5
7		KO^{t}Bu	**6b**	−13.56	4.13×10^5
8^b	**1b**	P$_2$-^{t}Bu	**2a**	−17.90	1.93×10^3
9		KO^{t}Bu	**2a**	−17.90	1.98×10^3
10^b		P$_2$-^{t}Bu	**2b**	−17.29	3.63×10^3
11		KO^{t}Bu	**2b**	−17.29	3.72×10^3
12		Verkade	**6a**	−14.68	1.34×10^4
13		Verkade	**4a**	−13.97	1.86×10^4
14		Verkade	**5a**	−13.84	3.85×10^4
15		Verkade	**6b**	−13.56	6.09×10^4
16		Verkade	**5b**	−12.76	1.65×10^5
17		Verkade	**2e**	−13.39	3.87×10^5
18	**1c**	P$_2$-^{t}Bu	**2a**	−17.90	4.90×10^2
19^b		P$_2$-^{t}Bu	**2b**	−17.29	9.77×10^2
20		KO^{t}Bu	**2b**	−17.29	1.04×10^3
21^b		KO^{t}Bu^a	**6a**	−14.68	5.64×10^3
22		KO^{t}Bu	**6a**	−14.68	5.78×10^3
23		KO^{t}Bu	**4a**	−13.97	1.04×10^4
24^b		Verkade	**5a**	−13.84	1.47×10^4
25		KO^{t}Bu	**5a**	−13.84	1.51×10^4
26		Verkade	**6b**	−13.56	2.54×10^4
27		Verkade	**5b**	−12.76	6.00×10^4
28		KO^{t}Bu	**2e**	−13.39	1.84×10^5
29	**1d**	Verkade	**2c**	−16.11	6.71×10^1
30		Verkade	**2d**	−15.83	1.10×10^2
31		Verkade	**6c**	−11.32	2.34×10^4
32		Verkade	**5c**	−10.37	5.53×10^4
33		Verkade	**6d**	−10.11	9.27×10^4
34		Verkade	**3b**	−10.04	2.85×10^6
35		Verkade	**3a**	−9.45	6.58×10^6

[a] Addition of equimolar amounts of 18-crown-6. [b] Rate constants not used for further evaluations.

^{t}Bu-P$_2$- or ^{t}Bu-P$_4$-phosphazene base, or Verkade's football-shaped proazaphosphatrane base (Scheme 5). In DMSO, the large differences between the pK_a values of the sulfones **1** (pK_a = 15.8–21.6)[17] and Schwesinger's P$_4$-^{t}Bu base (pK_{BH^+} = 30.2),[26] potassium *tert*-butoxide (pK_{BH^+} = 29.4),[27] and Verkade's base (pK_{BH^+} ~ 27)[28,29] warrant the quantitative formation of the carbanions under these conditions. Complete deprotonation of the sulfones **1b** and **1c** by 1.05 equivalents of Schwesinger's P$_2$-^{t}Bu base (pK_{BH^+} = 21.5)[26] was indicated by the observation that the UV-Vis absorbances of the solutions of the carbanions **1b**$^-$ and **1c**$^-$ at λ_{max} = 350 nm and λ_{max} = 375 nm, respectively, could not be increased by adding a second equivalent of the P$_2$-^{t}Bu base.



Scheme 5 Sterically hindered bases used for the deprotonation of sulfones **1a–d**.

As demonstrated for the additions of the sulfonyl-stabilized carbanion **1b**$^-$ to the quinone methides **2a–b** (entries 8/9 and 10/11, Table 1) and for the reaction of **1c**$^-$ with **2b** (entries 19/20, Table 1), the rate of the reaction is not significantly affected by the nature of the base used for the deprotonation of the sulfones **1**. Analogously, for the reaction of **1c**$^-$ with the Michael acceptor **5a**, a second-order rate constant of 1.48×10^4 M^{-1} s^{-1} was observed with Verkade's base, and $k_2 = 1.51 \times 10^4$ M^{-1} s^{-1} was observed when KO^{t}Bu was used for the deprotonation of **1c** (entries 24/25, Table 1). The addition of equimolar amounts of 18-crown-6 as complexing agent for the potassium ions does not influence the rate either, as shown for the reactions of **1a** with **2a** (entries 1/2, Table 1) and of **1c** with **6a** (entries 21/22, Table 1). These comparisons show that the carbanions **1**$^-$ are not paired under the conditions used for the kinetic experiments. The situation is different when Li$^+$ is used as a counterion.[30]

Due to the yellow colour of the carbanions (**1a–c**)$^-$ in DMSO solution, electrophiles with UV-Vis maxima >475 nm (*i.e.*, **2a–b**, **2e**, **4a**, **5a–b**, **6a–b**) had to be employed for kinetic investigations. In contrast, the *p*-nitro-substituted carbanion **1d**$^-$ absorbs at λ_{max} = 540 nm, and electrophiles with UV-Vis maxima at λ = 375–475 nm (*e.g.*, the yellow compounds **2c–d**, **5c**, **6c–d**) were used to study the reactivity of this carbanion.

Discussion

In order to determine the nucleophilicity parameters N and s of the sulfonyl-stabilized carbanions (**1a–d**)$^-$, the logarithmic second-order rate constants logk_2 were plotted *versus* the E-parameters of the corresponding electrophiles. As expected, the plots for the reactions of sulfonyl-stabilized carbanions (**1a–d**)$^-$ with the reference electrophiles **2** and **3** yield linear correlations. However, systematic deviations are found for the rate constants of the corresponding additions to the Michael acceptors **4–6** (Fig. 1 and 2). The rate constants of these reactions are about 5–24 times smaller than expected on the basis of the correlation with the reference electrophiles **2** and **3**.

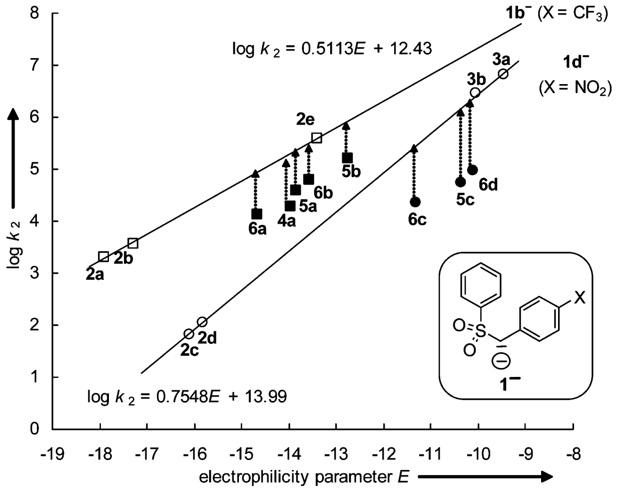


Fig. 1 Plot of logk_2 (DMSO, 20 °C) *versus* the electrophilicity parameters E for the reactions of the carbanions **1b**$^-$ and **1d**$^-$ with the reference electrophiles **2**, **3** and the Michael acceptors **4–6**.

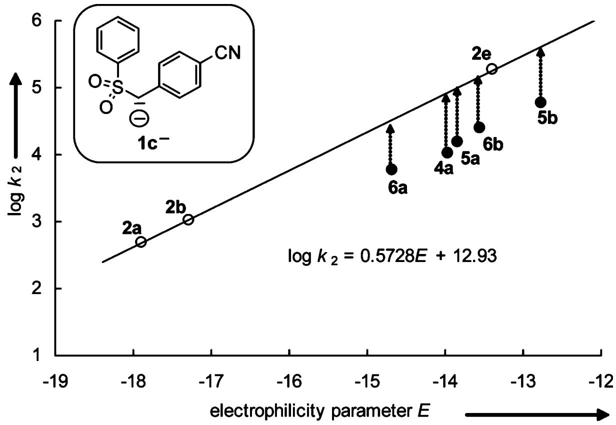


Fig. 2 Plot of $\log k_2$ (DMSO) *versus* electrophilicity parameters E for the reactions of carbanion **1c**⁻ with the quinone methides **2** and the Michael acceptors **4–6**.

Table 2 N and s parameters for the sulfonyl-stabilized carbanions (**1b–d**)⁻

Carbanion	N	s
1b⁻	24.3	0.51
1c⁻	22.6	0.57
1d⁻	18.5	0.75

From the correlation lines drawn in Fig. 1 and 2, which are based on the reactions of the carbanions (**1b–d**)⁻ with the reference electrophiles **2a–e**, we have derived the nucleophile-specific parameters N and s, which are listed in Table 2. As the reactivity of the carbanion **1a**⁻ was only investigated towards two reference compounds of comparable electrophilicity (see ESI†), the corresponding N and s values have not been calculated.

According to Fig. 3, the benzenesulfonyl-stabilized benzyl anions (**1b–d**)⁻ are considerably more nucleophilic than their trifluoromethanesulfonyl-stabilized analogues[31–33] (4 to 7 units in N) and the corresponding α-nitrobenzyl anions.

To include the carbanion **1a**⁻, detailed structure–reactivity correlations shall, therefore, be based on individual rate constants. Second-order rate constants for the reactions of the quinone methide **2b** have been measured with all sulfonyl-stabilized carbanions **1**⁻ except **1d**⁻. Because the electrophilicity of **2b** is only slightly smaller than that of **2c** and **2d**, the rate constant for the reaction of **1d**⁻ with **2b** can reliably be calculated from the lower correlation line of Fig. 1 as $k_2 = 8.70\ \text{M}^{-1}\ \text{s}^{-1}$.

Fig. 4 shows that the rate constants for the reactions of the carbanions (**1a–d**)⁻ with the quinone methide **2b** correlate only moderately with Hammett's σ^- parameters. The correlation with σ_p is even worse, and because of the deviation of *p*-CN and *p*-NO$_2$ in opposite directions from the correlation line, a Yukawa–Tsuno treatment[34] would not improve the fit.

In agreement with a higher negative charge density at the benzylic carbon of carbanions (**1a–d**)⁻, the Hammett reaction constant ρ is more negative than for the analogous reactions of the corresponding trifluoromethanesulfonyl-stabilized anions (Fig. 4, lower graph).

In contrast, the Brønsted correlation shown in Fig. 5 is of high quality though the rate constant for the *p*-cyano substituted compound lies slightly above the depicted correlation line as previously found in the Hammett plot (see Fig. 4). The slope of the Brønsted correlation in Fig. 5 (β = 0.58) is 1.44 times larger than that of the corresponding Brønsted plot for the reactions of the carbanions **1**⁻ with *n*-butyl chloride ($\beta = 0.402$),[12,13] in agreement with previous observations that the variation of nucleophiles affects the reactivities toward C_{sp^3} electrophiles to a smaller degree than the reactivities toward C_{sp^2} electrophiles.[35] Systematic investigations of S_N2 reactions with sulfonyl-stabilized carbanions are presently under investigation.

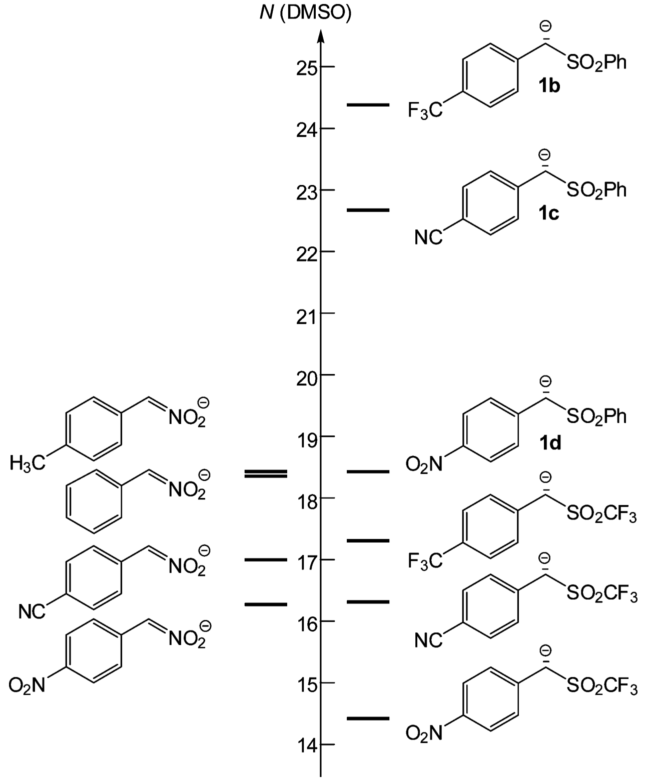


Fig. 3 Comparison of the nucleophilicities of differently substituted benzyl anions in DMSO.

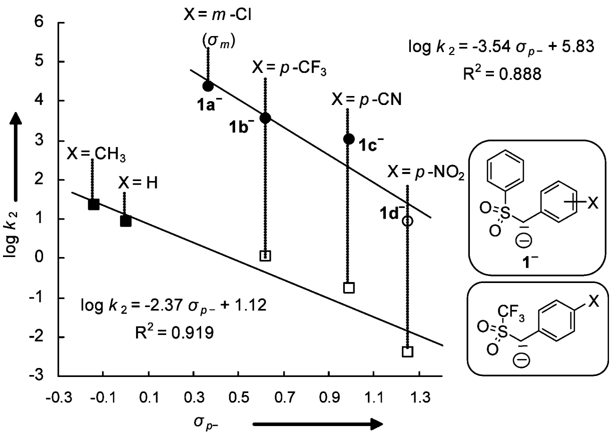


Fig. 4 Correlations of the logarithmic second-order rate constants of the reactions of quinone methide **2b** with the carbanions (**1a–d**)⁻ and the trifluoromethanesulfonyl-stabilized carbanions (DMSO) with the Hammett σ_p^- values. Filled symbols: experimental rate constants; open symbols: k_2 calculated by eqn (1).

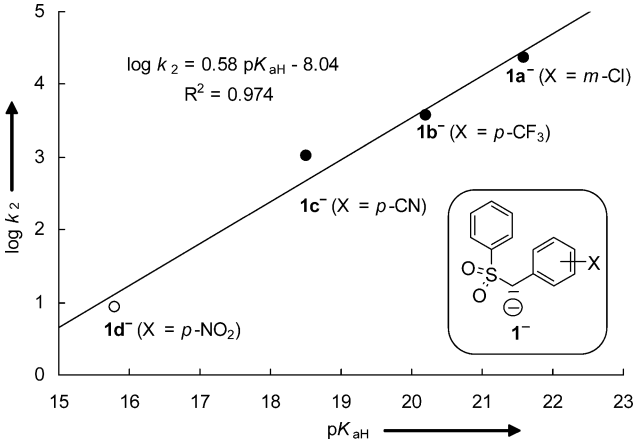


Fig. 5 Brønsted plot for the reactions of sulfonyl-stabilized carbanions (**1a–d**)$^-$ with the quinone methide **2b** (DMSO). Filled symbols: experimental rate constants; open symbol: calculated (eqn (1)) rate constant.

Conclusions

The second-order rate constants for the reactions of the benzenesulfonyl-stabilized carbanions (**1a–d**)$^-$ with the electrophiles **2–6** can be described by eqn (1) within the postulated accuracy of a factor 10–100. However, all second-order rate constants for the additions of (**1a–d**)$^-$ to the electrophiles **4–6** are 5–24 times smaller than predicted by eqn (1) based on the N and s parameters derived from the reactions of **1**$^-$ with the reference electrophiles **2** and **3**. This observation is in line with the previously reported systematic deviations of the reactions of the dimedone anion and the anion of diethyl malonate with the Michael acceptors **4–6**.[20] Though these systematic deviations suggest that one should derive correlation equations for separate groups of electrophiles, we rather stick to a single set of universal parameters and accept the relatively low accuracy of eqn (1) in order to have a simple and unambiguous correlation, which makes reliable estimates in a reactivity range of more than thirty orders of magnitude. Nevertheless, further investigations are going on in order to understand the origin of these deviations.

Experimental

^{1}H and ^{13}C NMR chemical shifts are expressed in ppm and refer to the corresponding solvents (δ_H 2.50, δ_C 39.5 for DMSO-d_6 and δ_H 7.26, δ_C 77.2 for CDCl$_3$), J values are given in Hz. DEPT and HSQC experiments were employed to assign the signals. All reactions were performed under an atmosphere of dry argon. Dry DMSO for kinetics was purchased (<50 ppm H$_2$O). Sulfones **1a–d** were synthesized from the corresponding benzyl bromides and sodium benzenesulfinate in DMSO according to ref. 36.

General procedure for the synthesis of anionic addition products

Under an argon atmosphere equimolar amounts of potassium *tert*-butoxide (~0.6 mmol) and sulfone **1** were dissolved in freshly distilled THF (10 mL). The electrophile (~0.6 mmol) was then added to this stirred solution and after 10 min the product was precipitated by adding diethyl ether (10 mL).

7$^-$**.** Yellow crystals, isolated as a mixture of diastereomers (3 : 2), which contain 0.5 equivalents of THF (from ^{1}H NMR), 41% yield. Major diastereomer: δ_H(400 MHz; DMSO-d_6) 2.78 (9 H, s, NMe and NMe$_2$), 2.87 (3 H, s, NMe), 4.99 (1 H, d, J 12.0, C$^-$CH), 6.17 (1 H, d, J 12.0, CH), 6.30 (2 H, d, J 8.7, Ar) and 7.24–7.64 (11 H, m, Ar); δ_C(100 MHz; DMSO-d_6) 26.3 (NMe), 27.0 (NMe), 40.3 (CH), 40.6 (NMe$_2$), 73.0 (CH), 88.5 (C$^-$), 112.0 (C$_{Ar}$-H), 123.7 (C$_{Ar}$-H), 127.1–127.6 and 128.2–132.1 (5 × C$_{Ar}$-H and C_{Ar}-CF$_3$), 132.3–140.8 (3 × C$_{Ar}$), 148.6 (C$_{Ar}$-N), 152.5 (CO), 160.6 (CO) and 161.3 (CO). Minor diastereomer: δ_H(400 MHz; DMSO-d_6) 2.65 (6 H, s, NMe$_2$), 2.87 (s, 3 H, NMe), 5.07 (1 H, d, J 11.9, C$^-$CH), 6.27 (2 H, d, J 8.7, Ar), 6.56 (1 H, d, J 11.9, CH), 7.11 (2 H, d, J 8.7, Ar) and 7.24–7.64 (9 H, m, Ar); δ_C(100 MHz; DMSO-d_6) 26.3 (NMe), 27.0 (NMe), 40.3 (CH), 40.6 (NMe$_2$), 68.5 (CH), 86.8 (C$^-$), 111.6 (C$_{Ar}$-H), 124.3 (C$_{Ar}$-H), 127.1–127.9 and 128.2–132.1 (5 × C$_{Ar}$-H and C_{Ar}-CF$_3$), 132.3–140.8 (3 × C$_{Ar}$), 147.6 (C$_{Ar}$-N), 152.1 (CO), 160.6 (CO) and 161.3 (CO).

8$^-$**.** Yellow crystals, isolated as a mixture of diastereomers (5 : 4), which contain 0.3 equivalents of THF (from ^{1}H NMR), 81% yield. Major diastereomer: δ_H(400 MHz; DMSO-d_6) 2.78 (3 H, s, NMe), 2.78 (6 H, s, NMe$_2$), 2.87 (3 H, s, NMe), 4.97 (1 H, d, J 12.0, C$^-$CH), 6.12 (1 H, d, J 12.0, CH), 6.31 (2 H, d, J 8.8, Ar) and 7.08–7.68 (11 H, m, Ar); δ_C(100 MHz; DMSO-d_6) 26.3 (NMe), 27.0 (NMe), 40.2 (CH), 40.6 (NMe$_2$), 73.2 (CH), 88.5 (C$^-$), 110.0 (C_{Ar}-CN), 112.0 (C$_{Ar}$-H), 118.9 (CN), 127.1–132.2 (6 × C$_{Ar}$-H), 132.2 (C$_{Ar}$), 140.5 (C$_{Ar}$), 140.6 (C$_{Ar}$), 148.6 (C$_{Ar}$-N), 152.5 (CO), 160.5 (CO) and 161.3 (CO). Minor diastereomer: δ_C(400 MHz; DMSO-d_6) 2.66 (6 H, s, NMe$_2$), 2.87 (3 H, s, NMe), 5.04 (1 H, d, J 11.8, C$^-$CH), 6.27 (2 H, d, J 8.9, Ar), 6.56 (1 H, d, J 11.9, CH), 7.10 (2 H, d, J 8.8, Ar) and 7.08–7.68 (9 H, m, Ar); δ_C(100 MHz, DMSO-d_6) 26.3 (NMe), 27.0 (NMe), 40.2 (CH), 40.6 (NMe$_2$), 68.7 (CH), 86.7 (C$^-$), 110.0 (C_{Ar}-CN), 111.5 (C$_{Ar}$-H), 118.7 (CN), 127.1–132.3 (6 × C$_{Ar}$-H), 132.8 (C$_{Ar}$), 139.9 (C$_{Ar}$), 140.5 (C$_{Ar}$), 147.7 (C$_{Ar}$-N), 152.1 (CO), 160.5 (CO) and 161.3 (CO).

9$^-$**.** Orange crystals, isolated as a mixture of diastereomers (7 : 3), which contain 0.2 equivalents of THF (from ^{1}H NMR), 69% yield. Major diastereomer: δ_H(400 MHz; DMSO-d_6) 2.78 (6 H, s, NMe$_2$), 4.53 (1 H, d, J 11.9, C$^-$CH), 5.97 (1 H, d, J 11.9, CH), 6.34 (2 H, d, J 8.9, Ar) and 6.69–7.63 (15 H, m, Ar); δ_C(100 MHz; DMSO-d_6) 40.2 (CH), 40.5 (NMe$_2$), 72.8 (CH), 106.8 (C$^-$), 109.9 (C_{Ar}-CN), 112.1 (C$_{Ar}$-H), 115.9 (C$_{Ar}$-H), 118.7 (CN), 127.4–132.3 (6 × C$_{Ar}$-H), 132.0 (C$_{Ar}$), 140.0–140.6 (4 × C$_{Ar}$), 148.6 (C$_{Ar}$-N) and 186.8 (2 × CO). Minor diastereomer: δ_H(400 MHz; DMSO-d_6) 2.65 (6 H, s, NMe$_2$), 4.57 (1 H, d, J 11.3, C$^-$CH), 6.27–6.35 (3 H, m, CH and Ar) and 6.69–7.63 (15 H, m, Ar); δ_C(100 MHz, DMSO-d_6) 40.2 (CH), 40.2 (NMe$_2$), 69.5 (CH), 105.1 (C$^-$), 109.9 (C_{Ar}-CN), 111.7 (C$_{Ar}$-H), 115.8 (C$_{Ar}$-H), 118.7 (CN), 127.4–132.3 (6 × C$_{Ar}$-H), 133.0 (C$_{Ar}$), 140.0–140.6 (4 × C$_{Ar}$), 147.6 (C$_{Ar}$-N) and 187.3 (2 × CO).

General procedure for the synthesis of neutral addition products 10–13

Under an argon atmosphere equimolar amounts of potassium *tert*-butoxide (~0.4 mmol) and sulfone **1** were dissolved in freshly distilled THF (15 mL). A solution of the quinone methide **2** (~0.4 mmol) in THF (20 mL) was then added to this solution and stirred for 1.5 h. After removal of the solvent in the vacuum the residue was washed with saturated NH_4Cl solution, extracted with EtOAc, and dried over Na_2SO_4. In order to obtain the major diastereomer, the crude product was purified by column chromatography (SiO_2, hexane–EtOAc) twice and crystallized from ethanol. The absolute conformation of the diastereomer was not determined.

4-[2-Benzenesulfonyl-2-(3-chlorophenyl)-1-(4-dimethylaminophenyl)ethyl]-2,6-di-*tert*-butylphenol 10. Yellow crystals, 7% yield, mp 222–224 °C. δ_H(300 MHz; $CDCl_3$) 1.19 (18 H, s, 2 × $C(CH_3)_3$), 2.84 (6 H, s, NMe_2), 4.80 (1 H, s, OH), 4.82 (1 H, d, *J* 10.4, CH), 4.86 (1 H, d, *J* 10.1, CH), 6.55 (2 H, br s, Ar), 6.75 (2 H, s, Ar) and 6.90–7.38 (11 H, m, Ar); δ_C(75.5 MHz; $CDCl_3$) 30.3 (6 × CH_3), 34.3 (2 × $C(CH_3)_3$), 41.0 (NMe_2), 51.7 (CH), 75.9 (CH), 113.2 (C_{Ar}), 125.3 (C_{Ar}-H), 128.1 (C_{Ar}-H), 128.6 (2 × C_{Ar}-H), 128.9 (C_{Ar}-H), 129.1 (C_{Ar}-H), 131.1 (C_{Ar}-H), 132.3 (C_{Ar}-H), 132.9 (C_{Ar}-H), 133.8 (C_{Ar}), 135.5 (C_{Ar}), 135.6 (C_{Ar}), 140.0 (C_{Ar}) and 152.1 (C_{Ar}); *m/z* (EI) 603.2567 (M^+. $C_{36}H_{42}ClNO_3S$ requires 603.2574), 603 (M^+, 1%), 461 (55), 338 (100), 322 (45), 280 (17), 134 (19), 127 (17) and 125 (55).

4-[2-Benzenesulfonyl-1-(4-dimethylaminophenyl)-2-(4-trifluoromethylphenyl)ethyl]-2,6-di-*tert*-butylphenol 11. Colourless crystals, 9% yield, mp 209–211 °C. δ_H(300 MHz; $CDCl_3$) 1.16 (18 H, s, 2 × $C(CH_3)_3$), 2.82 (6 H, s, NMe_2), 4.79 (1 H, s, OH), 4.85 (1 H, d, *J* 10.1 Hz, CH), 4.95 (1 H, d, *J* 10.1, CH), 6.50 (2 H, d, *J* 7.7, Ar), 6.72 (2 H, s, Ar) and 7.11–7.37 (11 H, m, Ar); δ_C(75.5 MHz; $CDCl_3$) 30.3 (6 × CH_3), 34.2 (2 × $C(CH_3)_3$), 41.0 ($N(CH_3)_2$), 51.8 (CH), 76.1 (CH), 113.3 (C_{Ar}-H), 122.2 (CF_3), 124.8 (2 × C_{Ar}-H), 125.3 (C_{Ar}-H), 128.5 (C_{Ar}-H), 128.7 (C_{Ar}-H), 128.9 (C_{Ar}-H), 129.9 (C_{Ar}), 130.4 (C_{Ar}), 131.3 (C_{Ar}-H), 132.0 (C_{Ar}), 133.0 (C_{Ar}-H), 135.6 (C_{Ar}), 137.8 (C_{Ar}), 140.0 (C_{Ar}), 149.4 (C_{Ar}) and 152.1 (C_{Ar}); *m/z* (EI) 637.2820 (M^+. $C_{37}H_{42}F_3NO_3S$ requires 637.2838), 637 (M^+, 2%), 338 (100).

4-[1-Benzenesulfonyl-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(julolidin-9-yl)ethyl]benzonitrile 12. Yellow crystals, 22% yield, mp >165 °C (dec.). δ_H(300 MHz; $CDCl_3$) 1.17 (18 H, s, 2 × $C(CH_3)_3$), 1.79 (4 H, m, CH_2), 2.45 (4 H, m, CH_2), 2.95 (4 H, t, *J* 5.5, CH_2), 4.56 (1 H, d, *J* 10.8, CH), 4.78 (1 H, s, OH), 4.93 (1 H, d, *J* 10.8, CH), 6.46 (2 H, s, Ar), 6.68 (2 H, s, Ar) and 7.17–7.40 (9 H, m, Ar); δ_C(75.5 MHz; $CDCl_3$) 22.2 (CH_2), 27.7 (CH_2), 30.3 (6 × CH_3), 34.3 (2 × $C(CH_3)_3$), 50.0 (CH_2), 52.7 (CH), 76.2 (CH), 111.8 (C_{Ar}-CN), 118.6 (CN), 121.6 (C_{Ar}), 124.9 (C_{Ar}-H), 126.7 (C_{Ar}-H), 127.5 (C_{Ar}), 128.2 (C_{Ar}-H), 128.4 (C_{Ar}-H), 131.6 (C_{Ar}-H), 132.2 (C_{Ar}), 132.7 (C_{Ar}-H), 135.7 (C_{Ar}), 139.0 (C_{Ar}), 140.5 (C_{Ar}), 142.2 (C_{Ar}) and 152.0 (C_{Ar}); *m/z* (EI) 646.3231 (M^+. $C_{41}H_{46}N_2O_3S$ requires 646.3229), 646 (M^+, 2%), 504 (17), 390 (100), 374 (10) and 116 (11).

4-[1-Benzenesulfonyl-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(4-dimethylaminophenyl)ethyl]benzonitrile 13. Colourless crystals, 16% yield, mp 237–238 °C. δ_H(300 MHz; $CDCl_3$) 1.17 (18 H, s, 2 × $C(CH_3)_3$), 2.81 (6 H, s, NMe_2), 4.81 (1 H, s, OH), 4.82 (1 H, d, *J* 10.3, CH), 4.96 (1 H, d, *J* 10.4, CH), 6.45 (2 H, d, *J* 8.3, Ar), 6.72 (2 H, s, Ar) and 7.07–7.36 (11 H, m, Ar); δ_C(75.5 MHz; $CDCl_3$) 30.3 (6 × CH_3), 34.3 (2 × $C(CH_3)_3$), 40.8 ($N(CH_3)_2$), 51.8 (CH), 76.1 (CH), 111.8 (C_{Ar}-CN), 113.1 (C_{Ar}), 118.5 (CN), 125.1 (C_{Ar}), 128.4 (C_{Ar}-H), 128.7 (C_{Ar}-H), 128.8 (C_{Ar}-H), 131.5 (C_{Ar}-H), 131.9 (C_{Ar}), 133.1 (C_{Ar}-H), 135.8 (C_{Ar}), 139.2 (C_{Ar}), 139.9 (C_{Ar}), 149.5 (C_{Ar}) and 152.1 (C_{Ar}); *m/z* (EI) 594.2901 (M^+. $C_{37}H_{42}N_2O_3S$ requires 594.2916), 594 (M^+, 2%), 338 (100).

Kinetic experiments

During all kinetic studies the temperature of the solutions was kept constant (20 ± 0.1 °C) by using a circulating bath thermostat. Dry DMSO for kinetics was purchased (<50 ppm H_2O). For the evaluation of kinetics the stopped-flow spectrophotometer systems Hi-Tech SF-61DX2 or Applied Photophysics SX.18MV-R stopped-flow reaction analyzer were used. Rate constants k_{obs} (s^{-1}) were obtained by fitting the single exponential $A_t = A_0 \exp(-k_{obs}t) + C$ to the observed time-dependent electrophile absorbance (averaged from at least 3 kinetic runs for each nucleophile concentration). For the stopped-flow experiments 2 stock solutions were used: a solution of the electrophile in DMSO and a solution of the carbanion, which was generated by the deprotonation of the CH acid with 1.05 equivalents of base.

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