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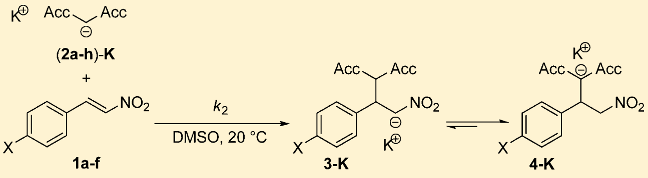
Electrophilicities of *trans-β*-Nitrostyrenes

Ivo Zenz and Herbert Mayr*

Department Chemie, Ludwig-Maximilians-Universität München, Butenandtstrasse 5-13 (Haus F), 81377 München, Germany

Supporting Information



ABSTRACT: The kinetics of the reactions of the *trans-β*-nitrostyrenes **1a–f** with the acceptor-substituted carbanions **2a–h** have been determined in dimethyl sulfoxide solution at 20 °C. The resulting second-order rate constants were employed to determine the electrophile-specific reactivity parameters *E* of the *trans-β*-nitrostyrenes according to the correlation equation $\log k_2(20\ °C) = s_N(N + E)$. The *E* parameters range from −12 to −15 on our empirical electrophilicity scale (www.cup.lmu.de/oc/mayr/DBintro.html). The second-order rate constants for the reactions of *trans-β*-nitrostyrenes with some enamines were measured and found to agree with those calculated from the electrophilicity parameters *E* determined in this work and the previously published *N* and s_N parameters for enamines.

INTRODUCTION

Nitroalkenes **1** are important reagents in organic chemistry. They are readily accessible via Henry reaction of aldehydes or ketones with nitroalkanes, and the nitro group can easily be converted into a large variety of functional groups like the carbonyl, the amino, the hydroxylamino, or the azo group.[1,2] As the nitro group is one of the strongest electron-withdrawing substituents known, nitroalkenes are highly reactive Michael acceptors, and their use as electrophiles in organocatalytic reactions has led to a renaissance of nitroalkene chemistry.[3,4] Recent examples of organocatalytic reactions include highly enantioselective thiourea-catalyzed additions[5−7] to indoles[8,9] and *β*-diketones.[10,11] Enamine activation[12,13] in reactions of nitroalkenes with ketones[14−17] and aldehydes[18−23] has also been reported. Highly diastereo- and enantioselective additions of aldehydes to nitrostyrenes have been achieved with as little as 0.1% of a tripeptide catalyst.[23] Furthermore, guanidine derivatives and cinchona alkaloids have been employed as catalysts for additions of malonates[24] and *β*-ketoesters[25] to nitroalkenes. Additions of oxindols to nitroalkenes have been performed under conditions of phase-transfer catalysis,[26] and tandem cycloadditions of nitroalkenes[27,28] have been applied to the synthesis of natural products.[29]

Kinetics of the reactions of nitroalkenes with benzylamines,[30] sodium alkoxides,[31] and hydroxide anions[32] have been investigated in order to elucidate the mechanism of nucleophilic additions to the electron-deficient double bond of nitroalkenes.[33]

In previous work, we have shown that a large variety of reactions of electrophiles with nucleophiles can be described by eq 1, where *N* and s_N (previously called *s*) are nucleophile-specific parameters, *E* is an electrophilicity parameter, and k_2 is the second-order rate constant.[34]

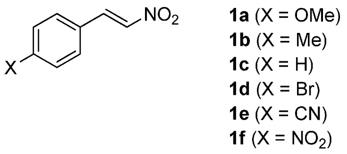
$$\log k_2(20\ °C) = s_N(N + E) \qquad (1)$$

Diarylcarbenium ions have been employed as reference electrophiles for the determination of the nucleophile-specific parameters *N* and s_N of neutral and anionic nucleophiles.[35]

Furthermore, the kinetics of the reactions of carbanions with Michael acceptors such as quinone methides,[36−38] benzylidenemalononitriles,[39] benzylidene-1,3-indandiones,[40] benzylidenebarbituric- and thiobarbituric acids,[41] benzylidene Meldrum's acids,[42] and iminium ions[43] have been employed to determine the *E* parameters of these electrophiles according to eq 1.

We will now report on the kinetics of the reactions of the *trans-β*-nitrostyrenes **1a–f** (Scheme 1) with the stabilized carbanions **2a–h** (Table 1) in DMSO and demonstrate that the second-order rate constants k_2 of these reactions follow eq 1. These rate constants will then be used for the determination of the *E* parameters for *trans-β*-nitrostyrenes **1a–f** as part of our program of developing comprehensive nucleophilicity and electrophilicity scales.[44−47]

Scheme 1. Structures of the *trans-β*-Nitrostyrenes 1a–f



RESULTS

Product Studies. Combination of the *trans-β*-nitrostyrenes **1a–f** with equimolar amounts of the potassium salts **2a-K** and **2b-K** in DMSO gave the adducts (**4aa–4fa**)-K and (**4ab–4fb**)-K, respectively (Scheme 2), which were identified by ^{1}H and ^{13}C NMR spectroscopy (Table 2). The origin of the adducts

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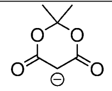
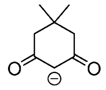
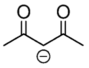
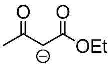
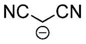
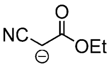
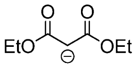
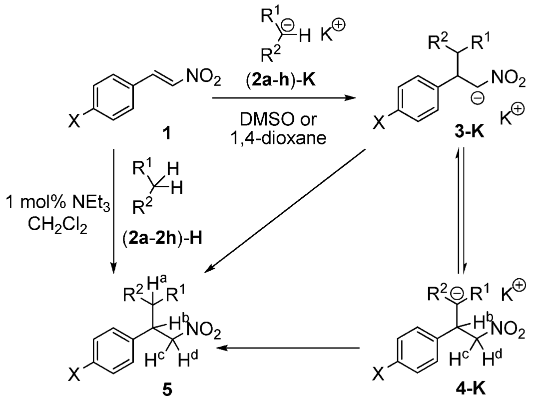
Table 1. Reactivity Parameters N and s_N of the Carbanions 2a–h in DMSO

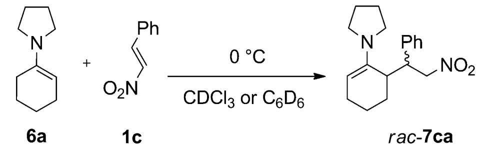
	Nucleophile	N, s_N[a]	pK_{aH} (in DMSO)
2a		13.91, 0.86	7.3[c]
2b		16.27, 0.77	11.2[d]
2c		17.64, 0.73	13.3[d]
2d		18.82, 0.69	14.2[e]
2e		19.36, 0.67	11.1[f]
2f		19.62, 0.67	13.1[g]
2g		20.22, 0.65	16.4[d]
2h	$H_2C{=}NO_2^{\ominus}$	20.71, 0.60[b]	17.2[f]

[a] Reference 38. [b] Reference 36. [c] Reference 48. [d] Reference 49. [e] Reference 50. [f] Reference 51. [g] Reference 52.

Scheme 2. Reactions of the *trans-β*-Nitrostyrenes 1a–f with the Carbanions 2a–h



Scheme 3. Reaction of *trans-β*-Nitrostyrene 1c with 1-Pyrrolidinocyclohexene 6a



can be derived from the formula abbreviations **4xy**; the first letter identifies the electrophile, while the second letter identifies the nucleophile. Thus, compound **4fa** is an adduct from **1f** and **2a**. The higher acidity of Meldrum's acid (**2a-H**, pK_a^{DMSO} = 7.3)[48] and dimedone (**2b-H**, pK_a^{DMSO} = 11.2)[49] compared with nitromethane (**2h-H**, pK_a^{DMSO} = 17.2)[51] rationalizes why the initially formed adducts **3** obtained from the nitrostyrenes **1** and **2a-K** or **2b-K** immediately tautomerize with formation of the carbanions **4**.

Analogously, **4ce-K** was obtained from *trans-β*-nitrostyrene **1c** and **2e-K** due to the higher aciditiy of malononitrile (**2e-H**, pK_a^{DMSO} = 11.1)[51] relative to nitromethane. The anions **4** show ^{1}H NMR spectra with resonances in the range of δ = 4.7–5.6 ppm for the diastereotopic protons H^c and H^d (Table 2). Protons H^c and H^d of the products **4aa-K** to **4fa-K** are nearly isochronous (δ = 5.1 to 5.3 ppm) and show similar vicinal coupling constants of J_{bc} = 8.2–9.0 Hz and J_{bd} = 7.5–8.1 Hz (see Tables 2 and S1, Supporting Information). In contrast, the chemical shifts of the protons H^c and H^d of **4ab-K** to **4fb-K** differ by about 0.5 ppm [H^c (δ = 5.4 to 5.6 ppm), H^d ($\delta \approx$ 4.9 ppm)], and the vicinal coupling constants differ by about 3 Hz (J_{bc} = 9.1–9.5 Hz, J_{bd} = 5.9–6.3 Hz).

The Michael adducts **5ac–5 fc**, which were obtained in 38–79% isolated yields from **1a–f** and 2 equiv of pentane-2,4-dione **2c-H** in CH_2Cl_2 in the presence of NEt_3 (1 mol %) following a report by Brunner and Kimel[53] (Table 2), showed ^{1}H NMR spectra with resonances in the range of δ = 4.3–4.4 ppm for H^a, δ = 4.2–4.4 ppm for H^b, and δ = 4.6–4.7 ppm for H^c and H^d.

The reaction of *trans-β*-nitrostyrene **1c** with enamine **6a** in $CDCl_3$ and C_6D_6 solution gave *rac*-**7ca** (Scheme 3) with a vinylic proton at δ = 4.54 (t, J = 3.9 Hz). Though unidentified impurities were detected in the NMR spectra, the ^{1}H NMR signals from δ = 3.6 to 5.1 ppm indicated the formation of a single diastereomer. The intermediate formation of cyclobutanes[57–59] could not be observed.

Kinetics. The kinetic investigations were performed at 20 °C in DMSO as the solvent. The carbanions **2a–h** were either used as preformed potassium salts (CAUTION: **2h-K** must not be isolated as it is known to be explosive) or generated in the solutions used for the kinetic investigations by treatment of the corresponding CH acids with 1.05 equiv of potassium *tert*-butoxide, which is sufficient for the complete deprotonation of the CH acids.[42] The rates of the consumptions of the *trans-β*-nitrostyrenes **1a–d** ($\lambda_{\max}$ = 310–363 nm) were generally followed photometrically at their absorption maxima. Due to an overlap of the absorption bands, the rates of the reactions with the carbanions **2f** and **2h** were followed at the shoulders of the absorption bands of the electrophiles **1a–f**. Measurements at the shoulders of the absorption bands of the *trans-β*-nitrostyrenes **1e** and **1f** were also performed to determine the kinetics of their reactions with the carbanions **2a–d**. In these cases, the absorbances at the monitored wavelengths did not reach 0 at the end of the reactions. Only partial conversion was observed for the reactions of **1a–d** with the carbanion **2e**; the corresponding equilibrium constants could not be determined, however, because of unknown subsequent reactions.

Only the reactions of **1a–d** with the carbanion **2a** were slow enough to be studied by conventional UV–vis spectroscopy ($\tau_{1/2}$ > 30 s); in all other cases, the stopped-flow technique was employed. By using a high excess of the carbanions **2** (10–50 equiv), pseudo-first-order conditions were achieved (eq 2), as revealed by the exponential decays of the concentrations of the nitrostyrenes **1a–f**.

$$-\mathrm{d}[\mathbf{1}]/\mathrm{d}t = k_{\text{obs}}[\mathbf{1}] \tag{2}$$

The first-order rate constants k_{obs} were obtained by least-squares fitting of the time-dependent absorbances A_t of the electrophiles to the exponential function $A_t = A_0 \cdot e^{-k_{\text{obs}}t} + C$. As shown in Figure 1 for the reaction of **1a** with **2a**, plots of k_{obs} versus the concentrations of the carbanions [**2**] were linear with

Table 2. Characteristic ^{1}H and ^{13}C NMR Chemical Shifts of the Michael Adducts 4-K and 5

electrophile	nucleophile	product	yield (%)	$\delta(H^a)^f$	$\delta(H^b)^f$	$\delta(H^c)$, $\delta(H^d)^f$	$\delta(C-H^b)$
1a	**2a-K**	**4aa-K**	*a*		4.53	5.09, 5.08	40.0
1b	**2a-K**	**4ba-K**	*a*		4.55	5.10, 5.10	39.8
1c	**2a-K**	**4ca-K**	*a*		4.59	5.15, 5.13	40.1
1d	**2a-K**	**4da-K**	*a*		4.56	5.15, 5.11	39.6
1e	**2a-K**	**4ea-K**	*a*		4.66	5.23, 5.14	40.1
1f	**2a-K**	**4fa-K**	*a*		4.72	5.28, 5.17	39.9
1a	**2b-K**	**4ab-K**	*a*		4.87	5.38, 4.88	38.6
1b	**2b-K**	**4bb-K**	*a*		4.90	5.40, 4.88	38.8
1c	**2b-K**	**4cb-K**	*a*		4.95	5.42, 4.93	39.2
1d	**2b-K**	**4db-K**	*a*		4.92	5.46, 4.88	38.6
1e	**2b-K**	**4eb-K**	*a*		5.04	5.51, 4.94	38.8
1f	**2b-K**	**4fb-K**	*a*		5.10	5.59, 4.92	38.8
1a	**2c-H**	**5ac**	79	4.33	4.19	4.59, 4.58	42.2
1b	**2c-H**	**5bc**	71	4.35	4.20	4.60, 4.59	42.6
1c	**2c-H**	**5cc**	71	4.34	4.21	4.61, 4.59	42.9
1d	**2c-H**	**5dc**	63	4.32	4.21	4.61, 4.60	42.3
1e	**2c-H**	**5ec**	38	4.36	4.31	4.66, 4.64	42.7
1f	**2c-H**	**5fc**	50	4.39	4.38	4.69, 4.66	42.4
1c	**2d-H**	**5cd**	55[d]	4.09	4.17	4.72, 4.72	42.4
1c	**2e-K**	**4ce-K**	*a*		3.70	4.70, 4.67	43.0
1c	**2f-H**	**5cf**	67[e]	3.93	4.22	5.01, 4.92	42.8
1c	**2g-K**	**5cg**[b]	42	3.79	4.20	4.89, 4.83	43.1
1c	**2h-H**	**5ch**[c]	50		4.31	4.78, 4.75	41.8

[a] The potassium salts **4-K** were generated in DMSO-d_6 solution and identified in situ by ^{1}H and ^{13}C NMR spectroscopy. [b] From **1c** and **2g-K** in 1,4-dioxane and subsequent protonation with aqueous acetic acid (2 mol/L), as reported in ref 54. [c] From **1c** (1.15 mmol) in nitromethane **2h-H** (10 mL) in the presence of NEt_3 (1 mol %), as reported in ref 55. [d] Yield of a mixture of diasteromers (dr ≈ 8:1). [e] Yield of a mixture of diasteromers (dr ≈ 1.4:1). [f] Chemical shifts (in ppm) extracted by using DAVINX software (ref 56). Chemical shifts for diastereomeric mixtures refer to the major isomer.

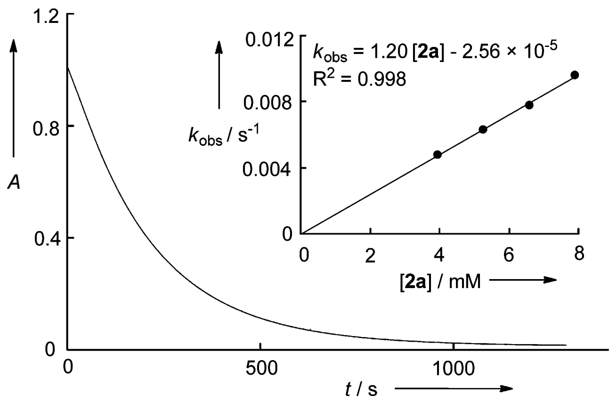


Figure 1. Exponential decay of absorbance (A at λ = 363 nm) and linear correlation of the pseudo-first-order rate constants k_{obs} with [**2a**] for the reaction of **1a** (c = 1.06 × 10^{-4} M) with **2a** (the individual kinetics is shown for c = 3.95 × 10^{-3} M) in DMSO at 20 °C.

almost 0 intercepts. According to the relation $k_2 = k_{obs}/[2]$, the slopes of these correlations gave the second-order rate constants k_2 listed in Table 3.

DISCUSSION

The rate constants k_2 listed in Table 3 reveal that the reactivity order of the carbanions **2a–h** toward nitrostyrenes is generally the same as that toward benzhydrylium ions and quinone methides, the reference electrophiles of our scales. Slight deviations from this order will be discussed below.

Substitution of the rate constants k_2 (Table 3) and the previously published N and s_N parameters of the carbanions (Table 1) into eq 1 allows one to calculate the electrophilicity parameters E for the *trans*-β-nitrostyrenes **1a–f**. The values of E, which are listed in Table 3, were obtained by minimization of Δ^2, that is, the squares of the deviations between experimental and calculated rate constants, $\Delta = (\log k_2^{exp}) - s_N(N + E)$.

The correlations in Figure 2 show that the rate constants for the reactions of **1a–f** with the carbanions **2b–f** are fairly reproduced by eq 1, that is, the experimental points are close to the calculated correlation lines. Some systematic deviations are obvious, however. Thus, the anion of Meldrum's acid **2a** reacts faster with all nitrostyrenes, particularly with the less reactive nitrostyrenes **1a–d**. Furthermore, the malonate anion **2g** reacts more slowly, and the nitromethyl anion **2h** reacts faster with the nitrostyrenes **1b–d** than expected from their benzhydrylium-derived reactivity parameters N and s_N. While the origin of these deviations is not known, it should be noted that analogous deviations have also been observed for the reactions of these carbanions with benzylidene Meldrum's acids[42] and benzylidene dimethylbarbituric and thiobarbituric acids.[41] The last column of Table 3 quantifies these deviations and shows that the absolute value of $\log(k_2^{exp}/k_2^{calcd})$ is always smaller than 0.76, corresponding to a maximum deviation between calculated and experimental rate constants of a factor of 6, which we consider tolerable for a reactivity model covering a reactivity range of almost 40 orders of magnitude with only three parameters.

The nucleophilic reactivities of most carbanions are reduced in protic solvents, and the reactivity parameters of stabilized carbanions have been determined in several solvents.[60−62] Table 4 shows that also the rate constants for the reactions of

Table 3. Second-Order Rate Constants k_2 for the Reactions of Carbanions **2a**–**h** with *trans*-β-Nitrostyrenes **1a**–**f** in DMSO at 20 °C

electrophile	E^a	nucleophile	k_2^{exp} ($\mathrm{M^{-1}\,s^{-1}}$)	k_2^{calcd} ($\mathrm{M^{-1}\,s^{-1}}$)	$\log (k_2^{\mathrm{exp}}/k_2^{\mathrm{calcd}})$
1a	−14.70	**2a**	1.20 ± 0.04	2.09×10^{-1}	0.76
1a		**2b**	$(2.02 \pm 0.04) \times 10$	1.61×10	0.10
1a		**2c**	$(1.49 \pm 0.05) \times 10^{2}$	1.40×10^{2}	0.03
1a		**2d**	$(4.5 \pm 0.1) \times 10^{2}$	7.0×10^{2}	−0.20
1a		**2e**	$(9.8 \pm 0.4) \times 10^{2}$	1.3×10^{3}	−0.13
1a		**2f**	$(1.26 \pm 0.01) \times 10^{3}$	1.98×10^{3}	−0.19
1a		**2g**	$(1.00 \pm 0.02) \times 10^{3}$	3.87×10^{3}	−0.59
1a		**2h**	$(3.7 \pm 0.2) \times 10^{3}$	4.0×10^{3}	−0.03
1b	−14.23	**2a**	2.35 ± 0.04	5.32×10^{-1}	0.65
1b		**2b**	$(4.7 \pm 0.1) \times 10$	3.7×10	0.10
1b		**2c**	$(3.01 \pm 0.02) \times 10^{2}$	3.09×10^{2}	−0.01
1b		**2d**	$(1.25 \pm 0.04) \times 10^{3}$	1.47×10^{3}	−0.07
1b		**2e**	$(1.71 \pm 0.09) \times 10^{3}$	2.74×10^{3}	−0.20
1b		**2f**	$(2.77 \pm 0.04) \times 10^{3}$	4.09×10^{3}	−0.17
1b		**2g**	$(2.09 \pm 0.06) \times 10^{3}$	7.84×10^{3}	−0.57
1b		**2h**	$(9.6 \pm 0.3) \times 10^{3}$	7.7×10^{3}	0.09
1c	−13.85	**2a**	4.7 ± 0.2	1.1	0.62
1c		**2b**	$(9.2 \pm 0.4) \times 10$	7.3×10	0.10
1c		**2c**	$(4.87 \pm 0.05) \times 10^{2}$	5.80×10^{2}	−0.08
1c		**2d**	$(2.09 \pm 0.08) \times 10^{3}$	2.67×10^{3}	−0.11
1c		**2e**	$(2.76 \pm 0.02) \times 10^{3}$	4.89×10^{3}	−0.25
1c		**2f**	$(6.02 \pm 0.05) \times 10^{3}$	7.30×10^{3}	−0.08
1c		**2g**	$(3.4 \pm 0.2) \times 10^{3}$	1.4×10^{4}	−0.61
1c		**2h**	$(2.11 \pm 0.07) \times 10^{4}$	1.30×10^{4}	0.21
1d	−13.37	**2a**	8.2 ± 0.3	2.9	0.45
1d		**2b**	$(1.46 \pm 0.01) \times 10^{2}$	1.70×10^{2}	−0.07
1d		**2c**	$(1.32 \pm 0.01) \times 10^{3}$	1.30×10^{3}	0.01
1d		**2d**	$(4.58 \pm 0.08) \times 10^{3}$	5.72×10^{3}	−0.10
1d		**2e**	$(7.1 \pm 0.5) \times 10^{3}$	1.0×10^{4}	−0.16
1d		**2f**	$(1.23 \pm 0.02) \times 10^{4}$	1.53×10^{4}	−0.09
1d		**2g**	$(1.18 \pm 0.06) \times 10^{4}$	2.82×10^{4}	−0.38
1d		**2h**	$(4.3 \pm 0.3) \times 10^{4}$	2.5×10^{4}	0.23
1e	−12.61	**2a**	$(2.32 \pm 0.04) \times 10$	1.32×10	0.24
1e		**2b**	$(4.5 \pm 0.2) \times 10^{2}$	6.6×10^{2}	−0.17
1e		**2c**	$(3.74 \pm 0.08) \times 10^{3}$	4.73×10^{3}	−0.10
1e		**2d**	$(1.9 \pm 0.1) \times 10^{4}$	1.9×10^{4}	−0.01
1f	−12.37	**2a**	$(3.23 \pm 0.04) \times 10$	2.10×10	0.19
1f		**2b**	$(7.1 \pm 0.3) \times 10^{2}$	1.0×10^{3}	−0.15
1f		**2c**	$(5.5 \pm 0.2) \times 10^{3}$	7.0×10^{3}	−0.11
1f		**2d**	$(3.1 \pm 0.1) \times 10^{4}$	2.8×10^{4}	0.04

[a] The E parameters for **1a**–**f** result from a least-squares minimization of Δ^2, with $\Delta = \log k_2^{\mathrm{exp}} - s_N(N + E)$; k_2^{exp} is taken from this table, and N and s_N of the carbanions **2a**–**h** are from Table 1.

1b with **2e** and **2f** in methanol are almost perfectly (within a factor of 2.1) reproduced by eq 1.

In order to check the applicability of the electrophilicity parameters E of the *trans*-β-nitrostyrenes **1** for the prediction of the rates of their reactions with other types of nucleophiles, we measured the rates of the reactions of the *trans*-β-nitrostyrenes **1b** and **1c** with the enamines **6a** and **6b** in dichloromethane. We then compared these measured rate constants with those calculated by eq 1 from the previously published parameters N and s_N for these enamines[63] and the E parameters of the *trans*-β-nitrostyrenes **1** listed in Table 3. Table 5 shows that also in these cases, the deviations between calculated and experimental rate constants are around a factor of 2 or less, despite the fact that the E values for **1b** and **1c** were determined in DMSO.

Table 6 shows that also the rate constants for the reactions of piperidine and morpholine with β-nitrostyrenes calculated by eq 1 agree within a factor of 3–20 with those previously measured by Bernasconi in aqueous solution of ion strength $\mu = 0.5$ M.[64] As the electrophilicity parameters of the nitrostyrenes determined in DMSO were used for these calculations, the fair agreement between experimental and calculated numbers again confirms that the use of solvent-independent electrophilicity parameters is justified in many cases because solvent effects are considered in the nucleophile-specific parameters N and s_N.[65]

The Hammett plot in Figure 3 shows a good correlation between the electrophilicity parameters E of the *trans*-β-nitrostyrenes **1** and the Hammett σ_p values for the para-substituents.[67] One can see that the reactivities of the *trans*-β-nitrostyrenes **1** are affected more by variation of the para-substituents than the reactivities of the aryl-substituted quinone methides **8** but less than the reactivities of the arylidenemal-

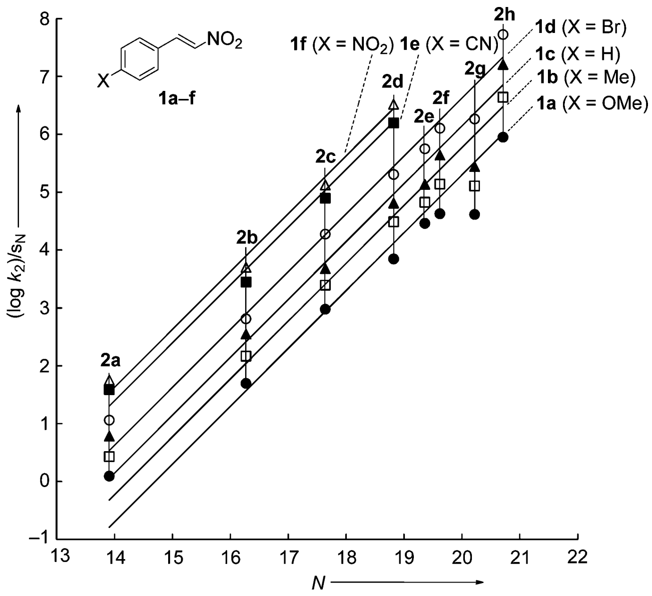


Figure 2. Correlation of $(\log k_2)/s_N$ versus the nucleophilicity parameters N of the carbanions **2a**–**h** for their reactions with *trans*-β-nitrostyrenes **1a**–**f** in DMSO at 20 °C. Correlation lines are fixed at a slope of 1.0, as required by eq 1.

Table 4. Comparison of Measured and Calculated Second-Order Rate Constants k_2 for the Reactions of the Carbanions 2e and 2f with *trans*-4-Methyl-β-nitrostyrene (1b) in MeOH at 20 °C

nucleophile	N, s_N[a]	k_2^{exp} (M^{-1} s^{-1})	k_2^{calcd} (M^{-1} s^{-1})
2e (malononitrile-Na)	18.21, 0.69	384 ± 15	557
2f (ethyl cyanoacetate-Na)	18.59, 0.65	322 ± 8	682

[a] Reactivity parameters N and s_N for carbanions in methanol from ref 60.

onates **9**. Multiplication of the slopes of these correlations (1.79–3.45, Figure 3) with the s_N values of the nucleophilic reaction partners yields the Hammett reaction constants ρ.

■ CONCLUSION

The reactivities of the *trans*-β-nitrostyrenes **1** toward nucleophiles can be described by eq 1; the experimental rate constants of the reactions of **1** with carbanions in DMSO and in methanol as well as with enamines in dichloromethane and with secondary amines in water agree within 1 order of magnitude with the rate constants calculated by eq 1. As illustrated in Figure 4, the β-nitrostyrenes **1** are considerably more electrophilic than substituted benzylidenemalonates and less electrophilic than analogously substituted benzylidenemalononitriles. The fairly good correlation between E and Hammett's σ_p values (Figure 3) allows one to estimate the electrophilicity parameter E for almost any *trans*-β-nitrostyrene, which can be combined with the numerous published N and s_N parameters of nucleophiles[69] to predict scope and limitations of nucleophilic additions to *trans*-β-nitrostyrenes on the basis of eq 1.

Table 6. Comparison of Measured[a] and Calculated Rate Constants k_2 for the Reactions of β-Nitrostyrenes 1a,c–f with Secondary Amines in Water at 20 °C

amine (N, s_N)[b]	β-nitrostyrene	k_2^{exp} (M^{-1} s^{-1})	k_2^{calcd} (M^{-1} s^{-1})
piperidine (18.13, 0.44)	**1a**	622	32.3
	1c	661	76.4
	1d	796	124
	1e	989	268
	1f	1100	342
morpholine (15.62, 0.54)	**1c**	137	9.03

[a] Experimental second-order rate constants k_2^{exp} from ref 64. [b] Reactivity parameters N and s_N from ref 66.

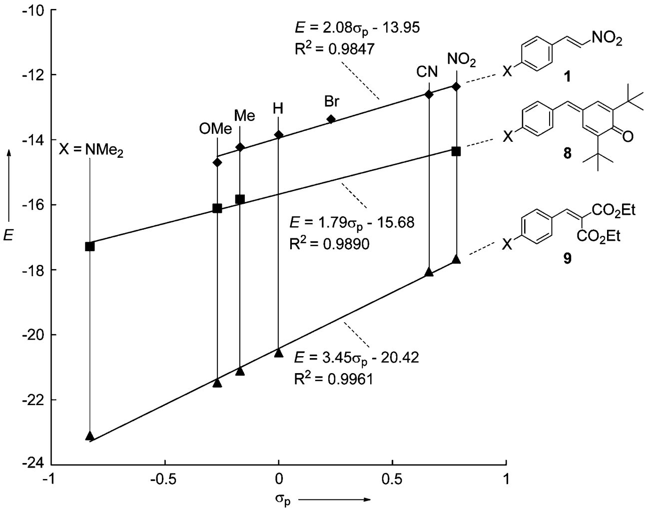
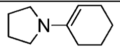
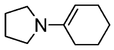
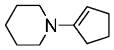


Figure 3. Correlations of the electrophilicity parameters E of **1**, **8** (from ref 37), and **9** (from ref 68) with Hammett's σ_p values (from ref 67).

■ EXPERIMENTAL SECTION

Materials. Commercially available DMSO (with <50 ppm H_2O content), MeOH (HPLC grade), and triethylamine (pure, <0.5% H_2O content) were used without further purification. Dichloromethane was freshly distilled over CaH_2. *n*-Pentane was freshly distilled over

Table 5. Comparison of Measured and Calculated Second-Order Rate Constants k_2 for the Reactions of the Enamines 6a and 6b with Electrophiles 1b and 1c in Dichloromethane at 20 °C

	Enamine	N, s_N[a]	β-Nitrostyrene	k_2^{exp} (M^{-1} s^{-1})	k_2^{calcd} (M^{-1} s^{-1})
6a		14.91, 0.86	**1b**	3.1 ± 0.1	3.8
6a		14.91, 0.86	**1c**	7.1 ± 0.3	8.2
6b		15.06, 0.82	**1c**	21.1 ± 0.7	9.82

[a] Reactivity parameters N and s_N from ref 63.

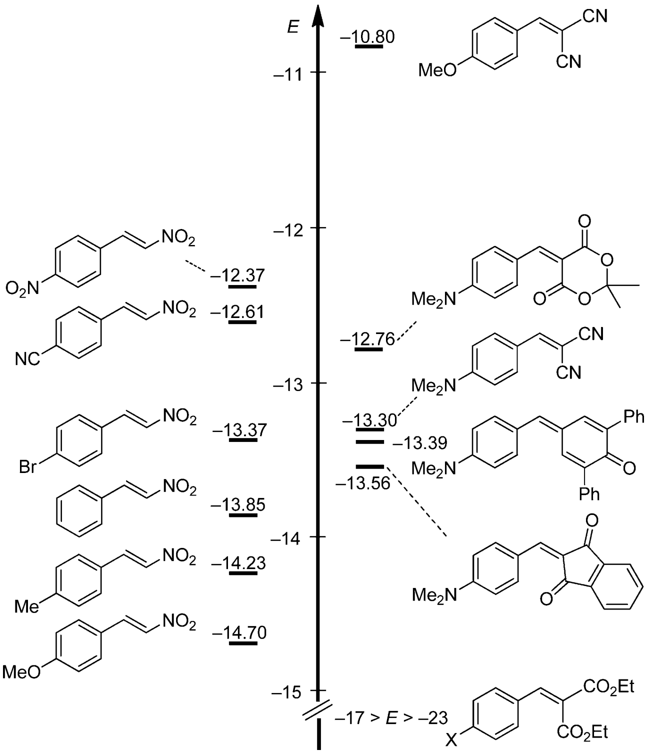


Figure 4. Comparison of electrophilicity parameters E for differently substituted Michael acceptors and quinone methides.[69]

sodium. All reactions were performed under an atmosphere of dry nitrogen. Compounds **1a**−**d** were purchased and purified by recrystallization from ethanol. The cyano- and nitro-substituted β-nitrostyrenes **1e** and **1f** were synthesized by Henry reactions.[2] The ^{1}H and ^{13}C NMR chemical shifts are given in ppm and refer to DMSO-d_6 (δ_H = 2.50 ppm, δ_C = 39.52 ppm) or to CDCl$_3$ (δ_H = 7.26 ppm, δ_C = 77.16 ppm) as internal standards.[70] The chemical shifts given in brackets are extracted from product spectra using DAVINX software.[56] The coupling constants are given in Hz. The following abbreviations are used for chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. NMR signal assignments in Table 2 are based on additional 2D-NMR experiments (COSY, HSQC). Diastereomeric ratios were determined by ^{1}H NMR spectroscopy.

Preparation of Potassium Salts 2-K. The potassium salts (**2a**−**g**)-**K** were generated by mixing solutions of KOEt in dry EtOH with a solution of the corresponding CH acids (**2a**−**g**)-**H** in dry EtOH under nitrogen atmosphere. To precipitate the product, dry n-pentane was added. The precipitates were filtered and dried in vacuo (40 °C/5 × 10^{-3} mbar) to obtain (**2a**−**g**)-**K** as colorless solids. CAUTION: Neat **2h-K** must not be isolated as it is known to be explosive.

Product Studies. *General Procedure A.* The nitrostyrenes **1** (0.090 mmol) and the potassium salts **2-K** (0.090 mmol) were dissolved in dry DMSO-d_6 (0.7 mL) in an NMR tube and shaken vigorously. The resulting solutions of the addition products were directly characterized by ^{1}H and ^{13}C NMR spectroscopy.

General Procedure B. The nitrostyrenes **1** and the CH acids **2-H** (2 equiv) were dissolved in dry dichloromethane (5 mL) under a nitrogen atmosphere. After addition of triethylamine (1 mol %), the mixture was stirred for 24 h at ambient temperature. Then, the solvent was removed under reduced pressure. The crude products were recrystallized from ethanol.

*Potassium 5-(1-(4-Methoxyphenyl)-2-nitroethyl)-2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ide (**4aa-K**).* From **1a** and **2a-K** by following general procedure A. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 1.39 (s, 6 H), 3.69 (s, 3 H), [ABC system at δ = 4.53 (J = 7.5, 9.0 Hz), 5.08 (J = −11.3, 7.5 Hz), 5.09 (J = −11.3, 9.0 Hz)], 6.73−6.77 (m, 2 H), 7.25−7.29 (m, 2 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 25.8, 40.0, 54.9, 72.9, 79.0, 99.2, 113.0, 128.6, 135.8, 157.3, 164.7.

*Potassium 2,2-Dimethyl-5-(2-nitro-1-p-tolylethyl)-4,6-dioxo-1,3-dioxan-5-ide (**4ba-K**).* From **1b** and **2a-K** by following general procedure A. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 1.38 (s, 6 H), 2.22 (s, 3 H), [ABC system at δ = 4.55 (J = 8.0, 8.4 Hz), 5.10 (J = −13.0, 8.4 Hz), 5.10 (J = −13.0, 8.0 Hz)], 6.98−7.00 (m, 2 H), 7.22−7.24 (m, 2 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 20.6, 25.8, 39.8, 72.8, 78.8, 99.2, 127.5, 128.1, 134.3, 140.7, 164.7.

*Potassium 2,2-Dimethyl-5-(2-nitro-1-phenylethyl)-4,6-dioxo-1,3-dioxan-5-ide (**4ca-K**).* From **1c** and **2a-K** by following general procedure A. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 1.39 (s, 6 H), [ABC system at δ = 4.59 (J = 8.1, 8.2 Hz), 5.13 (J = −12.4, 8.1 Hz), 5.15 (J = −12.4, 8.2 Hz)], 7.08−7.11 (m, 1 H), 7.17−7.21 (m, 2 H), 7.34−7.36 (m, 2 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 25.8, 40.1, 72.7, 78.6, 99.2, 125.5, 127.57, 127.59, 143.7, 164.7.

*Potassium 5-(1-(4-Bromophenyl)-2-nitroethyl)-2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ide (**4da-K**).* From **1d** and **2a-K** by following general procedure A. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 1.39 (s, 6 H), [ABC system at δ = 4.56 (J = 7.9, 8.4 Hz), 5.11 (J = −12.1, 7.9 Hz), 5.15 (J = −12.1, 8.4 Hz)], 7.30−7.32 (m, 2 H), 7.37−7.39 (m, 2 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 25.7, 39.6, 72.5, 78.2, 99.4, 118.5, 129.8, 130.4, 143.1, 164.6.

*Potassium 5-(1-(4-Cyanophenyl)-2-nitroethyl)-2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ide (**4ea-K**).* From **1e** and **2a-K** by following general procedure A. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 1.38 (s, 6 H), [ABC system at δ = 4.66 (J = 7.8, 8.4 Hz), 5.14 (J = −12.4, 7.8, Hz), 5.23 (J = −12.4, 8.4 Hz)], 7.52−7.54 (m, 2 H), 7.66−7.68 (m, 2 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 25.7, 40.1, 72.3, 77.6, 100.0, 108.3, 119.1, 128.4, 131.6, 149.5, 164.5.

*Potassium 2,2-Dimethyl-5-(2-nitro-1-(4-nitrophenyl)ethyl)-4,6-dioxo-1,3-dioxan-5-ide (**4fa-K**).* From **1f** and **2a-K** by following general procedure A. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 1.39 (s, 6 H), [ABC system at δ = 4.72 (J = 7.7, 8.5 Hz), 5.17 (J = −12.6, 7.7 Hz), 5.28 (J = −12.6, 8.5 Hz)], 7.59−7.62 (m, 2 H), 8.08−8.10 (m, 2 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 25.7, 39.9, 72.3, 77.5, 99.5, 122.9, 128.5, 145.5, 151.7, 164.5.

*Potassium 1-(1-(4-Methoxyphenyl)-2-nitroethyl)-4,4-dimethyl-2,6-dioxocyclohexan-1-ide (**4ab-K**).* From **1a** and **2b-K** by following general procedure A. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 0.86 (s, 6 H), 1.85 (s, 4 H), 3.66 (s, 3 H), [ABC system at δ = 4.87 (J = 6.3, 9.4 Hz), 4.88 (J = −12.0, 6.3 Hz), 5.38 (J = −12.0, 9.4 Hz)], 6.66−6.69 (m, 2 H), 7.24−7.27 (m, 2 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 28.9, 31.2, 38.6, 51.0, 80.2, 107.5, 112.6, 128.9, 137.0, 156.8, 187.3.

*Potassium 4,4-Dimethyl-1-(2-nitro-1-p-tolylethyl)-2,6-dioxocyclohexan-1-ide (**4bb-K**).* From **1b** and **2b-K** by following general procedure A. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 0.86 (s, 6 H), 1.85 (s, 4 H), 2.19 (s, 3 H), [ABC system at δ = 4.88 (J = −12.0, 6.3 Hz), 4.90 (J = 6.3, 9.3 Hz), 5.40 (J = −12.0, 9.3 Hz)], 6.90−6.92 (m, 2 H), 7.20−7.22 (m, 2 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 20.6, 28.9, 31.2, 38.8, 51.0, 79.9, 107.5, 127.79, 127.84, 133.5, 141.8, 187.3.

*Potassium 4,4-Dimethyl-1-(2-nitro-1-phenylethyl)-2,6-dioxocyclohexan-1-ide (**4cb-K**).* From **1c** and **2b-K** by following general procedure A. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 0.86 (s, 6 H), 1.86 (s, 4 H), [ABC system at δ = 4.93 (J = −12.1, 6.3 Hz), 4.95 (J = 6.3, 9.1 Hz), 5.42 (J = −12.1, 9.1 Hz)], 7.00−7.04 (m, 1 H), 7.09−7.13 (m, 2 H), 7.33−7.35 (m, 2 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 28.9, 31.2, 39.2, 51.0, 79.7, 107.3, 124.9, 127.2, 127.9, 144.9, 187.4.

*Potassium 1-(1-(4-Bromophenyl)-2-nitroethyl)-4,4-dimethyl-2,6-dioxocyclohexan-1-ide (**4db-K**).* From **1d** and **2b-K** by following general procedure A. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 0.85 (s, 6 H), 1.86 (s, 4 H), [ABC system at δ = 4.88 (J = −12.4, 6.1 Hz), 4.92 (J = 6.1, 9.5 Hz), 5.46 (J = −12.4, 9.5 Hz)], 7.30 (s, 4 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 28.8, 31.2, 38.6, 50.8, 79.2, 107.0, 117.8, 130.0, 130.1, 144.3, 187.3.

*Potassium 1-(1-(4-Cyanophenyl)-2-nitroethyl)-4,4-dimethyl-2,6-dioxocyclohexan-1-ide (**4eb-K**).* From **1e** and **2b-K** by following general procedure A. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) =

0.85 (s, 6 H), 1.89 (s, 4 H), [ABC system at δ = 4.94 (*J* = −12.7, 6.3 Hz), 5.04 (*J* = 6.3, 9.3 Hz), 5.51 (*J* = −12.7, 9.3 Hz)], 7.49−7.51 (m, 2 H), 7.59−7.61 (m, 2 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 28.6, 31.3, 38.8, 50.2, 78.2, 107.1, 107.7, 119.2, 128.5, 131.4, 150.3, 187.2.

*Potassium 4,4-Dimethyl-1-(2-nitro-1-(4-nitrophenyl)ethyl)-2,6-dioxocyclohexan-1-ide (**4fb-K**).* From **1f** and **2b-K** by following general procedure A. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 0.84 (s, 6 H), 1.87 (s, 4 H), [ABC system at δ = 4.92 (*J* = −12.8, 5.9 Hz), 5.10 (*J* = 5.9, 9.5 Hz), 5.59 (*J* = −12.8, 9.5 Hz)], 7.57−7.59 (m, 2 H), 8.01−8.04 (m, 2 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 28.7, 31.2, 38.8, 50.5, 78.2, 106.7, 122.6, 128.5, 145.0, 153.0, 187.4.

*3-(1-(4-Methoxyphenyl)-2-nitroethyl)pentane-2,4-dione (**5ac**).* Obtained from **1a** (129 mg, 0.720 mmol) and **2c-H** following general procedure B: 158 mg (0.566 mmol, 79%), yellow solid, mp 115−117 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) = 1.94 (s, 3 H), 2.28 (s, 3 H), 3.77 (s, 3 H), [ABCD system at δ = 4.19 (*J* = 4.5, 8.3, 11.0 Hz), 4.33 (*J* = 11.0 Hz), 4.58 (*J* = −12.4, 4.5 Hz), 4.59 (*J* = −12.4, 8.3 Hz)], 6.81−6.86 (m, 2 H), 7.07−7.12 (m, 2 H). ^{13}C NMR (75.5 MHz, CDCl$_3$): δ (ppm) = 29.6, 30.5, 42.2, 55.4, 71.0, 78.6, 114.8, 127.7, 129.2, 159.6, 201.3, 202.0. Anal. Calcd for $C_{14}H_{17}NO_5$: C, 60.21; H, 6.14; N, 5.02. Found: C, 60.07; H, 6.17; N, 4.99.

*3-(2-Nitro-1-p-tolylethyl)pentane-2,4-dione (**5bc**).* Obtained from **1b** (124 mg, 0.760 mmol) and **2c-H** following general procedure B: 142 mg (0.539 mmol, 71%), colorless solid, mp 104 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 1.93 (s, 3 H), 2.28 (s, 3 H), 2.30 (s, 3 H), [ABCD system at δ = 4.20 (*J* = 4.4, 8.5, 10.9 Hz), 4.35 (*J* = 10.9 Hz), 4.59 (*J* = −12.3, 4.4 Hz), 4.60 (*J* = −12.3, 8.5 Hz)], 7.04−7.07 (m, 2 H), 7.11−7.13 (m, 2 H). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 21.2, 29.6, 30.6, 42.6, 70.9, 78.5, 127.9, 130.1, 132.9, 138.5, 201.3, 202.0. Anal. Calcd for $C_{14}H_{17}NO_4$: C, 63.87; H, 6.51; N, 5.32. Found: C, 63.83; H, 6.53; N, 5.31.

*3-(2-Nitro-1-phenylethyl)pentane-2,4-dione (**5cc**).* Obtained from **1c** (179 mg, 1.20 mmol) and **2c-H** following general procedure B: 212 mg (0.851 mmol, 71%), pale yellow solid, mp 111−112 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) = 1.93 (s, 3 H), 2.28 (s, 3 H), [ABCD system at δ = 4.21 (*J* = 4.3, 8.5, 10.8 Hz), 4.34 (*J* = 10.8 Hz), 4.59 (*J* = −12.4, 4.3 Hz), 4.61 (*J* = −12.4, 8.5 Hz)], 7.16−7.20 (m, 2 H), 7.28−7.36 (m, 3 H). ^{13}C NMR (75.5 MHz, CDCl$_3$): δ (ppm) = 29.7, 30.6, 42.9, 70.8, 78.3, 128.1, 128.7, 129.5, 136.1, 201.1, 201.9. Anal. Calcd for $C_{13}H_{15}NO_4$: C, 62.64; H, 6.07; N, 5.62. Found: C, 62.51; H, 6.04; N, 5.60.

*3-(1-(4-Bromophenyl)-2-nitroethyl)pentane-2,4-dione (**5dc**).* Obtained from **1d** (141 mg, 0.618 mmol) and **2c-H** following general procedure B: 127 mg (0.387 mmol, 63%), colorless solid, mp 135−137 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) = 1.97 (s, 3 H), 2.29 (s, 3 H), [ABCD system at δ = 4.21 (*J* = 3.8, 8.9, 10.8 Hz), 4.32 (*J* = 10.8 Hz), 4.60 (*J* = −12.6, 3.8 Hz), 4.61 (*J* = −12.6, 8.9 Hz)], 7.05−7.09 (m, 2 H), 7.44−7.48 (m, 2 H). ^{13}C NMR (75.5 MHz, CDCl$_3$): δ (ppm) = 29.8, 30.6, 42.3, 70.6, 78.0, 122.8, 129.8, 132.6, 135.2, 200.7, 201.5. Anal. Calcd for $C_{13}H_{14}BrNO_4$: C, 47.58; H, 4.30; N, 4.27. Found: C, 47.56; H, 4.40; N, 4.22.

*4-(3-Acetyl-1-nitro-4-oxopent-2-yl)benzonitrile (**5ec**).* Obtained from **1e** (127 mg, 0.729 mmol) and **2c-H** following general procedure B. The crude product was purified by column chromatography (silica gel 70−230 mesh; gradient eluent: *n*-pentane/ethyl acetate = 12/1 to 3/1) and then recrystallized from ethanol: 76 mg (0.28 mmol, 38%), colorless solid, mp 127−128 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) = 2.00 (s, 3 H), 2.31 (s, 3 H), [ABCD system at δ = 4.31 (*J* = 4.1, 8.7, 10.6 Hz), 4.36 (*J* = 10.6 Hz), 4.64 (*J* = −13.0, 4.1 Hz), 4.66 (*J* = −13.0, 8.7 Hz)], 7.31−7.35 (m, 2 H), 7.62−7.66 (m, 2 H). ^{13}C NMR (75.5 MHz, DMSO-d_6): δ (ppm) = 30.1, 30.7, 42.7, 70.1, 77.5, 112.8, 118.1, 129.0, 133.1, 141.7, 200.1, 201.0. Anal. Calcd for $C_{14}H_{14}N_2O_4$: C, 61.31; H, 5.14; N, 10.21. Found: C, 61.14; H, 5.30; N, 10.19. IR (ATR) ν (cm^{-1}) = 726, 833, 860, 956, 1075, 1119, 1144, 1176, 1211, 1242, 1268, 1361, 1419, 1439, 1508, 1555, 1609, 1701, 1732.

*3-(2-Nitro-1-(4-nitrophenyl)ethyl)pentane-2,4-dione (**5fc**).* Obtained from **1f** (132 mg, 0.680 mmol) and **2c-H** following general procedure B. The crude product was purified by column chromatography (silica gel 70−230 mesh; gradient eluent: *n*-pentane/ethyl acetate = 11/1 to 4/1) and then recrystallized from ethanol: 100 mg (0.340 mmol, 50%), yellowish solid, mp 127−130 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) = 2.03 (s, 3 H), 2.32 (s, 3 H), [ABCD system at δ = 4.38 (*J* = 4.0, 8.9, 10.1 Hz), 4.39 (*J* = 10.1 Hz), 4.66 (*J* = −13.0, 4.0 Hz), 4.69 (*J* = −13.0, 8.9 Hz)], 7.38−7.43 (m, 2 H), 8.18−8.21 (m, 2 H). ^{13}C NMR (75.5 MHz, CDCl$_3$): δ (ppm) = 30.1, 30.7, 42.4, 70.2, 77.5, 124.6, 129.3, 143.7, 148.0, 200.0, 200.9. Anal. Calcd for $C_{13}H_{14}N_2O_6$: C, 53.06; H, 4.80; N, 9.52. Found: C, 53.07; H, 4.89; N, 9.52.

*Ethyl 2-Acetyl-4-nitro-3-phenylbutanoate (**5cd**).* Obtained from **1c** (160 mg, 1.07 mmol) and **2d-H** following general procedure B: 165 mg (0.591 mmol, 55%, dr ≈ 1:8 from ^{1}H NMR integrals of the CH_3 signals of CH_3CO and OCH_2CH_3), colorless solid, mp 73−75 °C. ^{1}H NMR (300 MHz, CDCl$_3$, major diastereomer): δ (ppm) = 1.00 (t, *J* = 7.1 Hz, 3 H), 2.30 (s, 3 H), 3.96 (q, *J* = 7.1 Hz, 2 H), [ABCD system at δ = 4.09 (*J* = 10.0 Hz), 4.17 (*J* = 4.6, 8.3, 10.0 Hz), 4.72 (*J* = −13.1, 8.3 Hz), 4.72 (*J* = −13.1, 4.6 Hz)], 7.18−7.21 (m, 2 H), 7.26−7.34 (m, 3 H); additional signals for the minor diastereomer: δ (ppm) = 1.27 (t, *J* = 7.1 Hz, 0.4 H), 2.05 (s, 0.4 H). ^{13}C NMR (75.5 MHz, CDCl$_3$, major diastereomer): δ (ppm) = 13.8, 30.2, 42.4, 62.1, 78.0, 128.1, 128.4, 129.1, 136.5, 167.0, 201.3. HRMS (ESI): calcd for $C_{14}H_{16}NO_5^-$ $[M - H]^-$, 278.1034; found, 278.1038. Anal. Calcd for $C_{14}H_{17}NO_5$: C, 60.21; H, 6.14; N, 5.02. Found: C, 60.14; H, 6.28; N, 4.98.

*Potassium 1,1-Dicyano-3-nitro-2-phenylpropan-1-ide (**4ce-K**).* From **1c** and **2e-K** by following general procedure A. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = [ABC system at δ = 3.70 (*J* = 8.2, 8.4 Hz), 4.67 (*J* = −12.3, 8.4 Hz), 4.70 (*J* = −12.3, 8.2 Hz)], 7.18−7.31 (m, 5 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 40.0, 43.0, 79.8, 126.6, 127.0, 128.3, 129.9, 142.5.

*Ethyl 2-Cyano-4-nitro-3-phenylbutanoate (**5cf**).* Obtained from *trans-β*-nitrostyrene (**1c**) (298 mg, 2.00 mmol) and **2f-H** following general procedure B: 349 mg (1.33 mmol, 67%, dr ≈ 1.4:1 from ^{1}H NMR integrals of the CH_3 signals), colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$, major diastereomer): δ (ppm) = 1.13 (t, *J* = 7.2 Hz, 1.6 H), [ABCD system at δ = 3.93 (*J* = 5.7 Hz), 4.22 (*J* = 5.7, 6.2, 8.7 Hz), 4.92 (*J* = −13.6, 8.7 Hz), 5.01 (*J* = −13.6, 6.2 Hz)], 7.21−7.39 (m, 5 H); additional signals for the minor diastereomer: δ (ppm) = 1.22 (t, *J* = 7.2 Hz, 1.2 H), 4.09−4.15 (m, 1.6 H), 4.75−4.85 (m, 0.9 H). ^{13}C NMR (100 MHz, CDCl$_3$, major diastereomer): δ (ppm) = 13.8, 41.7, 42.8, 63.4, 76.1, 76.4, 114.4, 127.6, 128.0, 129.4, 129.5, 163.9.

*Diethyl 2-(2-Nitro-1-phenylethyl)malonate (**5cg**).* *trans-β*-Nitrostyrene (**1c**) (97 mg, 0.65 mmol) and **2g-K** (129 mg, 0.651 mmol) were dissolved in dry 1,4-dioxane (15 mL) and stirred for 10 min under nitrogen atmosphere. Subsequent addition of 2 M aqueous acetic acid (1 mL) furnished a precipitate, which was filtered. The crude product was purified by column chromatography (silica gel 70−230 mesh; gradient eluent: *n*-pentane/ethyl acetate =10/1 to 3/1) and then recrystallized from ethanol: 82 mg (0.27 mmol, 42%), yellow solid, mp 63−64 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) = 1.04 (t, *J* = 7.1 Hz, 3 H), 1.26 (t, *J* = 7.1 Hz, 3 H), 4.00 (q, *J* = 7.1 Hz, 2 H), 4.21−4.27 (m, 2 H), [ABCD system at δ = 3.79 (*J* = 9.4 Hz), 4.20 (*J* = 4.6, 9.4, 9.4 Hz), 4.83 (*J* = −13.1, 9.4 Hz), 4.89 (*J* = −13.1, 4.6 Hz)], 7.22−7.32 (m, 5 H). ^{13}C NMR (75.5 MHz, CDCl$_3$): δ (ppm) = 13.9, 14.1, 43.1, 55.1, 62.0, 62.3, 77.8, 128.1, 128.5, 129.0, 136.3, 166.9, 167.6.

*(1,3-Dinitroprop-2-yl)benzene (**5ch**).* *trans-β*-Nitrostyrene (**1c**) (171 mg, 1.15 mmol) was dissolved in nitromethane (10 mL) under nitrogen atmosphere; then, triethylamine (1 mol %) was added. The mixture was stirred at ambient temperature for 24 h. The solvent was removed in vacuo, and then, the crude product was purified by column chromatography (silica gel 70−230 mesh; gradient eluent: *n*-pentane/ethyl acetate =10/1 to 3/1): 121 mg (0.576 mmol, 50%), colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = [AA′BB′C system at δ = 4.31 (*J* = 7.0, 7.4 Hz), 4.75 (*J* = −13.4, 7.4 Hz), 4.78 (*J* = −13.4, 7.0 Hz)], 7.21−7.24 (m, 2 H), 7.36−7.41 (m, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 41.8, 76.8, 127.5, 129.2, 129.7, 134.3.

*1-(6-(2-Nitro-1-phenylethyl)cyclohex-1-enyl)pyrrolidine (rac-**7ca**).* *trans-β*-Nitrostyrene (**1c**) (298 mg, 2.00 mmol) and 1-

cyclohex-1-enylpyrrolidine (**6a**) (303 mg, 2.00 mmol) were dissolved in $CDCl_3$ (10 mL) at 0 °C. After 5 min, a sample was taken for NMR spectroscopy. Purification by column chromatography resulted in decomposition of the product. ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) = 1.32−1.44 (m, 3 H), 1.47−1.55 (m, 1 H), 1.74−1.86 (m, 4 H), 1.95−2.01 (m, 1 H), 2.04−2.09 (m, 1 H), 2.55−2.57 (m, 1 H), 2.69−2.72 (m, 2 H), 2.98−3.02 (m, 2 H), 3.63−3.68 (m, 1 H), 4.54 (t, J = 3.9 Hz, 1 H), 4.66 (dd, J = 10.6, 12.8 Hz, 1 H), 5.04 (dd, J = 5.5, 12.8 Hz, 1 H), 7.08−7.13 (m, 2 H), 7.15−7.18 (m, 1 H), 7.22−7.24 (m, 2 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) = 17.2, 23.8, 24.3, 25.2, 38.2, 47.9, 48.8, 79.6, 101.1, 127.4, 128.1, 128.8, 139.7, 144.6.

Kinetics. For the investigation of fast kinetics ($\tau_{1/2} < 30$ s), stopped-flow spectrophotometer systems were used. Slow kinetics ($\tau_{1/2} > 30$ s) were followed by using a conventional UV−vis diode array spectrophotometer system that was connected to a quartz immersion probe via fiber optic cables. Due to an overlap of the absorption bands, the rates of the reactions with the carbanions **2f** and **2h** were followed at the shoulders of the absorption bands of the electrophiles **1a**−**f**. Measurements at the shoulders of the absorption bands of the *trans*-β-nitrostyrenes **1e** and **1f** were also performed to determine the kinetics of their reactions with the carbanions **2a**−**d**. All measurements were carried out under first-order conditions (in general $[\mathbf{2}]_0/[\mathbf{1}]_0 > 10$). The first-order rate constants k_{obs} were obtained by least-squares fitting of the time-dependent absorbances A_t of the electrophiles to the exponential function $A_t = A_0 e^{-k_{obs}t} + C$. Second-order rate constans k_2^{exp} were then derived from linear correlations of k_{obs} versus $[\mathbf{2}]$.

Evaluating the kinetics of the reactions of the carbanions **2e** and **2f** with *trans*-β-nitrostyrene **1b** in methanol required consideration of the competing reactions of methoxide anions and methanol (eq 3).[71]

$$k_{obs} = k_2^{exp}[\mathbf{2}] + k_{2,MeO}[MeO^-] + k_{1,MeOH} \qquad (3)$$

Because the rate constant $k_{2,MeO}$ for the reaction between methoxide anion (N = 15.78 and s_N = 0.56 for MeO^- in MeOH)[71a] and **1b** (E = −14.23) was calculated by using eq 1 and $[MeO^-]$ was calculated based on the known K_{CH} values of the CH acids **2e-H** and **2f-H** in methanol,[71b] the terms for the reactions of **1b** with the carbanions and with methanol (eq 4, right) can be derived by rearranging eq 3 to eq 4.

$$k_{1\psi} = k_{obs} - k_{2,MeO}[MeO^-] = k_2^{exp}[\mathbf{2}] + k_{1,MeOH} \qquad (4)$$

Second-order rate constants k_2^{exp} for the reactions of **2e** and **2f** with **1b** in methanol were obtained from the slopes of the linear plots of $k_{1\psi}$ against the concentrations of the carbanions **2e** and **2f**, in analogy to the procedure described in ref 71b.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of the kinetic experiments, synthetic procedures, and NMR spectra of all characterized compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: herbert.mayr@cup.uni-muenchen.de.

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