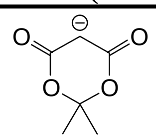
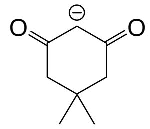
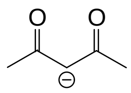
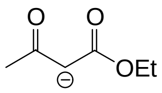
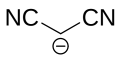
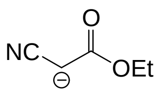
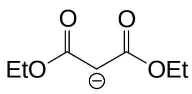
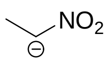
Supporting Information for *Angew. Chem. Int. Ed.* Z 17 625

Kinetics of Carbocation Carbanion Combinations: Key to a General Concept of Polar Organic Reactivity

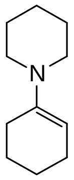
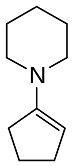
Roland Lucius, Robert Loos, Herbert Mayr*

Table S1. Comparison of the measured second-order rate constants k (from ref. 3) with k_{calc} calculated from equation (1) for the reactions of the quinone methides **1j**-**m** with the carbanions **2a**-**h** (DMSO, 20 °C).

nucleophile (N / s)		counterion[a]	quinone methide	k[b] / M^{-1} s^{-1}	k_{calc}[c] / M^{-1} s^{-1}
 (13.91 / 0.856)	**2a**[d]	K^+ / 18-crown-6	**1j**	$(2.06 \pm 0.01) \times 10^{-2}$	2.27×10^{-2}
			1k	$(1.38 \pm 0.01) \times 10^{-2}$	1.32×10^{-2}
 (16.27 / 0.767)	**2b**[d]	K^+ / 18-crown-6	**1j**	1.96 ± 0.03	2.19
			1k	1.26 ± 0.01	1.34
			1l	$(1.87 \pm 0.08) \times 10^{-1}$	1.65×10^{-1}
			1m	$(8.15 \pm 0.17) \times 10^{-2}$	5.67×10^{-2}
 (17.64 / 0.729)	**2c**[d]	K^+ / 18-crown-6	**1j**	$(2.15 \pm 0.06) \times 10^{1}$	2.07×10^{1}
			1k	$(1.31 \pm 0.02) \times 10^{1}$	1.30×10^{1}
			1l	1.97 ± 0.02	1.78
			1m	$(5.57 \pm 0.04) \times 10^{-1}$	6.43×10^{-1}
 (18.82 / 0.688)	**2d**[d]	K^+ / 18-crown-6	**1j**	$(1.28 \pm 0.03) \times 10^{2}$	1.14×10^{2}
			1k	$(7.98 \pm 0.21) \times 10^{1}$	7.38×10^{1}
			1l	$(1.07 \pm 0.05) \times 10^{1}$	1.12×10^{1}
			1m	3.52 ± 0.06	4.30
 (19.36 / 0.671)	**2e**	K^+ / 18-crown-6	**1j**	$(2.16 \pm 0.01) \times 10^{2}$	2.34×10^{2}
			1k	$(1.39 \pm 0.01) \times 10^{2}$	1.53×10^{2}
			1l	$(2.55 \pm 0.05) \times 10^{1}$	2.44×10^{1}
			1m	9.90 ± 0.05	9.58
 (19.62 / 0.668)	**2f**	$N(nBu)_4^+$	**1j**	$(3.49 \pm 0.05) \times 10^{2}$	3.40×10^{2}
			1k	$(2.13 \pm 0.04) \times 10^{2}$	2.22×10^{2}
			1l	$(3.39 \pm 0.04) \times 10^{1}$	3.58×10^{1}
			1m	$(1.43 \pm 0.02) \times 10^{1}$	1.41×10^{1}
 (20.22 / 0.654)	**2g**	$N(nBu)_4^+$	**1j**	$(8.65 \pm 0.07) \times 10^{2}$	7.42×10^{2}
			1k	$(5.17 \pm 0.07) \times 10^{2}$	4.89×10^{2}
			1l	$(6.99 \pm 0.13) \times 10^{1}$	8.18×10^{1}
			1m	$(2.89 \pm 0.02) \times 10^{1}$	3.28×10^{1}
 (21.93 / 0.568)	**2h**	$N(nBu)_4^+$	**1k**	$(2.06 \pm 0.05) \times 10^{3}$	2.03×10^{3}
			1l	$(4.12 \pm 0.10) \times 10^{2}$	4.30×10^{2}
			1m	$(2.00 \pm 0.05) \times 10^{2}$	1.95×10^{2}

[a] The potassium salts were combined with 1.01 to 1.10 equivalents 18-crown-6. [b] The listed rate constants have been averaged from two to five experiments with different anion concentrations. [c] The values of k_{calc} were calculated with more decimals of E, N and s than indicated in the table. The use of the E, N and s parameters given in this table leads to slightly deviating numbers. [d] With addition of 0.5 to 2.5 equivalents of the corresponding acid of the carbanion **2**.

Table S2. Comparison of the second order rate constants k for the reactions of the quinone methides **1g**,**h** with the enamines **3a**,**b** in DMSO and CH_2Cl_2 at 20 °C.

nucleophile		electrophile	solvent	k[a] / M^{-1} s^{-1}	k_{calc} [eq.(1)] / M^{-1} s^{-1}
 **3a**	N = 13.36[b] s = 0.81[b]	**1g**	DMSO	(1.67 ± 0.03) × 10^4	6.78 × 10^3
		1g	CH_2Cl_2	(2.45 ± 0.02) × 10^3	6.78 × 10^3
		1h	DMSO	(2.11 ± 0.09) × 10^1	9.03
		1h	CH_2Cl_2	2.75 ± 0.05	9.03
 **3b**	N = 14.95[c] s = 0.83[c]	**1g**	DMSO	(2.65 ± 0.12) × 10^5	1.76 × 10^5
		1g	CH_2Cl_2	(4.13 ± 0.03) × 10^4	1.76 × 10^5
		1h	DMSO	5.95 × 10^2	1.99 × 10^5
		1h	CH_2Cl_2	(6.02 ± 0.04) × 10^1	1.99 × 10^5

[a] The listed rate constants have been averaged from three to five experiments with different enamine concentrations. [b] Reactivity parameters from ref. [2a]. [c] Reactivity parameters from ref. [13b].

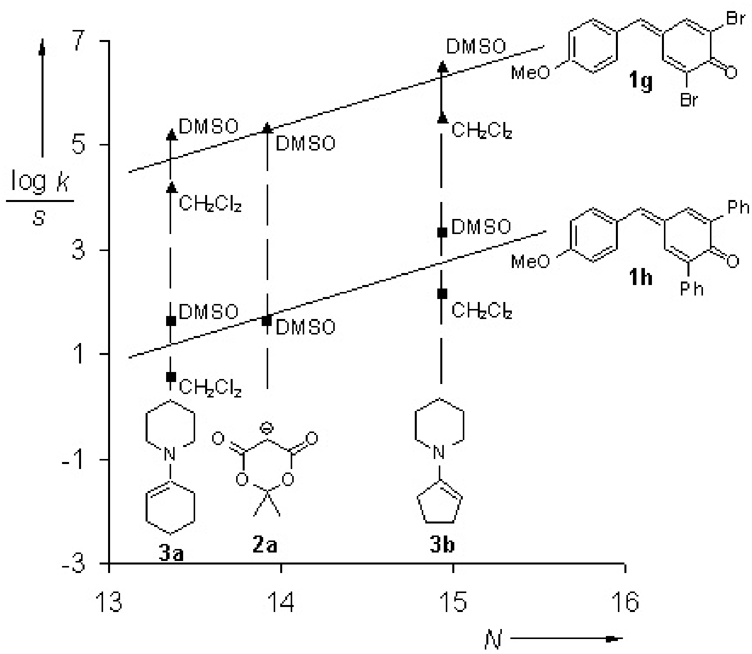


Figure S1. Rate constants for the reactions of the quinone methides **1g** and **1h** with the enamines **3a** and **3b** in DMSO and CH_2Cl_2. The correlation lines are calculated from E, N and s in Tables 2, 3 and S2.