[15] (−)-Me-DuPHOS (−)-**7** = (−)-1,2-bis((2*R*,5*R*)2,5-dimethylphospholanyl)benzene; M. J. Burk, J. E. Feaster, W. A. Nugent, R. L. Harlow, *J. Am. Chem. Soc.* **1993**, *115*, 10125 – 10138.

[16] (−)-JOSIPHOS (−)-**8** = (−)-(*R*-(1)-[(*S*)-2-(diphenylphosphanyl)ferrocenyl]ethyldicyclohexylphosphane; A. Togni, C. Breutel, A. Schnyder, F. Spindler, H. Landert, A. Tijani, *J. Am. Chem. Soc.* **1994**, *116*, 4062 – 4066.

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[19] Treatment of (−)-**7** in Et_2O with 1 equiv. $HBF_4 \cdot Et_2O$ precipitates (−)-**7** · HBF_4 but generation and isolation of (−)-**7** · $2HBF_4$ by reaction with excess $HBF_4 \cdot Et_2O$, and comproportionation with 1 equiv. (−)-**7** (see Experimental Section) is somewhat more convenient. Both salts can be isolated as analytically pure, crystalline solids. The solid-state structure of (−)-**7** · HBF_4 was determined by X-ray diffraction. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-138771. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[22] ^{31}P NMR (161.9 MHz, CD_2Cl_2, 300 K): $\delta = 79.2$, 86.2 (d, $J_{PP} = 30.5$ Hz).

[23] This quality still contains ~5% of **12**, as determined by ^{31}P NMR.

Constant Selectivity Relationships of Addition Reactions of Carbanions**

Roland Lucius and Herbert Mayr*

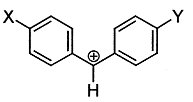
Dedicated to Professor Rolf Saalfrank
on the occasion of his 60th birthday

Reactions of carbocations and related electrophiles with uncharged nucleophiles obey the linear free-energy relationship given in [Eq. (1)], where E = electrophilicity parameter, N = nucleophilicity parameter, and s = nucleophile-specific slope parameter.[1]

$$\log k\ (20\,^{\circ}\text{C}) = s(N + E) \qquad (1)$$

Since the slope parameter s is usually close to unity, it may be neglected for qualitative considerations, so that in practice reactions will be sufficiently fast at 20 °C if $(N + E) > -5$. Since the change of polarity is small in the rate-determining step of these ion – molecule reactions, the solvent effects on reaction rates are also small and can, to a first approximation, be neglected.[1c]

For the development of reactivity scales for uncharged nucleophiles, the benzhydryl cations **1** proved to be extraordinarily suitable reference electrophiles since their electrophilicities can be altered by almost 20 orders of magnitude by varying the substituents X and Y but the steric situation at the reactive site remains constant. Benzhydryl cations with amino groups in the *p*-position are the weakest reference electrophiles used so far to characterize the nucleophilicities of silyl enol ethers,[2] silyl ketene acetals,[2] and enamines.[3] In order to perform kinetic investigations with still stronger nucleophiles, a further reduction of the electrophilicity of benzhydryl cations is necessary, which may be achieved be employing the strong electron donor O^- at the position X or Y of compound **1**. Thus, the quinone methides **2** represent uncharged analogues of the benzhydryl cations **1**, which again allows a variation of electrophilicity under a constant steric situation. Richard et al.,[4] have already reported that quinone methides behave as highly resonance-stabilized carbocations.



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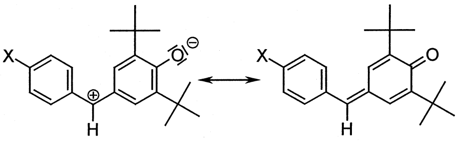

2

The quinone methides **2a – d** are accessible through a Mannich-type reaction from 2,6-di-*tert*-butylphenol in a one-pot procedure.[5] For the determination of the reaction rates, the potassium[6] or tetra-*n*-butylammonium[7] salts of the carbanions **3** were dissolved in DMSO. After addition of 0.02 to 0.2 equivalents of **2**, the change in their UV/Vis absorbance between $\lambda = 200 - 600$ nm was monitored with a diode-array spectrometer,[8a] and featuring a fiber-optic immersion probe.[8b] The pseudo first-order rate constants, $k_{1\psi}$, determined from the exponential decay of the absorbance at the absorption maximum, were divided by the carbanion concentration to yield the concentration-independent rate constant k [Eq. (2)], to prove that second-order kinetics are present.

$$-\,\mathrm{d}[\mathbf{2}]/\mathrm{d}t = k[\mathbf{2}][\mathbf{3}] = k_{1\psi}[\mathbf{2}]$$
$$k = k_{1\psi}/[\mathbf{3}] \qquad (2)$$

The observation of isosbestic points (Figure 1) excludes long-lived intermediates, and one can assume the simple mechanism outlined in Scheme 1.

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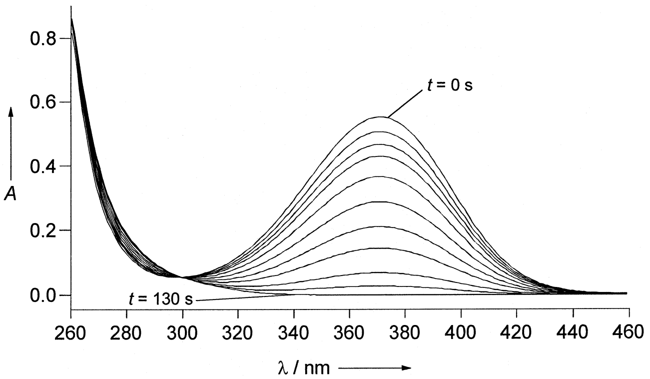
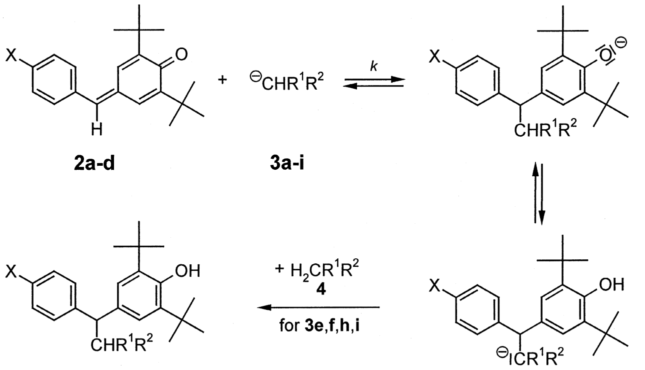


Figure 1. UV spectra during the reaction of the quinone methide **2d** with the tetra-*n*-butylammonium salt of ethyl cyanoacetate **3c** (DMSO, 20 °C).



Scheme 1. Reactions of the quinone methides **2a–d** with the carbanions **3a–i**.

Table 1 shows that under these reaction conditions, at carbanion concentrations $10^{-4}-10^{-3}$ mol L^{-1}, equal reaction rates are found for the tetra-*n*-butylammonium and potassium salts in presence or absence of crown ether or cryptand. The addition reactions of the carbanions **3e,f,h,i** do not proceed quantitatively. In the presence of an excess of **4**, the corresponding acids of the carbanions **3**, the equilibrium is shifted so far towards the products that the final concentrations of the quinone methides **2** are negligibly small.

Table 1. Influence of the counterion on the rate constants of the addition reactions of **2** with the anions **3** in DMSO at 20 °C.

Electrophile	⊖CHR¹R²	Counterion	k[d] [L mol^{-1} s^{-1}]
2c	**3b**	K$^+$/[18]crown-6[a]	$(5.28 \pm 0.04) \times 10^2$
		N(nBu)$_4^+$[b]	$(5.17 \pm 0.07) \times 10^2$
2d	**3c**	K$^+$	$(3.35 \pm 0.08) \times 10^2$
		K$^+$/[18]crown-6[c]	$(3.25 \pm 0.09) \times 10^2$
		K$^+$/Cryptofix 222[c]	$(3.29 \pm 0.07) \times 10^2$
		N(nBu)$_4^+$[b]	$(3.49 \pm 0.05) \times 10^2$
2d	**3g**	K$^+$	3.90
		K$^+$/[18]crown-6[c]	3.81 ± 0.03

[a] 1.05 equivalents. [b] The existence of dimers, derived by Reetz et al. (ref. [7a–d]) from cryoscopic measurements in benzene, does not affect the rate constant under the conditions employed in these experiments. [c] 1.1 equivalents. [d] The listed rate constants have been averaged from two to five experiments with different anion concentrations.

Table 2. Rate constants for the reactions of the quinone methides **2a–d** with the carbanions **3a–i** in DMSO at 20 °C.

⊖CHR¹R²	M[a]	Electrophile	k[c] [L mol^{-1} s^{-1}]
3a	N(nBu)$_4^+$	**2a**	$(2.00 \pm 0.05) \times 10^2$
		2b	$(4.12 \pm 0.10) \times 10^2$
		2c	$(2.06 \pm 0.05) \times 10^3$
3b	N(nBu)$_4^+$	**2a**	$(2.89 \pm 0.02) \times 10^1$
		2b	$(6.99 \pm 0.13) \times 10^2$
		2c	$(5.17 \pm 0.07) \times 10^2$
		2d	$(8.65 \pm 0.07) \times 10^2$
3c	N(nBu)$_4^+$	**2a**	$(1.43 \pm 0.02) \times 10^1$
		2b	$(3.39 \pm 0.04) \times 10^1$
		2c	$(2.13 \pm 0.04) \times 10^2$
		2d	$(3.49 \pm 0.05) \times 10^2$
3d	K$^+$/[18]crown-6	**2a**	9.90 ± 0.05
		2b	$(2.55 \pm 0.05) \times 10^1$
		2c	$(1.39 \pm 0.01) \times 10^2$
		2d	$(2.16 \pm 0.01) \times 10^2$
3e	K$^+$/[18]crown-6	**2a**[b]	3.52 ± 0.06
		2b[b]	$(1.07 \pm 0.05) \times 10^1$
		2c[b]	$(7.98 \pm 0.21) \times 10^1$
		2d[b]	$(1.28 \pm 0.03) \times 10^2$
3f	K$^+$/[18]crown-6	**2a**[b]	$(5.57 \pm 0.04) \times 10^{-1}$
		2b[b]	1.97 ± 0.02
		2c[b]	$(1.31 \pm 0.02) \times 10^1$
		2d[b]	$(2.15 \pm 0.06) \times 10^1$
3g	K$^+$/[18]crown-6	**2b**	$(4.28 \pm 0.03) \times 10^{-1}$
		2c	2.69
		2d	3.81 ± 0.03
3h	K$^+$/[18]crown-6	**2a**[b]	$(8.15 \pm 0.17) \times 10^{-2}$
		2b[b]	$(1.87 \pm 0.08) \times 10^{-1}$
		2c[b]	1.26 ± 0.01
		2d[b]	1.96 ± 0.03
3i	K$^+$/[18]crown-6	**2c**[b]	$(1.38 \pm 0.01) \times 10^{-2}$
		2d[b]	$(2.06 \pm 0.01) \times 10^{-2}$

[a] The potassium salts were combined with 1.01 to 1.10 equivalents of [18]crown-6. [b] With addition of 0.5 to 2.5 equivalents of the corresponding acid **4**. [c] The listed rate constants have been averaged from two to five experiments with different anion concentrations.

When the rate constants of the addition reactions of the carbanions **3a–i** to the quinone methides **2a–d** (Table 2) are plotted against the rate constants of the reference reactions of **3c** with **2a–d**, linear correlations are observed (Figure 2). The parallel correlation lines imply that the relative reactivities of the carbanions **3a–i** are independent of the electrophilicity of the reaction partners, that is, the vertical arrangement of the carbanions **3a–i** corresponds to a nucleophilicity scale. Vice versa, the relative reactivities of the quinone methides **2a–d** are independent of the nature of the carbanions and an electrophilicity scale of the quinone methides **2a–d** can be derived from their positions on the abscissa of Figure 2. Like the reactions of carbocations with nucleophiles,[1, 9, 10] these reactions are controlled by constant selectivity relationships which appear to be more general than the inverse relationships between reactivity and selectivity postulated by the reactivity–selectivity principle.[11, 12]

The reactivities of the carbanions **3a–i** towards the quinone methides **2** correlate only moderately ($r = 0.88$, nine points) with the corresponding pK_a values[13] (Figure 3). The correlation between the oxidation potentials of the carbanions **3b–f**[14] and **3h**[14a] and their nucleophilic reactivities is even weaker ($r = -0.69$, six points). In an analogous case, Bordwell et al. reported a considerable scatter in the correlation of pK_a values with oxidation potentials of these carbanions.[14a]

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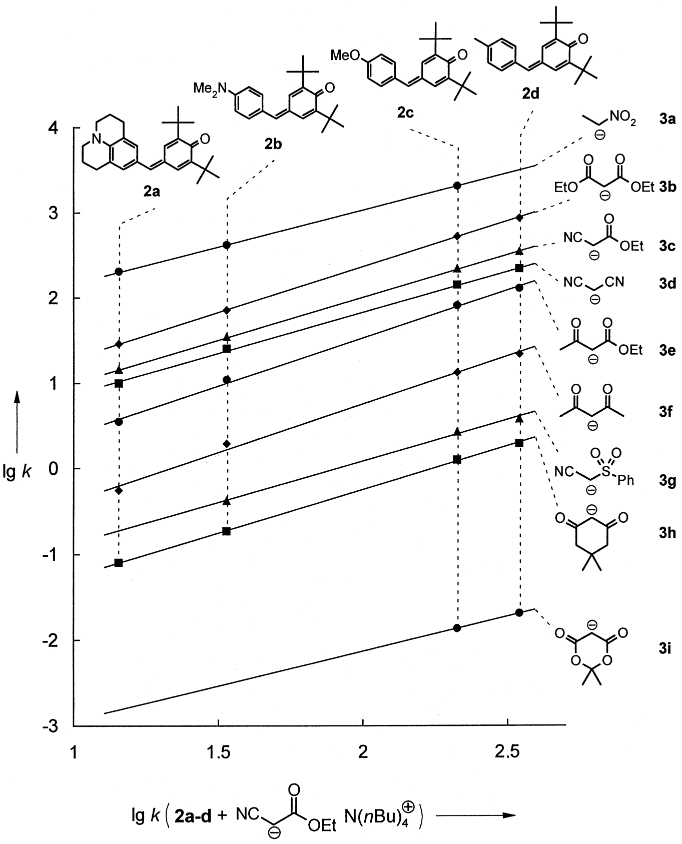

Figure 2. Constant selectivity relationships for the reactions of the quinone methides **2a–d** with the carbanions **3a–i** (DMSO, 20 °C).

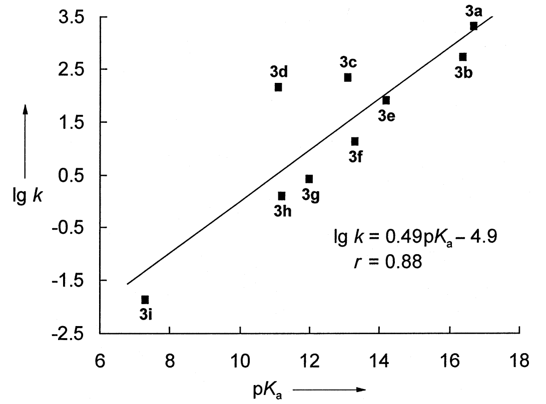

Figure 3. Linear correlation between the rate constants lg$k$ for the reactions of the quinone methide **2c** with the carbanions **3a–i** (DMSO, 20 °C) and the pK_a values (DMSO)[13] of the corresponding acids.

Constant selectivity relationships have also been reported for S_N2 reactions of phenylsulphonyl-substituted benzyl anions with 1-chlorobutane and 1-bromobutane,[15] as well as for the reactions of 9-substituted fluorenyl anions with eight different benzyl chlorides.[16] Only few kinetic data on addition reactions of carbanions to electron-deficient π-electron systems have been reported.[17–20] While some of these data[20] can be interpreted in terms of constant selectivity relationships, the paucity of electrophiles investigated prevents definite conclusions.

Having demonstrated that the reactions of carbanions with uncharged electrophiles follow analogous relationships as the reactions of carbocations with uncharged nucleophiles, we will now attempt to connect the two reactivity scales.

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