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Letter

Electrophilic Reactivities of Vinyl *p*-Quinone Methides

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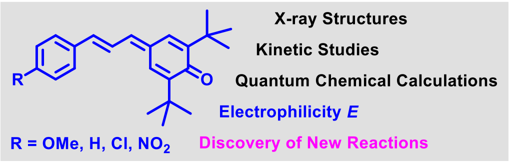
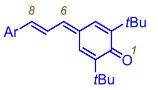
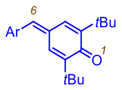
ABSTRACT: The electrophilic reactivity of a series of 8-arylated vinyl *p*-quinone methides (*p*VQMs) was determined by analyzing the kinetics of their reactions with carbanions in DMSO at 20 °C according to the linear free energy relationship log $k = s_N(N + E)$. The electrophilicity parameters E for *p*VQMs were used to successfully predict Michael-additions with structurally diverse C-, N-, S-, and H-nucleophiles.



The interest in vinyl *p*-quinone methides (*p*VQMs)[1−4] increased recently because it was shown that applying a 1,6-addition/cyclization strategy in reactions of *p*VQMs with sulfonium ylides,[5] carbanions,[6] or ammonium ylides[7a] gave rise to vinyl cyclopropanes that rearranged to chiral spirocyclopentenes. Hence, *p*VQMs are versatile building blocks for the stereocontrolled synthesis of complex molecules.[5−7] The further development of *p*VQM-based organic synthesis could clearly benefit from the knowledge of their electrophilic reactivity to define scope and limitations of their reactions with nucleophiles.[1−3]



8-aryl *p*VQM



6-aryl *p*QM

The electrophilicity of 6-aryl-substituted *p*-quinone methides (*p*QMs) had been studied by Mayr and co-workers[8] who analyzed the second-order rate constants of the reactions of nucleophiles with *p*QMs according to the linear free energy relationship eq 1:[9]

$$\log k(20\ °\mathrm{C}) = s_N(N + E) \quad (1)$$

In this work, we set out to characterize the electrophilic reactivity E of *p*VQMs **1a−d** (Figure 1) by studying the kinetics of their reactions with the carbanions **2a−d** as reference nucleophiles in DMSO at 20 °C. In this way, *p*VQMs are integrated into Mayr's reactivity scales, which allows chemists to reliably predict the scope of their reactions with structurally diverse nucleophiles when exploring novel organic syntheses.[10]

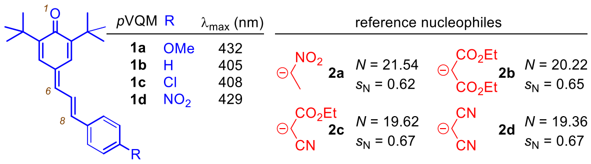


Figure 1. *p*VQMs **1a−d** and reference nucleophiles **2a−d** used for the determination of their electrophilicities E. Nucleophilicity parameters N and s_N (in DMSO) were obtained from previous literature.[8a,11]

The *p*VQMs **1a−d** were synthesized according to literature procedures and characterized by spectroscopic and electrochemical methods (Supporting Information). Single crystal X-ray crystallography (Figure 2) revealed that the conjugated π-systems in **1a−d** are slightly bent. The *p*VQMs **1a−d** are dyes with λ_{max} between 405 and 432 nm (in DMSO) and molar absorption coefficients in the range of 5×10^4 M^{-1} cm^{-1} (Figure 1), which enabled us to follow their reactions with the colorless nucleophiles **2a−d** by photometry.

When solutions of the colored *p*VQMs **1** in DMSO (or d_6-DMSO) were treated with the potassium salts of nucleophiles **2**, a rapid fading of the color of **1** was observed. As described in Scheme 1, the reaction mixtures were then either analyzed by NMR methods or worked-up to isolate the Michael adducts. Mixtures of the regioisomers **3** and **4** were obtained via 1,6- and 1,8-additions of **2a**, **2c**, and **2d** to *p*VQMs **1**, which are ambident electrophiles. Only **2b** underwent selective 1,8-additions to **1a−d**, and the exclusive formation of regioisomers **4** could be detected in the crude reaction mixtures. Subsequent acidic workup of the reaction mixtures yielded the isolated products in good to excellent yields.

In the kinetic experiments the presence of a Brønsted acid is required to ensure fast protonation of the initial Michael adducts.[8a] Solutions of the corresponding CH acids **2**-H in DMSO were therefore only partially deprotonated by 0.5 equiv of KO*t*Bu to generate DMSO stock solutions of the carbanions **2** as 1:1 mixtures with the CH acids **2**-H. The reaction kinetics were determined by employing stopped-flow UV/vis photometry to follow the fading of the colored *p*VQMs **1** in their reactions with the colorless carbanions **2**. By using a large

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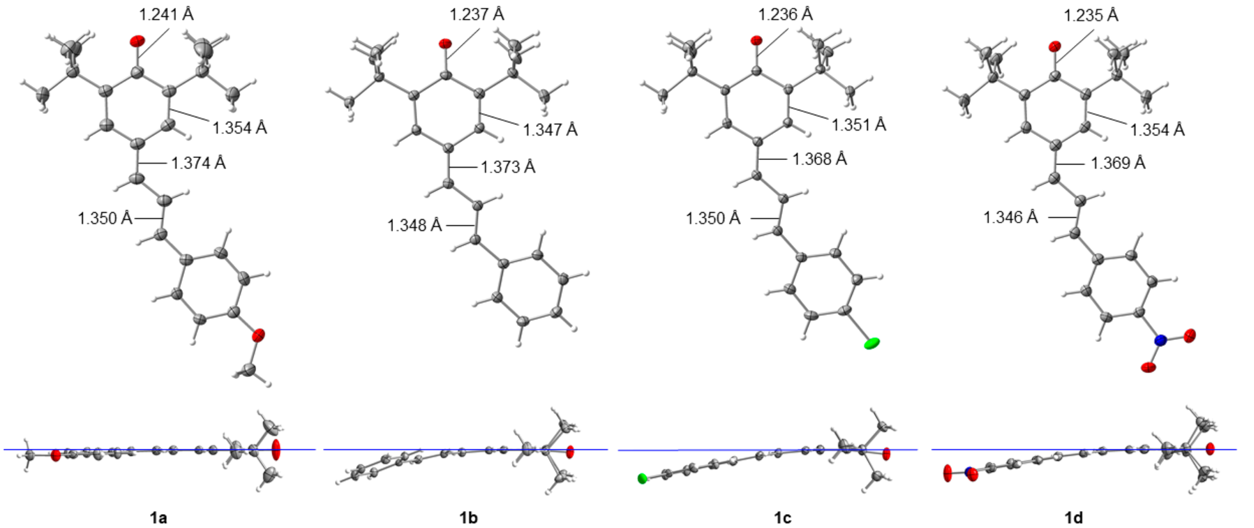
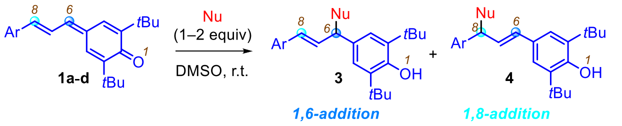


Figure 2. Single crystal X-ray structures of the *p*VQMs **1a–d**. Thermal ellipsoids are shown at a 50% probability level. Bottom: Side views on **1a–d**. The blue lines indicate the planes through the carbon atoms of the quinone moieties.

Scheme 1. Products of the Reactions of 1 with 2 in DMSO



*p*VQM	Nu	3	:	4	Yield[a]
1a	**2a**-K	60 (d.r.: 1.8/1) (**3aa**)	:	40 (d.r.: 1.1/1) (**4aa**)	84%
1a	**2b**-K	<1	:	>99 (**4ab**-K)	—[b]
1b	**2b**-K	<1	:	>99 (**4bb**)	90%
1b	**2b**-K	<1	:	>99 (**4bb**)	77%[c]
1b	**2b**-K	<1	:	>99 (**4bb**-K)	—[b]
1c	**2b**-K	<1	:	>99 (**4cb**-K)	—[b]
1d	**2b**-K	<1	:	>99 (**4db**-K)	—[b]
1b	**2c**-K	77 (**3bc**-K)	:	23 (**4bc**-K)	—[d]
		>95 (d.r.: 1/1) (**3bc**)	:	<5	75%
1a	**2d**-K	40 (**3ad**)	:	60 (**4ad**)	74%
1b	**2d**-K	42 (**3bd**)	:	58 (**4bd**)	63%
1c	**2d**-K	40 (**3cd**)	:	60 (**4cd**)	90%
1d	**2d**-K	70 (**3dd**)	:	30 (**4dd**)	99%

[a] Yields of isolated products after chromatographic workup. [b] Reaction performed in d_6-DMSO; the initially formed potassium phenolates **4Xb**-K were directly analyzed by NMR spectroscopic methods. [c] Reaction at 1 mmol scale. [d] Reaction performed in d_6-DMSO; the mixture of potassium salts **3bc**-K and **4bc**-K (both with deprotonated malononitrile moiety) was directly analyzed by NMR spectroscopic methods.

excess of the carbanions over the electrophiles, the resulting absorbance decays followed first-order kinetics. First-order rate constants k_{obs} were calculated by least-squares fitting of the single-exponential $A_t = A_0 \exp(-k_{obs}t) + C$ to the experimentally observed time-dependent absorbances (Figure 3a). Second-order rate constants k_2^{exptl} were subsequently obtained as the slopes of the linear correlations of k_{obs} with the concentrations of the carbanions [**2**] (Figure 3b; analogous correlations for all other electrophile–nucleophile combinations studied in this work are shown in the Supporting Information). Table 1 gathers the measured k_2^{exptl} values for the investigated reactions of *p*VQMs **1** with the carbanionic reference nucleophiles **2**.

Next, we used eq 1 to perform a least-squares analysis, which allowed us to determine the electrophilicity parameters *E* for the *p*VQMs **1a–d** from k_2^{exptl} and the known nucleophilicity

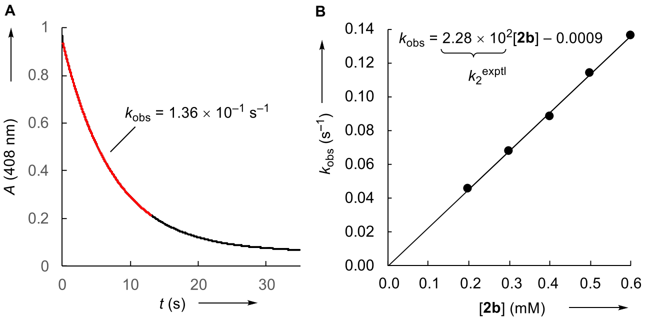


Figure 3. (A) Decay of the absorbance *A* of **1c** ($c = 1.75 \times 10^{-5}$ M) at 408 nm in the reaction (DMSO, 20 °C) with **2b** ($c = 6.00 \times 10^{-4}$ M). (B) The slope of the linear correlation of k_{obs} with the concentration of **2b** yields the second-order rate constant k_2.

Table 1. Second-Order Rate Constants for the Reactions of 1 with the Reference Nucleophiles 2 in DMSO at 20 °C

1	2	k_2^{exptl} (M^{-1} s^{-1})	$k_2^{eq\ 1,a}$ (M^{-1} s^{-1})	$k_2^{exptl}/k_2^{eq\ 1}$
1a	**2a**	5.72×10^2	3.59×10^2	1.6
	2b	7.88×10^1	6.62×10^1	1.2
	2c	3.09×10^1	2.98×10^1	1.0
	2d	1.06×10^1	2.00×10^1	0.53
E(**1a**) = −17.42				
1b	**2a**	7.11×10^2	6.49×10^2	1.1
	2b	1.65×10^2	1.23×10^2	1.3
	2c	6.16×10^1	5.65×10^1	1.1
	2d	2.39×10^1	3.79×10^1	0.63
E(**1b**) = −17.00				
1c	**2a**	1.14×10^3	8.21×10^2	1.4
	2b	2.28×10^2	1.58×10^2	1.5
	2c	7.44×10^1	7.30×10^1	1.0
	2d	2.47×10^1	4.88×10^1	0.51
E(**1c**) = −16.84				
1d	**2a**	3.44×10^3	1.91×10^3	1.8
	2b	5.92×10^2	3.82×10^2	1.5
	2c	1.66×10^2	1.82×10^2	0.91
	2d	5.08×10^1	1.22×10^2	0.42
E(**1d**) = −16.25				

[a] Second-order rate constant k_2 by applying eq 1.

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parameters N (and s_N) of the reference nucleophiles (Table 1 and Figure S1, Supporting Information).

If compared to the analogously substituted *p*QMs the electrophilicity of *p*VQMs **1** is reduced by 1−2 orders of magnitude (Figure 4).[8] Moreover, electronic substituent effects have a stronger impact on the electrophilicity of *p*QMs than on analogous *π*-extended *p*VQMs: While a change from a methoxy- to a nitro-substituent in *p*QMs increases their electrophilicity E by 1.7 units,[8b] the same change in the series of *p*VQMs results in an increase of E by only 0.9 units.[12] This might be rationalized by the observed deviations from planarity in the solid state structures (Figure 2), which weaken the conjugation and thus attenuate the substituent effects.[13]

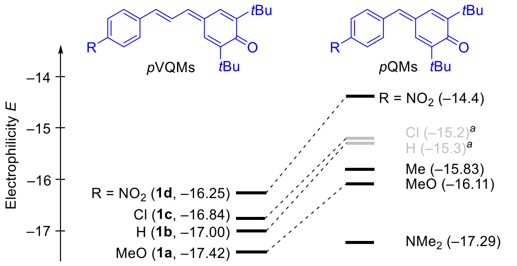


Figure 4. Comparison of electrophilicities E of *p*VQMs **1** with those of analogously substituted *p*QMs.[8] [a] Gray values are interpolated on the basis of the Hammett correlation described in ref 8b.

Quantum-chemical calculations were performed to gain a deeper understanding of the ambident reactivity of *p*VQMs. We calculated the Gibbs activation and reaction energies for the addition of nucleophiles **2b** and **2d** to the electrophile **1b** at the M06-2X/6-31+G(d,p) level considering solvation by the SMD solvation model for DMSO (Figure 5).[14] In line with our experimental results and previous reports on the formation of regioisomeric mixtures upon concomitant attack of different types of nucleophiles at 1,6- and 1,8-positions of simple vinyl *p*-quinone methides,[1c,3] the calculations show that the barriers for 1,6- and 1,8-addition differ only by 4−8 kJ mol^{-1}. For a given combination of **1** and **2**, also both intermediates **P1**(1,6) and **P1**(1,8) are formed with similar Gibbs reaction energies.

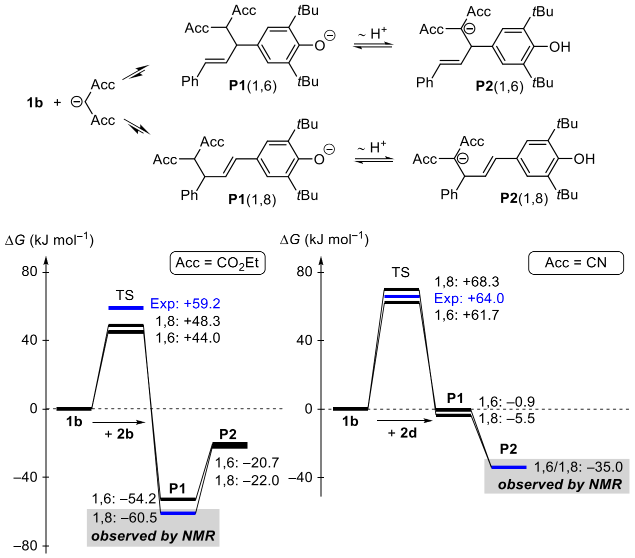


Figure 5. Reaction paths for additions of the nucleophiles **2b** (Acc = CO_2Et) and **2d** (Acc = CN) to *p*VQM **1b** (calculated at the SMD(DMSO)/M06-2X/6-31+G(d,p) level of theory).

Depending on the acidity of the $(Acc)_2CH$ moiety, the initially formed phenolate group in the adduct **P1** might be protonated to yield the corresponding phenol **P2**. In line with NMR spectroscopic studies of the reactions (Supporting Information), the proton transfer is unfavored for **2b** (pK_{aH} 18.7 for $(EtO_2C)_2MeC^-$)[15] and the phenolate form **P1**(1,8) persists as detectable species in the reaction mixture (pK_{aH} 17.7 for 2,6-*tert*-butyl-4-methylphenolate).[16] In additions of **2d** (pK_{aH} 12.4 for $(NC)_2MeC^-$)[17] to *p*VQMs, proton transfer from C−H to O−H occurs to yield a phenol. Owing to the energetic similarity of the competing reaction paths, the observed regiochemistry (1,6- vs 1,8-attack) for the attack of nucleophiles at *p*VQMs does not follow a clear pattern but seems to depend on subtle effects, which are introduced by the nature of the nucleophile.

Nevertheless, the determined electrophilicity parameters E for **1a−d** can be used to rationalize reported reactions and, more intriguingly, to predict new reactions. In Figure 6, the electrophilicity and nucleophilicity scales are arranged such that $(E + N) = -3$. Reaction partners on the same horizontal level react (somewhat dependent on the s_N parameter) with second-order rate constants of 10^{-3} to 10^{-2} M^{-1} s^{-1} at 20 °C. Accordingly, reactions of *p*VQMs **1** with sulfonium ylides, such as **12**, and *α*-bromo malonate (N determined for the chloro-derivative **6**) have been described in the literature.[5,6] Nucleophiles located at levels below that of the *p*VQMs can be expected to react even more rapidly.

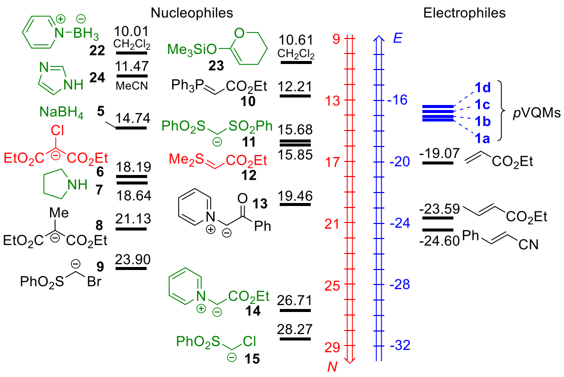
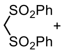
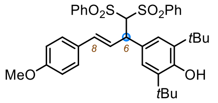
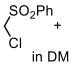
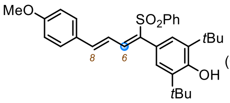
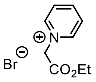
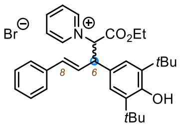
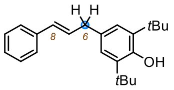
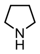
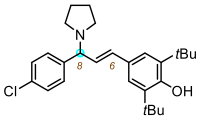
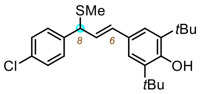


Figure 6. Ranking of *p*VQMs **1a−d** in the Mayr reactivity scales (nucleophilicities N in DMSO if not mentioned otherwise).[10]

Based on the prediction that reactions of **1** with nucleophiles of $N > 13$ should occur at 20 °C,[18] we studied the reactions of *p*VQMs **1** with carbanions (**11** and **15**), the pyridinium ylide **14**, the heteroatom nucleophiles MeS^- and pyrrolidine (**7**), and the hydride donor $NaBH_4$ (**5**). For all combinations, the reaction products could be isolated in good to excellent yields without further optimization (Table 2).

As found in the initial product studies (Scheme 1), different regioisomers were also observed for the reactions of **1a−d** with the nucleophiles in Table 2: While 1,6-addition was the preferred reaction mode for $NaBH_4$ (**5**), highly nucleophilic carbanions (**11** and **15**), and the pyridinium ylide **14**, products of 1,8-attack were observed for **7** and NaSMe. We rationalize the formation of the butadienyl-substituted phenol **17** (Table 2, entry 2) by a cyclopropanation/ring opening sequence as previously observed for reactions of *p*QMs with *α*-halo-tosylmethyl anions.[19,20] Interestingly, the reaction of the

Table 2. Scope of *p*VQM (1) Reactions with Nucleophiles

Entry	1	Nucleophile	Product (Yield)
1	**1a**	 + KO*t*Bu (**11**) in DMSO	 **16** (68%)
2	**1a**	 + KO*t*Bu (**15**) in DMSO	 **17** (66%)
3	**1b**	 (**14**) + NEt$_3$ in MeCN	 **18** (60%) d.r. = 64/36
4	**1b**	NaBH$_4$ in MeOH (**5**)	 **19** (91%)
5	**1c**	 (**7**) in DMSO	 **20** (54%)
6	**1c**	NaSMe in DMSO	 **21** (79%)

pyridinium ylide **14** with the *p*VQM **1a** gave the pyridinium bromide **18** (Table 2, entry 3), which is in contrast to reactions of ammonium ylides with *p*VQMs which furnish spirocyclic products.[7]

In conclusion, we have characterized the Mayr electrophilicities *E* of the vinyl *p*-quinone methides **1a**−**d** by analyzing the kinetics and products of their reactions with carbanions in DMSO. In agreement with earlier findings on the regioselectivities of nucleophile additions to 2,6-dimethoxy-4-(2-propenylidene)-2,5-cyclohexadien-1-one and eugenol-derived vinylic *p*-quinone methides,[1c,3] the *p*VQMs **1** are ambident electrophiles that have similar 1,6- and 1,8-reactivities. While the results of our experiments do not allow us to predict the regiochemistry of the nucleophilic attack at *p*VQMs, the determined Mayr *E* parameters reliably reflect the general electrophilic reactivity of these electron-deficient π-systems. Application of the electrophilicity parameters *E* in eq 1 not only rationalizes reported reactions but also empowers chemists to systematically predict novel combinations of *p*VQMs with nucleophiles. We demonstrated that uncatalyzed reactions of **1a**−**d** with different types of C-, N-, S-, and H-nucleophiles with $N > 14$ are feasible at ambient temperature[21] and lead to novel types of conjugate 1,6- and 1,8-adducts of *p*VQMs.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c00338.

Synthetic procedures, analytical data, X-ray structure determinations, details on kinetic measurements and quantum-chemical calculations, and copies of NMR spectra (PDF)

Coordinates of optimized structures (ZIP)

Accession Codes

CCDC 1973228−1973231 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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