(t, 3 CH_3), 0.9–1.7 (m, 20 CH_2), 2.55 (br t, 3 CH_2 next to ring), 6.83 (s, 3 Ar H); mass spectrum, *m/e* 442 (M^+). Anal. Calcd for $C_{32}H_{58}$: C, 86.88; H, 13.12. Found: C, 87.08; H, 13.42.

Registry No. **1a**, 29536-28-5; **1b**, 29536-29-6; **1c**, 7694-77-1; **1d**, 29536-30-9; **1e**, 87969-78-6; **2**, 87969-79-7; **4**, 87969-80-0; **8**, 87969-81-1; **9a**, 87969-82-2; **9b**, 87969-83-3; **9c**, 87969-84-4; **10a**, 87969-85-5; **10b**, 87969-86-6; **10c**, 87969-87-7; **10d**, 87969-88-8; **10e**, 87969-89-9; **10f**, 87969-90-2; 1,3,5-$Cl_3C_6H_3$, 108-70-3; 1,2,3-$Cl_3C_6H_3$, 87-61-6; 1,2,4-$Cl_3C_6H_3$, 120-82-1; 1,2,4,5-$Cl_4C_6H_2$, 95-94-3; *n*-$C_6H_{13}MgBr$, 3761-92-0; *n*-$C_7H_{15}MgBr$, 13125-66-1; *n*-$C_8H_{17}MgBr$, 17049-49-9; *n*-$C_9H_{19}MgBr$, 39691-62-8; *n*-$C_{10}H_{21}MgBr$, 17049-50-2; $NiCl_2$(dppe), 38754-20-0; Ni(acac)$_2$, 3264-82-2; (*n*-$C_8H_{17})_2ClC_6H_3$, 87969-91-3.

Nucleophilic Addition to Olefins. 9.[1] Kinetics of the Reaction of Benzylidenemalononitrile with Malononitrile Anion

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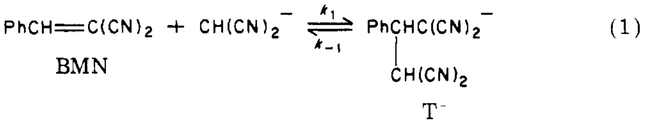
The rates of the reversible addition of $CH(CN)_2^-$ to benzylidenemalononitrile, to form $PhCH(CH(CN)_2)C(CN)_2^-$, have been measured in water and in 50% Me_2SO–50% water. In water at 20 °C, $k_1 = 2.30 \times 10^5$ M^{-1} s^{-1}, $k_{-1} = 5.95$ s^{-1}, and $K_1 = 3.86 \times 10^4$ M^{-1}. In 50% Me_2SO–50% water at 20 °C, $k_1 = 9.50 \times 10^5$ M^{-1} s^{-1}, $k_{-1} = 6.52$ s^{-1}, and $K_1 = 1.45 \times 10^5$ M^{-1}. The pK_a of the adduct is about 5 p*K* units lower than that of malononitrile. K_1 for the addition of $CH(CN)_2^-$ is much higher than K_1 for piperidine addition, despite the slightly lower proton basicity of $CH(CN)_2^-$. This reflects the common observation that the carbon basicity of carbanions is higher than that of amines. The intrinsic rate constant for nucleophilic attack by $CH(CN)_2^-$ appears to be somewhat smaller than for amine attack, just as the intrinsic rate constant for protonation of $RC(CN)_2^-$ is lower than for the protonation of amines. This is not unexpected, since structural factors should affect the coordination of bases with Lewis acids in a similar way as coordination with the proton. The change from water to 50% Me_2SO–50% water has the effect of increasing k_1 by a slightly larger factor (4.13) than K_1 (3.75). This implies that the intrinsic rate constant is higher in the less aqueous solvent, which is consistent with the notion that solvent reorganization contributes to the intrinsic barrier of the reaction.

We report a kinetic study of the Michael addition of malononitrile anion to benzylidenemalononitrile (BMN; eq 1). Reaction 1 and similar additions of malononitrile



$$\underset{\text{BMN}}{PhCH{=}C(CN)_2} + CH(CN)_2^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{T^-}{PhCH(CH(CN)_2)C(CN)_2^-} \qquad (1)$$

anion to ylidenemalononitriles represent the first step in many synthetically useful reactions[2,3] and thus are of considerable interest to organic chemists. Our own main interest in studying reaction 1 is aimed at expanding our systematic investigations of structure–reactivity relationships in nucleophilic additions to activated double bonds[1,4] by including carbanionic nucleophiles.

On a more practical level, kinetic information on reaction 1 is also needed in order to carry out a full analysis of the hydrolysis of BMN (eq 2). This is because reaction 1

$$PhCH{=}C(CN)_2 + OH^- \rightarrow PhCH{=}O + CH(CN)_2^- \qquad (2)$$

occurs in competition with reaction 2; i.e., the malononitrile anion produced during the hydrolysis of BMN can attack unreacted BMN under certain reaction conditions.[5]

Results

Upon mixing of an aqueous solution of BMN with a solution of malononitrile anion, the adduct T^- is rapidly formed. This manifests itself by the disappearance of the absorption of BMN (λ_{max} 309 nm) and the appearance of a new species whose spectrum is similar to that of malononitrile anion, as shown in Figure 1. Due to the rapid hydrolysis of BMN at a pH greater than $pK_a^{CH_2(CN)_2}$, the spectrum of T^- was obtained in a borate buffer at pH ~8.5. Even at this pH, hydrolysis is not negligible, and absorbance values had to be obtained by extrapolation to zero time. Further complications arose owing to the nonquantitative conversion of BMN into T^-, and because $CH(CH)_2^-$ contributes to the observed spectrum. This necessitated appropriate corrections, as detailed in the Experimental Section, and affected the accuracy of the spectrum of T^-, for which we estimate a ±10 to ±15% uncertainty in ϵ.

Table I. Reaction of BMN with $CH(CN)_2^-$ at pH 12.52 in Water at 25 °C, $\mu = 0.5$ M[a]

$[CH(CN)_2^-]^b \times 10^4$, M	τ^{-1}, s^{-1}	k_{hyd}, s^{-1}
0		8.0
0.11	~17.0	~7.0
0.22	~22.0	~5.0
1.07	40.8	~2.6
1.60	54.4	~1.7
1.91	75.0	
2.13	74.3	
2.86	110	
3.82	136	
4.05	132	~0.36
5.72	211	
7.63	265	

[a] $[BMN]_0 = 6.6 - 22.8 \times 10^{-6}$ M. [b] Calculated from $[CH_2(CN)_2]_0$ based on $pK_a^{CH_2(CN)_2} = 11.19$.

The kinetics of reaction 1 were measured in aqueous solution at 25 and 20 °C and also in 50% Me_2SO–50%

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(1) Part 8: Bernasconi, C. F.; Murray, C. J.; Fox, J. P.; Carré, D. J. *J. Am. Chem. Soc.* **1983**, *105*, 4349.

(2) Fatiadi, A. J. *Synthesis* **1978**, 165.

(3) Freeman, F. *Chem. Rev.* **1980**, *80*, 329.

(4) For a recent review, see: Bernasconi, C. F. *Pure Appl. Chem.* **1982**, *54*, 2335.

(5) Bernasconi, C. F.; Howard, K. A.; Kanavarioti, A., to be published.

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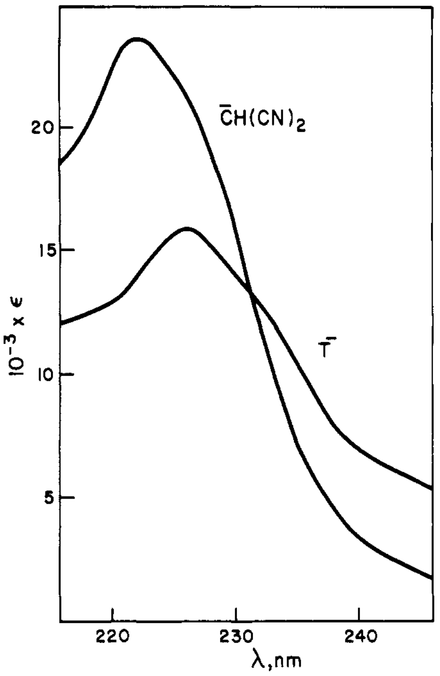


Figure 1. Absorption spectra of T^- and of $CH(CN)_2^-$ in water at 25 °C.

water (v/v) at 20 °C. All experiments were conducted under pseudo-first-order conditions, with the $CH(CN)_2^-$ (or $CH_2(CN)_2$ at low pH) as the excess component. The ionic strength was maintained at 0.5 M with KCl. The rates were measured by the stopped-flow technique.

In water, the reaction was mainly followed by monitoring the disappearance of BMN at 309 (λ_{max}) or 330 nm. In a number of experiments we also monitored the formation of T^- around 250 nm. In all cases we found the rates to be the same at the different wavelengths.

In 50% Me_2SO-50% water, the reaction was only monitored at 310 nm; absorption by the solvent precluded direct observation of the adduct.

Table I summarizes the reciprocal relaxation times, τ^{-1}, for reaction 1 in water at pH 12.52. It also includes a few pseudo-first-order rate constants, k_{hyd}, for hydrolysis of BMN. These latter rate constants are only approximate values because the very small OD change associated with this process made an accurate determination very difficult.[6] The reason for measuring k_{hyd} was to assess the extent of coupling between reactions 1 and 2 rather than to get accurate data on the hydrolysis; this latter reaction is, of course, more easily studied in the absence of $CH(CN)_2^-$.[5]

For $[CH(CN)_2^-] \geq 10^{-4}$ M, τ^{-1} is seen to exceed k_{hyd} at least tenfold (Table I). Hence, reaction 1 can be regarded as essentially decoupled from reaction 2, and τ^{-1} should obey eq 3, while k_{hyd} should be given by eq 4, with k_{hyd}^0 being the hydrolysis rate constant in the absence of malononitrile.

$$\tau^{-1} = k_1[CH(CN)_2^-] + k_{-1} \qquad (3)$$

$$k_{hyd} = k_{hyd}^0/(1 + K_1[CH(CN)_2^-]) \qquad (4)$$

Figure 2 shows a plot of τ^{-1} vs. $[CH(CN)_2^-]$. The points for $[CH(CN)_2^-] \geq 10^{-4}$ M are seen to fall on a very good straight line as called for by eq 3. However, at the lowest two concentrations (0.11×10^{-4} and 0.22×10^{-4} M) τ^{-1} deviates significantly from the straight line: at 0.22×10^{-4} M, the deviation is 77%; at 0.11×10^{-4} M, it is 112%. Here τ^{-1} exceeds k_{hyd} by less than fivefold (Table I), indicating substantial coupling between reactions 1 and 2 and, hence, a breakdown of eq 3 and 4; this breakdown is the most likely reason for the positive deviations from the plot (filled circles in Figure 2).

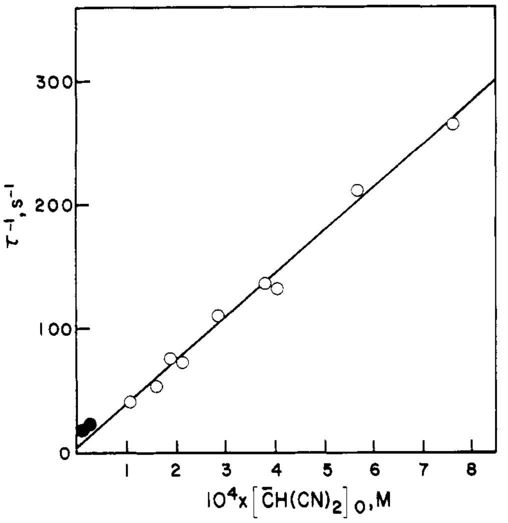
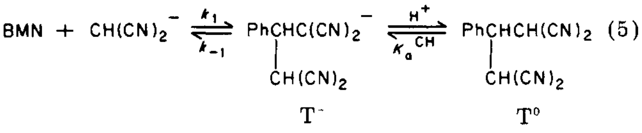


Figure 2. Reaction of BMN with $CH(CN)_2^-$ in water at 25 °C, pH 12.52: (○) points for which eq 3 is valid; (●) points for which eq 3 breaks down. See text.

The above analysis shows that at this pH, τ^{-1} cannot be measured at low enough $[CH(CN)_2^-]$ to obtain a reliable intercept (k_{-1}). The data afford $k_1 = 3.44 \pm 0.3 \times 10^5$ M^{-1} s^{-1} and $k_{-1} = 8 \pm 3$ s^{-1}.

Additional experiments were performed at low pH values where coupling with reaction 2 is negligible even at very low $[CH(CN)_2^-]$ because of slower hydrolysis.[5] These experiments were primarily aimed at obtaining a more reliable k_{-1} value and also at determining the pK_a of the carbanionic site in T^- according to eq 5 and 6.



$$BMN + CH(CN)_2^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{T^-}{\underset{CH(CN)_2}{PhCHC(CN)_2^-}} \underset{K_a^{CH}}{\overset{H^+}{\rightleftharpoons}} \underset{T^0}{\underset{CH(CN)_2}{PhCHCH(CN)_2}} \qquad (5)$$

$$\tau^{-1} = k_1[CH(CN)_2^-] + k_{-1}\left(\frac{K_a^{CH}}{K_a^{CH} + a_{H^+}}\right) \qquad (6)$$

In a first series of experiments, τ^{-1} was determined as a function of four to five concentrations of $CH(CN)_2^-$ in borate buffers at pH 9.11 and 7.97. The results are summarized in Table S1.[7] Based on $pK_a^{CH_2(CN)_2} = 11.19$ to calculate $[CH(CN)_2^-]$, one obtains $k_1 = 3.84 \pm 0.40 \times 10^5$ M^{-1} s^{-1} at pH 9.11 and $k_1 = 2.86 \pm 0.40 \times 10^5$ M^{-1} s^{-1} at pH 7.97, for an average of 3.35×10^5 M^{-1} s^{-1}. This average value is in close agreement with $k_1 = 3.44 \times 10^5$ M^{-1} s^{-1} obtained at pH 12.52.

In a second series of experiments, τ^{-1} was measured at single malononitrile concentrations ($[CH_2(CN)_2] \approx 0.05$ M, $[CH(CN)_2^-] \approx 10^{-6}$ to 10^{-7} M) as a function of pH in a range from pH 5.48 to 6.62. Since under these conditions the equilibrium strongly favors BMN, the experiments were performed by approaching equilibrium from the adduct

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[6] k_{hyd} was measured by following the appearance of benzaldehyde at 250 nm. Since T^- also absorbs at this wavelength, ΔOD is very small. Monitoring BMN was not feasible, since in the presence of $CH(CN)_2^-$ most of the BMN is in the form of T^-.

[7] See paragraph concerning supplementary material at the end of this paper.

[8] We thank Dr. A. Kanavarioti for measuring the pK_a values under the current experimental conditions.

Table II. Summary of Rate and Equilibrium Constants for the Reaction of BMN with CH(CN)$_2^-$, Piperidine, and Morpholine

constant	$CH(CN)_2^-$			piperidine[a] 50% Me_2SO–50% H_2O, 20 °C	morpholine[a] 50% Me_2SO–50% H_2O, 20 °C
	water, 25 °C	water, 20 °C	50% Me_2SO–50% H_2O, 20 °C		
k_1, M^{-1} s^{-1}	$3.44 (\pm 0.17) \times 10^5$	$2.30 (\pm 0.10) \times 10^5$	$9.50 (\pm 0.15) \times 10^5$	2.10×10^5	5.9×10^4
k_{-1}, s^{-1}	$7.69 (\pm 1.00)$	$5.95 (\pm 1.0)$	$6.52 (\pm 1.00)$	1.36×10^4	2.6×10^5
$K_1 = k_1/k_{-1}$, M^{-1}	$4.47 (\pm 0.90) \times 10^4$	$3.86 (\pm 1.0) \times 10^4$	$1.45 (\pm 0.26) \times 10^5$	15.4	0.23
pK_a^{CH} [b]	$6.19 (\pm 0.08)$	$6.35 (\pm 0.08)$	$5.07 (\pm 0.08)$	~8.43	~8.43
pK_a^{Nuc} [c]	$11.19 (\pm 0.03)$	$11.39 (\pm 0.04)$	$10.21 (\pm 0.02)$	11.00	8.72

[a] Reference 9. [b] Refers to T^0. [c] Refers to $CH_2(CN)_2$, piperidine H^+ and morpholine H^+, respectively.

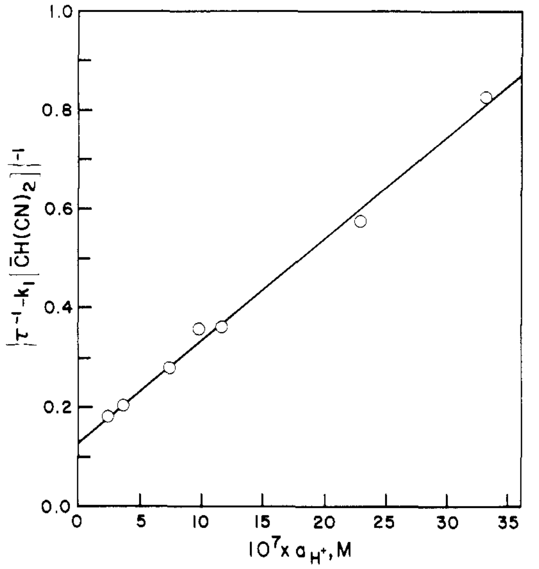

Figure 3. Inversion plot according to eq 8.

side by first generating the adduct at high pH and then adding an acidic buffer in the stopped-flow apparatus ("pH jumps"). The results are summarized in Table S2.[7] From these, the term $k_{-1}K_a^{CH}/(K_a^{CH} + a_{H^+})$ was obtained as eq 7. Figure 3 shows an inversion plot according to eq 8. It affords $k_{-1} = 7.69 \pm 1.00$ s^{-1} and $pK_a^{CH} = 6.19 \pm 0.08$.

$$k_{-1}K_a^{CH}/(K_a^{CH} + a_{H^+}) = \tau^{-1} - k_1[CH(CN)_2^-] \quad (7)$$

$$\{\tau^{-1} - k_1[CH(CN)_2^-]\}^{-1} = 1/k_{-1} + a_{H^+}/k_{-1}K_a^{CH} \quad (8)$$

For purposes of comparison with previously studied systems (see Discussion), we also carried out similar measurements at 20 °C, both in water and in 50% Me_2SO–50% water (v/v). The τ^{-1} values are summarized in Tables S2–S5,[7] while the rate and equilibrium constants are summarized in Table II.

Discussion

Rate and equilibrium constants for the reaction of BMN with malononitrile anion, including the acid-base equilibrium shown in eq 5, have been determined under various conditions and are summarized in Table II. Table II also includes data for the reaction of BMN with piperidine and morpholine.[9] The following features are noteworthy.

(1) Carbon Basicity. As is apparent from the K_1 values, the carbon basicity of $CH(CN)_2^-$ toward BMN is much larger than that of piperidine. In 50% Me_2SO–50% water, the ratio $K_1(CH(CN)_2^-)/K_1$ (Pip) $= 9.41 \times 10^3$, even though the proton basicity of $CH(CN)_2^-$ is 0.79 pK_a units lower than that of piperidine (see $pK_a^{Nuc} = pK_a^{CH_2(CN)_2}$ in Table II). After taking into account this pK_a difference, one calculates a corrected K_1 $(CH(CN)_2^-)/K_1$ (Pip) ratio of 5.80×10^4. This high ratio is consistent with numerous observations showing that carbon bases have considerably higher carbon basicities than nitrogen bases of comparable pK_a.[10]

(2) Intrinsic Rate Constants. The higher carbon basicity of $CH(CN)_2^-$ compared to that of piperidine does not appear to be accompanied by a correspondingly enhanced nucleophilic reactivity ("kinetic" carbon basicity). In fact, the following considerations suggest that, after due correction for the different equilibrium constants, $CH(CN)_2^-$ is kinetically somewhat less effective than the amine.

Based on the reactions of piperidine and morpholine with BMN,[9] one can calculate, by linear interpolation, an "intrinsic rate constant" $k_0 = 8.70 \times 10^4$ in 50% Me_2SO_4–50% water for nucleophilic addition to BMN by a hypothetical cyclic secondary amine for which $K_1 = 1$ and, thus, $k_0 = k_1 = k_{-1}$. These data also provided a normalized β_{nuc} value ($\beta_{nuc}^n = \partial \log k_1/\partial \log K_1$) of 0.30. If one assumes that the reaction of BMN with substituted malononitrile anions has the same β_{nuc}^n as the reaction with the amines, one can estimate, by linear extrapolation, a $k_0 = 2.69 \times 10^4$. This estimate suggests that k_0 for $CH(CN)_2^-$ addition is approximately threefold lower than for amine addition.

Not much significance should, of course, be attached to the exact value estimated for k_0, since a different value would be obtained if β_{nuc}^n were different from 0.30. However, as long as $\beta_{nuc}^n > 0.20$, k_0 for $CH(CN)_2^-$ addition would always come out lower than k_0 for amine addition.

A lower k_0 for $CH(CN)_2^-$ addition is consistent with the somewhat lower intrinsic rate constant for protonation of substituted malononitriles ($\sim 10^7$)[11] compared to that of amines ($\sim 10^9$).[12] This analogy is not surprising, since the coordination of a nucleophile with an electrophile, such as BMN, must have similar structural and solvational effects on the nucleophile as a protonation reaction, and thus one expects that the intrinsic rate constants show a similar dependence on the nature of the nucleophile.[4]

On the basis of our results, one further expects that the addition of carbanions which are more resonance stabilized than $CH(CN)_2^-$ would have still lower intrinsic rate constants, since their intrinsic protonation rates are also lower due to more extensive structural and solvational reorganization during the reaction.[4] Work is in progress to test this prediction. For the case where the electrophile is

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(9) Bernasconi, C. F.; Fox, J. P.; Fornarini, S. *J. Am. Chem. Soc.* **1980**, *102*, 2810.

(10) (a) Hine, J.; Weimar, R. D. *J. Am. Chem. Soc.* **1965**, *87*, 3387. (b) Hine, J. "Structural Effects on Equilibria in Organic Chemistry"; Wiley-Interscience: New York, 1975; p 225.

(11) (a) Hibbert, F.; Long, F. A.; Walters, E. A. *J. Am. Chem. Soc.* **1971**, *93*, 2829. (b) Hibbert, F. *Compr. Chem. Kinet.* **1977**, *8*, 97.

(12) (a) Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 1. (b) Ahrens, M.-L.; Maass, G. *Ibid.* **1968**, *7*, 818. (c) Grunwald, E.; Eustace, D. In "Proton Transfer Reactions"; Caldin, E.; Gold, V., Eds.; Wiley: New York, 1975; p 103.

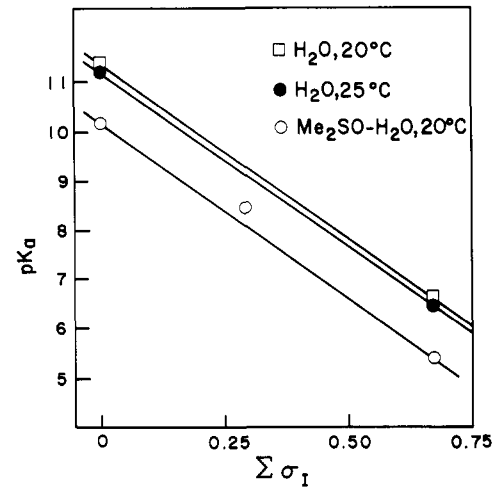


Figure 4. Correlation of the pK_a of $CH_2(CN)_2$, 1 (in 50% Me_2SO–50% water only), and T^0 with σ_I.

benzaldehyde, preliminary data suggest that k_0 for the addition of $CH_2NO_2^-$ is, indeed, about 10^5 fold lower than for the addition of $CH(CN)_2^-$.[4]

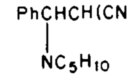
(3) Solvent Effects. There is a 3.75-fold increase in the equilibrium constant (K_1) for addition when changing from water to 50% Me_2SO–50% water. This result might seem surprising in view of the 1.18-unit drop in p$K_a^{CH_2(CN)_2}$, which implies a comparable decrease in the carbon basicity of $CH(CN)_2^-$. However, the change in solvent is expected to have a compensating effect on the Lewis acidity of BMN. This is because the carbanionic portion of T^- has essentially the same structure as CH(CN$_2^-$, and hence its stability should respond in a similar way to a change in solvent as that of $CH(CN)_2^-$. In other words, the reduced basicity of $CH(CN)_2^-$ should be matched by a comparable increase in reactivity of BMN. The results show that this increase in reactivity of BMN even overcompensates the drop in p$K_a^{CH_2(CN)_2}$ by about fourfold.

With respect to the rate constants, the change from water to 50% Me_2SO–50% water increases k_1 4.13-fold, while k_{-1} increases by 10%. This result shows that k_1 increases by a slightly larger factor than K_1, which implies a larger intrinsic rate constant in the less aqueous solvent. If we use the same β_{nuc}^n (0.30) as in 50% Me_2SO–50% water to estimate k_0 in water, we obtain $k_0 = 9.70 \times 10^3$, which is almost threefold lower than k_0 estimated in 50% Me_2SO–50% water.

The larger k_0 in the less aqueous solvent is consistent with the notion that solvent reorganization is an important contributor to the intrinsic barrier of nucleophilic additions to activated olefins, as described in detail elsewhere.[4]

(4) pK_a of T^0. The pK_a^{CH} values are about 5 units lower than the pK_a of $CH_2(CN)_2$ in both solvents. This sharp decrease in pK_a reflects mainly the strong polar effect exerted by the $CH(CN)_2$ moiety ($\sigma_I = 0.55$[13]). There is also a small contribution by the polar effect of the phenyl group ($\sigma_I = 0.12$[13,14]) and a 0.3-log unit contribution by a statistical factor, owing to the fact that T^0 has two equivalent protons.

Figure 4 shows plots of p$K_a^{CH_2(CN)_2}$, pK_a^{CH} of T^0 (statistically corrected), and pK_a^{CH} of the piperidine adduct 1 (in 50% Me_2SO–50% water only) vs. $\sum\sigma_I$. In view of the uncertainties in σ_I for the piperidine moiety and its possible solvent dependence,[15] as well as the approximate



$PhCH(NC_5H_{10})CH(CN)_2$

1

nature of the pK_a^{CH} of **1**,[9] the plot shows a reasonably straight line. ρ_I based on $CH_2(CN)_2$ and T^0 only is 7.46 and 7.52 in water at 25 and 20 °C, respectively, and 7.67 in 50% Me_2SO–50% water. These ρ_I values appear to be reasonable. For example, ρ_I for the pK_a of X–CH_2COOH is 3.95.[13] The substituent in T^0 or 1 is one atom closer to the acidic site than in X–CH_2COOH, which should enhance ρ_I. However, this enhancement is not expected to be quite as large as the commonly used fall-off factor of 2.8,[13] since the negative charge in the carbanion is more dispersed than on an oxy anion.

Experimental Section

Materials. Benzylidenemalononitrile, available from a previous study,[9] was recrystallized from ethanol, mp 85–86 °C (lit. mp 84 °C).[17] Malononitrile (Aldrich Chemical Co.) was distilled and stored over P_2O_5, mp 31–33 °C (lit. mp 32 °C).[18] Dimethyl sulfoxide was stored over 4A molecular sieves prior to use. Buffers and inorganic salts were reagent grade and were used without further purification.

Spectrum of Adduct T^-. A few microliters of an ethanol solution of BMN was injected into the cuvette of a Perkin-Elmer double-beam spectrophotometer which contained 3×10^{-3} M malononitrile in a borate buffer at pH 8.58 to 8.95. Since the solution started to decompose shortly after mixing, the absorbance was measured as a function of time and extrapolated to $t = 0$. This procedure was repeated at 2- to 3-nm intervals over a range from 215 to 245 nm. In order to compensate for the absorption by $CH(CN)_2^-$, the reference cuvette contained the same solution as the sample cuvette, except for BMN. The extinction coefficient at any wavelength was calculated as

$$\epsilon_{T^-} = \frac{A - \epsilon_{BMN}[BMN]_{eq}}{[T]_{eq}}$$

where A is the absorbance at $t = 0$, ϵ_{BMN} is the extinction coefficient of BMN, and where the concentrations refer to their equilibrium values, calculated from K_1, p$K_a^{CH_2(CN)_2}$, pH, and initial concentrations.

pK_a of Malononitrile. The pK_a was determined by standard spectrophotometric procedures. In water, measurements were made at λ_{max} 223 nm, but in 50% Me_2SO–50% water, the strong absorption by the solvent necessitated a change to a λ of 250 nm. Our value (11.19) in water at 25 °C and μ = 0.5 M compares well with literature values (11.19,[18] 11.20,[19] and 11.23[20]) at different ionic strengths and suggests that the dependence on ionic strength is very small.

Kinetic Experiments. All experiments were carried out in a Durrum stopped-flow spectrophotometer with a computerized data acquisition and analysis system. Since basic solutions of malononitrile decompose rather rapidly, the following mixing procedures were adopted. One syringe of the stopped-flow apparatus was filled with a slightly acidic solution containing both BMN and malononitrile. The other syringe was filled with KOH or a basic buffer solution. In this manner, malononitrile could be kept in an acidic environment until the reaction was triggered by mixing in the stopped-flow apparatus. Since deprotonation of malononitrile is very fast[11] on the time scale of reaction 1, equilibration between $CH_2(CN)_2$ and $CH(CN)_2^-$ was always es-

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[13] Exner, O. In "Correlation Analysis in Chemistry"; Chapman, N. B.; Shorter, J.; Plenum Press: New York, 1978; p 439.

[14] Based on the pK_a of substituted acetic acids.

[15] σ_I values for amines are notoriously uncertain.[16] We use σ_I = 0.16, corresponding to the value estimated for the NEt_2 group.[13]

[16] See, for example: (a) More O'Ferrall, R. A.; Larkin, F.; Walsh, P. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1573. (b) Concilio, C.; Bongini, A. *Ann. Chim.* (*Rome*) **1966**, *56*, 417.

[17] Patai, S.; Rappoport, Z. *J. Chem. Soc.* **1962**, 383.

[18] Pearson, P. G.; Dillon, R. L. *J. Am. Chem. Soc.* **1953**, *75*, 2439.

[19] Boyd, R. H.; Wang, C. *J. Am. Chem. Soc.* **1965**, *87*, 430.

[20] Jencks, W. P.; Lienhard, G. E. *J. Am. Chem. Soc.* **1965**, *87*, 3863.

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tablished before the start of reaction 1.

For the pH-jump experiments, the addition complex had to be generated at high enough pH to assure nearly complete conversion of BMN into T^- but at low enough pH to avoid rapid decomposition of malononitrile and/or hydrolysis of BMN. A pH ~8 borate buffer gave the best results.

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Registry No. T^-, 88157-08-8; $CH(CN)_2^-$, 41470-37-5; benzylidenemalononitrile, 2700-22-3; malononitrile, 109-77-3; piperidine, 110-86-1; morpholine, 110-91-8.

Supplementary Material Available: Tables S1–S5, containing data on the following reactions: reaction of BMN with $CH(CN)_2^-$ at pH 9.11 and 7.97 in water at 25 °C (Table S1), reaction of BMN with $CH(CN)_2^-$ at single $CH(CN)_2^-$ concentrations (pH jumps) in water at 25 and 20 °C (Table S2), reaction of BMN with $CH(CN)_2^-$ at pH 12.72 in water at 20 °C (Table S3), reaction of BMN with $CH(CN)_2^-$ in 50% Me_2SO–50% water at 20 °C (Table S4), reaction of BMN with $CH(CN)_2^-$ at single $CH(CN)_2^-$ concentrations (pH jumps) in 50% Me_2SO–50% water at 20 °C (Table S5) (5 pages). Ordering information is given on any current masthead page.

Relative Reactivities of Nucleophiles Derived from Group 6A toward Aryl Radicals[1]

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Competition experiments have been carried out in liquid ammonia at reflux temperature to determine the relative rate constants for the coupling reactions of nucleophiles derived from group 6A of the periodic table toward aryl radicals. The nucleophiles studied were of the type PhZ^- (Z = S, Se, Te). It has been proposed that these nucleophiles react under photochemical stimulation with haloaromatic substrates through the $S_{RN}1$ mechanism of aromatic substitution. The experimental results suggest that the coupling reaction aryl radical–PhZ^- anion can be reversible or irreversible depending on the nature of the aryl moiety and the PhZ^- nucleophile. Relative rate constants have been determined under conditions of irreversible coupling of the nucleophiles PhZ^- (Z = S, Se, Te) with 2-quinolyl radicals. Results here reported indicate an increasing reactivity as we go down the group: PhO^- (0.0), PhS^- (1.00), $PhSe^-$ (5.8), $PhTe^-$ (28). The relative rate constant when one of the coupling reactions is reversible supports our mechanistic suggestions.

We have reported the photostimulated reaction of phenyl selenide ion and phenyl telluride ion nucleophiles with haloaromatic substrates in liquid ammonia. It has been proposed that these reactions occur by the $S_{RN}1$ mechanism of aromatic nucleophilic substitution.[2,3]

Inspection of the species PhZ^- nucleophilicities, Z being an element of group 6A of the periodic table, shows that phenoxide ion does not react with haloarenes,[4] while benzenethiolate ion,[5] phenyl selenide ion,[3] and phenyl telluride ion[3] react with good yields of substitution products in general. We determined the relative reactivity of the last three nucleophiles just mentioned toward aryl radicals.

All the reactions were carried out in liquid ammonia as the solvent at −33 °C and under photostimulation. Similar competition experiments have been previously reported.[6] In these experiments two nucleophiles were allowed to react with aromatic radicals generated from the haloaromatic substrate.

The propagation steps for $S_{RN}1$ reactions of one aromatic substrate with two nucleophiles Nu_1 and Nu_2 are shown in Scheme I.

Scheme I

$$(ArX)^{-}\cdot \rightarrow Ar\cdot + X^- \tag{1}$$

$$Ar\cdot + Nu_1^- \xrightarrow{k_{Nu1}} (ArNu_1)^{-}\cdot \tag{2}$$

$$Ar\cdot + Nu_2^- \xrightarrow{k_{Nu2}} (ArNu_2)^{-}\cdot \tag{3}$$

$$(ArNu_1)^{-}\cdot + ArX \rightarrow ArNu_1 + (ArX)^{-}\cdot \tag{4}$$

$$(ArNu_2)^{-}\cdot + ArX \rightarrow ArNu_2 + (ArX)^{-}\cdot \tag{5}$$

As it has been pointed out, the ratio of concentration of substitution products, $ArNu_1$ and $ArNu_2$, derived from the nucleophiles Nu_1^- and Nu_2^-, respectively, would be indicative of the relative rate constants (k_{Nu_1}/k_{Nu_2} of both reactions (eq 2 and 3). This will be so if the propagation steps are more frequent than the termination steps and if the nucleophiles and the intermediate radical anions are not involved in side reactions.[6]

It is known that the benzenethiolate ion reacts with aryl radicals to give an intermediate radical anion, whose main reaction is the electron transfer to the aromatic substrate. The reaction products of this nucleophile with different

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(2) Pierini, A. B.; Rossi, R. A. *J. Organomet. Chem.* **1978**, *144*, c12; **1979**, *168*, 163.

(3) Pierini, A. B.; Rossi, R. A. *J. Org. Chem.* **1979**, *44*, 4667.

(4) Rossi, R. A.; Pierini, A. B. *J. Org. Chem.* **1980**, *45*, 2914.

(5) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413.

(6) Galli, C.; Bunnett, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 7140.

0022-3263/84/1949-0486$01.50/0