# Kinetics and Mechanism of the Addition of Benzylamines to Benzylidenemalononitriles in Acetonitrile

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Nucleophilic addition reactions of benzylamines (BA) to benzylidenemalononitrile (BMN) have been studied in acetonitrile at 15.0 °C. The rate is first-order with respect to both BA and BMN and no base catalysis is observed. The rate decreases as the electron-withdrawing power of the substituent (Y) in the substrate increases ($\rho_Y < 0$). This is in contrast to the similar reactions of $\beta$-nitrostyrenes (NS) with BAs in acetonitrile and the addition reactions of NS and BMN in aqueous solution ($\rho_Y > 0$). This sign change of $\rho_Y$ is considered to result from the strong electron-withdrawing power of the $(CN)_2$ group in BMN, which leads to polarization of $C_\alpha{}^{\delta+}C^{\delta-}(CN)_2$ in the transition state. The mechanism of amine addition to BMN in acetonitrile is radically different from that in water. The reaction is predicted to proceed concertedly in a single step with a hydrogen-bonded, four-center cyclic transition state.

## Introduction

Addition of anionic or neutral base nucleophiles to olefins is an important class of reaction. It may occur in a nucleophilic vinylic substitution[1] or in an adduct formation.[2] In any of these classes of reactions, the role of an activating group is similar. The activating groups are normally electron acceptors, which act to stabilize the intermediate carbanion in the stepwise pathways.[1] The addition reactions of amine nucleophiles to olefins containing activating groups have been extensively studied.[2] One of the goals of such studies has been to demonstrate the transition state "imbalance" in which a lag in the charge delocalization into the activating group behind C−Nu bond formation occurs in the transition state. This type of "imbalance" arises from a delayed development of product (or carbanionic intermediate) stabilizing resonance in the transition state, in which a delayed solvation of the carbanionic center plays an important role especially in aqueous solution.[3]

Nucleophilic addition reactions of amine bases to substituted benzylidenemalononitriles (BMN) have been studied by Bernasconi et al.,[2] with the view of demonstrating a transition state (TS) imbalance[2,3] involved in a carbanion-forming reaction (eq 1, where Nu = second-



$$(1)$$
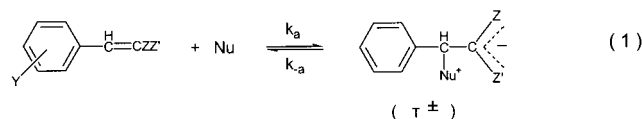
ary amines and Z = Z′ = CN) in which the carbanion is

weakly resonance stabilized. Their work was carried out in aqueous solution, since delocalization of the negative charge into the activating groups (Z = Z′ = CN) is strongly dependent on the solvation of this negative charge.[2,3] They found that even though the reactions show the typical behavior of a carbanion-forming process, the carbanion is largely stabilized by polar effects while resonance effects playing a more modest role.

On the other hand, our recent work on the nucleophilic addition reactions of benzylamines (BA) to $\beta$-nitrostyrenes (NS) in acetonitrile[4] showed that proton transfer to the $\beta$-carbon occurs concurrently and the neutral adducts are formed in a single step, not through a zwitterionic addition intermediate, T$^\pm$ (of the type in eq 1). We attributed this change of mechanism in acetonitrile to (i) weak solvation by acetonitrile to stabilize the carbanion (and benzylammonium ion) in the putative intermediate and (ii) hydrogen bonding to negative charge localized on $C_\beta$ in the TS due partly to the well-known "imbalance", which causes a lag in charge delocalization into the $NO_2$ moiety behind C−N bond formation.

In view of this surprising mechanistic change observed in the additions of amines to $\beta$-nitrostyrenes (NS) in acetonitrile, we extend this series of work to confirm such a change of mechanism using carbanion-forming reactions involving relatively weak activating groups, Z = Z′ = CN, in acetonitrile. The resonance stabilization of the carbanion is reported to be much weaker with the activating groups of $(CN)_2$ than with $H(NO_2)$.[2,3]

Another point of interest is the sign and magnitude of the cross-interaction constant, $\rho_{XY}$ in eqs 2[4]

$$log(k_{XY}/k_{HH}) = \rho_X\sigma_X + \rho_Y\sigma_Y + \rho_{XY}\sigma_X\sigma_Y \qquad (2a)$$

$$\rho_{XY} = \partial\rho_X/\partial\sigma_Y = \partial\rho_Y/\partial\sigma_X \qquad (2b)$$

where X and Y are substituents in the nucleophile, benzylamine (BA), and in the substrate, benzylidene-

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(1) (a) Apeloig, Y.; Rappoport, Z. *J. Am. Chem. Soc.* **1979**, *101*, 5095. (b) Rappoport, Z. *Acc. Chem. Res.* **1981**, *14*, 7. (c) Cohen, D.; Bar, R.; Shaik, S. S. *J. Am. Chem. Soc.* **1986**, *108*, 231. (d) Bernasconi, C. F.; Schuck, D. F.; Ketner, R. J.; Weiss, M.; Rappoport, Z. *J. Am. Chem. Soc.* **1994**, *116*, 11764. (e) Beit-Yannai, M.; Rappoport, Z.; Shainyan, B. A.; Danilevich, Y. S. *J. Org. Chem.* **1997**, *62*, 8049. (f) Chen, X.; Rappoport, Z. *J. Org. Chem.* **1998**, *63*, 5684.

(2) (a) Bernasconi, C. F.; Killion, R. B., Jr. *J. Org. Chem.* **1989**, *54*, 2878. (b) Bernasconi, C. F. *Tetrahedron* **1989**, *45*, 4017.

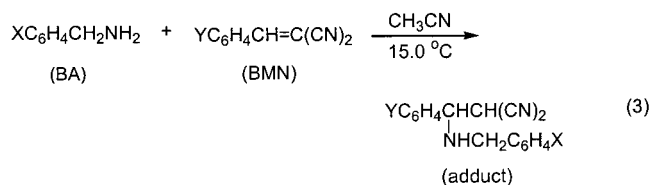(3) Bernasconi, C. F. *Acc. Chem. Res.* **1987**, *20*, 301.

(4) Oh, H. K.; Yang, J. H.; Sung, D. D.; Lee, I. *J. Chem. Soc., Perkin Trans. 2*, in press.

**Table 1. Second-Order Rate Constants, $k_2 \times 10$ L mol$^{-1}$ s$^{-1}$ for the Addition of X-Benzylamines to Y-Benzylidenemalononitriles in Acetonitrile at 15.0 °C**

| | Y | | | | | |
|---|---|---|---|---|---|---|
| X | *p*-Me | H | *p*-Cl | *p*-Br | *p*-NO$_2$ | $\rho_Y{}^a$ |
| *p*-OMe | 44.4$^b$ | | | | 16.5 | $-0.47 \pm 0.02$ |
| | 30.7 | 25.7 | 19.3 | 18.7 | 11.1 | |
| | 20.9$^c$ | | | | 7.38 | |
| *p*-Me | 23.9 | 19.2 | 14.6 | 13.9 | 7.73 | $-0.52 \pm 0.02$ |
| H | 13.3 | 10.1 | 7.66 | 7.21 | 3.94 | $-0.55 \pm 0.03$ |
| *p*-Cl | 8.31 | | | | 2.04 | $-0.63 \pm 0.04$ |
| | 5.68 | 4.12 | 2.92 | 2.77 | 1.40 | |
| | 3.82 | | | | 0.943 | |
| $\rho_X{}^d$ | $-1.49 \pm 0.07$ | $-1.62 \pm 0.06$ | $-1.67 \pm 0.08$ | $-1.69 \pm 0.07$ | $-1.81 \pm 0.07$ | $\rho_{XY}{}^e = -0.31$ |
| $\beta_X{}^f$ | $1.42 \pm 0.10$ | $1.54 \pm 0.10$ | $1.59 \pm 0.12$ | $1.60 \pm 0.11$ | $1.73 \pm 0.10$ | |

$^a$ The $\sigma$ values were taken from ref 6. Correlation coefficients were better than 0.995 in all cases $^b$ At 25.0 °C. $^c$ At 5.0 °C. $^d$ The source of $\sigma$ is the same as for footnote a. Correlation coefficients were better than 0.998 in all cases. $^e$ Correlation coefficients was 0.998. $^f$ The p$K_a$ values were taken from Fischer, A.; Galloway W. J.; Vaughan, J. *J. Chem. Soc.* **1964**, 3588. Oh, H. K.; Lee, J. Y.; Lee, I. *Bull. Korean Chem. Soc.* **1998**, *19*, 1198. Correlation coefficients were better than 0.995 in all cases.

malononitrile (BMN), respectively, in eq 3. The $\rho_{XY}$ has been shown to have a negative sign in addition processes,[5] e.g., bond formation in the $S_N2$ reactions[4a] and in the addition of amines to a vinyl carbon[4] with ca. $-0.6$ to $-0.8$.

$$XC_6H_4CH_2NH_2 \ + \ YC_6H_4CH=C(CN)_2 \ \xrightarrow[15.0\ °C]{CH_3CN}$$

$$\text{(BA)} \qquad\qquad \text{(BMN)}$$

$$\underset{\substack{|\\ NHCH_2C_6H_4X}}{YC_6H_4CHCH(CN)_2} \qquad (3)$$

$$\text{(adduct)}$$

## Results and Discussion

The kinetic law found for all the reactions studied in this work is given by eqs 4 and 5 where $k_0$ ($= 0$) and $k_2$ are the rate constants for solvolysis and aminolysis of the substrate (BMN), respectively.

$$-\mathrm{d[BMN]}/\mathrm{d}t = k_{obs}[BMN] \qquad (4)$$

$$k_{obs} = k_o + k_2[BA] \qquad (5)$$

No catalysis by a second benzylamine molecule was detected, which is in contrast to the benzylamine catalysis ($k_{obs} = k_2[BA] + k_3[BA]^2$) found for the aminolysis of $\beta$-nitrostyrenes (NSs).[4] Plots of $k_{obs}$ vs [BA] were linear, and the $k_2$ values obtained from the slopes of these plots are summarized in Table 1. The rate of benzylamine addition to BMN is faster by more than $10^2$ times than those to NS, e.g., for X = Y = H in acetonitrile, $k_2 = 1.01$ L mol$^{-1}$ s$^{-1}$ at 15.0 °C for BMN, but it is $2.63 \times 10^{-2}$ L mol$^{-1}$ s$^{-1}$ at 25.0 °C for NS.[4] The faster rates observed with BMN should be due to a stronger electron-deficient center, $C_\alpha$, in BMN than in NS since both the inductive ($\sigma_I$) and resonance ($\sigma_R$) electron-withdrawing power of the two CN groups ($2 \times \sigma_I = 2 \times 0.60 = 1.20$ and $2 \times \sigma_R = 0.36$)[6] in the BMN is much greater than that of one NO$_2$ group ($\sigma_I = 0.65$ and $\sigma_R = 0.16$)[6] in the NS. However, these rates are extremely slower (by a factor of ca. $\sim10^{-5}$–$10^{-6}$) than those corresponding reactions in aqueous solution.[2] We note in Table 1 that the rate decreases as the electron-withdrawing power of the substituent (Y)

**Table 2. Kinetic Isotope Effects on the Second-Order Rate Constants ($k_2$) for the Reactions of Y-Benzylidenemalononitriles with Deuterated X-Benzylamines in Acetonitrile at 15.0 °C**

| X | Y | $k_H/10^{-1}$ M$^{-1}$ s$^{-1}$ | $k_D/10^{-1}$ M$^{-1}$ s$^{-1}$ | $k_H/k_D$ |
|---|---|---|---|---|
| *p*-OMe | *p*-Me | $3.07 \pm 0.03$ | $1.30 \pm 0.01$ | $2.36 \pm 0.03^a$ |
| *p*-OMe | H | $2.57 \pm 0.02$ | $1.05 \pm 0.01$ | $2.45 \pm 0.03$ |
| *p*-OMe | *p*-Cl | $1.93 \pm 0.02$ | $0.757 \pm 0.007$ | $2.55 \pm 0.04$ |
| *p*-OMe | *p*-Br | $1.87 \pm 0.02$ | $0.728 \pm 0.005$ | $2.57 \pm 0.03$ |
| *p*-OMe | *p*-NO$_2$ | $1.11 \pm 0.01$ | $0.410 \pm 0.004$ | $2.71 \pm 0.04$ |
| *p*-Cl | *p*-Me | $0.568 \pm 0.005$ | $0.253 \pm 0.002$ | $2.25 \pm 0.03$ |
| *p*-Cl | H | $0.412 \pm 0.004$ | $0.173 \pm 0.002$ | $2.38 \pm 0.04$ |
| *p*-Cl | *p*-Cl | $0.292 \pm 0.003$ | $0.118 \pm 0.001$ | $2.47 \pm 0.03$ |
| *p*-Cl | *p*-Br | $0.277 \pm 0.002$ | $0.108 \pm 0.001$ | $2.56 \pm 0.03$ |
| *p*-Cl | *p*-NO$_2$ | $0.140 \pm 0.001$ | $0.0528 \pm 0.0003$ | $2.65 \pm 0.03$ |

$^a$ Standard deviations.

in the substrate increases, e.g., $k_2$ (Y = *p*-NO$_2$)/$k_2$(Y = H) $\cong 0.3$–0.4. This is opposite to the trend found for the reactions of NSs[4] with BA in acetonitrile [$k_2(p\text{-NO}_2)/k_2(H) = 31$–49] and also to that of $k_1$ for the rate-limiting $T^\pm$ formation of the reactions of BMN with piperidine (and morpholine) in water [$k_1(Y = p\text{-NO}_2)/k_1(Y = H) \cong 4$].[2a] Consequently, the sign of $\rho_Y$ ($= -0.47$ to $-0.63$) is negative for the present reaction series in contrast to the all positive $\rho_Y$ values for other similar reactions compared above.[2] The magnitudes of $\rho_X(\rho_{nuc})$ ($= -1.49$ to $-1.81$) and $\beta_X(\beta_{nuc})$ ($= 1.42$–1.73) are somewhat greater than those corresponding values of the NS reactions.[4] The negative $\rho_Y$ obtained in this work indicates that the reaction center carbon ($C_\alpha$) becomes more positive on going from the reactant to the TS. This is certainly not consistent with the TS for rate-limiting formation of the addition intermediate, $T^\pm$, for which negative charge ($\rho_Y > 0$) develops normally.[2–5]

The normal kinetic isotope effects ($k_H/k_D > 1.0$ in Table 2) involving deuterated benzylamines ($XC_6H_4CH_2ND_2$) provide evidence for partial N–H(D) bond cleavage in the TS.[7] This means that proton transfer to $C_\beta$ occurs concurrently with the N–$C_\alpha$ bond formation in the TS, **I**, i.e., the reaction does not proceed through an addition intermediate, $T^\pm$, but occurs concertedly in a single step. This mechanism is similar to that proposed for the addition reactions of benzylamines to NS in acetonitrile.[4] We stress that this mechanism is radically different from the rate-limiting formation of $T^\pm$ in water.[2] We propose again that this mechanistic change can be attributed to the weak solvation by acetonitrile of the carbanion and

(5) (a) Lee, I. *Prog. Phys. Org. Chem.* **1992**, *27*, 57. (b) Lee, I. *Chem. Soc. Rev.* **1990**, *19*, 317. (c) Isaacs, N. S. *Physical Organic Chemistry*, 2nd ed.; Longman: Harlow, 1995; p 186.
(6) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

(7) Lee, I. *Chem. Soc. Rev.* **1995**, *24*, 223.

benzylammonium ion in the putative $T^{\pm}$. As to the TS imbalance, the instantaneously localized negative charge on $C_\beta$ may facilitate the proton shift to $C_\beta$ in the TS.



**I**
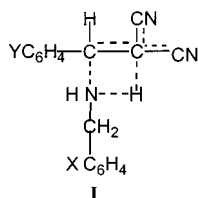
There remains an important result of the negative $\rho_Y$ for the addition of benzylamines to BMN in contrast to the positive $\rho_Y$ for the addition to NS to be explained consistently with our proposed mechanism: For this purpose, we should consider relative extent of resonance delocalization within the reactants, BMN and NS (**II** and **III**), as well as that within the activating groups of the carbanion intermediates. The resonance delocalization in



**II**                                                **III**
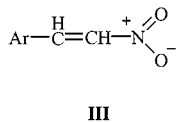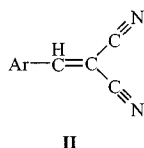
**II** should be stronger than that in **III** since the two CN groups provide a stronger $\pi$-electron-accepting ability. The resonance parameters such as $R$ (Swain–Lupton) and $\sigma_R$ (NMR chemical shift) show that two CN groups are much stronger resonance electron acceptors than an $NO_2$ group; $R$ (0.30 for $(CN)_2$ and 0.13 for $NO_2$) and $\sigma_R$ (0.36 for $(CN)_2$ and 0.16 for $NO_2$).[6] On the other hand, resonance stabilization of the carbanion in $T^{\pm}$ by $H(NO_2)$ groups in NS is known to be much stronger than that by the $(CN)_2$ groups in BMN.[2] However, this should apply to the reactions in aqueous solution, where the terminal anionic $NO_2$ group in NS is strongly stabilized by hydration, **IV**, while stabilization by hydration of the anionic $(CN)_2$ groups in BMN is small, **V**. This difference in the extent of solvation between the two, **IV** and **V**, should be the main reason for the large difference in the strength of resonance stabilization of the carbanions on the two activating groups, $(CN)_2 \ll H(NO_2)$, in aqueous solution. In acetonitrile, however, weaker solvation of carbanions on the two activating groups, $H(NO_2)$ in NS and $(CN)_2$ in BMN, may cause to reduce the large difference of solvating power, and the stronger electron withdrawing power of the $(CN)_2$ group in BMN may prevail.



**IV**                                                **V**
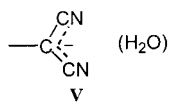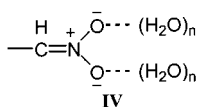
A measure of the electron-withdrawing power of the $(CN)_2$ group in the TS can be provided by the $R^-$ value, which has been defined for $\pi$-electron acceptor substituents in the reaction with strong conjugation with electron-rich reaction centers. The $R^-$ values for $(CN)_2$ and $NO_2$ are 0.98 and 0.62, respectively;[6] these are much greater than the $R$ values (0.30 and 0.13, respectively), and the difference between the two ($\Delta R^- = 0.36$) is also very large. Since both the inductive and resonance electron-withdrawing power of the $(CN)_2$ group are much stronger than those of the $NO_2$ group (vide supra),

**Table 3. Activation Parameters[a] for the Reactions of Y-Benzylidenemalononitriles with X-Benzylamines in Acetonitrile**

| X | Y | $\Delta H^{\ddagger}$/kcal mol$^{-1}$ | $-\Delta S^{\ddagger}$/cal mol$^{-1}$ K$^{-1}$ |
|---|---|---|---|
| *p*-OMe | *p*-Me | 5.6 | 32 |
| *p*-OMe | *p*-NO$_2$ | 5.8 | 35 |
| *p*-Cl | *p*-Me | 6.1 | 33 |
| *p*-Cl | *p*-NO$_2$ | 5.8 | 38 |

[a] Calculated by the Eyring equation. The maximum errors calculated (by the method of Wiberg, K. B. *Physical Organic Chemistry*; Wiley: New York, 1964; p 378) are $\pm 0.5$ kcal mol$^{-1}$ and $\pm 2$ eu for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, respectively.

polarization of the $\alpha$-carbon to $C_\alpha^+$ should be much stronger in BMN than in NS.

The relatively lower electron density on $C_\alpha \cdots C_\beta$ due to strong electron acceptor ability of the $(CN)_2$ group should lead to smaller primary kinetic isotope effects[7] for the reaction of NS ($k_H/k_D \cong 2.30-3.08$).[4]

There is almost a linear increase of $k_H/k_D$ with $\sigma_Y$ (e.g., for X = *p*-MeO, $k_H/k_D = 0.36\sigma_Y + 2.45$, $r = 0.981$) suggesting that a greater degree of bond formation ($\beta_x$ increases with $\sigma_Y$) results in a greater degree of proton transfer in the TS, **I**.

The cross-interaction constant, $\rho_{XY}$, calculated by subjecting 20 rate data to multiple linear regression using eq 2a is $-0.31$. This is also reasonable considering the values for $S_N2$ reaction ($\rho_{XY} = -0.6$ to $-0.8$)[5a] if we account for the falloff ($\cong 0.47$)[8] due to an intervening group, $CH_2$, in benzylamine (leading to $\rho_{XY} \cong -0.7$). The negative sign of $\rho_{XY}$ also ensures us an involvement of the normal $N-C_\alpha$ bond formation process in the TS, excluding any possibilities of $T^{\pm}$ intermediate formation for which the sign of $\rho_{XY}$ has been found to be positive in the carbonyl addition reactions.[9] The smaller magnitude of $\rho_{XY}$ found for the addition to BMN than to NS is again a manifestation of the dissociative nature of the TS for the addition to BMN, since the magnitude of $\rho_{XY}$ is a measure of the degree of bond formation.

The activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ in Table 3, are consistent with the concurrent addition of nucleophile and proton transfer, **I**.

The bond formation process normally requires small activation energy, since exclusion repulsion energy is partially offset by the bond energy of the forming bond. In the present reactions, a $\pi$ bond is broken concurrently, but this is facilitated by the imbalance of the TS in which reactant resonance stabilization is lost ahead of the bond formation. The large negative entropy of activation ($-32$ to $-38$ eu) is consistent with the four-membered type of constrained TS structure, **I**.

In summary, the addition of benzylamine (BA) to benzylidenemalononitrile (BMN) occurs in a single step in which the addition of BA to $C_\alpha$ of BMN and proton transfer from BA to $C_\beta$ of BMN take place concurrently with a four-membered cyclic TS structure, **I**. The reaction center carbon, $C_\alpha$, becomes more positive ($\rho_Y < 0$) on going from the reactant to transition state due to strong polarization of the $\alpha$-carbon, $C_\alpha^+$, in the TS by the strong electron-withdrawing polar effects of the two CN groups.

(8) (a) Page, M.; Williams, A. *Organic and Bio-organic Mechanisms*; Longman: London, 1997; p 250. (b) Hansch, C.; Hoekman, D.; Gao, H. *Chem. Rev.* **1996**, *96*, 1045.

(9) (a) Lee, I. *Bull. Korean Chem. Soc.* **1994**, *15*, 985. (b) Oh, H. K.; Shin, C. H.; Lee, I. *J. Chem. Soc., Perkin Trans. 2* **1995**, 1169. (c) Lee, I.; Koh, H. J. *New J. Chem.* **1996**, *20*, 131. (d) Koh, H. J.; Kim, O. S.; Lee, H. W.; Lee, I.. *J. Phys. Org. Chem.* **1997**, *10*, 725. (e) Kim, T. H.; Huh, C.; Lee, B. S.; Lee, I. *J. Chem. Soc., Perkin Trans. 2* **1995**, 2257.

The proton transfer in the TS to $C_\beta$ of BMN is viable also due to polarization of double bond in the imbalanced TS. The sign and magnitude of the cross-interaction constant, $\rho_{XY}$, is comparable to those found in the normal bond formation processes in the $S_N2$ and addition reactions. The normal kinetic isotope effect ($k_H/k_D > 1.0$) and relatively low $\Delta H^\ddagger$ and large negative $\Delta S^\ddagger$ values are also consistent with the mechanism proposed.

## Experimental Section

**Materials.** Merck GR acetonitrile was used after three distillations. The Aldrich benzylamine nucleophiles were used after recrystallization. Aldrich malononitrile and benzaldehydes were used.

**Preparations of Benzylidenemalononitriles.** The benzylidenemalononitriles were prepared by the literature method of Zabicky.[10] Equimolar amounts of benzaldehyde (10 mmol) and malononitrile (10 mmol) were dissolved in the minimal amount of 95% ethanol. After the addition of a few drops of 10% potassium hydroxide solution the mixture was set aside for 1 h. The precipitate was filtered off and purified by repeated recrystallizations from ethanol (yield > 85%). Melting points, IR, and $^1$H and $^{13}$C NMR data were found to agree well with the literature values.[2a]

**Kinetic Measurement.** The reaction was followed spectrophotometrically by monitoring the decrease in the concentration of benzylidenemalononitrile, [BMN], at $\lambda_{max}$ of the substrate to over 80% completion. The reaction was studied under pseudo-first-order conditions, $[BMN] = 8 \times 10^{-5}$ M and $[BA] = (1.0\sim8.0) \times 10^{-3}$ M at $15.0 \pm 0.1$ °C. The pseudo-first-order rate constant, $k_{obs}$, was determined from the slope of the plot of $\ln[BMN]$ vs time ($r > 0.994$). Second-order rate constants, $k_2$, were obtained from the slope of the plot of $k_{obs}$ vs [BA] ($r > 0.995$) with more than eight concentrations of benzylamine, carried out more than three runs, and were reproducible to within $\pm3$%. Typical examples of $k_{obs}$ vs [BA] data are shown in Table 4.

**Product Analysis.** Benzylidenemalononitrile (0.05 mol) and benzylamine (0.06 mol) were reacted in acetonitrile at 15.0 °C. After more than 15 half-lives, solvent was removed under reduced pressure and product was separated by column chromatography (silica gel, 20% ethyl acetate$-n$-hexane). Analytical data of the product gave the following results.

$p$-CH$_3$C$_6$H$_5$CH(NHCH$_2$C$_6$H$_4$-$p$-OCH$_3$)CH(CN)$_2$: mp 213–15 °C, IR(KBr), 3341 (NH, stretch), 3057 (CH, alkene), 2919 (CH, CH$_3$), 2233 (C≡N), 1589 (C=C, aromatic); $^1$H NMR (400 MHz, CDCl$_3$), 1.40 (1H, s, NH), 1.43 (2H, s, benzyl), 2.36 (1H, d, HC(CN)$_2$, $J = 1.08$ Hz), 2.40 (1H, d, CHN, $J = 0.68$), 2.45

(10) Zabicky, J. *J. Chem. Soc.* **1961**, 683.

**Table 4. The $k_{obs}$ and $k_2$ Values for the Reactions of Y$-$Benzylidenemalononitriles with $p$-OMe-Benzylamine Varying Concentrations in Acetonitrile at 15.0 °C**

| Y | [$p$-OMe-BA]/M | $k_{obs}/10^{-3}\cdot s^{-1}$ | $k_2$/M$^{-1}$ s$^{-1}$ | corr coeff |
|---|---|---|---|---|
| $p$-CH$_3$ | 0.001 | 2.78 | $3.07 \pm 0.13$ | 0.995 |
| | 0.002 | 6.18 | | |
| | 0.003 | 9.50 | | |
| | 0.004 | 13.7 | | |
| | 0.005 | 14.4 | | |
| | 0.006 | 17.7 | | |
| | 0.007 | 21.1 | | |
| | 0.008 | 25.3 | | |
| H | 0.001 | 2.88 | $2.57 \pm 0.08$ | 0.997 |
| | 0.002 | 5.31 | | |
| | 0.003 | 8.34 | | |
| | 0.004 | 11.5 | | |
| | 0.005 | 13.9 | | |
| | 0.006 | 16.1 | | |
| | 0.007 | 17.8 | | |
| | 0.008 | 21.1 | | |
| $p$-Cl | 0.001 | 1.93 | $1.93 \pm 0.08$ | 0.995 |
| | 0.002 | 4.48 | | |
| | 0.003 | 7.26 | | |
| | 0.004 | 8.66 | | |
| | 0.005 | 10.8 | | |
| | 0.006 | 12.3 | | |
| | 0.007 | 14.1 | | |
| | 0.008 | 15.8 | | |
| $p$-Br | 0.001 | 2.27 | $1.87 \pm 0.07$ | 0.996 |
| | 0.002 | 4.46 | | |
| | 0.003 | 6.81 | | |
| | 0.004 | 8.36 | | |
| | 0.005 | 10.0 | | |
| | 0.006 | 11.5 | | |
| | 0.007 | 13.3 | | |
| | 0.008 | 16.2 | | |
| $p$-NO$_2$ | 0.001 | 0.864 | $1.11 \pm 0.04$ | 0.996 |
| | 0.002 | 1.77 | | |
| | 0.003 | 2.85 | | |
| | 0.004 | 3.94 | | |
| | 0.005 | 5.27 | | |
| | 0.006 | 6.80 | | |
| | 0.007 | 7.41 | | |
| | 0.008 | 8.23 | | |

(3H, s, CH$_3$), 3.84 (3H, s, OCH$_3$), 6.69–7.82 (8H, m, aromatic ring); $^{13}$C NMR (100.4 MHz, CDCl$_3$), 158.5, 137.5, 130.8, 130.2, 128.5, 117.7, 113.8, 68.2, 59.2, 31.6, 22.7, 14.1.