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Kinetics and Mechanism of the Addition of Benzylamines to Benzylidene-3,5-heptadione in Acetonitrile

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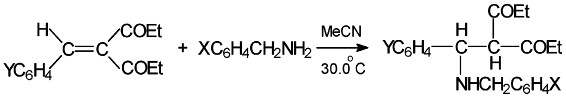
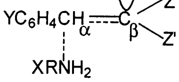


The addition reaction of benzylamine ($XC_6H_4CH_2NH_2$) to benzylidene-3,5-heptadione (BHD; YC_6H_4-$CH{=}C(COEt)_2$) in acetonitrile is investigated. The rate is slower than the corresponding rate for benzylidenediethylmalonate ($YC_6H_4CH{=}C(OOEt)_2$) as the result of a greater steric hindrance in the *planar* dicarbonyl transition state. The kinetic isotope effects (k_H/k_D) involving deuterated amine nucleophiles ($XC_6H_4CH_2ND_2$) are greater than 1 (1.37−2.04), indicating N−H bond stretching with concurrent $N-C_\alpha$ and $H-C_\beta$ bond formation in the TS. The trend of change in k_H/k_D with variation of substituent X in the nucleophile conforms to the Bell−Evans−Polanyi principle. It has been stressed that the dicarbonyl group activated olefins exhibit insignificant charge imbalance in the TS for the benzylamine additions in acetonitrile as a result of the two strong $n_c \rightarrow \pi^*_{C=O}$ vicinal charge-transfer interactions.

Introduction

Nucleophilic addition of amines ($XRNH_2$) to olefins ($YC_6H_4CH{=}CZZ'$) activated by electron acceptors (Z, Z′) occurs through a zwitterionic intermediate, $T^\pm$, in aqueous solution.[1] An imbalanced transition state (TS) is often observed due mainly to the poorly developed resonance into Z,Z′ and solvation with the negative charge largely localized on carbon (C_β), an exaggerated form of which can be given as **1**.[1] The imbalance is stronger in the amine additions in aqueous solution than in the corresponding addition reactions in acetonitrile in which the reactions are known to proceed by concerted formation of the $N-C_\alpha$ and C_β-H bonds, **2**, in a single-step to a neutral product,[2] eq 1.



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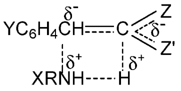

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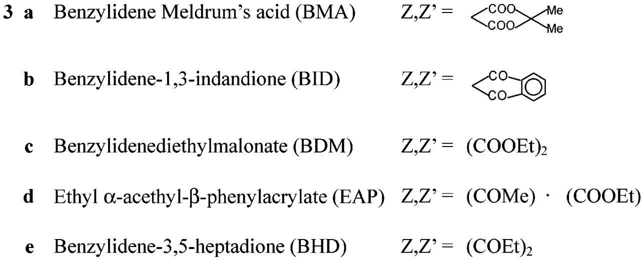
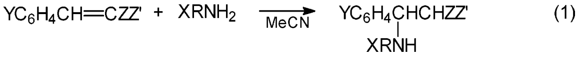


3	a	Benzylidene Meldrum's acid (BMA)	Z,Z' =
	b	Benzylidene-1,3-indandione (BID)	Z,Z' =
	c	Benzylidenediethylmalonate (BDM)	Z,Z' = $(COOEt)_2$
	d	Ethyl α-acethyl-β-phenylacrylate (EAP)	Z,Z' = (COMe) · (COOEt)
	e	Benzylidene-3,5-heptadione (BHD)	Z,Z' = $(COEt)_2$

FIGURE 1.



$$YC_6H_4CH{=}CZZ' + XRNH_2 \xrightarrow[MeCN]{k_2} YC_6H_4\underset{\displaystyle XRNH}{\underset{|}{C}}HCHZZ' \qquad (1)$$

Recently, we found that amine additions to dicarbonyl activated olefins (**3a**−**d**, Figure 1), in general, and those with the cyclic structures (**3a** and **3b**), in particular,

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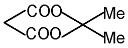
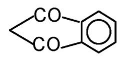
TABLE 1. Second-Order Rate Constants, $k_2 \times 10^2$ dm^3 mol^{-1} s^{-1}, for Addition Reactions of Benzylidene-3,5-heptadiones with X-Benzylamines in Acetonitrile at 30.0 °C

	Y					
X	*p*-OMe	*p*-Me	H	*p*-Cl	*p*-Br	ρ_Y[a]
p-OMe	1.04 0.706[b] 0.494[c]	1.38	2.20	3.85	4.26 2.89[b] 1.99[c]	1.18 ± 0.01
p-Me	0.920	1.20	1.90	3.25	3.48	1.13 ± 0.03
H	0.770	0.985	1.47	2.45	2.73	1.06 ± 0.04
p-Cl	0.584 0.392[b] 0.266[c]	0.697	1.04	1.65	1.77 1.20[b] 0.804[c]	0.95 ± 0.03
ρ_X[d]	−0.50(±0.01)	−0.59(±0.02)	−0.66(±0.02)	−0.74(±0.05)	−0.75(±0.03)	ρ_{XY}[e]= −0.46
β_X[f]	0.48(±0.01)	0.56(±0.03)	0.63±(±0.02)	0.70(±0.02))	0.72(±0.02)	

[a] The σ values were taken from ref 9. Correlation coefficients were better than 0.998 in all cases. [b] At 20.0 °C. [c] At 10.0 °C. [d] The source of σ is the same as for footnote a. Correlation coefficients were better than 0.998 in all cases. [e] Correlation coefficients was 0.999. [f] The pK_a values were taken from Fischer, A.; Galloway, W. J.; Vaughan, J. *J. Chem. Soc.* **1964**, 3588. Correlation coefficients were better than 0.999 in all cases. pK_a = 9.67 was used for X = *p*-CH$_3$O. (Oh, H. K.; Lee, J. Y.; Lee, I. *Bull. Korean Chem Soc*. **1998**, *19*, 1198).

TABLE 2. Comparison of Rate, Selectivity, and Activation Parameters for Benzylamine Additions to Olefins with Dicarbonyl Activating Groups

substrate	Z,Z′	k_2 (°C)	β_x[a]	ρ_{XY}	k_H/k_D	$\Delta H^{\ddagger b}$	$-\Delta S^{\ddagger}$	ρ_Y[c]	ref
3a BMA		86.6 (20)	0.23	−0.33	1.45−1.74	3.8	38	0.40	3c
3b BID		1.48 (25)	1.09	−0.33	1.25−1.81	6.0	36	0.41	8
3c BDM	(COOEt)$_2$	2.48 × 10^{-2} (20)	0.88	−0.45	1.52−2.07	6.5	50	1.05	3a
3d EAP	COMe, COOEt	0.81 × 10^{-2} (20)	0.90	−0.38	1.78−2.38	4.9	54	0.90	2c
3e BHD	(COEt)$_2$	1.47 × 10^{-2} (30)	0.63	−0.46	1.37−2.04	6.1	48	1.06	this work

[a] For Y = H. [b] For X = *p*-Cl and Y = *p*-OMe. [c] For X = H.

4 a	β-Nitrostyrene (NS)	Z,Z' =	H, NO$_2$
b	β-Nitrostilbene (NSB)	Z,Z' =	Ph, NO$_2$
c	β-Cyano-4'-nitrostilbene (CNS)	Z,Z' =	C$_6$H$_4$·NO$_2$, CN
d	Benzylidenemalononitrile (BMN)	Z,Z' =	(CN)$_2$
e	Benzylidene-α-cyanocinnamate (ECC)	Z,Z' =	CN, COOEt

FIGURE 2.

exhibit insignificant imbalance in acetonitrile.[2c,3] This has been demonstrated by relatively smaller kinetic isotope effects, k_H/k_D(<2.0), involving deuterated benzylamine nucleophiles (XC$_6$H$_4$CH$_2$ND$_2$)[4] and the trend of change in k_H/k_D with the substituent X, which is consistent with thermodynamically controlled reactions where the Hammond postulate and Bell−Evans−Polanyi (BEP) principle hold.[2c,5] In contrast, for amine additions to nondicarbonyl activated olefins (**4a**−**e**, Figure 2) the k_H/k_D values are relatively large (>2.3) and the trend of change in k_H/k_D with the substituent X conforms to that expected from intrinsically controlled reactions[6a] where an anti-Hammond effect applies.[5a] For this class of nondicarbonyls, the imbalance is relatively stronger than that for the dicarbonyls. In this work, we explore further with an acyclic dicarbonyl activated olefin, benzylidene-3,5-heptadione (BHD), why dicarbonyls behave differently from other nondicarbonyl activated olefins in the amine addition reactions in acetonitrile. Furthermore, we are interested in the major factors influencing the TS structure for the amine additions to dicarbonyl as well as nondicarbonyl activated olefins in acetonitrile.

Results and Discussion

The reactions of benzylidene-3,5-heptadione (BHD), YC$_6$H$_4$CH=C(COEt)$_2$, with benzylamines (XC$_6$H$_4$CH$_2$NH$_2$) in acetonitrile at 30.0 °C obey a clean second-order rate law, eqs 2 and 3 where [BHD] and [BA] are the concentration of benzylidene-3,5-heptadione and benzylamine, respectively.

$$\text{rate} = k_{\text{obs}}[\text{BHD}] \tag{2}$$

$$k_{\text{obs}} = k_2[\text{BA}] \tag{3}$$

The second-order rate constants, k_2, summarized in Table 1 are obtained from a straight line plot of k_{obs} vs [BA]. The rates of benzylamine additions to dicarbonyl activated olefins in acetonitrile are compared in Table 2 together with relevant selectivity parameters, including

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TABLE 3. Kinetic Isotope Effects on Second-Order Rate Constants (k_2) for Reactions of Benzylidene-3,5-heptadiones with Deuterated X-Benzylamines ($XC_6H_4CH_2ND_2$) in Acetonitrile at 30.0 °C

X	Y	$k_H \times 10^2$ ($M^{-1}\ s^{-1}$)	$k_D \times 10^2$ ($M^{-1}\ s^{-1}$)	k_H/k_D
p-OMe	*p*-Me	1.38(±0.01)	0.696(±0.004)	1.98 ± 0.02[a]
p-OMe	H	2.20(±0.02)	1.24(±0.01)	1.77 ± 0.02
p-OMe	*p*-Cl	3.85(±0.04)	2.46(±0.03)	1.56 ± 0.03
P-OMe	*p*-Br	4.26(±0.06)	3.10(±0.04)	1.37 ± 0.03
p-Cl	*p*-Me	0.697(±0.004)	0.341(±0.002)	2.04 ± 0.02
p-Cl	H	1.04(±0.01)	0.556(±0.003)	1.87 ± 0.02
p-Cl	*p*-Cl	1.65(±0.01)	0.993(±0.001)	1.66 ± 0.03
p-Cl	*p*-Br	1.77(±0.02)	1.20(±0.01)	1.47 ± 0.02

[a] Standard deviation.

the cross-interaction constant, ρ_{XY}, which is defined as eqs 4 and 5.[6]

$$\log\left(\frac{k_{XY}}{k_{HH}}\right) = \rho_X\sigma_X + \rho_Y\sigma_Y + \rho_{XY}\sigma_X\sigma_Y \tag{4}$$

$$\rho_{XY} = \frac{\partial\rho_X}{\partial\sigma_Y} = \frac{\partial\rho_Y}{\partial\sigma_X} \tag{5}$$

The β_X values listed are those determined by the plots of log k_2(MeCN) against pK_a(H_2O) of benzylamines. This procedure was found to be reliable, since the pK_a(MeCN) varies in parallel with the pK_a(H_2O) with a reasonably constant difference of δpK_a (= pK_a(MeCN) − pK_a(H_2O)) ≅ 7.5.[7] The sign of ρ_{XY} is negative in all cases, which is consistent with those reported for nucleophilic bond formation in the TS.[6] The size of ρ_{XY} for the cyclic series (−0.33) are somewhat smaller than those for the noncyclic series (−0.38 to −0.46), which suggests an earlier TS for the cyclic series. This is also evident from smaller k_H/k_D values for the cyclic compared to those of acyclic series. The kinetic isotope effect involving deuterated amines ($XC_6H_4CH_2ND_2$) reflects N−H (N−D) bond stretching in the TS[4] due to the hydrogen bonding of the amine proton toward the anionic center developing on C_β forming a four-membered type structure, **2**. The k_H/k_D values determined in the present work are summarized in Table 3. The trend of change in k_H/k_D with variation of X in the nucleophile, $\delta\sigma_X < 0 \rightarrow \delta(k_H/k_D) < 0$, is in agreement with those found for other dicarbonyl series.[2c,3a,c,8]

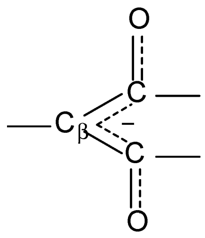
The activation parameters, $\Delta H^\ddagger$ and $\Delta S^\ddagger$, are shown in Table 4. The $\Delta H^\ddagger$ values are rather low since the reaction proceeds by a concurrent formation of N−C_α and H−C_β bonds, and the $\Delta S^\ddagger$ values are large due to a constrained hydrogen bonded TS structure, **2** (with Z,Z′ = $(COEt)_2$ and R = C_6H_4).

TABLE 4. Activation Parameters[a] for Reactions of Benzylidene-3,5-heptadiones with X-Benzylamines in Acetonitrile

X	Y	$\Delta H^\ddagger$ (kcal mol^{-1})	$-\Delta S^\ddagger$ (cal mol^{-1} K^{-1})
p-OMe	*p*-MeO	5.7	48
p-OMe	*p*-Br	5.9	45
p-Cl	*p*-MeO	6.1	48
p-Cl	*p*-Br	6.2	46

[a] Calculated by the Eyring equation. The maximum errors calculated (by the method of Wiberg, K. B. *Phys. Org. Chem.*; Wiley, New York, **1964**, p378) are ±0.5 kcal mol^{-1} and ±2 eu for $\Delta H^\ddagger$ and $\Delta S^\ddagger$, respectively.

Reference to Table 2 reveals that the rates of three acyclic dicarbonyl compounds[2c,3a] are substantially slower than those of the cyclic dicarbonyl activated olefins.[3c,8] This has been attributed to a built-in *planar* structure, **5**, in the cyclic dicarbonyls, which will strongly enhance delocalization of anionic charge on the carbanionic center,[2c] **1**, into the two carbonyl groups in the TS. For the acyclic dicarbonyls reorganization is required to form such a planar structure in the TS, which should result in a higher activation barrier.[2c] Among the acyclic dicarbonyls, the rate of BHD (**3e**; Z,Z′ = $(COEt)_2$) is slower than that of BDM (**3c**; Z,Z′ = $(COOEt)_2$).[3a] This is rather unexpected since the amine addition reactions to olefins are in general faster for the olefins with stronger electron acceptors; the resonance electron accepting ability is greater for COEt (R = 0.14, R^- = 0.51, σ^- = 0.84)[9] than for COOEt (R = 0.11, R^- = 0.41, σ^- = 0.75),[9] so that the rate order observed is in reverse of that predicted according to the electron acceptor strength of Z,Z′.



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However, this reversal can be rationalized by a greater steric hindrance within the *planar* TS for BHD than for BDM, since the insertion of an extra oxygen atom i.e., -C(=O)-Et → -C(=O)-O-Et, ameliorates the steric hindrance[10] in the *planar* (TS) structure for BDM. In the *nonplanar* structure, as in the final adduct (product), steric requirement for planarity will be relaxed and the product stability will be greater with $(COEt)_2$ than with $(COOEt)_2$, i.e., thermodynamically the BHD product is more stable and hence the TS for the BHD will occur at an earlier position (β_X = 0.63) along the reaction coordinate than for the BDM (β_X = 0.88) in accordance with the BEP principle.[5] However, all other parameters (ρ_{XY}, k_H/k_D, $\Delta H^\ddagger$, $\Delta S^\ddagger$, and ρ_Y) for the two compounds (in Table 2) are quite reasonably similar. For the cyclic dicarbonyls, BMA[3c] and BID,[8] there will be no such streic hindrance effect in the planar TS, and hence the faster rate (with BMA) leads to an earlier TS (β_X = 0.23 and 1.09 for BMA[3c] and BID,[8] respectively) relative to BID, which is again consistent with the BEP principle.[5] Thus the TS position along the reaction coordinate for the

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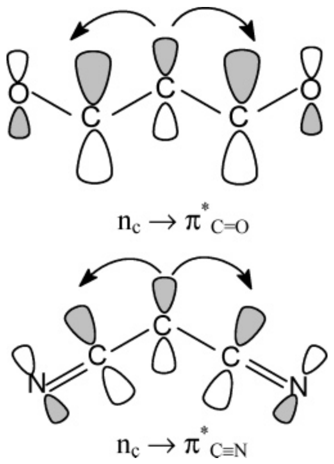
(10) For example, E_s values for $PhCH_2$ and $PhOCH_2$ are −0.38 and −0.33, respectively. Taft, R. W. In *Steric Effects in Organic Chemistry*; Newman, M. S., Ed.; Wiley: New York, 1956; Chapter 13.

amine additions to cyclic as well as acyclic dicarbonyl activated olefins is controlled by the thermodynamic effect.[5b,6a] The trend of change in the kinetic isotope effect (k_H/k_D) involving deuterated benzylamine nucleophiles[4] ($XC_6H_4CH_2ND_2$) with variation of substituent X in the nucleophile, $\delta\sigma_X < 0 \rightarrow \delta(k_H/k_D) < 0$, for the dicarbonyl substrates are also consistent with the thermodynamic controlled reaction series; a faster rate with a strong electron donor in the nucleophile ($\delta\sigma_X < 0$) leads to an earlier TS with a lower degree of N−H bond stretching and C_β−H bond formation in the concurrent C_α−N and C_β−H bond formation in the TS, **2**. In the thermodynamic control reaction series, the product stability dictates the progress of reaction in the TS.[5,6a] This means that for the amine additions to dicarbonyl activated olefins, the charge imbalance, **1**, seems minimal, and there is a marginal or insignificant delay or lag in the anionic charge delocalization into the dicarbonyl activating groups in the TS. This has been attributed to the two strong vicinal charge transfers of the carbanioic charge of a nonbonding orbital, n_c, on C_β into the two π^* orbitals of the carbonyl groups ($\pi^*_{C=O}$) by $n_c \rightarrow \pi^*_{C=O}$ interactions,[11] leading to a planar structure, **5**, of the TS. The two strong $n_c \rightarrow \pi^*_{C=O}$ interactions occurring concurrently in the dicarbonyls seem to provide sufficient electronic charge transfer to prevent the buildup of anionic charge on C_β in the TS, **1**. A single carbonyl group is not sufficient to prevent the charge imbalance as evidenced with ECC (Z,Z′ = CN, COOEt).[3b]

In contrast, the amine additions to nondicarbonyl activated olefins, **4a**−**e**, the charge imbalance is relatively strong and the TS position in the reaction coordinate becomes controlled by an intrinsic effect.[6a] For example, the rate of benzylamine addition to BMN (**4d**) in acetonitrile is much faster ($k_2 = 1.48$ M^{-1} s^{-1} at 25.0 °C)[12] than those for the corresponding reactions for CNS (**4c**; $k_2 = 1.02 \times 10^{-3}$ M^{-1} s^{-1} at 25.0 °C)[2b] and ECC (**4e**; $k_2 = 1.62 \times 10^{-2}$ M^{-1} s^{-1} at 30.0 °C)[3b] with a TS ($\beta_X = 1.54$) that is later than the latter two ($\beta_X = 1.09$). Moreover, the trend of change in k_H/k_D with the nucleophile is opposite to that found for the dicarbonyl series, $\delta\sigma_X < 0 \rightarrow \delta(k_H/k_D) > 0$, i.e., a faster rate with a stronger electron donor in the nucleophile ($\delta\sigma_X < 0$) leads to a later TS with a greater degree of N−H bond stretching and C_β−H bond formation in the concerted C_α−N and C_β−H bond formation in the TS. Furthermore, the magnitude of k_H/k_D values for the nondicarbonyl series ($k_H/k_D \cong 2.2-3.1$)[2a,b: 3b,12] is significantly greater than that for the dicarbonyl series ($k_H/k_D \cong 1.3-2.1$).[2c,3a,c,8] These results for the nondicarbonyl series can be interpreted as manifestations of substantial anionic charge localization on C_β in the TS due to the lag in the charge delocalization into activating groups, Z,Z.[1] These observations in acetonitrile are in line with the stronger TS imbalance with a significant retardation of the intrinsic rate of the amine additions to nondicarbonyls in aqueous solution.[1b]

It is interesting to compare the benzylamine addition to BMN (**4d**)[12] with that to BID[8] (**3b**). The two reactions in acetonitrile proceed with the same rate ($k_2 = 1.48$ M^{-1} s^{-1} at 25.0 °C), although the former is a nondicarbonyl in contrast to the latter, a cyclic dicarbonyl, i.e., the charge imbalance in the TS is significant in the former, whereas it is insignificant in the latter. The fast rate observed with BMN[12] is understandable in view of its strong electron accepting power by the two CN groups ($\sum C_p^- = 2.00$; $\sum R^- = 9.8$).[9] The vicinal charge transfer of the developing lone pair, n_c, on C_β in the TS can be, however, quite smaller to the two CN groups, $n_c \rightarrow \pi^*_{C\equiv N}$, in BMN than to the two CO groups $n_c \rightarrow \pi^*_{C=O}$, in BID, Scheme 1, since the charge-transfer energy stabilization, $\Delta E^{(2)}$, depends on two factors,[11,13] the energy gap, $\Delta\epsilon = \epsilon_{\pi^*} - \epsilon_n$, and the Fock matrix element, which is propotional to the overlap, $S_{n\pi^*}$, between the two interacting orbitals, eq 6:

SCHEME 1



$$\Delta E^{(2)} = -\frac{2F^2_{n\sigma^*}}{\Delta\epsilon} \qquad (6)$$

Thus, the $n_c \rightarrow \pi^*_{C\equiv N}$ interaction should be much weaker than the $n_c \rightarrow \pi^*_{C=O}$ charg -transfer based on the following grounds: (i) The $\pi^*_{C\equiv N}$ level is higher than the $\pi^*_{C=O}$ level,[14] so that $\Delta\epsilon$ will be greater and $-\Delta E^{(2)}$ will be small for BMN than for BID. (ii) The overlap of the nonbonding orbital (n_c) occurs only with the carbon of the C≡N group in $\pi^*_{C\equiv N}$, whereas a facial overlap of n_c with $\pi^*_{C=O}$ is possible in dicarbonyls so that $S_{n\pi^*}$ ($F_{n\pi^*}$) should be much smaller in BMN than in BID. (iii) The lobe size of the carbon in $\pi^*_{C\equiv N}$ is smaller than that in $\pi^*_{C=O}$[15] so that the overlap, $S_{n\pi^*}$ ($F_{n\pi^*}$), is smaller for BMN than for BID.

In summary, the benzylamine addition to benzylidene-3,5-heptadione (BHD) in acetonitrile proceeds by concurrent formation of N−C_α and H−C_β bonds with a cyclic TS structure. The kinetic isotope effect, k_H/k_D (>1.0), involving deuterated benzylamine is smaller ($\delta(k_H/k_D) < 0$ for a stronger nucleophile ($\delta\sigma_X < 0$) in accordance with the BEP principle. The progress of reaction at the TS for benzylamine additions to all the dicarbonyl activated olefins including BHD in acetonitrile are dependent on

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the product stability, i.e., thermodynamically controlled, indicating insignificant lag in the charge delocalization into the activating groups in the TS. This is in quite contrast to the substantial charge imbalance in the corresponding addition reactions to other nondicarbonyl activated olefins, for which the TS structure is intrinsic controlled. There are two very strong $n_c \rightarrow \pi^*_{C=O}$ vicinal charge-transfer interactions in the planar TS for the dicarbonyl activated olefins, and anionic charge buildup on C_β, i.e., lag in the charge delocalization, in the TS becomes insignificant.

Experimental Section

Materials. GR grade acetonitrile was used after three distillations. GR grade benzylamine nucleophiles were used after recrystallization. 3,5-Heptanedione and benzaldehydes were also GR grade.

Preparartions of Benzylidene-3,5-heptadiones. The benzylidene-3,5-heptadiones (BHDs) were prepared by the literature method of Horning et al.[16] Equimolar amounts of benzaldehyde (10 mmol) and 3,5-heptanedione (10 mmol) were dissolved in the minimal amount of pyridine and refluxed for 1 h. Solvent was removed under reduced pressure and product was separated by column chromatography (silica gel, 10% ethyl acetate−*n*-hexane) (yield >85%). IR (FT-IR) and ^{1}H and ^{13}C NMR (400 MHz) data were found to agree well with the literture value.[16]

Deuterated Benzylamines. The deuterated benzylamines ($XC_6H_4CH_2ND_2$) were prepared as described before.[17] The analysis (NMR) of dried benzylamines had more than 99% deuterium content.

Kinetic Measurement. The reaction was followed spectrophotometrically by monitoring the decrease in the concentration of benzylidene-3,5-heptadione, [BHD], at λ_{max} (282 nm) of the substrate to over 80% completion. The reaction was studied under pseudo-first-order conditions, $[BHD] = 6.0 \times 10^{-5}$ M and [BA] = 0.04−0.10 M at 30.0 ± 0.1 °C. The pseudo-first-order rate constant, k_{obs}, was determined from the slope of the plot ($r > 0.994$) ln[BHD] (2.303 log[BHD]) vs time. Second-order rate constants, k_2, were obtained from the slope of a plot ($r > 0.995$) of k_{obs} vs benzylamine with more than six concentrations. The values reported are the averages of more than three runs and were reproducible to within ±3%.

Product Analysis. The analysis of final products was difficult because of partial decomposition during product separation and purification. We therefore analyzed the reaction mixture by NMR (400 MHz) at appropriate intervals under exactly the same reaction conditions as the kinetic measurement in CD_3CN at 30.0 °C. Initially we found a peak for CH in the reactant, *p*-$MeOC_6H_4CH{=}C(COCH_2CH_3)_2$ at 7.53 ppm, which was gradually reduced, and two new peaks for CH−CH in the product, *p*-$MeOC_6H_4(C_6H_5CH_2NH)CH{-}CH(COCH_2CH_3)_2$, grew at 3.57 and 4.72 ppm as the reaction proceeds. No other peaks or complications were found during the reaction except the three peak height changes, indicating that the reaction proceeds with no other side reactions.

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Supporting Information Available: A sample of kinetic measurements (plot for k_{obs}) and determination of k_2 value. This material is available free of charge via the Internet at http://pubs.acs.org.

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