

Kinetic and Mechanism of the Addition of Benzylamines to α -Phenyl- β -thiophenylacrylonitriles in Acetonitrile

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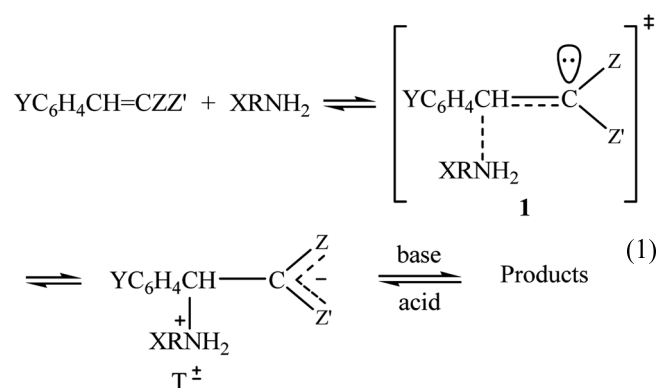
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Nucleophilic addition reactions of *p*-substitutedbenzylamines ($\text{XC}_6\text{H}_4\text{CH}_2\text{NH}_2$) to α -phenyl- β -thiophenylacrylonitriles ($\text{YC}_4\text{SH}_2\text{CH}=\text{C}(\text{CN})\text{C}_6\text{H}_4\text{Y}'$) have been studied in acetonitrile at 25.0, 30.0, and 35.0 °C. The reactions take place in single step in which the C_β -N bond formation and proton transfer to C_α of α -phenyl- β -thiophenylacrylonitriles occur concurrently with four-membered cyclic transition structure. These mechanistic conclusions are drawn based on (i) the large negative ρ_X and large positive ρ_Y values and also large magnitude of ρ_X , (ii) the negative sign and large magnitude of the cross-interaction constants (ρ_{XY}), (iii) the normal kinetic isotope effects ($k_{\text{H}}/k_{\text{D}} > 1.0$), and (iv) relatively low ΔH^\ddagger and large negative ΔS^\ddagger values.

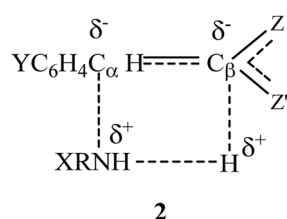
Key Words : Nucleophilic addition reaction, Cross-interaction constant, Kinetic isotope effects, Four-center cyclic transition state

Introduction

In nucleophilic additions of amines (XRNH_2) to activated alkenes ($\text{YC}_6\text{H}_4\text{CH}=\text{CZZ}'$), development of resonance and solvation of the incipient carbanion in the TS often lag behind C-N bond formation,¹ an exaggerated form of this can be given as **1** in eq. (1). In aqueous solution,



The reaction proceeds through a zwitterionic intermediate,¹ T^\ddagger , (eq. 1) whereas in acetonitrile the adduct was found to form in a single step,² **2**. The transition state (TS) imbalance, **1**, is far more pronounced for the reaction in



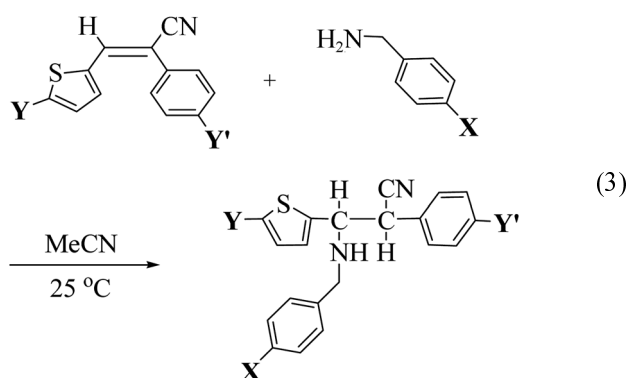
aqueous solution than in acetonitrile. Due to weak solvation by acetonitrile to stabilize the carbanion T^\ddagger and hydrogen bonding by N-H proton to negative charge localized on C_β in the TS(**2**), the imbalance in the amine additions in acetonitrile becomes very weak. Nevertheless,

The partially localized incipient anionic charge on C_β (**1**) due to the imbalance was found to manifest itself in the strength of hydrogen bonding in the TS (**2**); thus a relatively strong imbalance has led to a stronger kinetic isotope effect ($k_{\text{H}}/k_{\text{D}} > 1.0$) involving deuterated amines (XRND_2).³ Another interesting observation is that the sign and magnitude ($\rho_{XY} = -0.6$ to -0.8) of the cross-interaction constant,^{3,4} ρ_{XY} in eqs. 2 where X and Y are substituents in the nucleophile and substrate, respectively, are in general agreement with those for bond formation in the concerted bimolecular nucleophilic substitution ($\text{S}_{\text{N}}2$) reactions.^{2,4(a)}

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

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

In this work, we carried out kinetic studies of the benzylamine (BA, $\text{XC}_6\text{H}_4\text{CH}_2\text{NH}_2$) addition in acetonitrile at 25.0, 30.0, and 35.0 °C to α -phenyl- β -thiophenyl acrylonitriles (PTA: $\text{YC}_4\text{SH}_2\text{CH}=\text{C}(\text{CN})\text{C}_6\text{H}_4\text{Y}'$) where substituents Y and Y' in phenyl ring and thiophene ring are varied respectively (eq. 3). In this paper we report the nature and substituents effect of the thiophene ring with a sulfur atom for the BA addition reaction to PTA. We try to demonstrate that there is TS imbalance in the one step amine addition to olefins in acetonitrile, by determining various selectivity parameters (ρ_X , ρ_Y , ρ_{XY} and β_X) and the kinetic isotope effects, $k_{\text{H}}/k_{\text{D}}$.



Results and Discussion

The kinetic law obeyed in the present reactions is given by eq. (4). No catalysis by a second benzylamine molecule was detected. Plots of pseudo-first-order rate constant, k_{obs} against $[\text{BA}]$ were linear as shown Figure 1, and the second-order rate constants, k_2 , determined from the slopes of these plots are summarized in Table 1.

$$\text{rate} = k_2[\text{BA}][\text{PTA}] = k_{\text{obs}}[\text{PTA}] \quad (4)$$

The selectivity parameters, Hammett coefficients ρ_X , ρ_Y and $\rho_{Y'}$ values and Brønsted β_X values, are also shown in Table 1 together with the cross-interaction constant ρ_{XY} (eqs. 2). The ρ_Y values were determined by the plots $\log k_2$ versus normal σ_p substituents constant. The 5,2-substituted thiophene system is considered formally analogous to para-substituted benzene derivatives; such set have generally been correlated with σ_p constants depending on the nature of reaction site.⁵ Ionization constants of 5-substituted thiophene-2-carboxylic acid in pure water at 25.0 °C give very good correlation with σ_p constants ($\rho = 1.10$, $n = 5$, $r =$

Table 1. Second-order rate constants, $10^4 k_2$, $\text{M}^{-1}\text{s}^{-1}$ for addition reactions of α -phenyl- β -thiophenylacrylonitriles with X-substituted benzylamines in acetonitrile at 25.0 °C

Y	Y'	X				
		<i>p</i> -OMe	<i>p</i> -Me	H	<i>p</i> -Cl	<i>p</i> -NO ₂
Me	<i>p</i> -OMe	0.922	0.891	0.670	0.572	0.370
	<i>p</i> -Me	1.53	1.24	0.993	0.754	0.441
	H	2.02	1.65	1.21	0.882	0.483
	<i>p</i> -Cl	4.72	3.75	2.62	1.62	0.584
	<i>p</i> -NO ₂	13.8	7.44	5.05	2.79	0.751
H	<i>p</i> -OMe	1.74	1.45	1.12	0.881	0.532
	<i>p</i> -Me	2.67	2.02	1.51	1.09	0.571
	H	5.29	4.08	2.70	1.56	0.704
	<i>p</i> -Cl	8.91	5.95	3.88	2.39	0.802
	<i>p</i> -NO ₂	36.0	18.4	11.4	5.93	1.10
Br	<i>p</i> -OMe	4.19	3.48	2.53	1.71	0.682
	<i>p</i> -Me	5.68	4.67	3.13	1.98	0.784
	H	11.8	8.97	6.02	3.74	1.18
	<i>p</i> -Cl	18.9	13.2	8.47	4.67	1.30
	<i>p</i> -NO ₂	139	83.9	46.9	20.9	2.29

0.988).^{5(c)} Both the Hammett (for Y and Y') and Brønsted plots are very good linear as shown in Figures 2, 3 and 4. The β_X (β_{nuc}) values were determined by the plots of $\log k_2$ (MeCN) versus $\text{p}K_{\text{a}}(\text{H}_2\text{O})$ of benzylamines. This procedure was found to be reliable⁶ since the $\text{p}K_{\text{a}}(\text{MeCN})$ varies in parallel with the $\text{p}K_{\text{a}}(\text{H}_2\text{O})$ with a reasonably constant difference of $\Delta K_{\alpha} (= \text{p}K_{\text{a}}(\text{MeCN}) - \text{p}K_{\text{a}}(\text{H}_2\text{O})) = 7.5$.

As shown in Table 1, the second-order rate constant (k_2) increases as the substituents Y' and Y in the phenyl and thiophene moiety changes from an electron-donating group to an electron-withdrawing group, and increases as the

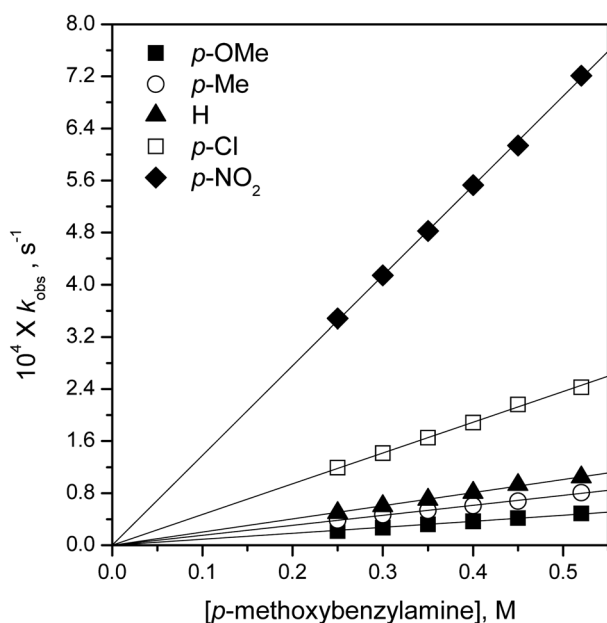


Figure 1. Plots of k_{obs} vs. $[\text{p-methoxybenzylamine}]$ for the addition reactions of $\text{MeC}_4\text{SH}_2\text{CH}=\text{C}(\text{CN})\text{C}_6\text{H}_4\text{Y}'$ at 25.0 °C.

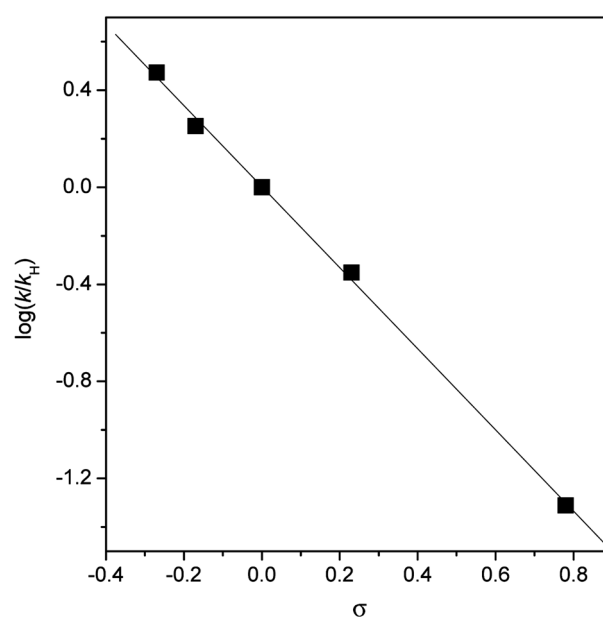


Figure 2. The typical Hammett plot of $\text{NH}_2\text{CH}_2\text{C}_6\text{H}_4\text{X}$ for the addition reactions of $\text{C}_4\text{SH}_3\text{CH}=\text{C}(\text{CN})\text{C}_6\text{H}_4\text{NO}_2$ at 25.0 °C.

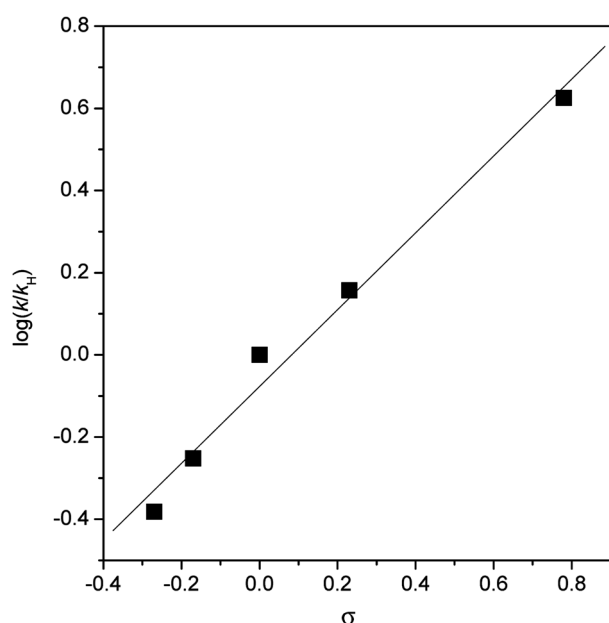


Figure 3. The typical Hammett plot of $\text{NH}_2\text{CH}_2\text{C}_6\text{H}_5$ for the addition reactions of $\text{C}_4\text{SH}_3\text{CH}=\text{C}(\text{CN})\text{C}_6\text{H}_4\text{Y}'$ at 25.0°C .

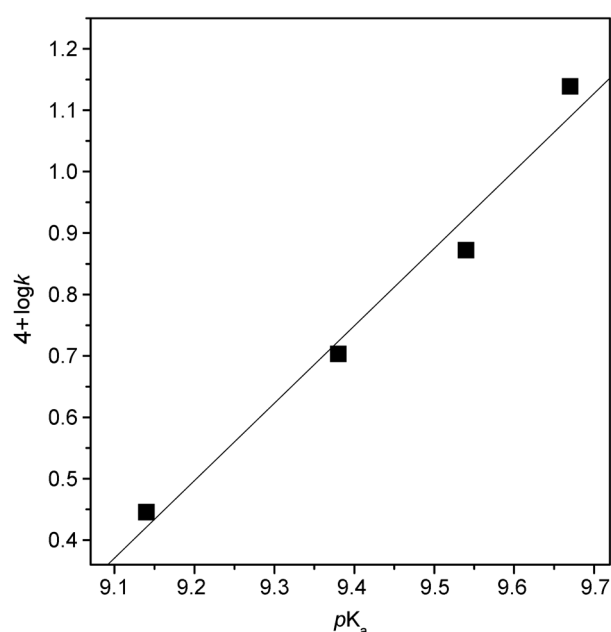


Figure 4. The typical Brønsted plot of $\text{NH}_2\text{CH}_2\text{C}_6\text{H}_4\text{X}$ for the addition reactions of $\text{MeC}_4\text{SH}_2\text{CH}=\text{C}(\text{CN})\text{C}_6\text{H}_4\text{NO}_2$ at 25.0°C .

substituent X in the benzylamine changes from an electron-withdrawing group to an electron-donating group for the addition reaction of PTA with benzylamines. This result indicates that the rates are faster for a stronger nucleophile

($\delta\sigma_X < 0$) and for the substrate (PTA) with a stronger electron-withdrawing group in phenyl ring ($\delta\sigma_Y > 0$) and thiophene ring ($\delta\sigma_Y > 0$) as exhibit in a typical nucleophilic addition reaction. The ρ_Y value in the present system is

Table 2. Hammett (ρ_X , ρ_Y and ρ_Z) and Brønsted (β_X) coefficients for the reactions of α -phenyl- β -thiophenylacrylonitriles with X-substituted benzylamines in acetonitrile at 25.0°C

(i) ρ_X and (β_X) values^a

Y/Y'	<i>p</i> -OMe	<i>p</i> -Me	H	<i>p</i> -Cl	<i>p</i> -NO ₂
Me	-0.38 ± 0.02	-0.50 ± 0.09	-0.58 ± 0.05	-0.86 ± 0.05	-1.14 ± 0.03
Me	(0.43 ± 0.06)	(0.58 ± 0.08)	(0.69 ± 0.03)	(0.89 ± 0.09)	(1.26 ± 0.03)
H	-0.48 ± 0.09	-0.50 ± 0.03	-0.83 ± 0.04	-0.96 ± 0.05	-1.37 ± 0.07
H	(0.56 ± 0.04)	(0.73 ± 0.07)	(1.01 ± 0.09)	(1.07 ± 0.03)	(1.43 ± 0.04)
Br	-0.75 ± 0.09	-0.85 ± 0.03	-0.94 ± 0.01	-1.09 ± 0.03	-1.67 ± 0.09
Br	(0.75 ± 0.08)	(0.89 ± 0.07)	(0.95 ± 0.07)	(1.15 ± 0.03)	(1.55 ± 0.01)

^aThe correlation coefficients were better than 0.992 in all cases.

(ii) ρ_Y values^b

Y/X	<i>p</i> -OMe	<i>p</i> -Me	H	<i>p</i> -Cl	<i>p</i> -NO ₂
Me	1.09 ± 0.06	0.881 ± 0.03	0.822 ± 0.05	0.652 ± 0.06	0.283 ± 0.08
H	1.24 ± 0.05	1.02 ± 0.04	0.941 ± 0.07	0.781 ± 0.06	0.301 ± 0.09
Br	1.43 ± 0.04	1.30 ± 0.07	1.20 ± 0.08	1.03 ± 0.09	0.494 ± 0.09

^bThe correlation coefficients were better than 0.995 in all cases.

(iii) ρ_Y values^c

X/Y'	<i>p</i> -OMe	<i>p</i> -Me	H	<i>p</i> -Cl	<i>p</i> -NO ₂
<i>p</i> -OMe	1.65 ± 0.09	1.43 ± 0.03	1.89 ± 0.08	1.50 ± 0.09	2.51 ± 0.02
<i>p</i> -Me	1.49 ± 0.06	1.45 ± 0.04	1.82 ± 0.07	1.37 ± 0.02	2.64 ± 0.06
H	1.45 ± 0.04	1.25 ± 0.08	1.73 ± 0.04	1.28 ± 0.08	2.43 ± 0.03
<i>p</i> -Cl	1.19 ± 0.08	1.05 ± 0.02	1.57 ± 0.01	1.16 ± 0.06	2.20 ± 0.03
<i>p</i> -NO ₂	0.654 ± 0.02	0.624 ± 0.02	0.970 ± 0.01	0.872 ± 0.03	1.22 ± 0.02

^cThe correlation coefficients were better than 0.992 in all cases.

much smaller than ρ_Y value. This differs from the result for the addition of benzylamines to β -cyanostilbenes in acetonitrile.^{2(c)} However, this is not surprising since sulfur atom is in the vicinity of the reaction center in the present system. The higher ρ_Y value is due to the strong electron transmission efficiencies between sulfur atom and reaction center and also short range interaction of 5-membered ring.⁷ The large positive ρ_Y and $\rho_{Y'}$ values and the large negative ρ_X values indicate that the negative charge development at C_β in the TS. The large positive ρ_Y and $\rho_{Y'}$ are indication of a strong anionic charge development at the C_α and C_β in the TS, and also the anionic charge development at the C_α in the TS as a result of the lag (1) in the resonance development into the activating group, $Z=CN$.

The sign of ρ_{XY} and $\rho_{XY'}$ shown in Table 2 are negative, as observed in all the bond formation process in nucleophilic substitution and addition reactions.^{2(c),4(a),8} The large magnitude of ρ_{XY} and $\rho_{XY'}$ is reflecting a stronger interaction of the substituents in the nucleophile with those in the phenyl and thiophene ring. Another important result is that the sign of $\rho_{YY'}$ is positive. The positive ρ_{ij} is normally obtained between substituents i and j in the bond cleavage process between them.^{4(a),8} In the present reaction, as the nucleophile (benzylamine) attacks C_β , the pi-bond between C_β (linked to thiophene ring) and C_α (linked to phenyl ring) is partially broken in the TS so that the sign of $\rho_{YY'}$ becomes positive. The positive $\rho_{YY'}$ also indicates that a stronger electron

Table 3. Cross-interaction constant, ρ_{XY} , $\rho_{XY'}$ and $\rho_{YY'}$ for the reactions of α -phenyl- β -thiophenylacrylonitriles with X-substituted benzylamines in acetonitrile at 25.0 °C

(i) ρ_{XY}^a

Y'	ρ_{XY}
<i>p</i> -OMe	-0.94 ± 0.06
<i>p</i> -Me	-0.91 ± 0.08
H	-0.88 ± 0.02
<i>p</i> -Cl	-0.57 ± 0.06
<i>p</i> -NO ₂	-0.32 ± 0.03

^aThe correlation coefficients were better than 0.993 in all cases.

(ii) $\rho_{XY'}^b$

Y	$\rho_{XY'}$
Me	-0.72 ± 0.03
H	-0.83 ± 0.03
Br	-0.87 ± 0.03

^bThe correlation coefficients were better than 0.992 in all cases.

(iii) $\rho_{YY'}^c$

X	$\rho_{YY'}$
<i>p</i> -OMe	0.85 ± 0.08
<i>p</i> -Me	1.06 ± 0.01
H	0.96 ± 0.06
<i>p</i> -Cl	0.96 ± 0.08
<i>p</i> -NO ₂	0.54 ± 0.08

^cThe correlation coefficients were better than 0.995 in all cases.

Table 4. Kinetic isotope effects on the second order rate constants, $10^4 k_2$, $M^{-1}s^{-1}$ for the addition reactions α -phenyl- β -thiophenylacrylonitriles with deuterated X- substituted benzylamines in acetonitrile at 25.0 °C

X	Y	Y'	k_H	k_D	k_H/k_D
<i>p</i> -OMe	Me	<i>p</i> -NO ₂	13.8	5.76	2.40
<i>p</i> -NO ₂	Me	<i>p</i> -Cl	2.79	1.43	2.08
<i>p</i> -OMe	H	H	5.29	2.42	2.19
<i>p</i> -OMe	H	<i>p</i> -NO ₂	36.0	16.8	2.14
H	H	<i>p</i> -OMe	1.12	0.528	2.12
<i>p</i> -OMe	Br	<i>p</i> -OMe	4.19	2.11	1.99
<i>p</i> -Cl	Br	H	3.74	1.85	2.02

acceptor Y ($\delta\sigma_Y > 0$) or Y' ($\delta\sigma_{Y'} > 0$) will result in greater charge development, $\delta\sigma_Y > 0$ or $\delta\sigma_{Y'} > 0$, since $\rho_{YY'} = \delta\rho_{Y'}/\delta\sigma_Y = \delta\rho_{Y'}/\delta\sigma_{Y'} > 0$. This is supported by the greater magnitude of ρ_X (and β_X) for stronger acceptor Y and Y' as can be seen in Table 2; the greater the magnitude of ρ_X (and β_X), the greater is the degree of bond formation and hence the greater becomes the pi-bond cleavage in the TS with a stronger anionic charge development on C_α as well as on C_β in the TS.

The kinetic isotope effects involving deuterated benzylamine nucleophiles^{2,9} ($XC_6H_4CH_2ND_2$) are quite large with a $k_H/k_D = 1.99$ -2.40 (Table 4) indicating that strong hydrogen bonding of the N-H(D) proton toward the anionic center, C_α , in the TS. Thus the reaction proceeds in a single step with concurrent formation N-C_β and H-C_α bond, **3**.

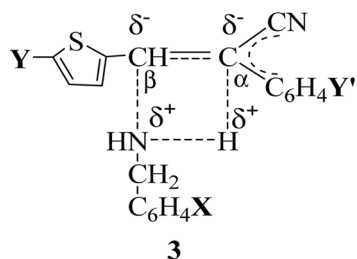
The relatively low activation enthalpies, ΔH^\ddagger , and large

Table 5. Activation parameters for the reactions of α -phenyl- β -thiophenylacrylonitriles with X-benzylamines in acetonitrile^a

X	Y	Y'	T (°C)	k ($10^4 M^{-1}s^{-1}$)	ΔH^\ddagger (kcalmol ⁻¹)	$-\Delta S^\ddagger$ (calmol ⁻¹ K ⁻¹)
<i>p</i> -OMe	Me	H	25	2.02	9.2	45
			30	2.73		
			35	3.45		
<i>p</i> -OMe	H	<i>p</i> -Me	25	2.67	8.6	46
			30	3.42		
			35	4.38		
<i>p</i> -OMe	Br	H	25	11.8	9.3	41
			30	15.5		
			35	20.3		
<i>p</i> -NO ₂	Me	H	25	0.483	11	43
			30	0.653		
			35	0.892		
<i>p</i> -NO ₂	H	H	25	0.704	9.8	45
			30	0.931		
			35	1.25		
<i>p</i> -NO ₂	Br	<i>p</i> -Me	25	0.784	11	42
			30	1.07		
			35	1.45		

^aCalculated by using Eyring equation. The maximum errors calculated (by the method of K. B. Wiberg, Physical Organic Chemistry; Wiley, New York, 1964, p 378) are ± 0.5 e.u. and ± 2 e.u. for ΔH^\ddagger and ΔS^\ddagger , respectively.

negative entropies of activation, ΔS^\ddagger , in Table 5, are consistent with a four-centered constrained TS structure, **3**, proposed.²



Experimental Section

General procedure. GR grade acetonitrile was purchased from Merck and used without distillation. The benzylamine nucleophiles, Merck GR grade were used without re crystallization. Melting points were measured using a Tomas Hoover 6427-H10. Infrared spectra were taken using a Shimadzu FT-IR spectrophotometer. ¹H NMR spectra were recorded on Bruker Advance 300 MHz instrument using CDCl₃ as solvent, unless otherwise stated, with TMS as an internal standard. UV-Vis spectra were obtained on a Shimadzu UV-2401PC spectrophotometer. Kinetic experiments were performed using a Shimadzu UV-2401PC spectrophotometer.

Preparations of α -phenyl- β -thiophenylacrylonitriles. The *p*-substituted acrylonitriles (20 mmol; 4-OCH₃, 4-CH₃, 4-H, 4-Cl, 4-NO₂) was prepared by condensation of 2-substituted thiophene aldehyde (2-Me, 2-H, 2-Br) with a appropriate arylacetonitrile in the presence of base; a solution of the aldehyde (20 mmol) and arylacetonitrile (20 mmol) were shaken in warm ethanol with a few drops of 30% aqueous potassium hydroxide. The mixture was stirred at room temperature. The reaction controlled by TLC showed quickly disappearance of the starting reagents. The substance precipitated was washed with water and recrystallized from EtOH.

4-CH₃C₄SH₂CH=C(CN)C₆H₄OCH₃-*p*. IR (KBr): 2210 (CN), 1591 (C=C), ¹H NMR (300 MHz, CDCl₃) (δ) 2.55 (s, 3H, CH₃), 3.84 (s, 3H, OCH₃), 6.78 (m, 1H (thiophene)), 6.93 (d, *J* = 9.0 Hz, 2H (aromatic)), 7.36 (d, *J* = 3.6 Hz, 1H (thiophene)), 7.45 (s, 1H (alkene)), 7.55 (d, *J* = 9.0 Hz, 2H (aromatic)).

4-CH₃C₄SH₂CH=C(CN)C₆H₄CH₃-*p*. IR (KBr): 2208 (CN), 1590 (C=C), ¹H NMR (300 MHz, CDCl₃) (δ) 2.37 (s, 3H, CH₃ (thiophene)), 2.55 (s, 3H, CH₃ (aromatic)), 6.79 (m, 1H (thiophene)), 7.21 (d, *J* = 7.8 Hz, 2H (aromatic)), 7.38 (d, *J* = 3.6 Hz, 1H (thiophene)), 7.49-7.53 (m, 3H ((2H, aromatic), (1H, alkene))).

4-CH₃C₄SH₂CH=C(CN)C₆H₅. IR (KBr): 2209 (CN), 1592 (C=C), ¹H NMR (300 MHz, 4-CDCl₃) (δ) 2.56 (s, 3H, CH₃ (thiophene)), 6.8 (m, 1H (thiophene)), 7.31-7.44 (m, 4H ((3H, aromatic), (1H, thiophene))), 7.57 (s, 1H (alkene)), 7.60-7.63 (m, 2H (benzene)).

4-CH₃C₄SH₂CH=C(CN)C₆H₄Cl-*p*. IR (KBr): 2210

(CN), 1589 (C=C), ¹H NMR (300 MHz, CDCl₃) (δ) 2.56 (s, 3H, CH₃ (thiophene)), 6.80 (m, 1H (thiophene)), 7.38 (d, *J* = 8.7 Hz, 2H (aromatic)), 7.41 (s, *J* = 3.9 Hz, 1H (thiophene)), 7.54 (s, 1H (alkene)), 7.55 (d, *J* = 8.7 Hz, 2H (aromatic)).

4-CH₃C₄SH₂CH=C(CN)C₆H₄NO₂-*p*. IR (KBr): 2211 (CN), 1590 (C=C), ¹H NMR (300 MHz, CDCl₃) (δ) 2.60 (s, 3H, CH₃ (thiophene)), 6.88 (m, 1H (thiophene)), 7.52 (d, *J* = 3.9 Hz, 1H (thiophene)), 7.73 (s, 1H (alkene)), 7.78 (d, *J* = 9.0 Hz, 2H (aromatic)), 8.28 (d, *J* = 9.0 Hz, 2H (aromatic)).

C₄H₃SCH=C(CN)C₆H₄OCH₃-*p*. IR (KBr): 2208 (CN), 1590 (C=C), ¹H NMR (300 MHz, CDCl₃) (δ) 3.87 (s, 3H, OCH₃ (aromatic)), 6.97 (d, *J* = 9.0 Hz, 2H (aromatic)) 7.15 (m, 1H (thiophene)), 7.52 (d, *J* = 5.1 Hz, 1H (thiophene)), 7.56 (s, 1H (alkene)), 7.59 (d, *J* = 9.0 Hz, 2H (aromatic)), 7.64 (d, *J* = 3.6 Hz, 2H (thiophene)).

C₄H₃SCH=C(CN)C₆H₄CH₃-*p*. IR (KBr): 2207 (CN), 1594 (C=C), ¹H NMR (300 MHz, CDCl₃) (δ) 2.39 (s, 3H, CH₃ (aromatic)), 7.14 (m, 1H (thiophene)), 7.24 (d, *J* = 8.1 Hz, 2H (aromatic)), 7.52-7.55 (m, 3H (2H (aromatic), 1H (thiophene))), 7.62 (s, 1H (alkene)), 7.64 (d, *J* = 3.9 Hz, 1H (thiophene)).

C₄H₃SCH=C(CN)C₆H₅-*p*. IR (KBr): 2206 (CN), 1591 (C=C), ¹H NMR (300 MHz, CDCl₃) (δ) 7.14 (m, 1H (thiophene)), 7.33-7.45 (m, 3H (aromatic)), 7.53 (d, *J* = 5.1 Hz, 1H (thiophene)), 7.62-7.66 (m, 4H (1H (alkene), 2H (aromatic), 1H (thiophene))).

C₄H₃SCH=C(CN)C₆H₄Cl-*p*. IR (KBr): 2210 (CN), 1600 (C=C), ¹H NMR (300 MHz, CDCl₃) (δ) 7.15 (m, 1H (thiophene)), 7.40 (d, *J* = 8.7 Hz, 2H (aromatic)) 7.55-7.58 (m, 3H (2H (aromatic), 1H (thiophene))), 7.63 (s, 1H (alkene)), 7.66 (d, *J* = 3.6 Hz, 1H (thiophene)).

C₄H₃SCH=C(CN)C₆H₄NO₂-*p*. IR (KBr): 2212 (CN), 11593 (C=C), ¹H NMR (300 MHz, CDCl₃) (δ) 7.21 (m, 1H (thiophene)), 7.67 (d, *J* = 5.1 Hz, 1H (thiophene)), 7.72 (d, *J* = 3.9 Hz, 1H (thiophene)), 7.80-7.83 (m, 3H (2H (aromatic), 1H (alkene))), 8.29 (d, *J* = 8.7 Hz, 2H (aromatic)).

4-BrC₄SH₂CH=C(CN)C₆H₄OCH₃-*p*. IR (KBr): 2200 (CN), 1596 (C=C), ¹H NMR (300 MHz, CDCl₃) (δ) 3.84 (s, 3H, OCH₃ (aromatic)), 6.94 (d, *J* = 9.0 Hz, 2H (aromatic)), 7.08 (d, *J* = 3.9 Hz, 1H (thiophene)), 7.28 (d, *J* = 3.9 Hz, 2H (thiophene)), 7.40 (s, 1H (alkene)), 7.55 (d, *J* = 8.7 Hz, 2H (aromatic)).

4-BrC₄SH₂CH=C(CN)C₆H₄CH₃-*p*. IR (KBr): 2209 (C=C), 1591 (C=C), ¹H NMR (300 MHz, CDCl₃) (δ) 2.38 (s, 3H, CH₃ (aromatic)), 7.09 (d, *J* = 4.2 Hz, 1H (thiophene)), 7.23 (d, *J* = 8.4 Hz, 2H (aromatic)), 7.31 (d, *J* = 3.9 Hz, 1H (aromatic)), 7.48 (s, 1H (alkene)), 7.51 (d, *J* = 8.1 Hz, 2H (aromatic)).

4-BrCS₄H₂CH=C(CN)C₆H₅. IR (KBr): 2210 (CN), 1594 (C=C), ¹H NMR (300 MHz, CDCl₃) (δ) 7.10 (d, *J* = 4.2 Hz, 1H (thiophene)), 7.33 (d, *J* = 3.9 Hz, 1H (thiophene)), 7.37-7.46 (m, 3H (aromatic)), 7.53 (s, 1H (alkene)), 7.60-7.64 (m, 2H (aromatic)).

4-BrC₄SH₂CH=C(CN)C₆H₄Cl-*p*. IR (KBr): 2212 (CN), 1600 (C=C), ¹H NMR (300 MHz, CDCl₃) (δ) 7.11 (d, *J* = 3.9 Hz, 1H (thiophene)), 7.33 (d, *J* = 4.2 Hz, 1H (thiophene)), 7.40 (d, *J* = 8.7 Hz, 2H (aromatic)), 7.50 (s, 1H (alkene)),

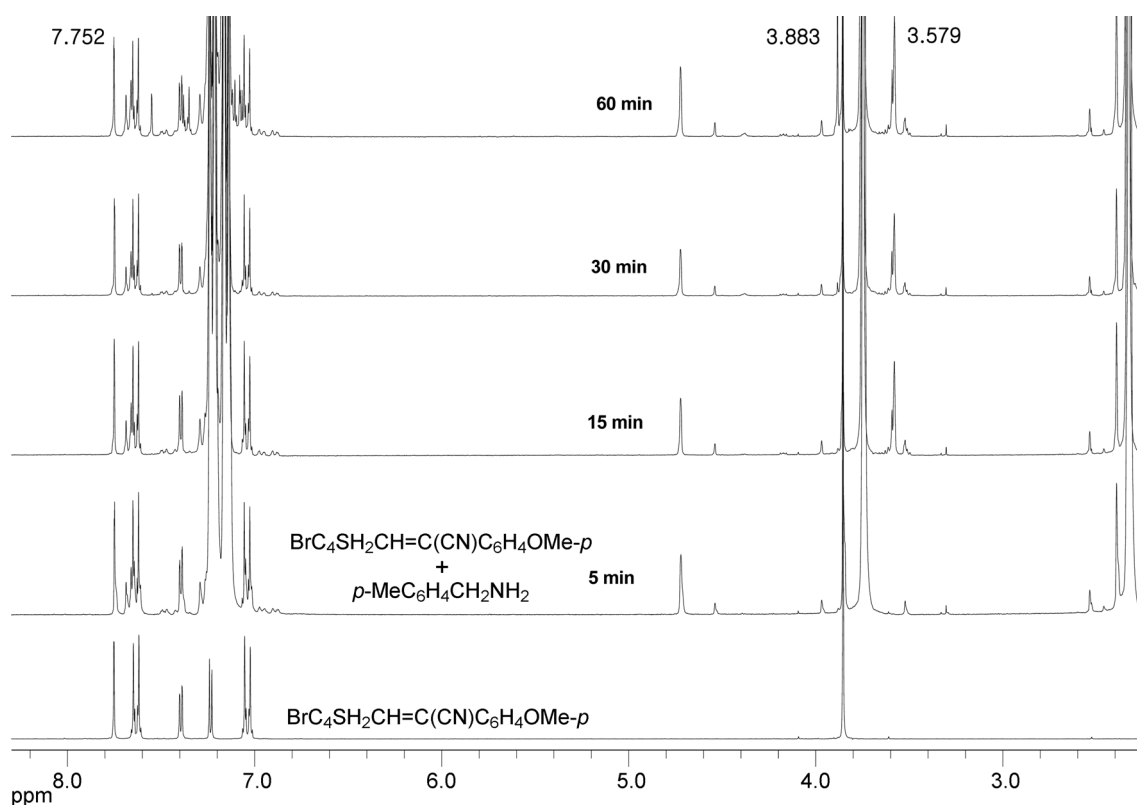


Figure 5. $^1\text{H-NMR}$ spectra for the reaction $\text{BrC}_4\text{SH}_2\text{CH}=\text{C}(\text{CN})\text{C}_6\text{H}_4\text{OMe-}p$ with $p\text{-MeC}_6\text{H}_4\text{CH}_2\text{NH}_2$ in CD_3CN at $25.0\text{ }^\circ\text{C}$.

7.55 (d, $J = 8.7\text{ Hz}$, 2H (aromatic)).

4- $\text{BrC}_4\text{SH}_2\text{CH}=\text{C}(\text{CN})\text{C}_6\text{H}_4\text{NO}_2\text{-}p$. IR (KBr): 2207 (CN), 1592 (C=C), $^1\text{H NMR}$ (300 MHz, CDCl_3) (δ) 7.18 (m, 1H (thiophene)), 7.49 (d, $J = 4.2\text{ Hz}$, 1H (thiophene)), 7.63 (d, 2H, $J = 9.0\text{ Hz}$ (aromatic)), 7.63 (s, 1H (alkene)), 7.80 (d, 2H, $J = 9.0\text{ Hz}$ (aromatic)).

Kinetic Measurement. The reactions was followed spectrophotometrically by monitoring the decrease in the concentration of α -phenyl- β -thiophenylaclylonitriles, [PTA], at λ_{max} of the substrate to over 80% completion. The reaction was studied under pseudo-first-order condition, $[\text{PTA}] = 5.5 \times 10^{-5}\text{ M}$ and $[\text{BA}] = (2.5\text{-}5.2) \times 10^{-1}\text{ M}$ at $25.0\text{ }^\circ\text{C}$. The pseudo first-order rate constant, k_{obs} , was determined from the slope of the plot ($r > 0.996$) of $\ln[\text{PTA}]$ vs time. Second-order rate constants, k_2 , were obtained from the slope of a plot ($r > 0.996$) of k_{obs} vs $[\text{BA}]$ with more than four concentrations of benzylamine, carried out more than two runs, and were reproducible to within $\pm 3\%$.

Product Analysis. The analysis of final product was difficult due to partial decomposition during product separation and purification. We therefore analyzed the reaction mixture by NMR (Bruker 300 MHz) at appropriate intervals under exactly the same reaction conditions as the kinetic measurement in CD_3CN at $25.0\text{ }^\circ\text{C}$ using larger amount of reactants. Initially we found a peaks for olefin CH in the products, 4- $\text{BrC}_4\text{SH}_2\text{CH}=\text{C}(\text{CN})\text{C}_6\text{H}_4\text{OMe-}p$, at 7.752 ppm, which was gradually reduced, and two new peaks for CH-CH in the product, 4- $\text{BrC}_4\text{SH}_2(p\text{-MeC}_6\text{H}_4\text{CH}_2\text{NH})\text{-CHCH}(\text{CN})\text{C}_6\text{H}_4\text{OMe-}p$, grew at 3.883 and 3.579 ppm as the reaction proceeded. 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 (Figure 5).

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