Kinetics and Mechanism of the Addition of Anilines to β-Nitrostilbenes in Acetonitrile

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Addition reactions of anilines ($XC_6H_4NH_2$) to β-nitrostilbene ($YC_6H_4CH=C(NO_2)C_6H_4Y'$) have been investigated in acetonitrile at 30.0 °C. The magnitude of β_X values (=0.11-0.34) indicates relatively earlier transition state for additions with anilines than with benzylamines. The signs of ρ_Y and $\rho_{Y'}$ are positive with $\Delta\rho = \rho_Y - \rho_{Y'} = 0.04$, demonstrating a TS imbalance with a negative charge development on the C_β in the TS. The signs of cross-interaction constants ρ_{XY} (<0), $\rho_{XY'}$ (<0) and $\rho_{YY'}$ (>0) are consistent with bond forming and breaking processes. The relatively weak normal kinetic isotope effects involving deutarated nucleophiles, $k_H/k_D>1$, suggest an early, hydrogen-bonded, 4-member cyclic TS.

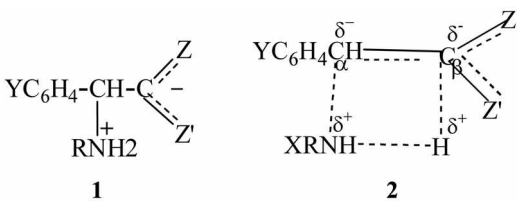
Key Words : β-Nitrostilbene, Addition reaction, Cross-interaction constant, Hydrogen-bonded TS, TS imbalance

Introduction

Nucleophilic additions of amines ($XRNH_2$) to olefins ($YC_6H_4CH=CZZ'$) activated by electron-acceptors (Z,Z'), eq. 1, have attracted considerable interests due to the strong transition state

$$XRNH_2 + YC_6H_4CH=CZZ' \xrightarrow{k_2} YC_6H_4CHCHZZ' \quad (1)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad HNRX$$

imbalance observed in aqueous solution. Bernasconi and coworkers[1] treated the TS imbalance (l_m) semiquantitatively by expressimg the lag in resonance development of the incipient carbanion as $l_m = \alpha_{nuc} - \beta_{nuc}$, where α_{nuc} and β_{nuc} are Brönsted type coefficients obtained by varying substituents in the substrate (Y in eq. 1) and basicity of the amine nucleophile, respectively. The imbalance was found to increase with increasing resonance stabilization of the carbanionic intermediate, **1**, in aqueous solution,[1] *e.g.* Z,Z' = CN, CN < H, NO_2. In contrast to the stepwise amine addition in aqueous solution, the reaction was found to occur concertedly with a hydrogen-bonded four-center, cyclic TS, **2**, proceeding to the neutral product in acetonitrile.[2,3] The TS imbalance, albeit much weaker than in aqueous solution, was found also in acetonitrile.[2]



1 **2**

In a previous work we reported kinetic results on the benzylamine (BA) additions to β-cyanostilbene in acetonitrile,[4] where we varied substituents in the nucleophile (X) and in both, α (Y) and β (Y'), rings, and invoked mechanistic criteria based on the cross-interaction constants,[5] eqs. 2. Here i and j are substituents X, Y, or Y', and we can determine cross-interaction constants ρ_{XY}, $\rho_{XY'}$, or $\rho_{YY'}$ using eqs. 2.

$$\log(k_{ij}/k_{HH}) = \rho_i\sigma_i + \rho_j\sigma_j + \rho_{ij}\sigma_i\sigma_j \quad (2a)$$

$$\rho_{ij} = \rho_i/\sigma_j = \rho_j/\sigma_i \quad (2b)$$

In this work we investigated aniline ($XC_6H_4NH_2$) additions to β-nitrostilbenes (Z=NO_2; Z'=C_6H_4Y' in eq. 1) in acetonitrile. Our interests in this work are (i) effects of the stronger acceptor, NO_2, (compared to CN) and the weaker nucleophiles, anilines, (relative to benzylamines), and (ii) effects of substituents (Y') in the b ring, on the mechanism and the TS structure. We have applied the multiple substituent effect mechanistic criteria based on eqs. 2.

Results and Discussion

The reactions followed a simple kinetic law given by eqs. 3 and 4 where S and AN denote the substrate (β-nitrostilbene) and aniline, respectively.

$$\text{Rate} = k_{obs}[S] \quad (3)$$

$$k_{obs} = k_2[AN] \quad (4)$$

There was no catalysis by a second aniline base. Plots of k_{obs} versus [AN] were linear, and the second-order rate constants, k_2, determined from the slope of the plots are summarized in Table 1. Addition rates of anilines are substantially slower than those of the benzylamines, *e.g.*, for X=Y=Y'=H in acetonitrile, k_2(AN) = 1.92 × 10^{-3} $M^{-1}s^{-1}$ at 30 °C whereas k_2(BA) = 2.69 × 10^{-3} $M^{-1}s^{-1}$ at 25 °C.[2b] The Hammett ρ_X, ρ_Y and $\rho_{Y'}$ values are collected in Table 2 together with the Brönsted β_X values. For determination of β_X values, we used the pK_a values measured in acetonitrile at

Table 1. Second-order rate constants, $k_2 \times 10^3$ $M^{-1}s^{-1}$, for addition of X-anilines to β-nitrostilbenes in MeCN at 30 °C

		X			
Y	Y'	*p*-OMe	*p*-Me	H	*p*-Cl
p-Me	*p*-Me	1.26	1.13	0.881	0.651
	H	1.85	1.59	1.21	0.840
	p-Cl	3.09	2.53	1.84	1.16
	p-NO_2	9.17	7.02	4.72	2.65
H	*p*-Me	2.05	1.71	1.24	0.825
	H	3.27	2.62	1.85	1.12
	p-Cl	5.80	4.49	2.98	1.70
	p-NO_2	20.3	14.4	8.87	4.23
p-Cl	*p*-Me	3.45	2.73	1.68	1.03
	H	6.37	4.75	2.85	1.61
	p-Cl	12.2	8.63	4.63	2.54
	p-NO_2	57.5	38.1	19.9	7.23
p-NO_2	*p*-Me	11.1	8.62	5.23	2.65
	H	22.4	16.1	9.50	4.44
	p-Cl	–	38.8	21.6	9.15
	p-NO_2	–	–	140	47.8

Table 2. Hammett, ρ_X, ρ_Y and $\rho_{Y'}$, and Brönsted coefficients, β_x in acetonitrile at 30 °C

(i) ρ_X and (β_x) values[a]

Y/Y'	*p*-Me	H	*p*-Cl	*p*-NO_2
p-Me	−0.58 ± 0.01	−0.69 ± 0.01	−0.85 ± 0.01	−1.10 ± 0.05
	(0.11 ± 0.01)	(0.13 ± 0.01)	(0.16 ± 0.01)	(0.20 ± 0.01)
H	−0.79 ± 0.01	−0.93 ± 0.01	−1.10 ± 0.03	−1.40 ± 0.05
	(0.15 ± 0.01)	(0.17 ± 0.01)	(0.19 ± 0.01)	(0.25 ± 0.01)
p-Cl	−1.10 ± 0.04	−1.20 ± 0.01	−1.40 ± 0.08	−1.80 ± 0.01
	(0.20 ± 0.02)	(0.22 ± 0.02)	(0.26 ± 0.02)	(0.34 ± 0.02)
p-NO_2	−1.30 ± 0.01	−1.40 ± 0.03	−1.60 ± 0.04	
	(0.23 ± 0.02)	(0.26 ± 0.01)	(0.31 ± 0.01)	

[a]The correlation coefficients were better than 0.994 in all cases.

(ii) $\rho_{Y'}$ values[b]

Y/X	*p*-OMe	*p*-Me	H	*p*-Cl
p-Me	0.90 ± 0.02	0.83 ± 0.01	0.77 ± 0.01	0.64 ± 0.01
H	1.00 ± 0.03	0.97 ± 0.03	0.89 ± 0.02	0.75 ± 0.01
p-Cl	1.40 ± 0.03	1.30 ± 0.03	1.10 ± 0.04	0.88 ± 0.04
p-NO_2	1.80 ± 0.04	1.60 ± 0.06	1.50 ± 0.01	1.30 ± 0.02

[b]The correlation coefficients were better than 0.998 in all cases.

(iii) ρ_Y values[c]

X/Y'	*p*-Me	H	*p*-Cl	*p*-NO_2
p-OMe	1.00 ± 0.03	1.10 ± 0.04	1.50 ± 0.06	2.00 ± 0.01
p-Me	0.93 ± 0.02	1.10 ± 0.06	1.30 ± 0.01	1.80 ± 0.04
H	0.81 ± 0.04	0.94 ± 0.02	1.10 ± 0.03	1.50 ± 0.04
p-Cl	0.64 ± 0.02	0.76 ± 0.01	0.94 ± 0.04	1.32 ± 0.02

[c]The Correlation coefficients were better than 0.996 in all cases.

25 °C.[6] The values not reported were interpolated using the Hammett correlation of pK_a versus σ. Cross-interaction constants ρ_{XY}, $\rho_{XY'}$ and $\rho_{YY'}$ are determined by multiple regression analysis using eq. 2a and are shown in Table 3.

Table 3. Cross interaction constants, ρ_{XY}, $\rho_{XY'}$ and $\rho_{YY'}$, in acetonitrile at 30 °C[a]

(i) ρ_{XY}

Y'	ρ_{XY}
p-Me	−0.68 ± 0.08
p-H	−0.71 ± 0.09
p-Cl	−0.79 ± 0.12

(ii) $\rho_{XY'}$

Y	$\rho_{XY'}$
p-Me	−0.51 ± 0.03
p-H	−0.57 ± 0.05
p-Cl	−0.77 ± 0.09

(iii) $\rho_{YY'}$

X	$\rho_{YY'}$
p-OMe	1.11 ± 0.12
p-Me	0.92 ± 0.07
H	0.78 ± 0.04
p-Cl	0.72 ± 0.06

[a]Correlation coefficients were better than 0.997 in all cases.

Reference to Table 2 reveals that the β_X values range from 0.11 to 0.34, which is quite small so that N-C_α bond formation is relatively small in the TS. The magnitude of ρ_X as well as β_X increases with electron acceptor ability of substituents Y and Y' in the substrate, indicating that the extent of bond formation increases in the TS with the increase in the electrophilicity, or positive charge, of the reaction center carbon, C_α. We note that the sign of ρ_Y and $\rho_{Y'}$ is positive reflecting negative charge development at both carbon centers, C_α and C_β, in the TS. Moreover the magnitude of $\rho_{Y'}$ is marginally different from that of ρ_Y, *e.g.*, $\rho_Y = 0.93$ for X=Y=H, while $\rho_Y = 0.89$ for X=Y'=H. This means that the development of negative charge on the β carbon atom is strong in the TS, since charge on C_β ($\rho_{Y'}$) should have been much smaller than that at C_α (ρ_Y) considering the attenuation of susceptibility due to an intervening carbon atom C_α, where the attack of the aniline nucleophile actually occurs. Experimentally the dehydration of 1,2-diphenylethane gave ($\rho_Y/\rho_{Y'}$) = 3.87 so that there is a fall-off factor of approximately 3.8[7] (3.5 from bromination).[7] *i.e.*, the magnitude of ρ_Y should have been larger by *ca* 3.8 than that of $\rho_{Y'}$. Thus, the negative charge developed on the β carbon has not resonance delocalized into the strong electron acceptors, Z,Z'=NO_2, C_6H_4Y', and largely remains localized on the C_β atom[1-3] in the TS. This is a direct demonstration of the lag in the resonance development of the incipient carbanionic charge into the strong electron acceptors, Z, Z', *i.e.*, the TS imbalance, which is in this work presented by investigating substituent effects of both the α- and β-rings. The TS imbalance in the present reaction series is, however, somewhat smaller than that found for the benzylamine additions to β-cyanostilbenes,[4] where Z,Z' =

CN, C_6H_4Y' and $\Delta\rho = \rho_{Y'} - \rho_Y = 0.44$. The larger imbalance observed in the latter series, despite weaker electron accepter CN than NO_2 in the present case, may result from the more advanced N-C_α bond formation in TS for the β-cyanostilbenes, for which the β_X values (=0.69-2.06)[4] were much larger. Thus, the TS imbalance is most probably dependent on the degree of bond formation in the TS.

It is also notable that a weaker nucleophile, aniline, leads to an earlier TS (β_X = 0.17) than a stronger nucleophile,benzylamine (β_X = 1.0).[4] This is consistent with the trend expected from an intrinsic barrier controlled, single step (concerted) reaction series,[5a] for which the anti-Hammond effect[8] applies. In quite contrast, amine additions to dicarbonyl activated olefins (such as benzylidene Meldrum's acid,[3c] benzylidene-1-3-indandione,[3d] benzylidenediethylmalonate,[3b] ethyl α-acetyl-β-phenylacrylate[3a] and benzylidene-3,5-heptadione[3e]) are thermodynamic controlled reactions for which the Hammond postulate and Bell-Evans-Polanyi (BEP) principle[8] hold so that a weaker nucleophile leads to a later TS.[5a] These dicarbonyl activated olefins were found to exhibit insignificant TS imbalance in acetonitrile[3] such that the lag in the resonance development of carbanionic charge on the β carbon practically did not exist. The progress of reaction at the TS for amine additions to all the dicarbonyl activated olefins in acetonitrile is dependent on the product stability, *i.e.*, thermodynamically controlled, with insignificant lag in the charge delocalization into the dicarbonyl activating groups in the TS.[3e] Although the TS imbalance was reported for the dicarbonyl activated olefins *in aqueous solution*, the magnitude, I_m, was much smaller than that for the nondicarbonyl activated olefin series.[1] This is in striking contrast to the substantial charge imbalance observed in the corresponding addition reactions to *nondicarbonyl* activated olefins in acetonitrile as well as in aqueous solution, for which the TS structure is intrinsic controlled. This is in accord with the fact that the imbalance phenomenon is an intrinsic, a kinetic, nature.[1] Another criterion to distinguish between the two reaction types, intrinsic or thermodynamic control, is whether the reactivity-selectivity principle (RSP)[9] holds or not. It has been shown that for thermodynamically controlled reaction series a more reactive reagent is less selective.[5a,9] For the nondicarbonyl activated olefin series (intrinsic control) the RSP is violated, while for the dicarbonyl activated reaction series (thermodynamic control) the RSP holds. Reference to Tables 1 and 2 indeed shows that the RSP is violated (anti-RSP) as expected from an amine additions to a nondicarbonyl activated olefin series.

The signs of cross-interaction constant ρ_{XY} (< 0) and $\rho_{XY'}$ (< 0) are negative, which are consistent with bond formation occurring between the nucleophile (X) and the two interacting reaction centers of the substituted-rings (Y or Y') in the TS.[5a] The magnitude of the former (−0.71) is a typical value for the aminolysis with anilines proceeding by an S_N2 pathway.[5] The magnitude of ρ_{XY} (= −0.71 for Y'=H) is larger than that of $\rho_{XY'}$ (= −0.57 for Y=H) because the distance involved in the two interacting reaction centers is shorter for N-C_α than N-C_β.[5a] The magnitudes of selectivity parameters ρ_X, ρ_Y, $\rho_{Y'}$, β_X, ρ_{XY} and $\rho_{XY'}$ are greater for a stronger electron withdrawing substituent in the ring, *e.g.*, for Y' or Y = *p*-NO_2, indicating a greater degree of bond formation in the TS. In contrast, the sign of $\rho_{YY'}$ (> 0) is positive, which predicts correctly the bond cleavage of a p bond between the two carbon atoms, C_α and C_β in the TS.[5a] The larger $\rho_{YY'}$

Table 4. Kinetic Isotope Effects on the Second Order Rate Constants, $k_2 \times 10^3$ dm^3 mol^{-1} s^{-1} for the Addition Reactions of *p*-, and *p'*-Substituted (Y and Y') β-Nitrostilbene with *p*-Substituted (*p*-X) Anilines in Acetonitrile at 30 °C

X	Y	Y'	k_H	k_D	k_H/k_D
p-OMe	*p*-Me	*p*-NO_2	9.17	7.40	1.24
p-OMe	H	H	3.27	2.75	1.19
p-OMe	H	*p*-NO_2	20.3	16.2	1.25
p-OMe	*p*-Cl	H	6.37	5.31	1.20
p-Me	*p*-Me	H	1.59	1.39	1.14
p-Me	H	H	2.62	2.30	1.14
p-Me	*p*-Cl	H	4.75	4.24	1.15
p-Me	*p*-Me	*p*-Cl	2.53	2.18	1.16
p-Cl	*p*-Cl	H	1.61	1.56	1.03
p-Cl	H	H	1.12	1.10	1.02
p-Cl	H	*p*-Cl	1.70	1.63	1.04

Table 5. Activation Parameters[a] for Addition of X-Anilines to β-Nitrostilbenes in acetonitrile

X	Y	Y'	T (°C)	k_2 (10^3 M^{-1} s^{-1})	$\Delta H^\ddagger$ (kcal/mol)	$-\Delta S^\ddagger$ (cal·mol^{-1}·K^{-1})
p-OMe	*p*-Me	H	25	1.62	4.1	58
			30	1.85		
			35	2.10		
p-OMe	H	*p*-Me	25	1.80	4.0	58
			30	2.05		
			35	2.32		
p-Me	H	H	25	2.32	3.8	58
			30	2.62		
			35	2.95		
p-Me	*p*-Cl	*p*-Cl	25	7.57	4.2	54
			30	8.63		
			35	9.84		
H	*p*-Me	*p*-Cl	25	1.62	4.0	58
			30	1.84		
			35	2.08		
H	*p*-NO_2	*p*-Me	25	4.67	3.5	53
			30	5.23		
			35	5.86		
p-Cl	*p*-Me	H	25	0.731	4.5	58
			30	0.840		
			35	0.965		
p-Cl	H	H	25	0.984	4.2	58
			30	1.12		
			35	1.28		

[a]Calculated using the Eyring equation. The maximum errors calculated by the method of Wiberg[12] were ± 0.5 kcal/mol and ± 2 e.u. respectively for $\Delta H^\ddagger$ and $\Delta S^\ddagger$.

value for a stronger nucleophile, (*e.g.*, for X = *p*-OMe and *p*-Cl, the values are 1.11 and 0.72, respectively) correctly reflects the greater degree of π-bond cleavage between C_α and C_β in the TS with a greater degree of N-C_α bond formation (anti-RSP).

The kinetic isotope effects involving deuterated aniline ($XC_6H_4ND_2$) nucleophiles are summarized in Table 4. The normal isotope effects, $k_H/k_D > 1$, are relatively weak indicating that weak hydrogen bonding of the N-H(D) proton toward the anionic center, C_β, occurs in the earlier TS.[10] Thus the reaction is proposed to proceed in a single step with concurrent formation of N-C_α and H-C_β bonds, **2** with Z,Z' = NO_2, C_6H_4Y' and R=C_6H_4. We note that a stronger nucleophile, X = *p*-OMe, with a faster rate has a larger selectivity, k_H/k_D, value (1.19) compared to that for X = *p*-Me (1.14) and X = *p*-Cl (1.02, for Y=Y'=H), reflecting a stronger hydrogen bonding in a later TS compared with the weaker nucleophiles. This trend of variation of k_H/k_D with substituents is therefore in accord with that expected for an anti-RSP reaction series, which in turn is in line with the intrinsic barrier controlled reactions of a nondicarbonyl activated olefin series.[3e]

The relatively low activation enthalpies, $\Delta H^{\neq}$ ($\cong$ 4 kcal/mol), and large negative activation entropies, $\Delta S^{\neq}$ (= 50-60 e.u.) in Table 5, are consistent with the formation of a more constrained (four-centered cyclic) TS structure proposed.

Experimental

Materials. General procedure. GR grade acetonitrile was purchased from Aldrich and used after re-distillation. The aniline nucleophiles, Aldrich GR grade were used after re-crystallization and re-distillation. FT-IR spectra were taken using a Bruker IFS 55 spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker DPX 300 MHz-NMR instrument using $CDCl_3$ and C_6D_6 as solvent, unless otherwise stated, with TMS as an internal standard. UV/Vis spectra were obtained on a JASCO V-500 spectrophotometer. Kinetic runs were performed using a JASCO V-500 spectrophotometer.

Preparations of α-nitro-4'-substituted phenyl-β-4'-substituted stilbenes. The α-nitro-4'-substituted phenyl-β-4'-substituted stilbenes were prepared by the literature methods of Robertson[10] and Schonne[11] *et al.* To a solution of 0.1 mol. of phenylnitromethane in 25ml. of glacial acetic acid is added 0.1 mol. of the appropriate Schiff's base. The clear homogeneous mixture is allowed to stand at room temperature. When crystallization is completed, the solid is filtered, washed with the mixture of water and acetic acid (50:50 v/v %). The Schiff's bases were prepared by the following reactions; a solution of 0.1 mol. each of an aromatic aldehyde and *n*-butylamine in 30 mL. of benzene in a 100 mL. round bottom flask is attached to a water separator as a modified Dean and Stark moisture trap and refluxed until the theoretical amount of water has been collected for 20 min. The solvent is then removed by distillation, finally under aspirator pressure. The crude Schiff's bases are used directly in the next step.

***p*-$CH_3C_6H_4CH$=$C(NO_2)C_6H_4CH_3$-*p*.** IR(KBr): 3052 (CH, Ar), 1649 (C=C), 1335 (NO_2), 2970 (CH_3, asym. stretch), 1461 (CH_3, asym) cm^{-1}, ^{1}H NMR (300 MHz, $CDCl_3$) (δ) 2.46 (s, 6H, CH_3), 7.90 (s, 1H (alkene)), 7.04-7.07 (m, 4H (aromatic)), 7.33-7.40 (m, 4H (aromatic)).

***p*-$CH_3C_6H_4CH$=$C(NO_2)C_6H_5$.** IR (KBr): 3051 (CH, Ar), 1650 (C=C), 1337 (NO_2), 2971 (CH_3, asym. stretch) cm^{-1}, ^{1}H NMR (300 MHz, $CDCl_3$) (δ) 2.46 (s, 3H, CH_3), 8.10 (s, 1H (alkene)), 7.06-7.11 (m, 3H (aromatic)), 7.34-7.39 (m, 4H), 7.74-7.79 (d, 2H (aromatic)).

***p*-$CH_3C_6H_4CH$=$C(NO_2)C_6H_4Cl$-*p*.** IR (KBr): 3050 (CH, Ar), 1649 (C=C), 1339 (NO_2), 2978 (CH_3, asym. stretch) cm^{-1}, ^{1}H NMR (300 MHz, $CDCl_3$) (δ) 2.46 (s, 3H, CH_3), 7.98 (s, 1H (alkene)), 6.90-7.14 (d, 2H (aromatic)), 7.37-7.60 (m, 6H (aromatic)).

***p*-$CH_3C_6H_4CH$=$C(NO_2)C_6H_4NO_2$-*p*.** IR (KBr): 3049 (CH, Ar), 1650 (C=C), 1338 (NO_2, asym. stretch), 1341 (NO_2, asym. stretch), 2979 (CH_3, asym. stretch) cm^{-1}, ^{1}H NMR (300 MHz, $CDCl_3$) (δ) 2.46 (s, 3H, CH_3), 7.04-7.06 (d, 2H (aromatic)), 7.30-7.34 (d, 2H (aromatic)), 7.66-7.69 (d, 2H (aromatic)), 7.99 (s, 1H (alkene)), 8.17-8.20 (d, 2H (aromatic)).

C_6H_5CH=$C(NO_2)C_6H_4CH_3$-*p*. IR (KBr): 3051 (CH, Ar), 1651 (C=C), 1339 (NO_2), 2979 (CH_3, asym. stretch) cm^{-1}, ^{1}H NMR (300 MHz, $CDCl_3$) (δ) 2.46 (s, 3H, CH_3), 7.06-7.11 (m, 3H (aromatic)), 7.33-7.39 (m, 4H (aromatic)), 7.77-7.81 (d, 2H (aromatic)), 7.99 (s, 1H(alkene)).

$C_6H_5(H)CH$=$C(NO_2)C_6H_5$. IR (KBr): 3058 (CH, Ar), 1650 (C=C), 1337 (NO_2) cm^{-1}, ^{1}H NMR (300 MHz, $CDCl_3$) (δ) 8.01 (s, 1H (alkene)), 7.33-7.39 (m, 6H (aromatic)), 7.77-7.81 (m, 4H (aromatic)).

C_6H_5CH=$C(NO_2)C_6H_4Cl$-*p*. IR (KBr): 3051 (CH, Ar), 1649 (C=C), 1339 (NO_2) cm^{-1}, ^{1}H NMR (300 MHz, $CDCl_3$) (δ) 8.02 (s, 1H (alkene)), 6.87-7.17 (m, 1H (aromatic)), 7.11-7.13 (m, 2H (aromatic)), 7.24-7.27 (m, 4H (aromatic)), 7.42-7.46 (m, 4H (aromatic)).

C_6H_5CH=$C(NO_2)C_6H_4NO_2$-*p*. IR (KBr): 3060 (CH, Ar), 1648 (C=C), 1340 (NO_2) cm^{-1}, ^{1}H NMR (300 MHz, $CDCl_3$) (δ) 8.17-8.19 (d, 2H (aromatic)), 7.98 (s, 1H (alkene)), 6.97-7.11 (m, 1H (aromatic)), 7.24-7.27 (m, 2H (aromatic)), 7.42-7.47 (d, 2H (aromatic)), 7.66-7.69 (d, 2H (aromatic)).

***p*-ClC_6H_4CH=$C(NO_2)C_6H_4CH_3$-*p*.** IR (KBr): 3056 (CH, Ar), 1649 (C=C), 1337 (NO_2), 2978 (CH_3, asym. stretch) cm^{-1}, ^{1}H NMR (300 MHz, $CDCl_3$) (δ) 2.46 (s, 3H, CH_3), 7.90 (s, 1H (alkene)), 7.03-7.11 (d, 2H (aromatic)), 7.25-7.59 (m, 6H (aromatic)).

***p*-ClC_6H_4CH=$C(NO_2)C_6H_5$.** IR (KBr): 3058 (CH, Ar), 1649 (C=C), 1338 (NO_2) cm^{-1}, ^{1}H NMR (300 MHz, $CDCl_3$) (δ) 8.02 (s, 1H (alkene)), 7.10-7.16 (m, 1H (aromatic)), 7.25-7.28 (m, 4H (aromatic)), 7.34-7.39 (m, 4H (aromatic)).

***p*-ClC_6H_4CH=$C(NO_2)C_6H_4Cl$-*p*.** IR (KBr): 3057 (CH, Ar), 1640 (C=C), 1339 (NO_2) cm^{-1}, ^{1}H NMR (300 MHz, $CDCl_3$) (δ) 8.04 (s, 1H (alkene)), 7.24-7.27 (d, 4H (aromatic)), 7.34-7.36 (d, 4H (aromatic)).

***p*-ClC_6H_4CH=$C(NO_2)C_6H_4NO_2$-*p*.** IR (KBr): 3059 (CH, Ar), 1648 (C=C), 1339 (NO_2) cm^{-1}, ^{1}H NMR (300 MHz,

$CDCl_3$) (δ) 7.98 (s, 1H (alkene)), 7.24-7.27 (d, 2H (aromatic)), 7.34-7.37 (d, 2H (aromatic)), 7.64-7.66 (d, 2H (aromatic)), 8.20-8.24 (d, 2H (aromatic)).

p*-$NO_2C_6H_4CH$=$C(NO_2)C_6H_4CH_3$-*p. IR (KBr): 3054 (CH, Ar), 1651 (C=C), 1337 (NO_2, asym. stretch), 1340 (NO_2, asym. stretch), 2978 (CH_3, asym. stretch) cm^{-1}, ^1H NMR (300 MHz, $CDCl_3$) (δ) 2.46 (s, 3H, CH_3), 7.06-7.09 (d, 2H (aromatic)), 8.04 (s, 1H (alkene)), 7.36-7.38 (d, 2H (aromatic)), 7.64-7.69 (d, 2H (aromatic)), 8.19-8.21 (d, 2H (aromatic)).

***p*-$NO_2C_6H_4CH$=$C(NO_2)C_6H_5$**. IR (KBr): 3047 (CH, Ar), 1652 (C=C), 1339 (NO_2, asym. stretch), 1341 (NO_2, asym. stretch) cm^{-1}, ^1H NMR (300 MHz, $CDCl_3$) (δ) 7.98 (s, 1H (alkene)), 7.10-7.14 (m, 1H (aromatic)), 7.24-7.29 (m, 2H (aromatic)), 7.42-7.46 (d, 2H (aromatic)), 7.64-7.69 (d, 2H (aromatic)), 8.14-8.19 (d, 2H (aromatic)).

p*-$NO_2C_6H_4CH$=$C(NO_2)C_6H_4Cl$-*p. IR (KBr): 3051 (CH, Ar), 1648 (C=C), 1343 (NO_2, asym. stretch), 1346 (NO_2, asym. stretch) cm^{-1}, ^1H NMR (300 MHz, $CDCl_3$) (δ) 7.26-7.29 (d, 2H (aromatic)), 7.34-7.37 (d, 2H (aromatic)), 7.64-7.68 (d, 2H (aromatic)), 8.10 (s, 1H (alkene)), 8.19-8.22 (d, 2H (aromatic)).

p*-$NO_2C_6H_4CH$=$C(NO_2)C_6H_4NO_2$-*p. IR (KBr): 3048 (CH, Ar), 1647 (C=C), 1342 (NO_2, asym. stretch), 1338 (NO_2, asym. stretch) cm^{-1}, ^1H NMR (300 MHz, $CDCl_3$) (δ) 8.30 (s, 1H (alkene)), 7.64-7.68 (d, 4H (aromatic)), 8.18-8.20 (d, 4H (aromatic)).

Kinetic procedure. The reaction was followed spectrophotometrically by monitoring the decrease in the concentration of the substrate (β-nitrostilbene) at λ_{max} (=250-269 nm) of the substrate up to *ca* 80% completion. The reaction was studied under pseudo-first-order condition, [S] = 5×10^{-5} M and [AN] = $(3-5) \times 10^{-1}$ M at 30.0 ± 0.1 °C. The seudo-first-order rate constants, k_{obs}, was obtained from the slope of the plot of ln[S] *vs* time ($r > 0.995$). The second-order rate constant, k_2, was determined from the slope of the plot of k_{obs} *vs* [AN] ($r > 0.995$) with more than four [AN], carried out more than three runs, and were reproducible to within ± 3%.

Product analysis. The final products, 1-nitro-1'-phenyl-2'-*N*-benzylaniline ethanes were unstable to collect as pure compounds at room temperature. The product analyses were accomplished using a Bruker DPX 300 MHz-NMR at appropriate intervals under exactly the same conditions as the kinetic measurement in CD_3CN. For the reaction of 4-$ClC_6H_4(H)CH$=$C(NO_2)C_6H_4CH_3$-*p* with aniline at 25.0 °C, at 7.90 ppm, which was gradually reduced, and new peaks for CH-CH in the product, 4-$ClC_6H_4(C_6H_5NH)CH$-$CH(NO_2)C_6H_4CH_3$-*p*, grew at 4.73 and 5.48 ppm, as the reaction proceeded. Other reactions were followed similarly. No other peaks or complications were found during the reaction except the 3 peak hights change showing as the reaction proceeds with no side reactions.

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