Kinetics and Mechanism of Triethylamine Catalysed Michael Addition of Benzenethiol to 1-(2-Nitrovinyl)benzene in Acetonitrile

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Nucleophilic addition reaction of benzenethiols (PhSH) to 1-(2-nitrovinyl) benzenes (βNS) in the presence of triethylamine (TEA) has been studied in acetonitrile at 25 °C. The rate is first order with respect to [PhSH], [TEA] and [βNS]. The reaction is found to proceed with the formation of ion-pair between benzenethiol and TEA. A suitable mechanism with the formation of an adduct between ion-pair and substrate in a slow step followed by its rearrangement to 1,2-addition product in a fast step has been proposed and corresponding rate law derived. From the rate law, the rate constants for the interaction between ion-pair and βNS have been evaluated. Interestingly, in both *para*-substituted substrates and benzenethiols the rate increases with the electron-withdrawing power of the substituents. The positive sign of ρ_x in benzenethiols has been explained. The magnitude of cross-interaction constant, ρ_{xy} is small (0.08). The magnitude of the Hammett ρ_x values is higher than that of the Bronsted, β_x values for benzenethiols. The kinetic isotope effect, k_H/k_D, is found to be greater than unity. A suitable transition state with simultaneous formation of C_β-H and C_α-S bonds involving the ion-pair and βNS in a single concerted step has been proposed to account for these observations.

Key Words : Kinetics, Michael addition, 1-(2-Vinylnitro)benzene, Ion-pair and concerted addition

Introduction

Addition of neutral or anionic nucleophiles to activated olefins is an important class of reactions and has been studied extensively.[1-5] The activating groups are normally electron acceptors which act to stabilize the intermediate carbanion in the stepwise pathway.[1] The addition reactions of amine nucleophiles to olefins containing activating groups have been investigated.[3] In these reactions, solvent plays an important role on the mechanism. In aqueous medium the reaction proceeds through the formation of zwitterion with charge imbalanced transition state.[1] It is observed that even though the reactions show typical behaviour of a carbanion forming process, the carbanion is largely stabilized by the polar effects while resonance effects playing a more modest role.[2] On the other hand, the nucleophilic addition of amines to activated olefins in acetonitrile[4] shows that proton transfer to β-carbon and N-C_α bond formation occur concertedly and the neutral adducts are formed in a single step but not through zwitterion formation. This change in mechanism has been attributed to weak solvating power of acetonitrile to stabilize carbanion. This supporting mechanistic change has also been reflected in high reduction in rate constants in acetonitrile for the addition of neutral nucleophiles to activated olefins.[5] The addition of thiols to such olefinic system has received attention recently.[6] Even though thiols are reported to be very good nucleophiles for Michael addition to activated olefins, the addition reactions have been carried out in the presence of a catalyst[7-10] or in a buffer medium.[11-13] The present work is to study the mechanism of Michael addition reaction of benzenethiol (PhSH) to 1-(2-nitrovinyl)benzene (βNS) in pure acetonitrile in the presence of a suitable catalyst, triethylamine (TEA) by examining the structure-reactivity behaviour of nucleophiles and substrates.

Results and Discussion

The rate of addition reaction of 1-(2-nitrovinyl)benzene with benzenethiol in the presence of triethylamine in acetonitrile was followed by monitoring the disappearance of UV absorption maxima of the substrate (λ_{max} = 310 nm). The plot of log OD versus time is linear showing first order dependence on [substrate]. Further the variation of [substrate] at constant [PhSH] and [TEA] does not alter the pseudo-first order rate constants (Table 1) confirming the first order dependence of the substrate.

The effect of [PhSH] on the rate of addition reactions with βNS was studied by varying [PhSH] and keeping other factors constant. The rate constant increases with an increase in [PhSH]. The plot of log k_{obs} versus log [PhSH] is linear with unit slope. Similarly the effect of [TEA] on the rate was also studied by varying the concentration of TEA, keeping other factors constant. The plot of log k_{obs} versus log [TEA] is also linear with unit slope. Further, the plot of k_{obs} against [TEA] is linear without any intercept which indicates that non-catalytic addition reaction of PhSH with βNS, under the given experimental conditions, is absent. This is in contrast to the observations made for the same reaction in aqueous acetonitrile.[14] This reaction in acetonitrile at 298 K follows total third order; first order with respect to each reactant; βNS, PhSH and TEA.

In order to understand the electronic effects of substituents on the addition reaction of benzenethiol with βNS in the

Table 1. Effect of varying [βNS], [PhSH] and [TEA] in acetonitrile at 298 K on the rate of addition of benzenethiol to 1-(2-nitrovinyl)-benzene

[βNS] × 10^4 (mol dm^{-3})	[PhSH] × 10^3 (mol dm^{-3})	[TEA] × 10^4 (mol dm^{-3})	$k_{obs} \times 10^4$ (s^{-1})	$k_2' = \frac{k_{obs}}{[PhSH]}$ (dm^3 mol^{-1} s^{-1})	$k_2'' = \frac{k_{obs}}{[TEA]}$ (dm^3 mol^{-1} s^{-1})
0.8	1.0	0.10	6.46 ± 0.2	–	–
1.0	1.0	0.10	6.32 ± 0.1	0.632	63.2
1.2	1.0	0.10	6.28 ± 0.1	–	–
1.0	0.6	0.10	3.81 ± 0.1	0.635	–
1.0	0.8	0.10	5.02 ± 0.1	0.630	–
1.0	1.2	0.10	7.52 ± 0.2	0.630	–
1.0	1.0	0.08	5.29 ± 0.1	–	66.1
1.0	1.0	0.20	12.7 ± 0.1	–	63.5
1.0	1.0	0.50	32.2 ± 0.1	–	64.4

Table 2. Second order rate constants, k_2' (dm^3 mol^{-1} s^{-1}) for the addition reactions of *p*-Y-$C_6H_4CH{=}CHNO_2$ with *p*-X-C_6H_4SH in the presence of TEA in acetonitrile at 298 K

X	Y								
	p-OMe	*p*-Me	*p*-H	*p*-F	*p*-Cl	*p*-Br	*p*-CF_3	*p*-CN	*p*-NO_2
p-OMe	0.256 ± 0.001	0.825 ± 0.002	1.53 ± 0.03	1.94 ± 0.04	2.46 ± 0.05	2.81 ± 0.06	9.43 ± 0.19	17.1 ± 0.3	12.4 ± 0.2
p-Me	0.169 ± 0.001	0.433 ± 0.001	0.952 ± 0.002	1.23 ± 0.02	2.29 ± 0.05	2.45 ± 0.05	7.60 ± 0.15	13.9 ± 0.3	10.6 ± 0.2
p-H	0.092 ± 0.001	0.229 ± 0.001	0.632 ± 0.001	0.698 ± 0.002	0.966 ± 0.002	1.01 ± 0.03	4.26 ± 0.09	7.98 ± 0.16	5.04 ± 0.10
p-F	0.152 ± 0.001	0.384 ± 0.001	0.801 ± 0.002	0.866 ± 0.002	1.46 ± 0.03	1.55 ± 0.05	5.67 ± 0.11	9.93 ± 0.20	8.53 ± 0.17
p-Cl	0.307 ± 0.001	0.691 ± 0.001	1.54 ± 0.03	2.30 ± 0.05	3.22 ± 0.06	3.37 ± 0.09	10.9 ± 0.2	19.9 ± 0.4	11.9 ± 0.2

[βNS] = 1.0 × 10^{-4} mol dm^{-3}; [PhSH] = (0.3-0.5) × 10^{-3} mol dm^{-3}; [TEA] = (0.1-0.5) × 10^{-4} mol dm^{-3}

presence of TEA, the addition reaction was carried out with different *para*-substituted 1-(2-nitrovinyl)benzenes and benzenethiols. The relevant data at 298 K are given in Table 2.

Analysis of rate data in Table 2 reveals that the rate increases with increase in electron-attracting power of *para*-substituents in βNS. The rate of addition of *para*-substituted benzenethiols with different *para*-substituted 1-(2-nitrovinyl)benzene in the presence of TEA increases with both electron-withdrawing and electron-releasing substituents in benzenethiol.

The reaction of PhSH with βNS in the presence of TEA is initiated through the formation of intimate ion-pair in acetonitrile.[15,16] IR spectrum of a mixture of PhSH and TEA shows a peak corresponding to $>NH^+$ group (~2493 cm^{-1})[17] in acetonitrile. Similarly a mixture of PhSH and TEA under kinetic condition shows a new weak absorption band at 273 nm in UV spectrum which is in favour of the ion-pair (IP) formation between PhSH and TEA. This is further confirmed by recording the UV spectrum for a mixture of PhSH and TEA with [PhSH] < [TEA]. When [TEA] is varied with constant [PhSH], intensity of the corresponding peak at 273 nm undergoes a change. Hence it was thought of interesting to determine equilibrium constant for the formation of IP between PhSH and TEA.

$$\text{PhSH} + \text{TEA} \underset{}{\overset{K}{\rightleftharpoons}} \text{IP}$$

The corresponding equilibrium constant (K) may be represented as

$$K = \frac{[IP]}{[PhSH][TEA]} \quad \text{or} \quad \frac{[C]}{[A][D]}$$

$$K = \frac{[C]}{([A]_o - [C])([D]_o - [C])} \tag{1}$$

where [C], [A] and [D] denote the concentration of ion-pair, acceptor (PhSH) and donor (TEA). Further $[A]_o$ and $[D]_o$ represent initial concentration of PhSH and TEA respectively. From the measurement of OD of the ion-pair at different initial concentrations of donor, keeping the concentration of acceptor as constant, K has been evaluated by making use of Benesi-Hildebrand equation.[18]

$$\frac{[A]_o}{OD} = \frac{1}{K\varepsilon[D]_o} + \frac{1}{\varepsilon} \tag{2}$$

where OD is the optical density of the ion-pair, ε is molar extinction coefficient and K is the equilibrium constant for the formation of ion-pair.

For a series of solutions of different concentrations of donor (TEA) in which $[D]_o > [A]_o$, optical densities were recorded. A plot of $[A]_o$/OD against $1/[D]_o$ is linear with a definite intercept. By making use of intercept ($1/\varepsilon$) and slope ($1/K\varepsilon$), the equilibrium constants are obtained (Table 3) for different substituted benzenethiols. The free energy of formation of IP has also been calculated and the values are given in Table 3.

Table 3. Equilibrium constants and free energy changes for the formation of ion-pair between *para*-substituted benzenethiols and triethylamine in acetonitrile at 298 K

	p-OCH_3	*p*-CH_3	*p*-H	*p*-F	*p*-Cl
K/10(dm^3 mol^{-1})	218	61.5	20.1	36.7	43.9
$-\Delta G_f$ (kJ mol^{-1})	19.0	15.9	13.1	14.6	15.1

$$\text{PhSH} + \text{TEA} \underset{}{\overset{K}{\rightleftharpoons}} \text{IP}$$

$$\text{IP} + \beta\text{NS} \xrightarrow[k_2]{\text{slow}} \text{Adduct}$$

$$\text{Adduct} \xrightarrow{\text{fast}} \text{Product} + \text{TEA}$$

Scheme 1

The equilibrium constant is also found to increase with increase in electron-withdrawing as well as electron-releasing power of substituents in benzenethiol. This may be due to the fact that electron-withdrawing substituents favour the formation of the ion-pair whereas electron-releasing substituents favour the stabilization of the ion-pair.

In general, rates of amine addition to activated olefins are much faster in aqueous medium (*ca.* > 10^2 fold) than those for the corresponding reactions in acetonitrile.[4,5] But in the present study the rate of addition of benzenethiol to 1-(2-nitrovinyl)benzene in the presence of TEA in acetonitrile is found to be faster than the same reaction in aqueous acetonitrile.[14] The formation of a less polar transition state from the ion-pair and βNS may be the probable reason for the higher reactivity in acetonitrile.

All these observations indicate that the addition of benzenethiol to βNS in the presence of TEA in pure acetonitrile is predicted to proceed by the attack of intimate ion-pair to βNS to form adduct followed by its rearrangement (Scheme 1).

The rate law for the above mechanism is

$$v = k_2[\text{IP}][\beta\text{NS}]$$

On substituting the value for [IP] in the rate law, the observed pseudo-first order rate constant is given as

$$k_{obs} = \frac{v}{[\beta\text{NS}]} = k_2K[\text{PhSH}][\text{TEA}]$$

$$\text{or} \quad k_2' = \frac{k_{obs}}{[\text{PhSH}]} = k_2K[\text{TEA}]$$

By using equilibrium constant *K*, [PhSH] and [TEA], the second order rate constant for the second step (k_2) can be evaluated.

$$k_2 = \frac{k_2'}{[\text{TEA}]}\left(\frac{1}{K}\right) \tag{3}$$

The second order rate constants (k_2) for the addition of various substituted benzenethiols to various *para*-substituted 1-(2-nitrovinyl)benzene at 298 K in acetonitrile are presented in Table 4. The rate data for the addition reactions of 1-(2-nitrovinyl)benzenes and substituted benzenethiols are analysed in terms of the corresponding Hammett σ constants.[19] Further, the rate constants of substituted benzenethiols are also correlated with pK_a values of benzenethiols in water.[20] It has been proved that the β_x values determined by correlating the rate constants in acetonitrile with pK_a of benzenethiols in water are reliable in spite of the difference in solvent.[21] Relevant ρ_x, ρ_y and β_x values are presented in Table 4.

Analysis of rate data in Table 4 reveals that the rate of addition of ion-pair to βNS increases with electron-withdrawing substituents in *para*-substituted βNS and also in *para*-substituted benzenethiols. In the case of *para*-substituted βNS, good correlations are obtained with normal σ-constants (ρ_y = 1.73-1.91) whereas in the case of *para*-substituted benzenethiols, good correlations are obtained with σ^+ constants (ρ_x = 0.60-0.75). In the correlation of rate data of *para*-substituted βNS, *p*-$NO_2\beta$NS has not been included since the observed rate constants are lower than those expected based on its σ value. A similar trend has been observed in the reactions of βNS with benzylamines in acetonitrile.[4a] The lower rate for the *p*-$NO_2\beta$NS may be due to the fact that the two nitro groups present on both sides are

Table 4. Values of second order rate constants (k_2/10 $dm^3mol^{-1}s^{-1}$) for the addition reactions of various substituted benzenethiols to *p*-Y-$C_6H_4CH{=}CHNO_2$ at 298 K in acetonitrile

X	Y									
	p-OMe	*p*-Me	*p*-H	*p*-F	*p*-Cl	*p*-Br	*p*-CF_3	*p*-CN	*p*-NO_2	ρ_y
p-OMe	1.18	3.79	7.05	8.91	11.3	12.9	43.4	78.7	56.8	1.73 ± 0.14
p-Me	2.75	7.05	15.5	20.0	37.2	39.8	123	226	172	1.91 ± 0.10
p-H	4.58	11.4	31.3	34.7	48.1	50.2	212	397	251	1.90 ± 0.13
p-F	4.14	10.5	21.8	23.6	39.8	42.2	154	270	232	1.80 ± 0.10
p-Cl	7.00	15.7	35.0	52.5	73.5	76.8	248	453	273	1.80 ± 0.10
ρ_x	0.74 ± 0.06	0.60 ± 0.05	0.69 ± 0.11	0.70 ± 0.13	0.75 ± 0.14	0.71 ± 0.10	0.74 ± 0.10	0.74 ± 0.11	0.70 ± 0.08	ρ_{xy} = 0.08 ± 0.01
β_x	−0.29 ± 0.05	−0.24 ± 0.03	−0.26 ± 0.05	−0.27 ± 0.06	−0.28 ± 0.08	−0.25 ± 0.06	−0.28 ± 0.07	−0.28 ± 0.08	−0.27 ± 0.07	

Correlation coefficients were better than 0.970 in all the cases.

operating the electronic effects in opposite directions. This results in lowering of polarization of >C=C< and its reactivity.[6]

The mode of rate variation with *para*-substituted benzenethiols in the addition reactions is opposite to the general behaviour observed in nucleophilic addition reactions of neutral nucleophiles with activated olefinic bonds.[1-5] In all these cases ρ_x is observed to be negative.

A larger negative value of ρ_x is observed in the addition of benzylamine to 1-(2-nitrovinyl)benzene in acetonitrile[4a] and also in the addition of benzenethiols to 4'-[*N*-(9-Acridinyl)]-1'-(*N*-methanesulfonyl)-3'-methoxyquinine diimide.[12] But, the observed ρ_x value in the present study is positive and less than unity. Further, exalted σ^+ constants are required to correlate the rate data for the addition of various *para*-substituted benzenethiols to 1-(2-nitrovinyl)benzenes. This is accounted by the fact that the addition of ion-pair to βNS is the slow step. The presence of electron-withdrawing groups polarizes the -S-H bond in the ion-pair and the transfer of proton to C_β becomes much easier, whereas the presence of electron-releasing substituents in benzenethiol increases the electron density at the sulphur atom in the ion-pair, thereby the polarization of S-H bond in ion-pair decreases and hence its reactivity.

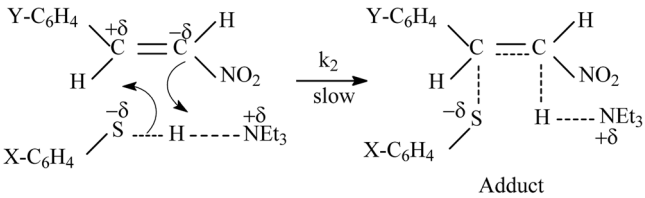
For the addition of benzenethiol to various *para*-substituted 1-(2-nitrovinyl)benzenes in the presence of triethylamine in acetonitrile, ρ_y values are also found to be positive and are in the range 1.73-1.91. These values are more or less comparable with those ρ_y values for the addition of benzylamine to *para*-substituted 1-(2-nitrovinyl)benzenes in acetonitrile.[4a] The addition of ion-pair to βNS depends on the extend of polarization of >C=C< in βNS. The extend of polarization and development of partial positive charge on C_α and negative charge on C_β carbon atoms is enhanced by electron-withdrawing substituents in βNS whereas it is decreased by electron-releasing substituents. This is reflected by the observed positive ρ_y values for βNS in the present study.

Further, the nature of the transition state in amine addition reactions in acetonitrile[3-5] has been explained in terms of cross-interaction constant, ρ_{xy} which has been evaluated by making use of the equation (4).

$$\log(k_{ij}/k_{HH}) = \rho_i\sigma_i + \rho_j\sigma_j + \rho_{ij}\sigma_i\sigma_j \quad (4)$$

The observed value of the cross-interaction constant, ρ_{xy} for the present investigation in acetonitrile is almost equal to zero (0.08). Whenever bond formation occurs in the transition state ρ_{xy} is negative,[4] whereas for bond breaking in transition state ρ_{xy} is found to be positive.[22,23]

A cyclic transition state with bond formation has been envisaged on the basis of sign and magnitude of ρ_{xy} values (−0.24 to −0.90) in the addition reaction of benzylamine to activated olefins. In contrast, the aminolysis of thiophenyl acetates with benzylamines in acetonitrile which is believed to proceed by rate-limiting expulsion of leaving group, gives positive ρ_{xy}(0.90) value.[23] In the present investigation, ρ_{xy} value is nearer to zero(0.08). Since the magnitude of ρ_{xy} is a measure of the degree of bond formation,[5] it may be expected the occurrence of both bond-breaking and bond-making in the transition state. Therefore, the present addition reaction proceeds with the simultaneous formation of C_β-H and C_α-S bonds involving the ion-pair in a single step to form an adduct during which -S-H bond undergoes cleavage. The plots of ρ_x *vs* σ_y (slope = 0.08) and ρ_y *vs* σ_x (slope = 0.08) are linear which are also in favour of occurrence of simultaneous bond making and bond breaking in the transition state.



The observed ρ_x, ρ_y, ρ_{xy} and β_x values are in support of the mechanism (Scheme 1). The observed β_x values are much lower than the corresponding ρ_x values in the addition reaction of benzenethiols to βNS. These relative lower β_x values to those of ρ_x values are similar to the addition reaction of aniline to βNS in acetonitrile at 25 °C (β_x ~ 0.68 and ρ_x ~ 1.89 ± 0.13).[24] This is an indication of lower degree of bond formation in the transition state in benzenethiol addition to βNS.

The rate of addition of benzenethiol to βNS in the presence of TEA in acetonitrile has been measured at four different temperatures (Table 5).

Activation parameters $\Delta H^\#$ (15.2 kJ mol^{-1}), $\Delta S^\#$ (−146 J K^{-1} mol^{-1}) and $\Delta G^\#$ (53.1 kJ mol^{-1}) are all similar to those observed in benzylamine addition to βNS with the formation of cyclic transition state.[4a] Low $\Delta H^\#$ and large negative $\Delta S^\#$ values are in line with the concerted proton transfer to C_β and C_α-S bond formation involving βNS and IP to form TS with less polarity.

Proton transfer from the ion-pair to negatively charged C_β-carbon in the transition state is further confirmed by the primary kinetic isotope effect; (k_H/k_D > unity) given in Table 6 involving deuterated benzenethiols. In the case of *p*-chlorobenzenethiol and *p*-methoxybenzenethiol, k_H/k_D values are significantly higher (~7). In the case of *p*-chlorobenzenethiol and *p*-methoxybenzenethiol, the ion-pair formation with TEA is high (Table 3) and hence the formation of C_β-H bond is significant in the transition state which is reflected in

Table 5. Effect of temperature on the rate of addition of C_6H_5SH with $C_6H_5CH{=}CHNO_2$ in the presence of TEA in acetonitrile

S.No.	T (K)	$k_{obs} \times 10^4$ (s^{-1})	K (dm^3 mol^{-1})	k_2 (dm^3 mol^{-1} s^{-1})
1.	298	6.32	201	313
2.	303	6.22	178	349
3.	308	6.06	156	388
4.	313	5.83	132	442

[βNS] = 1.0 × 10^{-4} mol dm^{-3}; [PhSH] = 1.0 × 10^{-3} mol dm^{-3}; [TEA] = 0.1 × 10^{-4} mol dm^{-3}

Table 6. Kinetic isotope effects on the second order rate constants (k_2) for the reactions of *p*-Y-$C_6H_4CH{=}CHNO_2$ with deuterated *p*-X-C_6H_4SH in acetonitrile at 298 K

Y	X	$k_H/10$ ($dm^3\ mol^{-1}\ s^{-1}$)	$k_D/10$ ($dm^3\ mol^{-1}\ s^{-1}$)	k_H/k_D
p-OMe	*p*-H	4.58 ± 0.01	3.30 ± 0.01	1.39 ± 0.01
p-H	*p*-H	31.3 ± 0.5	22.0 ± 0.2	1.42 ± 0.03
p-CN	*p*-H	397 ± 7	236 ± 5	1.68 ± 0.02
p-OMe	*p*-Cl	7.0 ± 0.05	1.59 ± 0.07	4.40 ± 0.07
p-H	*p*-Cl	35.0 ± 0.5	16.6 ± 0.9	2.11 ± 0.05
p-CN	*p*-Cl	453 ± 3	64.7 ± 1.6	7.01 ± 0.15
p-OMe	*p*-OMe	1.18 ± 0.02	0.167 ± 0.01	7.01 ± 0.15
p-H	*p*-OMe	7.05 ± 0.13	2.79 ± 0.06	2.53 ± 0.04
p-CN	*p*-OMe	78.7 ± 1.3	37.7 ± 1.1	2.09 ± 0.06

the value of k_H/k_D for these substituents in benzenethiol. The electron-releasing substituent(*p*-OMe) in βNS enhances the polarization of >C=C< bond and favours the formation of C_β-H bond in the transition state.

Materials and Methods

Solvent, acetonitrile (merck GR) was used after three distillations. Benzenethiols (Aldrich GR) were used after fractional distillation/crystallization. The 1-(2-nitrovinyl)-benzenes were prepared by the literature method.[6]

Kinetic measurements. The reaction was followed spectrophotometrically using Shimadzu UV-1601 spectrophotometer by monitoring the decrease in the concentration of 1-(2-nitrovinyl)benzenes at the corresponding λ_{max} of the substrates to over 60% completion. The reaction was studied under pseudo-first order conditions, [βNS] = (0.8-1.2) × 10^{-4} mol dm^{-3}, [PhSH] = (0.6-1.2) × 10^{-3} mol dm^{-3} and [TEA] = (0.08-0.5) × 10^{-4} mol dm^{-3} at 25 ± 0.1 °C. The pseudo-first order rate constant was determined from the slope of the plot of log OD versus time.

Product analysis. 1-(2-nitrovinyl)benzene (0.02 mol), benzenethiol (0.1 mol) and triethylamine (0.02 mol) were mixed in acetonitrile at 25 °C and kept for more than 10 half-lives. The resultant mixture was poured into excess water and the product was extracted with ethyl acetate. The organic layer was washed with dil.HCl and then with water. The separated organic layer was dried over anhy.Na_2SO_4 and the solvent was removed under reduced pressure. The separated solid was purified by column chromatography (Silica gel, 20% ethyl acetate - *n*-hexane). The separated solid (yield: 85%) was identified as 1,2-addition product (C_6H_5-$CH(SC_6H_5)$-CH_2NO_2) from its melting point (72 °C) which is confirmed by preparing authentic sample.[6] The nature of the product was further confirmed by NMR and Mass spectral data. The ^{1}H NMR (300 MHz) spectrum in $CDCl_3$ showed signals in the region 4.56-4.91 δ (3H, m, CH and CH_2) and 7.4 δ (10H, m, aromatic). The ^{13}C NMR showed signals at 50.25 (C-H), 78.92 (CH_2), 128.04, 129.06, 129.26, 129.40, 129.77 and 134.17 (aromatic) ppm. The mass spectral data showed the following fragment ions having m/e values 259 (M^+), 212, 150, 135, 125, 121, 109, 104 (base peak), 91, 77 and 65.

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References

1. Bernasconi, C. F. *Tetrahedron* **1989**, *45*, 4017.
2. (a) Bernasconi, C. F.; Schuck, D. F.; Ketner, R. J.; Weiss, M.; Rappoport, Z. *J. Am. Chem. Soc.* **1994**, *116*, 11764. (b) Chem, X.; Rappoport, Z. *J. Org. Chem.* **1998**, *63*, 5684.
3. Oh, H. K.; Kinn, I. K.; Lee, H. W.; Lee, J. *J. Org. Chem.* **2004**, *69*, 3806.
4. (a) Oh, H. K.; Yang, J. H.; Sung, D. D.; Lee, I. *J. Chem. Soc. Perkin Trans. 2* **2000**, 101. (b) Oh, H. K.; Yang, J. H.; Hwang, Y. H.; Lee, H. W.; Lee, I. *Bull. Korean Chem. Soc.* **2002**, *23*, 221.
5. Oh, H. K.; Yang, J. H.; Lee, H. W.; Lee, I. *J. Org. Chem.* **2000**, *65*, 2188 and 5391.
6. Ananthakumar, K.; Sarathi, A.; Gnanasekaran, C.; Shunmugasundaram, A. *Indian J. Chem.* **2003**, *42B*, 1943.
7. Miyata, O.; Naito, T.; Ninomiya, I. *Pure and Applied Chem.* **1994**, *66*, 2115.
8. Kanimura, A.; Sasatani, H.; Hashimoto, T.; Kawai, T.; Hori, K.; Ono, N. *J. Org. Chem.* **1990**, *55*, 2437.
9. Kotrusz, P.; Toma, S. *Molecules* **2006**, *11*, 197.
10. Meciarova, M.; Toma, S.; Kotrusz, P. *Org. & Biomol. Chem.* **2006**, *4*, 1420.
11. Kim, T. R.; Hall, T. S.; Han, I. S. *Bull. Korean Chem. Soc.* **1982**, *3*, 162.
12. Kim, T. R.; Chung, D. I.; Pyun, S. Y. *Bull. Korean Chem. Soc.* **1997**, *18*, 374.
13. da Silva, F. M.; Jones Jr, J. J. *J. Braz. Chem. Soc.* **2001**, *12*, 135.
14. Sarathi, P. A.; Vijayakumar, A.; Gnanasekaran, C.; Shunmugasundaram, A. *J. Indian Chem. Soc.* **2004**, *81*, 1157.
15. Berkessel, A.; Grogee, H. *Asymmetric Organocatalysis*: *From Biomimetic Concepts to Applications in Asymmetric Synthesis*; Wiley-VCH: 2005; p 73.
16. Nag, S.; Datta, D. *Indian J. Chem.* **2007**, *46A*, 1263.
17. Detar, D. F.; Novak, R. W. *J. Am. Chem. Soc.* **1970**, *92*, 1361.
18. Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703.
19. Dean, J. A. *Handbook of Organic Chemistry*; McGraw-Hill: New York, 1987; Table 7-1.
20. Bukingham, J. *Dictionary of Organic Compounds*, 5th Ed.; Chapman Hall: New York, 1982.
21. (a) Oh, H. K.; Woo, S. Y.; Shim, C. H.; Pak, Y. S.; Lee, I. *J. Org. Chem.* **1997**, *62*, 5780. (b) Koh, H. J.; Han, K. L.; Lee, I. *J. Org. Chem.* **1999**, *64*, 4783.
22. Lee, H. W.; Yun, Y. S.; Lee, B. S.; Koh, H. J.; Lee, I. *J. Chem. Soc. Perkin Trans. 2* **2000**, 2302.
23. Oh, H. K.; Yang, J. H.; Lee, H. W.; Lee, I. *Bull. Korean Chem. Soc.* **1999**, *20*, 1418.
24. Varghese, R.; Kothari, S.; Banerji, K. K. *J. Chem. Res. (S)* **1998**, 422.