Mechanism of Debromination of 1-Aryl-1,2-dibromo-2-nitropropanes Promoted by Secondary Amines in Acetonitrile

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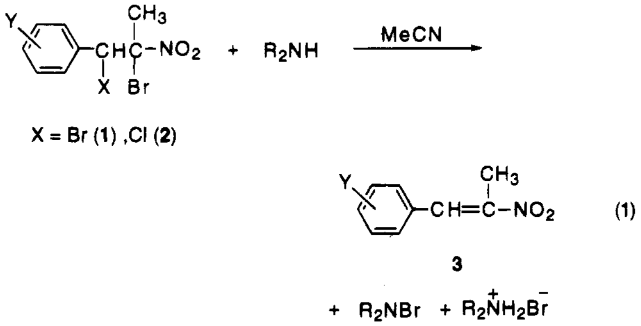
Debromination reactions of *erythro-dl*-1-aryl-1,2-dibromo-2-nitropropanes with secondary amines in MeCN have been investigated kinetically. Reactions of *erythro-dl*-1-aryl-1,2-dibromo-2-nitropropanes with secondary amines in MeCN are stereospecific, producing (*E*)-1-aryl-2-nitropropenes quantitatively. The rate equation for the reaction is $k_{obs} = k_2[R_2NH] + k_3[R_2NH]^2$, indicating that the reactions proceed by both uncatalyzed and base-catalyzed pathways. The Hammett ϱ, Brønsted β, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ values for the k_2 and k_3 processes are 1.22 ± 0.04 and 1.20 ± 0.02, 0.77 ± 0.05 and 1.05 ± 0.13, 5.6 ± 0.3 and 1.7 ± 0.1 kcal/mol, and −49.1 ± 4.5 and −60.7 ± 204 eu, respectively. For dehalogenation reactions from vicinal dibromo and bromochloro compounds, the element effect of the leaving group k_{Br}/k_{Cl} = 7.8 and 25 have been determined for the k_2 and k_3 processes. From these results, the mechanism and the transition-state character of these reactions are assessed.

The mechanisms of debromination reactions of vicinal dibromides have been investigated under various conditions.[1–6] The conversion of vicinal dibromides to olefins by reaction with iodides has been shown to follow a direct mechanism involving nucleophilic attack of iodide on bromine in a typical E2 process resulting in trans elimination[5] or may involve S_N2 replacement of bromine on carbon by iodide followed by rapid collapse of the iodobromide to afford cis elimination.[6] Solvolytic and reductive debromination reactions have also been reported.[1–4]

Very recently we investigated the reactions of 1-aryl-1,2-dibromo-2-nitropropanes with 2-nitro-2-propyl anion in DMSO in an attempt to find the first example of elimination reactions that proceed by the SET mechanism.[7] The reactions were almost instantaneous, producing 1-aryl-2-nitropropenes, 2-bromo-2-nitropropane, and 2,3-dimethyl-2,3-dinitrobutane. Addition of 1 equiv of *p*-dinitrobenzene or di-*tert*-butyl nitroxide decreased the yield of 2,3-dimethyl-2,3-dinitrobutane, but increased the yields of 1-aryl-2-nitropropenes. The results were interpreted as resulting from an ionic mechanism induced by the attack of the base on the bromine atom of the C−Br bond. The propensity of the ionic pathway over the SET process was attributed to the higher exothermicity of the former. However, the detailed mechanism and the transition state of the debromination reaction were not rigorously examined because the reaction was too fast to follow even by stopped-flow spectrophotometry.

To better understand the mechanism of this reaction, we have conducted kinetic studies on the reactions of 1-aryl-1,2-dibromo-2-nitropropanes with secondary amines in acetonitrile (eq 1).



X = Br (**1**), Cl (**2**)

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(1)

	Y	R_2NH
a	H	2,6-dimethylpiperidine
b	*p*-CH_3O	diisobutylamine
c	*m*-Br	diisopropylamine
d	*p*-NO_2	benzylisopropylamine

It was expected that the reaction may be sufficiently slowed to measure the rates conveniently since the reaction should be much less exothermic than the 2-nitro-2-propyl anion-promoted debromination due to the much weaker strength of the N−Br than the C−Br bond.[8,9] In addition, sterically bulky amines have been employed to avoid the complication that may be caused by a subsequent addition of the base to the alkene product. In this work, we have determined the mechanism and the transition state structure for these reactions. The results of these studies are now reported.

Results

erythro-dl-1-Aryl-1,2-dibromo-2-nitropropanes **1a–d** were prepared by known methods.[10,11] *erythro-dl*-2-Bromo-1-chloro-1-phenyl-2-nitropropane (**2a**) was prepared by the addition of bromine chloride to 2-nitro-1-

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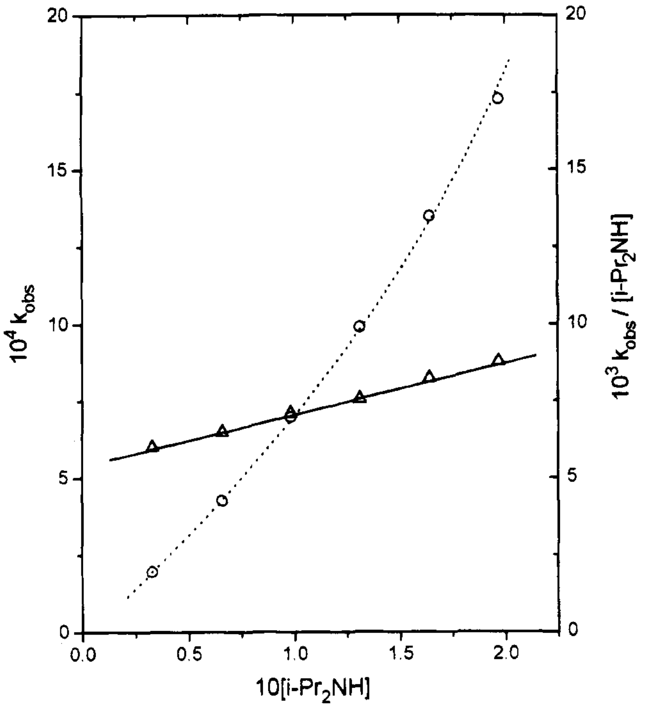


Figure 1. Plots of k_{obs}(○) and k_{obs}/[i-Pr$_2$NH](△) vs base concentration for debromination from 1,2-dibromo-2-nitro-1-phenylpropane promoted by diisopropylamine in MeCN at 20.0 °C.

phenylpropene. The spectral and analytical data for the compounds were consistent with the proposed structures.

The reaction of **1a** with benzylisopropylamine in MeCN produced (*E*)-2-nitro-1-phenylpropene and *N*-isopropylbenzylideneamine in 90 and 76% yields, respectively. The yields of the dehalogenation product for all reactions as determined by comparison of the UV absorption of the infinity sample of the kinetic run with that for an authentic sample were in the range of 90–98%. For reaction of **1a** with diisopropylamine, a small amount of *N*-bromodiisopropylamine was detected by NMR. When the reaction was quenched after approximately one half-life by the addition of HCl, only the starting material and the debromination product were obtained. No trace of 1-bromo-2-nitro-1-phenylpropane could be detected.

The rates of the reactions were followed by monitoring the increase in the absorption at the λ_{max} for **3a–d** in the range of 306–344 nm. Excellent pseudo-first-order kinetic plots which covered at least three half-lives were obtained. The pseudo-first-order rate constants are listed in Tables S1–S8 in the supplementary material. The k_{obs} values were not influenced by the addition of an excess of p-dinitrobenzene and di-*tert*-butyl nitroxide (Tables S1 and S7).

A plot of k_{obs} vs [R$_2$NH] shows upward curvature (Figure 1). However, when k_{obs}/[R$_2$NH] is plotted against [R$_2$NH], straight lines are obtained for all reactions (Figure 1), indicating that the rate equation can be expressed as $k_{obs} = k_2\,[\mathrm{R_2NH}] + k_3[\mathrm{R_2NH}]^2$. The k_2 and k_3 values are obtained from the intercepts and the slopes of the plots. The rate constants are summarized in Table 1.

Rates of debromination from **1a** promoted by diisopropylamine in MeCN were measured at five temperatures spanning 40 °C. Since the k_3 process became negligible at 35 °C, the k_3 values could not be obtained accurately at higher temperatures (Table 2). The Arrhenius plots for the two reactions were linear with excellent correlation (plots not shown), although the standard deviation of the intercept on the plot for the latter was very large due to the lack of the data at higher temperatures. The calculated enthalpies and entropies of activation are presented in Table 4.

Table 1. Second- and Third-Order Rate Constants for Dehaloganation from 1-Aryl-1,2-dibromo-2-nitropropane (1a–d) and 2-Bromo-1-chloro-2-nitro-1-phenylpropane (2a)[a] Promoted by Diisopropylamine[b] in MeCN at 25.0 °C

compd	10^3k_2, $M^{-1}s^{-1}$ [c]	10^2k_3, $M^{-1}s^{-1}$ [c]	compd	10^3k_2, $M^{-1}s^{-1}$ [c]	10^2k_3, $M^{-1}s^{-1}$ [c]
1a	6.04	1.81	**1d**	53.2	16.6
1b	2.95	0.91	**2a**	0.772	0.0723
1c	20.2	5.38			

[a] [Substrate] = 6.19 × 10^{-5}M. [b] [i-Pr$_2$NH] = 0.0328–0.197 M. [c] Estimated uncertainty, ±5%.

Table 2. Effect of Temperature on the k_2 and k_3 Values for Debromination from 1,2-Dibromo-2-nitro-1-phenylpropane (1a)[a] Promoted by Diisopropylamine[b] in MeCN

T, °C	10^3k_2, $M^{-1}s^{-1}$ [c]	10^2k_3, $M^{-2}s^{-1}$ [c]	T, °C	10^3k_2, $M^{-1}s^{-1}$ [c]	10^2k_3, $M^{-2}s^{-1}$ [c]
15.0	4.37	1.57	35.0	9.06	
20.0	5.42	1.70	45.0	12.1	
25.0	6.04	1.81			

[a] [Substrate] = 6.19 × 10^{-5} M. [b] [i-Pr$_2$NH] = 0.0328–0.197 M. [c] Estimated uncertainty, ±5%.

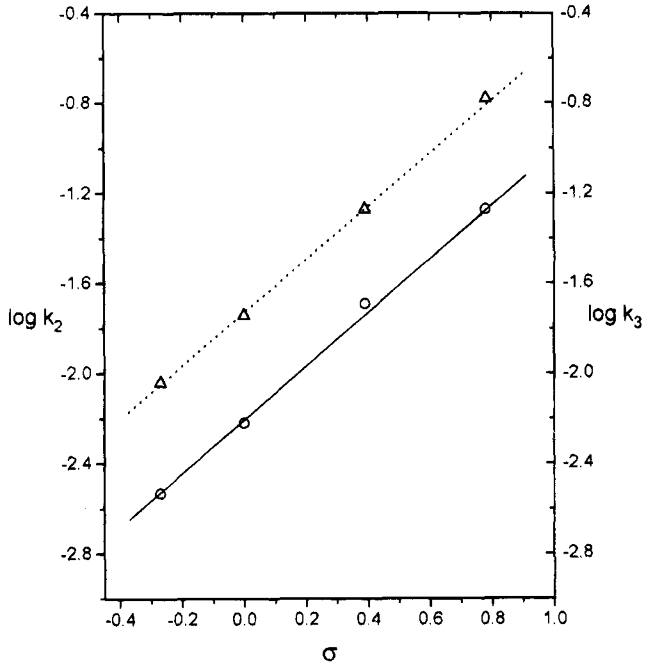


Figure 2. Hammett plots for the k_2 (○) and k_3 (△) processes for debromination from 1-aryl-1,2-dibromo-2-nitropropane promoted by diisopropylamine in MeCN at 25.0 °C.

Hammett plots for debromination from **1** are shown in Figure 2. The influence of aryl substituents (**a–d**) upon the rates gave excellent correlations with σ values. Hammett ρ values for the k_2 and k_3 processes are 1.22 ± 0.04 and 1.20 ± 0.02, respectively (Table 4).

The pK_a values of the secondary amines were determined by measuring the equilibrium constants for reactions between R$_2$NH and p-nitrophenol spectrophotometrically.[12] The pK_a values in MeCN were 16.8 ± 0.1, 18.2 ± 0.1, 18.5 ± 0.2, and 18.9 ± 0.02 for benzylisopropylamine, diisobutylamine, diisopropylamine, and 2,6-dim-

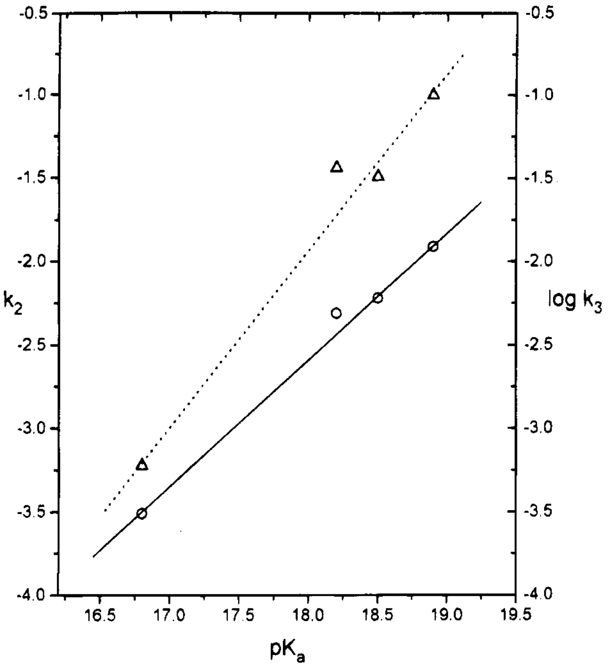


Figure 3. Brønsted plots for the k_2 (○) and k_3 (△) processes for debromination from 1-phenyl-1,2-dibromo-2-nitropropane promoted by secondary amines in MeCN at 25.0 °C.

Table 3. Effect of Base Strength upon the k_2 and k_3 Values for Debromination from 1,2-Dibromo-2-nitro-1-phenylpropane (1a)[a] Promoted by Secondary Amines in MeCN at 25.0 °C

R_2NH[b]	pK_a[c]	10^3k_2, $M^{-1}s^{-1}$[d]	10^2k_3, $M^{-1}s^{-1}$[d]
benzylisopropylamine	16.8	0.309	0.06
diisobutylamine	18.2	4.90	3.65
diisopropylamine	18.5	6.04	3.22
2,6-dimethylpiperidine	18.9	12.3	10.0

[a] [Substrate] = (6.26–7.86) × 10^{-5} M. [b] [R_2NH] = 0.0328–0.197 M. [c] Estimated uncertainty, ±3%. [d] Estimated uncertainty, ±5%.

ethylpiperidine, respectively (Table 3). The pK_a value determined for diisobutylamine is in reasonable agreement with the literature value.[13]

Brønsted plots for debromination from **1** are depicted in Figure 3. Excellent correlation was obtained between the log k_2 and pK_a values, although the correlation was not as good for the k_3 process. The β values for the k_2 and k_3 processes are 0.77 ± 0.05 and1.05 ± 0.13, respectively (Table 4).

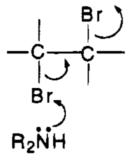
Discussion

The reactions of *erythro-dl*-1-aryl-1,2-dihalo-2-nitropropanes **1** and **2** with secondary amines in MeCN are stereospecific, producing only (*E*)-1-aryl-2-nitropropenes **3** almost quantitatively. For reaction of **1a** with benzylisopropylamine *N*-bromodiisopropylamine and *N*-isopropylbenzylideneamine were also produced. Since the *N*-bromoamine is known to react with the secondary amine to produce the corresponding imine, amine, and dialkylammonium ion products under the same condition,[14] the initial products of the reactions must be **3a–d**, the *N*-bromoamine, and the dialkylammonium bromide as shown in eq 1. Moreover, the rates were not influenced by the radical scavengers. Therefore, the debromination reactions must proceed by an ionic mechanism induced by the attack of the base on the bromine atom of **1a–d** with anti stereochemistry.

Table 4. Activation Parameters for Bimolecular and Termolecular Processes of Debromination Reaction of 1,2-Dibromo-2-nitro-1-phenylpropane (1a–d) with Diisopropylamine in MeCN at 25.0 °C

	k_2 path	k_3 path
ϱ	1.22 ± 0.04	1.20 ± 0.02
β	0.77 ± 0.05	1.05 ± 0.13
k_{Br}/k_{Cl}	7.8	25
$\Delta H^{\ddagger}$, kcal/mol	5.6 ± 0.3	1.7 ± 0.1
$\Delta S^{\ddagger}$, eu	−49.1 ± 4.5	−60.6 ± 204

The rate equation for the debromination reaction consists of both second- and third-order terms, indicating that the reactions proceed by both uncatalyzed (**I**) and base-catalyzed (**II**) pathways. Moreover, the third-order term disappeared at higher temperature. The result can be attributed to the larger negative entropy of activation for the latter (Table 4). The enthalpy of activation for the latter is somewhat lower than that of the former apparently due to the much greater basicity of the amide ion than the amine. Although the entropy of activation for the latter has large standard deviation due to the absence of data for the higher temperatures, the value is more negative than that for the former probably because three molecules are associated in the latter's transition state. Therefore, the rates of the both processes should not be very different. The absence of the competing k_3 process at higher temperature can also be attributed to the larger negative entropy of activation because the entropic term becomes more important at higher temperature. It is interesting to note that both reactions exhibit small $\Delta H^{\ddagger}$ and large negative $\Delta S^{\ddagger}$ values. The small enthalpy of activation apparently results from the relative strength of the bonds involved in these reactions. Since the C—Br bonds are rather weak and the C=C bond of **2a** must be stronger than a normal double bond due to the extended conjugation with phenyl and nitro groups, the energy required to cleave both of the C—Br bonds should be largely compensated by the formation of partial C=C and N—Br bonds in the transition state. The large negative entropies of activation for these reactions are typical for reactions of this charge type and can be attributed to the large solvent reorganization required to solvate the charged transition state.[14,15]



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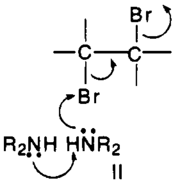

II

The reaction site was determined by the Hammett plots. For debromination of **1a–d**, the rate data for the k_2 and k_3 processes correlated with the σ values with excellent correlation (Figure 2). This result strongly indicates that the reaction site is the C-2–Br bond. On the other hand, if the benzylic C–Br bond were the

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reaction site, the rate data for **1b** and **1d** should have been correlated with σ^- values because the developing negative charge on the benzylic carbon would be stabilized by resonance with the para substituents.

With this information in hand, it is now possible to elucidate the mechanism of this reaction. The reaction exhibits second- and third-order kinetics which indicates that there are two competing pathways. For both reactions, the $(E1cb)_{rev}$ mechanism is negated by the results of a trapping experiment and the Brønsted studies.[16,17] If the carbanion intermediate were in equilibrium with the substrate, it should have been trapped as 1-bromo-1-phenyl-2-nitropropane upon the addition of HCl to the reaction mixture after half reaction. Moreover, the β values would also be greater than unity (vide infra) because the C_β-Br bond[18] must be completely broken in the $(E1cb)_{rev}$ transition state. Neither of these expectations was borne out by the experiments.

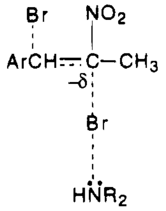
The distinction between the E2 and $(E1cb)_{irr}$ mechanisms has been made by the leaving group element effect (Table 4). The $(E1cb)_{irr}$ mechanism predicts that the k_{Br}/k_{Cl} value should be smaller than unity because the negative charge developed on the β-carbon in the transition state could be better stabilized by the polar or inductive effect of the chloride.[17] In contrast, a much larger value of the leaving group element effect is anticipated for the E2 mechanism because the C_α−X bond must be broken significantly in the transition state. For example, the k_{Br}/k_{Cl} values for the E2 debromination of *meso*-stilbene dibromide promoted by iodide ion were 87 (MeOH) and 260 (DMF), respectively.[19] Therefore, the observed $k_{Br}/k_{Cl} = 7.8$ and 25 for the k_2 and k_3 processes of the R_2NH-promoted dehalogenation from **1a** and **2a** are entirely consistent with an E2 mechanism.

The structure of the transition states for the debromination reactions may be deduced by comparing the Hammett ρ, Brønsted β, and k_{Br}/k_{Cl} values. Hammett ρ values indicate the extent of negative charge development at the reaction site in the transition state. For debromination of **1a**−**d**, Hammett ρ values of 1.22 ± 0.04 and 1.20 ± 0.02 have been determined for the k_2 and k_3 processes. Although these values are rather small, they indicate extensive negative charge development at C-2 in both transition states because the reaction site is insulated from the effect of the substituent in the aromatic ring by an sp^3 hybridized carbon.

Brønsted β values are usually taken as the measure of the extent of proton transfer in the transition state. In order to use the β values as a probe for the degree of C−Br bond cleavage in the transition state, they should be calculated using $-\log K_e$ for $R_2NHBr^+ \rightleftharpoons R_2NH + Br^+$ because it is the bromine rather than the proton that is transferred from the carbon to the amine base. However, the β values for these reactions were calculated using the pK_a values of $R_2NH_2^+$ rather than the $-\log K_e$ for R_2NHBr^+ because they cannot be determined experimentally. Since R_2NHBr^+ should be less stable than $R_2NH_2^+$ due to the weaker strength of the N−Br than the N−H bond, the effects of the alkyl group on the energies of the former is anticipated to be greater than those of the former. This would predict that the real β values should be smaller than the experimental values of ca. 0.8−1.0 (Table 4). Therefore, the results can most reasonably be interpreted with extensive C−Br bond cleavage in the transition state.

The k_{Br}/k_{Cl} values for these reactions can be taken as the measure of the extent of C−Br bond cleavage.[17,19] For dehalogenation from **1a** and **2a**, k_{Br}/k_{Cl} values of 7.8 and 25 are calculated for the k_2 and k_3 processes. These values are much smaller than those for the iodide-promoted debromination from *meso*-stilbene dibromide (vide supra) and indicate small, yet significant, extents of C_α−Br bond cleavage in the transition state.

The combined results reveal that the debromination reaction of 1-aryl-1,2-dibromo-2-nitropropanes **1a**−**d** with secondary amines in MeCN proceed by an E2 mechanism induced by the attack of the base at the C-2−Br bond via an E1cb-like transition state with extensive C_β−Br bond cleavage, some negative charge development at the β-carbon, and a limited extent of C_α−Br bond rupture (**III**).



III

The transition state structure changes toward productlike with greater extents of C_β−Br and C_α−Br bond cleavage in the k_3 process as indicated by the larger values of β and k_{Br}/k_{Cl} than those for the k_2 pathway. Since the C_β−Br bond is broken more in the k_3 than in the k_2 pathway, more electron density should be transferred to the C_β−C_α bond to form the partial double bond in order for the β-carbon to retain similar negative charge density. This would in turn increase an extent of the C_α−Br bond cleavage, as observed.

Experimental Section

Materials. Secondary amines and acetonitrile have been purified as described before.[20] 1-Aryl-2-nitropropenes **3a**−**d** and *erythro-dl*-1-aryl-1,2-dibromo-2-nitropropanes **1a**−**d** were prepared by known methods.[10,11] *erythro-dl*-2-Bromo-1-chloro-1-phenyl-2-nitropropane (**2a**) was prepared in high yield by slowly adding a CH_2Cl_2 solution of BrCl to a solution of 1-phenyl-2-nitropropene in CH_2Cl_2 at room temperature. The spectral and analytical data of the compounds were consistent with the proposed structures. The melting point (°C), NMR ($CDCl_3$), IR (k_{Br}, NO_2, cm^{-1}), and combustion analysis data for the new compounds are as follows. *m*-$BrC_6H_4CH(Br)C(Br)(NO_2)CH_3$ (**1c**): mp 66−68; IR (KBr) 1332,1565 (NO_2); ^1H NMR ($CDCl_3$) δ 7.75 (s, 1H), 7.59−7.50 (m, 2H), 7.33−7.28 (m, 1H), 5.92 (s, 1H), 2.43 (s, 3H). Anal. Calcd for $C_9H_8Br_3NO_2$: C, 26.90; H, 2.01; N, 3.49. Found: C, 26.87; H, 2.04; N, 3.44. $C_6H_5CH(Cl)C(Br)(NO_2)CH_3$ (**2a**): mp 72−74; IR (KBr) 1335, 1567 (NO_2); ^1H NMR ($CDCl_3$) δ 7.58 (m, 2H), 7.42 (m, 3H), 6.02 (s, 1H), 2.43 (s, 3H). Anal. Calcd for $C_9H_9ClBrNO_2$: C, 38.81; H, 3.26; N, 5.03. Found: C, 38.50; H, 3.34; N, 4.78. Since the proton NMR of **1a** and **2a** were nearly identical, ^{13}C NMR spectra were also taken to determine the structure of the latter more rigorously. They are as follows: for C_6H_5CH-

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(Br)C(Br)(NO_2)CH_3 (**1a**) ^{13}C NMR ($CDCl_3$) δ 135.2, 131.5, 130.5, 129.1, 94.8, 57.3, 24.9; for $C_6H_5CH(Cl)C(Br)(NO_2)CH_3$ (**2a**) ^{13}C NMR ($CDCl_3$) δ 134.7, 131.0, 130.7, 129.1, 95.1, 66.6, 23.8.

Kinetic Studies. The rates of the reactions were followed by monitoring the increase in the absorption at the λ_{max} for **2a–d** in the range 306–344 nm as described before.[15] Plots of -ln ($A_\infty - A_t/A_\infty - A_o$) vs time were linear over at least three half-lives. The slope was the pseudo-first-order rate constant. Plots of $k_{obs}/[R_2NH]$ vs $[R_2NH]$ were linear for all reactions. The k_2 and k_3 values were obtained from the intercept and the slope of the straight lines.

Product Studies. The yields of 1-aryl-2-nitropropenes, determined by comparison of the UV absorbances of the infinity samples for the kinetic runs with those of 1-aryl-2-nitropropenes were in the range of 90–98%. To determine the yield of the debromination product by GC, 1,2-dibromo-2-nitro-1-phenylpropane (0.10 g, 3.1×10^{-4} mol) and benzylisopropylamine (0.31 g, 3.1×10^{-3} mol) were reacted in 5.0 mL MeCN for 2 days. A small amount of chloroform was added to the solution and the mixture was washed several times with water to remove the ammonium salt. The product was analyzed by GC as described before.[7] The product was a mixture of (*E*)-2-nitro-1-phenylpropene and *N*-isopropylbenzylideneamine in 90 and 76% yields, respectively.

To detect the presence of *N*-bromoamine as the reaction product, 0.10 g of 1,2-dibromo-2-nitro-1-phenylpropane was reacted with an equimolar amount of diisopropylamine and the products were taken up in $CDCl_3$ as described above. The NMR spectrum showed a clean septet at δ 3.6 corresponding to the methyne proton of authentic *N*-bromodiisopropylamine along with other peaks arising from 1-phenyl-2-nitropropene and unconsumed reactants.

In an attempt to trap the carbanion intermediate, the debromination reaction was conducted by the preceding procedure. An excess amount of HCl solution was added to the solution after one half-life and the products were isolated. The products were a mixture of unreacted dibromide and alkene. No trace of 1-bromo-2-nitro-1-phenylpropane could be detected in the NMR spectrum.

p*K*ₐ Values of the Secondary Amines. The pK_a values of the seconary amines were determined by measuring the equilibrium constant, *K*, between *p*-nitrophenol and R_2NH in MeCN by the modified procedure of Bordwell (eq 2 and 3).[12] To a solution containing (1.4–7.0) $\times 10^{-5}$ M of *p*-nitrophenol in MeCN, (1.0–70) $\times 10^{-3}$ M of R_2NH was added in small increments and the absorbances were determined at 425 nm. The absorbance was divided by the molar extinction coefficient for *p*-nitrophenoxide ion to afford the concentration of the *p*-nitrophenoxide *x*. The equilibrium constants were calculated with eq 3 using the *p*-nitrophenoxide ion concentration. The pK_a values of the seconary amines were then calculated with the pK_a value of the *p*-nitrophenol[13] and the equilbrium constants (eq 4)

$$\underset{[R_2NH]_o - x}{R_2NH} + \underset{[p\text{-}O_2NC_6H_4OH]_o - x}{p\text{-}O_2NC_6H_4OH} \rightarrow \underset{x}{R_2NH_2^+} + \underset{x}{p\text{-}O_2NC_6H_4O^-} \qquad (2)$$

$$K = [R_2NH_2^+][p\text{-}O_2NC_6H_4O^-]/[R_2NH][p\text{-}O_2NC_6H_4OH] = x^2/([R_2NH]_o - x)([p\text{-}O_2NC_6H_4OH]_o - x) \qquad (3)$$

$$pK_a\ (R_2NH) = 20.7 - \log K \qquad (4)$$

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Supplementary Material Available: Pseudo-first-order rate constants for dehalogenation reactions of 1-aryl-1,2-dibromo-2-nitropropanes (**1a–d**) and 2-bromo-1-chloro-2-nitro-1-phenylpropane (**2a**) promoted by secondary amines in MeCN at various temperatures (3 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current head masthead page for ordering information.

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