then prepared in the usual manner. If the D_2O exchange step is omitted, the isotopic purity in the α-deuteriotosylhydrazone drops, due to scrambling in the salt-formation step.

1-Naphthaldehyde Tosylhydrazone. Prepared from 1-naphthaldehyde (Aldrich) in 91% yield: mp 132–133 °C (lit.[24] 144–146 °C); ^{1}H NMR ($CDCl_3/Me_2SO$-d_6) δ 2.33 (s, 3 H), 7.22–8.00 (m, 10 H), 8.42–8.65 (m, 1 H), 8.50 (s, 1 H), 11.33 (s, 1 H).

1-Naphthyldiazomethane (1a). IR (Ar, 15 K) 3078 m, 2065 s, 1594 m, 1582 s, 1523 m, 1515 m, 1471 s, 1453 m, 1418 s, 1386 w, 1370 w, 1338 s, 1267 w, 1252 m, 1220 w, 1173 w, 1148 w, 1093 w, 1012 m, 854 w, 807 w, 792 s, 773 s, 649 m, 632 w, 565 m, 411 m cm^{-1}. The deep red diazocompound was sublimed at 30 °C (10^{-6} torr) and codeposited with argon to form a matrix.

α-Deuterio-1-naphthaldehyde Tosylhydrazone. Prepared from α-deuterio-1-naphthaldehyde in 70% yield: mp 128–129 °C dec; ^{1}H NMR ($CDCl_3/Me_2SO$-d_6) δ 2.35 (s, 3 H), 7.17–8.00 (m, 10 H), 8.48–8.68 (m, 1 H); mass spectrum (16 eV), m/z (relative intensity) 325 (M^+, 4.3), 141 (100) (324 not detected).

(α-Deuterio-1-naphthyl)diazomethane (1b). IR (Ar, 15K) 3065 m, 2055 s, 1595 m, 1590 m, 1580 s, 1520 m, 1510 m, 1468 s, 1450 m, 1412 s, 1408 s, 1327 s, 1013 m, 851 m, 844 w, 802 m, 791 s, 787 s, 770 s, 649 m, 647 m, 562 m, 504 w, 453 w, 432 w, 419 w, 409 w cm^{-1}. The deep red diazocompound was sublimed at 40 °C (10^{-6} torr) and codeposited with argon to form a matrix.

2-Naphthaldehyde Tosylhydrazone. Prepared from 2-naphthaldehyde (Aldrich) in 85% yield: mp 169–170 °C dec (lit.[25] 174 °C); ^{1}H NMR ($CDCl_3/Me_2SO$-d_6) δ 2.37 (s, 3 H), 7.23–7.93 (m, 11 H), 8.03 (s, 1 H), 11.40 (s, 1 H).

2-Naphthyldiazomethane (5a). IR (Ar, 15 K) 3060 m, 2055 s, 1632 m, 1626 m, 1604 s, 1511 s, 1478 m, 1471 m, 1443 m, 1398 s, 1357 m, 1328 m, 1201 m, 1187 m, 1182 m, 1146 m, 872 m, 842 s, 809 s, 740 s, 600 m, 582 m, 460 s cm^{-1}; ^{1}H NMR (CCl_4) δ 5.03 (s, 1 H), 6.9–7.9 (m, 7 H). The deep red diazocompound was sublimed at 30 °C (10^{-6} torr) and codeposited with argon to form a matrix.

α-Deuterio-2-naphthaldehyde Tosylhydrazone. Prepared from α-deuterio-2-naphthaldehyde in 66% yield: mp 164–165 °C dec; ^{1}H NMR ($CDCl_3/Me_2SO$-d_6) δ 2.33 (s, 3 H), 7.20–7.97 (m, 11 H), 11.33 (s, 1 H); mass spectrum (16 eV), m/z (relative intensity) 325 (M^+, 1.2), 141 (100) (324 not detected).

(α-Deuterio-2-naphthyl)diazomethane (5b). IR (Ar, 15 K) 3059 m, 3020 w, 2060 s, 1633 s, 1603 s, 1511 s, 1506 m, 1475 m, 1390 s, 1368 m, 1331 m, 1313 m, 872 m, 844 s, 810 s, 741 s, 602 m, 580 m, 472 m, 411 w, 372 w cm^{-1}. The deep red diazocompound was sublimed at 36 °C (10^{-6} torr) and codeposited with argon to form a matrix.

***1H*-Cyclobuta[*de*]naphthalene (4).** Prepared from 1,8-naphthalic anhydride by literature methods.[26] IR (Ar, 15 K) 3072 m, 3065 m, 3057 m, 3041 m, 2982 w, 2949 m, 2818 w, 1920 w, 1775 w, 1608 m, 1602 m, 1477 m, 1344 m, 1339 m, 1170 w, 1164 w, 1002 m, 966 w, 792 s, 761 s, 707 m, 478 m, 402 w cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.80 (s, 2 H), 7.05–7.83 (m, 6 H); mass spectrum (70 eV), m/z (relative intensity) 141 (13), 140 (M^+, 100), 139 (87), 113 (10), 89 (10), 87 (8), 74 (8), 70 (8). The compound was sublimed at −5 °C (10^{-6} torr) and codeposited with argon to form a matrix.

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Registry No. **1a**, 10378-55-9; **1b**, 78377-25-0; **3a**, 7078-38-8; **3b**, 100447-97-0; **4**, 24973-91-9; **5a**, 10378-56-0; **5b**, 78377-21-6; **7a**, 38617-06-0; **7b**, 100447-98-1; **8**, 52783-97-8; 1-naphthaldehyde tosylhydrazone, 19350-73-3; α-deuterio-1-naphthaldehyde, 42007-09-0; α-deuterio-2-naphthaldehyde tosyhydrazone, 100447-96-9; 2-naphthaldehyde tosylhydrazone, 19350-74-4; α-deuterio-2-naphthaldehyde, 42007-10-3; α-deuterio-2-naphthaldehyde tosylhydrazone, 78377-20-5; 1-naphthaldehyde tosylhydrazone lithium salt, 100447-99-2; α-deuterio-1-naphthaldehyde tosylhydrazone lithium salt, 100448-00-8; 2-naphthaldehyde tosylhydrazone lithium salt, 100448-01-9; α-deuterio-2-naphthaldehyde tosylhydrazone lithium salt, 100448-02-0; 1-naphthaldehyde, 66-77-3; 2-naphthaldehyde, 66-99-9.

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Reactions of *N*-Chlorobenzylmethylamines with Secondary Amines in Acetonitrile. Effect of Base Strength upon the Imine-Forming Transition State

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Reactions of *N*-chlorobenzylmethylamines 1 with R_2NH in MeCN have been investigated kinetically. Eliminations from 1 were quantitative and regiospecific, producing only benzylidenemethylamines. For the elimination reaction of 1 with Bu_2NH, $k_H/k_D = 8.8$, $\rho = 0.96$, $\Delta H^{\ddagger} = 7.6$ kcal/mol, and $\Delta S^{\ddagger} = -45.1$ eu were determined. The transition state structure is assessed as being highly symmetrical with similar extents of C_β–H and N_α–Cl bond cleavage, little carbanionic character, and significant π bond formation. The k_H/k_D and ρ values first increase and then decrease with enhancing amine base strength. Comparison of these results with those for related olefin-forming eliminations provides insight into the transition state differences between imine- and olefin-forming eliminations.

An understanding of the effect of changes in reactant structure and reaction conditions on the energies and structures of transition states is an important element for the detailed description of organic reaction pathways. Several studies of this type have been conducted for elimination reactions which form carbon–nitrogen double bonds.[2-11]

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Table I. Rate Coefficients for Elimination from $ArCH_2N(Cl)CH_3$[a] Promoted by R_2NH in MeCN at 25.0 °C

		10^3k_2,[d] $M^{-1}\ s^{-1}$					
base[b]	pK_a[c]	**1a**	**1b**	**1c**	**1d**	**1e**	**1f**
piperidine	18.9	4.20	0.635	2.99	12.3	16.8	48.9
Et_2NH	18.7	2.51	0.291	1.35	4.90	9.63	28.0
Bu_2NH	18.3	2.27[f]	0.258	1.19	6.17	11.4	30.1
$(i\text{-}Bu)_2NH$	17.9	0.385 (9.28)[g]	0.060	0.265	1.13	1.80	4.37
$PhCH_2NHCH_3$	17.1[e]	0.667	0.133	0.600	1.90	3.23	8.00

[a] [Substrate] = 5.0×10^{-5} M. [b] [Base] = $1.50 \times 10^{-3} - 2.00 \times 10^{-2}$ M. [c] Reference 15. [d] Estimated uncertainty ±3%. [e] Estimated from $(pK_a)_w$[16] and $\Delta pK_a(MeCN{-}H_2O)$.[15,19] [f] $k_2 = 3.69 \times 10^{-3}$ at 35.0 °C and 5.40×10^{-3} at 45.0 °C. [g] Substrate was $PhCH_2N(Br)CH_3$.

Previously, it has been shown that the reactions of *N*-chlorobenzylmethylamine with MeONa–MeOH or *t*-BuOK–*t*-BuOH are normal E2 reactions.[6] Comparison of transition state parameters for this reaction with those for closely related eliminations from 1-aryl-2-chloropropanes reveals that the transition state structures are quite similar. Effects of β-carbon substituents[10] and leaving group variation[11] upon the transition states are quite similar to those for olefin-forming elimination reactions. These results are somewhat surprising in view of the much greater facility of imine-forming eliminations.

The most significant differences between imine- and olefin-forming elimination reactions are the lower stability of the leaving group bond and the higher energy of the resultant double bond for the former.[12] Thus, transition state differences for such reactions might be anticipated if they were conducted under conditions where either of these ground state differences would have important influence. Accordingly, we have investigated the reactions of *N*-chlorobenzylmethylamines with secondary amines in MeCN (eq 1). It was expected that the poor anion-solvating abilities of a dipolar aprotic solvent might increase the degree of double bond character in the transition state.

$$\underset{\mathbf{1}}{XC_6H_4CL_2N(Cl)CH_3} + R_2NH \xrightarrow{MeCN} \underset{\mathbf{2}}{XC_6H_4CL{=}NCH_3} \quad (1)$$

	X	L	R_2NH
a	H	H	piperidine
b	H	D	Et_2NH
c	$p\text{-}CH_3O$	H	Bu_2NH
d	*m*-Br	H	$(i\text{-}Bu)_2NH$
e	$m\text{-}NO_2$	H	$PhCH_2NHCH_3$
f	$p\text{-}NO_2$	H	

In this study we have determined the transition state differences for eliminations from **1** wrought by the change in base–solvent from MeONa–MeOH to Bu_2NH–MeCN. The influence of base-strength variation for amine bases upon the transition state structure was also studied. Finally, the results are compared with those of related olefin-forming eliminations[13] to assess transition state differences for imine- and olefin-forming elimination reactions.

Results

Reactions of **1** with secondary amine bases in MeCN produced only benzylidenemethylamines **2**. Eliminations were followed by monitoring the appearance of absorption at the λ_{max} for **2**. Excellent pseudo-first-order kinetic plots which covered at least 2 half-lives were obtained. Pseudo-first-order rate constants were divided by the base concentrations to provide second-order rate constants which remained constant for two–tenfold variations in base concentrations.

A Brønsted plot for reactions of **1** with the series of amine bases is shown in Figure 1. With the exception of $(i\text{-}Bu)_2NH$, the rate constants correlate well with the Brønsted equation. The large negative deviation of $(i\text{-}Bu)_2NH$ may be due to a base steric effect. The β value calculated for the series of secondary amine bases, but without the data for $(i\text{-}Bu)_2NH$, is 0.41 (r = 0.998).

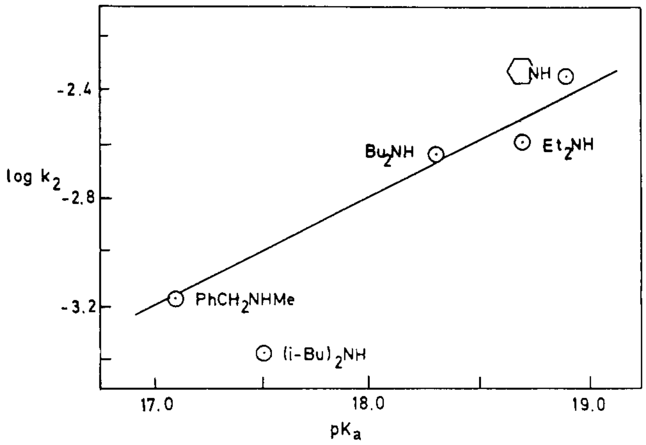

Figure 1. Brøsted plot for reactions of $ArCH_2N(Cl)CH_3$ with R_2NH in MeCN at 25.0 °C. The β value is calculated without the data for $(i\text{-}Bu)_2NH$.

Table II. Transition State Parameters for Eliminations from $ArCH_2N(Cl)CH_3$ Promoted by MeONa–MeOH and by Bu_2NH–MeCN

base–solvent	MeONa–MeOH[a]	Bu_2NH–MeCN
pK_a	18.3[b]	18.3
ρ	1.58[c]	0.96
k_H/k_D	6.4	8.8 (β = 0.41)
k_{Br}/k_{Cl}	15.8	24.1[d] (β_{lg} = −0.41)[e]
$\Delta H^{\ddagger}$, kcal/mol	14.2	7.6
$\Delta S^{\ddagger}$, eu	−19.9	−45.1
$\Delta G^{\ddagger}$, kcal/mol	20.1	21.0

[a] Reference 11. [b] Reference 17. [c] Calculated from rate coefficients for **1a–e** given in ref 11 and for **1f**.[18] [d] Base was $(i\text{-}Bu)_2NH$. [e] See text.

Table III. Effects of Base Strength upon k_H/k_D and Hammett ρ Values for Eliminations from $ArCH_2N(Cl)CH_3$ Promoted by R_2NH–MeCN at 25.0 °C

base	pK_a[a]	k_H/k_D	ρ
piperidine	18.9	6.6	0.84 (r = 0.993)[b]
Et_2NH	18.7	8.6	0.89 (r = 0.998)
Bu_2NH	18.3	8.8	0.96 (r = 0.994)
$(i\text{-}Bu)_2NH$	17.9	6.4	0.86 (r = 0.993)
$PhCH_2NHCH_3$	17.1	5.0	0.82 (r = 0.993)

[a] See footnote in Table I for references. [b] Correlation coefficient.

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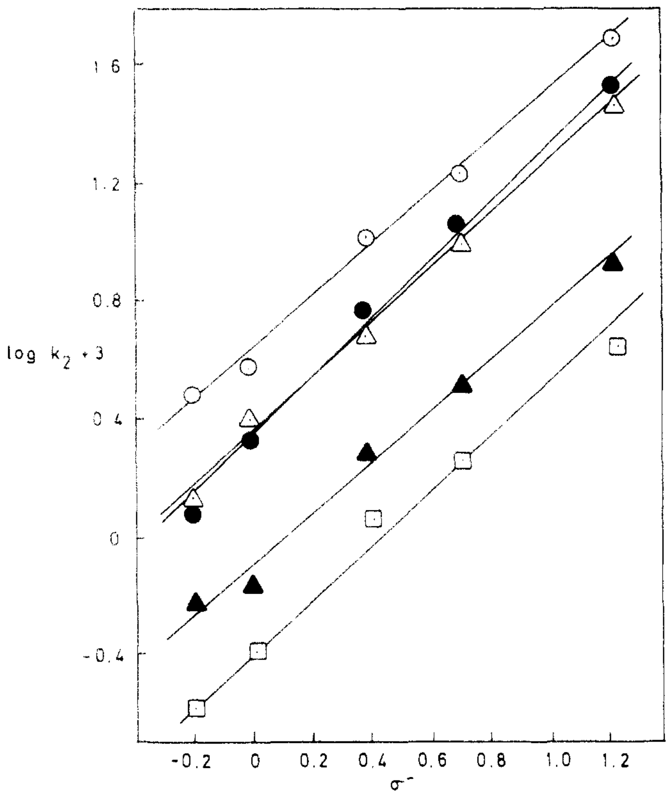

Figure 2. Hammett plots for eliminations from $ArCH_2N(Cl)CH_3$ promoted by R_2NH in MeCN at 25.0 °C. Bases are the following: piperidine (○); Bu_2NH (●); Et_2NH (△); $C_6H_5CH_2NHCH_3$ (▲); and $(i\text{-}Bu)_2NH$ (□).

Rates of elimination from **1a** promoted by Bu_2NH–MeCN were measured at three temperatures spanning 20 °C. An Arrhenius plot was linear with excellent correlation. Calculated enthalpies and entropies of activation are presented in Table II.

From the rate coefficients for elimination from **1a** and its deuterated analogue **1b**, primary deuterium isotope effect values were calculated. These values are listed in Tables II and III.

The influence of aryl substituents upon elimination rates correlated satisfactorily with Hammett σ^- values (Figure 2).

The reactions of *N*-bromobenzylmethylamine with R_2NH–MeCN were also briefly examined. The products were benzylidenemethylamine and benzylmethylamine. The amine product apparently arises by nucleophilic displacement of the amine on the bromine leaving group of the substrate.[11] In most cases, the yield of the elimination product was too low to determine the rate constants accurately. However, when $(i\text{-}Bu)_2NH$ was used as the promoting base, the imine yield increased and good pseudo-first-order kinetic plots were obtained. The overall second-order rate constant was multiplied by the imine yield to obtain the rate constant for imine formation. For elimination from *N*-halobenzylmethylamines at 25.0 °C, the leaving group effect k_{Br}/k_{Cl} was 2.41 with $(i\text{-}Bu)_2NH$–MeCN.

Discussion

Transition State for Elimination from 1 Promoted by Bu_2NH–MeCN. Results of the kinetic investigations and control experiments clearly establish that the reaction of 1 with Bu_2NH–MeCN proceeds via an E2 mechanism. Since reactants 1 were found to be stable in MeCN and the reaction exhibited second-order kinetics, all except bimolecular pathways can be ruled out. In addition an E1cb mechanism is negated by the substantial values of the primary deuterium isotope effect and the element effect of the leaving group (Table II).[14]

Comparison of transition state parameters for base-promoted eliminations from 1 (Table II) reveals that the structure of the transition state changes significantly when the base–solvent is varied from MeONa–MeOH[11] to Bu_2NH–MeCN even though the base strength remains constant. The Hammett ρ value for the Bu_2NH-promoted eliminations from 1 is 0.96, which is much lower than that for MeONa-promoted eliminations for the same substrates. Thus the carbanionic character of the transition state decreases significantly with this variation of the base–solvent system.

The primary deuterium isotope effect and Brønsted β values indicate the extent of proton transfer in the transition state. For reaction of 1 with Bu_2NH–MeCN a deuterium isotope effect value of 8.8 and a Brønsted β value of 0.41 were determined. Moreover, this isotope effect is the maximum value observed for the series of reactions with different secondary amine bases (Table III). Since the isotope effect is expected to be a maximum with 0.42 proton transfer for a reaction between C–H and a nitrogen base,[19] the k_H/k_D and β values are in agreement and indicate about 0.4 proton transfer in the transition state. In comparison, the k_H/k_D value for MeONa-induced elimination is 6.4, which is smaller than that observed for the amine base. In view of the prediction that the maximum isotope effect occurs with 0.38 proton transfer for reaction of an oxygen base with a carbon acid,[20] the result may be interpreted as either a greater or smaller extent of proton transfer than 0.38. However, the former interpretation seems more compatible with the larger ρ value observed with MeONa as the base. Therefore, the extent of C_β–H bond cleavage in the transition states appears to be reasonably similar for reactions with both base–solvent systems.

The leaving group element effect for eliminations from *N*-halobenzylmethylamines promoted by $(i\text{-}Bu)_2NH$ in MeCN is 24.1. Utilizing this k_{Br}/k_{Cl} ratio and pK_a's of HCl and HBr in MeCN,[21] $\beta_{lg} = -0.41$ is calculated. This indicates a moderate amount of N–Cl bond cleavage in the transition state. Assuming that the structure of the transition state does not vary significantly with the change in base from $(i\text{-}Bu)_2NH$ to Bu_2NH, a similar extent of N–Cl bond cleavage would be expected in the transition state for Bu_2NH-promoted elimination from 1. In contrast, the k_{Br}/k_{Cl} ratio for MeONa-induced elimination from 1 is 15.8. Thus, an increase in the extent of N–Cl bond cleavage is indicated as the base–solvent is changed to Bu_2NH–MeCN.

The lower enthalpy of activation for reaction of 1 with Bu_2NH–MeCN may in part be attributed to a greater amount of π-bond formation in the transition state. Since the C=N bond strength is approximately 75 kcal/mol^{-1} stronger than the corresponding single bond and the bond

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dissociation energy of the N–Cl bond is approximately 60 kcal/mol^{-1},[22] the enthalpy of activation should decrease if the extent of C_β–H bond cleavage remains nearly the same but more of the π-bond is formed. The small ρ values observed for the amine-promoted reactions support this interpretation, i.e., little carbanionic character is developed in the transition state because most of the charge density on the benzylic carbon has been transferred between carbon and nitrogen to form the double bond.

The combined results reveal that the extent of C_β–H bond cleavage is similar, but the transition state carbanionic character decreases, and the extents of N_α–Cl bond and π-bond formation increase in the transition state when the base–solvent system is changed from MeONa–MeOH to Bu_2NH–MeCN. Thus it appears that the structure of transition state for the Bu_2NH-promoted elimination from 1 is highly symmetrical with similar extents of C_β–H and N_α–Cl bond cleavage, little carbanionic character, and well-developed double bond character.

The change in transition structure with this base–solvent variation may be attributed to a solvent effect. Since the carbanion and chloride ion would be good hydrogen bond acceptors, partial negative charges developed at these sites in the transition state cannot be stabilized by solvation in an aprotic solvent. Therefore, E1- or E1cb-like transition states will be destabilized, and a symmetric transition state with maximum charge dispersal becomes the favored alternative.

Effect of Base Strength upon Imine-Forming Transition States. For elimination reactions of 1 with secondary amine bases in MeCN, the deuterium isotope effect first increases, passes through the maximum value of 8.8, and then decreases as the base strength increases (Table III). The Hammett ρ values change similiarly (Table III), although the differences are too small to suggest appreciable changes in the transition state structure.

The results may readily be rationalized by considering relative effects of parallel and perpendicular motions in the reaction coordinate diagram (Figure 3).[25,26a,b] Since the pK_a's of MeONa-MeOH and Bu_2NH–MeCN are the same,[15,17] the relative energy of the base with respect to its conjugate acid will be nearly the same in both base–solvent systems. However, the carbanion and chloride ion would be much better solvated in MeOH than in MeCN.[26] Hence, although the neutral molecules and cationic intermediate may be slightly more stable in MeCN,[27] the overall effect of base–solvent variation from MeONa–MeOH to Bu_2NH–MeCN would be to increase the energy of E1 and E1cb intermediates and the product compared to that of the reactant in the reaction coordinate diagram[12,26a,b] (Figure 3). On the other hand, the free energy of activation for elimination from 1 is increased only slightly by the change in base–solvent system. Therefore, the curvature of the potential energy surface should decrease along the reaction coordinate but increase in the perpendicular direction when the base–solvent system is changed to Bu_2NH–MeCN. This would predict that the parallel effect will be predominant since the transition state will move easier in the direction where curvature of the surface is smaller.[25]

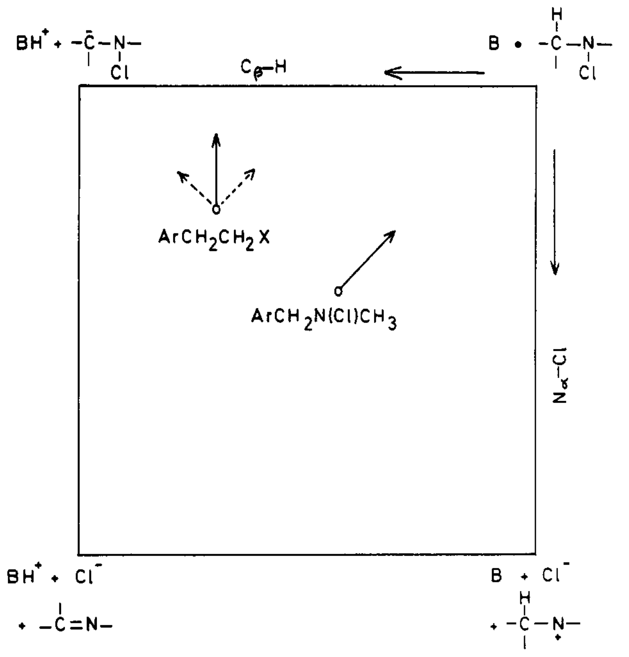

Figure 3. Reaction coordinate energy diagram for elimination reactions from $ArCH_2N(Cl)CH_3$ with R_2NH–MeCN and $ArCH_2CH_2X$ with ArO^-–DMF. Energy contours are omitted. Effects of change in a stronger base upon the transition state position are shown by the solid lines.

As previously mentioned, the transition state of elimination from 1 promoted by Bu_2NH–MeCN appears to be highly symmetrical with moderate amounts of C_β–H and N_α–Cl bond cleavage and thus can be located somewhat toward the reactant from the center in the reaction coordinate diagram (Figure 3). An increase in base strength would increase the energy of the reactant and the E1cb intermediate. Since the parallel effect is assumed to be predominant, the transition state is predicted to move toward the reactant.[25,26a,b] Conversely, a decrease in basicity should shift the transition state toward the product.[25,26a,b] In either case the k_H/k_D values are expected to decrease,[20,29] from the maximum value found with Bu_2NH, in agreement with the observed results (Table III).

A parallel shift of transition state character with base strength variations has been observed in a number of elimination reactions that proceed via highly carbanionic transition states.[20,30,31] In contrast, for eliminations that proceed through central transition states, such as 2-arylethyl substrates, with ArO^-–DMF, the change in k_H/k_D and ρ values with base strength variation has been interpreted by assuming similar effects on parallel and perpendicular motions in the reaction coordinate diagram (Figure 3).[13] Since the basicities of ArO^- and R_2NH[13,15] and solvating powers of MeCN and DMF[32] are similar, the different base

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(27) The free energy of transfer of Cl^- from CH_3OH to MeCN, $\Delta G_{tr}^{CH_3OH\rightarrow CH_3CN}(Cl^-)$ is 8.6 kcal/mol.[26c] Since the carbanion is a stronger base and probably a better hydrogen bond acceptor than Cl^-, $\Delta G_{tr}^{CH_3OH\rightarrow CH_3CN}(R_2CH^-)$ should be much greater than that for Cl^-.[28] On the other hand that for bulky a cation is rather small, i.e., $\Delta G_{tr}^{CH_3OH\rightarrow CH_3CN}(Bu_4N^+) \simeq 2.2$ kcal/mol.[26c,28]

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(32) That the solvating powers of DMF and MeCN are similar for anions is indicated by $\Delta G_{tr}^{DMF\rightarrow CH_3CN}(Y^-) = 0$.[26c,28] Although DMF is a better solvent than MeCN for cations ($\Delta G_{tr}^{DMF\rightarrow CH_3CN}(Bu_4N^+) = 2$ kcal/mol),[26c,28] the difference will be partially compensated by the difference in energy of the carbocation and nitrenium ion in the reaction coordinate diagram.

strength effect for eliminations from **1** and $ArCH_2CH_2X$ may in part be attributed to the lower free energy of activation for the former.[33] If the free energy of activation is increased without changing the relative energy of any corner in the reaction coordinate diagram, the effects on parallel and perpendicular motions would become similar (Figure 3), and constant k_H/k_D and larger ρ values would be expected for the change to a stronger base, as observed for the latter.[13] Therefore, it appears that the most significant difference in transition states for related imine- and olefin-forming eliminations is a lower free energy of activation for the former which manifests itself in different base strength effects.

Experimental Section

Benzylidenemethylamines **2**, benzylmethylamines, and *N*-chlorobenzylmethylamines **1** were prepared as described previously.[6] The solvent and amines were purified by known methods.

Product studies of the reactions of *N*-chloro- and *N*-bromobenzylmethylamines with piperidine were carried out by refluxing the solution of the *N*-haloamine (2.0 mmol), piperidine (10.0 mmol), and benzene (internal standard, 2.0 mmol) in 20 mL of MeCN for 12 h. The solution was analyzed by gas chromatography on a 2 ft × $^1/_8$ in. column of 20% PEG 400 on Chromosorb P at 130 °C. The products were benzylidenemethylamine (95.0%) from **1a** and benzylidenemethylamine (22.2%) and benzylmethylamine (74.5%) from *N*-bromobenzylmethylamine. Yields of **2** from reactions of other chloroamines **1c–f** were determined by comparing the UV absorbances of the reaction products with those for authentic samples. On the basis of the starting amine concentrations, the yields of **2** were 88–95%.

Stability of *N*-haloamines in MeCN was demonstrated by the previously used method.[6]

Kinetic studies were carried out as before on a Cary 17D spectrophotometer.[6] The pseudo-first-order rate constants were divided by the base concentrations to afford the second-order rate constants, k_2. The k_2 values were found to be constant for two–tenfold variation in base concentration.

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Registry No. **1a**, 3555-71-3; **1c**, 70972-89-3; **1d**, 70972-94-0; **1e**, 70972-96-2; **1f**, 70972-95-1; Et_2NH, 109-89-7; Bu_2NH, 111-92-2; $(i\text{-}Bu)_2NH$, 110-96-3; $PhCH_2NHCH_3$, 103-67-3; D_2, 7782-39-0; piperidine, 110-89-4.

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[33] Although the activation energy for elimination from $ArCH_2CH_2X$ promoted by ArO^--DMF is not available in the literature, it has been demonstrated that the $\Delta G^\ddagger$ for reaction 1 with MeONa–MeOH is about 6 kcal/mol lower than that for olefin-forming elimination from closely related $PhCH_2CH(Cl)CH_3$ under similar conditions.[6]

Solvolysis of 1-(1-Naphthyl)- and 1-(9-Anthryl)-2,2,2-trifluoroethyl Sulfonates

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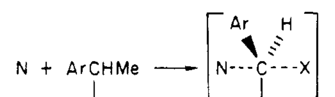
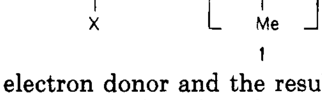
Solvolyses of $ArCH(O_3SR)CF_3$ (**13**, Ar = 1-naphthyl; R = *p*-Tol; **14**, Ar = 9-anthryl; R = Me) give *m* values for the rate dependence on solvent of 0.94 (**13**) and 0.64 (**14**) and a reactivity order **14** > **13** > Ar = *p*-Tol. The substitution products from **14** in EtOH, HOAc, or CF_3CH_2OH involve extensive or exclusive attack on the ring. The polarimetric rate constant of (*R*)-(–)-**14** in CF_3CH_2OH was 1.3 times greater than that for product formation, and in EtOH this substrate gave exclusive ring substitution with loss of optical activity. These results are interpreted in terms of initial reaction of **13** and **14** to form intimate ion pairs, which either return to reactant or form products through further steps which may involve other ion pairs. No evidence for solvent attack concurrent with sulfonate departure is observed. The strongly electron-withdrawing α-CF_3 substituent may enhance ring attack in the solvolysis of **14**.

The study of the solvolytic reactivity of 1-arylethyl systems has been of continuing utility in investigations of nucleophilic substitution.[1-5] The results of these studies have generally been interpreted that for substrates with electron-donating aryl groups in ionizing solvents the reactions involve initial formation of an ion pair that leads to products through further steps (eq 1), sometimes involving other ion pairs or free ions.[1-5] When the aryl group is not a good electron donor and the resulting cation is relatively less stable and when the solvent is a reasonably good nucleophile, rate-limiting nucleophilic solvent displacement should become relatively more significant (eq



$$\underset{\displaystyle X}{\mathrm{ArCHMe}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ArC^{+}(Me)(H)}\quad X^{-} \xrightarrow{k_2} \text{products} \qquad (1)$$



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