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Eliminations Forming Carbon–Heteroatom Multiple Bonds. Base-Promoted Dehydrochlorination of *N*-Chlorobenzylmethylamines[1]

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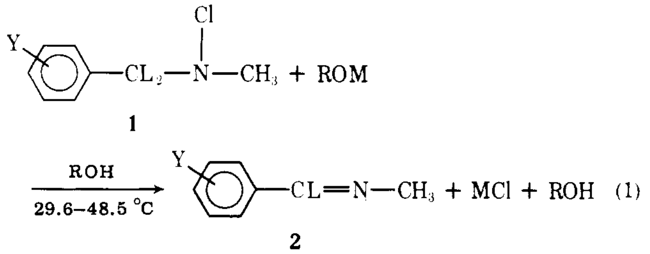
Abstract: Reactions of *N*-chlorobenzylmethylamines, **1**, with MeONa-MeOH and *t*-BuOK-*t*-BuOH have been studied kinetically. The eliminations are quantitative and regiospecific, producing only benzylidenemethylamines. The reactions are first order in base and first order in chloramine and an E2 mechanism is evident. Reactions of **1** with MeONa-MeOH and *t*-BuOK-*t*-BuOH give Hammett ρ values of +1.52 and +1.68, respectively. From eliminations of $PhCD_2N(Cl)CH_3$ and its undeuterated analogue induced by MeONa-MeOH and *t*-BuOK-*t*-BuOH, k_H/k_D values of 5.1–6.5 were calculated. For eliminations from *N*-halobenzylmethylamines, k_{Br}/k_{Cl} = 11.9 and 10.8 were observed with MeONa-MeOH and *t*-BuOK-*t*-BuOH, respectively. Comparison of these results with those for eliminations from 2-halo-1-phenylpropanes provides insight into closely related imine- and alkene-forming eliminations.

Olefin formation by base-promoted 1,2 elimination of HX from vicinal carbon atoms has been extensively investigated.[3a,4a] Similarly, base-induced HX eliminations from vinylic substrates have received considerable attention.[3b,4b,5,6] In sharp contrast, if the reverse of simple carbonyl and Schiff's base addition reactions are excluded, relatively little is known about the formation of multiple bonds between carbon and the heteroatoms N, O, and S by base-promoted 1,2 elimination of HX.[3c,4c]

Significant differences between carbon–heteroatom and carbon–carbon multiple bond forming eliminations are readily apparent. In general, the former are much more facile than the latter. For instance, eliminations from 1,1-difluoroalkanes require strong bases such as *t*-BuOK-*t*-BuOH.[7] However, even water is sufficiently basic to cause elimination from alkyldifluoramines.[8,9]

The greater facility of carbon–heteroatom multiple bond forming eliminations has been attributed to a lower stability of the heteratom–leaving group bond, greater strength of the resultant multiple bond, or increased acidity of the β hydrogen.[10] The relative importance of these three factors has not been assessed.

In order to compare closely related imine- and alkene-forming eliminations, we have investigated reactions of *N*-chlorobenzylmethylamines, **1**, with alkali metal alkoxides in the corresponding alcohols (eq 1). Corresponding alkene-forming eliminations from 1-aryl-2-halopropanes have been studied by other workers.[11,12]



	Y	L		Y	L
a	H	H	**f**	*m*-Me	H
b	H	D	**g**	*p*-Cl	H
c	*p*-MeO	H	**h**	*m*-Br	H
d	*m*-MeO	H	**i**	*p*-NO_2	H
e	*p*-Me	H	**j**	*m*-NO_2	H

Results

N-Chlorobenzylmethylamines, **1**, were prepared by quantitative N-chlorination of the corresponding benzylmethylamines with *N*-chlorosuccinimide in pentane. Following filtration to remove succinimide, the pentane was exchanged with the desired alcoholic solvent (see Experimental Section).

Eliminations from **1** were induced by mixing the alcoholic solution of **1** with MeONa-MeOH or *t*-BuOK-*t*-BuOH. Kinetics of the eliminations were followed by measuring the appearance of absorption at the λ_{max} for the *N*-benzylidenemethylamines, **2**, in the region 240–280 nm. Pseudo-first-order conditions (base in at least tenfold excess) were employed. 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 concentration to provide the second-order rate coefficients recorded in Tables I and II.

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Table I. Rate Coefficients for Eliminations from **1**[a] Induced by MeONa-MeOH

entry	compd	temp, °C	[MeONa], M	$k_2 \times 10^2$, $M^{-1}\ s^{-1}$
1	**1a**	29.6	0.103	1.53 ± 0.02[b]
2	**1b**	29.6	0.103	0.241 ± 0.001
3	**1a**	39.0	0.005 13	3.65 ± 0.05
4	**1a**	39.0	0.103	3.66 ± 0.04
5	**1b**	39.0	0.103	0.614 ± 0.001
6[c]		39.0	0.101	43.7 ± 0.2
7	**1a**	48.5	0.103	7.92 ± 0.08
8	**1b**	48.5	0.103	1.56 ± 0.05
9	**1c**	39.0	0.005 13	2.07 ± 0.05
10	**1e**	39.0	0.005 13	2.55 ± 0.06
11	**1f**	39.0	0.005 13	3.19 ± 0.01
12	**1d**	39.0	0.005 13	4.69 ± 0.04
13	**1g**	39.0	0.005 13	11.4 ± 0.02
14	**1h**	39.0	0.005 13	16.1 ± 1.0
15	**1j**	39.0	0.003 08	64.7 ± 0.7
16	**1j**	39.0	0.103	62.8 ± 0.4
17	**1i**	39.0	0.103	274 ± 8

[a] [Substrate] = 3.0-8.5 × 10^{-5} M. [b] Average rate coefficient and standard deviation from the average for two or more kinetic runs. [c] Substrate was $PhCH_2N(Br)CH_3$. Imine yield was 61.9 ± 0.8%.

Table II. Rate Coefficients for Eliminations from $YC_6H_4CL_2N(Cl)CH_3$[a] Induced by *t*-BuOK-*t*-BuOH

entry	compd	temp, °C	[*t*-BuOK], M	k_2, $M^{-1}\ s^{-1}$
1	**1a**	29.6	0.0145	0.539 ± 0.006[b]
2	**1b**	29.6	0.0145	0.0831 ± 0.0010
3	**1a**	39.0	0.001 39	0.921[c]
4	**1a**	39.0	0.006 50	0.935 ± 0.001
5	**1a**	39.0	0.0139	1.03 ± 0.01
6	**1a**	39.0	0.0145	1.03 ± 0.01
7	**1a**	39.0	0.0695	1.05[c]
8[d]		39.0	0.005 11	10.8 ± 0.3
9	**1b**	39.0	0.0145	0.174 ± 0.002
10	**1a**	48.5	0.0145	1.75 ± 0.04
11	**1b**	48.5	0.0145	0.346 ± 0.006
12	**1c**	39.0	0.0145	0.419 ± 0.008
13	**1e**	39.0	0.0145	0.626 ± 0.012
14	**1f**	39.0	0.0145	0.797 ± 0.015
15	**1d**	39.0	0.0145	1.45 ± 0.02
16	**1g**	39.0	0.0145	2.72 ± 0.08
17	**1h**	39.0	0.0145	4.91 ± 0.19
18	**1j**	39.0	0.0145	17.4 ± 0.1
19	**1i**	39.0	0.0145	117 ± 4

[a] [Substrate] = 3.0-8.5 × 10^{-5} M. [b] Average rate coefficient and standard deviation from the average for two or more kinetic runs. [c] Rate coefficient for a single kinetic run. [d] Substrate was $PhCH_2N(Br)CH_3$.

Comparison of the absorption in infinity samples with that for authentic samples of **2** allowed product yields to be calculated. Reactions of **1** with MeONa-MeOH and *t*-BuOK-*t*-BuOH at 29.6-48.5 °C produced 85-96% yields of **2** (based upon the original amines). Considering the moderate losses which undoubtedly attend generation of **1** from the parent amines, the lack of evidence for other possible products (see Experimental Section), and the regiospecificity exhibited in eliminations from *N*-chlorobenzyl-*n*-butylamine with several base-solvent systems,[13] the yields of **2** were assumed to be quantitative. Conceivable base-promoted isomerization[14] of initially formed *N*-methylidenebenzylamines to the measured **2** is rendered highly unlikely by the report that *N*-*n*-butylidenebenzylamine was unaffected by MeONa-MeOH or *t*-BuOK-*t*-BuOH under conditions comparable to those employed for eliminations from **1**.[13]

No **2a** was formed when **1a** was heated in methanol at 48.5 °C for a period of time similar to that used for the base-promoted eliminations from **1**. Therefore solvolytic elimination from **1** was deemed unimportant.

The rate coefficients presented in Tables I and II provide ample evidence that the elimination reactions are first order in base, as well as first order in **1**. Second-order rate coefficients for reactions of **1a** and **1j** with MeONa-MeOH and of the former with *t*-BuOK-*t*-BuOH are constant for 20-50-fold variations in base concentration (entries 3, 4 and 15, 16 in Table I; entries 3-7 in Table II).

Rates of elimination from **1a** promoted by MeONa-MeOH and *t*-BuOK-*t*-BuOH were measured at three temperatures spanning nearly 20 °C. Arrhenius plots exhibited excellent linearity. Calculated enthalpies and entropies of activation are presented in Table III.

From the rate coefficients for eliminations from **1a** and its deuterated analogue **1b** at 29.6, 39.0, and 48.5 °C, primary deuterium isotope effect values for MeONa-MeOH and *t*-BuOK-*t*-BuOH induced reactions were calculated. The values are listed in Table IV.

The influence of aryl ring substituents upon elimination rates correlated satisfactorily with the Hammett equation using σ^- values (Figures 1 and 2). Hammett ρ values and correlation coefficients are given in Table IV.

The reactions of *N*-bromobenzylmethylamine with MeONa-MeOH and *t*-BuOK-*t*-BuOH were also briefly examined (entry 6, Table I, and entry 8, Table II). In contrast

Table III. Activation Parameters for Base-Promoted Eliminations from $PhCH_2N(Cl)CH_3$ and $PhCH_2CH(Cl)CH_3$

substrate	base-solvent	temp, °C	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
$PhCH_2N(Cl)CH_3$	MeONa-MeOH	39.0	16.6 ± 0.1	−12.1 ± 0.3
	t-BuOK-*t*-BuOH	39.0	11.7 ± 0.3	−21.1 ± 1.1
$PhCH_2CH(Cl)CH_3$[a]	EtONa-EtOH	25.0	22.3 ± 0.2	−10.1 ± 0.4
	t-BuOK-*t*-BuOH	25.0	17.9 ± 0.2	−19.4 ± 0.5

[a] Reference 12.

Table IV. Hammett Correlations and Deuterium Isotope Effect Values for Eliminations from $ArCH_2N(Cl)CH_3$ Promoted by MeONa-MeOH and *t*-BuOK-*t*-BuOH

		k_H/k_D		
base-solvent	ρ at 39.0 °C (r[a])	29.6 °C	39.0 °C	48.5 °C
MeONa-MeOH	1.52 ± 0.06 (0.994)	6.4 ± 0.1	6.0 ± 0.1	5.1 ± 0.1
t-BuOK-*t*-BuOH	1.68 ± 0.03 (0.999)	6.5 ± 0.1	5.9 ± 0.1	5.1 ± 0.2

[a] r = correlation coefficient.

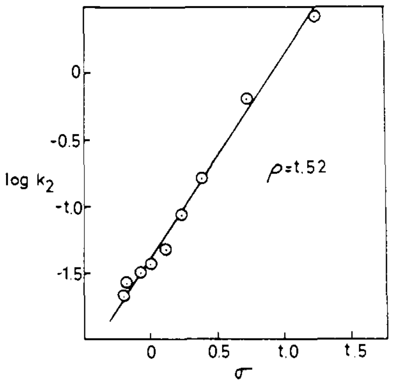

Figure 1. Hammett plot for reactions of **1** with MeONa-MeOH at 39.0 °C.

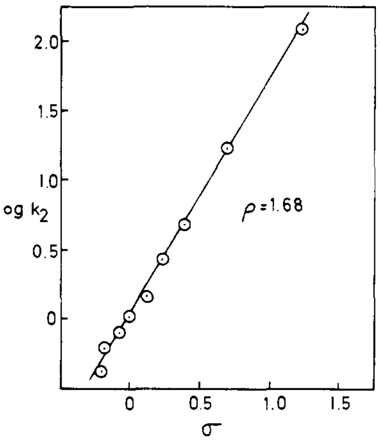

Figure 2. Hammett plot for reactions of **1** with *t*-BuOK-*t*-BuOH at 39.0 °C.

to reactions of **1** with MeONa-MeOH and *t*-BuOK-*t*-BuOH and of *N*-bromobenzylmethylamine with *t*-BuOK-*t*-BuOH, reaction of *N*-bromobenzylmethylamine with MeONa-MeOH produced **2a** and benzylmethylamine. The reduction product apparently arises by nucleophilic displacement of methoxide on the bromine atom of the substrate. The overall pseudo-first-order rate constant was multiplied by the imine yield to obtain the pseudo-first-order rate constant for imine formation. For eliminations from *N*-halobenzylmethylamines at 39.0 °C, k_{Br}/k_{Cl} = 11.9 with MeONa-MeOH and 10.8 with *t*-BuOK-*t*-BuOH.

Discussion

To our knowledge, there are only three previous kinetic investigations of base-promoted imine formation from -CH-NX- compounds. Brauman and Hill[8,9] have studied eliminations from the rather exotic alkyldifluoramines, RCH_2NF_2, in aqueous media. Eliminations from $(ArCH_2)_2NOC(O)Ar'$ promoted by azide, chloride, and cyanide ion in Me_2SO have been reported by Oae and Sakuri.[15] Most recently, Hoffman and Cadena[16] have probed amine-induced eliminations from $ArCH_2NHOSO_2C_6H_4$-*p*-NO_2 and related compounds in water-THF-ethyl acetate. Although each of these investigations has added to the meager store of information available concerning imine-forming eliminations, each employs a substrate, leaving group, or base-solvent system which has little analogy in previously studied reactions leading to alkenes. Since reactions of 1-aryl-2-halopropanes with alkoxides in the corresponding alcohols have been investigated by other workers,[11,12] eliminations from **1** provide valuable insight into the similarities and differences between closely related alkene- and imine-forming eliminations.

Mechanism of Elimination from 1. The kinetic investigation and control experiments provide convincing evidence that eliminations from **1** promoted by MeONa-MeOH and *t*-BuOK-*t*-BuOH proceed via an E2 mechanism. Solvolytic elimination was demonstrated to be negligible for **1a** in methanol, the more polar alcoholic solvent. Also observed second-order kinetics, first order in **1** and first order in base, rule out all but bimolecular reaction pathways. A reversible ElcB mechanism is negated by substantial values of the primary deuterium isotope effect (Table IV). The E2 and irreversible ElcB mechanisms may be differentiated by the element effect of the leaving group.[3d] For eliminations from *N*-halobenzylmethylamines, leaving group element effect (k_{Br}/k_{Cl}) values of 11.9 and 10.8 were determined with MeONa-MeOH and *t*-BuOK-*t*-BuOH, respectively. Utilizing kinetic data from two sources,[11,12] a k_{Br}/k_{Cl} value of approximately 80 is calculated for E2 elimination from 2-halo-1-phenylpropanes induced by EtONa-EtOH at 25.0 °C. Since the differences in bond energy between N-Br and N-Cl bonds is anticipated to be significantly less than that between C-Br and C-Cl bonds,[17] the lower value of k_{Br}/k_{Cl} noted for eliminations from *N*-halobenzylmethylamines is entirely consistent with an E2 mechanism.

Regioselectivity in Eliminations from *N*-Chloramines. Eliminations from **1** promoted by MeONa-MeOH and *t*-BuOK-*t*-BuOH produced essentially quantitative yields of the conjugated imine **2**. Detection of only the conjugated imine has previously been reported in reactions of *N*-chlorobenzyl-*n*-butylamine with MeONa-MeOH, EtONa-EtOH, *t*-BuOK-*t*-BuOH, and *t*-BuOK-hexane.[13] The regiospecificity observed in these *N*-chloramine eliminations parallels observations for alkoxide-induced eliminations from 2-halo-1-phenylpropanes[11,12] and suggests well-developed double-bond character in the imine-forming transition states.

In sharp contrast to the high regioselectivity noted for alkoxide-induced eliminations from **1** and other *N*-chloramines,[13] 2-halo-1-phenylpropanes,[11,12] and 1-phenyl-2-tosyloxypropane,[11] Hoffman and Cadena[16] have noted the formation of both conjugated and unconjugated imine products in reactions of $PhCH_2N(R)OSO_2C_6H_4$-*p*-NO_2 with amine bases in water-THF-ethyl acetate at −10 °C. The statistically corrected ratio of products resulting from benzyl H:alkyl H removal for different R groups was 5.0:1 with R = Me, 2.1:1 with R = Et and *n*-heptyl, and 0.7:1 with R = isopropyl. The results were interpreted in terms of a "late" transition state. However, these findings also appear to be consistent with an El-like transition state in the variable E2 transition state spectrum[3e] resulting from the weak base and good leaving group. At this time, the reasons for the much lower regioselectivity observed with Hoffman and Cadena's system than with ours remain uncertain.

Rates of Closely Related Imine- and Alkene-Forming Eliminations. The second-order rate constant for reaction of **1a** with MeONa-MeOH at 29.6 °C is $1.53 \times 10^{-2}\ M^{-1}\ s^{-1}$. That for reaction of 2-chloro-1-phenylpropane[12] with EtONa-EtOH at 25.0 °C is $1.86 \times 10^{-6}\ M^{-1}\ s^{-1}$. Considering the slightly different reaction conditions, the replacement of α carbon by α nitrogen produces a minimal 1000-fold increase in rate of elimination.

Activation parameters for base-promoted eliminations from **1a** and 2-chloro-1-phenylpropane are recorded in Table III. The entropies of activation for these closely related imine- and alkene-forming eliminations are remarkably similar when base-solvent combinations of similar type (dissociated or associated bases) are compared. Thus, the large rate enhancement for eliminations from **1a** results from enthalpic (energy of bond making and bond breaking) factors. The similarity of activation entropies provides additional evidence for a common E2 mechanism for the imine- and alkene-forming eliminations.

Transition States for Elimination from *N*-Chloramines. Much of our present knowledge of the details of olefin formation by the E2 mechanism has been derived from investigations of eliminations from β-arylethyl halides, arenesulfonates, and onium salts. Measurements of the primary deuterium isotope effect and determination of the Hammett ρ value for β-aryl groups have been instrumental in assessing the character of the E2 transition state and the changes wrought by variation of leaving group, base-solvent combination, etc.[3f]

Because of anticipated experimental problems due to the facile hydrolysis and polymerization of benzaldehyde imines, **1a–j** rather than *N*-chlorobenzylamines were selected as substrates for this study. Available data for alkoxide-induced eliminations from the structurally similar 2-halo-1-phenylpropanes[11,12] is collected in Table V.

From previous investigations of base-promoted imine formation, the transition state charge development at the β carbon remains uncertain. Reactions of (p-Y-$C_6H_4CH_2)_2NOCOC_6H_4$-*p*-NO_2 with NaN_3 in Me_2SO[15] failed to obey the Hammett relationship for a limited group of substituents (Y = Cl, H, Me). A Hammett ρ value of +0.5 to +1.3 has been estimated for the amine-promoted eliminations from $ArCH_2NHOSO_2C_6H_4$-*p*-NO_2 in water-THF-ethyl acetate.[16]

For reactions of **1** with MeONa-MeOH and *t*-BuOK-*t*-BuOH at 39.0 °C, we calculate Hammett ρ values (correlation with σ^-) of $+1.52 \pm 0.06$ and $+1.68 \pm 0.03$, respectively. The indicated carbanionic character at the β carbon in the transition state is of approximately the same magnitude as that reported for alkoxide-promoted eliminations from 1-phenyl-2-propyl bromide.[11] For eliminations from **1**, the ρ value increases slightly as the base is changed from dissociated (MeONa-MeOH) to associated (*t*-BuOK-*t*-BuOH). Similar variation of base-solvent combination produces a considerably larger decrease in ρ (Table V) for comparable olefin-forming eliminations. Although the factors responsible for the opposing effects wrought by the change in base-solvent system in imine- and alkene-forming eliminations remain uncertain at present, the results suggest a lesser sensitivity of E2 transition state character to variation of the base-solvent system for the former.

Table V. Hammett Correlations and Deuterium Isotope Effect Values for Eliminations from 1-Phenyl-2-X-propanes Promoted by EtONa-EtOH and *t*-BuOK-*t*-BuOH

X	base-solvent	temp, °C	k_H/k_D	ρ
Cl[a]	EtONa-EtOH	25.0	6.1	
	t-BuOK-*t*-BuOH	25.0	8.7	
Br[b]	EtONa-EtOH	50.0		1.84
	t-BuOK-*t*-BuOH	50.0		1.37

[a] Reference 12. [b] Reference 11.

Considerable C_β-H bond rupture is indicated in transition states for the alkoxide-promoted eliminations from **1**. Primary deuterium isotope effect values vary from 5.1 to 6.5 depending upon the temperature (Table IV). These results are consistent with the substantial k_H/k_D values reported by Oae and Sakuri[15] and by Hoffman and Cadena[16] in earlier studies of base-promoted imine formation.

The primary deuterium isotope effect values for elimination from **1a** are unchanged by variation of base-solvent combination from MeONa-MeOH to *t*-BuOK-*t*-BuOH. A similar change of base-solvent system for eliminations from 2-chloro-1-phenylpropane produces a large increase in k_H/k_D (Table V). Although the double-valued nature of the primary deuterium isotope effect introduces some uncertainty, the present results are consistent with the insensitivity of imine-forming transition-state character to change in base-solvent system indicated by the ρ values.

Arrhenius parameters for eliminations from **1a** and **1b** may be used to calculate the difference in activation energies ($E_a{}^D - E_a{}^H$) and the ratio of preexponential factors, A_H/A_D. With MeONa-MeOH, $E_a{}^D - E_a{}^H = 2.3 \pm 0.6$ kcal mol^{-1} and $A_H/A_D = 0.14$. With *t*-BuOK and *t*-BuOH, $E_a{}^D - E_a{}^H = 2.6 \pm 0.3$ kcal mol^{-1} and $A_H/A_D = 0.08$. In both cases, the difference in activation energies is greater than the classical maximum of approximately 1.3 kcal mol^{-1} and the A_H/A_D ratio is less than the lower limit of 0.5 anticipated in the absence of tunneling.[19] This indicates that the isotope effect values for eliminations from **1a** are complicated by a tunneling contribution. However, this conclusion must be considered in light of the limited (20 °C) range of kinetic measurements.[20] Regardless of possible tunneling corrections which would diminish the k_H/k_D values observed for the base-promoted eliminations from **1a**, values of the primary deuterium isotope effect will remain of sufficient magnitude to indicate considerable C_β-H rupture in the imine-forming transition states.

The leaving group element effect, k_{Br}/k_{Cl}, for eliminations from *N*-halobenzylmethylamines at 39.0 °C is 11.9 with MeONa-MeOH and 10.8 with *t*-BuOK-*t*-BuOH. The k_{Br}/k_{Cl} values show little sensitivity to variation of the base-solvent system. As previously mentioned, these values are consistent with a significant degree of N_α-X bond rupture in the imine-forming transition states.

The combined results reveal that transition states for base-promoted eliminations from **1** have appreciable scission of the C_β-H and N_α-Cl bonds, significant carbon-nitrogen double bond character, and limited carbanionic character. Thus, it appears that the transition states lie somewhat to the E1cB side of central in the spectrum of E2 transition states. Noteworthy is the insensitivity of transition-state structure to variation of the base-solvent system when compared with closely related alkene-forming eliminations.

Experimental Section

Materials. *N*-Benzylidenemethylamines, **2**, were prepared in high yield (>80%) from the corresponding benzaldehydes and methylamine using one of two literature methods.[21,22] The imines **2** were reduced to the amines either by catalytic hydrogenation over Raney nickel (W-2) in MeOH[22] or by reaction with $NaBH_4$ in MeOH.[23] The prepared benzylmethylamines and **2** were all known compounds which gave infrared and proton magnetic resonance spectra consistent with the proposed structures.

The $PhCD_2NHCH_3$ was prepared by reduction of *N*-methylbenzamide with $LiAlD_4$ (minimum 99 atom % D, Merck) in absolute ether[24,25] in 87% yield. The proton magnetic resonance spectrum ($CDCl_3$) of $PhCD_2NHCH_3$ was exactly the same as that for $PhCH_2NHCH_3$ except for the complete absence of the benzylic proton singlet of the latter at 3.65 ppm.

N-Chlorobenzylmethylamines, **1**, were prepared by dissolving approximately 0.3 mmol of the benzylmethylamine in 20 mL of pentane and adding a 20-30% molar excess of *N*-chlorosuccinimide. The mixture was stirred for 20 min and filtered with a sintered glass funnel. Five milliliters of MeOH or *t*-BuOH was added to the pentane solution and the pentane was removed in vacuo. The resulting alcoholic solution of **1** was diluted to 10.0 mL by addition of the appropriate alcohol.

N-Bromobenzylmethylamine was prepared in similar fashion using *N*-bromosuccinimide. Owing to a lower stability of this bromoamine than **1a**, alcoholic solutions were freshly prepared before kinetic runs.

Methanol (Fisher, reagent) was purified by reaction with magnesium and distillation. Solutions of MeONa-MeOH were prepared by adding clean pieces of sodium metal to anhydrous MeOH under nitrogen.

tert-Butyl alcohol (Mallinckrodt, reagent) was distilled three times from potassium metal. Solutions of *t*-BuOK-*t*-BuOH were prepared by adding clean pieces of potassium metal to the purified *t*-BuOH under nitrogen. The solutions were stored in a drybox and used within 1 week.

Ultraviolet Spectra of 2. Molar extinction coefficients (λ_{max}) measured in absolute MeOH were the following: **2a**, 15 300 (244 nm); **2c**, 19 600 (266 nm); **2d**, 11 300 (249 nm); **2e**, 17 200 (252.5 nm); **2f**, 14 400 (248 nm); **2g**, 19 800 (252 nm); **2h**, 14 000 (245 nm); **2i**, 15 800 (280 nm); **2j**, 26 400 (234 nm). The molar extinction coefficient and λ_{max} of **2a** were the same in *t*-BuOH as in MeOH. It was therefore assumed that the extinction coefficients and λ_{max} for other **1** were the same in the two solvents.

Kinetic Studies of Elimination from 1. Base-promoted eliminations from **1** were followed in almost every case using a Beckman Acta V ultraviolet spectrometer with thermostated cuvette holders. Reactions were followed under pseudo-first-order conditions employing at least a tenfold excess of base. The desired base-solvent solution (3.0 mL) was placed in a quartz cuvette and allowed to equilibrate in the cuvette compartment for 20 min. The cuvette was removed and 6 μL of the alcoholic solution of **1** was injected with a microsyringe. The cuvette was quickly shaken and returned to the cuvette compartment. The increase of absorption at the λ_{max} for **2** with time was monitored. Plots of $-\ln (A_\infty - A_t/A_\infty - A_0)$ vs. time were linear over at least 2 half-lives of the reaction. The slope was the pseudo-first-order rate constant. Second-order rate constants were obtained by dividing the pseudo-first-order rate constant by the base concentration.

Reactions of **1i** and **1j** with *t*-BuOK-*t*-BuOH (entries 18 and 19, Table II) were too fast to be measured by this ordinary kinetic method, so the rate studies utilized a Durrum D-110 stopped-flow spectrophotometer.

Product Studies of Eliminations from 1. For reactions of **1** with MeONa-MeOH, the absorbance of infinity samples from the kinetic reactions was compared with that of authentic samples of **2**. Based upon the starting benzylmethylamine, the yields of **2** were 85-96%. For reactions of **1a** with *t*-BuOK-*t*-BuOH, the yield of **2a** was 95 ± 2%. Quantitative yields of **2** were assumed in reactions of other **1** with *t*-BuOK-*t*-BuOH.

The absence of the corresponding benzylmethylamines as products from reactions of **1a,c,i** with MeONa-MeOH and *t*-BuOK-*t*-BuOH was established using more concentrated reagents. Reaction of 2.0 mmol of a chloramine and 60 mL of 0.10 M base-solvent solution was conducted by refluxing overnight. The solvent was removed in vacuo and the residue was extracted with pentane. Solvent exchange was accomplished by adding $CDCl_3$ and evaporating the pentane in vacuo. Proton magnetic resonance spectra of the $CDCl_3$ solution showed a clean doublet centered at 3.52 ppm for the *N*-methyl group of **2**, but no trace of the *N*-methyl singlet of the benzylmethylamine at 2.22 ppm.

Product Studies of Eliminations from N-Bromobenzylmethylamine. In infinity samples from kinetic studies of the reaction of *N*-bromobenzylmethylamine with *t*-BuOK-*t*-BuOH, a 88 ± 2% yield of **2a** indicated essentially quantitative conversion. However, with MeONa-MeOH a yield of only 62% of **2a** was observed. Using more concentrated solutions and the proton magnetic resonance spectral method outlined in the previous section, it was demonstrated that the reaction of *N*-bromobenzylmethylamine with MeONa-MeOH produces benzylmethylamine in addition to **2a.**

Control Experiments. When solutions of **1a** or *N*-bromobenzylmethylamine in MeOH and *t*-BuOH were heated at 48.5 °C for times comparable to those required to obtain infinity samples from the base-promoted eliminations, no increase in ultraviolet absorption at 244 nm was noted.

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References and Notes

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