the toluene layer was diluted in MeOH and quantitatively assayed by the HPLC system described above for catalyst, indanone 1, and methylindanone 2. The basicity of the toluene layer was determined by adding a weighed amount of the toluene layer to water and titrating with standardized acetic acid to a phenolphthalein end point.

C. Determination of Enantiomeric Excess. The (+/-) isomer ratio of the methylindanone 2 was determined by NMR from 10 mL of reaction sample worked up as follows: washed with 2 × 5 mL of 4 N HCl and then 5 mL of H_2O; concentrated and flushed with 2 × 10 mL of $CHCl_3$ to remove all toluene; 100 mg of residue plus 100 mg of tris[3-((heptafluoropropyl)hydroxymethylene)-*d*-camphorato]europium (III) in 0.5 mL of $CDCl_3$.

D. Catalyst Preparation. The catalysts were prepared from cinchonine (Fluka) and the appropriate benzyl halide in refluxing toluene or isopropyl alcohol. The bromides required 1-2 h reflux, while the chlorides required 24-48 h reflux for complete reaction.

Commercial cinchonine usually contains 15% of dihydrocinchonine, which forms the dihydro analogue of the catalyst during the reaction. The catalytic activity of this analog is very similar to that of the title catalyst. Therefore the presence of dihydrocinchonine does not present a problem.

E. Catalyst Dimer. 1. Preparation and Characterization of the Dimer. *p*-CF_3BCNB (76 mg) was added to toluene (10 mL) and 50% NaOH (8 mL) and stirred for 0.5 h until the solution was clear. HPLC of the toluene layer showed that all the catalyst had dissolved in toluene (14.3 mM). The toluene layer (2.16 mL) was added to 25 mL of water and titrated to a phenolphthalein end point with 1.11 mL of 13.8 mM HOAc, giving a basicity of 7.1 mM in the toluene layer. Similarly, catalyst (450 mg), benzene (20 mL), and 50% NaOH (10 mL) were stirred for 0.5 h. The benzene layer was separated, dried over 4A powdered sieves, filtered, concentrated to approximately 5 mL, and stored overnight. The resulting solid was filtered, washed with 1 mL of benzene, and dried to afford 213 mg of crystalline (microscopy) catalyst dimer, mp 120-125 °C dec. Anal. Calcd for $C_{54}H_{55}N_4BrF_6O_2$ (dimer): C, 65.8; H, 5.6; N, 5.7; Br^-, 8.1. Anal. Calcd for $C_{27}H_{28}N_2BrF_3O$ (monomer): C, 60.8; H, 5.3; N, 5.25; Br^-, 15.0. Found: C, 65.8; H, 6.0; N, 5.2; Br^-, 7.6.

BCNB (95 mg) was added to toluene (10 mL) and 50% NaOH (8 mL) and stirred at room temperature for 5 h. HPLC of the toluene layer showed all the catalyst had dissolved (20.4 mM). The toluene layer (0.64 mL) in 20 mL of water was titrated with 1.99 mL of 3.45 mM HOAc, giving a basicity in toluene of 10.7 mM. Similarly, catalyst (550 mg), benzene (20 mL), and 40% NaOH were stirred for 3 h. The benzene layer was separated, dried over 4A powdered sieves, filtered, and concentrated to 5 mL. After 2 h at 25 °C the resulting solid was filtered, washed with 1 mL of benzene, and dried at 25 °C (1 mm) to afford 74 mg of dimer. Anal. Calcd for $C_{52}H_{57}N_4BrO_2$ (dimer): C, 73.5; H, 6.7; N, 6.6; Br, 9.4. Anal. Calcd for $C_{26}H_{29}N_2BrO$ (monomer): C, 67.1; H, 6.0; N, 6.0; Br, 17.2. Anal. Calcd for $C_{52}H_{57}BrN_4O_2 \cdot {}^1/_2C_6H_6 \cdot 3H_2O$ (dimer benzene hemisolvate trihydrate: presence of $^1/_2$ mol of C_6H_6 confirmed by NMR; H_2O by Karl Fisher analysis): C, 70.0; H, 7.1; N, 5.9; Br, 8.5. Found: C, 70.3; H, 6.7; N, 6.2; Br, 8.3.

2. Methylation of Catalyst Dimer. *p*-CF_3BCNB (1.28 mmol) was stirred 1 h in 50 mL of toluene and 50 mL of 50% NaOH. The toluene layer (45 mL) was separated, MeI (2.8 g) was added, and the solution was aged 43 h. A precipitate was recovered (0.23 g), which showed, by ^1H NMR, 40% starting material (6) and 60% of the methyl ether 8. HPLC also gave a 60/40 ratio. Evaporation of the solution gave an additional 0.26 g, which showed, by LC, 68% catalyst 6 and 32% methyl ether 8. Overall, then, 87% of material was recovered; 55% was catalyst 6 and 45% was methyl ether 8, in line with the proposed dimeric species in toluene.

Registry No. 1, 60769-26-8; 2, 88494-66-0; 6 (G = H)·Cl^-, 69221-14-3; 6 (G = H)·Br^-, 85653-34-5; 6 (G = *p*-MeO)·Cl^-, 110097-80-8; 6 (G = *p*-Me)·Cl^-, 110097-81-9; 6 (G = *p*-F)·Cl^-, 110097-82-0; 6 (G = *p*-Cl)·Cl^-, 110097-83-1; 6 (G = *m*-Cl)·Cl^-, 110097-84-2; 6 (G = *m*-Cl)·Br^-, 110097-85-3; 6 (G = *p*-CF_3)·Br^-, 95088-20-3; 6 (G = *m*-CF_3)·Cl^-, 110097-86-4; 6 (G = *m*-CF_3)·Br^-, 110097-87-5; 6 (G = *p*-NO_2)·Cl^-, 110097-88-6; 6 (G = 3,4-Cl_2)·Cl^-, 110171-18-1; 6 (G = 3,4-Cl_2)·Br^-, 110171-19-2; 6 (G = *p*-CF_3) dimer, 110097-90-0; 6 (G = H) dimer, 110097-93-3; 8, 110097-91-1.

Reactions of *N*-Chlorobenzylalkylamines with Sodium Methoxide in Methanol. Steric Effects in Elimination Reactions[1]

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Reactions of *N*-chlorobenzylalkylamines in which the alkyl group is Me, Et, *i*-Pr, *t*-Bu, and *sec*-Bu with MeONa-MeOH have been investigated kinetically. The eliminations are quantitative and regiospecific, producing only benzylidenealkylamines. The reactions are first order in base and first order in substrate, and an E2 mechanism is evident. The relative rates of elimination at 25 °C are 1/0.5/0.3/0.2/0.01 for Me/Et/*i*-Pr/*sec*-Bu/*t*-Bu alkyl substituents, respectively. The results are attributed to repulsive interaction between the alkyl group and the base in the transition state. Hammett ρ and k_H/k_D values decreased, but the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values increased with bulkier alkyl substituents. Changes in the transition-state parameters with the substrate steric effect are interpreted with variation in structure of the imine-forming transition states.

Steric and electronic effects are among the most important factors that influence organic reaction pathways. It is well-known that the rate of S_N2 reaction decreases with steric hindrance in the substrate. In contrast, there is considerable controversy regarding the explanation of the effect of alkyl groups on reaction rates and orientation in elimination reactions.[2-6] From a series of reactions of $RCH_2C(X)Me_2$ and $RCH_2CH(X)Me$ (X = Br, I, OTs, S^+Me_2, SO_2CH_3, N^+Me_3), Brown concluded that the steric effects are the cause of the observed effects of alkyl groups on the rate and orientation in both E1 and E2 reactions.[2] On the other hand, Ingold proposed that the inductive and electromeric effects of the R groups dominate the E2 reactions of RCH_2CH_2X (X = S^+Me_2, N^+Me_3) compounds and the steric effect is insignificant except when the alkyl

(1) Presented at the 192nd American Chemical Society National Meeting, Anaheim, CA, Sept 1986.

(2) Brown, H. C.; Moritani, I.; Nakagawa, M. *J. Am. Chem. Soc.* **1956**, *78*, 2190-2193. Brown, H. C.; Wheeler, O. H. *Ibid.* **1956**, *78*, 2199-2202. Brown, H. C.; Moritani, I. *Ibid.* **1956**, *78*, 2203-2210. Brown, H. C.; Moritani, I. *Ibid.* **1955**, *77*, 3607-3610. Brown, H. C.; Nakagawa, M. *Ibid.* **1955**, *77*, 3614-3619.

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Table I. Rate Constants for Elimination from $XC_6H_4CL_2N(Cl)R$ Promoted by MeONa-MeOH[a]

entry	temp, °C	X	L	10^3k_2,[b] M^{-1} s^{-1} R = Et	R = i-Pr	R = t-Bu
1	25.0	H	H	5.10 (64.4)[c]	2.73 (33.3)[c]	0.114
2	35.0	H	H	11.6	6.87	0.488
3	45.0	H	H	26.6	15.6	1.09
4	25.0	H	D	0.991	0.894	0.0354
5	25.0	p-CH_3O	H	2.53	1.63	0.0941
6	25.0	m-Br	H	22.1	10.6	0.381
7	25.0	m-NO_2	H	85.3	35.6	1.55
8	25.0	p-NO_2	H	343	189	6.77

[a] [MeONa] = 1.60×10^{-2}–1.60×10^{-1} M; [substrate] = $(5.0–7.0) \times 10^{-5}$ M. [b] Estimated uncertainty, ±3%. [c] Substrate was $PhCH_2N(Br)Et$.

group is very large.[3] More recently, Charton examined the available data statistically by means of correlations with the modified Taft equations (eq 1 and 2),[4] where ν and ν'

$$\log k_2 = \psi\nu + h \quad (1)$$

$$\log k_2 = \psi'\nu' + h \quad (2)$$

are steric parameters defined from the esterification of carboxylic acids and S_N2 reactions of substituted alkyl bromides,[5,6] respectively. He found excellent correlation of the rate and orientation data for E1 and E2 reactions with eq 1. However, when the electronic effects of the alkyl substituents were included, no correlation was observed.[4] This result seemed to refute the conclusion of Ingold and support the position of Brown.

To better understand the effect of alkyl substituents upon E2 reactions, it seems necessary to design a system that reacts by an E2 mechanism and whose steric requirement can be varied without affecting the electronic effect. This can be accomplished if the alkyl substituents are varied on the α-atom rather than on the β-carbon as Brown and Ingold did. Accordingly, we have investigated the reactions of N-chlorobenzylalkylamines **1–5** with MeONa–MeOH.

It has been demonstrated that the dehydrochlorinations of N-chlorobenzylmethylamines proceed by an E2 mechanism under various conditions.[7–11] Moreover, the steric requirement of such substrates can readily be modified by utilizing different N-alkyl substituents, while maintaining the C_β—H bond acidity and C=N bond stability relatively constant. The results of kinetic investigation of these reactions are now reported.

$$XC_6H_4CL_2N(Cl)R + MeONa\text{-}MeOH \rightarrow XC_6H_4CL{=}NR \quad (3)$$

1–5 **6**

1: R = Me
2: R = Et
3: R = i-Pr
4: R = t-Bu
5: R = sec-Bu

a: X = H; L = H
b: X = H; L = D
c: X = p-CH_3O; L = H
d: X = m-Br; L = H
e: X = m-NO_2; L = H
f: X = p-NO_2; L = H

Results

Benzylidenealkylamines **6**, benzylalkylamines, and N-chlorobenzylalkylamines were prepared in high yields by known methods.[12] The spectral and analytical data of the compounds were consistent with the proposed structures.

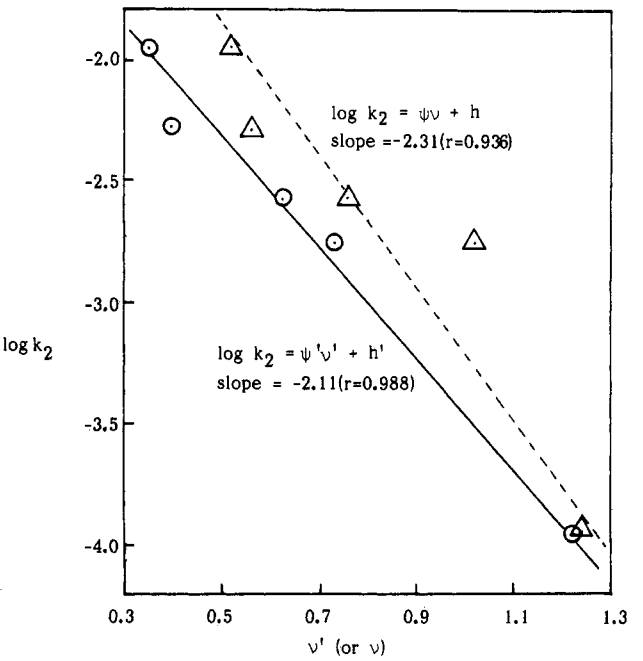

Figure 1. Correlation of E2 rates with Charton's ν or ν' values.

Table II. Susceptibility of Various Reactions to Steric Effects under Comparable Conditions

reaction	ψ or ψ'	ref
RCH_2Br + EtONa-EtOH → RCH_2OEt	−5.48	6
RCH_2Br + MeONa-MeOH → RCH_2OMe	−3.37	6
RCO_2H + MeOH $\xrightarrow{H^+}$ $RCO_2Me + H_2O$	−2.14	5
$RCH_2CH_2N^+Me_3$ + EtONa-EtOH → RCH=CH_2	−2.36	4
$PhCH_2N(Cl)R$ + MeONa-MeOH → PhCH=NR	−2.11	this work

Table III. Transition-State Parameters for Eliminations from $ArCH_2N(Cl)R$ Promoted by MeONa-MeOH

R	ρ (r)[a]	k_H/k_D	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu
Me[b]	1.58 (0.999)	6.4	14.2	−19.9
Et	1.52 (0.996)	5.1	14.9	−18.8
i-Pr	1.47 (0.999)	3.0	16.9	−16.2
t-Bu	1.36 (0.993)	2.8	20.7	−6.2

[a] Correlation coefficient. [b] Reference 9.

Reactions of **2–5** with MeONa–MeOH produced only benzylidenealkylamines **6**. 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 10-fold variations in base concentration (Table I for **2a**, **3a**, and **4a**). The rate of elimination from N-chlorobenzyl-sec-butylamine **5a** was also determined under the same condition. The k_2 value at 25.0 °C was 1.77×10^{-3} M^{-1} s^{-1}. Relative rates

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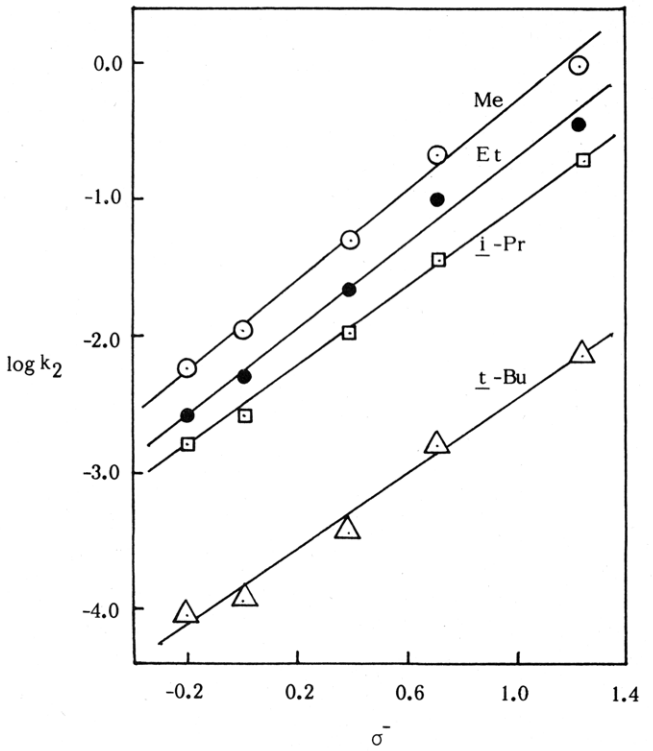


Figure 2. Hammett plots for eliminations from $ArCH_2N(Cl)R$ promoted by MeONa–MeOH; R = Me, Et, *i*-Pr, and *t*-Bu in descending order.

of elimination are 1/0.5/0.3/0.2/0.01 for **1a/2a/3a/4a/5a**, respectively.

A plot of log k_2 vs. ν and ν' values[5,6,23] is shown in Figure 1. The rate data correlate better with ν' than ν parameters. The ψ and ψ' values are given in Table II.

Rates of elimination from **2a–4a** promoted by MeOHa–MeOH were measured at three temperatures spanning 30 °C. The Arrhenius plots were linear with excellent correlation. Calculated enthalpies and entropies of activation are presented in Table III.

The influence of aryl substituents upon elimination rates correlated statisfactorily with the Hammett equation, using σ^- values (Figure 2). Hammett ρ values are given in Table III.

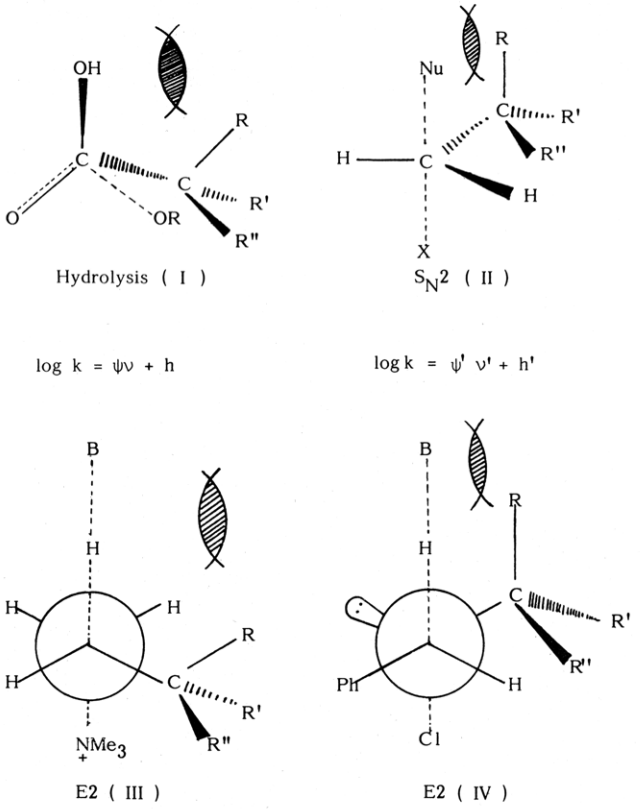
From the rate coefficients for eliminations from **2a–4a** and their deuteriated analogues **2b–4b** at 25.0 °C, primary deuterium isotope effect values were calculated. The values are listed in Table III.

Reactions of *N*-bromobenzylalkylamines with MeONa–MeOH were also briefly examined. The products were benzylidenealkylamine and benzylalkylamine. The amine products apparently arise by nucleophilic displacement of the methoxide on the bromine leaving group of these substrates.[9] The imine yield decreased with increasing steric requirement of the *N*-alkyl substituents. Rate constants for elimination from the *N*-bromamines were obtained by multiplying the overall second-order rate constants by the imine yields. However when the *N*-alkyl group was *t*-Bu, the elimination product yield was too low for the rate constant to be determined accurately. For eliminations from *N*-halobenzylalkylamines at 25.0 °C, the leaving group element effect k_{Br}/k_{Cl} was 15.8, 12.6, and 12.2 for R = Me, Et, and *i*-Pr, respectively.

Discussion

Steric Effects of *N*-Alkyl Groups in Eliminations from 1–5. Earlier we reported that the reactions of **1** with MeONa–MeOH proceed by a normal E2 mechanism.[8,9]

Chart I



The results of kinetic investigation and control experiments reveal that the reactions of **2–4** with MeONa–MeOH also proceed by the same E2 mechanism. Since **2–4** were stable in MeOH and the reactions exhibited second-order kinetics, all except bimolecular pathways can be ruled out. In addition, an Elcb mechanism is negated by the substantial values of the primary deuterium isotope effect and the element effect of the leaving group.[13]

The rate of elimination from the *N*-chlorobenzylalkylamines decreases systematically as the steric requirement of the *N*-alkyl group is increased. When log k_2 was plotted against Charton's ν' values, a straight line was obtained with excellent correlation (Figure 1). Anticipating little change in N—Cl bond strength and C=N bond stability with different *N*-alkyl substituents,[14] the result can be accounted for entirely by a steric effect. Thus, our findings provide additional support for the conclusions of Brown and of Charton.

Correlation of the rate data with ν' rather than ν values can be explained by considering the structure of the transition states (Chart I). As pointed out by Charton, the transition state for elimination from $RCH_2CH_2N^+Me_3$ compounds (III) must, in so far as the steric interactions between the base and alkyl substituents are concerned, bear closer relationship to the transition state for hydrolysis (I) than it does to the transition state for bimolecular nucleophilic substitution (II). However, the corresponding steric interactions in the transition state for *N*-chlorobenzylalkylamine elimination (IV) appear more similar to that for the S_N2 reaction (II) as depicted in Chart I. Therefore, similarity in the way in which the base and alkyl group interact in the transition states II and IV must be responsible for the correlation of the rate data with ν'

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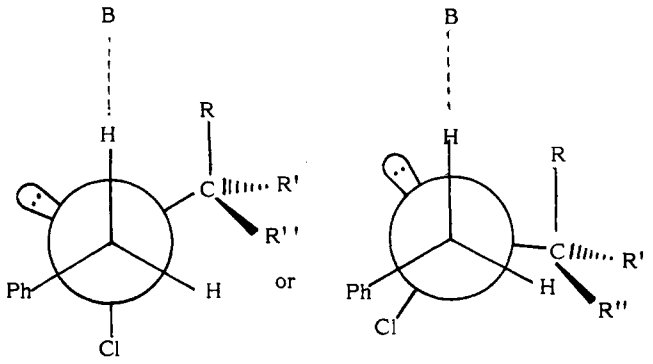
Chart II



anti (V) partially eclipsed (VI)

	anti	eclipsed
ρ	decrease	increase
k_H/k_D	decrease	same
$\Delta H^{\neq}$	increase	increase
$\Delta S^{\neq}$	increase	decrease

values for the chloramine eliminations.

The susceptibilities of various reactions to alkyl group steric effects under comparable conditions are summarized in Table II. The data reveal that S_N2 reactions are most sensitive to the substrate steric effect and the steric effect in eliminations from **1–5** is similar to those observed in esterification and in E2 reactions of $RCH_2CH_2N^+Me_3$ compounds. It is interesting to note that the sensitivity of E2 reactions to the alkyl group steric effect is similar irrespective of whether the alkyl substituent is located on the α- or β-atom.

Influence of Alkyl Group upon Imine-Forming Transition State. There are two possibilities by which the alkyl group steric effect may operate in these reactions[15] (Chart II). If the reactions proceed via anti transition states (V), the bulky substituent may hinder the approach of the base to the C_β–H bond in the transition state. The C_β–H bond would then be less broken, and less π-bond character would be developed in the transition state as the alkyl group becomes bulkier. Alternatively, the reaction might proceed through a partially eclipsed transition state (VI) to relieve the nonbonding interactions between the alkyl group and the attacking base. The transition state would then become more distorted from the anti stereochemistry for a bulkier alkyl group, without much affecting the extent of C_β–H bond breaking in the transition state.

To determine which of these transition states the reactions might actually pass through, the transition-state parameters for reactions of **1–4** with MeONa–MeOH were determined (Table III). The Hammett ρ values decrease in the order **1 > 2 > 3 > 4**, indicating decreased carbanionic character of the transition state with increasing substrate steric effect. The k_H/k_D values also decrease in the same order. Although the latter result could be interpreted by either a decrease or an increase in the extent of proton transfer in the transition state,[17] the former interpretation seems more compatible with the decreased ρ values observed for bulkier alkyl substituents.

These results are clearly in accord with the anti transition state (V). In contrast, if the reaction were to proceed via VI, the k_H/k_D values should remain constant, since in VI little change in the degree of proton transfer is required with alkyl group variation. Moreover, the ρ values should increase as the transition state (VI) becomes more eclipsed by the bulkier alkyl group, because less of the π-bond would be formed by the poorer overlap of the developing p orbitals on the C_β and N_α atoms and hence less of the charge density on the β-carbon could be transferred between the carbon and nitrogen atoms.

The changes in $\Delta H^{\neq}$ and $\Delta S^{\neq}$ with alkyl group variation are also in agreement with the anti transition state (V). The enthalpy of activation is expected to increase with increased substrate steric effect because of less base–proton bond and π-bond formation. The entropy of activation should also increase since the transition state becomes less associated with respect to the base–proton bond. On the other hand, for the partially eclipsed transition state (VI), the enthalpy of activation should increase with bulkier substituents due to the decreased π-bond formation (vide supra) and increased van der Waals repulsion between the C_β–H and N_α–R groups, but the entropy of activation should decrease since more solvent reorganization would be required to solvate the charged transition states (vide supra).

Thus, it appears that the reactions of **1–4** with MeO-Na–MeOH proceed via anti transition states, and the extent of C_β–H bond cleavage, carbanionic character, and double-bond character in the transition state decreases as the steric requirement of the alkyl substituent increases.

Experimental Section

The NMR spectra were recorded with an EM-360 spectrometer. Chemical shifts are reported to the nearest 0.1 ppm with TMS as an internal standard. IR spectra were recorded with a Perkin-Elmer Model 710B spectrophotometer. UV spectra were measured with a Cary-17D ultraviolet spectrophotometer with thermostated cuvette holders. Elemental analyses were performed by the Korea Advanced Institute of Science and Technology, Seoul, Korea.

Materials. Benzylidenealkylamines **6** were prepared in high yields (>80%) by reaction of substituted benzaldehydes with appropriate alkylamines.[8,12]

The physical, spectral, and analytical data for **6** were consistent with the proposed structures.[18–20] The boiling points or melting points (°C/mmHg or °C) of the new compounds are as follows: *p*-$CH_3OC_6H_4CH$=NEt, 95–96/4; *m*-BrC_6H_4CH=NEt, 85/0.8; *m*-$NO_2C_6H_4CH$=NEt, 94–96/0.2; *p*-$CH_3OC_6H_4CH$=N-*i*-Pr, 90/3; *m*-BrC_6H_4CH=N-*i*-Pr, 81/3; *m*-$NO_2C_6H_4CH$=N-*i*-Pr, 55–59; PhCH=N-*sec*-Bu, 73–74/9; *p*-$CH_3OC_6H_4CH$=N-*t*-Bu, 103/1; *m*-BrC_6H_4CH=N-*t*-Bu, 93/0.5; *m*-$NO_2C_6H_4CH$=N-*t*-Bu, 115/0.5; *p*-$NO_2C_6H_4CH$=N-*t*-Bu, 71–75.

The benzylidenealkylamines were reduced by $NaBH_4$ in MeOH to afford benzylalkylamines.[8] The $PhCD_2NHR$ compounds were prepared by reduction of the corresponding *N*-alkylbenzamides with $LiAlD_4$ (98 atom % D, Aldrich) in dry THF in moderate to high yields.[8] The physical, spectral, and analytical data for these compounds were consistent with the proposed structure.[18–22]

(15) Linear proton transfer was assumed in these transition states since it has been demonstrated that the k_H/k_D values for MeONa-promoted eliminations from **1a** decreased with temperature.[8] Nonlinear proton transfer was indicated by constant k_H/k_D values with temperature variation in a few cases where soft bases were utilized.[16]

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The boiling points or melting points (°C/mmHg or °C) of the new compounds are as follows: $PhCD_2NHEt$, 40/8; *p*-$CH_3OC_6H_4CH_2NHEt$, 131/26; *m*-$BrC_6H_4CH_2NHEt$, 102/5; *m*-$NO_2C_6H_4CH_2NHEt$, 108/3; *p*-$NO_2C_6H_4CH_2NHEt$, 131/6; $PhCD_2NH$-*i*-Pr, 34/5; *p*-$CH_3OC_6H_4CH_2NH$-*i*-Pr, 72/3; *m*-$BrC_6H_4CH_2NH$-*i*-Pr, 62/3; *m*-$NO_2C_6H_4CH_2NH$-*i*-Pr, 91-92/5; *p*-$NO_2C_6H_4NH$-*i*-Pr, 80/5; $PhCH_2NH$-*t*-Bu, 82/5; $PhCD_2NH$-*t*-Bu, 60/3; *p*-$CH_3OC_6H_4CH_2NH$-*t*-Bu, 101/1; *m*-BrC_6H_4NH-*t*-Bu, 95/0.5; *m*-$NO_2C_6H_4CH_2NH$-*t*-Bu, 113/0.5; *p*-$NO_2C_6H_4CH_2NH$-*t*-Bu, 32.

N-Halobenzylalkylamines were prepared by reaction of the benzylalkylamines with *N*-chloro- or *N*-bromosuccinimide in pentane as described previously.[8]

Methanol was purified by reaction with magnesium and distillation. Solutions of MeONa in MeOH were prepared by adding clean pieces of sodium metal to anhydrous MeOH under nitrogen.

Kinetic Studies of Elimination from 2-5. Kinetic studies of eliminations from **2-5** were carried out as before[8] using a Cary 17D or Pye Unicam SP 500 UV spectrophotometer with thermostated cuvette holders. The pseudo-first-order rate constant was divided by the base concentration to afford the second-order rate constant k_2. For reactions of *N*-bromobenzylalkylamines with MeONa-MeOH, the k_2 values were multiplied by the imine yields to obtain the second-order rate constant for imine formation.

Product Studies for Reactions of *N*-Halobenzylalkylamines with MeONa-MeOH. For reactions of *N*-halobenzylalkylamines with MeONa-MeOH, the absorbances of infinity samples from the kinetic reactions were compared with those of authentic samples of **6**. Based upon the starting benzylalkylamines, the yields of **6** were 85-96% from *N*-chloramines **2-5** and 40-80% from the corresponding *N*-bromamines.

The products of reactions of *N*-halobenzylalkylamines with MeONa-MeOH were identified by using more concentrated solutions and the proton magnetic spectral method outlined previously.[8] From reactions of **2a-5a** with MeONa-MeOH, benzylidenealkylamines were obtained as the only products in 72-76% yields. On the other hand, the reactions of *N*-bromobenzylalkylamines with MeONa-MeOH produced benzylalkylamines in addition to **6**.

Control Experiments. The stability of the *N*-haloamines and benzylidenealkylamines under the experimental conditions was demonstrated by the previously used method.[8]

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Registry No. $PhCH_2N(Cl)Et$, 110079-23-7; $PhCH_2N(Cl)Pr$-*i*, 110079-24-8; $PhCH_2N(Cl)Bu$-*t*, 33863-73-9; 4-$H_3CO_6H_4CH_2N(Cl)Et$, 110079-25-9; 4-$H_3COC_6H_4CH_2N(Cl)Pr$-*i*, 110079-26-0; 4-$H_3COC_6H_4CH_2N(Cl)Bu$-*t*, 110079-27-1; 3-$BrC_6H_4CH_2N(Cl)Et$, 110079-28-2; 3-$BrC_6H_4CH_2N(Cl)Pr$-*i*, 110079-29-3; 3-$BrC_6H_4CH_2N(Cl)Bu$-*t*, 110079-30-6; 3-$O_2NC_6H_4CH_2N(Cl)Et$, 110079-31-7; 3-$O_2NC_6H_4CH_2N(Cl)Pr$-*i*, 110079-32-8; 3-$O_2NC_6H_4CH_2N(Cl)Bu$-*t*, 110079-33-9; 4-$O_2NC_6H_4CH_2N(Cl)Et$, 110079-34-0; 4-$O_2NC_6H_4CH_2N(Cl)Pr$-*i*, 110079-35-1; 4-$O_2NC_6H_4CH_2N(Cl)Bu$-*t*, 110079-36-2; 4-$H_3COC_6H_4CH{=}NEt$, 17972-12-2; 3-$BrC_6H_4CH{=}NEt$, 110079-37-3; 3-$O_2NC_6H_4CH{=}NEt$, 110079-38-4; 4-$H_3COC_6H_4CH{=}NPr$-*i*, 13033-52-8; 3-$BrC_6H_4CH{=}NPr$-*i*, 110079-39-5; 3-$O_2NC_6H_4CH{=}NPr$-*i*, 27895-80-3; $PhCH{=}NBu$-*sec*, 40051-50-1; 4-$H_3COC_6H_4CH{=}NBu$-*t*, 15875-74-8; 3-$BrC_6H_4CH{=}NBu$-*t*, 28405-57-4; 3-$O_2NC_6H_4CH{=}NBu$-*t*, 25115-54-2; 4-$O_2NC_6H_4CH{=}NBu$-*t*, 718-36-5; $PhCD_2NHEt$, 56052-04-1; 4-$H_3COC_6H_4CH_2NHEt$, 22993-76-6; 3-$BrC_6H_4CH_2NHEt$, 90389-91-6; 3-$O_2NC_6H_4CH_2NHEt$, 4319-19-1; 4-$O_2NC_6H_4CH_2NHEt$, 17847-35-7; $PhCD_2NHPr$-*i*, 110079-40-8; 4-$H_3COC_6H_4CH_2NHPr$-*i*, 70894-74-5; 3-$BrC_6H_4CH_2NHPr$-*i*, 110079-41-9; 3-$O_2NC_6H_4CH_2NHPr$-*i*, 90390-05-9; 4-$O_2NC_6H_4NHBu$-*t*, 25186-43-0; 3-$BrPhCH_2NHBu$-*t*, 3378-72-1; $PhCD_2NHBu$-*i*, 15185-03-2; 4-$H_3COC_6H_4CH_2NHBu$-*t*, 22675-83-8; 3-BrC_6H_4NHBu-*t*, 40686-63-3; 3-$O_2NC_6H_4CH_2NHBu$-*t*, 110079-42-0; 4-$O_2NC_6H_4CH_2NHBu$-*t*, 3489-67-6; D_2, 7782-39-0.

(23) The ν' value of 0.73 was estimated for *sec*-Bu from the relationship between the ν and ν' values for structurally related alkyl substituents.[5,6]

Surface Photochemistry: The CdS-Mediated Reactions of 1,1-Di-*p*-anisylethylene[1]

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The CdS-photomediated reaction of 1,1-di-*p*-anisylethylene (**1b**) leads to the formation of two cyclized (2 + 4) and two open chain dimeric products. All four reactions were quenched by 1,2,4,5-tetramethoxybenzene. Comparison of the product distribution in the CdS-induced reaction with those obtained by using cyanoaromatic sensitizers showed that the CdS distribution fell within the range found in the homogeneous systems by varying the nature of the sensitizer and of the solvent. It can be concluded that in this system, at least, the fact of adsorption on the semiconductor surface plays a minor role in directing the nature of the products. One sample of CdS used, which was of high purity, appeared able, even when washed, to induce the acid-catalyzed "dark" dimerization of **1b**. This sample yielded, on irradiation, the same four dimeric materials obtained previously, together with 1,2-dimethyltetra-*p*-anisylethane.

Introduction

Although the study of photochemically induced electron-transfer organic reactions has received much attention in recent years the parallel study of the mediation of photostimulated semiconductors in such processes has attracted much less. Aside from oxidation/reduction processes,[2] examples of semiconductor induced reactions now include dimerization,[3,4] cis-trans isomerization,[5] va-

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