Reactions of N-(Arylsulfonoxy)-N-alkylbenzylamines with MeONa–MeOH. Steric Effect on the Structure of the Imine-Forming Transition State

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Abstract: Elimination reactions of N-(arylsulfonoxy)-N-alkylbenzylamines 1–5 with MeONa–MeOH have been studied kinetically. The elimination reactions are regiospecific, producing only corresponding benzylidenalkylamines. The rate equation for the reactions is $k_{obs} = k_0 + k_2[MeONa]$, indicating that the reactions proceed by competing solvolytic- and base-promoted pathways. The relative rates of elimination for the k_2 and k_0 pathways are 1, 0.67, 0.53, 0.35, and 0.27 for R = Me, Et, i-Pr, s-Bu, and t-Bu and 1, 4.1, 5.1, and 8.7 for R = Et, i-Pr, s-Bu, and t-Bu, respectively. For MeONa-promoted elimination from 1–5, Hammett ρ and k_H/k_D decrease but ρ_{lg} and $|\beta_{lg}|$ increase with a bulkier alkyl substituent. However, the values for the solvolytic eliminations are nearly the same for all substrates and are similar to those for the base-promoted pathway, except for the ρ values, which have opposite signs. From these results, the changes in transition-state structure wrought by variation of N-alkyl substituents are assessed.

In an earlier paper, we have demonstrated that the transition state for elimination from $ArCH_2N(X)CH_3$ can be shifted from E2-central toward the E1-like by utilizing a better leaving group and a weaker base.[1] The extent of C_β–H bond cleavage and negative charge density on the β-carbon decreased but the degree of N_α–X bond rupture increased when the leaving group was changed from Cl to OSO_2Ar and the base from MeONa to benzylamine. A similar change of the transition-state structure was also noted in eliminations from N-chloro-N-alkylbenzylamines, with the N-alkyl group varying from Me to Et, i-Pr, s-Bu, and t-Bu, although the change was only modest.[2,3] A bulky substituent appeared to hinder the approach of the base to the β-hydrogen, decreasing the extent of the C_β–H bond cleavage in the transition state. It is conceivable that the rupture of the N–Cl bond would increase as the proton transfer is lessoned by the steric effect. However, the effect of alkyl group steric bulk upon the N_α–X bond cleavage has not been determined.

To further expand our understanding of the steric effect on the imine-forming transition state, the reactions of N-(arylsulfonoxy)-N-benzylalkylamines 1–5 with MeONa–MeOH (eq 1) have now been studied. It has been shown that the transition-state structure for elimination from N-(arylsulfonoxy)benzylamine is very sensitive to the variation of the substrate structure and the reaction condition.[4]

$$XC_6H_4CL_2N(OSO_2C_6H_4Y)R + MeONa \xrightarrow{\text{MeOH}} XC_6H_4CL{=}NR$$

<div style="text-align:right">(1)</div>

    1: R = Me   6
    2: R = Et
    3: R = i-Pr
    4: R = t-Bu
    5: R = s-Bu

    a, X = H; Y = m-CF₃; L = H
    b, X = H; Y = m-CF₃; L = D
    c, X = p-CH₃; Y = m-CF₃; L = H
    d, X = p-Cl; Y = m-CF₃; L = H
    e, X = m-Br; Y = m-CF₃; L = H
    f, X = p-CN; Y = m-CF₃; L = H
    g, X = H; Y = H; L = H
    h, X = H; Y = p-Cl; L = H
    i, X = H; Y = 3,5-(CF₃)₂; L = H

Thus, it was expected that the transition state my be shifted toward borderline E1–E2 by the steric effect if a bulkier N-alkyl group were used in the N-(arylsulfonoxy)amine substrate. It was found in the present research that the reactions of 1–5 with MeONa–MeOH proceed via solvent- and base-promoted pathways. The alkyl steric effects on both of these reactions pathways are reported in this paper.

Results

N-(Arylsulfonoxy)-N-alkylbenzylamines 1–5 were prepared in situ from the reactions of the benzylalkylamines and arylsulfonyl peroxides in EtOAc at –78 °C.[1,5,6] Reactions of 1–5 with MeONa–MeOH produced only benzylidenalkylamines 6. Eliminations were followed by monitoring the appearance of the absorption at the λ_{max} for 6. Excellent pseudo-first-order kinetic plots that covered at least 2 half-lives were obtained. However, the change in the absorption (ΔA) for the reactions of 3i and 4i were so small that the rate constants could not be determined. The rate constants are listed in Tables S1–S9 in the supplementary material. For all substrates, the plots of k_{obs} vs [MeONa] were straight lines with positive intercept, except for 1 and 2f for which the intercepts were negligible. This indicates that the rate equation for the reactions of 1–5 is $k_{obs} = k_0 + k_2[MeONa]$ and $k_0 = 0$ for 1 and 2f. The slopes and intercepts of these straight lines were calculated by linear regression. The k_2 and k_0 values are listed in Tables I and II, respectively.

The k_2 decreased but k_0 increased with the increase in the steric requirement of the N-alkyl group. The relative rates of elimination for the k_2 and k_0 pathways are 1, 0.67, 0.53, 0.35, and 0.27 for 1a, 2a, 3a, 5a, and 4a and 1, 4.1, 5.1, and 8.7 and 2a, 3a, 5a, and 4a, respectively. Plots of log k_2 and the log k_0 vs Charton's ν and ν' values[7–10] are shown in Figures 1 and 2, respectively. The rate data correlated better with ν than ν' parameters, although the rate data for the k_0 path scattered significantly from the Charton plot.

The influence of aryl substituents X and Y in 1–5 upon the k_2 and k_0 values correlated with the Hammett equation with use of σ^- values (Figures 3–6). The plots of log k_2 and log k_0 vs $pK_{lg}^{CH_3}$ values[11] of the arylsulfonate leaving groups are depicted in Figures

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(3) Cho, B. R.; Suh, Y. W. J. Org. Chem. 1989, 54, 2855–2858.
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Table I. Second-Order Rate Constants k_2 (M^{-1} s^{-1})[a] for Eliminations from $XC_6H_4CL_2N(Y)R$[b] Promoted by MeONa–MeOH[c]

X	L	Y	R = Me	R = Et	R = i-Pr	R = t-Bu
H	H	m-CF$_3$	1.93 ± 0.01	1.30 ± 0.01	1.03 ± 0.01	0.522 ± 0.010
H	D	m-CF$_3$	0.542 ± 0.002	0.500 ± 0.02	0.448 ± 0.005	0.272 ± 0.004
p-Me	H	m-CF$_3$	1.30 ± 0.01	1.01 ± 0.01	0.719 ± 0.007	0.463 ± 0.020
p-Cl	H	m-CF$_3$	4.25 ± 0.02	2.74 ± 0.01	1.88 ± 0.02	1.10 ± 0.02
m-Br	H	m-CF$_3$	4.81 ± 0.02	2.77 ± 0.01	2.23 ± 0.02	1.11 ± 0.03
p-CN	H	m-CF$_3$	23.3 ± 0.5	11.8 ± 0.3	7.55 ± 0.20	2.85 ± 0.09
H	H	H	0.399 ± 0.003	0.283 ± 0.002	0.184 ± 0.003	0.0933 ± 0.0007
H	H	p-Cl	0.914 ± 0.004	0.699 ± 0.003	0.427 ± 0.006	0.273 ± 0.003
H	H	2,4-(CF$_3$)$_2$	9.04 ± 0.04	7.48 ± 0.04		

[a] k_2 = 0.669 ± 0.010 M^{-1} s^{-1} for **5a**. [b] [substrate] = 5.0×10^{-5} – 1.0×10^{-4} M. [c] [MeONa] = 1.70×10^{-3} – 3.40×10^{-2} M.
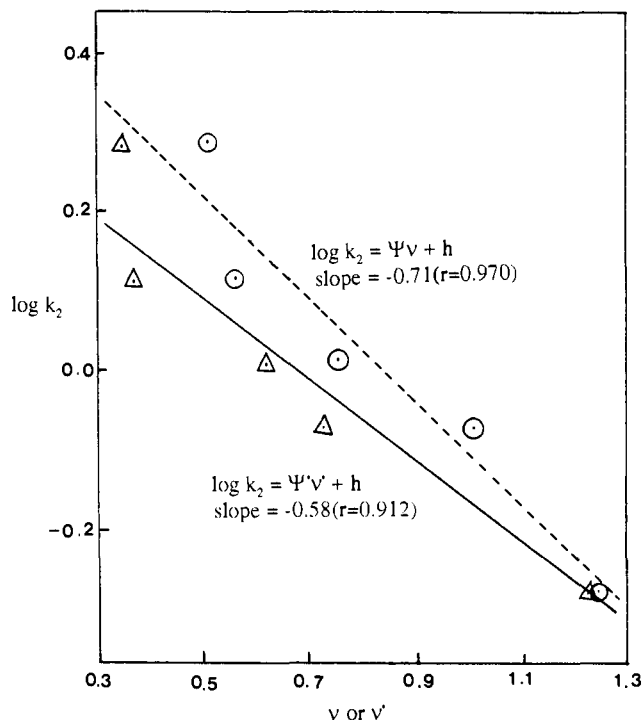
Figure 1. Charton's plot for MeONa-promoted eliminations from PhCH$_2$N(OSO$_2$C$_6$H$_4$-m-CF$_3$)R.
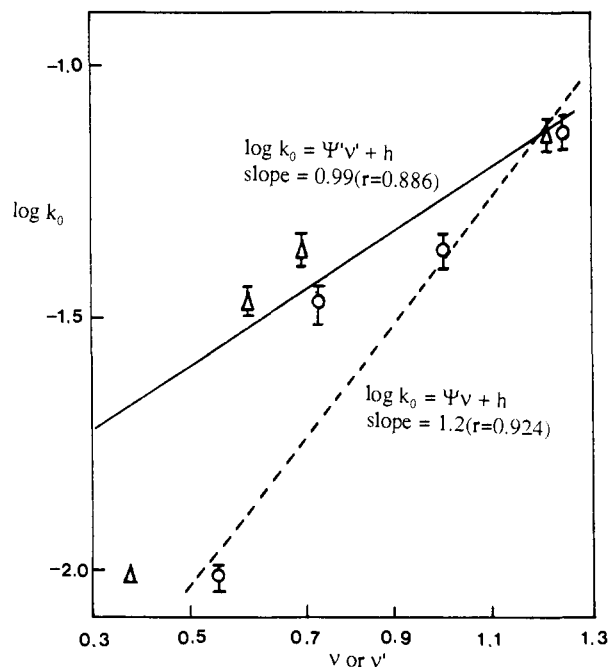
Figure 2. Charton's plot for solvolytic eliminations from PhCH$_2$N-(OSO$_2$C$_6$H$_4$-m-CF$_3$)R.

7 and 8. In all cases, the correlation of the plots for the solvolytic elimination is worse than that for the MeONa-promoted elimi-

Table II. Zero-Order Rate Constants k_0[a] (s^{-1})[b] for Eliminations from $XC_6H_4CL_2N(Y)R$ Promoted by MeONa–MeOH

X	L	Y	R = Et	R = i-Pr	R = t-Bu
H	H	m-CF$_3$	0.828 ± 0.300	3.40 ± 0.20	7.23 ± 0.30
H	D	m-CF$_3$	0.406 ± 0.050	2.56 ± 0.10	3.30 ± 0.10
p-CH$_3$	H	m-CF$_3$	1.20 ± 0.20	4.35 ± 0.20	10.9 ± 0.04
p-Cl	H	m-CF$_3$	0.953 ± 0.340	3.43 ± 0.50	6.30 ± 0.50
m-Br	H	m-CF$_3$	0.614 ± 0.200	3.20 ± 0.40	4.69 ± 0.70
p-CN	H	m-CF$_3$		3.15 ± 0.60	3.33 ± 0.30
H	H	H	0.118 ± 0.040	0.797 ± 0.060	1.13 ± 0.02
H	H	p-Cl	0.167 ± 0.070	1.12 ± 0.10	2.33 ± 0.06
H	H	2,4-(CF$_3$)$_2$	4.79 ± 0.90		

[a] Values are given as $10^2 k_0$. [b] k_0 = (4.20 ± 0.30) × 10^{-2} for **5a**. [c] [Substrate] = 5.0×10^{-5} – 1.0×10^{-4} M.

**Table III.** Transition-State Parameters for MeONa-Promoted Eliminations from ArCH$_2$N(OAs)R in MeONa–MeOH

R	ρ	k_H/k_D	$ρ_{lg}$	$β_{lg}$
Me	1.2 ± 0.1	3.6 ± 0.1	1.6 ± 0.1	−0.53 ± 0.01
Et	1.0 ± 0.1	2.6 ± 0.1	1.6 ± 0.1	−0.55 ± 0.01
i-Pr	0.95 ± 0.04	2.3 ± 0.1	1.7 ± 0.1[a]	−0.56 ± 0.04[a]
t-Bu	0.76 ± 0.07	1.9 ± 0.1	1.8 ± 0.1[a]	−0.57 ± 0.01[a]

[a] Calculated without the data for AsO⁻ = ⁻OSO$_2$C$_6$H$_3$-3,5-(CF$_3$)$_2$.

Table IV. Transition-State Parameters for Solvolytic Eliminations from ArCH$_2$N(OAs)R in MeONa–MeOH

R	ρ	k_H/k_D	$ρ_{lg}$	$β_{lg}$
Et	−0.42 ± 0.39	2.0 ± 1.0	2.0 ± 0.1	−0.66 ± 0.03
i-Pr	−0.10 ± 0.02	1.3 ± 0.1	1.4 ± 2.6[a]	−0.46 ± 0.89[a]
t-Bu	−0.42 ± 0.03	2.2 ± 0.2	1.9 ± 0.1[a]	−0.60 ± 0.08[a]

[a] Calculated without the data for AsO⁻ = ⁻OSO$_2$C$_6$H$_3$-3,5-(CF$_3$)$_2$.
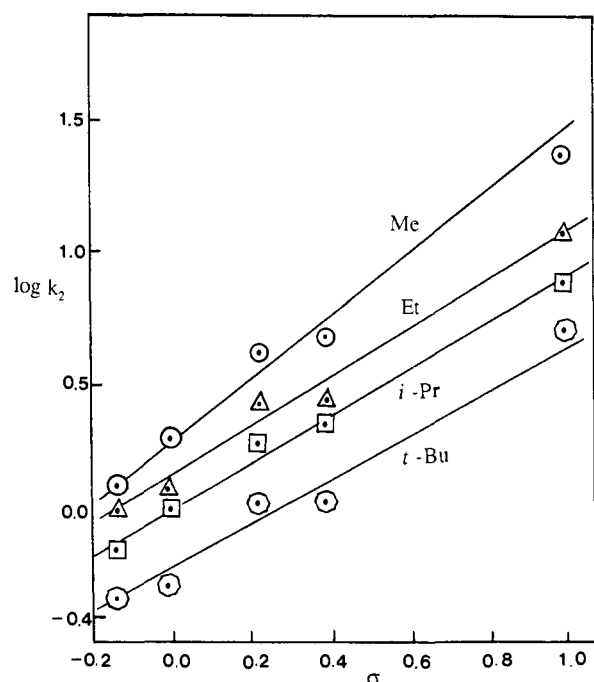
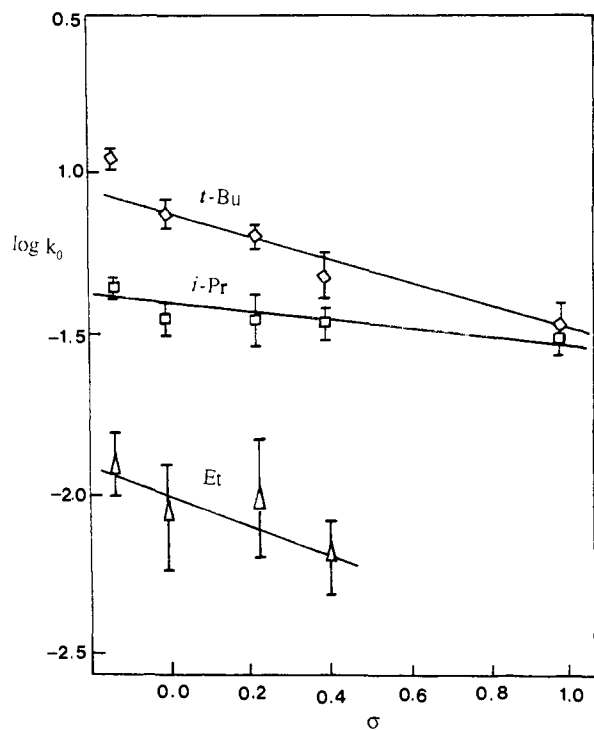**Figure 3.** Hammett plots for MeONa-promoted eliminations from $XC_6H_4CH_2N(OSO_2C_6H_4$-m-CF$_3)$R.

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Figure 4. Hammett plots for solvolytic eliminations from $XC_6H_4CH_2N$-$(OSO_2C_6H_4$-m-$CF_3)R$.

Figure 6. Hammett plots for solvolytic eliminations from $PhCH_2N$-$(OSO_2C_6H_4Y)R$.

Figure 5. Hammett plots for MeONa-promoted eliminations from $PhCH_2N(OSO_2C_6H_4Y)R$.
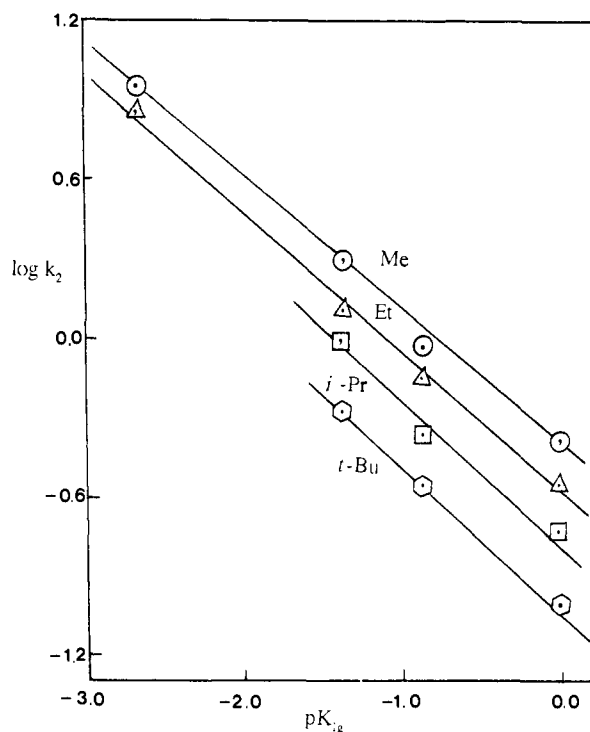
Figure 7. Bronsted plot for MeONa-promoted eliminations from $PhCH_2N(OSO_2C_6H_4Y)R$.

nation. Hammett ρ, ρ_{lg}, and $\beta_{lg}{}^{CH_3}$ values for the k_2 and k_0 paths are summarized in Tables III and IV, respectively.

From the rate coefficients for eliminations from **1–4a** and their deuterated analogues **1–4b**, the isotope effect values were calculated. The values are listed in Tables III and IV.

Discussion

Mechanism of Eliminations from 1–5. The mechanism of eliminations from **1–5** changes depending upon the N-alkyl and β-aryl substituent. It has been established that the reaction of **1** with MeONa–MeOH proceeds by an E2 mechanism.[1] However, for the reactions of **2–5** with MeONa–MeOH, the solvolytic
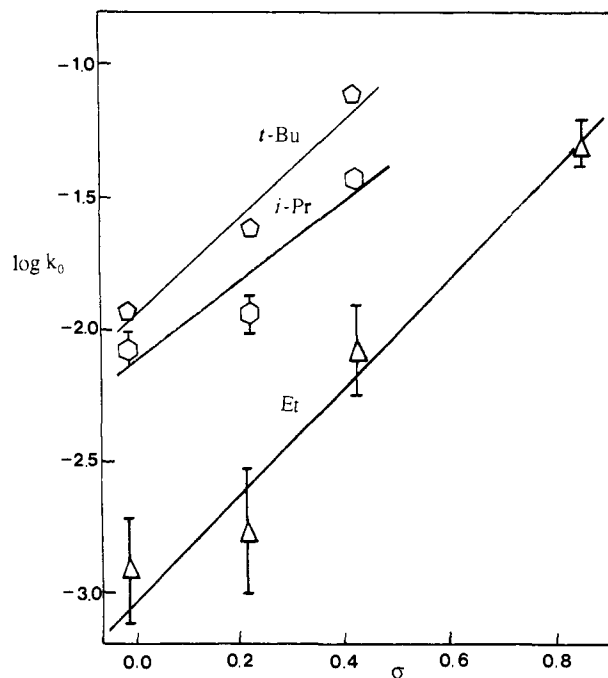
pathway competes with the MeONa-promoted elimination as indicated by the rate equation $k_{obs} = k_0 + k_2[\text{MeONa}]$. When the electron-withdrawing p-CN group is used, the solvolytic elimination of **2** becomes negligible.

Results of kinetic and product studies reveal that the MeONa-promoted eliminations from **2–5** proceed by an E2 mechanism. The reactions are second-order and produce benzylidenalkylamines **6** as the only product. Thus, all but bimolecular reaction pathways can be ruled out. In addition, an E1cB mechanism is negated by the substantial values of k_H/k_D and β_{lg} (Table IV).[12] An al-

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ternative mechanism is the one involving an ion pair (eq 2). If

$$HCNOSO_2Ar \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$$

$$HCN^{+-}OSO_2Ar \underset{k_2}{\overset{B}{\rightleftharpoons}} BH + \diagup C{=}N\diagdown + ArSO_3^- \quad (2)$$
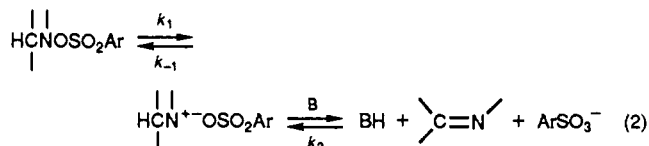
attack by base on the ion pair is rate-determining, the rate equation would become $k_{obs} = k_1k_2[B]/k_{-1}$, which is kinetically indistinguishable from that for the E2 reaction. However, this mechanism would require a negative ρ value because positive charge is developed in the transition state, which is opposite to what we have observed.

On the other hand, the solvolytic elimination appears to proceed by the ion pair mechanism (eq 2).[13] The observation of the negative ρ value (Table IV) rules out the E2 mechanism, for which a positive ρ value is expected (vide supra). The E1 mechanism can be negated by the absence of solvolysis products. In the solvolysis of N-[(p-nitrobenzyl)sulfonoxy]-p-methoxybenzylamine in ethyl acetate, Hoffman obtained p-methoxyaniline in 40% yield.[14] If the methanolysis of 2–5 proceeded via a nitrenium ion intermediate, O-methyl-N-alkyl-N-benzylhydroxylamine, alkylidenaniline, and/or aniline should have been observed. However, no trace of such products was detected in the GC–MS analysis of the product mixtures.

The rate-determining step of the reaction may be decided by the k_H/k_D, ρ, and $\beta_{lg}^{CH_3}$ values. The k_H/k_D values of 1.3–2.2 correspond to values of 1.14–1.48 per deuterium. The values are too large for a secondary β-deuterium isotope effect but within the range for the reversible formation of the contact ion pair followed by the rate-limiting deprotonation of the ion pair to the elimination product.[15–17] The ρ values of –0.1 to –0.46 observed in these reactions are consistent with this mechanism. For the solvolysis of 2-chloro-2-methyl-1-phenylpropane, a Hammett ρ value of –1.1 was observed.[18] Since the nitrenium ion intermediate is expected to be less stable than the tertiary carbocation, it should be more susceptible to the electron-donating ability of the aryl substituents. Therefore, a negative ρ value of greater magnitude should have been observed if the first step were rate-determining. Finally, the $\beta_{lg}^{CH_3}$ values of –0.60 to –0.66 for the solvolysis of 2 and 4 are similar to $\beta_{lg}^{CH_3} = -0.61$ calculated for the ethanolysis of 2-adamantyl arylsulfonate,[11] which is known to proceed by a limiting S_N1 reaction. This indicates a complete rupture of the N–leaving group bond in the transition state and is in full accord with the rate-limiting deprotonation of the ion pair intermediate.

Steric Effect on the Rate of Eliminations from 1–5. The rate of MeONa-promoted elimination from 1–5 decreased as the steric requirement of the N-alkyl group increased. The influence of the alkyl substituent upon the k_2 value correlated satisfactorily with the Charton equation with use of a ν value. Correlation of the rate data with ν rather than ν' values can be explained by considering the structure of the transition state (Chart I). As reported earlier, the rate of elimination from N-chloro-N-alkylbenzylamines correlated better with ν' values due to the similarity in the way in which the base and alkyl group interact in the transition states II and IV.[2] However, since the transition-state structure for the N-(arylsulfonoxy)amine elimination is looser with a smaller degree
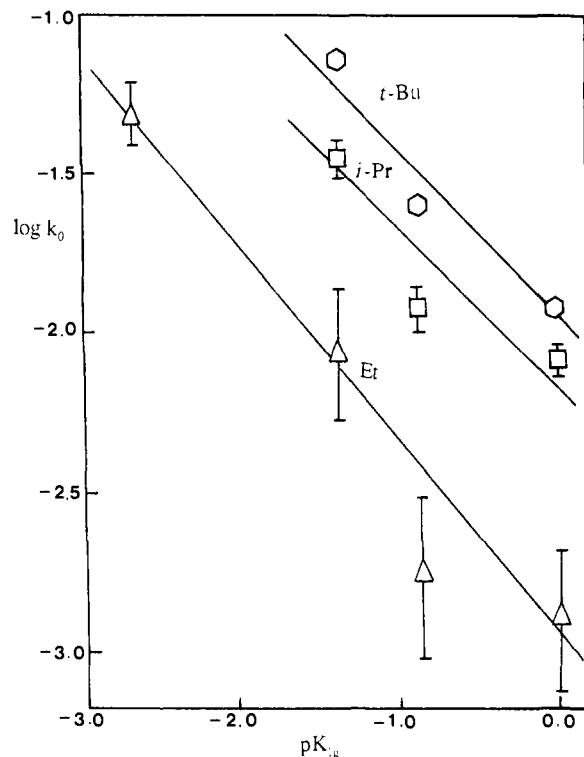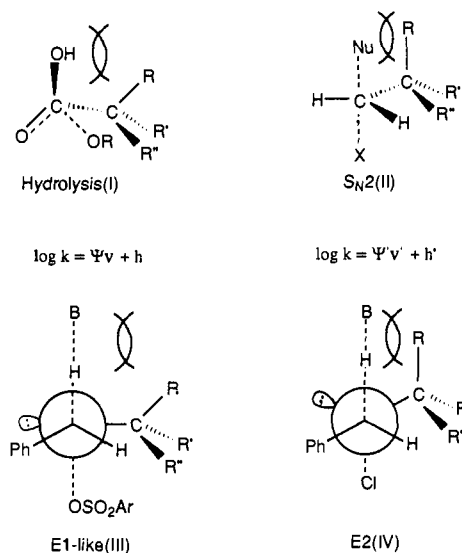
Figure 8. Bronsted plot for solvolytic eliminations from $PhCH_2N$-$(OSO_2C_6H_4Y)R$.

Chart I

Hydrolysis(I) S_N2(II)

$\log k = \Psi v + h$ $\log k = \Psi'v' + h'$

E1-like(III)   E2(IV)

of base–proton bond formation and a greater extent of N_α–X bond cleavage than that of the N-chloramine elimination,[1,4–6] the steric interaction between the base and the alkyl group in the former transition state III should be less than that in IV and appear more similar to that for the hydrolysis (I). Therefore, it is reasonable to expect that the rate of MeONa-promoted elimination should correlate with ν values.

The ψ values for imine-forming eliminations are quite sensitive to the structure of the transition states. Thus, the $|\psi|$ values for eliminations from 1–5 and N-chloramines are 0.71 and 2.11, respectively.[2] The smaller $|\psi|$ value for the former can be attributed to the smaller repulsive interaction between the base and the alkyl group in the looser transition state III (vide supra). In contrast, the ψ value for the solvolytic elimination from 2–5 is 1.2, indicating moderate rate enhancement with a bulkier substituent. To our knowledge, this is the first example of the steric acceleration observed in elimination reactions, although such an effect has already been noted in S_N1 reactions.[19] The positive

(13) A reviewer has suggested that the very low k_H/k_D values for the solvolytic eliminations may be consistent with an E1-like E2 transition state. However, the negative ρ and positive ψ values observed in these reactions are exactly opposite to those for MeONa-promoted elimination from 4, which is assumed to proceed by an extreme E1-like transition state (see text), even though the k_H/k_D values are similar. Therefore, an ion pair mechanism appears more consistent with the observed kinetic parameters.

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ψ value for the solvolytic reaction is consistent with the ion pair mechanism (eq 2). If the transition state resembles the contact ion pair, the repulsive interaction between the alkyl group and the leaving group in the reactant would be diminished in the transition state. Moreover, this effect would be more pronounced for a sterically more congested substrate. Therefore, the activation energy for the solvolytic elimination should decrease with a bulkier alkyl substituent to increase the rate.

Steric Effect on the Structure of Imine-Forming Transition State. For MeONa-promoted eliminations from 1–4, the k_H/k_D and ρ decreased but $|\beta_{lg}|$ and ρ_{lg} values increased as the steric requirement of the alkyl group increased. This indicates a decrease in the extent of C–H bond cleavage and negative charge development at the β-carbon and an increase in the N–leaving group bond rupture and the negative charge density on the leaving group oxygen atom in the transition state. Moreover, the transition-state parameters for the MeONa-promoted elimination from 4 (Table III) are similar to $k_H/k_D = 1.2$ and $\beta_{lg} = -0.55$ determined for the PhCH$_2$NH$_2$-promoted elimination from N-(arylsulfonoxy)-benzylamine, which is known to proceed via an extreme E1-like transition state.[6] Therefore, a shift of the transition state toward E1-borderline is clearly indicated by the increase in the alkyl group steric effect. It should be noted, however, that the change in the N$_\alpha$–leaving group bond cleavage with the N-alkyl group variation is smaller than that of the C$_\beta$–H bond rupture in the transition state as indicated by the smaller changes in $|\beta_{lg}|$ and ρ_{lg} than in ρ and k_H/k_D values (Table III). It appears that the instability of the nitrenium ion prevents the N$_\alpha$–OSO$_2$Ar bond from breaking further in the E2 transition state.

The transition-state parameters for the solvolytic eliminations from 2–4 are similar, implying similar transition-state structure.[20] The relative insensitivity of the transition-state structures for the solvolytic eliminations to the N-alkyl group variation may presumably be because the transition states closely resemble the intermediates, which are expected to have similar structures regardless of the nature of the N-alkyl group.

It is interesting to note that the transition-state parameters for the solvolytic and the MeONa-promoted eliminations from 2–5 are not very much different from each other, except for the ρ values, which have opposite signs. It appears that the transition-state structures for both of these reaction pathways are similar with respect to the degree of C$_\beta$–H and N$_\alpha$–X bond cleavage even though the mechanisms are different. The most significant difference is the nature of the charge developed in the transition state; i.e., positive charge is developed on the α-nitrogen in the former transition state, and negative charge is developed on the β-carbon in the latter transition state.

Experimental Section

Reagents. Benzylidenalkylamines (6) and benzylalkylamines were prepared as described previously.[2] Arylsulfonyl peroxides were prepared by known methods.[21,23] N-(Arylsulfonoxy)-N-benzylalkylamines 1–5 were prepared from arylsulfonyl peroxides and benzylamines in EtOAc at -78 °C according to the procedure of Hoffman.[5,6]

Kinetic Studies of Elimination from 1–5. Kinetic studies of elimination from 1–5 were carried out as before with a Perkin-Elmer 552 UV–vis spectrophotometer with thermostated cuvette holders.[1] 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 k_{obs}. Values of k_{obs} were determined at 8–10 base concentrations. Plots of k_{obs} vs [MeONa] were straight lines for all substrates. The rate constants for the solvolytic (k_0) and MeONa-promoted (k_2) eliminations were obtained from the intercept and the slope, respectively.

Product Studies of Eliminations from 2–4. For reactions of 2–4 with MeONa–MeOH, the yields of 6 determined by the absorbance of infinity samples from the kinetic reactions were 50–90%, based upon the starting arylsulfonyl peroxide.

The products of reactions of 2a–4a with MeONa–MeOH were identified with use of more concentrated solutions and gas chromatographic analysis outlined previously.[1] The products were benzaldehyde and benzylidenalkylamines 6. The yields of elimination products (benzaldehyde + 6) for 1a, 2a, 3a, and 4a were 92.7, 63.5, 61.9, and 50.1%, respectively, based on the starting peroxide. For reactions of 2a–4a, 36–50% of the unreacted benzylalkylamines were recovered.

Registry No. PhCH$_2$NHMe, 103-67-3; PhCH$_2$NHEt, 14321-27-8; PhCH$_2$NHPr-i, 102-97-6; PhCH$_2$NHBu-s, 46120-25-6; PhCH$_2$NHBu-t, 3378-72-1; CF$_3$-m-C$_6$H$_4$So$_2$OOSo$_2$C$_6$H$_4$-m-CF$_3$, 35673-10-0; D$_2$, 7782-39-0; p-CH$_3$C$_6$H$_4$CH$_2$NHMe, 699-04-7; p-CH$_3$C$_6$H$_4$CH$_2$NHEt, 39099-13-3; p-CH$_3$C$_6$H$_4$CH$_2$NHPr-i, 70894-75-6; p-CH$_3$C$_6$H$_4$CH$_2$NHBu-t, 55980-45-5; p-ClC$_6$H$_4$CH$_2$NHMe, 104-11-0; p-ClC$_6$H$_4$CH$_2$NHEt, 69957-83-1; p-ClC$_6$H$_4$CH$_2$NHPr-i, 40066-21-5; p-ClC$_6$H$_4$CH$_2$NHBu-t, 46234-01-9; m-BrC$_6$H$_4$CH$_2$NHMe, 67344-77-8; m-BrC$_6$H$_4$CH$_2$NHEt, 90389-91-6; m-BrC$_6$H$_4$CH$_2$NHPr-i, 10049-41-9; m-BrC$_6$H$_4$CH$_2$NHBu-t, 133042-85-0; p-CNC$_6$H$_4$CH$_2$NHMe, 34403-48-0; p-CNC$_6$H$_4$CH$_2$NHEt, 133042-86-1; p-CHC$_6$H$_4$CH$_2$NHPr-i, 91350-01-5; p-CNC$_6$H$_4$CH$_2$NHBu-t, 133042-87-2; PhSo$_2$OOSo$_2$Ph, 29342-61-8; p-Cl-C$_6$H$_4$SO$_2$OOSO$_2$C$_6$H$_4$-p-Cl, 1886-69-7; 3,5-(CF$_3$)$_2$C$_6$H$_3$SO$_2$OOSO$_2$C$_6$H$_3$(CF$_3$)$_2$-3,5, 80953-39-5.

Supplementary Material Available: Tables SI–SIX, listing observed rate constants for eliminations from XC$_6$H$_4$CH$_2$N-(OAs)R promoted by MeONa–MeOH (9 pages). Ordering information is given on any current masthead page.

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