In systems possessing a rigid torsional constraint, such as cation **2** and *trans*-1-thioniabicyclo[4.4.0]decane,[6] pyramidal ylides will be formed, giving rise to kinetic acidity differentials related to the energy differentials of the corresponding ylides. The PMO analysis above suggests that, although no single factor determines the relative energy of the ylides, the hyperconjugative $n_{C_\alpha}\sigma^*_{SC_{\alpha'}}$ interactions play a special role insofar as their trend is the same as that for the total energy. Since such interactions are at maxima when the n_{C_α} and the $S–C_{\alpha'}$ or $S–C_{\alpha''}$ bond orbitals are syn or anti aligned and the geometry of the ylide is very much the same as that of the cation precursor, it is often possible to guess, purely on geometrical grounds, which pair of ylides will enjoy greater hyperconjugative stabilization. That ylide is also likely to be the more stable one and the proton, whose removal gives rise to it, the more acidic. In the case of torsionally constrained ylides, the overall stereochemistry of products arising from their reaction with electrophiles will depend on (i) the ylide populations and (ii) the rates of ylide interconversions relative to their rate of reaction with electrophile. Lacking this kinetic information, the overall stereochemical course may not be simply related to the relative thermodynamic stability of the various ylides. A fortiori, a parallelism is not to be expected between kinetic acidity in one solvent (such as water) and stereochemistry of alkylation of ylides in another nonpolar solvent such as THF, where, in addition, the Li cation may complicate the issue by associating with the carbanionic carbon.[38,39] In view of the above, it is not surprising that a system such as **2**, while exhibiting highly stereoselective base-catalyzed H–D exchange in water,[9] undergoes nonstereoselective alkylation (LDA followed by CH_3I) in tetrahydrofuran.[37]

Registry No. $2\cdot BF_4^-$, 80996-27-6.

Supplementary Material Available: Talbes of positional and thermal parameters for hydrogen and for nonhydrogen atoms (Tables S1 and S2), structure amplitudes (Table S3), and molecular packing (Figure S1) (12 pages). Ordering information is given on any current masthead page.

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(39) Graham, S. L.; Heathcock, C. H. *Tetrahedron Lett.* **1980**, 5865.

Transition-State Structures of Base-Promoted, Imine-Forming Eliminations from *N*-Benzyl-*O*-(arylsulfonyl)hydroxylamines[1]

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Abstract: Eliminations in $XC_6H_4CH_2NHOSO_2C_6H_4Y$ promoted by amine bases were examined in 2.25 M H_2O in THF–EtOAc (3:1) and methanol. Transition-state parameters in methanol were found to be $\rho = 0.11$, $k_H/k_D = 1.2$, for the benzylic group and $\rho = 1.65$ for the leaving group. These data indicate that the polar solvent methanol causes an E1-like transition state in this elimination. Brønsted parameters were determined for both solvents and found to be $\alpha = 0.3$ and $\beta = 2.32$ for the former and $\alpha = 0.1$ and $\beta = 2.65$ for methanol. These parameters can be used to map the transition-state structure in a More-O'Ferrall–Jencks diagram. Values of β_{lg} for a variety of reactions are found to be a useful gauge of reaction type and leaving group loss in the transition state.

In an earlier paper it was established that *N*-benzyl-*O*-(arylsulfonyl)hydroxylamines, **3**, produced from the reaction of benzylamines, **1**, with arylsulfonyl peroxides, **2**, undergo base-promoted elimination of imines **4** (eq 1).[2] A variety of mechanistic

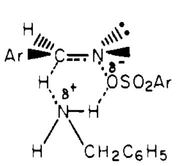
$$\underset{\textbf{1a–f}}{XC_6H_4CH_2NH_2} + \underset{\textbf{2a–e}}{(YC_6H_4SO_2O)_2} \rightarrow \underset{\textbf{3x,y}}{XC_6H_4CH_2NHOSO_2C_6H_4Y} \xrightarrow[k_2]{:B} \underset{\textbf{4}}{XC_6H_4CH{=}NH} + BH^+ + ArSO_3^- \quad (1)$$

1: **a**, X = H; **b**, X = *p*-CH_3; **c**, X = *m*-CH_3; **d**, X = *p*-Cl; **e**, X = *m*-Cl; **f**, X = *m*-CF_3

2: **a**, Y = *p*-NO_2; **b**, Y = *m*-CF_3; **c**, Y = *p*-Br; **d**, Y = H; **e**, Y = 3,5-$(CF_3)_2$

probes indicated that the transition state is E1-like in that the loss of the arylsulfonate leaving group is well-advanced while benzylic proton removal lags behind.[1c]

Several interesting features were noted for this elimination. In the first place it exhibits a rather large, negative entropy of activation, which is significantly more negative than other common E2 types. Since benzylamine was used as the promoting base, hydrogen bonding between the promoting base and the anionic leaving group via a cyclic, syn-transition state, **5**, would result in



5

a highly ordered transition state and a large negative activation entropy.[3] Alternatively, the elimination is of an unusual charge type—neutral reactants giving charged products.[4] Since the transition state would be more charged than the reactants, electrostatic solvation of the transition state and consequent solvent

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(1) (a) Taken in part from the Ph.D. Thesis of ELB submitted to the Graduate School of New Mexico State University, May 1981. (b) Presented in part at the 179th Meeting of the American Chemical Society, Houston, Texas, March, 1980, (c) Part 6 in "The Oxidation of Amines with Sulfonyl Peroxides"; for part 5 see: Hoffman, R. V.; Belfoure, E. L. *J. Am. Chem. Soc.* **1979**, *101*, 5687–5691.

(2) Hoffman, R. V.; Cadena, R. *J. Am Chem. soc.* **1977**, *99*, 8226–8232.

(3) Harris, J. M.; Wamser, C. C. "Fundamentals of Organic Reaction Mechanisms"; Wiley; New York, 1976; pp 108–110.

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Table I. Temperature Dependence of the Second-Order Rate Constants for Imine-Forming Elimination in 3a,b

	solvent		
	2.25 M H_2O-THF·EtOAc		CH_3OH
temp, °C	benzylamine[a]	Et_3N[a]	benzylamine[a]
−10	4.46×10^{-3}	1.98×10^{-2}	2.64×10^{-4}
0	1.11×10^{-2}	4.74×10^{-2}	4.55×10^{-4}
10	2.46×10^{-2}	9.39×10^{-2}	1.08×10^{-3}
20	5.18×10^{-2}	1.90×10^{-1}	2.80×10^{-3}

[a] Promoting base.

ordering might account for the more negative entropy.[4,5] Regardless of the origin of the entropy loss, the charge type of this elimination is little studied,[4] and it might be expected that solvent effects would be very pronounced. The present system provides a convenient and thorough way to evaluate the role of solvent in these reactions.

A second useful feature of imine-forming eliminations in *N*-benzyl-*O*-sulfonylhydroxylamines is that they proceed readily under the influence of amine bases. With use of a series of amine bases of known pK_a's and use of a series of arylsulfonate leaving groups, the Brønsted coefficients α and β_{lg} respectively can be determined and used in a reaction coordinate diagram[6] (More-O'Ferrall–Jencks diagram) to further define the transition-state structure. We wish to present the results of studies on imine-forming eliminations which address these points.

Results

Cyclic Transition State. When benzylamine is treated with *m*-(trifluoromethyl)benzenesulfonyl peroxide, *N*-benzyl-*O*-(*m*-(trifluoromethyl)benzenesulfonyl)hydroxylamine, **3a,b**, is produced. Addition of excess benzylamine promotes elimination to benzaldimine, **4a**. The activation parameters determined previously for this reaction in 2.25 M H_2O in THF–ethyl acetate (3:1) were $\Delta H^\ddagger = 12.0 \pm 0.1$ kcal/mol and $\Delta S^\ddagger = -23.5 \pm 0.3$ eu.[1c] Triethylamine was used as the promoting base in the same solvent, and from the rate data in Table I, the activation parameters were $\Delta H^\ddagger = 11.0 \pm 0.1$ kcal/mol and $\Delta S^\ddagger = -24.4 \pm 0.3$ eu. The similarity of the activation entropy of the base benzylamine, which is capable of H bonding with the leaving group as in **5**, to that of the base triethylamine, which is not capable of such interaction, discounts the involvement of a cylic transition state in this elimination. Therefore, solvation effects probably account for the large negative activation entropy.

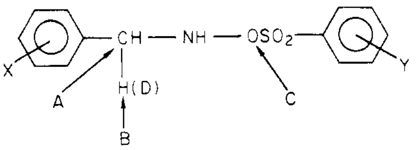
Solvent Effects on Transition-State Structure. Our earlier work on imine-forming eliminations utilized 2.25 M aqueous THF–ethyl acetate (3:1) (TEW) and 3.0 M aqueous THF as solvents.[1c,2] These mixtures contained 4.05% water and 5.4% water, respectively, and had calculated dielectric constants of $D = 10.2$ and $D = 11.6$, respectively.[7] For determination of the effects of a more polar solvent, methanol ($D = 32.6$) was used as the reaction medium. While the dielectric constant is a poor predictor of microscopic solvent behavior, other empirical solvent parameters such as Z, $E_T(30)$, and Y values[8] support the contention that methanol is significantly more polar than the aqueous mixtures used in our earlier work. Specific solvent parameters are not available for TEW or 3 M H_2O in the THF, but comparable aqueous acetone and dioxane solvent mixtures might serve as models since the organic components are all oxygenated solvents with similar polarities as neat liquids.[8] With these analogies, methanol is shown to be appreciably more polar than the above aqueous mixtures.

Table II. Rate Constants for Base-Promoted Eliminations in 3x,y in Methanol

		temp, °C ± 0.02		
entry	substrate	−10	10.0	20.0
1	3a,b	6.36×10^{-4} [a]	5.80×10^{-2} [a]	2.25×10^{-3} [b]
	3b,b	6.03×10^{-4} [a]	4.87×10^{-2} [a]	2.14×10^{-3} [b]
	3e,b	6.05×10^{-4} [a]	6.59×10^{-2} [a]	2.46×10^{-3} [b]
	3f,b	8.6×10^{-4} [a]	8.64×10^{-2} [a]	2.51×10^{-3} [b]
2	3a,d	4.27×10^{-5} [b]		4.2×10^{-4} [b]
	3a,b	2.43×10^{-4} [b]		2.25×10^{-3} [b]
	3a,e	6.05×10^{-4} [b]		1.1×10^{-2} [b]

[a] Using pyrrolidine as promoting base. [b] Using benzylamine as promoting base.

The transition-state parameters for base-promoted, imine-forming eliminations in hydroxylamine adducts **3x,y** were determined in methanol. Rates were monitored conductometrically.[2] By appropriate choice of amine and peroxide components of eq 1, it was possible to determine: A, the Hammett ρ value for charge development at the benzylic position; B, the kinetic deuterium isotope effect for proton removal; and C, the Hammett ρ value for charge development on the leaving group.



3X,Y

The rates of bimolecular elimination in substituted *N*-benzyl-*O*-(*m*-(trifluoromethyl)benzenesulfonyl)hydroxylamines, **3x,b**, were measured in methanol and the bimolecular rate constants, k_2, are given in Table II, entry 1. The previous studies[1c] were carried out at −10 °C, but it was found that the rates in methanol at −10 °C were quite slow and the infinity points difficult to determine accurately. Therefore, reactions were also studied in methanol at +10 °C and +20 °C where the kinetics were much smoother and more reliable.

Hammett plots of the rate data in Table II, entry 1, are not conclusive at −10 °C, $\rho = 0.14$ ($r = 0.58$) and only somewhat better at +10 °C, $\rho = 0.32$ ($r = 0.91$). Pyrrolidine was used as the promoting base in these series. The only conclusion that can be made from the above data is that the benzylic ρ value is low, since when pyrrolidine is used to promote elimination in TEW, $\rho = 0.84$ ($r = 0.98$). At +20 °C, with benzylamine as the promoting base in methanol, $\rho = 0.11$ ($r = 0.99$) which indicates minimal charge development at the benzylic position in the transition state. The corresponding value in TEW is $\rho = 0.68$.[1c]

The rate constants for elimination in *N*-benzyl-*O*-(*m*-(trifluoromethyl)benzenesulfonyl)hydroxylamine, **3a,b**, and its α,α-d_2 analogue were found to be 2.43×10^{-3} and 2.02×10^{-3} M^{-1} s^{-1}, respectively, at 20 °C in methanol. The kinetic deuterium isotope effect for proton removal is thus $k_H/k_D = 1.21$. Since the elimination in methanol is first order in both base and substrate, proton removal is involved in the transition state so this value probably represents a very low primary kinetic isotope effect.

Arylsulfonyl peroxides, **2b,d,e**, were reacted with excess benzylamine, and the resulting hydroxylamine adducts underwent elimination. Hammett plots for data at −10 and 20 °C (Table II, entry 2) gave $\rho = 1.34$ ($r = 0.984$) and $\rho = 1.65$ ($r = 0.999$) respectively. As noted above the data at 20 °C are more reliable and the ρ-value indicates a significant amount of charge development on the leaving group in the transition state.

Activation parameters were measured for adduct **3a,b** by carrying out rate studies in methanol over a 30 °C temperature range from −10 to +20 °C. Plotting the rate data in Table I by the Eyring equation gave $\Delta H^\ddagger = 14.5 \pm 0.3$ kcal/mol and $\Delta S^\ddagger = -34.8 \pm 1$ eu.

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(5) Amis, E. S.; Hinton, J. F. "Solvent Effects on Chemical Phenomena"; Academic Press: New York, 1973; pp 300–306.

(6) (a) Jencks, W. P. *Chem. Rev.* **1972**, *72*, 705–718. (b) Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry"; Harper and Row: New York, 1976; pp 246–250. (c) More-O'Ferrall, R. A. *J. Chem. Soc. B* **1970**, 247–277. (d) Jencks, D. A.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 7948–7960.

(7) Lewis, F. D.; Ho, T.; Devoe, R. J. *J. Org. Chem.* **1980**, *45*, 5283–5287.

(8) Kosower, E. M. "An Introduction to Physical Organic Chemistry"; Wiley; New York, 1968; pp 293–315. This section contains several tables of solvent parameters from which this analogy was derived. References to the primary literature are also given.

Table III. Rate Constants for Base-Promoted Elimination in *n*-Benzyl-*O*-(arylsulfonyl)hydroxylamines for Various Bases

		2.5 M H_2O–THF–EtOAc (−10 °C)		CH_3OH	
base	pK_a	3a,a	3a,b	3a,b (−10 °C)	3a,b (20 °C)
benzylamine (6a)	9.33	8.5×10^{-3}			
cyclohexylamine (6b)	10.66	1.3×10^{-2}			
n-butylamine (6c)	10.77	1.61×10^{-2}			
diethylamine (6d)	11.09	4.15×10^{-2}			
morpholine (6e)	8.33	1.61×10^{-2}	9.44×10^{-3}	3.12×10^{-4}	5.5×10^{-3}
pyrrolidine (6f)	11.27	1.07×10^{-1}	7.07×10^{-2}	5.95×10^{-4}	1.17×10^{-2}
piperidine (6g)	11.12	5.96×10^{-2}		7.25×10^{-4}	9.95×10^{-3}
N-methylbenzylamine (6h)	9.60		1.30×10^{-2}	5.14×10^{-4}	7.41×10^{-3}
triethylamine (6i)	11.01	2.12×10^{-2}			
pyridine (6j)	5.21	6.02×10^{-4}			
tert-butylamine (6k)	10.83	9.01×10^{-3}			
di-*n*-butylamine (6l)	11.25	4.03×10^{-2}			
diisopropylamine (6m)	11.13	7.00×10^{-3}			
tri-*n*-butylamine (6n)	10.89	1.5×10^{-2}			
2,6-dimethylpyridine (6o)	6.60	7.38×10^{-4}			

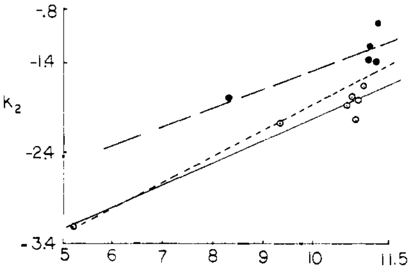

Figure 1. Brønsted plot of the bimolecular rate constants (log k_2) vs. pK_a for base-promoted elimination in **3a,a** in TEW at −10 °C. Open circles (○) are for primary and tertiary amines in Table IV, and closed circles (●) are for secondary amines. Line (---) is a linear fit to all points while the lines (—) and (– –) are linear fits for primary–tertiary and secondary amines, respectively.

Brønsted Studies. A series of amine bases was used to promote elimination in adducts **3a,a** and **3a,b** in TEW at −10 °C and adduct **3a,b** in methanol at −10 °C and 20 °C. The rate constants and pK_a's are given in Table III. A Brønsted plot for adduct **3a,a** is shown in Figure 1. Disregarding two sterically bulky amines, diisopropylamine, **6m**, and 2,6-dimethylpyridine, **6p**, which have obviously low rate constants, the slope of the Brønsted plot gave $\alpha = 0.29$ ($r = 0.83$). Scrutiny of the data reveals, however, that there appear to be two separate correllations. Primary and tertiary amines fall on one line, $\alpha = 0.24$ ($r = 0.98$), and secondary amines fall on a second line, $\alpha = 0.20$. The adduct **3a,b** under the same conditions gave $\alpha = 0.30$ ($r = 0.96$), using only secondary amines to promote the elimination.

The appearance of two or more lines of equal slope is not unusual in Brønsted studies utilizing amine bases in aqueous solution.[9] This is normally attributed to differences in solvation via H bonding of the corresponding ammonium ions of primary, secondary and tertiary amines[10] (the amines themselves have similar solvation energies[11]). The solvent system employed is sufficiently aqueous that these solvation differences are expressed as multiple lines. That primary and tertiary amines fall on the same line is probably fortuitous.

Application of pK_a values of amines, determined in aqueous solution, in Brønsted studies using the mixed and alcohol solvents of this work has much experimental justification. Aqueous pK_a values for amine bases have been plotted vs. pK_a values of the same bases in certain nonaqueous solvents, and excellent linear relationships are found.[12] Likewise, linear relationships are found for the pK_a values of amines in water and alcohols.[13] Thus although the actual pK_a values in the present solvents are probably not equal to the aqueous pK_a values, the α values are not affected significantly.[14]

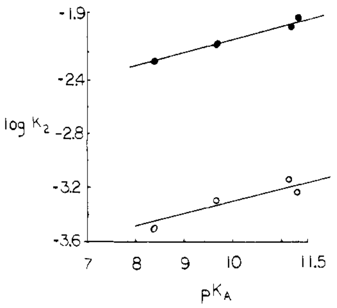

Figure 2. Brønsted plot for elimination in **3a,b** in methanol at −10 °C (○) and 20 °C (●) promoted by secondary amines.

Table IV. Products From 3a,b at 20 °C with Benzylamine as the Promoting Base

		promoting base		
entry	solvent	base equiv	% C_6H_5-CHO[a]	% C_6H_5-NH_2[a]
1	TEW[b]	6	29	0
2	CH_3OH	3.5	36	14
3	CH_3OH	6	44	11
4	CH_3OH	12	52	6

[a] Average values from two or more identical runs. [b] 2.25 M H_2O in THF–ethyl acetate (3:1).

Elimination in adduct **3a,b** promoted by secondary amines in methanol at −10 and +20 °C yielded $\alpha = 0.10$ ($r = 0.94$) and $\alpha = 0.10$ ($r = 0.98$), respectively (Figure 2). These results indicate much less benzylic proton removal in methanol than in the aqueous THF–ethyl acetate system. These results, corroborate the much lower benzylic ρ value and k_H/k_D value in methanol (vide supra). It is also seen from the correlation coefficients that the results in methanol at −10 °C are less precise than at 20 °C.

Product Studies. The reaction products of adduct **3a,b** were determined by using benzylamine as the promoting base and by using higher concentrations to permit analysis. The reaction mixture was hydrolyzed in acid and the benzaldehyde analyzed by gas chromatography. The acidic hydrolysis residue was ba-

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(9) (a) Bell, R. P. "The Proton in Chemistry", 2nd ed.; Cornell University Press: Ithaca, NY, 1963. (b) Jencks, W. P. "Catalysis in Chemistry and Enzymology"; McGraw-Hill: New York, 1969.

(10) Trotman-Dickenson, A. F. *J. Chem. Soc.* **1949**, 1293–96. Evans, A. G.; Harmen, S. D. *Trans. Faraday Soc.* **1951**, *47*, 34–37.

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(12) Trotman-Dickenson, A. F.; Bell, R. P. *J. Chem. Soc.* **1949**, 1288–1293. Bell, R. P.; Bayles, J. W., Jr. *Ibid.* **1952**, 1518–1522.

(13) Goldschmidt, H.; Mathiesen, E. *Z. Phys. Chem.* **1926**, *119*, 439–442.

(14) See Bronsted, J. N.; Nicholson, A. L.; Belbonco, A. *Z. Phys. Chem.* **1934**, *169A*, 379–384 and references therein for example.

Table V. Transition-State Parameters for the Benzylamine-Promoted Elimination in Hydroxylamine **3a**,b in TEW[a] and Methanol

parameter	TEW[1c] (−10 °C)	MeOH (20 °C)
benzylic ρ	0.68[b]/0.84[c]	0.11/0.32[c]
k_H/k_D	4.2[b]	1.2
ρ-leaving groups	1.32[b]	1.65
Brønsted α	0.30	0.10
$\Delta H^\ddagger$	11.7[b] ± 0.1 kcal/mol	14.5 ± 0.3 kcal/mol
$\Delta S^\ddagger$	−25.0[b] ± 0.3 eu	−34.8 ± 1 eu

[a] 2.25 M H_2O in ThF–ethyl acetate (3:1). [b] From ref 1c. [c] Using pyrrolidine as the promoting base.

sified, and the amine fraction was also analyzed gas chromatographically. The results are presented in Table IV.

The yields of benzaldehyde are predictably low since we showed earlier that the first formed imine product decomposes significantly at the temperatures employed here.[15] Of greater interest is the formation of aniline which results from carbon-to-nitrogen migration of the phenyl group. Aniline is only produced in methanol solvent, and its yield varies inversely with the amount of catalyzing base.

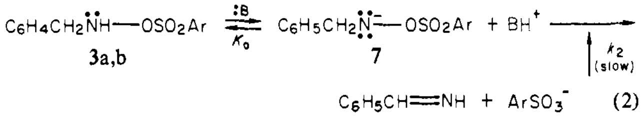
Discussion.

Transition States. The present study was undertaken to delineate factors which influence transition-state structures in imine-forming eliminations. From previous work it is clear that in *N*-benzyl-*O*-(arylsulfonyl)hydroxylamines, the transition state is skewed toward the E1 mechanistic extreme. The removal of the benzylic proton is significant, but loss of leaving group is the leading feature, and π-bond formation is probably well developed.[1c] The elimination is characterized by a rather low activation enthalpy and a high negative activation entropy. The origin of entropy loss at the transition state could be due to increased solvent organization around the polar transition state or to a cyclic transition state as shown in **5**. Since both triethylamine and benzylamine as promoting bases give the same activation entropy, it is possible to discount the cyclic **5** as a transition state.

Thus solvent organization around the transition state is a very important factor in the reaction energetics. This is not unexpected since neutral reactants yield charged products in these eliminations. To the extent that the transition state develops charged character, solvation of the transition state becomes quite important. It also follows that changes in solvent may affect the structure and energy of the transition state profoundly. Recent work on the Menschutkin reaction, an S_N2 displacement reaction of the same charge type, has shown that solvation forces are the dominant constituents in the free energies of activation and reaction.[16]

Comparison of transition-state parameters for **3a**,**b** in TEW and methanol reveal that the solvent does in fact play a crucial role in determining these descriptors (Table V). The data for methanol were obtained at +20 °C where the kinetics are more reliable while those in TEW are for −10 °C. However, there is no significant changes in these values between −10 and +20 °C in methanol so that the comparison remains valid. The change to the more polar solvent methanol results in an even greater skewing toward an E1 mechanism. The reaction is still bimolecular, but removal of the benzylic proton by base is minimal as evidenced by the low charge buildup on the benzylic position, the low kinetic isotope effect, and the low Brønsted coefficient. Using the stronger base pyrrolidine results in increased benzylic charge, but the extent is much less in methanol than TEW. Conversely, leaving group removal is more advanced in the more polar solvent as indicated by increased charge (ρ value) on the leaving group. Since the amount of proton removal is smaller in methanol, the amount of π bonding is also probably lower. Thus the more polar solvent increases the ionic character of the transition state. π-Bond formation, which might be considered a nonpolar feature of the transition state, is diminished in the more polar solvent.

The product studies rule out the possibility that in methanol the mechanism changes to an α elimination (eq 2). Such a mechanism would involve hydrogen migration in a nitrene/nitrenoid intermediate.[17] With use of the steady-state approximation, it is seen that the rate equals K_ak_2[B][A] for a fast preequilibrium, K_a; thus second-order kinetics would obtain. The transition-state parameters, particularly the low kinetic deuterium isotope effect, could fit this model also. The presence of aniline in the products implies that phenyl migration is competetive with hydrogen migration. This would also expected for a nitrenoid mechanism where migratory preferences are known to be small.[17]



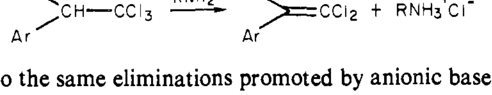
3a,b **7** (2)

However, product partitioning between hydrogen and phenyl migration takes place in the decomposition of intermediate **7** and must therefore be independent of the base concentration. The results of the product studies indicate that the amount of phenyl arrangement is dependent on the base concentration and thus an α elimination is highly unlikely.

The product studies, in which small (6–12 equiv) excesses of base were used, can be more reasonably interpreted in terms of competing bimolecular elimination (E2) and unimolecular, cationic rearrangement of **3** (E1). Increasing the base concentration increases the rate of the bimolecular elimination at the expense of unimolecular phenyl rearrangement. The kinetic studies reported here utilized much larger excesses of base (50–75 equiv). It is therefore safe to assume that negligible rearrangement would be observed under the conditions of the kinetic studies.

The production of aniline in methanol, but not in TEW, is also supportive of the change in transition-state structure toward the E1 extreme. Phenyl rearrangement can be considered an "E1 product" and is seen in the solvent which also yields transition-state parameters which are more E1-like.

The activation parameters are consistent with the above interpretation. The increase in $\Delta H^\ddagger$ in methanol is probably due to the combination of greater breaking of the bond to the leaving group and less base–proton bond and π-bond formation. The entropy decrease can be attributed entirely to solvent reorganization.[16] Furthermore, it is reasonable to assert that nearly all of the entropy change is associated with solvent reorganization around the partially charged leaving group, the major component of which is most likely H bonding. Support for this claim is found in Table V where it is seen that the decrease in entropy is related to increased charge on the leaving group; the decreased charge at the benzylic position should lead to lowered electrostatic solvation and a less negative entropy of activation. Since TEW is a mixed solvent system, it is quite likely that some solvent sorting (preferential solvation by the more polar component) around the transition state takes place.[5,8,18] It is therefore not appropriate to attempt to correlate structure with macroscopic solvent parameters.



(3)

Eliminations of the charge type studied here are rare in the literature. The most complete work is that on amine-promoted eliminations in 2,2-diaryl-1,1,1-trichloroethanes (eq 3).[19] Compared to the same eliminations promoted by anionic bases, these

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Table VI. pK_a Values of Arylsulfonic Acids in Sulfuric Acid

	substituent	$-\mathrm{p}K_a$	σ
measured[a]	-H	6.65	0
	m-CH_3	6.56	−0.07
	p-CH_3	6.62	−0.17
	p-Br	6.86	0.23
	m-SO_3H	7.0 (±0.2)	0.56
calculated	m-NO_2	7.10	0.71
	p-NO_2	7.15	0.78
	m-CF_3	6.93	0.43
	3,5-di-CF_3	7.20	0.86

[a] Reference 24.

charge-producing eliminations have low (~8 kcal/mol) activation energies and very negative activation entropies (~−50 eu). Furthermore, the change to amine bases causes reduced proton removal at the transition state. These trends parallel the results reported here. Finally, the amine-promoted DDT eliminations (eq 3) are very sensitive to the polarity of the solvent; however, more polar environments from salt additions cause significant *increases* in rate.[19] This observation is, at the moment, unexplained.

It does, however, emphasize the need to consider solvent contributions in discussions of transition states. As noted for displacement reactions,[16,18c] the role of solvent is often neglected when discussing reaction energetics, yet it is becoming clear that solvation can be a crucial factor in reactivity differences. For example, analyses of leaving group effects such as tosylate:bromide rate ratios in E2 eliminations usually neglect solvation of the leaving group at the transition state.[20] The conclusions that have been reached concerning bond-making, bond-breaking processes are valid only if leaving-group solvation changes are similar. Since this is probably not the case,[16,18] such conclusions are actually speculative, and this work points out the need to address the role of solvent in more detail.

Brønsted Studies. The discussion of transition-state structures in biomolecular eliminations is aided considerably by the use of More-O'Ferrall–Jencks diagrams[6] which are projections of the energy surface for elimination reactions. A great deal of qualitative use has been made of these diagrams in describing parallel and perpendicular shifts of transition-state structure[20b,c,21] for eliminations. Two bonding parameters describe the progression of reactants to products. The C–H bond is one coordinate, and the L–X bond to the leaving group is the other. The transition state for an elimination can be moved parallel to the concerted diagonal or perpendicular to it. The amount and direction of movement depend on structural and electronic features in the reactants which can change the relative energies of products and/or intermediates.[20b]

Using typical transition-state descriptors, it is easy to show relative differences between transition states for elimination reactions, but the actual position on the MOFJ diagram is not accessible because the descriptors are not absolute (i.e., the upper limits are not known) or because descriptors measuring charge buildup are not necessarily related directly to the extent of bond cleavage.[22] Parameters which are available and which have a finite range (0–1) mechanistically are Brønsted coefficients. These have been very useful when applied to MOFJ diagrams for a variety of reactions.[6,23] We have determined the Brønsted coefficients of proton removal for imine-forming eliminations to be $\alpha = 0.24$ for **3a,a** and $\alpha = 0.30$ for **3a,b** in TEW. In methanol the value for **3a,b** is $\alpha = 0.1$.

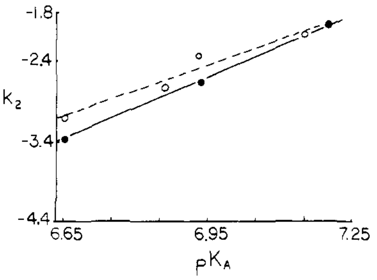

Figure 3. Brønsted plot for elimination in **3** incorporating various arylsulfonate leaving groups in TEW (○, ---) and methanol (●, —).

To obtain the Brønsted coefficients for loss of leaving group β_{lg}, the pK_a values for the arylsulfonate leaving groups are needed. These have been determined for arylsulfonic acids by the Hammett method in sulfuric acid solution by Cerfontain and appear in Table VI.[24] The method used yields pK_a values extrapolated to dilute aqueous solution. A Hammett plot of these data gave $\rho = 0.61$ ($r = 0.96$) from which were calculated the pK_a values of the other arylsulfonic acids used in the present study. These calculated values are also found in Table VI. Brønsted plots of the rates for elimination vs. the pK_a of the arylsulfonic acid are shown in Figure 3. In TEW at −10 °C the Brønsted coefficient $\beta_{\mathrm{lg}} = 2.19$ while in methanol at 20 °C, $\beta_{\mathrm{lg}} = 2.58$. These β_{lg} values are outside the normal range (0–1) for Brønsted coefficients. Brønsted coefficients greater than unity for proton transfer have been observed in some systems.[25] However, in many examples where explusion of a leaving group is part of the rate-determining step, β_{lg} is found to be greater than one.[26] The Brønsted coefficient measures the relative sensitivity of polar substituents to the energy required to develop some negative charge on the leaving group at the transition state (log k) compared with that required to develop negative charge by loss of a proton (pK_a). Comparing these processes in eq 4 and 5, in order for β_{lg} to fall between the limits of zero and one, then the reactant and product of Equation 5 must serve as accurate models for the energy extremes needed to achieve the transition state in eq 4. Since R, from which the leaving group is lost, is *not* a proton, the bond strengths and stabilities of the transition state may not be well modeled by a proton. Additionally, the solvation of the transition state of eq 4 might suffer due to steric effects of R, relative to solvation of the sulfonate anion in eq 5. This latter factor may be extremely important in the present case as determined by the high entropy of activation.

$$\mathrm{R{-}OSO_2Ar} \rightarrow [\mathrm{R}^{\delta+}\text{- - -}{}^{\delta-}\mathrm{OSO_2Ar}]^{\ddagger} \rightarrow \mathrm{R}^+ + {}^-\mathrm{O_3SAr} \quad (4)$$

$$\mathrm{H{-}OSO_2Ar} \rightleftarrows \mathrm{H}^+ + {}^-\mathrm{O_3SAr} \quad (5)$$

In order to establish some yardstick for the extent of cleavage of the bond in the leaving group, we have chosen to calculate β_{lg} for several model reactions. (Of course, ρ values for leaving groups (ρ_{lg}) could also be used; β_{lg} was chosen since it implies the amount of leaving-group removal at the transition state whereas ρ_{lg} implies the amount of charge development on the leaving group. The difference is semantic since the two quantities are related by $\beta_{\mathrm{lg}} = \rho_{\mathrm{lg}}/\rho_{\mathrm{p}K_a}$ where $\rho_{\mathrm{p}K_a}$ is the free-energy relationship between pK_a

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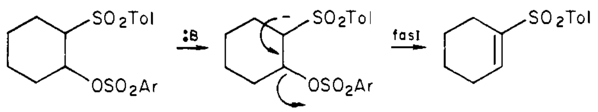
Table VII. Brønsted Coefficients for Reactions Involving Loss of Arenesulfonate Groups

	reaction	β_{lg}	ref
1	elimination in 2-(*p*-tolylsulfonyl)cyclohexyl arenesulfonates, 50% dioxane, 25 °C	(OH^-) 0.82 cis (OH^-) 0.97 trans (Me_3N) 0.54 trans	27 27 27
2	E2 elimination in 2-phenethyl arenesulfonates, *tert*-butyl alcohol 40 °C	1.8	28
3	concerted rearrangement in *t*-butyl arenesulfonate peresters (t-$BuOOSO_2Ar$), methanol, 25 °C	2.08	29
4	solvolysis of methyl arenesulfonates, ethanol, 70 °C	2.21	30
5	solvolysis of ethyl arenesulfonates, ethanol, 70 °C	2.16	30
6	solvolysis of methyl arenesulfonates, methanol, 50 °C	2.12	30
7	solvolysis of methyl arenesulfonates, 50% dioxane, 50 °C	2.08	30
8	ethoxide substitution of ethyl arenesulfonates, ethanol, 35 °C	2.25	31
9	ionization of 1-adamantyl arenesulfonates, ethanol, 25 °C	2.94	32
10	ionization of 2-adamantyl arenesulfonates, ethanol, 25 °C	3.01	32
11	imine-forming elimination in 3a,b, methanol, 20 °C	2.58	this work
12	imine-forming elimination in 3a,b, TEW, −10 °C	2.19	this work

and the substituent constant.[24]) The results of plots of rate constants versus pK_a values are collected in Table VII. These reactions were chosen to represent the spectrum of leaving-group loss possible in elimination transition states. Remarkably, these data fall into three distinct ranges which depend on the reaction type but are relatively insensitive to charge type, solvent, and temperature. Reactions run in alcohol solvents were chosen where possible, but aqueous dioxane gives no large difference. Furthermore, changes in temperature cause no large changes either.

The first range of β_{lg} values, 0.5–1, are found for E1cb eliminations in **8**,[27] entry 1 (eq 6). This range of β_{lg} values probably represents a loosening of the bond to leaving group caused by dipolar effects of the adjacent negative charge, and it varies only slightly with the charge type of the base. Alternatively the loss of leaving group could be considered very early in a Hammond sense. These data permit a lower limit of β_{lg} = 0.5 to be assigned for the E1cb mechanistic limit in the MOFJ diagram for eliminations. The next group of β_{lg} values, ~2.1 ± 0.1 (entries 3–8), are for reactions in which leaving-group loss is accompanied by electron donation to the site from which the leaving group departs. The diversity of reactions which fall in this range is quite surprizing. Electron donation can result from concerted migration (entry 3), donation by a negatively charged nucleophile (entry 8) or donation by neutral nucleophiles such as alcohols or water. Furthermore, similar β_{lg} values are obtained for leaving-group loss from oxygen or carbon and for various charge types of reactions.



8

(6)

The final group of β_{lg} values, 3.0 ± 0.1, are for the E1 mechanism. The ionizations for 1- and 2-adamantyl derivatives give these values, and 3.0 might be considered an upper limit for β_{lg} in the MOFJ diagram. These ionizations are somewhat extreme examples since the bridged systems used prevent backside nucleophilic solvation.[32,3c] Less encumbered molecules might be expected to exhibit slightly lower β_{lg} values for the E1 process, since nucleophilic solvation is a weak analogy of nucleophilic attack.

With these analogies in hand, it is now possible to examine elimination reactions using Brønsted coefficients α = 0–1 and β_{lg} = 0.5–3 as coordinates in a MOFJ diagram (Figure 4). For the imine-forming eliminations investigated, the Brønsted coefficients α = 0.3 and β_{lg} = 2.19 for **3a,b** in TEW at −10 °C indicate a transition-state structure skewed[1c] toward an E1 mechanism. A change to methanol as the reaction solvent gives α = 0.1 and β_{lg} = 2.58. The transition state is very close to being E1, yet the kinetics show the reaction to be bimolecular. Of interest is the requirement that the nitrogen attached to the leaving group bears substantial positive charge. In the absence of large amounts of base, phenyl rearrangement to electron-deficient nitrogen is seen.

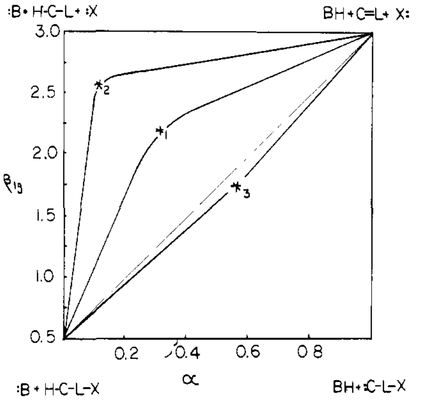
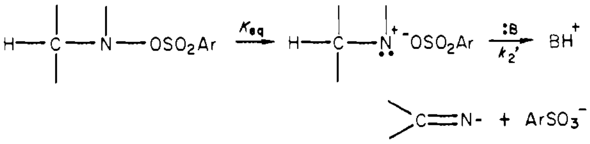


Figure 4. More-O'Ferrall–Jencks diagram for bimolecular elimination in *O*-(arylsulfonyl)-*N*-benzylhydroxylamines, **3**. The E1 character of the transition state in TEW ($*_1$) is skewed even further to the E1 extreme in methanol as solvent ($*_2$). In contrast, bimolecular eliminations in β-phenylethyl arenesulfonates have transition states ($*_3$) very close to the concerted (- - -).

A mechanistic pathway that remains a possibility is one involving an ion pair (eq 7). If attack by base on the ion pair is rate determining, it is easily shown by the steady-state approximation that the rate = $K_{eq}k_2'$[B][3], which has the same kinetic form as is observed. However, our reported second-order rate constants would be given by $k_2 = K_{eq}k_2'$. We cannot specifically rule out this mechanism, but it can be argued that in TEW, the transition-state parameters are similar to those of other reactions not involving ion pairs (Table V). If solvent merely skews the transition state, then the results in methanol would result from a more E1-like transition state and not a different ion-pair mechanism. Furthermore, hydroxylamines **3** would give primary nitrenium ion pairs. Since it is generally accepted that primary carbenium ion pairs are not produced in solvolyses,[34] it can also be argued that primary nitrenium ion pairs would not be expected.



(7)

Analogous olefin-forming eliminations in 2-phenylethyl bromides promoted by phenoxide bases, α = 0.56,[35] and for 2-phenylethyl arenesulfonates β_{lg} = 1.8.[28] This indicates that in the 2-phenylethyl system, bond-making–bond-breaking processes

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are much more equally advanced, and this system can be best described as concerted. It must be recognized that this formulation is based on a bromide leaving group for α and arenesulfonates for β_{1g}. However, it should be a resonable estimation of the transition state.

The other transition-state parameters for imine-forming eliminations (Table V) discussed earlier are consistent with this mechanistic formulation; however, they do not provide such a graphic demonstration of the differences that result from changes in solvent. While solvent is not specifically parameterized in the MOFJ diagram, its effect on the transition state is clearly apparent. From entropies of activation we conclude that hydrogen bonding to the leaving group is the dominant solvation feature. By using the more polar solvent methanol, this hydrogen bonding is increased and the transition state is skewed toward loss of leaving group. That this is distinctly a solvent effect is assured by noting that the same substrates, bases, and leaving groups have been used throughout.

Having established the coordinates for proton removal and leaving group departure in the MOFJ diagram, many diverse elimination reactions can be compared mechanistically. At present, only a limited number of studies of the type required have been reported.[20a] To obtain the most meaningful comparison: (a) the same pure solvent should be employed, (b) several arenesulfonate groups should be used in order that leaving group solvation remain the same, and (c) bases much weaker than the lyate anion be used so that the promoting base is well-defined (i.e., concentration of lyate ion very low). If these conditions are fulfilled, then α and β_{1g} can be easily obtained, and thus a comprehensive view of structure–reactivity relationships for eliminations in arenesulfonates can be achieved. It may then be possible to include other leaving groups, solvent systems, and charge types into the data base in a systematic fashion. This has been the goal of many studies on elimination reactions,[20] and that goal is now more clearly in sight.

Furthermore, it is our belief that the described Brønsted plots using arenesulfonate groups can be extremely profitable when applied to other reactions in which leaving groups are lost in the rate-determining step (e.g., solvolyses). The β_{1g} values thus obtained may permit accurate mechanistic mapping and the detection of charge stabilizing events like backside solvation, neighboring group participation, and bridging—all points of considerable current interest.

Experimental Section

Amines **1a–f** and peroxides **2a–d** were prepared and purified as described earlier.[1c] Peroxide **2e** was prepared from 3,5-bis(trifluoromethyl)benzenesulfonyl chloride in the standard way.[36] It had a melting point of 72 °C dec and was 99% pure by iodometric titration. The sulfonyl chloride was prepared from 3,5-bistrifluoromethyl)aniline (PCR) by the Meerwein procedure.[37] The solvent system TEW was prepared as described earlier,[1c] and methanol was dried by treatment with magnesium, distilled, and stored under nitrogen.

Kinetics were carried out as before,[1c] and Brønsted studies were done by using various amines as catalyzing bases. These amines were purified by conversion to the ammonium chloride salt, which was recrystallized and returned to the free base with sodium hydroxide. The amine was finally distilled and stored under nitrogen.

All rate constants reported are the average of at least two runs and the kinetic runs usually agreed to within ±2% in TEW and ±4% in methanol.

Product studies were carried out as described earlier.[2,15] A solution of **2b** (1.5 mmol) in the appropriate solvent (20 ml) was equilibrated at 20 °C and added to a known excess of benzylamine in the same solvent also at 20 °C. The reaction mixture was maintained at 20 °C for 10 min and then evaporated on a rotary evaporator without application of heat. Aqueous hydrochloric acid (2.5 M, 50 mL) was added, and the mixture was steam distilled until 20 mL of distillate was collected. The steam distillate was extracted with dichloromethane (3 × 10 mL) which was dried ($MgSO_4$) and analyzed for benzaldehyde by gas chromatography. The acidic steam distillation residue was taken to pH 14 with potassium hydroxide and extracted with dichloromethane (3 × 15 mL) which was dried ($MgSO_4$) and analyzed for aniline by gas chromatography.

Acknowledgment. We wish to thank Professor Dennis Davis of this department for his timely comments. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society. Data management was facilitated greatly by the NIH Prophet Computer System which is supported at NMSU by the National Institues of Health.

Registry No. 1a, 100-46-9; **1b**, 104-84-7; **1c**, 100-81-2; **1d**, 104-86-9; **1e**, 4152-90-3; **1f**, 2740-83-2; **2a**, 6209-72-9; **2b**, 35673-10-0; **2c**, 29342-58-3; **2d**, 29342-61-8; **2e**, 80953-39-5; **3a,a**, 80953-40-8; **3a,b**, 80953-41-9; **3a,d**, 80953-42-0; **3a,e**, 80953-43-1; **3b,b**, 80953-44-2; **3e,b**, 80953-45-3; **3f,b**, 80953-46-4.

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