using 85:15 hexane–ethyl ether (relative R_f of **4i** and **5i** on analytical plate, 1.9:1) as the eluant.

4i: mp 111–113 °C (from methanol); ^{1}H NMR δ 8.30 (s, 4 Ar H), 5.60 (m, $W_{1/2}$ = 14 Hz, CHO, 1 H), 4.75 (2 overlapping m, $W_{1/2}$ = 8 Hz, CHBr, 2 H), 2.75–1.45 (6 cyclohexane H); IR (Nujol) 2920, 2860, 1730, 1605, 1520, 1460, 1375, 1350, 1275, 1160, 1105, 1015, 940, 875, 835, 720, 660 cm^{-1}. Anal. Calcd for $C_{13}H_{13}Br_2NO_4$: C, 38.36; H, 3.22; Br, 39.26; N, 3.44. Found: C, 38.42; H, 3.31; Br, 39.46; N, 3.38.

5i: mp 105–107 °C (from ethanol) (lit.[8a] mp 103–105 °C, lit.[3c] mp 108–110 °C); ^{1}H NMR δ 8.30 (s, 4 Ar H), 5.30 (m, $W_{1/2}$ = 16 Hz, CHO, 1 H), 4.35 (2 overlapping m, W = 25 Hz, CHBr, 2 H), 2.75–1.35 (6 cyclohexane H); IR (Nujol) 2930, 2860, 1720, 1600, 1520, 1460, 1370, 1350, 1310, 1280, 1120, 1100, 1010, 830, 710, 690 cm^{-1}. Anal. Found: C, 38.51; H, 3.30; Br, 39.38; N, 3.49.

Product Analyses. The mixtures of **4b–5b**, **4d–5d**, and **4e–5e** were analyzed by GLC.[3a,c] The relative retention times were as follows: **4b** and **5b**, 1:2.3; **4d** and **5d**, 1:1.4; **4e** and **5e**, 1:1.5. Identical products ratios were found for mixtures obtained both under the conditions of the kinetic runs and under the preparative conditions.

The analyses of the mixtures of **4c–5c** obtained under preparative conditions were carried out by integration of the signals of the protons α to bromine in the NMR spectra.[11a]

The mixtures of **4f–5f**, **4g–5g**, **4h–5h**, and **4i–5i** were analyzed by HPLC using respectively 99:1, 96:4, 96:4, and 98:2 mixtures of hexane–ethyl acetate as the eluants. The relative retention times were as follows: **4f** and **5f**, 1:1.6; **4g** and **5g**, 1:2; **4h** and **5h**, 1:1.5; **4i** and **5i**, 1:1.3. Also in these cases identical product ratios were found for mixtures obtained under the conditions of the kinetic runs and under the preparative conditions.

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Registry No. **1a**, 110-83-8; **16**, 591-48-0; **1c**, 14072-87-8; **1d**, 1521-51-3; **1e**, 2441-97-6; **1f**, 3352-93-0; **1g**, 103437-97-4; **1h**, 103437-98-5; **1i**, 38313-01-8; **4e**, 103437-99-6; **4f**, 103438-00-2; **4g**, 103438-01-3; **4h**, 103438-02-4; **4i**, 103530-08-1; **5e**, 103530-04-7; **5f**, 103530-05-8; **5g**, 103530-06-9; **5h**, 103530-07-0; **5i**, 53119-31-6.

Mechanism of Base-Promoted Eliminative Fragmentations of 2-Alkyl-3-Phenyloxaziridines

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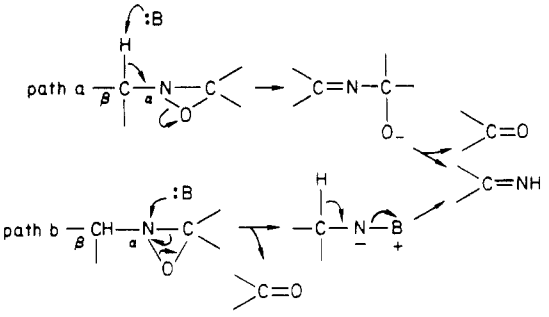
The base-promoted fragmentations of 2-benzyl-3-(4-substituted-phenyl)oxaziridines **1** and 2-(4-substituted-benzyl)-3-phenyloxaziridines **2** in anhydrous organic solvents give benzaldehydes and unstable benzylideneimines. The subsequent trimerization of the imines provides the benzylidene animals with the liberation of ammonia. The fragmentations can be regarded as an α,β-elimination and have been studied kinetically with triethylamine in acetonitrile at 40 °C. The (*Z*)-oxaziridines react more rapidly than the corresponding (*E*)-oxaziridines. The Hammett ρ values for the *E* isomers of **1** and **2** are 0.68 and 0.89, respectively. The primary kinetic β-deuterium isotope effects (k_H/k_D) are 6.1 for (*E*)-2-benzyl-3-(4-nitrophenyl)oxaziridine [(*E*)-**1a**] and 6.9 for (*E*)-2-benzyl-3-(4-methoxyphenyl)oxaziridine [(*E*)-**1e**]. From these results and considerations on the magnitudes of the Brønsted β (0.46), the activation parameters and the Arrhenius parameters for (*E*)-**1a**, the triethylamine-promoted fragmentations of **1** and **2** are best interpreted in terms of a near central E2 mechanism; for the transition state of (*E*)-**1a** the N_α–O bond breaking is slightly ahead of the β-proton removal. The triethylamine-promoted fragmentations of (*E*)- and (*Z*)-2-methyl-3-(4-nitrophenyl)oxaziridines (**9**) in acetonitrile are slower than those of **1a**, but give comparable primary isotope effects; k_H/k_D = 6.1 for (*Z*)-**9** and 6.6 for (*E*)-**9**. The Arrhenius plot for (*Z*)-**9** shows excellent linearity, suggesting neither change in mechanism nor the necessity for a tunneling correction. The fragmentation of (*Z*)-**9** in chloroform is slightly slower than that in acetonitrile, with k_H/k_D = 6.2. These data suggest that the tertiary amine promoted fragmentations of 2-alkyl-3-phenyloxaziridines with β-hydrogen exclusively proceed through an E2 mechanism.

Oxaziridines represent a unique class of three-membered heterocyclic compounds of which three bonds are severed respectively under appropriate conditions.[1] The chemistry of these compounds is relatively new and, at present, has received considerable attention in connection with some biological processes.[2] Oxaziridines with a proton on the carbon adjacent to the ring nitrogen undergo a base-promoted fragmentation to aldehydes or ketones and imines.[3]

Scheme I



The transformation of amino acids to oxaziridines via the corresponding imines and the subsequent fragmentation of the oxaziridines are of interest in connection with a biological oxidative deamination of amino acids.

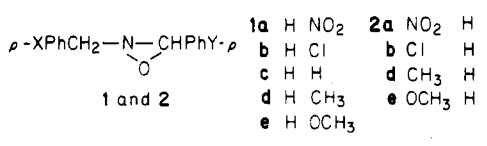
For the base-promoted fragmentation of 2-alkyloxaziridines mainly two reaction pathways concerning the rupture of the N-O bond have been suggested (Scheme

(1) (a) Emmons, W. D. *Heterocycl. Compd.* **1964**, *19*, 624–646. (b) Schmitz, E. *Adv. Heterocycl. Chem.* **1963**, *2*, 83–122; **1979**, *24*, 63–95. (c) Orf, H. W.; Dolphin, D. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 264[illegible]50. (b) Frost, J. W.; Rastetter, W. H. *J. Am. Chem. Soc.* **1981**, *103*, [illegible]2–5244. (c) Rastetter, W. H.; Gadek, T. R.; Tane, J. P.; Frost, J. [illegible]*d.* **1979**, *101*, 2228–2231.

(2) Emmons, W. D. *J. Am. Chem. Soc.* **1957**, *79*, 5739–5754. (b) Dir[illegible]S. E.; Watt, D. S. *Ibid.* **1975**, *97*, 6900–6901. (c) Rastetter, W. H.; Fros[illegible]J. W. *Tetrahedron Lett.* **1979**, 3353–3356. (d) Yijima, C.; Hino, F.; Suda, K. *Tetrahedron Lett.* **1980**, 4725–4726. (e) Rastetter, W. H.; Wagner, W. R.; Findeis, M. A. *J. Org. Chem.* **1982**, *47*, 419–422. (f) Boyd, D. R.; Hamilton, R.; Thompson, N. T.; Stubbs, M. E. *Tetrahedron Lett.* **1979**, 3201–3204. (g) Boyd, D. R.; McCombe, K. M.; Sharma, N. D. *Tetrahedron Lett.* **1982**, 2907–2908.

0022-3263/86/1951-4232$01.50/0

Scheme II



I).[3e,4] Path a is a general base catalyzed reaction involving initial β-proton abstraction, and path b represents nucleophilic attack of a base at oxaziridine nitrogen.

These pathways, though the former seems to be favorable for oxaziridines with a bulky substituent on the ring nitrogen, must be distinguished on the basis of the results of careful product analyses with a variety of bases and the kinetic investigations. Another important subject is to elucidate the detailed mechanism of the elimination involved in path a, because little is known about imine-forming eliminations involving the cleavage of such strained rings. Although large β-deuterium isotope effects have been estimated for the elimination of several oxaziridines,[3e,g] there has been neither systematic investigation on a series of oxaziridines with an appropriate structure nor information on the participation of the ring system in the fragmentations.

We wish to report here the results on the product analyses and the kinetic investigation for the amine-promoted fragmentations of a series of 2-benzyl-3-(4-substituted-phenyl)oxaziridines **1** and 2-(4-substituted-benzyl)-3-phenyloxaziridines **2** in nonaqueous solvents (Scheme II). The use of **1** and **2** will be one of the best choice for the above purposes because the substituent effects at the 2-benzyl and C3-phenyl groups are expected to provide valuable information on the mechanism. We have also reinvestigated the triethylamine-promoted fragmentation of 2-methyl-3-(4-nitrophenyl)oxaziridines (**9**), for which a nucleophilic substitution mechanism (path b) was proposed,[4] and found that the fragmentation also proceeds through an E2 mechanism.

Experimental Section

Melting points were determined with a YANACO Micro Melting Point apparatus and are uncorrected. ^{1}H NMR spectra were obtained with a JEOL PS-100 spectrometer with tetramethylsilane as an internal standard. IR spectra were obtained with a JASCO DS-710G spectrophotometer. Microanalyses were performed on a Perkin-Elmer Model 240 elemental analyzer.

Materials. Acetonitrile[5] and methanol[6] were purified according to the literature methods. Methylene chloride was dried over phosphorus pentoxide and then distilled. Triethylamine, morpholine, *N*-methylmorpholine, and 2,6-lutidine were respectively dried over potassium hydroxide for a day and then distilled. 2-(Diethylamino)ethanol was purified by repeated fractional distillation. Trifluoroacetic acid (99.5%) and lithium aluminium deuteride (minimum 98 atom % D) were obtained from Merck Co. and methyl-d_3-amine (minimum 98 atom % D) from Aldrich.

General Method for Preparation of Oxaziridines 1 and 2. The oxaziridines were prepared just before use by oxidation of appropriate imines with *m*-chloroperbenzoic acid in methylene chloride according to the literature methods[7,8] with a little modification. The spectral and analytical data for the oxaziridines **1** and **2** are presented in the supplementary material. Most of the oxaziridines are mixtures of *E* and *Z* forms and are oils except for **1a** at ambient temperature. They decompose gradually even at a temperature lower than 0 °C. The elemental analyses not always gave enough results owing to the instability of the compounds during their analyses but their purities were also checked by ^{1}H NMR and TLC after repeated crystallization of the *E* and *Z* mixtures from *n*-hexane or benzene–*n*-hexane at −60 °C.

Syntheses of Dideuterio Oxaziridines 1a-d_2 and 1e-d_2. α,α-Dideuteriobenzylamine was prepared by reduction of benzonitrile (1.0 g, 9.7 mmol) with $LiAlD_4$ (0.3 g, 7.0 mmol) in absolute tetrahydrofuran according to the literature method[9] [bp 88 °C (12 mmHg)]. The amine was converted into imines with appropriate aldehydes by general method. Oxidation of the imines with *m*-chloroperbenzoic acid in methylene chloride yielded mixtures of the (*E*)- and (*Z*)-dideuterio oxaziridines. (*E*)-2-(α,α-Dideuteriobenzyl)-3-(4-nitrophenyl)oxaziridine [(*E*)-**1a**-d_2] was purified by repeated crystallization from benzene–*n*-hexane at −60 °C. (*E*)-2-(α,α-Dideuteriobenzyl)-3-(4-methoxyphenyl)oxaziridine [(*E*)-**1e**-d_2] was purified by the same procedure from *n*-hexane. Their purities were checked by ^{1}H NMR and TLC.

Separation of (*E*)- and (*Z*)-2-Benzyl-3-(4-nitrophenyl)-oxaziridines (1a). A mixture of *E* and *Z* oxaziridines was separated into each isomer by means of preparative TLC on a silica gel plate with benzene. The isomers were respectively purified by recrystallization from benzene–*n*-hexane.

(*Z*)-**1a**: mp 107–108 °C. Anal. Calcd for $C_{14}H_{12}N_2O_3$: C, 65.62; H, 4.72; N, 10.93. Found: C, 65.41; H, 4.63; N, 11.00. ^{1}H NMR (CH_3CN) δ 5.45 (s, 1 H), 3.61 (s, 2 H).

(*E*)-**1a**: mp 110–112 °C. Anal. Calcd for $C_{14}H_{12}N_2O_3$: C, 65.62; H, 4.72; N, 10.93. Found: C, 65.37; H, 4.56; N, 11.03. ^{1}H NMR (CH_3CN) δ 5.04 (s, 1 H), 4.24 (d, J = 15 Hz, 1 H), 3.90 (d, J = 15 Hz, 1 H).

2-Benzyl-3-methyloxaziridines (3). The oxaziridine was prepared according to the literature method[10] and distilled under nitrogen atmosphere: bp 92 °C (1 mmHg) [lit. bp 95–96 °C (1 mmHg), a pale yellow oil.

2-Methyl-3-(4-nitrophenyl)oxaziridine (9) and 2-(Trideuteriomethyl)-3-(4-nitrophenyl)oxaziridine (9-d_3). The oxaziridines were prepared according to the literature method.[11] The *E* and *Z* isomers were preparatively separated on silica gel using benzene and then recrystallized from benzene. Their purities were checked by ^{1}H NMR and MS. (*E*)-**9**: mp 94–96 °C (lit. mp 94–96 °C). (*E*)-**9**-d_3: mp 93.5 °C; mass spectrum, M^+ = 182 (100%). (*Z*)-**9**: mp 80–81 °C (lit. mp 80–81 °C). (*Z*)-**9**-d_3: mp 78–79 °C; mass spectrum, M^+ = 182 (100%).

Product Analyses and Stoichiometry for Fragmentations of 1–3. The fragmentations of **1** with triethylamine in acetonitrile at ambient temperature were rapid and exothermic and gave **4c** and benzaldehyde with evolution of ammonia which was detectable by use of Nesslar's reagent. After removal of the solvent in vacuo, **4c** was recrystallized from ethanol–*n*-hexane (mp 104–105 °C) and identified as *N*,*N*′-dibenzylidenebenzylidenediamine by comparison of its mp and ^{1}H NMR and IR spectra with those of an authentic sample:[12] ^{1}H NMR (in CCl_4) δ 8.44 (s, 2 H, PhCH=N), 5.85 (s, 1 H, NCHN). The fragmentations of **1** also take place in solvents such as 1,4-dioxane, ether, methylene chloride, and methanol with triethylamine or morpholine and in methanol with sodium methoxide.

In the fragmentation of **1a** with triethylamine in acetonitrile-d_3 at 25 °C, the ^{1}H NMR spectrum of the reaction mixture at infinite time showed three characteristic singlets at δ 9.98, 8.58, and 5.90 in a ratio of 3:2:1. They were assigned in that order to be the formyl proton of *p*-nitrobenzaldehyde and the azomethyne and methyne protones in **4c**, respectively. No other products such as hydrazines[4a] were detected by ^{1}H NMR. After removal of the solvent in vacuo **4c** was isolated in 95% yield according to the stoichiometry (see Scheme III). In the same reactions of (*E*)-**1a**-d_2 and (*E*)-**1e**-d_2 in acetonitrile, the benzlidene animals **4** isolated and then recrystallized from ethanol–*n*-hexane were both assigned to be **4c**-d_3 by ^{1}H NMR: neither methyne proton [δ 5.85 (s)] nor

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(6) Bjerrum, N.; Zechmeister, L. *Ber. Dtsch. Chem. Ges.* **1923**, *56*, 894–899.
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(8) Pews, R. G. *J. Org. Chem.* **1967**, *32*, 1628.
(9) Friedmann, L.; Jurewicz, A. T. *J. Org. Chem.* **1968**, *33*, 1254–1255.
(10) Tolsttikov, G. A.; Jemilev, U. M.; Jurjev, V. P.; Gershanov, F. B. *Tetrahedron Lett.* **1971**, 2807–2808.
(11) Boyd, D. R.; Neil, D. C.; Watson, C. G. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1813–1818.
(12) Ogata, Y.; Kawasaki, A.; Okumura, N. *J. Org. Chem.* **1964**, *29*, 1985–1988.

azomethyne proton [δ 8.44 (s)] was observed in their ^{1}H NMR spectra (in CCl_4).

The fragmentation of **1c** (39.4 mg, 187 μmol) with triethylamine (10 μL, 71.9 μmol) in acetonitrile (400 μL) containing anisole (3 μL, 27.7 μmol) as a reference for determination of the yield of the products was followed by ^{1}H NMR at 25 °C. In the spectrum three characteristic signals due to benzaldehyde and **4c** were rapidly developed at δ 10.01 and 8.60, 5.93 in a ratio of 3:2:1 during 1 h. The yields of benzaldehyde and **4c** were determined spectrometrically: benzaldehyde/**4**/time, 163 μmol (91%)/53 μmol (90%)/ h; 133 μmol (75%)/74 μmol (124%)/24 h. A similar fragmentation of **3** with triethylamine in acetonitrile give **4c** in 60% yield (isolated).

Trapping of 4-Chlorobenzylideneimine as an Intermediate from 2b. The cavity of the NMR spectrometer was maintained at −53 °C by the air of liquid nitrogen. After addition of triethylamine (50 μL) to a NMR tube containing (*E*)-**2b** (25 mg in 0.35 mL CH_2Cl_2) at this temperature, the solution was shaken and then cooled again to −53 °C. The ^{1}H NMR spectrum showed characteristic two doublets due to 4-chlorobenzylideneimine at δ 8.7 (1 H, *J* = 16 Hz, C*H*=NH) and 10.18 (1 H, *J* = 16 Hz, CH=N*H*) along with a singlet due to benzaldehyde [δ 9.95 (1 H, CHO)]. On addition of methanol-d_1 (CH_3OD, 30 μL) to the reaction mixture, the former doublet gradually transfered into a singlet with the decreasing latter doublet. The imine was stable over a period of several hours at the temperature, but, on standing the solution at 25 °C overnight, the imine was transformed exclusively into the corresponding trichlorobenzylidene animal **4b**.[13] No other intermediates but the imine could be observed during the reaction by ^{1}H NMR.

Kinetic Measurements. All the oxaziridines synthesized were purified just before use for kinetic measurement.

^{1}H NMR Method. Kinetic measurements for **1** and **2** were carried out with a JEOL PS-100 NMR spectrometer equipped with a thermostated cavity. A freshly prepared solution of 2-benzyl-3-phenyloxaziridines (0.23–0.26 M in acetonitrile, 0.4 mL) in a NMR tube was equilibrated (within a 3 min) at a desired temperature (normally 40 ± 0.3 °C) in the cavity. A small amount (30–50 μL) of the acetonitrile solution of amines, which had been also equilibrated at the same reaction temperature, was added with a microsyringe, and the mixture was quickly shaken for a few seconds. The rate of elimination was then followed by monitoring the decrease in peak height of the ring proton signal (singlet) (method A) or of the methylene signal (two doublets) in the 2-benzyl group (method B) of the oxaziridines or by monitoring the increase in peak height of the formyl proton signal of benzyladehydes (method C).

Measurements of 15–50 points were made in each run. Plot of the logarithm of the peak height against time showed a good linear correlation ($\gamma > 0.997$) over 80% completion of the reaction in each run to give the pseudo-first-order rate constant. The second-order rate constants (k_2) were obtained by dividing the pseudo-first-order rate constants by the base concentrations. All the rate constants were estimated from the average of at least three runs.

HPLC–Spectrophotometric Method. Kinetic studies for **9** and **9**-d_3 and some kinetic runs for (*E*)-**1a** were carried out in acetonitrile under pseudo-first-order conditions with concentrations of (0.7–5.7) × 10^{-3} in substrates and of (0.3–1.8) × 10^{-1} M in bases. A reaction flask equipped with a septum seal was filled with 3 mL of a base solution. After thermostating at the reaction temperature (normally 40.0 ± 0.1 °C), 30 μL of substrate solution was injected with a syringe. Aliquots were withdrawn periodically with a syringe and analyzed by HPLC. The concentrations of remaining **9** and (*E*)-**1a** and that of producing *p*-nitrobenzaldehyde were monitored at 265 or 260 nm and determined from the area under the separated peaks. The reactions were follwed more than 90% completion and good pseudo-first-order kinetics ($\gamma > 0.999$) were obtained.

Results

Product Analyses and Stoichiometry. The reactions of a mixture of the *E* and *Z* forms of **1** with triethylamine

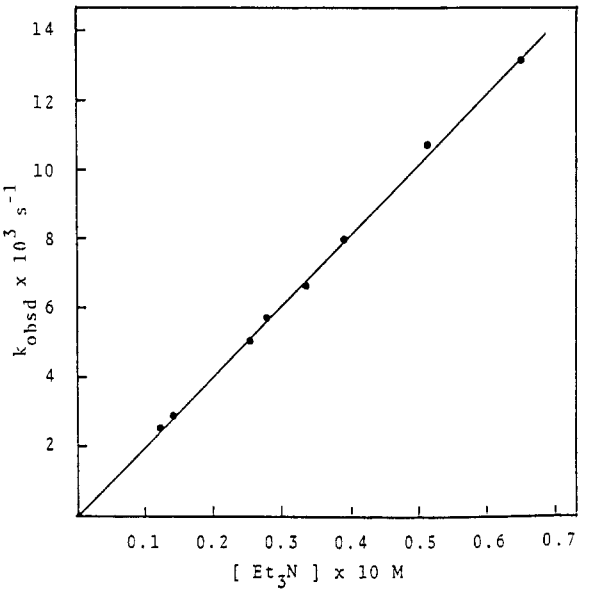
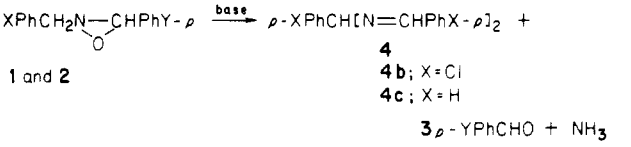


Figure 1. Plot of the observed pseudo-first-order rate constants k_{obsd} against the concentration of triethylamine for the fragmentation of (*Z*)-**1a** in acetonitrile at 40 °C.

Scheme III



in various anhydrous solvents such as acetonitrile, ether, methylene chloride, 1,4-dioxane, and methanol or with sodium methoxide in methanol gave unsubstituted benzylidene aminal **4c** and benzaldehyde in a molar ratio of 1:3 along with the evolution of ammonia. Triethylamine-promoted fragmentations of (*E*)-**1a**-d_2 and (*E*)-**1e**-d_2 in acetonitrile gave **4c**-d_3 exclusively (Scheme III). These reactions were rapidly and almost quantitative according to the following stoichiometry.

In the fragmentation of **1c** an additional amount of **4c** was obtained by a slower condensation[12] between the benzaldehyde and ammonia, both generated in the initial stage of the reaction, and the yield of **4c** finally exceeded the theoretical value calculated from the stoichiometry. Attempts to trap other intemediates during the fragmentation failed in acetonitrile because of the rapid reaction in the solvent and the high melting point of the solvent itself. In the triethylamine-promoted fragmentation of 2-(4-chlorobenzyl)-3-phenyloxaziridine (**2b**), however, the intermediacy of *p*-chlorobenzylideneimine[14] was confirmed by ^{1}H NMR at −53 °C in methylene chloride. The imine trimerized rapidly at ambient temperature to give the corresponding benzylidene aminal (**4b**), exclusively. With various amines no intermediate other than the imine was detected by ^{1}H NMR during the reaction. A similar fragmentation of 2-benzyl-3-methyloxaziridine (**3**) with triethylamine also gave **4c**. The amine-promoted rapid fragmentations of oxaziridines **1**–**3** can be, therefore, separated into two reactions: an α,β-elimination to give a

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(14) Boyd et al. have first assigned a series of N-unsubstituted aldo imines as a transient intermediate of a base-promoted fragmentation of 2-alkyloxaziridines and observed transformation of the imines to bis(aldo imines) or benzylidene aminals (see ref 3f).

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Table I. Effects of Additives on the Rate of Triethylamine-Promoted Fragmentation of (*E*)-1a in Acetonitrile[a]

10[Et_3N], M	10[additive], M	temp, °C	$10k_2$, M^{-1} s^{-1}
	p-Nitrobenzaldehyde		
0.449	0.602	34	1.55
0.581	0.973	34	1.70
0.706	1.33	34	1.57
	N,N'-Dibenzylidenebenzylidenediamine (4c)		
0.178	0.204	34	1.60
0.237	0.287	34	1.58
0.178	0.519	34	1.58
	Triethylammonium Trifluoroacetate[b]		
0.210	0.239	40	2.02
0.242	0.275	40	2.02
0.315	0.359	40	2.04
0.362	0.413	40	2.16
0.420	0.479	40	1.98
0.483	0.550	40	1.92
	Methanol (Molar Ratio to (*E*)-1a)		
0.403	7.10 (3)	40	1.95
0.403	10.8 (5)	40	1.55
0.403	23.7 (10)	40	1.50
0.403	47.3 (20)	40	1.36
0.403	71.0 (30)	40	1.24

[a] [(*E*)-1a] = 0.236 M. [b] [$Et_3N^+HO^-COCF_3$]/[Et_3N] = 1.14, was maintained without addition of an inert salt.

Table II. Substituent Effects on the Rates of the Triethylamine-Promoted Fragmentations of (*E*)-1 and (*E*)-2 in Acetonitrile at 40 °C[a]

compd	$10k_2$, M^{-1} s^{-1} [b]	compd	$10k_2$, M^{-1} s^{-1} [b]
1a	2.04 ± 0.06[c]	**2a**	2.76 ± 0.16
1b	1.00 ± 0.02	**2b**	0.953 ± 0.033
1c	0.610 ± 0.007	**2d**	0.380 ± 0.016
1d	0.465 ± 0.010	**2e**	0.326 ± 0.019
1e	0.391 ± 0.008		

[a] [Oxaziridines] = (3.3–3.8) × 10^{-1} M, [triethylamine] = (0.8–4.25) × 10^{-2} M. [b] Average of at least five determinations. [c] Average of the rates shown in Table B in the supplementary material.

benzylideneimine and an aldehyde and the subsequent trimerization of the former.

Kinetics. Kinetic measurements were performed in acetonitrile. Kinetic data for the triethylamine-promoted fragmentation of (*E*)-1a are presented in the supplementary material. The rate of the fragmentation showed first-order dependence on the concentrations of 1 and triethylamine, respectively (Figure 1). The rate constants estimated from the disappearance of oxaziridine ring hydrogen (method B) agreed with those estimated from the disappearance of β-hydrogen in the 2-benzyl group (method A) within a limit of experimental error. The rate of formation of *p*-nitrobenzaldehyde also obeyed pseudo-first-order kinetics (method C) with a correlation coefficient ~0.99, but the second-order rate constant, k_2, was smaller than those estimated from the disappearance of the oxaziridine and decreased with an increase in the concentration of triethylamine. All the rates of the fragmentation were thereafter measured by method A and/or method B.

Table I shows effect of additives on the rate constant k_2 of the fragmentation of (*E*)-1a. *p*-Nitrobenzaldehyde and 4c exhibited no appreciable effect on the rate. Triethylammonium trifluoroacetate added as the conjugate acid of triethylamine showed essentially no effect either, provided that a constant ratio of the buffer constituents was maintained. On the other hand, the rate constant decreased with an increase in the amount of added methanol and gradually approached a limiting value (Figure 2).

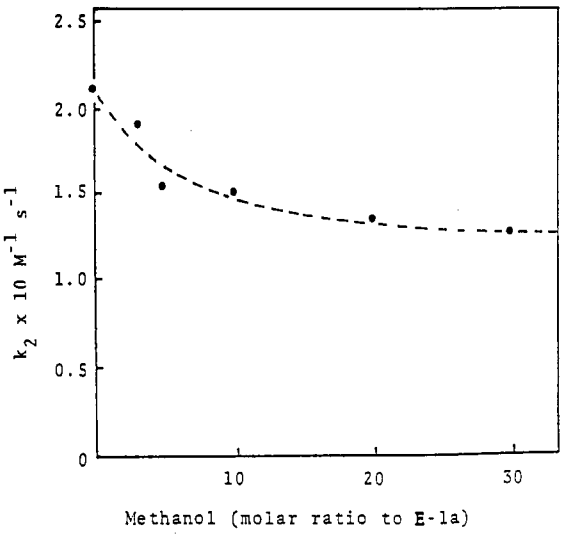

Figure 2. Effect of added methanol on the rate of fragmentation of (*E*)-1a in acetonitrile at 40 °C.

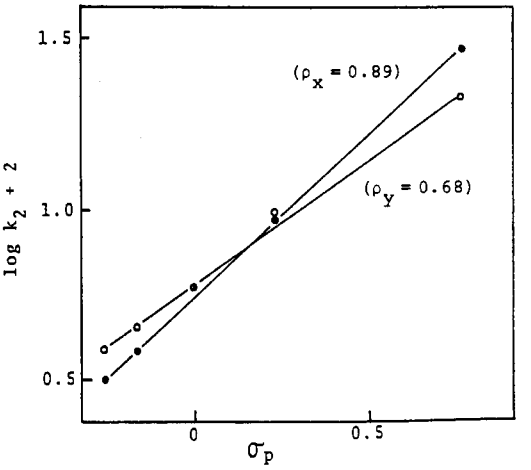

Figure 3. Hammett plots for the triethylamine-promoted fragmentations of (*E*)-1 (○) and (*E*)-2 (●) in acetonitrile at 40 °C.

The effects of substituents in the phenyl rings of 1 and 2 on the fragmentation rates are summarized in Table II. The rate constants for 1 and 2 correlate in good linear fashions with the Hammett equation using σ_p values (Figure 3). The reaction constants, ρ_x and ρ_y, were estimated to be 0.89 (γ = 0.998) and 0.68 (γ = 0.995), respectively, from the slopes.

Kinetic β-deuterium isotope effects (k_H/k_D) for the triethylamine-promoted fragmentations of (*E*)-1a and (*E*)-1e were 6.1 and 6.9, respectively (Table III). A Brønsted plot for the tertiary amine-promoted fragmentation of (*E*)-1a is shown in Figure 4 by the use of approximate pK_a's of the amines in acetonitrile (Table III). The slope lies between 0.46 and 0.38, depending on the pK_a value estimated for *N*-methylmorpholine (15.3–14.8).[29] Arrhenius plots for the fragmentations of (*E*)-1a and (*E*)-1a-d_2 (the figures are not shown) exhibited good linearity over a temperature range from 24.0 to 55.0 °C. The activation parameters are summarized in Table IV together with the rate constants obtained. The differences in Arrhenius parameters, ΔE_a^{D-H} = 1.14 kcal/mol and A^H/A^D = 0.99, are quite normal and do not suggest the necessity for a tunneling correction. Effects of the structure and strength of catalyst amines on the relative rate of the fragmentations of (*E*)- and (*Z*)-1a were briefly examined (Table V). The rate for the *Z* form is larger than that for

Table III. Primary Kinetic Isotope Effects and Rate Constants for Tertiary Amine Promoted Fragmentations of (*E*)-1 in Acetonitrile at 40 °C

compd	amine	p*K*a[a]	$10k_2$, M^{-1} s^{-1}	k_H/k_D
1a	triethylamine	18.0	2.04 ± 0.01	
1a(D)	triethylamine		0.334 ± 0.003	6.1 ± 0.1
1a	2-(diethylamino)ethanol	17.1	0.614 ± 0.038	
1a	*N*-methylmorpholine	15.3[b]	0.109 ± 0.002[c]	
1e	triethylamine		0.391 ± 0.011	
1e(D)	triethylamine		0.0560 ± 0.0012	6.9 ± 0.4

[a] See ref 29. [b] Derived from the difference in pK_a values, $\Delta(pK_a)_{A-W}$ = 8.25 for morpholine.[36] A pK_a = 14.8 is estimable from the difference of 7.8 for triethylamine. [c] Obtained by a HPLC method.

Table IV. Temperature Dependence of Triethylamine-Promoted Fragmentation of (*E*)-1a and (*E*)-1a-d_2 and the Activation Parameters in Acetonitrile

temp, °C	$10k_2$, M^{-1} s^{-1} [a] (*E*)-1a	$10k_2$, M^{-1} s^{-1} [a] (*E*)-1a-d_2
24.0	1.10 ± 0.02	
25.0		0.173 ± 0.003
30.0	1.36 ± 0.02	0.200 ± 0.002
36.0	1.84 ± 0.04	0.272 ± 0.003
40.0	2.04 ± 0.01	0.334 ± 0.003
43.0	2.26 ± 0.09	0.374 ± 0.013
48.5	2.95 ± 0.04	0.495 ± 0.001
54.0	3.73 ± 0.15	0.647 ± 0.013
55.0	3.83 ± 0.01	0.663 ± 0.001

E_a^H = 7.90 ± 0.22 kcal/mol $\Delta H^{\ddagger}$ = 7.3 ± 0.2 kcal/mol
$\Delta S^{\ddagger}$ = −38.5 ± 0.7 eu
E_a^D = 9.04 ± 0.11 kcal/mol $\Delta G^{\ddagger}$ = 19.4 ± 0.4 kcal/mol

[a] Average of at least three determinations by a HPLC method.

Table V. Effects of the Structure and Strength of Bases on the Rates of Fragmentations of (*E*)-1a and (*Z*)-1a in Acetonitrile at 43 °C

base[a]	10 k_2, M^{-1} s^{-1} (*Z*)-1a	10 k_2, M^{-1} s^{-1} (*E*)-1a	$k_{2[(Z)\text{-1a}]}/k_{2[(E)\text{-1a}]}$
triethylamine	5.91 ± 0.21	2.25 ± 0.05	2.6
morpholine[b]	1.51 ± 0.08	0.417 ± 0.006	3.6
2,6-lutidine	0.0357 ± 0.0006	0.00489 ± 0.00013	7.7

[a] [Triethylamine] = 3 × 10^{-2} M, [morpholine] = (0.3–3) × 10^{-2} M, [2,6-lutidine] = 0.8–1.2 M. [b] By a HPLC method.

the *E* form, and the rate ratio, $k_{2[(Z)\text{-1a}]}/k_{2[(E)\text{-1a}]}$, increased gradually with a decrease in the basicity and with an increase in the bulkiness of the amines used.

Fragmentations of (*E*)- and (*Z*)-2-methyl-3-(4-nitrophenyl)oxaziridines (**9**) with triethylamine were briefly reexamined in acetonitrile. *p*-Nitrobenzaldehyde was the only stable product characterized. The reaction obeyed second-order kinetics, first order in **9** and first order in triethylamine, and the results are shown in Table VI. The rate constants (k_2) for (*E*)- and (*Z*)-**9** were about 0.02 and 0.025 times, respectively, those for the corresponding isomers of **1a** at 40 °C. The rate of (*Z*)-**9** was nearly three times that of (*E*)-**9**. These findings are consistent with the previous observation by Hata and Watanabe.[4] The kinetic β-deuterium isotope effects were 6.6 for (*E*)-**9** and 6.1 for (*Z*)-**9** at 40 °C. Temperature dependence of the fragmentation of (*Z*)-**9** is shown in Table VII. The Arrhenius plot showed good linearity ($\gamma > 0.999$) over a temperature range from 22.4 to 55.6 °C, and the Arrhenius parameters were calculated: ΔE_a^{D-H} = 1.13 kcal/mol, and A^H/A^D = 0.98. The same fragmentation of (*Z*)-**9** in chloroform was slightly slower than that in acetonitrile, but the primary β-deuterium isotope effect remained unchanged.

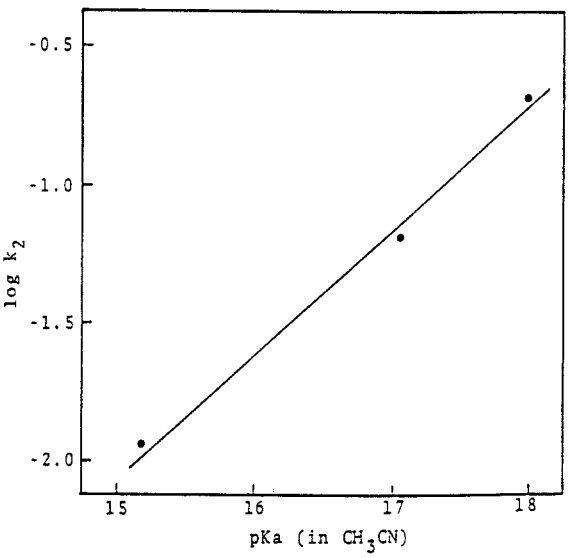

Figure 4. Brønsted plot for tertiary amine promoted fragmentations of (*E*)-**1a** in acetonitrile at 40 °C. β = 0.46.[29]

Table VI. Kinetic Data for the Triethylamine-Promoted Fragmentations of 2-Methyl-3-(4-nitrophenyl)oxaziridine (9) at 40 °C[a]

	solvent: acetonitrile (*Z*)-9	acetonitrile (*Z*)-9-d_3	acetonitrile (*E*)-9	acetonitrile (*E*)-9-d_3	$CHCl_3$[b] (*Z*)-9	$CHCl_3$[b] (*Z*)-9-d_3
10^3k_2, M^{-1} s^{-1}	12.8 ± 0.1	2.10 ± 0.02	4.48 ± 0.08	0.675 ± 0.023	7.48	1.20
k_H/k_D	6.1 ± 0.1		6.6 ± 0.3		6.2	

[a] [Oxaziridine] = (0.7–9.64) × 10^{-3} M, [triethylamine] = (3.29–32.9) × 10^{-2} M. [b] A single kinetic run.

Table VII. Temperature Dependence of Triethylamine-Promoted Fragmentation of (*Z*)-2-Methyl-3-(4-nitrophenyl)oxaziridine [(*Z*)-9] in Acetonitrile

	temp, °C: 55.6	47.4	40.0	29.6	22.4
	10^3 k_2, M^{-1} s^{-1}				
(*Z*)-9[a]	29.4 ± 0.1	19.7 ± 0.2	12.8 ± 0.2	7.27 ± 0.02	4.54 ± 0.04
(*Z*)-9-d_3[b]	5.47 ± 0.05	3.33 ± 0.03	2.10 ± 0.02	1.15 ± 0.02	0.679 ± 0.019

[a] E_a^H = 10.83 ± 0.12 kcal/mol. [b] E_a^D = 11.96 ± 0.20 kcal/mol.

Discussion

Reactions of 2-Benzyl-3-phenyloxaziridines. Observed second-order kinetics, first order in 1 and first order in base, rule out all but bimolecular reaction pathways. Mechanisms characterized by nucleophilic catalysis (Scheme I, path b) are also ruled out for the fragmentation catalyzed by triethylamine on the basis of the large primary β-deuterium isotope effects (k_H/k_D) observed for (*E*)-**1a** and (*E*)-**1e** and the substituent effect obtained for the C3-phenyl group in **2**. The base-promoted eliminative ring fission of the oxaziridines can therefore be regarded as an α,β-elimination to form carbon–nitrogen double bond from compounds of a type H–C_β–N_α–X. In such an elimination, X should become a better leaving group than in the formation of carbon–carbon double bond from H–C_β–C_α–X-type compounds[15] since the bond energy of N_α–X bond is less than that of C_α–X bond. Ring strain in oxaziridines may also increase the leaving group ability of the "alkoxy group". The transition state of such eliminations would therefore become more skewed toward the loss of the leaving group than those of the corresponding olefin-forming eliminations.[16]

The primary β-deuterium isotope effect is clearly one of the best means of determining the extent of hydrogen transfer in the transition state. The effects for (*E*)-**1a** and (*E*)-**1e** are larger than those previously reported for similar fragmentations of 2-propyl-3-isobutyl-3-methyloxaziridine[3e] and 2-(diphenylmethyl)-3-(4-nitrophenyl)oxaziridine[3g] and are of close to the theoretical maximum. A reversible E1cB mechanism, $(E1cB)_R$, is also excluded on the basis of the magnitude of the kinetic isotope effects and the nondetectable effect of the conjugate acid of triethylamine. If, as has been indicated by recent calculations,[17] the magnitude of k_H/k_D can be interpreted in terms of the transition-state proton transfer in E2 eliminations, the values obtained for (*E*)-**1a** and (*E*)-**1e** suggest a transition state in which the β-proton is almost half-transferred to base. Although it is sometimes difficult to distinguish an irreversible E1cB mechanism, $(E1cB)_I$, from a concerted E2, the substituent effects observed for the C_β-phenyl and C3-phenyl groups in **1** and **2** and the following considerations lead us to the latter mechanism.

An $(E1cB)_I$ mechanism, in which proton transfer from C_β to form a carbanion is rate-determining, is characterized by a well-broken C_β–H bond, an excess of negative charge on C_β and intact C_α (or N_α) leaving group bond. Therefore, one should expect a larger positive ρ value for substitution in C_β-phenyl group, a smaller leaving group effect, and a faster rate of reaction, compared to similar elimnations with an E2 mechanism.[18,19] Indeed, for the amine-promoted dehydration of *N*-(α-cyanobenzyl)-*N*-phenylhydroxylamines, a closely related reaction to the present elimination, the ρ values for substitution in the C_β-phenyl and the N_α-phenyl groups have been reported to be 2.90 and 1.57, respectively.[20] If the present elimination proceeds through an $(E1cB)_I$ mechanism, the magnitude of the substituent effects should be in the order of $\rho_x > \rho_y > 0$. The positive reaction constant, $\rho_x = 0.89$, obtained for the C_β-phenyl ring might imply the development of negative charge on C_β in the transition state. However, a better correlation not with σ^- ($\rho = 0.59$, $\gamma = 0.978$) but with σ ($\gamma = 0.998$) in the Hammett plots, and the much smaller ρ_x value than those for the reactions accepted as $(E1cB)_I$ mechanism are both inconsistent with a carbanion mechanism. Furthermore, the reaction constant ($\rho_y = 0.68$) for the C3-phenyl ring is relatively large in spite of the insertion of two atoms between the C_β- and the C3-phenyl groups. Provided that the transmission factor of one sp^3 carbon is 0.43,[21] this value of ρ_y would be comparable in effect to a reaction constant, $\rho_y' = 1.58$, for the hypothetical elimination of a system which has the phenyl group directly on the N_α atom and reacts by a similar mechanism. The order $\rho_y' > \rho_x > 0$, thus obtained, excludes the possibility of an $(E1cB)_I$ mechanism. There must be no effective charge on the C_β. The positive value in ρ_y means that the transition state has considerable negative charge on the O atom in the leaving group, i.e., the rupture of the N_α–O bond is involved in the transition state.

For concerted E2 eliminations forming a carbon–carbon double bond, it is now widely accepted that there exists a spectrum of transition-state structures ranging from the E1cB-like to E1-like. Between these two extremes there is a central structure, exhibiting equal extent of C_β–H and C_α–X bond breaking and no development of charge at either C_β or C_α.[15] An E1cB-like E2 mechanism is, however, less plausible in the present system, because many C_β-phenyl activated systems classified into this category of mechanism are usually best correlated with σ^- and the magnitudes of their ρ values are nearly or more than twice the value of ρ_x obtained.[22,23] Therefore, the same considerations as mentioned in eliminating an $(E1cB)_I$ mechanism can be accepted on the relative magnitude of the two reaction constants observed. In the present system the C3-phenyl groups of **1** and **2** can behave not only as a part of the N_α substituent but also as a part of the N_α-benzyloxy leaving group. Electron-withdrawing substituents on the C3-phenyl group of **1** will enhance the ability of the leaving group through the oxygen atom ($\rho_{y(lg)} > 0$) but, on the contrary, reduce that through the N_α atom ($\rho_{y(sub)} < 0$). However, another effect of the C3-phenyl substituents on the C_β ($\rho > 0$) will be negligible because of insertion of two atoms between C_β and the phenyl group. The magnitude of ρ_y (+0.68) obtained, therefore, should represent the net effect reflecting such opposing effects of the C3-phenyl group. If $\rho_{y(lg)} > \rho_{y(sub)}$ or $\rho_{y(sub)} \simeq 0$, $\rho_{y(lg)}$ will be equivalent to the slope ρ_{lg}, which can be estimated from the plots of the log k_2 against the pK_a's of benzyl alcohols and should provide a measure of the N_α–O bond cleavage in the transition state. The slope estimated is considerably negative, $\rho_{lg} = -0.72$ ($\gamma = 0.987$), and broadly suggests that the N_α–O bond is more than half breaking. On the other hand, it is, at present, difficult to estimate a reliable value for $\rho_{y(sub)}$. It is, however, known that in

(16) In eliminative ring fission of oxiranes the leaving-group ability of the "alkoxy group" has been predicted to be comparable to bromo or iodo. It has been noticed also that change of leaving group from methoxy through acetoxy to bromo or iodo produces change in mechanism from $(E1cB)_R$ through $(E1cB)_I$ to E2. (a) Thomas, P. J.; Stirling, C. J. M. *J. Chem. Soc., Perkin Trans. 2* **1978**, 1914–1919. (b) Palmer, R. J.; Stirling, C. J. M. *J. Am. Chem. Soc.* **1980**, *102*, 7888–7892.

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(20) The presence of a better carbanion stabilizing group, CN, and of a poorer leaving group, OH, compared to our system, seems to shift the transition state structure of the elimination to an E1cB region.

(21) Jones, R. A. Y. *Physical and Mechanistic Organic Chemistry*; Cambridge University: Cambridge, 1979; p 39.

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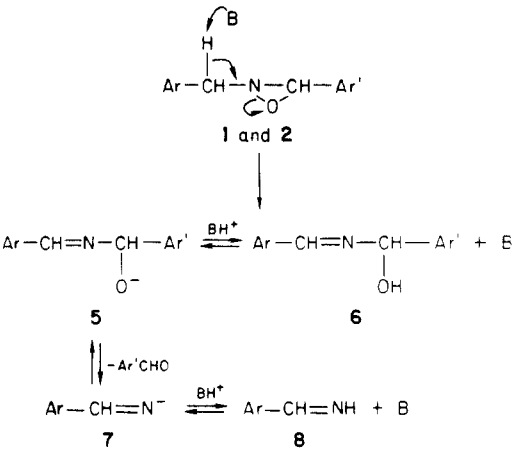
(23) Baciocchi, E.; Perucci, P.; Rol, C. *J. Chem. Soc., Perkin Trans. 2* **1975**, 329–333.

E1cB-like E2 reactions of 2-phenylethyl chlorides in $EtO^-/EtOH$ the introduction of an α-phenyl group has shifted the transition-state structure somewhat toward the central region.[23] For more central E2 reactions of 1-phenylethyl halides, the introduction of substituents into the phenyl group has caused a large change in mechanism from an E1cB-like to an E1-like.[17b,26] In the present elimination such effects of the phenyl group and its substituents are weakened by the intervening CH group, but the large ring strain and partial sp^2 character of the oxaziridine ring[24] and the longer N_α–O and shorter N_α–C bonds[25] relative to the corresponding bond lengths in usual compounds should permit us to estimate a small value without sacrifice of the good Hammett correlations observed. The value of $\rho_{y(sub)}$ will enhance and increase its importance as the transition state of E2 reactions shift toward an E1-like from an E1cB-like through the central.[17b,23,26] If $\rho_{y(sub)} = -0.2$ to -0.5 is allowed, $\rho_{y(lg)} = +0.9$ to $+1.2$ can be expected. The magnitudes of ρ_x (+0.89) and $\rho_{y(lg)}$ (+1.2), thus estimated for **2** and **1**, respectively, are comparable to the corresponding substituent effects for an imine-forming elimination of *N*-benzyl-*O*-(arylsulfonyl)hydroxylamines ($\rho_{benzyl} = 0.6$–0.8, and $\rho_{lg} = 1.36$),[27] in which leaving group loss is well ahead of benzylic proton removal but there is no effective positive charge on the N_α atom. Therefore, the fragmentations of **1** and **2** with triethylamine in acetonitrile are best interpreted by a near central E2 mechanism, in which there are virtually no positive and negative charges at the N_α and C_β atoms, respectively. In the transition state of (*E*)-**1a**, β-proton transfer is on the slightly early side of symmetric and the degree of N_α leaving group bond breaking is slightly more advanced than the proton removal. An increase in magnitude of the primary β-deuterium isotope effect from (*E*)-**1a** (6.1) with an electron-withdrawing substituent in the leaving group toward (*E*)-**1e** (6.9) with an electron-donating substituent in that group means a small change of the transition state from a slightly E1-like (for (*E*)-**1a**) toward the central (for (*E*)-**1e**). The leaving group ability of the "alkoxy group" in the oxaziridines seems to be slightly smaller than that of arylsulfonates.

It is known that the Brønsted parameter β also provides a means of determining the transition-state structure of E2 reactions.[28] The value of 0.46 estimated from the least-squares slope of Brønsted plots for a series of tertiary amines (Figure 4)[29] also suggests that for the fragmentation of (*E*)-**1a** β-proton transfer is slightly less than half-transferred in the transition state. The negative deviation of the point for 2-(diethylamino)ethanol from the Brønsted slope can be rationalized by the intramolecular five-membered hydrogen bonding of ethanolamines in aprotic solvents,[30] which is masked in water. The presence of hydrogen bonding between tertiary amines and alcohols in acetonitrile is also suggested from the effect of added

Scheme IV



methanol (Table I and Figure 2). Such intra- and intermolecular hydrogen bondings of ethanolamines must reduce the concentration of the free amines in acetonitrile and result in a decrease in the rate of the fragmentation. Although an E1cB mechanism with internal return provides a possible alternative to a concerted E2 mechanism,[31] such a mechanism is ruled out on the bases of the magnitude of the Brønsted β (0.46), the better correlation with σ than with σ^- in the Hammett plot for **2**, and the normal Arrhenius behavior ($\Delta E_a^{D-H} = 1.14$ kcal/mol, $A^H/A^D = 0.99$) observed for (*E*)-**1a**.

Activation parameters (Table IV) are also consistent with an E2 mechanism. Hoffman and Belfoure have reported that for base-promoted olefin- or imine-forming E2 reactions with comparable energy changes for β-proton removal in the transition state ($k_H/k_D \simeq 6$), the steady change in mechanism from an E1cB-like toward an E1-like, reflected in the decreasing activation enthalpies, can be correlated with the bond energy changes in the bonds connecting the leaving-groups to the substrates.[32] The much smaller activation enthalpy for (*E*)-**1a** (less than 65%) than those for the compared E2 reactions seems to reflect the weaker N_α–O bond of the oxaziridine (~30 kcal/mol),[33] which is well stretched by a large ring strain and is consistent with an earlier transition state for the E2 reaction of (*E*)-**1a**. Such a large decrease in activation energy by ring strain has been reported in a nucleophilic eliminative ring fission of an oxirane.[16b] Regardless of a relief of the ring strain, the observed large negative activation entropy can be attributed to a restricted orientation between 1 and the attacking base,[34] solvation of charged transition state formed from the uncharged substrate and base, and increased solvent organization for the extended charge. Aprotic polar solvents should give much larger negative activation entropies for such reactions than protic solvents do.[35]

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(28) Yano, Y.; Oae, S. *Tetrahedron* **1970**, *26*, 27–35.
(29) As the pK_a values of the amines in acetonitrile at 40 °C are not available they were estimated from the difference, $\Delta(pK_a)_{A-W}$, between the pK_a values of structurally related amines in acetonitrile and those in water at 25 °C[36] and the temperature change, $[-d(pK_a)/dT]$, of the conjugated acids BH^+ in water.[37,38] If the value for 2-(diethylamino)ethanol is not included in the Brønsted plots, one obtains essentially the same slope.
(30) (a) Freeman, H. H. *J. Am. Chem. Soc.* **1961**, *83*, 2900–2902. (b) Bergmann, E. D.; Gil-Av, E.; Pinchas, S. *Ibid.* **1953**, *75*, 68–71.
(31) (a) Koch, H. F.; Dahlberg, D. B. *J. Am. Chem. Soc.* **1980**, *102*, 6102–6167. (b) Koch, H. F.; McLennan, D. J.; Koch, J. G.; Tumas, W.; Dobson, B.; Koch, N. H. *Ibid.* **1983**, *105*, 1930–1937. (c) Koch, H. F. *Acc. Chem. Res.* **1984**, *17*, 137–144.
(32) Reference 27, p 5690 and references cited therein.
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(34) The benzylic protons of (*E*)-**1a** are in different circumstances showing two doublets in the ^1H NMR spectrum.
(35) Bunnett, J. F. In *Technique of Chemistry, Investigation of Rates and Mechanisms of Reactions*; Lewis, E. S., Ed.; Wiley: New York, 1974; Vol. 6, Part 1, p 424.
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(37) Perin, D. D.; Dempsey, B.; Sergeant, E. P. pK_a *Prediction for Organic Acids and Bases*; Chapman and Hall: London, 1981.

A brief investigation of the effect of the structure and strength of catalyst amines on the relative rate of the fragmentations of (*E*)- and (*Z*)-**1a** (Table V) shows that the reaction of the *Z* isomer would be accelerated by its larger ring strain. Such a reactivity has been observed in a similar fragmentation of 2-methyl-3-phenyloxaziridine (**9**)[4] for which we must discuss later. The rate ratios ($k_{2[(Z)\text{-}1a]}/k_{2[(E)\text{-}1a]}$) are, however, small and seem to be in such magnitudes as reasonably ascribed to the difference in steric hindrance between the *E* and *Z* oxaziridines toward bases in an E2 mechanism.[34] Thus, change in mechanism between the *E* and *Z* forms is not probable in the fragmentation of **1**. The small ratios also exclude the possibility of an E2C mechanism, in which a loose covalent interaction between catalyst bases and the N_α atom of **1** would be involved and a considerably different steric effect of amines should be expected.

The reaction in Scheme IV is proposed for the base-promoted fragmentations of 2-benzyl-3-phenyloxaziridines (**1** and **2**). The decrease in the rate constant k_2 with an increase in the initial concentration of the base in method C may be attributed to the addition of **7** to benzaldehydes to give **6**, a reaction which is accelerated by an increased dissociation of benzylideneimines **8**.

Preferential deuterium incorporation in the methyne and azomethyne moieties of **4c** by the fragmentation of (*E*)-**1a**-d_2 and preferential formation of trichlorobenzylidene animal **4b** from **2b** strongly support that **4** is produced by a rapid trimerization of **8**. An alternative mechanism reported by Ogata et al.,[12] in which intermediate **6** reacts with **8** to give **4**, will involve a slower step than the trimerization of **8** and can be excluded.

Reactions of 2-Methyl-3-phenyloxaziridines. For the fragmentations of 2-methyl-3-phenyloxaziridines promoted by various amines and nucleophiles, a nucleophilic substitution mechanism which involves the intermediacy of an ylide has been proposed (Scheme I, path b).[4] Among the reported 2-alkyl-3-phenyloxaziridines **9** seems to be the most appropriate probe for differentiating path b from path a; the N_α atom is relatively electron deficient by the presence of an electron-withdrawing nitro group and the attack of a nucleophile onto the N_α atom would be most favorable. However, the smaller fragmentation rate for **9** compared to the rate for **1a** with a more bulky group around N_α atom is inconsistent with the nucleophilic substitution mechanism. The observed large primary β-deuterium isotope effects for (*E*)-**9** and (*Z*)-**9** clearly indicate rate-determining C_β–H bond rupture. The excellent linearity of the Arrhenius plot and the normal Arrhenius behavior in the fragmentation of (*Z*)-**9**, though they have been obtained from a restricted range of temperature, suggest the absence of an alternative pathway. Therefore, the triethylamine-promoted fragmentation of **9** proceeds through an elimination mechanism (path a), and the nucleophilic substitution mechanism (path b) must be excluded. Depending on the absence of a β-phenyl group as an activating group or a carbanion-stabilizing group in **9** and the E2 character observed for **1** and **2**, the $(E1cB)_I$ mechanism should be ruled out. The small solvent effect on the rate of the fragmentation of (*Z*)-**9** accompanied by a constant β-deuterium isotope effect also consistents with an E2 mechanism.

On the bases of kinetics and thermodynamic data for the three representative 2-alkyloxaziridines **1**, **2**, and **9** we can generally conclude that the tertiary amine promoted fragmentations of 2-alkyl-3-phenyloxaziridines with β-hydrogen exclusively proceed through an E2 mechanism in aprotic solvents.

Confirmation of the competition between E2 and S_N2 mechanisms or determination of E2–S_N2 borderline for the fragmentation of 2-alkyloxaziridines must be further conducted with various amines or bases with different basicities or nucleophilicities and structures.

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Registry No. **1a**, 25105-62-8; **1b**, 102852-83-5; **1c**, 7731-37-5; **1d**, 102852-84-6; **1e**, 102852-85-7; **2a**, 102852-86-8; **2b**, 102852-87-9; **2d**, 102852-88-0; **2e**, 102852-89-1; **4c**, 92-29-5; (*E*)-**9**, 102918-84-3; (*Z*)-**9**, 102852-90-4; D_2, 7782-39-0; 4-chlorobenzylideneimine, 45709-05-5; *p*-nitrobenzaldehyde, 555-16-8; triethylammonium trifluoroacetate, 454-49-9; methanol, 67-56-1; 2-(diethylamino)-ethanol, 100-37-8; *N*-methylmorpholine, 109-02-4; triethylamine, 121-44-8; morpholine, 110-91-8; 2,6-lutidine, 108-48-5.

Supplementary Material Available: Analytical and ^1H NMR data for oxaziridines **1** and **2** (Table A) and kinetic data for the fragmentation of (*E*)-**1a** (Table B) (2 pages). Ordering information is given on an current masthead page.

(38) (a) Hall, H. K., Jr. *J. Am. Chem. Soc.* **1957**, *79*, 5441–5444. (b) Perrault, G. *Can. J. Chem.* **1967**, *45*, 1063–1067.