times from cyclohexanone to give bright yellow needles: mp 375–377°; uv λ_{max} 330, 220 mμ; ir λ_{max} 3.30, 5.60, 5.69, 5.80, 6.23, and 6.81 μ. *Anal.* Calcd for $C_{20}H_8N_4O_4S_2$: C, 55.54; H, 1.86; N, 12.96. Found: C, 55.40; H, 1.78; N, 13.19.

This material did react with hydrazine to give an amino product (**18**) and subsequently a benzoyl derivative. However, neither of these has so far been purified or otherwise adequately characterized.

***n*-Propyl 2-Thiazolothiazolecarbamate (19).** To 2-thiazolothiazolecarbonyl hydrazide (**12**, 710 mg, 3.55 mmol) in 20 ml of aqueous hydrochloric acid, stirred with 400 ml of ether at 10°, was added 420 mg (5.9 mmol) of sodium nitrite. A precipitate of the azide was formed but was extracted by the ether as stirring was continued for 15 min. The ether phase and an ether extract of the aqueous phase was dried (magnesium sulfate and then Drierite) and then diluted with 100 ml of *n*-propyl alcohol. The ether was distilled and the alcohol solution was refluxed for 1 hr, concentrated to 10 ml, and allowed to stand at 20°. There was obtained 470 mg (55%) of the *n*-propyl carbamate (**19**), mp 185–192°. The material was dissolved in ether, the solution was filtered and diluted with propyl alcohol, and the ether distilled to give colorless crystals, mp 192–194°. This process was repeated twice followed by sublimation (115–123°, 0.01 mm) for the analytical sample: mp 198–200.5°; uv λ_{max} 289 (log ε = 4.22), 246 mμ (log ε = 3.78); ir λ_{max} 3.18, 3.30, 3.42, 3.62, 5.83, 6.39, 6.80, 6.96, 10.43 μ. *Anal.* Calcd for $C_8H_9N_3O_2S_2$: C, 39.49; H, 3.73; N, 17.27. Found: C, 39.71; H, 3.89; N, 17.37.

Allyl (26%, mp 190–192°) and *t*-amyl (26%, mp 230° dec) carbamates were prepared by similar procedures.

2-Phthalimidothiazolothiazole (20). The *n*-propyl carbamate (**19**, 465 mg, 1.93 mmol) and 610 mg (4.12 mmol) of phthalic anhydride were heated at 225° for 40 min to give a dark liquid melt. The reaction mixture was cooled, broken up, and stirred overnight with 60 ml of aqueous sodium bicarbonate. The solid phthalimide derivative was collected, washed with water, and dried to give 440 mg (80%) of dark beige solid, mp 275–278°. Crystallization from chloroform–cyclohexane gave bright yellow needles: mp 279–280°; uv λ_{max} 300 (log ε = 4.26), 230 mμ; ir λ_{max} 3.30, 3.35, 5.60 (m), 5.69 (m), 5.80 (s), 6.26, 6.78, 7.00, and 10.50 μ. *Anal.* Calcd for $C_{12}H_5N_3O_2S_2$: C, 50.16; H, 1.75; N, 14.63. Found: C, 50.38; H, 1.85; N, 14.80.

2-Aminothiazolothiazole (21). 2-Phthalimidothiazolothiazole (**20**, 127 mg, 0.44 mmol), 1 ml of 95% ethanol, and 0.026 ml (27 mg, 0.54 mmol) of 100% hydrazine hydrate were stirred at room temperature for 1.5 hr. The yellow solid dissolved slowly and a white precipitate formed. Addition of 5 ml of 5% hydrochloric acid dissolved most of the suspended matter. Filtration removed 40 mg of unidentified material. Removal of ethanol and some water precipitated 12 mg (17%) of phthalhydrazide which was removed by filtration. The acidic filtrate was washed with ether, neutralized with solid sodium bicarbonate, and extracted with ether. Concentration of the ether solution afforded crops of 20 mg (29%, mp 213–214° dec) and 12 mg (17%, mp 203–207° dec). Crystallization of the first crop from chloroform gave rhombic crystals: mp 215–215.5° dec; uv λ_{max} 297 (log ε = 3.97), 235; in acid 225, 283 mμ; ir λ_{max} 3.10, 3.28, 3.70, 6.09, 6.58, 6.92, and 10.42 μ. *Anal.* Calcd for $C_4H_3N_3S_2$: C, 30.56; H, 1.92; N, 26.73. Found: C, 30.30; H, 2.36; N, 26.72.

The Effect of Substituents on the Rate of Pyramidal Inversion of 1-Aryl-2,2-dimethylaziridines[1]

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Abstract: The influence of electronic effects on the barrier to pyramidal inversion in *meta*- and *para*-substituted N-phenyl-2,2-dimethylaziridines has been investigated by an examination of the temperature-dependent nmr spectrum. Rate constants and free energies of activation at the coalescence temperature have been determined. The inversion barrier shows a linear correlation with the Hammett substituent constant σ^- (ρ = 2.8–3.3 at −60°). The direction of the substituent effect parallels that previously found for pyramidal inversion at sulfur in sulfoxides and at phosphorus in phosphines, but the magnitude of the effect is greatest in the aziridines. These results are ascribed to conjugation of the lone pair on the inverting center with the attached arene π system, an effect which is more pronounced for first- than for second-row elements, and which finds its maximum expression in the transition state for the inversion process.

It is generally accepted that conjugation of a nitrogen lone pair with a π system decreases the barrier to inversion of the pyramidal nitrogen site, which at the same time is flattened more or less depending on the amount of conjugation. A wide variety of compounds (*e.g.*, amides, cyanamides, aromatic amines) present such characteristics. However, a homogeneous series of substrates is needed in order to study the electronic effects more quantitatively and eventually to allow a separation of the empirically defined concepts of substituent electronegativity and conjugative ability.

Such studies have previously been carried out in related systems. Recent investigations into the factors influencing the pyramidal stability of sulfoxides have shown that the inversion barrier for these compounds is remarkably insensitive to attached substituent groups.[3] Thus acyclic dialkyl, alkyl aryl, and diaryl sulfoxides racemize at 210° with free energies of activation[4a] covering the relatively narrow range[4b] of 38–41 kcal/mol. Parallel investigations into the pyramidal stability of phosphines have shown that the inversion barrier in these compounds is only slightly more sensitive to attached substituent groups.[5] Thus, acy-

(1) This work was supported in part by the Air Force Office of Scientific Research under Grant No. AF-AFOSR-1188-B.

(2) U. S. Public Health Service Predoctoral Fellow, 1968–1970.

(3) (a) D. R. Rayner, A. J. Gordon, and K. Mislow, *J. Amer. Chem. Soc.*, 90, 4854 (1968); (b) D. R. Rayner, E. G. Miller, P. Bickart, A. J. Gordon, and K. Mislow, *ibid.*, 88, 3138 (1966).

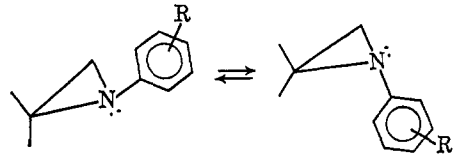
(4) (a) Calculated from one-point rate constants reported in ref 3a using the Eyring equation and assuming a transmission coefficient equal to unity. (b) Excluded from this range are two compounds (1 and 2 of ref 3a) for which a steric effect on the rate is indicated.

clic trialkyl-, dialkylaryl-, and diarylalkylphosphines racemize at 130° with free energies of activation in the range of 29–36 kcal/mol.

The relative insensitivity of the inversion barrier of sulfoxides and phosphines to the effect of aryl substituents is in marked contrast to the results found in the nitrogen series.[6] Thus the inversion rate of 1-phenylaziridine (**1**)[7] at −40° is already equal to the inversion rate of 1,2,2-trimethylaziridine (**2**)[8] at 70°. The free energies of activation at −40° reflect this difference in pyramidal stability of a N-alkyl *vs.* a N-arylaziridine: a value of 12.8 kcal/mol for **1** compared to 19.3 kcal/mol for **2**.[9]

While previous investigations[3,5] have shown that electronic effects exert only small influence on the inversion barrier for second-row elements, only limited information is available for first-row elements.[10] It thus became of interest to examine the influence of electronic effects on the pyramidal inversion of nitrogen, and to compare the results of such a study with the related case of inversion at sulfur and phosphorus.

For the present study, the temperature-dependent nmr spectra of a homogeneous series of N-aryl-2,2-dimethylaziridines (**3**) as dilute solutions in dichlorodifluoromethane were examined.[11] The *gem*-methyl groups were included to serve as a convenient nmr signal for study uncomplicated by strong AB coupling. Pyramidal inversion of nitrogen serves to interconvert the diastereotopic *gem*-methyl groups as well as the diastereotopic *gem*-hydrogens. These compounds are



3a, R = 4-OCH_3
b, R = H
c, R = 4-Cl
d, R = 3-CF_3
e, R = 4-CF_3
f, R = 4-NO_2

readily available through photolysis of the corresponding 1-aryl-5,5-dimethyl-Δ^2-1,2,3-triazolines, which are in turn available through the cycloaddition of aryl azides with isobutylene.[12] Substituents were chosen so that the present results could be directly compared to the results found[3,5] for second-row elements.

While it would clearly have been simpler to obtain the inversion rate of each aziridine at its coalescence temperature, T_c, such an approach would have prevented direct rate comparisons at the same temperature making interpretation within this system and comparison with other systems difficult. Instead, adopting the procedure of Anet, *et al.*,[13] the temperature-dependent rate of two compounds, **3a** and **3b**, was determined while for the other aziridines only one-point rate constants at T_c were obtained. Extrapolation of the rate constant of **3a** down to the T_c of each of the other aziridines permitted the rate of each compound to be compared with that of **3a**.

Results

At 23°, the nmr spectrum of **3a** shows four singlets at τ 8.90, 8.15, 6.38, and 3.35 corresponding to the *gem*-methyls, the *gem*-hydrogens, the *p*-methoxy, and the aromatic protons (which are accidentally degenerate).[14] As the temperature is lowered, the signals at τ 8.90 and 8.15 broaden until they coalesce at −26 and −30°, respectively. As the temperature is reduced still further to −68°, the peaks originally at τ 8.90 and 8.15 are each replaced by a cleanly resolved asymmetric doublet showing chemical shift differences of 25.4 and 20.2 Hz. The line widths of the two signals for the *gem*-methyl groups are unequal; the low-field signal has a smaller line width at half-height than the upfield signal (line widths 1.5 and 1.8 Hz). The same is true for the *gem*-hydrogen signals except that here the upfield signal is now the more narrow of the two (line widths 2.2 and 1.8 Hz). This asymmetry is probably the result of stereospecific long range ^1H–^1H or ^1H–^{14}N coupling.[15] The presence of such unresolved coupling is indicated by the appreciable line width of these signals in the absence of exchange broadening compared to the line width of TMS.[8,16] The remaining aziridines **3b–3f** display similar temperature-dependent spectra but the temperature at which the spectral changes occur becomes progressively lower.

The nitrogen inversion rate, k_{inv}, of **3a** and of **3b** was determined by an analysis of the temperature-dependent line shape of the *gem*-methyl protons. Treating the methyl groups as an uncoupled[17] AB system, theoretical spectra were calculated and visually compared to the experimental spectra using the program CLATUX[19a] (Princeton) and a program based on the Alexander equations[19b] (Strasbourg). The unequal line widths were simulated by assuming unequal transverse relaxation times for the two methyl groups.[15] An effective transverse relaxation time for each methyl group was calculated from the minimum observed line width of each group under

(5) R. Baechler and K. Mislow, *J. Amer. Chem. Soc.*, **92**, 3090 (1970).
(6) For a recent review with leading references see S. J. Brois, *N. Y. Acad. Sci.*, **31**, 931 (1969).
(7) F. A. L. Anet and J. M. Osyany, *J. Amer. Chem. Soc.*, **89**, 352 (1967).
(8) M. Jautelat and J. D. Roberts, *ibid.*, **91**, 642 (1969).
(9) $\Delta G^{\ddagger}$ for **2** at −40° was calculated from the data given in ref 8 for neat 2.
(10) A limited substituent study of diaryldiazetidinones has appeared [E. Fahr, W. Fischer, A. Jung, L. Sauer, and A. Mannschreck, *Tetrahedron Lett.*, 161 (1967)].
(11) Aziridine 3f was examined in dichlorofluoromethane.
(12) (a) P. Scheiner, *Tetrahedron*, **24**, 349 (1968); (b) *ibid.*, **24**, 2757 (1968); (c) *J. Amer. Chem. Soc.*, **90**, 988 (1968), and references therein.
(13) F. A. L. Anet, R. D. Trepka, and D. J. Cram, *ibid.*, **89**, 357 (1967).
(14) Line positions are in parts per million and refer to internal TMS (line width about 0.5 Hz over the temperature range 23° to −77°).
(15) The unequal line widths of the N-methyl protons of N,N-dimethylacetamide-d_3 have been explained in terms of such couplings [R. C. Neuman, Jr., and V. Jonas, *J. Amer. Chem. Soc.*, 90, 1970 (1968)].
(16) The average line width of the *gem*-methyl protons and that of the *gem*-hydrogens (1.65 and 2.0 Hz, respectively) of **3a** in the absence of exchange agree well with those found for the similar aziridine 2.[8]
(17) Jautelat and Roberts[8] have concluded that coupling between the *gem*-methyl protons makes no contribution to the observed line width. While the presence of unresolved coupling with either the methylene protons or with the ^{14}N nucleus is indicated by the appreciable line width of the methyl protons in the absence of exchange, it has been shown that the effect of such couplings on the rate is only important for very large and very small values of k.[18]
(18) (a) H. S. Gutowsky and P. A. Temussi, *J. Amer. Chem. Soc.*, **89**, 4358 (1967); (b) A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *ibid.*, **88**, 3185 (1966).
(19) (a) G. Binsch in "Topics in Stereochemistry," Vol. 3, E. L. Eliel and N. L. Allinger, Ed., John Wiley & Sons, Inc., New York, N. Y., 1968, p 97 ff; (b) P. Linscheid and J. M. Lehn, *Bull. Soc. Chim. Fr.*, 992 (1967).

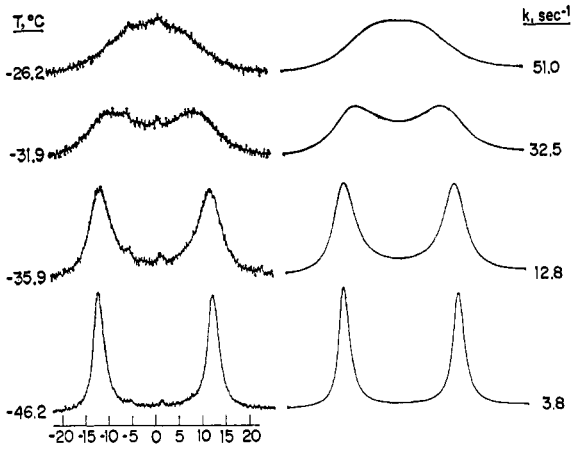


Figure 1. Comparison of simulated (right) and experimental (left, scale in hertz) nmr spectra for N-(*p*-methoxyphenyl)-2,2-dimethylaziridine, **3a**, and rate constants of inversion at four temperatures.

conditions of slow exchange.[19a] The relaxation times so calculated were assumed to be constant throughout the temperature range studied.[20]

For **3a**, it was not possible to obtain satisfactory fit of theoretical to experimental spectra using a fixed value for the chemical-shift difference between the methyl groups, ν_{ab}.[21a] Nevertheless, treating both k_{inv} and ν_{ab} as variables, an excellent fit of theoretical to experimental curves was obtained. Illustrative experimental and simulated spectra are included in Figure 1. Values of k_{inv} and ν_{ab} found in this analysis are given in Table I.

Table I. Chemical-Shift Differences and Rate Constants for Pyramidal Inversion at Different Temperatures of 1-(*p*-Methoxyphenyl)-2,2-dimethylaziridine (**3a**)

Temp, °C	ν_{ab}, Hz[a]	k_{inv}, sec^{-1}
−77.0	25.8	
−68.0	25.4	
−51.2	25.0	1.4
−46.2	25.0	3.8
−43.1	24.9	7.4
−35.9	24.8	12.8
−35.3	24.7	17.4
−31.9	24.0	32.5
−30.0	23.4	40.7
−26.2	22.5	51.0

[a] Values of ν_{ab} refer to the *gem*-methyl protons.

Standard least-squares treatment of the data gave the following Eyring activation parameters for **3a**: $\Delta H^{\pm}$ = 15.2 ± 1 kcal/mol; $\Delta S^{\pm}$ = 11.4 ± 6 eu.

A similar analysis of the spectral data (neglecting changes in ν_{ab}[21b]) gave the following Eyring activation parameters for **3b**: $\Delta H^{\pm}$ = 13.6 ± 1 kcal/mol; $\Delta S^{\pm}$ = 10.4 ± 5 eu.

(20) This assumption is not strictly valid since the line width of the methyl singlet in the fast-exchange limit (0.9 Hz) is smaller than the average line width of the methyl signals in the slow-exchange limit (about 1.6 Hz). However, this factor is only expected to introduce error under conditions of rapid exchange.

(21) (a) Similar behavior has been observed previously.[8,22] (b) The influence of small changes in ν_{ab} on the calculated rates is, however, of relatively minor importance here as ν_{ab} itself is quite large.

(22) (a) M. Rabinovitz and A. Pines, *J. Chem. Soc., B*, 1110 (1968); (b) M. Rabinovitz and A. Pines, *J. Amer. Chem. Soc.*, 91, 1585 (1969), and references cited therein.

For the remaining aziridines, one-point inversion rate constants, k_c, were obtained at the coalescence temperature of the *gem*-methyl protons using the relationship[18b] in eq 1[23] where ν_{ab} is the value of the

$$k_c = \pi\nu_{ab}/\sqrt{2} = 2.22\nu_{ab} \quad (1)$$

chemical-shift difference at T_c. Because of the temperature variation of ν_{ab} found for **3a**, a measure of ν_{ab} at T_c was obtained using the procedure of Gutowsky and coworkers.[18b,24] From the values of k_c and T_c so determined, the free energy of activation at T_c, denoted $\Delta G_c^{\pm}$, was calculated using the Eyring equation and assuming a value of unity for the transmission coefficient. Values of k_c, T_c, $\Delta G_c^{\pm}$, and the inversion rate, k_T, of **3a** extrapolated to the T_c of each of the other aziridines are collected in Table II. Although it is difficult to estimate the error in such one-point rate constants, it can be shown that the value of $\Delta G_c^{\pm}$ is rather insensitive to the exact choice in k_{inv}. Comparison of the inversion rate for **3a** determined by coalescence measurements shows that the one-point rate constant agrees to within 15% with the value determined at T_c by the total line-shape analysis. Such an error in k_{inv} represents an error in $\Delta G_c^{\pm}$ of less than 0.2 kcal/mol.

Comment should be made on the observed temperature variation of ν_{ab}. As indicated in Table II, variation appears to be greatest for the *p*-OCH_3 compound, **3a**, and of lesser importance for the other aziridines.[25] If, as is the case for N,N-dimethylformamide,[22] the variation in ν_{ab} with temperature is the result of association phenomena, the possibility exists that the measured rates (and the activation parameters thence derived) do not represent the true inversion rate of a "free" aziridine but rather represent the apparent inversion rate of an associated species.[26]

Discussion

An effect of steric origin is disclosed by a comparison of $\Delta G^{\pm}$ for 1-phenylaziridine (**1**) and 1-phenyl-2,2-dimethylaziridine (**3b**), 12.8 and 11.2 kcal/mol, respectively. While the rate-enhancing effect of the *gem*-methyl groups may be the result of a relief of nonbonded strain in going to the planar transition state, the possibility exists that the lower $\Delta G^{\pm}$ for **3b** results from a gain in rotational freedom in the transition state. The former effect would be expected to manifest itself in the $\Delta H^{\pm}$ term, while the latter effect should be reflected by the $\Delta S^{\pm}$ term. Indeed, in the thermal racemization of sulfoxides,[3a] the importance of the entropy factor was demonstrated. However, although the $\Delta S^{\pm}$ of 11.4 and 10.4 eu found for **3a** and **3b**, respectively, in this study might indicate a loss of rotational freedom in the ground state that is relieved in going to the transition

(23) Equation 1 is valid for an uncoupled AB system under conditions where ν_{ab} is much greater than the line width of the signals in the absence of exchange.[18b] This condition was easily met for all the aziridines in the present study.

(24) At T_c, the full line width at half-height of the exchange-broadened peak is equal to ν_{ab}.

(25) (a) Because of the significant change in line width of the *gem*-methyl signals in the neighborhood of T_c, the value of ν_{ab} determined at T_c[24] possesses an uncertainty of about 1 Hz; (b) the *p*-Cl compound, **3c**, precipitated from solution below −70°; therefore ν_{ab} could only be obtained at T_c.

(26) Evidence has recently been presented that aziridines associate in the neat state as well as in solution in carbon tetrachloride [H. Saitô, K. Nukada, T. Kobayashi, and K. Morita, *J. Amer. Chem. Soc.*, **89**, 6605 (1967)].

Table II. Rates and Free Energies of Activation at the Coalescence Temperature for 1-Aryl-2,2-dimethylaziridines

Compd no.	Aryl group	ν_{ab},[a] Hz	T_c, °C	k_c,[b] sec^{-1}	k_T,[c] sec^{-1}	k_c/k_T	$\Delta G_c^{\ddagger}$,[d] kcal/mol
3a	$4\text{-}CH_3OC_6H_4$	25.4 (−68°) 22.5[e]	−26	50		1.0	12.5
3b	C_6H_5	25.3 (−92°) 25.3[e]	−49	56	2.3	24.4	11.2
3c	$4\text{-}ClC_6H_4$	25.2[e]	−53	56	1.2	46.7	11.0
3d	$3\text{-}CF_3C_6H_4$	25.1 (−91°) 24.9[e]	−59	55	0.5	110	10.7
3e	$4\text{-}CF_3C_6H_4$	26.0 (−105°) 26.9[e]	−72	60	0.04	1500	10.0
3f	$4\text{-}O_2NC_6H_4$	22.2 (−125°, $CHFCl_2$)	−107	49	<0.04	>1500	8.2

[a] Refers to *gem*-methyl protons, solvent CF_2Cl_2 unless otherwise specified (temperature in parentheses). [b] Rate at T_c from eq 1. [c] Rate of **3a** at T_c of the other aziridine, calculated by extrapolation of Arrhenius plot of **3a**. [d] Calculated from the Eyring equation. [e] Refers to T_c.[24]

state, the limited temperature range employed in these studies and the known sensitivity of the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ terms to even slight errors in the determination of the rates make an interpretation based on this determination quite risky.[18b,27,28]

Examination of Table II indicates that electronic effects exert a significant influence on the barrier to pyramidal inversion, as measured by $\Delta G^{\ddagger}$. Proceeding down the series **3a–3f**, the free energy of activation decreases from 12.5 to 8.2 kcal/mol. The decrease in barrier to pyramidal inversion along the series parallels the ability of the substituent to withdraw electron density from the aromatic ring ($4\text{-}CH_3O$ < H < 4-Cl < $3\text{-}CF_3$ < $4\text{-}CF_3$ < $4\text{-}NO_2$). Using the free energy form of the Hammett equation,[30] the free energies of activation for these compounds show a good correlation (Figure 2) with the substituent constant σ^-, giving a value of $\rho = 2.8$ at −60°.[31,32]

Such a pronounced acceleration of inversion with increasing electron withdrawal of substituents is contrary to expectations based on a naive inductive model. Both simple valence bond arguments[34] and nonempirical calculations without[35a,b] or with[35c] orbital localization indicate that increasing the electronegativity of substituents directly attached to nitrogen should increase the barrier to pyramidal inversion.[36] The influence of substituents on a distant reaction center, however, is known to be complex. Five distinct interactions have been enumerated,[38] of which the classical σ-inductive effect is but one. Moreover, the importance of the simple σ-inductive effect has been questioned in aromatic[38] and also aliphatic[39] systems, where the substituent is separated from the reaction center by more than one or two bonds.

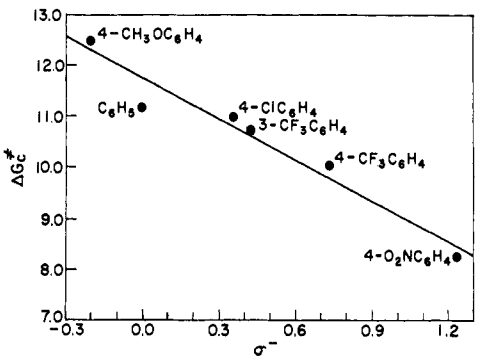


Figure 2. Hammett plot of free energies of activation at T_c *vs.* σ^- for N-aryl-2,2-dimethylaziridines, **3**.

While a detailed analysis of the influence of substituents on the barrier to pyramidal inversion in N-arylaziridines is thus likely to be quite complex, an explanation based solely on factors affecting the ability of the nitrogen to conjugate with the aromatic ring is possible. Quite simply, for substituents which withdraw electron density from the aromatic ring, conjugation of the amine nitrogen lone pair with the ring is facilitated in the transition state and the barrier to pyramidal inversion is lowered in consequence. Conversely, substituents which release electrons into the ring increase the barrier by decreasing such delocalization. That the barrier to inversion correlates with σ^- substituent constants indicates the possibility of

(27) For a discussion of the problems involved in determining $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ by nmr line-shape analysis see A. Allerhand, F. M. Chen, and H. S. Gutowsky, *J. Chem. Phys.*, 42, 3040 (1965).

(28) For N-methyl- and N-*t*-butyldiphenyloxaziridines **4a** and **4b**, respectively, the 8000-fold difference in rate of racemization at 100° is reflected almost totally in the $\Delta H^{\ddagger}$ term. Also, steric interactions in the pyramidal ground state of **4a** should be similar to those for aziridine **3a**, yet for **4a** a value of $\Delta S^{\ddagger} = 5$ eu was reported.[29]

(29) F. Montanari, I. Moretti, and G. Torre, *Chem. Commun.*, 1086 (1969).

(30) (a) For a related application see M. Raban and F. B. Jones, Jr., *J. Amer. Chem. Soc.*, **91**, 2180 (1969); (b) C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, 2, 323 (1964).

(31) To obtain this result, it is necessary to assume that all $\Delta G^{\ddagger}$ values refer to the same temperature. If not, as in the present case, it is further necessary to assume that $\Delta S^{\ddagger} = 0$. However, it can be shown that even for a fixed value for $\Delta S^{\ddagger}$ of 11.4 eu (the value found for **3a** by line-shape anaysis), ρ is 3.3 at −60°, which does not greatly deviate from 2.8.

(32) Correlation coefficient −0.975; standard deviation 0.29 kcal/mol. For the $3\text{-}CF_3$ substituent (**3d**), the σ_m value[30b] was used. For the 4-Cl substituent (**3c**), the value of σ^- was calculated using the correlation developed by Swain and Lupton.[33]

(33) C. G. Swain and E. C. Lupton, Jr., *J. Amer. Chem. Soc.*, 90, 4328 (1968).

(34) H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

(35) (a) J. M. Lehn, B. Munsch, Ph. Millié, and A. Veillard, *Theor. Chim. Acta*, 13, 313 (1969); (b) A. Rauk, L. C. Allen, and K. Mislow, unpublished work; (c) B. Lévy, Ph. Millié, J. M. Lehn, and B. Munsch, submitted for publication.

(36) The opposite conclusion has been reached by Dewar.[37] However, his arguments are based on the effect of electronegativity changes of the central atom itself from which no conclusion concerning the effect of substituents *attached* to the atom undergoing inversion may be drawn.

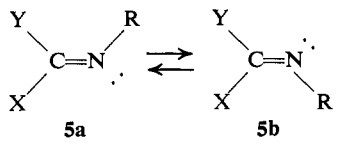
(37) M. J. S. Dewar and M. Shanshal, *J. Amer. Chem. Soc.*, **91**, 3654 (1969).

(38) M. J. S. Dewar and P. J. Grisdale, *ibid.*, **84**, 3539, 3541, 3546, 3548 (1962).

(39) C. F. Wilcox and C. Leung, *ibid.*, 90, 336 (1968), and references therein.

direct conjugation between the inversion center (nitrogen) and strong electron-withdrawing groups.[40]

Of related interest to the inversion of nitrogen in amines is the *syn–anti* isomerization of N-arylimines (**5**), for which two mechanisms have been discussed.[41]



5a **5b**

In one of these, isomerization occurs by rotation about the carbon–nitrogen double bond, whereas in the other mechanism, termed the "lateral-shift mechanism," isomerization proceeds through a linear transition state in which the lone pair on nitrogen has rehydridized to a p orbital. Experimental[41,42] as well as theoretical[43] evidence has been advanced supporting the lateral shift mechanism, although the bond rotation mechanism has been invoked for certain systems.[44] A third possibility, that of a continuum of mechanisms intermediate to these two limiting pathways, has also been advanced.[41,44b]

The lateral-shift mechanism possesses a striking resemblance to the mechanism for amine inversion. Thus, for both processes, isomerization involves rehybridization of the lone pair on nitrogen to a p orbital in the transition state for the conformational change. Indeed, both systems show the same general response to substituents on nitrogen; for both processes, a phenyl group speeds up the isomerization rate relative to an alkyl group while an attached heteroatom such as oxygen or chlorine drastically reduces the rate.[45] As shown in Table III, the response of both systems to electronic effects is also quite similar.[41,42a,46] However, the same trend of increase in rate with increasing electron-withdrawing power of substituent could also have been predicted for a bond rotation mechanism.

Having examined the electronic effects of substituents on the barrier to pyramidal inversion for a first-row element, attention is now directed at comparing such findings with the results known for other systems in which the inverting center is a second-row element. Such comparison will be facilitated if the rates of pyramidal inversion for the N-arylaziridines can all be compared at the same temperature. Strictly, this requires a knowledge of $\Delta S^{\ddagger}$ for each compound. However, it was found that the relative rates of isomerization are not a sensitive function of the choice of $\Delta S^{\ddagger}$, as illustrated in Table IV, which lists rate constants of inversion for compounds **3a–3f** extrapolated to a common temperature of −60° using two values of $\Delta S^{\ddagger}$ (11.4 and 0.0 eu).[47]

Table III. Comparison of Electronic Effects on the Isomerization of N-Arylimines and the Pyramidal Inversion of N-Arylaziridines

Compd		ρ^a	T, °C	Ref
N-Arylimines (**5**)				
X	Y			
p-Anisyl	*p*-Anisyl	1.7[b]	62	*e*
Phenyl	H	2.0[c]	30	*f*
NMe_2	NMe_2	1.5[c]	*Ca.* 40	*g*
N-Aryl-2,2-dimethyl-aziridines (**3**)		2.8[b]	−60	Present work
		2.0[b,d]	25	Present work

[a] Parameter obtained from Hammett $\sigma\rho$ treatment. [b] Correlation with σ^-. [c] Correlation with σ_p. [d] The ρ value at −60° has been extrapolated to 25°.[30a] [e] Reference 41. [f] Reference 46. [g] Reference 42a.

Table IV. Calculated Inversion Rate Constants of N-Arylaziridines at −60° Using Assumed Values of $\Delta S^{\ddagger}$

Compd	k, sec^{-1} ($\Delta S^{\ddagger}$ = 11.4)[a]	k, sec^{-1} ($\Delta S^{\ddagger}$ = 0.0)
3a	0.38	0.73
3b	10.8	14.6
3c	19.7	23.8
3d	47.4	48.7
3e	358	259
3f	4.7×10^4	1.7×10^4

[a] The value of 11.4 eu corresponds to that found for **3a** by the complete line-shape method.

Electronic effects on the pyramidal inversion of second-row elements have been observed for arylmethylphenylphosphines (**6**),[5] for aryl *p*-tolyl sulfoxides (**7**),[3] and for sulfonium salts.[48] Limited substituent studies have also been reported for diphosphines[50] and for aryl arenethiolsulfinates;[51] however, in these systems further complications are introduced by the presence of a second-row heteroatom bonded to the central inverting nucleus. Nevertheless, for all systems studied, electronic effects are quite small (less than a factor of 10 in relative rates within each of the cited series). By contrast, the results found for the N-arylaziridines (**3**) show a substantial sensitivity to changes in the substituent (Table V), corresponding to a range of rate constant of 10^4 at −60°. Table V presents a comparison of the relative rates of pyramidal inversion for similarly substituted compounds in series **3**, **6**, and **7**.

While the difference in magnitude of electronic effects among the three series is at least in part due to the differences in the comparison temperatures, it can be shown that this factor is insufficient to account for more than a portion of the observed effect. Thus, if the

(40) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953); R. W. Taft, Jr., *J. Amer. Chem. Soc.*, **79**, 1045 (1957).

(41) D. Y. Curtin, E. J. Grubbs, and C. G. McCarty, *ibid.*, **88**, 2775 (1966).

(42) (a) H. Kessler, *Tetrahedron Lett.*, 2041 (1968); (b) H. Kessler, *Angew. Chem. Intern. Ed. Engl.*, **6**, 977 (1967); D. W. Gerlich, F. Vögtle, A. Mannschreck, and H. A. Staab, *Ann.*, **708**, 36 (1967); F. Vögtle, A. Mannschreck, and H. A. Staab, *ibid.*, **708**, 51 (1967).

(43) J. M. Lehn and B. Munsch, *Theor. Chim. Acta*, **12**, 91 (1968).

(44) (a) N. P. Marullo and E. H. Wagener, *J. Amer. Chem. Soc.*, **88**, 5034 (1966); (b) E. Carlson, F. B. Jones, Jr., and M. Raban, *Chem. Commun.*, 1235 (1969); N. P. Marullo and E. H. Wagener, *Tetrahedron Lett.*, 2555 (1969); (c) H. Kessler and D. Leibfritz, *ibid.*, 427 (1969). In this last study, a rotation mechanism was assured by tying up the lone pair in salt formation.

(45) For substituent effects on imines see ref 41 and references cited therein. For a review of similar effects on aziridine inversions, see ref 6.

(46) G. Wettermark, J. Weinstein, J. Sousa, and L. Dogliotti, *J. Phys. Chem.*, **69**, 1584 (1965).

(47) A similar insensitivity has been shown in the case of N-arylimines.[41]

(48) Darwish, *et al.*, found that electron-withdrawing groups have an insignificant effect on the inversion of *para*-substituted benzylethylmethylsulfonium salts [D. Darwish, S. H. Hui, and R. Tomilson, *J. Amer. Chem. Soc.*, **90**, 5631 (1968)].[49] In these systems, however, the inverting center is effectively insulated from direct interaction with the aryl group.

(49) For electron-donating groups such as *p*-OCH_3, racemization is proposed to occur by carbon–sulfur bond heterolysis.

(50) J. B. Lambert, G. F. Jackson, III, and D. C. Mueller, *J. Amer. Chem. Soc.*, **92**, 3093 (1970).

(51) P. Koch and A. Fava, *ibid.*, **90**, 3867 (1968).

Table V. Relative Rate Constants of Pyramidal Inversion for N-Arylaziridines, Arylmethylphenylphosphines, and Aryl *p*-Tolyl Sulfoxides

Aryl group	Subst index	Relative rates[a] Aziridines, 3 at −60°	Phosphines, 6[c] at 130°	Sulfoxides, 7[d] at 210°
4-$CH_3OC_6H_4$	a	1.0 (1.0)[b]	1.0	1.0
4-$CH_3C_6H_4$	g		1.8	
C_6H_5	b	28.4 (20.0)		1.74
4-ClC_6H_4	c	51.9 (32.6)		1.35
3-$CF_3C_6H_4$	d	125 (66.7)		1.85
4-$CF_3C_6H_4$	e	942 (355)	8.5	3.38

[a] Rates in each series are relative to the *p*-OCH_3 compound of that series. [b] See Table IV. Values are based on $\Delta S^{\ddagger} = 11.4$ eu and, in parentheses, on $\Delta S^{\ddagger} = 0.0$ eu. [c] Reference 5. [d] Reference 3a.

inversion rates for phosphines **6a** and **6e** are extrapolated to −60°,[52] the new rate for **6e** relative to the new rate for **6a** is still only equal to 58. That electronic effects appear more important for first- than for second-row elements is due, presumably, to more effective overlap of the benzene π system (formed by C 2p atomic orbitals) with the lone pair on the central atom when this is a first-row element (2p orbital) than when it is a second- (3p orbital) or higher row element; the weight of this is felt more strongly in the transition than in the ground state. Thus for phosphines, conjugation of the lone pair with an aromatic ring appears to be much less important than for the corresponding amines.[53] For sulfoxides, such conjugation seems even less important.[54,55]

The direction of substituent effects found for the pyramidal inversion of N-arylaziridines (**3**) in general parallels that previously found for the pyramidal inversion of second-row elements (Table V). Indeed, there is a linear correlation between the log k_{inv} values of the aziridines (**3**) and the phosphines (**6**) which is shown in Figure 3.[56,57] Although a similar correlation of log k_{inv} values between aziridines (**3**) and sulfoxides (**7**) is obviated by the fact that the effect of the chloro substituent, relative to hydrogen, is different for the two systems,[58] for three substituents (*p*-OCH_3, H, and *p*-CF_3), an excellent linear correlation is found between these systems as well.

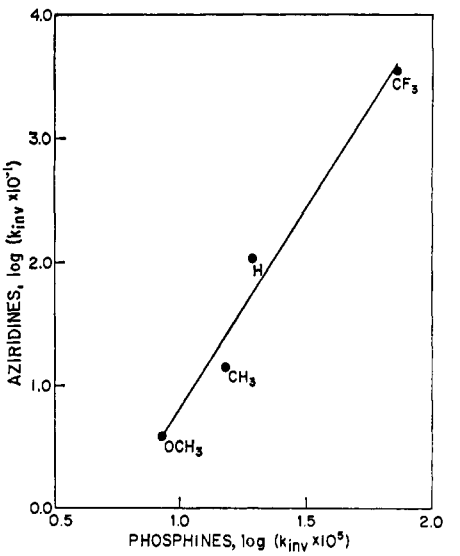


Figure 3. Correlation of log k_{inv} values of N-aryl-2,2-dimethylaziridines (**3**) at −60° and arylmethylphenylphosphines (**6**) at 130°; aryl = *p*-RC_6H_4.

In summary, the results of the present study, combined with those of related studies on sulfoxides[3] and phosphines,[5] clearly demonstrate that the magnitude of the barrier to pyramidal inversion is a function of the electron-releasing or -withdrawing capacity of substituents in benzene rings attached to the central inverting atom, whether this be nitrogen, sulfur, or phosphorus. In all three systems, electron-withdrawing substituents lower the barrier to inversion, and this lowering roughly correlates to the Hammett substituent constant.

Experimental Section[59]

Aziridines used in this study were prepared by the photolytic decomposition of 1-aryl-5,5-dimethyl-Δ^2-1,2,3-triazolines. The triazolines were prepared by the cycloaddition of the appropriate aryl azide with isobutylene.[12]

Aryl Azides. The amines[60] were converted to the corresponding azides using method A of Smith and Brown,[61a] except that hydro-

(52) Extrapolation was made using an assumed $\Delta S^{\ddagger} = -4$ eu for both **6a** and **6e**. This value of $\Delta S^{\ddagger}$ was found for the racemization of allylmethylphenylphosphine in benzene.[5]

(53) (a) J. W. Rakshys, R. W. Taft, and W. A. Sheppard, *J. Amer. Chem. Soc.*, 90, 5236 (1968); (b) A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus," Elsevier Publishing Co., New York, N. Y., 1967, Chapter 1; R. F. Hudson, "Structure and Mechanism in Organo-Phosphorus Chemistry," Academic Press, New York, N. Y., 1965, Chapter 2.

(54) The resonance substituent constant for the methylsulfinyl group (0.007)[33] indicates that sulfoxide sulfur, unlike phosphine phosphorus[53a] or amine nitrogen,[33] actually acts as a net resonance acceptor of electron density.

(55) C. C. Price and S. Oae, "Sulfur Bonding," The Ronald Press Co., New York, N. Y., 1962, Chapter 4.

(56) The k_{inv} values for the phosphines are taken from ref 5. As explained in the cited paper, the value for the *p*-H substituent is calculated by interpolation from the Hammett plot (σ_p) of the other three substituents (R = OCH_3, CH_3, and CF_3). The k_{inv} values for the aziridines are taken from Table IV and correspond to $\Delta S^{\ddagger} = 11.4$ eu, the value found for **3a** by the complete line-shape analysis. The k_{inv} value for the *p*-CH_3 substituted aziridine was calculated by interpolation from the Hammett plot (σ^-) of the other six substituents (**3a**–**3f**).

(57) Correlation coefficient 0.985, standard deviation 0.192. The slope of the line, 3.25, may be considered a measure of the sensitivity of the aziridine relative to the phosphine system to electronic substituent effects.

(58) In the aziridines (**3**), k_{Cl}/k_H = *ca.* 1.7 at −60°, whereas in the sulfoxides (**7**), k_{Cl}/k_H = 0.78 at 210°. However, it is noteworthy that for the inversion of *para*-substituted 1-phenyl-2,2,3,4,4-pentamethylphosphetanes, k_{Cl}/k_H = *ca.* 1.4 at 145° (S. E. Cremer, private communication; we thank Professor Cremer for permission to cite these unpublished results). Thus, the response of aziridines to electronic substituent effects is seen to parallel more closely that of phosphines than that of sulfoxides. While resonance substituent effects appear to dominate the barrier in the case of sulfoxides,[3a] the interplay of both inductive (field) and resonance substituent effects combine to determine the barrier in phosphines and aziridines. Thus for the above pentamethylphosphetane system, k_F/k_H = *ca.* 0.6 at 145° (S. E. Cremer, unpublished results), indicating that in going from a chloro to a fluoro substituent the increase in inductive electron withdrawal is more than compensated for by an increase in resonance release of electron density. Physical evidence for such resonance donation in a nitrogen system is also indicated by the increase in nonplanarity of *p*-fluoroaniline as compared to aniline itself [A. Hastie, D. G. Lister, R. L. McNeil, and J. K. Tyler, *Chem. Comm.*, 108 (1970)].

(59) Elemental analyses by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y., and by the Centre de Microanalyse du C.N.R.S. All pmr spectra were recorded on a Varian A-60A spectrometer; chemical shifts are in parts per million and refer to internal TMS.

(60) The amines were commercially available and were distilled from zinc dust immediately prior to use. Each sample was checked for isomeric purity using tlc or glpc by comparison with authentic samples of all possible isomers.

(61) (a) P. A. S. Smith and B. B. Brown, *J. Amer. Chem. Soc.*, 73, 2438 (1951); P. A. S. Smith and J. H. Boyer, "Organic Syntheses," Coll. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1963, p 475; (b) G. Smolinsky, *J. Org. Chem.*, 26, 4108 (1961).

chloric acid was used in place of sulfuric acid. The isolation procedure was that described by Smolinsky.[61b] All azides except for 3-(trifluoromethyl)azidobenzene have been reported previously;[62] the new azide was prepared in the same manner as the *para* isomer[62] but was used without purification.

Triazolines. General Procedure. A solution of the aryl azide (10–20 g) in hexane or heptane (60 ml) was placed in a 300-ml stainless steel high-pressure bomb (or a thick-walled glass tube) and the bomb and contents were cooled to about −78°. Isobutylene (about a threefold excess) was condensed directly into the cooled mixture. The sealed bomb was then heated at 85° for 3 days (70° for 2 days in the case of the 4-nitro compound). Removal of solvent on a rotary evaporator gave a mixture of product triazoline together with unreacted azide and small quantities of thermal decomposition product. The unreacted azide and decomposition products were removed by distillation (kugelrohr, 70° or less, 0.05 mm), leaving behind the crude triazoline in an average yield of 35%.[63] The triazoline so obtained was pure by nmr and was used without further purification. The 4-nitrotriazoline was recrystallized from methanol; mp 187°.

Aziridine Preparations. General Procedure. A solution of the triazoline (5–12 g) in acetone (250 ml) was placed in a water-cooled Pyrex vessel and was irradiated at 3500 Å (Rayonet photochemical reactor) until evolution of nitrogen had ceased (8–20 hr). Removal of solvent and distillation (kugelrohr) gave the aziridine in high yield except in the case of **3f** (15%) (see also ref 12b). Nmr and analytical samples were further purified by glpc on a 4 ft × $^3/_8$ in. Apiezon L column (5%) on Fluoropak 80 using a column temperature of 125–150° or a 3 ft Carbowax 20M column (10%) on Chromosorb W at 120–140° or at 190° in the case of **3f**. Material collected by glpc was redistilled (kugelrohr) before use. During these last operations the aziridine was protected from moisture.

1-(*p*-Methoxyphenyl)-2,2-dimethylaziridine (3a) obtained by the above procedure as a colorless oil (kugelrohr, bp 80° (0.02 mm)) displayed the following signals in the pmr spectrum ($CFCl_3$, 41°): $(CH_3)_2C$, s, τ 8.92; CH_2, s, τ 8.18; OCH_3, s, τ 6.87; C_6H_4, s, τ 3.4.

Anal. Calcd for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.13; H, 8.67; N, 7.95.

1-Phenyl-2,2-dimethylaziridine (3b) obtained as a colorless oil (kugelrohr, bp 45° (0.75 mm)) displayed the following signals in the pmr spectrum ($CDCl_3$, 41°): $(CH_3)_2C$, s, τ 8.85; CH_2, s, τ 8.0; C_6H_5, m, τ 2.7–3.4.

Anal. Calcd for $C_{10}H_{13}N$: C, 81.59; H, 8.90; N, 9.51. Found: C, 81.61; H, 8.96; N, 9.77.

1-(*p*-Chlorophenyl)-2,2-dimethylaziridine (3c) obtained as a colorless oil (kugelrohr, bp 80° (0.05 mm)) displayed the following signals in the pmr spectrum ($CFCl_3$, 41°): $(CH_3)_2C$, s, τ 8.88; CH_2, s, τ 8.08; C_6H_4, m (AA'BB'), centered at τ 3.13.

Anal. Calcd for $C_{10}H_{12}NCl$: C, 66.12; H, 6.66; N, 7.71; Cl, 19.52. Found: C, 66.23; H, 6.83; N, 7.41; Cl, 19.76.

1-(*m*-Trifluoromethylphenyl)-2,2-dimethylaziridine (3d) obtained as a colorless oil (kugelrohr, bp 40° (0.05 mm)) displayed the following signals in the pmr spectrum (CCl_4, 41°): $(CH_3)_2C$, s, τ 8.79; CH_2, s, τ 7.98; C_6H_4, m, τ 2.9–3.2.

Anal. Calcd for $C_{11}H_{12}NF_3$: C, 61.39; H, 5.62; N, 6.51; F, 26.48. Found: C, 60.95; H, 5.62; N, 6.76; F, 26.45.

1-(*p*-Trifluoromethylphenyl)-2,2-dimethylaziridine (3e) obtained as a colorless oil (kugelrohr, bp 50° (0.03 mm)) displayed the following signals in the pmr spectrum (CCl_4, 41°): $(CH_3)_2C$, s, τ 8.81; CH_2, s, τ 7.99; C_6H_4, apparent AB centered at τ 2.88.

Anal. Calcd for $C_{11}H_{12}NF_3$: C, 61.39; H, 5.62; N, 6.51; F, 26.48. Found: C, 61.19; H, 5.76; N, 6.64; F, 26.80.

1-(*p*-Nitrophenyl)-2,2-dimethylaziridine (3f) obtained as a yellow oil (bp 95–100° (0.1 mm)) displayed the following signals in the pmr spectrum ($CDCl_3$, 34°): $(CH_3)_2C$, s, τ 8.75; CH_2, s, τ 7.83; C_6H_4, apparent AB centered at τ 2.52.

Anal. Calcd for $C_{10}H_{12}N_2O_2$: C, 62.48; H, 6.29; N, 14.58. Found: C, 62.92; H, 6.23; N, 14.33.

Nmr Measurements. Nmr spectra were recorded on a Varian A-60A spectrometer equipped with a variable temperature accessory. Temperature measurements were based on the chemical-shift separation of the protons of methanol using the temperature-shift correlation of Van Geet.[64] Temperatures are believed accurate to 2° although within a series of measurements differences of 0.5° are considered significant. Low temperatures (in the case of **3f** in $CHFCl_2$) have been measured using a copper–constantan thermocouple. Spectra were recorded on chart paper which was precalibrated using a Hewlett-Packard 200CD wide-range oscillator and a Hewlett-Packard 5212A electronic counter. Nmr samples were prepared on a vacuum line and contained 15% by volume of the aziridine in dichlorodifluoromethane with about 1% TMS.[11] Samples were degassed by the standard freeze–thaw technique and were sealed in precision thin-wall nmr tubes. In the recording of spectra, care was taken to avoid saturation of the signal. All nmr samples remained liquid at low temperatures with the exception of the *p*-chloro compound (**3c**) which precipitated from solution below −70°.

Nmr line-shape analysis was performed on an IBM 360/91 or an IBM 360/65 computer equipped with a Calcomp or a Benson plotting accessory. Activation parameters were obtained by the method of least squares from the slope and intercept of the line defined by $\log (k/T) = f(1/T)$. Error limits in the determination of $\Delta H^{\pm}$ and $\Delta S^{\pm}$ were estimated by drawing lines of maximum and minimum slope containing between them all the experimental points as previously reported.[65]

(62) 4-Methoxyazidobenzene: H. Rupe and K. von Majewski, *Ber.*, **33**, 3401 (1900); azidobenzene: R. O. Lindsay and C. F. H. Allen, "Organic Syntheses," Coll. Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1955, p 710; 4-chloroazidobenzene: P. K. Dutt, H. R. Whitehead, and A. Wormall, *J. Chem. Soc.*, **119**, 2088 (1921); 4-(trifluoromethyl)azidobenzene: I. N. Zhmurova and A. V. Kirsanov, *Zh. Obsch. Khim.*, **36** (7), 1248 (1966); 4-nitroazidobenzene: H. H. Hogdson and W. H. H. Norris, *J. Chem. Soc.*, 762 (1949).

(63) Based on the initial amount of azide.

(64) A. L. Van Geet, *Anal. Chem.*, **42**, 679 (1970).

(65) J. E. Anderson and J. M. Lehn, *J. Amer. Chem. Soc.*, **89**, 81 (1967).