Electrophilic Substitution at Saturated Carbon. XXXI. Effects of Attached Second-Row Elements on the Rates of Nitrogen Inversion in Aziridines[1]

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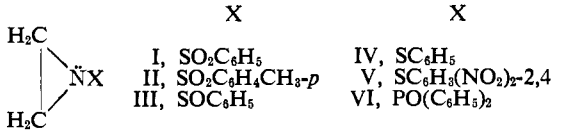
Abstract: The rates of nitrogen inversion have been measured with nuclear magnetic resonance (nmr) techniques in a series of aziridines substituted on nitrogen with a series of functional groups centered around sulfur and phosphorus. The rates of nitrogen inversion assumed the following order: 1-diphenylphosphinoxyaziridine $\gg$ 1-benzenesulfonylaziridine $>$ 1-(2,4-dinitrobenzenesulfenyl)aziridine $>$ 1-benzenesulfenylaziridine $>$ 1-benzenesulfinylaziridine. The rate order is discussed in terms of steric conjugative (or overlap), inductive, and electrostatic effects. No relationship is visible between the configuration-holding power of the group X in aziridine system $(CH_2)_2NX$ and in the carbanion system $R_2\bar{C}X$. Thus, amines appear to be unsatisfactory models for carbanions as far as substituent effects that control stereochemistry are concerned. It is concluded that electrostatic effects in the charged anions which are absent in the neutral aziridines dominate the stereochemistry of carbanions substituted with these functional groups. The nmr spectra of the aziridines were interpreted.

The effects on the stabilization of carbanions of attached atoms with low-lying empty d orbitals have been much studied in recent years.[2] Anions such as open-chain sulfonyl carbanions appear to have appreciable configurational stability, while others such as sulfinyl carbanions do not. The origin of the asymmetry in the sulfonyl carbanions has yet to be settled. One possible explanation is that the asymmetry is associated with pyramidal carbon which resists inversion. A second possibility is that the carbon atom is planar, the preferred conformation is asymmetric, and the formation and capture of the anion involve only one face of the anion. In either case, proton capture would have to compete favorably with either inversion of the pyramidal anion or rotation of the planar anion, possibly because of either electrostatic or overlap effects.

Amines are isoelectronic with carbanions. The barriers to inversion and to rotation in compounds of the type $R_2\ddot{N}X$ (X represents atoms or groups with available d orbitals) might provide clues as to the size of such barriers in the corresponding carbanions. In both classes of compounds, interaction between the electron pair and the d orbitals of the attached atom is possible. However, the difference in charge type between carbanions and amines places a severe limitation on the value of such a comparison.

Aziridine derivatives were selected for study since the constrictions of the three-membered ring slow the nitrogen inversion rate to the point where it can be measured with nuclear magnetic resonance (nmr) techniques.[3] In a previous paper,[4] 1-acylaziridines were found to have much higher rates of nitrogen inversion than simple 1-alkylaziridines, and the barrier to inversion appeared to depend mainly and conversely on the conjugative ability of the 1 substituent. Although the nmr spectra of a number of aziridines substituted on nitrogen with second-row elements have been reported,[5] the rates of inversion of the compounds were not measured.

Six compounds were selected for study (I–VI) and were prepared by standard methods (sulfonamides I and II were already known).[5a] Compound IV was an oil which was not isolated in a completely pure state, but the impurities did not prevent analysis of the substance's nmr spectrum. The 2,4-dinitro derivative, V, of compound IV was obtained in a pure crystalline state.



Results

Figures 1, 2, and 3 record the nmr spectra of the aziridine protons of I, III, and VI taken at various temperatures. The spectra of II, IV, and V were similar in type to that of I. Chemical shifts and coupling constants are given in Table I. Coalescence temperatures (T_c) and rate constants (k) are found in Table II. The temperature dependence of the spectrum of I was examined above the coalescence temperature by the line-width method, and k was calculated from eq 1.[6] In this equation, ν_{AB} is the chemical shift in cps between A and B protons, and $\Delta\nu$ is the full line width in cps at half-height.

This equation is strictly valid when the only broadening process is the exchange of protons between two equally populated sites and spin coupling is absent. A correction for magnetic-field inhomogeneities and finite T_2 in the absence of exchange was obtained by

(1) This investigation was supported in part by Public Health Service Grant No. GM12640-02 from the Department of Health, Education, and Welfare, and in part by National Science Foundation Grant No. GP-3780. The authors express their appreciation.

(2) For a review, see D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, p 71.

(3) A. T. Bottini and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 5126 (1956).

(4) F. A. L. Anet and J. M. Osyany, *ibid.*, **89**, 352 (1967).

(5) (a) T. G. Traylor, *Chem. Ind.* (London), 650 (1963); (b) V. F. Bystrov, R. G. Kostyanovskii, O. A. Panshin, A. U. Stepanyants, and O. A. Iuzhakova, *Opt. Spectry.* (USSR), **19**, 122 (1965); (c) O. J. Scherer and M. Schmidt, *Chem. Ber.*, **98**, 2243 (1965).

(6) F. A. L. Anet and J. S. Hartman, *J. Am. Chem. Soc.*, **85**, 1204 (1963); see also J. S. Hartman, M.Sc. Thesis, University of Ottawa, 1963.

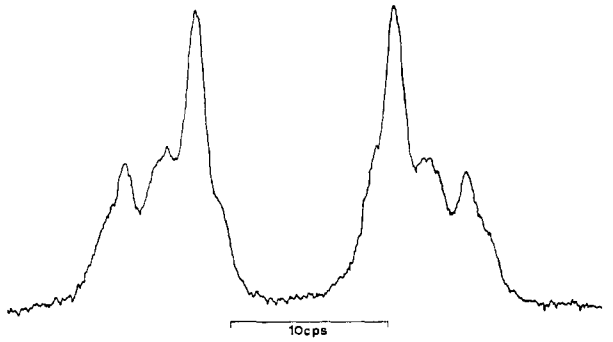


Figure 1. Aziridine protons (nmr) of 1-benzenesulfonylaziridine (I) in $CDCl_3$ at −67°.

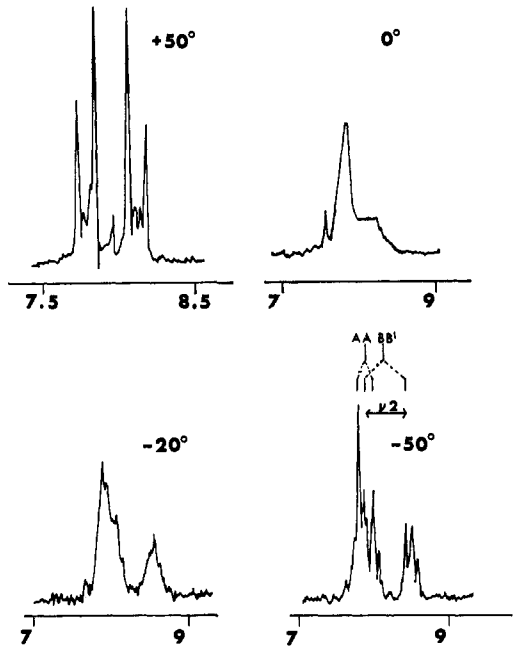


Figure 2. Aziridine protons (nmr) of 1-benzenesulfinylaziridine (III) in $CDCl_3$.

measuring the line width of tetramethylsilane, and this quantity was subtracted from the observed line width of the aziridine protons to give $\Delta\nu$. When the line is relatively narrow, this correction is important, and the procedure is quite valid. When the line is much broader and is no longer Lorentzian in shape, this type of correction is less valid, but fortunately k is then no longer a sensitive function of the correction.

$$k = \pi[\nu_{AB}^4 + 2\nu_{AB}^2\Delta\nu^2 - \Delta\nu^4]^{1/2}/2\Delta\nu \quad (1)$$

Equation 1 is much better than the usual fast-exchange approximation (eq 2), where $\Delta\nu$ is the line broadening measured at half-height. The two expressions give essentially the same results for very rapid exchange. Because of the presence of spin coupling in the low-temperature spectra, no attempt was made to obtain rate constants at temperatures below T_c.

$$k = \pi\nu_{AB}^2/2\Delta\nu \quad (2)$$

The second moment of the low-temperature spectrum of I was used to calculate the chemical shift for I shown in Table I. The procedure and equations were the same as used in the previous paper.[4]

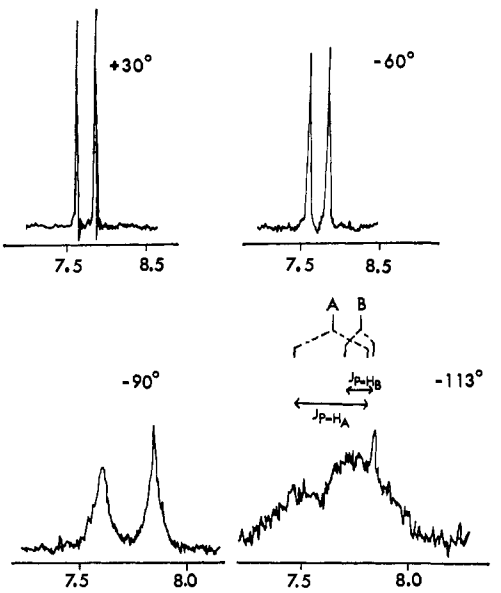


Figure 3. Aziridine protons (nmr) of 1-(diphenylphosphinoxy)aziridine in CH_2Cl_2.

The rate constants at the coalescence temperatures were calculated[6] by means of eq 3 which is valid under the same conditions as eq 1. Because coupling constants are much smaller than the chemical shifts, this equation should be applicable. Thus, calculations[7]

Table I. Chemical Shifts and Coupling Constants in Aziridines I–VI

Compound	τ_{CH_2} at 25°	ν_{AB} at low temp
I[a]	7.6	16.4[b]
II[a]	7.6	16.0
III[a]	7.73, 8.1	~36[c]
IV[a]	8.02	32
V[a]	7.74	28.5
VI[d]	7.86[e]	~22

[a] In $CDCl_3$ solution. [b] Calculated from second moment. [c] Frequency separation ν_2 shown in Figure 2. [d] In CH_2Cl_2 solution. [e] J_{P-H} = 14.5 cps.

Table II. Comparison of the Coalescence Temperatures (T_c) and Rate Constants (k) for Nitrogen Inversion in Aziridines I–VI

Compound	N-Substituent	T_c,[a] °C	k,[b] sec^{-1} at T_c	k, sec^{-1} for I at T_c for other compd
I	$SO_2C_6H_5$	−30	36	
II	$SO_2C_6H_4CH_3$	−30	36	36
III	SOC_6H_5	0	79	500
IV	SC_6H_5	−11	71	210
V	$SC_6H_3(NO_2)_2$-2,4	−18	63	115
VI	$PO(C_6H_5)_2$	−108	48	0.0018

[a] Coalescence temperatures. [b] Calculated from eq 3.

show that in an AB system with $J_{AB}/\nu_{AB} = 0.2$, the error in k made by neglecting J_{AB} is only 10%. In an

(7) R. J. Kurland, M. B. Rubin, and W. B. Wise, *J. Chem. Phys.*, **40**, 2426 (1964).

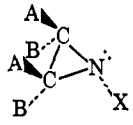
A_2B_2 system the magnitude of the error should be roughly the same as in an AB system.

$$k = \pi\nu_{AB}/\sqrt{2} \quad (3)$$

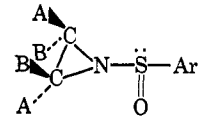
Discussion

Nmr Spectra. The aziridine protons in compounds I, II, IV, and V produced a single sharp line at room temperature. As the temperature was lowered, this line broadened and then split into two broad bands, and ultimately a temperature-independent A_2B_2 spectrum was obtained.

The aziridine protons of III gave an A_2B_2 spectrum at room temperature because the sulfur atom is an asymmetric center. The appearance of this A_2B_2 spectrum is appreciably different from that given at low temperatures by I, II, IV, or V, which results from slow nitrogen inversion. The arrangements of chemically shifted protons are different in the two cases, as is apparent through a comparison of a generalized formula for I, II, IV, and V, and a time-average formula for III (IIIa). When inversion of the nitrogen atom and rotation around the nitrogen–sulfur bond are both rapid in III, the sulfinyl group on



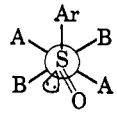
I, II, IV, or V
(N inverting slowly)



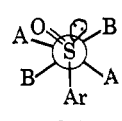
IIIa (N inverting rapidly, shown in its average planar configuration)

a time-average basis has an infinitefold axis of symmetry which is coincident with the nitrogen–sulfur bond (only the local symmetry of the sulfinyl group is considered here). The aziridine ring itself in III has a (local) 2-fold axis of symmetry, which also lies along the nitrogen–sulfur bond. Thus, the molecule as a whole has a 2-fold axis of symmetry on a time-average basis, and the chemically shifted protons A and B have the arrangement depicted in formula IIIa.

These symmetry properties are also shown by projection formulas IIIb and c, which depict two equivalent conformations of III. The two A protons have different environments in IIIb, but they exchange on going to IIIc, so on the average they have identical chemical shifts. The same situation holds for the two B protons, which always remain distinct from the A protons, provided that the sulfur atom does not undergo inversion. The sulfur atoms in similar compounds such as sulfites are configurationally stable.[8]



IIIb



IIIc

Although the two A protons have the same chemical shift in IIIa as they have in Ia, they are not magnetically equivalent because in either case two distinct AB coupling constants are involved. If the four hydrogen nuclei are labeled A, A′, B, and B′, there are four different coupling constants:[9] J_{AB} (= $J_{A'B'}$), $J_{AB'}$ (= $J_{A'B}$), $J_{AA'}$ and $J_{BB'}$. These coupling constants are expected to depend[4] largely on the relationship of the pairs of protons in the aziridine ring, and to a minor extent on the substituent attached to the nitrogen atom. Thus, the largest coupling constant (~6 cps) is assigned[4] to the *cis* vicinal protons, *i.e.*, $J_{AA'}$ in I, II, IV, or V and J_{AB} in IIIa. Much larger splittings were observed in both the A and B bands of III compared to those of I, II, IV, and V, a fact undoubtedly associated with the *cis* and eclipsed arrangement of the A,B protons of III.[9] Because only a limited number of lines were clearly resolved in these spectra, a complete analysis was not attempted. No simple unambiguous way of assigning chemical shifts to the different types of aziridine protons is evident.

The aziridine proton spectrum of III at −50° passed from an A_2B_2 to an unsymmetrical ABCD system (Figure 2). This change produced a much larger chemical shift split for the pair of high-field protons than for the low-field pair. This effect was evident in the greater broadening of the upfield band at intermediate temperatures. As with I, II, IV, and V, the temperature-dependent spectral changes observed in III are probably associated with a decrease in rate of nitrogen inversion. Although a slowing down of rotation about the nitrogen–sulfur bond would produce the same effect, this possibility is much less likely. In 1-carboxacylaziridines, restriction of rotation is unimportant,[4] and the effect in such compounds should be more important than in compounds such as III.

The aziridine protons of VI gave a sharp doublet at room temperature associated with spin coupling to the phosphorus nucleus (^{31}P, spin 0.5). The doublet broadens at very low temperatures (Figure 3). The spectrum at −113°, the lowest temperature reached, can best be interpreted on the basis of two kinds of protons which have quite different coupling constants to ^{31}P. It is not possible to obtain chemical shifts and coupling constants from the poorly resolved spectrum at −113°, but a qualitative representation of possible parameters is shown in Figure 3.

Rates of Nitrogen Inversion. Rate constants obtained by nmr are most easily obtained at the coalescence temperature (T_c) since this is where the greatest spectral changes take place. The rate constants for compounds I–VI were determined at their coalescence temperatures. Rate constants can be meaningfully compared only at the same temperature. Accordingly, the rate constant for nitrogen inversion in I was measured by the line-width method above T_c over the temperature range −28 to +2°, and rough values for the activation parameters were determined[10] (Table III). The rate constant for I was corrected to those temperatures at which the rate constants for the other compounds were determined, and this allowed the rate for each compound to be compared to that for I (Table III).

Several effects are expected to be important in determining rates of nitrogen inversion (k) in the compounds listed in Table II.

(8) J. G. Pritchard and P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 2105 (1961).

(9) (a) K. B. Wiberg and B. J. Nist, "Interpretation of NMR Spectra," W. A. Benjamin, Inc., New York, N. Y., 1962, p 309; (b) D. M. Grant, *Ann. Rev. Phys. Chem.*, **15**, 492 (1964).

(10) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 218.

Table III. Changes in Rates of Inversion of Nitrogen in 1-Phenylsulfonylaziridine with Changes in Temperature, and Activation Parameters for the Process[a]

Temp, °C	ν,[b] cps	k, sec^{-1}
+2.0	0.70	600
−4.7	1.22	340
−9.3	1.81	230
−13.0	2.2	195
−19.4	3.8	118
−23.8	6.1	77
−28.8	13.7	43

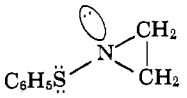
[a] $\Delta F^{\pm} = 10.0 \pm 0.1$ kcal/mole, $\Delta H^{\pm} = 10.9 \pm 2$ kcal/mole, $\Delta S^{\pm} = 3.6 \pm 6$ eu. [b] Line width at half-height of CH_2 protons minus line width of TMS (0.53 cps).

a. Steric Effects. A large group attached to the nitrogen atom should be more compressed in the nonplanar ground state than in the presumably planar transition state for nitrogen inversion. Thus, large groups should increase k, and there is some evidence,[3] which is not unambiguous,[4] that suggests this conclusion. In the series of compounds studied here, there are quite large variations in the size of the group attached to nitrogen. As in other cases of steric hindrance, the size of the group at a distance close to nitrogen is of the greatest significance, *i.e.*, the nonbonded repulsions between the ring protons and the N-substituent are the most important.

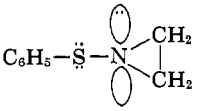
b. Inductive Effects. Electronegative substituents on nitrogen are expected to decrease the rate of inversion because of the tendency of such substituents to increase the s character of the unshared electron pair on nitrogen.[11] In the planar transition state this electron pair must be in a p orbital.

c. Conjugative Effects. Conjugative or overlap effects, especially of the p–p type, should increase the rate of inversion because such effects are greater in a planar than in a nonplanar system. The configurational requirements for providing maximum stabilization for an atom with an unshared electron pair attached to a d orbital containing elements have not been established, although calculations exist that suggest that overlap is maximal when the electron pair is in a p orbital.[12]

d. Electrostatic or Electron Repulsion Effects. When the atom attached to nitrogen carries an unshared electron pair, repulsion between this pair and that on nitrogen is less in the ground state than in the transition state. An example is formulated which involves compound IV. The preferred conformation of hydrazine has the two-electron pair in orbitals whose dihedral angle is 90°.[13] Other examples are known



ground state of IV



transition state for inversion of IV

where electron-pair repulsions are important in determining the geometry of molecules.[14]

In the series of compounds I, II, and IV, in which X changes from $SO_2C_6H_5$ to SOC_6H_5 to SC_6H_5, increased steric and overlap effects would tend to increase the rate of inversion, and increased inductive and electrostatic effects would tend to decrease the rate of inversion. The importance of steric effects in the series is doubtful since the rates of inversion of the aziridine with SO_2CH_3 and $SO_2C_6H_5$ as N-substituents are almost the same.[4] Little appears to be known about the size of these various groups. The A value for only C_6H_5S has been determined.[15] The overlap effect of the methanesulfonyl group is known to be greater than that of the methanesulfinyl group. Thus, σ_p^- for SO_2CH_3 is 0.98, whereas the σ_p^- for $SOCH_3$ is 0.73.[16] About half of this effect has been ascribed to p–d overlap, and the other half to the inductive effect in both compounds. Normal Hammett σ constants for the series SO_2CH_3, $SOCH_3$, and SCH_3 are 0.72, 0.54, and 0.00, respectively, in the *para* position and 0.60, 0.52, and 0.15, respectively, in the *meta* position.[17] Thus, the inductive and overlap effects with these substituents should be quite marked, but since they operate in opposite directions, they probably largely cancel. The electrostatic effect clearly should produce a decreasing value for k in the series I, II, and IV, but the magnitude of the effect is unknown.

A comparison of IV with V shows that V has the slightly higher valued k, and hence the nitro groups of the benzenesulfenyl group tend to speed up inversion. This small change may reflect delocalization of electrons of the sulfur into the nitro groups, and a consequent decrease in the electrostatic inhibition of inversion. Perhaps the most striking feature of the data is that the rate constants are so close together for compounds I–V, a fact that clearly indicates cancellation of the above opposing effects.

The phosphinoxy compound VI has a very large k compared with the sulfur-containing aziridine derivatives. Possibly, steric effects play some role in this. The σ constants for this group are not known. However, the $PO(C_6H_5)_2$ and SOC_6H_5 groups are known to have about the same acidifying (kinetic) effect on an attached R_2CH group,[18] and yet the $PO(C_6H_5)_2$ group enhances the rate of inversion of aziridine VI by an estimated five powers of ten compared to the SOC_6H_5 group. Possibly, the absence of an unshared electron pair on the phosphorus of the phosphinoxy group increases the rate of inversion compared to that of the sulfinyl group, whose sulfur does possess an unshared electron pair whose electrostatic properties would slow inversion.

No relationship is visible between the configuration-holding power[19] of the group X in the carbanion system, R_2CX, and in the aziridine system, $(CH_2)_2NX$. In fact, this study demonstrates that amines are un-

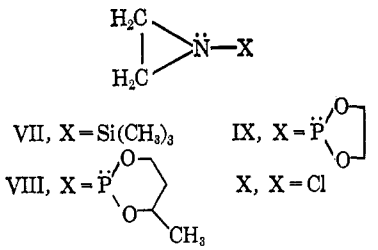
(11) H. A. Bent, *Chem. Rev.*, 61, 275 (1961); see also ref 2, p 56.
(12) T. Jordan, H. W. Smith, L. L. Lohr, Jr., and W. N. Lipscomb, *J. Am. Chem. Soc.*, 85, 846 (1963).
(13) T. Kasuya and T. Kojima, *Proc. Intern. Symp. Mol. Struct. Spectry., Tokyo*, C 404 (1962); *Chem. Abstr.*, 61, 2616 (1964).
(14) R. J. Gillespie and R. S. Nyholm, *Progr. Stereochem.*, 2, 261 (1958).
(15) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1955, p 44.
(16) Reference 2a, p 73.
(17) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 23, 420 (1958).
(18) (a) D. J. Cram and R. D. Partos, *J. Am. Chem. Soc.*, 85, 1093 (1963); (b) D. J. Cram and S. H. Pine, *ibid.*, 85, 1096 (1963).
(19) D. J. Cram, R. D. Trepka, and P. St. Janiak, *ibid.*, 88, 2749 (1966).

satisfactory models for carbanions as far as substituent effects that control stereochemistry are concerned. This lack of correlation probably reflects the dominance of electrostatic effects in the negatively charged anions and the absence of charge in the amines.

The rates of inversion of nitrogen in alkylaziridines are strongly influenced by solvents.[20] Hydroxylic solvents decrease the rate of inversion, presumably by hydrogen bonding to the unshared electron pair of nitrogen. In the present study, changes of solvent for the inversion of sulfonyl compound I from deuteriochloroform to methylene chloride to methanol changed the coalescence temperature from −30 to −32 to −34°, respectively. This effect is very small and is attributed to the relatively low basicity and hence low hydrogen-bonding ability of I.

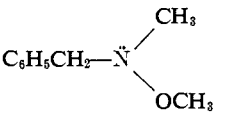
The activation parameters for inversion in I given in Table III can be compared with those of alkylaziridines.[20] The value of $\Delta S^{\ddagger}$ for I is close to zero, unlike that given for 1,2,2-trimethylaziridine.[20,21]

After the completion of the present work, syntheses and nmr spectra of compounds VII–XI were described.[5b,c] The aziridine protons of the silicon derivative VII consisted of a sharp line at room temperature. Low-temperature spectra were not taken. Probably the rate of nitrogen inversion in VII is much higher than in 1-alkylaziridines. This presumption is consistent with the overlap effects in VII, the low electronegativity, and the large bulk of the trimethylsilyl group, all of which effects would tend to increase the rate of nitrogen inversion.



XI

The nmr spectra (20.5 Mc/sec) of compounds VII–XI were reported by Russian workers.[5b] They concluded that rapid nitrogen inversion was taking place in these compounds even at −100°. At the low frequency used, the relative chemical shift, ν_{AB}, might be quite small, and thus possibly a retardation of rate of inversion might not make itself evident. Nevertheless, it is probable that the rates of nitrogen inversion in VIII–XI are high. Compounds VIII, IX, and X are interesting because the atom attached to nitrogen possesses at least one unshared pair of electrons. On the basis of the previous discussion, X would be predicted to have a low rate of inversion because of the high electronegativity and electrostatic effects. Significantly, N-chlorimines have lower rates of nitrogen inversion than N-alkylimines.[22] The stability of oximes and oxime ethers to inversion is so great that isomers can often be isolated. The marked ability of an alkoxyl group to reduce the rate of nitrogen inversion is also exhibited by the low rate observed[23] in XII. The low rate compared to ordinary tertiary amines was attributed to the electronegativity of the oxygen and to the presence of unshared electrons on the oxygen atoms. Thus, a high inversion rate in X could be anomalous, should it be firmly established with higher resolution instruments.



XII

Experimental Section

Nmr Spectra. A Varian A-60 spectrometer was used, and temperatures were determined by measurements of peak separation in neat methanol. Spectra were taken on 0.4 ml samples containing 5–20% substrate and 2% tetramethylsilane. The line-broadening measurements on I were carried out with a sweep time of 500 sec and a sweep width of 50 cps, and duplicate measurements were made at each temperature. The spectra of VI at −90 and −113° were taken on a Varian HR-60 instrument by Dr. A. J. R. Bourn, whom we wish to thank.

Preparation of Aziridines. Procedure A.[24] The sulfonyl chloride was shaken with excess ethylenimine (Matheson Coleman and Bell) in the presence of dilute sodium hydroxide until the sulfonyl chloride had completely reacted. The disappearance of the sulfonyl chloride was followed by thin layer chromatography. The resulting oil was separated and dissolved in ether, and the ether was washed with water until the washings were neutral. The ether solution was dried and evaporated on a rotary evaporator.

Procedure B.[25] The acid chloride in benzene or ether was added dropwise to a cooled solution of excess ethylenimine in benzene or ether. The solution was filtered and evaporated on a rotary evaporator.

1-Benzenesulfonylaziridine (I). Procedure A gave an oil which spontaneously began to crystallize exothermically. Unless cooled immediately, the partially crystallized material polymerized in a few seconds. The crystalline aziridine I was recrystallized from 90% ligroin–10% ether to give large white needles, mp 47.6–48.0°; 20% yield. *Anal.* Calcd for $C_8H_9NO_2S$: C, 52.44; H, 4.95. Found: C, 52.59; H, 5.17.

1-(*p*-Tolylsulfonyl)aziridine (II). Aziridine II was prepared by means of procedure A. No polymerization was observed. Two recrystallizations from ligroin gave pure material, mp 66.0–66.5°; 33% yield (lit.[5a] mp 64.2–64.4°). *Anal.* Calcd for $C_9H_{11}NO_2S$: C, 54.80; H, 5.62. Found: C, 54.95; H, 5.65.

1-Benzenesulfinylaziridine (III). Benzenesulfinyl chloride was prepared by the published procedure.[26] The aziridine III was prepared in 61% by means of procedure B. The resulting oil was shown to be pure by tlc; $n^{25}D$ 1.5750. *Anal.* Calcd for C_8H_9NOS: C, 57.46; H, 5.42. Found: C, 57.46; H, 5.55.

1-Benzenesulfenylaziridine (IV). Benzenesulfenyl chloride was prepared by the published procedure.[27] Aziridine IV was prepared by means of procedure B and was obtained as a light yellow oil. This material was contaminated by an impurity which comprised about 20% of the total product. Attempts to purify this material were not successful as the product decomposed extensively when subjected to tlc.

1-(2,4-Dinitrobenzenesulfenyl)aziridine (V). Aziridine V was prepared from 2,4-dinitrobenzenesulfenyl chloride (Matheson Coleman and Bell) by means of procedure B. Five recrystalliza-

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(21) A value for $\Delta S^{\ddagger}$ is not given in ref 19, but from the very low frequency factor (5×10^7 sec^{-1}), $\Delta S^{\ddagger}$ must be about −23 eu. In other cases where early nmr work indicated large negative values for $\Delta S^{\ddagger}$, systematic errors were found to be responsible [A. Allerhand and H. S. Gutowsky, *J. Chem. Phys.*, 41, 2115 (1964); C. W. Fryer, F. Conti, and C. Franconi, *Ric. Sci. Rend.*, [2] 8, 788 (1965)].

(22) D. Y. Curtin, E. J. Grubbs, and C. M. McCarty, *J. Am. Chem. Soc.*, 88, 2775 (1966).

(23) D. L. Griffith and J. D. Roberts, *ibid.*, 87, 4089 (1965).

(24) C. C. Howard and W. Marchwald, *Ber.*, 32, 2036 (1899).

(25) H. Bestian, *Ann.*, 566, 210 (1950).

(26) H. Phillips, *J. Chem. Soc.*, 2552 (1925).

(27) H. Lecher and F. Holschneider, *Ber.*, 57, 755 (1924).

tions from 10% benzene–90% ligroin gave pure material, mp 144.5–145.0°; 70% yield. *Anal.* Calcd for $C_8H_7N_3O_4S$: C, 39.83; H, 2.93. Found: C, 40.08; H, 2.84.

1-Diphenylphoshinoxyaziridine (VI). The compound was prepared from diphenylphosphinous chloride (Stauffer Chemical Co.) by means of procedure B. The resulting oil was titrated with potassium permanganate in acetone to give aziridine VI. Six recrystallizations from 25% benzene–75% *n*-hexane gave pure material, mp 119.0–119.5°; 26% yield. *Anal.* Calcd for $C_{14}H_{14}NOP$: C, 69.13; H, 5.80. Found: C, 69.37; H, 5.94.

α-Lactams. IV.[1] A Stable α-Lactam, 1,3-Di-*t*-butylaziridinone[2]

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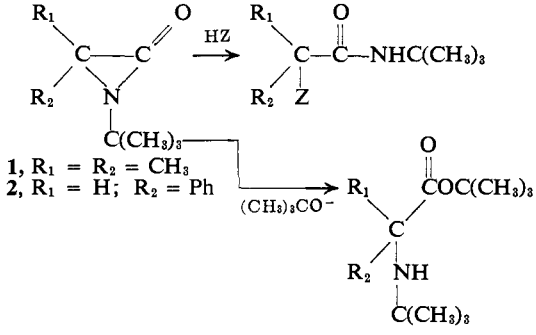
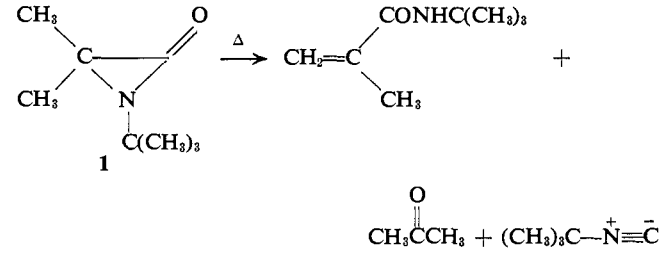
Abstract: The dehydrobromination of 2-bromo-3,3-dimethyl-N-*t*-butylbutyramide with potassium *t*-butoxide has been found to give 1,3-di-*t*-butylaziridinone. This α-lactam has also been prepared by the addition of dichlorocarbene to N-neopentylidene-*t*-butylamine. The chemical properties of this α-lactam differ remarkably from other reported cases. It is cleaved only very slowly by refluxing methanol to give 2-methoxy-3,3-dimethyl-N-*t*-butylbutyramide and methyl 2-(N-*t*-butylamino)-3,3-dimethylbutyrate. The acidic and basic methanolyses of this α-lactam give the amide and methyl ester, respectively. Reaction of the aziridone with dimethylsulfoxonium methylide produces a carbonyl-stabilized ylide. At 450° pyrolysis of 1,3-di-*t*-butylaziridinone gives *t*-butyl cyanide and pivalaldehyde.

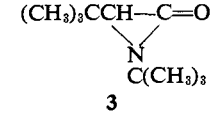
Since the suggestion in 1949 that 1-phenylaziridinone might be an intermediate in the reaction of phenyl isocyanate with diazomethane,[3] several attempts have led to the synthesis of three authentic α-lactams[1a,b,4] and the isolation and characterization of two of these, 1-*t*-butyl-3,3-dimethylaziridinone (**1**)[1b] and 1-*t*-butyl-3-phenylaziridinone (**2**).[4] Attack of nonionic nucleophiles (HZ = alcohols, amines, etc.) on the α-lactams **1** and **2** was found to proceed with cleavage of the alkyl–nitrogen bond to yield the corresponding α-substituted amide. Reaction of **1** or **2** with potassium *t*-butoxide produces the *t*-butyl ester from cleavage of the acyl–nitrogen bond.



In refluxing ether the thermal decomposition of the α-lactam **1** was complete in less than 1 hr, producing N-*t*-butylmethacrylamide, acetone, and *t*-butyl isocyanide in yields of 65, 12, and 12%, respectively.



If nucleophilic cleavage is retarded sterically and eliminative isomerization is avoided, then an α-lactam of greater stability should be obtained. Multiple phenyl substitutions appear to fulfill these requirements; however, attempts to produce 1,3,3-triphenylaziridinone by dehydrochlorination of 2-chloro-2,2-diphenylacetanilide have led only to rearranged products of the oxindole type.[5]



A more promising substitution pattern appeared to be that of 1,3-di-*t*-butylaziridinone (**3**). In this system one mode of decomposition, direct elimination to form an α,β-unsaturated amide, is blocked completely. There is precedent for the steric hindrance to nucleophilic attack at the α position in the failure of *n*-butyl 2-bromo-3,3-dimethylbutyrate to react with iodide ion in acetic acid or alcohol.[6] This hindrance should be

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(2) Taken in part from the Ph.D. Thesis of J. H. B., Massachusetts Institute of Technology, June 1966. This work was aided by National Institutes of Health Grant No. CA 02239-11,12 and a National Institutes of Health predoctoral fellowship (J. H. B.).

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