Although the nature of the species responsible for the intense colors has not been conclusively established, these results do show that silacyclopentadienide anions are *not* formed from treatment of the hydrides with *n*-butyllithium at low temperatures. Further studies are in progress to determine if the silacyclopentadienide anions can be prepared by other methods. The germanium hydride X does form the germyllithium derivative XII, but triphenylgermane also forms triphenylgermyllithium under the same conditions. It thus appears that the ring structure does not confer enhanced acidity to the hydrides (I, Y = H).

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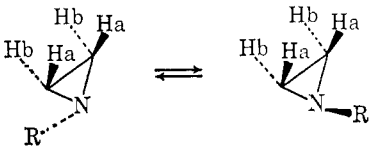
Aziridines. X. The Influence of Steric Factors on Nitrogen Inversion Rates and Ring Proton Shifts in Aziridines

Sir:

The study of nitrogen inversion in aziridines has become an active field of interest in recent years. In many aziridines, the rates of nitrogen inversion are of suitable magnitude for study by nmr spectroscopy.[1] At *ca.* 25°, the ring proton spectrum of 1-alkylaziridines (I, R = Me, Et, *i*-Pr) gives rise to an A_2B_2 pattern indicating that the rate constant (k_i) for the nitrogen inversion process (Ia ⇌ Ib) is small compared to the chemical



Ia Ib

shift, ν_{AB}. At higher temperatures, the ring proton spectrum of I (R = Et), for example, broadens and then at ~108° the coalescence temperature (T_c) collapses to a singlet. At T_c, the inversion rate constant becomes equal to $2.22\nu_{AB}$, or approximately 60 sec^{-1}.[1b] Replacing the ethyl group by methyl, benzyl, phenethyl, or cyclohexyl does not greatly affect the latter value. On the other hand, the bulky *t*-butyl group appears to increase the rate of nitrogen inversion dramatically. Thus, Bottini and Roberts[1b] report that the 40-Mc/sec nmr spectrum of 1-*t*-butylaziridine (II) even at −77° possesses only a single sharp line for the ring protons, "indicating that inversion occurs too rapidly for measurement." The lower inversion barrier was ascribed[1b] to nonbonded interactions between the ring protons and the *t*-butyl group in the ground state of II.[2]

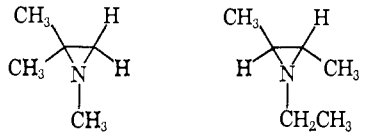
In this communication we present new data concerning nitrogen inversion in 1-*t*-butylaziridine (II) and discuss the factors which govern the magnitude of ν_{AB} in 1-alkylaziridines.

In contrast to the study of Bottini and Roberts,[1b] we have found that the ring protons in the 40- and 60-Mc/sec spectrum of II as the neat liquid or a 50% CCl_4 solution form *two peaks* separated by ~2 and 3 cps, respectively, at room temperature. The magnitude of ν_{AB} was found to be solvent and concentration dependent. For example, the proton spectrum of II as a 20% benzene solution (w/v) exhibits an A_2B_2 pattern with $\nu_{AB} \approx 11$ cps at 34° and lower.

On heating a benzene solution of II the ring proton spectrum broadens and then collapses to a single band at about 52°, the coalescence temperature.[3] The thermodynamic parameters for the inversion process in 1-*t*-butylaziridine-2,2-d_2 ($T_c \approx 52°$) are currently being assessed from the deuterium-decoupled spectra in various solvents.

The present study clearly demonstrates that steric factors do indeed accelerate the nitrogen inversion process in 1-alkylaziridines.[4] However, the rate of nitrogen inversion in the case of 1-*t*-butylaziridine (II) is far less than that previously claimed by Bottini and Roberts.[1b]

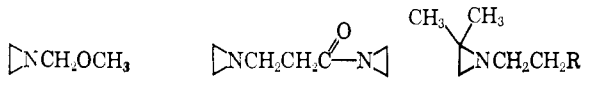
Of particular relevance is the similarity of the present data and those reported for 1-alkyl-2,2-dimethylaziridines (iii,[1b] III[1c,e]) and *trans*-1-ethyl-2,3-dimethylaziridine[1b,e] (IV). Such similarities strongly imply that the degree of steric assistance to the inversion process in these molecules is comparable.[6]



III IV

In addition to accelerating the nitrogen inversion process, steric factors also play a prominent role in determining the magnitude of ring proton shifts (ν_{AB}) in aziridines.

In harmony with our earlier studies[7] on styrenimines (2-phenylaziridines), we find that ring protons *cis* to the magnetically anisotropic N-alkyl bond in I (R = Me, Et, *i*-Pr) are shifted over 25 cps upfield relative to the ring protons in aziridine (I, R = H). A comparison of the ν_{AB} values for the 1-alkylaziridines recorded in



i ii iii

i and ii,[5] respectively.

(1) (a) H. S. Gutowsky, *Ann. N. Y. Acad. Sci.*, 70, 786 (1958); (b) A. T. Bottini and J. D. Roberts, *J. Am. Chem. Soc.*, **80**, 5203 (1958); (c) A. Loewenstein, J. F. Neumer, and J. D. Roberts, *ibid.*, **82**, 3599 (1960); (d) T. J. Bardos, V. Szantay, and C. K. Navada, *ibid.*, **87**, 5796 (1965); (e) F. A. L. Anet and J. M. Osyany, *ibid.*, **89**, 352 (1967); (f) F. A. L. Anet, R. D. Trepka, and D. J. Cram, *ibid.*, **89**, 357 (1967); (g) V. F. Bystrov, R. G. Kostyanovskii, O. A. Panshin, A. U. Stepanyants, and O. A. Iuzhakova, *Opt. Spectry.* (USSR), **19**, 122 (1965).

(2) After completion of this paper, Anet and Osyany[1e] suggested that the effect of the *t*-butyl group could not be regarded as firmly established because the ring protons still formed a single band at −77°. If ν_{AB} is about 0–3 cps, the authors[1e] argue that, as a result of coupling, a single line would result regardless of the value of k_i. An explanation for this unusually small ν_{AB} value for II, however, was not proposed by Anet and Osyany.[1e]

(3) Interestingly, 1-(1-adamantyl)aziridine as a 20% benzene solution exhibited a coalescence temperature of about 41°.

(4) In several instances, the presence of heteroatoms on the alkyl chain allegedly increases k_i *via* an electronic effect.[1g] Thus, Bystrov and co-workers[1g] report T_c values of approximately 30 and 57° for

(5) The very similar T_c values of 57 and 55° reported for ii[1g] and iii (R = CH_2OH, CO_2Et),[1b] respectively, cannot be easily rationalized.

(6) Arguing that steric repulsions were not very different in II, III, and IV, as shown by molecular models, Anet and Osyany[1e] recently proposed that the rate of nitrogen inversion in these three compounds would be similar.

(7) S. J. Brois, Abstracts of Papers, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 9–14, 1967, No. O-72.

Table I. ν_{AB} Values for 1-Alkylaziridines (I)[a]

R	ν_{AB}, cps
Me	42
Et	39
i-Pr	36
t-Bu	3[b]

[a] 60-Mc/sec spectra recorded as 50% CCl_4 solutions. [b] Peak separation. A value of 5 cps was obtained from the deuterium-decoupled proton spectrum of 1-*t*-butylaziridine-2,2-d_2.

Table I reveals that the magnitude of the anisotropy shift decreases with the steric requirements of the N-substituent, *i.e.*, Me > Et > *i*-Pr ≫ *t*-Bu. The observed trend in ν_{AB} is surprising since one would have expected increased shielding from the anisotropy of the N-alkyl carbon–carbon bonds.[8] In light of our earlier studies,[7] however, we propose that intramolecular van der Waals (dispersion) interactions between the N-alkyl and ring protons account for the observed chemical shift trend.

Presumably, nonbonded interactions between the ring and N-substituent hydrogens cause a distortion of the electron cloud around the ring protons, *i.e.*, H_a in conformer Ib. These time-dependent distortions of the ring C–H bond symmetry lead to a reduction in shielding.[9] Such dispersion effects become especially important as the steric requirements of the N-alkyl group increase. Thus, the van der Waals contribution to ν_{AB} in 1-ethyl- and 1-isopropylaziridine relative to 1-methylaziridine is, as expected, rather small. On the other hand, the strong intramolecular dispersion effect due to the bulky *t*-butyl group in II (CCl_4) virtually *nullifies* the magnetic anisotropy contribution to ν_{AB}.

It is plausible that the magnitude of such intramolecular dispersion shifts in aziridines may be a sensitive function of the steric requirements of the N substituent. We are presently investigating this possibility.

(8) A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **83**, 231 (1961); **84**, 2784 (1962); F. A. Bovey and F. P. Hood, III, *ibid.*, **87**, 2060 (1965).

(9) For pertinent discussions see A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, **32**, 1227 (1960); T. Schaefer, W. F. Reynolds, and T. Yonemoto, *Can. J. Chem.*, **41**, 2969 (1963); V. M. S. Gil and W. A. Gibbons, *Mol. Phys.*, **8**, 199 (1964).

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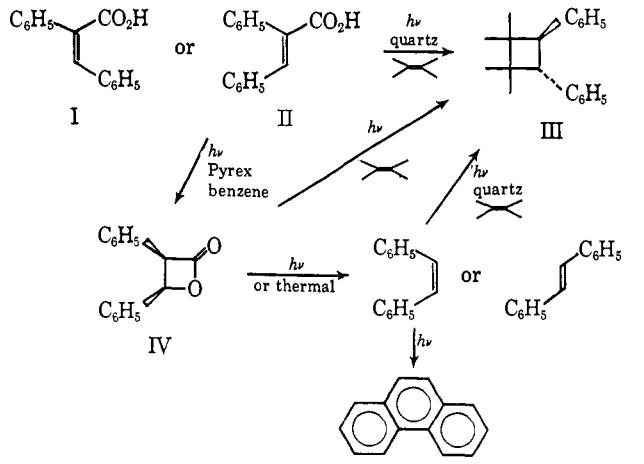
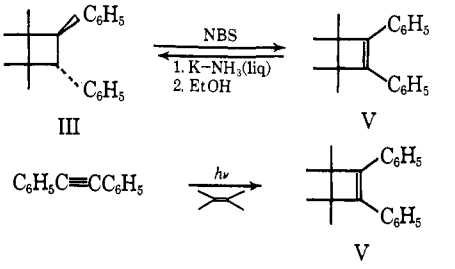
Photochemical Isomerization of α,β-Unsaturated Acids to β-Lactones and α,β-Unsaturated Amides to β-Lactams[1]

Sir:

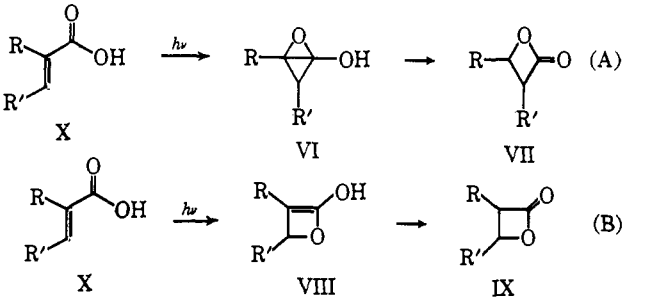
Attempts to add I or its isomer II to tetramethylethylene gave only *trans*-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane (III, mp 105–106°, 67%). The structure of the product was established by the molecular weight (mass spectrometry, mol wt 264), nmr (δ 7.07 (10 H, singlet), 3.55 (2 H, singlet), 1.12 (6 H, singlet), 0.77 (6 H, singlet)), and oxidation by N-bromosuccinimide to 1,2-diphenyl-3,3,4,4-tetramethylcyclobutene (V, 80%) which was identical with an authentic sample prepared by photocycloaddition of diphenylacetylene to tetramethylethylene (30%). Reduction of the cyclobutene with potassium in liquid ammonia gave the original cyclobutane III, which is thus assigned *trans* stereochemistry.





The formation of III in high yield naturally raises questions concerning mechanism. Irradiation of I or II in degassed benzene gave the *cis*-β-lactone IV (mp 120–121°, isolated in 79% yield). The product showed λ_{max}^{KBr} 5.45 μ and ν_A = δ 5.30, ν_B = δ 5.84 (J_{AB} = 7.0 cps), δ 6.90–7.20 (10 H). Pyrolysis of the β-lactone gave *cis*-stilbene (up to 99%) and CO_2 (92%). Irradiation of the β-lactone in the presence of tetramethylethylene gave III. Irradiation of the β-lactone in the absence of tetramethylethylene gave a complex mixture from which phenanthrene (a photoproduct of *cis*-stilbene)[2] could be isolated. Irradiation of either *cis*- or *trans*-stilbene in the presence of tetramethylethylene gave only *trans*-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane (III).

Two structurally different paths may be considered for the formation of the β-lactone IV from the unsaturated acid I or II. Path A involves valence isomerization to a substituted oxabicyclobutane VI which can isomerize to β-lactone VII. Path B involves valence isomerization to hydroxy oxetene VIII which could keton-



(1) Photochemical Transformations. XXI. All irradiations were carried out with degassed solutions.

(2) F. R. Stermitz in "Organic Photochemistry," Vol. 1, O. L. Chapman, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, p 247.