

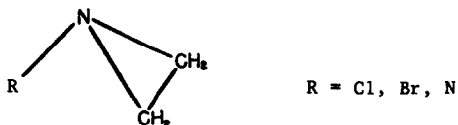
STABLE NITROGEN PYRAMIDS III. N-AMINOAZIRIDINES

Stanley J. Brois

Esso Research and Engineering Company
Linden, New Jersey

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Recently, we discovered (1,2) that N-haloaziridines (3) exist as stable pyramidal structures at room temperature. In our continuing studies in this area, we now find that replacement of halogen by nitrogen also affords a stable nitrogen pyramid.



The present communication describes nmr spectral evidence for the remarkable configurational stability of N-aminoaziridine (I) and N-amino-2,2-dimethylaziridine (II).



The model N-aminoaziridines I and II were prepared in low yields via amination of ethylenimine and isobutylenimine with hydroxylamine-O-sulfonic acid in an alkaline medium at ca. 0° (6).

The 60-MHz spectra of the gc purified N-aminoaziridines I and II were recorded as 25% (w/v) CCl_4 solutions at room temperature. The ring protons of I featured a complex multiplet centered at 1.75τ . The 2,2-dimethyl analog, II, showed two sharp methyl resonances at 1.06 and 1.27τ and two sharp ring proton signals at 1.10 and 1.63τ . The conspicuous nonequivalence of the geminal nuclei in I and II clearly reveals that pyramidal inversion in these molecules is slow on the nmr time scale at $\sim 25^\circ$.

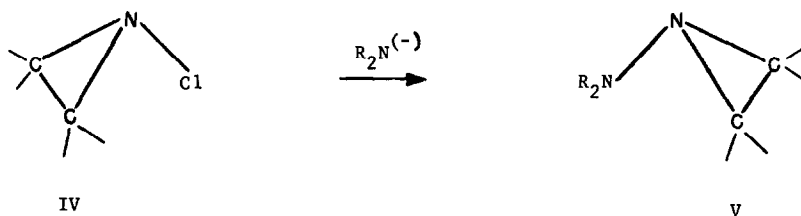
Moreover, the spectra of the N-aminoaziridines as dilute solutions in xylene remained unchanged even at $\sim 150^\circ$. The thermal instability of I and II has discouraged further attempts to ascertain their coalescence temperature. However, in light of the remarkable configurational stability of I and II as assessed by nmr spectroscopy, we are actively pursuing the synthesis and isolation of the cis and trans isomers of 1-amino-2-methylaziridine (III).



Presumably, the appreciable inversion barrier ($\Delta F^\ddagger > 22$ Kcal/mole) to pyramidal inversion observed for the N-aminoaziridines (7) may be attributed, in part, to increased repulsions between the lone-pair electrons on the nitrogen atoms in the planar transition state for inversion.

Significantly, the present study lends further substance to the concept (1,4,8,9) that an adjacent heteroatom substantially decreases the rate of nitrogen inversion in cyclic and acyclic systems.

Two especially important corollaries emerge from the present study. First, the configurationally stable aminoaziridines readily lend themselves to resolution studies (cf. 2) via conventional methods. Second, the realization of stable nitrogen pyramids IV and V opens the door to mechanistic studies on nucleophilic displacements at nitrogen employing



the known reactions of N-haloaziridines with ammonia (10) and 1-lithium aziridine (11). These studies will be described in due course.

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