LETTERS TO THE EDITOR

A THERMODYNAMICALLY STABLE 1,2-CIS-DIAZIRIDINE

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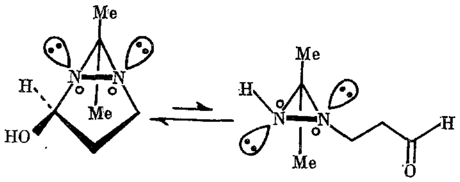
Mannschreck and Seitz [1] have proposed an inversion equilibrium between cis and trans isomers of 1-alkyl- and 1,2-dialkyldiaziridines. However, 1,2-cis-diaziridines are not observed in the equilibrium mixture due to destabilization by steric and four-electron interaction of the cis-oriented N-substituents and the unshared electron pairs [1, 2].

We have obtained a bicyclic cis-diaziridine (Ia) which predominates in the equilibrium mixture with the monocyclic trans form (Ib)



(Ia) (Ib)

PMR spectroscopy showed that the (Ia)/(Ib) ratio at 28°C is 85:15 in $C_6D_5CD_3$ and 77:23 in $CDCl_3$. The thermodynamic equilibrium parameters were obtained from the temperature dependence in $C_6D_5CD_3$:$\Delta H^0 = 7.04 \pm 0.01$ kcal/mole and $\Delta S^0 = -19.9 \pm 0.4$ cal/mole·deg. The interconversion of the cis and trans isomers, (Ia) and (Ib), is accomplished not by inversion but rather by reversible nucleophilic addition to the C=O group. Thus, the enthalpy of the reaction is greater than the strain energy of the 1,5-diazabicyclohexane system and destabilizing interaction of the unshared electron pairs.

Diaziridine (I) was obtained by the reaction of 3,3-dimethyldiaziridine with acrolein in methanol at 20°C in 30% yield (after sublimation at 60°C (1 mm)), mp 62-69°C. Found: C 55.97; H 9.46; N 21.75%. Calculated for $C_6H_{12}N_2O$: C 56.21; H 9.44; N 21.85%. PMR spectrum at 400 MHz in C_6D_6 (δ, ppm, J, Hz): for (Ia), 0.55 and 1.23 s (6,6-Me_2), 1.74 m (3-H_a), 2.14 m (3-H_e, J = 14.0); 2.31 m (4-H_e, J = 11.9, 10.7, 5.2); 3.40 m (4-H_a, J = 11.6, 11.6, 7.0), 4.69 m (2-H, J = 2.1, 5.8), 6.35 br.s (OH); for (Ib), 0.93 and 0.97 s (3,3-Me_2), 2.24 m (2'-H_2), 2.38 and 2.65 (3'-H_2, J = 12.5, 6.7, 6.4), 9.52 m (1'-H, J = 1.6).

LITERATURE CITED

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