THERMOLYSIS OF TRANS-2-METHYL-1-AMINOAZIRIDINE

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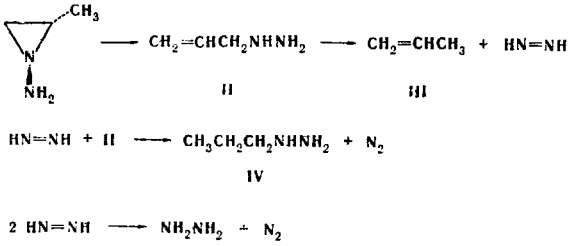
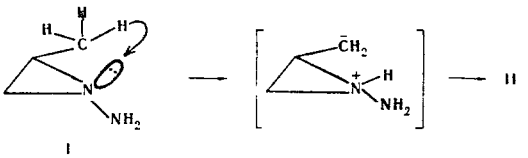
We have found that the character of the PMR spectrum does not change, i.e., the cis isomer is not formed, when chromatographically pure trans-1-amino-2-methylaziridine (I) is heated in a sealed ampule under helium at 100°C. The pattern of the PMR spectrum is complicated substantially after I is heated at 160° for 2.5 h. An analysis of the reaction mixture and of the isolated (by preparative gas-liquid chromatography) reaction products by PMR spectroscopy showed that allylhydrazine (II), propylene (III), propylhydrazine (IV), hydrazine, and nitrogen are formed in the mixture. The structures of II and IV were confirmed by comparison of their physicochemical characteristics with the characteristics of genuine samples. Propylene was characterized in the form of 1,2-dibromopropane. The relative percentages of the reaction products depend on the thermolysis time, and the percentages of III and IV increase proportionally as the amount of allyl hydrazine II decreases.

On the basis of these results, the thermolysis of aziridine I can be represented by the following scheme:



A 1,3 proton shift with simultaneous cleavage of the N_1-C_2 bond probably occurs in the rearrangement of aziridine I to allylhydrazine.



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