

THE DECOMPOSITION OF *exo*-7-AZIDOBICYCLO [4.1.0] HEPTANE

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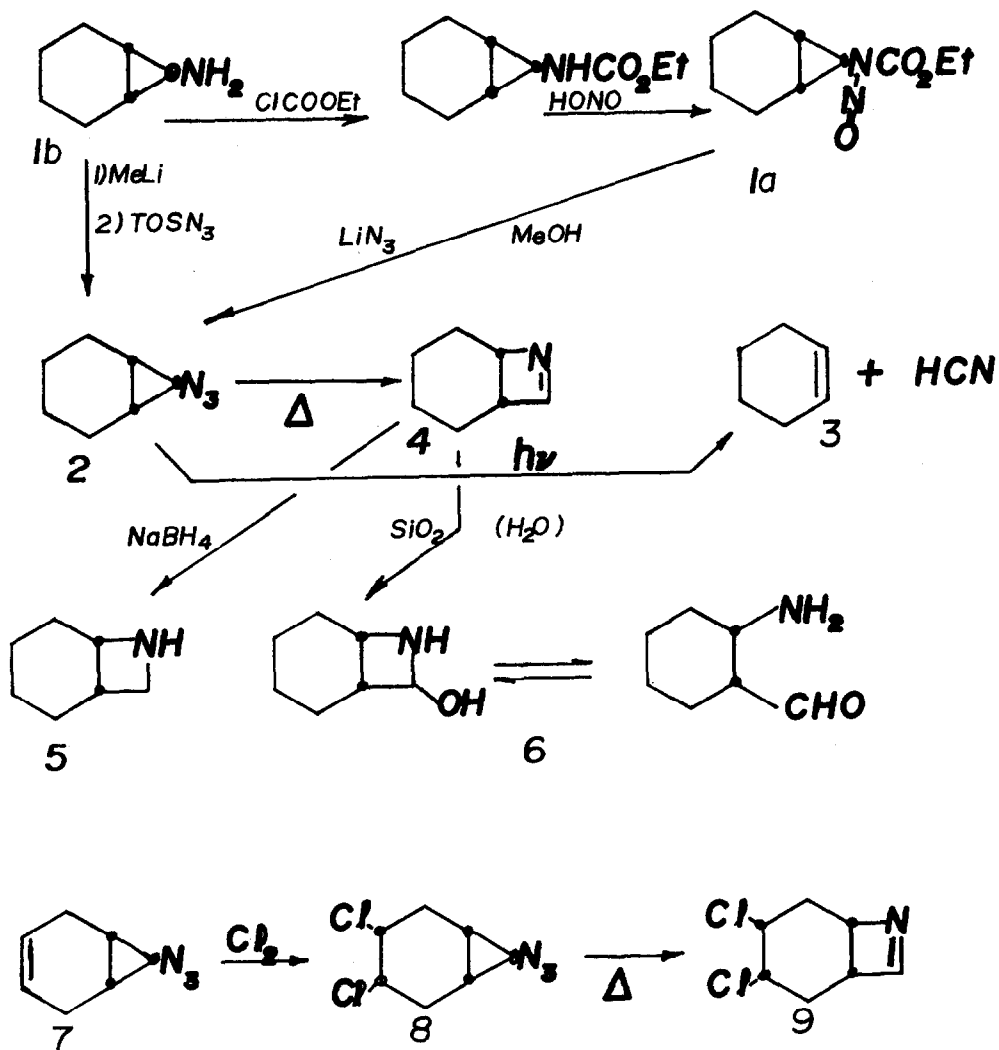
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(Received in USA 12 June 1972; received in UK for publication 14 August 1972)

The reported decomposition of dichlorocyclopropyl azides to yield dichloro-1-azetines¹ prompts us to report our related results with norcaranyl azides.

As a model for continuing efforts to synthesize the parent azabullvalene and azocine molecules, we have examined the photolytic and thermal decomposition of 7-azidobicyclo [4.1.0] heptane (2). The azide is obtained in 40% isolated yield from treatment of *N*-nitroso-*N*-bicyclo [4.1.0] heptyl ethyl carbamate (1a) with a threefold excess of lithium azide² in anhydrous methanol or by diazo transfer upon (1b) in 50% yield. The former procedure is superior because of freedom from mechanical operation and purification problems³.

Irradiation of small samples of (2) in anhydrous ether for one hour at 0°C using a 450-watt Hanovia apparatus furnished no isolatable basic products and negligible residues. Hydrogen cyanide was detected in the reaction mixture colorimetrically in 70% of theoretical yield by direct comparison of its picric acid complex with standards⁴. This observation suggests that the initially generated nitrene intermediate collapses rapidly to hydrogen cyanide either directly or via the 1-azetine derivative. The results are identical when the reaction was carried out through a pyrex filter, vycor filter, or without any filter. The cyclohexene formed was swept with a dry nitrogen stream into a cold bromine-methylene chloride solution and assayed by gas chromatography as dibromocyclohexane (40% recovery). Previous investigations in this laboratory demonstrated that 7-azidocyclohepta-1,3,5-triene (troyl azide) undergoes vaporphase thermolysis and photolysis to furnish benzene, hydrogen cyanide, and nitrogen gas⁵.



The facile loss of hydrogen cyanide via photolysis of the 1-azetine is consistent thermodynamically and on an orbital symmetry conservation basis⁶. Furthermore, it appears that ejection of hydrogen cyanide will be a very important process in isomerization reactions of the pure aza analogues of C_8H_8 and $C_{10}H_{10}$ hydrocarbons. Upon comparison with the imidate ester analogues of these hydrocarbons⁷, it becomes apparent that a considerable barrier will exist toward elimination of $ROC=N$. We therefore conclude that they are not representative of the C_7H_7N and C_9H_9N systems.

The thermal decomposition of (2) was also examined. Thermolysis of 2.0 gm sample was accomplished in refluxing toluene. Cessation of nitrogen gas evolution and disappearance of the 2095 cm^{-1} ir band indicated no azide remained after three hours. Removal of the solvent in vacuo followed by careful column chromatography on silica gel furnished 1.0 gm of a light tan oil. The ir and uv spectral parameters were consistent with the structure of 2-aminohexahydrobenzaldehyde in equilibrium with the isomeric carbinolamine (major peaks at 3440, 3350, and 1750 cm^{-1} , λ_{max} at 227 nm, $\epsilon = 345$). A red ppt. (mp 201°C) was obtained upon addition of 2,4-DNP reagent. Hydrolysis during chromatography of 2-azabicyclo[4.1.0]oct-2-ene, (4), accounts for the formation of 2-aminohexahydrobenzaldehyde. When the thermolysis was followed immediately by reduction with sodium borohydride in ethanol a basic material was obtained (major peaks at 3305, 2850, 1450, 990, and 730 cm^{-1})⁸. Treatment with benzoyl chloride gave a benzamide (mp $179-81^\circ\text{C}$)⁹.

The exhibition of a weak uv absorbance at 227 nm is surprising for the 2-aminohexahydrobenzaldehyde. It therefore was of paramount importance to determine the identity of the reduction product. This material was subjected to nmr analysis which revealed three groups of multiplets of non-aromatic proton resonances. The elemental analysis of the extensively purified benzoyl derivative coupled with the nmr data including no vinyl H in the reduction product and the fact that the physical properties of the derivatives are not those reported for heptamethylenimine derivatives only supports the assignments (4) and (5).

We are forced to conclude that the uv absorbance at 227nm results from an interaction created by the close proximity of the amino and carbonyl groups.

Similar results have been realized from the thermolysis of 7-exo-azido-trans-4,5-dichloronorcarane (8 + 9).

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- (9) Correct spectral parameters and elemental analysis were obtained.