

# SYNTHESIS OF A 2-AMINO AZIRIDINE

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2-amino aziridines have been mentioned as intermediates in the literature but have <sup>not</sup> been characterized as such <sup>(1)</sup>. A 2-pyridinium aziridine has been prepared <sup>(2)</sup>. We now wish to report the synthesis of a 2-dimethylamino aziridine from the photolysis of the corresponding  $\Delta^2$ -triazoline.

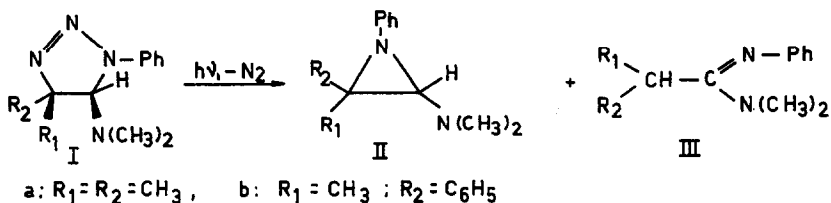
The thermal decomposition of a  $\Delta^2$ -triazoline affords, in most cases, a mixture of aziridine and imine <sup>(3)</sup>. However, heating 5-amino- $\Delta^2$ -triazolines only yields an amidine <sup>(4)</sup>. Scheiner <sup>(5)</sup> has observed that the photolysis of a  $\Delta^2$ -triazoline affords a greater yield of aziridine. It was hoped that 2-amino aziridines could be synthesized through the photolysis of 5-amino- $\Delta^2$ -triazolines.

1-Phenyl-4, 4-dimethyl-5-dimethylamino- $\Delta^2$ -triazoline (Ia) and 1, 4-diphenyl-4-methyl-5-dimethylamino- $\Delta^2$ -triazoline (Ib) are synthesized by the cycloaddition reaction between the corresponding enamines <sup>(6)</sup> and phenyl azide in chloroform. The solutions are refluxed two hours, the solvent evaporated, and the resulting oils give white needles from pentane. (Ia) ( $R_1=R_2=CH_3$ ): m.p. 50°; yield 50%; (Ib) ( $R_1=CH_3$ ,  $R_2=C_6H_5$ ): m.p. 43.5°; yield 25%. The direction of the addition was proved by the mass spectral fragment  $m/e=148$  <sup>(7)</sup>.

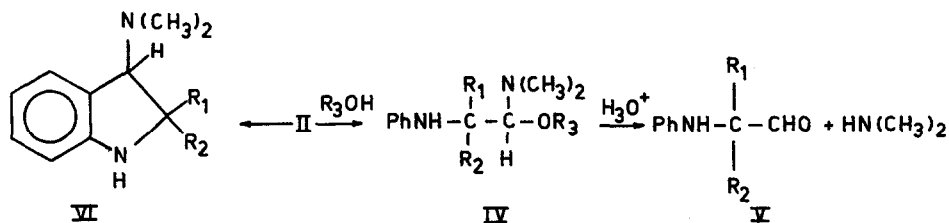
Photolysis of the triazolines in dry benzene is fast, and yield oils after the theoretical amount of nitrogen, measured with a gas burette, has evolved, and the solvent is evaporated. Pure aziridine is distilled at reduced pressure (b.p. 83°C, 0.1 mm).

Analysis of (IIa): NMR ( $CDCl_3, \delta$ ): 0.92 (s, 3H), 1.41 (s, 3H), 2.22 (s, 1H), 2.39 (s, 6H), 6.5-7.35 (m, 5H). IR (film,  $cm^{-1}$ ): 1260 ( $C(CH_3)_2$ ), 1258 (ring breathing), 1310 (N-Ph), 1369, 1379, 1388, 2765, 2810 ( $N(CH_3)_2$ ). Mass spectrum:  $m/e (M^+)=190$  (100%).

Typical fragmentations  $190 \rightarrow 134$  (49%) and  $190 \rightarrow 175$  ( $-CH_3$ , 36%)  $\rightarrow$  118 (20%). The ratio of aziridine to amidine, as determined by NMR, is respectively 3;2.



Aziridines (IIa) and (IIb) are very sensitive to moisture. Hydrolysis of II yields an hemi-aminal (IV) that decomposes into an aldehyde (V) and dimethylamine.



a:  $\text{R}_1 = \text{R}_2 = \text{CH}_3$ ; a<sub>1</sub>:  $\text{R}_1 = \text{R}_2 = \text{CH}_3$ ,  $\text{R}_3 = \text{H}$ ; a<sub>2</sub>:  $\text{R}_1 = \text{R}_2 = \text{R}_3 = \text{CH}_3$ ; b:  $\text{R}_1 = \text{CH}_3$ ,  $\text{R}_2 = \text{C}_6\text{H}_5$ ,  $\text{R}_3 = \text{H}$

Photolysis of triazoline (Ia) in methanol results in the formation of a gem-amino ether (IVa<sub>2</sub>) and amidine (IIIa) in 3:2 ratio as determined by NMR. Hydrolysis and alcoholysis of 2-alkoxy aziridines are known<sup>(8)</sup>. The products that were obtained were essentially of the same nature as the products of the hydrolysis and the methanolysis of the 2-amino aziridine.

IIa could also be converted on heating in the presence of acid to 2, 3 dihydro-indole VIa in high yields. An aminoaziridine had been postulated as intermediate in the synthesis of indole from p-chlorophenyl-1-azirine and N-methylaniline.<sup>(9)</sup>

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