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SYNTHESIS AND PROPERTIES OF 4-AMINOTETRAZOLO[1,5-*a*]PERIMIDINE*

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We have shown recently that 1-amino-2-azidobenzimidazole (I) is converted into 3-amino-1,2,4-triazine (III) in good yield on heating in chlorobenzene [2]. The reaction probably goes via the highly reactive nitrene II which undergoes a rearrangement, perhaps through an open chain intermediate. Other N-amino-α-azido azoles also undergo this rearrangement readily [2]. We were interested in discovering whether N-amino-α-azidoazoles which exist in the tetrazole form show a similar reactivity. The 2-azidoperimidines IV [3, 4] are the only known compounds of this type. The previously unknown amine V, which was essential for our study, was obtained by electrophilic amination of tetrazolo[1,5-*a*]perimidine (IVa) with hydroxylamine-O-sulfonic acid in a basic borate buffer (cf. [5]). Hydroxylamine-O-sulfonic acid (90%, 4.13 g, 33 mmol) was added to a suspension of unpurified compound IVa [3] (2.28 g, 11 mmol) was heated to 50°C in a borate buffer (55 cm^3 ($Na_2B_2O_4$–NaOH, pH 10) containing ethanol (10 cm^3) and sodium hydroxide (2.61 g, 66 mol). The mixture was stirred for 4h at 60-65°C, cooled, and the brownish precipitate was separated, washed with water, dried in air, and purified on a short chromatographic column packed with alumina. The colorless fraction with R_f 0.15 was collected (chloroform eluent). Since the amine V has a low solubility in chloroform the purification was carried out in several batches to give pure V (0.7 g, 29%) as light grey needles, m.p. 243-244°C dec. (from butanol). UV spectrum (methanol), λ_{max} (lgε): 220 (4.55), 247 (4.17), 306 (3.87), 345 nm (3.93). IR spectrum (Nujol): 3320, 3210 cm^{-1} (NH_2). ^1H NMR spectrum ($CDCl_3$, 300 MHz); 4.65 (2 H, s, NH_2), 7.37 (1 H, dd, 5-H), 7.39 (1 H, dd, 10-H), 7.48 (2 H, m, 7-H, 8-H), 7.60 ppm (2 H, m, 6-H, 9-H). Mass spectrum, *m/z (I, %)*: 224 (M^+, 100), 168 ($M^+ - N_2$, 77), 152 (9), 141 (29), 140 (56). There are three places in which amino groups may exist in an ambident ion: atoms $N_{(1)}$, $N_{(3)}$ and $N_{(4)}$. We consider the product to be a 4-amino derivative on the basis of the similarity of the aromatic proton region of its ^1H NMR spectrum to that of the 4-methyl substituted compound IVb [3,4]. The IR spectrum of amine V shows no absorptions in the azide region (2100-2200 cm^{-1}) which indicates that it exists in the tetrazole form in the solid state.

It might have been hoped that amine V would undergo thermolysis via a small equilibrium amount of the azido form VI as discussed above to give the previously unknown heterocyclic system naphtho[1,8-*e,f*]-1,2,4-triazepine. However, compound V underwent no noticeable change on heating in chlorobenzene for 8-10 h which shows how stable the tetrazole ring in compound V is. In this connection it is worth noting that there is no peak in the mass spectrum of amine V corresponding to the loss of a molecule of nitrogen from the molecular ion. However there is a very intense peak at *m/z* 168 which corresponds to the loss of two molecules of N_2 and formation of a pseudomolecular ion of perimidine. In contrast, there is an intense ($M^+ - N_2$) peak in the mass spectrum of compound IVb.

In contrast with other N-aminoazoles, we were unable to prepare the benzylidene derivative of amine V. When compound V was refluxed with benzaldehyde in acetic acid for 20 min, deamination occurred to give compound IVa in 80% yield. We suggest that this results from scission of the N–N bond in the hydrazone formed as an intermediate (with the elimination of benzonitrile) (cf [6]). Although the amine V is itself deaminated on boiling in acetic acid, the process is much slower.

*Paper 64 in the series "Heterocyclic analogs of pleiadiene." For paper 63, see [1].

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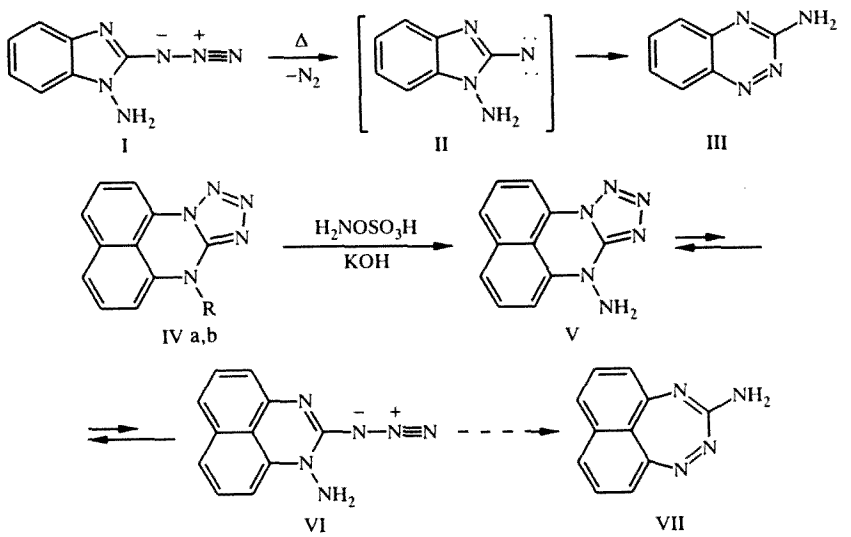

IV a R = H, b R = Me

Results of elemental analysis agree with calculated values.

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