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IMIDAZO[1,2-d]TETRAZOLE AND TETRAZOLO[1,5-a]BENZIMIDAZOLE

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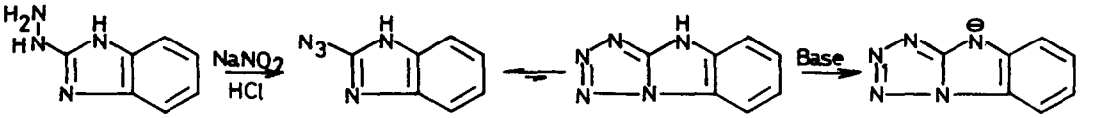
Research into azapentalenes[1] has been extended to the 1,2,3,3a,6-penta-azapentalenes IIb and Vb. The azidoazoles IIa and Va were prepared from I and IV as indicated. IR and NMR spectra show that the neutral molecules II and V exist as expected[2] only as the azides IIa and Va: ν_{as} N_3 occurred for both compounds at 2200-2130 cm^{-1} in KBr, $CHCl_3$ and DMSO, and all NMR signals were attributable to the structures IIa (A_2 system) and Va (AA'BB' system).

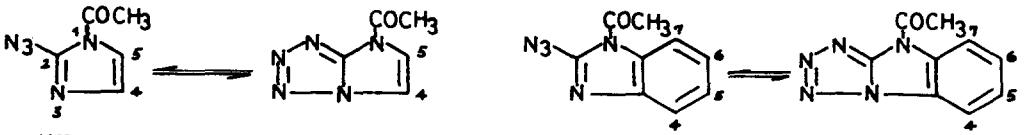
I IIa IIb III



IV Va Vb VI

However, the equilibrium is completely shifted to the tetrazole form in the corresponding anions III and VI [See reference 3 for the azidopyrazole anions]. Infrared spectra in EtONa-EtOH showed the disappearance of the azido band and the NMR in DMSO-NaH indicated the presence of AB (J_{AB} = 1.2 Hz) and ABCD systems for III and VI.

The azidoazoles with acetic anhydride gave the acetyl derivatives VII and VIII which exist as an equilibrium between the azido and tetrazole forms.



VIIa VII b VIII a VIII b

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The equilibrium ratio of azide/tetrazole in DMSO-d_6 is 3/2 for both compounds VII and VIII. At high temperature the proportion of azido form increases. In $CDCl_3$ we observed for VII only the azido form and for VIII a mixture of azide and tetrazole in the ratio 10/1. In the solid state VIIIa isomerises to the tetrazole VIIIb which on melting reverts to the azido form. [See reference 4 for similar examples in six membered rings]. The influence of N-acyl substituents on the azide/tetrazole relationship is now under investigation, but it is worth noting that in the case of 1-acetyl-3-azidopyrazoles only the azido form has been detected[3].

NMR of acetyl derivatives.

Compound	VIIa	VIIb	VIIIa	VIIIb
$CDCl_3$	2.58 ($COCH_3$) 6.86 (H_4) 7.38 (H_5) $J_{4,5}$ = 2Hz	-	2.68 ($COCH_3$) 7.2-7.7 (H_{456}) 8.16 (H_7)	2.98 ($COCH_3$) 7.2-7.7 (H_{456}) 8.53 (H_7)
DMSO-d_6	2.56 ($COCH_3$) 6.89 (H_4) 7.51 (H_5) $J_{4,5}$ = 2Hz	2.78 ($COCH_3$) 8.06 (H_4) 8.32 (H_5) $J_{4,5}$ = 2.8Hz	2.63 ($COCH_3$) 7.2-7.7 (H_{456}) 8.06 (H_7)	2.86 ($COCH_3$) 7.2-7.7 (H_{456}) 8.58 (H_7)

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