

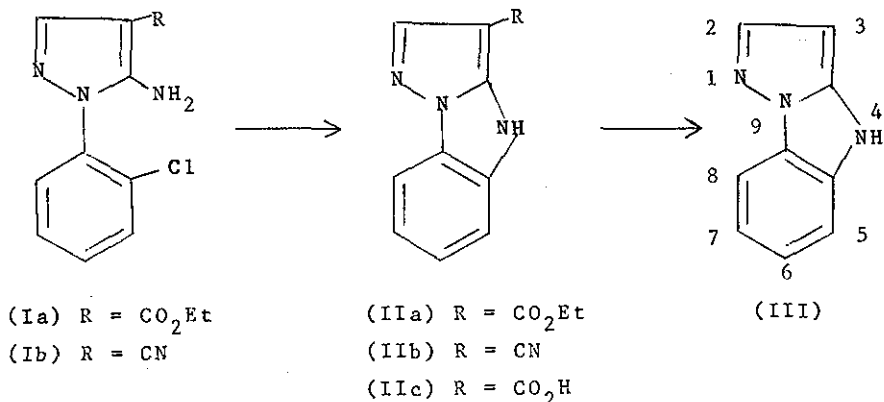
4H-PYRAZOLO[1,5-a]BENZIMIDAZOLE

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The parent ring system pyrazolo[1,5-a]benzimidazole has been obtained from the decarboxylation of the acid received in the hydrolysis of ethyl 4H-pyrazolo[1,5-a]-benzimidazole-3-carboxylate.

Although derivatives of 4H-pyrazolo[1,5-a]benzimidazole have been known for some time as dye intermediates in color photography¹ and were obtained by reductive cyclization of 1-o-nitrophenylpyrazol-5-one² while intramolecular cyclization of 5-amino-3-methyl-1-o-chlorophenylpyrazole by potassium in liquid ammonia led to another derivative³, the parent ring system has so far not been reported in the literature.

During our investigations of the scope of the Ullmann arylations of azoles⁴, we prepared ethyl 5-amino-1-o-chlorophenylpyrazole-4-carboxylate (Ia) and 5-amino-1-o-chlorophenylpyrazole-4-carbonitrile (Ib) from the reaction of o-chlorophenylhydrazine with ethyl ethoxymethylenecyanoacetate⁵, and with ethoxymethylene-malononitrile⁶ respectively. Ia and Ib on heating in N,N-dimethyl-



formamide in the presence of copper(II) oxide undergo intramolecular cyclizations to give ethyl 4H-pyrazolo[1,5-a]benzimidazole-3-carboxylate (IIa), mp 171-172°, and 4H-pyrazolo[1,5-a]benzimidazole-3-carbonitrile (IIb), mp 281-282° in yields of 14.5% and 42% respectively. IIa on hydrolysis affords the corresponding acid IIc, mp 210-212° in 72.7% yield.

When IIc was heated at 180-190°/ 2mm in a sublimation apparatus it decarboxylated to give the parent ring system 4H-pyrazolo[1,5-a]benzimidazole (III) in 90% yield. III: mp 220°; ir $\nu_{\text{max}}^{\text{KBr}}$: 3240-2500 (br., NH), 1590, 1200, 740, and 700 cm⁻¹; nmr (DMSO-d₆) δ : 11.30 (s, 1H, NH), 7.62 (d, 1H, J = 2.25 Hz, C₂H); 7.80 - 7.55 (m, 1H, C₈H), 7.50 - 6.90 (m, 3H, C₅H, C₆H, and C₇H); 5.72 (d, 1H, J = 2.25 Hz, C₃H), mass:m/e 157 (M⁺). all the compounds reported here gave satisfactory elemental analyses.

Further studies on this system are in progress.

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