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

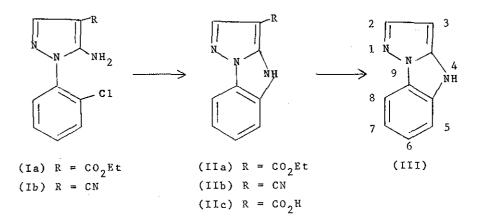
M<u>isbahul</u> A<u>in</u> K<u>han</u>^{*} and V<u>era</u> L<u>ucia</u> T<u>eixeira</u> R<u>ibeiro</u> Seção de Quimica, Instituto Militar de Engenharia, Urca, Rio de Janeiro, RJ, Brasil

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

Although derivatives of $4\underline{H}$ -pyrazolo $[1,5-\underline{a}]$ benzimidazole have been known for some time as dye intermediates in color photography 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-4carbonitrile (Ib) from the reaction of o-chlorophenylhydrazine with ethyl ethoxymethylenecyanoacetate⁵, and with ethoxymethylenemalononitrile⁶ respectively. Ia and Ib on heating in <u>N,N</u>-dimethyl-

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formamide in the presence of copper(II) oxide undergo intramolecular cyclizations to give ethyl $4\underline{H}$ -pyrazolo $[1,5-\underline{a}]$ benzimidazole-3carboxylate (IIa), mp 171-172°, and $4\underline{H}$ -pyrazolo $[1,5-\underline{a}]$ 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 $180-190^{\circ}$ / 2mm in a sublimation apparatus it decarboxylated to give the parent ring system $4\underline{H}$ -pyrazolo $[1,5-\underline{a}]$ benzimidazole (III) in 90% yield. III: mp 220°; ir v_{max}^{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 (A⁺). all the compounds reported here gave satisfactory elemental analyses.

Further studies on this system are in progress. ACKNOWLEDGEMENT We are grateful to Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) for the grant of a fellow-

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ship to Vera Lucia Teixeira Ribeíro.

REFERENCES

1.see for example H.Schellenberger, W.Pueschel, K.Loeffler, and K.H.Menzel, <u>Ger.</u>, 1961, 1.116.534 (<u>Chem. Abstracts</u>, 1962, <u>56</u>, 10332), and M.Fujihara, Y.Takei, T.Endo, and T.Masukawa, <u>Japan</u> <u>Kokai</u>, 1974, 74 53.435 (<u>Chem. Abstracts</u>, 1974, <u>81</u>, 162088). 2.K.H.Menzel, O.Wahl, and W.Pelz, <u>Ger.</u>, 1959, 1.070.030 (<u>Chem.</u> <u>Abstracts</u>, 1961, <u>55</u>, 23139). 3. S. Mignonac-Mondon, J. Elguero, and E. Lazaro, C. B. Acad. Sci. Ser C.

3.S.Mignonac-Mondon, J.Elguero, and R.Lazaro, <u>C.R.Acad.Sci.,Ser.C.</u> 1973, 276, 1533.

4.M.A.Khan, <u>Rec.Chem.Progr.</u>, 1970, <u>31</u>, 43.

5.C.Alberti and C.Tironi, Farmaco, Ed.Sci., 1967, 22, 58.

6.C.C.Cheng and R.K.Robins, <u>J.Org.Chem.</u>, 1956, 21, 1240.

Received, 9th May, 1977