ACIDIC FISSION OF 1,4-DIFORMYL-2,3,5,6-TETRA SUBSTITUTED

PIPERAZINES

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The mild removal of the N-formyl group by the action of hydrochloric acid is known from [1].

With the aim of obtaining unknown 2,3,5,6-tetra substituted piperazines by the deformylation of their 1,4-diformyl derivatives (I) [2] we have studied the behavior of the latter in hydrochloric acid and have found that together with the expected deformylation there also occurred a destruction of the piperazine ring with the formation of the hydrochloride salts of 1,2-di-substituted ethylenediamines (II).

Thus on treatment of substances (Ia) and (Ib) with concentrated hydrochloric acid for 72 and 24 h respectively at 20°C compound (IIa) dihydrochloride was formed in yields of 35 and 50% having decomposition temperature 132-133°C. IR spectrum (mull in Nujol and in fluorinated vaseline oil): 3070, 2610, 1590 (NH_3^+), 3620, 1290, 1100 cm⁻¹ (OH).

Diamine (IIc) dihydrochloride was obtained in 50% yield having decomposition temperature 138°C from compound (Ic) by the action of concentrated hydrochloric acid for 24 h at 20°C. IR spectrum (mull in Nujol and in fluorinated vaseline oil): 3100, 2590, 1610 ($\rm NH_3^+$), 740 cm⁻¹ (C1).

The data of elemental analysis for C, H, N, and C1 corresponded to the calculated values for all the obtained compounds.

The described conversion, fission of C-N bonds of the piperazine ring, is apparently explained by the instability in acid media of deformylated compound (I), which decomposed in a similar manner to α -hydroxy- [3] and α -haloamines [4] with the formation of the salt of the corresponding amine and an aldehyde. A more profound destruction to ammonium salts is possible, confirmation of which is the quantitative formation of ammonium perchlorate from compound (IIa) dihydrochloride in 42% hydrochloric acid at 20°C.

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