DECARBOXYLATION OF PIPERAZINIUM MONO- AND DIOXALATES

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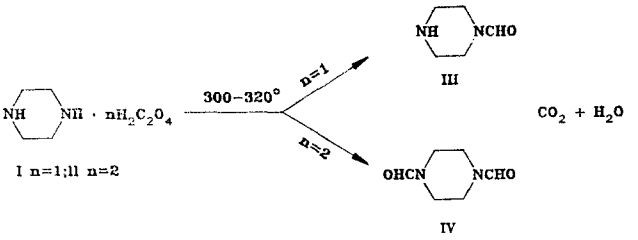
1-Formyl and 1,4-diformylpiperazines form by the reaction of methyl formate with piperazine; because of the low boiling point of one of the reagents the process is carried out in an autoclave [1].

We have studied the reaction of oxalic acid with piperazine. Contrary to expectations, instead of 2,3-dioxo-1,4-diazabicyclo[2.2.2]octane, on heating to 300-320° we separated 1-formyl- (III) and 1,4-diformylpiperazines (IV). The thermolysis is preceded by the formation of oxalates I and II. We found that the monoformyl derivative III comes from I; when the dioxalate II is heated, IV forms, with an insignificant (∿5%) admixture of III.



In the presence of formic acid, formylation of piperazine does not occur. Apparently the active intermediate in the thermolysis is the product of oxalic acid decomposition at the carbon—carbon bond; this process goes very quickly at 280-300° [2].

1-Formylpiperazine (III) [1]: yield 50%, bp 115-120° (4 mm). Mass spectrum, m/z (relative intensity, %): M^+ 114 (24); $[M - CHO]^+$ 85 (20).

1,4-Diformylpiperazine (IV) [1]: yield 60%, bp 154-158° (0.2-0.3 mm). mp 126-127° (from benzene). Mass spectrum: M^+ 142 (34); $[M - CHO]^+$ 114 (6); $[M - 2CHO]^+$ 85 (20).

The structure of the products is confirmed by the mass spectra and by comparison with authentic samples.

LITERATURE CITED

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