SYNTHESIS OF CHLORO ALDEHYDES OF THE HETEROCYCLIC SERIES

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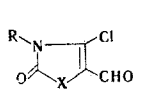
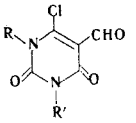
A method was developed for the preparation of 4-chloro-5-formylimidazolones, Δ^4-thiazolinones, and 4-chloro-5-formyluracils by reaction of 4-azolidones or barbituric acids with dimethylformamide and phosphorus oxychloride.

We have obtained 4-chloro-5-formylimidazolones (Ia-c) and the corresponding Δ^4-thiazolinones (Id) and 4-chloro-5-formyluracils (IIa-c) by reaction of 4-azolidones or barbituric acids with dimethylformamide (DMFA) and phosphorus oxychloride in a molar ratio of 1 : 1.5 : 3, respectively.



Ia-d



IIa-c

The optimum conditions for the formation of Ia-d and IIa-c are heating of the reaction mixture at 80°C for 16 h with subsequent brief heating at 115-130°. The reaction mixture is decomposed with ice, and the product is removed by filtration. The filtrate is extracted with ether to isolate an additional amount of product. The yields are 40-60%. The results of elementary analysis for carbon, hydrogen, and chlorine for Ia-d and IIa-c are in satisfactory agreement with the calculated values.

Under similar conditions, selenazolidine-2,4-diones and thiazolidine-2,5-dione undergo ring cleavage. The azomethines of 5-formylazolidinediones obtained by condensation of anilines with hydrolysis products Ia-d are identical with those previously described in the literature.

EXPERIMENTAL

4-Chloro-5-formyl-1-phenyl-2-imidazolone (Ia). This compound had mp 243-245° (from dioxane). IR spectrum, cm^{-1}: 1690 (CO), 1720 (CO), and 2720 (aldehyde CH).

4-Chloro-5-formyl-1-(p-methoxyphenyl)-2-imidazolone (Ib). This compound had mp 170° (from dioxane). IR spectrum, cm^{-1}: 1700 (CO) 1725 (CO), and 2730 (aldehyde CH).

4-Chloro-5-formyl-1-(p-tolyl)-2-imidazolone (Ic). This compound had mp 185° (from dioxane). IR spectrum, cm^{-1}: 1690 (CO), 1730 (CO), 2720 (aldehyde CH).

4-Chloro-5-formyl-Δ^4-thiazoline-2-one (Id). This compound had mp 219° (dec., from propanol). UV spectrum, λ_{max}, nm (log ε): 245 (3.44), 330 (3.77). IR spectrum, cm^{-1}: 1720 (CO), 1690 (CO), and 2710 (aldehyde CH).

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