NUCLEOPHILIC SUBSTITUTION IN THE O-PYRIMIDINYL KETOXIME SERIES

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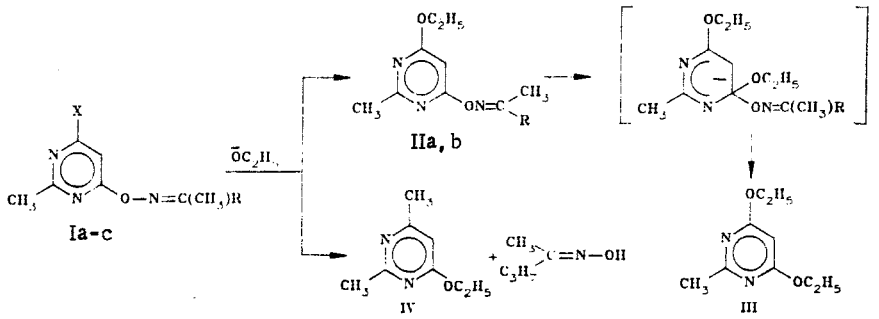
We have shown that treatment of the O-(2-methyl-4-chloropyrimidin-6-yl)oximes of acetone (Ia) and ethylmethylketone (Ib) with an alcoholic solution of sodium ethylate leads to the expected 4-ethoxy drivatives (IIa, b) and also to 2-methyl-4,6-diethoxypyrimidine (III). Thus, along with nucleophilic exchange of chlorine there is also observed a previously unreported substitution of the isopropylidene(isobutylidene)iminoxy group.

A similar substitution was also noted for the O-(2,4-dimethylpyrimidin-6-yl)oxime of methylpropylketone (Ic) which gave the corresponding ethoxypyrimidine IV and the dissociation product methylpropyl ketoxime.



The molecular weight of the products as determined mass spectrometrically and the results of elemental analysis were in agreement with those calculated. The PMR spectrum of the diethoxy derivative supported the proposed structure. Compounds III and IV were chromatographically identical to known samples.

Compound Ia, b (15 mmole) was added to sodium ethylate which had been prepared from sodium (0.69 g, 30 mmole) of absolute ethanol (60 ml). After refluxing for 6 h the alcohol was distilled off, the residue treated with water (2-3 ml), neutralized with dilute HCl solution (1:1), and extracted with ether. Removal of ether and distillation gave 2-methyl-4,6-diethoxypyrimidine (III) with bp 63-64.5°C (2.5 mm) and n_D^{24} 1.4820 (1.5 g, 55% from oxime Ia or 1.22 g, 45% from oxime Ib). It can be crystallized on standing to mp 29-30°C (according to [1] the bp is 107°C at 20 mm Hg). PMR Spectrum (CCl_4): 1.26 (6H, 5, CH_3CH_2), 2.39 (3H, s, CH_3), 4.34 (4H, q, CH_3CH_2), 5.68 ppm (1H, s, 5-H).

Similar treatment of Ic (20 mmole) in ethanol with sodium ethylate (40 mmole), neutralization with an alcohol solution of HCl, removal of solvent, extraction with ether, and distillation gave methylpropyl ketoxime (0.7 g, 35%) and 2,4-dimethyl-6-ethoxypyrimidine (0.8 g, 27%) which were identical to known samples by PMR spectroscopy and TLC.

LITERATURE CITED

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