

LETTERS TO THE EDITOR

SIMPLE METHOD FOR THE PREPARATION OF Z-(ANTI)-PYRIDINE-2- AND -4-ALDOXIMES

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We have established that the difficult-to-obtain thermodynamically unstable Z isomers of pyridine-2- and pyridine-4-aldoximes (I, II) are primarily formed in the nitrosation of the sodium and potassium derivatives of α - and γ -picolines in liquid ammonia. Only the E isomers were previously obtained by this method [1], and this was evidently due to the severe treatment of the reaction product, during which Z \rightarrow E isomerization occurred.

The reaction mixture obtained in accordance with [1] from α -picoline, sodium, and n-butyl nitrite, was decomposed with water, after which the ammonia was removed, and the residual alkaline solution was washed with ether four times and acidified with glacial acetic acid to pH 9. The bulk of anti-oxime I was removed by filtration. The filtrate was acidified to pH 7, and the mixture of isomers (E/Z ratio 2 : 1) was removed by filtration. This mixture was dissolved in 10% NaOH, the solution was acidified to pH 9 with acetic acid, and an additional amount of anti-oxime I was isolated to give a product with mp 99-101° (from dry ether) in an overall yield of 52%. The reaction mixture obtained similarly from γ -picoline, potassium, and n-butyl nitrite was decomposed with ammonium chloride, after which the ammonia was removed, and the solid product was washed with water 10 times and removed by filtration. The yield of anti-oxime II, with mp 176-178° (from water), was 86%.

The purity and configurational individuality of the products were monitored by means of the PMR spectra (in DMSO); the signals of the methylidyne proton of the oxime group were most characteristic: I 7.59 (Z) and 8.10 (E); II 7.50 (Z) and 8.06 (E) ppm. Prior to recrystallization, the samples of the oximes contained no less than 98% of the Z isomer. According to the results of spectrophotometric analysis based on the formation of a colored I-E complex with Fe^{2+} , the recrystallized I-Z samples contained less than 0.5% I-E impurity.

The melting points were determined with a Boethius apparatus.

LITERATURE CITED

1. E. Forman, J. Org. Chem., 29, 3323 (1964).

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