CONVERSION OF O-VINYL ALKYL ARYL (HETARYL) KETOXIMES TO PYRROLES IN THE KOH—DMSO SYSTEM

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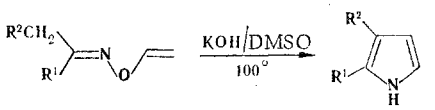
It has been previously shown [1] that O-vinyl derivatives of oximes of aliphatic ketones do not form pyrroles upon thermolysis.

However, we have found that O-vinyl aryl (hetaryl) ketoximes I-IV, which can be obtained in up to 50% yields via the reaction of ketoximes with acetylene, are converted to the corresponding pyrroles V-VIII when they are heated (at ∿100°C) in the KOH—DMSO superbase system for 1.5 h.



I–IV V–VIII

V R^1=Ph, R^2=H; VI R^1=*p*-ClC_6H_4, R^2=H; VII R^1=2-furyl, R^2=H; VIII R^1=2-thienyl, R^2=H

Under similar conditions O-vinyl acetoxime primarily undergoes resinification (2-methylpyrrole is obtained in ∿5% yield). Only traces of 2-phenylpyrrole [thin-layer chromatography (TLC), Silufol UV-254, hexane—ether (3:1)] are formed when KOH—DMSO is absent. At 150°C thermolysis of oxime I goes to completion after 1 h but is accompanied by resinification (a spot of pyrrole V is recorded by TLC).

Thus the superbase-catalyzed rearrangement of O-vinyl oximes may be one of the pathways for the formation of pyrroles in their synthesis from ketoximes and acetylene in the KOH—DMSO system.

Thus 0.17 g (96%) of 2-phenylpyrrole (V) was obtained by heating 0.2 g (0.8 mmole) of oxime I and 0.03 g of KOH in 2 ml of DMSO at 95°C for 80 min.

Pyrroles VI-VIII were similarly obtained in 87, 60, and 50% yields, respectively.

The results of elementary analysis for C, H, N, and Cl in the case of pyrrole VI were in agreement with the calculated values, and the IR and PMR spectra confirmed its structure.

LITERATURE CITED

1. B. A. Trofimov, A. I. Mikhaleva, A. N. Vasil'ev, and M. V. Sigalov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 3, 695 (1979).

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