FORMATION OF 3-ETHYLPYRROLES IN THE SYNTHESIS OF 3H-PYRROLES FROM ISOPROPYL KETOXIMES IN THE TROFIMOV REACTION

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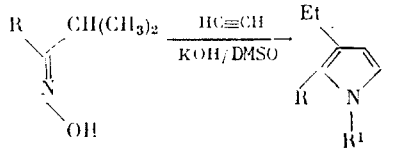
The condensation of isopropyl phenyl ketoxime (Ia), isopropyl 2-thienyl ketoxime (Ib), and isopropyl methyl ketoxime (Ic), which do not contain traces of n-propyl ketoximes as indicated by gas-liquid chromatography, with acetylene at 10-12 atm and atmospheric pressure in KOH/DMSO at 90-100°C proceeds through a previously unreported pathway, leading to 2-phenyl- (IIa), 2-(2-thienyl)- (IIb), and 2-methyl-3-ethylpyrroles (IIc) (1-2%) and their N-vinyl derivatives (IIIa)-(IIIc) (5-8%) in addition to the ordinary reaction products, namely, O-vinylketoximes, hydroxypyrrolines [1], identified in the reaction mixture by gas-liquid chromatography, and 3H-pyrroles (40% [2]).

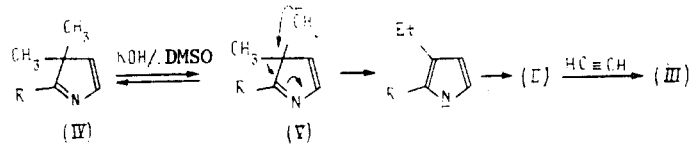


(Ia — c) (IIa — c), (IIIa — c)

R = Ph (Ia): R^1 = H (IIa), CH = CH_2 (IIIa); R = 2-thienyl (Ib); R^1 = H (IIb), CH=CH_2 (IIIb); R = CH_3 (Ic); R^1 = H (IIc); CH=CH_2 (IIIc)

Pyrroles (IIa)-(IIc) and vinylpyrroles (IIIa)-(IIIc) were isolated from the reaction mixture obtained after its treatment with water, extraction with ether, drying over potassium carbonate, removal of the solvent, and fractionation by thin-layer chromatography on unattached neutral alumina using 3:1 hexane–ether as the eluent and identified by gas-liquid chromatography by comparison with authentic samples obtained in the reaction of n-propyl phenyl ketoxime, n-propyl 2-thienyl ketoxime, and n-propyl methyl ketoxime with acetylene. The physical indices of (IIa)-(IIc) and (IIIa)-(IIIc) correspond to previous data [3].

The observed rearrangement apparently proceeds in carbanion (V) formed as a result of the deprotonation of the corresponding 3H-pyrrole (IV) by the action of a superbase.



(IV) (V)

The driving force should be the significant difference in the energies between the nonaromatic system in (IV) and aromatic systems in (II) and (III).

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3. B. A. Trofimov and A. I. Mikhaleva, N-Vinylpyrroles, Nauka, Novosibirsk (1984).

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