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Taking as an example the reaction of isopropyl phenyl ketoxime (I) with acetylene in the system KOH-DMSO, we have found that ketoximes which have only one 'aliphatic' hydrogen atom in the α -position to the oxime function can be used as starting materials for the synthesis of the difficultly-accessible 3H-pyrroles.

Since the corresponding 2-hydroxypyrrole (IV) (the rearrangement product of the 0-vinyl oxime (III) [1] is converted under the reaction conditions into the 3H-pyrrole (II), this finding may be regarded as confirming one of the mechanisms proposed previously for a new synthesis of pyrroles [2, 3] in which 0-vinyloximes undergo rearrangement.

The oxime (I) (4.08 g), 1.4 g of KOH, and 60 ml of DMSO, were mixed, and acetylene passed into the mixture with stirring at 70°C for 5 h. Treatment with water, extraction with ether, and chromatography (alumina, hexane—ether, 2:1) gave 0.4 g (9%) of 3,3-dimethyl-2-phenyl-3H-pyrrole (II), d_4^{20} 1.0290, np^{20} 1.5648. IR spectrum (film): 1370, 1387 (gem-dimethyl group), 2880, 2930, 2970 (CH₃), 1510, 1570 (Ph), 3030, 3070, 3085 (ring CH), 1675 cm⁻¹ (C=N), no OH absorption in the region 3200-3600 cm⁻¹. PMR spectrum (acetone-D₆): 1.39 (6H, 2CH₃), s), 6.30, 7.00 (2H, -CH=CH, d.d, $^3J_{4.5}$ = 3.2 Hz), 7.39-7.48, 8.04-8.09 ppm (5H, Ph, m). Mass spectrum: M⁺ 171. The elemental analyses agreed with the calculated values.

3H-Pyrroles function as intermediates if only one hydrogen atom is present in the 3-po-sition

The hydroxypyrrole (IV) (1.19 g), 0.35 g of KOH, and 15 ml of DMSO were stirred and heated at 70° C for 5 h while passing in acetylene. GLC showed the presence of the 3-H-pyrrole (II).

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