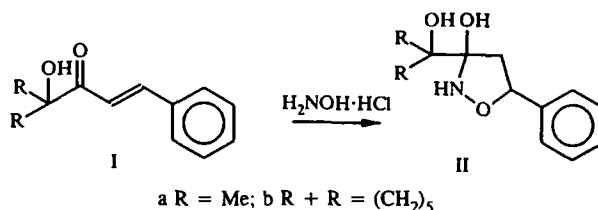


FORMATION OF A 5-MEMBER SATURATED HETEROCYCLE IN OXIMATION OF ARYLIDENE KETONES

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The reaction of α,β -unsaturated carbonyl compounds with nitrogen-containing nucleophiles yields different products of heterocyclization [1]. We found that the reaction of arylideneketones (Ia, b) with hydroxylamine in water-methanol medium (in the presence of NaOH) unexpectedly does not yield the corresponding isoxazolines but instead 3-hydroxyisoxazolidines IIa, b, whose structure follows from the data from elemental analysis, IR, PMR, and mass spectrometry.



The mass spectrum contains the peaks of a molecular ion M^+ (1-2%) and the peaks of ions characterizing fragmentation of M^+ . There are no absorption bands of the C=N group in the 1610-1670 cm^{-1} region in the IR spectrum; OH and NH groups appear in the form of a broad band at 3100-3400 cm^{-1} . There is a double set of signals ABX of protons of a 5-member ring in the PMR spectra, indicating that it is a mixture of diastereomers. Products II are probably formed through the stage of addition of the H_2NO^- nucleophile at the double bond of ketone I and subsequent conversion into a hydroxyisoxazolidine ring. The hypothetical direction of the reaction is in agreement with the published data on the participation of hydroxylamine as an O-nucleophile [2].

Arylideneketones Ia, b were obtained by the method in [3].

3-Hydroxy-3-(2-hydroxypropyl-2)-5-phenylisoxazolidine (IIa). Yield of 42%; mp = 131-132°C (butyl acetate). IR spectrum (KBr): 3220. PMR spectrum (CDCl_3): 1.29; 1.48 and 1.56 (6H, three s, CH_3); 2.32 and 2.71 (2H, two q, CH_2); 4.48 and 4.73 (1H, two t, CHO); 7.39 ppm (5H, m, C_6H_5). Mass spectrum, m/z (%): 223 (1), 192 (9), 131 (17), 105 (24), 59 (100). Found, %: C 64.22; H 7.79; N 6.41. $\text{C}_{12}\text{H}_{17}\text{NO}_3$. Calculated, %: C 64.55; H 7.69; N 6.27.

3-Hydroxy-3-(1-hydroxycyclohexyl-1)-5-phenylisoxazolidine (IIb). Yield of 47%; mp = 146-147°C (butyl acetate). IR spectrum (KBr): 3210. PMR spectrum ($\text{CDCl}_3 - \text{CD}_3\text{OD}$, 1:1): 1.1-1.5 (10H, m, CH_2); 1.76, 2.12, and 2.53 (2H, q m and q, CH_2); 3.92 and 4.23 (1H, two t, CHO); 6.98 ppm (5H, m, C_6H_5). Mass spectrum, m/z (%): 263 (1), 231 (6), 146 (21), 105 (21), 99 (98), 81 (100). Found, %: C 68.21; H 7.78; N 5.44. $\text{C}_{15}\text{H}_{21}\text{NO}_3$. Calculated, %: C 68.41; H 8.04; N 5.32.

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