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5-HYDRAZINO-2-ISOXAZOLINES

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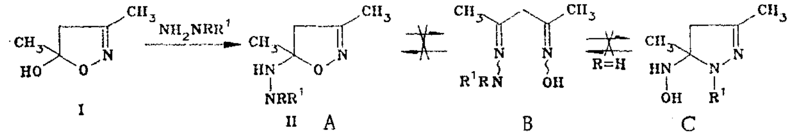
In view of the high and varied biological activity of many isoxazole derivatives [1], to find new methods for their synthesis is becoming timeyl. We have established that a simple method of obtaining some 5-hydrazino-2-isoxazolines IIa-c is the reaction of the readily available 5-hydroxy-3,5-dimethyl-2-isoxazolines I [2] with the respectivey hydrazines.



II a R=H, R^1=COC$_6$H$_5$; b R=H, R^1=COC$_6$H$_4$NO$_2$-*p*; c R=R^1=CH$_3$

According to ^{1}H and ^{13}C NMR data, the compounds IIa-c have the cyclic structure A, and show no tendency to go over in various solvents to the linear form B. Incidentally the hydrazinooximes of 1,3-dioxo compounds are unknown.

With IIa,b the theoretical possibility of formation of a pyrazoline ring C must also be considered. But this variant must be excluded because in the ^{13}C NMR spectra, the C$_{(5)}$ atom of tautomer C ought to be located in the 80-90 ppm range [3]. In the case of IIc, however, which is incapable of such a transition, the C$_{(5)}$ signal appears at a weaker field (98.9 ppm). The value for the C$_{(5)}$ signal in IIa, viz., 100.2 ppm, is also evidence that it is located in a N,O-, and not a N,N environment. An attempt to synthesize a type C compound by another route, by the reaction of hydroxylamine and 1-benzoyl-5-hydroxy-3,5-dimethyl-2-pyrazoline [4] yielded benzhydrazide and a mixture of I with acetylacetone dioxime.

II was synthesized by boiling equimolar amounts of the reagents in benzene solution in the presence of KU-2 carion exchanger in the H$^+$ form. The elemental compositions of IIa-c agree with those calculated.

IIa: yield 72%, mp 107-108° (from hexane—ethyl acetate mixture). PMR spectrum (DMFA-D$_7$): 1.69 (s, 3H), and 2.01 (t, 3H, J = 1.0 Hz) — 2 CH$_3$ groups; 2.99 and 3.21 (2H, J$_{AB}$ = 18.0, J = 1.0 Hz, 4-H); 5.85 (d, 1H, J = 6.0 Hz, NH); 7.53-8.0 (m, 5H, H$_{arom}$); 9.85 ppm (d, 1H, J = 6.0 Hz, NHCO). ^{13}C NMR spectrum (CDCl$_3$): 13.6 J$_{CH}$ = 129.0 Hz) and 23.6 (J$_{CH}$ = 129.0, J$_{CCCH}$ = 4.0 Hz) — 2 CH$_3$ groups; 47.0 (J$_{CH}$ = 136.0, J$_{CCCH}$ = 4.0 Hz, C$_{(4)}$); 100.2 (C$_{(5)}$); 158.3 (J$_{CCH}$ = 4.5 Hz, C$_{(3)}$); 170.2 (J$_{CCH}$ = 6.8 Hz, C=O); 128.7-134.6 ppm (C$_{arom}$).

IIb: yield 62%, mp 153-155° (from toluene). PMR spectrum (DMFA-D$_7$): 1.50 (s, 3H) and 1.83 (t, 3H, J = 1.0 Hz) — 2 CH$_3$ groups; 2.92 and 3.10 (2H, J$_{AB}$ = 18.0, J = 1.0 Hz, 4-H); 5.93 (d, 1H, J = 5.0 Hz, NH); 8.07 (d, 2H, J = 9.0 Hz) and 8.31 (d, 2H, J = 9.0 Hz, H$_{arom}$) 10.13 ppm (d, 1H, J = 5.0 Hz, NHCO).

IIc: yield 85%, mp 48-49° (from hexane—ethyl acetate mixture). PMR spectrum (DMFA-D$_7$): 1.44 (s, 3H), and 1.92 (t, 3H, J = 1.0 Hz) — 2 CH$_3$ groups; 2.46 (s, (CH$_3$)$_2$N); 2.72 and 3.00 (2H, J$_{AB}$ = 16.0, J = 1.0 Hz, 4-H); 3.94 ppm (br. s, 1H, NH). ^{13}C NMR spectrum (CD$_3$OD): 13.1 (J$_{CH}$ = 129.0 Hz) and 24.1 (J$_{CH}$ = 129.0, J$_{CCCH}$ = 4.5 Hz) — 2 CH$_3$ groups; 45.3 (J$_{CH}$ = 135.0, J$_{CCCH}$ = 3.0 Hz, C$_{(4)}$); 49.5 (J$_{CH}$ = 132.0, J$_{CCCH}$ = 4.5 Hz, (CH$_3$)$_2$N); 98.9 (J$_{CCH}$ = 3.0 Hz, C$_{(5)}$, 154.9 ppm (J$_{CCH}$ = 6.5 Hz, C$_{(3)}$).

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