PROTOTROPIC ISOMERIZATION INDUCED BY LANTHANIDE SHIFT REAGENTS IN THE PYRAZOLINE SERIES

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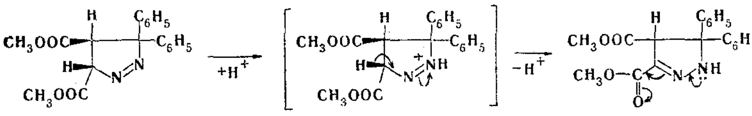
We have realized the prototropic isomerization of trans-3,4-di(methoxycarbonyl)-5,5-diphenyl-1-pyrazoline (I) to the corresponding 2-pyrazoline (II) by means of tris[1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionato]europium(III) [Eu(FOD)$_3$]. The reaction proceeds in the same way as that effected by a strong protic acid.



I

II

1-Pyrazoline I was obtained in 70% yield by the action of diphenyldiazomethane on dimethyl maleate in absolute ether (in the absence of traces of acid, for otherwise 2-pyrazoline II is formed immediately (see [1]); the product had mp 130°. PMR spectrum (with respect to tetramethylsilane in CDCl$_3$): 3.97 (3-CH$_3$), 3.16 (4-CH$_3$), 4.29 (d, $J_{3,4}$=7.3 Hz, 3-H) and 5.19 (d, 4-H). After the addition of 5-6 mg of Eu(FOD)$_3$ or CF$_3$COOH to a solution of 20 mg of pyrazoline I in 0.5 ml of CDCl$_3$ the signals of its protons begin to vanish, and the peaks of pyrazoline II appear simultaneously. PMR spectrum [the specific shifts induced by Eu(FOD)$_3$ are given in parentheses]: 7.20 (8.45) [1-H], 3.95 (7.73) [3-CH$_3$], 3.26 (2.83 [4-CH$_3$], 4.96 [14.47) [4-H], 7.35 (3.10) and 7.40 (2.63 [o-H], 7.35 (0.40) and 7.40 ppm (0.40) [m- and p-H]. The isomerization of pyrazoline I is complete after 5-10 min and proceeds quantitatively. With Eu(DPM)$_3$ the reaction takes place only when the mixture is heated to 50-60°C. When a mixture of 3 g of pyrazoline I, 10 ml of methanol, and 0.5 ml of CF$_3$COOH is refluxed (1 h), individual pyrazoline II precipitates as prisms with mp 144° (dec.) [1] when the mixture is cooled.

We assume that the addition of both the proton and the europium reagent takes place at the N$_{(1)}$ atom and is accompanied by detachment of the 3-H proton, which subsequently also participates in the catalysis. It is characteristic that the peaks of 1-pyrazoline I undergo almost no change in position after the addition of Eu(FOD)$_3$ of Eu(DPM)$_3$, whereas considerable lanthanide shifts are observed in the spectrum of 2-pyrazoline II. We explain the low affinity of 1-pyrazoline for the europium reagent by steric hindrance in the vicinity of the nitrogen atoms. On the other hand, in the case of 2-pyrazoline one of the carbonyl groups becomes more basic because of conjugation with the N$_{(1)}$ atom and may serve as a convenient coordination center for the addition of europium.

Satisfactory analysis for C, H, and N were obtained for I.

LITERATURE CITED

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