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INTRAMOLECULAR HYDROGEN BONDS IN 1-VINYL-5-PYRAZOLE CARBOXYLATE ESTERS

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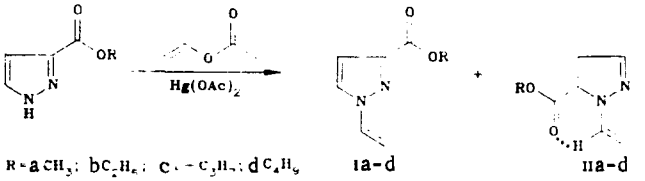
The presence of an intramolecular CH—N hydrogen bond has recently [1] been demonstrated in 2-vinylhydroxy(vinylthio)pyridine and -quinoline. We have discovered a similar interaction in 1-vinyl-5-pyrazole carboxylate esters II.

N-Vinylation of 3(5)-pyrazole carboxylate esters with vinyl acetate using mercuric acetate catalyst led to a mixture of the isomeric 1-vinyl-3- and -5-pyrazole carvoxylates I and II in 88-92% yield which were separated by straight distillation.



R = a CH_3; b C_2H_5; c C_3H_7; d C_4H_9 Ia-d IIa-d

According to PMR spectroscopy (CCl_4, internal standard HMDS) II have intermolecular hydrogen bonds between the vinyl α-proton and the carbonyl oxygen p-electrons (CH—O=C) resulting in a low field shift of the α-proton to 7.98, 8.03, 7.97, and 8.03 ppm (corresponding to the above named R substituents). Because deshielding of the α-proton by the carbonyl is impossible for steric reasons in the isomers I the chemical shift value is at higher field in a narrow range 7.10-7.20 ppm.

The boiling points (1 mm) of the synthesized compounds were: Ia 85; Ib 108; Ic 85; Id 124; IIa 54; IIb 75; IIc 69; IId 85°C. Elemental analysis for nitrogen agreed with that calculated.

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