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INFLUENCE OF THE HYDROGEN FLUORIDE-PYRIDINE MOLAR RATIO ON THE REGIO- AND STEREO-SELECTIVITY IN SEVERAL FLUORINATION REACTIONS

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We used the hydrogen fluoride-pyridine mixture of different molar ratio as a solvent for different fluorination reactions:

(i) bromofluorination of unsubstituted and substituted ethyl cinnamates $ZC_6H_4C(2)X{=}C(1)HCO_2Et$ with N-bromosuccinimide;

(ii) fluorodeamination of α-amino-esters $RR'C(2)HC(1)H(NH_2)CO_2Et$ with sodium nitrite;

(iii) fluorodehydroxylation of alkyl-phenyl carbinols Ph C(2)H(OH)C(1)HRR'.

The regiochemistry and the stereochemistry of the reaction products were unambiguously established by ^{13}C and ^{19}F NMR spectroscopy.

The influence of the HF:pyridine molar ratio on the regio- and stereo-selectivity can be described as the influence of solvation by the solvent mixture of the cationic intermediates in the reactions (bridged or open-chain carbenium ions): hindrance to free rotation of the C(1)C(2) bond in the carbenium ion, mono or bifacial attack of this ion or rearrangement of the carbenium ion (positive charge on carbon C(1) or C(2). The importance of this solvation is depending on the HF:pyridine molar ratio and on the nature of the substituents (Z, X, R or R').