Reactions of Aryl Acetates with Secondary Alicyclic Amines in Ethanol/Water Mixtures: Effect of the Solvent Composition on the Kinetics and Mechanism

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Resumen

We report a kinetic study on the reactions of secondary alicyclic amines toward 4-nitrophenyl, 2,4-dinitrophenyl, and 2,4,6-trinitrophenyl acetates (1, 2, and 3) in ethanol/water mixtures of different compositions. It is found that (i) the intermediate in the reaction of 1 is stabilized in a mixture of 90 vol% ethanol; (ii) for the reaction of 2, the mechanism is stepwise in water but concerted in the mixtures; (iii) For the reaction of 3, the mechanism is concerted along the whole range of composition; (iv) the effect of -NO(2) outweighs the solvent effect; (v) preferential solvation in the core of reaction can be ruled out. (C) 2011 Wiley Periodicals, Inc. Int J Chem Kinet 43: 687-693, 2011

Palabras clave

KeyWords Plus: STRUCTURE-REACTIVITY CORRELATIONS; X-SUBSTITUTED BENZOATES; 2,4,6-TRINITROPHENYL METHYL CARBONATE; RATE-DETERMINING STEP; AQUEOUS-ETHANOL; 2,4-DINITROPHENYL ACETATE; ESTER AMINOLYSIS; PHENYL CARBONATE; NONLEAVING GROUP; PYRIDINOLYSIS