Synthetic Applications and Mechanistic Studies of the Hydroxide-Mediated Cleavage of Carbon-Carbon Bonds in Ketones

The hydroxide-mediated cleavage of ketones into alkanes and carboxylic acids has been reinvestigated and the substrate scope extended to benzyl carbonyl compounds. The transformation is performed with a 0.05 M ketone solution in refluxing xylene in the presence of 10 equiv of potassium hydroxide. The reaction constitutes a straightforward protocol for the synthesis of certain phenyl-substituted carboxylic acids from 2-phenylcycloalkanones. The mechanism was investigated by kinetic experiments which indicated a first order reaction in hydroxide and a full negative charge in the rate-determining step. The studies were complemented by a theoretical investigation where two possible pathways were characterized by DFT/M06-2X. The calculations showed that the scission takes place by nucleophilic attack of hydroxide on the ketone followed by fragmentation of the resulting oxyanion into the carboxylic acid and a benzyl anion.

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