The kinetics of sequential addition of a distinct Grignard species onto a lactone is studied by flow chemistry. The experimental data are shown to be consistent with a kinetic model based on four reaction steps, reaction of ester to magnesium hemiacetal, rearrangement to ketone (forward and backward) and reaction of ketone to tertiary alcohol upon quenching. The experimental derived reaction mechanism is supported by ab initio molecular computations, and the predicted activation energy is in good agreement with the experimental observations. The Grignard reaction follows a substrate-independent, reductive [2+2] cycloaddition of the Meisenheimer/Casper type. Moreover, the rearrangement equilibrium between magnesium hemiacetal and ketone is characterized and found to be feasible. Monoaddition of the ester carbonyl group is demonstrated for fluorophenyl magnesium bromide, but at reaction conditions at -40 °C with several hours of residence time. Working under cryogenic temperature conditions is essential to realizing monoaddition of the ester carbonyl group with Grignard reagents.