

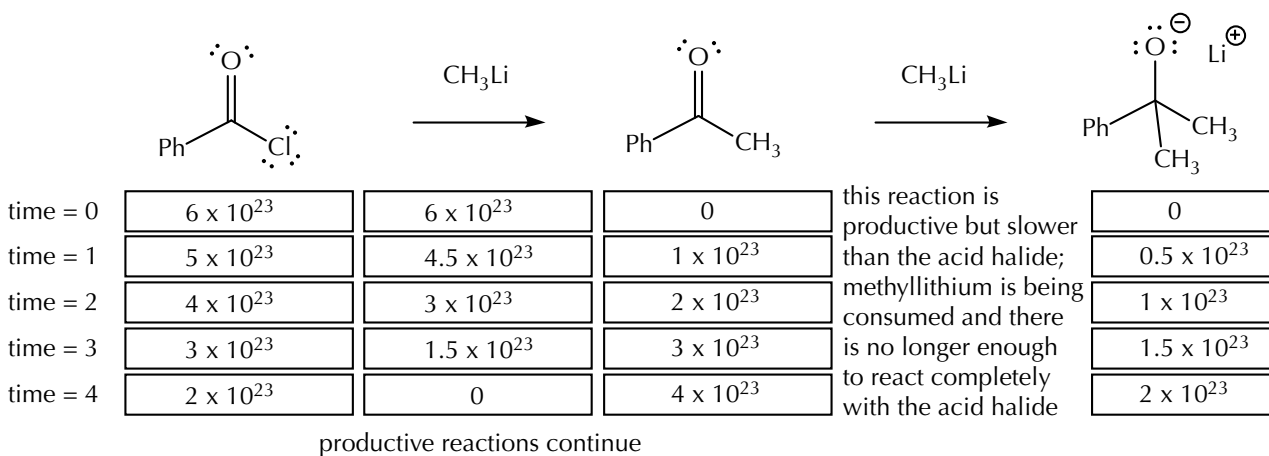
As soon as the ester forms, it begins to compete with the acid halide for the methoxide nucleophile, but the concentration of the nucleophile does not change. Every time the ester reacts with methoxide, a methoxide is released, so this transesterification can continue to run in the background, and it does not affect the intended acylation reaction with the acid halide.

If the product of a reaction continues to react with the same reagent as the starting material, then the relative reactivities of the starting material and the product dictate the observed outcome.

Instead of sodium methoxide, what if the reagent in the previous example was methyllithium? Start with 6×10^{23} molecules of each one and then look at what happens (Figure 1353).

Figure 1353

Productive reactions consume the nucleophile: Second reaction is slower.



As the first ketone molecules are formed, they are now competing for the methyllithium. And even though the reaction between the acid halide and methyllithium is faster than the reaction of the ketone with methyllithium, it is not fast enough to stop the ketone from irreversibly removing some of organometallic reagent from the reaction mixture. In this model of the reactivity, when the methyllithium has been consumed, the ketone will be the major product. There will be unreacted acid halide and an equivalent amount of the tertiary alkoxide.

If the starting material was an ester rather than an acid halide, the second reaction (addition of methyllithium to the ketone) would be substantially faster than the first reaction (acylation of methyllithium) because the electron delocalization provided by the oxygen atom reduces the electrophilicity of the carbonyl carbon of the ester (Figure 1354).

Figure 1354

Productive reactions consume the nucleophile: Second reaction is faster.

