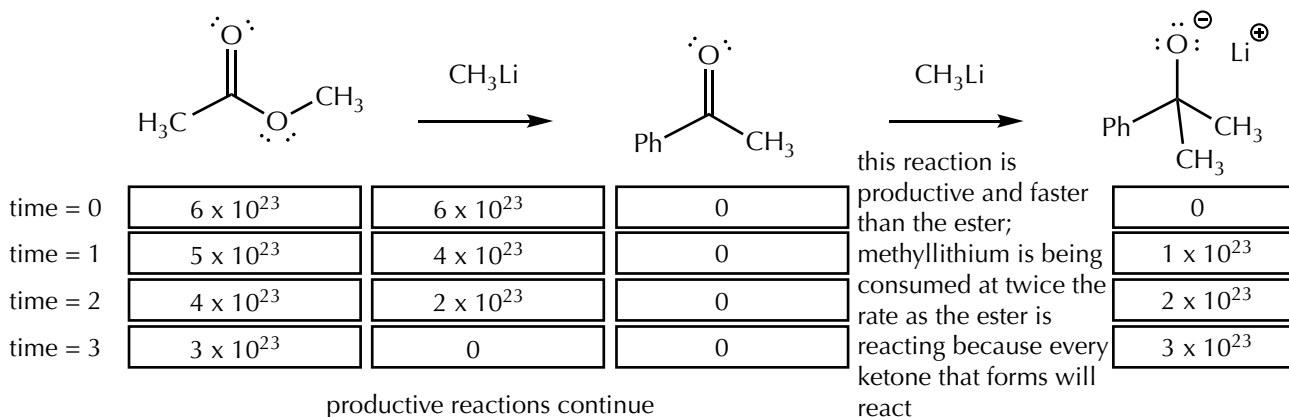
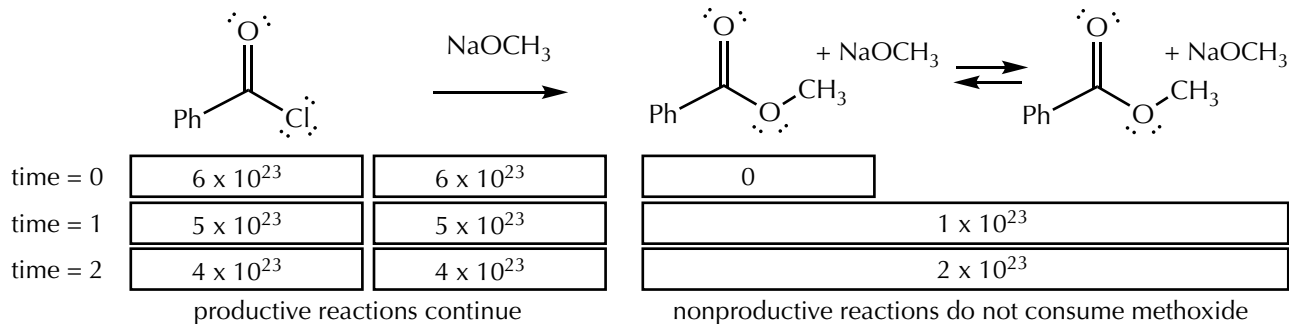


Problem of the Day 16  
 CH 13  
 Question 1352 & 1354

Do not be distracted by the quantitative information used to illustrate the difference between heteroatom and organometallic nucleophiles. Be sure to be able to explain the difference in what is happening in a real solution of molecules as the first acylation products form and why



Reactions take place using incredibly large numbers of molecules, and they do not all react at the same moment. When a typical reaction takes place ( $A + B \rightarrow C$ ), product C forms in the presence of both A and B.

Product C could have one of three properties:

- (a) is it inert, and does not itself react with either A or B
- (b) it reacts with A and/or B, but it reacts quite slowly than with them
- (c) it reacts with A and/or B, and it reacts more quickly than with them

In the top reaction, A (the acid halide) reacts with B (methoxide) to give C (the ester). The ester (C) can react with methoxide (B), too, as it is after all an acylating agent. But here, when C (the ester) reacts with methoxide (B), it simply makes another molecule of C!  $C + B \rightarrow C$ , and you can never really detect that this reversible process is taking place

In the lower reaction, the ester (A') reacts with methyllithium (B') to give C' (a ketone). The ketone (C') as it forms, is significantly more reactive than the ester (A'), so as the ketone (C') forms, it reacts immediately with methyllithium (B') and a new compound, a 3° alcohol (D). The concentration of the ketone never builds up because it reacts faster than the ester. If only 1 equivalent of the methyllithium is used, 50% of the ester will remain unreacted because each ester consumes two methyllithiums on the way to form D.