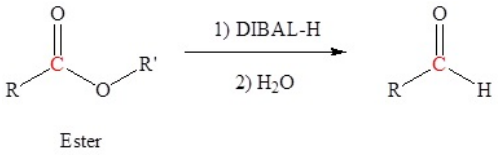
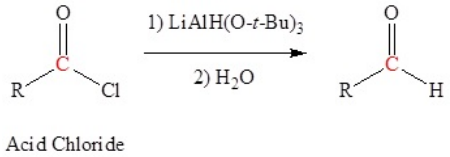
19.4: 19.4 NEW SYNTHESIS OF ALDEHYDES AND KETONES

ESTER, ACID CHLORIDE, AND NITRILE REDUCTION TO FORM ALDEHYDES

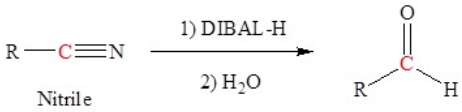
The reduction of esters, acid chlorides, and nitriles require reducing agents that are derivatives of lithium aluminum hydride ($LiAlH_4$). For esters and nitriles, $LiAlH_4$ is modified into the organometallic reagent diisobutyl aluminum hydride which can be represented as DIBAL or DIBAL-H or DIBAH or DIBALH. To reduce acid chlorides, t-butoxide groups are combined with $LiAlH_4$ to form lithium tritert-butoxy aluminum hydride.



Ester



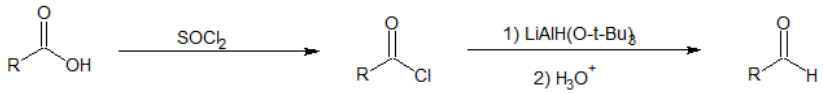
Acid Chloride



Nitrile

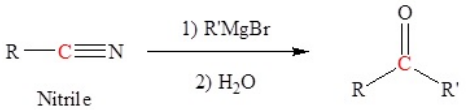
CARBOXYLIC ACIDS CAN BE CONVERTED TO ALDEHYDES

Carboxylic acids cannot be reduced directly to aldehydes. Carboxylic acids can be converted to acid chlorides using thionyl chloride which can then be reduced to aldehydes using LiAlH(O-t-Bu)$_3$.



GRIGNARD REAGENTS REACT WITH NITRILES TO FORM KETONES

Nitriles can also be used to synthesize ketones when they react with Grignards as shown below.

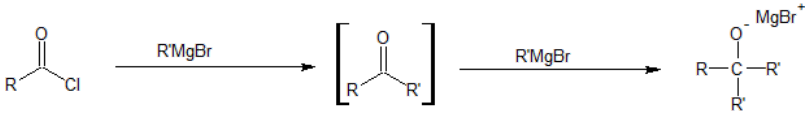


Nitrile

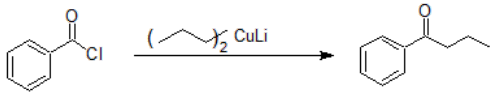
ORGANOCUPRATE REAGENTS REACT WITH ACID CHLORIDES TO FORM KETONES

Organocuprate reagents are the least reactive of the organometallic reagents studied so far. While we learned to synthesize alcohols by reacting Grignard reagents with aldehydes and ketones, organocuprates will not react with aldehydes and ketones.

Grignard reagents will keep reacting with the product of the acid chloride reaction.

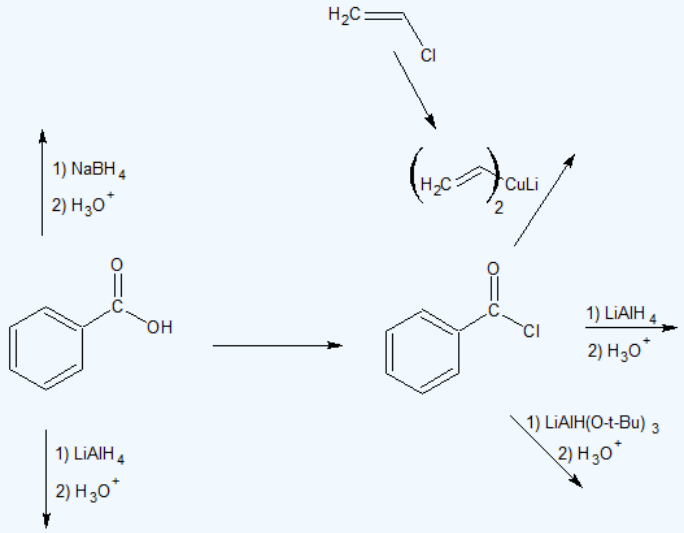


Organocuprate reactions with acid chlorides stop at the ketone as shown below.



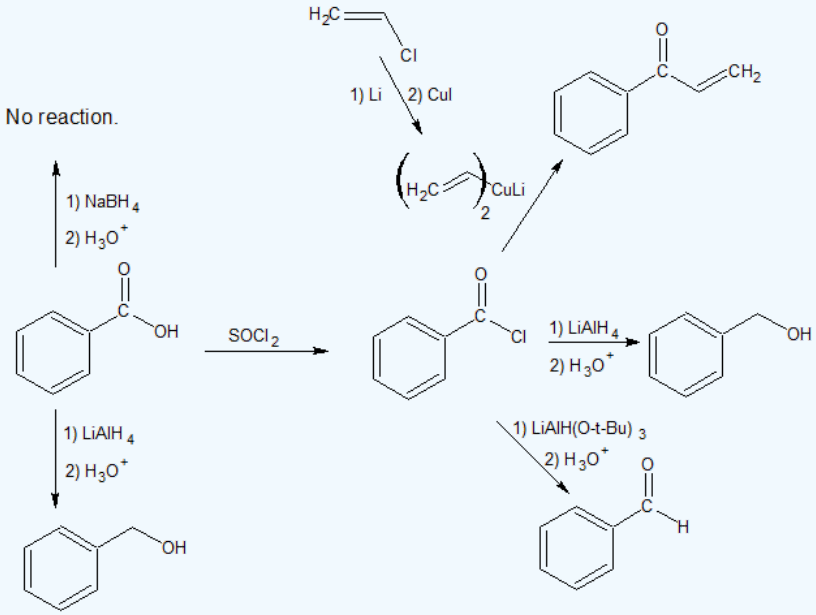
Exercise

3. Complete the reaction map below.



Answer

3.



CONTRIBUTORS AND ATTRIBUTIONS