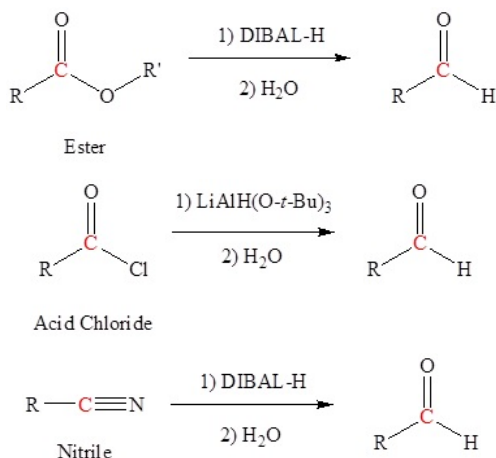


19.4: 19.4 NEW SYNTHESIS OF ALDEHYDES AND KETONES

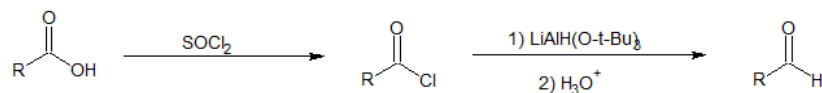
ESTER, ACID CHLORIDE, AND NITRILE REDUCTION TO FORM ALDEHYDES

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-butoxy groups are combined with LiAlH_4 to form lithium tritert-butoxy aluminum hydride.



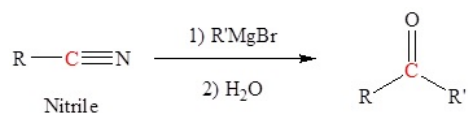
CARBOXYLIC ACIDS CAN BE CONVERTED TO ALDEHYDES

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 $\text{LiAlH}(\text{O}-t\text{-Bu})_3$.



GRIGNARD REAGENTS REACT WITH NITRILES TO FORM KETONES

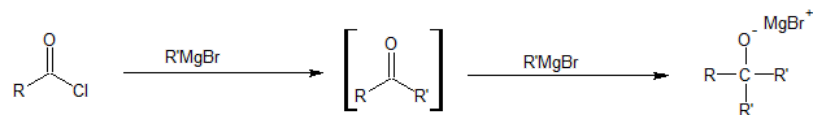
Nitriles can also be used to synthesize ketones when they react with Grignards as shown below.



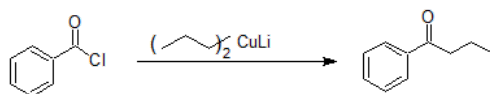
ORGANOCUPRATE REAGENTS REACT WITH ACID CHLORIDES TO FORM KETONES

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.



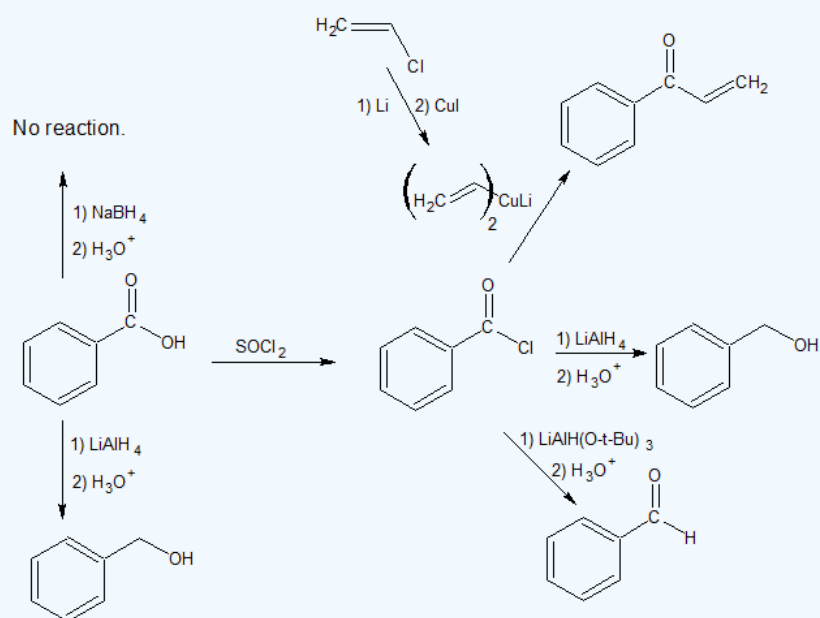
Reaction scheme for the synthesis of 1-phenylethanol from benzoic acid:

Benzoic acid (c1ccccc1C(=O)O) can be reduced to 1-phenylethanol (c1ccccc1C(O)C) via two main pathways:

- Left Pathway:** Direct reduction using $1) \text{NaBH}_4$ followed by $2) \text{H}_3\text{O}^+$.
- Right Pathway:** Conversion of benzoic acid to benzoyl chloride (c1ccccc1C(=O)Cl) followed by reduction.
 - Option 1: $1) \text{LiAlH}_4$ followed by $2) \text{H}_3\text{O}^+$.
 - Option 2: $1) \text{LiAlH}(\text{O}-t\text{-Bu})_3$ followed by $2) \text{H}_3\text{O}^+$.

A side reaction is also shown: Vinyl chloride (H2C=CHCl) reacts with a lithium dialkylcuprate ($(\text{H}_2\text{C}=\text{CH})_2\text{CuLi}$) to form a vinyl lithium species ($\text{H}_2\text{C}=\text{CHLi}$).

3.



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