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ORGANIC CHEMISTRY 2 LECTURE GUIDE 2019

BY RHETT C. SMITH, PH.D.

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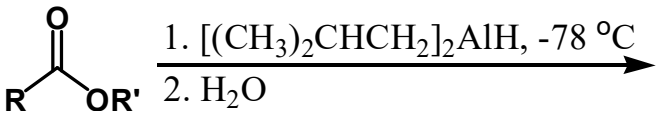
Lesson VI.13. Reaction of Carboxylic Acid Derivatives with H or C Nucleophiles

DIBALH makes aldehydes from esters

Recall when we examined the hydride sources to be used in this chapter, we noted that DIBALH is the least reactive of the hydride sources under discussion. In fact, if we use DIBALH as the hydride source and keep the temperature low (typically –78 °C, we are able to stop the reduction of an ester at the aldehyde:



A

This is an important reaction for preparing aldehydes.

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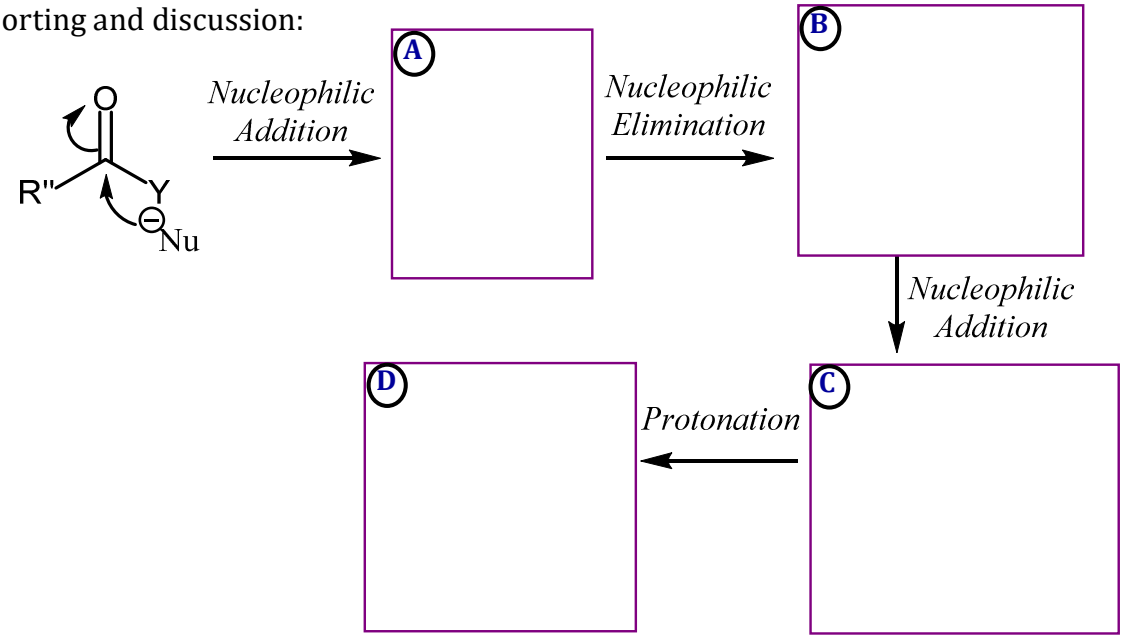
Lesson VI.13. Reaction of Carboxylic Acid Derivatives with H or C Nucleophiles

Carbonyl reaction Type C is Type B followed by Type A

Some carbonyls undergo reaction that is essentially reaction Type B (S_NAc) followed by reaction Type A (nucleophilic addition then protonation). In this Lecture Guide, we will refer to these reactions as **Type C** for the purpose of sorting and discussion:



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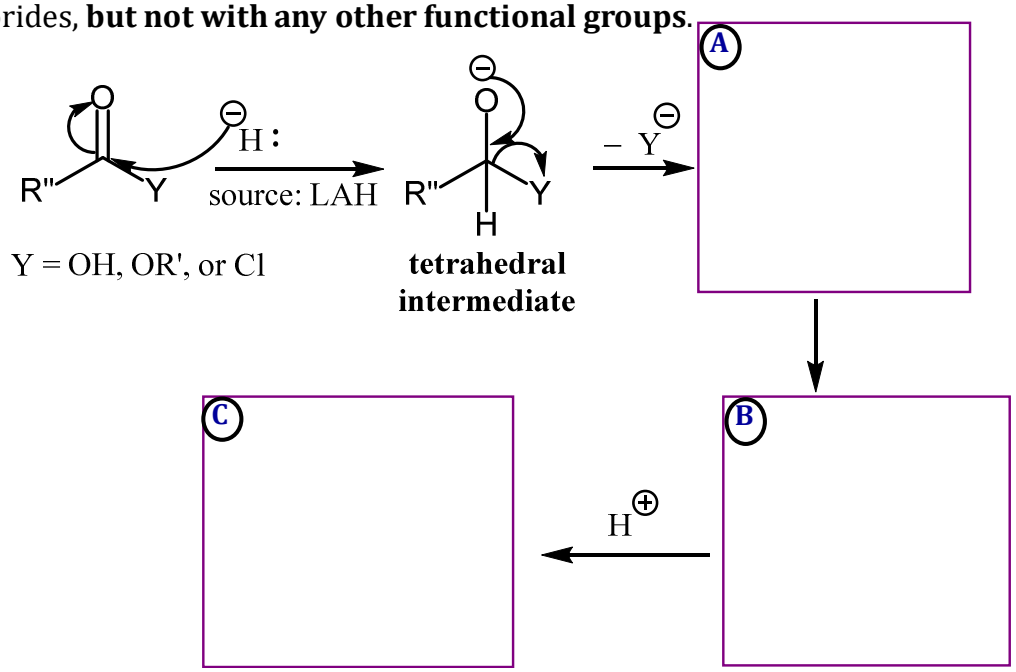
Lesson VI.13. Reaction of Carboxylic Acid Derivatives with H or C Nucleophiles

Metal hydrides with carboxylic acids, esters and acid chlorides

Type C reactions occur between $LiAlH_4$ and either carboxylic acids, esters, or acid chlorides to give 1° alcohols. $NaBH_4$ can also facilitate this reaction with acid chlorides, **but not with any other functional groups**.



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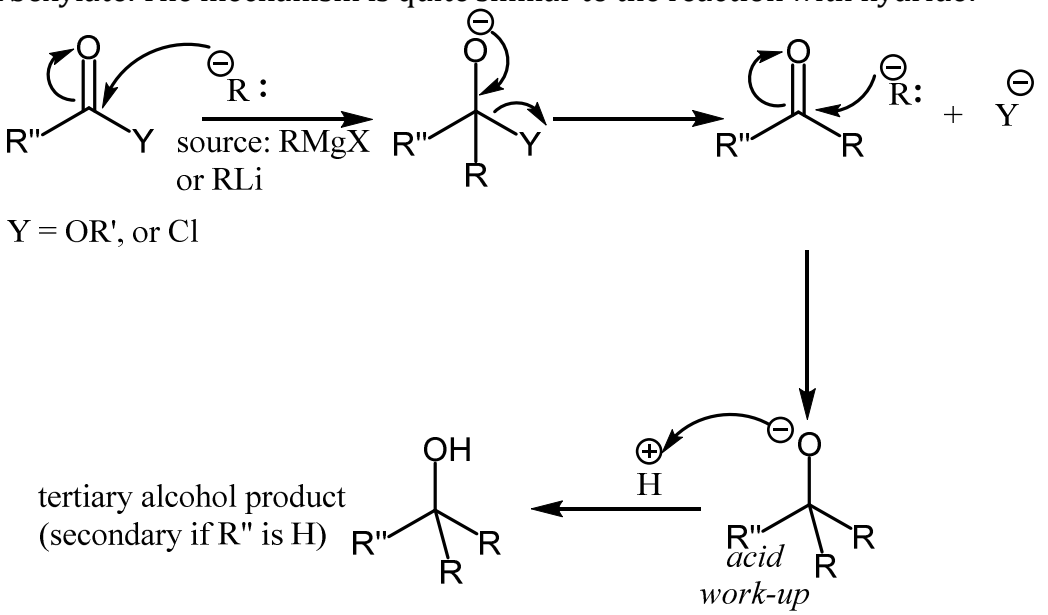
Lesson VI.13. Reaction of Carboxylic Acid Derivatives with H or C Nucleophiles

Organometallics with carboxylic acids, esters and acid chlorides

Type C reactions occur between LiR or RMgX and either esters, or acid chlorides to give alcohols as well. LiR can also facilitate this reaction with carboxylic acids, but Grignard reagents will only deprotonating carboxylic acids to make the carboxylate. The mechanism is quite similar to the reaction with hydride:



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