

Organic Chemistry

2th Edition

Paula Yurkanis Bruice

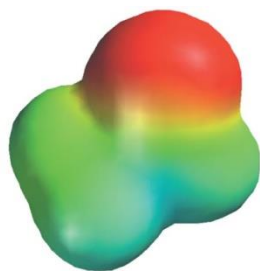
Chapter 12

Carbonyl Compounds II

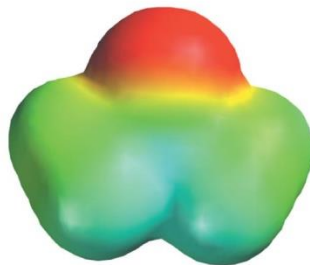
Reactions of Aldehydes and Ketones



formaldehyde

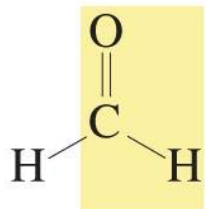


acetaldehyde



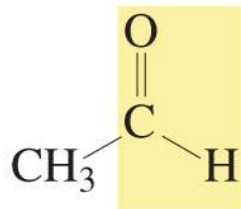
acetone

Nomenclature of Aldehydes

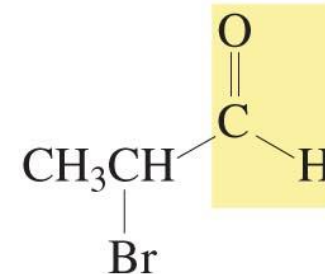


systematic name:
common name:

methanal
formaldehyde

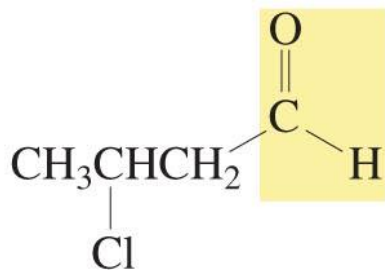


ethanal
acetaldehyde

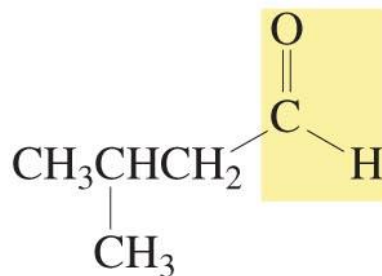


2-bromopropanal
 α -bromopropionaldehyde

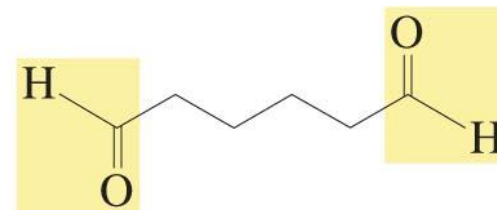
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systematic name: **3-chlorobutanal**
common name: **β -chlorobutyraldehyde**



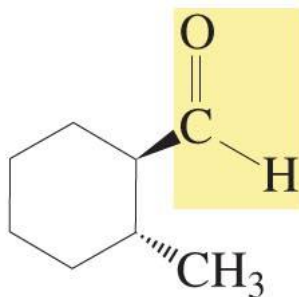
3-methylbutanal
isovaleraldehyde



hexanedial

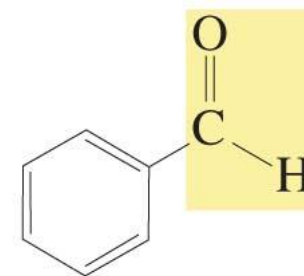
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If the aldehyde group is attached to a ring,



systematic name: *trans*-2-methylcyclohexanecarbaldehyde

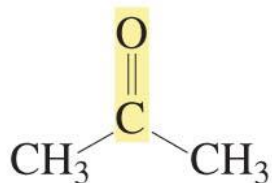
common name:



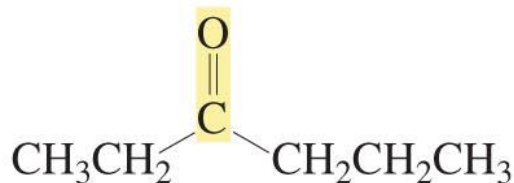
systematic name: benzenecarbaldehyde
common name: benzaldehyde

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Nomenclature of Ketones



systematic name: propanone
common name: acetone
derived name: dimethyl ketone



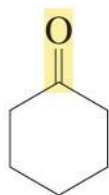
3-hexanone
ethyl propyl ketone



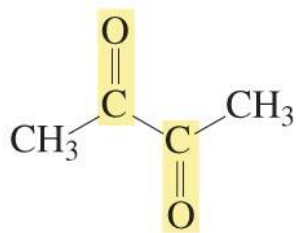
6-methyl-2-heptanone
isohexyl methyl ketone

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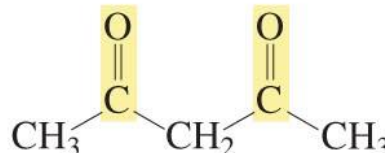
The carbonyl is assumed to be at the 1-position in cyclic ketones:



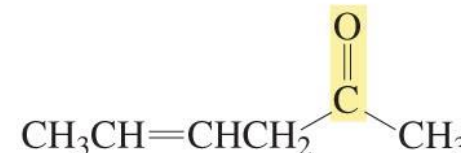
systematic name: cyclohexanone
common name:



butanedione



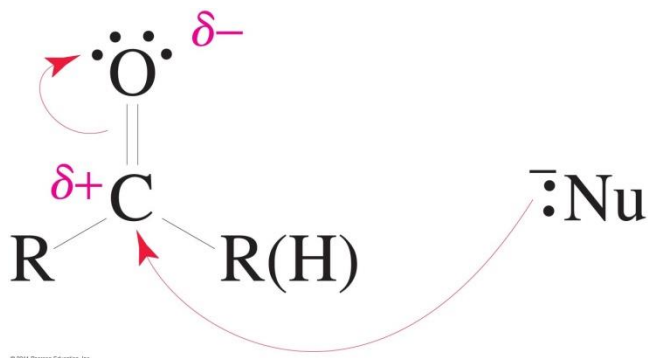
2,4-pentanedione
acetylacetone



4-hexen-2-one

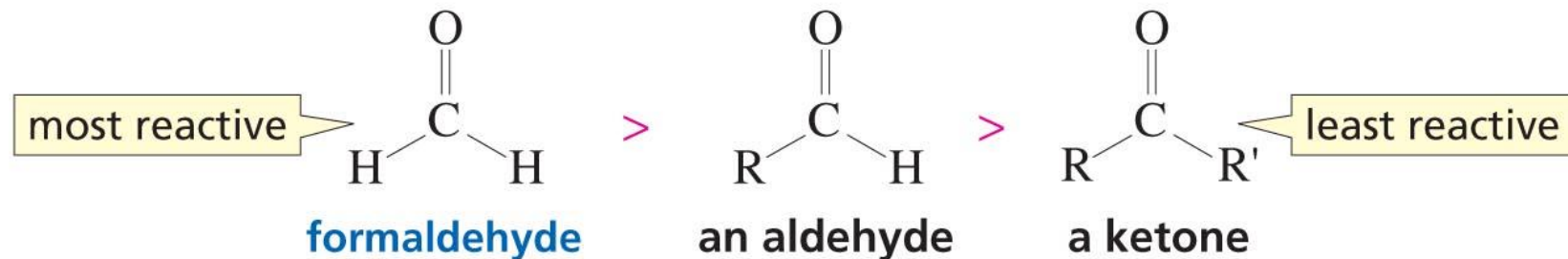
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The partial positive charge on the carbonyl carbon causes that carbon to be attacked by nucleophiles:



An aldehyde has a greater partial positive charge on its carbonyl carbon than does a ketone:

relative reactivities

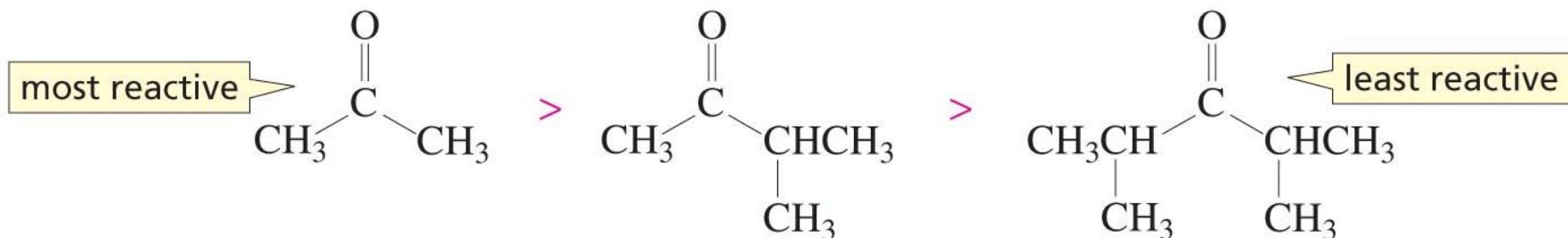


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Aldehydes Are More Reactive Than Ketones

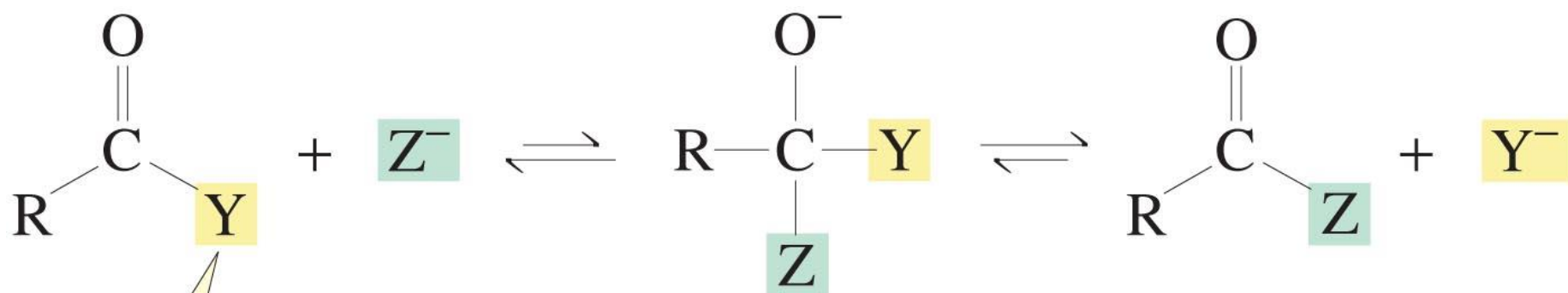
- Steric factors contribute to the reactivity of an aldehyde.
- The carbonyl carbon of an aldehyde is more accessible to the nucleophile.
- Ketones have greater steric crowding in their transition states, so they have less stable transition states.

relative reactivities



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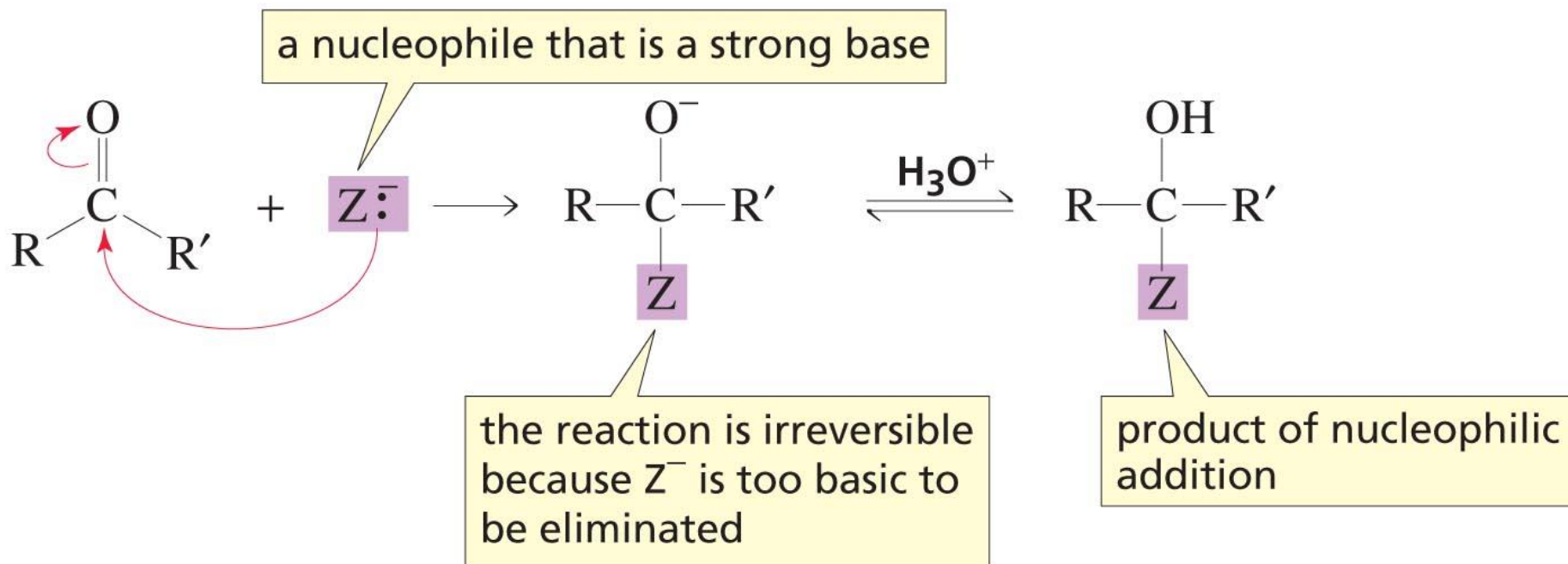
Carboxylic acid derivatives undergo nucleophilic acyl substitution reactions with nucleophiles:



a group that can be replaced by another group

product of nucleophilic addition-elimination

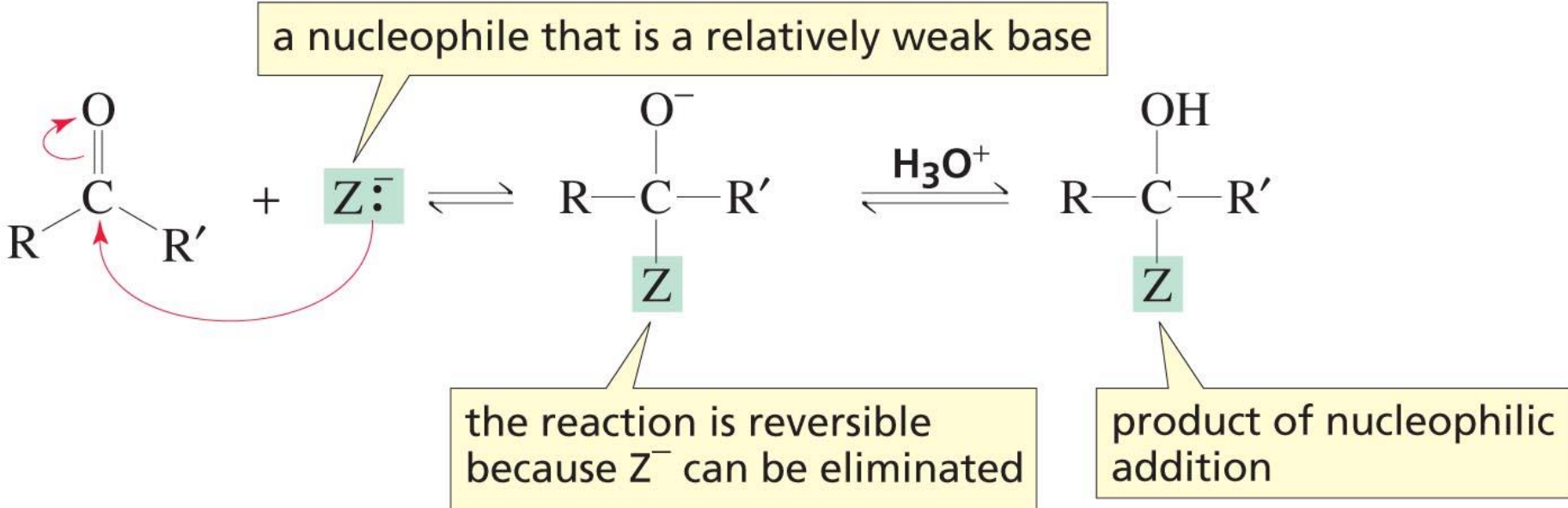
Aldehydes and ketones undergo nucleophilic addition reactions with nucleophiles:



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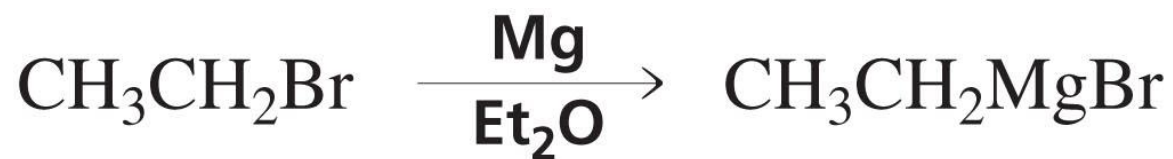
This is an irreversible nucleophilic addition reaction if the nucleophile is a strong base

A reversible nucleophilic addition reaction:



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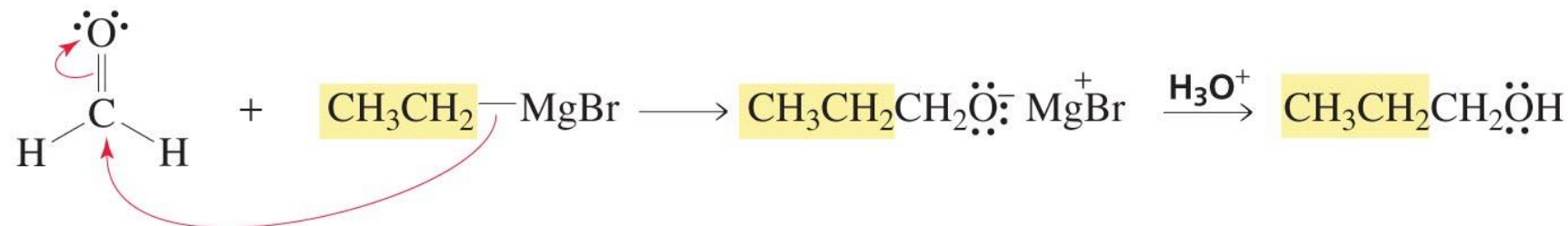
Formation of a New Carbon–Carbon Bond Using Grignard Reagents



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Grignard reagents react with aldehydes, ketones, and carboxylic acid derivatives

Grignard reagents are used to prepare alcohols:



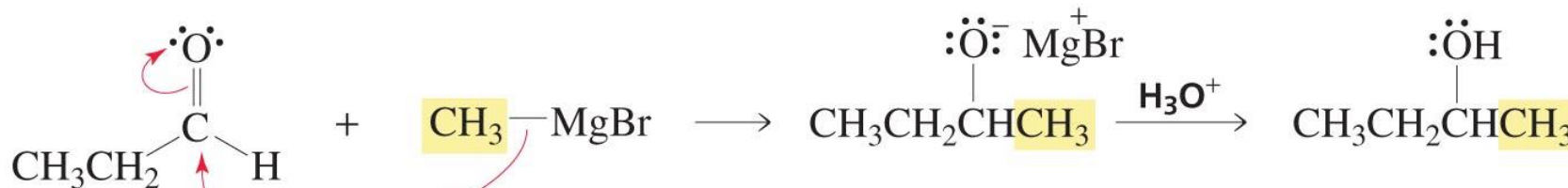
formaldehyde

ethylmagnesium
bromide

an alkoxide ion

1-propanol
a primary alcohol

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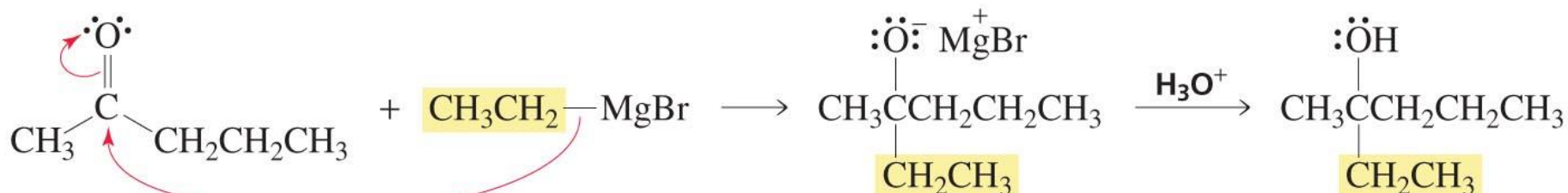


propanal

methylmagnesium
bromide

2-butanol
a secondary alcohol

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2-pentanone

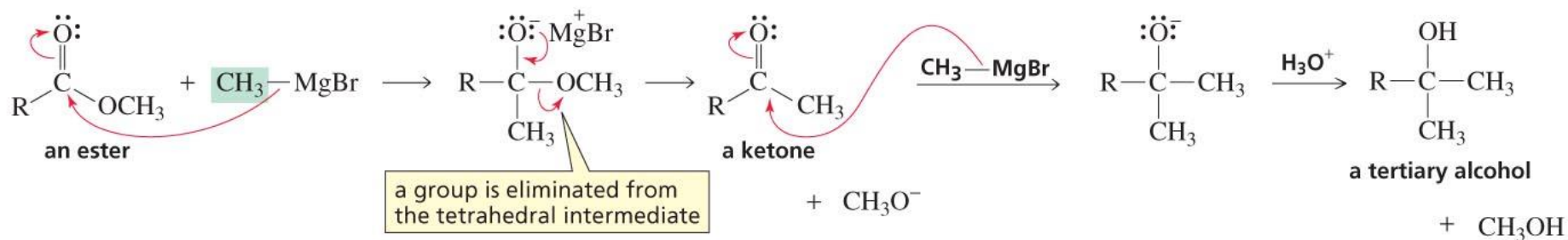
ethylmagnesium
bromide

3-methyl-3-hexanol
a tertiary alcohol

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Mechanism for the reaction of an ester with a Grignard reagent:

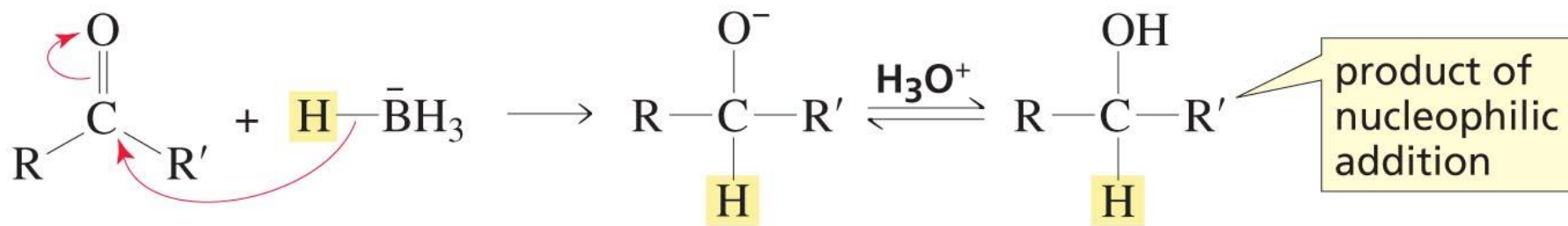
mechanism for the reaction of an ester with a Grignard reagent



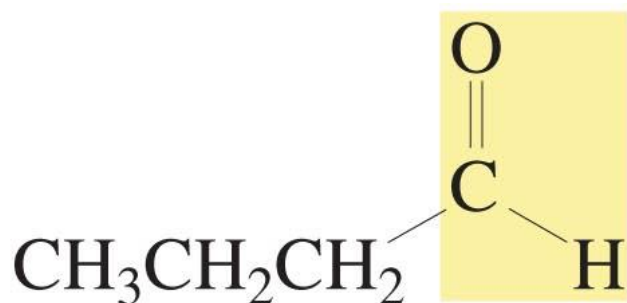
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Reactions of Carbonyl Compounds with Hydride Ion

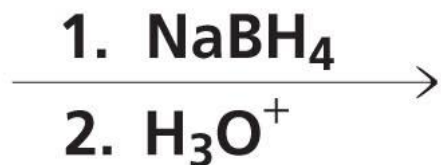
mechanism for the reaction of an aldehyde or a ketone with hydride ion



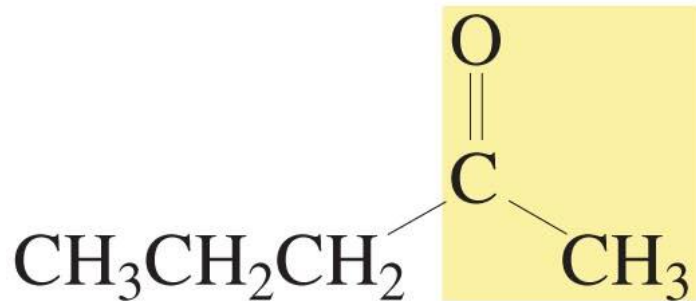
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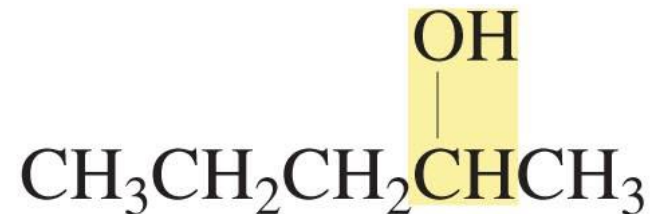
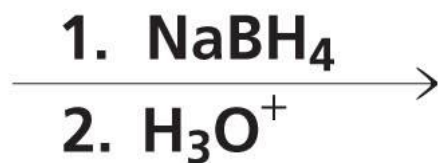
butanal
an aldehyde



1-butanol
a primary alcohol



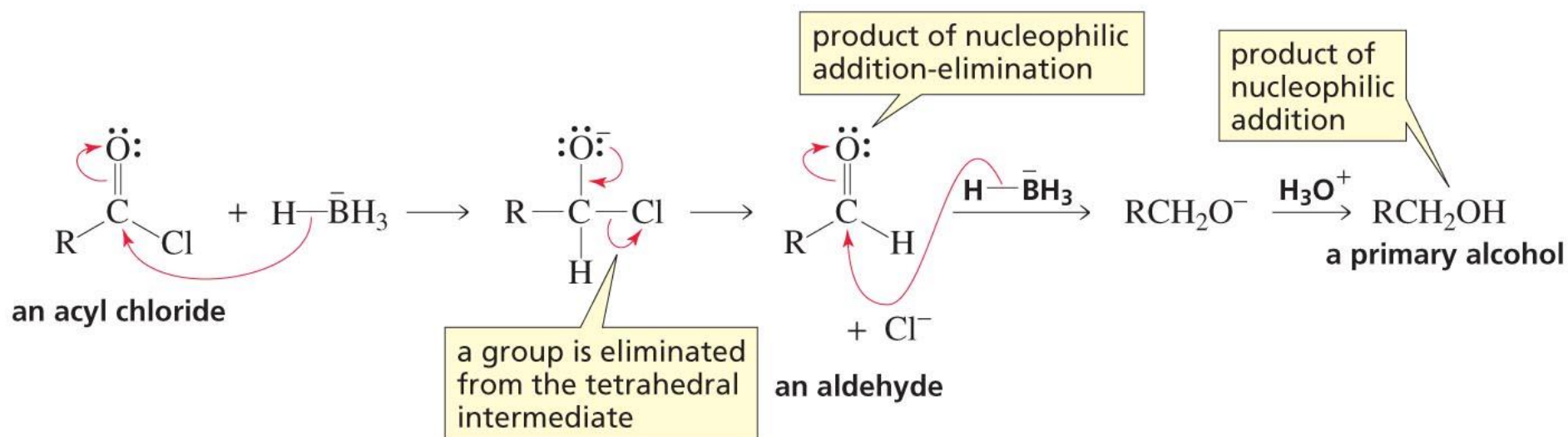
2-pentanone
a ketone



2-pentanol
a secondary alcohol

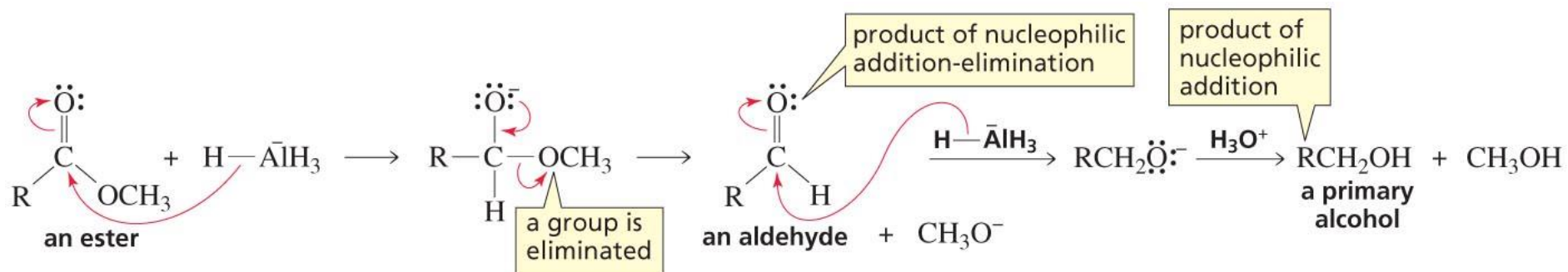
Mechanism for the reaction of an acyl chloride with hydride ion:

mechanism for the reaction of an acyl chloride with hydride ion



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Mechanism for the reaction of an ester with hydride ion:

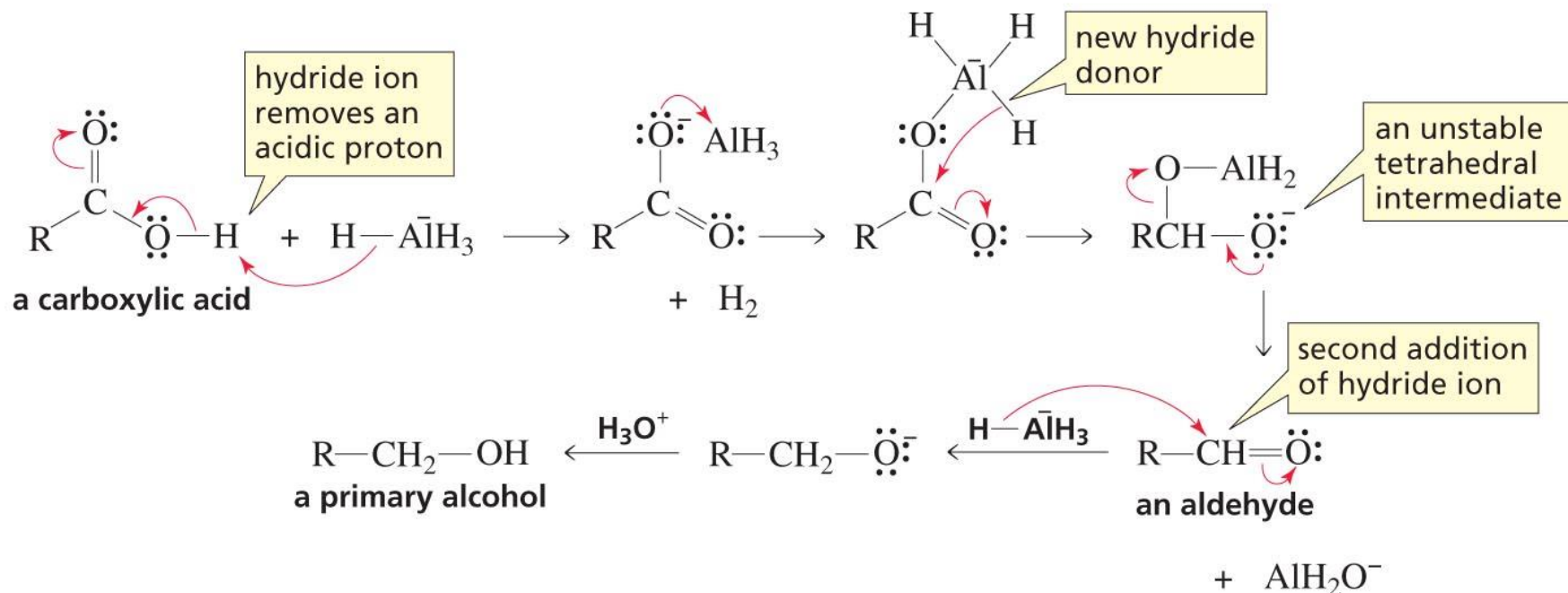


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Esters and acyl chlorides undergo two successive reactions with hydride ion and Grignard reagents

The reduction of a carboxylic acid with LiAlH_4 forms a single primary alcohol:

mechanism for the reaction of a carboxylic acid with hydride ion



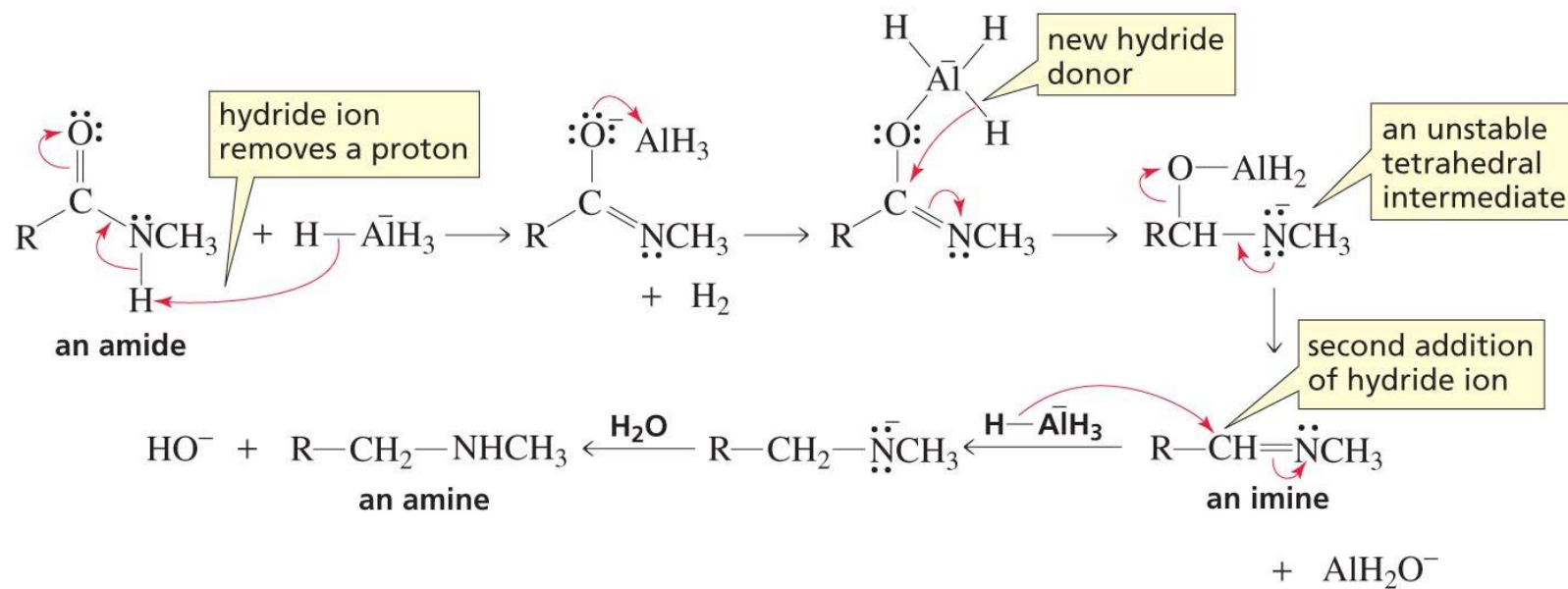
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Acyl chloride is also reduced by LiAlH_4 to yield an alcohol

An amide is reduced by LiAlH_4 to an amine

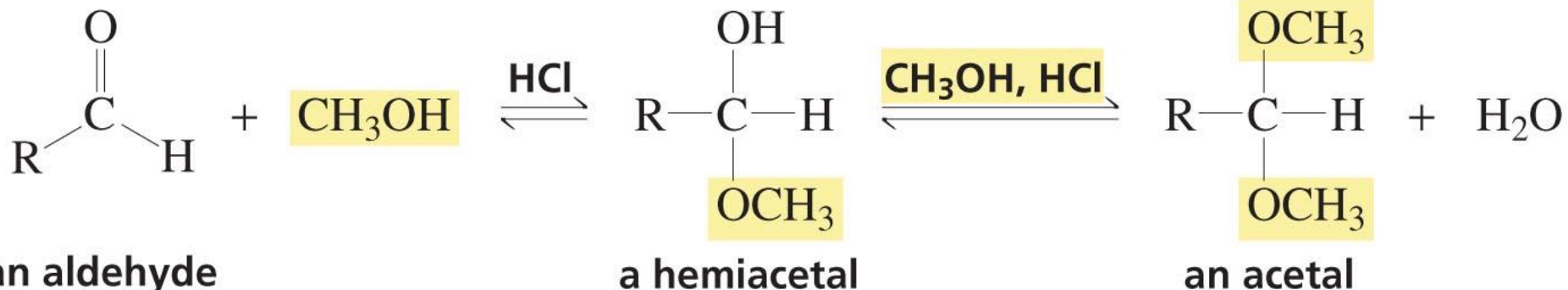
Mechanism for the reaction of an *N*-substituted amide with hydride ion:

mechanism for the reaction of an *N*-substituted amide with hydride ion

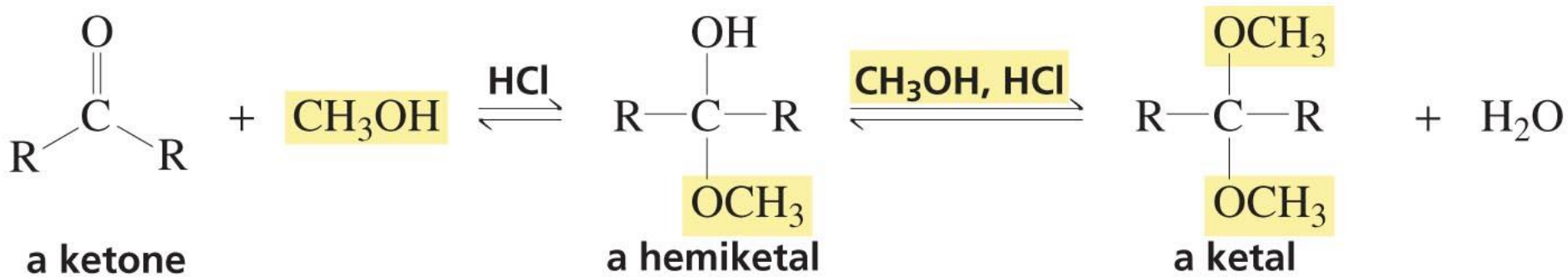


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Addition of an Alcohol to an Aldehyde or a Ketone



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