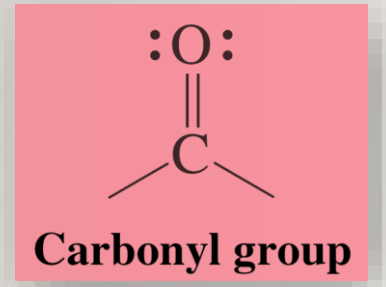
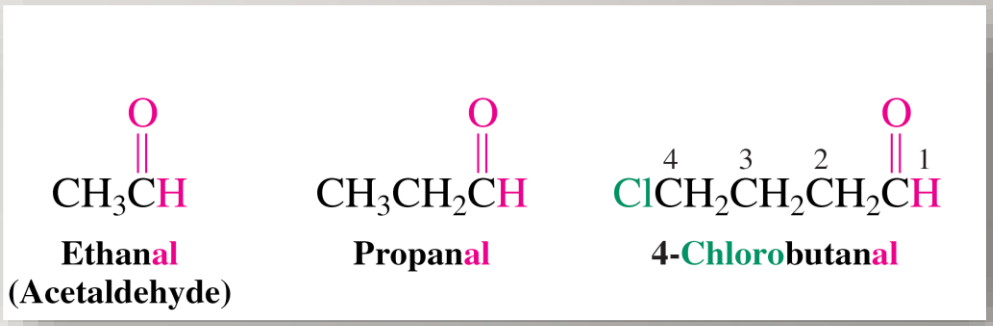
CHM-134 ORGANIC CHEMISTRY
CHAPTER-9: ALDEHYDES & KETONES

Aldehydes

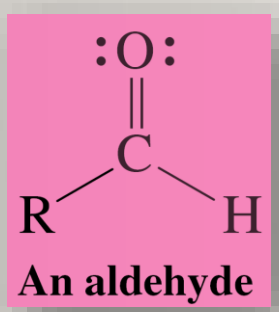
Functional Group: Carbonyl



Alkane → Alkanal. Longest chain starts at -CH=O, which contains C1.



Aldehyde: RCHO



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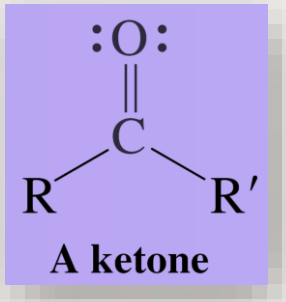
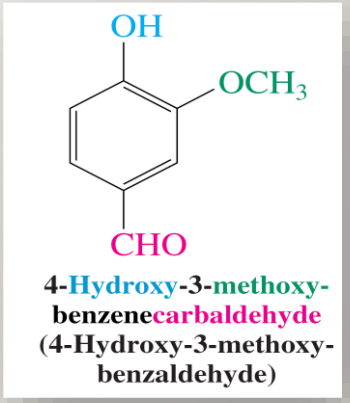
Ketone: RCOR'



Priority of nomenclature

The carbonyl group of aldehydes and ketones has priority over all other polar or functions used so far.

Cyclic aldehydes have the ending -carbaldehyde after cycloalkane name. The carbon attached to -CH=O is C1.



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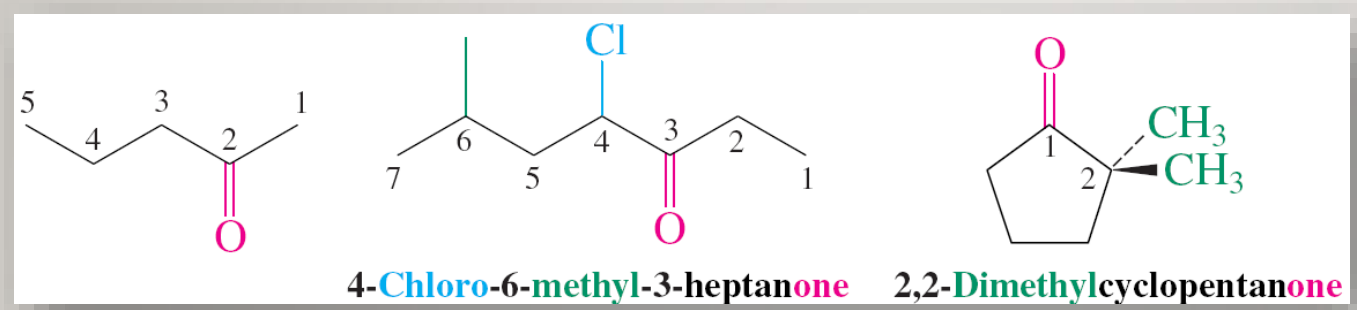
9.1 NOMENCLATURE RULES

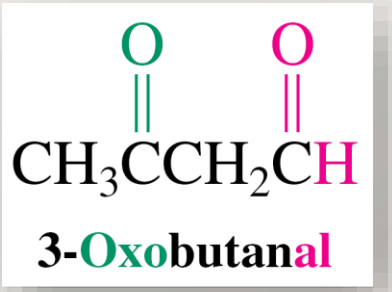
Ketones

Alkane → Alkanone. Longest chain incorporates carbonyl carbon and is numbered from terminus close to C=O.

Cyclic ketones are cycloalkanones; C=O is C1.



An aldehyde containing a ketone C=O is called an oxoalkanal.



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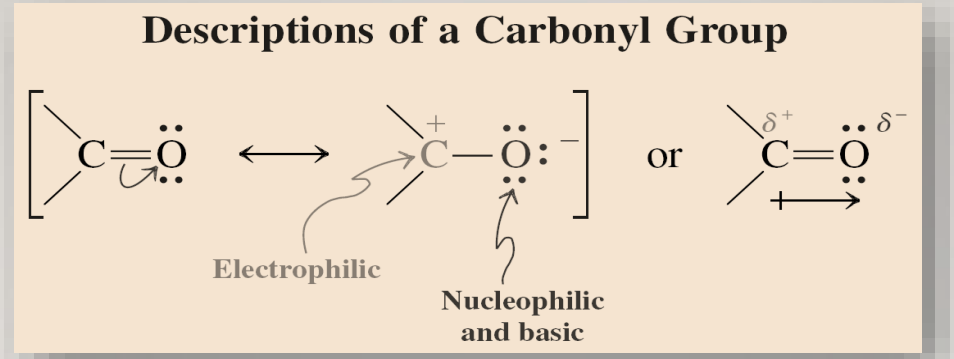
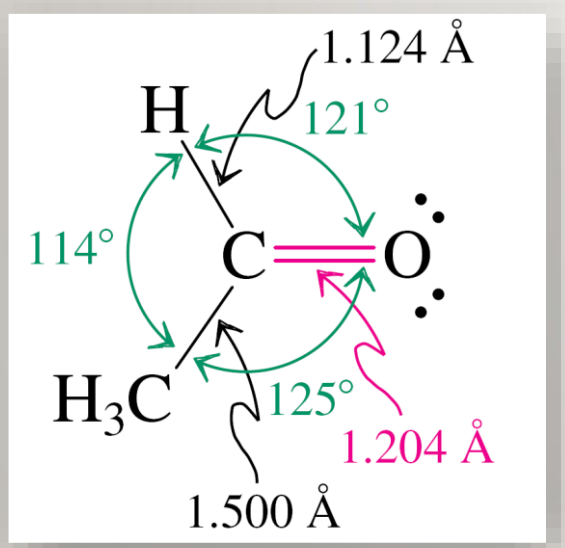
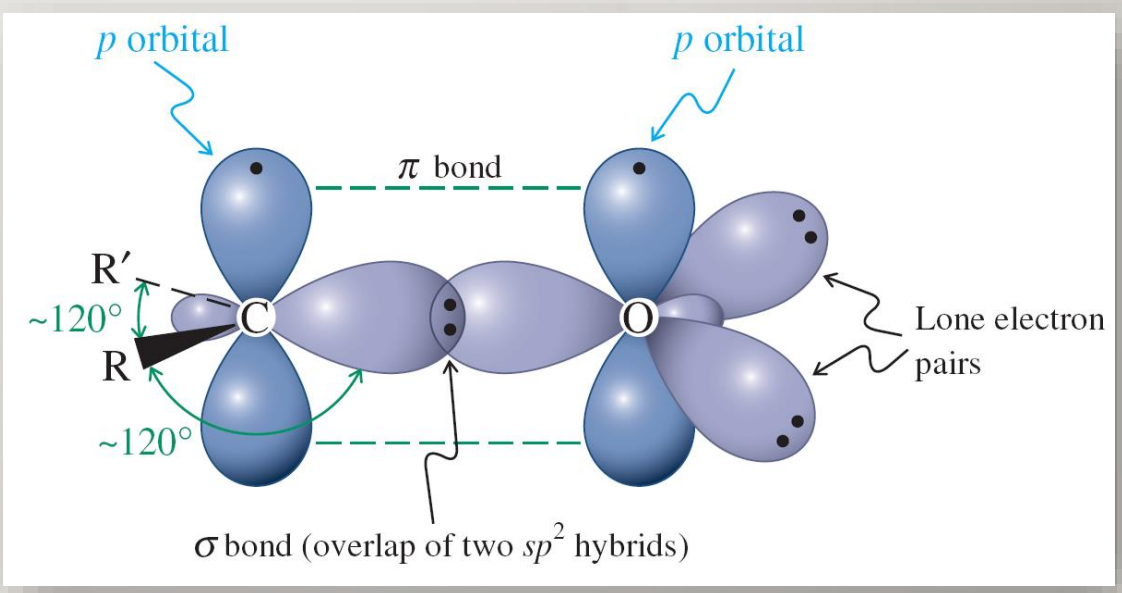
9.2 STRUCTURAL PROPERTIES

The carbonyl group contains a short, strong, and very polar bond.







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9.3 SYNTHESIS OF ALDEHYDES AND KETONES

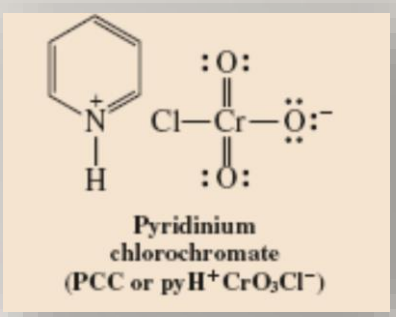
Oxidation of Alcohols

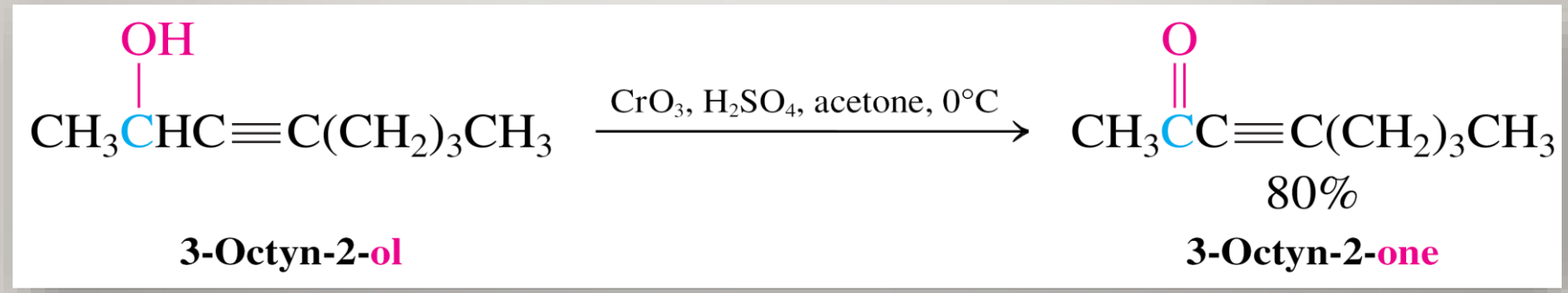
Primary alcohols → aldehydes

Secondary alcohols → ketones

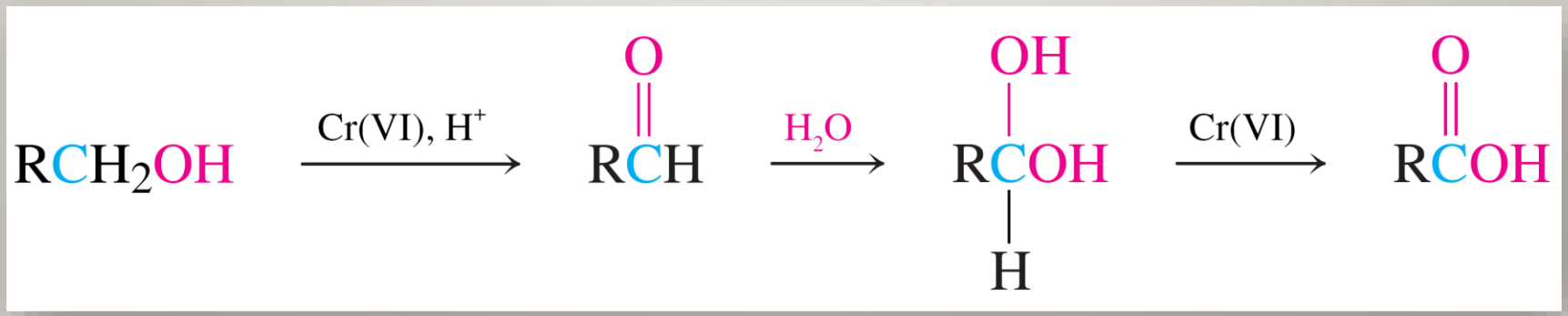
Use chromium(VI) reagents (CrO_3, $Na_2Cr_2O_7$)

Selective: Will not oxidize alkene or alkyne units. Especially mild is PCC:





PCC avoids water, which causes overoxidation of primary alcohols



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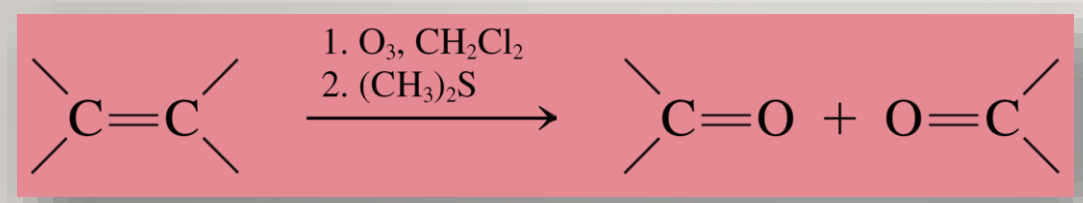
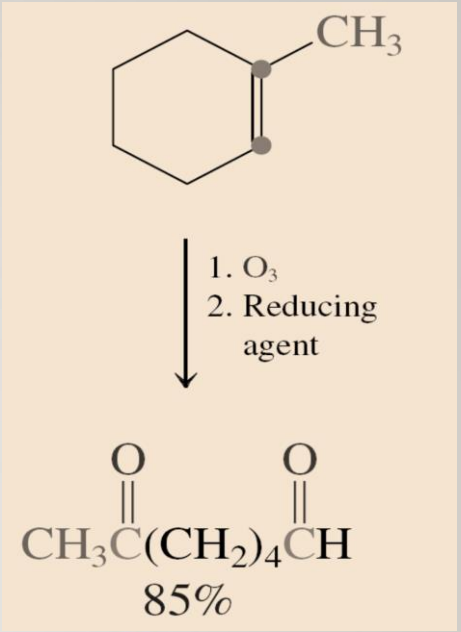
9.3 SYNTHESIS OF ALDEHYDES AND KETONES

Ozonolysis of Alkenes:

Oxidative cleavage of Carbon-Carbon double bonds.



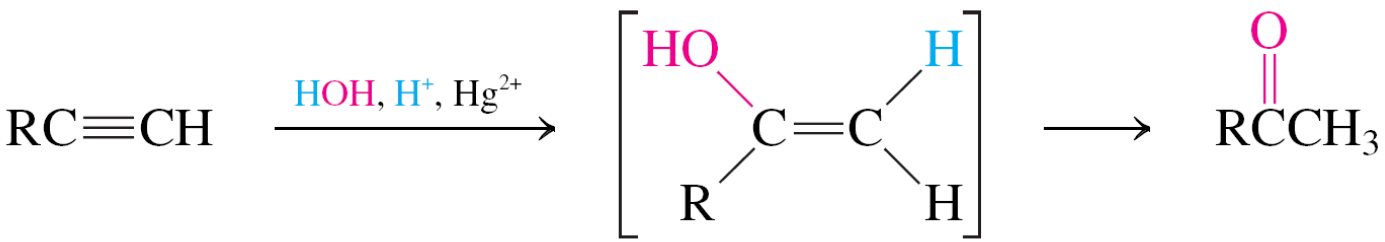


Hydration of Alkynes

Hydration of the carbon–carbon triple bond yields enols that tautomerize to carbonyl compounds

Markovnikov: **Use Hg^{2+}, H_2O, H^+:**

Markovnikov Hydration of Alkynes



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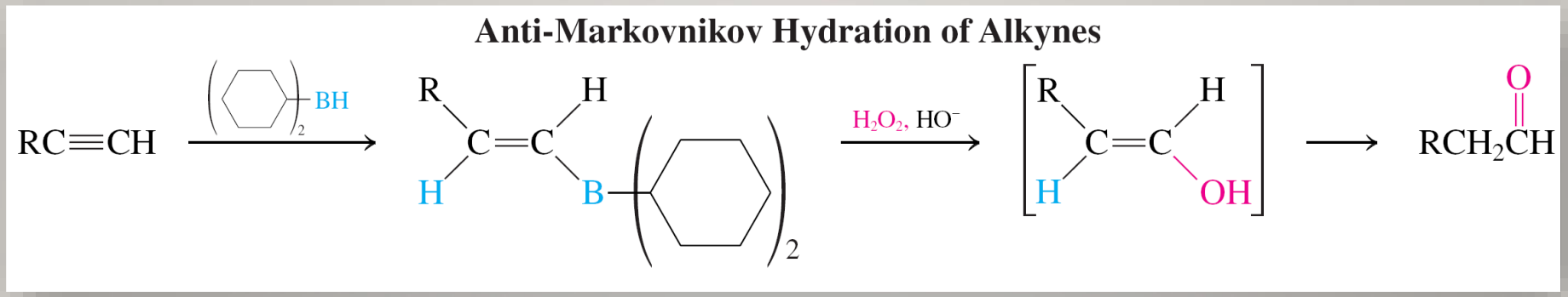
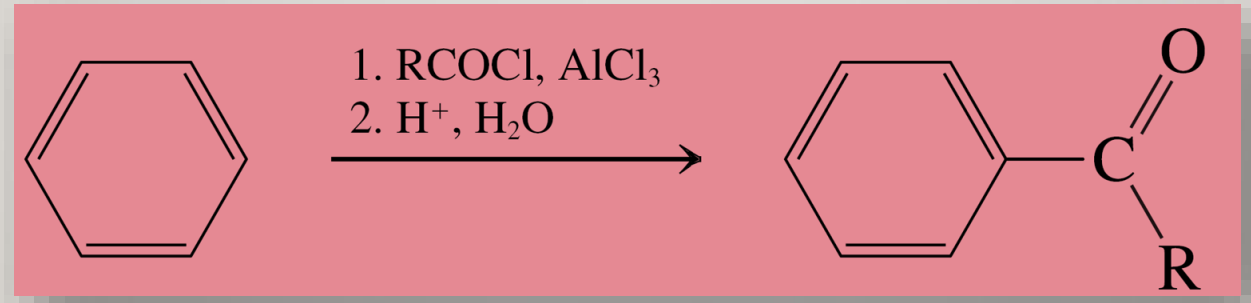
9.3 SYNTHESIS OF ALDEHYDES AND KETONES

Anti-Markovnikov: Use hydroboration-oxidation



Friedel-Crafts acylation
(Electrophilic Aromatic Substitution)



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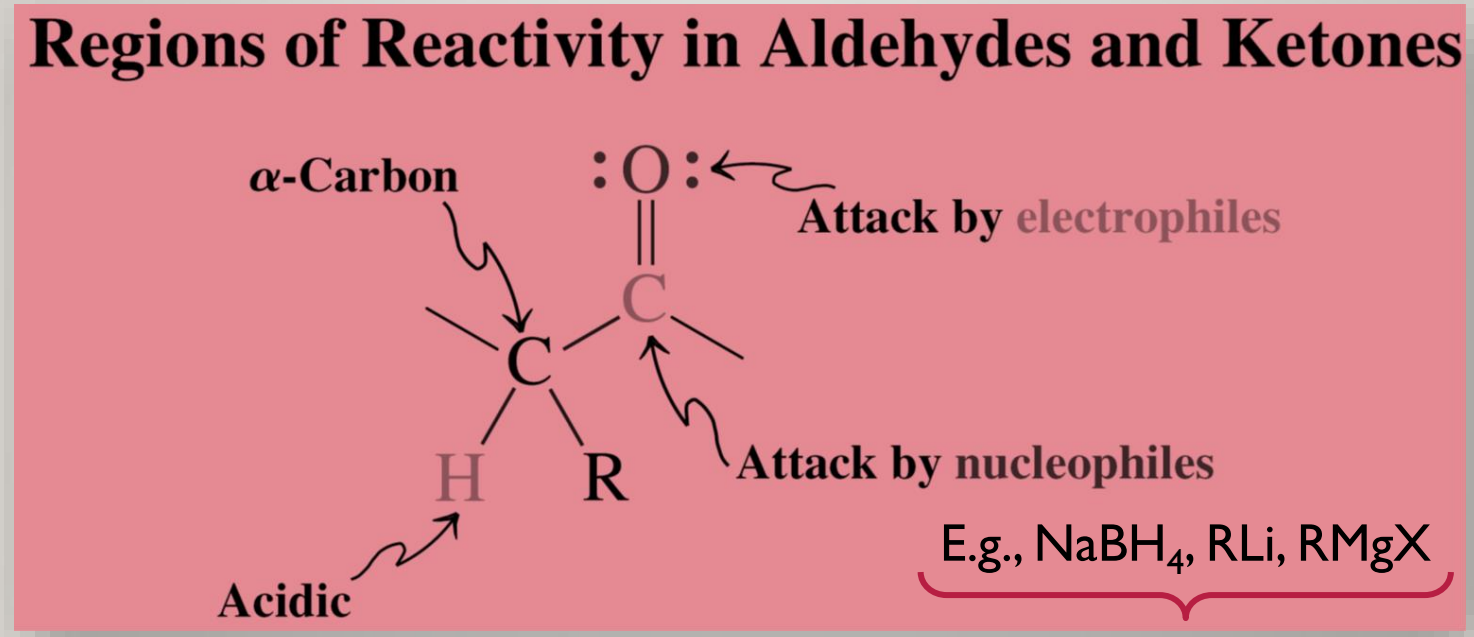
9.4 REACTIONS OF ALDEHYDES AND KETONES



Review

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9.4 REACTIONS OF ALDEHYDES AND KETONES

TABLE 17-3 Additions of Hydride and Organometallic Reagents to Aldehydes and Ketones

Reaction	Equation			
1. Aldehyde + hydride reagent	$RCHO$	$\xrightarrow{NaBH_4,\ CH_3CH_2OH}$	RCH_2OH	Primary alcohol
2. Ketone + hydride reagent	R_2CO	$\xrightarrow{NaBH_4,\ CH_3CH_2OH}$	R_2CHOH	Secondary alcohol
3. Formaldehyde + Grignard reagent	H_2CO	$\xrightarrow{R'MgX,\ (CH_3CH_2)_2O}$	$R'CH_2OH^a$	Primary alcohol
4. Aldehyde + Grignard reagent	$RCHO$	$\xrightarrow{R'MgX,\ (CH_3CH_2)_2O}$	$R'RCHOH^a$	Secondary alcohol
5. Ketone + Grignard reagent	R_2CO	$\xrightarrow{R'MgX,\ (CH_3CH_2)_2O}$	$R'R_2COH^a$	Tertiary alcohol

[a]After aqueous acid work-up.

Addition reactions also occur with milder nucleophiles, such as water, alcohols, and amines. To speed them up, acid or base catalysis is required. Moreover: They are reversible.

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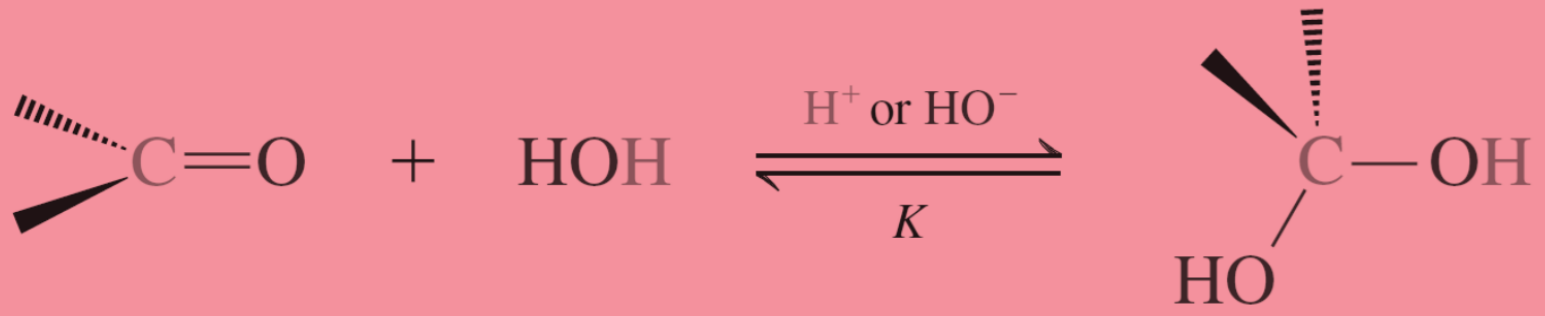
9.4 REACTIONS OF ALDEHYDES AND KETONES

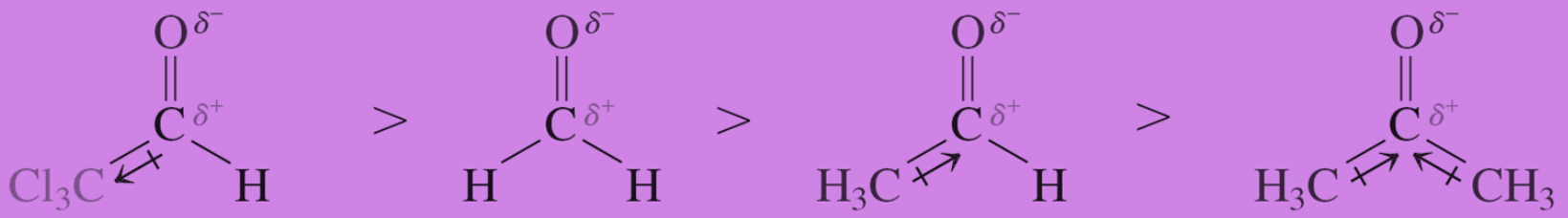
1. Hydration: Geminal Diols (Carbonyl Hydrates)

Hydration of the Carbonyl Group



Geminal diol

Relative Reactivities of Carbonyl Groups



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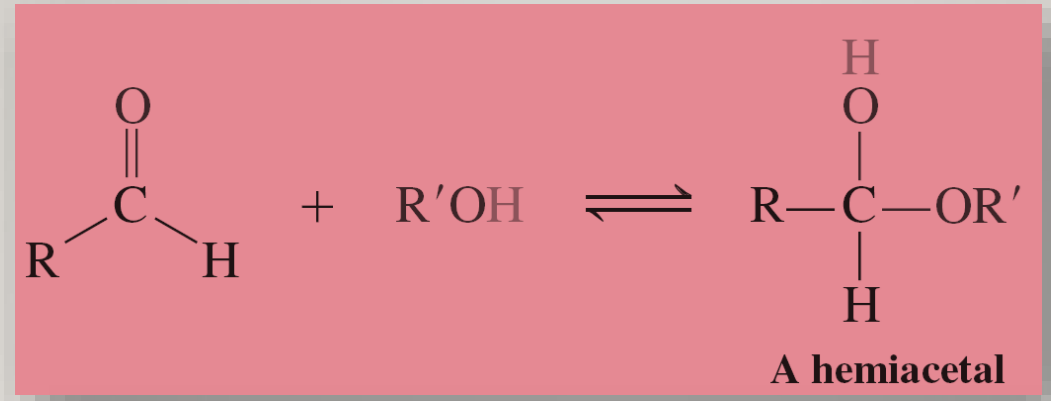
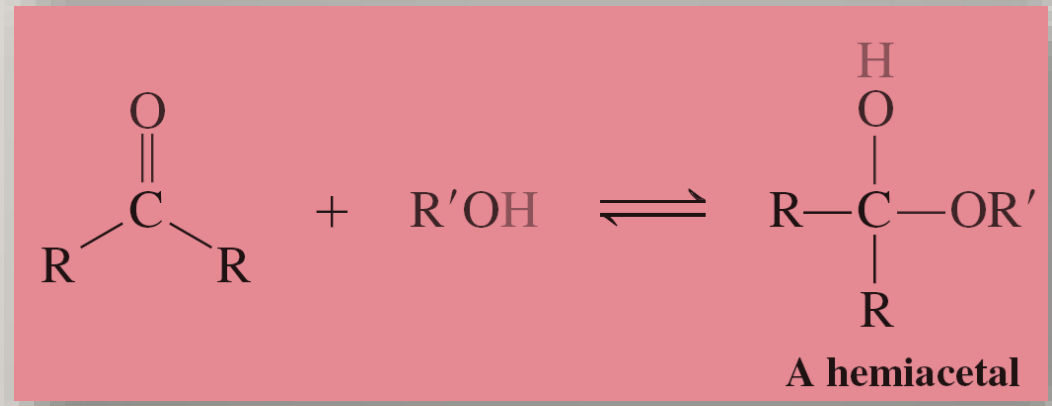
9.4 REACTIONS OF ALDEHYDES AND KETONES

2. Addition of Alcohols

Same as water, initially, to form hemiacetals





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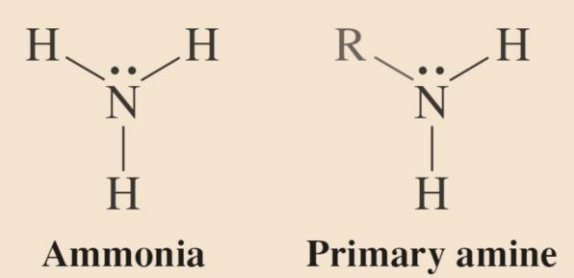
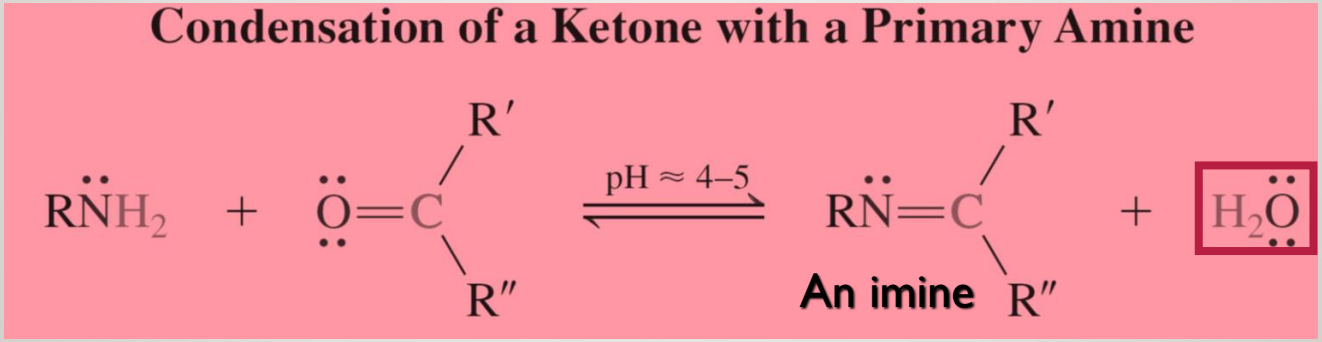
9.4 REACTIONS OF ALDEHYDES AND KETONES

3. Addition of Amines

NH_3 and RNH_2 add to the carbonyl function, followed by dehydration:
A "condensation" reaction.
Water is lost with simultaneous C=N bond formation (opposite of hydrolysis).





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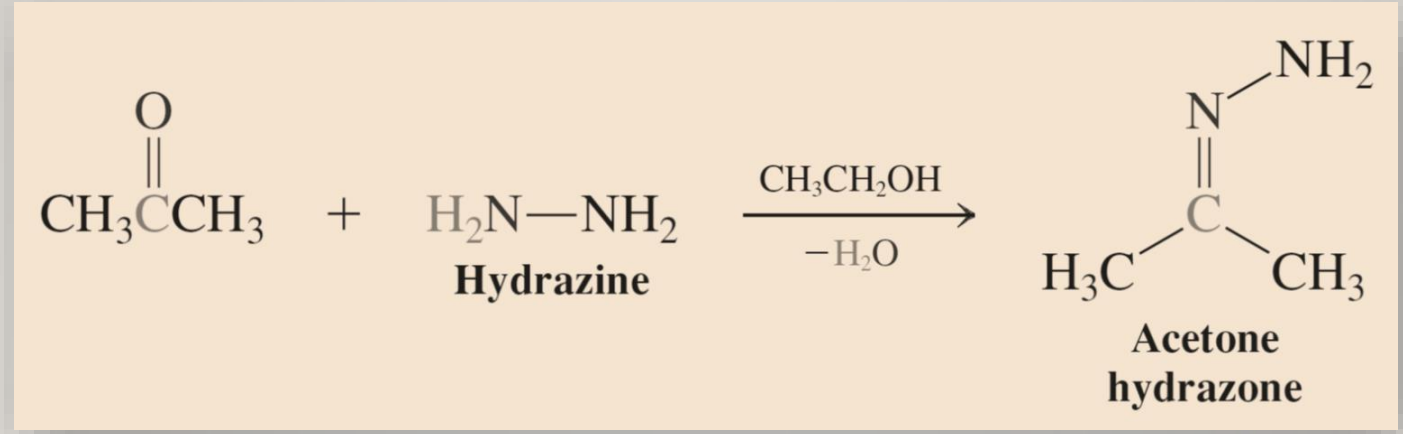
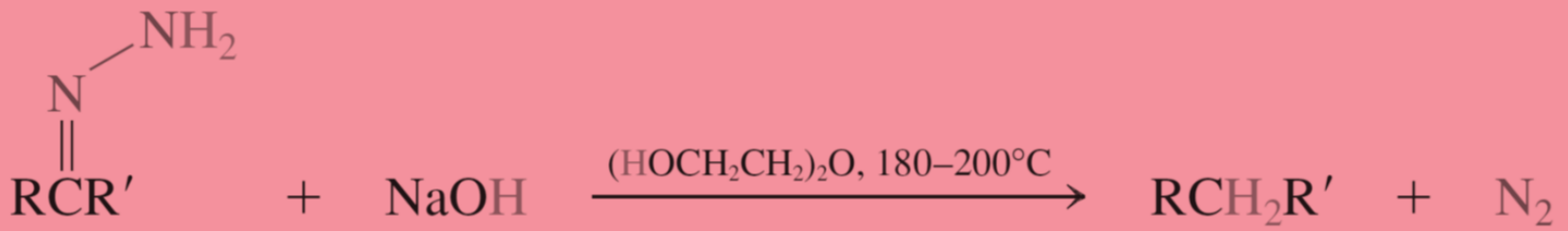
9.4 REACTIONS OF ALDEHYDES AND KETONES

Wolff-Kishner Reduction An Application of Hydrazones

Synthesis of a Hydrazone by Imine Formation



Wolff-Kishner Reduction



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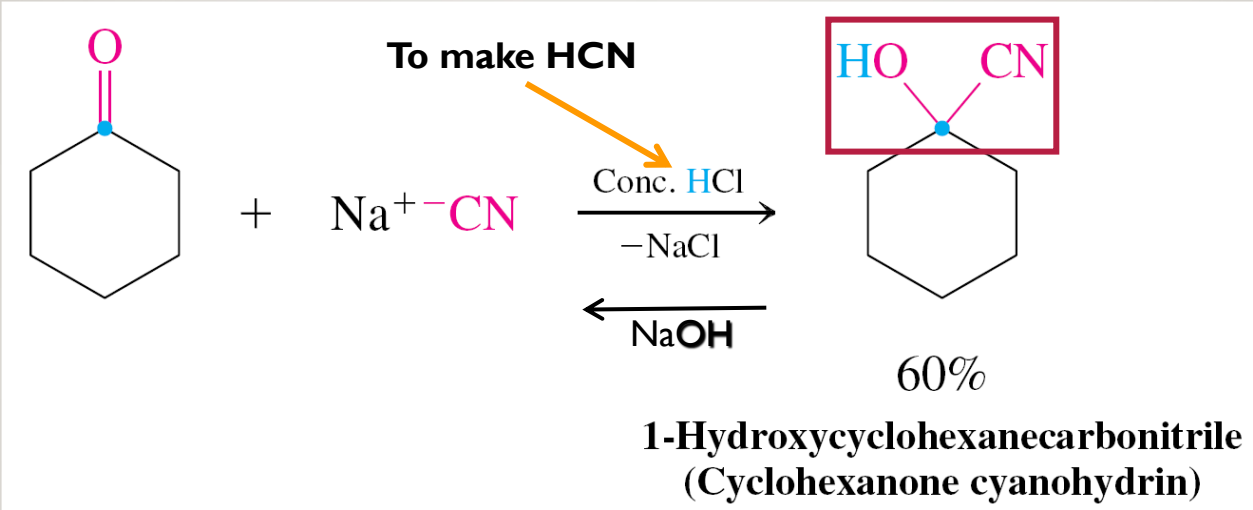
9.4 REACTIONS OF ALDEHYDES AND KETONES

4. Addition of Non-organometallic Carbon Nucleophiles

a. Cyanide makes cyanohydrins



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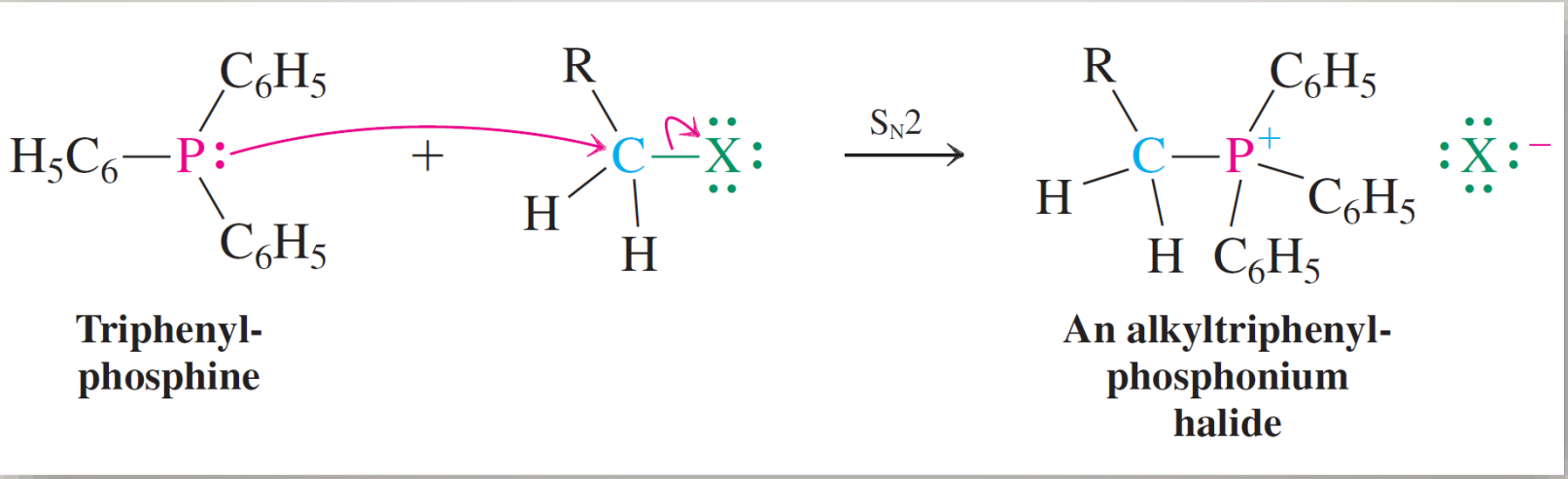
9.4 REACTIONS OF ALDEHYDES AND KETONES

4. Addition of Non-organometallic Carbon Nucleophiles

b. The Wittig Reaction

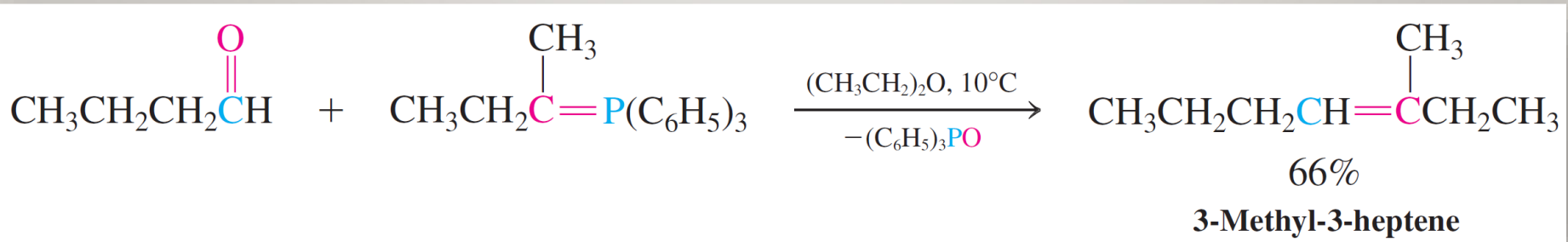
Discovered during an investigation of SN_2 reactions of phosphines with haloalkanes.

Phosphonium salt synthesis



Triphenyl-phosphine

An alkyltriphenyl-phosphonium halide



3-Methyl-3-heptene

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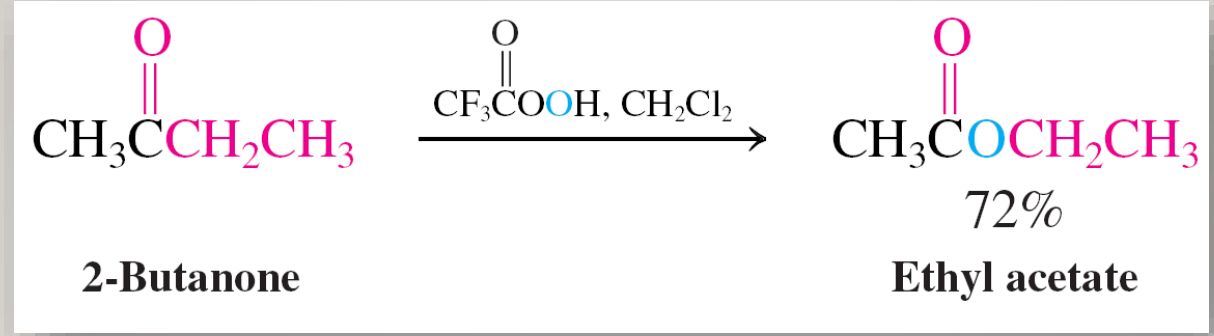
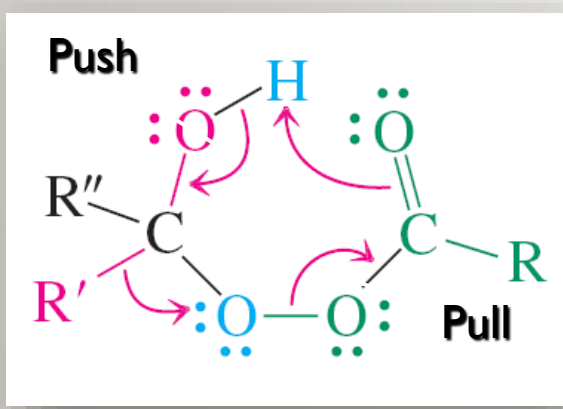
9.4 REACTIONS OF ALDEHYDES AND KETONES

5. Baeyer-Villiger Oxidation

Oxidation of ketones by peroxycarboxylic acids gives esters:





Migratory Aptitudes in the Baeyer-Villiger Reaction

Methyl < primary < phenyl ~ secondary < tertiary

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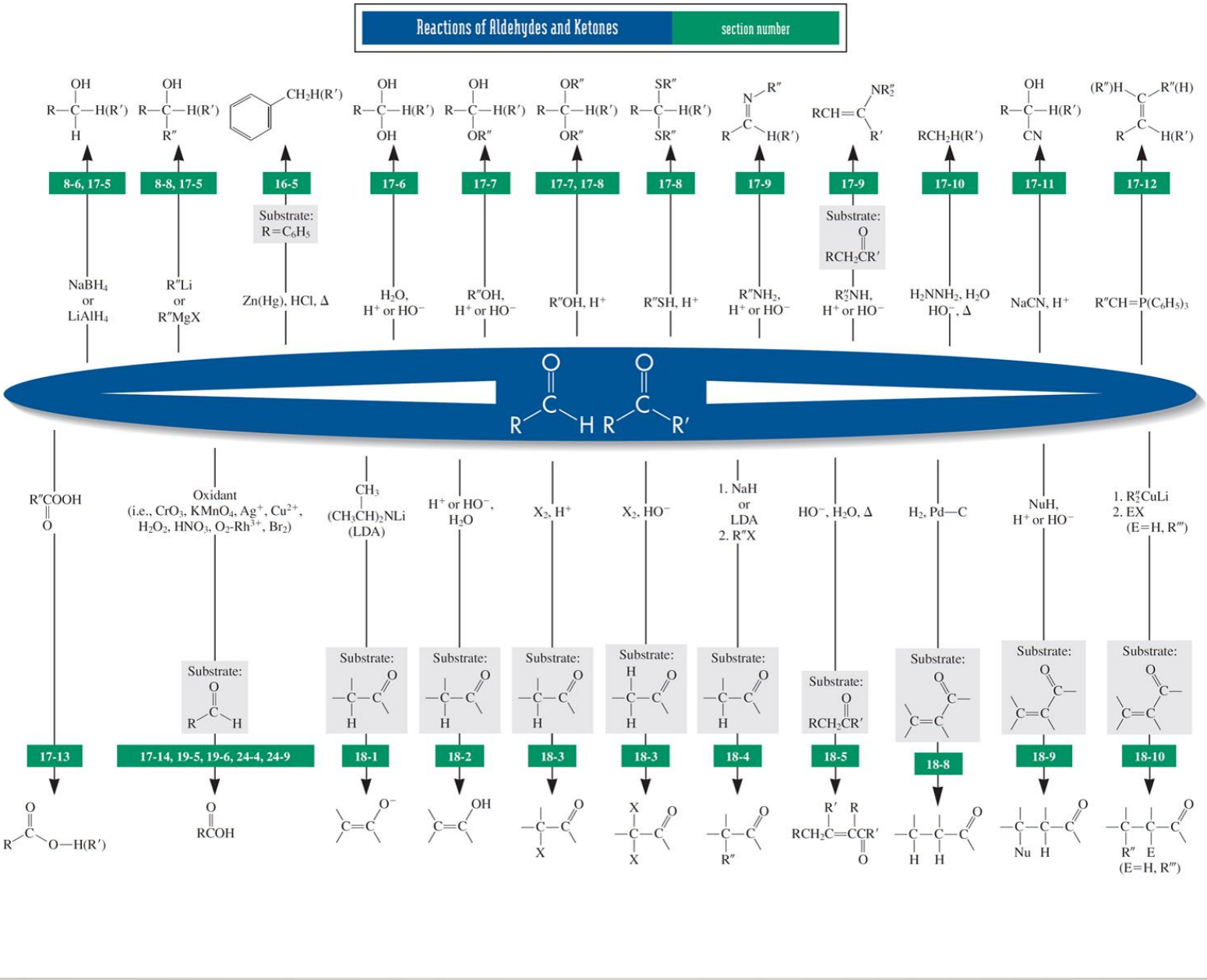

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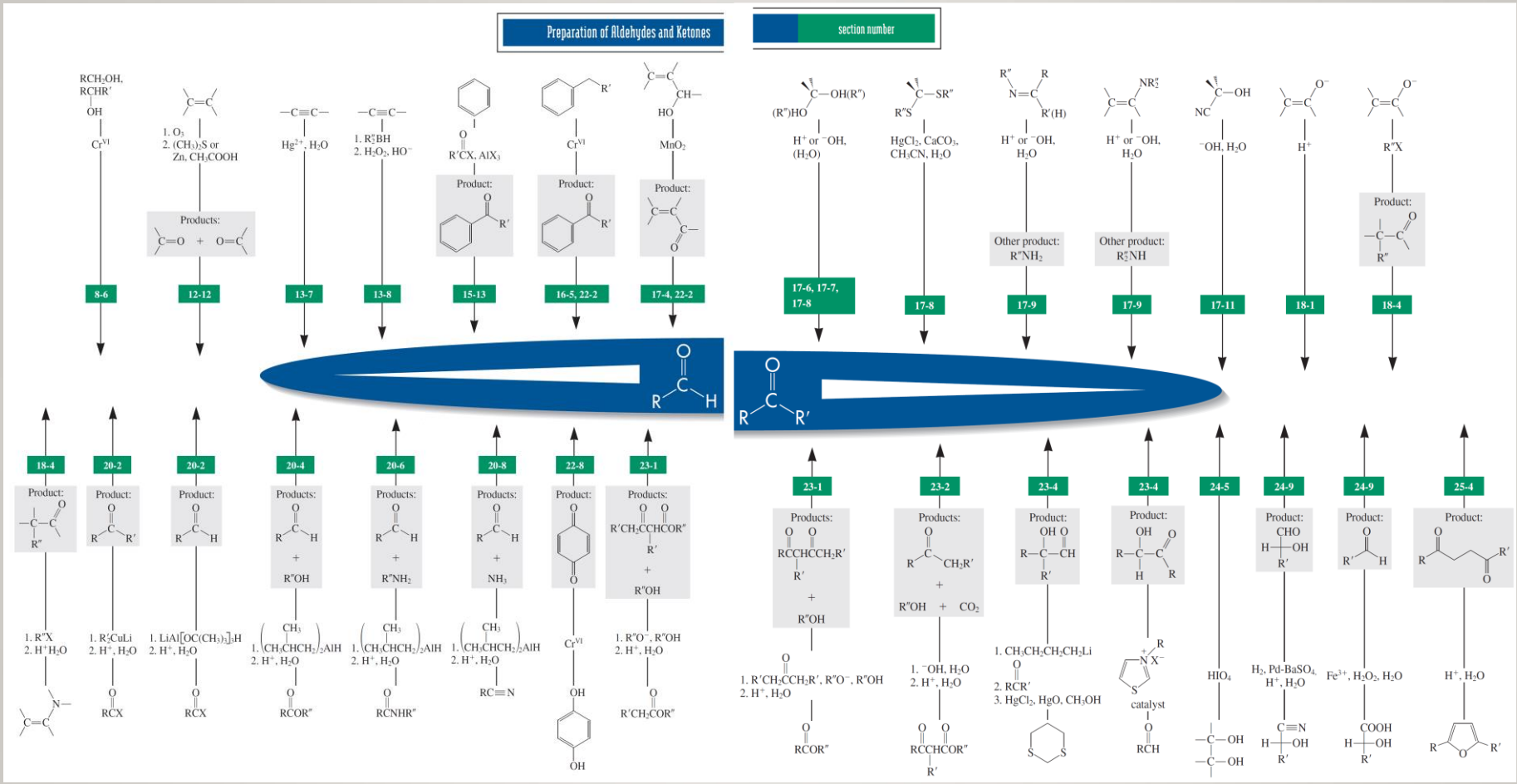

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