Organic Chemistry

Aromatic Compounds

by
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Chapter Description

- Aims
  - The students should **understand** the fundamental of organic chemistry in terms of aromatic compounds
  - The students should be able to **explain** the fundamental of organic chemistry in terms of aromatic compounds

- Expected Outcomes
  - Explain the basic knowledge in aromatic compounds
  - Describe the chemical reactions and conditions for aromatic compounds reactions
  - Describe the aromatic compound reactions in certain industrial application

- References
  - Janice Gorzynski Smith (2008), Organic chemistry,Mc Graw-Hill
  - T. W. Graham Solomons. (2008). Organic chemistry, 9th ed, Mc Graw-Hill
  - K. Peter C. Vollhardt, Neil E. Schore, (2009). Organic chemistry, Fourth Edition: Structure and Function, Pub Chem

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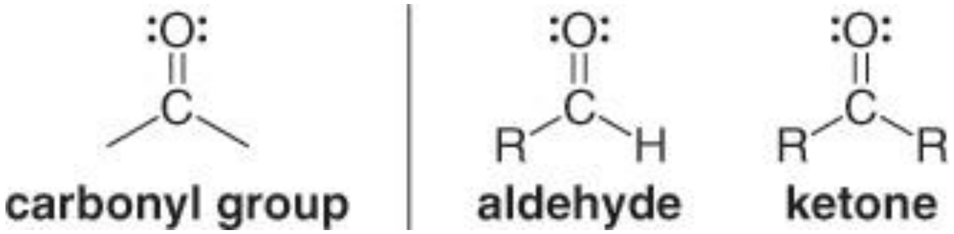
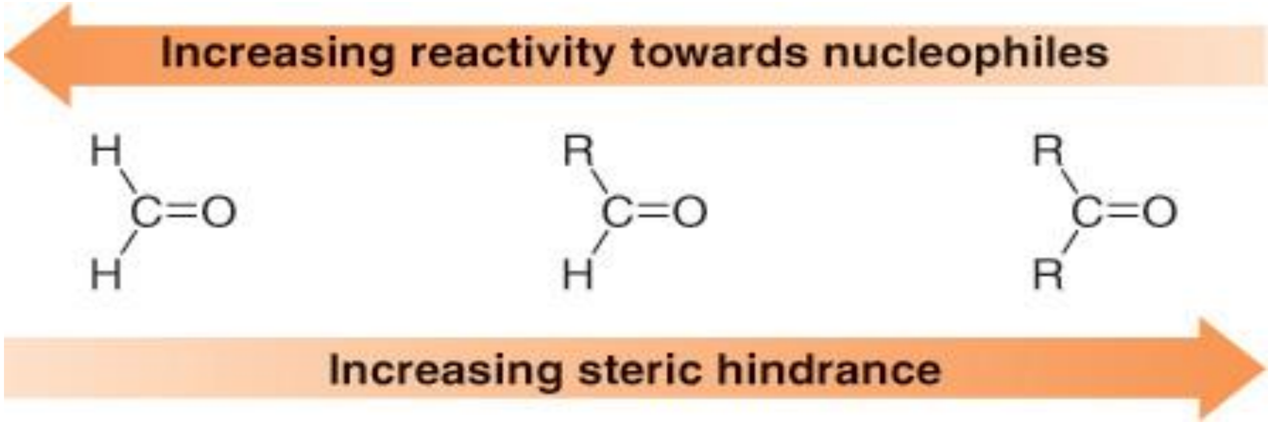
Introduction

- Aldehydes and ketones contain a carbonyl group.
- An aldehyde contains at least one H atom bonded to the carbonyl carbon, whereas the ketone has two alkyl or aryl groups bonded to it.



Introduction

- **Aldehydes and ketones react with nucleophiles.**
- **As the number of R groups around the carbonyl carbon increases, the reactivity of the carbonyl compound decreases (WHY?), resulting in the following order of reactivity:**



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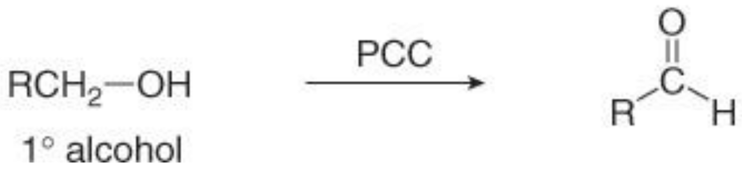
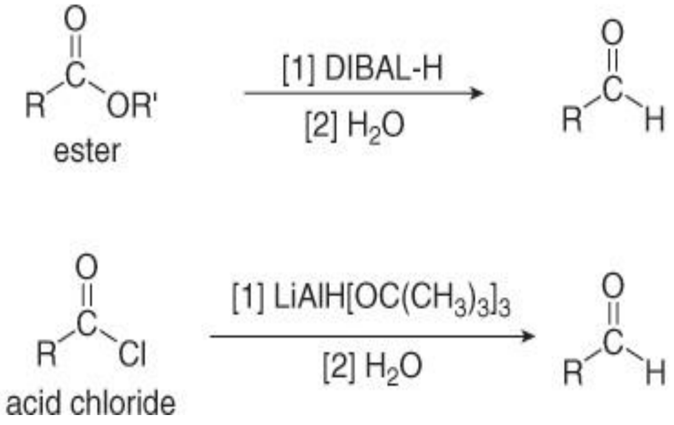
Preparation of Aldehydes and Ketones

Common methods to synthesize aldehydes:

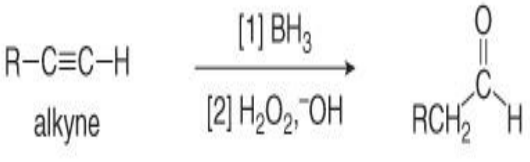
- **By oxidation of 1° alcohols with PCC**



- **By reduction of esters and acid chlorides**



- **By hydration of an alkyne using hydroboration-oxidation**



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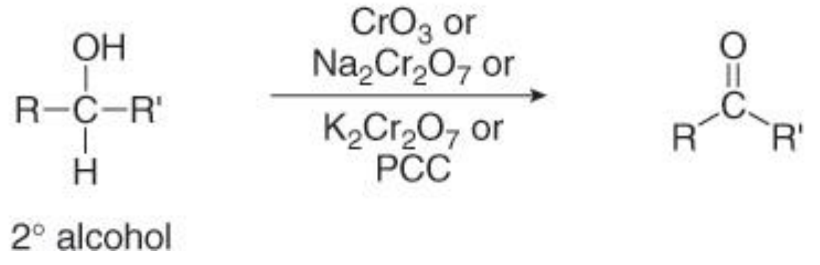
Preparation of Aldehydes and Ketones

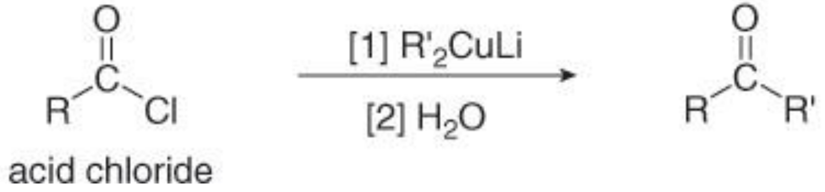
Common methods to synthesize ketones:

- **By oxidation of 2° alcohols with Cr^{6+} reagents**



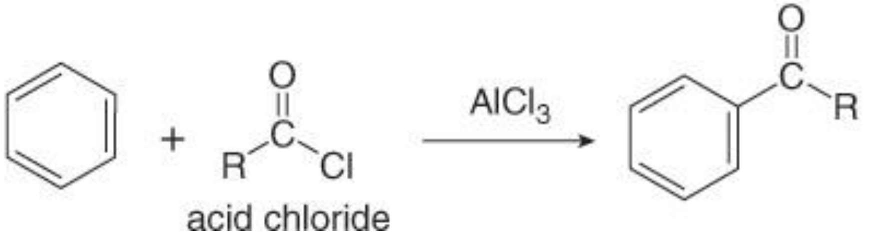
(Section 12.12A)

- **By reaction of acid chlorides with organocuprates**



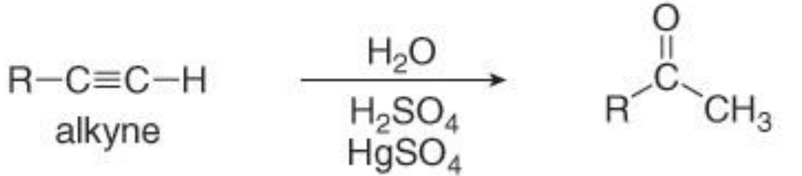
(Section 20.13)

- **By Friedel–Crafts acylation**



(Section 18.5)

- **By hydration of an alkyne**



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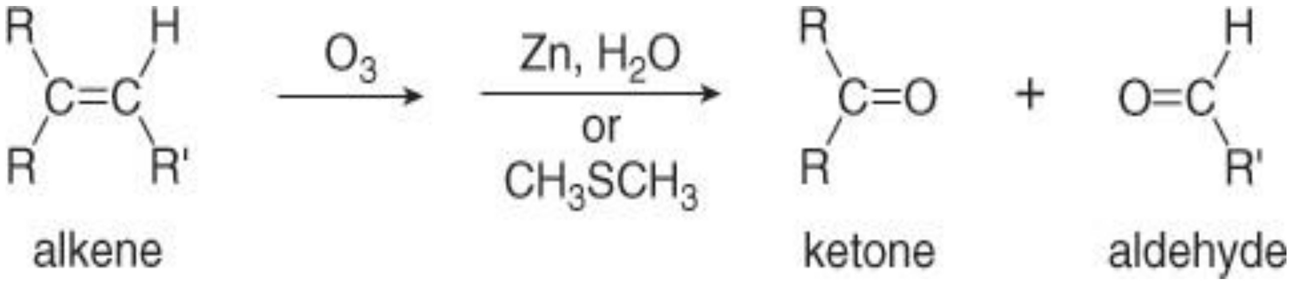
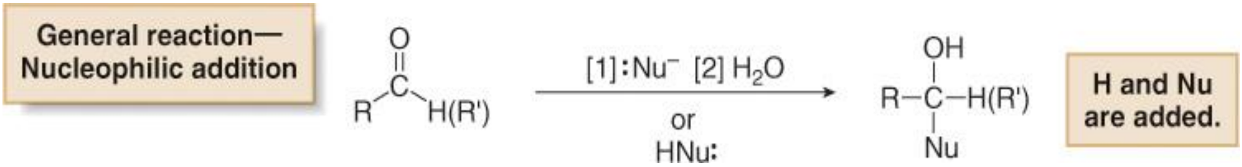
Preparation of Aldehydes and Ketones

Aldehydes and ketones are also both obtained as products of the oxidative cleavage of alkenes.

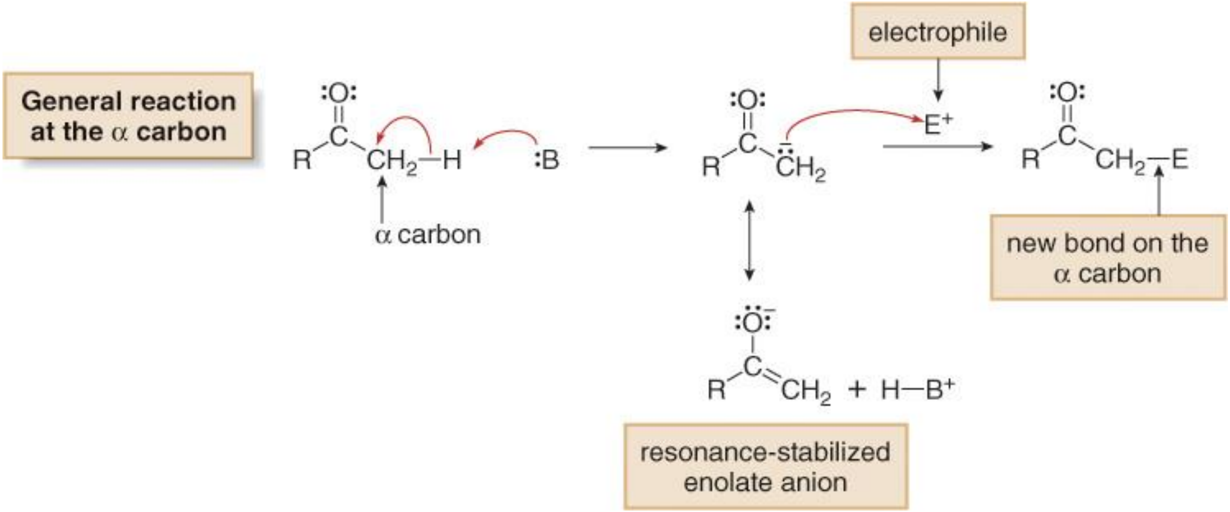


Reactions of Aldehydes and Ketones— General

[1] Reaction at the carbonyl carbon—the elements of H and Nu are added to the carbonyl group.



[2] Reaction at the α carbon.



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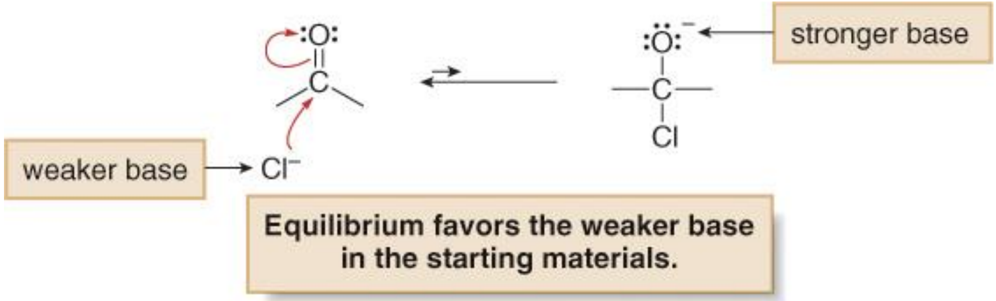
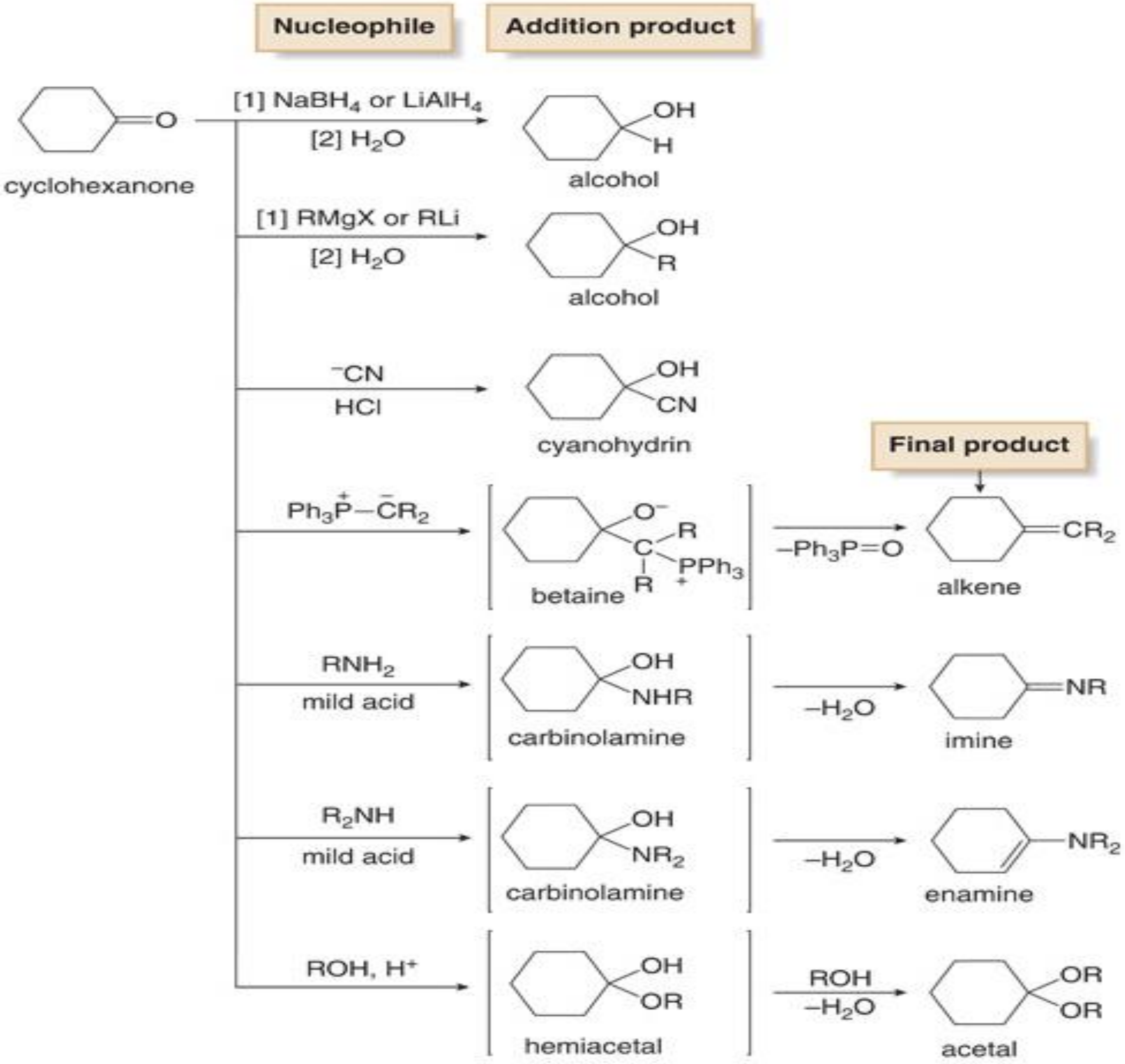
Reactions of Aldehydes and Ketones—General

It is important to know what nucleophiles will add to carbonyl groups.

- **Cl^{-}, Br^{-} and I^{-} are good nucleophiles in substitution reactions at *sp*^{3} hybridized carbons, but they are ineffective nucleophiles in addition.**
- **When these nucleophiles add to a carbonyl, they cleave the C—O π bond, forming an alkoxide. Since X^{-} is a much weaker base than the alkoxide formed, equilibrium favors the starting materials, not the addition product.**

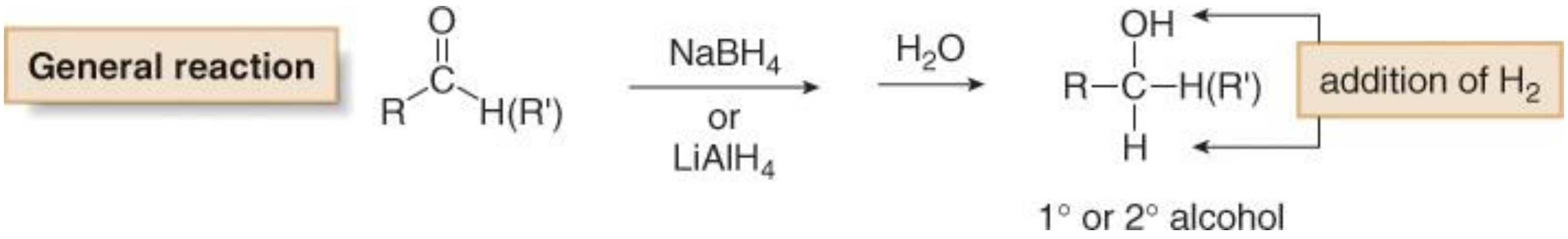


Equilibrium favors the weaker base in the starting materials.

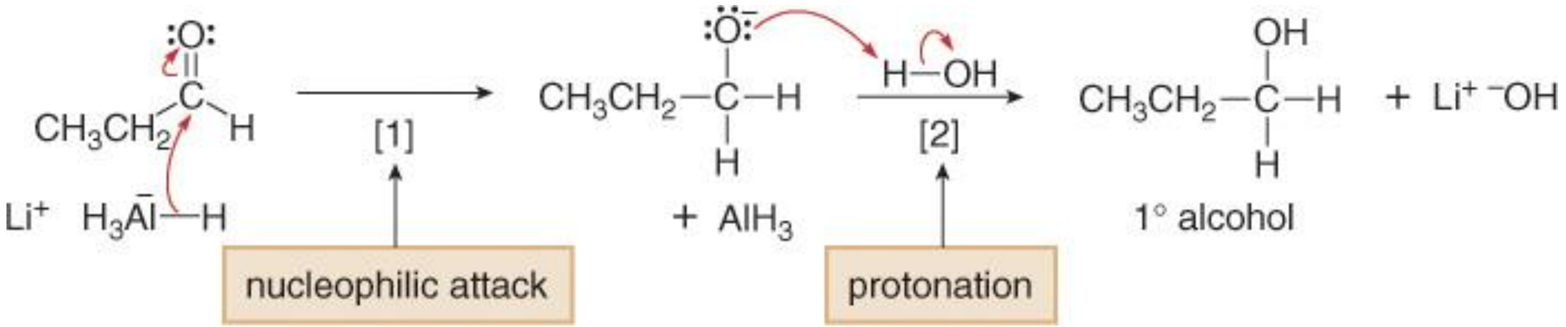

Nucleophile
Addition product
cyclohexanone
[1] NaBH4 or LiAlH4
[2] H2O
alcohol
[1] RMgX or RLi
[2] H2O
alcohol
⁻CN
HCl
cyanohydrin
Final product
Ph3P⁺–C⁻R2
betaine
–Ph3P=O
alkene
RNH2
mild acid
carbinolamine
–H2O
imine
R2NH
mild acid
carbinolamine
–H2O
enamine
ROH, H⁺
hemiacetal
ROH
–H2O
acetal

Nucleophilic Addition of H^- and R^-—A Review

Treatment of an aldehyde or ketone with either $NaBH_4$ or $LiAlH_4$ followed by protonation forms a 1^0 or 2^0 alcohol. The nucleophile in these reactions is $H:^-$.

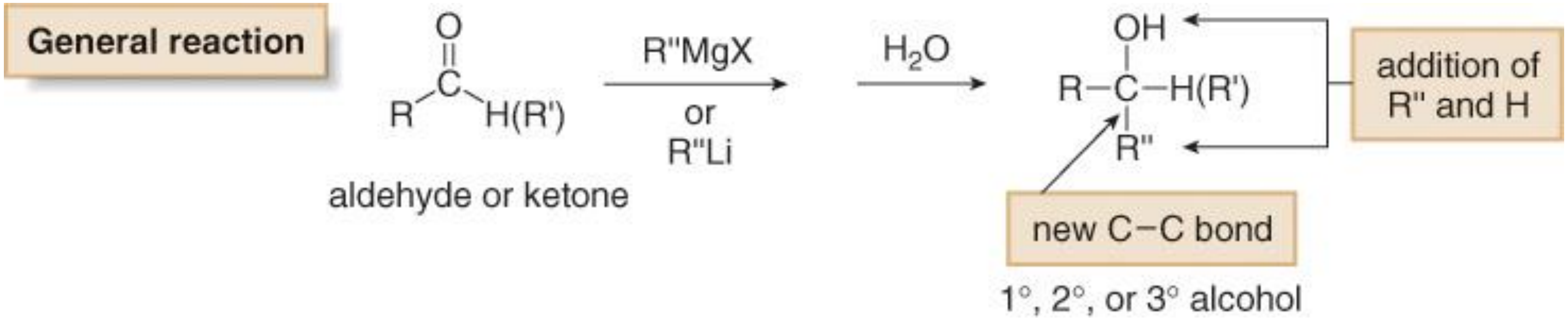


Hydride reduction occurs via a two-step mechanism.

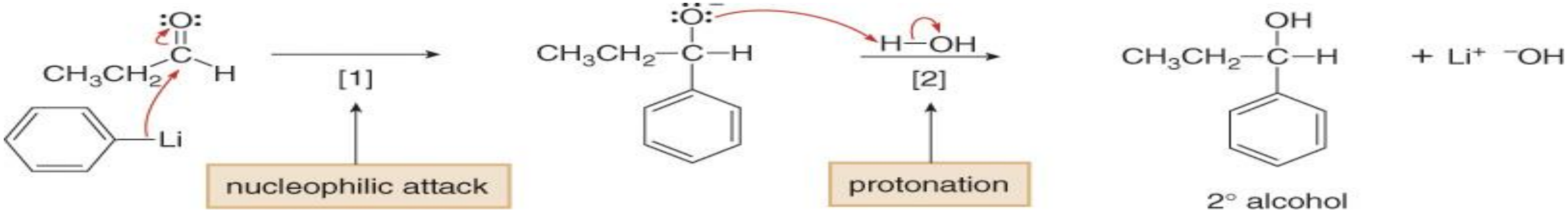


Nucleophilic Addition of H^- and R^-—A Review

Treatment of an aldehyde or ketone with either an organolithium (R"Li) or Grignard reagent (R"MgX) followed by water forms a 1^0, 2^0, or 3^0 alcohol containing a new C—C bond. In these reactions, $R"^-$ is the nucleophile.



Nucleophilic addition occurs via a two-step mechanism.



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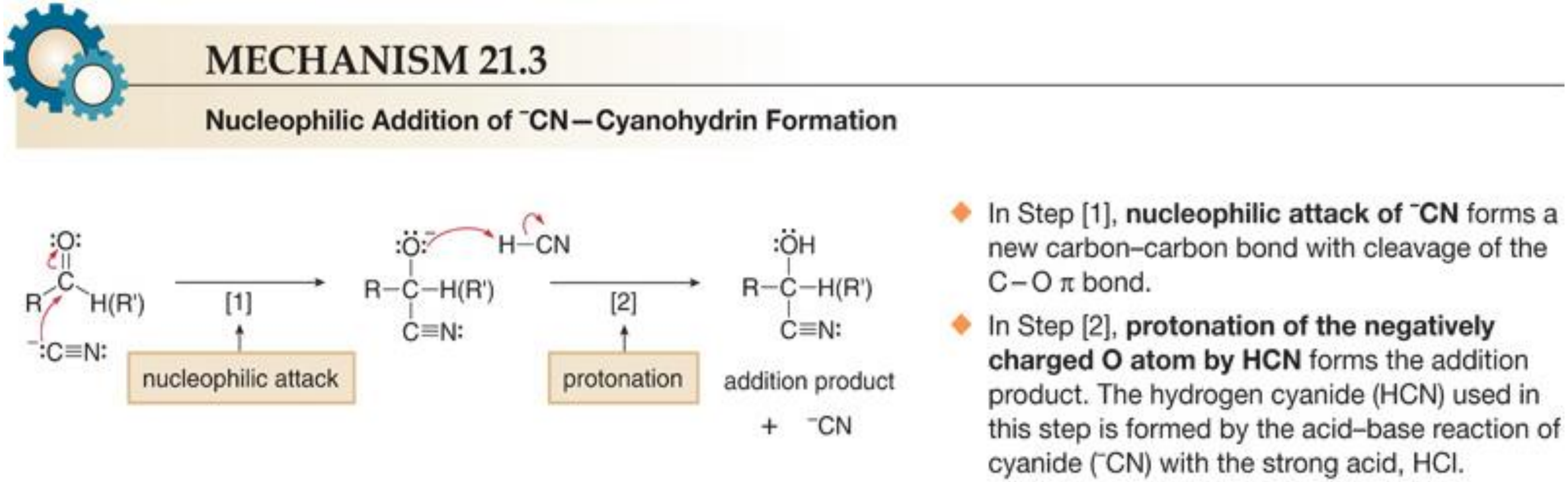
Nucleophilic Addition of $^{-}$CN

- Treatment of an aldehyde or ketone with NaCN and a strong acid such as HCl adds the elements of HCN across the C—O π bond, forming a cyanohydrin.
- The mechanism involves the usual two steps of nucleophilic addition—nucleophilic attack followed by protonation.



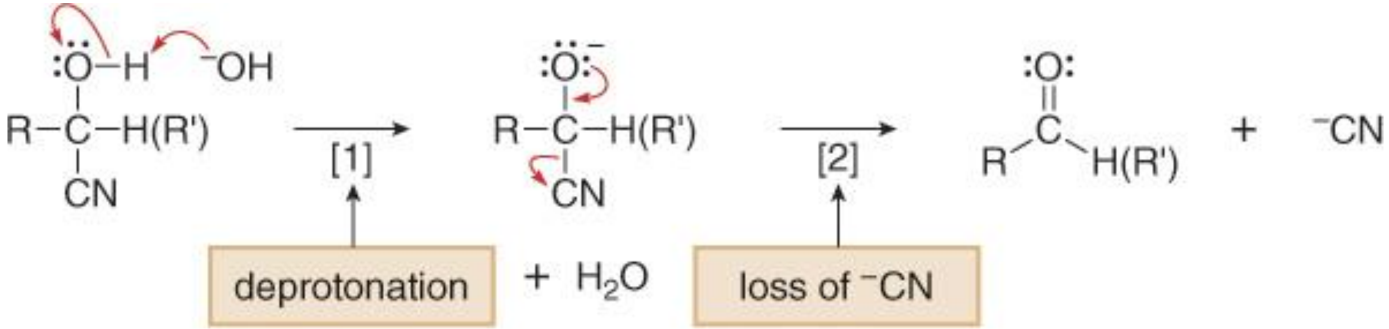
MECHANISM 21.3

Nucleophilic Addition of $^{-}$CN—Cyanohydrin Formation

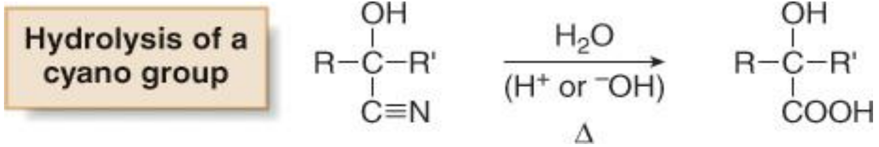
- In Step [1], **nucleophilic attack of $^{-}$CN** forms a new carbon–carbon bond with cleavage of the C–O π bond.
- In Step [2], **protonation of the negatively charged O atom by HCN** forms the addition product. The hydrogen cyanide (HCN) used in this step is formed by the acid–base reaction of cyanide ($^{-}$CN) with the strong acid, HCl.

Nucleophilic Addition of ^{-}CN

- **Cyanohydrins can be reconverted to carbonyl compounds by treatment with base.**
- **This process is just the reverse of the addition of HCN: deprotonation followed by elimination of ^{-}CN.**

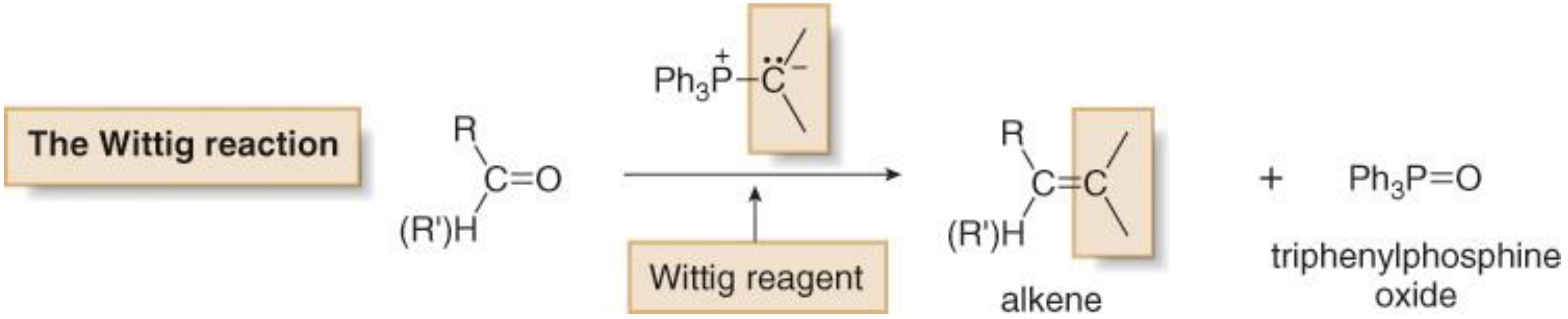


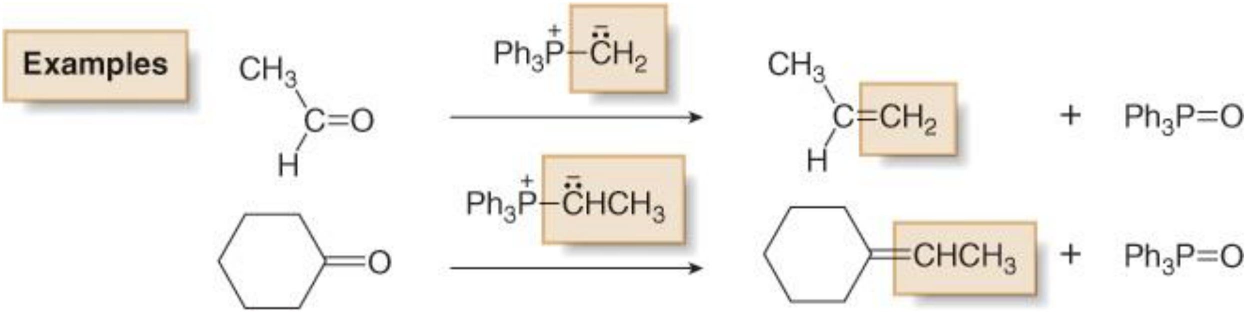
- **The cyano group of a cyanohydrin is readily hydrolyzed to a carboxy group by heating with aqueous acid or base.**



The Wittig Reaction

- **The Wittig reaction uses a carbon nucleophile (the Wittig reagent) to form alkenes—the carbonyl group is converted to a C=C.**





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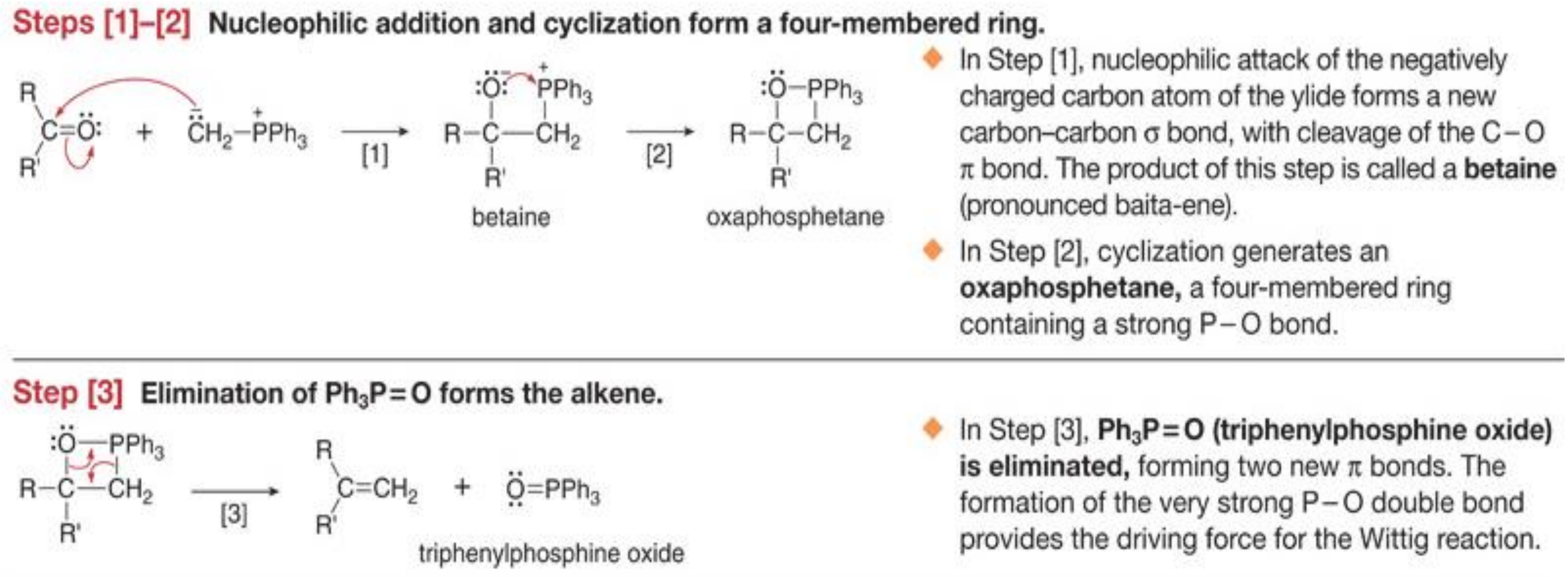
The Wittig Reaction

Wittig reactions occur by an addition-elimination sequence that involves three steps.



Steps [1]–[2] Nucleophilic addition and cyclization form a four-membered ring.

- In Step [1], nucleophilic attack of the negatively charged carbon atom of the ylide forms a new carbon–carbon σ bond, with cleavage of the C–O π bond. The product of this step is called a **betaine** (pronounced baita-ene).
- In Step [2], cyclization generates an **oxaphosphetane,** a four-membered ring containing a strong P–O bond.

Step [3] Elimination of $Ph_3P{=}O$ forms the alkene.

- In Step [3], **$Ph_3P{=}O$ (triphenylphosphine oxide) is eliminated,** forming two new π bonds. The formation of the very strong P–O double bond provides the driving force for the Wittig reaction.

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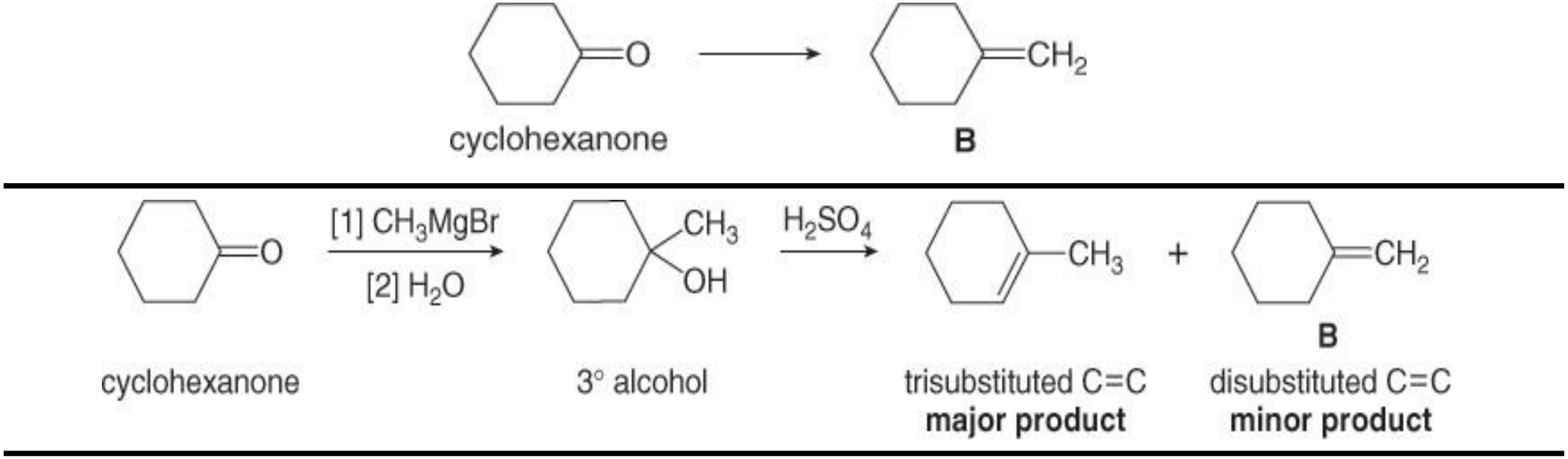
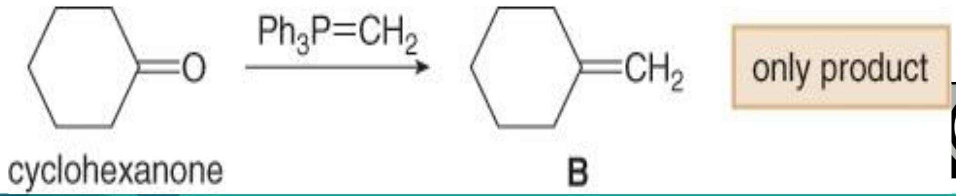
The Wittig Reaction

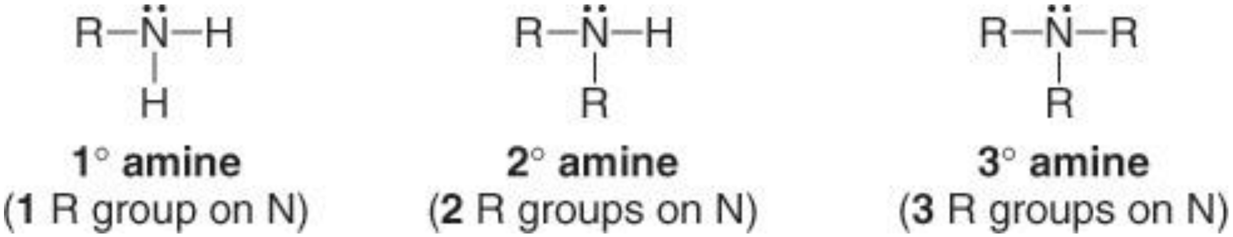
- An advantage of the Wittig reaction over elimination methods used to synthesize alkenes is that you always know the location of the double bond—the Wittig reaction always gives a single constitutional isomer.
- Consider the two methods that can be used to convert cyclohexanone into cycloalkene B.



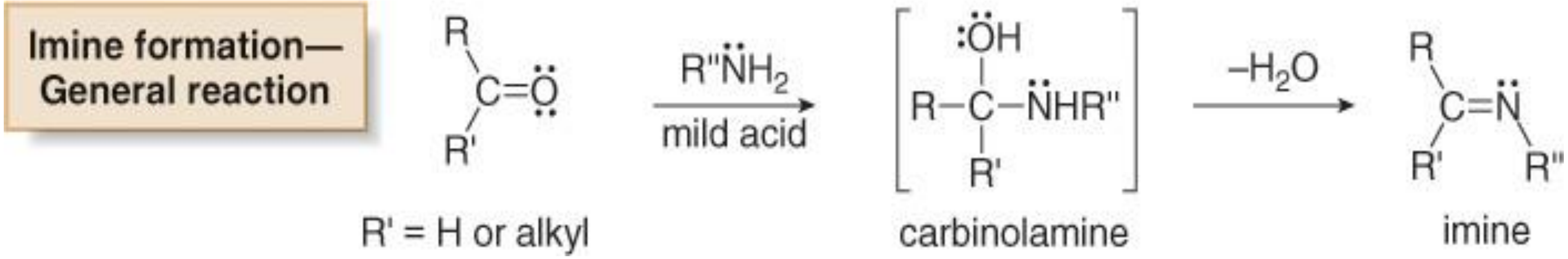


Addition of 1^0 Amines

- **Amines are classified as 1^0, 2^0, or 3^0 by the number of alkyl groups bonded to the nitrogen atom.**



- **Treatment of an aldehyde or a ketone with a 1^0 amine affords an imine (also called a Schiff base).**



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Conclusion of The Chapter

- Conclusion #1
  - The fundamental of aromatic compounds with its nomenclature were understandable.

- Conclusion #2
  - The fundamental of aromatic compounds included its reactions involves were practically explained.

- Conclusion #3
  - The fundamental of aromatic compounds reaction was practically shown in industrial application such as Wittig reaction.

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Co-author Information

Nurlin Abu Samah is an analytical chemistry lecturer since 2010 and currently she further her PhD study in Universitat Autonoma de Barcelona, Spain. She was graduated from Universiti Kebangsaan Malaysia for her Master of Science in Chemistry. During her undergraduate, she was studied in Universiti Sains Malaysia, Penang.

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