

Chapter 12. Alcohols from Carbonyl Compounds

Study Worksheet – CHE212

Section 12.1 – Read carefully. This is an important introduction.

- Be sure to ask questions if anything in this section is not clear.
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Section 12.2 – Defining oxidation and reduction

SKIP 12.2A and instead read this:

Technically, an atom is said to undergo oxidation if its formal charge increases; likewise, reduction is when its formal charge decreases. Formal charge increases when atoms that are more electronegative attach.

Since we focus on carbon in this course, we often speak of an “oxidation” or a “reduction” as if it was possible to have only one of these reactions in the absence of the other. THIS IS NOT TRUE. For every oxidation there is a reduction. If the organic molecule is oxidized we speak of the reagent used to perform this reaction as an oxidizing agent. The oxidizing agent is reduced. When the organic molecule is reduced we speak of the reagent used to perform this reaction as a reducing agent. The reducing agent is oxidized.

Here are some oxidizing agents we have previously discussed:

KMnO₄ OsO₄ NMO H₂O₂ mCPBA

The only reducing agent we have discussed so far is H₂. By the way, NaH is also a reducing agent but we have only discussed its role as a base up to now.

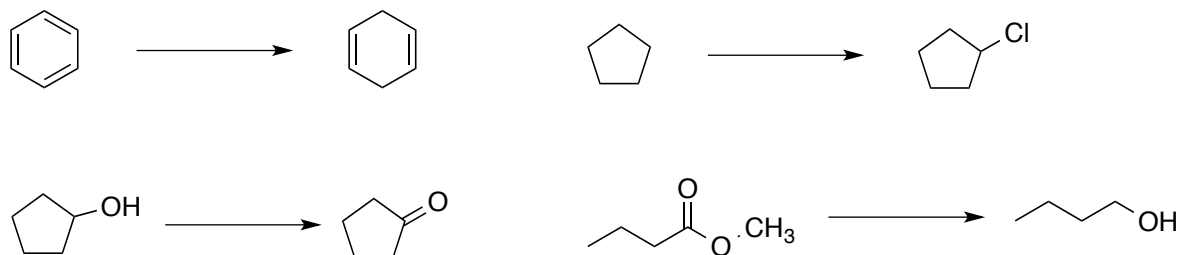
- Question: Show an example of a reaction that uses KMnO₄ and explain why we say the organic molecule it reacted with was oxidized. Remember to use charge on the carbon atom as your rule.

In general, whenever a carbon gains bonds to hydrogens – or loses bonds to O, N, or X – the carbon is said to be reduced. On the other hand, if a carbon gains a bond to an electronegative atom (O, N, or X) – or loses bonds to H – we say that the carbon has been oxidized.

The general symbol used over an arrow in a chemical reaction to show that a process is an oxidation or a reduction is [O] or [H].

- Question: Why [O] or [H] rather than [O] or [R]?

- Question: Write [O] or [H] over the arrows to describe these reactions. (Don't worry about how these reactions are performed; just categorize them)



Section 12.3 – Important section!

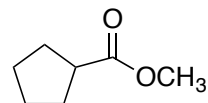
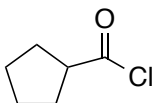
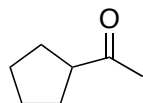
New factoid – We have learned in the first half of the course that when a carbocation forms in a mechanism, the next step will always be a rearrangement, if one can occur to make the molecule more stable. Always so.

With the reaction of a carbonyl there is a new important fact to remember. When a nucleophile breaks the π bond of carbonyl, the next step will always be to reform the π bond by eliminating a leaving group from the carbon. For the purposes of this step, any group can be made to leave *except* an H atom or an R group.

- Question: What is the nucleophilic specie in each of these reducing agents:



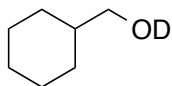
- Question: Demonstrate this new factoid by showing the mechanism that would occur when hydride, $\text{H}^{(-)}$, reacts with each of the following molecules. Use curved-arrow notation.



- Question: What is T₂O? What is D₂O?

- Question: Do Practice Problem 12.3

- Question: Repeat Practice Problem 12.3e to give the following product.



- Add these facts to your reaction database:

1° alcohol => aldehyde
1° alcohol => carboxylic acid
1° alcohol => carboxylic ester
2° alcohol => ketone
alkane => alkyl halide

Section 12.4 – Skip the mechanism for these reactions. You will not need to know them.

- Skip Sections 12.4A and 12.4B
- Be sure to carefully read 12.4C, D, and E.
- Question: Do Practice Problem 12.5
- Add these facts to your reaction database:

ketone => 2° alcohol
aldehyde => 1° alcohol
carboxylic acid => 1° alcohol

• Create a table that clearly shows what the following oxidizing and reducing reagents can do. For each reagent, state whether it is an oxidizing or a reducing agent and then include all of the retrosynthetic facts that pertain to the reagent. Be specific. For example, instead of “alcohol” you would say “1° alcohol” in your fact.

KMnO₄

PCC/CH₂Cl₂

H₂CrO₄

NaBH₄

LiAlH₄

Sections 12.5 and 12.6

- Read carefully!
- Question: Which type of alkyl halide makes the best choice in the formation of Grignard reagent? Which is the least useful?
- Question: Using reactions from this chapter as well as from the previous chapter, show how 1-hexanol can be converted into a Grignard reagent. (Summary reactions, not mechanisms)

Section 12.7 – The Grignard Synthesis – VERY IMPORTANT

- Do a Google search of Victor Grignard. When and where did he do his work? Any other interesting facts about him?
- Section 12.7A – This is never a desired reaction unless one is trying to place a D or T atom on a carbon. Do Practice Problem 12.7
- Section 12.7B – 1° alcohol => Grignard reagent & epoxide
- Section 12.7C – Carefully study the mechanism
- Question: With a Grignard reagent, R-MgX, what is the apparent nucleophile?
- Question: Look at the mechanism on page 561 and explain what would be different if a carboxylic ester had been used instead of a ketone. Write the mechanism out.

Hint: Remember our new mechanism fact about mechanisms that involve a nucleophile attacking a carbonyl.

Section 12.8 – IMPORTANT!

Read Section 12.8A carefully!

- Add these facts to your reaction database

Grignard reagent => alkyl halide (include exceptions)

1° alcohol => Grignard reagent & formaldehyde – Boring fact.

2° alcohol => Grignard reagent & aldehyde (except formaldehyde)

3° alcohol => Grignard reagent & ketone

3° alcohol => Grignard reagent & carboxylic ester

- Do Practice Problems 12.9 and 12.10
- Section 12.8B – the book makes this too complicated.

Here's the easy fact; it is not possible to prepare a Grignard reagent from an alkyl halide if the alkyl halide contains any of these groups:

carbonyl moiety, epoxide, nitrile or anything with a $K_a > 10^{-30}$
(YAY! The Chap 3 table comes to the rescue again!)

SKIP Section 12.9

END OF CHAPTER PROBLEMS

12.11, 12.12, 12.14, 12.16, 12.21, 12.22, 12.24, 12.28

Good review problem: 12.30