Cornell University

Alcohol Oxidations

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OCSP Lecture #15

Lecture 15 Learning Objectives

- Assigning Oxidation Numbers (3 Steps)
- Alcohol Oxidation Reactions
  - Classifying Alcohols (Primary, Secondary, and Tertiary Alcohols)
  - Primary Alcohol Oxidation
    - “Weak” Oxidants
    - “Strong” Oxidants
  - Secondary Alcohol Oxidation
  - Tertiary Alcohol Oxidation

What is Oxidation and Reduction?

We are now moving into reactions in which one species is reduced and the other is oxidized. The fastest way to determine whether a species is being reduced or oxidized is using oxidation numbers for the product and the reactants.

Assigning Oxidation Numbers (Step 1)

Step 1: Assign oxidation level to each carbon that changes (from reactant → product)

- For every bond from carbon to a less electronegative atom, and for every negative charge on carbon, assign a "-1"
- For every bond from carbon to another carbon atom and for every unpaired electron on the carbon, assign a "0"
- For every bond from carbon to a more electronegative atom, and for every positive charge on the carbon, assign a "+1"
- Add all the above numbers to obtain the oxidation level of the specific carbon

Assigning Oxidation Numbers (Step 2)

Step 2: Determine the oxidation number (N_{ox}) of reactants and products by adding within each compound the oxidation numbers of all carbon considered in Step 1 (only consider carbons that undergo a change in the reaction)

Assigning Oxidation Numbers (Step 3)

Step 3: Compute the difference $N_{ox\ (products)}$ -$N_{ox\ (reactants)}$ to determine whether the transformation is an oxidation, reduction, or neither.

- Difference = positive number (oxidation)
- Difference = negative number (reduction)
- Difference = 0 (neither)

Putting it all together…

Ex. What type of reaction is this (oxidation, reduction, or neither)?

Practice Problems: Assigning Oxidation Numbers

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Note: this is a "formalism/bookkeeping" so the charge on the carbon isn't real. The oxidation state formalism is a way to help us keep track of where electrons are going (which will come in handy for our next reactions... alcohol oxidations!)

Alcohol Oxidation Reactions: Classifying Alcohols

What are alcohols? : compounds in which one or more hydrogen atoms in an alkane have been replaced by an OH group. Alcohols fall into three different classes depending on how the OH group is positioned on the chain of carbon atoms

- 1° (Primary) Alcohols: the carbon atom that carries the OH group is only attached to one alkyl group

Note: methanol is the exception to this rule (it is classified as a primary alcohol despite not having alkyl groups)

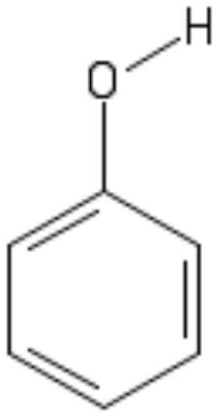
Alcohol Oxidation Reactions: Classifying Alcohols

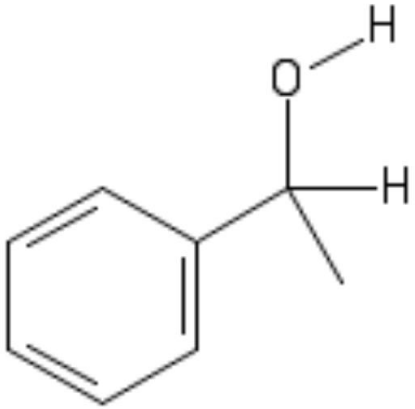
- 2° (Secondary) Alcohols: the carbon atom that carries the OH group is joined directly to two alkyl groups

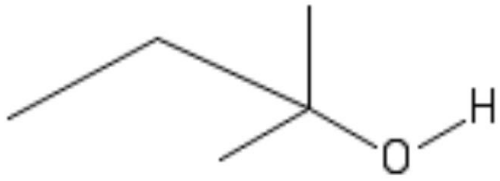
- 3° (Tertiary) Alcohols: the carbon atom that carries the OH group is attached to three alkyl groups

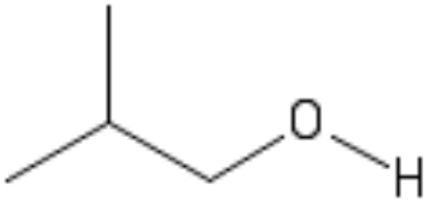
Practice Problems: Classifying Alcohols

- Classify the following alcohols (1°, 2°, 3°):

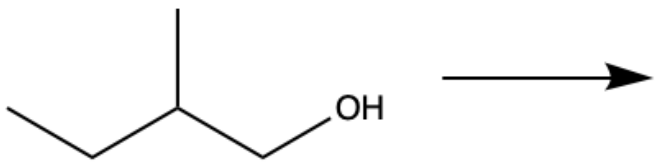








Reactions of Primary Alcohols



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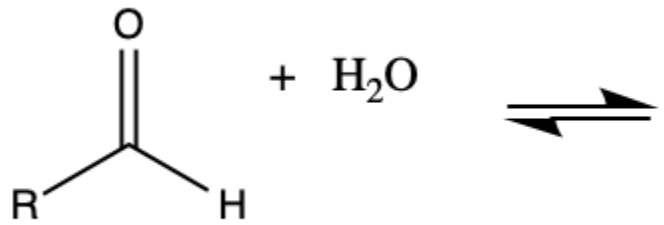


Reactions of Primary Alcohols

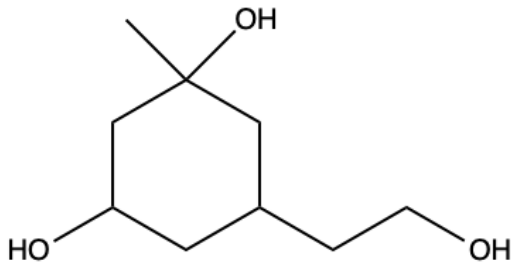
Reactions of Secondary & Tertiary Alcohols

- Reactions of Secondary alcohols: secondary alcohols are oxidized to a ketone in either $K_2Cr_2O_7$ (or other Cr(VI) reagents) in aqueous acid or PCC.

- Reactions of Tertiary Alcohols: tertiary alcohols can't be oxidized under these normal conditions because they lack the alpha C-H bonds that must be broken in the mechanisms.

Example Problems

Treat the compound shown below with the following reagents.



1) $\xrightarrow[2.\ H_3O^+]{1.\ KMnO_4,\ NaOH,\ rt.}$

2) $\xrightarrow[CH_2Cl_2\ (solvent)]{DMP}$

3) $\xrightarrow[H_3O^+/H_2O]{CrO_3}$

4) $\xrightarrow[H_2SO_4]{Na_2Cr_2O_7}$

Practice Problems

Find the product of the following reactions.