Objective 2: Identify and understand an organic oxidation and reduction reactions.

Quiz Practice problems

Key ideas:

In Chem 1A/B, we learned oxidation is the loss of electrons, reduction is the gain of electrons.

In Organic chemistry, think of oxidation as the gain of O or loss of H or both and reduction as the loss of O or gain of H or both.

Skills:

Given reactants and products, identify the reaction as an oxidation or reduction. Identify the carbon at which the oxidation or reduction occurs. Determine the number of O or H gained/lost.

1. Identify each reaction as an oxidation or reduction. Identify the carbon at which oxidation or reduction occurs. How many O's are gained/lost? How many H's are gained/lost?

Note: treat a C=O bond as a C bonded to two O's when counting O's.



g. Benedict's reagent is a test for glucose in urine (diabetes). The first reactant is the reducing sugar. Is the reducing sugar oxidized or reduced?



Answers:

Treat a C=O bond as a C bonded to two O's when counting O's.

a. reduction. Carbon 2 (C bonded to O). Reactant (ketone) has 2 O's and 0 H's bonded to C. Product (alcohol) has 1 O and 1 H. So 1 O lost and 1 H gained ==> reduction.

b. oxidation. Carbon 1 (C bonded to O). Reactant (alcohol) has 1 O's and 2 H's bonded to C. Product (acid) has 3 O and 0 H. So 2 O gained and 2 H lost ==> oxidation.

c. reduction. Carbon 1 and Carbon 2. Reactant (alkyne) has 1 H bonded to C-1 and 0 H bonded to C-2. Product (alkane) has 3 H bonded to C-1 and 2 H bonded to C-2. So 4 H gained ==> reduction.

d. oxidation. N and C bonded to N. Reactant (amine) has 2 H bonded to N and 2 H bonded to C. Product (nitrile) has 0 H bonded to N and 0 H bonded to C. So 4 H lost ==> oxidation.

e. reduction. Carbon 4 and Carbon 5. Reactant (alkene) has 1 H bonded to C-4 and 1 H bonded to C-5. Product (alkane) has 2 H bonded to C-4 and 2 H bonded to C-5. So 2 H gained ==> reduction.

f. reduction. Carbon 1 (C bonded to O). Reactant (aldehyde) has 2 O and 1 H bonded to C. Product (alcohol) has 1 O and 2 H. So 1 O lost and 1 H gained ==> reduction.

g. oxidation. Carbon 1 (C bonded to O). Reactant (aldehyde) has 2 O and 1 H bonded to C. Product (acid) has 3 O and 0 H. So 1 O gained and 1 H lost ==> oxidation.

2. Ethanol is treated with KMnO₄. The product is:

(a) ethylene (b) acetaldehyde (c) acetic acid

Identify the reagent type. Draw the structures of the reactant and product. State the number of O's and H's gained or lost. Answers:

Ethanol is treated with $KMnO_4$ to produce acetic acid. Oxidation reaction.

See C bonded to O in ethanol. 2 O's gained and 2 H's lost.

3. Ethanol is treated with PCC. The product is:

(a) ethylene (b) acetaldehyde (c) acetic acid Identify the reagent type. Draw the structures of the reactant and product. State the number of O's and H's gained or lost. Answers:

Ethanol is treated with PCC to produce acetaldehyde. Oxidation reaction.

See C bonded to O in ethanol. 1 O's gained and 1 H lost.

4. Isopropanol is treated with bleach. The product is:

(a) ethylene (b) acetaldehyde (c) acetone

Identify the reagent type. Draw the structures of the reactant and product. State the number of O's and H's gained or lost. Answers:

Isopropanol is treated with bleach to produce acetone. Oxidation reaction.

O^{-H} bleach

See C bonded to O in Isopropanol. 1 O's gained and 1 H lost.

5. What reagent type would you use to make these reactions go in the reverse direction? Answers:

Use a reducing agent, e.g., NaBH₄.

6. The reaction below is similar to a reaction in cellular respiration.

a. Is this an oxidation or reduction reaction? What C is involved in the redox?



b. Would you use NAD⁺ or NADH in this reaction? Answers:

- a. Oxidation reaction.
- b. Oxidizing agent = NAD^+ .

7. Grignard reaction:

a. In the most common Grignard reaction, a Grignard reagent (RMgX) reacts with an aldehyde or ketone to form an alcohol and a new C-C bond (makes a bigger molecule).

The Grignard reagent is made by reacting Mg metal with an alkyl halide (RX) to form RMgX.

E.g., CH₃Br + Mg --> CH₃MgBr

(i) CH₃MgBr has a C-Mg bond. Carbon is more electronegative than Mg so this makes the C behave like a _____. You can look at CH₃MgBr as (CH₃)(MgBr⁺) to help remind you the C behaves like a _____.

RMgX reacts at the carbonyl carbon (carbon bonded to oxygen in a double bond (C=O)). The carbonyl carbon is less electronegative than O so this makes the C behave like a _____.



as $(CH_3)(MgBr^+)$

intermediate

+ MgBr⁺

A C-C bond forms when the nucleophilic C in the Grignard reagent reacts with the electrophilic C in the ketone. (ii) Circle the C-C bond that forms in the tetrahedral intermediate.

(iii) Box the carbon in the tetrahedral intermediate that was the carbonyl carbon.

NOTE 1: (ii) and (iii) will help you when you want to make an alcohol using the Grignard reaction and want to figure out the aldehyde or ketone to start with. See Question 7d.)

(iv) How is the $(CH_3)_3CO^2$ ion converted to an alcohol? What reagent could you use?

NOTE 2: The Grignard reagent is a nucleophile so it can react with any electrophile besides the carbonyl C in an aldehyde or ketone.

NOTE 3. The Grignard reaction is a type of nucleophilic addition reaction. We will look at this reaction type later in Chem 12B.

(v) In a Grignard reaction, you don't want any water to be present. Why?

b. Ethyl magnesium bromide reacts with acetone to form 2-methyl-2-butanol. Draw the tetrahedral intermediate that forms. Use curved arrows to show bonds breaking and forming.

Water is added to the intermediate. Draw the structure of the alcohol that is produced.

c. Phenyl magnesium bromide reacts with $R_2C=O$. Is the alcohol that forms a 1°, 2°, or 3° alcohol? Use curved arrows to show bonds breaking and forming. Note: this reaction is similar to the reaction that makes the precursor to the breast cancer drug Tamoxifen.

d. Propose a synthesis of each alcohol. There are at least two ways to make each alcohol. <u>Hint</u>: identify carbon that comes from the carbonyl carbon that reacts with the Grignard reagent. Identify the bond that forms when the carbonyl carbon reacts with the Grignard reagent.





Answers:

a. The Grignard reagent is made by reacting Mg metal with an alkyl halide (RX) to form RMgX.

E.g., $CH_3Br + Mg --> CH_3MgBr$

(i) CH_3MgBr has a C-Mg bond. Carbon is more electronegative than Mg so this makes the C behave like a nucleophile. You can look at CH_3MgBr as $(CH_3)(MgBr^{+})$ to help remind you the C behaves like a nucleophile.

RMgX reacts at the carbonyl carbon (carbon bonded to oxygen in a double bond (C=O)). The carbonyl carbon is less electronegative than O so this makes the C behave like a electrophile.



A C-C bond forms when the nucleophilic C in the Grignard reagent reacts with the electrophilic C in the ketone. (ii) and (iii).



tetrahedral internediate (iv) Use an acid, e.g., HCI, to convert (CH₃)₃CO⁻ ion to an alcohol? (v) Water reacts with a Grignard reaction. b.



c. A 3° alcohol forms.







