Lecture Note 8 – Fundamental Organic Chemistry 2

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[Pre-Reading]: Organic Chemistry with a Biological Emphasis Volume I (open textbook) by Tim Soderberg, University of Minnesota, Morris

[Learning Objectives]

- 1. Oxidation of alcohols and aldehydes
- 1.1 Primary, secondary, tertiary alcohols



1.2 Oxidation of alcohols – break ______ and _____ bonds, form C–O (<u>pi</u> bond) on the same carbon.



[USNCO Example – *L2017-Q57*]

Which compound reacts readily with Cr(VI) reagents?



1.3 Oxidation of aldehydes and tests for aldehydes

 \circ Strong oxidants – KMnO₄ and K₂Cr₂O₇

Example: Jones Oxidation





What is the color change? *Balance the above reaction.

How about ketone? Does it have the similar reaction, why or why not?

• Weak oxidant - Tollens' test (silver mirror)

Tollens' reagent is a chemical reagent used to determine the presence of an **aldehyde**, aromatic aldehyde and ^{*}alpha-hydroxy ketone functional groups. The reagent consists of a solution of silver nitrate and ammonia to form a complex ______. [*What's the color of the complex?]

Tollens' reagent is indicated by the precipitation of elemental silver, often producing a characteristic "silver mirror" on the inner surface of the reaction vessel.

 $2[Ag(NH_3)_2]^+ + RCHO + H_2O \rightarrow 2Ag(s) + 4NH_4^+ + _$

Which of the following will give a negative Tollens' test? A. acetaldehyde B. formic acid C. ethyl formate D. acetone E. *glucose [CH₂OH(CHOH)₄CHO]



• Weak oxidant - Fehling's Test

Fehling's solution is a chemical reagent used to differentiate between water-soluble carbohydrate and ketone functional groups, and as a test for *reducing sugars* and *non-reducing sugars*, supplementary to the Tollens' reagent test.

The *deep blue* active ingredient in Fehling's solution is the bis(tartrate) complex of Cu^{2+} . The tartrate tetraanions serve as bidentate alkoxide ligands.



How to tell a sugar is reducing or non-reducing based on the observation? The brick _____ precipitate produced in the test is copper(I) oxide, _____. Write down the equation of the reaction.

Summary



In each case the aldehyde has been oxidized to a carboxylic acid and the metal salt (Cu^{2*} or Ag*) has been reduced.

2. Nucleophilic substitutions

Nucleophile and Nucleophilic substitution

A *nucleophile* is a chemical species that ______ an electron pair to form a chemical bond in relation to a reaction. All molecules or ions with a *free pair of electrons* or at least *one pi bond* can act as nucleophiles. Because nucleophiles donate electrons, they are by definition Lewis _____.

The most general form of the reaction may be given as the following:

Nu:
$$+ R-LG \rightarrow R-Nu + LG$$
:

The electron pair (:) from the nucleophile (Nu) attacks the substrate (R–LG) forming a new bond, while the leaving group (LG) departs with an electron pair. The principal product in this case is R–Nu. The nucleophile may be electrically neutral or negatively charged, whereas the substrate is typically neutral or positively charged.



An example of nucleophilic substitution is the hydrolysis of an alkyl bromide, R-Br, under basic conditions, where the attacking nucleophile is the OH⁻ and the leaving group is Br⁻.

$$R-Br + OH^{-} \rightarrow R-OH + Br^{-}$$

	S _N 1 (molecular)	S _N 2 (molecular)
mechanism	$\begin{array}{c} X \\ Y \\ Y \\ Z \end{array} \begin{array}{c} X \\ Z \end{array} \begin{array}{c} V \\ S \\ Z \end{array} \begin{array}{c} V \\ S \\ V \\ Y \end{array} \begin{array}{c} V \\ C \\ Y \\ Z \end{array} \begin{array}{c} V \\ C \\ Y \\ Z \end{array} \begin{array}{c} V \\ T \\ T \\ T \\ T \end{array} \begin{array}{c} V \\ T \\$	$\begin{array}{c} H_{3}C \\ H_{H} \\ H \\ H \\ H \end{array} \xrightarrow{C - CI} +Br \\ H \\ $
analogue		
*energy profile		
rate law		
substrate	Tertiary > secondary >> primary > methyl $C_{R} \rightarrow R$ Fast $R \rightarrow R^{+} C_{I}^{\odot}$ Tertiary carbocation: most stable $C_{R} \rightarrow R$ Slow $R \rightarrow R^{+} C_{I}^{\odot}$ Secondary carbocation $C_{R} \rightarrow R$ $R \rightarrow R^{+} C_{I}^{\odot}$ Secondary carbocation $C_{R} \rightarrow R^{+} \rightarrow R^{+} C_{I}^{\odot}$ Secondary carbocation: least stable (methyl carbocations are even more unstable)	Nu: HHA R Nu: HA R Nu: R R Nu: R HA R Nu: R R A R A R A R A R A R A A R A A R A A R A A A R A A A A A A A A A A A A A
*big barrier	Carbocation stability	Steric hindrence

*Summary and Comparison

[USNCO Example – *L2017-Q56*]

What is the role of hydroxide ion in the reaction below?

$\mathrm{CH_3CH_2CH_2CH_2Br} + \mathrm{OH^-} \rightarrow \mathrm{CH_3CH_2CH_2CH_2OH} + \mathrm{Br^-}$

- (A) Oxidizing agent (B) Lewis acid
- (C) Catalyst (D) Nucleophile



[*USNCO Example – *N2016P1-Q55*]

Which alkyl halide reacts most rapidly with aqueous sodium hydroxide solution?

(A)	CH ₃ Cl	(B)	CH ₃ I
(C)	(CH ₃) ₃ CCH ₂ Cl	(D)	(CH ₃) ₃ CCH ₂ I

3. Aromatic substitutions

3.1 Aromaticity – benzene vs alkene

Hydrogenation: more difficult with aromatic compounds



How would like to describe the stability of benzene?

*What is the observation if benzene(l) is added to bromine water with swirl?

3.2 An introduction to resonance energy and aromaticity

Hydrogenation of alkenes liberates 119 kJ/mol of energy

 $\frac{Pd/C}{H_2}$

 $\Delta H = -119 \text{ kJ/mol} (28.4 \text{ kcal/mol})$

We would expect hydrogenation of benzene to liberate 3 × 119 = 357 kJ/mol.



 $\Delta H = -207 \text{ kJ/mol} (49 \text{ kcal/mol})$

We would expect hydrogenation of benzene to liberate _____ kJ/mol if all of the C=C bonds are independent. The extra stability of benzene is called the "*resonance energy*", which is _____ kJ/mol. Benzene has a particularly large resonance energy, which leads us to classify it as "*aromatic*".



3.3 4*n* + 2 rule

A cyclic ring molecule that follows Hückel's rule when the number of its π -electrons equals 4n + 2 where *n* is a non-negative integer, is aromatic, and more stable than theoretically predicted using hydrogenation data of simple alkenes.

*Figure out which of the following are aromatic.



[USNCO Examples – L2019-Q59]

Which compound is NOT considered aromatic?



[*USNCO Examples – N2015P1-Q57]

Which of the following is a difference between benzene and cyclooctatetraene?

- (A) Benzene reacts rapidly with bromine and cyclooctatetraene does not.
- (B) Benzene contains sp^2 -hybridized carbon atoms and cyclooctatetraene does not.
- (C) Benzene has the formula C_nH_n and cyclooctatetraene does not.
- (D) Benzene is planar and cyclooctatetraene is not.

3.4 Mechanism of electrophilic aromatic substitutions



Substituents that stabilize this carbocation (relative to H) are called activating groups.

*What is the *similarity* and *difference* between this mechanism with that of the electrophilic addition of alkenes?

How to interpret the name of reaction, electrophilic aromatic substitution?





3.5 Summary of electrophilic aromatic substitutions

[USNCO Example – *L2019-Q58*]

What is the maximum number of monosubstitution products of the aromatic substitution reaction shown?



4. Polymerization

Addition vs Condensation





polymerization			polymerization	
0	It is formed by reaction of large	0	It is formed by the combination of large number	
	number of having double bond		of monomers having multifunctional groups to	
	without any loss of small molecules.		form polymers with loss of small molecules like	
0	It is chain growth polymerization, e. g. polythene		H ₂ O, NH ₃ , etc.	
		0	It is step growth polymerization, e.g. Nylon-6,6	

[Practice Example] Draw the structures of the polypropylene and polystyrene following the example.



Examples of condensation polymers - polyamide



Biopolymers and their hydrolysis

Biopolymers are natural polymers produced by the cells of living organisms. There are three main classes of biopolymers, classified according to the monomers used and the structure of the biopolymer formed: *polynucleotides*, *polypeptides*, and *polysaccharides*.

Polynucleotides, such as ______ and _____, are long polymers composed of 13 or more nucleotide monomers. Polypeptides and proteins are polymers of ______, and some major examples include collagen, actin, and fibrin. Peptides links are ______ bonds.

Polysaccharides are linear or branched polymeric carbohydrates and examples include _____, ____, glycogen, and alginate. Other examples of biopolymers include *natural rubbers* (polymers of isoprene _____).





