235 – Organic II
Final Exam Review

REATIONS OF CONJUGATED DIENES:
Just like alkenes, conjugated dienes undergo the
ionic addition of HBr; however, the addition to
congjugated dienes proceeds by two pathways.

REATIONS OF CONJUGATED DIENES:
In the 1,4-addition, protonation on the terminal
carbon generates the allylic carbocation, with
cationic character on both carbons #1 and #3.

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1,2 vs 1,4 ADDITION REATIONS OF CONJUGATED DIENES
For 1,2 and 1,4-additions the following trends are
observed:
- The 1,2-addition product forms rapidly at low
temperatures.
- The 1,4-addition product is predominant at higher
temperatures.
- Even at low temperatures, 1,4-addition products
will predominate if given enough time.
- The addition of HBr to butadiene is reversible and
isolated 1,2-addition product will convert to the
1,4-product at higher temperatures or at longer
times.

REATIONS OF CONJUGATED DIENES:
The two products are also referred to as the kinetic
product; and the thermodynamic product.

The addition of Br⁻ to carbon #1 of the diene
gives the 1,4-addition product.

Kinetic product (faster).

Thermodynamic product (slower, but more stable).
**In-Class Problem**

Predict the major products for the following reactions:

1. \( \text{HBr} + \text{1,2-addition} \)
2. \( \text{HBr} + \text{1,2-addition} \)
3. \( \text{HBr} + \text{1,2-addition} \)
4. \( \text{HBr} + \text{1,2-addition} \)

**Reactions of Conjugated Dienes**

The Diels-Alder reaction; **4 + 2 Cycloadditions**.

[Diagram showing Diels-Alder reaction with a diene and a dienophile forming a cyclic product.]

This is called an electrocyclic reaction.

**Reactions of Conjugated Dienes**

The Diels-Alder reaction; **4 + 2 Cycloadditions**.

[Diagram showing Diels-Alder reaction producing a cyclic product from a diene and a dienophile.]

**The (4n + 2) Rule**

The resonance description of benzene will explain the geometry of the molecule and the isomer distribution of benzene derivatives, but does not explain the unusual stability of benzene and its derivatives.

The stability of benzene is suggested to arise from the fact that the conjugated \( n \) system is planar and contains \( 4n + 2 \) electrons (with \( n = 1 \)), and it is suggested that all compounds having planar, conjugated \( n \) systems containing \( 4n + 2 \) electrons will share this stability. This property, described originally by Hückel, is referred to as aromaticity.

Consider the following molecules:

- 4 \( \pi \) electrons **not aromatic**
- 6 \( \pi \) electrons **aromatic**
- 8 \( \pi \) electrons **not aromatic**

**The (4n + 2) Rule**

Consider the following molecules:

- 6 \( \pi \) electrons **aromatic**
- 6 \( \pi \) electrons **aromatic**
### REACTIONS OF AROMATIC SIDE-CHAINS

**Oxidation with neutral MnO₄⁻**

- \( \text{CH}_3 \)
- \( \text{CH}_3 \text{CH}_2 \text{CH}_3 \)
- \( \text{MnO}_4^-/\text{H}_2\text{O, heat} \)

**Allylic bromination with NBS**

- \( \text{CH}_3 \)
- \( \text{CH}_3 \text{CH}_2 \text{CH}_3 \)
- \( \text{NBS/CCl}_4 \) (radical initiator)

**Dissolving Metal Reduction of Benzene Derivatives**

- The Birch Reduction

- \( \text{Li/NH}_3 \)

**Electrophilic Aromatic Substitution**

- Halogenation
- Acylation
- Nitrilation
- Sulfonation
- Alkylation

**Predict the products of the following reactions**

- NBS/CCl₄ (radical initiator)
- MnO₄⁻/H₂O
- Li/NH₃
1. Reaction limited to alkyl halides; aryl or vinyl halides do not react.
2. Reaction does not occur on rings containing strong electron withdrawing substituents.
3. Multiple substitutions often occur.
4. Carbobation rearrangements can occur, particularly with 1° alkyl halides.
1. Multiple substitutions do not occur.
2. Carbocation rearrangements do not occur.
3. Reaction does not occur on rings containing strong electron withdrawing substituents.
4. Acid anhydrides can also be used.

Reactions that yield alcohols:

1. BH₄⁻
2. H₂O³⁻
Reactions that yield alcohols:

1. LiAlH₄, ether
2. H₂O³⁻

from a carboxylic acid

1. Mg, ether
2. H₂O³⁻

from an ester

Suggest two syntheses for the molecule shown below, using a Grignard Reaction.

Utilizing any one of the starting materials shown on the right, suggest a synthesis of the following compound:
**In-Class Problem**

Predict the products for the following substitution reactions.

\[ \text{CH}_2\text{Br} \xrightarrow{\text{CH}_2\text{OH}} \text{CH}_2\text{OH} \]

\[ \text{CH}_2\text{Br} \xrightarrow{\text{H}_2\text{O}} \text{CH}_2\text{OH} \]

H\text{C}\text{C}\text{CH}_2\text{O}_\text{Tos} \xrightarrow{1.\text{MgBr, ether}} \text{CH}_2\text{O}_\text{Tos} \xrightarrow{2.\text{H}_2\text{O}} \text{H}_2\text{O} \]

**In-Class Problem**

Predict the products for the following reactions of epoxides.

\[ \text{CH}_2\text{CH}_3 \xrightarrow{1.\text{MgBr, ether}} \text{CH}_2\text{CH}_3 \]

\[ \xrightarrow{2.\text{H}_2\text{O}} \]

\[ \text{CH}_2\text{CH}_3 \xrightarrow{1.\text{CH}_3\text{COOH}} \text{CH}_2\text{CH}_3 \]

\[ \xrightarrow{2.\text{H}_2\text{O}} \]

**In-Class Problem**

Beginning with benzyl bromide, suggest a synthesis of the compound shown below:

\[ \text{CH}_2\text{Br} \xrightarrow{?} \text{CH}_3\text{CH}_2\text{O}\text{CH}_3 \]

**In-Class Problem**

Beginning with benzyl bromide, suggest a synthesis of the compound shown below:

\[ \text{CH}_2\text{Br} \xrightarrow{?} \text{CH}_3\text{CH}_2\text{O}\text{CH}_3 \]

**Carbonyl Condensation Reactions**

The base-catalyzed condensation of two aldehydes or ketones to form a β-hydroxy aldehyde or ketone is known as the **Aldol Condensation**.

\[ 2\text{CH}_2\text{CHO} \xrightarrow{\text{HO}^-} \text{CH}_2\text{CH(OH)}\text{CHO} \]

**Carbonyl Condensation Reactions**

The base-catalyzed condensation of two moles of an ester is called the **Claisen Condensation**.

\[ 2\text{CH}_2\text{CH}_3\text{CO}_2\text{H} \xrightarrow{\text{CH}_2\text{O}} \text{CH}_2\text{CH}_3\text{CO}_2\text{H} \]

\[ +\text{CH}_2\text{CH}_3\text{CO}_2\text{H} \]

\[ \xrightarrow{\text{CH}_2\text{OH}} \]

\[ \text{CH}_2\text{CH}_3\text{CO}_2\text{H} \]
**CARBONYL CONDENSATION REACTIONS**

An intramolecular Claisen is called the Dieckman Condensation.

![Dieckman Condensation](image)

**REACTIONS OF α,β-UNSATURATED CARBONYLS**

The Michael Reaction of α,β-unsaturated ketones and aldehydes.

![Michael Reaction](image)

Conjugated ketones and aldehydes can undergo an analogous reaction in which a nucleophile adds to the terminal carbon of the double bond.

**REACTIONS OF α,β-UNSATURATED CARBONYLS**

The Michael additions of α,β-unsaturated ketones and aldehydes that we covered include:

- (CH₂CH₂)₂ACN
- (CH₃)₂CCL₂
- CH₃NH₂

![Michael Additions](image)

**REACTIONS OF α,β-UNSATURATED CARBONYLS**

Enolate anions also undergo the Michael Reaction:

![Enolate Reaction](image)

**REACTIONS OF α,β-UNSATURATED CARBONYLS**

Michael addition of enamines and nitroalkanes.

![Michael Addition](image)

**IN-CLASS PROBLEM**

3-Buten-2-one is subjected to the four steps shown below; what will be the major product of this reaction sequence?

1. CH₃
2. H²⁺H₂O; heat
3. OH⁻/H₂O
4. H²⁺H₂O

![Problem Reaction](image)
**IN-CLASS PROBLEM**

Beginning with cyclohexanone, suggest a simple synthesis for the following compound:

1. **IN-CLASS PROBLEM**

Beginning with cyclohexanone, suggest a simple synthesis for the following compound:

2. **IN-CLASS PROBLEM**

Beginning with cyclohexanone, suggest a simple synthesis for the following compound:

3. **IN-CLASS PROBLEM**

Beginning with cyclohexanone, suggest a simple synthesis for the following compound:

4. **IN-CLASS PROBLEM**

Predict the products for the following reactions:

   -  \( \text{Br} + \text{CO} \rightarrow \text{Cl} \)
   -  \( \text{H}_2\text{N} + \text{SO}_2\text{Cl} \rightarrow \text{NH}_2 \)
   -  \( \text{K}^+ + \text{CN} \rightarrow \text{CN}^- \)
   -  \( \text{NaN}^+ + \text{H}_2\text{O} \rightarrow \text{Na}^- + \text{H}_2\text{O} \)

5. **IN-CLASS PROBLEM**

Predict the products for the following reactions:

   -  \( \text{H} + \text{NH} + \text{CH}_2\text{Br} \rightarrow \text{H}_2\text{O} \)
   -  \( \text{NaBH}_4 + \text{CN} \rightarrow \text{H}_2\text{O} \)
   -  \( \text{NaNO}_3 \rightarrow \text{H}_2\text{O} \)
**In-Class Problem**

Predict the products for the following reactions:

1. $\text{CH}_3\text{NH}_2$ (excess)
2. $\text{Ag}_2\text{O, H}_2\text{O}$, heat

**Formation of Diazonium Salts**

...a diazonium salt...

**Reactions of Diazonium Salts**

- $\text{H}_3\text{PO}_4, \text{H}_2\text{O}$
- $\text{HCl, CaCl}_2$
- $\text{HBr, CuBr}$
- $\text{KI}$

**Reactions of Diazonium Salts**

- $\text{KCN, CuCN}$
- $\text{H}^+\text{H}_2\text{O}$
- $\text{CH}_3$ addition

**Integrated Spectroscopy: Compound #1**

- $\text{C}_9\text{H}_10\text{O}$, $\text{MW} = 134.18$

- Absorbance
  - $3400 \text{ cm}^{-1}$
  - $3100 \text{ cm}^{-1}$
  - $2900 \text{ cm}^{-1}$
  - $2750 \text{ cm}^{-1}$
  - $1710 \text{ cm}^{-1}$
  - $1610 \text{ cm}^{-1}$
**INTEGRATED SPECTROSCOPY: COMPOUND #1**

C₉H₁₀O    MW = 134.18

°C Spectral Data:
- singlet, 196.5 ppm
- singlet, 142.1 ppm
- singlet, 134.4 ppm
- doublet, 129.1 ppm
- doublet, 128.5 ppm
- quartet, 22.8 ppm
- quartet, 20.9 ppm

**INTEGRATED SPECTROSCOPY: COMPOUND #2**

C₅H₉O₂Br  MW = 181.03

°C Spectral Data:
- singlet, 172.0 ppm
- triplet, 59.5 ppm
- doublet, 57.7 ppm
- quartet, 20.4 ppm
- quartet, 13.6 ppm

**INTEGRATED SPECTROSCOPY: COMPOUND #2**

C₅H₉O₂Br  MW = 181.03

Ω: 3400 cm⁻¹:
- 3100 cm⁻¹:
- 2900 cm⁻¹:
- 2200 cm⁻¹:
- 1710 cm⁻¹:
- 1610 cm⁻¹:

**INTEGRATED SPECTROSCOPY: COMPOUND #2**

C₅H₉O₂Br  MW = 181.03

Ω: 3400 cm⁻¹:
- 3100 cm⁻¹:
- 2900 cm⁻¹:
- 2200 cm⁻¹:
- 1710 cm⁻¹:
- 1610 cm⁻¹: