Organic Chemistry-III
CH-423

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Syllabus

CH-423 (2013)/Chem/IIT-B
Organic Chemistry III

Dr. Kaliappan, Krishna P.

Classification of reactions: A brief introduction to substitution, elimination, addition, oxidation, reduction, rearrangement and pericyclic reactions.

Functional group transformations: alcohols to alkylating agents, Mitsunobu and related reactions, introduction of functional groups by nucleophilic substitution at saturated carbon, nucleophilic cleavage of C-O bonds in ethers and esters and inter-conversion of carboxylic acid derivatives.

Oxidation: Metal based oxidizing reagents: A review and detailed discussion of chromium, manganese, ruthenium, silver and other metal-based reagents. Non-metal based oxidizing reagents: DMSO, peroxide, peracid and oxygen based oxidation. Miscellaneous oxidizing reagents like IBX, DMP, CAN, DDQ, periodate etc.
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Organic Chemistry III

Reduction: Homogeneous and heterogeneous hydrogenations; Discussion on borane based racemic and chiral reagents, aluminum, tin, silicon based reducing agents. Dissolving metal reductions.

Selectivity and protecting groups: Illustration of chemoselectivity, regioselectivity and stereoselectivity with examples; protecting groups for alcohols, amines, acids, ketones and aldehydes.

Cycloaddition reactions: Diels-Alder reaction; general features, dienes, dienophiles, selectivity, intramolecular and intermolecular reactions, hetero-Diels Alder reaction. 1,-3-dipolar cycloaddition reactions; general features, dipoles, dipolarophiles. [2+2] cycloaddition reactions; general features, selected examples.

Molecular rearrangements: Illustration of electron deficient and electron rich skeletal rearrangements with examples; Sigmatropic rearrangements-Claisen and related rearrangements, Cope and oxy-Cope rearrangements; 2,3-sigmatropic rearrangements and ene reaction.
Syllabus

Suggested Books/Reviews:


Evaluation Pattern

<table>
<thead>
<tr>
<th>Evaluation Pattern</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mid-Semester</td>
<td>30%</td>
</tr>
<tr>
<td>End Semester + Assignment</td>
<td>50%</td>
</tr>
<tr>
<td>Quiz (2 Nos)</td>
<td>20%</td>
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</tbody>
</table>

-There will be a total of 36 (1h) lectures, and 7 tutorials
Functional Groups

Only with carbon and hydrogen

With heteroatoms

With one oxygen atom:

1. Alcohol

   R–OH

   Primary alcohol

   secondary alcohol

   tertiary alcohol

2. Ether

   Diethyl ether

   anisole

   diphenyl ether

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Functional Groups

With one oxygen atom:

3. Ketone

\[
\begin{align*}
\text{Acetone} & : & \text{Acetophenone} \\
\text{Acetaldehyde} & : & \text{Benzaldehyde} \\
\text{Epoxide} & : & \text{Oxetane}
\end{align*}
\]
Functional Groups

With heteroatoms

With two oxygen atoms:

1. Acid

\[
\text{Acetic acid} \quad \text{Benzoic acid}
\]

2. Ketal

\[
R \quad R \quad OR' \quad OR'
\]

3. Acetal

\[
R \quad H \quad OR' \quad OR'
\]

4. Ester

\[
\text{Ethyl acetate} \quad \text{Ethyl benzoate}
\]
Functional Groups

With heteroatoms

With two oxygen atoms:

5. Lactone (Cyclic ester)

\[
\begin{align*}
\gamma\text{-lactone} & : \quad \overset{\text{C}}{\text{=O}} \quad \overset{\text{C}}{\text{=O}} \\
\delta\text{-lactone} & : \quad \overset{\text{C}}{\text{=O}} \quad \overset{\text{C}}{\text{=O}}
\end{align*}
\]

6. Peroxides

\[
\begin{align*}
\overset{\text{R}}{\text{O}} \overset{\text{O}}{\text{O}} \overset{\text{R}}{\text{R}}
\end{align*}
\]

With three oxygen atoms:

1. Anhydrides

\[
\begin{align*}
\overset{\text{O}}{\text{O}} \overset{\text{O}}{\text{O}}
\end{align*}
\]

Acetic anhydride
Functional Groups

With heteroatoms

With three oxygen atoms:

2. Hydroxy acid

α-hydroxy acid

β-hydroxy acid

γ-hydroxy acid

3. Peracid

meta-chloro perbenzoic acid
Functional Groups

With heteroatoms

With One Nitrogen atom

1) Amines

- Methyl amine (primary amine)
  \[ \text{H}_3\text{C} \equiv \text{NH}_2 \]

- Dimethyl amine (secondary amine)
  \[ \text{H}_3\text{C} - \text{N} - \text{CH}_3 \]

- Triethyl amine (tertiary amine)
  \[ \text{CH}_3 \text{N} \]

2) Aromatic amine

- Aniline
  \[ \text{NH}_2 \]

3) Nitriles

- Acetonitrile
  \[ \text{H}_3\text{C} \equiv \text{CN} \]
Functional Groups

With heteroatoms

With One Nitrogen atom

4) Aziridine

\[
\text{aziridine}
\]

5) Aromatic amines

\[
\begin{align*}
\text{Pyridine} & \\
\text{Pyrrole} & 
\end{align*}
\]

6) Imine

\[
\begin{align*}
\text{Primary aldimine} & \\
\text{Secondary aldimine} & \\
\text{Primary Ketimine} & \\
\text{Secondary Ketimine} & 
\end{align*}
\]
Functional Groups

With heteroatoms

With Two Nitrogen atoms
1) Diazo
\[ \text{H}_2\text{C}=\text{N}_2 \]
Diazomethane

2) Azo
\[ \text{N}=\text{N} \]

3) Diazonium
\[ \text{N}^+=\text{N} \]
Benzenediazonium cation

With Three Nitrogen atoms
1) Azides
\[ \text{R}^-\text{N}=\text{N}^+\text{N}=\text{N}^- \]

2) Triazole
\[ \text{1,2,3-triazole} \quad \text{1,2,4-triazole} \]

With Four Nitrogen atoms
1) Tetrazole
\[ \text{1-triatrazole} \]
Functional Group

With heteroatoms

With One Nitrogen atom and One oxygen atom

1) Amide

\[ \text{R} \text{NH}_2 \text{CONH}_2 \]

2) Lactams

\[ \text{NH}_2 \text{CONH} \]

\[ \text{NH}_2 \text{CONH} \]

\[ \text{R} \text{NH}_2 \text{CONH}_2 \]

3) Oximes

\[ \text{R} \text{NH} \text{OH} \]

\[ \text{R} \text{NH} \text{OH} \]

4) Nitroso

\[ \text{R} \text{N} \text{O} \]

5) Nitrile oxide

\[ \text{R} \equiv \text{N} \equiv \text{O} \]

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Functional Group
With heteroatoms

With One Nitrogen atom and Two oxygen atoms

1) Nitro
\[
R\text{NO}_2
\]

2) Nitrones
\[
\begin{align*}
\text{R} & \equiv \text{N}^+ \\
\text{O}^{-} & \equiv \text{R}
\end{align*}
\]

With Two Nitrogen atom and One oxygen atom

1) Urea
\[
\begin{align*}
\text{H}_2\text{N} & \equiv \text{C} \\
\text{NH}_2 & \equiv \text{O}
\end{align*}
\]
Functional Group

With heteroatoms (Sulfur)

1) Thiols

\[
\text{Thiophenol} \quad \text{Ethanethiol}
\]

2) Thio ethers

\[
R - S - R
\]

3) Thio carbonyl

\[
R - S - R
\]

4) Thiirane

\[
\text{Thiophene}
\]

5) Heterocycles
Functional Group
With heteroatoms (Halogen)

1) Halides
- Methyl iodide: \( \text{H}_3\text{C}^-\text{I} \)
- Ethyl bromide: \( \text{Br} \)

2) Halohydrin
- \( \text{R}^-\text{I} \)
- \( \text{OH} \)

3) Dihalides
- \( \text{Cl}^-\text{Cl} \)
- 1,2-dichloroethane

4) Acid Chloride
- Acetyl chloride: \( \text{Acetyl chloride} \)

5) Halolactones
- \( \text{O} \)
- \( \text{I} \)