Exam 3 Review

4/26/2023

Ch 21: Conjugate addition and Michael addition

- 1,2- vs 1,4- addition
  - Only Grignard and Hydride ($LiAlH_4$ or $NaBH_4$) do 1,2-addition.
    - Unstabilized enolates give a mixture of 1,2- and 1,4-
    - Doubly resonance stabilized enolate – 1,4- only (Michael addition)
  - Mechanism (don't need to show tautomerization or true "1,4-" addition – can just show alpha-carbanion after nucleophile attacks.
- Quenching with H_3O^+ vs quenching with an alkyl halide or electrophile
- Recognize Michael donors/acceptors
- Other Ch 21 reactions will not be on the exam

Ch 16: Diels-Alder

- Drawing product
  - Rotating to s-cis correctly
  - Regioselectivity (lining up partial charges)
  - Stereospecificity (trans on alkene → trans on ring; cis on alkene → cis on ring; for diene and dieneophile)
  - Stereoselectivity (EWG on dienophile faces “out”)
  - **+ enantiomer**
- Back-tracking from product to draw diene and dienophile
  - You can leave the diene in the s-cis conformation
- Comparing rates of Diels-Alder reactions
  - Steric hindrance of s-cis conformation of diene
  - Strength of EWG and EDG on diene/dienophile
- Mechanism

Ch. 24: Carbohydrates

- Bond-line → Fischer projection → Haworth projection → chair structure
- Generic naming (aldohexose, ketotetrose, etc)
- Assigning D- vs L-
  - Don't forget that D- and L- sugars of the same name (e.g. D-Glucose and L-Glucose) are <u>always</u> enantiomers of each other.
- Epimers (a type of diastereomer)
- Anomers (a type of diastereomer – ring form only)
- Reactions of carbohydrates
  - OH groups as nucleophiles
  - Glycoside formation (and mechanism)
  - Oxidation and Reduction
  - Chain lengthening (mechanism for cyanohydrin formation only)

Ch 25: Amino Acids and Peptides

- Drawing peptides using the amino acid table
  - N-terminus always goes on the left. Any given amino acid sequence (e.g. Ala-Cys-His) will follow this rule.
  - R group up → wedge; R group down → dash; for L-amino acids with N-terminus drawn on the left side

- Determining pI of amino acids and small peptides (using table of amino acid pKa's) Drawing Zwitterion form

- Drawing most prevalent protonation state of an amino acid or peptide at a given pH (using table of amino acid pKa's)
  - pH is above pKa of group – group is deprotonated [A:$^-$]
  - pH is below pKa of group – group is protonated [HA]

Ch 25: Amino Acids and Peptides

- Peptide synthesis
  - Amine + carboxylic acid + DCC → amide
    - this is not limited to amino acids! Works with simple amine + simple carboxylic acid too.
    - Mechanism
  - Be able to recognize all of the protection/deprotection groups and appropriate reagents
    - All protection mechanisms
    - Deprotection with HBr mechanism (no other deprotection mechanisms)
  - Tripeptide synthesis (like on practice exam)
      - can use whichever protecting and deprotecting method you want as long as it's correct

Exam format

- There's a limited number of things I can even ask you about!
- You should be able to predict most of the questions on the exam as a result.
- No open-ended synthesis – just ONE peptide synthesis (like practice exam)
- Rest is all fair game!
- I will be in my office on Monday, May 1st from 11-3:30pm to hand back Exam 3 and answer questions about it. Any unclaimed exams will be left in a box outside my office.

Final Exam

Thursday, May 4th @ 9:30 am - 12:30 am in Park 25

- 100 points
- Same length as first three exams
- Mechanisms will be limited to "common themes" from the class.
  - Don't try to memorize every mechanism from the whole class! That's not the point!
  - No EAS mechanisms. No Chromium mechanisms. No "unusual" or "weird" mechanisms.
- No open-ended synthesis
  - May still have a peptide synthesis like practice exam 3.
- Roughly equal distribution between content from all 3 exams.
- Email me if you have questions during finals week!! We can meet on Zoom.