FS25-CEM 351 Final Exam Objectives

(When studying, it is better for you to look up these concepts (alone or, better, with a team) rather than asking a T.A. or instructor to "remind [me] what that is again.")

Also, continue to do the worksheets handed out throughout the semester to help you see the format of problems as they may appear on quizzes/Exams

1. **Bonding and Shapes of Molecules**
   a. Identification of Ionic bonds and (polar & non-polar) Covalent bonds
   b. Calculation of formal charge
   c. Lewis and Resonance Structures
   d. Electron configuration
   e. Hybridization (sp^x; where you determine x based on item f below; also, know how more *p*-character in a hybridized bond affects orbital size/length)
   f. Know how to predict the geometry of orbitals used by an atom in a molecule based on the following:
      - Electron group (E.G.) geometry
      - Molecular geometry (M.G.)

2. **Acid-Base reactions**
   a. Know how to identify Acids, Bases, Conjugate Acid (C.A.), and Conjugate Base (C.B.), as Lowry or Lewis Acids and Bases.
   b. Determine the position of equilibrium when comparing the C.A. or C.B. in an acid/base reaction
   c. Rules of identifying Strong Acids via:
      - pK_a and K_a values
      - Structure of the compound (stability of conjugate base). How (do differences in Atom electronegativity, Resonance, Induction, and Orbital Size – i.e., hybridization) affect the stability of the negative charge on a conjugate base
   d. Know how to identify Lewis Acid (L.A.) and Lewis Base (L.B.)

3. **Thermodynamics**
   a. Keq, ΔH, ΔG
   b. Transition States, Intermediates identification on a reaction curve

4. **Alkanes and Cycloalkanes**
   a. Alkane & Cycloalkane Nomenclature
      - IUPAC Rules
      - Important substituent common names
      - *R*/*S* rules
      -
   b. Identify a 1°, 2°, 3°, and 4° carbon and know which ones contain a similarly designated H. This knowledge helps with our limited coverage of radical chemistry.
   c. Newman Projection
      - Know how to draw Newman projection
      - Know how to convert Newman projection into a bond-line structure
   d. Know to determine isomeric relationships (D.I.C.E.N. – Diastereoisomers, Identical, Constitutional Isomers, Enantiomers, or Not related)
   e. Cyclohexane Chair conformation
      - Know how to convert flat cyclohexane structure to its chair conformation

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- Know ring flipping and how it affects the orientation of attached bonds/substituents
- Stability of cyclohexane chair conformation (be able to take 1,3-diaxial interaction energies (given data) and determine which chair conformation is more stable)

5. **Stereoisomerism and Chirality**
   a. How to determine chiral carbons
   b. *R*/*S* configuration rules
   c. How to determine more D.I.C.E.N work + Meso. Know the definition of chiral vs. achiral
   d. Determine *R*/*S* on Fischer projection and correctly draw a Fischer Projection. Make sure you use the workspace on the exam to determine configurations without marking work on an answer already given; this practice confuses the graders.

6. **Alkene Nomenclature**
   a. IUPAC Rules
   b. Important substituent common names
   c. *E*/ *Z* and *cis*/ *trans* rules
   d. *R*/*S* rules

7. **Alkene Classification and Stability**
   a. How to determine different types of alkenes (mono, di, tri, tetra)
   b. Alkenes stability rules

8. **Alkene (Reactions + *Mechanisms*), Including concepts in the in-class worksheets.**
9. Halogenation reaction (Addition of X_2)
   a. Halo-hydrogenation reaction (Addition of H-X)
      - H-X (alone)
      - H-X, peroxides
   b. Halohydrin
   c. Hydration (Addition of H-OH)
      - H_2SO_4 /H_2O
      - Oxymercuration
      - Hydroboration
   d. Addition of (H-OR): Make sure that you get the R group drawn correctly
   e. Hydrogenation (Reduction reaction)
   f. Dihydroxylation (Addition of two hydroxy groups (O.H.)) OsO_4, H_2O_2
   g. Epoxidation (mCPBA)
   h. Oxidation Cleavage
      - Ozonolysis
   i. Carbenes (stereoselectivity -- syn addition)
      - diazomethane
      - CH_2I_2, Zn-Cu
      - $CHCl_3$, base
   j. Grignard Reagent
      - Mg metal insertion into the C=C-Br bond --> C=C-Mg-Br
         - C behaves like S_N2 nucleophile

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Alkyne Nomenclature

a. IUPAC rules, know priority -ol > -ene > yne
   - #-en-#-yn-#-ol

b. Important substituent common names

c. *R*/*S* rules

9. Alkyne Classification

a. How to determine Internal and Terminal alkyne

10. Alkyne (Preparation and *Mechanisms*)

a. Two consecutive E2 reactions with dihaloalkanes (using $^{-}NH_2$ equivalent to $NaNH_2$)

11. Alkyne (Reactions + Mechanisms)

a. Halogenation (1 or 2 equiv, Addition of X_2)

b. Halo-hydrogenation (1 or 2 equiv, Addition of H-X)

c. Reduction reactions
   - H_2/Pd or Pt
   - H_2/ Lindlar's Catalyst
   - Li or Na / NH_3

d. Hydration (Addition of H-OH, Dilute H_2SO_4, $HgSO_4$, H_2O)

e. **Enol-carbonyl** Tautomerization

f. Oxymercuration reaction

g. Disiamylborane ($(Sia)_2BH$) reaction (dicyclohexylborane, etc)

h. S_N2 reactions (to convert a Terminal alkyne (or acetylene H-C≡C-H) into an Internal alkyne) via an acetylide anion ($^{-}$:C≡C-H) – the structure of the reactant with the leaving group can be inferred from the structural intermediates

12. Synthesis

a. Be able to link reaction steps into a logical progression from starting material to final product while given ***significant***(!) hints along the way

13. Alkyl Halides Nomenclature

a. IUPAC rules (drop the "ine" suffix of the halogen atom and at "o". For example, fluor*ine* becomes fluor*o*.

b. Important substituents, namely the common names

c. *R*/*S* rules

14. Alkyl Halides Classification

a. Know how to determine each alkyl halide as 1°, 2°, and 3°.

15. Alkyl Halides (Preparation + ***Mechanisms***)

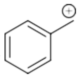
a. Free radical reaction using: X_2/uv light (X: F, Cl , Br, I)

16. Know how to determine Polar Protic and Polar Aprotic Solvents

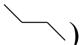
17. Alkyl Halides (Substitution Reaction + Mechanisms)

a. S_N2 mechanism

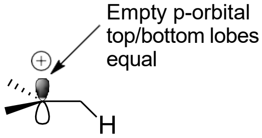
b. S_N1 mechanism

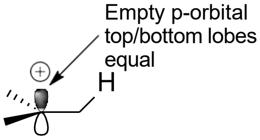
- Know carbocation stability rules ( benzylic > allylic > 3° > 2° > 1°. Why are benzylic and allylic C^+ more stable?

18. Alkyl Halides (Elimination Reaction + Mechanisms)

a. E2 mechanism
  - Know how to determine (α and β) (carbon and hydrogen)
  - Know the stereochemistry (Leaving group MUST be *anti* to and *planar* () with the β hydrogen**). ONE step reaction, in part, limits the stereoisomerism of E2 reactions with some halo cycloalkanes and some acyclic compounds with limited β-hydrogens.**

b. E1 mechanism
  - Know carbocation stability rules and alkene stability and remember that a *p*-orbital has a top and bottom lobe that electrons from an acid H can add to and form a pi-bond. Ask: How does this affect your assessment of the stereoisomers made for an E1 rxn?





18. ^{1}H and ^{13}C NMR, including DEPT 135 and DEPT 90

a. Equivalent H

b. Diastereotopic, Homotopic (Identical), Enantiotopic, Not Related. Do a 'Br' replacement for each of the Hs being compared. Evaluate the stereoisomeric relationship between the 'Bromo' compounds made. If they are, for example, 'Enantiomers' (identical chemical and physical properties), then the protons are 'Enantiotopic' and therefore will have the same chemical shifts in the ^{1}H NMR. If the compounds are, for example, 'Diastereomers' (different chemical and physical properties), then the protons are 'Diastereotopic' and therefore will have different chemical shift values.

c. Multiplicity (N + 1 rule). NOTE: Equivalent Hs DO NOT couple. ($CH_3CH_2CH_2CH_3$) – In this symmetrical molecule (butane), the Hs of the CH_2 do not split one another. For example, the observed CH_2 protons are split into a **quartet** (N + 1) by adjacent CH_3 nuclear spins only.

d. Carbon spectra show the number of magnetically unique carbons in a molecule, while the DEPT 135 and 90 (Distortionless Enhancement by Polarization Transfer) data show additional data regarding the hydrogens attached to a carbon. DEPT 135 shows (+) peaks for CH and CH_3, while CH_2 peak is (-). DEPT 90 shows a (+) peak for CH_3. If a Carbon signal is 135 (+) and 90 (+), then the observer is looking at a CH. If the number of carbons signals observed in a ^{13}C spectrum is fewer than the number of carbons in the molecular formula then some of the carbons are chemically equivalent by symmetry within the molecular structure.

18. IR Spectroscopy

a. Understand the significance of higher energy IR frequencies (heavy atom attached to a lower atomic weight atom, e.g., C-H, N-H, O-H stretching frequencies).

b. O-H stretches tend to be broad absorbances due to differential hydrogen bond interactions that spread the vibrational energies across across a broader range. N-H stretches tend to also be higher energy, yet have lower absorbance and less broad relative to O-H; however, the synchronous and asynchronous stretching of the Hs on an NH_2 typically show two distinct energy stretch absorbances, while an NH only shows 1 absorbance.

c. To the left of 3000 cm^{-1} are generally sp or sp^2 C-H stretches and to the left of 3000 cm^{-1} are sp^3 C-H stretches. While the IR spectrum is valuable, another clearly diagnostic absorbance appear around 1720 cm^{-1} and is associated with C=O stretches.