CHEM 223 (2024) SI Session #8

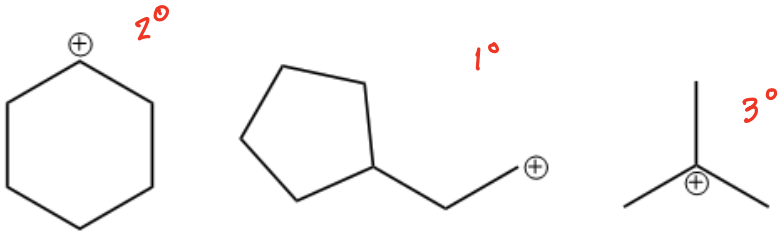
Learning Objectives: By the end of this session, students should be able to:

- Discuss the stability of carbocations, carbon radicals, and carbanions
- Practice Chapter 4 using previous exam questions
- Use the Cahn-Ingold-Prelog rules to label chiral molecules.

Section 1: Stability of Intermediates

1. Use the molecules in each question set to fill out the tables.
   a. Carbocations

Q MMS

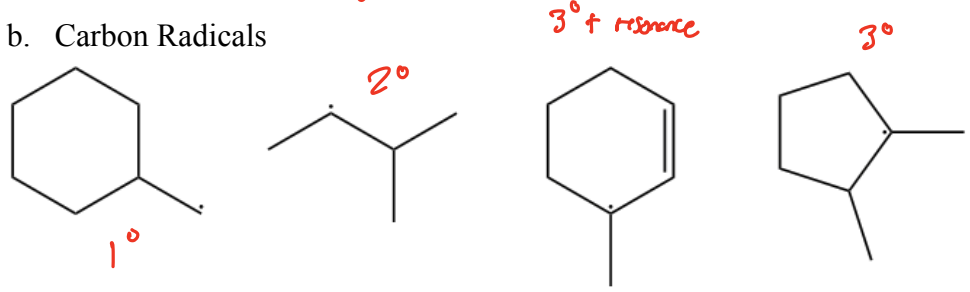


FQ: hybridization?

Order of Stability	Explanation	Nucleophile / Electrophile
$3^\circ > 2^\circ >> 1^\circ$	• Inductive effect: e^- rich alkyl groups donate e^- density to e^- poor carbons. • Hyperconjugation: empty p-orbital overlaps w/ sp^3 orbitals nearby, donating e^- density	Electrophile

sp^2 hybridized!

   b. Carbon Radicals



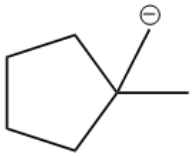
FQ: hybridization?

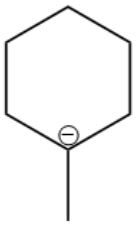
Order of Stability	Explanation	Nucleophile / Electrophile
3° + resonance $> 3^\circ > 2^\circ >> 1^\circ$	• Inductive effect • Hyperconjugation • Resonance	Electrophile

sp^2 hybridized!

c. Carbanions

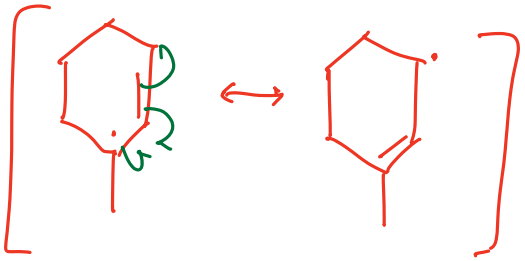
FQ: hybridization? usually sp^3!





Order of Stability	Explanation	Nucleophile / Electrophile
methyl > 1° > 2° > 3° (not shown)	• e^- donating effects (hyperconjugation, inductive effect) destabilize the ⊖ charge.	Nucleophile

2. Draw the resonance forms of the structure in 1b that has resonance (Hint: watch your arrows!)

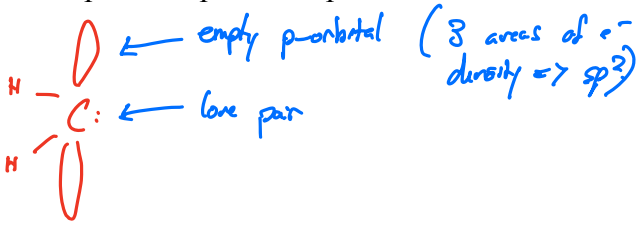


use 1 fishhook!

Do not use 2 fishhooks with radicals ever!

3. Carbenes can act both as a nucleophile and electrophile. Explain this phenomenon.

- Nucleophile b/c lone pair
- Electrophile b/c empty p-orbital



Section 2: Exam-Based Practice (All from 2021 & 2022 Exam 2)

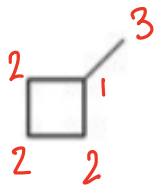
10 mins

4. The rate of a reaction typically increases as the temperature increases because _____.
   a. the A term in the Arrhenius equation increases
   b. the fraction of molecules with kinetic energy greater than Ea increases
   c. the activation energy decreases

d. the activation energy increases
e. the molecules make more collisions with the wall of the reaction vessel

5. How do alkyl substituents stabilize a carbocationic center to which they are attached?
   a. through an inductive donation of electron density to the cationic center
   b. through an inductive removal of electron density from the cationic center
   c. through hyperconjugation
   d. both A and C
   e. both B and C

6. For the compound below, the number of primary, secondary, and tertiary carbons is ___, ___, and ___, respectively.

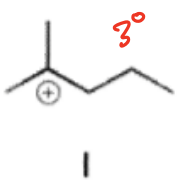


hydrogens

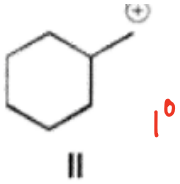
3, 6, 1

   a. 1, 3, 1
   b. 3, 6, 2
   c. 3, 6, 1
   d. 1, 6, 0

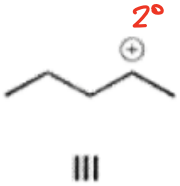
7. Rank the carbocations in terms of decreasing stability.



I



II



III

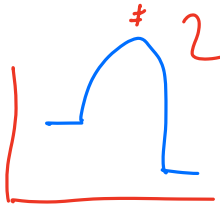
   a. I > III > II
   b. III > II > I
   c. II > III > I
   d. I > II > III

3° >> 2° > 1°

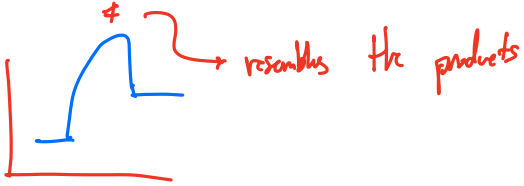
I > III > II

8. Which reactive intermediate is both nucleophilic and strongly basic?
   a. Carbanion
   b. Carbocation
   c. Carbene → not necessarily basic.
   d. Carbon Radical

9. Which statement best describes Hammond's Postulate?
   a. In an exothermic reaction, the transition state closely resembles the products

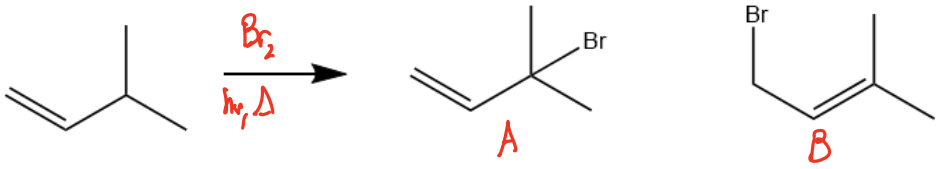


→ resembles the reactants

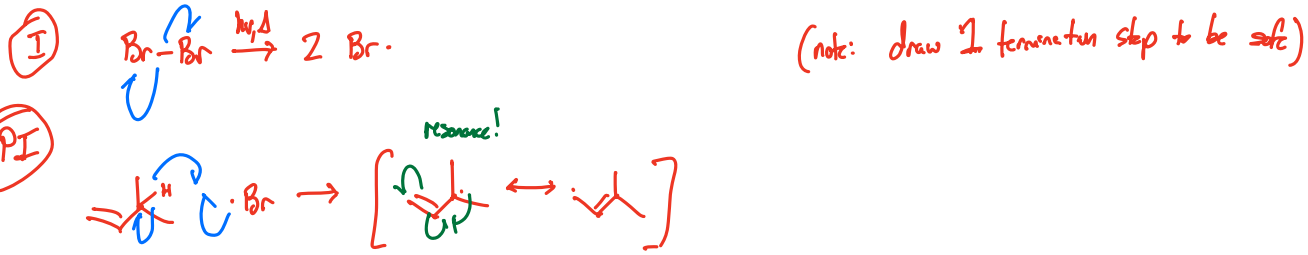


b. In an endothermic reaction, the transition state closely resembles the products
c. In an endothermic reaction, the transition state closely resembles the reactants
d. Transition states are reactive intermediates that can be probed using free radicals.

10. Using the reaction below, answer the following questions.

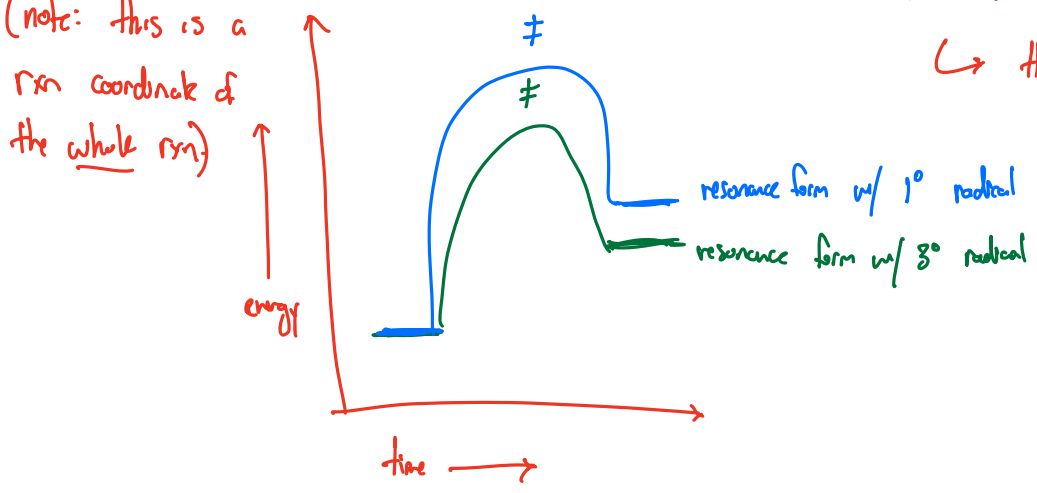


a. Draw a mechanism that accounts for the production of both products.



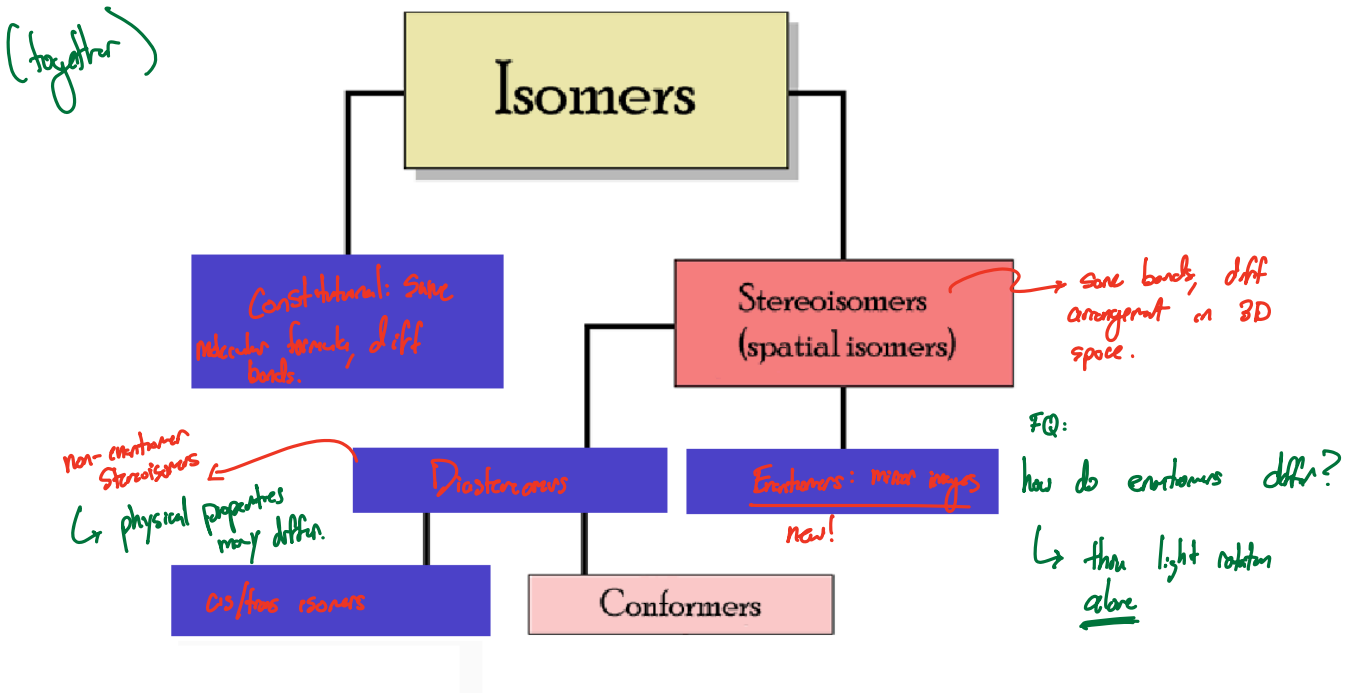
b. Explain which product is major, using a reaction coordinate diagram and Hammond's Postulate.

(A) is more stable.
Chlorination is exothermic
Bromination is endothermic, so both transition states will contain a carbon with radical character.
↳ the stability of the carbon radical product dictates the stability of the transition state.
↳ 3° > > > 1° in terms of carbon radical stability, so the



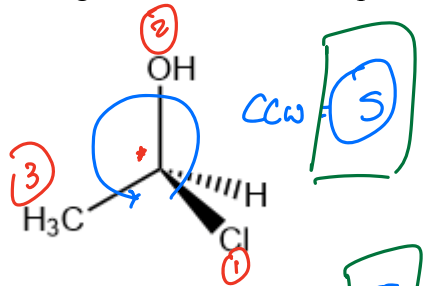
Section 3: Stereoisomers and Chirality

11. Fill in the missing terms (the blue boxes) in the tree of isomers, and provide definitions for each term.

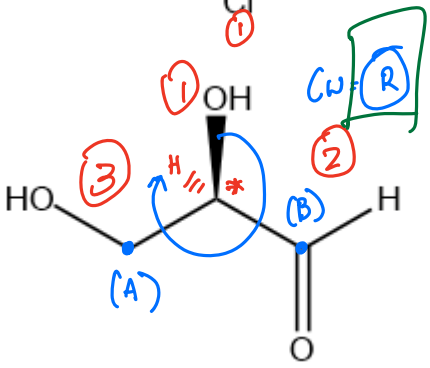


12. For each of the following compounds, do the following: (1) label the asymmetric carbon with an asterisk, (2) assign priorities using the Cahn-Ingold-Prelog rules, and (3) assign an (R/S) configuration based on the priorities given.

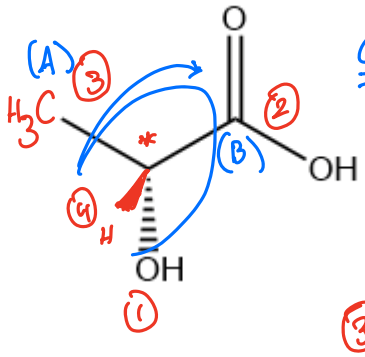
a.



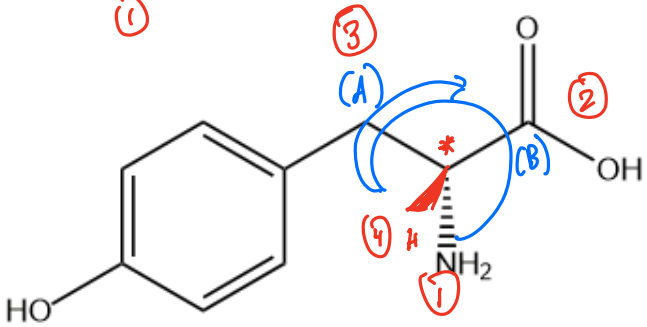
b.



(glyceraldehyde, a biochemical intermediate)

c. 

(lactic acid, another biochemical intermediate)

d. 

(tyrosine, an amino acid)