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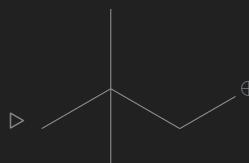
### Week 1

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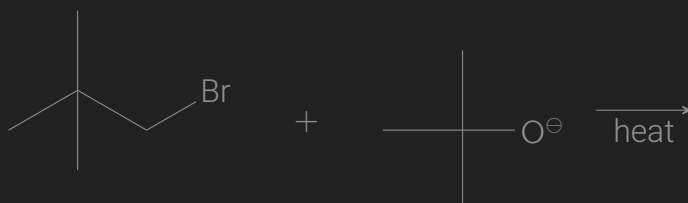
## Week 10

### Friday, November 30 - Quiz 21

1. Which of the following is the most stable carbocation?



2. What mechanism is most likely for the following?



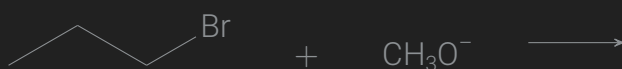
☐  $S_N1$

☐  $S_N2$

☐ E1

☒ E2

3. Which mechanism is most likely for the following?



☐  $S_N1$

☒  $S_N2$

☐ E1

☐ E2







## Week 8

### Friday, November 20 - Quiz 20

1. What is the rate law for an  $S_N1$  reaction of an alkyl halide?
  - ▷  $\text{rate} = k[\text{alkyl halide}]^2$
  - ▷  **$\text{rate} = k[\text{alkyl halide}]$**
  - ▷  $\text{rate} = k[\text{nucleophile}]$
  - ▷  $\text{rate} = k[\text{alkyl halide}]$
  - ▷ Unimolecular:  $S_N1$  and E2 reactions that are linearly dependent on the concentration of only one compound (the substrate).
  - ▷ A first order rate:  $v_0 = k[\text{substrate}]$ 
    - The substrate varies, and can be more than just an alkyl halide, but alkyl halides are very common.
2. What is the rate limiting step for an  $S_N1$  reaction?
  - ▷ **formation of carbocation**
  - ▷ loss of an  $H^+$  ion from the nucleophile
  - ▷ backside attack of the nucleophile
  - ▷ The alkyl halide often acts as the rate-determining step for  $S_N1$  reactions.
    - I think the better answer would be that the loss of the alkyl halide (leaving group) acts as the rate-determining step, but the loss of the leaving group is what forms the carbocation.
  - ▷  $S_N1$  reactions are often just two-steps (formation of carbocation  $\rightarrow$  nucleophilic attack), but the transfer of an  $H^+$  can occur if the nucleophile is uncharged, which is done by a solvent molecule.
3. Which reaction proceeds with an inversion of configuration?
  - ▷  $S_N1$
  - ▷  **$S_N2$**
  - ▷ acid base reactions
  - ▷ addition reactions
  - ▷  $S_N2$  reactions always invert, but technically both  $S_N1$  and  $S_N2$  reactions can do so as well.

- ▷ If the halogen in a  $S_N1$  reaction is bonded to an asymmetric center then it produces a pair of enantiomers, one of which will be inverted.
  - This is because the nucleophile can attack the carbocation in either direction.
  - Note: observation evidence shows a there is sometimes a slight preference for the inverted product, probably due to the type of ion pairs created.
- 4. Which conditions are most favorable an  $S_N1$  reaction?
  - ▷ a bulky nucleophile and a  $1^\circ$  alkyl halide
  - ▷ a bulky nucleophile and a  $2^\circ$  alkyl halide
  - ▷ **a bulky nucleophile and a  $3^\circ$  alkyl halide**
  - ▷ a small unhindered nucleophile and a  $1^\circ$  alkyl halide
  - ▷ Primary and secondary alkyl halides don't undergo  $S_N1$  reactions. The carbocation needs to be stabilized (hyperconjugation), and can need the most stable form ( $3^\circ$ ) in order to do so.
- 5. For either an  $S_N1$  or an  $S_N2$  reaction, which is the best leaving group?
  - ▷  **$I^-$**
  - ▷  $F^-$
  - ▷  $Cl^-$
  - ▷  $Br^-$
  - ▷ Alkyl iodides are the most reactive, while fluorides are the least.
    - $I^- > Br^- > Cl^- > F^-$
  - ▷ This is in large part determined by **polarizability**, which **increases with size of atom** since electrons occupy more space around the atom and thus have a higher chance of randomly forming differences in charge due to uneven distribution of electrons.
- 6. Why is a tertiary carbocation so much more stable than a primary carbocation?
  - ▷ steric bulk helps stabilize the tertiary carbocation
  - ▷ **hyperconjugation provides more stability in a tertiary carbocation than in primary carbocation.**
  - ▷ a tertiary carbocation is more stabilized by the leaving group
  - ▷ a tertiary carbocation is more ideal trigonal planar geometry

- ▷ **Hyperconjugation:** nearby electron sharing of electrons with adjacent empty, or partially filled orbitals, that give rise to more stability.
  - ▷ A primary carbocation has no such orbitals to share with, so the instability is increased.
7. According to the Hammond Postulate, the transition state for a reaction that proceeds with a large activation energy
- ▷ will be more likely to go by an  $S_N2$  pathway
  - ▷ **looks more like the products**
  - ▷ will be more likely to go by an  $S_N1$  pathway
  - ▷ looks more like the reactants
  - ▷ A higher energy transition state (larger activation energy) means it takes more energy to make any sort of change at all, which means change occurs rapidly once it finally can—creating transition states that look more like the products.
    - This is why they are **endothermic**; more energy is required, resulting in more energy **entering** the system from the outside.
    - This also explains why the products are less stable; more energy remains in the system due to these products.
8. The choice of a solvent affects the rate of the reaction by
- A changing the stability of the reactants
  - B changing the stability of the transition state
  - C changing the stability of the products
  - ▷ all of the above
  - ▷ **A and B**
  - ▷ The choice of solvent, often protic or aprotic, changes the stability of the added nucleophiles (increasing/decreasing respectively).
  - ▷ Stronger, less stable nucleophiles increase the potential energy in the reaction, which decreases the activation energy. The inverse is true for weaker, more stable
  - ▷ A change the activation energy often results in different products being formed, which usually differ in stability, but this does not affect the rate.



**Tuesday, November 17 - Quiz 19**

1. In an  $S_N2$  reaction in which  $\text{OH}^-$  is the nucleophile, in which solvent will the rate be the fastest?
  - ▷ **a polar aprotic solvent**
  - ▷ a nonpolar solvent
  - ▷ a polar protic solvent
  - ▷ **Polar aprotic solvents:** protic solvents lacking a hydrogen atom connected to electronegative atoms.
    - Lack of hydrogen **fails to stabilize added nucleophiles**, leaving compounds with higher potential energy and thus a **lower activation energy** for a reaction to take place.
    - $S_N2$  reactions are generally much **faster in polar aprotic solvents**.
2. The carbon center in an alkyl halide is
  - ▷ an unsaturated center
  - ▷ a nucleophile
  - ▷ a cation
  - ▷ **an electrophile**
  - ▷ **Alkyl halides:** compounds in which a halogen (Cl, Br, I) is connected to an  $sp^3$  hybridized carbon atom.
    - Alkyl halides are electrophiles since they contain such electron deficient halogens—making them easily accept new electrons.
3. Why is the rate of reaction for an  $S_N2$  reaction so much slower for a  $3^\circ$  alkyl halide than for a  $1^\circ$  alkyl halide?
  - ▷ the leaving group is more reactive in an  $1^\circ$  alkyl halide
  - ▷ steric crowding is much less in  $3^\circ$  alkyl halides
  - ▷ because  $\Delta G^\circ$  is much smaller for a  $3^\circ$  alkyl halide
  - ▷ **steric crowding is much greater in  $3^\circ$  alkyl halides**
  - ▷ The more substituents, the more bonds that need to be broken/changed and the more steric interactions there are during the transition state—leading to higher activation energy and thus a slower reaction.
    - Steric crowding refers to the steric interactions that act to increase such interference.
    - $3^\circ$  refers to the number of  $\beta$  positions (max  $3^\circ$ , min  $1^\circ$ )

- **$\alpha$  position:** the position connected directly next to the halogen.
- **$\beta$  position:** positions connected to the  $\alpha$  position.

4. At the transition state of an  $S_N2$  reaction reaction

- ▷ **the C–Nu bond is *partially* formed and the C–LG bond is *partially* broken.**
- ▷ the C–Nu bond is *partially* formed and the C–LG bond is *completely* broken.
- ▷ the C–Nu bond is *completely* formed and the C–LG bond is *partially* broken.
- ▷ the C–Nu bond is *partially* formed and the C–LG bond is *completely in tact*.
- ▷ **Transition states:** represent local maxima of the reaction.
  - Cannot be isolated.
  - Represents high-energy states where bonds are being simultaneously broken and formed.
    - I.e., partially broken and partially formed.

5. The rate law expression for an  $S_N2$  reactions reaction has the form

- ▷ rate =  $k[\text{electrophile}]$
- ▷ rate =  $k[\text{electrophile}]^2$
- ▷ rate =  $k[\text{nucleophile}]^2$
- ▷ **rate =  $k[\text{electrophile}][\text{nucleophile}]$**
- ▷ **Kinetics of  $S_N2$  reactions:** a biomolecular (2) nucleophilic (N) substitution (S) reaction.
  - **Biomolecular:** a step that involves two chemical entities, such as when the alkyl halide and nucleophile collide during the reaction mechanism.
  - Rate:  $v_0 = k[\text{alkyl halide}][\text{nucleophile}]$ 
    - As mentioned above, alkyl halides are electrophiles.

6. What is the meaning of  $S_N2$ ?

- ▷ substitution nucleophilic two transition states
- ▷ substitution nucleophilic two two reagents
- ▷ **substitution nucleophilic two second order**
- ▷ substitution nucleophilic two twice
- ▷  $\text{Rate} = k[A]^x[B]^y$ 
  - **Rate order:** the sum of exponents of the reactants.
    - E.g.,  $kA$  = first,  $kAB$  = second,  $kA^2B$  = third.

7. Which would you expect to be the best nucleophile?

- ▷  $F^-$
- ▷  $(CH_3)_2CH^-$
- ▷  **$CH_3^-$**
- ▷  $(CH_3)_3C^-$
- ▷ **Nucleophilicity:** the rate at which a nucleophile will attack a suitable electrophile.
  - There are multiple factors that contribute, but three main factors at play here: the role electron density, electronegativity, and steric hinderance (crowding).
    - $(CH_3)_2CH^-$  ( $2^\circ$ ) and  $(CH_3)_3C^-$  ( $3^\circ$ ) have more  $\beta$  branching, thus more hinderance.
    - $F^-$  electron density is so small that it causes low polarizability (more sable), which reduces reactivity.
    - Nucleophilicity also decreases as electronegativity increases ( $F > O > N > C$ ), so carbon will be have higher Nucleophilicity.

8. In substitution reactions with alkyl halides,

- ▷ the nucleophile is the leaving group
- ▷ a hydrogen becomes the leaving group
- ▷ **the halide is the leaving group**
- ▷ the electrophile is the leaving group
- ▷ In an alkyl halide, the halogen serves two critical functions that render the alkyl halide reactive:

- The halogen withdraws electron density via **induction**, rendering the adjacent carbon atom electrophilic, and therefore subject to attack.
- The halogen can serve as the **leaving group** for the compound, vital for substitution or an elimination to occur.
  - Good leaving groups are conjugate bases of strong acids, i.e., good groups are weak bases.
  - Generally an acid with a  $pK_a < 0$  generates a stable enough base to be a good leaving group, which is another reason why F ( $pK_a$  of HF is 3.2) is not one, despite being a halogen.

9. Of the following, which is the better nucleophile?

- ▷  $H_2O$
- ▷  $NH_3$
- ▷  $RNH^-$
- ▷  **$NH_2^-$**
- ▷ This question has more to do with the solvent effects on nucleophilicity.
  - **Protic solvents:** polar solvent that **contains** a hydrogen atom connected directly to an electronegative atom.
  - **Polar aprotic solvents:** protic solvents **lacking** a hydrogen atom connected to electronegative atoms.
  - Both  $H_2O$  and  $NH_3$  have are protic solvents, with hydrogen on the electronegative oxygen and nitrogen.
- ▷ Comes down to  $RNH^-$  and  $NH_2^-$ .
  - I believe the R is a functional group, which shares more of the negative charge, decreases strength relative to  $NH_2^-$ .
  - Although, I'm not completely sure, and I welcome a better explanation.

## Week 7

### Friday, November 13 - Quiz 18

1. Which parameter, kinetic or thermodynamic, gives us information about the rate and mechanism of the reaction?

▷ **Kinetics**

- Kinetics refers to the rate of a reaction, while thermodynamics refers to the equilibrium concentrations of the reactants and products.

2. For a reaction to be spontaneous,  $\Delta G^\circ$  must be

▷ **Negative**

**Gibbs free energy ( $\Delta G^\circ$ ):** the maximum amount of non-expansion work that can be extracted from a closed system.

- Essentially a repackaged way of expressing entropy in a closed system.
- $\Delta G^\circ$  is just  $\Delta S^\circ$  multiplied by the negative temperature in order to measure the entropy of the surroundings.
- Thus,  $\Delta G^\circ$  must be **negative** for a reaction to be spontaneous. (second law of thermodynamics)

3. Which part of the energy level diagram shown below, represents the kinetic component, and which represents the thermodynamic component?

▷ **A is kinetic, B is thermodynamic**

- **A** represents the activation energy ( $E_a$ ,  $\Delta G_{\text{act}}$ ) required for a reaction to form products.
- **B** represents the difference in free energy ( $\Delta G^\circ$ ) of the products from the initial reactants.
  - **Endergonic:** nonspontaneous ( $+\Delta G^\circ$ ) processes.
  - **Exergonic:** spontaneous ( $-\Delta G^\circ$ ) processes.

4. Which factors affect the equilibrium of a reaction?

▷ **a and b** (temperature and concentration)

- Rate of the reaction and catalysts effect the kinetics (rate), not equilibrium (thermodynamics)

5. Which factors affect the rate of a reaction?

▷ **a, c, and c** (concentration, temperature, and presences of catalysts)

- There are more, such as, substrate type, physical state, surface area, concentration, temperature, catalysts, pressure, and light absorption.
- Essentially concentration effects the *rate order*, while everything else effects the rate constant  $k$  ( $\text{rate} = k[\text{reactants}]$ )
- As described above, endergonic and exergonic has to do with  $\Delta G^\circ$  (equilibrium).

6. A small activation energy,  $\Delta G_{\text{act}}$ , corresponds to a

▷ **a fast reaction**

- Lower the activation energy, the less potential energy is needed for a reaction to occur, and thus more likely (faster) that a larger portion of molecules will undergo the reaction upon collision.

7. Which parameter, kinetic or thermodynamic, determines the equilibrium constant and how much product will form?

▷ **Thermodynamic**

- Kinetics refers to the rate of a reaction, while thermodynamics refers to the equilibrium concentrations of the reactants and products.

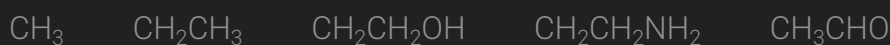
8. A large and negative  $\Delta G^\circ$  will correspond to

▷ **a large  $K_{\text{eq}}$**

- A large  $-\Delta G^\circ$  means the **products** are favored. ( $1 < K_{\text{eq}}$ )
- A large  $+\Delta G^\circ$ : the **reactants** are favored. ( $K_{\text{eq}} < 1$ )
- $K_{\text{eq}}$  says nothing about rate, that is determined by the kinetics, instead it just determines the direction and spontaneity.

## Tuesday, November 10 - Quiz 17

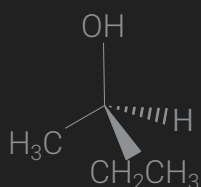
1. Based on the Cahn Ingold Prelog rules, rank the following in order of lowest to highest priority.



▷ **CH<sub>3</sub> < CH<sub>2</sub>CH<sub>3</sub> < CH<sub>2</sub>CH<sub>2</sub>NH < CH<sub>2</sub>CH<sub>2</sub>OH < CH<sub>3</sub>CHO**

- Relevant notes (highlighted applies to this problem):
  - **Chan-Ingold-Prelog system:** a system of nomenclature for Identifying each enantiomer individually.
    - (a) Assign priorities to each of the four groups based on atomic number; the highest atomic number has the highest priority.
    - (b) Rotate the molecule so that the fourth priority group is on a dash (behind)
    - (c) Determin the configuration, i.e., sequence of 1-2-3 groups.
      - clockwise (R) or counterclockwise (S).
  - If there is a tie between the atoms connected, then continue outward until a difference is found.
    - Do not add the sum all atomic numbers attached to each atom, just the first in which the atoms differ.
    - Any multiple bonded atom, (2 or 3) is treated as if connected to multiple atoms equal to number of bonds.
- First difference is the NH<sub>2</sub> vs OH<sub>2</sub>; oxygen has more mass.
- Leaves difference between CH<sub>2</sub>OH vs CHO; oxygen is double bonded in the latter, so really CHOO (O beats H).

2. Determine the absolute configuration of the following molecule.

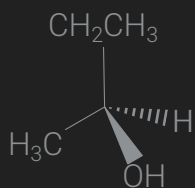


▷ **R**

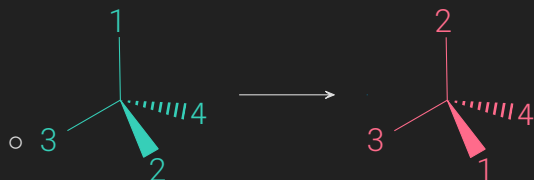


- H = 4, CH<sub>3</sub> = 3, CH<sub>2</sub>CH<sub>3</sub> = 2, OH = 1.
- Lowest priority is already in the back, leave as is.

3. The molecule shown below is the enantiomer of the molecule shown in the previous question. What is its absolute configuration?

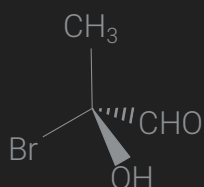


▷ **S**

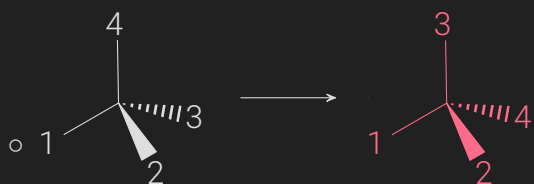


- Swap 1 and 2, swap the configuration; R  $\rightarrow$  S

4. What is the absolute configuration of the molecule shown below?



▷ **R**

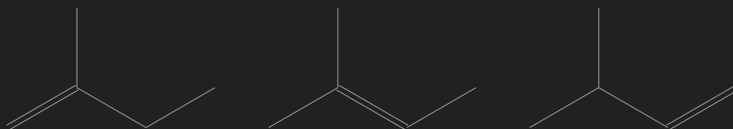


- Once lowest priority is assigned to dashed wedge(aka cram), then one can tell sequence.
- The **original (absolute) configuration is R** since the new configuration is **S** due to the swap between positions 4 and 3.



## Monday, November 9 - Quiz 16

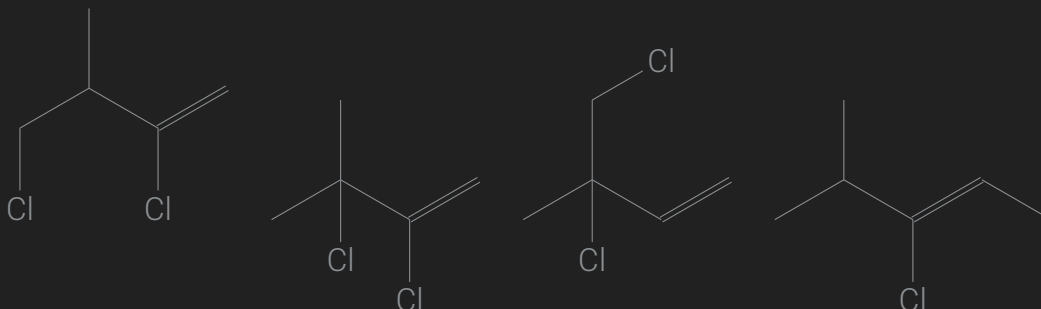
1. Which of the following molecules is not capable of existing in cis and trans isomeric forms?



▷ **All of the above**

- Option 1 and 3 both have a  $\pi$  bonded carbon ( $sp^2$ ), which has two hydrogens as the substituents—compounds with same substituents on both sides are unable to be cis–trans.
- Likewise, option 2, has  $CH_3$  on both sides of one end of the  $\pi$  bond, making them the have same substituents.

2. Which of the following molecules corresponds to a cis isomer?



▷ **D**

- A, B, and C all cannot be cis–trans isomers due to double hydrogen substituents.

3. What condition causes a carbon center to be classified as asymmetric?

▷ **The C must have four different groups bonded to it**

- Asymmetric carbon center = **chiral center**, i.e., a tetrahedral carbon that bears four different groups.

4. Suppose a sample of 2-methyl-1-butanol (see lecture notes), when placed in plane polarize light, showed a rotation of  $-4.32^\circ$ . What is the enantiomeric excess of the enantiomer that rotates light to the left?

▷ **75.1%**

- $\% ee = \frac{|\text{observed } (\alpha)|}{|\text{specific } [\alpha]|} \times 100\%$
- (from slides) 2-methyl-1-butanol: specific  $[\alpha]_D^{20} = \pm 5.75$ ; observed  $(\alpha) = -4.32$ .
- $ee = \frac{4.32^\circ}{5.75^\circ} \times 100\% = 75.1\%$

5. While nature, i.e., enzymes, synthesize molecules with chiral centers in 100% enantiomeric purity, that often proves very difficult for synthetic organic chemists to do. What most often results in the lab is a mixture containing equal concentrations of both enantiomers. What term is used to describe this mixture?

▷ **Racemic mixture**

- (from notes) **Racemic mixture**: a solution containing equal amounts of both enantiomers, resulting in an optically inactive appearance.

6. What physical properties distinguish the R enantiomer from the S enantiomer of a molecule?

▷ **they rotate plane polarized light in equal, but opposite, directions**

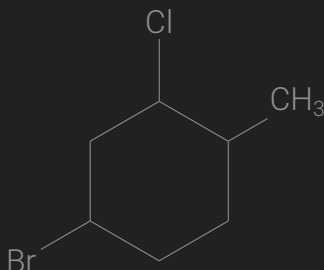
▷ Relevant notes:

- Specific rotation for enantiomers are **equal in magnitude** but **opposite in direction**.
  - **dextrorotatory**: a compound exhibiting **positive** rotation.
  - **levorotatory**: a compound exhibiting **negative** rotation.
  - No direct relationship between R/S system of nomenclature, as that is independent of conditions, but dependent on observation angle.
  - The **direction** of polarized light, however, is **dependent on conditions**, and can change based on temperature or wavelength even with the same given configuration.

## Week 6

### Monday, November 2

1. What is the name of the following molecule?



▷ **4-bromo-1-chloro-2-methylcyclohexane**

- Lowest sum and alphabetically ordered.

2. What is the definition of a molecular conformation?

▷ **A geometric arrangement in space of a molecule that has a low energy pathway to rearrangement**

- **Conformations:** the variety of possible three-dimensional shapes of a molecule that are interchangeable by low energy pathways.
  - Conformations vary in potential energy.
  - Changes due to rotation about  $\sigma$  bonds.

3. What is the following molecule?

(The package that draws newman projections is not compatible with the font I use... working on a fix, but can't draw them at the moment)

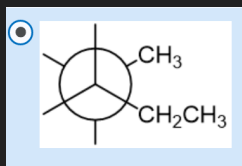
▷ **pentane**

- Front portion has 3 carbons in the chain: CH<sub>3</sub> (1), CH<sub>2</sub> (2), and the 4° carbon (3) in the center.
- The circle represents the  $\sigma$  bond between the carbon behind it, so that's (4).
- The methyl (CH<sub>3</sub>) on the back portion is (5).

4. For the molecule in the previous question, which conformer is the gauche form of the molecule?

▷ **choice 1**

▷ Can't draw newman projections currently; it's broken... but here's this lame screenshot:

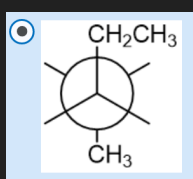


- **Gauche interaction:** unfavorable intereaction between groups, causing an increases in energy due to electron cloud repulsion.
- Gauche intereaction is a type of steric intereactions present at  $\approx \pm 60^\circ$  the next eclipsed conformation.

5. For the same molecule, which conformation corresponds to the most stable form?

▷ **pick number 1 m'lord**

▷ ugggghhhhhhhhhhhhhhhhh so ugly :(



- Other forms represent an eclipsed form and the gauche interaction, both which increases potential energy due to increased torsional strain.
- More notes for reference:
  - **dihedral (torsional) angle:** the angle between substituents of front and back carbons as the  $\sigma$  bonds rotates.
  - **Staggered conformation:** **lowest energy** conformation, when two substituents are at maximum dihedral angle from each other.
  - **Eclipsed conformation:** the **highest energy** conformation, when two substituents are at the minimum dihedral angle from each other.

6. For which molecule will the energy of conversion ( $E_{\text{act}}$ ) be the greatest?

▷ **butane**

- I don't really know what  $E_{\text{act}}$  is, but I assume it's the energy required to go through the interchangeable pathway.
- Costs of butane:
  - 19 kJ/mol (eclipsed with methyl overlap; once)
  - 16 kJ/mol (eclipsed, no methyl, but with gauche; twice)
  - 3.8 kJ/mol (gauche only; twice)
- I'm not sure if you add them up or just take max, but either way butane has the greatest out of ethane, propane, and methane.

7. Why is the cyclohexane ring more stable than rings of other sizes?

- ▷ the bond angles are all nearly  $109.5^\circ$
- ▷ the ring strain is at a minimum
- ▷ the overlap of the  $sp^3$  hybrid orbitals is at a maximum

▷ **all of the above**

- This is true in the most stable, chair conformations at least.

8. Why can't the cyclobutane ring be square planar?

▷ **the  $sp^3$  orbitals wouldn't overlap well**

- Cyclobutane adopts a slightly puckered conformation in order to reduce angle strain (and eclipsed H)... which I guess are the  $sp^3$  orbitals. I got this wrong multiple times; need to review orbitals I guess.

9. In the cartoon picture shown below, who's on the chair and who's on the boat forms of cyclohexane?

▷ **she's on the chair and he's on the boat**

- Hmmmmmmmmmmmm....

10. What is the total energy for the cyclohexane ring flipping process?

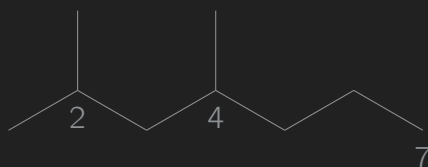
▷ **12.1**

- Appears to be just the cost of the first flip to the half chair.
- Can't seem to find good explanation to why, however.

## Week 5

### Friday, October 30

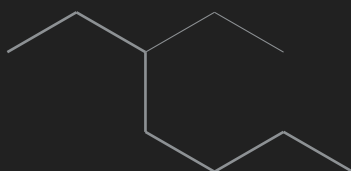
1. The name of the molecule shown below is



▷ **2,4-dimethylheptane**

- Parent chain, 7—heptane.
- Two methyl groups—dimethyl
- Locations of methyls—2,4

2. What is incorrect about the name, 3-butylpentane, for the following molecule?



▷ **the longest chain is a heptane**

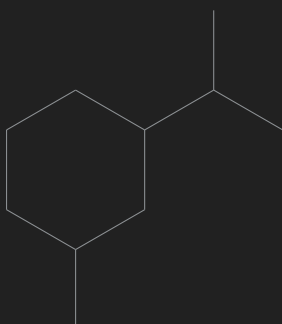
3. What is the name of the following molecule?



▷ **1-ethyl-3-methylcyclohexane**

- Parent chain: cyclohexane
- One ethyl, one methyl.
- First substituent receives lowest number, but if there is a tie then number is assigned alphabetically; starts with 1-ethyl.

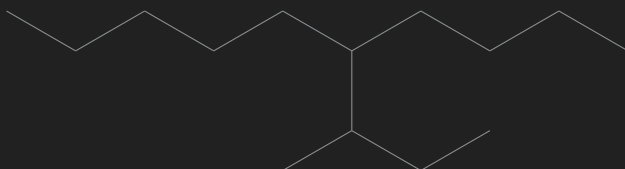
4. What is the name of the following molecule?



▷ **1-isopropyl-3-methylcyclohexane**

- Parent chain: cyclohexane
- One isopropyl (name for complex substituent bearing three carbons, aka 1-methylpropyl), one methyl.
- Same as before, i is before m.

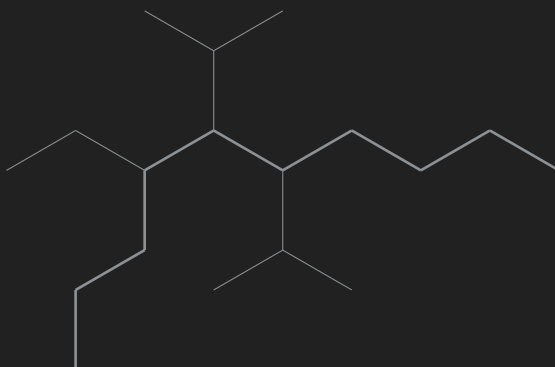
5. What is the name of the following molecule?



▷ **5-sec-butyldecane**

- Parent chain: decane
- one sec-butyl (1-methylpropyl)
- Lowest locant(location of a carbon on a numbered parent chain): 5

6. What is the name of the following molecule?



▷ **4-ethyl-5,6-diisopropyldecane**

- Parent chain: decane
- 1 ethyl, 2 isopropyl (1-methylpropyl)
- Alphabetical tiebreaker again, 4-ethyl wins.

7. For any two molecules to be constitutional isomers of each other, they must have

▷ **the same molecular formula**

- Constitutional isomers have the same molecular formula, different systematic names, and different atom connectivity.

8. Why aren't hexane and cyclohexane constitutional isomers?

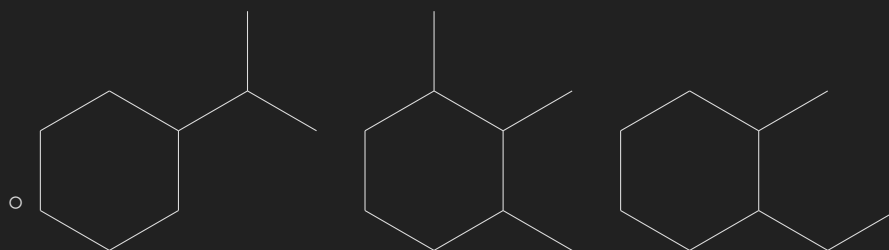
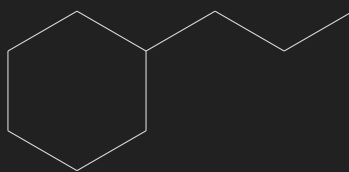
▷ **all of the above**

- cyclohexane is missing 2 H due to C—C bond making it a ring, which the chemical formula different and HDI different... also different names.

9. Which molecule(s) represents a constitutional isomer of propylcyclohexane?

▷ **all of the above**

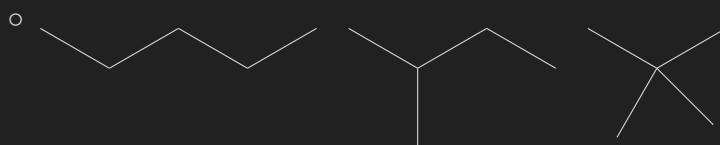
- Propylcyclohexane:



10. 2,2-dimethylpropane and pentane represent

▷ **constitutional isomers**

- $C_5H_{12}$ , pentane, can be arranged in three ways.





**Wednesday, October 28**

1. Comparing the following, which is the strongest acid?

▷  **$\text{CH}_3\text{COOH}$   $pK_a = 4.8$**

- $pK_a$  generally ranges from -10 (strong acid: positive charge) to 50 (strong base: negative charge).

2. Which of the following alcohols would you predict to be the most acidic?

▷  **$\text{FH}_2\text{COH}$**

- Fluorine has the greatest electronegativity compared to bromine and chlorine.
- Inductive effect of the electronegative atom withdraws more of the negative charge, making the conjugate base more stable (weaker).
- Weaker conjugate base = stronger acid.

3. Why is  $\text{H}-\text{C}\equiv\text{C}-\text{H}$  ( $pK_a = 25$ ) more acidic than  $\text{H}_2\text{C}=\text{CH}_2$  ( $pK_a = 44$ )?

▷ **the  $\text{H}-\text{C}\equiv\text{C}^-$  anion is more stable than  $\text{H}_2\text{C}=\text{CH}^-$**

- $sp$ -hybridization of carbon results in a triple bond, while  $sp^2$  results in a double bond.
- The negative charge on carbon anion is more stable when closer to the positive nucleus in a triple bond vs a double bond.
- More stable (weaker) conjugate base (deprotonated molecule) results in stronger acid.

4. Why is  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHBrCOOH}$  ( $pK_a = 2.97$ ) nearly two orders of magnitude less acidic than  $\text{CH}_2\text{BrCH}_2\text{CH}_2\text{CH}_2\text{COOH}$  ( $pK_a = 4.71$ ),

▷ **the inductive effect of Br is more pronounced in  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHBrCOOH}$  than in  $\text{CH}_2\text{BrCH}_2\text{CH}_2\text{CHCOOH}$**

- The further the electronegative atom (Br) causing the inductive effect from the deprotonated atom (O), the less stable (stronger) conjugate base and the weaker the acid.

5. The greater acidity of a carboxylic acid,  $\text{RCOOH}$  ( $pK_a = 4.76$ ) compared to an alcohol,  $\text{ROH}$  ( $pK_a = 16$ ) can almost entirely be attributed to

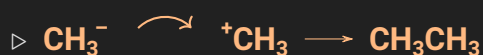
▷ **the resonance stabilization of the  $\text{RCOO}^-$  anion compared to the  $\text{RO}^-$  anion**

- The two oxygen atoms allows for electron delocalization, increasing stability of the conjugate base, resulting in a stronger acid.

- No delocalization is possible in the  $\text{RO}^-$ ; the negative charge is stuck only on the one oxygen.
6. We are going to see that most reactions in organic chemistry do not involve the  $\text{H}^+$  ion (from a Brønsted acid), other than as a catalyst. Instead, reactions are viewed in terms of the interaction between a Lewis acid and a Lewis base. Which of the following statements is true?

▷ **a Brønsted acid is also a Lewis acids**

- All Brønsted acids are also Lewis acids, but the reverse is not always true.
  - An  $\text{H}^+$  ion can be a Lewis acid, as it can accept a pair of electrons.
7. Which of the following shows the correct way to draw the curved arrows for the indicated reaction?



- Tail of arrow goes on negative charge, indicating electron donor (base).
- Head of arrow goes on positive charge, indicating electron acceptor (acid).

## Week 4

### Friday, October 23

1.  $\text{H}_3\text{PO}_4$  can lose one, two, or three protons. When it loses just one proton, what is the conjugate base?

▷  $\text{H}_2\text{PO}_4^-$

- Removing a  $\text{H}^+$  reduces H by one and decreases charge on the now deprotonated molecule by one.

2. Acetic acid,  $\text{CH}_3\text{COOH}$ , has a  $pK_a$  of 4.76 while phenol,  $\text{C}_6\text{H}_5\text{OH}$ , has a  $pK_a$  of 9.4. Which is the strongest acid?

▷ **acetic acid**

- $pK_a$  generally ranges from -10 (strong acid: positive charge) to 50 (strong base: negative charge).

3. In the following reaction, is  $\text{H}_2\text{O}$  acting as an acid, base, or neither?

▷ **base**

- $\text{acid} + \text{base} \rightleftharpoons \text{conjugate base} + \text{conjugate acid}$
- Symbolically:  $\text{HA} + \text{B} \rightleftharpoons \text{A}^- + \text{HB}^+$
- Our case:  $\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+$

4. In the following reaction, is  $\text{H}_2\text{O}$  functioning as an acid, a base, or neither?

▷ **acid**

- Our case:  $\text{CH}_3\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{NH}_3^+ + \text{OH}^-$

5. In a reaction of an acid with a base, equilibrium is favored if

▷ **the reaction proceeds from a stronger acid to a weaker acid**

- Equilibrium favors formation of the weaker (higher  $pK_a$ ) acid.
- Favored means to have the reaction proceed in a particular direction. Once it's reached nothing is favored. That means you need a stronger base  $\rightarrow$  weaker acid to have a favored direction.

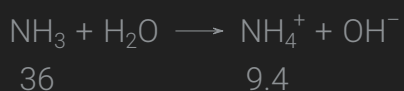
6. Which of the following statements is true?

- A. a strong acid will produce a strong conjugate base
- B. a weak acid will produce a weak conjugate base
- C. a weak acid will produce a strong conjugate base
- D. a strong acid will produce a weak conjugate base.

▷ **both C and D are true**

- The strength of the acid/base is **inversely proportional** to the strength of the conjugate acid/base.

7. Based upon the information given in Table 1 (chapter 6) in Strongin's book, will equilibrium favor the reactants or the products in the following reaction?

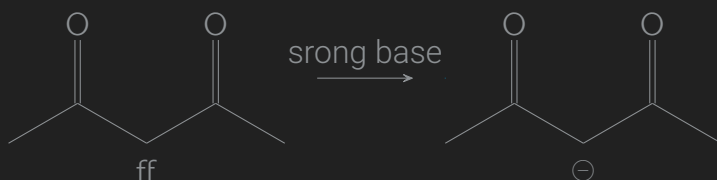


▷ **reactants**

- $pK_a$  for  $\text{NH}_4^+$  is 9.4 and  $pK_a$  for  $\text{NH}_3$  is 36 — Thanks @Winterho\_\_\_ for numbers, I have no access to the book.
- Equilibrium **favors formation** of the **weaker** (higher  $pK_a$ ) **acid**.

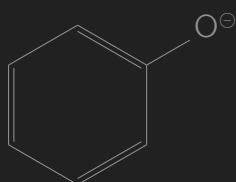
## Wednesday, October 21

1. A common reaction for carbonyls occurs by removing an alpha hydrogen to generate a carbanion, as shown for 2,4-pentanedione. Most C–H bonds are not acidic enough to react with any base, no matter how strong the base. Why do you think that this happens in 2,4-pentanedione?

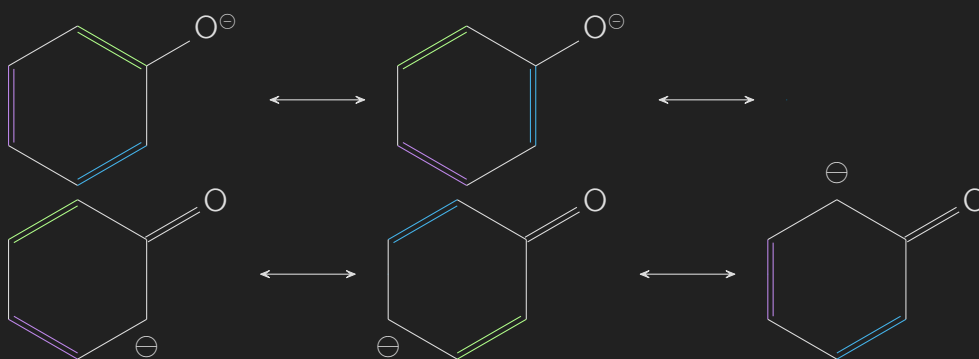


▷ **the negative charge is resonance stabilized over two C=O bonds**

- The negative charge on the carbanion can be pushed to the double bond between the carbon and the oxygen, which then pushes those electrons into lone pairs around the oxygen.
  - Negative charges prefer to be on the most electronegative element, in this case oxygen.
  - Both C=O bonds can share the charge, as sharing between each one forms separate resonance structures that form together form the resonance hybrid.
2. Most alcohols, ROH, are not very acidic, an exception is phenol, ArOH, which is "mildly" acidic. Including the starting structure, how many resonance forms can be drawn for the benzylic anion (shown below)?



▷ **5**

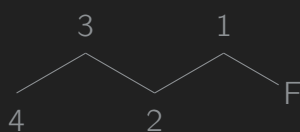


3. For the molecule in the previous question, how will the C–O bond length compare to C–O single bonds and C=O double bonds?

▷ **shorter than a single bond and longer than a double bond**

- Electron delocalization around the ring makes the C–O in the stronger than a normal single bond, but weaker than a double bond.
- The stronger the bond, the shorter the length.
- So after delocalization its now **shorter/stronger** than C–O, but **longer/weaker** than C=O.

4. For the molecule 1-fluorobutane, on which carbon will the inductive effect of the F be most prominent?



▷ **1**

- Inductive effects only influence atoms they are bonded to due to unequal sharing of electrons.

## Monday, October 19

1. When electrons are delocalized over several carbon centers, this results in

▷ **greater stability of the molecule**

- Resonance allows for delocalization of electrons, which spreads the charge between multiple atoms and lowers overall energy of molecule; termed **resonance stabilization**.

2. When showing electron movement with curved arrows,

▷ **the arrow head points towards the lewis acid**

- the tail "pushes" **electrons** from a **electronegative (lewis base:donor)** towards the **less electronegative (lewis acid:acceptor)**.

3. For electron delocalization, which of the following is allowed?

- ▷ electrons can move from a lone pair to an  $sp^2$  hybridized carbon.
- ▷ electrons can move as a pair from an anion to an  $sp^2$  hybridized carbon.
- ▷ electrons can move from pi bonding orbitals to an  $sp^2$  hybridized carbon.

▷ **all of the above**

- No good explanation. I don't think of it in terms of hybridized carbons.

4. What is wrong with the electron movement shown in the following

▷ **electrons cannot move towards an  $sp^3$  hybridized carbon**

- electrons from  $\pi$  bonding orbitals can move, just not towards a carbon with a full octet ( $sp^3$ ).

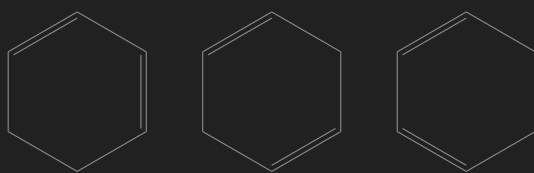
5. Is electron delocalization possible in the following molecule?



▷ **no**

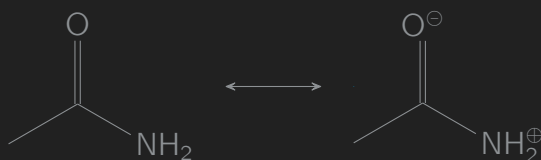
- Currently the  $CH_2$  in the middle has a full octet. You can't move the electrons from the  $\pi$  bonds
- There would have to be a carbocation in order to move the electrons.

6. Which of the following molecules will be resonance stabilized by electron delocalization?



▷ **A and C**

- A and C can push the electrons twice, since they are conjugated bonds ( $\pi$  bonds separated by a  $\sigma$  bond).
  - B would be too, if there was a carbocation on either of the carbons with two  $\sigma$  bonds.
7. Acetamide exists in a delocalized form that results from the two resonance forms shown below. Will the "real" structure be more like the one on the left, the one on the right, or an equal average of the two?



▷ **structure on the left**

- Rules for contributing significance, descending:
    - The greatest number of filled octets.
    - The greatest number of covalent bonds.
    - **Minimize formally charged atoms.**
    - Separation of unlike and like charges, minimized and maximized respectively.
    - Negative charges placed on the most electronegativity atoms, positive charges placed on the less electronegative atoms.
    - Do not deviate substantially from idealized bond lengths and angles.
    - Maintain aromatic substructures locally while avoiding anti-aromatic ones.
8. Which statement(s) is(are) true?
- ▷ the more resonance structures, the greater the stability of the molecule.
  - ▷ the more atoms over which the electrons can be delocalized, the greater the stability.

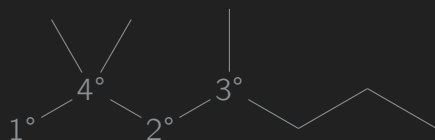


- ▷ when charges develop due delocalization, the structure with the negative charge on the most electronegative element is the most stable.
- ▷ a resonance structure in which all the atoms are neutral is more stable than one in which some of the atoms bear charges
- ▷ **all of the above**
  - see rules above on contributing significance; more of the major contributors result in more stability of the molecule, generally.

## Week 3

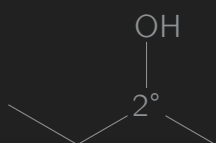
### Friday, October 16

1. What is the classification for the carbon centers, from left to right, in the following molecule?



▷ 1°, 4°, 2°, 3°

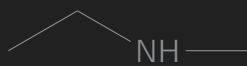
2. What is the classification of the following alcohol?



▷ 2°

- Two carbons are attached to the carbon with the alcohol.

3. How is the following amine classified?



▷ 2°

- $\text{CH}_3\text{CH}_2\text{NHCH}_3$ , looks like a dimethylamine with an extra  $\text{CH}_2$ . I don't know nomenclature yet, but the functional group (NH) remains the same. Has two carbons connected to it.

4. Which of the following is NOT an intermolecular force (IMF)?

▷ **covalent bonding**

- Any kind of bonding is not an intermolecular force. Hydrogen bonding isn't actually bonding, but instead just the strongest IMF mainly due to close proximity of charges compared to other IMFs.

5. Which of the following is the strongest IMF?

▷ **hydrogen bonding**

- See above answer.

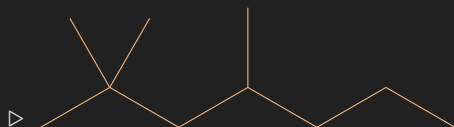
6. For a molecule to be polar, what conditions must exist?

▷ **all of the above**

- A molecule must have a molecular dipole moment in order to be polar, which means two or more bonds must not cancel each other out.

- Polar bonds must exist in order to create the net dipole moment.
- Has to have F O N Cl; I don't know why it must, but the other are true so this has to be true.

7. Of the following molecules, which will have the largest LDFs?



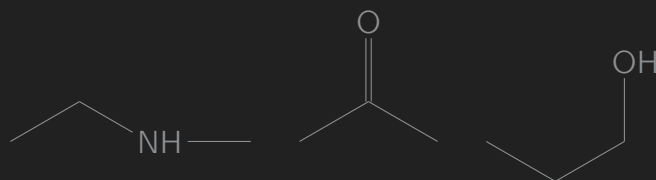
- London dispersion forces (LDF) related to molar mass, so generally the larger and heavier the compound, then the more atoms there are to randomly create dipole moments.

8. Which two molecules will be the least miscible?

▷ **O<sub>2</sub> and H<sub>2</sub>O**

- Least miscible means least likely to form a homogeneous mixture.
- "Like dissolves like" regarding to polar molecules, meaning polarity must match in order to become homogenous.
- All other choices are either both polar or both nonpolar.

9. Which molecule will have the highest boiling point?



▷ **C**

- When comparing boiling points of compounds, look for following factors:
  - Any dipole-dipole interactions? (increases boiling point)
  - Formation of hydrogen bonds? (increase boiling point)
  - Number of electrons. (more electrons, higher boiling point)
  - Number of carbon atoms. (more surface area, higher boiling point)
  - Degree of branching of compound. (more branching, more surface area)
- A and C both have more hydrogen bonding than B, but only really differ in the element (O vs N). Neither have dipole-dipole moments (no polar bonds). Oxygen is more electronegative, so it has more electrons.

## Wednesday, October 14

1. The reason that there is free rotation about any single sigma bond is because

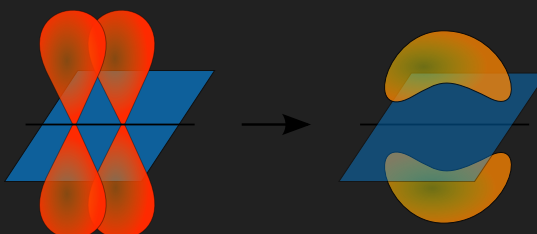
▷ **orbital overlap doesn't change with rotation**

- Electron density lies along the axis that connects the two nuclei forming the  $\sigma$  bond; no issue during rotation as one atom can freely rotate and stay connected.

2. The reason there is restricted rotation about a C=C double bond is because

▷ **rotation would eliminate the parallel overlap of the p orbitals**

- $\pi$  bonds lie above and below the axis and must break the overlap between the p orbitals during rotation, *unless they rotated in unison?*



3. What is a nucleophile?

▷ **all of the above**

- a nucleophile is an electron rich atom that is capable of **donating a pair of electrons**, which is the same definition as a **Lewis base**.
- Electron **rich** means **Lewis bases are negative** and thus attracted to a **positive charged** center (nuclei are generally positively charged) and capable of forming a bond due to excess of electrons.

4. What is an electrophile?

- a. a species that is attracted to a negative charge
- b. a species that contains extra electrons
- c. a Lewis acid

d. **a and c**

- An electrophile is an **electron-deficient** atom that is capable of **accepting a pair of electrons**, which is the same as a **Lewis acid**.

5. When drawing curved arrows, the arrow head always points towards the Lewis acid.

▷ **True**

- **Tails** must be placed on either a bond or a lone pair.
  - Shows the **source**, i.e., the electron donor (base).
  - Electrons can only be found in lone pairs or bonds, so **never place the tail** of a curved arrow on a **positive charge**.
- **Heads** must be placed so that it shows either the formation of a bond or the formation of a lone pair.
  - Shows the **destination**, i.e., the electron acceptor (acid).
  - Avoid drawing an arrow that violates the octet rule, so never draw an arrow that gives more than four orbitals to a second-row element.

6. What factors contribute to making something a good EWG?

▷ **all of the above**

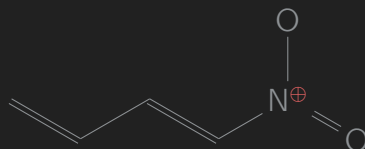
- Both inductive and resonance effects can have an impact on electronegativity, which governs substituent effects, such as the electron withdrawing group.

7. Given either the presence of a highly electronegative element that results in good inductive effects, or a group that, through resonance can delocalize positive charge, which has the greater effect as an EWG?

▷ **a group that is capable of delocalizing positive charge through resonance**

- The spreading of  $\pi$  bonds is called **delocalization**, which is a major **stabilizing factor** since the electrons are shared between multiple atoms.
- Inductive effect is due to electrons being shifted towards the more electronegative atom, but staying in the same place, providing less stability compared to resonance electron sharing.

8. On your own, you can show how electron distribution in the structure below results in the delocalization of positive charge, which increases the electronegativity at the terminal carbon atom.

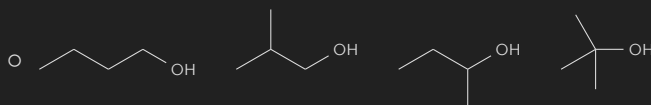


- ▷ I briefly read some sections on resonance, not expecting it to be on this quiz much since he talked about it very little. I'm not super confident in my explanation but I'll give it shot.
- ▷ There are some patterns for identifying lone pairs of oxygen and nitrogen, excerpt from today's notes:
  - **Associated Patterns for Oxygen**
    - A **negative** ( $\ominus$ ) charge corresponds with **one bond** and **three lone pairs**.
    - The absence of charge corresponds with **two bonds** and **two lone pairs**.
    - A **positive** ( $\oplus$ ) charge corresponds with **three bonds** and **one lone pair**.
  - **Associated Patterns for Nitrogen**
    - A **negative** charge corresponds with **two bond** and **two lone pairs**.
    - The absence of charge corresponds with **three bonds** and **one lone pair**.
    - A **positive** charge corresponds with **four bonds** and **no lone pairs**.
- ▷ Thus, the nitrogen should be have a **positive formal** charge, due to the four bonds (including the  $\pi$  bond) and no lone pairs.
- ▷ I don't know how to draw resonance arrows yet in the bond-line diagrams... but that charge is **delocalized** down the carbon chain, in reality it's being shared with **the four carbons and thus the electronegativity at the terminal carbon.**? (? Less confident about the validity of this statement, but seems reasonable)

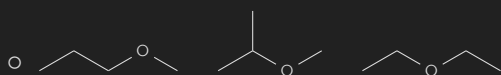
## Monday, October 12

1. How many isomers exist for a molecule with the molecular formula  $C_4H_{10}O$ ?

▷ 7



- These are the alcohols, or *all the possible combinations where the oxygen is on the end?* (? I'm sure when we get into nomenclature this will make more sense and lead to better explanation)



- These are the ethers, or *all the possible combinations where the oxygen is within the chain?* (? same disclaimer as above)
- Seems like drawing is only way to get good at this. Eventually we will probably get some intuition or memorize certain compounds with continual practice, similar to practicing math problems.

2. How many degrees of unsaturation are there in  $C_4H_{10}O$ ?

▷ 0

- Determining saturation using molecular formula:  $C_nH_{2n+2}$   
 $n$  = carbon atoms.
  - **Halogens:** takes the place of a hydrogen atom; *add one H* for each halogen.
  - **Oxygen:** no affect on saturation; *ignore*.
  - **Nitrogen:** needs an extra hydrogen; *subtract one H* for each nitrogen.
- Or use HDI formula:  $HDI = \frac{1}{2}(2C + 2 + N - H - X)$   $X$ : halogen atoms.
  - HDI: hydrogen deficiency index, which is the measure of degrees of freedom.
  - For  $C_4H_{10}O$ :  $\frac{1}{2}(8 + 2 + 0 - 10 - 0) = \frac{1}{2}(0) = 0$

3. Based upon the previous question, which structure(s) can be eliminated as possible for  $C_4H_{10}O$ ?

▷ **all of the above**

- Zero degrees of freedom means no double/triple bonds or rings are possible.
- Degrees of freedom help represent possible structures, indicating possible double bonds, triple bonds, rings, or various combinations of each.

4. How many degrees of unsaturation are there in  $C_5H_{13}$ ?

▷ **0**

- Again, general formula:  $HDI = \frac{1}{2}(2C + 2 + N - H - X)$  X: halogen atoms.
- For  $C_5H_{13}N$ :  $\frac{1}{2}(2(5) + 2 + 1 - 13 - 0) = \frac{1}{2}(0) = 0$

5. Based upon the previous question, what is a possible structure for  $C_5H_{13}N$ ?



- Same as question three, zero degrees of freedom means no double/triple bonds or rings are possible.

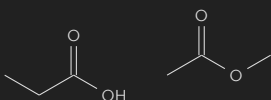

6. How many degrees of unsaturation exist for a molecule with the formula  $C_3H_6O_2$ ?

▷ **1**

- $\frac{1}{2}(2(3) + 2 + 0 - 6 - 0) = \frac{1}{2}(2) = 1$

7. What structures are possible for the  $C_3H_6O_2$  molecule?

▷ **both the first and second structures are possible**

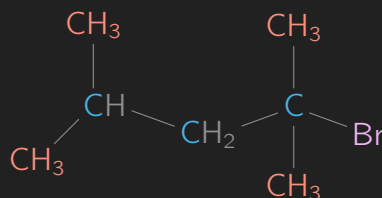
- For reference: 
- Has one degree of freedom so it has to have at least a double/triple bond or ring structure.
  - Makes  invalid due to lack of any double/triple/rings.



## Week 2

### Friday, October 9

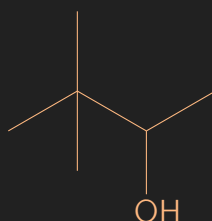
1. What is the condensed formula for the following molecule?



▷  **$(\text{CH}_3)_2\text{CHCH}_2\text{C}(\text{CH}_3)_2\text{Br}$**

- Breaking down answer:  $(\text{CH}_3)_2\text{CHCH}_2\text{C}(\text{CH}_3)_2\text{Br}$

2. What is the structural formula for  $(\text{CH}_3)_3\text{CCH}(\text{OH})\text{CH}_3$ ?



- ▷ Each line with an end is a  $\text{CH}_3$  (need 4)
  - ▷ Three points touching is a  $\text{CH}$ . (need 1)
  - ▷  $(\text{OH})$  is on the  $\text{CH}$
3. For any two molecules to be constitutional isomers of each other, at the very least, they:

▷ **must have the same chemical formula**

- isomers: same chemical formula.
- constitution: ways it connects; connect must be **different** to be a constitutional isomer.

4. How many constitutional isomers can be formed with the molecular formula  $\text{C}_4\text{H}_{10}\text{O}$ ?

▷ **7**

- See Monday, October 12 quiz. Same question asked and a better explanation given there.

5. The SO<sub>2</sub> molecule has two resonance forms, each of which is a constitutional isomer of the other. Which of the two structures shown below is the most stable? (The S→O bond is a dative bond in which both bonding electrons come from only one atom.)

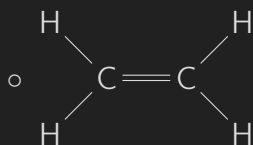
▷ **the structure on the right**

- *Delocalized electrons being shared in multiple bonds are more stable than a the dative bond.*? (? Not sufficient enough information yet to be confident of this explanation, though I'd be willing to bet that its along the right lines)

## Wednesday, October 7

1. What is the hybridization of the orbitals on C in ethylene?

▷  **$sp^2$**



- Each C has 3 groups (number of bonds,  $\pi$  bonds count as 1, or lone pairs)
- For atoms with groups between 1 and 4;  $sp^x$ ;  $x = \text{groups} - 1 = (2)$

2. What is the hybridization of the orbitals on C in acetylene?

▷  **$sp$**

- $\text{H} - \text{C} \equiv \text{C} - \text{H}$
- 2 groups, thus  $x = 1$ .

3. What type of bonds combine to make a  $\text{C}=\text{C}$  double bond?

▷ **one sigma and one pi bond.**

- First bond is a  $\sigma$  bond.
- Additional bonds are  $\pi$  bonds that go above and below the axis that connects the nuclei.

4. What is the  $\text{H}-\text{C}-\text{H}$  bond angle in ethylene?

▷  **$120^\circ$**

- $sp^2$  with no lone pairs, thus trigonal planar (according to VSEPR).
- $\frac{360}{3} = 120$ ; 3 angles maximized on a single plane.

5. Why is the geometry around the  $\text{CH}_2$  fragment in ethylene, trigonal planar?

▷ **there are three regions of electron density**

- *regions electron density = ? groups* (? I'm combining a past youtube video with his lecture...)

6. There is completely free rotation around a sigma bond such as a  $\text{C}-\text{C}$  single bond. Propose a reason for why there is no free rotation around a  $\text{C}=\text{C}$ .

▷ **the rotation would require the  $\text{C}-\text{C}$  pi bond to break**

- $\sigma$  bonds can rotate on the axis between the nuclei, but the  $\pi$  bonds are above and below and would break during rotation since *there are other orbitals that would block? their rotation*. (? not completely sure on the mechanism that doesn't allow for rotation)

7. As the percent s character increases in a bond, what happens to the bond angle?

▷ **it increases**

- The more **s character**, the **shorter** and **stronger** the bond, and the **larger** the bond angle.

8. As the percent p character in a bond increases, what happens to the bond angle?

▷ **it decreases**

- the more p character, the less s character; inverse of s character.

9. Why is a pi bond weaker than a sigma bond?

▷ **all of the above**

10. Which statement(s) is(are) correct?

- ▷ the shorter the bond, the stronger the bond
- ▷ the more s character in the hybridization, the stronger the bond
- ▷ the more s character in the hybridization, the greater the bond angle
- ▷ sigma bonds are stronger than pi bonds
- ▷ the geometry around the C in the ethylene is trigonal planar
- ▷ a C=C bond is composed of one sigma and one pi bond
- ▷ the hybridization around C in the methyl anion, isoelectronic with CH<sub>4</sub>, is sp<sup>3</sup>
- ▷ when 2s and 2p orbitals mix to form hybrid orbitals, the hybrid orbitals are higher in energy than the 2s orbitals, but lower in energy than the 2p orbitals
- ▷ the shapes of the hybrid orbitals match the electron domain geometry shapes predicted by VSEPR
- ▷ the potential energy of a covalent bond is lower than that of the potential energies of the free atoms from which it was formed
- ▷ **ALL OR THE ABOVE**
  - This seems to be a review of important concepts.

## Monday, October 5

1. The concept of orbital shapes comes directly from the wave model of the atom. What is the shape of an s orbital?

▷ **Spherical**

- S orbital is the most simple orbital, with only two electrons.
- Alternative shapes come from *nodes*; i.e. when *destructive interferences* cancels out the wave function.
- Not circular, orbitals are three-dimensional.

2. What is the shape of a p orbital?

▷ **Dumbbell shaped**

- P orbital can hold 6 electrons (3 pairs).
- Each pair has one angular node, squeezing shape into dumbbell in each direction (x, y, z).

3. When atomic orbitals overlap to form a covalent bond, the resultant bonding orbital is:

▷ **Lower in energy than the atomic orbitals from which it was formed**

- Electrons in a covalent bond are in a more stable (lower energy) state due to multiple nuclei holding them in place.
- Only when nodes are present do the electrons create a destabilized molecular orbit, increasing the energy.

4. Why can't pure p orbitals be used in forming four equivalent bonds as in methane?

▷ the three 2p orbitals can only hold 6 electrons.

- True, we need to make four bonds for methane.

▷ the bonds would have to be 90° apart.

- If p had enough space then it would result in planar geometry with 90°, but the true arrangement is tetrahedral with angles of 109.5°

▷ electron-electron repulsion would not be minimized.

- Planar minimization would be 90°, but we have 3d space to work with, so it's not minimized.

▷ **all of the above**

5. When s and p orbitals combine to form hybrid orbitals, the resultant hybridized orbitals are:

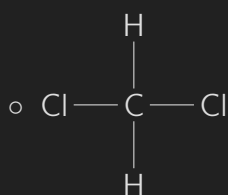
- ▷ lower in energy than the p orbitals
- ▷ higher in energy than the s orbitals
- ▷ **both of the above**
  - It takes energy to move the electron up from the s orbital and hybridize the p orbitals.
  - The new hybridized sp orbital also has more energy than the s orbital.

6. What is the difference between a sigma bond and a pi bond?

- ▷ **in a  $\pi$  bond, electron density lies above and below the axis that connects the two nuclei; in a  $\sigma$  bond, the electronegative density lies along the axis that connects the two nuclei**
  - $\sigma$  bond has circular symmetry with respect to the bond axis (axis that connects the two nuclei). i.e. it's along the axis.

7. What is the hybridization of the C in CH<sub>2</sub>Cl<sub>2</sub>?

▷ **sp<sup>3</sup>**



- Look at central atom – C
- Determin groups (number of bonds,  $\pi$  bonds count as 1, and lone pairs attached) – 4
- for groups 1-4; sp<sup>x</sup>; x = groups - 1 (**3**)

8. What is the hybridization of each C in benzene (shown below)?

▷ **sp<sup>2</sup>**

- Each carbon has 2H and  $\pi$  bond between, so groups = 3.
- Groups - 1 = 2, so sp<sup>2</sup>
- Though, each  $\pi$  bond is delocalized, or free to spread across all the carbons. Still counts as 1 group.

## Week 1

### Friday, October 2

▷ Determining formal charge:

◦ Formula:  $FC = V - N - \frac{B}{2}$

◦ V = valence electrons of element

◦ N = lone pair electrons; B = bonded electrons

1. What is the formal charge on P in the following structure? Each F and O has three lone pair of electrons.

◦  $P = 5 - 0 - 8(0.5)$ ; P = **+1**

2. What is the formal charge on O in the structure above?

◦  $O = 6 - 6 - 2(0.5)$ ; O = **-1**

3. What is the formal charge on P in the following structure? Each F still has three lone pairs of electrons, and O had the two pairs indicated.

◦  $P = 5 - 0 - 10(0.5)$ ; P = **0**

4. Of the two structures shown for  $\text{POF}_3$ , which is the most stable, and will, therefore, be the most abundant form?

◦ **Structure II**

◦ O has formal charge of **0** and is the **most electronegative** element with difference in charge between the resonance structures.

◦ F has greater electronegativity, but remains the same between both structures, so it's not relevant.

◦ Key difference: the double bond in structure II gives oxygen the **lower magnitude** formal charge between the two.

5. The fundamental concept upon which VSEPR, and hence molecular shapes, is based is that:

◦ Electron pairs repel each other;

– negative charge repels other negative charges.

◦ Electron repulsion is minimized by maximum angular separation;

– in other words, angular separation maximizes distance between electrons.

- Bonding pair electrons and lone pair electrons both occupy regions around the central atom;
  - if they didn't occupy the same space than they wouldn't interact and thus wouldn't affect shape.
- The electron domain geometry and the molecular geometry is identical if there all of the electrons are bonding electrons;
  - the lone pairs are have a greater influence than bonded pairs, resulting in less space for bonded pairs.

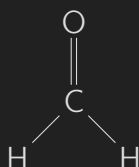
- **All of the above**

▷ General method of determining structure:

1. Count steric number—the total number of electron pairs in a molecule. Can be bonds or lone pairs.
  2. Determine predicted geometrical structure predicted (EDG) by VSEPR using steric number.
    - Octahedral:6, Bipyramid:5, Tetrahedral:4, Trigonal:3, Linear:2
  3. Determin impact (the MG) of lone pairs; more lone pairs results in less space between bonded pairs. Shape depends on EDG.
6. A resonance form of  $\text{SOF}_2$ , completely consistent with the octet rule, is shown below. What is the electron domain geometry (EDG), and molecular geometry (MG) of this molecule?

- **Tetrahedral EDG and trigonal pyramidal MG**

7. Draw a Lewis dot structure of formaldehyde ( $\text{CH}_2\text{O}$ ): what is the molecular shape of this molecule?



- Steric number = 3
  - Double bonds count as 1 for steric number.
- No lone pairs on central atom, C, so it's shape planar.

- **Trigonal planar**

8. The EDG for  $\text{CH}_3^-$  (a carbanion) is tetrahedral, and the MG is trigonal pyramidal. Why are the  $\text{H}-\text{C}-\text{H}$  bond angles less than  $109.5^\circ$  as in a perfect tetrahedron?



- **The lone pair electrons take up more space than bonding pair electrons.**