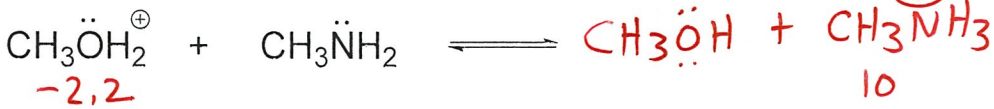
Key - Exam 2
Summer 2019

Multiple choice. Each of the following multiple choice questions (1-10) is worth 5 points and has only one correct answer. Select the best answer for each question and bubble it in on your Scantron.

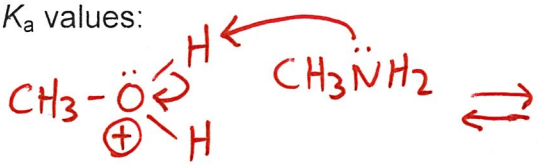
1. When the following two compounds are combined, a proton transfer occurs:



Some potentially useful pK_a values:

B

$CH_3OH_2^+$	–2.2
CH_3NH_2	36
CH_3OH	16
$CH_3NH_3^+$	10

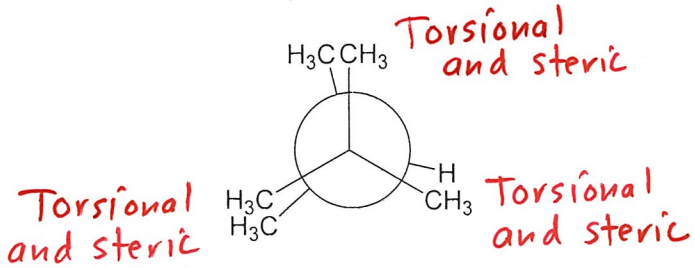


Which side of this proton transfer reaction is favored at equilibrium?

a. Reactants
b. Products
c. Neither side is favored
d. There is not enough information provided to answer the question

2. What types of strain exist in this conformation?

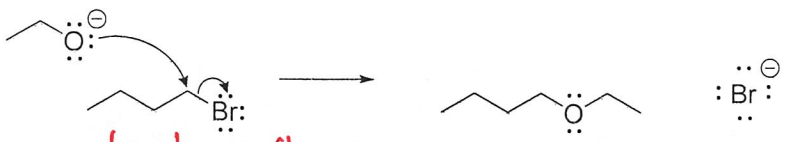
C



a. Steric strain only
b. Torsional strain only
c. Both steric and torsional strain
d. Neither steric nor torsional strain

3. The reaction of ethoxide ion and 1-bromobutane produces an ether, as shown in this mechanism:

nucleophile - HOMO



electrophile - LUMO

The LUMO in this reaction is

C-Br σ broke, so LUMO = C-Br σ*

D

a. nMO
b. C-O σ
c. C-O σ*
d. C-Br σ*
e. *p*

4. Propyne is a stronger acid than propane (structures shown, with acidic hydrogen explicitly drawn). When the conjugate bases of these acids are compared, which of the following factors best explains the difference in acidity of propyne and propane?

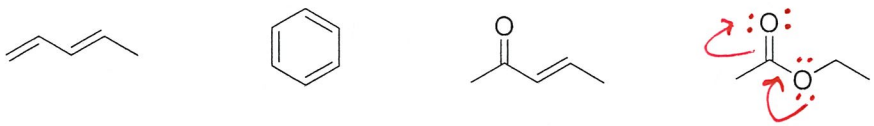
Propyne **Propane**

C

a. Resonance
b. Inductive effect
c. Hybridization
d. Size/Polarizability
e. Charge

5. Which of these molecules does not contain a pi system? (Lone pairs are not shown but all atoms are neutral.)

E



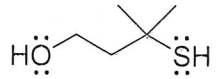
A **B** **C** **D**

All these molecules contain a π system

E

6. The compound 3-mercapto-3-methylbutan-1-ol ("MMB") is believed to be responsible for the odor of cat urine:

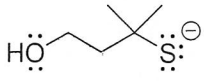
H attached to S is more acidic than H attached to O (O, S in same group → size/polarizability)



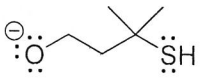
3-mercapto-3-methylbutan-1-ol

When one mole of MMB is combined with one mole of sodium hydroxide, a proton transfer occurs. Which of these structures is most likely to be a product of this proton transfer?

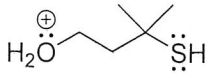
A



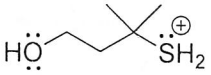
A



B



C

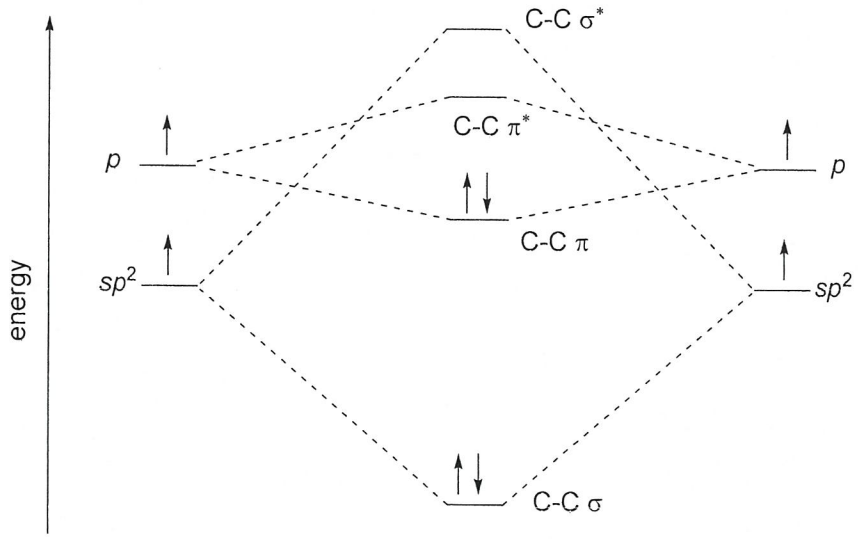


D

None of these structures

E

7. Here is a molecular orbital diagram for the C-C double bond in ethylene (C_2H_4):

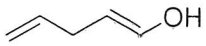


Select the true statement.

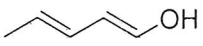
A

a. The bond order for the C-C double bond is 2. ✓ $\frac{4-0}{2} = 2$
b. The HOMO is the C-C σ*. No. C-C π
c. There are two nonbonding molecular orbitals. No. There are none.
d. The relative energies of the σ* and π* orbitals are incorrect; π* should be higher in energy than σ*. No. Order is correct
e. All of these statements are true.

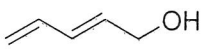
8. Select the answer choice that correctly places these three acids in order of *increasing* acidity. In each acid, the acidic proton is the one attached to the oxygen atom.



A



B



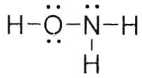
C

D

a. A < B < C
b. C < B < A
c. A < C < B
d. C < A < B
e. B < C < A

See next page

9. A compound called hydroxylamine can act as a Bronsted base:



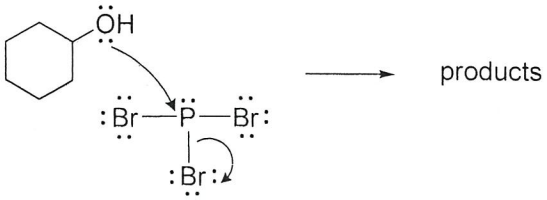
hydroxylamine

Which atom in hydroxylamine is more basic, N or O?

a. N
b. O
c. They are equally basic

Less EN than O; holds its e⁻ less tightly so they are more available to accept a H⊕

10. In the mechanistic step shown here,

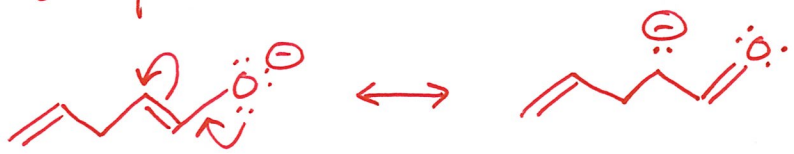


A

cyclohexanol is acting as a:

a. nucleophile
b. electrophile
c. Bronsted base
d. Bronsted acid
e. replacement for Kanye West, who couldn't be with us tonight for the exam

(8) Compare the three conjugate bases:

A: 

B: 

CB of B has the most reasonable resonance structures – thus most stable, weakest base → B is strongest acid

C: 

no resonance to delocalize ⊖ strongest CB, thus C is the weakest acid

Resonance exists here, but results in minor/less reasonable contributors (atoms w/o octets)

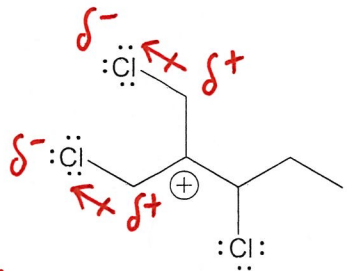
Free response. Provide the requested drawings or other information for the remaining questions.

11. For each proton transfer equation, draw curved arrows on the structures on the left to show how they react to produce the structures on the right. (6 pts)

a.

b.

12. An inductive effect exists in each of these structures. Circle the correct term to indicate whether this effect is electron donating or electron withdrawing and whether it exerts a stabilizing or destabilizing effect on the structure. (6 pts)



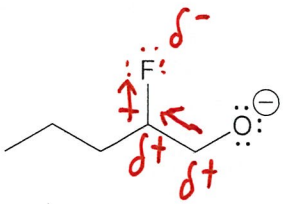
δ+ next to ⊕

Electron donating, stabilizing

Electron donating, destabilizing

Electron withdrawing, stabilizing

Electron withdrawing, destabilizing



Electron donating, stabilizing

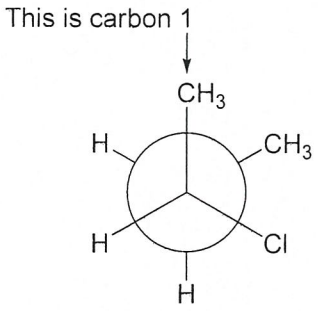
Electron donating, destabilizing

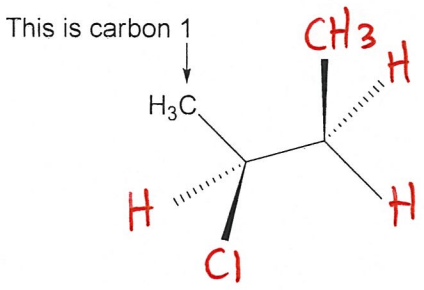
Electron withdrawing, stabilizing

Electron withdrawing, destabilizing

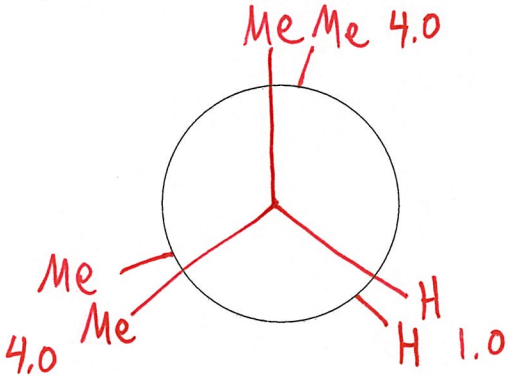
Effect of C-F dipole increases δ+ at this C and provides stabilization to the ⊖ on O

12. On the left is a Newman projection of one of the staggered conformations of 2-chlorobutane. Convert the Newman projection on the left to a wedge-and-dash ("perspective") drawing by writing the correct atom or group labels (e.g. H, CH_3, Cl) at the end of each bond. (5 pts)

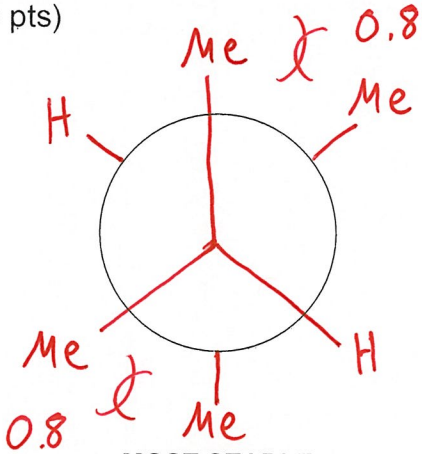




13a. Draw the least stable and most stable conformations of 2,3-dimethylbutane looking down the C2-C3 bond. Use the templates provided. (*Pro Tip™:* Be sure you are drawing the correct molecule!) (10 pts)



LEAST STABLE



MOST STABLE

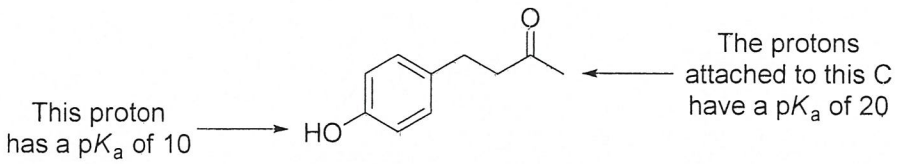
9.0 kcal/mol − 1.6 kcal/mol = 7.4 kcal/mol

13b. Calculate the barrier to rotation, in kcal/mol, around the C2-C3 bond in 2,3-dimethylbutane (see #13a!). A table of strain energies is provided for you. (Me = Methyl) (5 pts)

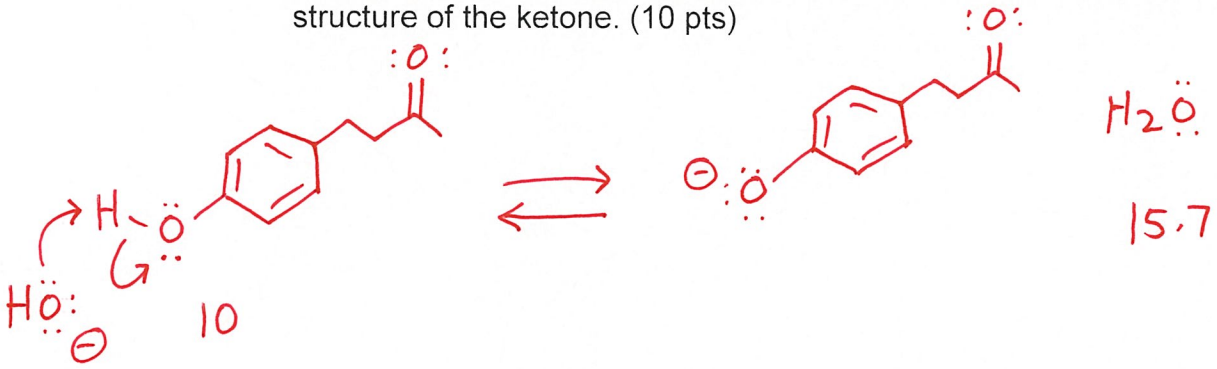
Interaction	Energy (kcal/mol)	Barrier to rotation =
Me-Me gauche	0.8	7.4 kcal/mol
H-H eclipse	1.0	
Me-H eclipse	1.3	
Me-Me eclipse	4.0	

14. A compound called raspberry ketone is found in raspberries and cranberries and is used as a flavoring additive in various foods:

Raspberry ketone (Frambinone)



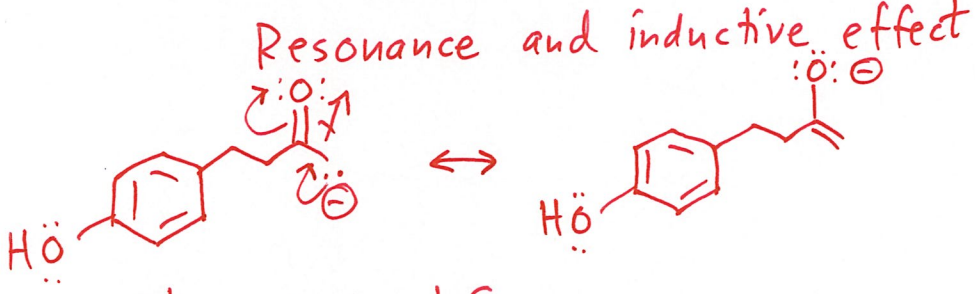
a. Using hydroxide ion as the Bronsted base, draw a mechanism to show the deprotonation of the OH group in raspberry ketone. Show all necessary curved arrows, lone pair electrons and nonzero formal charges. Draw the products of the proton transfer reaction. You will need to redraw the structure of the ketone. (10 pts)



b. Estimate the equilibrium constant for the proton transfer you drew in part "a". (4 pts) You can round 15.7 to 16:

$K \approx 10^{(16-10)} \approx 10^{6}$

c. On the right side of the raspberry ketone structure shown above is the second most acidic set of protons in raspberry ketone (p$K_a \approx 20$). List two factors that stabilize the conjugate base you get when one of those protons is removed. (4 pts)



δ^+ on carbonyl C
stabilizing to ⊖ shared by O and adjacent C