

CHEM 3311 (Richardson) Second Hour Exam – March 8, 2016

Your Name _____

Key

Student ID _____

- Recitation Time
- 3:00 Monday w/ Blaine McCarthy
 - 11:00 Tuesday w/ Thomas Carey
 - 1:00 Wednesday w/ Garrett Cairo
 - 8:00 Thursday w/ Blaine McCarthy
 - 3:00 Thursday w/ Garrett Cairo

Question	Score	Out of
1		30
2		18
3		10
4		12
5		10
6		10
7		10
8		6 e.c.
Total		100

This is a closed-book exam. The use of notes, calculators, or cell phones will not be allowed during the exam. You may use models sets brought in a clear ziplock bag. Use the backs of the pages for scratch work. If your final answer is not clearly specified, you will lose points. For mechanisms, show all intermediates including correct formal charges, but do not show transition states.

hydrogen 1 H 1.00794																	helium 2 He 4.00260						
lithium 3 Li 6.941	beryllium 4 Be 9.0122																	boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305																	aluminum 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078	scandium 21 Sc 44.956	titanium 22 Ti 47.887	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.38	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selecnium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80						
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	paladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29						
cesium 55 Cs 132.91	barium 56 Ba 137.33	lanthanum 57 La 138.905	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]						
francium 87 Fr [223]	radium 88 Ra [226]	* 57-70 Lr [257]	* Rf [261]	* Db [262]	* Sg [266]	* Bh [264]	* Hs [265]	* Mt [268]	* Uun [271]	* Uu [271]	* Uub [271]	* Uuq [271]											

* Lanthanide series

lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.05
actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

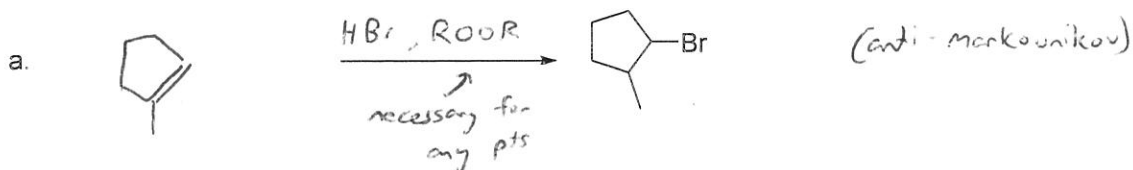
** Actinide series

pKa Values

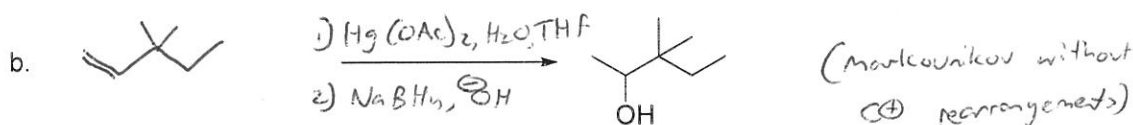
HI	-10	CH ₃ COOH	4.7	Phenol	10	H ₂	35
HBr	-8	HN ₃	4.7	RSH	10-12	NH ₃	36
HCl	-6	H ₂ S	7.0	H ₂ O	15.7	H ₂ C=CH ₂	45
H ₃ O ⁺	-1.7	NH ₄ ⁺	9.3	Alcohol (ROH)	16-18	CH ₄	60
HF	3.2	HCN	9.4	HC≡CH	26		

Average = 79.7
St. Dev = 15.0
Max = 104.0
Min = 42.0

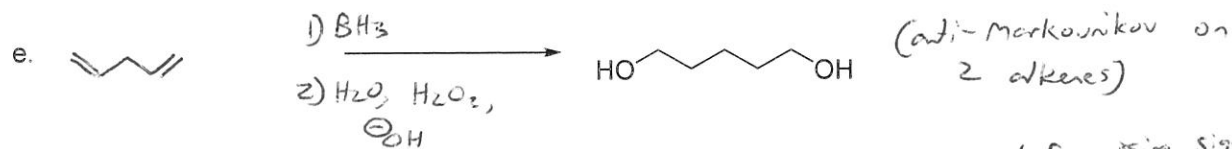
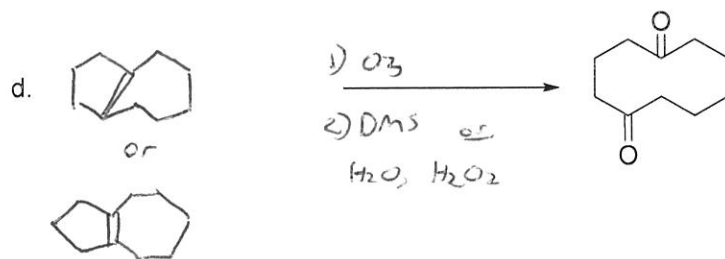
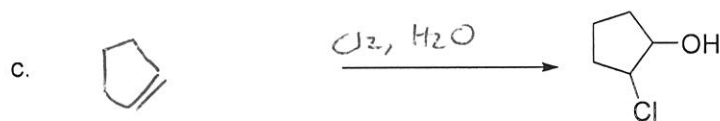
- 1) Starting from any hydrocarbon with the same number of carbon atoms as the product, and using any reactions that have been covered so far in class, show how you would create the products shown as **the only major product of the reaction**. Write your hydrocarbon starting material before the arrow, and the other reagents above or below the arrow. (30 pts).



6 pts each:
3 pts alkene
3 pts other reagents

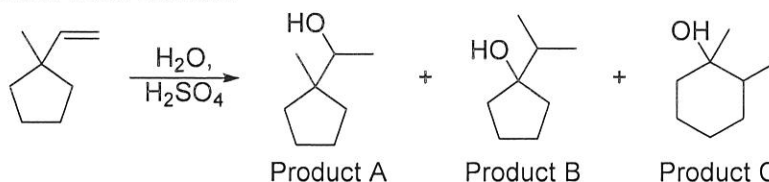


-1.5 pts for missing 1), 2).
-1.5 for missing any reagent.



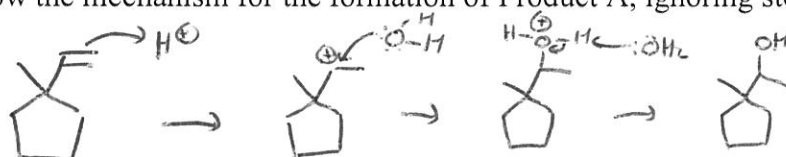
-1 pt for missing sign on OH

2) When an acid-catalyzed hydration was performed on the molecule shown below, some unexpected products were created.



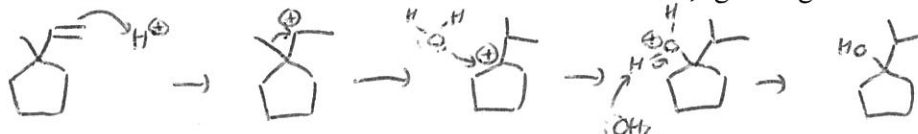
If basic conditions (OH⁻)
-4 for (a), -1 for (b) & (c).

a. Show the mechanism for the formation of Product A, ignoring stereochemistry. (4 pts)



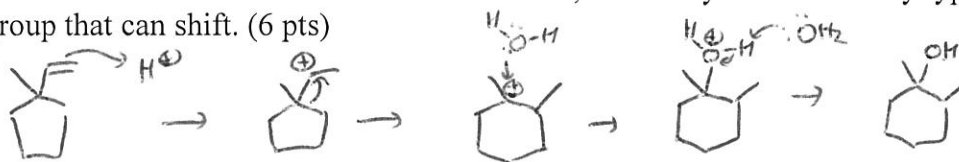
1 pt per intermediate/step
-0.5 for wrong charges

b. Show the mechanism for the formation of Product B, ignoring stereochemistry. (6 pts)



1 pt per intermediate/step
-0.5 for wrong charges

c. Show the mechanism for the formation of Product C, ignoring stereochemistry. Hint: It's almost identical to the formation of Product B, but methyl is not the only type of alkyl group that can shift. (6 pts)



1 pt per intermediate/step
-0.5 for wrong charges
-1 for missing methyl

d. Which of these three products is likely to be produced in the smallest quantity? (2 pts)

Product A - it has a 2° ct.

3) In your lab, you have found a mysterious bottle labeled "Terpinolene." In an attempt to discover its structure, you perform some reactions on it and observe the following results.

-3 pts for C=O or OH
-3 for one C=C in wrong place



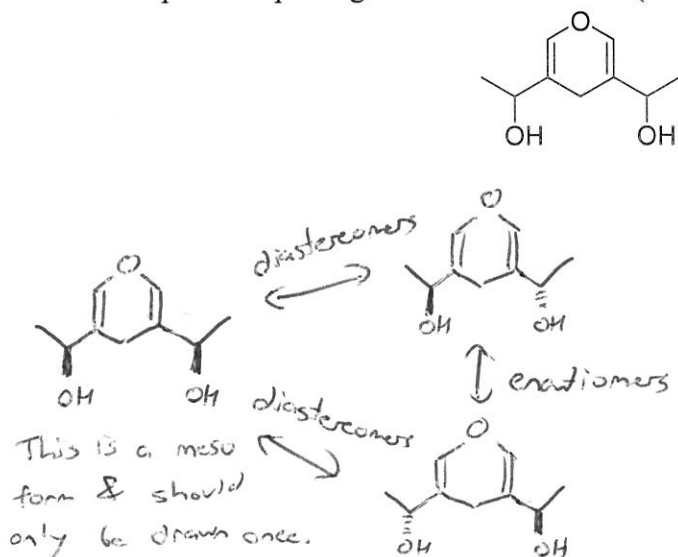
What is the structure of terpinolene? (10 pts)

4 pts for 6-member ring
4 pts for alkene
-2 pts for too many/too few alkenes



We know it has a 6-membered ring, so the only 2 carbons in ozonolysis product that could have been connected are 1 & 6. That means 3 & 9 were also connected to each other.

- 4) Using bold and dashed bonds, show all possible stereoisomers of the structure shown below. Leave all bonds in-plane (not bold or dashed) if they are part of the ring. Do not repeat any structures. What is the stereochemical relationship (enantiomers, diastereomers, identical) between each possible pairing of these molecules? (12 pts)



2 pts per structure,
2 pts per descriptor.

-1 pt for showing meso compound twice

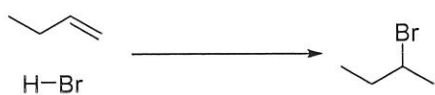
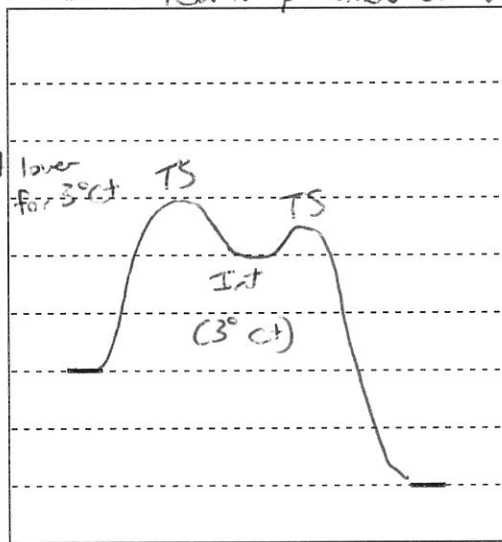
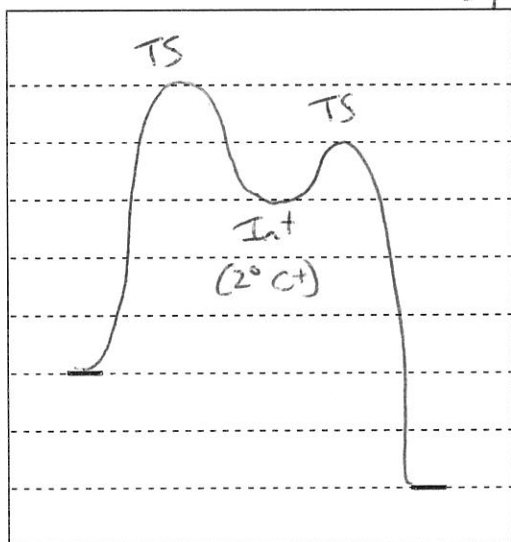
-2 pts for structures

M X or

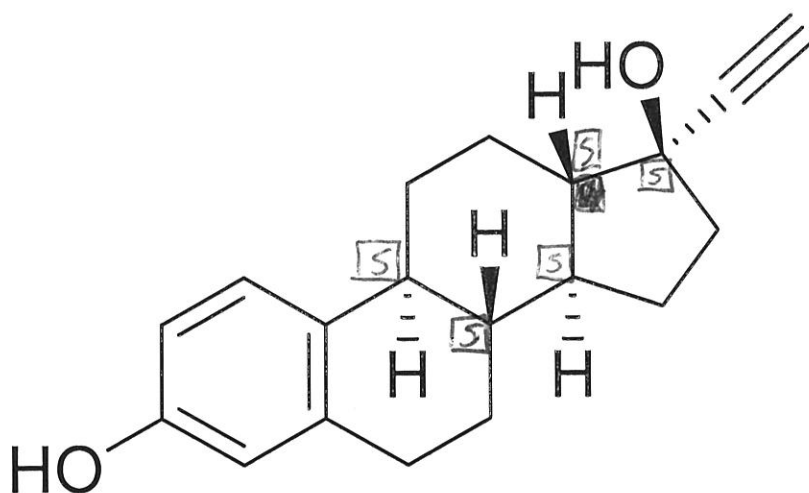
-2 for stereochem on sp^2 carbons.

- 5) Two reactions are shown below. Sketch the energy diagrams for each one, starting with the levels given for reactants and products. You don't need actual numbers, but the energy levels of each state should be correct relative to each other. Clearly label the location of each intermediate and transition state on the graph, though you do not need to draw the structures. (10 pts)

For each graph: 1 pt for each label, 2 pt for overall shape.
2 pts for correct relative placement of intermediates

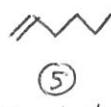
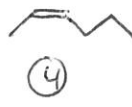
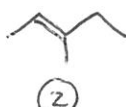
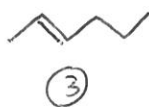


- 6) The structure of ethynyl estradiol, an oral contraceptive, is shown below. Label each stereocenter as R or S. (10 pts)



2 pts each

- 7) Put the following alkenes in order of stability, from most stable to least stable. (10 pts)
(E)-2-hexene, (E)-3-methyl-2-pentene, (Z)-2-hexene, 1-hexene, 2,3-dimethyl-2-butene



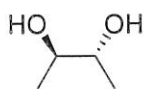
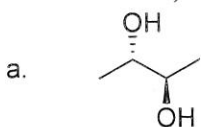
(least stable)

(most stable)

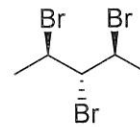
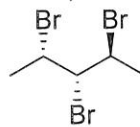
2 pts each

If only one is pulled out of sequence - 2 pts.

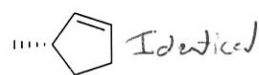
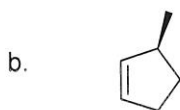
- 8) Extra credit! For each of the following pairs of molecules, are they identical, enantiomers, diastereomers, or constitutional isomers? (6 pts extra credit)



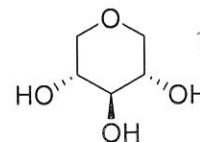
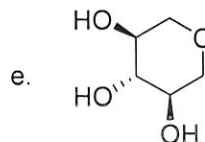
Diastereomers



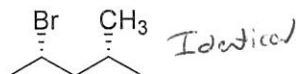
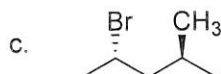
Diastereomers



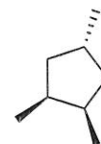
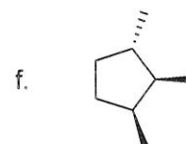
Identical



Identical



Identical



Const. isomers

1 pt each