

EXAM 3
CHEMISTRY 220
Friday, November 12, 2010

NAME (print): _____

TA:_____ Sect. Day:_____ Sect. Time:_____

Take a few moments to look over the exam. Answer each question on the exam paper.

No calculators or electronic devices. You may use molecular models. Important clues and structures are in **bold**. There is a **Periodic Table** on page 8.

Do all **preliminary** drawing or computations on the work sheets at the end of the exam. The work sheets will not be graded. You may detach the work sheets from the exam.

The exam is 55 minutes.

STOP writing and hand in your exam when you are asked to do so.

REMEMBER: Neatness is to your advantage.

1. (15 pts) Structure Determination _____

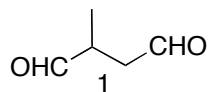
2. (30 pts) Reactions (Do 5 of 6) _____

3. (25 pts) Potpourri (Do 5 of 6) _____

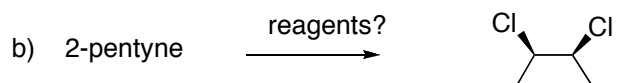
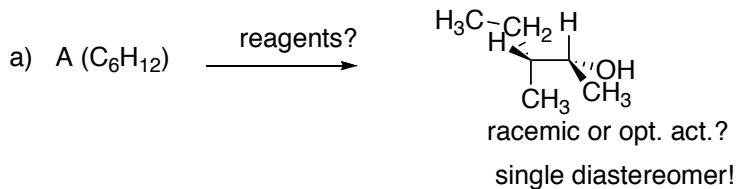
4. (30 pts) Mechanism _____

Total (100 pts)

- 1) **Structure Determination:** (15 pts.) Optically-active compound **A** ($C_{10}H_{16}$) [*Degrees of Unsaturation?*] reacts with Pt/H_2 to afford optically-active compound **B** ($C_{10}H_{20}$) [*Degrees of Unsaturation?*]. Ozonolysis of **A** followed by dimethyl sulfide reduction provides a **single** compound (*S*)-**1**. Draw (*S*)-**1**. What are the structures of **A** and **B**? **Explain your reasoning.**



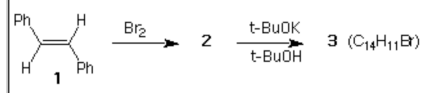
2) **Reactions:** (5 x 6 pts. = 30 pts.) Complete **5 of 6** of the following questions by providing structures, reagents, etc. Pay attention to stereochemistry, etc. Several steps may be required. **If you do more than 5 questions, clearly cross out the answer you do not want graded.**



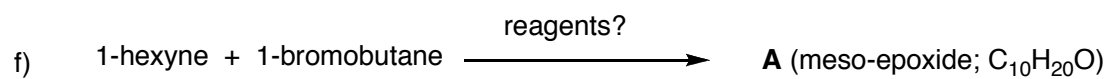
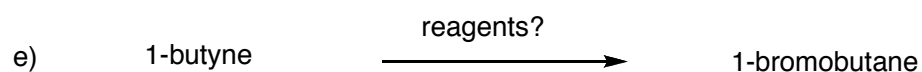
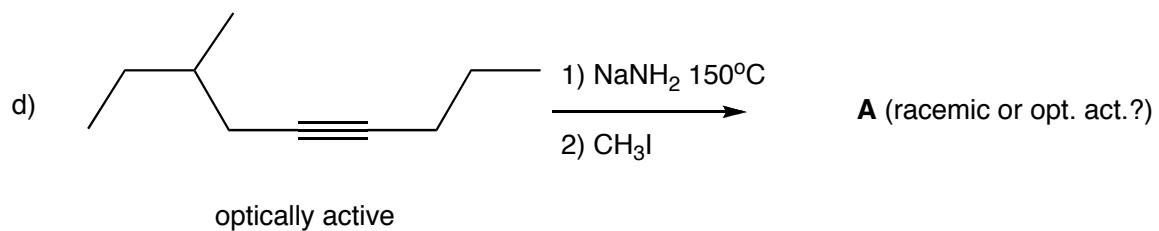
c) from ORGO/alkenes

Alkene 8:

Problem



...continued

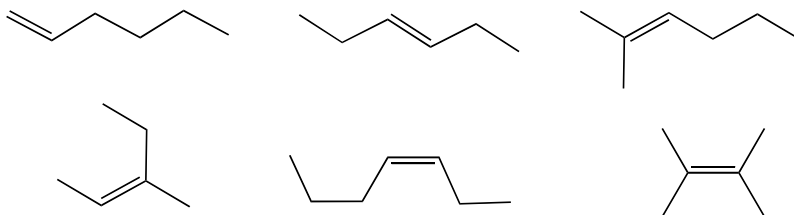


3) **Potpourri:** (5 x 5 pts. = 25 pts.) Provide the missing information in **5 of 6** of the following questions. **If you do more than 5 questions, clearly cross out the answer you do not want graded.**

a) **Circle** the terms that best apply to the hydration of 3-decyne with $\text{HgSO}_4/\text{aq. H}_2\text{SO}_4$.

regioselective stoichiometric Hg^{++} oxidation reduction enol tautomerization

b) **Circle** the **heptene** with the **greater** heat of hydrogenation.



c) **Circle** the compound(s) with a degree of unsaturation = 9.

$\text{C}_{17}\text{H}_{21}\text{NO}_4$
(cocaine)

$\text{C}_{17}\text{H}_{19}\text{NO}_3$
(morphine)

$\text{C}_{17}\text{H}_{17}\text{Cl}_2\text{N}$
(Sertraline – Zoloft)

d) **Circle** the terms that apply to the reaction of $\text{OsO}_4/\text{H}_2\text{O}_2$ with (*E*)-3-hexene.

catalytic regioselective d,l-pair reduction optically-active

e) Estimate the heat of formation of 5-decyne given that $\Delta H_f^\circ = +34.8$ kcal/mol for 2-butyne. **Show work.**

f) Write a brief description of the relevance of the work of Paul Sabatier (Nobel Prize 1912) to the chemistry covered on this exam.

4) **Mechanisms:** (5 x 5 pts. = 25 pts.) Complete each of the questions below.

iv) In the reaction of a terminal alkyne in a typical hydroboration procedure, why is diisoamylborane employed rather than borane? What is the downside?

v) For the preparation of secondary alcohols the hydroboration of the stereoisomers of 3-hexene is an acceptable procedure. The same cannot be said for the 2-hexenes. Explain.

BDE

http://classes.yale.edu/chem220/STUDYAIDS/thermo/BDE.html

Bond Dissociation Energies (kcal/mol)

$(X-Y \rightarrow X \cdot + Y \cdot)$

$\Delta H_f^\circ (RH) = \Delta H_f^\circ (R \cdot) + \Delta H_f^\circ (H \cdot) - \Delta H_f^\circ (RH)$

Note: These values are the one's used principally in Wade's text. We will use these values. Newer values have been determined by Blanksby and Ellison, *Acc. Chem. Res.* **2003**, *36*, 255. The Ellison paper is [here](#) in pdf format. For a discussion of heats of reaction, BDEs and heats of formation, [click here](#).

C-H Bonds

CH ₃ -H	CH ₃ CH ₂ -H	(CH ₃) ₂ CH-H	(CH ₃) ₃ C-H	CH ₂ =CHCH ₂ -H	PhCH ₂ -H	CH ₂ =CH-H
104	98	95	91	87	85	108

C-C Bonds

CH ₃ -CH ₃	CH ₃ CH ₂ -CH ₃	(CH ₃) ₂ CH-CH ₃	CH ₃ CH ₂ -CH ₂ CH ₃	(CH ₃) ₃ C-CH ₃
88	85	84	82	81

C-Cl Bonds

CH ₃ -Cl	CH ₃ CH ₂ -Cl	(CH ₃) ₂ CH-Cl	(CH ₃) ₃ C-Cl
84	81	80	79

C-Br Bonds

CH ₃ -Br	CH ₃ CH ₂ -Br	(CH ₃) ₂ CH-Br	(CH ₃) ₃ C-Br
70	68	68	65

C-I Bonds

CH ₃ -I	CH ₃ CH ₂ -I	(CH ₃) ₂ CH-I	(CH ₃) ₃ C-I
56	53	53	50

H-X and X-X Bonds

H-Cl	H-Br	H-I	H-H	Cl-Cl	Br-Br	I-I	HOOH
103	88	71	104	58	46	36	51

hydrogen 1 H 1.0079																		helium 2 He 4.0026																			
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 47.867		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 65.39		gallium 31 Ga 69.723		germanium 32 Ge 72.61		arsenic 33 As 74.922		selenium 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		palladium 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		57-70 ★		lutetium 71 Lu 174.97		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]		89-102 ★ ★		lawrencium 103 Lr [261]		rutherfordium 104 Rf [261]		dubnium 105 Db [262]		seaborgium 106 Sg [266]		bohrium 107 Bh [264]		hassium 108 Hs [265]		meitnerium 109 Mt [269]		unnilium 110 Uun [271]		ununium 111 Uuu [272]		unbium 112 Uub [273]		unennium 114 Uuq [289]											
																																		</			

* Lanthanide series

* * Actinide 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 173.04
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]

Name _____ 9

Work Sheets

Name _____ 10

Work Sheets

Work Sheets