CH 335

First Midterm Exam Thursday, January 30, 2014

Name_____

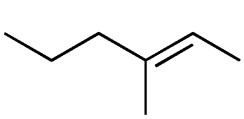
You may use model kits or drawing templates but no other material with chemical information without instructor approval.

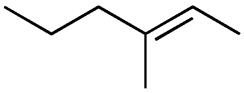
Please do not use ipods or other music players.

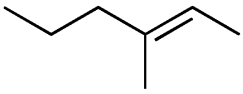
hydrogen 1 H 1.0079																	helium 2 He 4.0026
lithium 3 Li 6.941	beryllium 4 Be 9.0122											boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305											aluminium 13 Al 26.982	silicon 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
caesium 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 [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	ununnilium 110 Uun [271]	unununium 111 Uuu [272]	ununbium 112 Uub [277]		ununquadium 114 Uuq [289]				

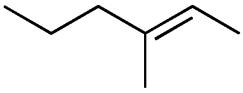
*Lanthanide series	lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
**Actinide series	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]

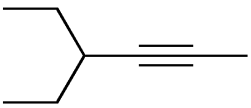
1. (30 points) Write the expected products for each of the following reactions. Specify stereochemistry where appropriate.

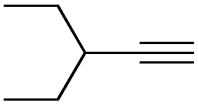
A.  D_2, Pt/C →

B.  HBr / CH_2Cl_2 →

C.  Br_2 / H_2O →

D.  1. BH_3-THF; 2. H_2O_2, NaOH, H_2O →

E.  Br_2 / (2 eq.) →

F.  $Hg(OAc)_2$, H_2O, / H_3O^+ →

2. (24 points) Write (over the arrow) the reagents needed to accomplish the following transformations.

A. 

(racemic)

B. 

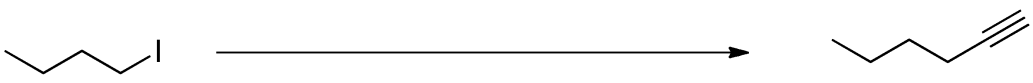
(racemic)

C. 

(racemic)

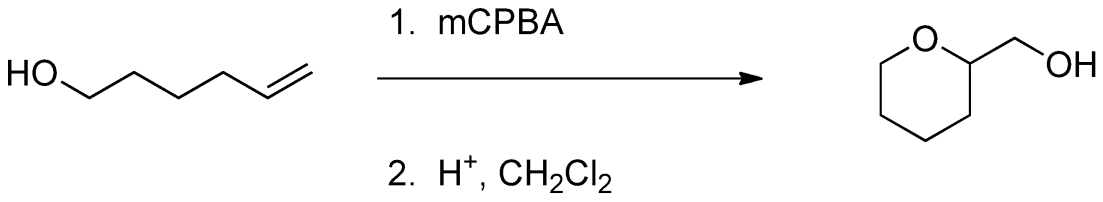
D. 

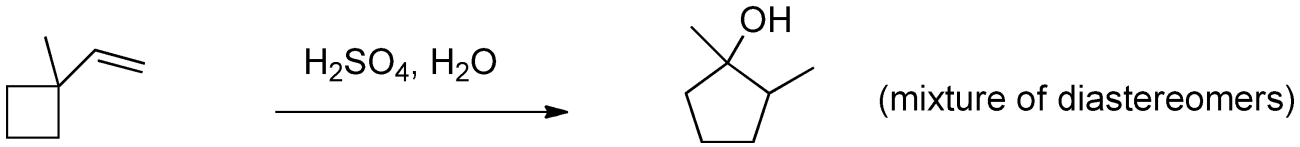
(racemic)

E. 

F. 

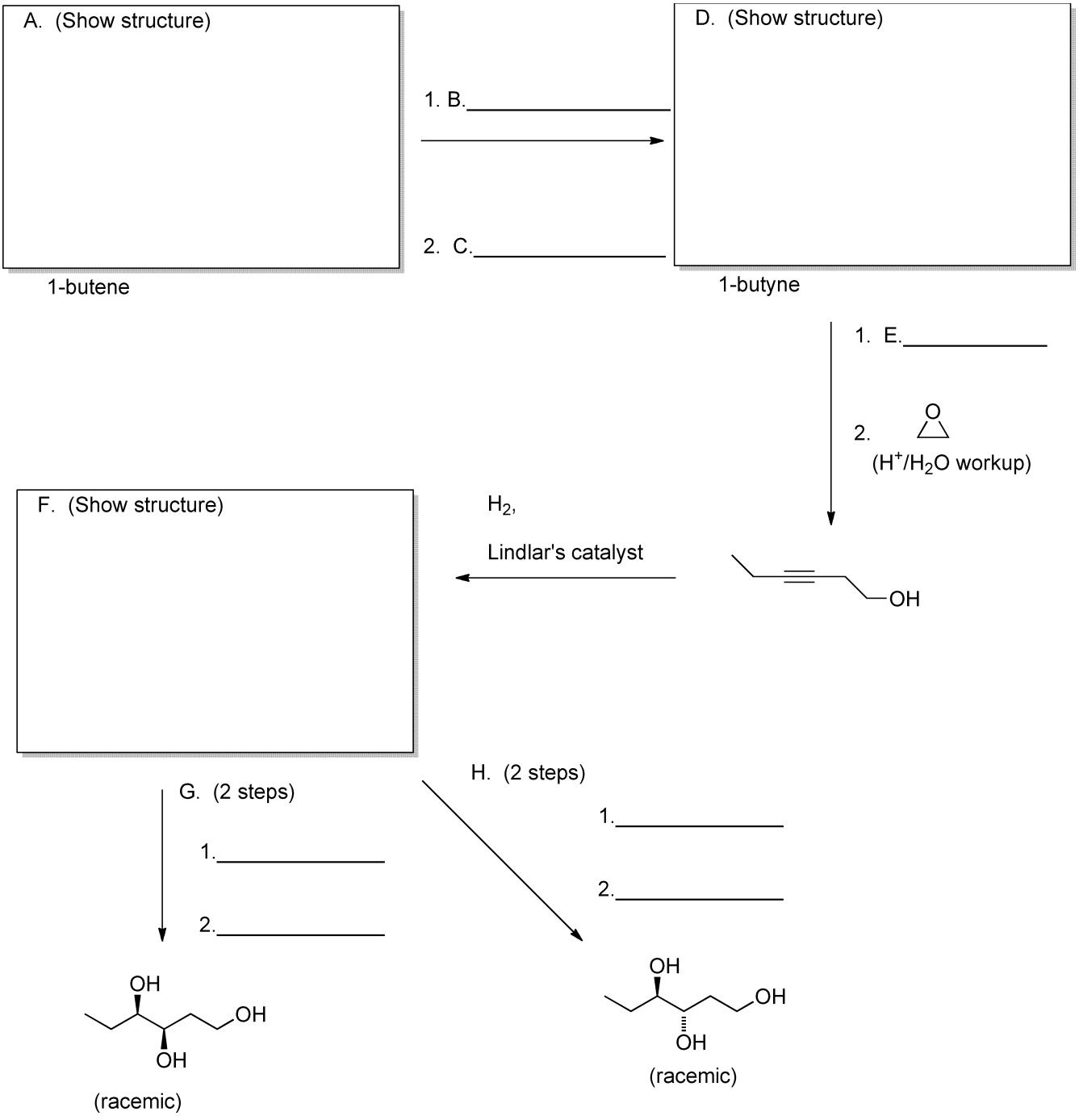
3. (20 points) Write mechanisms (using the correct electron-pushing formalism, and as many steps as needed) for each of the following transformations.





(mixture of diastereomers)

4. (14 points) Complete the multistep synthesis shown below. For each letter A-H, provide either a structure (for stable, isolated organic compounds) or the reagent(s) needed to accomplish the transformation. Note that I have given you names for structures A and D.



5. (12 points) Ethylene, as measured using its 1,2-dideuterio form (CHD=CHD) has a barrier to E/Z interconversion of 63.2 kcal/mol. This means that we would have to heat it to 500°C in order to see an appreciable rate of isomerization.

E-cyclooctene, in contrast, has a much lower barrier to isomerization: 46.2 kcal/mol. This means it will undergo isomerization at temperatures between 250-300°C—still a high temperature, but it shows that isomerization is easier than for most "normal" alkenes.

A. Describe what happens to the C=C bond during E/Z isomerization. You may wish to use an energy diagram and/or pictures of interacting orbitals in the bond. (You may use the back of the page if needed.)

B. Based on this description, why is the barrier to isomerization for E-cyclooctene so much lower? (There are, in fact two contributing effects; one is large and the other smaller.)

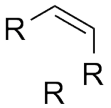
C. If the heat of hydrogenation of E-cyclooctene is -35.8 kcal/mol, and that for E-cycloheptene is -48.6 kcal/mol, what would you predict the barrier to isomerization of E-cycloheptene to be? Explain.

Bond strengths (kcal/mol):

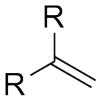
F-F	38
Cl-Cl	58
Br-Br	46
I-I	36
H-F	136
H-Cl	103
H-Br	87
H-I	71
CH_3-H	105
CH_3CH_2-H	101
$(CH_3)_2CH$-H	98.5
$(CH_3)_3C$-H	96.5
CH_3-F	110
CH_3-Cl	85
CH_3-Br	70
CH_3-I	57
CH_3CH_2-F	111
CH_3CH_2-Cl	84
CH_3CH_2-Br	70
CH_3CH_2-I	56
$(CH_3)_2CH$-F	111
$(CH_3)_2CH$-Cl	84
$(CH_3)_2CH$-Br	71
$(CH_3)_2CH$-I	56
$(CH_3)_3C$-F	110
$(CH_3)_3C$-Cl	85
$(CH_3)_3C$-Br	71
$(CH_3)_3C$-I	55

Typical Heats of Hydrogenation

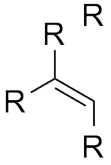
-30 kcal/mol



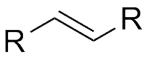
-28.2 kcal/mol



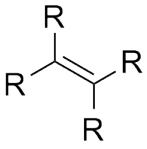
-27.9 kcal/mol



-26.5 kcal/mol



-27.4 kcal/mol



-26.3 kcal/mol