

Name \_\_\_\_\_

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

Please do not use any electronic gadgets.

hydrogen 1 <b>H</b> 1.0079																					helium 2 <b>He</b> 4.0026					
lithium 3 <b>Li</b> 6.941	beryllium 4 <b>Be</b> 9.0122																				boron 5 <b>B</b> 10.811	carbon 6 <b>C</b> 12.011	nitrogen 7 <b>N</b> 14.007	oxygen 8 <b>O</b> 15.999	fluorine 9 <b>F</b> 18.998	neon 10 <b>Ne</b> 20.180
sodium 11 <b>Na</b> 22.990	magnesium 12 <b>Mg</b> 24.305																				aluminum 13 <b>Al</b> 26.982	silicon 14 <b>Si</b> 28.086	phosphorus 15 <b>P</b> 30.974	sulfur 16 <b>S</b> 32.065	chlorine 17 <b>Cl</b> 35.453	argon 18 <b>Ar</b> 39.948
potassium 19 <b>K</b> 39.098	calcium 20 <b>Ca</b> 40.078	scandium 21 <b>Sc</b> 44.956	titanium 22 <b>Ti</b> 47.867	vanadium 23 <b>V</b> 50.942	chromium 24 <b>Cr</b> 51.996	manganese 25 <b>Mn</b> 54.938	iron 26 <b>Fe</b> 55.845	cobalt 27 <b>Co</b> 58.933	nickel 28 <b>Ni</b> 58.693	copper 29 <b>Cu</b> 63.546	zinc 30 <b>Zn</b> 65.39	gallium 31 <b>Ga</b> 69.723	germanium 32 <b>Ge</b> 72.61	arsenic 33 <b>As</b> 74.922	selenium 34 <b>Se</b> 78.96	bromine 35 <b>Br</b> 79.904	krypton 36 <b>Kr</b> 83.80									
rubidium 37 <b>Rb</b> 85.468	strontium 38 <b>Sr</b> 87.62	yttrium 39 <b>Y</b> 88.906	zirconium 40 <b>Zr</b> 91.224	niobium 41 <b>Nb</b> 92.906	molybdenum 42 <b>Mo</b> 95.94	technetium 43 <b>Tc</b> [98]	ruthenium 44 <b>Ru</b> 101.07	rhodium 45 <b>Rh</b> 102.91	palladium 46 <b>Pd</b> 106.42	silver 47 <b>Ag</b> 107.87	cadmium 48 <b>Cd</b> 112.41	indium 49 <b>In</b> 114.82	tin 50 <b>Sn</b> 118.71	antimony 51 <b>Sb</b> 121.76	tellurium 52 <b>Te</b> 127.60	iodine 53 <b>I</b> 126.90	xenon 54 <b>Xe</b> 131.29									
cesium 55 <b>Cs</b> 132.91	barium 56 <b>Ba</b> 137.33	57-70 *	lutetium 71 <b>Lu</b> 174.97	hafnium 72 <b>Hf</b> 178.49	tantalum 73 <b>Ta</b> 180.95	tungsten 74 <b>W</b> 183.84	rhenium 75 <b>Re</b> 186.21	osmium 76 <b>Os</b> 190.23	iridium 77 <b>Ir</b> 192.22	platinum 78 <b>Pt</b> 195.08	gold 79 <b>Au</b> 196.97	mercury 80 <b>Hg</b> 200.59	thallium 81 <b>Tl</b> 204.38	lead 82 <b>Pb</b> 207.2	bismuth 83 <b>Bi</b> 208.98	polonium 84 <b>Po</b> [209]	astatine 85 <b>At</b> [210]	radon 86 <b>Rn</b> [222]								
francium 87 <b>Fr</b> [223]	radium 88 <b>Ra</b> [226]	89-102 **	lawrencium 103 <b>Lr</b> [262]	rutherfordium 104 <b>Rf</b> [261]	dubnium 105 <b>Db</b> [262]	seaborgium 106 <b>Sg</b> [269]	bohrium 107 <b>Bh</b> [264]	hassium 108 <b>Hs</b> [269]	meitnerium 109 <b>Mt</b> [269]	ununilium 110 <b>Uun</b> [271]	unununium 111 <b>Uuu</b> [272]	unubium 112 <b>Uub</b> [277]		ununquadium 114 <b>Uuq</b> [289]												

\* Lanthanide series

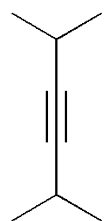
lanthanum 57 <b>La</b> 138.91	cerium 58 <b>Ce</b> 140.12	praseodymium 59 <b>Pr</b> 140.91	neodymium 60 <b>Nd</b> 144.24	promethium 61 <b>Pm</b> [145]	samarium 62 <b>Sm</b> 150.36	europium 63 <b>Eu</b> 151.96	gadolinium 64 <b>Gd</b> 157.25	terbium 65 <b>Tb</b> 158.93	dysprosium 66 <b>Dy</b> 162.50	holmium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

actinium 89 <b>Ac</b> [227]	thorium 90 <b>Th</b> 232.04	protactinium 91 <b>Pa</b> 231.04	uranium 92 <b>U</b> 238.03	neptunium 93 <b>Np</b> [237]	plutonium 94 <b>Pu</b> [244]	americium 95 <b>Am</b> [243]	curium 96 <b>Cm</b> [247]	berkelium 97 <b>Bk</b> [247]	californium 98 <b>Cf</b> [251]	einsteinium 99 <b>Es</b> [252]	fermium 100 <b>Fm</b> [257]	mendelevium 101 <b>Md</b> [258]	nobelium 102 <b>No</b> [259]
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1. (30 points) Write the expected products for each of the following reactions. Specify stereochemistry where appropriate (you may write "racemic" in place of drawing a second enantiomer).

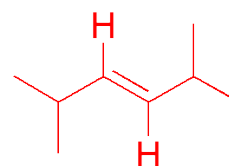
A.



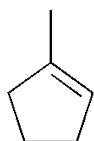
Na metal



NH<sub>3</sub> (liq.)



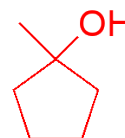
B.



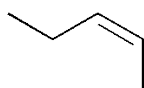
1. Hg(OAc)<sub>2</sub>, H<sub>2</sub>O



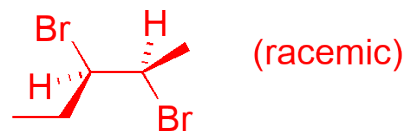
2. NaBH<sub>4</sub>



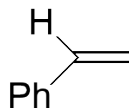
C.



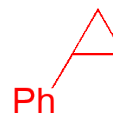
Br<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>



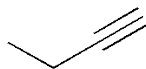
D.



CH<sub>2</sub>I<sub>2</sub>, Zn-Cu



E.



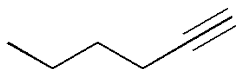
1. NaNH<sub>2</sub>



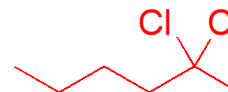
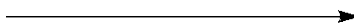
2. CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Br



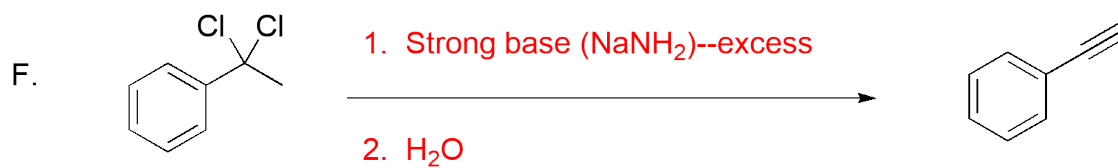
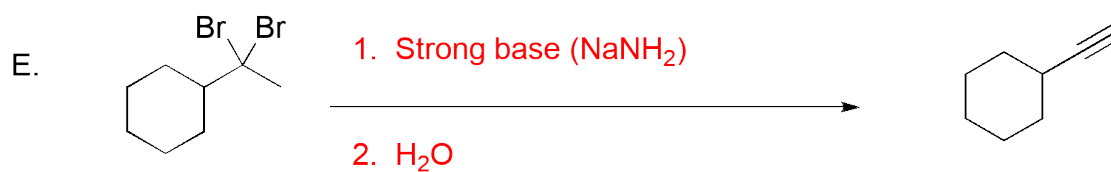
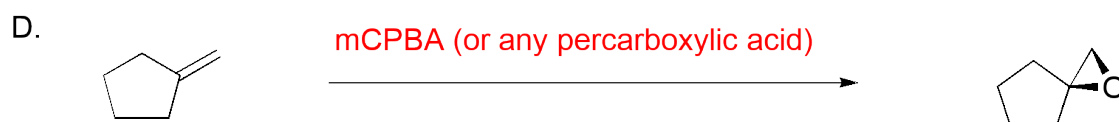
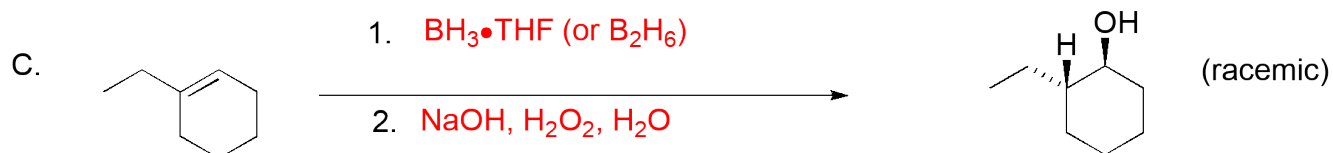
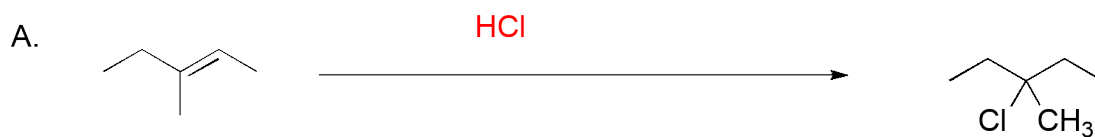
F.



HCl (excess)

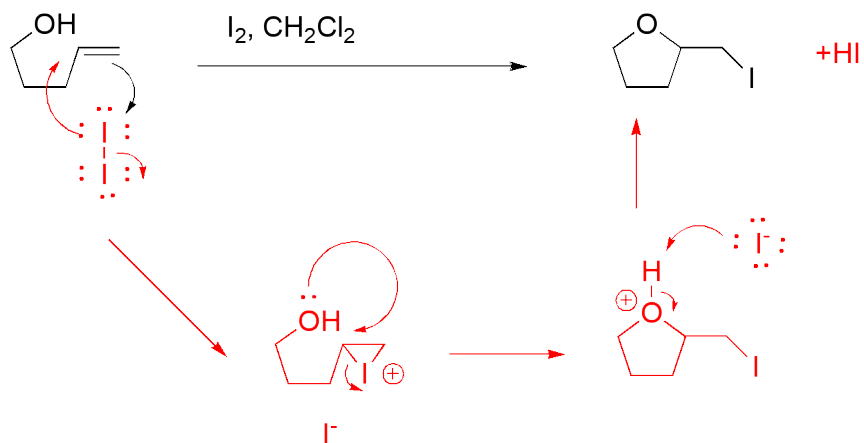


2. (25 points) Write (over the arrow) the reagents needed to accomplish the following transformations.

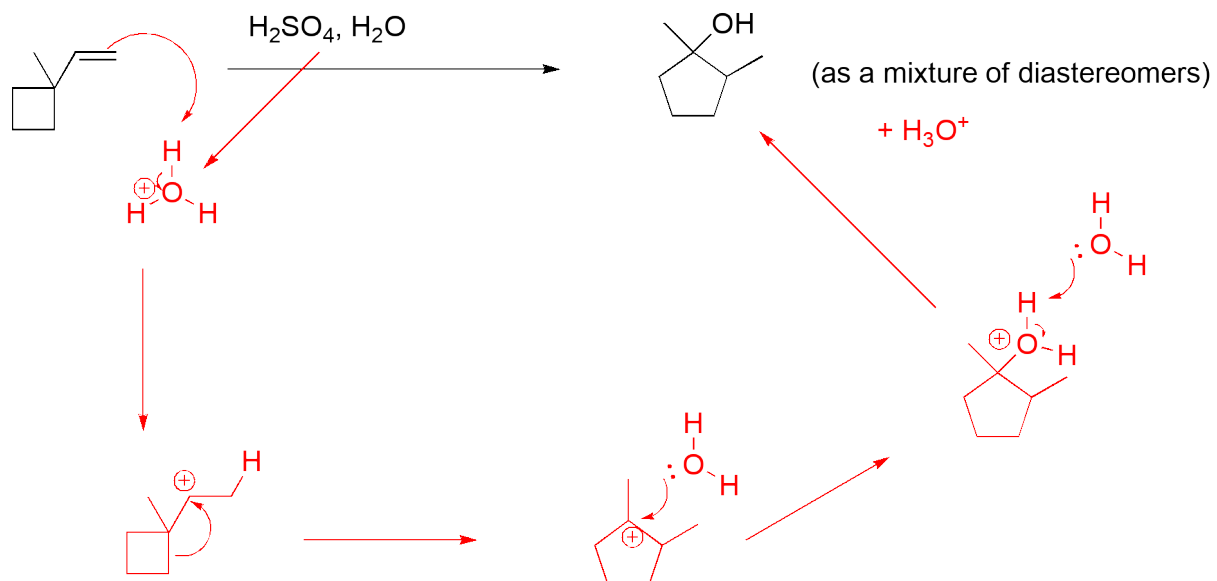


3. (20 points) Write mechanisms (using the correct electron-pushing formalism, and as many steps as needed) for each of the following transformations.

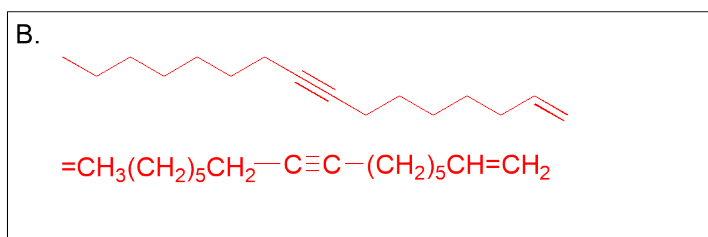
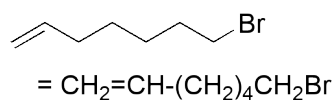
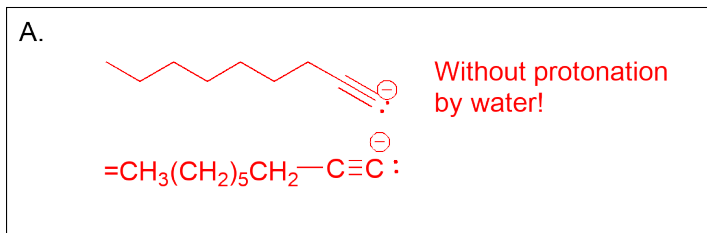
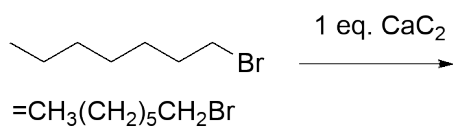
A.



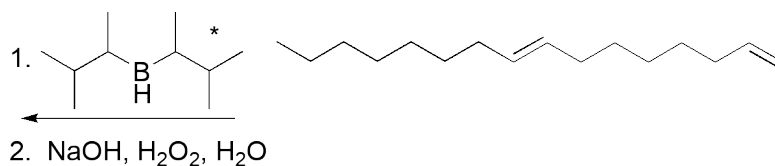
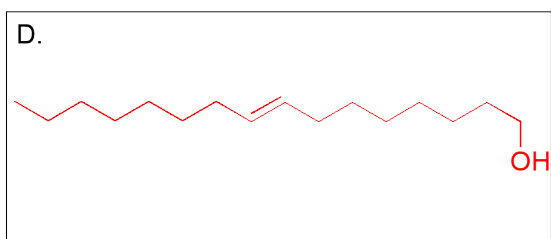
B.



4. (16 points) Long-chain fatty alcohols are often observed to be chemical signaling agents in insect biochemistry. Fill in the boxes for intermediate structures or reagents in the following synthesis of (8S, 9S)-1,8,9-hexadecanetriol. (You may abbreviate using the  $(\text{CH}_2)_n$  formalism.)

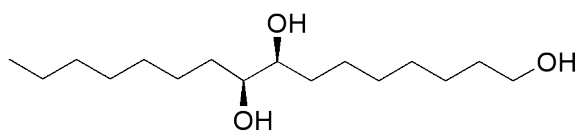


C. Na metal,  $\text{NH}_3$  (liquid)



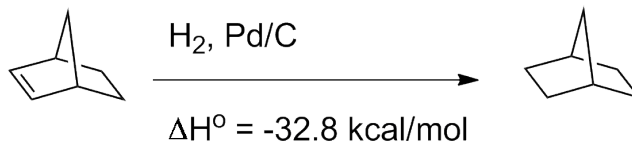
\* This reagent reacts selectively with monosubstituted alkenes in the presence of more highly substituted alkenes

1.  $\text{OsO}_4$   
2.  $\text{NaHSO}_3$

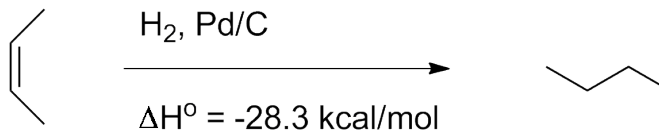


5. (9 points) The heat of hydrogenation for norbornene ([2.2.1]-bicyclo-hept-2-ene, shown at the right) is -32.8 kcal/mol.

Explain why this is different from that for Z-2-butene (-28.3 kcal/mol).



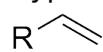

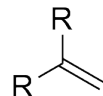

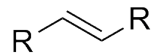
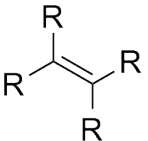
The C=C-C bond angles in the bicyclic compound are compressed versus what is normally seen in a cis alkene ( $107.2^\circ$  versus  $123.8^\circ$  for (Z)-2-butene). This destabilization energy is released in addition to the C-H bond formation energy on rehybridization, and leads to an extra 4.5 kcal/mol of hydrogenation energy.



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 <sub>3</sub> -H	105
CH <sub>3</sub> CH <sub>2</sub> -H	101
(CH <sub>3</sub> ) <sub>2</sub> CH-H	98.5
(CH <sub>3</sub> ) <sub>3</sub> C-H	96.5
CH <sub>3</sub> -F	110
CH <sub>3</sub> -Cl	85
CH <sub>3</sub> -Br	70
CH <sub>3</sub> -I	57
CH <sub>3</sub> CH <sub>2</sub> -F	111
CH <sub>3</sub> CH <sub>2</sub> -Cl	84
CH <sub>3</sub> CH <sub>2</sub> -Br	70
CH <sub>3</sub> CH <sub>2</sub> -I	56
(CH <sub>3</sub> ) <sub>2</sub> CH-F	111
(CH <sub>3</sub> ) <sub>2</sub> CH-Cl	84
(CH <sub>3</sub> ) <sub>2</sub> CH-Br	71
(CH <sub>3</sub> ) <sub>2</sub> CH-I	56
(CH <sub>3</sub> ) <sub>3</sub> C-F	110
(CH <sub>3</sub> ) <sub>3</sub> C-Cl	85
(CH <sub>3</sub> ) <sub>3</sub> C-Br	71
(CH <sub>3</sub> ) <sub>3</sub> C-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