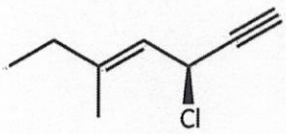
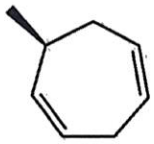
Answer Key

1. Name the following compounds. Don't forget about stereochemistry. (10 points)

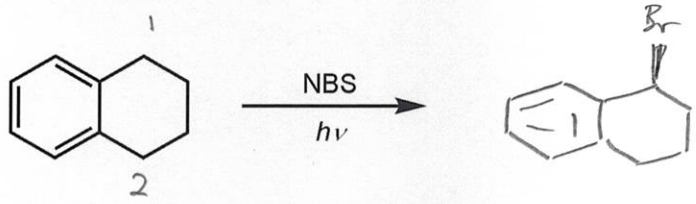
a. 

(3S, 4E)-3-chloro-5-methyl-hept-4-en-1-yne

b. 

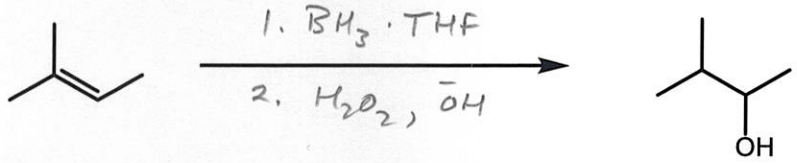
(S)-6-methyl cyclohepta-1,4-diene

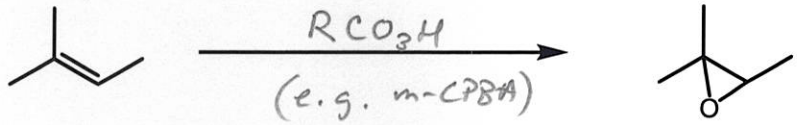
2. The reaction below produces only one product (and its enantiomer). Show the product and explain why it's the only one. (10 points)

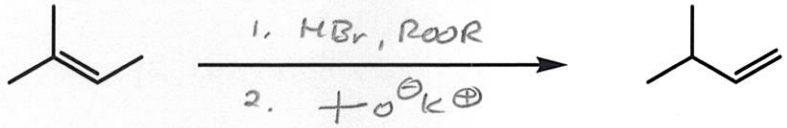


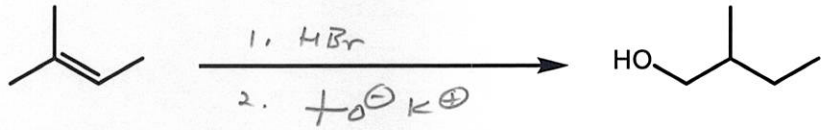
- bromination occurs at the benzylic position
- positions 1 & 2 are the same by symmetry

3. Show how to make the following compounds from the given starting materials. Some of the transformations require more than one step. (20 points)

a. 

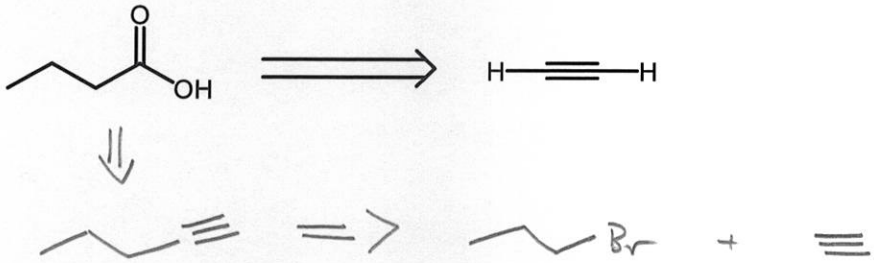
b. 

c. 

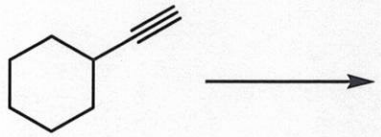
d. 

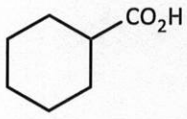
3. $BH_3 \cdot THF$
4. H_2O_2 $\bar{O}H$

4. Show the retrosynthetic analysis for how to prepare the product shown below starting from acetylene. (20 points) (See *Klein*, Organic Chemistry, Section 11.5, first)

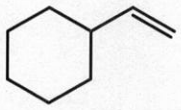


5. Show how to convert the alkyne below to each of the following compounds. List the reagents and conditions below each compound (some of these may require more than one step!). You don't need to show any intermediates (if there are any). (25 points)

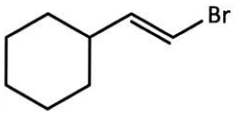


a. 

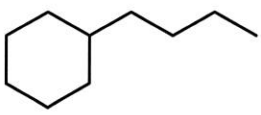
1. O_3
2. H_2O

b. 

H_2
Lindlar's catalyst

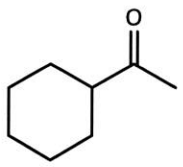
c. 

HBr
ROOR

d. 

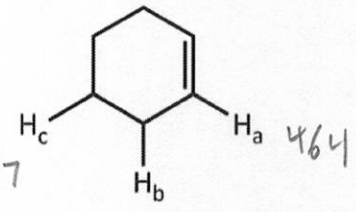
1. $NaNH_2$
2.

3. H_2, Pt

e. 

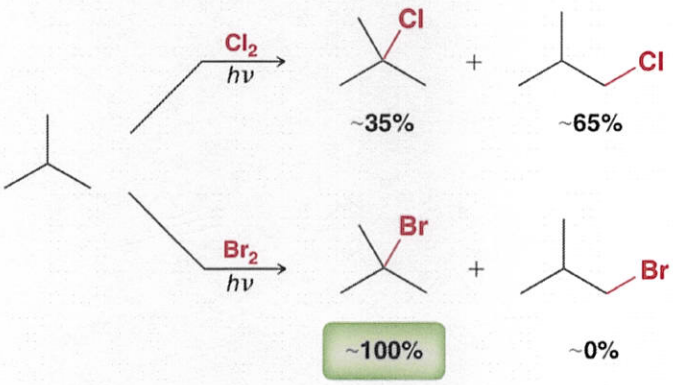
H_2SO_4
$HgSO_4$
H_2O

6. For the compound shown below, the carbon-hydrogen bonds to the highlighted hydrogens H_a, H_b, and H_c, have bond dissociation enthalpies (BDEs) of 397, 364, 464 kJ/mol, *irrespectively*. Assign these values to the correct hydrogens and indicate which one is most likely to be abstracted in a *radical* reaction. (20 points)



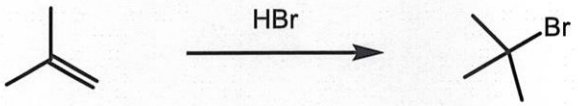
397
464
364 ← easiest H to remove
most likely to be abstracted – leads to the most stable allylic radical

7. Provide an explanation for the dramatic difference in the ratio of products produced below. (10 points)



8. In terms of the mechanism of the reaction explain why the addition of peroxides changes the course of the addition reaction shown below. (10 points)

Extra Credit Historically, where did the peroxides come from that led to the discovery of the "peroxide effect"? (5 EC points)



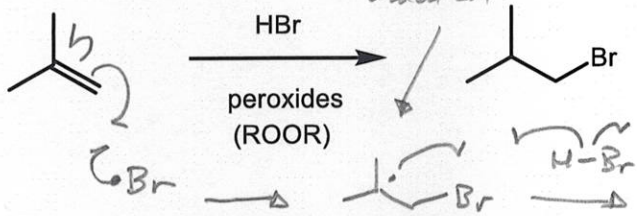
with peroxides, the reaction undergoes an initiation step

RO-OR → RO· + ·OR

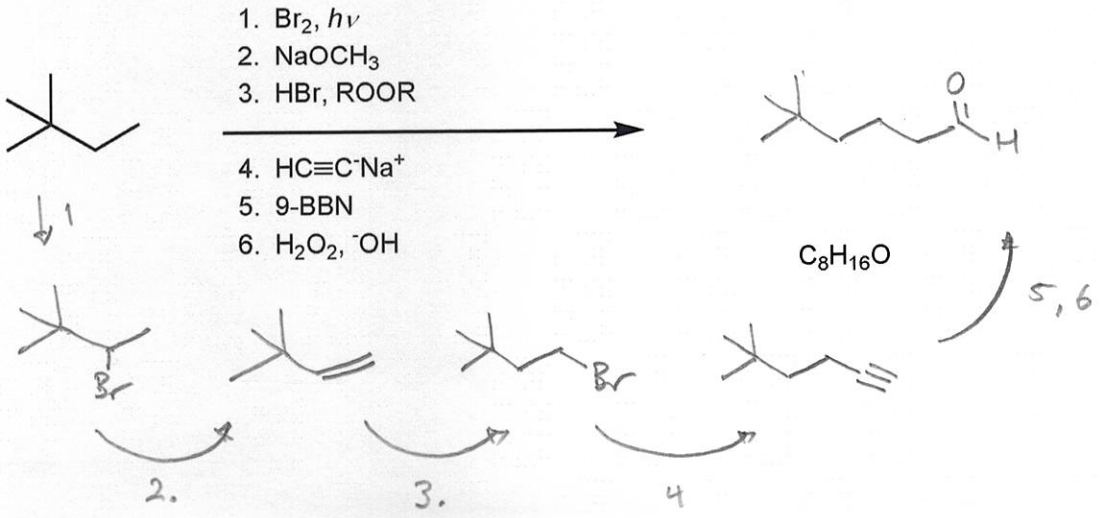
this abstracts a hydrogen to produce a bromine radical

RO· + H-Br → Br· + HOR

Bromine adds to give most stable radical



9. What is the final product? Show each intermediate compound. (20 points)



10. For the following diagram of reactions, fill in the reagents necessary to accomplish each transformation (some of them require more than one step – be sure to use 1. reagent 1, 2. reagent 2, etc. format when necessary). You do not need to show any intermediates.
Fill in your answers here: (55 points)

a. $HgSO_4$, H_2SO_4 H_2O

b. 1. Br_2 2. $NaNH_2$ 3. H_2O

c. H_2, Lindlar's

d. 1. 9-BBN 2. H_2O_2 ^-OH

e. step b., then step d.

f. NaH or DBN

g. HBr, ROOR

h. 1. BH_3-THF 2. H_2O_2 ^-OH

i. 1, Ts-Cl, pyridine 2. DBN

j. KOH

k. PBr_3