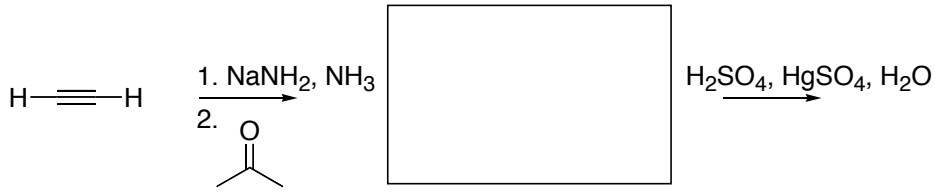
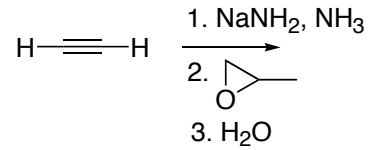
Massachusetts Institute of Technology 5.12, Spring 2005
Problem Set 5, Due 4pm March 31

1. Draw the products of the following reactions. Ignore stereochemistry.

a. 

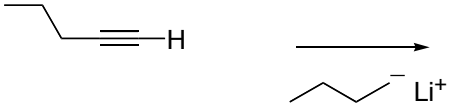
b. 

2.
a. Draw the molecular orbital diagram of ethyne.

b. What is the pKa of ethyne?

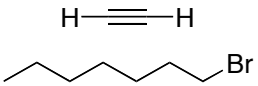
c. What is the pKa of ethane?

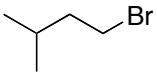
d. n-butyl lithium is a commercially available form of an alklyl anion. Draw the structure of the product of the following reaction.



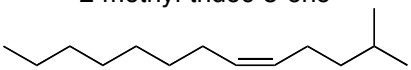
3.
Design a multistep synthesis for the following compound 2-methyl-tridec-5-ene. Organic starting materials are provided. You need to provide reagents.

starting materials

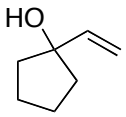




Product:
2-methyl-tridec-5-ene



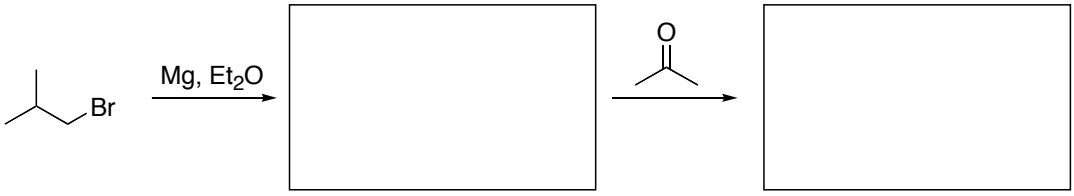
4.
Starting from acetylene (also known as ethyne) and a ketone, design a synthesis of the following compound (ignore stereochemistry).



5. Suggest a multi-step synthesis of 2-bromobutane from acetylene (ethyne).

6.

a. Fill in the missing intermediates.

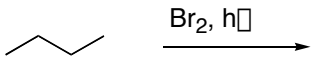


b. Design a multistep synthesis for 3-deutero-2,2,4,4-tetramethylpentane from 2,2,4,4-tetramethylpentane.

2,2,4,4-tetramethylpentane

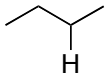
3-deutero-2,2,4,4-tetramethylpentane

7.

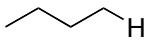


a. Write the structures of the products of the above reaction.

b. Use the following bond dissociation energies to calculate the ΔH° for the formation of the major and minor products.

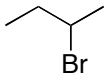


100 kcal/mol

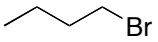


105 kcal/mol

Br—Br 46 kcal/mol



70 kcal/mol



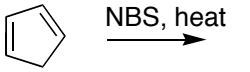
74 kcal/mol

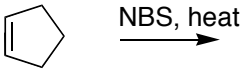
H—Br 87.5 kcal/mol

c. The relative rate of abstraction of a tertiary hydrogen is 1600; secondary is 82 and primary is 1. Calculate the percent yield for each product of the reaction.

d. Draw a mechanism for the formation of the major product.

8. Draw the major products of the following reactions.





9. Write the structures expected from the monochlorination of 2-methylbutane via a radical reaction. Using the relative reactivities of 1:4:5 for replacement of primary, secondary and tertiary hydrogens, determine the percentage of each of the monochloro compounds expected in the product mixture.