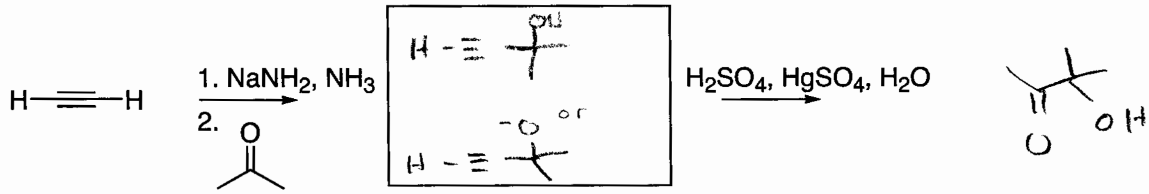
Massachusetts Institute of Technology — 5.12, Spring 2005

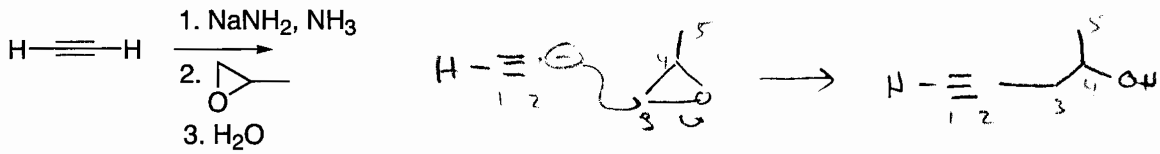
Problem Set 5, Due 4pm March 31

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

a.

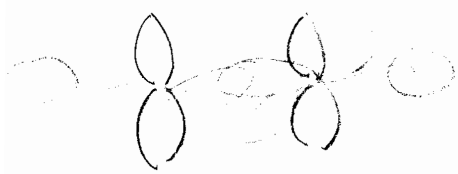


b.



2.

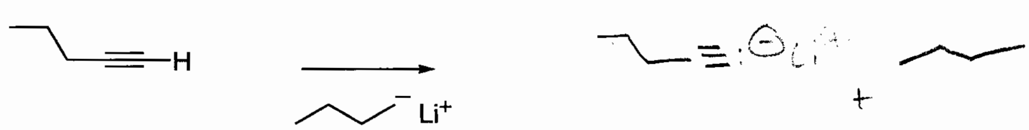
a. Draw the molecular orbital diagram of ethyne.



b. What is the pKa of ethyne? 25

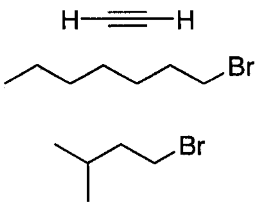
c. What is the pKa of ethane? ~50

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

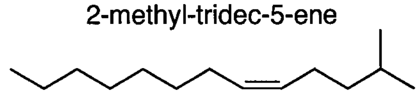


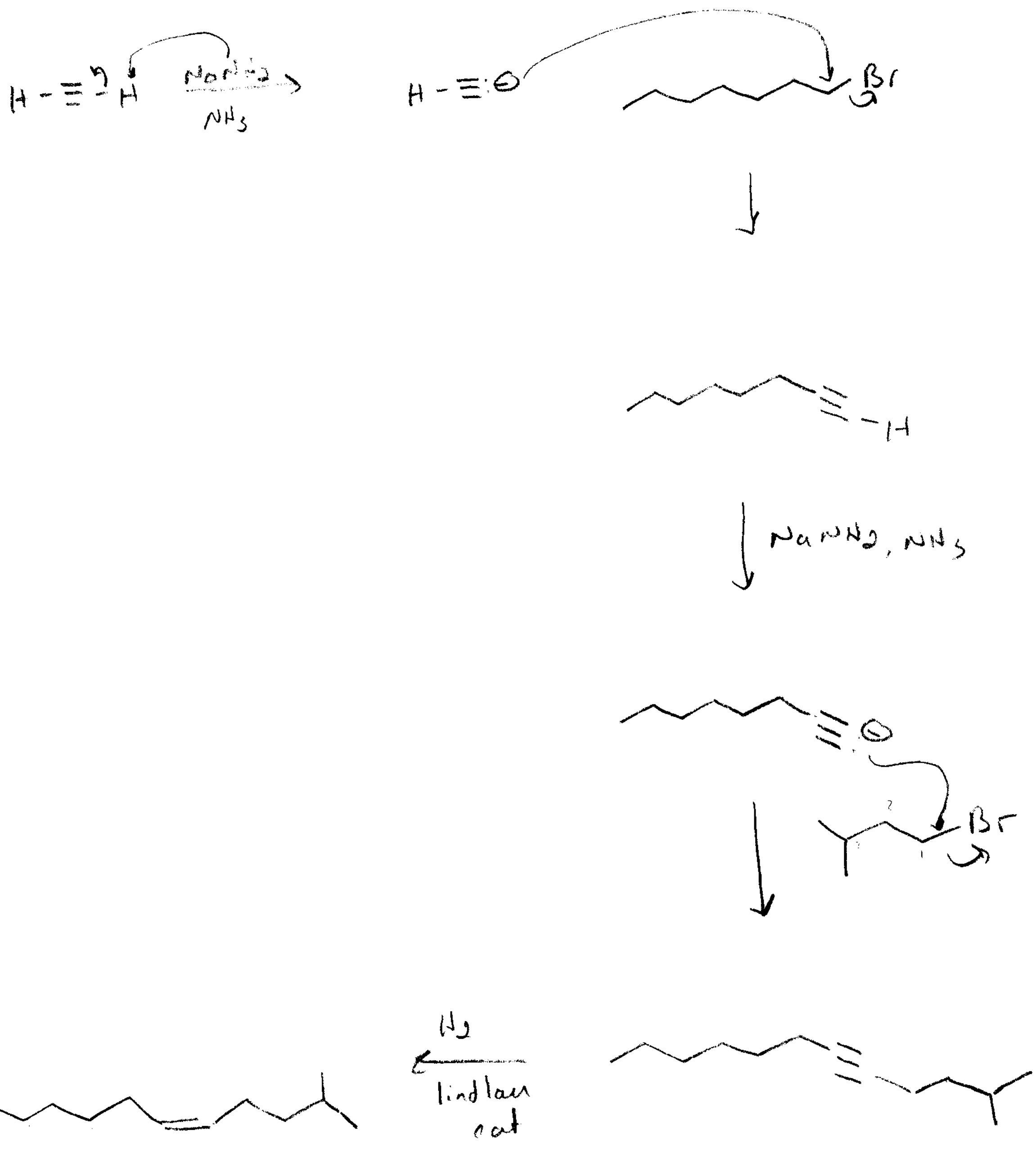
3.
Design a multistep synthesis for the following compound 2-methyl-tridec-5-ene. Organic starting materials are provided. You need to provide reagents.

starting materials

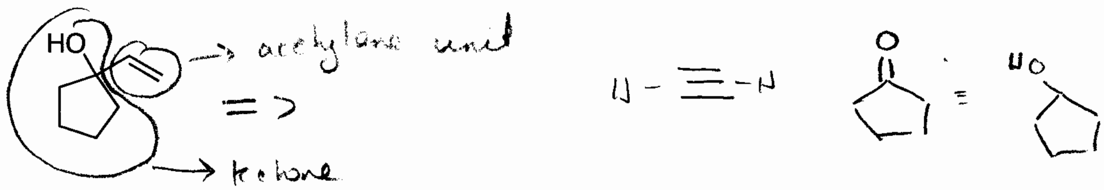


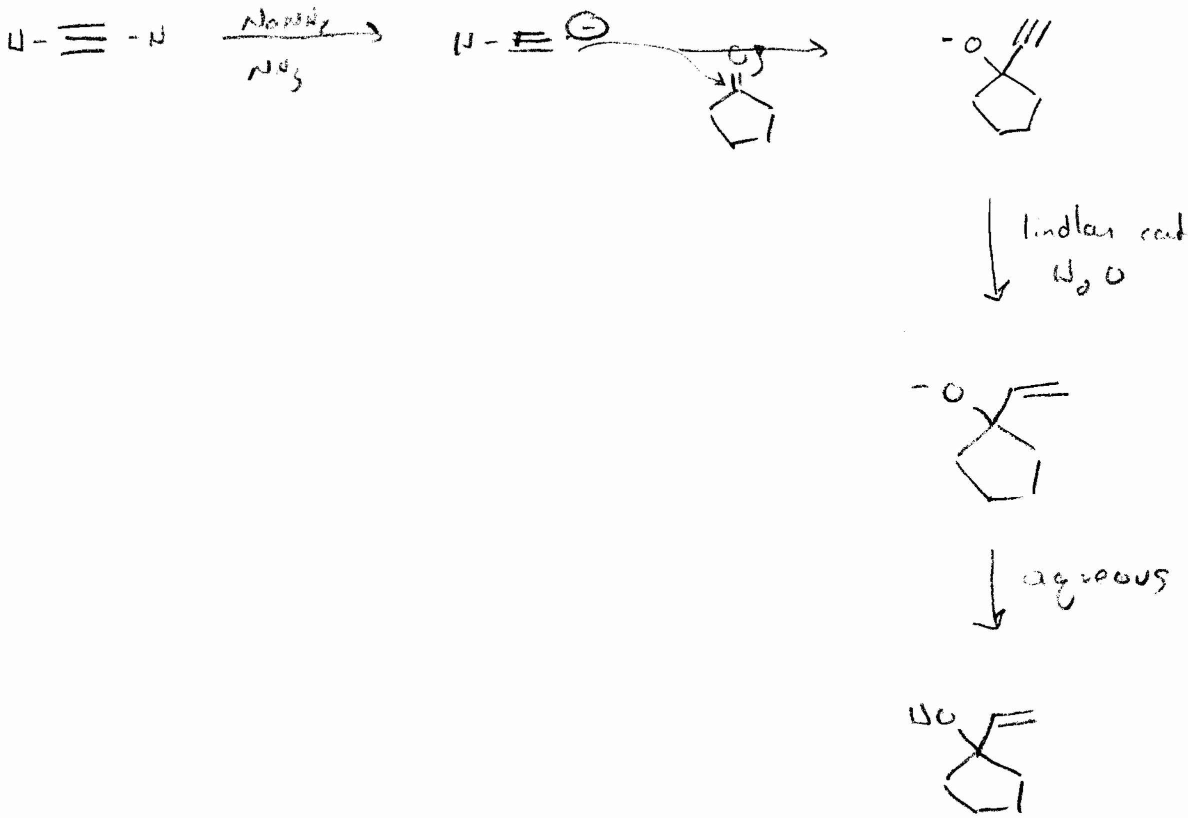
Product:
2-methyl-tridec-5-ene





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

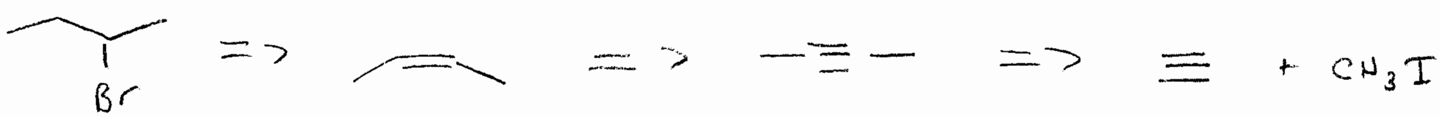


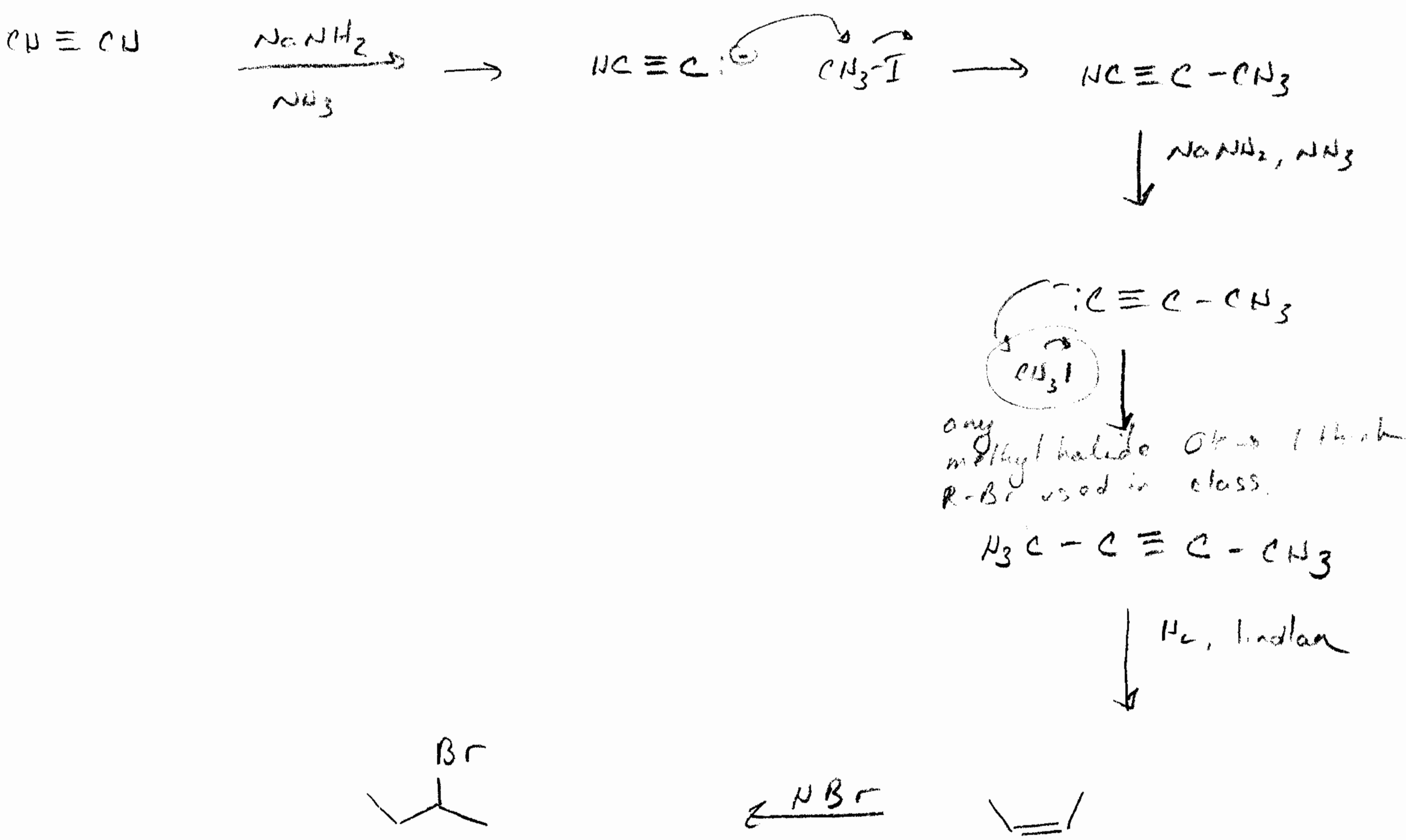


5. Suggest a multi-step synthesis of 2-bromobutane from acetylene (ethyne).

product

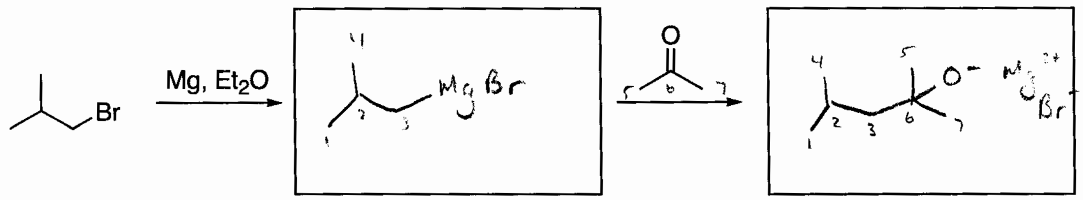
H - ≡ - H starting material



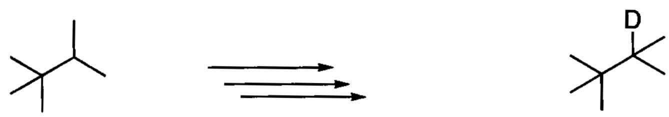


6.

a. Fill in the missing intermediates.

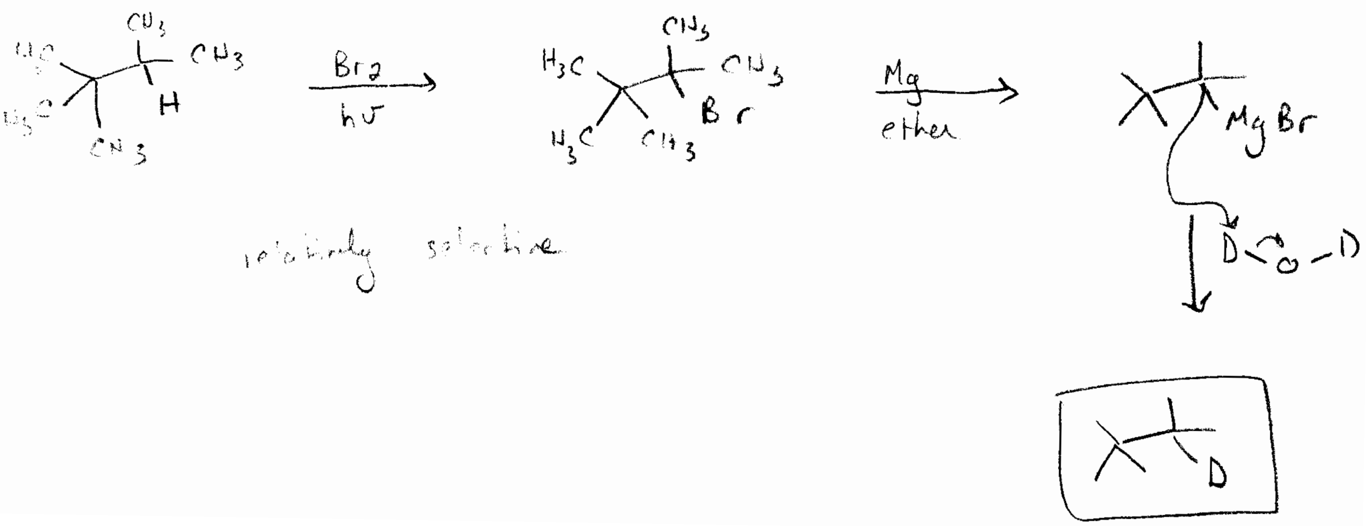


b. Design a multistep synthesis for 3-deutero-2,2,4,4-tetramethylpentane from 2,2,4,4-tetramethylpentane.

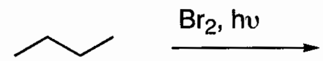


2,2,4,4-tetramethylpentane

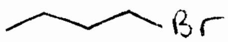
3-deutero-2,2,4,4-tetramethylpentane



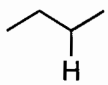
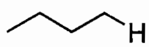
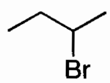
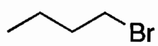
7.



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

ΔH° for 1 bromobutane

$(105 + 46) - (74 + 87.5) = 151 - 161.5$

bonds broken — bonds made

$= -10.5$ kcal/mol

ΔH° for 2 bromobutane.

$(100 + 46) - (70 + 87.5) = 146 - 157.5$

bonds broken — bonds formed

$= -11.5$ 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.

6 (1° H's) × 1 = 6 $\qquad \frac{6}{334} \times 100 = 1.8\%$

4 (2° H's) × 82 = 328 $\qquad \frac{328}{334} \times 100 = 98.2\%$

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

(d) <u>Initiation</u>

$Br-Br \xrightarrow{h\nu} Br\cdot \;\; \cdot Br$

<u>Propagation</u>

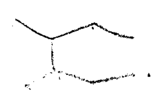
$Br\cdot \;\; CH_3-CH(H)-CH_2-CH_3 \longrightarrow HBr \;\; CH_3-\dot{C}H-CH_2-CH_3$

$CH_3-\dot{C}H-CH_2-CH_3 + Br-Br \longrightarrow CH_3-CH(Br)-CH_2-CH_3 + Br\cdot$

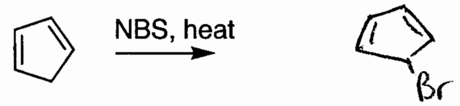
<u>Termination</u> (not necessary to show)

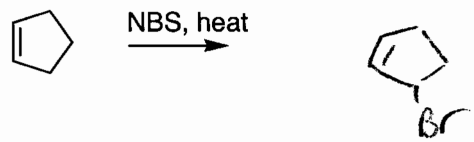
$Br\cdot \;\; \cdot Br \longrightarrow Br-Br$

$CH_3-\dot{C}H-CH_2-CH_3$

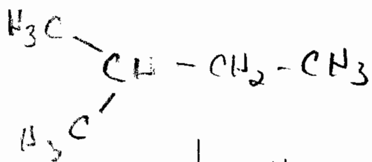
$CH_3-\dot{C}H-CH_2-CH_3$ $\longrightarrow$ 

8. Draw the major products of the following reactions.

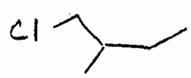
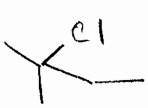
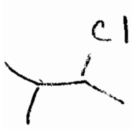




9. Write the structures expected from the monochlorination of 2-methylbutane via a radical reaction. Using the relative reactivities of 1:4:5 for replacement of primary, seconday and tertiary hydrogens, determine the percentage of each of the monochloro compounds expected in the product mixture.



↓ 4 possible products

	# Hydrogens	1°, 2° or 3° reactivity			
	6	1	=	6	$\frac{6}{22}$ = 27%
	3	1	=	3	$\frac{3}{22}$ = 14%
	1	5	=	5	$\frac{5}{22}$ = 23%
	2	4	=	8	$\frac{8}{22}$ = 36%
				22	