

CARLETON UNIVERSITY

MID-TERM
EXAMINATION
DECEMBER 1995

STUDENT NAME: _____

STUDENT # _____

DURATION: 3 HOURS

No. of Students: 210

Department Name & Course Number: Chemistry 65.220A

Course Instructor(s) P.H. Buist

AUTHORIZED MEMORANDA

NO INSTRUCTIONAL AIDS PERMITTED

Students **MUST** count the number of pages in this examination question paper before beginning to write, and report any discrepancy immediately to a proctor. This question paper has 9 pages.

This examination question paper **MAY NOT** be taken from the examination room.

ANSWER ALL QUESTIONS ON THE EXAMINATION PAPER IN THE SPACE PROVIDED.

TOTAL MARKS FOR THIS EXAM = 75

2003 Short answers (15 marks)

Physical Properties (5 marks)

Reagents (10 marks)

Starting Materials (10 marks)

Products (10 marks)

Mechanisms (3) (15 marks)

Synthesis (3) (10 marks)

(No Road Map)

P. Buist

1. GIVE SHORT ANSWERS TO THE FOLLOWING QUESTIONS IN THE SPACE PROVIDED. (15 marks).

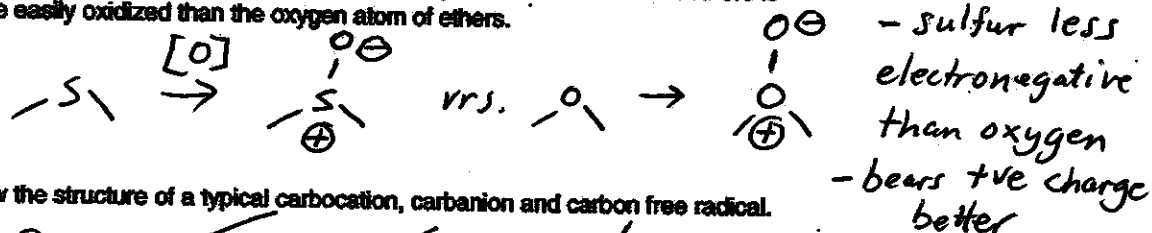
a. Give the three hybridization states of carbon commonly found in organic compounds.



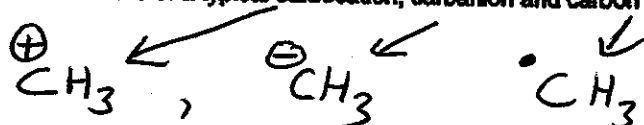
b. What is meant by the diagnostic region of an IR spectrum.

gives functional group information eg. $C=O$

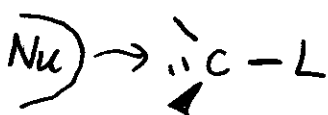
c. Use electronegativity arguments to explain why the sulfur atom of thioethers is more easily oxidized than the oxygen atom of ethers.



d. Draw the structure of a typical carbocation, carbanion and carbon free radical.

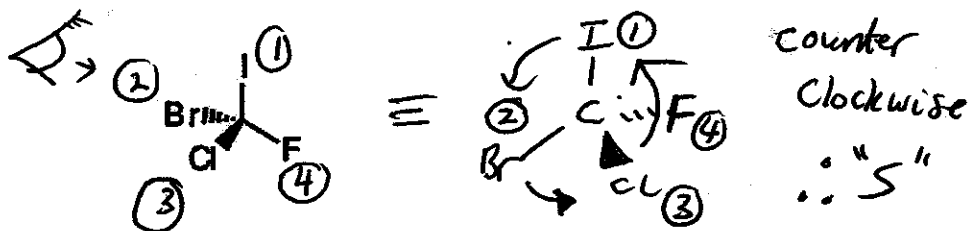


e. Explain what is meant by steric hindrance as it applies to S_N2 reactions.



large, bulky nucleophiles are prevented from attacking carbon.

f. Assign the (R)- or (S)-configuration to the chiral centre of the molecule shown.



g. Define what is meant by an enantiomer.

non superposable mirror image

h. Give the Huckel definition of an aromatic compound.

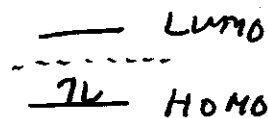
Compounds containing $(4n+2)e^-$ in cyclic, planar, contiguous array of p orbitals.

1. (cont'd)

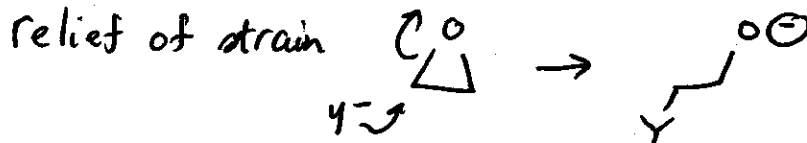
i. Define HOMO and LUMO.

HOMO = highest occupied molecular orbital

LUMO = lowest unoccupied molecular orbital



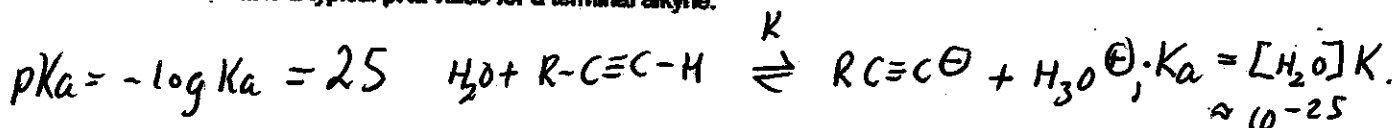
j. Epoxides react with nucleophiles while ordinary ethers are resistant to nucleophilic attack. Why?



k. Define what is meant by an electrophile.

any electron poor species such as M^+ , BF_3 , NO_2^+
(H^+ is a special case)

l. What is a typical pKa value for a terminal alkyne.

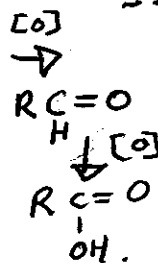


m. Which base might one use to quantitatively deprotonate an alcohol.

pK_a ROH is $\sim 16-18$. Need conjugate base of an acid with a higher pK_a , eg NaH ($pK_a H_2$ ≈ 35)

n. Define what is meant by an oxidant in the context of organic reactions.

removal of H atoms OR addition (insertion) of electronegative atoms.



o. Explain in your own words what is meant by a pKa value for a Bronsted acid.

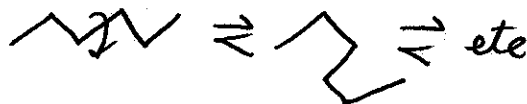
measures propensity of HA to donate a (H^+) proton to H_2O .

2. **PHYSICAL PROPERTIES:** (5 marks).

a. Explain why the melting point of benzene is so much higher than that of n-hexane.

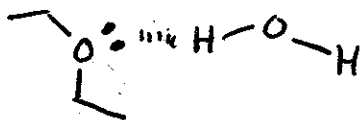


rigid discs
easier to stack!



many degrees of freedom
"floppy"

b. Show why ether dissolves an appreciable amount of water while pentane does not.

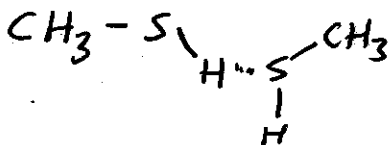


ether can accept H bonds from H_2O , both polar



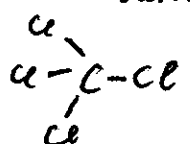
no H-bonds possible

c. Account for the fact that CH_3SH is a gas at R.T. while CH_3OH boils at $65^\circ C$.



H bonds between Sulfur + SH are weaker than for corresponding alcohol.

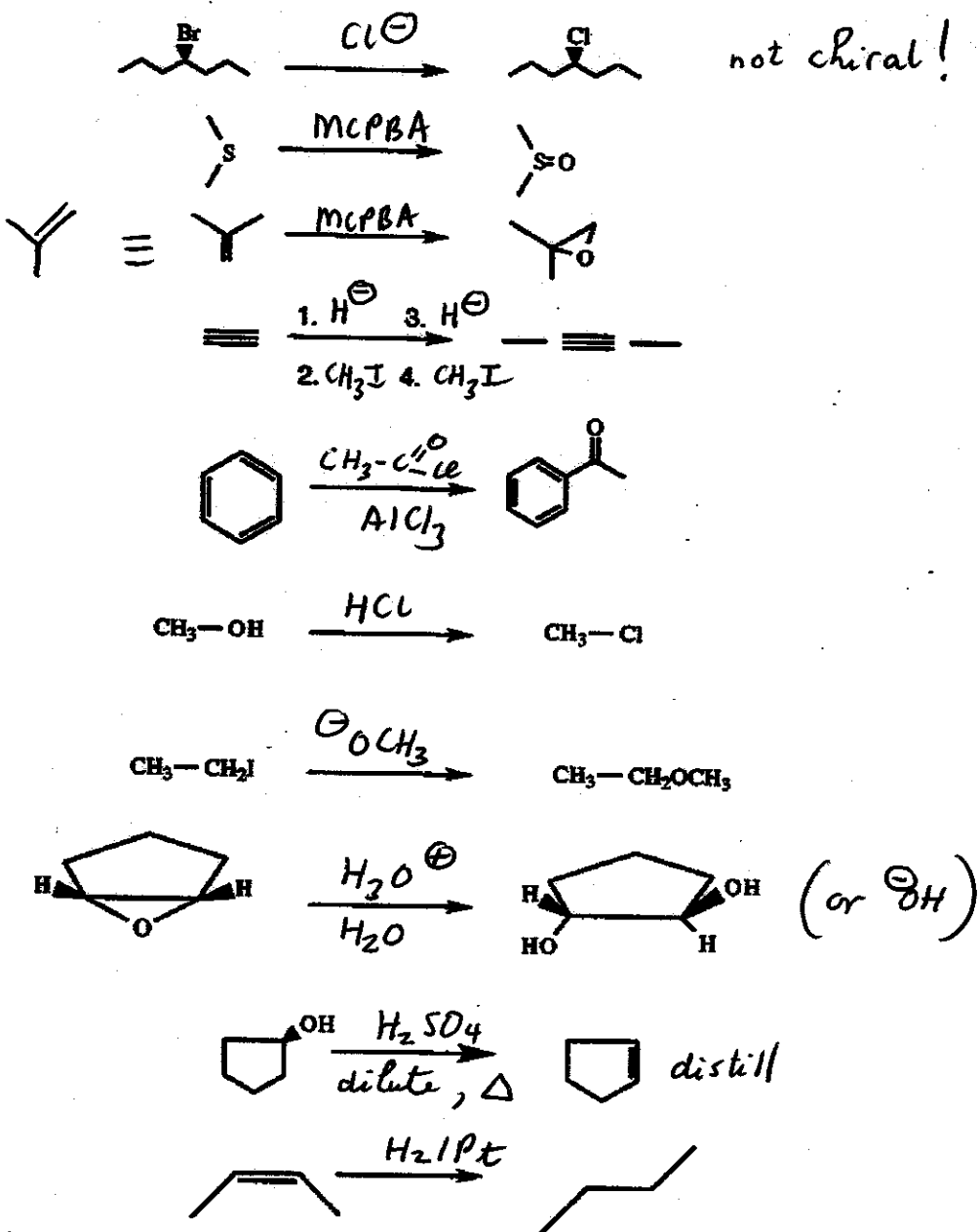
d. Why is CCl_4 not easily oxidized while CH_4 serves a fuel.

CH_4 undergoes facile H abstraction by oxy radicals during combustion. to give $CO_2 + H_2O$ eventually
 CCl_4 resists this chemistry.

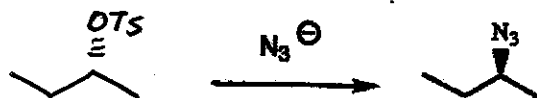
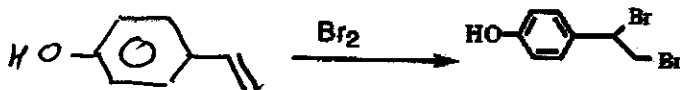
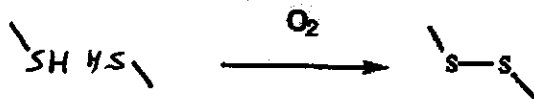
e. Why is t-butyl alcohol miscible with water in all proportions, while n-butanol is not?

t-butanol's compact shape fits more easily into hydration shell of H_2O . n-butanol's linear shape exposes too many mobile CH_2 groups.

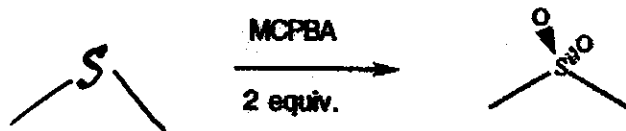
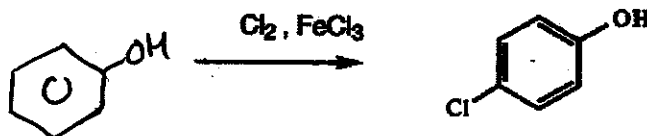
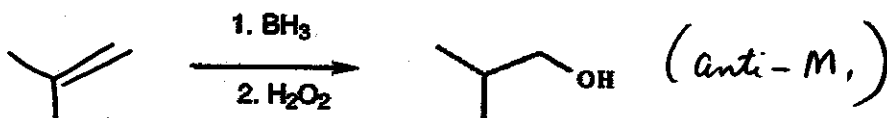
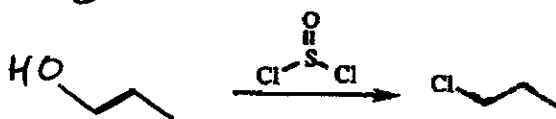
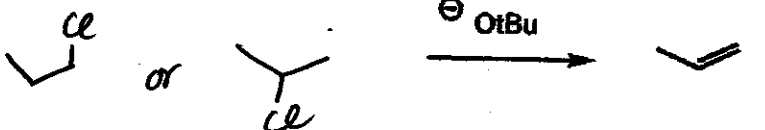
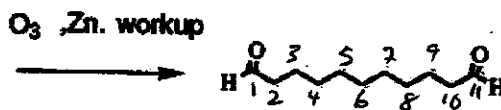
3. SHOW THE REAGENTS NECESSARY FOR EACH REACTION: (10 marks).



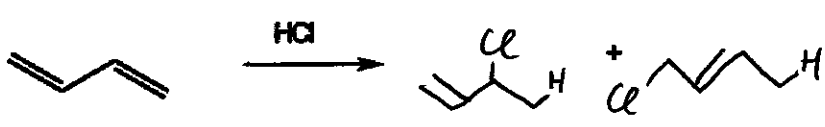
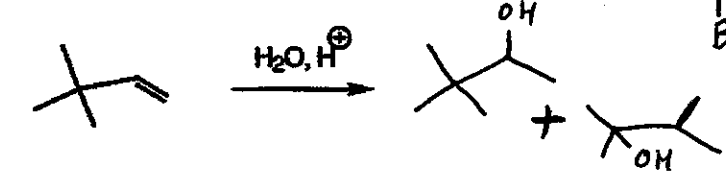
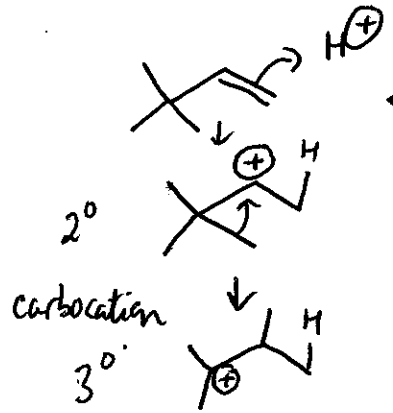
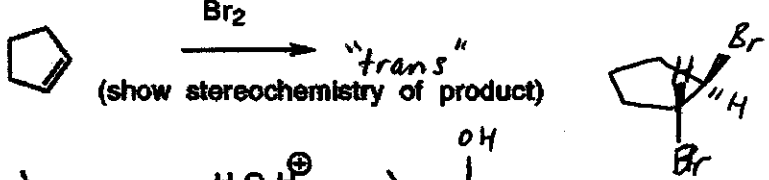
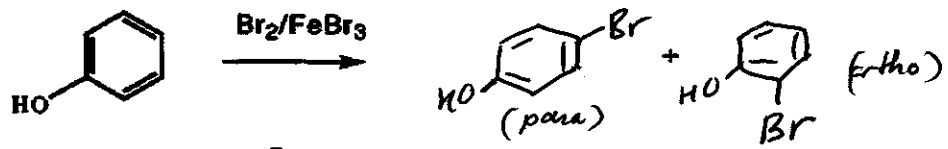
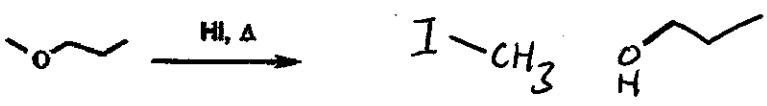
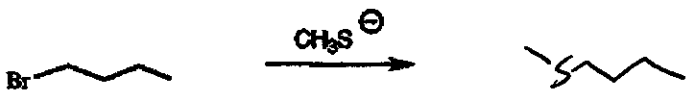
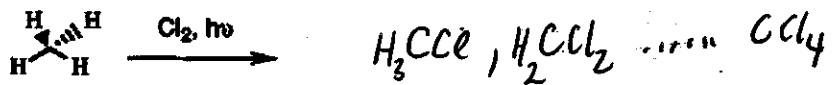
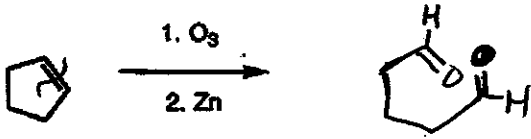
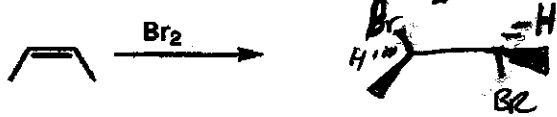
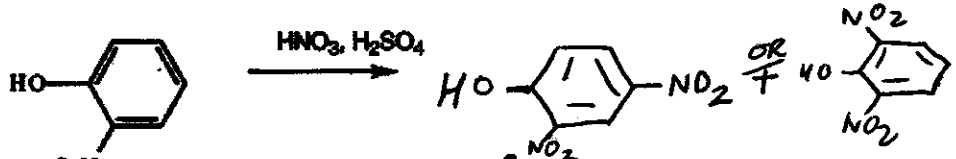
4. SHOW THE STARTING MATERIAL WHICH WOULD LEAD TO THE PRODUCTS SHOWN:
 (10 marks).



(Z)-cyclo
undecene



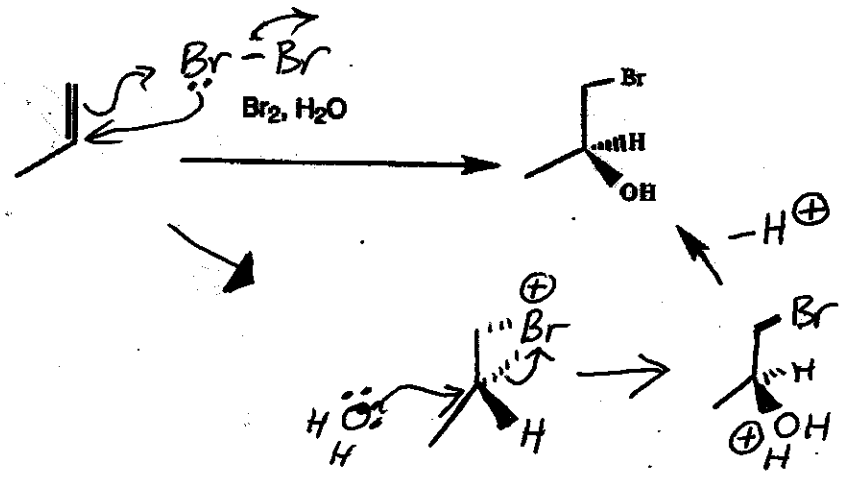
5. SHOW THE EXPECTED PRODUCT OF THE FOLLOWING REACTIONS: (10 marks).



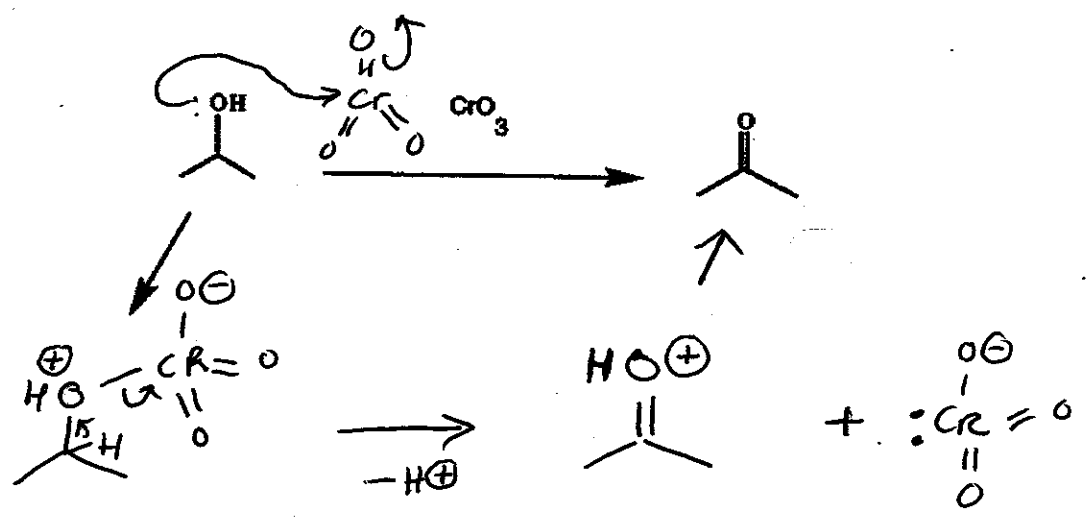
c.f. Jones 8.12
(Fig 8.82)

6. Draw a mechanism for the following reactions, showing all intermediates. Use curly arrows to show the flow of electrons from electron rich to electron poor sites. Give resonance forms where appropriate. (15 marks).

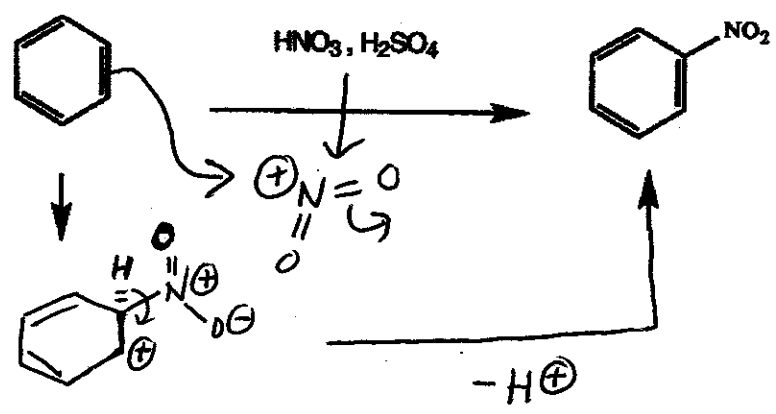
a.



b.

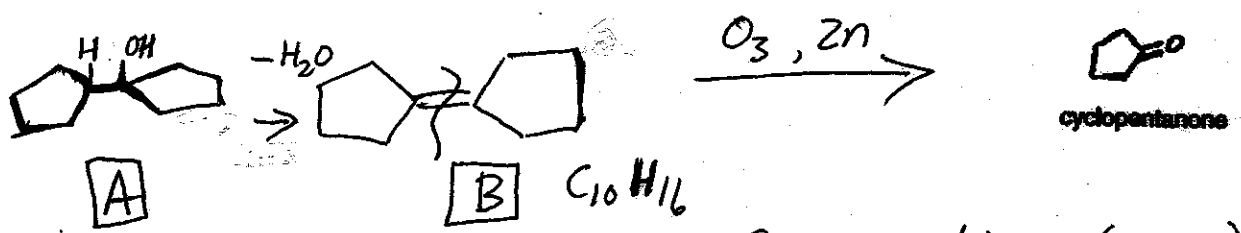


c.



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7a. A bicyclic alcohol, Compound A, $C_{10}H_{18}O$, undergoes reaction with dilute H_2SO_4 at $25^\circ C$ to yield a mixture of two alkenes, $C_{10}H_{16}$. The major alkene product, B, gives only cyclopentanone after ozone treatment followed by reduction with zinc in acetic acid. Formulate the reactions involved and identify A and B. (4 marks).

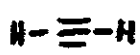


A
 $C_{10}H_{18}O$
2 deg. of unsat ($\frac{22-18}{2}$)
(2 rings)

B $C_{10}H_{16}$
3 deg. of unsaturation ($\frac{22-16}{2}$)
(2 rings, 1 db)

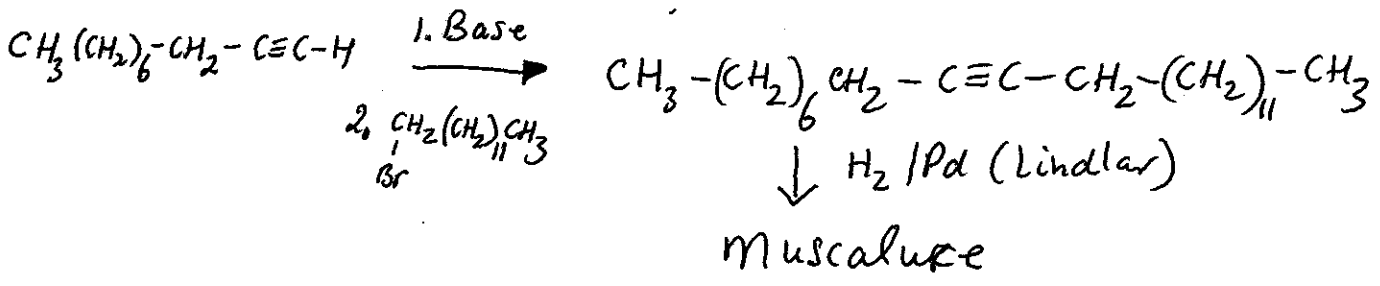
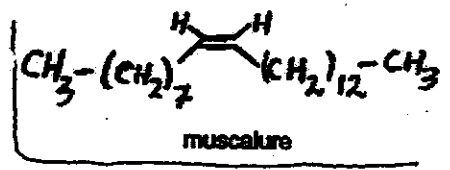
other alkene from **A**

b. The sex attractant given off by the common housefly is a simple alkene named muscalure. Propose a synthesis of muscalure starting from acetylene and any alkyl halides. (3 marks).



acetylene

1. Base
2. $CH_2(CH_2)_6CH_3$
Br



c. Assume that you have been given a sample of (S)-2-octanol. How would you prepare (R)-2-chlorooctane? How would you prepare (R)-2-octanol. (3 marks).

