Department of Chemistry and Biochemistry

Chemistry 59-230/232 **Final Exam**
Time: 3 h **Dec. 11, 2002**

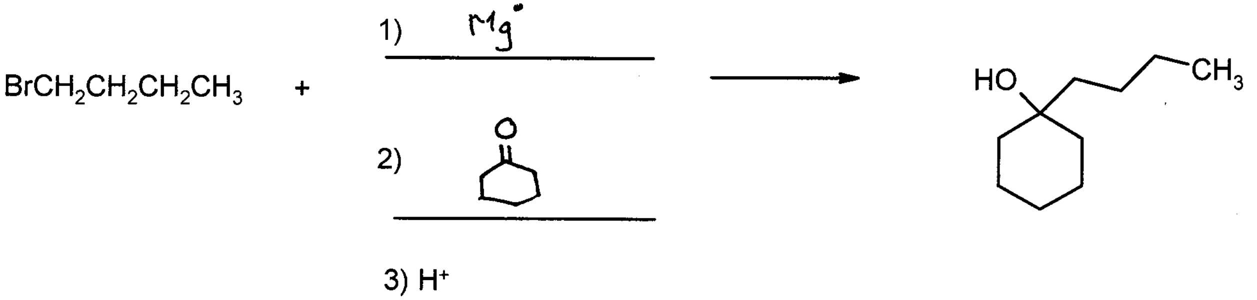
NAME ______________________ **ID#**______________________

LAB SECTION ***(enter 'no lab' if in 232 or not taking one)***______________________

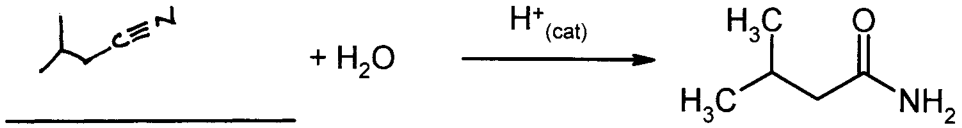
Note: **Please answer on the test paper.** There is an extra sheet for rough work at the back, but it will <u>not</u> be marked.

1. Fill in the blanks with the structural formula required to complete the equation. Show any required catalysts over the arrow. Make sure your drawings show stereochemistry if it is important. ***<u>Do any ten (10)</u>*** (40 marks)

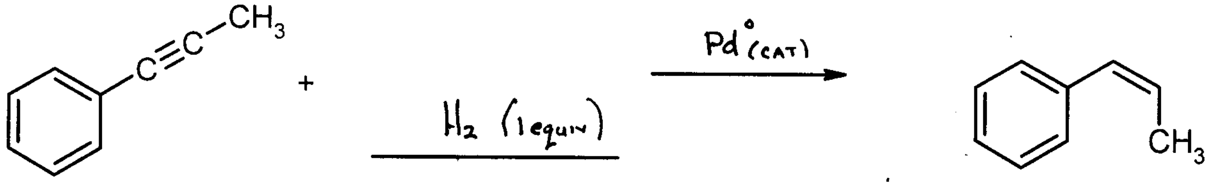
a.



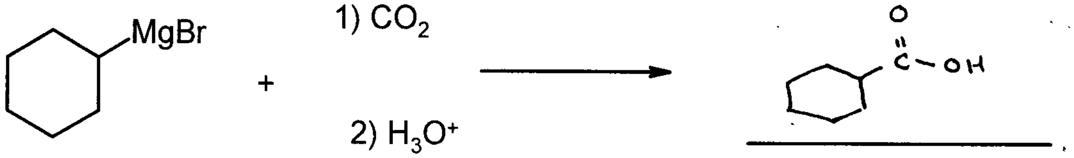
b.



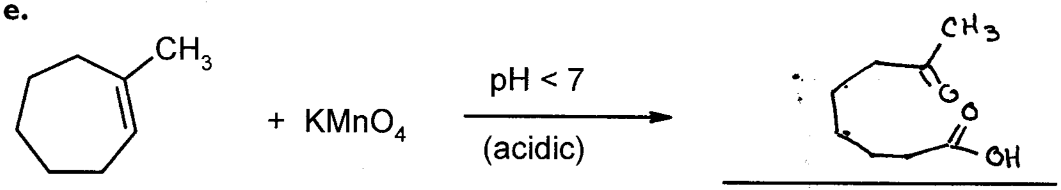
c.



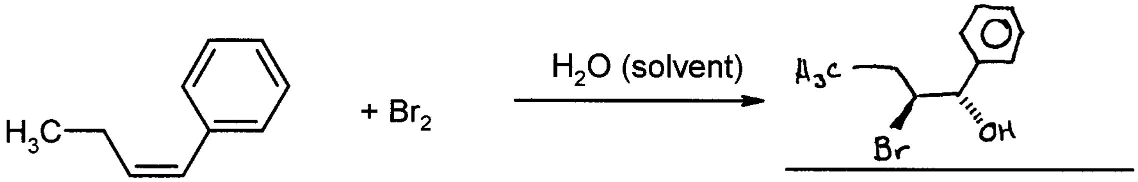
d.



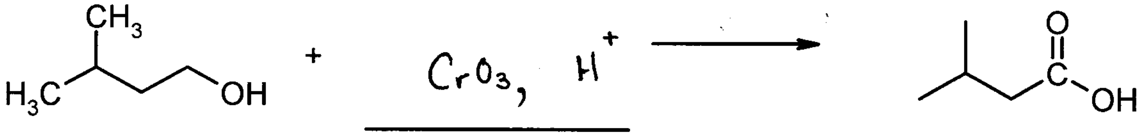
e.



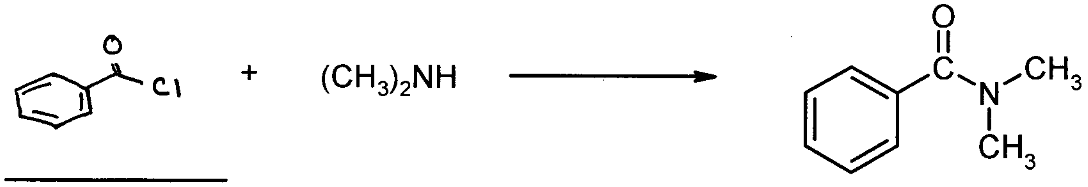
f.



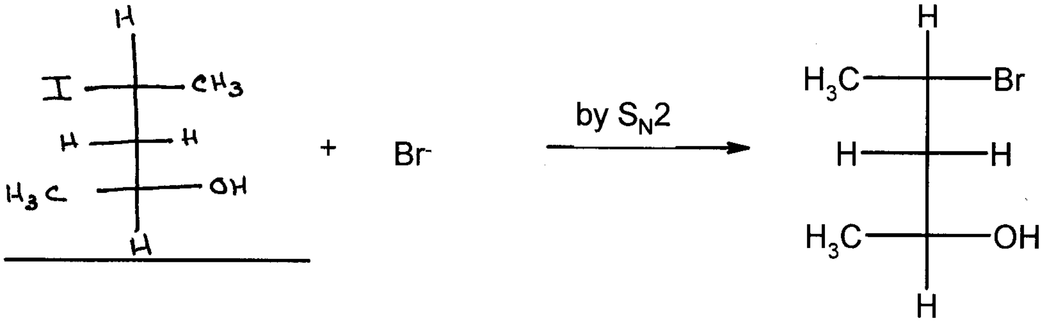
g.



h.

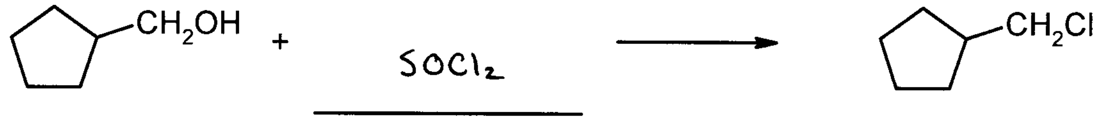


i.

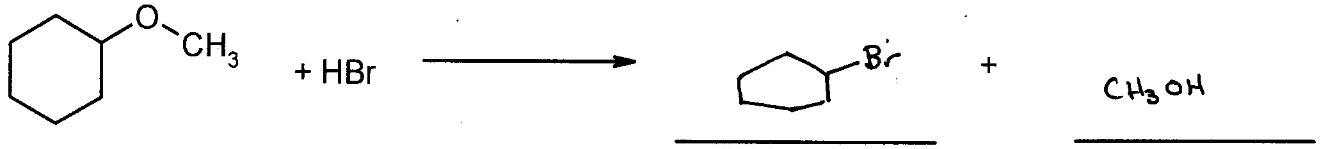


NOTE: Cl INSTED OF I (OR ANY OTHER GOOD LEAVING GROUP) IS ALSO FINE

j.

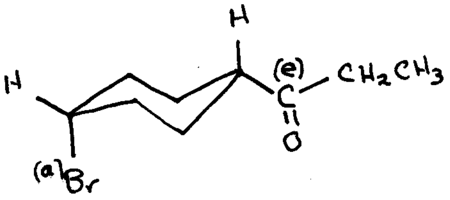


k.



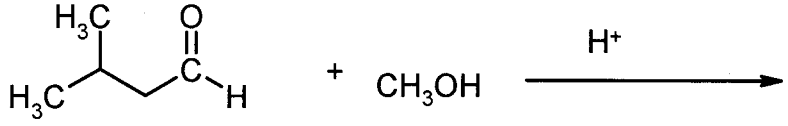
2 organic compounds

2. Draw the structure of *cis* 1-(4-bromocyclohexyl)-1-propanone is its most stable chair conformation. Label the non hydrogen substituents on the cyclohexane as axial or equatorial. In terms of size, a ketone group is larger than a bromine. (7 marks)

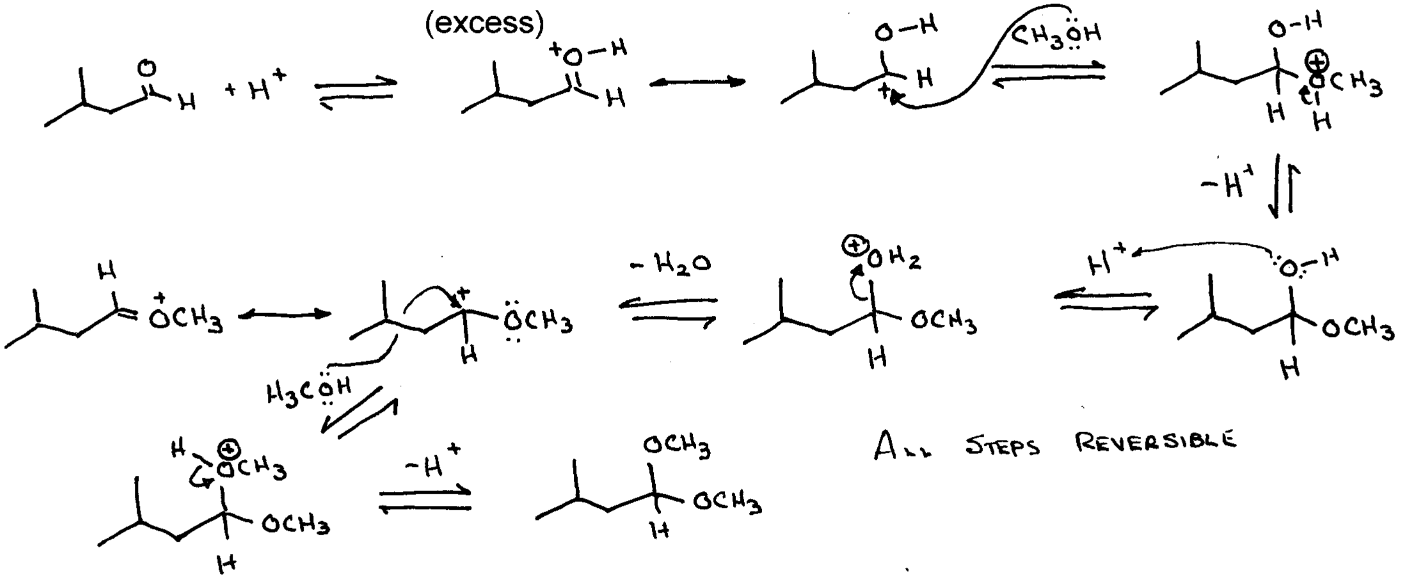


3. a.

Draw the complete mechanism for the following reaction. Take the reaction to completion. Indicate which steps are reversible (or irreversible). Provide a valid IUPAC name for the starting material. (12 marks)



(excess)

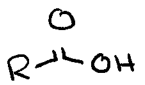
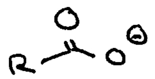


ALL STEPS REVERSIBLE

STARTING MATERIAL NAME : 3-METHYLBUTANAL

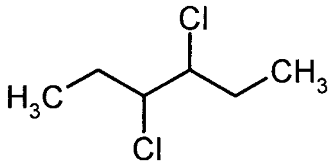
b. In the aqueous hydrolysis of an ester to a carboxylic acid, the reaction is more commonly done under basic rather than acidic conditions, even though both *are* feasible. Explain why this is the case, using structures to indicate the point, but I am *not* looking for the complete mechanism of hydrolysis (5 marks).

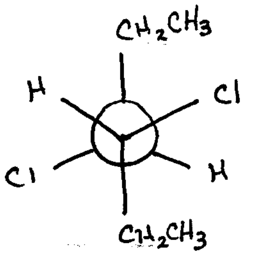
IN THE BASE INDUCED HYDROLYSIS OF  $+ HO^{\ominus}$, THE PRODUCTS ARE

 + $RO^{\ominus}$, WHICH DOES ⟶  + ROH IRREVERSIBLY,

DRIVING THE REACTION TO COMPLETION. ACID CATAYZED VERSIONS CAN BE REVERSIBLE.

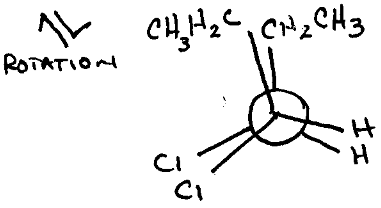
c. Draw the Newman projection of the following compound in its most stable configuration *and* conformation, as viewed down the C3-C4 bond. With respect to size, $CH_3 > Cl$. Is this molecule chiral, or a meso compound, or one with no chiral centres at all? (7 marks)





PUTTING BIGGEST GROUPS ANTIPERIPLANAR, WITH 2 BIG GROUP / MEDIUM GROUP GAUCHE (SYNCLINAL) INTERACTIONS

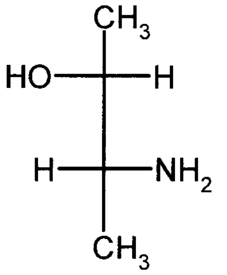
- THIS IS A MESO COMPOUND

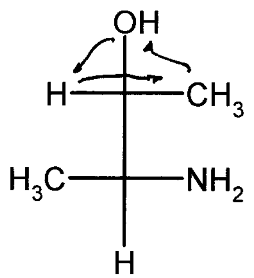


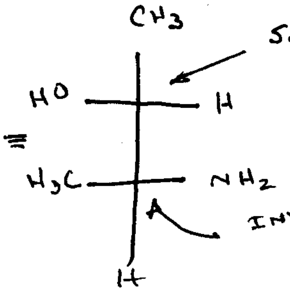
- MIRROR PLANE BETWEEN TWO CHIRAL CENTRES

4. Describe the relationship that exists between the following sets of compounds (i.e., enantiomer, diastereomer, geometric isomer, structural isomer, identical) (15 marks total)

a.







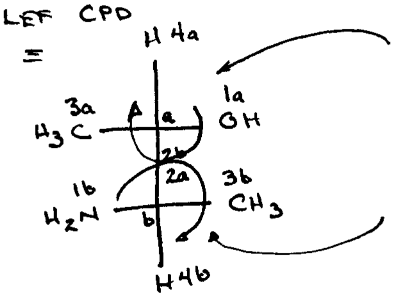
SAME AS LEFT CPD HERE

INVERTED REL. TO LEFT CPD. HERE

∴ THESE ARE DIASTEREOMERS

Also, identify the chiral centres for the left compound as (R)- or (S)-

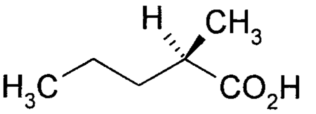
LEF CPD ≡

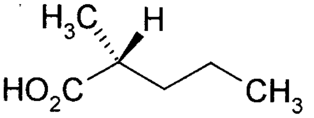


(R)-

(R)-

b.



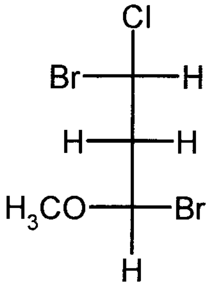


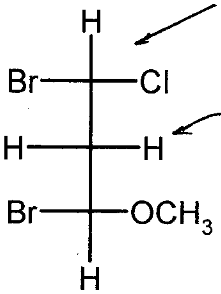
IDENTICAL

Also, give the complete IUPAC name of the compound on the left, including the stereochemical descriptor.

(R)- 2-METHYL PENTANOIC ACID

c.





H + Cl INVERTED RE LEFT CPD

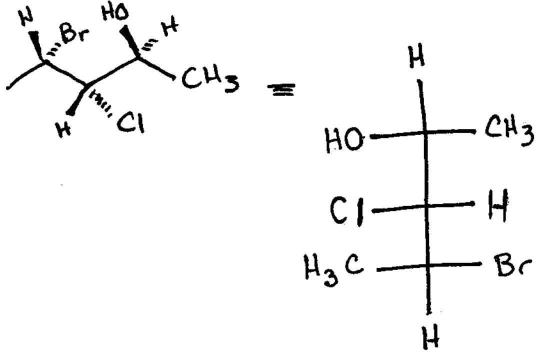
NOT CHIRAL CENTRE

Br + OCH_3 INVERTED RE LEF CPD.

BOTH CHIRAL CENTRES INVERTED

∴ ENANTIOMER.

d. Draw the Fischer projection of 4-bromo-3-chloro-2-pentanol in the 2S, 3R, 4S configuration. (5 *of the* 15 marks).



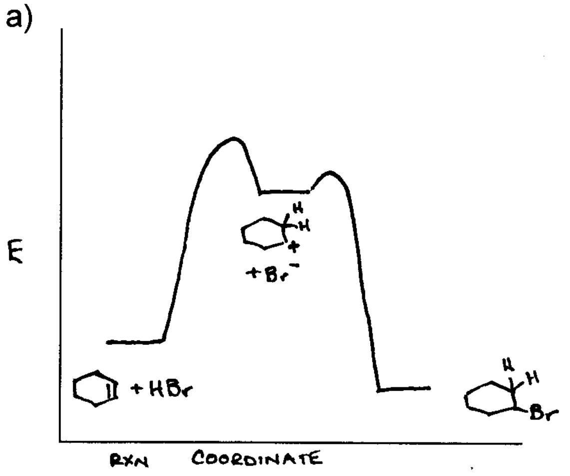
5. On the axes below, draw the energy reaction coordinate profile for:

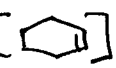
a. The reaction between cyclohexene and HBr

b. A two step reaction between A and B, where A is involved in the 1st step and B is involved in the 2nd step. The 2nd step is the slower one.

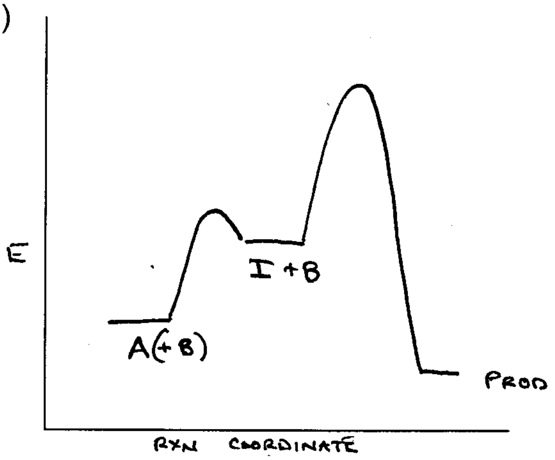
In each of these cases, give the rate equation for the reaction. (10 marks total)

a)



rate (v) = k[] [HBr]

b)



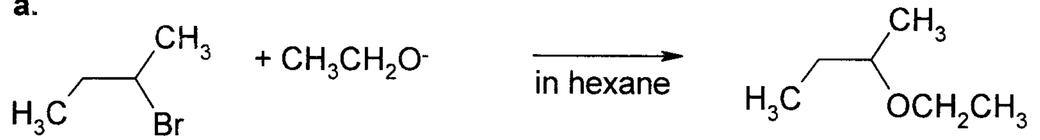
rate (v) = k [A][B]

6. Rank the following in terms of tendency to undergo S_N1 substitution (as opposed to S_N2) . Give reasons for you ordering. The solvent dielectric constants are (CH_3CH_2OH, 24; hexane , 2). (14 marks)

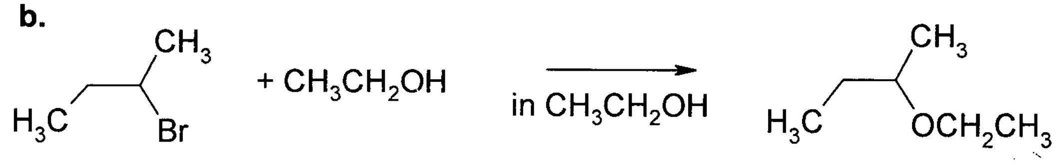
- Of the three, $CH_3CH_2O^-$ is a better nucleophile than CH_3CH_2OH
  - Therefore that one is pushed towards S_N2, since 'nucleophilicity' is important to the (bimolecular) S_N2, but doesn't affect the rate of an S_N1

- In the second one, the polar solvent stabilizes the charged intermediate () of the S_N1, and pushes the mechanism more in that direction
  - Therefore the 2nd one is the most S_N1 character

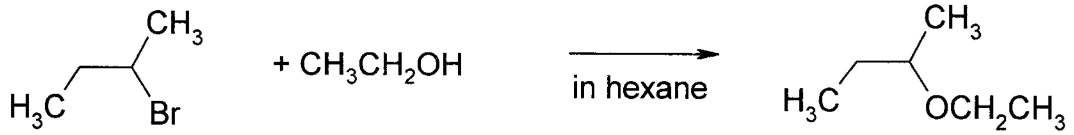
a.



b.



c.



- BY DEFAULT, c IS THE MIDDLE CASE (A LOUSY NUCLEOPHILE FAVOURS S_N1, BUT THE NON-POLAR SOLVENT DISFAVOURS S_N1)

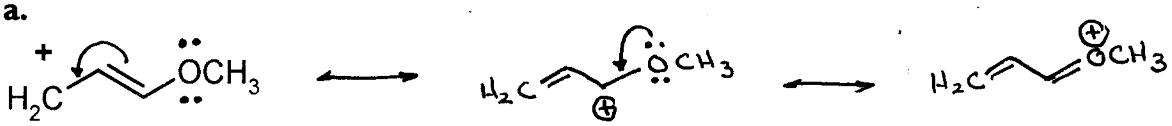
∴ b > c > a FOR S_N1 CHARACTER

d. Assuming each starting material is optically active, which of the above is the most likely to give an optically *inactive* product? (2 *of the* 14 marks)

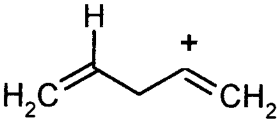
THE MOST S_N1 CASE, MEANING b.

7. Indicate all reasonable resonance forms of the following ions, using curved arrows to indicate electron movement. If there are no other resonance forms for any of the cases, state that fact.

a.

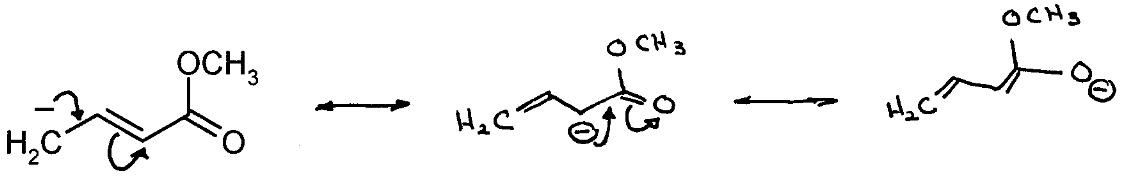


b.



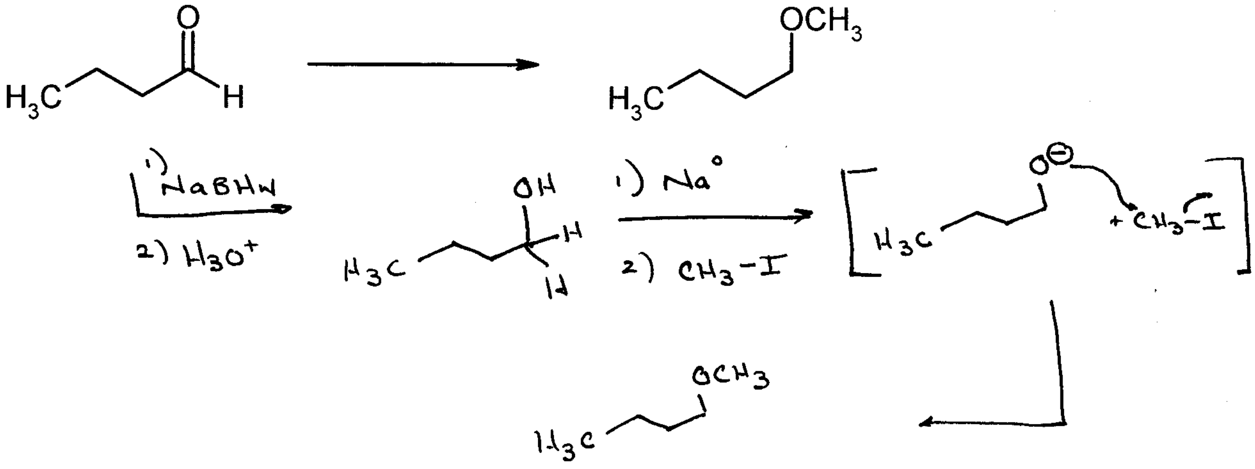
NO RESONANCE FORMS POSSIBLE

c.

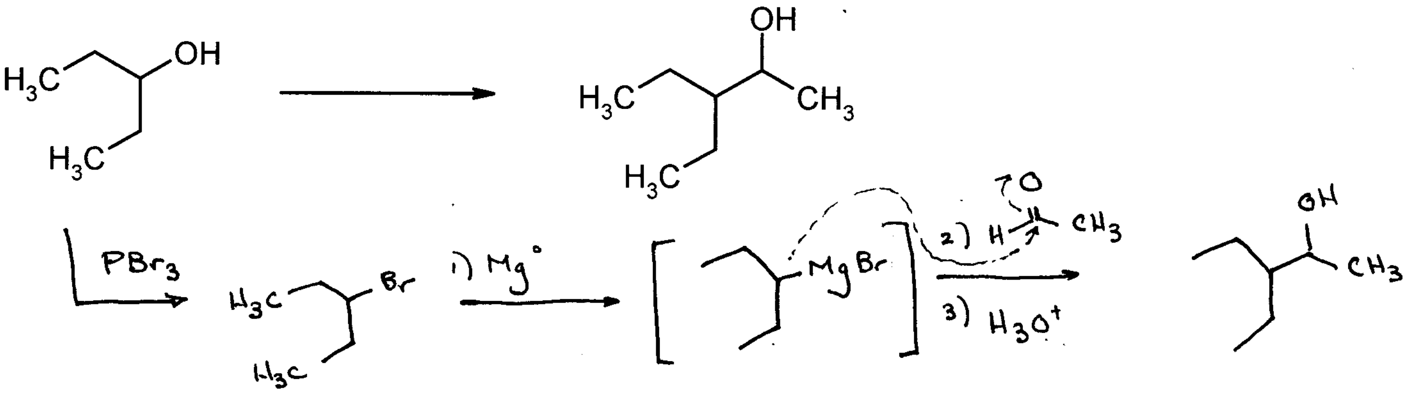


8. Show by equation how you carry out the following overall transformations. Show all reagents and the structures of each reaction product. There is quite possibly more than one correct way to accomplish this overall transformation. **DO any one of the following.**

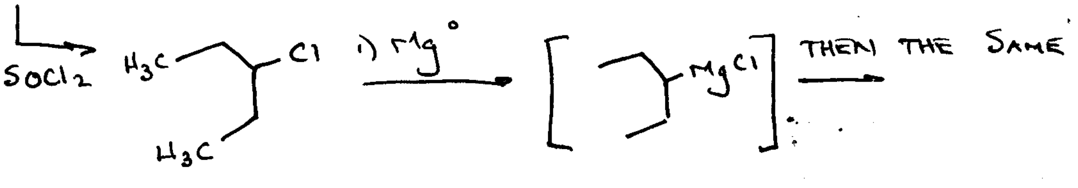
a.



b.

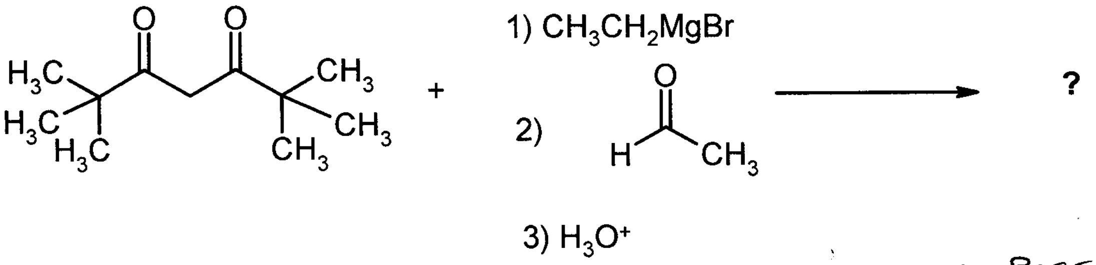


I'D ACCEPT

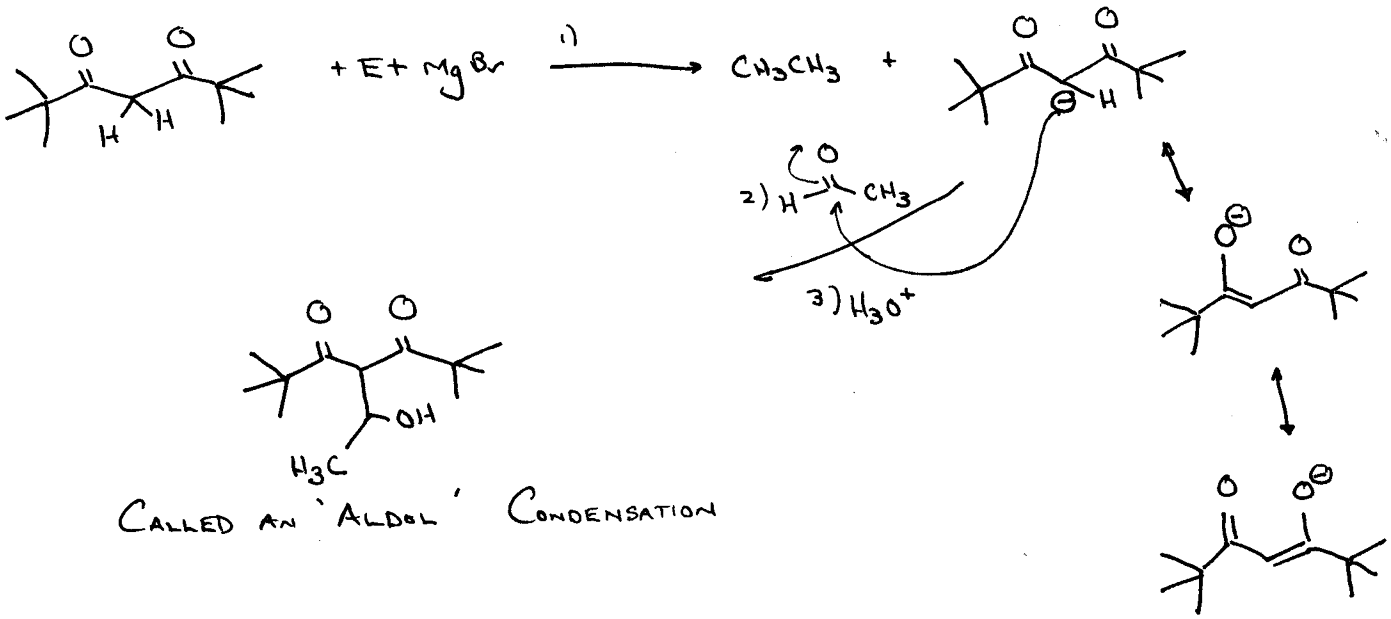


Bonus:

The nucleophilic attack of Grignard reagents with carbonyl compounds can be hindered by the presence of bulky functional groups. In such cases, other reactions occur which make sense based on the properties of the reagents involved. Suggest what the very reasonable outcome of the following 'failed' Grignard reaction might be.



- WHAT A GRIGNARD CAN ALSO DO IS ACT AS A BASE



CALLED AN 'ALDOL' CONDENSATION

HIGHLY RESONANCE STABILIZED