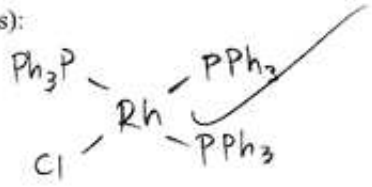
CHEM 3331 **Second Hour Exam** **Summer 2005**
July 19, 2005

Name: Key

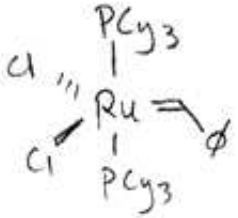
1a) Draw the structure of Wilkinson's catalyst (3 pts):



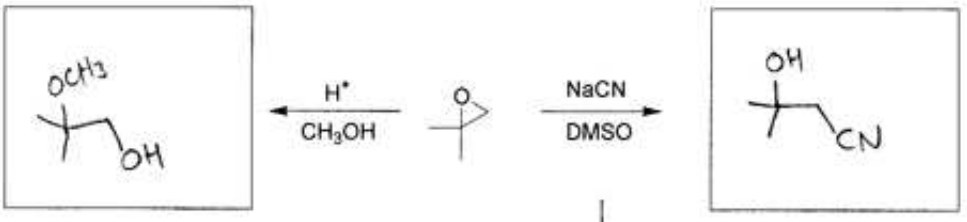
1b) What chemical reaction does Wilkinson's catalyst catalyze? (1 pt)

hydrogenation of alkenes/alkynes

1c) Draw the structure of Grubbs' catalyst (3 pts):



1d) Draw the products of each of the following reactions, and provide a brief explanation for the observed regiochemistry of epoxide opening for each case (8 pts).



+2 +2

H⊕-catalyzed epoxide opening occurs at more substituted side of epoxide, as that C is better able to accommodate partial positive charge

+1

Nucleophilic ring opening occurs at least hindered side of epoxide – kinetically faster

+2

15

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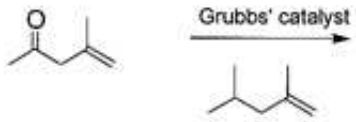
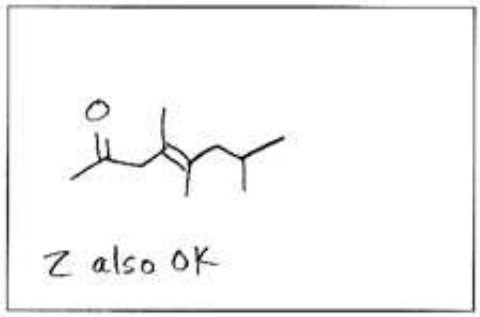
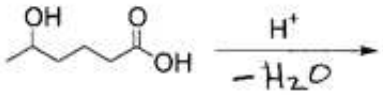
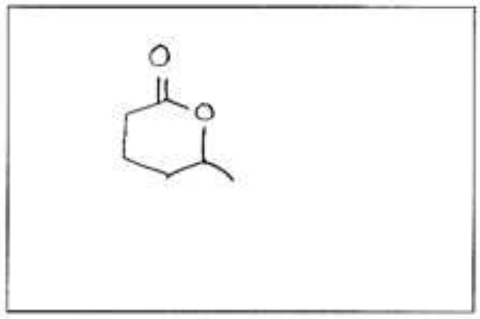
~-1 for not showing

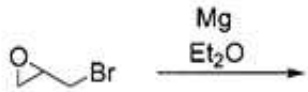
2a) Predict the products of the following reactions. Show stereochemistry where appropriate. (12 pts)

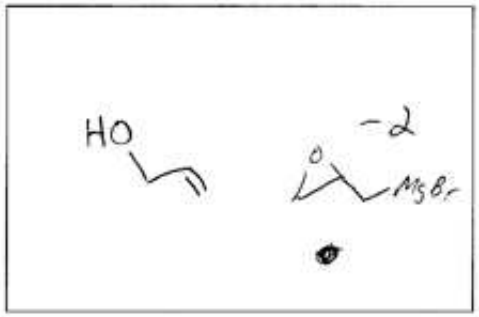


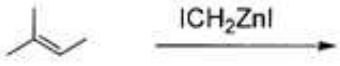


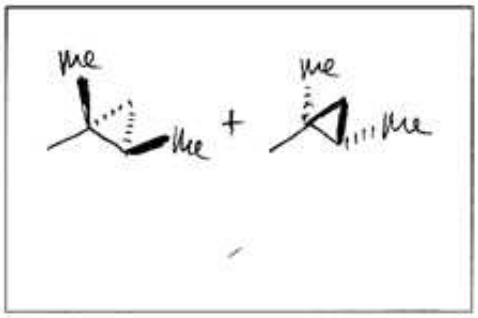








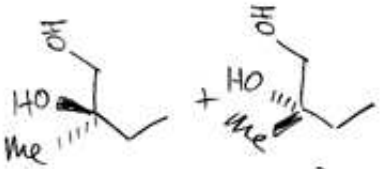




2b) Predict the products of the following reactions. Show all possible stereoisomers using bold and dashed lines for chirality centers and indicate whether the stereoisomers would be formed in equal or unequal amounts. (12 pts)

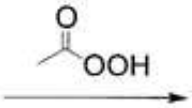
$K_2OsO_2(OH)_4$

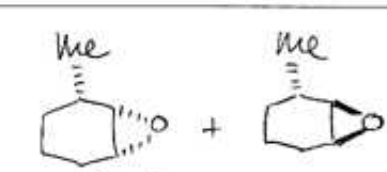
$K_3Fe(CN)_6$
DHQD ligand
(Sharpless dihydroxylation)



(enantioselective)

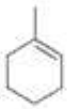
circle one: EQUAL UNEQUAL +1





diastereomers

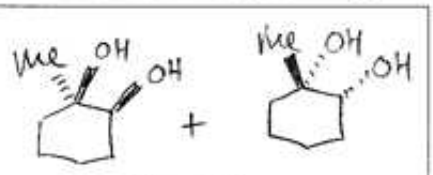
circle one: EQUAL UNEQUAL +1



OsO_4 (cat.)

tert-butanol
t-butyl hydroperoxide
sodium hydroxide

(non-Sharpless conditions)



enantiomers

circle one: EQUAL UNEQUAL +1

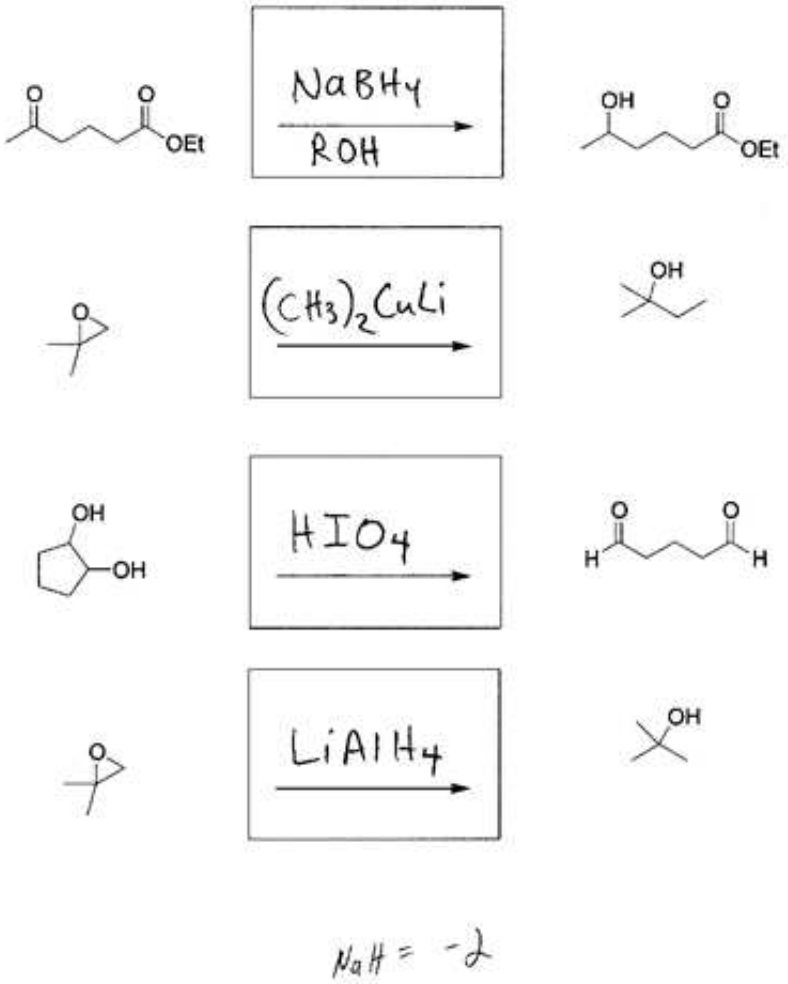
1. Br_2, H_2O

2. NaH

circle one: EQUAL UNEQUAL +1

-1 bromohydrin

2c) Provide the missing reagents for the following transformations. (12 pts)



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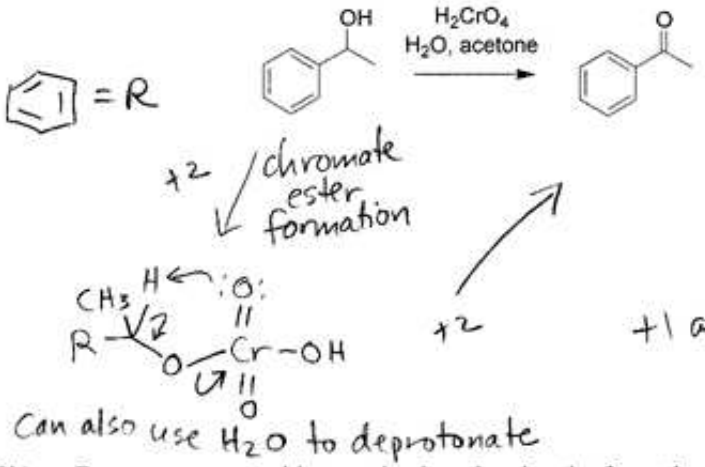
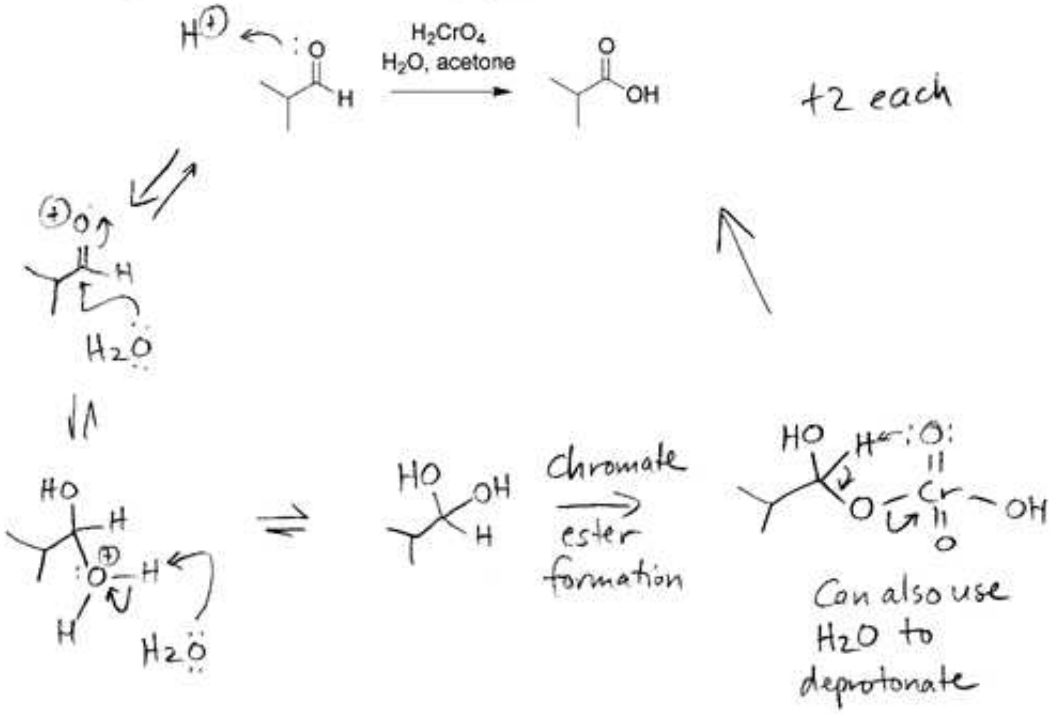
3a) Draw an arrow-pushing mechanism showing the formation of the ketone from the starting alcohol under Jones oxidation conditions. (5 pts)

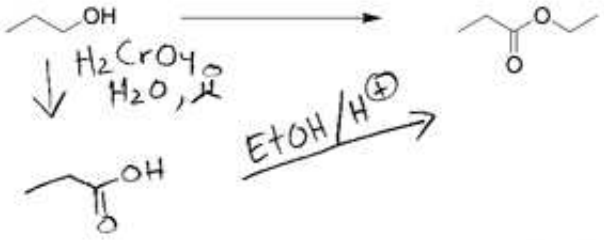


3b) Draw an arrow-pushing mechanism showing the formation of the carboxylic acid from the aldehyde under Jones conditions. (10 pts)



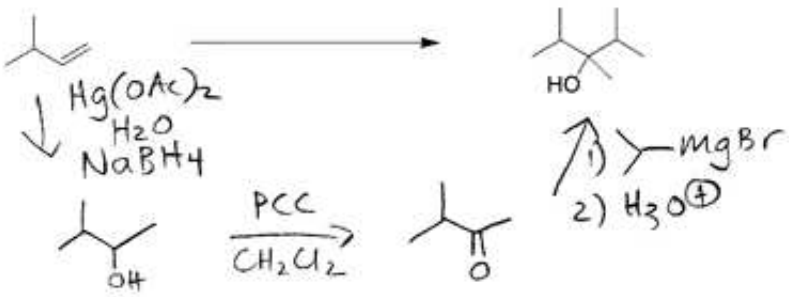
4) For each of the following, outline a synthesis of the compound from the indicated starting material and reagents of four or fewer carbons and any needed inorganic reagents. Do not show mechanisms, just reagents needed and the product of each step. Remember to work backwards from the target! (24 pts)

4a)



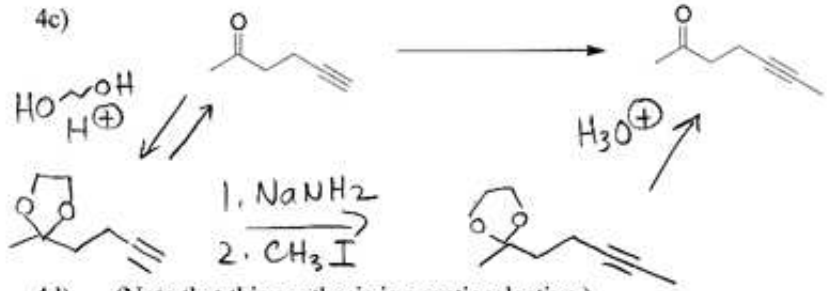
+4

4b)



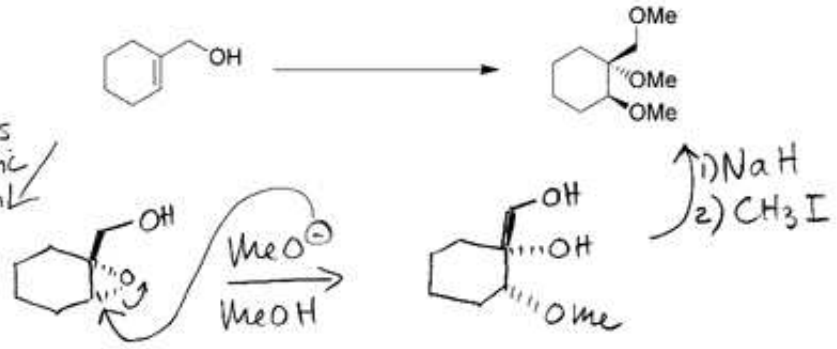
+6

4c)



+6

4d) (Note that this synthesis is enantioselective.)



+6

+2

5. Show a detailed mechanism for the following reaction. Include all arrows, lone pairs, formal charges and key intermediates to receive full credit (10 pts).