Chemistry 59-230/232 **Final Exam**
Time: 3 h **Dec. 15, 2005**

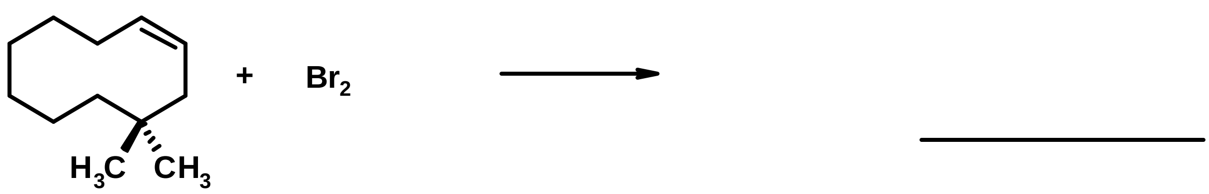
NAME ______________________________ **ID#** ____________________

LAB SECTION (or TA name) ______________________________

Note: **Please answer on the test paper.** There is an extra sheet for rough work at the back, but it will not be marked. In some questions, there is a choice of questions to answer. If all are answered, all will be marked. There are **140** marks on this exam.

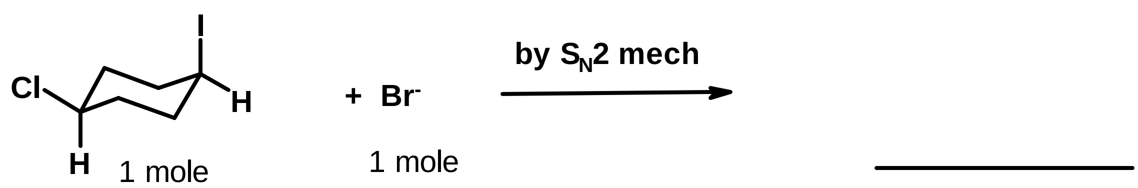
1. Fill in the blanks with the structural formula or reagents required to complete the equation. Show any required catalysts or additional reagents over the arrow. Make sure your drawings show stereochemistry if it is important. Note: Entry "i." is worth 2 entries. ***Do any ten (10), but including i.*** (**40 marks total)**

a.

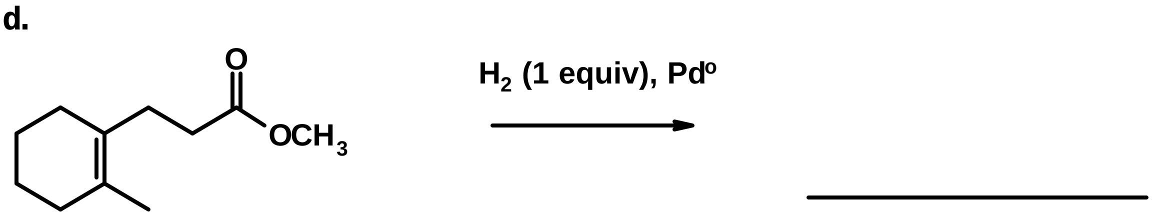


b.

c.

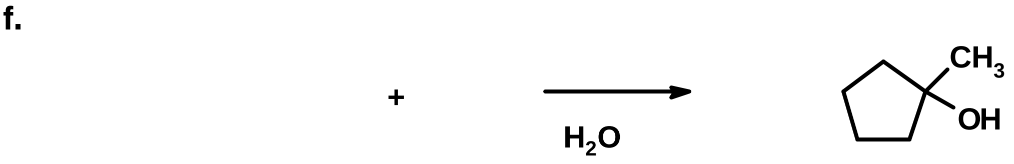


d.

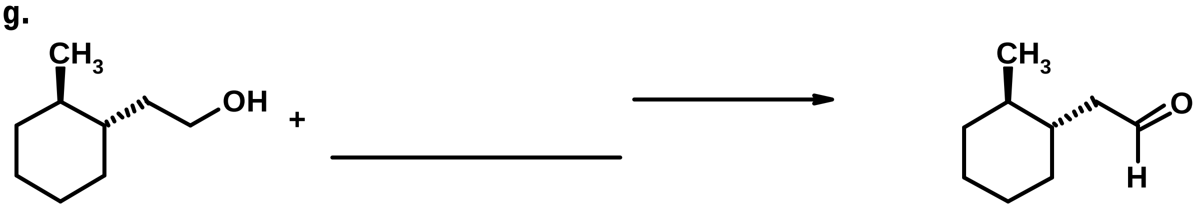


e.

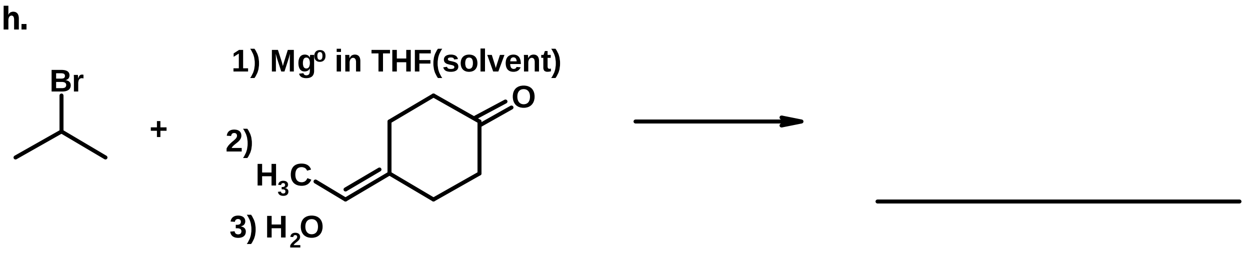
f.



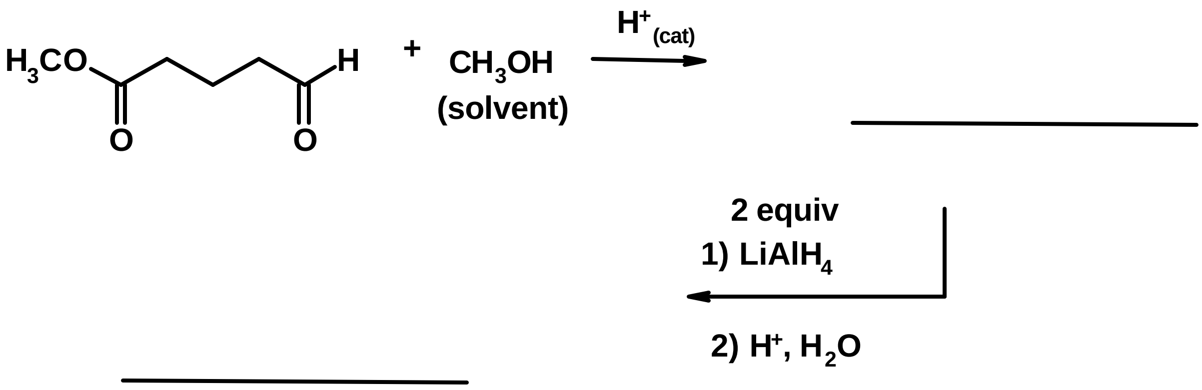
g.



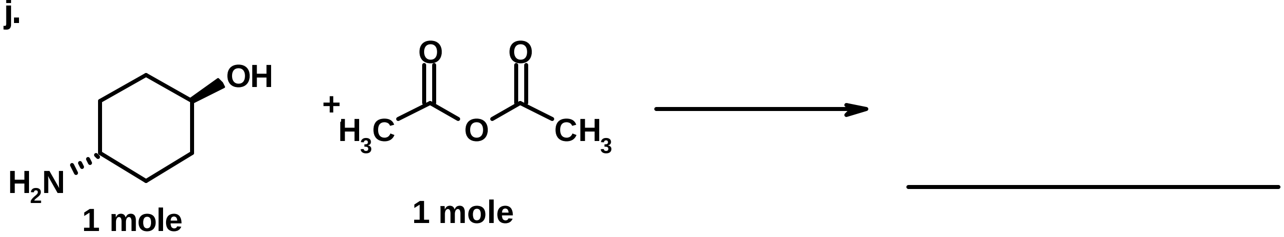
h.



i.

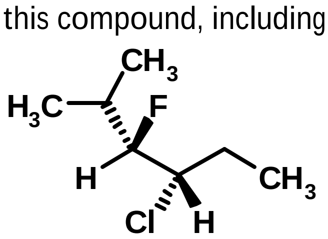


j.



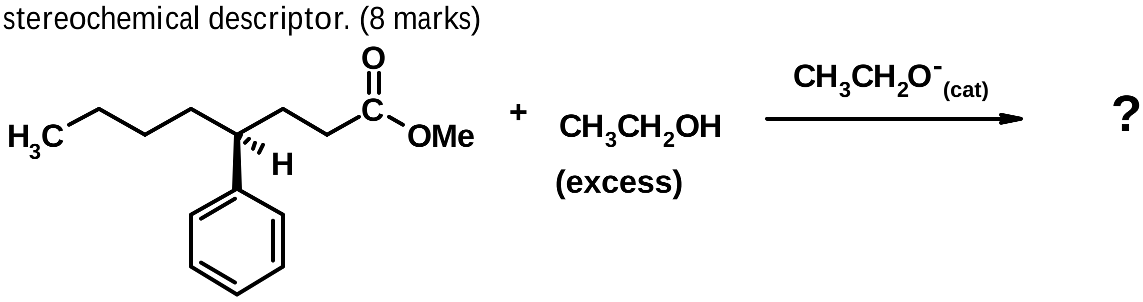
2a. (12 marks total) Draw the structure of *trans* 1-(1,1-dimethylethyl)-2-fluorocyclohexane in its most stable chair conformation. Label the non hydrogen substituents on the cyclohexane as axial or equatorial. In terms of size, a 1,1-dimethylethyl group (a.k.a *tert*-butyl group) is <u>larger</u> than an fluoro group. (5 marks)

b. Draw the Newman projection of the following compound in its *most* stable conformation, as viewed down the C3-C4 bond. With respect to size, $(CH_3)_2CH > CH_3CH_2 > CH_3 >$ Br ˜ Cl ˜ F > H. What is the <u>name</u> of this compound, including its stereochemical descriptor(s) ? (7 marks)



3. a. (13 marks total)

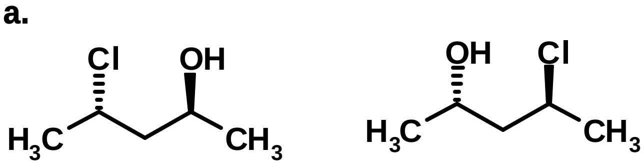
Draw the complete mechanism for the following reaction. Take the reaction to completion. Indicate which steps are reversible (or irreversible). Provide a valid IUPAC name for the starting material, including the stereochemical descriptor. (8 marks)



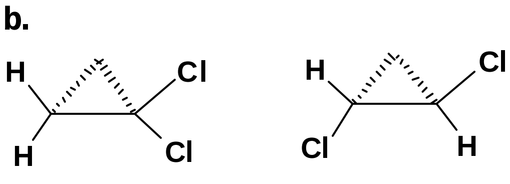
b. In the reaction of a ketone (lets say 2,6-dimethylheptan-4-one) with an alcohol (let's say it's CH_3OH) one never gets an acetal under base catalyzed conditions. Show by intermediates and reaction steps why is this is the case (5 marks). The complete answer will include the structure of 2,6-dimethylheptan-4-one.

4. (**33 marks total**) Describe the relationship that exists between the following sets of compounds (i.e., enantiomer, diastereomer, geometric isomer, structural/constitutional isomer, identical). Indicate any *meso* forms (9 of the 33 marks).

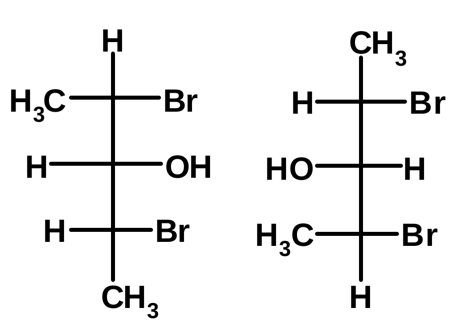
a.



b.



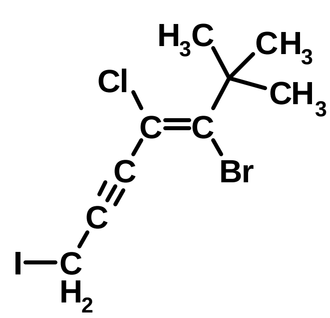
c.



Also, identify the chiral centres for the **left** compound in a) *and* c) as (R)- or (S)- (8 of 33 marks)

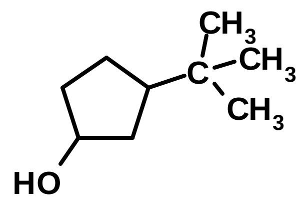
d. Draw the Fischer projection of (2S, 4R)-2-chloro-4-iodopentane. (4 *of the* 33 marks).

e. Identify the hybridization of each carbon atom in the following molecule. (3 of the 33 marks)



f. In the above compound (in e), assign the appropriate stereochemical descriptor to the alkene. Show your work (6 marks)

g. Identify the carbon atoms in the following compound as primary, secondary, tertiary, or quaternary (3 of the 33 marks).



5. On the axes below, draw the energy/reaction coordinate profile for the reaction between $(CH_3)_2C{=}CH_2$ + HBr (the mechanism should be implied in the answer). Label the intermediate(s)/products.

Give the rate equation for the reaction. (6 marks total)

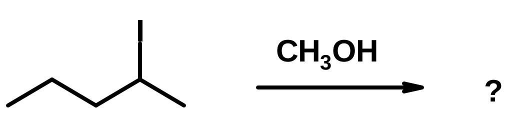
rate (v) =

6. (**16 marks** total) Rank the following in terms of tendency to undergo S_N2 substitution (as opposed to S_N1) . *Give reasons for your ordering* <u>and the expected products</u>. (13 of the 16 marks) Assume the same solvent for each of the reactions.

a)

b)

c)

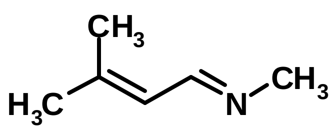


d. Rank the following from best nucleophile to worst nucleophile ? (3 *of the* 16 marks)

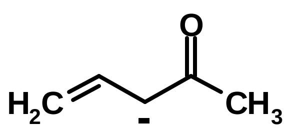
$CH_3C(O)O^-$, Br^-, I^-, HO^-, HS^-

7. (**9 marks**) a and b Indicate all *reasonable* resonance forms of the following ions, using curved arrows to indicate electron movement. If there are *unreasonable* resonance forms, <u>either</u> do not draw them or label them as unreasonable. If there is a case for which there are no other resonance forms, state that fact.

a.

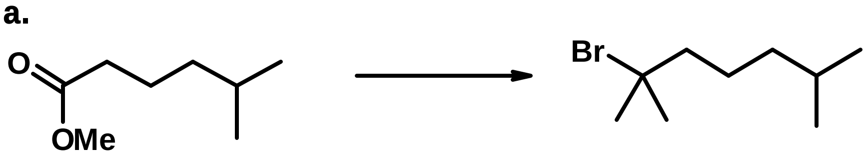


b.



8. (**11 marks total**) 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. ***<u>DO one of a and b, but answer c regardless.</u>***

a.

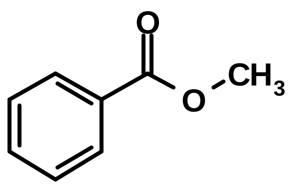


Note: Me = CH_3

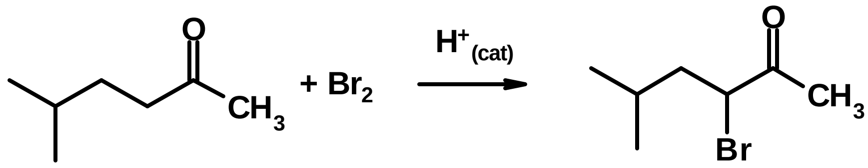
b.

c. What is the name of the final product compound in **8b**? (3 of the 11 marks)

Bonus: (up to +3) In esters, the 'carbonyl' oxygen is the basic one, and not the 'ether type' one. Why is this the case?



Another Bonus (up to +5**):** An excellent way to introduce a bromine a- to (next to) a ketone function is adding Br_2, with an acid catalyst. Can you propose a reasonable mechanism?



Periodic Table of the Elements

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
1 H 1.0079																1 H 1.0079	2 He 4.0026
3 Li 6.941	4 Be 9.0122											5 B 10.811	6 C 12.011	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.1797
11 Na 22.9898	12 Mg 24.3050											13 Al 26.9815	14 Si 28.0855	15 P 30.9738	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	21 Sc 44.9559	22 Ti 47.88	23 V 50.9415	24 Cr 51.9961	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.69	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62	39 Y 88.9059	40 Zr 91.224	41 Nb 92.9064	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.9055	46 Pd 106.42	47 Ag 107.8682	48 Cd 112.411	49 In 114.82	50 Sn 118.710	51 Sb 121.75	52 Te 127.60	53 I 126.9045	54 Xe 131.29
55 Cs 132.9054	56 Ba 137.327	57 *La 138.9055	72 Hf 178.49	73 Ta 180.9479	74 W 183.85	75 Re 186.207	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.9665	80 Hg 200.59	81 Tl 204.3833	82 Pb 207.2	83 Bi 208.9804	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 **Ac (227)	104 Unq (261)	105 Unp (262)	106 Unh (263)	107 Uns	108	109									

*	58 Ce 140.114	59 Pr 140.9076	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.965	64 Gd 157.25	65 Tb 158.9253	66 Dy 162.50	67 Ho 164.9303	68 Er 167.26	69 Tm 168.9342	70 Yb 173.04	71 Lu 174.967
**	90 Th 232.0381	91 Pa 231.0359	92 U 238.0289	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

Atomic masses are 1989 IUPAC values up to four decimal places.