Final Exam
Chemistry 343
Professor Gellman
18 December 2013

Last Name _____

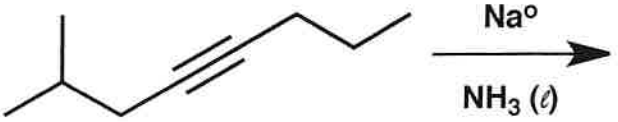
First Name _____

00205

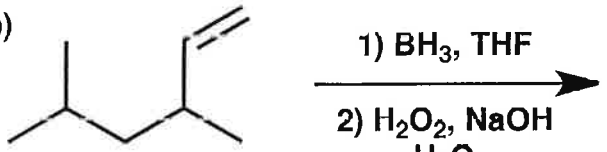
General Instructions:
(i) Use scratch paper at back of exam to work out answers; final answers must be recorded at the proper place on the exam itself for credit. Models are allowed.
(ii) Print your name on each page.
(iii) Please keep your paper covered and your eyes on your own work. Misconduct will lead to failure in the course.

1. (27 points) Show the major product or products expected from each reaction.

(a)

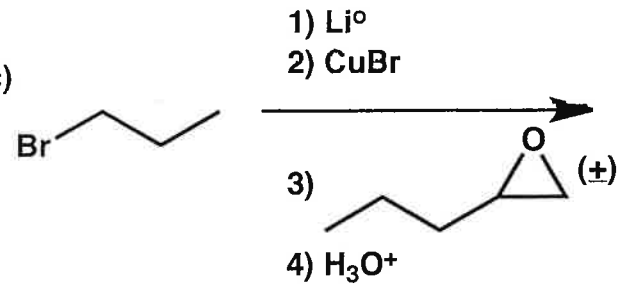


(b)

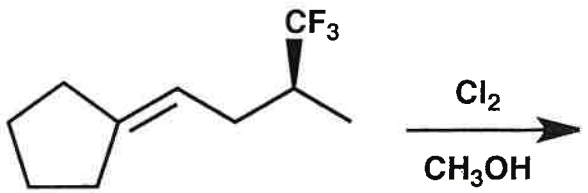


(racemic)

(c)



(d)



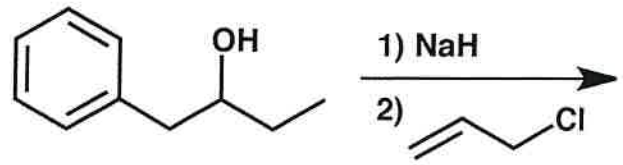
(single enantiomer)

(continued on next page)

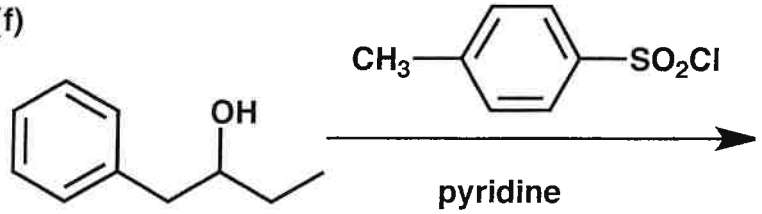
Name _____

1. (cont.)

(e)

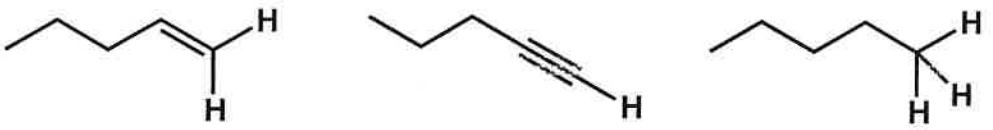


(f)

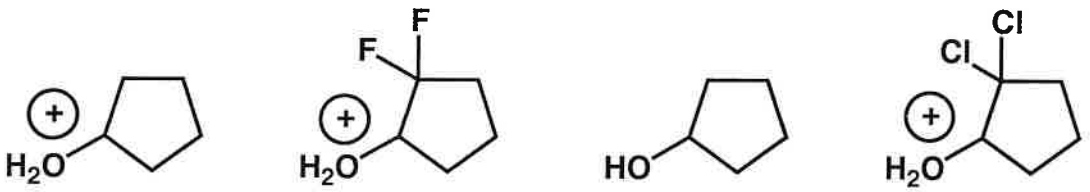


2. (10 points) For each set of molecules below, redraw them in order based on expected pK_a of the indicated protons, with the highest pK_a on the left and the lowest on the right.

(a) $H_2N—H$



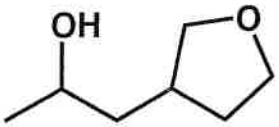
(b)



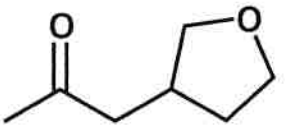
Name _____

3. (21 points) Show the reagents required to convert the starting molecule to the indicated product. If necessary, be sure to differentiate clearly between distinct steps, by using "1)," "2)," etc. over the arrow.

(a)

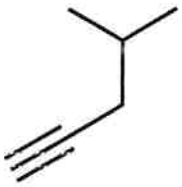


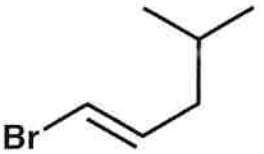
(mixture of 4 diastereomers)



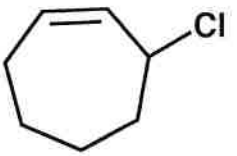
(racemic)

(b)



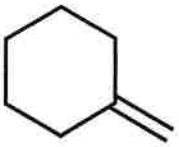


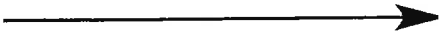
(c)

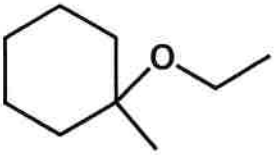


(racemic)

(d)



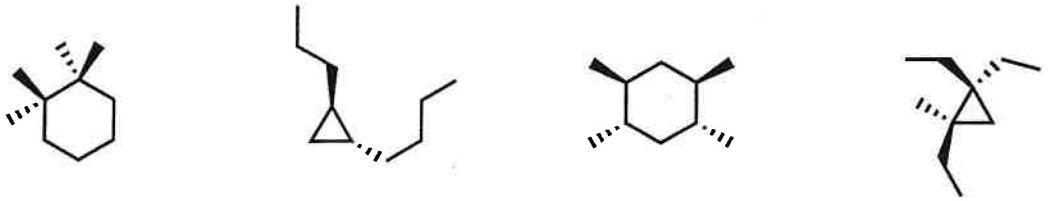




Name _____

4. (10 points)

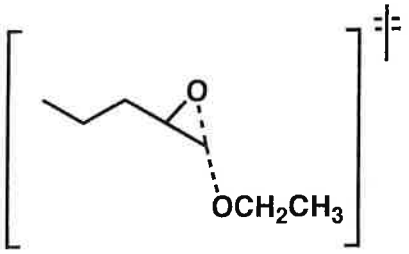
(a) Redraw the isomeric molecules below ordered according to heat of combustion, with the one that would give the largest heat of combustion (absolute value) on the left, and the one that would give the smallest heat of combustion on the right.

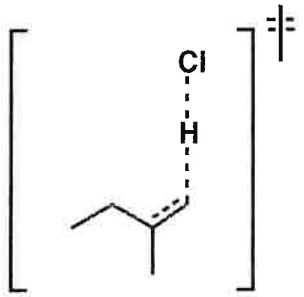


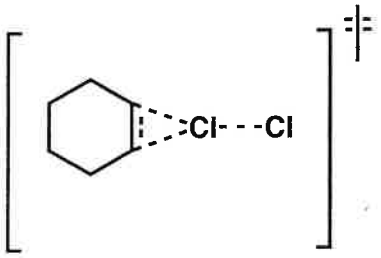
(b) Redraw the isomeric molecules below ordered according to heat of hydrogenation, with the one that would give the largest heat of hydrogenation (absolute value) on the left, and the one that would give the smallest heat of hydrogenation on the right.

5. (12 points) Shown below are transition states for reaction mechanisms that we have discussed in class. Add δ+ and/or δ- at the appropriate position(s) in each case.

NOTE: It is possible that some of the transition states have a net charge, but no counterions are shown.







Name _____ 00205

6. (30 points)

Indicate isomeric relationships to the structure drawn in each box among the structures drawn around the boxed structure. Follow the directions below. (Conformational differences are not relevant to this question.)

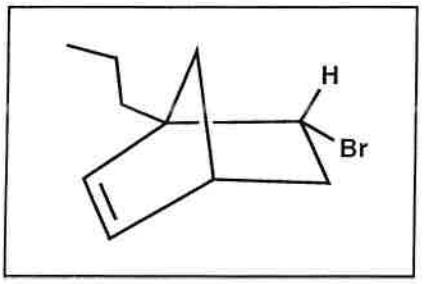
Put a CIRCLE around any structure that corresponds to boxed structure (i.e., a different drawing of the same molecule).

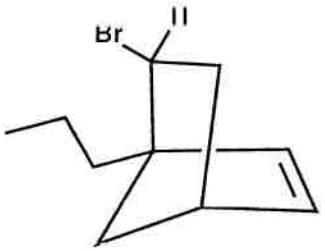
Put a SQUARE around any structure that corresponds to the ENANTIOMER of the boxed structure.

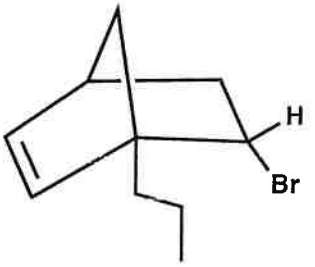
Put a TRIANGLE around any structure that corresponds to a DIASTEREOMER of the boxed structure.

Put an X across any structure that corresponds to a CONSTITUTIONAL ISOMER of the boxed structure.

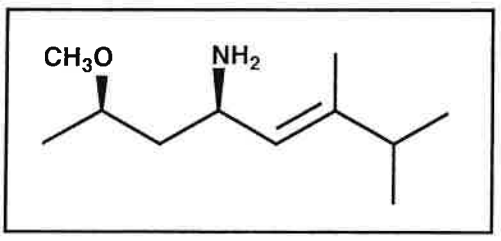
(a)

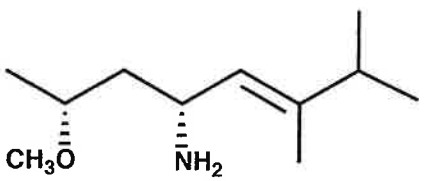


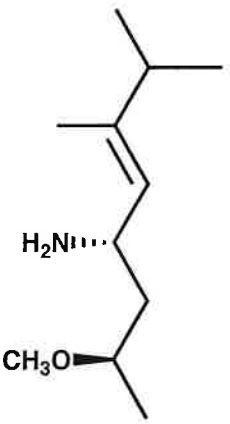


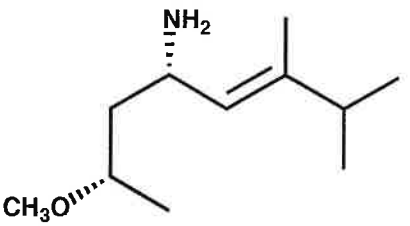


(b)



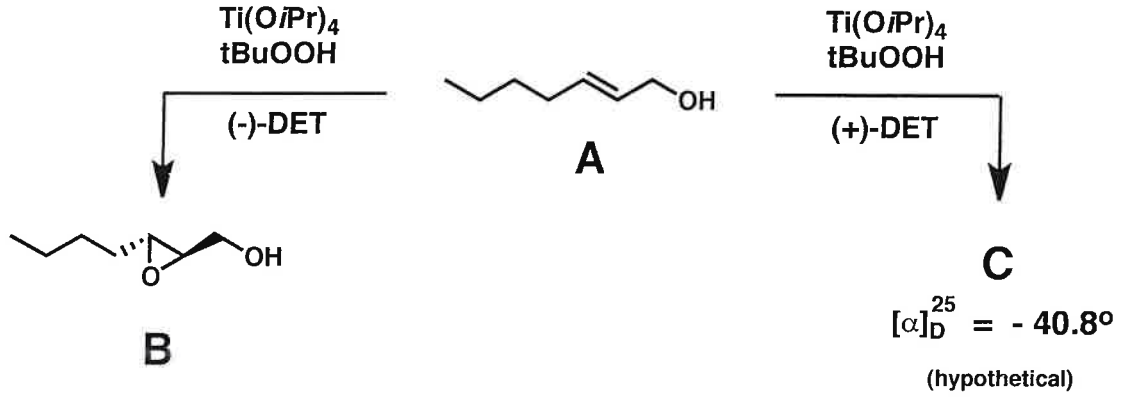






Name _____

7. (6 points) When molecule A is allowed to react as indicated below, either molecule B or molecule C is produced. In light of the information about B and C shown below, answer the questions below.

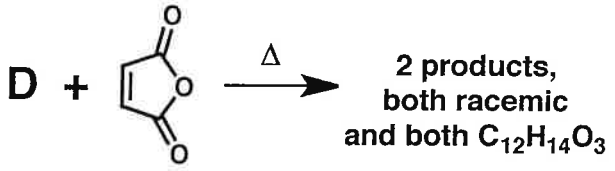


(a) For B, $[\alpha]_D^{25}$ = _____°

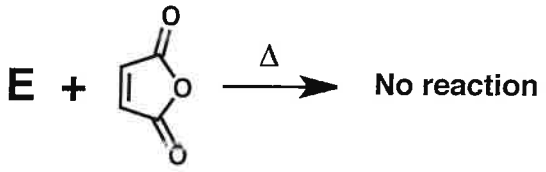
(b) The structure of C =

Name _____

8. (12 points) Two isomers, D and E, have the formula C_8H_{12}. Both react with two equivalents of H_2 in the presence of Pd/C to form ethylcyclohexane. However, exposing these isomers to the reaction conditions shown below gives divergent results.



vs.



Propose a structure for D and a structure E below (there may be more than one correct answer in each case).

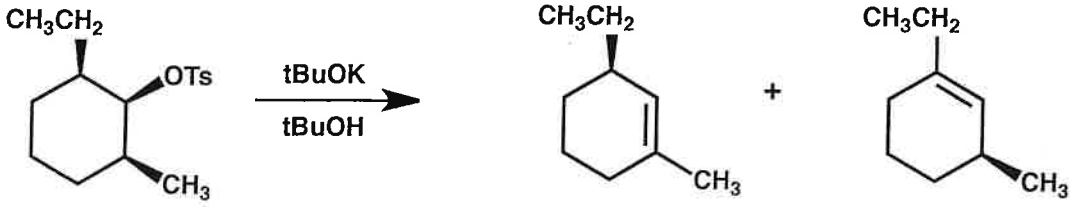
D =

E =

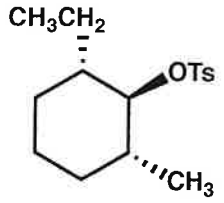
Name _____ 00205

9. (20 points)

(a) Provide a conformationally accurate drawing of the starting material below, and use that drawing as the starting point for a mechanism (curved arrows) that show how the products are formed. Be sure to show any intermediates.



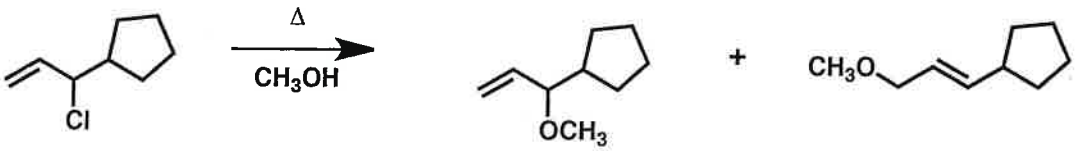
(b) Provide a conformationally accurate drawing of the molecule shown below. Your drawing will provide the basis of your answer to part (c); it may be helpful to show more than one conformation.



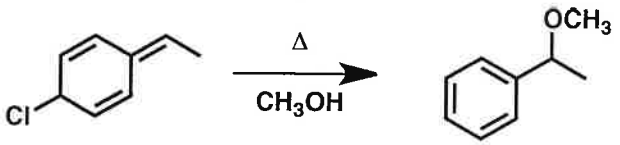
(c) In a <u>single sentence</u>, explain why the molecule in part (b) does not undergo any reaction when treated with the reagents used in part (a), i.e., when this molecule is treated with potassium *t*-butoxide in t-butanol.

10. (28 points) Name _____ 00205

(a) Provide a mechanism (curved arrows) for the reaction shown below. Be sure to show any intermediates.



(b) Provide a mechanism (curved arrows) for the reaction shown below. Be sure to show any intermediates.

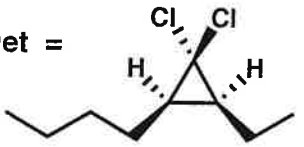


(c) In a single sentence, explain why there is only one product (actually, a racemic pair) from the reaction shown in part (b).

11. (24 points)

(a) Devise a synthetic route from the indicated starting material(s) to the indicated target. The route should be as short and as selective as possible. You may use <u>any</u> inorganic reagents in your synthetic plan. Show the expected product after each step in each synthetic route. (Do not provide mechanistic information.)

Starting materials = Any organic molecule(s) with 4 or fewer carbons

Target = 

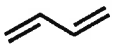
(±)

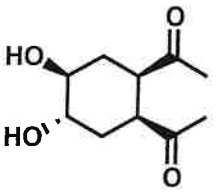
-- cont. on next page --

Name _____

11. (cont.)

(b) Devise a synthetic route from the indicated starting material to the indicated target. The route should be as short and as selective as possible. You may use <u>any</u> other organic molecules and any inorganic reagents in your synthetic plan. Show the expected product after each step in each synthetic route. (Do not provide mechanistic information.)

Starting material = 

Target = 

(racemic)

Name _____ 00205

Problem #	Score
1	/ 27
2	/ 10
3	/ 21
4	/ 10
5	/ 12
6	/ 30
7	/ 6
8	/ 12
9	/ 20
10	/ 28
11	/ 24

_____

Total: / 200

00205

Periodic Table of the Elements

																	2 He 4.003
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.011	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.7	29 Cu 63.5	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98.91	44 Ru 101.07	45 Rh 102.91	46 Pd 106.4	47 Ag 107.87	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.30
55 Cs 132.91	56 Ba 137.34	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.97	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.03	89 Ac (227)	104 Unq* (261)	105 Unp* (262)	106 Unh* (263)	107 Uns* (262)	108 Uno* (265)	109 Una* (266)									

Lanthanides	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
Actinides	90 Th 232.04	91 Pa (231)	92 U 238.03	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (249)	98 Cf (249)	99 Es (254)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

*Symbol (and name) provisional.

Numbers in parentheses: available radioactive isotope of longest half-life.