Chemistry 3719, Fall 2002 **Exam 3 Key** **Name:**

This exam is worth 100 points out of a total of 600 points for Chemistry 3719/3719L. You have 50 minutes to complete the exam and you may use molecular models as needed. Good Luck.

PERIODIC CHART OF THE ELEMENTS

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII		IB	IIB	IIIA	IVA	VA	VIA	VIIA	INERT GASES
1 H 1.00797															1 H 1.00797	2 He 4.0026
3 Li 6.939	4 Be 9.0122										5 B 10.811	6 C 12.0112	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.183
11 Na 22.9898	12 Mg 24.312										13 Al 26.9815	14 Si 28.086	15 P 30.9738	16 S 32.064	17 Cl 35.453	18 Ar 39.948
19 K 39.102	20 Ca 40.08	21 Sc 44.956	22 Ti 47.90	23 V 50.942	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.9216	34 Se 78.96	35 Br 79.909	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.905	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (99)	44 Ru 101.07	45 Rh 102.905	46 Pd 106.4	47 Ag 107.870	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.904	54 Xe 131.30
55 Cs 132.905	56 Ba 137.34	*57 La 138.91	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.967	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.980	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	‡89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 ? (271)	111 ? (272)	112 ? (277)					

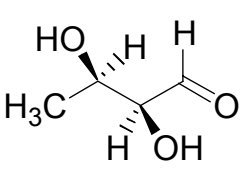
Numbers in parenthesis are mass numbers of most stable or most common isotope.

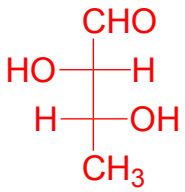
Atomic weights corrected to conform to the 1963 values of the Commission on Atomic Weights.

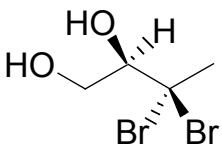
The group designations used here are the former Chemical Abstract Service numbers.

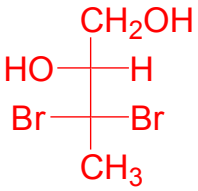
*Lanthanide Series	58 Ce 140.12	59 Pr 140.907	60 Nd 144.24	61 Pm (147)	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.924	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.97
‡Actinide Series	90 Th 232.038	91 Pa (231)	92 U 238.03	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (256)	103 Lr (257)

1. (6 pts) Convert the following structures into Fischer projections.









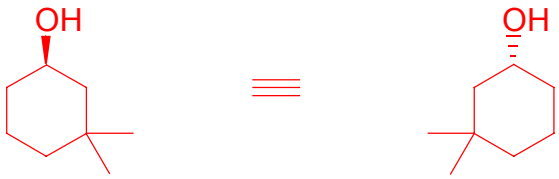
2. (12 pts) Draw each of the following compounds giving the correct configurations (*R* or *S*) for any asymmetric centers.

a. (*R*)-5-chloro-1-octyne

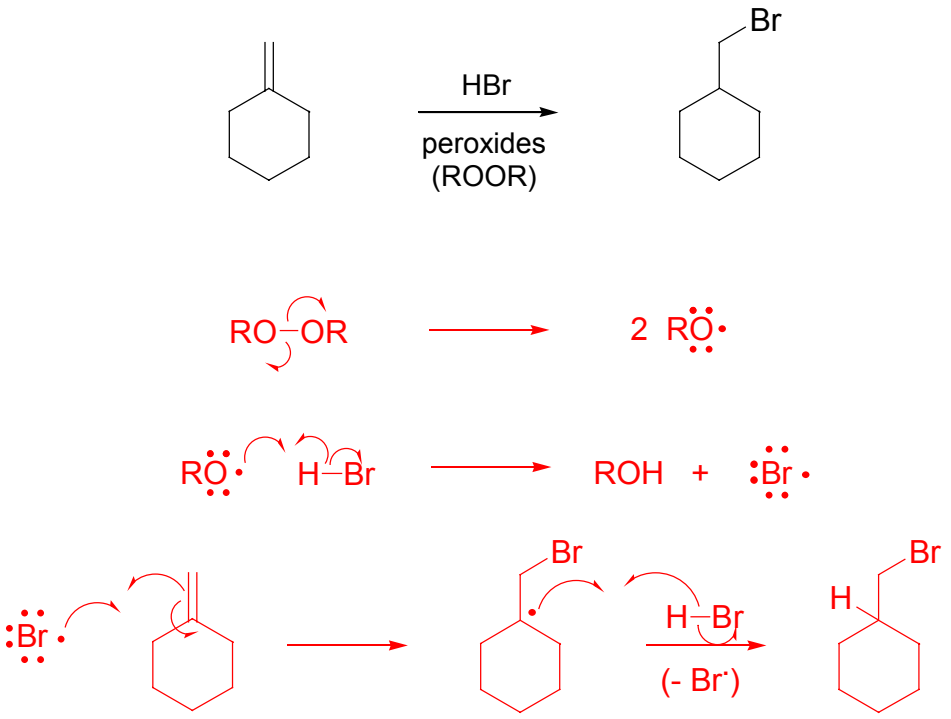
b. (*S*)-3-fluorocyclopentene

c. (2*R*, 3*S*)-2,3-dibromohexane

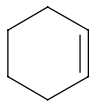
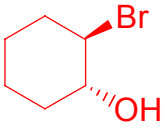
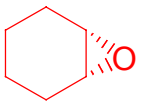
d. (*R*)-3,3-dimethylcylohexanol



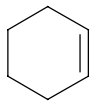
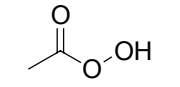
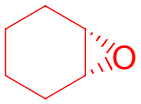
3. (10 pts) Provide a detailed mechanism, using arrows to show the breaking and forming of bonds, that details how the given product is formed in the reaction below.



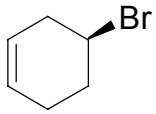
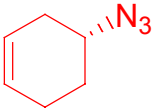
4. (18 pts) For each of the following reactions give the product(s) and indicate which will be major and minor when applicable. Where more than one set of reagents is given a product from each step is required.

a.  1. Br_2, H_2O 2. $NaNH_2$ → 1.  2. 

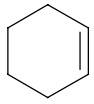
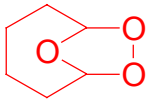
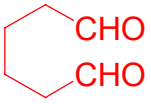
($NaNH_2$ depronates OH then the O kicks out Br)

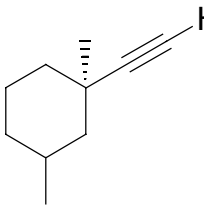
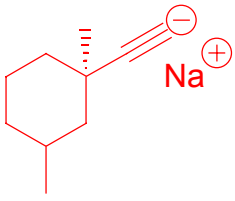
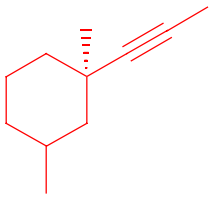
b.   → 

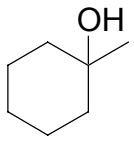
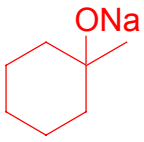
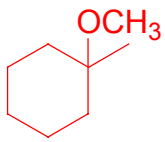
epoxidation with a peroxyacid (use of RCO_3H with alkene)

c.  NaN_3 in DMF → 

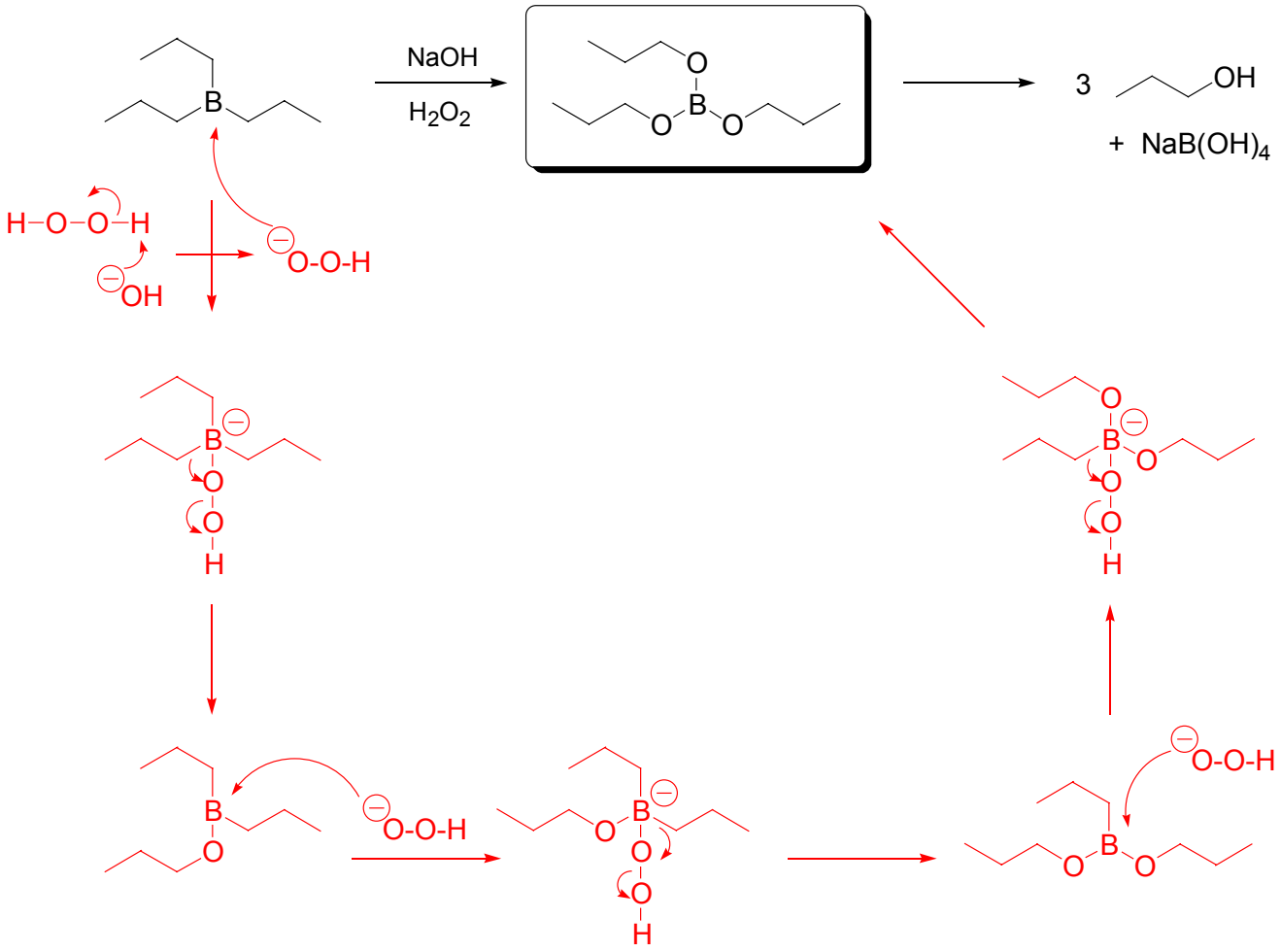
S_N2 with stereochemical inversion

d.  1. O_3 2. Zn, H_2O → 1.  2. 

e.  1. $NaNH_2$ 2. CH_3Br → 1.  2. 

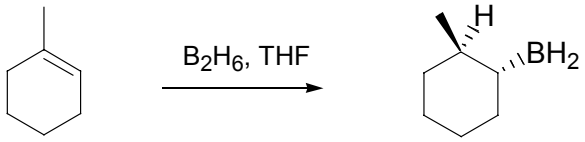
f.  1. $NaNH_2$ 2. CH_3Br → 1.  2. 

5. (10 pts) In the following portion of the hydroboration reaction, give a <u>complete</u> mechanism for how the highlighted material (in the box) is formed from the reactant on the left.



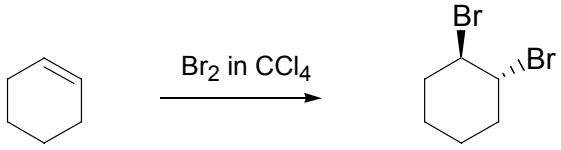
6. (12 pts) In each of the following reactions give a mechanistic explanation that accounts for the observed regiochemistry and/or stereochemistry in each product. Diagrams and/or words would suffice here.

a. Explain the observed stereochemistry and regiochemistry in the following hydroboration:



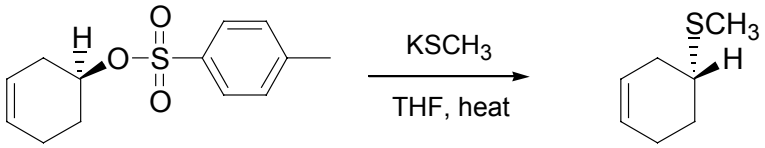
This reaction involves a syn addition of the BH_3 molecule hence the stereochemical outcome. The regiochemical preference is explained by the smaller H bonding to the less accessible carbon of the alkene and the larger BH_2 group adding to the less hindered carbon.

b. Explain the observed stereochemistry in the following addition of Br_2:



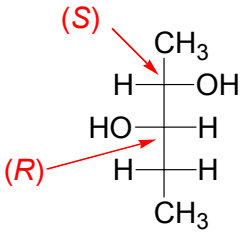
This addition reaction involves the formation of a carbocation that is stabilized by donation of electron density from the first Br that has added (bromonium ion). The large Br then blocks one face of the molecule such that the bromide ion may only attack from the opposite face, hence the *trans* stereochemistry.

c. Explain the observed stereochemistry in the following substitution reaction:

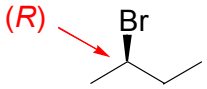


This is the classic S_N2 reaction in which the nucleophile must bond to the electrophile at ~180° to the direction that the leaving group will take off from. This results in inversion of stereochemistry.

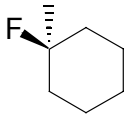
7. (10 pts) Decide which of the following molecules are chiral or achiral and, for those that are chiral, identify the asymmetric carbon(s) and work out whether they have the (*R*) or (*S*) configuration.



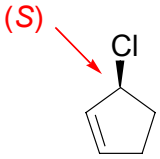
chiral



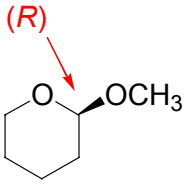
chiral



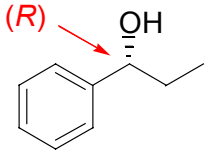
achiral



chiral



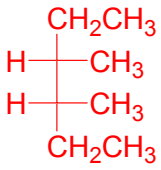
chiral



chiral

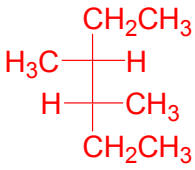
8. (6 pts) Draw all of the possible stereoisomers for the compound 3,4-dimethylhexane and relate them to each other as being either enantiomers or diastereomers. You may use either the "wedge-dash" notation or the Fischer projection convention.

1

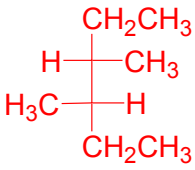


meso compound

2



3



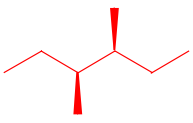
enantiomers

1 and 2; 1 and 3 are diastereomeric

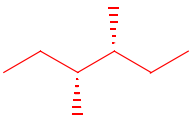
1

meso compound

2



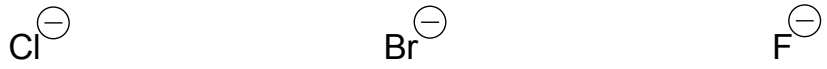
3



enantiomers

1 and 2; 1 and 3 are diastereomeric

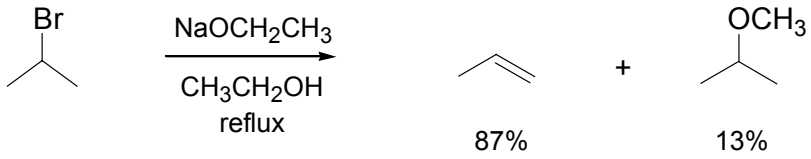
9. (6 pts) Rank the following species in terms of their relative ability to behave as leaving groups (**1** = best, **3** = worst). Explain your reasoning.



1 = Br anion, **2** = Cl anion, **3** = F anion

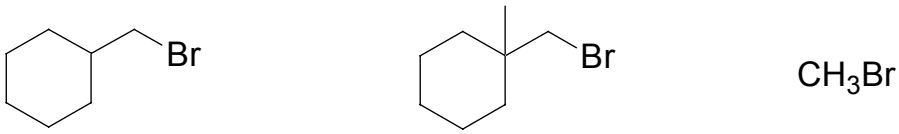
Stability of charge on a simple anion leads to leaving group ability and is related to the size of the anion and the ability of the anion to spread the charge out (larger surface area = more diffuse charge).

10. (4 pts) In the following reaction of a secondary alkyl halide with $NaOCH_2CH_3$, explain which mechanisms are operating to give the two products and explain why you get more alkene product than ether product.



The competing mechanisms are S_N2, in which $NaOCH_2CH_3$ behaves as a nucleophile, and E2, in which $NaOCH_2CH_3$ behaves as a base. When a secondary alkyl halide is used as the substrate the S_N2 is slowed down due to the electrophilic carbon being crowded by the β- methyl groups. The β-hydrogens are more accessible since they are simply pointing out into space and so the E2 mechanism is favoured.

11. (6 pts) Rank the following in the expected order of rate of reaction in the S_N2 reaction with NaN_3 in THF (**1** = fastest reaction, **3** = slowest reaction). Explain your reasoning.



2 **3** **1**

The accessibility of the electrophilic carbon is at issue here. Even groups at the beta carbon will slow the approach of the nucleophile so even though each of these substrates is a 1^0 alkyl bromide there will be a difference in reaction rates.