

Chemistry 3351
Organic Chemistry/Final Exam
Monday: Dec. 17th from 1:30 pm → 4:00pm

Name: Key (please print)

Page	Possible Points	Score
1	<u>1</u>	<u> </u>
2	<u>9</u>	<u> </u>
3	<u>10</u>	<u> </u>
4	<u>12</u>	<u> </u>
5	<u>14</u>	<u> </u>
6	<u>14</u>	<u> </u>
7	<u>10</u>	<u> </u>
8	<u>15</u>	<u> </u>
9	<u>10</u>	<u> </u>
10	<u>10</u>	<u> </u>
11	<u>10</u>	<u> </u>
12	<u>9</u>	<u> </u>
13	<u>16</u>	<u> </u>
14	<u>10</u>	<u> </u>
TOTAL	<u>150</u>	<u> </u>

1. (9 pts) Clickers in Action:

i) Your assignment is to convert (1*R*, 2*S*)-2-methylcyclopentanol to (1*R*, 2*S*)-1-cyano-2-methylcyclopentane. The reagents provided are:

- (1) NaCN, acetone
- (2) TsCl, pyridine
- (3) NaI, acetone

Select the best sequence of reactions, starting with substrate, to obtain the highest yield of product.

- (A) 1
- (B) 2, 1
- (C) 2, 3
- (D) 2, 3, 1

ii) Arrange the acids NH_3 , $\text{C}_2\text{H}_5\text{SH}$, $\text{C}_2\text{H}_5\text{OH}$, $\text{CH}_3\text{SO}_3\text{H}$, and HCO_2H in order of increasing strength.

- (A) $\text{C}_2\text{H}_5\text{OH} < \text{NH}_3 < \text{CH}_3\text{SO}_3\text{H} < \text{C}_2\text{H}_5\text{SH} < \text{HCO}_2\text{H}$
- (B) $\text{C}_2\text{H}_5\text{OH} < \text{NH}_3 < \text{C}_2\text{H}_5\text{SH} < \text{HCO}_2\text{H} < \text{CH}_3\text{SO}_3\text{H}$
- (C) $\text{NH}_3 < \text{C}_2\text{H}_5\text{OH} < \text{C}_2\text{H}_5\text{SH} < \text{HCO}_2\text{H} < \text{CH}_3\text{SO}_3\text{H}$
- (D) $\text{NH}_3 < \text{C}_2\text{H}_5\text{SH} < \text{C}_2\text{H}_5\text{OH} < \text{CH}_3\text{SO}_3\text{H} < \text{HCO}_2\text{H}$

iii) Which of these reactions involves a free radical mechanism?

- (I) Halogenation of alkanes in presence of light
- (II) Addition of HBr to alkenes
- (III) Addition of HBr to alkenes in the presence of ROOR

- (A) I and II
- (B) I and III
- (C) II and III
- (D) I, II and III

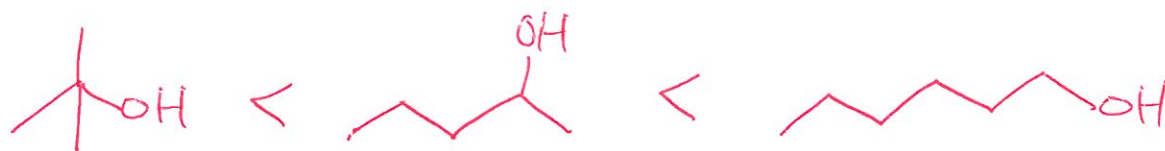
2. (10 pts) Arrange the compounds within each of the following sets in order of increasing boiling point, and give your reasoning (concisely).

(a) 1-pentanol, 2-methyl-1-butanol



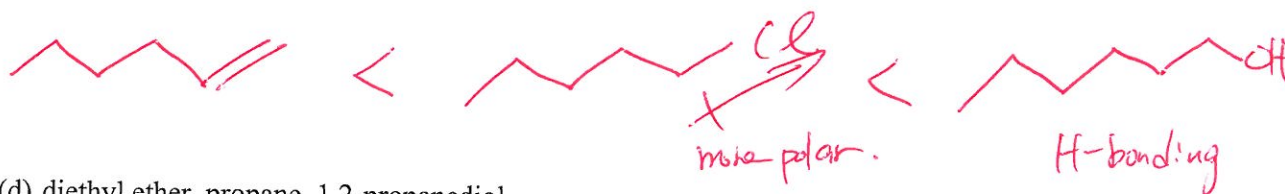
Unbranched alcohols have higher b.p.

(b) 1-hexanol, 2-pentanol, *tert*-butyl alcohol

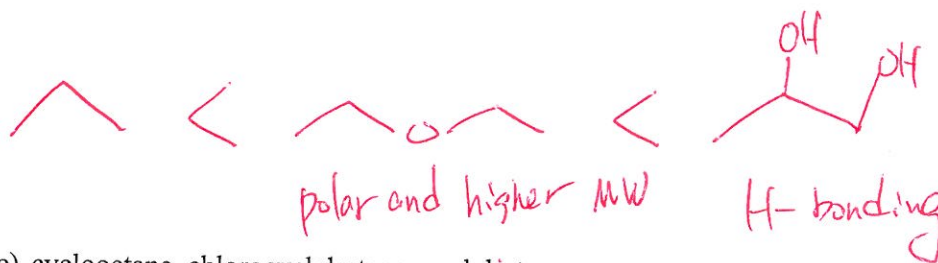


More carbon, higher b.p.

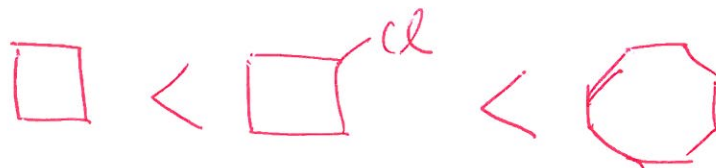
(c) 1-hexanol, 1-hexene, 1-chloropentane



(d) diethyl ether, propane, 1,2-propanediol



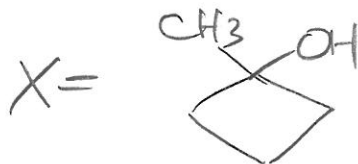
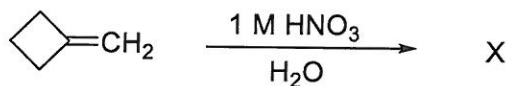
(e) cyclooctane, chlorocyclobutane, cyclobutane



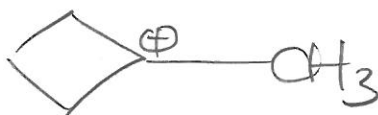
Higher MW, higher b.p.

3. (12 pts)

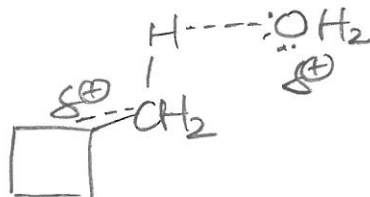
a) Give the product X expected when methylenecyclobutane undergoes acid-catalyzed hydration.



b) The rate-limiting step is protonation of the double bond; use H_3O^+ as the acid catalyst. Draw the structure of the reactive intermediate formed in the rate-limiting step.

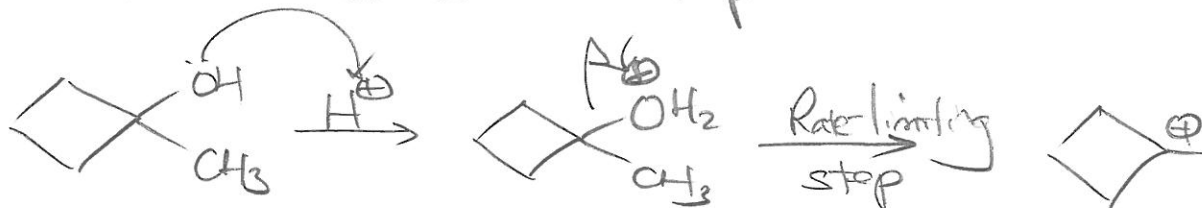


c) Draw the transition state for the rate-limiting step.

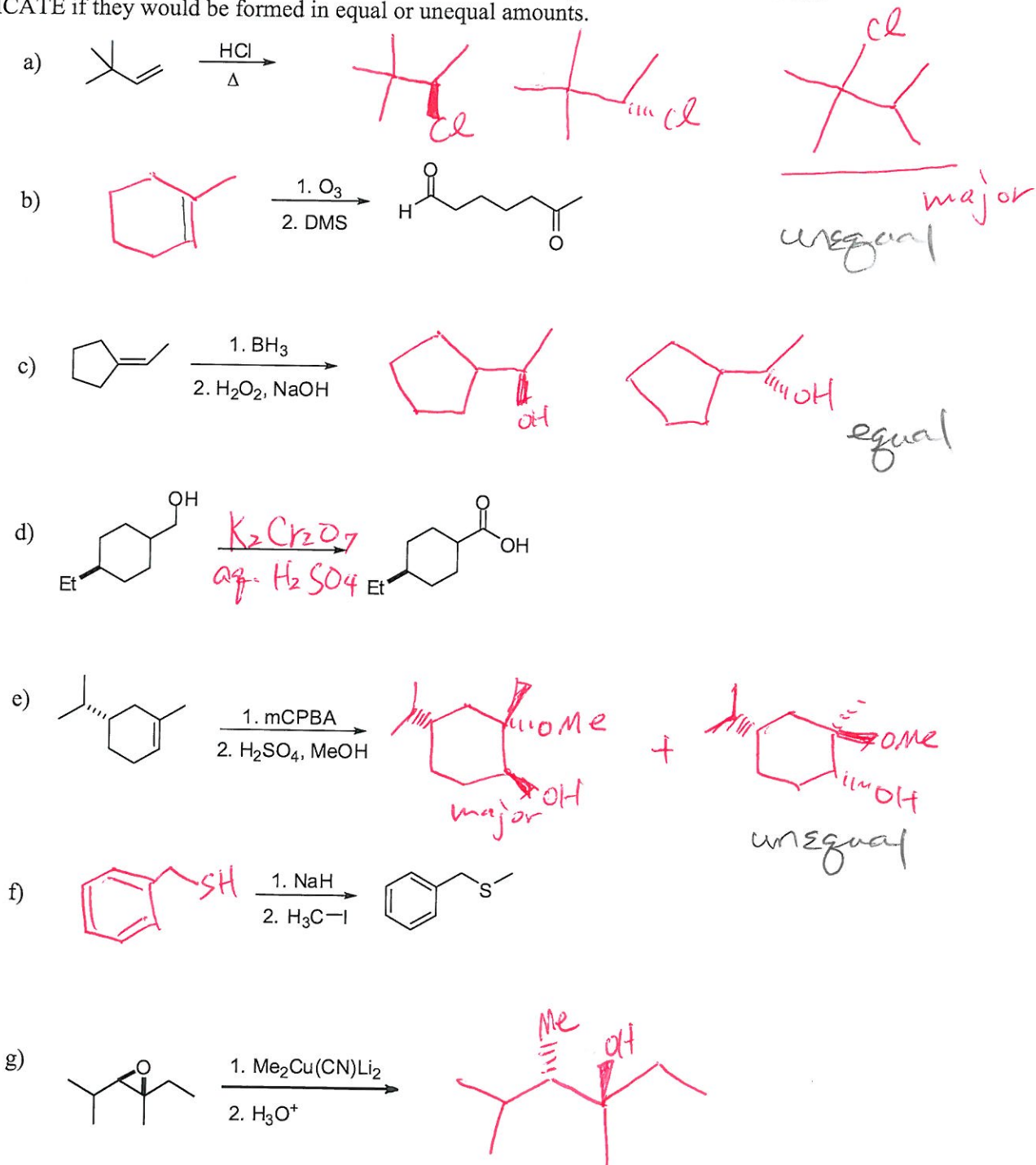


d) What is the rate-limiting step for dehydration of X (the reverse of the reaction shown above)?

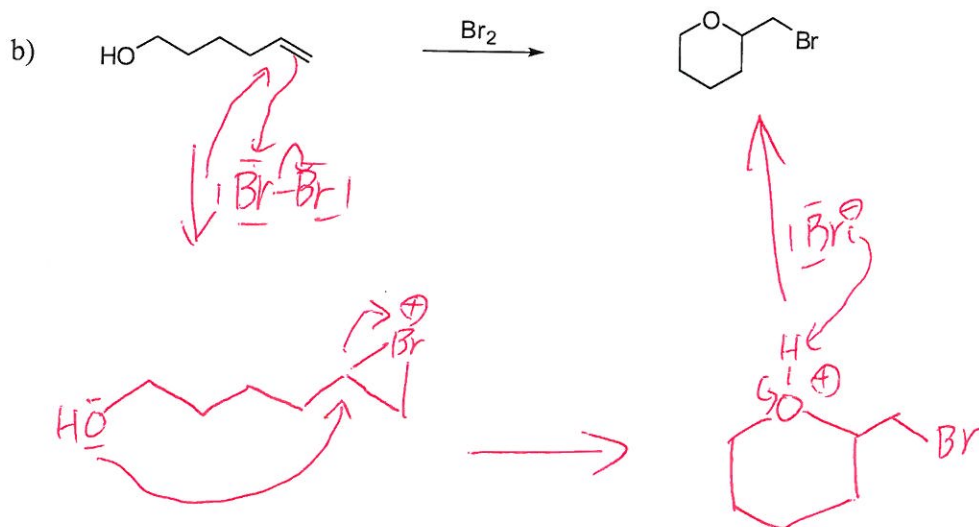
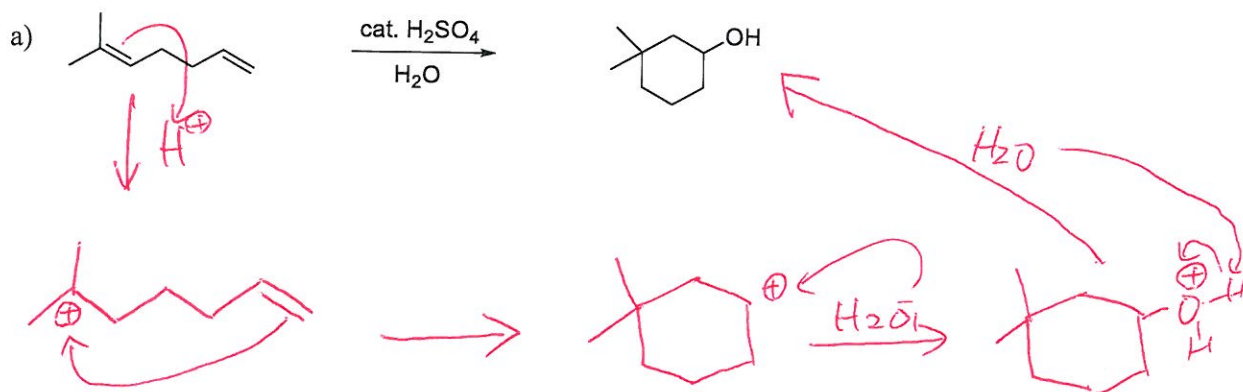
If the rate limiting step is protonation of the double bond in the forward direction, then the rate-limiting step in the reverse direction is the same step



4. (14 pts) Provide the missing products, reactants, or reaction conditions for the following reactions. For reactions that produce stereoisomers, draw ALL possible stereoisomers and INDICATE if they would be formed in equal or unequal amounts.

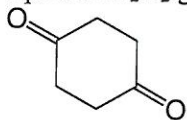


5. (14 pts) Provide full and complete mechanisms for the reactions below. Be sure to include every intermediate and all arrows required for each step of the reaction.



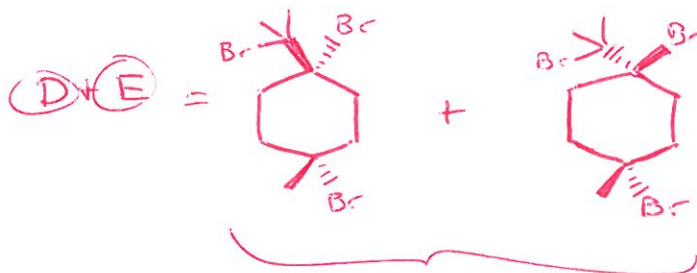
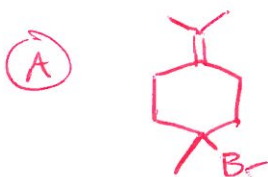
6. (10 pts). In the laboratory of the firm "Halides 'R' Us", compound **A** has been found in a vial labeled only "achiral alkyl halide $C_{10}H_{17}Br$ ". The management feels that the compound might be useful as a pesticide, but they need to know its structure. You have been called in as a consultant at a handsome fee.

Compound **A**, when treated with KOH in warm ethanol, yields two compounds (**B** and **C**), each with the molecular formula $C_{10}H_{16}$. Compound **A** rapidly reacts in aqueous ethanol to give an acidic solution, which, in turn, gives a precipitate of $AgBr$ when tested with $AgNO_3$ solution. Ozonolysis of **A** followed by treatment with $(CH_3)_2S$ affords $(CH_3)_2C=O$ (acetone) as one of the products plus an unidentified halogen-containing material. Catalytic hydrogenation of either **B** or **C** gives a mixture of both *trans*- and *cis*-1-isopropyl-4-methylcyclohexane. Compound **A** reacts with one equivalent of Br_2 to give a mixture of two separable compounds, **D** and **E**, both of which are achiral compounds. Finally, ozonolysis of compound **B** followed by treatment with aqueous H_2O_2 gives acetone and the diketone **F**.

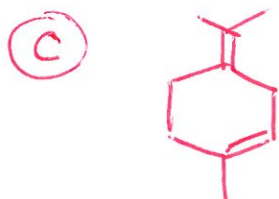
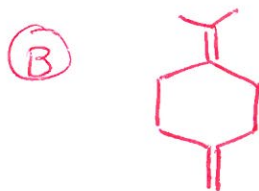


F

Propose structures for compounds **A** through **E** that best fit the data (and collect your fee).

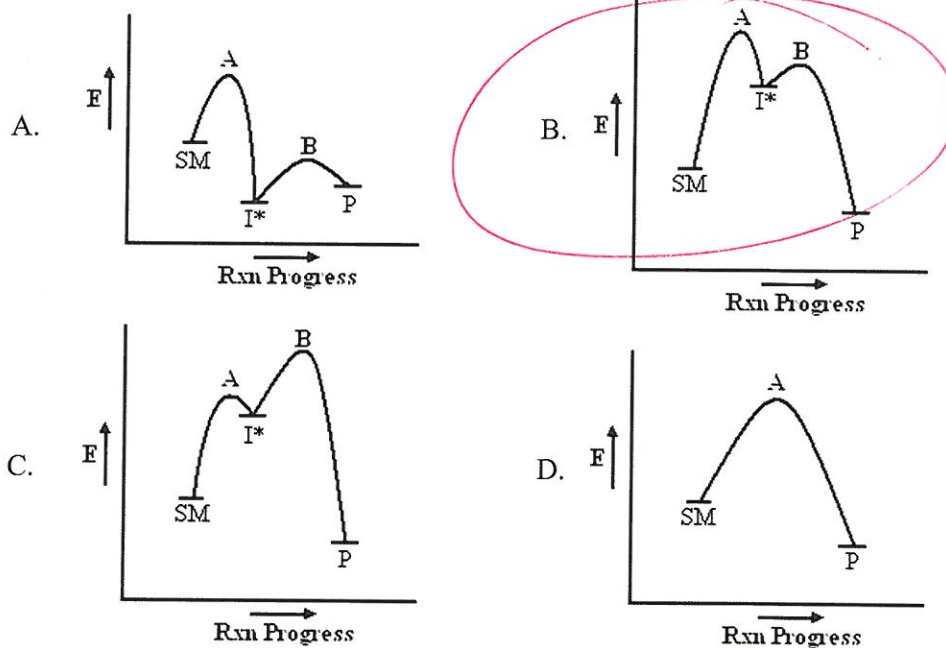
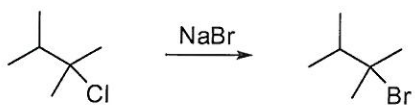


Can't tell
which is D,
which is E.



7. (15 pts)

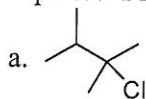
a) Which energy diagram best represents the reaction shown below? Please circle your answer. (SM: Starting material, I*: Intermediate, P: Product)



b) In regards to your answer for part a), which step is rate limiting? Please circle your answer.

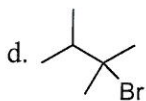
- i. Step A
- ii. Step B
- iii. Neither Step A nor Step B

c) In regards to the reaction above, which of the following compounds is the nucleophile? Please circle your answer.

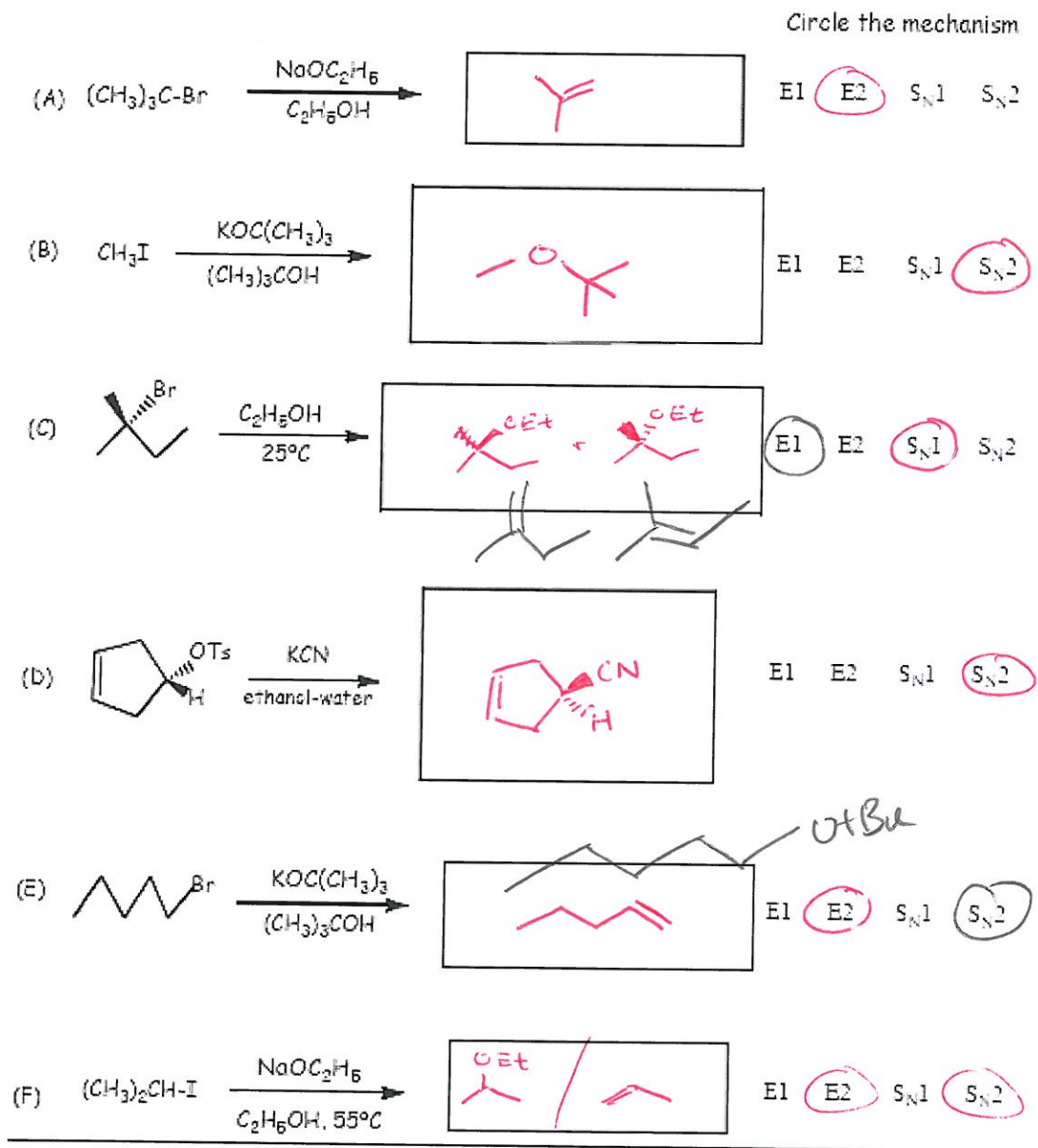


b. NaBr

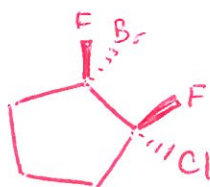
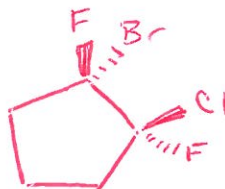
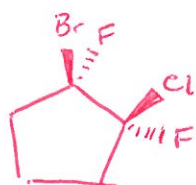
c. NaCl



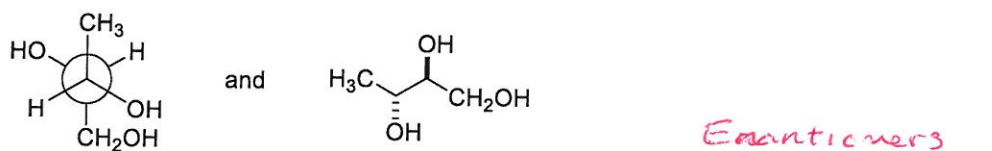
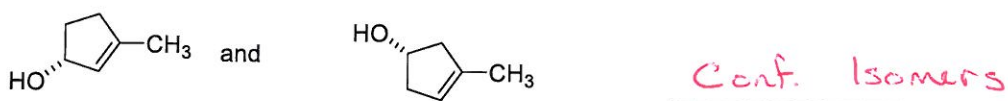
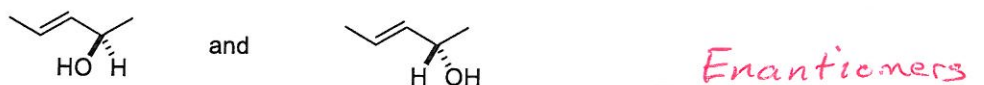
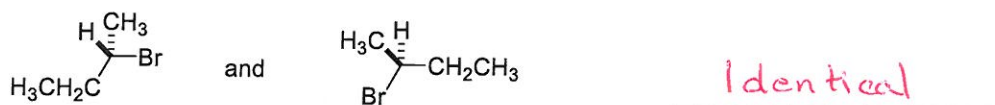
8. (10 pts) Draw the structure(s) of the major product(s) of each reaction. Be sure to include stereochemistry when appropriate. Circle the mechanism that accounts for the formation of this product:



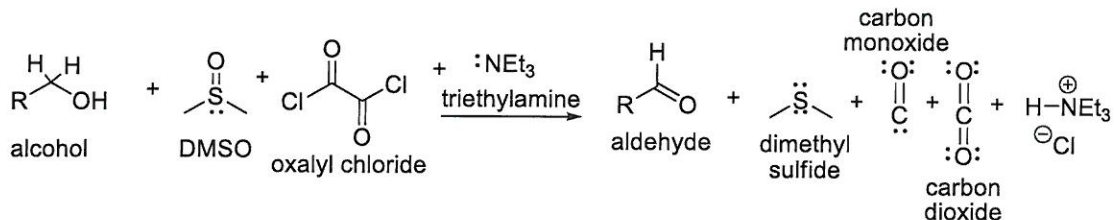
9. (10 pts) Draw every stereoisomer for 1-bromo-2-chloro-1,2-difluorocyclopentane. Use wedge-and-dash bonds for the substituent groups, and be sure that they are drawn on the outside of the ring, adjacent to each other.



10. (10 pts) Identify the relationship between the following pairs. Are they identical, constitutional isomers, enantiomers, or diastereomers?



11. (9 pts) The *Swern oxidation*, shown below is a very mild procedure for oxidizing primary and secondary alcohols.



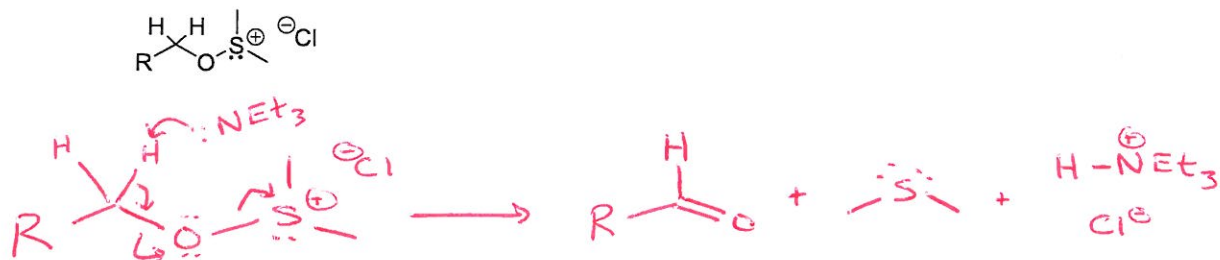
(a) How many electrons are involved in this oxidation from the alcohol to the aldehyde? Explain.

Alcohol to Aldehyde oxidation is a $2e^-$ oxidation.
Carbon goes from -1 to $+1$ oxidation state.

(b) What is the oxidizing agent?

DMSO, the sulfur goes from oxidation state of $+2$ to 0 .

(c) The following compound is a key intermediate in this oxidation. Give a curved-arrow mechanism for the reaction of this intermediate with triethylamine as the base to give the product aldehyde (RCHO).



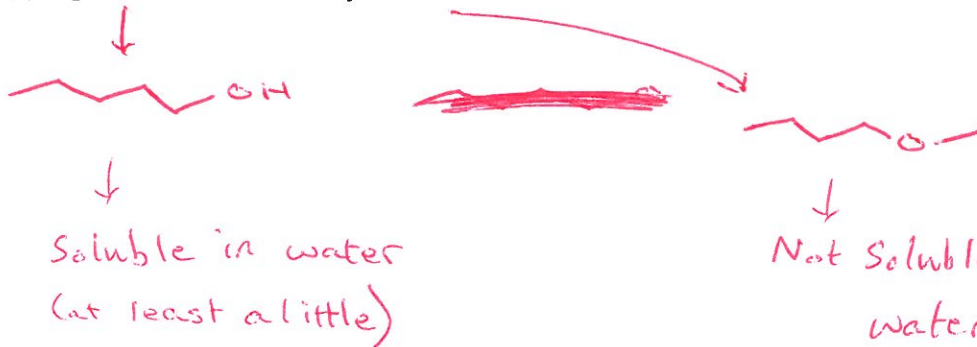
12. (16 pts) Explain how you could differentiate between the compounds in each of the following pairs by using simple physical or chemical tests that give readily observable results, such as obvious solubility differences, color changes, evolution of gases, or formation of precipitates.

(a) 3-ethoxypropene and 1-ethoxypropane



Br_2 will react with
alkene, color goes
from Brown to Clear.

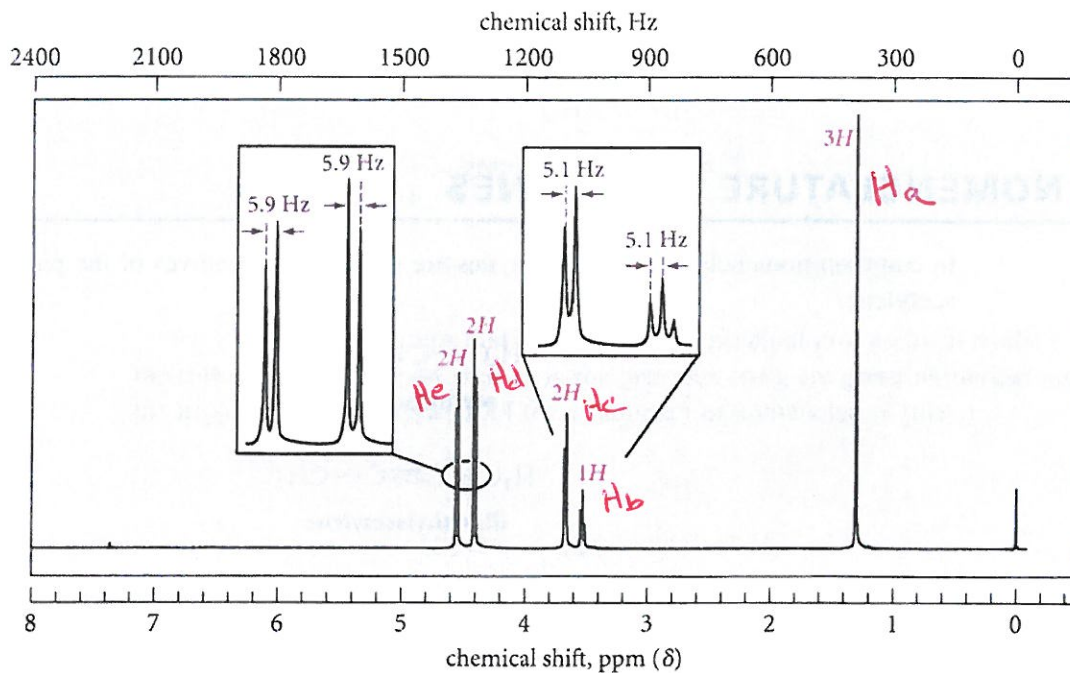
(b) 1-pentanol and 1-methoxybutane



Soluble in water
(at least a little)

Not Soluble in
water

13. (10 pts) A compound X with the molecular formula $C_5H_{10}O_2$ has an IR spectrum with strong absorption in the $1000-1100\text{ cm}^{-1}$ region; very strong, broad absorption in the $3000-3600\text{ cm}^{-1}$ region; and no absorption in the $1600-1700\text{ cm}^{-1}$ region. The proton NMR spectrum of X is given below. When the sample is shaken with D_2O , the triplet at $\delta 3.5$ disappears the doublet at $\delta 3.7$ becomes a singlet. Propose a structure for this compound, and explain your reasoning.



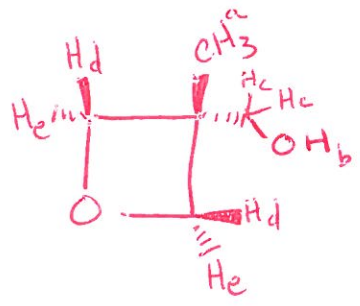
(IR)

$1600-1100\text{ cm}^{-1} = C-O$
 $3000-3600\text{ cm}^{-1} = O-H$
 No $1600-1700\text{ cm}^{-1} = \text{No } C=O$

$$n = [5(2) + 2 - 10] / 2$$

$$= [12 - 10] / 2$$

$n = 1$





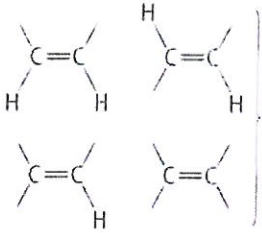
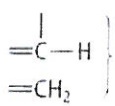

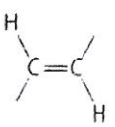
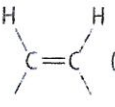
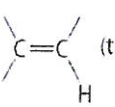
Hydrogen 1 1.008																	Helium 2 4.002																						
Lithium 3 6.941	Beryllium 4 9.012											Boron 5 10.811	Carbon 6 12.011	Nitrogen 7 14.007	Oxygen 8 15.999	Fluorine 9 18.998	Neon 10 20.180																						
Sodium 11 22.990	Magnesium 12 24.305											Aluminum 13 26.982	Silicon 14 28.086	Phosphorus 15 30.974	Sulfur 16 32.065	Chlorine 17 35.453	Argon 18 39.948																						
Potassium 19 39.098	Calcium 20 40.078	Scandium 21 44.956	Titanium 22 47.887	Vanadium 23 50.942	Chromium 24 51.996	Manganese 25 54.938	Iron 26 55.845	Cobalt 27 58.933	Nickel 28 58.693	Copper 29 63.546	Zinc 30 65.38	Gallium 31 69.723	Germanium 32 72.631	Arsenic 33 74.922	Selenium 34 78.96	Bromine 35 79.904	Krypton 36 83.8																						
Rubidium 37 85.468	Strontium 38 87.62	Yttrium 39 88.906	Zirconium 40 91.224	Niobium 41 92.906	Molybdenum 42 95.94	Technetium 43 [98]	Ruthenium 44 101.07	Rhodium 45 102.91	Palladium 46 106.32	Silver 47 107.87	Cadmium 48 112.41	Indium 49 114.82	Tin 50 118.71	Antimony 51 121.76	Tellurium 52 127.6	Iodine 53 126.905	Xenon 54 131.29																						
Cesium 55 132.91	Barium 56 137.33	* 57-70	Lanthanum 57 138.91	Hafnium 72 178.49	Tantalum 73 180.95	Tungsten 74 183.84	Rhenium 75 186.21	Osmium 76 190.23	Iridium 77 192.22	Platinum 78 195.08	Gold 79 196.97	Mercury 80 200.59	Thallium 81 204.38	Lead 82 207.2	Bismuth 83 208.98	Poisonium 84 [209]	Astatine 85 [210]	Radon 86 [222]																					
Francium 87 [223]	Radium 88 [226]	* * 89-102	Actinium 89 [227]	Rutherfordium 104 [261]	Dubnium 105 [262]	Seaborgium 106 [263]	Berkelium 107 [264]	Californium 108 [265]	Einsteinium 109 [266]	Mendelevium 110 [267]	Nobelium 111 [268]	Lutetium 112 [269]																											
												Uranium 92 238.03	Niobium 41 92.906	Plutonium 94 244.06	Uranium 92 238.03	Neptunium 93 237.05	Plutonium 94 244.06	Americium 95 [243]	Curium 96 [247]	Berkelium 97 [247]	Californium 98 [251]	Einsteinium 99 [252]	Mendelevium 101 [258]	Nobelium 102 [259]	Lutetium 63 174.967	Ytterbium 64 173.054	Lanthanum 57 138.905	Cerium 58 140.12	Praseodymium 59 140.908	Neodymium 60 144.24	Europium 62 151.964	Gadolinium 63 157.25	Terbium 64 158.925	Dysprosium 65 162.50	Hoium 67 164.930	Erbium 68 167.259	Thulium 69 168.930	Ytterbium 70 173.054	Lutetium 71 174.967

Group	Chemical shift, ppm	Group	Chemical shift, ppm
	0.7-1.5		9-11
	4.6-5.7		7.5-9.5
	varies with solvent and with acidity of O—H		0.5-1.5
	1.7-2.5		2.5-3.5
	6.5-8.5		

TABLE 12.1 Regions of the Infrared Spectrum

Wavenumber range, cm ⁻¹	Type of absorptions	Name of region
3400-2800	O—H, N—H, C—H stretching	Functional group
2250-2100	C≡N, C≡C stretching	
1850-1600	C=O, C=N, C=C stretching	
1600-1000	C—C, C—O, C—N stretching; various bending absorptions	Fingerprint
1000-600	C—H bending	C—H bending

TABLE 12.2 Important Infrared Absorptions of Alkenes

Functional group	Absorption*
 C=C stretching absorptions	
$-\text{CH}=\text{CH}_2$ (terminal vinyl)	1640 cm^{-1} (m, sh)
 $\text{C}=\text{CH}_2$ (terminal methylene)	1655 cm^{-1} (m, sh)
	$1660\text{--}1675\text{ cm}^{-1}$ (w) (absent in some compounds)
=C—H stretching absorptions	
	$3000\text{--}3100\text{ cm}^{-1}$ (m)
=C—H bending absorptions	
$-\text{CH}=\text{CH}_2$ (terminal vinyl)	$910, 990\text{ cm}^{-1}$ (s) two absorptions
 $\text{C}=\text{CH}_2$ (terminal methylene)	890 cm^{-1} (s)
 (<i>trans</i> -alkene)	$960\text{--}980\text{ cm}^{-1}$ (s)
 (<i>cis</i> -alkene)	$675\text{--}730\text{ cm}^{-1}$ (br) (ambiguous and variable for different compounds)
 (trisubstituted)	$800\text{--}840\text{ cm}^{-1}$ (s)

*Intensity designations: s = strong; m = moderate; w = weak
 Shape designations: sh = sharp (narrow); br = broad (wide)