Columbia University C99ORG12.DOC S3443D Summer 99
Professor Grace B. Borowitz Exam No. 2 June 14, 1999

Name: ***Sterie O'Chemistry*** *Grade:* _____

Please use a **non-red** pen. Answer questions in the provided space. If you write any answers on the back of the page, indicate this on the **front** of that page. Points appear in parentheses **( )**. ***Good Luck!***

Question	Points	Max. Points	Points Earned
1. (4 + 3) (6 + 3 + 4)	=	20	
2. 4 + (5 + 5) (3 + 3)	=	20	
3. (3 + 3 + 3) + 3	=	15	
4. 4 + 3 + (6 + 4 + 3)	=	20	
5. (3 + 3) + 4 + (3 + 3)+ 4	=	20	
6. 3 + 2	=	5	
Total	=	**100**	

1. **(20)** a. (1) Define enantiomers and give an original example (one not given in this exam) of a pair of enantiomers. ***Enantiomers:*** **Stereoisomers that are non-superimposable mirror images.**
Stereoisomers: Molecules with same molecular formula, same sequence or connectivity of atoms, but different arrangements in space.

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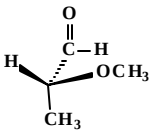
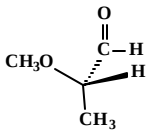




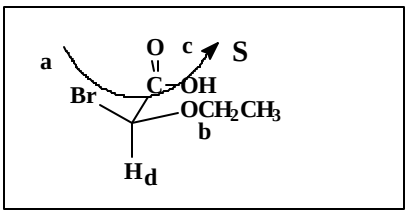
(2) Compare the properties of a pair of enantiomers with a pair of diastereomers.

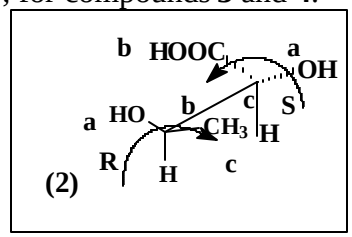
Enantiomers: **Enantiomers have similar physical properties except for the direction of rotation of the plane of polarized light. They might also react at a different rate with a particular enantiomer. They are difficult to separate physically as a racemic mixture. They require resolution or conversion to diastereomers before they can be separated.**

Diastereomers: **Diastereomers have different physical properties and may be easily separated by such means as recrystallization, chromatography (hplc, column, tlc, gc), and fractional distillation.**

3

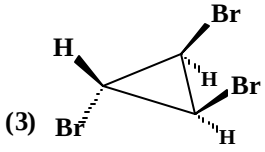
b. Which of the molecules below is/are chiral? Note that more than one answer is possible. For compounds **1** and **2,** determine the ***(R)*** or ***(S)*** chirality if any of the C_2 in compound **1** and of the C_2 and C_3 of compound **2**. Show how you determined your ***(R)*** or ***(S)*** chirality assignments using the Cahn-Ingold-Prelog Sequence rules. Name compound **(2)** by IUPAC nomenclature including the chirality of C-2 and C-3. Draw an enantiomer or enantiomers, if any, for compounds **3** and **4**.



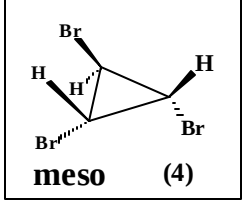


6 + 3

Name: (2S,3R)-dihydroxybutanoic acid



meso



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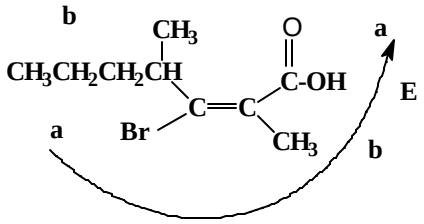
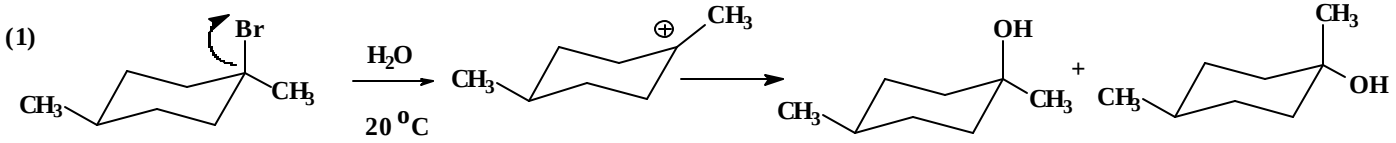
2. **(20)** a. Give the full IUPAC name of this compound including ***(E,Z)*** designation. Show how you arrived at your ***(E,Z)*** determination.

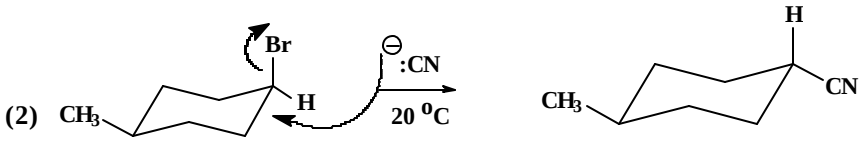


4 ***(E)*-3-bromo-2,4-dimethyl-2-heptenoic acid**

b. Show the structure(s) of be the major product(s) of the reactions shown? Show the mechanism by which you arrive at the product(s).



5 **S_N1**



5 **S_N2**

c. Label and show the energy profiles for these reactions. Label x and y axes with their appropriate designations. Locate the reactants and products and any transition states or intermediates formed. Note the energy of activation, $\mathbf{E_A}$ for the rate-determining step and the overall -D**H** (exothermic) for the reaction.

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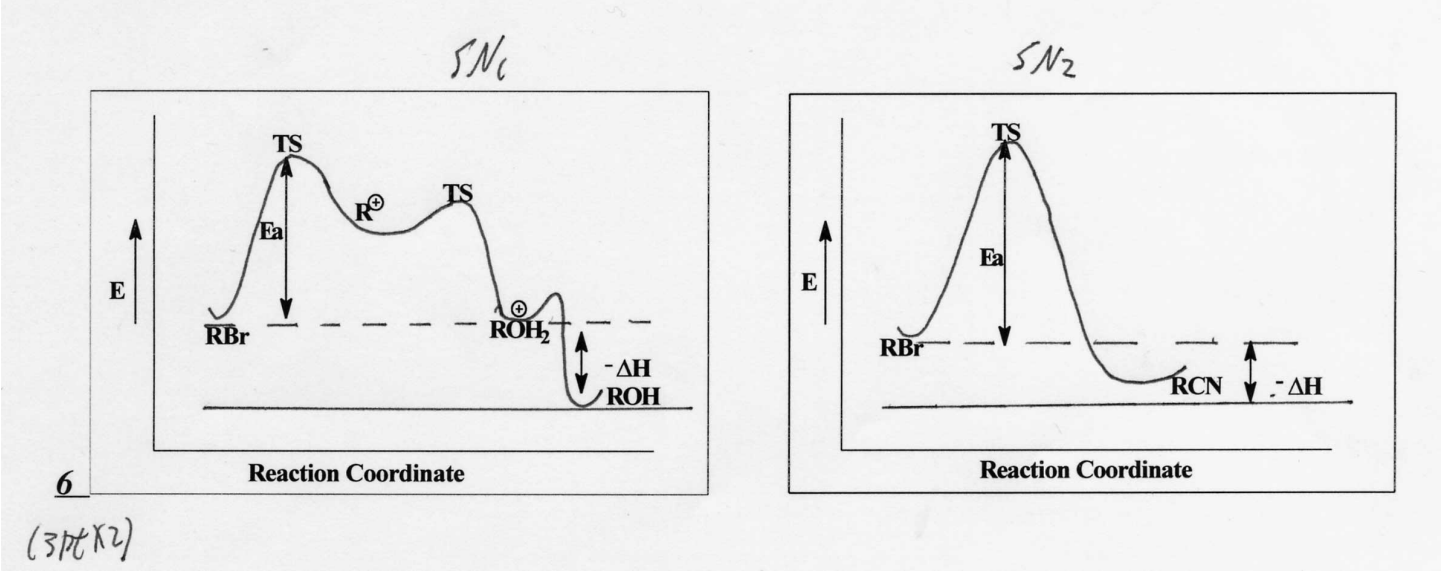
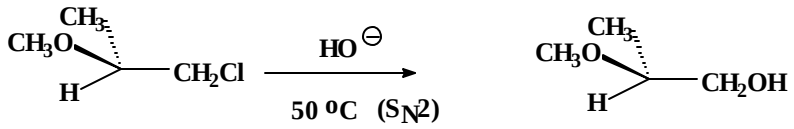

SN1
TS
Ea
R⊕
TS
E
RBr
ROH2⊕
-ΔH
ROH
Reaction Coordinate
SN2
TS
Ea
E
RBr
RCN
-ΔH
Reaction Coordinate

6

(3pt x2)

3. **(15)** a. Fill in the structure for the major product of the following reactions.

(1)



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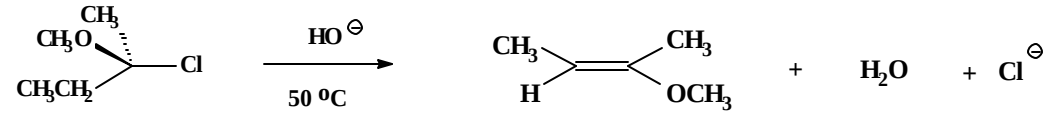
(2)



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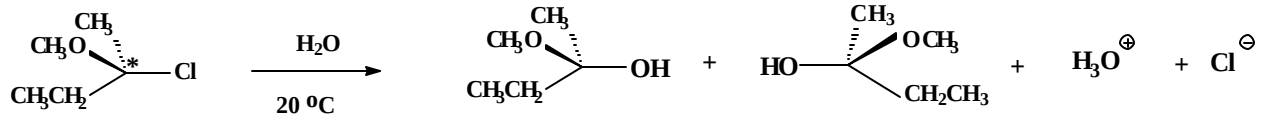
(3)



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b Which of the reactions in **3a** could safely be used to relate configuration. Briefly, why?

3. (1) This reaction proceeds with retention, so it is reliable and predictable.

3

c. Which ion is the strongest nucleophile in an aprotic solvent such as dimethylsulfoxide?

(1) $\mathbf{I^-}$ (2) $\mathbf{Br^-}$ (3) $\mathbf{Cl^-}$ * (4) $\mathbf{F^-}$ (5) These are all equal.

3

4. **(20)** a. Which of the following **is not/are not** good leaving group(s)?

4

b. Increasing the temperature of a chemical reaction usually greatly increases the rate of the reaction. The **most important** reason for this is that increasing the temperature markedly increases :

(1) the probability, orientation or entropy of activation factor.
(2) the collision frequency.
* (3) the fraction of collisions with energy greater than or equal to E_a
(4) the energy of activation.
(5) the amount of heat released in the reaction.

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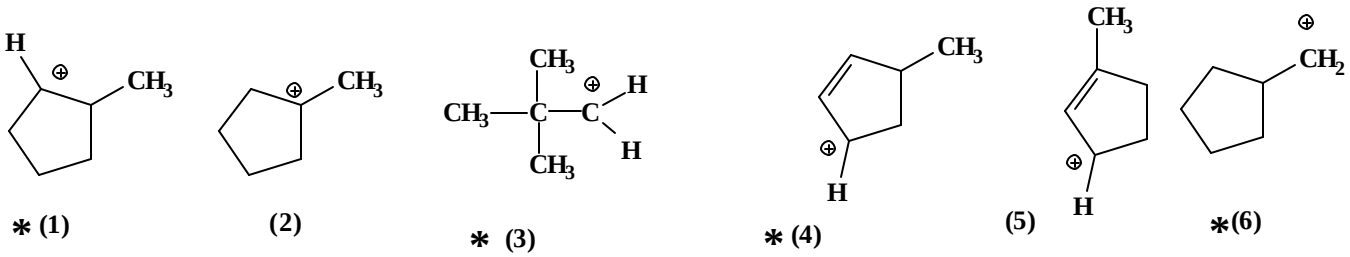
c. (1) Check all of the following carbocations that are quite likely to rearrange to a more stable carbocation intermediate in just one step?



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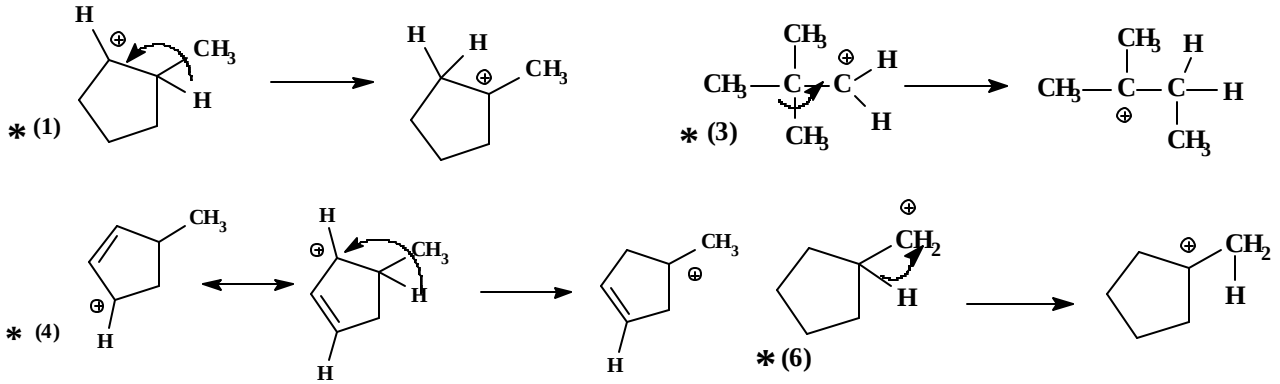
(2) Show the mechanism for **one** such rearrangement and the structure of the rearranged carbocation.



Note: The allylic C^+ and the 3^oC^+ forms in (5) are comparable in stability and would both exist as resonance forms-not a rearrangement.

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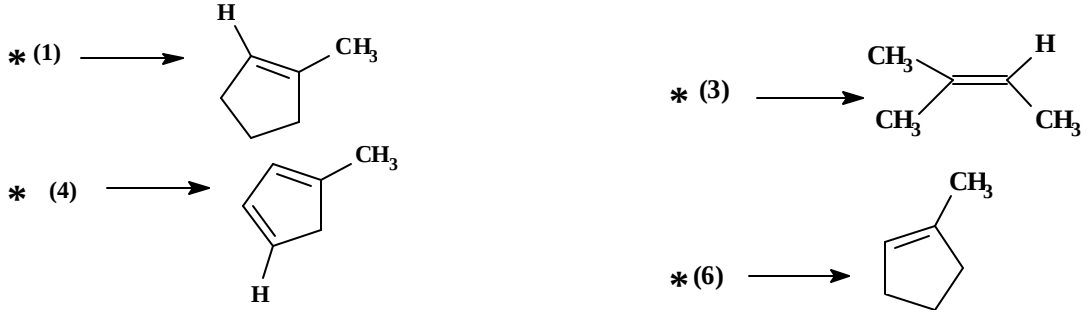
(3) Give the structure of the predominant alkene resulting by loss of a H^+ after that rearrangement.



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5. **(20)** a. S_N2 reactions of the type, **Nu:**^{¾} + **R-L** ⟶ **Nu-R** + **:L**^{¾} , are favored: (Choose all that apply).

(1) by high heating .
(2) by using a solvent of high polarity.
* (3) by using a high concentration of the nucleophile.
(4) by the use of tertiary substrates.
* (5) by the use of primary substrates.

3

Briefly, why?
Because the TS contains both nucleophile and alkyl halide, the rate of the reaction is 2nd order. Rate = k_2[Nu: $^-$] [R-L]. Thus rate is proportional to the concentration of nucleophile. Also, a primary substrate presents less steric hindrance to rear attack.

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b. Which alkyl halide would you expect to undergo S_N1 hydrolysis most rapidly?

(1) **$(CH_3)_3C$-F** (2) **$(CH_3)_3C$-Br** * (3) **$(CH_3)_3C$-I** (4) **$(CH_3)_3C$-Cl**
Briefly, why?

The C-I bond is easiest to break, because it is the weakest. I^- is the best leaving group because it is the weakest base (most stable anion) upon leaving.

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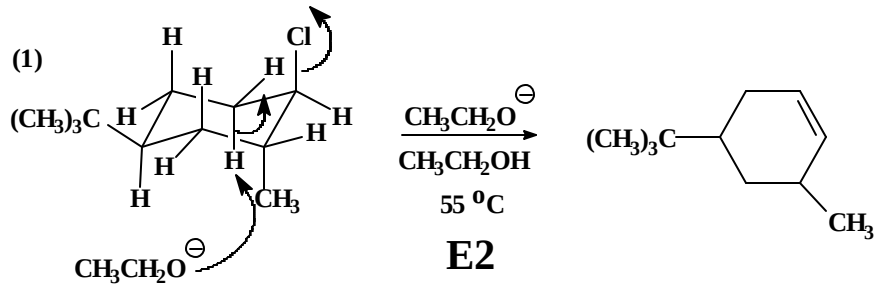
c. What would be the major product of each of the following reactions? Name and show the mechanism by which the major product is formed.



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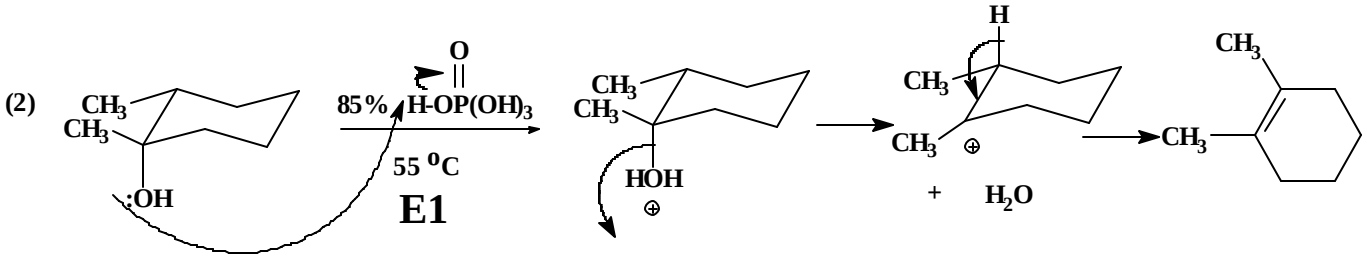

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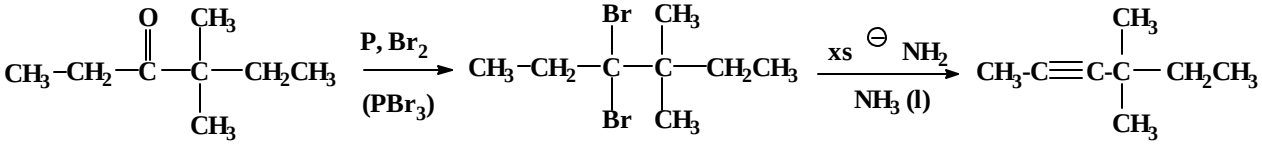
d. Fill in the missing reactants, reagents, intermediates, and products in the following synthesis. Show the proper stereochemistry.



6. **(05)** a. Which halide can give only one product from elimination of HBr with sodium ethoxide in ethanol?

(1) 2-bromo-4,4-dimethylpentane *** (3) 2-bromo-3,3-dimethylpentane**

(2) 3-bromo-2-methylhexane **(4) 3-bromo-2,2-dimethylpentane**

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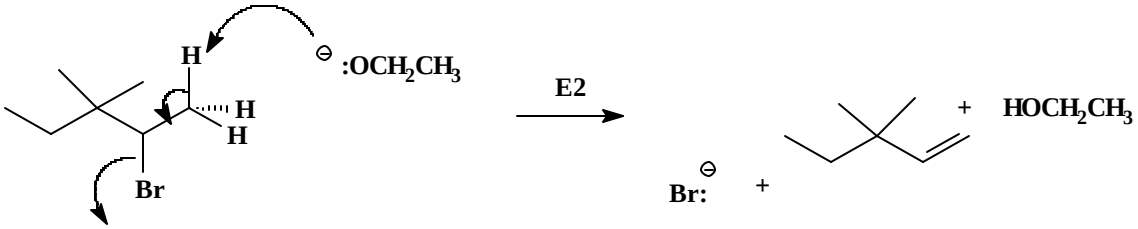
b. Using arrows to indicate the direction of electron flow, show and name the mechanism for the above reaction and give the structure of the product.



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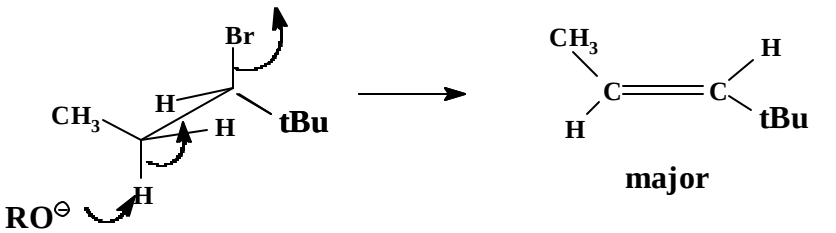
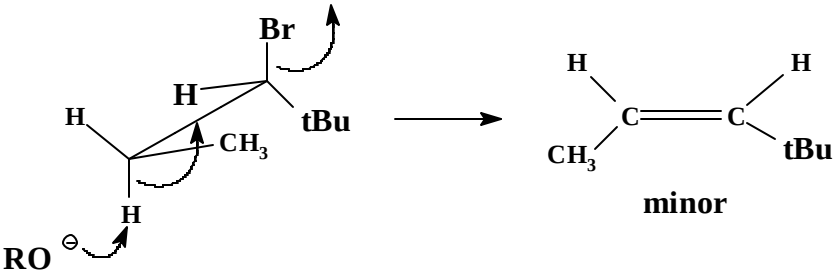
NOTE: Number (4) above gives a mixture of ***trans***- (major) and ***cis***-(minor) 4,4-dimethyl-2-pentene by antiperiplanar (E_2) elimination of HBr.





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