2310 Fall 2012 E2

I. Theory

1. Provide an equation, which shows how Gibb's free energy, enthalpy and entropy are related. (3 points)

$$\Delta G = \Delta H - T\Delta S$$

2. Provide an energy diagram for a reaction that proceeds through an E1 mechanism. Be sure to correctly label each axis. (4 points)

3. (Circle the correct answers) ((Homolytic) / Heterolytic) bond cleavage leads to radical intermediates and is always an (endothermic) exothermic) process. (4 points)

4. Provide a rate equation for the following reaction. (3 points)

$$\text{Rate} = k_r[\text{3° R-Br}][NaOCH_3]$$

$\Delta G = (-)$ favorable

5. If ΔG of a reaction is equal to a negative value then which of the following must also be true? (2 points)

$0 < K_{eq} < 1$

a) $\Delta S < 0$ (b) $K_{eq} > 1$ c) $\Delta H < 0$ d) $\Delta S > 0$ e) ~~$K_{eq} < 0$~~

6. For the chlorination of methane, which diagram most closely resembles the transition state of the rate determining step? (2 points)

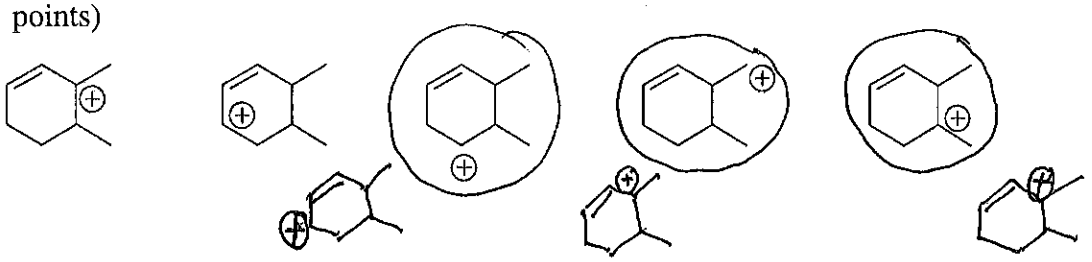
True for other HC's besides methane

a) $[H_3C\text{-}H\text{-----}Cl]^{\ddagger\bullet}$ b) $[H_3C\text{---}Cl\text{--}Cl]^{\ddagger\bullet}$ c) $[H_3C\text{-}Cl\text{----}Cl]^{\ddagger\bullet}$ (d) $[H_3C\text{----}H\text{--}Cl]^{\ddagger\bullet}$

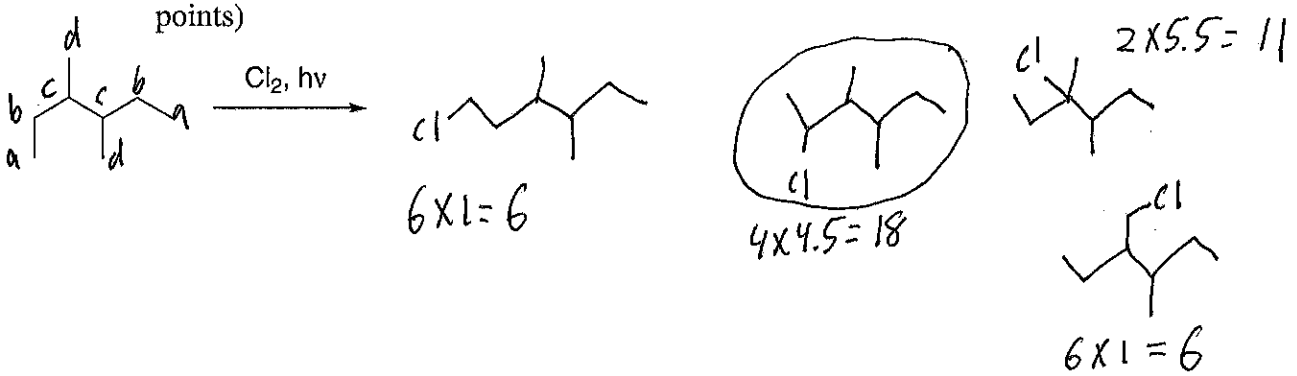
PI: $Cl^\bullet + H\text{-}CH_3 \rightarrow H\text{-}Cl + {}^\bullet CH_3$ RDS

PII: ${}^\bullet CH_3 + Cl\text{-}Cl \rightarrow CH_3Cl + Cl^\bullet$

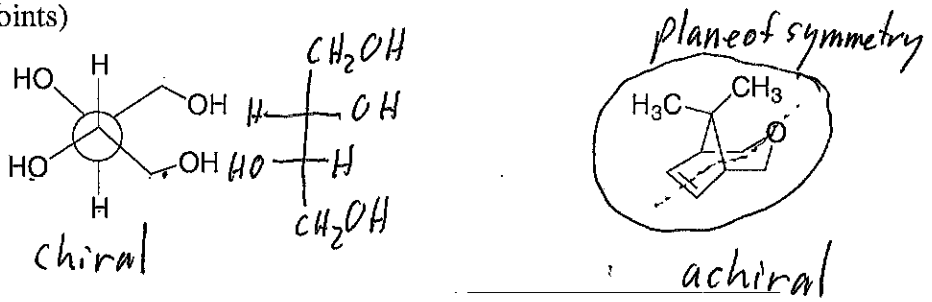
7. Circle all cations that would be expected to undergo a structural rearrangement. (4 points)



8. Draw structures for all monochlorination products resulting from the reaction below. Circle the major product and show all of your work for full credit. (10 points)



9. Label each structure below as being chiral or achiral. Circle any meso structures. (6 points)



10. A Racemic mixture is one that contains chiral compounds but overall is optically inactive. (2 points)

11. Glucose has a specific rotation of +52.8°. If 25.0 g of glucose is dissolved in 150 mL of water and a portion of this solution is placed in a 15 cm long sample cell, what would be the observed optical rotation of this solution? Show all of your work for full credit. (4 points)

$[\alpha]_D = +52.8^\circ$

$c = 25.0g/150mL$

$l = 1.5\ dm$

$\alpha = ?$

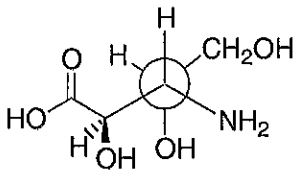
$[\alpha]_D = \frac{\alpha}{c \times l}$

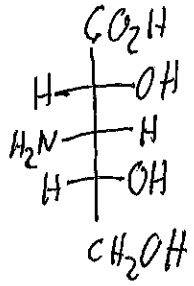
$+52.8^\circ = \frac{\alpha}{\left(\frac{25g}{150mL}\right)(1.5\ dm)}$

$\alpha = \left(+52.8^\circ\right)\left(\frac{25g}{150mL}\right)(1.5\ dm)$

$\alpha = +13.2^\circ$

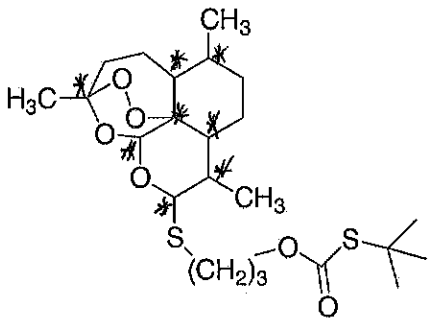
12. Translate the structure below to a Fischer projection. (5 points)





13. Draw (2*S*, 3*R*) 2-bromo-3-methoxypentane in a wedge-dash perspective structure. (4 points)

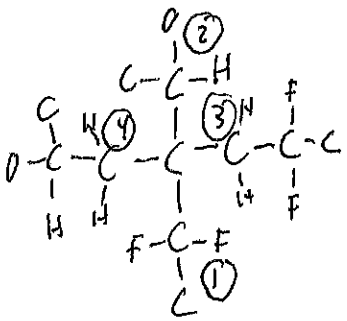
14. A stereoisomer of the following compound is a potent antimalarial agent derived from the natural product artemisinin (*J. Med. Chem.* **2012**, 7892). How many chiral centers are present in this compound? (3 points)



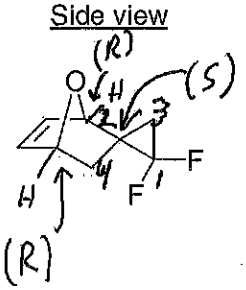
8 chiral centers

$2^8 = 256$ stereoisomers

15. The synthesis of the following compound was recently reported in the literature (*Tet. Lett.* **2012**, 5784). The two structures drawn are different views of the same compound. Label all chiral centers as having *R* or *S* configuration. (6 points)



Side view



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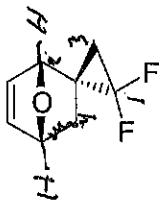
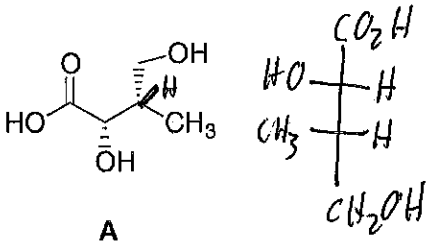
Top view

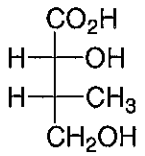


16. State the relationship between structure **A** and structure **B** as being same compound, enantiomer, diastereomer or constitutional isomers. Show all of your work for full credit. (3 points)



A

enantiomers



B

17. Circle all statements that are true of diastereomers. (3 points)

a) They have different boiling points.
b) They rotate plane polarized light to the same magnitude.
c) They must contain at least one chiral center.
d) A chiral probe is needed to separate diastereomers.

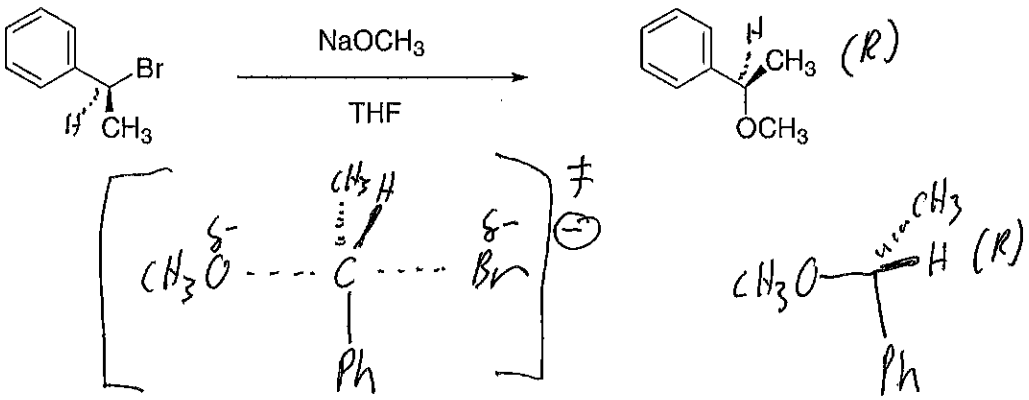
18. Trichloromethane is commonly known as chloroform. (2 points)

19. Circle all statements that describe favorable attributes of a leaving group. (3 points)

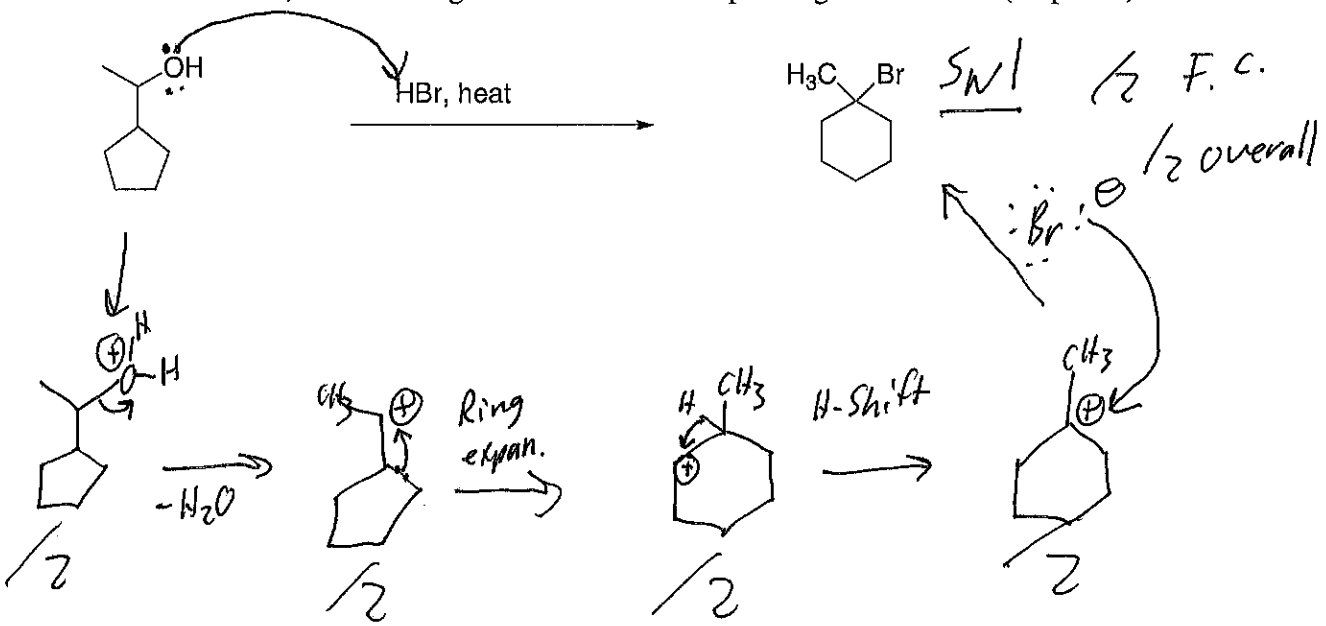
a) The leaving group should be highly polarizable
b) The lower the electronegativity of the leaving group the better.
c) Good leaving groups need to have low steric hindrance.
d) The departed leaving group should have low basicity.

II. Mechanisms

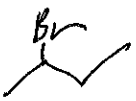
1. Provide a structure of the transition state for the following reaction. (4 points)



2. Provide a step-by-step mechanism for the reaction below. Include all intermediates, formal charges and correct arrow pushing of electrons. (12 points)



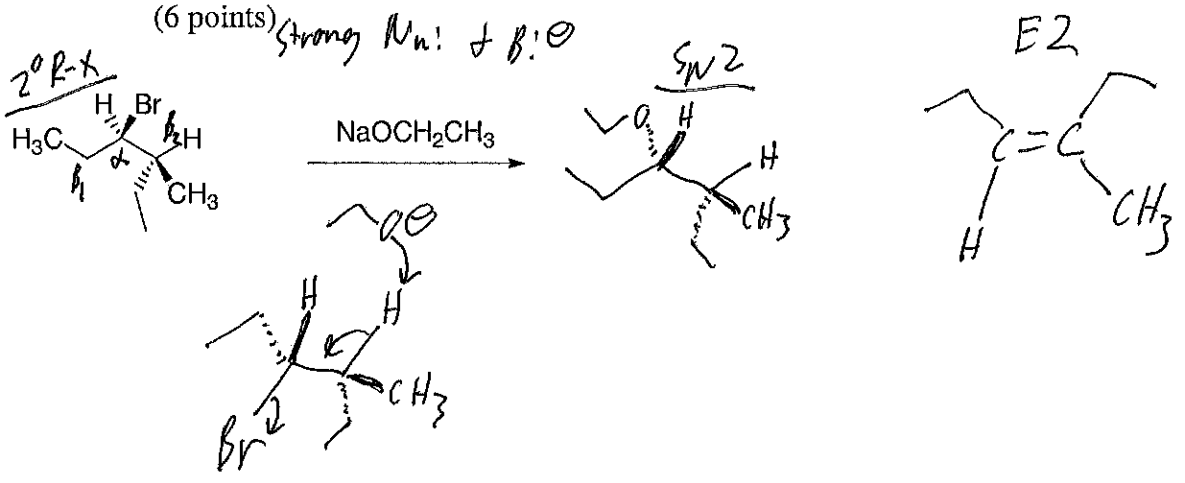
III. Reactions



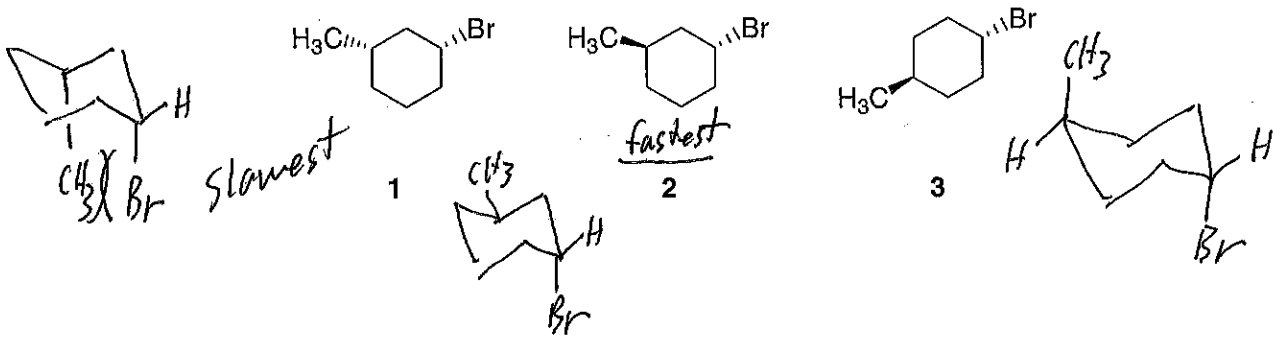
1. Which of the following bases will give the best yield of E1 products when reacted with 2-bromobutane? (2 points)

a) t-butyl alcohol b) CH_3CH_2SNa c) lithium diisopropyl amide (LDA) d) methanol

2. Provide structures for the major substitution and the major elimination product. (6 points)



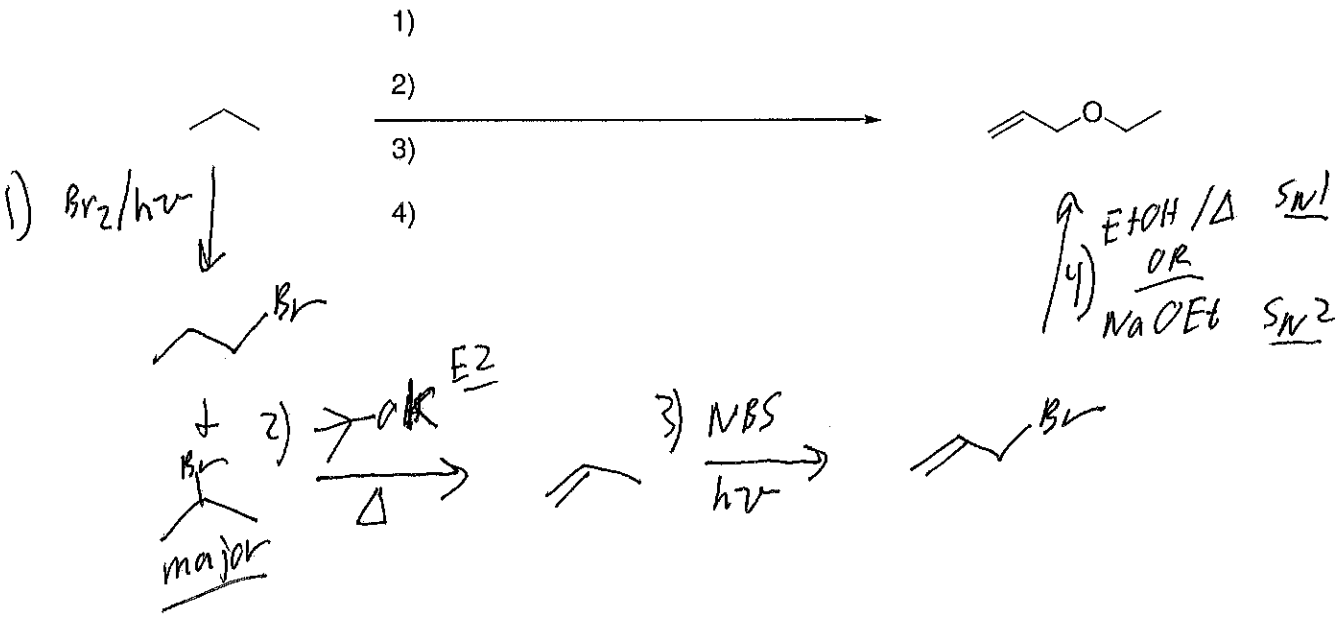
3. Which sequence ranks the following electrophiles in order of increasing rate of E2 elimination? (3 points)



a) 1<2<3 b) 2<3<1 c) 3<1<2 d) 3<2<1 e) 2<1<3 f) 1<3<2

IV. **Extra Credit** (5 points)

1. Complete the following reaction by filling in the missing reagents.



You received _____ points out of 100 points possible. To check your overall performance in lecture see http://canvas.weber.edu .