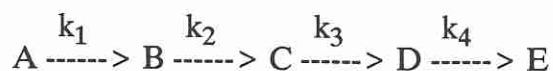


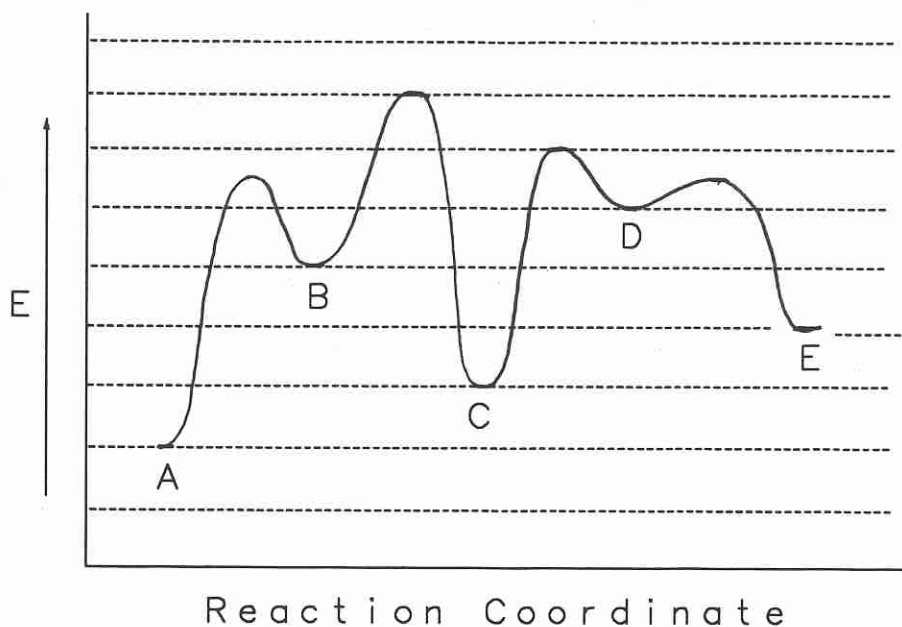
Organic Chemistry I, Exam 2, CH 3604/3703
October 25, 1989, 100 points

Name _____ ID# _____

1. (9 points) Consider the hypothetical reaction:



where the k 's are the rate constants for each mechanistic step of the reaction of $A \rightarrow E$. The reaction's energy profile is:



a. Which compound A B C D E (circle) is the least thermodynamically stable compound?

b. What is the correct order of magnitude for the rate constants?

- A) $k_2 > k_3 > k_1 > k_4$
- B) $k_4 > k_2 > k_3 > k_1$
- C) $k_2 > k_3 > k_1 = k_4$
- D) $k_1 > k_3 > k_2 > k_4$
- E) $k_4 > k_1 > k_3 > k_2$
- F) $k_4 = k_1 > k_3 > k_2$

2. (6 points) Calculate the equilibrium constant for a reaction that has a $\Delta H^\circ = -10 \text{ kcal mole}^{-1}$ and $\Delta S^\circ = -22 \text{ e.u.}$ at a temperature of 227°C . Place your final answer in the box provided (you must show your work to get credit)

3. (7 points) Calculate ΔH° for the reaction of hydrogen with 2-methylpropane to give methane and propane. Place your answer in the box provided. (no work no credit).

4. (9 points) In the box provided, give the major product from the monobromination of propane. Write equations showing the initiation, propagation, and termination steps. Compute the overall ΔH° of the reaction and place that in the box as well (no work no credit).

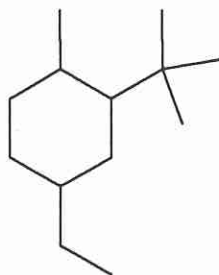
Initiation:

Propagation:

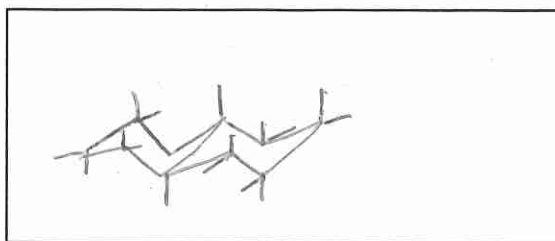
Termination:

5. (9 points) In the monobromination of 2-methylpropane, one major product is formed. Only trace amounts of a second monobrominated product is observed. In the box provided give the major product (2 points). Concisely explain, with an appropriate theory, why this product is preferred (7 points).

6. (5 points) In the box provided, give the IUPAC name for the following compound:



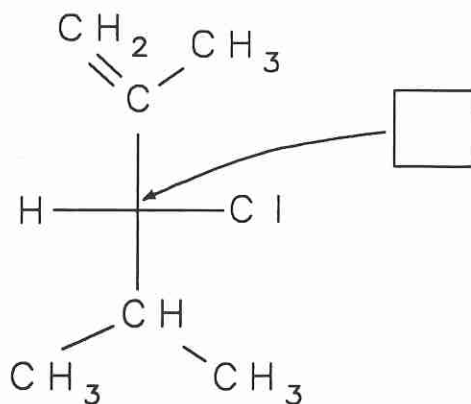
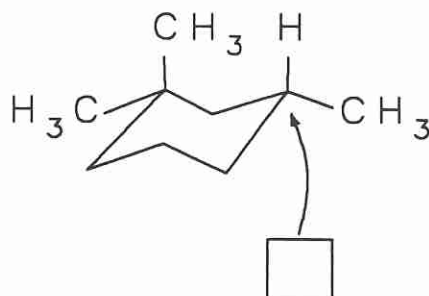
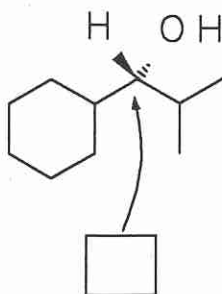
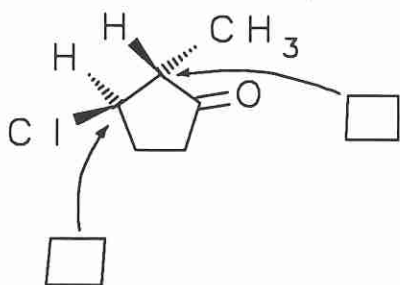
7. (5 points) In the box provided, draw *cis*-decalin (two fused 6-membered saturated rings) in chair form. Include the hydrogens connected to both rings



8. (10 points) Calculate the percentage of molecules having the substituent in the equatorial position for flourocyclohexane at 25 °C. Place your final answer in the box provided. You must show your work to get credit.

9. (7 points) Calculate the specific rotation of a solution containing 0.69g of 2-bromooctane in 10 mL of ether having an observed α of -1.80° in a 5 cm cell. Place your final answer in the box provided.

10. (10 points) For each of the following compounds, assign R or S to each indicated stereocenter.

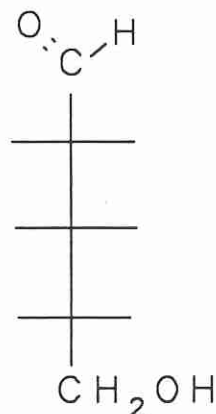
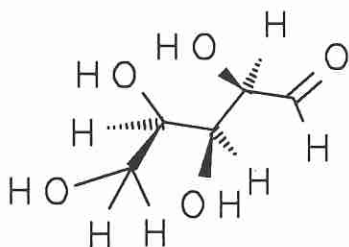


11. (6 points) Consider the free radical chlorination of (S)-2-fluorobutane. The monochlorination fraction of the reaction product contains 1% 1-chloro-2-fluorobutane. What is the absolute configuration of this material R or S (circle)

12. (8 points) When (+)-1-bromo-1-fluoropropane was treated with Cl_2 and light, 1-bromo-1-chloro-1-fluoropropane and 1-bromo-2-chloro-1-fluoropropane were isolated. These two compounds were separated from one another and the $[\alpha]_D^{25^\circ\text{C}}$ was determined. Which of the following statements is/are true? (more than one could be true)

- A. The $[\alpha]_D^{25^\circ\text{C}}$ of the 1-bromo-1-chloro-1-fluoropropane was not = 0.
- B. The $[\alpha]_D^{25^\circ\text{C}}$ of the 1-bromo-2-chloro-1-fluoropropane was not = 0.
- C. A pair of enantiomers are present in the 1-bromo-2-chloro-1-fluoropropane
- D. The 1-bromo-1-chloro-1-fluoropropane that is generated contains only one enantiomer.

13. (9 points) Xylose is a common sugar found in many woods such as maple and cherry. Because it is less prone to cause tooth decay than common sugar (sucrose), xylose has been used in candy and chewing gum. Complete the Fischer projection for xylose.



$$\Delta G^\circ = -RT \ln K = -2.303 RT \log K \text{ (in kcal mole}^{-1}\text{)}$$

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

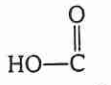
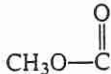
$$k = Ae^{-E_a/RT}$$

R is the gas constant (1.986 cal deg⁻¹ mole⁻¹)

$$\Delta G^\circ = -1.36 \log K \text{ (in kcal mole}^{-1}\text{)}$$

$$\left(\begin{array}{c} \text{Sum of strengths} \\ \text{of bonds broken} \end{array} \right) - \left(\begin{array}{c} \text{Sum of strengths} \\ \text{of bonds formed} \end{array} \right) = \Delta H^\circ$$

Free-energy differences between axial and equatorial cyclohexane conformers (in all examples, the equatorial form is more stable)

Substituent	ΔG° (kcal mole ⁻¹)	Substituent	ΔG° (kcal mole ⁻¹)
H	0	F	0.25
CH ₃	1.70	Cl	0.52
CH ₃ CH ₂	1.75	Br	0.55
(CH ₃) ₂ CH	2.20	I	0.46
(CH ₃) ₃ C	≈5	HO	0.94
	1.41	CH ₃ O	0.75
	1.29	H ₂ N	1.4

Bond-dissociation energies of some A-B bonds (DH° in kcal mole⁻¹)

A	B						
	H	F	Cl	Br	I	OH	NH ₂
H		135	103	87	71	119	107
CH ₃		110	85	71	57	93	80
CH ₃ CH ₂		107	80	68	53	92	77
CH ₃ CH ₂ CH ₂	98	107	81	68	53	91	78
(CH ₃) ₂ CH	94.5	106	81	68	53	92	93
(CH ₃) ₃ C	93	110	81	67	52	93	93

Bond-dissociation energies for some alkanes

Compound	DH° (kcal mole ⁻¹)	Compound	DH° (kcal mole ⁻¹)
CH ₃ -H	105	CH ₃ -CH ₃	90
C ₂ H ₅ -H	98	C ₂ H ₅ -CH ₃	86
C ₃ H ₇ -H	98	C ₃ H ₇ -CH ₃	87
(CH ₃) ₂ CHCH ₂ -H	98	C ₂ H ₅ -C ₂ H ₅	82
(CH ₃) ₂ CH-CH ₃	94.5	(CH ₃) ₂ CH-CH ₃	86
(CH ₃) ₃ C-H	93	(CH ₃) ₃ C-CH ₃	84
		(CH ₃) ₃ C-C(CH ₃) ₃	72

DH° (X ₂) in kcal mole ⁻¹	F ₂	Cl ₂	Br ₂	I ₂
	37	58	46	36

$$\ln k = \ln (Ae^{-E_a/RT})$$

Heats of formation of selected atoms and molecules (kcal mole⁻¹ normalized to 25°C)

Structure (state)	ΔH_f°	Structure (state)	ΔH_f°
(CH ₃) ₃ CH (gas)	-32.4	(CH ₃) ₃ CH ₃ (gas)	-35.1
CH ₃ (CH ₂) ₃ CH ₃ (gas)	-41.4	CH ₃ (CH ₂) ₃ CH ₃ (liquid)	0
H ₂ , O ₂ , N ₂ (gases)	52.1	H (atom)	59.6
O (atom)	171.3	C (atom)	12.5
CH ₂ =CH ₂ (gas)	54.2	HC≡CH (gas)	

$$\left\{ \alpha \right\}_\lambda^+ = \frac{\alpha}{2c}$$