

Name: Stereo Olchemistry

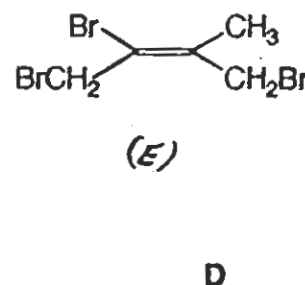
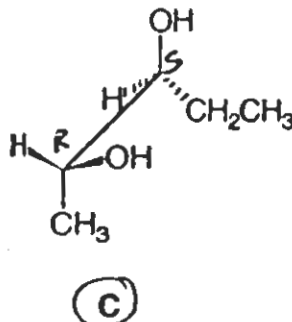
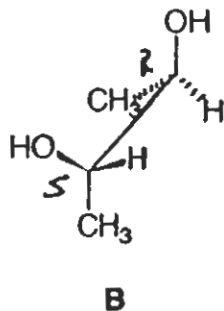
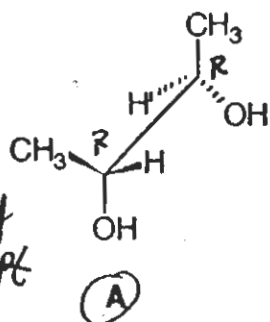
NOTE: THIS EXAM INCLUDES FREE RADICAL RXN - now on EXAM

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	Max. Pts.	Points
1. 4 + 8	=	12
2. 3 + 3 + 3 + 6	=	15
3. 4(3) + 2(3)	=	18
4. 6 + 3 + (2 + 2 + 2)	=	15
5. 8 + 4 + 3 + 5	=	20
6. (5+5+2)+3 + 3 + 2	=	20
<b>Total</b>	=	<b>100</b>

1. (12) a. Which of the following molecules is (are) chiral and give net rotation to the plane of polarized light.

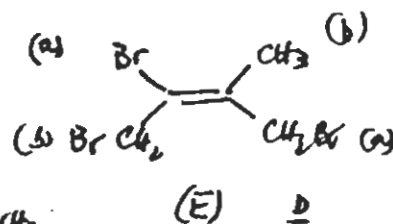
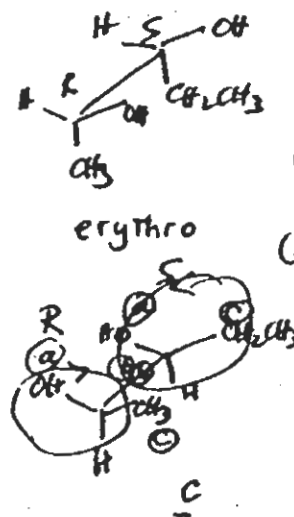
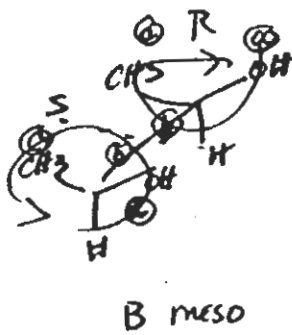
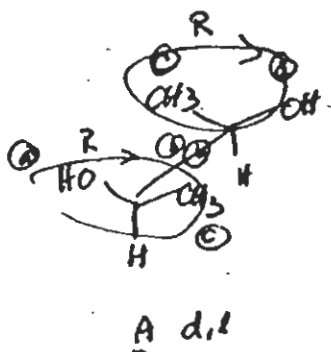


- (1) A only (2) B only (3) C only (4) D only (5) A and B only  
 (6) A and C only (7) B and C only (8) C and D only

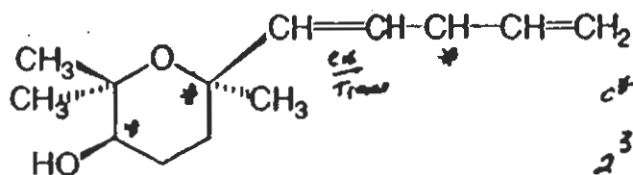
b. Determine the (R), (S) or (E), (Z) configurations of all chiral carbons, C\*, in molecules A, B, and C as well as the (E) or (Z) nature of molecule D. Show your method. For A, B, & C state meso/d,l or erythro/threo nature.

- (1) C\*(s) in A (2) C\*(s) in B (3) C\*(s) in C

(4) (E) or (Z) nature of D.



2. (15) a. The sesquiterpene (a 15 C compound) pictured below was isolated recently from the plant *Calea prunifolia*. How many stereoisomers, both Enantiomers (*R,S*) and (*E,Z*), are possible? Show your calculation. Specify their type and location on the molecule.



$c^* = \text{chiral ctr. cis/trans}$   
 $2^3 = 8$        $8(2) = 16$

- (1) 2      (2) 4      (3) 6      (4) 8      (5) 16

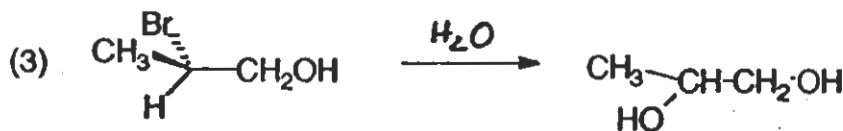
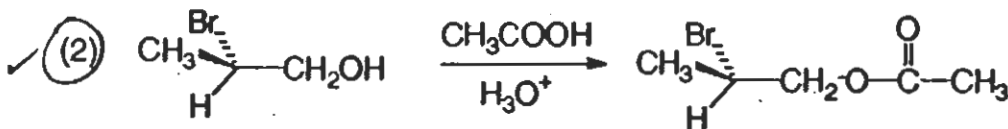
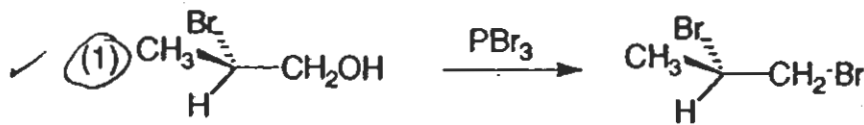
b. Enantiomers are:

- (1) molecules that have a mirror image.  
 (2) molecules that have stereogenic carbon atoms.  
 (3) non-superimposable molecules.  
 (4) non-superimposable constitutional isomers.  
 (5) non-superimposable molecules that are mirror images each other.

c. Resolution of racemic lactic acid,  $\text{CH}_3\text{-CH(OH)-COOH}$ , can be accomplished by:

- (1) Fractional distillation of the free acid.  
 (2) Fractional crystallization of the (-)-strychnine salt of the acid, followed by regeneration of the free acid.  
 (3) Fractional crystallization of the  $\text{Na}^+$  salt of the acid, followed by regeneration of the free acid.  
 (4) Lactic acid cannot be resolved since it is a *meso*-compound.

d. Which of the following reactions might be safely used to relate configurations? Briefly, why?



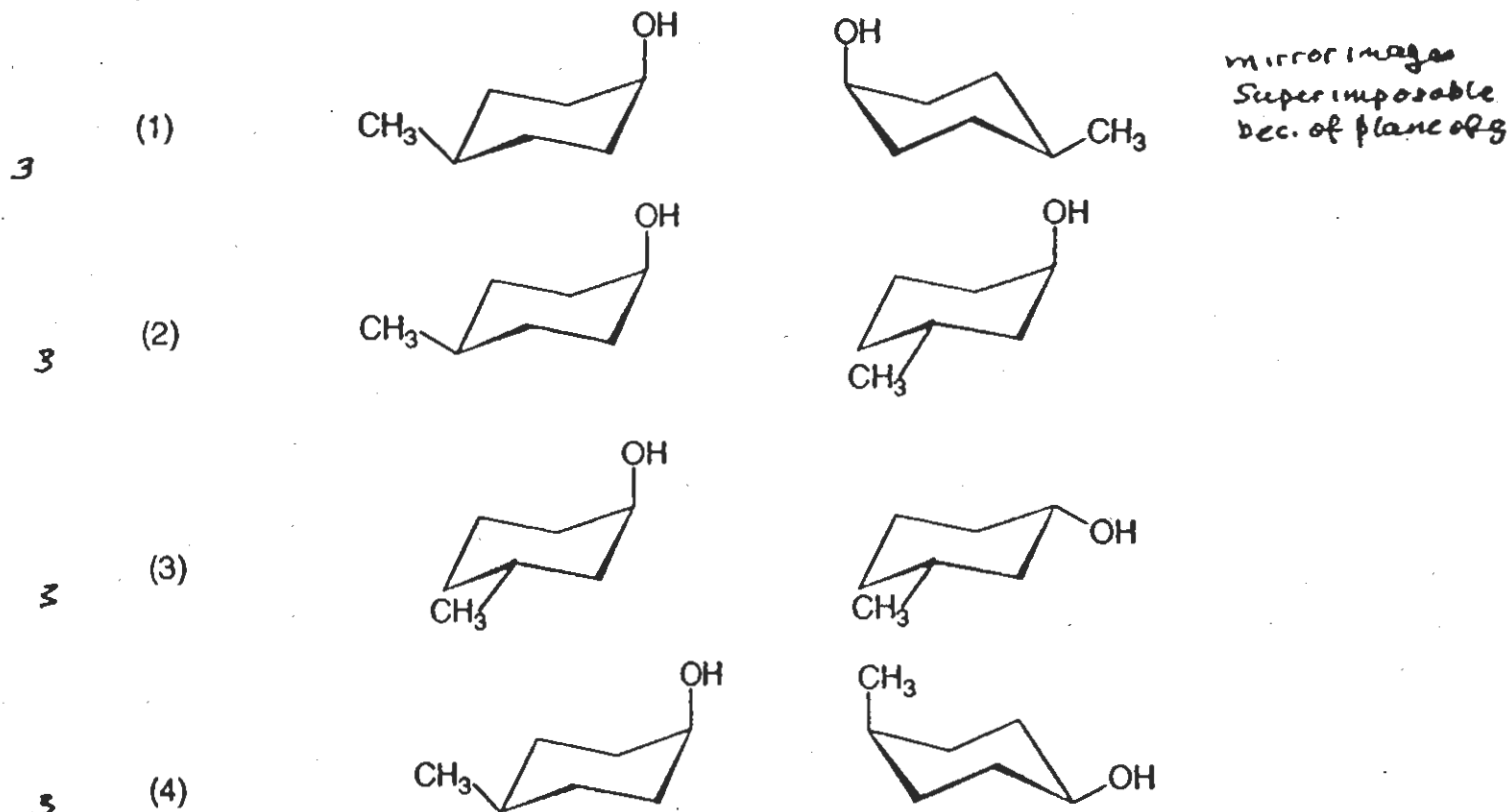
State why.

In no case is stereochemistry at the chiral center disturbed.

Reactions proceed with retention.

In case (3) inversion plus some racemization occurs at chiral center during the solvolysis. The chiral center is involved in an ambiguous way.

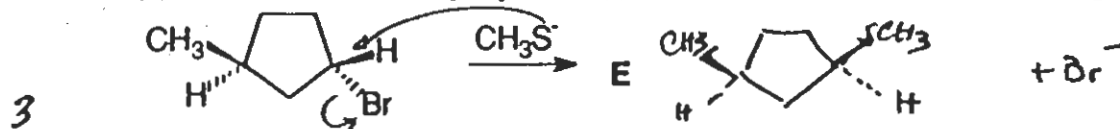
3. (18) a. What are the relationships between the following compounds? Choose from the following possibilities: constitutional isomers, enantiomers, diastereomers, conformers, or identical.



(1) identical (2) Constitutional isomers

(3) diastereomers (cis/trans) (4) conformers  
(Geometric)

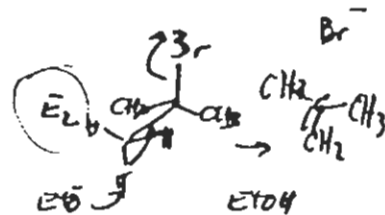
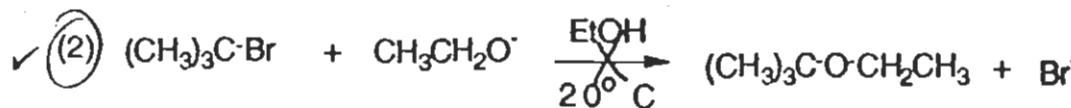
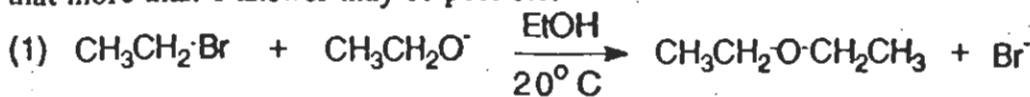
c. (1) What will be the major product(s) of the reaction shown? Show the specific structure(s).



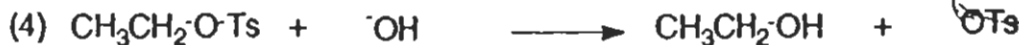
(2) What does this imply about the <sup>STEREOCHEMISTRY &</sup> mechanism of the reaction?

3  $S_N2$  inversion stereospecific

4. (15) a. Which of the following reactions will be unlikely to proceed as written? Briefly, why? Note that more than 1 answer may be possible.



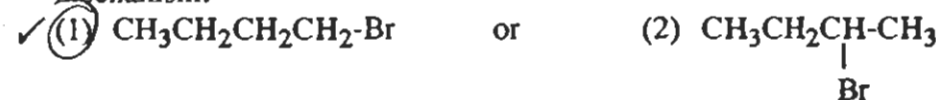
Cl<sup>-</sup> (weak base) cannot displace OH<sup>-</sup> (poor leaving group)



b. Which of the following statements is (are) true about S<sub>N</sub>1 reactions of alkyl halides in general?

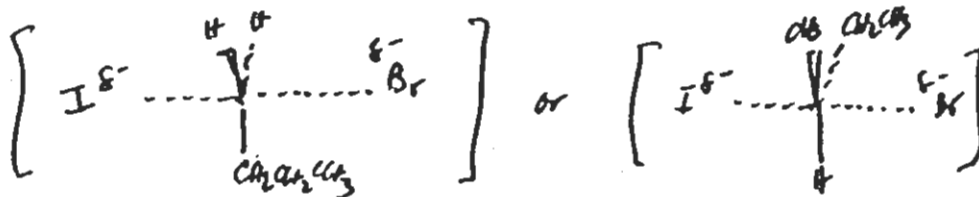
- ✓ (1) The rate of an S<sub>N</sub>1 reaction depends on the concentration of alkyl halide.
- (2) The rate of an S<sub>N</sub>1 reaction depends on the concentration of the nucleophile.
- ✓ (3) S<sub>N</sub>1 reactions of alkyl halides are favored by polar solvents.
- (4) S<sub>N</sub>1 reactions are favored over E1 or E2 by increase in temperature.
- 2pt ✓ (5) S<sub>N</sub>1 reactions may exhibit carbocation rearrangements.

c. Which of the following pairs of compounds would react more rapidly by an S<sub>N</sub>2 mechanism.

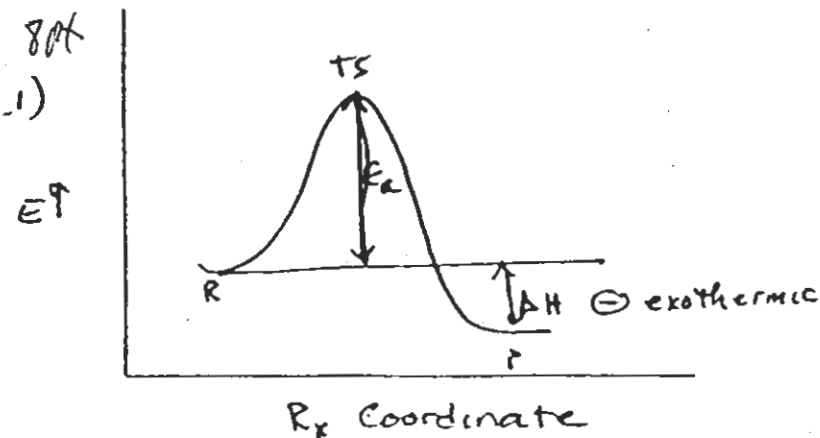


(2) Briefly, why? less steric hindrance. S<sub>N</sub>2 1° > 2° > 3°

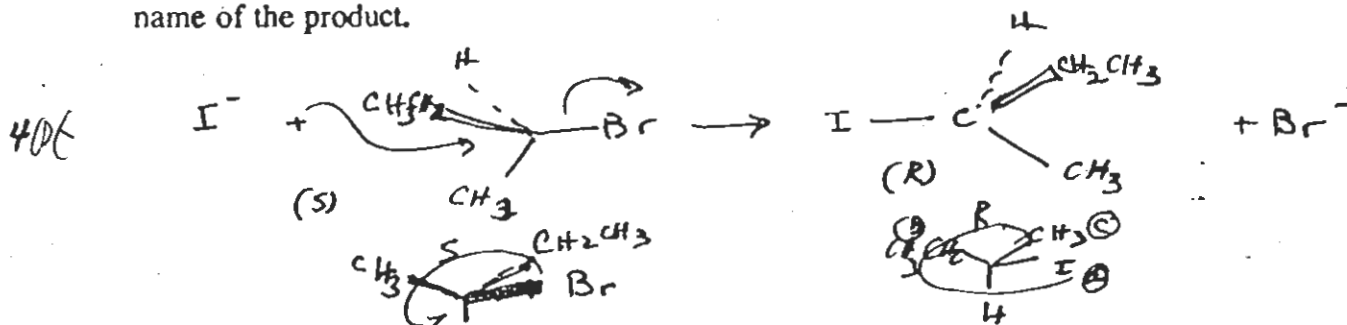
(3) Show the structure of the transition state for the alkyl halide which you chose in its reaction with the nucleophile I<sup>-</sup>.



5. (20) a. Show and completely label the energy profile for the  $S_N2$  reaction of (S)-2-bromobutane with  $I^-$ . Make sure to label the coordinates, R, P, TS(s), Intermediates (if any),  $E_a$ , and  $\Delta H$  (exothermic or endothermic).



- b. Use arrows to show the direction of electron flow for the  $S_N2$  reaction of (S)-2-bromobutane with  $I^-$ . Show the structure of the product(s), including the stereochemistry (R and/or S) and IUPAC name of the product.



- c. Give three ways in which you could increase the rate of the above  $S_N2$  reaction. Briefly show the reasons those methods work to increase the reaction rate.

1.  $Rate = k_2 [RBr] [I^-]$

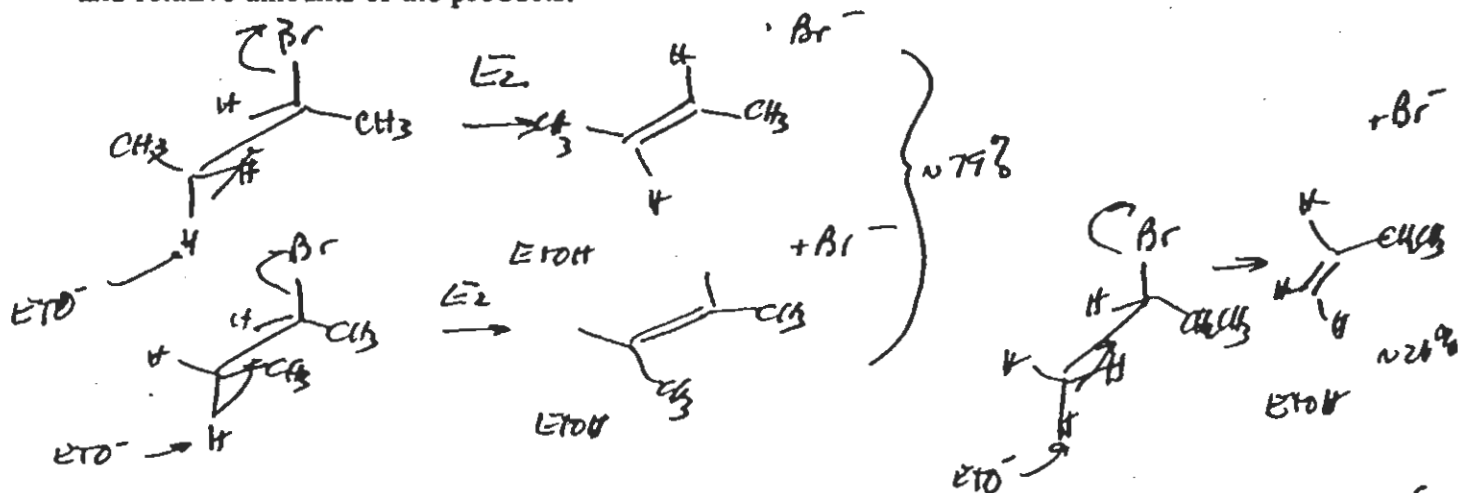
counts as 1 or 2 ways (1) inc  $[RBr]$  (2) inc  $[I^-]$   
inc  $[RBr]$  or  $[I^-]$  or both  $\rightarrow$  inc rate.

2.  $k = A e^{-E_a/RT}$

inc Temp. markedly inc Rate of Rx - many more effective collisions - those with  $E_a$  or better.

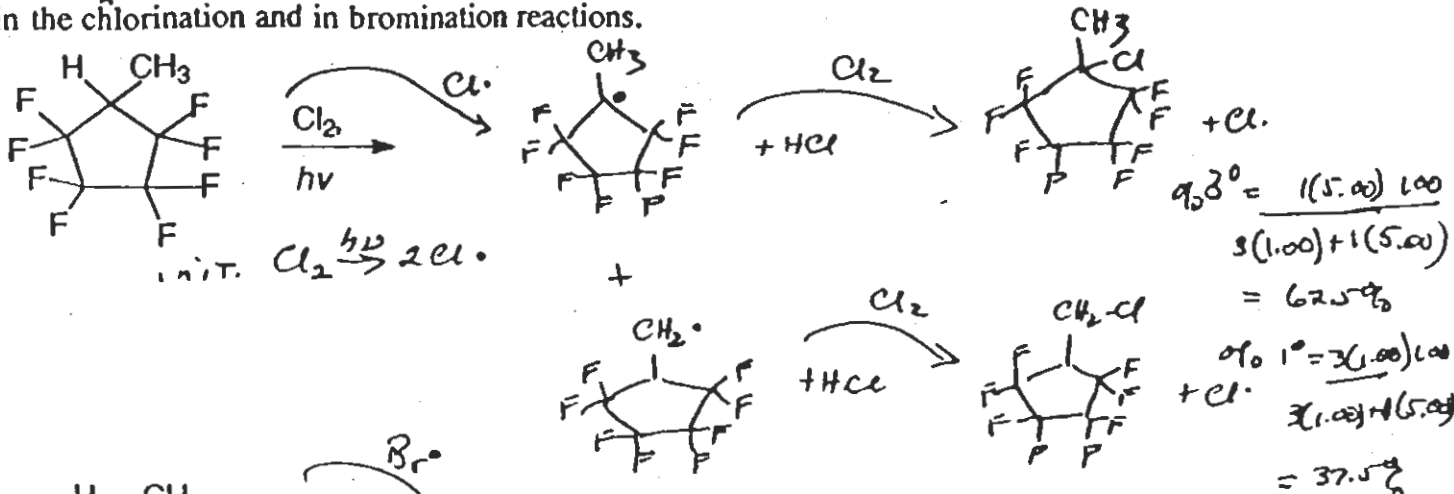
3. Run rx in polar aprotic solvent. Dec. solvation of  $I^-$  makes it stronger nucleophile.

- d. Describe what would happen if the 2-bromobutane above was reacted with sodium ethoxide in ethanol at  $55^\circ C$  by showing and naming both the mechanism of the new reaction and the structures and relative amounts of the products.

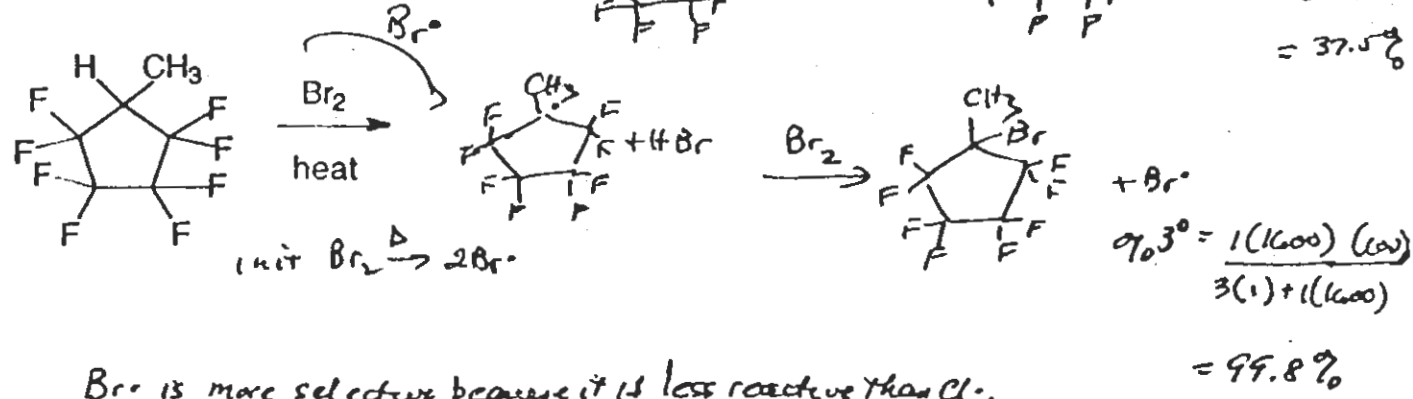


6. (20) a. Show the initiation steps and the missing intermediate(s) and product(s), indicating relative amounts, for the following reactions. Explain why the ratio of 3° to 1° substituted products is different in the chlorination and in bromination reactions.

1 init  
2 rxns  
2 calc  
5 pt



1 init  
1 rxn  
2 calc  
5 pt



Br• is more selective because it is less reactive than Cl•, a later TS is developed which looks more like free radical intermediate & has lots of free radical character. ∴ It is very important how stable that free radical is and 3° C• >> 1° C•.

2 pt

b. Choose a complete definition for a chain reaction from the following:

3 pt

- (1) A chain reaction involves a series of steps.
- (2) A chain reaction involves two steps of equal activation energy..
- (3) A chain reaction is one that can be initiated by light.
- (4) A chain reaction is one that involves free radicals that have an unusual stability and thereby cause a large quantum yield.
- (5) A chain reaction involves a series of steps, each of which generates a reactive intermediate that brings about the next step.

3 pt

c. The hybridization state of a methyl radical is:

- (1) sp (2)  sp<sup>2</sup> (3) sp<sup>3</sup> (4) sp<sup>5</sup>

2 pt

d. An example of a free radical reaction having E<sub>a</sub> = 0 is:

