

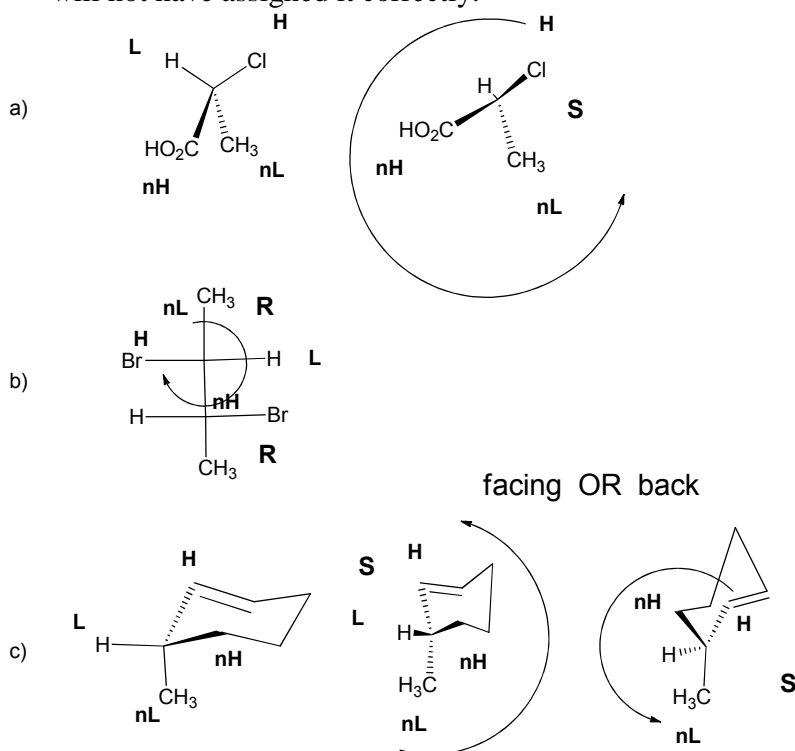
Answer all the questions.

- 1) (12 pts) Assign (R) or (S) to **all** the chiral centers in the following molecules and mark the priority of each group around a chiral center (just the top chiral carbon in molecule b).

a) 4 pts b) 3,1 pts c) 4 pts

To “*assign*” correctly you must 1) find the priorities for the four atoms, 2) draw the arrow in the correct direction according to whether you placed the molecule with the lowest group facing you or in back, 3) choose R or S according to whether the arrow is clock-wise or not.

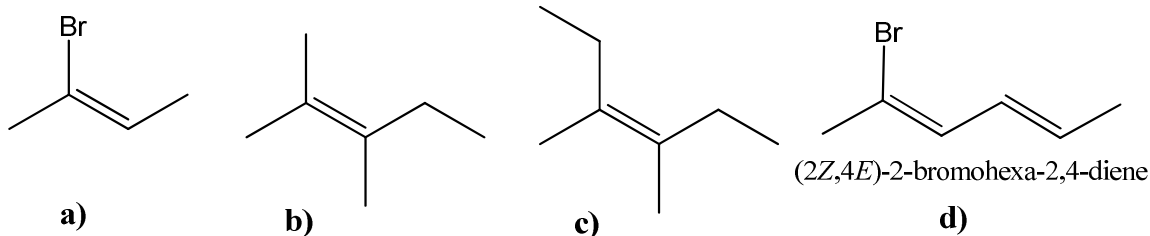
If you make two mistakes, you will have coincidentally found the designation, but you will not have assigned it correctly.



- 2) (1 pt) Identify all the compounds above as either chiral or achiral.

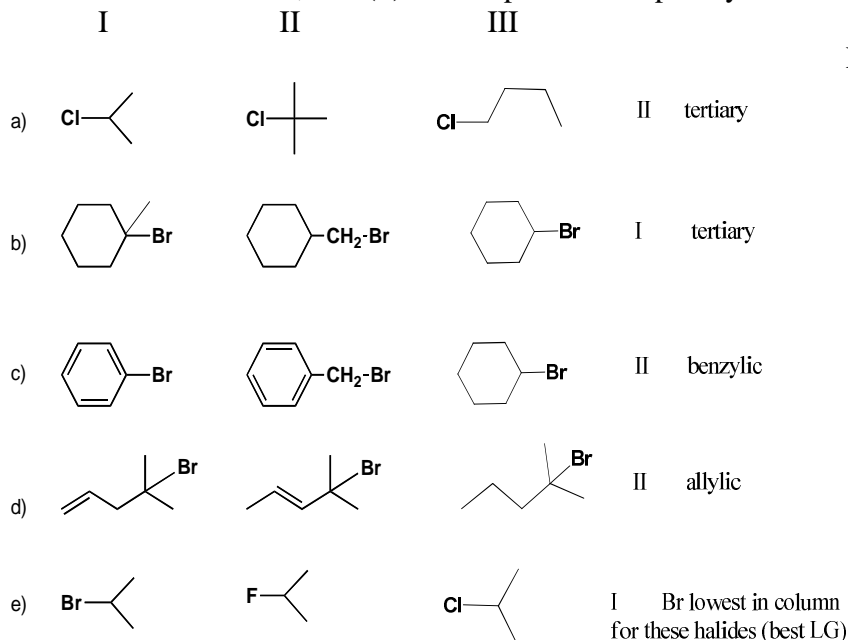
a) chiral b) chiral c) chiral

- 3) (8 pts) Name these alkenes in IUPAC form. E and Z designations must be used when applicable.



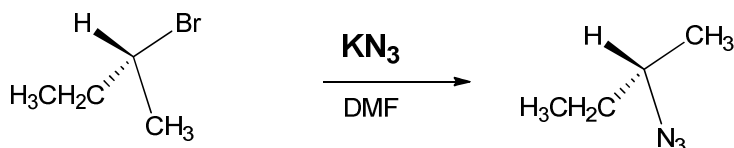
- a) (Z)-2-bromobut-2-ene
- b) 2,3-dimethylpent-2-ene
- c) (Z)-3,4-dimethylhex-3-ene
- d) (2Z,4E)-2-bromohexa-2,4-diene

- 4) (10 pts) For each series of molecules, (i) circle the one which will undergo S_N1 type reactions the fastest, and (ii) write a phrase to explain your answer/guess.



5) (7pts) The 2-bromobutane enantiomer below undergoes S_N2 reaction with potassium azide.

(i) Draw the product or products.
(Any drawing of the product showing the S configuration is acceptable.)



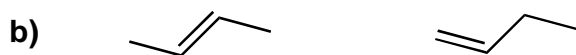
(ii) Will the product of this reaction be totally (R), totally (S) or a mixture of both?

S_N2 gives totally S

(iii) If two times as much *azide* and half as much *reactant* were added, what would happen to the rate of this reaction?

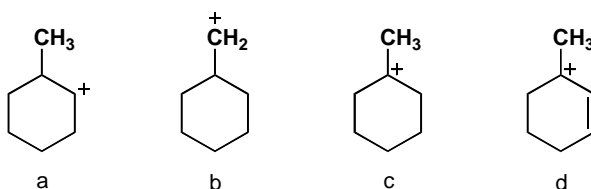
Rate remains the same. (because $\text{Rate} = k [\text{reactant}][\text{N}_3^-] = k [\text{halved}][\text{doubled}]$)

6) (2 pts) For the following alkenes, circle the one that is more stable.



a) trans b) the more substituted ene

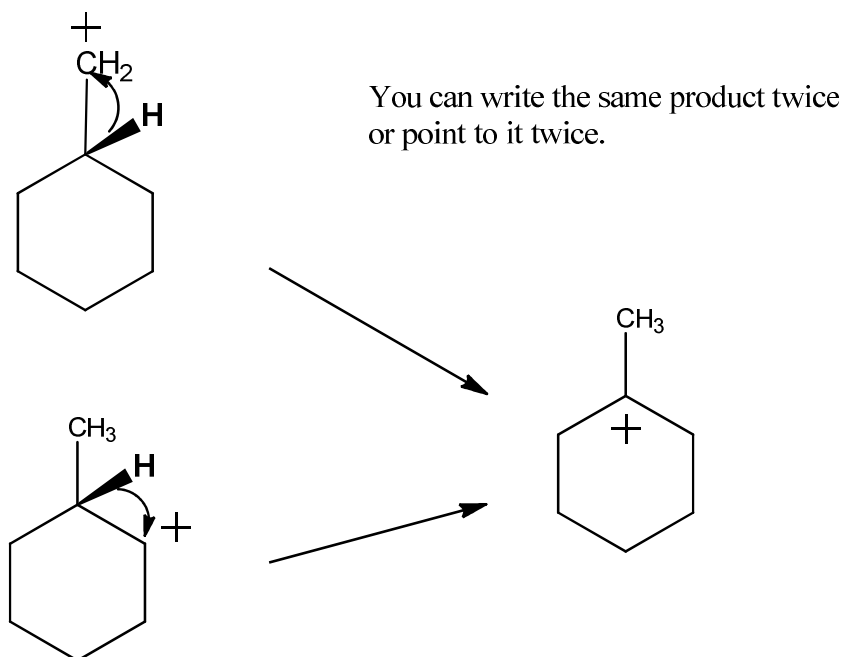
7) (4 pts) List the following carbocations in decreasing order of their stability.



Highest stability: d > c > a > b: lowest

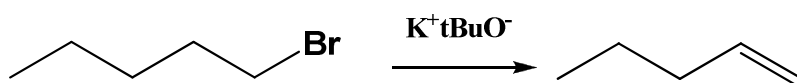
- 8) (6 pts) Two of the carbocations in the problem above are prone to rearrangements. Show mechanisms (with curly arrows) how they might rearrange to more stable carbocations.

The back of the curly arrows must start at the C-H bond and the arrowhead must be on the C with the + charge.



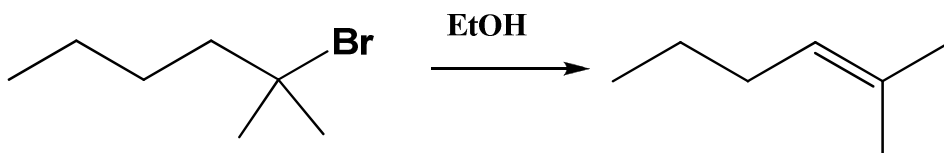
(Count the H atoms on each C atom)!!!

- 9) (7 pts) Write a mechanism (i.e. curly arrows) for this **E2** reaction:



See 2007, question 6

10) (7 pts) Write a mechanism (i.e. curly arrows) for this **E1** reaction:

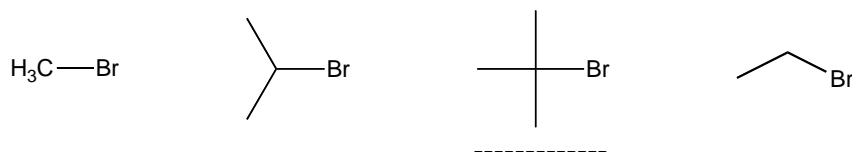


See 2007, question 7

11) (3 pts) What is the principal cause for the elimination reaction in question 9 being E2 while in question 10 it is E1?

The substrate in question 9 is a primary halide, while in question 10 it is tertiary.

12) a. Circle the best S_N1 substrate. (5 pts)



b. What happens to the stereochemistry of the substrate during an S_N1 ?

Retention

Inversion

Racemization

c. Circle the strongest nucleophile.

F^-

Br^-

Cl^-

I^-

d. Circle the strongest leaving group

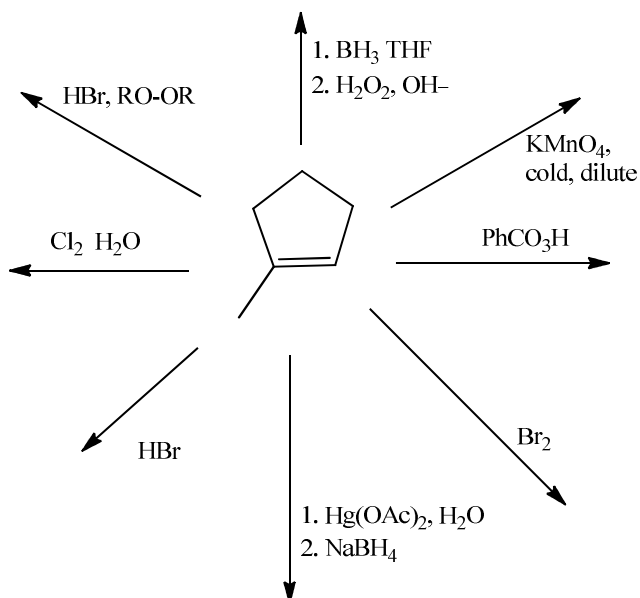
F⁻ Br⁻ Cl⁻ I⁻

e. Circle the best solvent for an S_N1 reaction and give the criterion for your choice.

dimethyl ether acetone methanol hexane

criterion: most polar of the solvents

12) (20 pts) Give the products formed in the following transformations of the below cyclic alkene, *paying attention to stereo- and regio-chemistry where relevant.*



See 2007, 2006, 2005 exams (PhCO₃H only, no subsequent H₃O⁺)

- (i) Circle the reagents in these reactions that give *anti Markovnikov* products.
(HBr, ROOR) (1[BH₃,THF],2[H₂O₂,OH⁻])
- (ii) Underline the reagents in these reactions that give pure *syn additions*.
(KMnO₄ cold)
(PhCO₃H is acceptable.)
- 13) (8 pts) Write the mechanism for either the H-Br addition **OR** the HBr/Peroxides addition in (11), and briefly explain why the reaction is *regioselective*.

See 2007, question 10 (but change HCl to HBr.)

BONUS: Draw two structures of the E1 products after the rearrangements in question 8 and circle the one that is more favored (3 pts)

