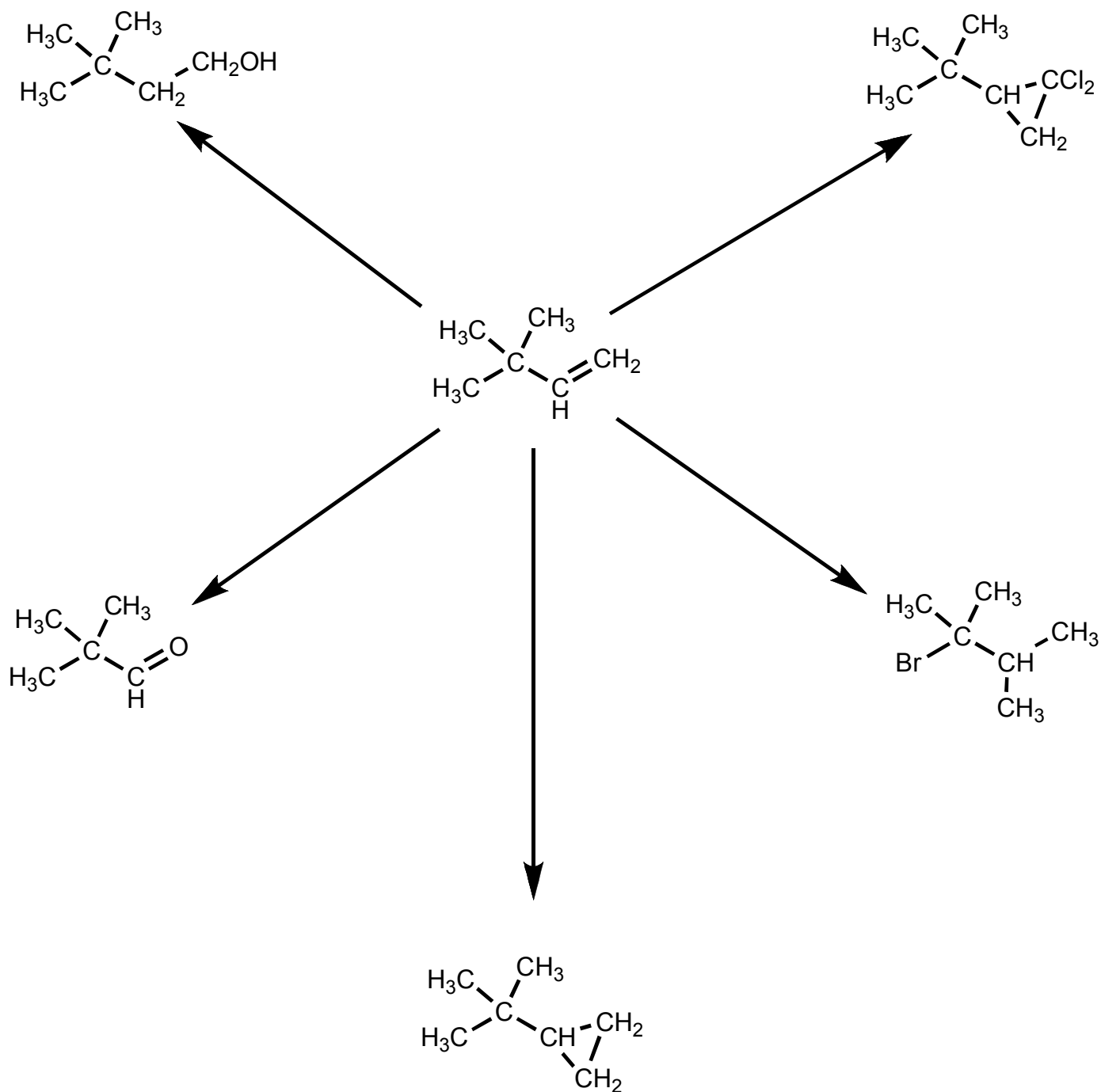


Chemistry 125 Fifth Examination Name _____
 February 6, 2009

The exam budgets 50 minutes, but you may have 60 minutes to finish it. Good answers can fit in the space provided.

1. (10 min) Complete this scheme by supplying a reagent (or reagents) for achieving each of the following five conversions in good yield.
 No mechanisms or curved arrows are required, just the reagents, but do indicate if two successive treatments are required by writing (1) reagent 1 (2) reagent 2.



2. (5 min) Consider these three **pairs** of C₄ isomers - radicals, cations, and alkenes. In two cases the energy difference between the members of a pair is about 2.5 kcal/mole, but in the other case it is estimated to be 21 kcal/mole.

Circle the more stable isomer in **each pair**, and provide a plausible **explanation** for the difference in each case, indicating why the difference is so much larger for one of the pairs.



3. Consider the chlorination reaction : $i\text{-Pr}_2\text{NCl} + \text{RH} \rightarrow i\text{-Pr}_2\text{NH} + \text{RCl}$

and these approximate bond dissociation energies (kcal/mole): N-Cl (46), R-Cl (85), N-H (92), R-H (100).

A. (3 min) Estimate the equilibrium constant for the transformation at room temperature:

- B. (3 min) The transformation requires light (or added free-radical initiators). If you doubled the amount of light (or initiator) would you expect the rate of transformation to (a) increase about 50%, (b) double, (c) quadruple, (d) stay the same, or (e) decrease? Why?

Question 3 (cont)

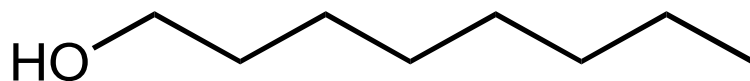
C. (5 min) Write a plausible mechanistic scheme for the chlorination of R'H by R₂NCl.

D. (5 min) One might change the rate of product formation by changing R or R'. Explain whether this rate should be more sensitive to changes in the strength of the R'-Cl bond, or to changes in the strength of the R₂N-H bond.

Question 3 (cont)

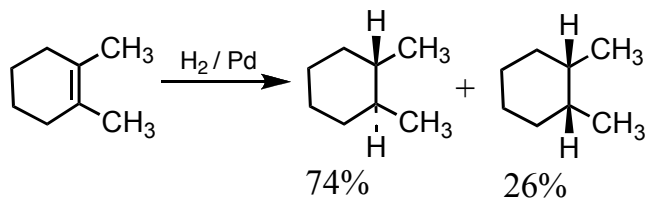
E. (3 min) Explain why the reaction fails unless the solution is made acidic.

F. (5 min) Explain **how and why** the reaction's regioselectivity changes dramatically as the medium is changed from 50% to 70% H_2SO_4 using 1-octanol as RH.



G. (3 min) Why should the BDEs of N-Cl and R-Cl be so different, when those for N-H and R-H are so similar?

4. (8 min) What is surprising about the yields of isomeric products from this catalytic hydrogenation?



Draw several key mechanistic steps with curved arrows to explain the yields. (You may abbreviate the structure to simplify your drawings.)

ALSO suggest an experiment with a different starting material to test your explanation.