Name: KEY **Advanced Organic Chemistry (4:172)**

ID #: _____ **Fall 2007**

EXAM 2, Wednesday, November 14, 2007

Before starting:

Check your exam to make sure that it is complete. There should be a total of 7 pages. Problems are on the front of each sheet.

Read each question carefully, making sure that you completely answer each question. You may use the back of a sheet for additional space if needed.

Remember: Questions answered in pencil, red ink, erasable ink, or that have white-out on them cannot be regraded.

Good luck.

Question #	Possible Points	Points Scored
1	16	_____
2	24	_____
3	25	_____
4	24	_____
5	36	_____

Total: _____

1. Multiple choice. Circle the correct answer (16 pts).

a) True or false?

The rate-determining step of a S_N1 reaction is ionization of the reactant.

i) True ii) False

b) A Lewis-acid catalyst serves to _____ electron pairs in organic reactions.

i) accept
ii) donate
iii) shield
iv) none of the above

C) Which of the following types of carbonyl compounds are least reactive toward nucleophilic addition?

i) esters
ii) ketones
iii) amides
iv) none of the above

D) True or false?

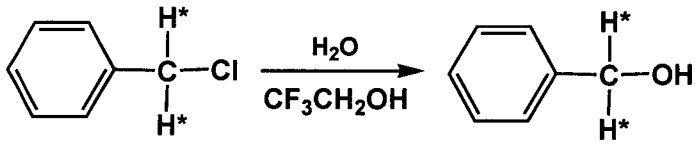
Crown ethers enhance nucleophilicity by solvating cations.

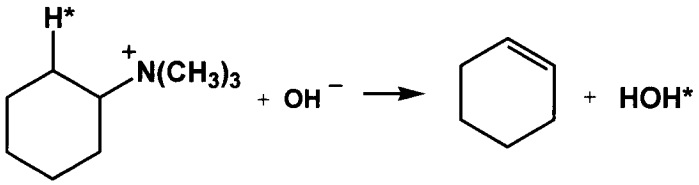
i) True ii) False

2. Consider the information below and answer the questions that follow (24 points).

a) In the spaces provided, indicate whether the reactions given below are expected to display either a primary or secondary kinetic isotope effect.

i) $PhCH_2{-}H^* + BrH^- \longrightarrow PhCH_2\cdot + H^*{-}Br$ 1°

ii)  2°

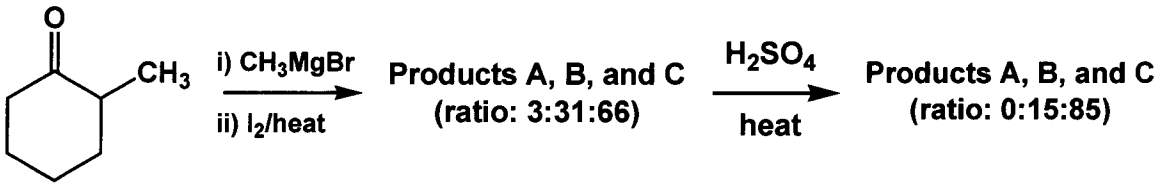
iii)  1°

b) Clearly explain why isotopic substitution of D for H has an effect on the rate of a chemical reaction.

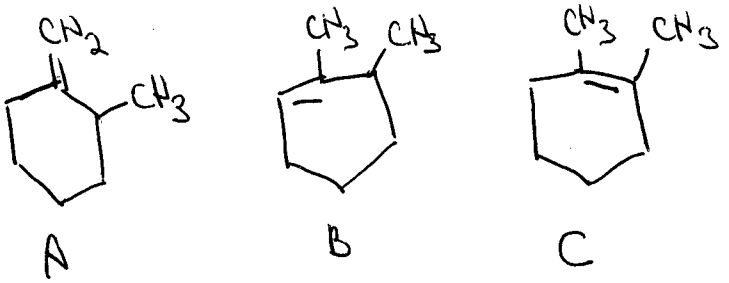
D isotope has a larger mass. The larger mass lowers the zero-point energy of a molecule, which has the effect of increasing the activation energy (i.e. bond dissociation) relative to H. A higher activation energy will mean a slower reaction rate

3. Consider the information below and answer the questions that follow (25 points).

Addition of methylmagnesium bromide to 2-methylcyclohexanone, followed by iodine-catalyzed dehydration of the resulting alcohol, gave three alkenes in the ratio A:B:C = 3:31:66. Each alkene gave a mixture of cis- and trans-1,2-dimethylcyclohexane upon catalytic hydrogenation. When the alkene mixture was heated with a small amount of sulfuric acid, the ratio of A:B:C changed to 0.0:15:85.



a) Assign structures to A, B, and C.



b) Clearly describe the rationale behind your assignments.

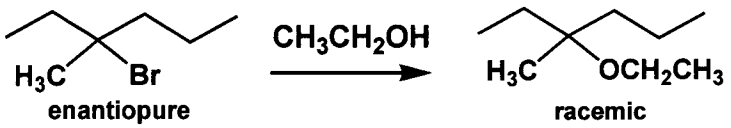
Most highly substituted olefin is most stable. Stability order is C > B > A. This order is reflected in the ratios.

c) Account for the change in the relative ratios of products A, B, and C.

Conditions that promote thermodynamic control of reactivity were created upon addition of the sulfuric acid. As a result, the kinetic product has completely disappeared.

4. Consider the information below and answer the question that follows (24 points).

3,3-chloro-methyl-hexane undergoes solvolysis and nucleophilic substitution in ethanol to produce a racemic mixture of the corresponding ether as shown below. Nucleophilic substitutions of 3,3-chloro-methyl-hexane can also proceed with 98% inversion of stereochemistry. Carbocations are intermediates in both cases.

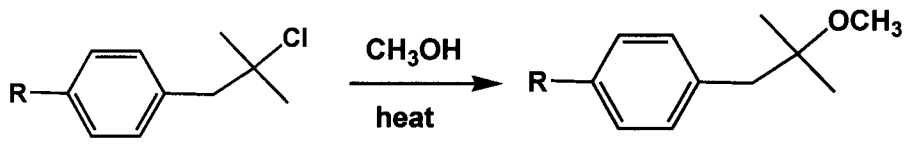


Explain how you could carry out a nucleophilic substitution of 3,3-chloro-methyl-hexane to achieve inversion of stereochemistry as described above. Clearly explain your reasoning. Be sure to indicate why you expect inversion to predominate.

Inversion of stereochemistry could be achieved by conducting the reaction in a nonpolar solvent so as to produce either a contact or/ solvent-separated ion pair. The ion pair would make the carbocation dissymmetric, which would enable inversion.

5. Consider the information below and answer the questions that follow (36 pts).

A student has discovered that para substituted 1-(2-chloro-2-methylpropyl)benzenes undergo solvolysis in methanol as shown below.



ρ = -2.1

a) What does the value and sign of the ρ value indicate?

Reaction involves a carbocation intermediate and is, therefore, promoted by electron-donating groups. Reaction is relatively sensitive to donating ability.

b) Give three examples of -R groups for the reaction above that would: (i) promote the reaction and (ii) inhibit the reaction:

promote:

EDGs (e.g. $-OR$, $-NR_2$, $-NH_2$, $-R$)

inhibit:

EWGs (e.g. $-NO_2$, $-CF_3$, $-\overset{O}{\overset{\|}{C}}OR$)

c) Would you expect the substituents that promote the reaction to have either positive or negative Hammett substituent constants? Clearly explain your reasoning.

Substituents that promote the reaction are expected to have negative σ values in line with the Hammett relationship: $\log \frac{K}{K_0} = \sigma\rho$

"+" "−" "−" should be negative

d) Propose a mechanism for the reaction and clearly indicate the species that accounts for the ρ value.