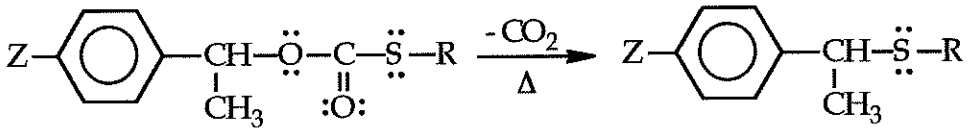
Advanced Organic Chemistry
Dr. M. J. Wieder
Examination #1

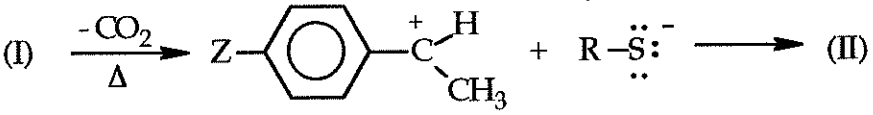
Name _____

(30) 1. Consider the following reaction:



(I) (II)

The above reaction is believed to proceed via a thermal decomposition-recombination pathway as shown below:



a) Devise a crossover experiment to test the above mechanism. Explain what results one would expect to obtain if the pathway shown is valid.

b) Explain how an optical activity study might help to elucidate the mechanism for the above reaction.

c) Explain how a consideration of Hammett substituent constants might help to elucidate the mechanism for the above reaction.

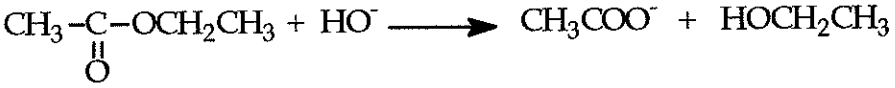
d) Explain how a kinetic study of the above reaction when Z is varied from a strongly electron-withdrawing group to a strongly electron-donating group might help to elucidate the mechanism for the above reaction. Assume that the formation of the benzylic carbocation is the rate determining step.

e) In the thermal decomposition-recombination pathway shown above, would one expect to observe a kinetic isotope effect using starting material deuterated at the benzylic carbon assuming:

i) the decomposition step is rate-determining?
ii) the recombination step is rate-determining?

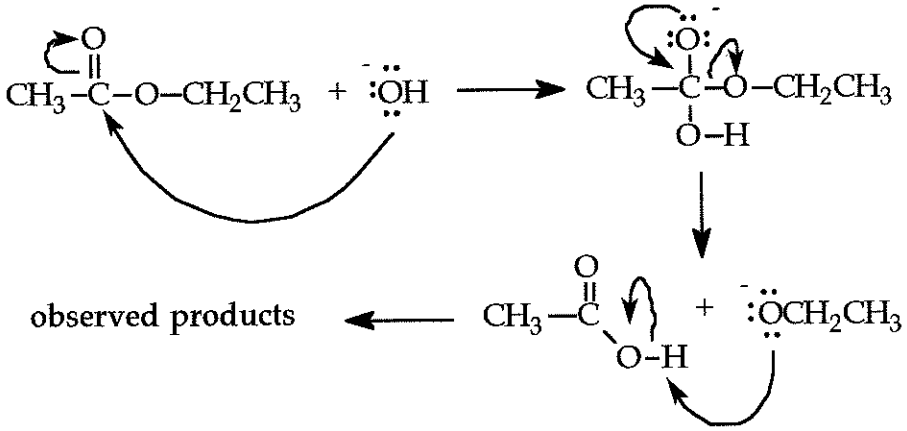
Explain the nature and magnitude of any kinetic isotope effect described for (i) and/or (ii).

(12) 2. Consider the basic hydrolysis of ethyl ethanoate:

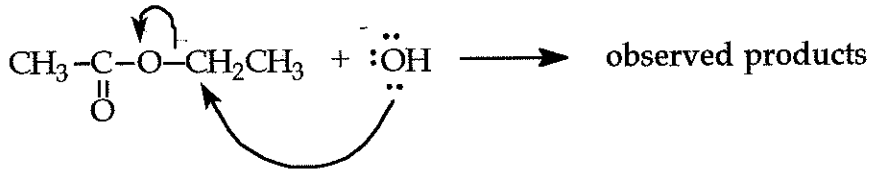


Two possible pathways that can account for product formation are presented below:

Pathway A:



Pathway B:



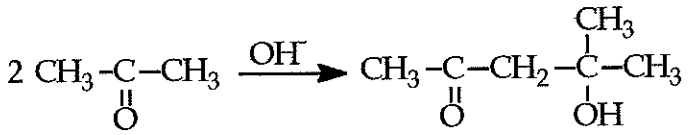
a) Based solely on the hydrolysis products obtained, would labeling the carbonyl oxygen of the ester starting material, enable one to differentiate between the two pathways shown above? If so, specify what results one would expect. If not, explain or illustrate.
(Yes, No)

b) Based solely on the hydrolysis products obtained, would labeling the ethoxy oxygen of the ester starting material enable one to differentiate between the two pathways shown above? If so, specify what results one would expect. If not, explain or illustrate.
(Yes, No)

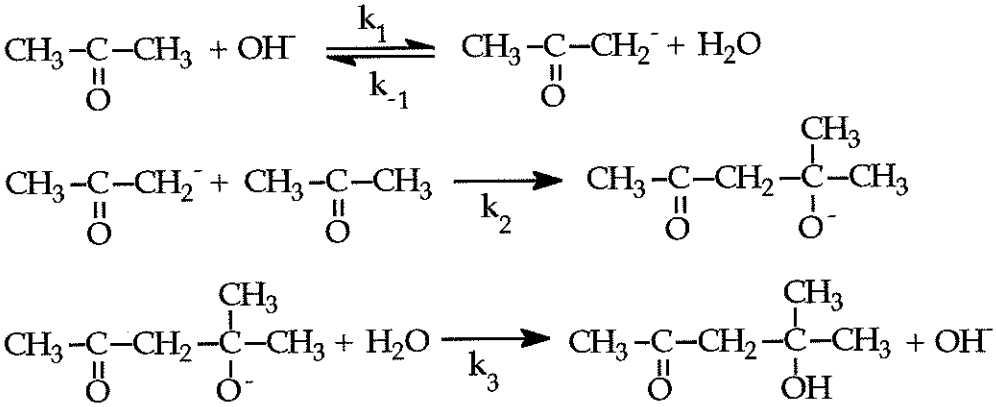
c) Based solely on the hydrolysis products obtained, would the use of $Na^{18}OH$ enable one to differentiate between the two possible pathways shown above? If so, specify what results one would expect. If not, explain or illustrate.
(Yes, No)

d) Based solely on the hydrolysis products obtained, would replacing one of the two methylene hydrogen atoms of the ester ethoxy group with deuterium enable one to differentiate between the two pathways shown above? If so, specify what results one would expect. If not, explain or illustrate.
(Yes, No)

(6) 3. Consider the base-catalyzed aldol condensation of acetone:



The following mechanistic pathway has been postulated:

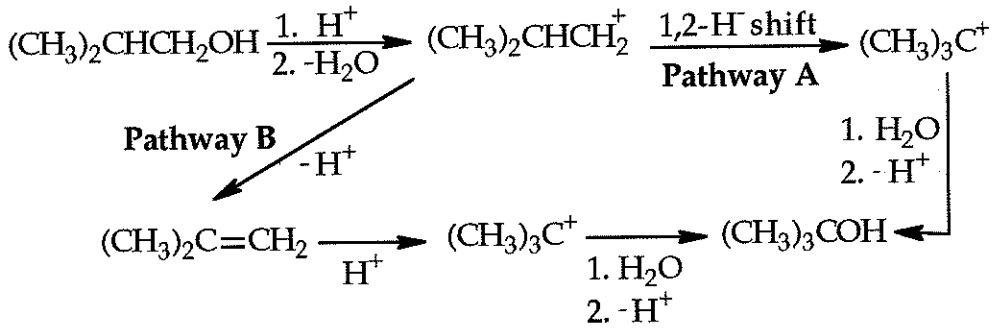


If the second step is the rate determining step, $k_{-1} >> k_2$, and $[H_2O]$ is a constant, derive the rate law expression for the above mechanism using the Steady State approximation for the α-carbanion of acetone. Show all work in the space provided below.

(6) 4. Consider the following reaction:

$$(CH_3)_2CHCH_2OH \xrightarrow[H_2O]{H^+} (CH_3)_3COH$$

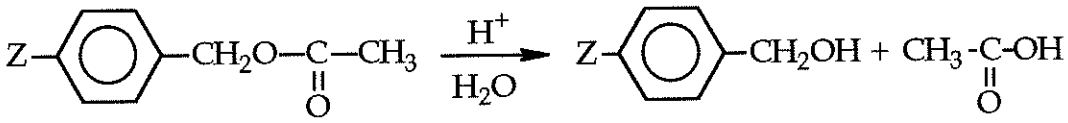
The above rearrangement reaction can proceed via one of the two pathways shown below:



In light of the following information, which one of the two pathways may be dropped from consideration? Explain.

Fact: $(CH_3)_2CHCH_2OH \xrightarrow[D_2O]{D^+} (CH_3)_3COD$ only organic product

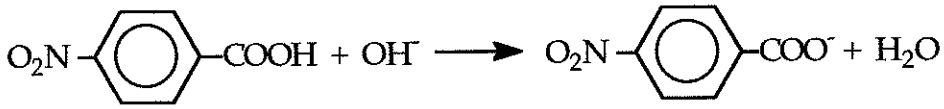
(10) 5. Consider the hydrolysis of para-substituted benzyl acetate esters under acidic conditions (see below):

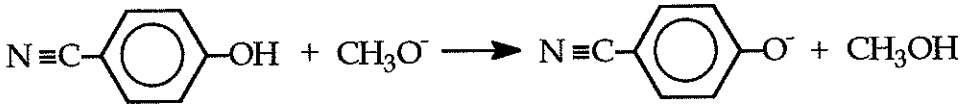


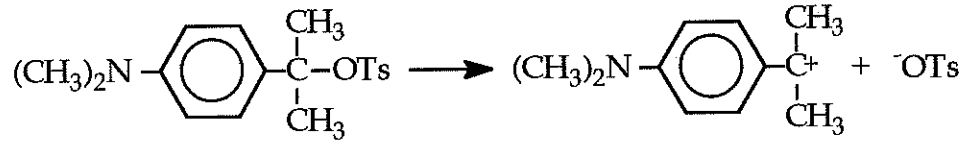
a) When Z = OH or OCH_3, the rho value for the hydrolysis reaction is negative, and the para-substituent gives an excellent Hammett correlation if σ_p^+ values are used instead of σ_p values. Suggest a plausible mechanism to account for these facts.

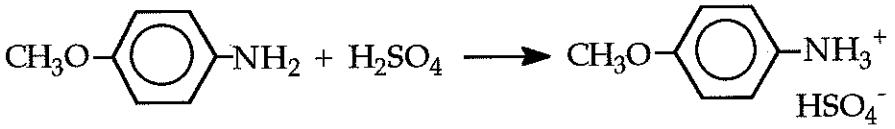
b) When Z = NO_2 or COOH however, the hydrolysis reaction proceeds via a different pathway from that in part (a). Explain the reason for the change, and describe/illustrate the second hydrolysis pathway.

(8) 6. For each of the following reactions, specify whether the use of σ_p, σ_p^+, or σ_p^- would give the best linear fit.

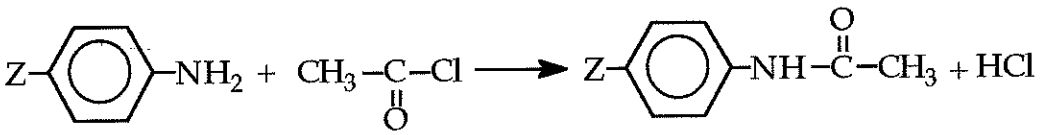
a) 

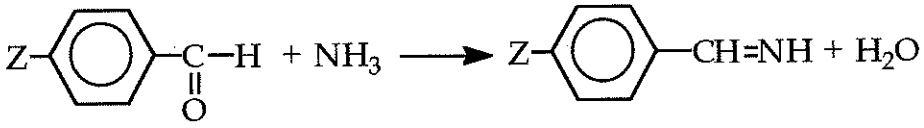
b) 

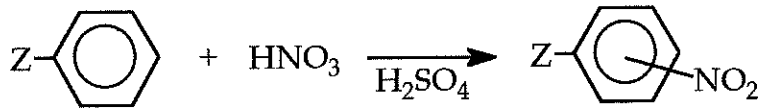
c) 

d) 

(12) 7. Predict the sign of the rho value for each of the following reactions. Briefly justify your response in each case.

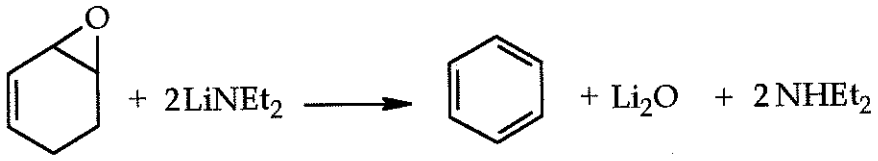
a) 

b) 

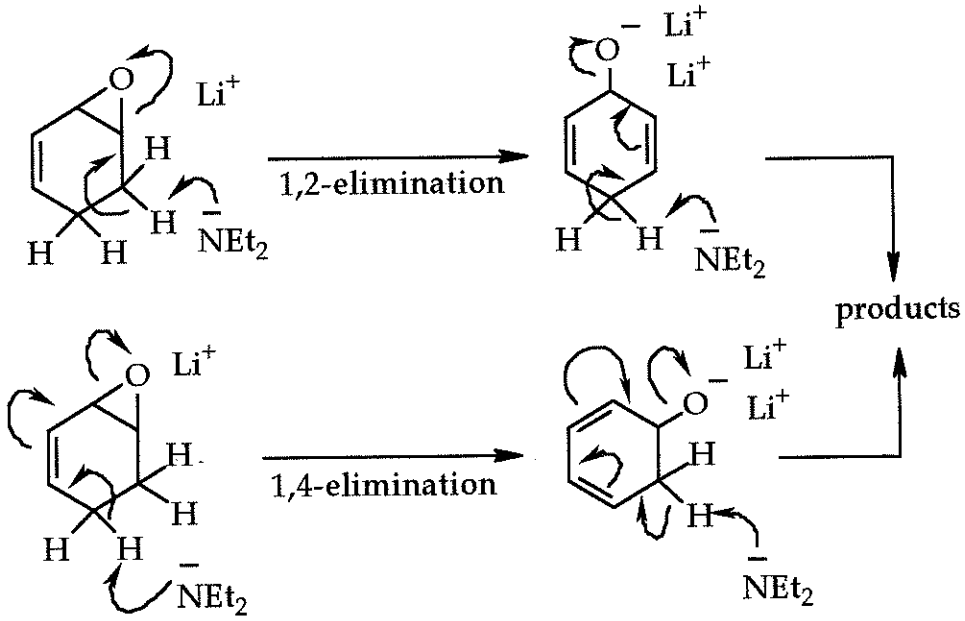
c) 

d) 

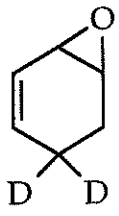
(8) 8. Consider the conversion of the following epoxide to benzene in the presence of lithium diethylamide:



The conversion can be envisioned as proceeding via one of the two elimination pathways shown below:



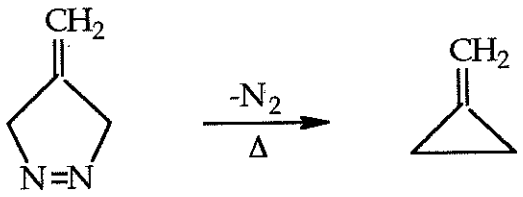
a) If the reaction were run using deuterated starting material, structure (I) below, would it be possible to differentiate between the pathways presented **based solely on product structure analysis**? Explain and/or illustrate.



(I)

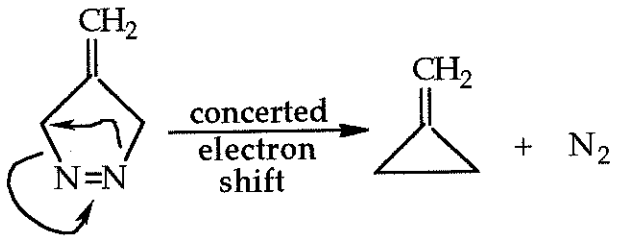
b) Could one differentiate between the two pathways presented using labeled (I) above and assuming that formation of intermediate is rate-determining? Explain and/or illustrate.

(8) 9. Consider the thermal decomposition reaction shown below:

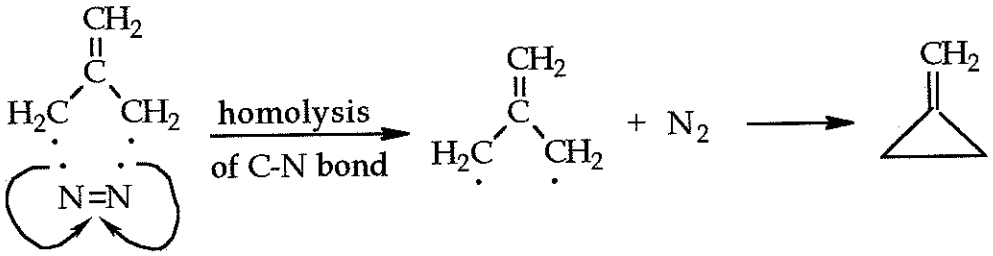


Two mechanistic pathways have been proposed to account for product formation:

Pathway (I):



Pathway (II):



a) Explain and/or illustrate how one could differentiate between the two pathways presented by running the thermal decomposition using starting material labeled with C-14 at the exocyclic vinyl methylene carbon atom (=CH_2).

b) Would it be possible to differentiate between the two pathways presented if the thermal decomposition were run using starting material labeled with C-14 at the endocyclic vinyl carbon atom? Explain and/or illustrate to justify your response.