Massachusetts Institute of Technology

Chemistry 5.43 *February 21, 2007*

Professor M. Movassaghi

Practice Exam #1

Question 1a	———/05 points	Question 1l	———/05 points
Question 1b	———/02 points	Question 1m	———/05 points
Question 1c	———/03 points	Question 2a	———/05 points
Question 1d	———/05 points	Question 2b	———/05 points
Question 1e	———/10 points	Question 2c	———/06 points
Question 1f	———/05 points	Question 2d	———/06 points
Question 1g	———/03 points	Question 2e	———/05 points
Question 1h	———/07 points	Question 2f	———/08 points
Question 1i	———/05 points		
Question 1j	———/05 points	**Total**	**———/100 points**
Question 1k	———/05 points		

NAME: _____

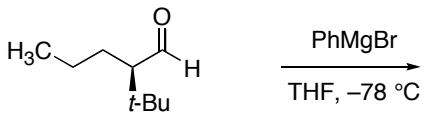
Signature: _____

T.A.: _____

There are 5 pages (2-6) of questions in this exam.

Question 1.

Consider the following reaction:



A
(optically pure)

B

C

1a) Provide the structure of the two principal addition products, clearly indicating stereochemistry, and assign the Cahn-Ingold-Prelog configuration to each stereocenter of the starting material A and products B and C.

1b) Indicate whether each product is a chiral or an achiral compound.

B ☐ **C** ☐

1c) What is the isomeric relationship between the products B and C (i.e. constitutional isomers, enantiomers, or diastereomers).

☐

1d) Do you expect the products to be formed in equal or unequal amounts.

☐

1e) Explain your answer to 1d using clear and informative drawings.

Question 1 (continued).

1f) Provide the topological relationship (homotopic, enantiotopic, diastereotopic) between the two faces of the carbonyl group of aldehyde A.

1g) Do you expect the addition of the nucleophile to the carbonyl group of aldehyde A to occur: (circle one)

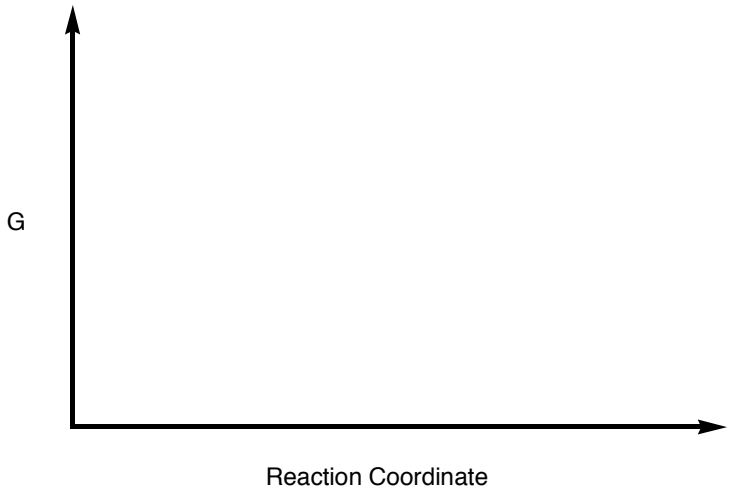
faster onto the *re*-face than the *si*-face.

faster onto the *si*-face than the *re*-face.

with equal rate to both faces.

1h) Describe two methods for determining the stereoselectivity of the reaction outlined in question 1a (after workup and isolation of the crude product mixture).

1i) Provide a detailed reaction coordinate diagram consistent with your answer to question 1d; include as much detail as possible.



Question 1 (continued).

1j) Describe two methods for determining the enatiomeric excess of the product B in your answer to question 1a.

1k) Consider an experiment similar to that described in question 1a with the exception that a racemic sample of aldehyde A is used. In addition to products B and C, what two other products do you expect to isolate; provide the structure of these compounds, clearly indicating stereochemistry, and assign the Cahn-Ingold-Prelog configuration to each stereocenter.

D **E**

1l) What is the isomeric relationship between the following pair of compounds (be consistent with you answers to questions 1a and 1k):

D and B:

D and C:

E and B:

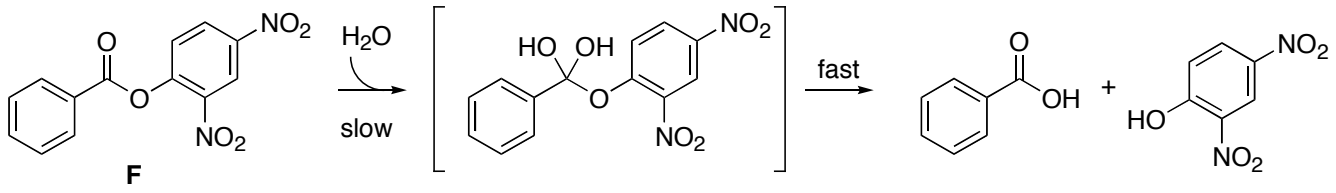
E and C:

1m) Describe the expected ratio of products B, C, D, and E in the experiment described in 1k.

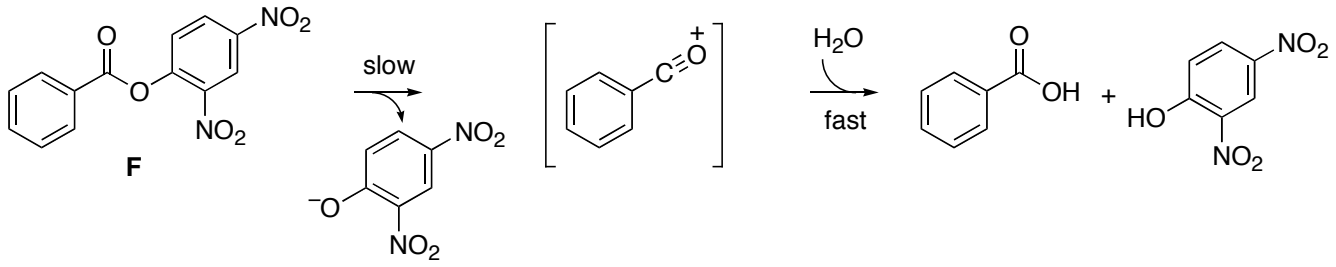
Question 2.

Consider the two mechanisms illustrated below for the hydrolysis of ester F by one equivalent of water:

Mechanism 1:



Mechanism 2:



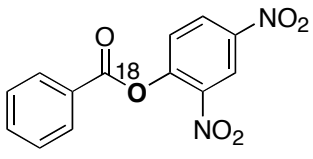
2a) Propose a rate law that would be expected for each scenario:

Mechanism 1:

Mechanism 2:

2b) Describe how the rate laws could be used to distinguish between these two mechanisms.

2c) Consider the experiment where the isotopically labeled substrate F-^{18}O is used. Observation of a 1° KIE is most consistent with which of the two mechanisms described above. Breifly explain your answer.

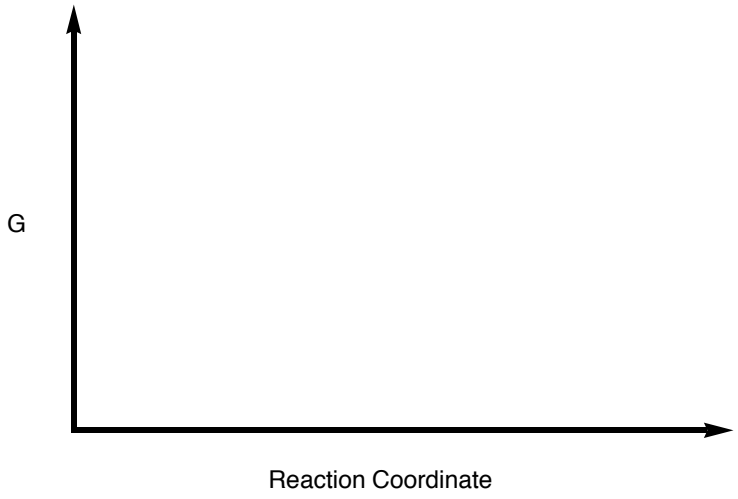


F-^{18}O

Question 2 (continued).

2d) For scenario 1, assumming a late transition state, provide a drawing and a detailed description of the transition state, based on the Hammond Postulate.

2e) In mechanism 1 we assumed the first step is rate-determining. Provide a detailed reaction coordinate diagram consistent with this scenario; include as much detail as possible.



2f) Assume for the moment that it is not known which step of Mechanism 1 is rate-determining. Consider an experiment conducted using $^{18}OH_2$ (oxygen-18 labeled water) and stopped prior to complete hydrolysis of the starting ester F. How would analysis of the recovered ester F from this experiment distinguish which of the two steps in Mechanism 1 is rate-determining. Breifly describe your reasoning and the method(s) you would use for this analysis.

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