

Fonctions et Réactions Organiques II

2018-2019 Fall Semester

Monday 28-Jan-2019, 12h15 to 15h15, CE3

Total time: 3h

Material allowed:

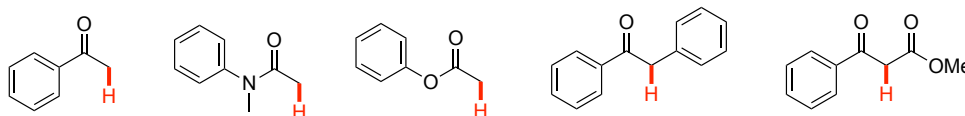
- Writing materials (pen, pencil, ...calculator)
- Drink and food
- ID or Student Card

Name:

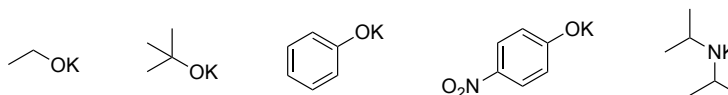
Signature:

Problem 1 (12 pts)

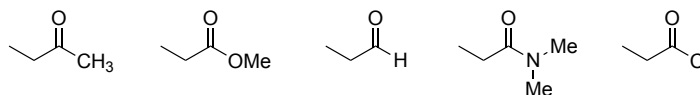
- a) Rank the α -CH acidity of the following carbonyl compounds in the order of increasing acidity and justify your answer:



- b) Rank the following compounds in the order of increasing basicity and justify your answer:



- c) Ranking the electrophilicity of the following carbonyl group:

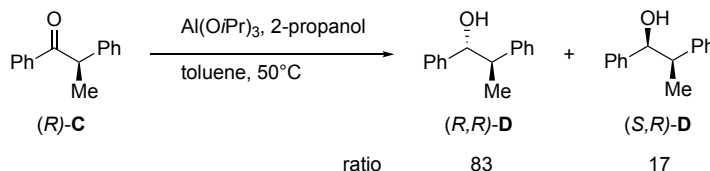


Problem 2 (15 pts)

- a) Draw two reaction energy diagrams corresponding to the S_N1 and the S_N2 mechanisms of the following nucleophilic substitution reaction, assuming that product **B** is thermodynamically more stable than starting material **A**.

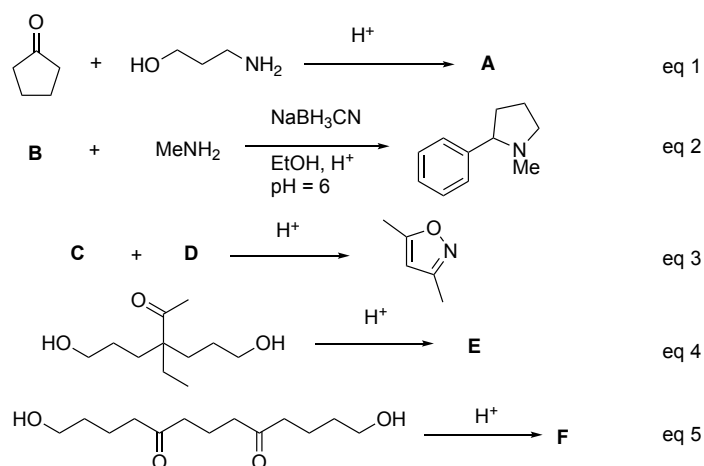


- b) Write the rate law for S_N1 and S_N2 reactions, according to their respective reaction energy diagrams.
- c) Diastereoselective Meerwein-Ponndorf-Verley reduction of ketone (*R*)-**C** afforded (*R,R*)-**D** and (*S,R*)-**D** in 83:17 ratio, respectively. Determine the difference in free energies of activation at 50°C for the formation of the two diastereomers. The reaction is kinetically controlled.



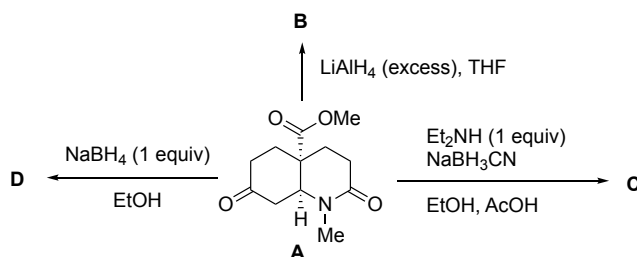
Problem 3 (15 pts)

- a) Provide the structures of **A**, **B**, **C**, **D**, **E** and **F**
- b) Provide a detailed reaction mechanism for the formation of compound **F**.

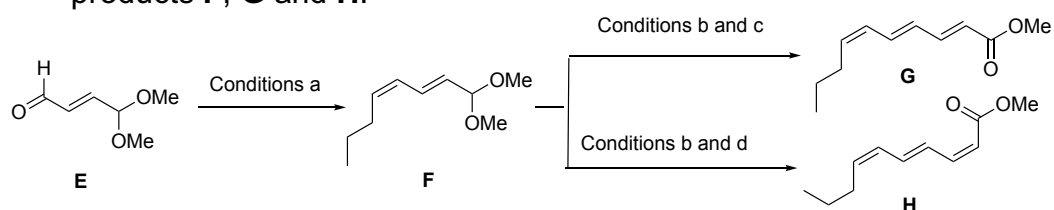


Problem 4 (16 pts)

- a) Compound **A** contains three different carbonyl functions that can be reduced chemoselectively. Give the structures of the expected products (**B**, **C**, **D**) in each case.

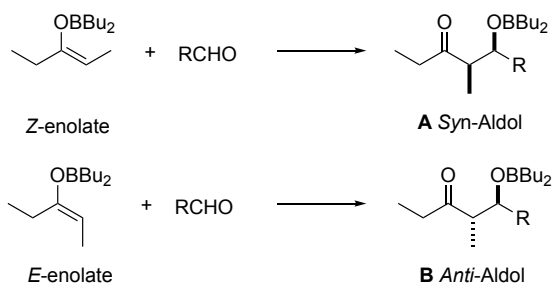


- b) Provide conditions (a, b, c and d) for the conversion of **E** to **F**, **F** to **G** and **F** to **H**. Please pay particular attention on the double bond geometry of the products **F**, **G** and **H**.



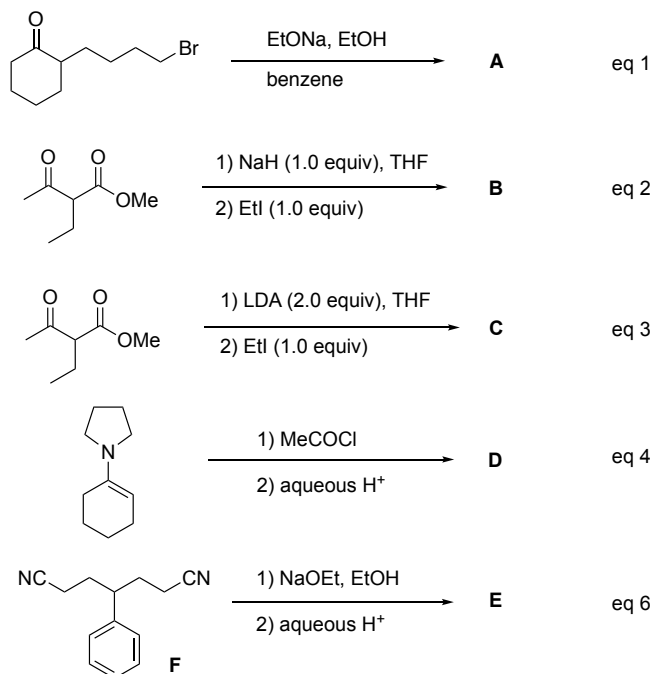
Problem 5 (10 pts)

Reaction of boron enolate with aldehyde is highly stereoselective. The *Z* enolate afford the *syn*-aldol **A**, while the *E* enolate provided the *anti*-aldol **B**. Please propose a transition state for both reactions to account for these experimental observation.



Problem 6 (18 pts)

- a) Please provide the structures of compounds **A**, **B**, **C**, **D** and **E**.
 b) Please propose a detailed mechanism for the conversion of **F** to **E**



Problem 7 (14 pts)

Provide the structures of **A**, **B**, **C**, **D**, **E**, **F** and **G**

