Chemistry 4321/8321	**Midterm Examination I** 6:00 – 8:00 PM	October 11, 2023
Organic Synthesis		T. R. Hoye

Name: ANSWERS

Part I	/ 16
Part II	/ 20
Part III	/ 20
Part IV	/ 44
Total	/100

Clearly **print** your name above.

There are 100 points and four questions on the exam.

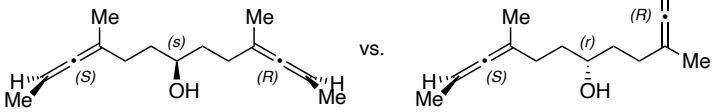
Answer all questions directly in the space provided on the five exam pages.

You may not use books, notes, phones, computers, etc.

Our diamond lattice is attached as a final page for your use, should you like.

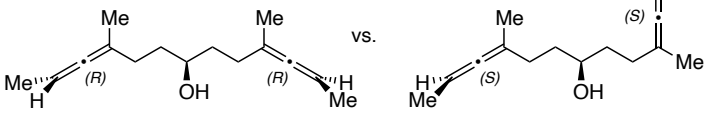
I. (**16 points**) For parts **a**-**c** indicate (circle the word) whether the two structures are the *same*, a pair of *enantiomers*, or a pair of *diastereomers*. *If* they are diastereomers, indicate the number of stereogenic centers that are different in the two structures. Ignore differences in conformation. For part d indicate (circle the word) whether the indicated pairs of atoms or groups are *homotopic*, *diastereotopic*, or *enantiotopic*.

4 **a)**



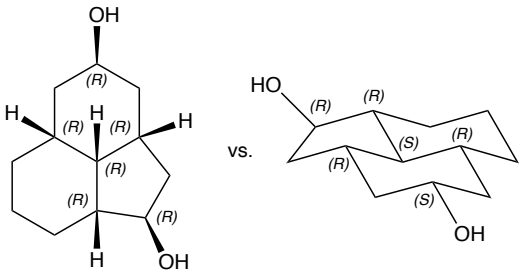
same enantiomeric **diastereomeric** (if so, how many stereogenic centers are different?) **1**

2 **b)**



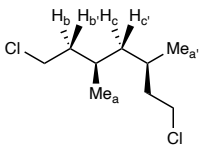
same **enantiomeric** diastereomeric (if so, how many stereogenic centers are different?)

4 **c)**



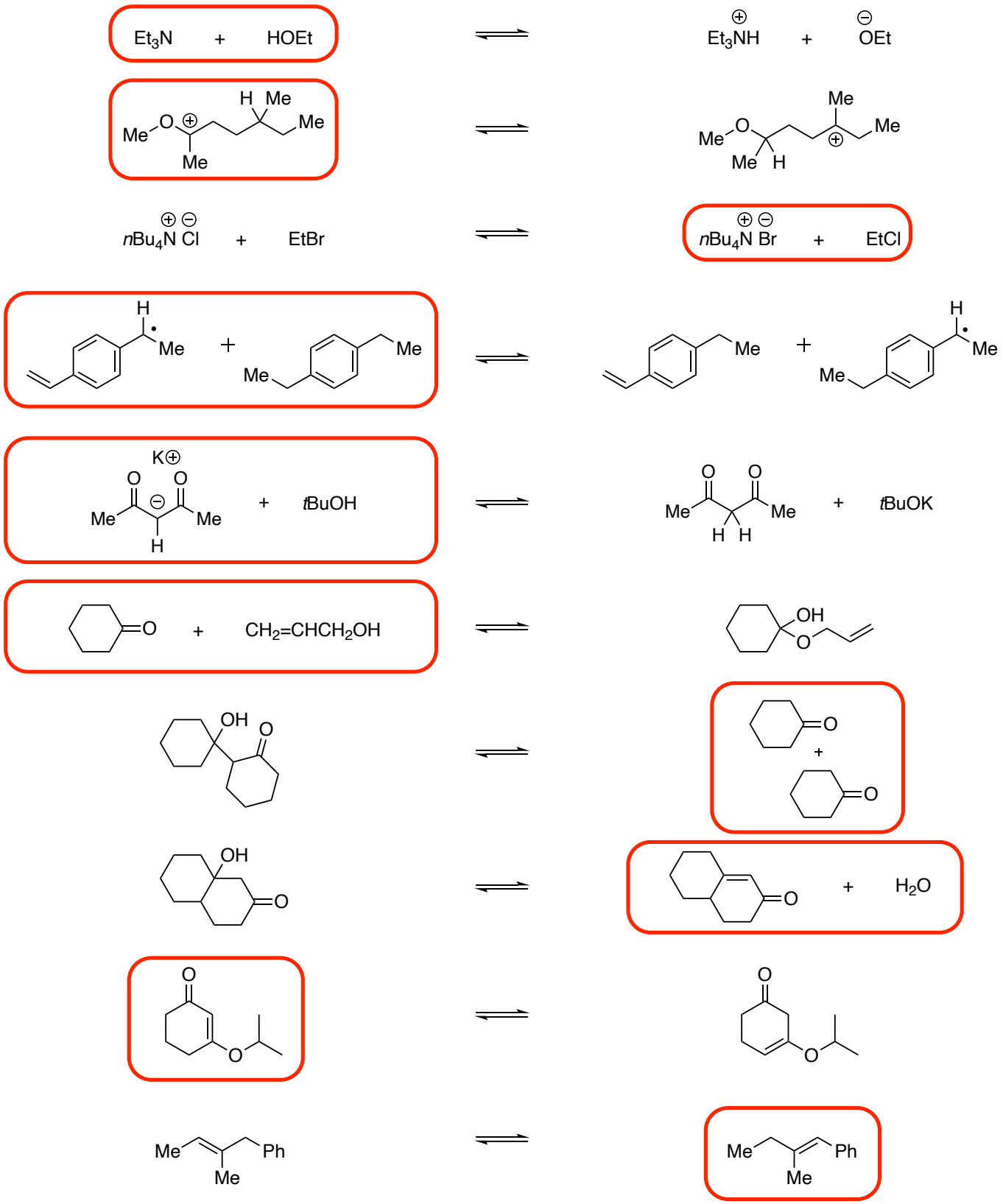
same enantiomeric **diastereomeric** (if so, how many stereogenic centers are different?) **2**

6 **d)**



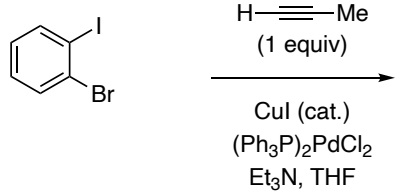
Me_a / $Me_{a'}$	**homotopic**	diastereotopic	enantiotopic
H_b / $H_{b'}$	homotopic	**diastereotopic**	enantiotopic
H_c / $H_{c'}$	**homotopic**	diastereotopic	enantiotopic

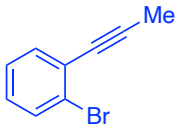
II. **(20 points)** Decide whether each of the following **equilibria** lies predominantly to the **left** or to the **right** as a solution in an organic solvent. **Circle** the species on the side that is more stable (i.e., lower in free energy and more highly populated at equilibrium).



III. (20 points) Provide the structure of the major product in each of the reactions **a**)-**e**).

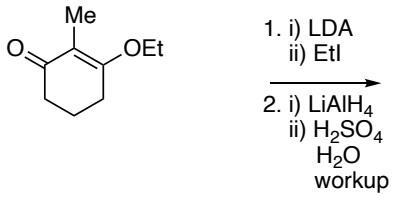
a)

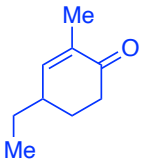




C_9H_7X

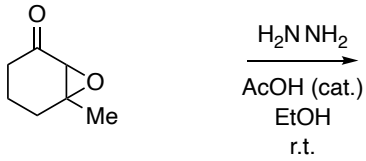
b)

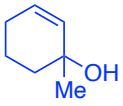




$C_9H_{14}O$

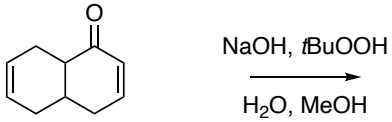
c)

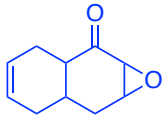




$C_7H_{12}O$

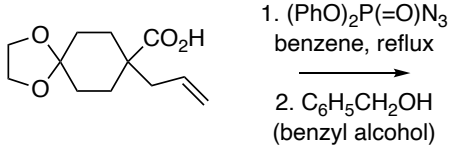
d)

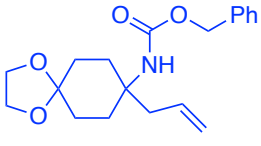




$C_{10}H_{12}O_2$

e)

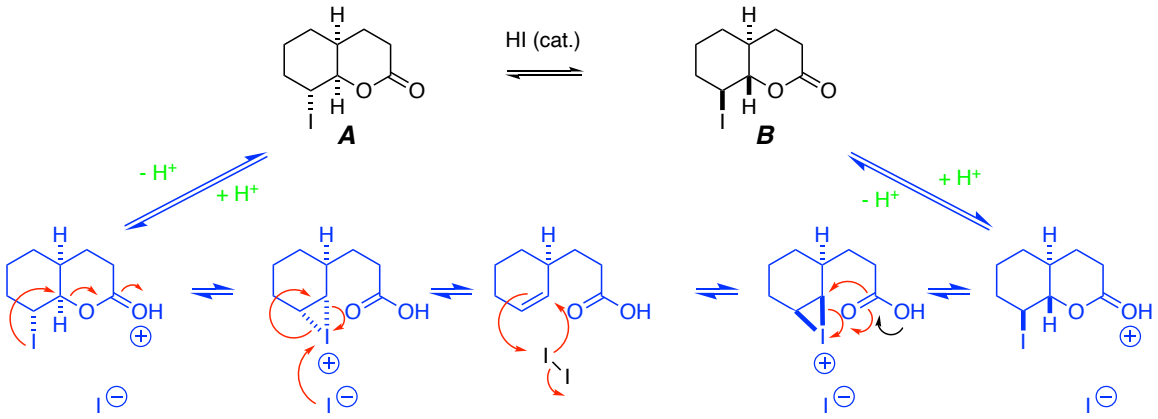




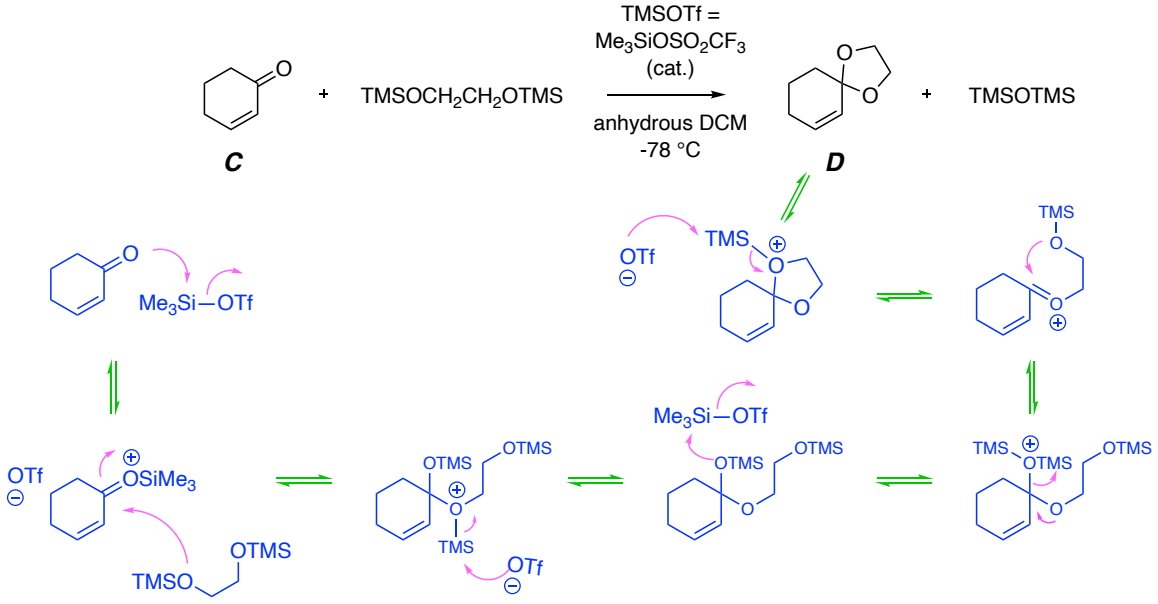
$C_{19}H_{25}NO_4$

IV. (44 pts) Provide a *detailed mechanism* to account for each of the following four reactions. Show *ALL* intermediates, equilibria, and bond-making and -breaking steps. For species that have more than one significant resonance contributor, you only need to show one of them.

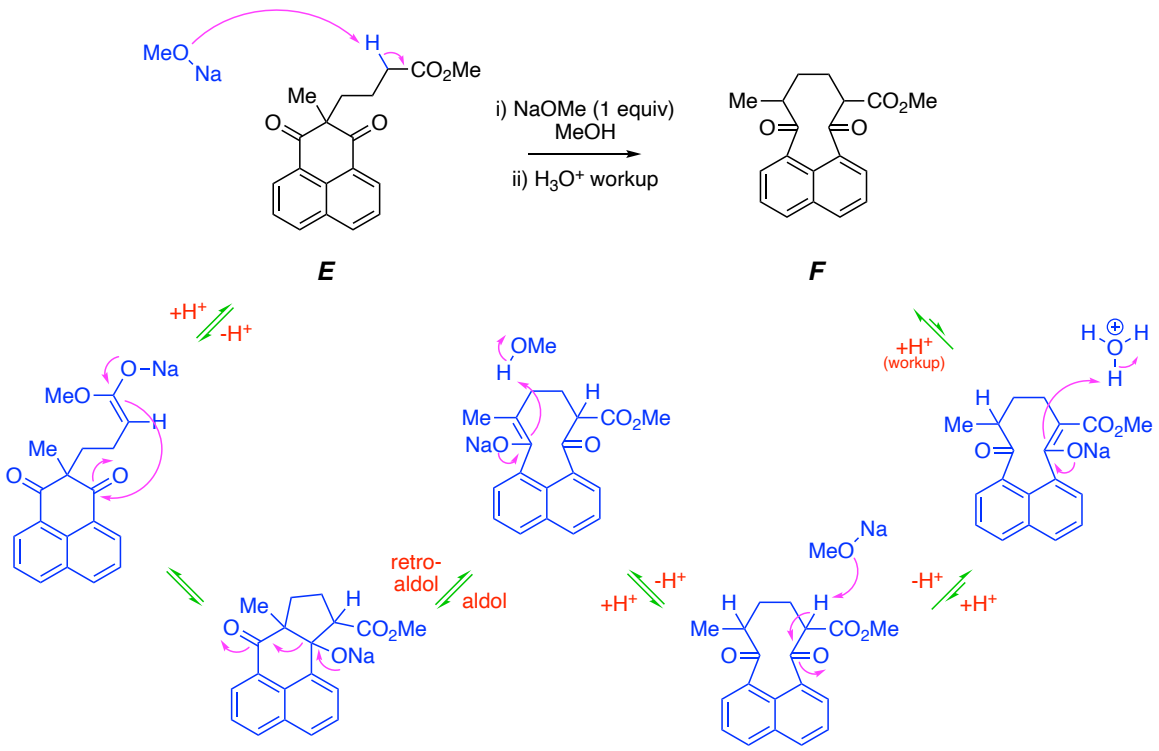
a) **(10)** The **isomerization** (i.e., there is no byproduct formed) of the cis-fused iodolactone **A** to the more stable, trans-fused diastereomer **B**. There is no water in this reaction (i.e., anhydrous HI is the Bronsted acid used to catalyze the process). [*hints:* recall the iodolactonization reaction and that iodonium ions can form reversibly when iodine engages an alkene.]



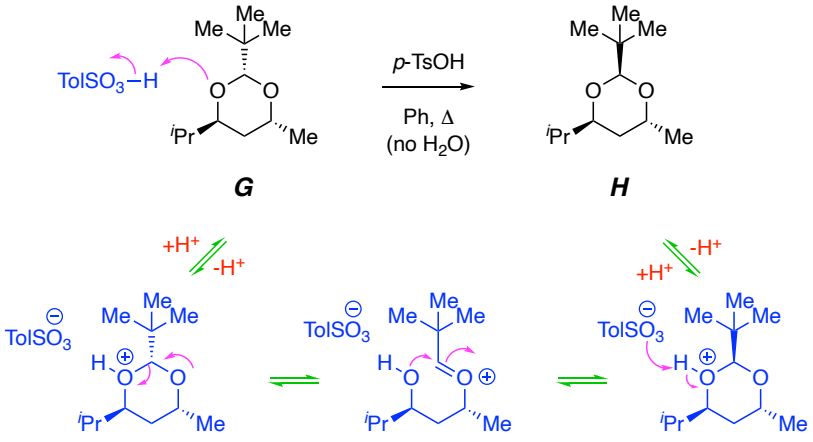
b) **(12)** The TMSOTf-catalyzed, low-temperature ketalization of cyclohexenone (**C**) to produce **D**. [*hints:* recall that a TMS group is often a surrogate for a hydrogen atom and there are no protic (i.e., Bronsted) acids present in the reaction mixture.]



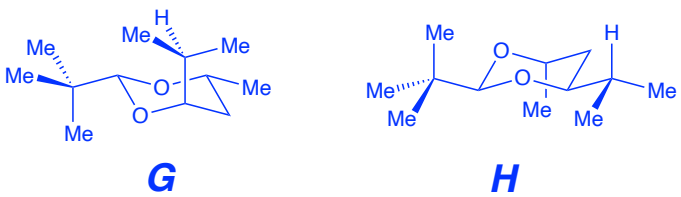
c) (**10**) The **isomerization** of the β-diketone **E** to the β-ketoester **F**.



d) (**6**) The **isomerization** (an epimerization) of acetal **G** to the more stable acetal **H**.



e) (**6**) Draw the most stable **conformation** of i) the starting material **G** and of ii) the product **H** in the above reaction.



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