

Name: ANSWERS

Please clearly print your name above.

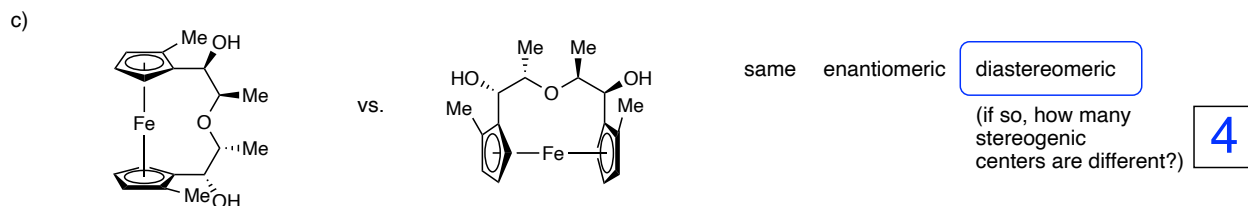
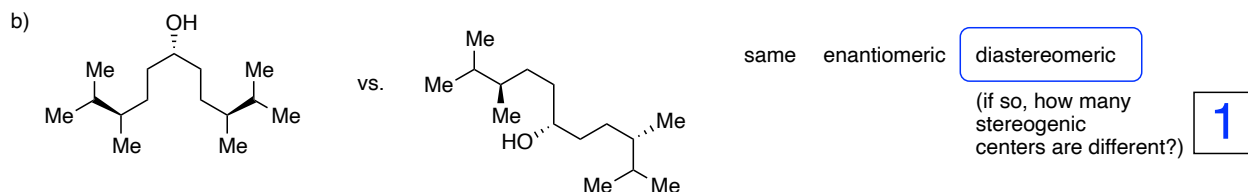
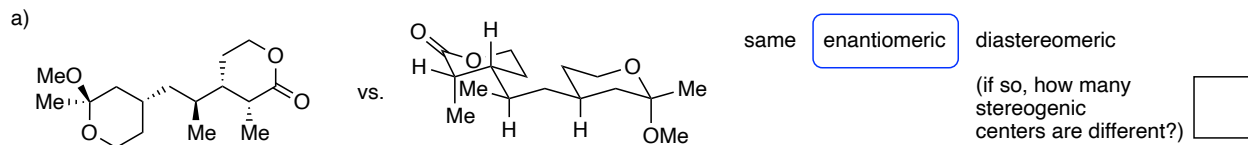
There are 160 points and eight questions on the exam.

Answer all questions directly in the space provided on the six exam pages (a diamond lattice has been provided on a seventh page).

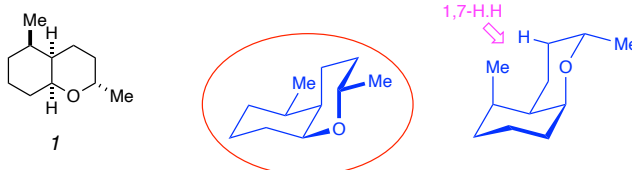
You may not use books, notes, phones, etc.

Part I 15 / 15Part II 9 / 9Part III 16 / 16Part IV 16 / 16Part V 16 / 16Part VI 15 / 15Part VII 25 / 25Part VIII 48 / 48Total 160 / 160

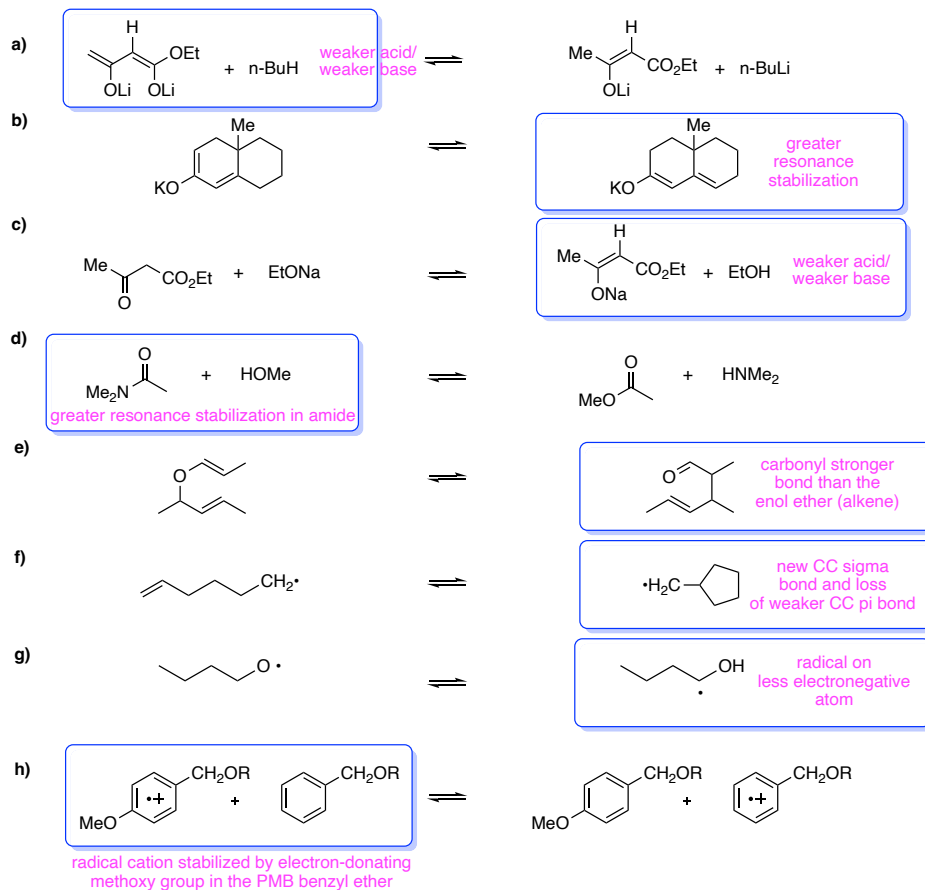
**I. (15 points)** Indicate (circle the word) whether the two stereoisomers for the following pairs of structures are the *same*, a pair of *enantiomers*, or a pair of *diastereomers*. If they are diastereomers, indicate the number of stereogenic centers that are different in the two structures. Ignore differences in conformation.



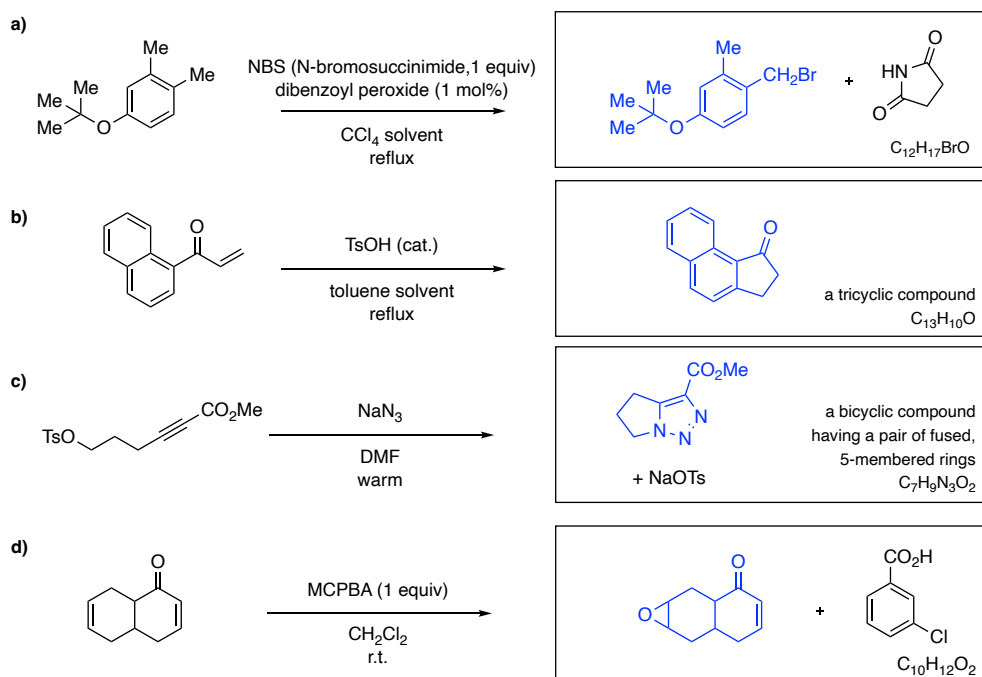
**II. (9 points)** The fused, bicyclic ether **1** can exist in either of two, cis-decalin-like conformations. In each, the two six-membered rings are chair-like. Provide the structure of each of these two conformations of **1**. Circle the more stable conformer.



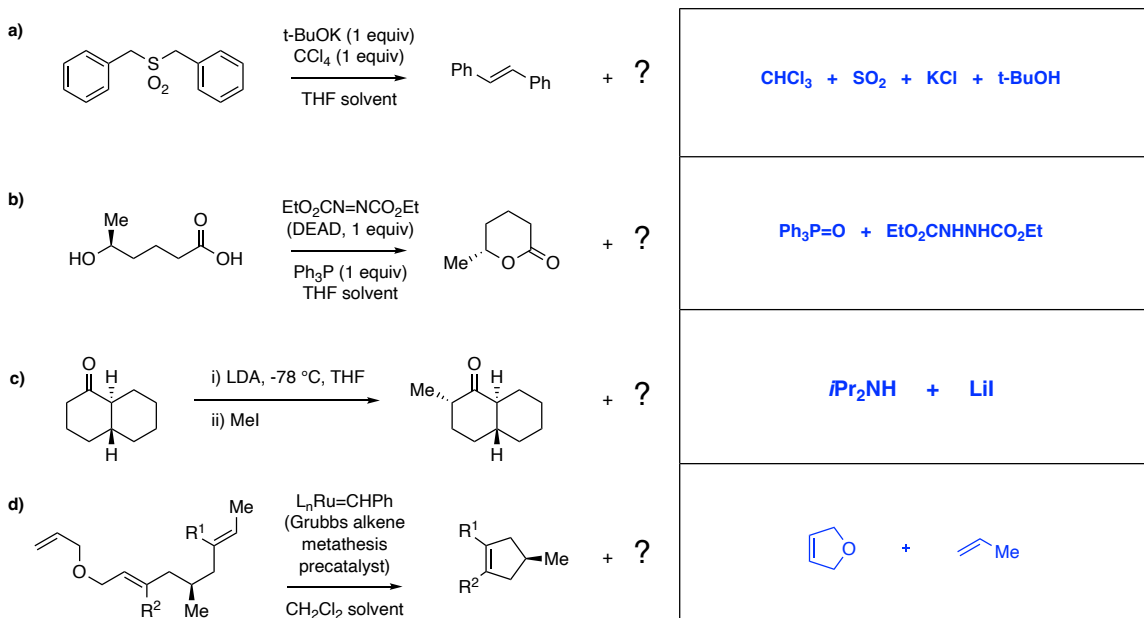
**III. (16 points)** Indicate whether each of the following equilibria lies predominantly to the left or to the right by circling the side corresponding to the more stable species.



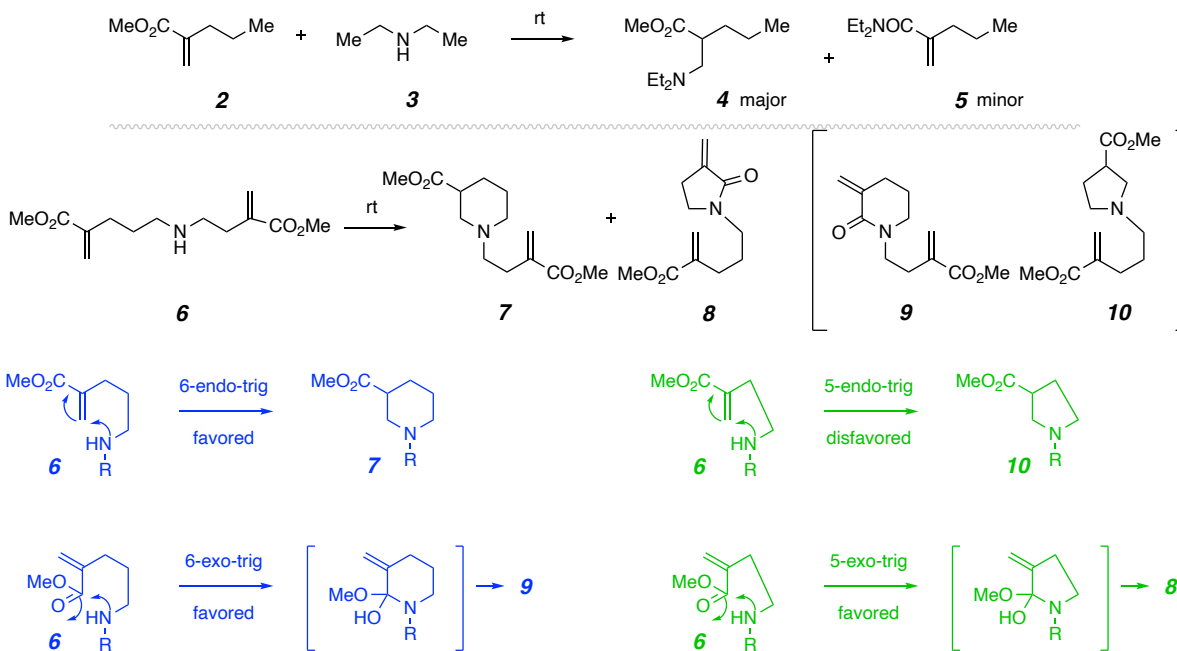
**IV. (16 points)** Provide the structure for the major product expected from each of the reactions a)-d). The molecular formula of the missing product is given in the lower right corner of each box.



**V. (16 points)** Provide the structure(s) of the byproduct(s) that, together with the provided main product, constitute(s) a stoichiometrically and fully balanced reaction equation for each of the following four (a-d) transformations. Note that in many instances, there is more than one byproduct.

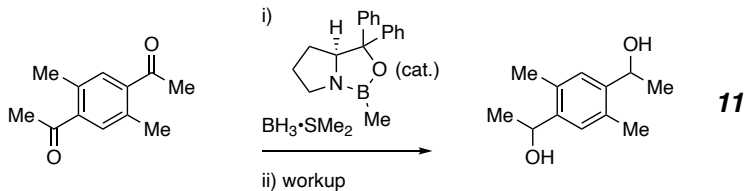
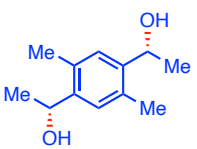
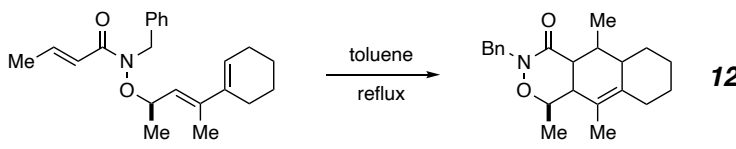
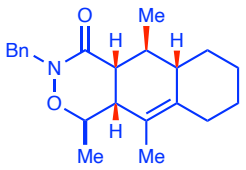
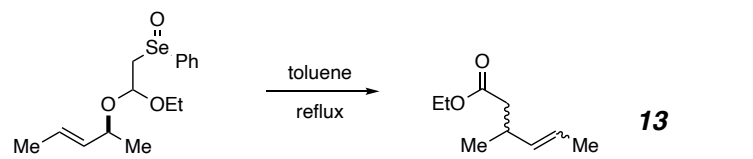
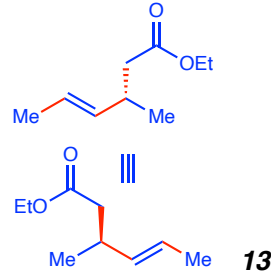
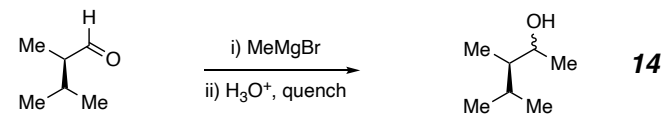
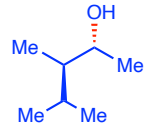
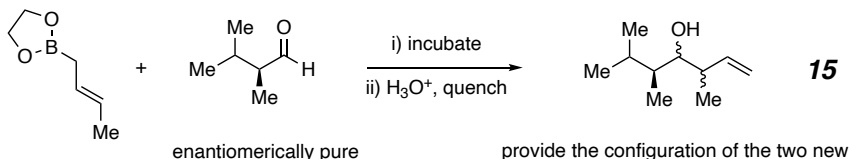
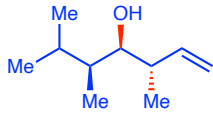


**VI. (15 points)** Facts: enoate **2** reacts with diethylamine (**3**) to provide, as the major product, the conjugate addition (i.e., aza-Michael) adduct **4** along with only a small amount of the amide **5**. Accordingly, the secondary amine **6** is a substrate that can be expected to give the amine **7** and lactam (cyclic amide) **8** as the principal products of intramolecular cyclization. Use Baldwin's rules for ring closure and the inherent preference for reactivity of amine **3** with enoate **2** to rationalize why **7** and **8** are the expected major products from **6** rather than the isomeric lactam **9** and amine **10**.



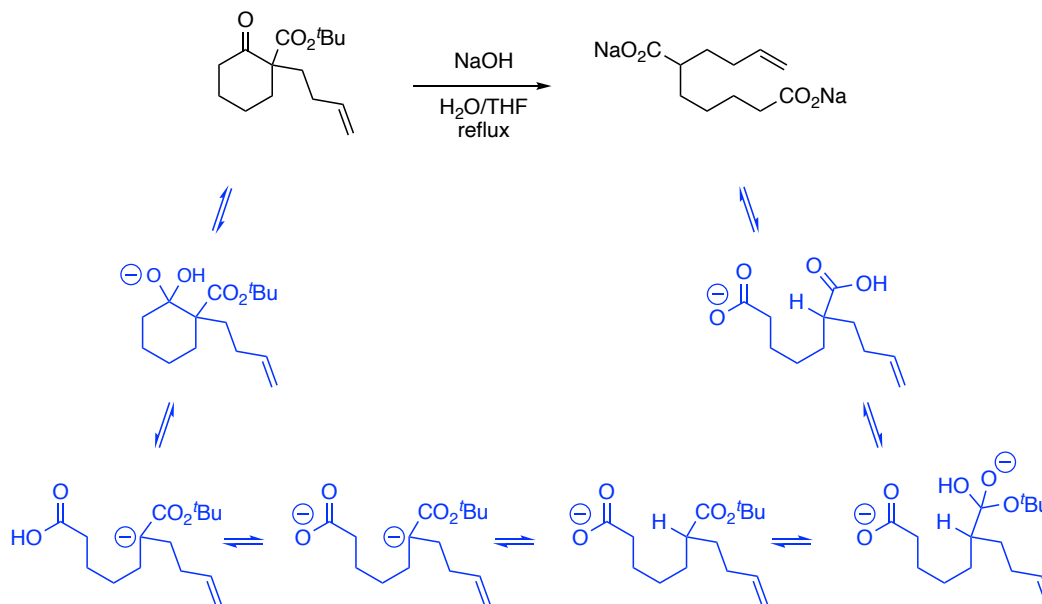
As learned from the formation of mostly **7** and a minor amount of **8**, the inherent energetic preference, in the absence of conformational and geometric constraints, is for conjugate addition of the secondary amine to the acrylate derivative rather than for amidation. Thus, in the formation of a six membered ring, for which both conjugate addition and amide formation are favored in the Baldwin sense, formation of amine **7** is preferred to lactam **9**. In contrast, with respect to formation a five-membered ring, amine **10** would involve a disfavored (5-endo-trig) geometry. Hence lactam **8** is preferred.

**VII. (25 points)** The constitution of the major product from each of the following five reactions is provided. For each of **11–15**, draw, in the box at the right, the fully defined structure of the major stereoisomer that you expect to be formed. (Hint: for the third example, recall that selenoxides will undergo thermal elimination of PhSeOH to produce an alkene.)

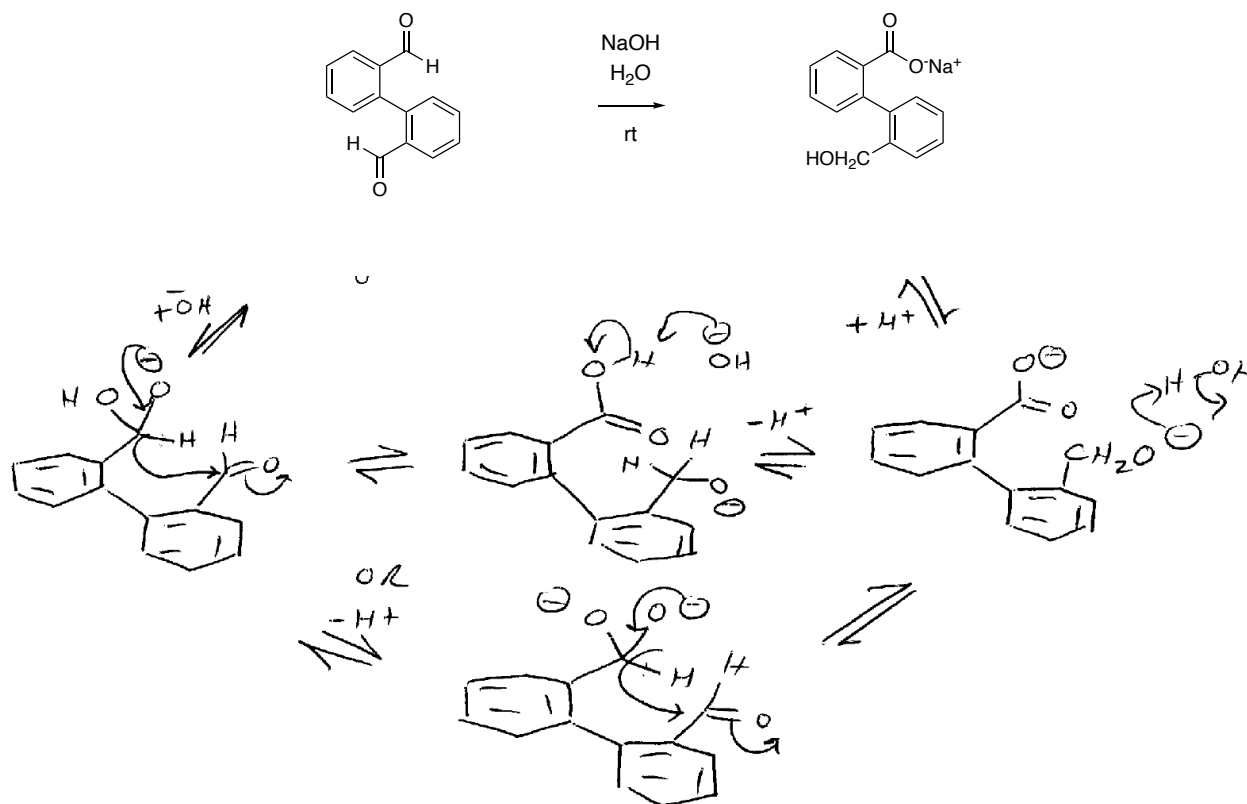
 <p>enantiomerically pure</p> <p>i) <math>\text{BH}_3 \cdot \text{SMe}_2</math> ii) workup</p> <p>provide the configuration of the two new stereogenic centers</p> <p><b>11</b></p>	 <p><b>11</b></p>
 <p>enantiomerically pure</p> <p>toluene reflux</p> <p>provide the configuration of the four new stereogenic centers</p> <p><b>12</b></p>	 <p><b>12</b></p>
 <p>enantiomerically pure</p> <p>toluene reflux</p> <p>provide both the alkene geometry and the configuration of the new stereogenic carbon atom</p> <p><b>13</b></p>	 <p><b>13</b></p>
 <p>enantiomerically pure</p> <p>i) MeMgBr ii) <math>\text{H}_3\text{O}^+</math>, quench</p> <p>provide the configuration of the two new stereogenic centers, which arise via Felkin-Ahn-controlled addition and a chair like transition-state geometry</p> <p><b>14</b></p>	 <p><b>14</b></p>
 <p>enantiomerically pure</p> <p>i) incubate ii) <math>\text{H}_3\text{O}^+</math>, quench</p> <p>provide the configuration of the two new stereogenic centers, which arise via Felkin-Ahn-controlled addition and a chair like transition-state geometry</p> <p><b>15</b></p>	 <p><b>15</b></p>

**VIII. (48 points)** 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.

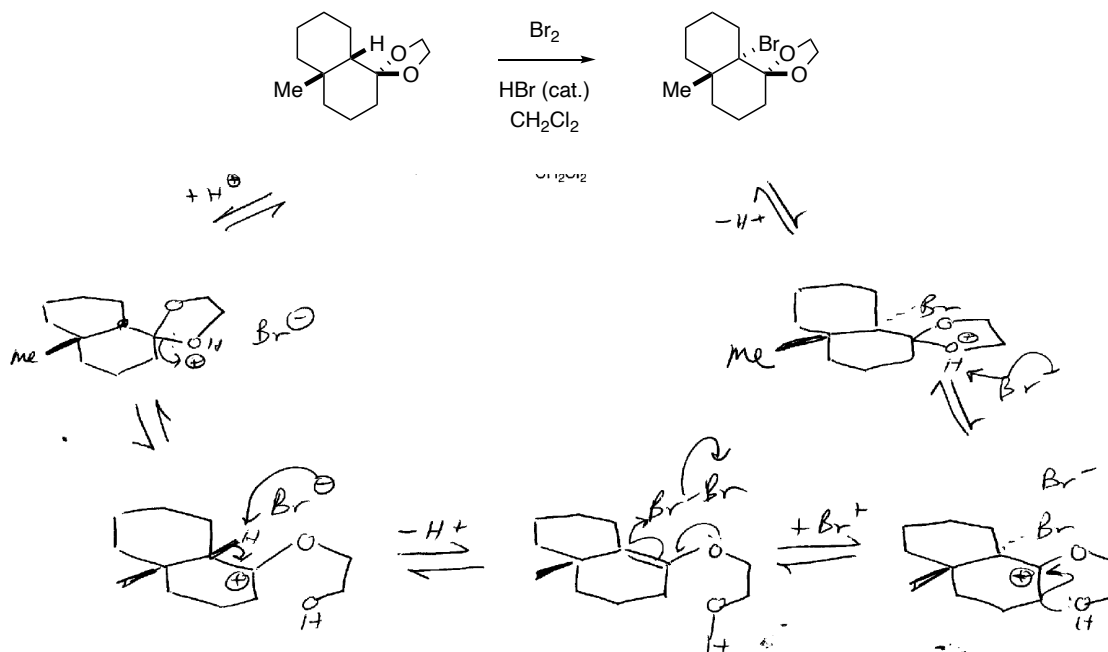
**a) (18 points)** (Hint: some of the intermediates are acyclic t-butyl esters)



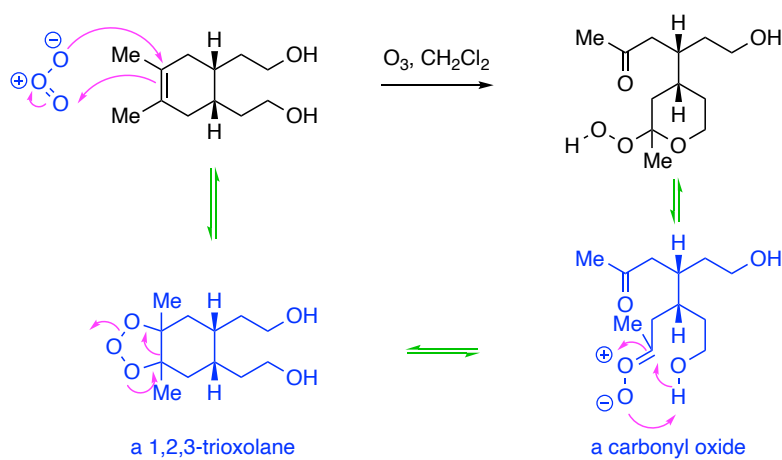
**b) (9 points)** This is an intramolecular Cannizzaro reaction.



c) (15 points) This reaction is autocatalytic because HBr, a byproduct of the reaction, further catalyzes the transformation. (Hint: think about the mechanistic implications of the change from a cis- to a trans-fused decalin in the starting substrate vs. product, respectively.)



d) (6 points)



\* \* \* end of exam \* \* \*

