Massachusetts Institute of Technology 5.13, Fall 2006

EXAM 4 EXTRA PROBLEMS

1. Provide the best mechanism for the following reaction.

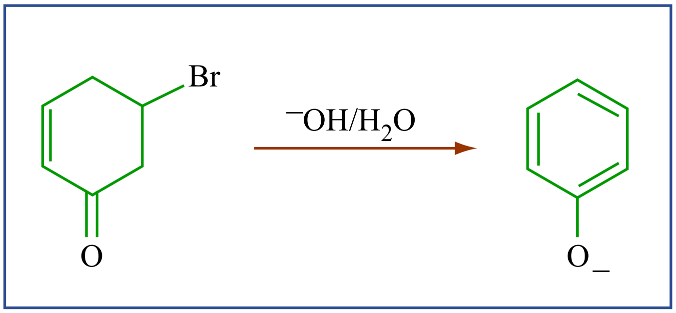

Figure by MIT OCW.

2. A useful diketone, dimedone, can be prepared in high yield by the synthesis below. Provide structures for the intermediate A and for dimedone, and show a mechanism for each step up to B.

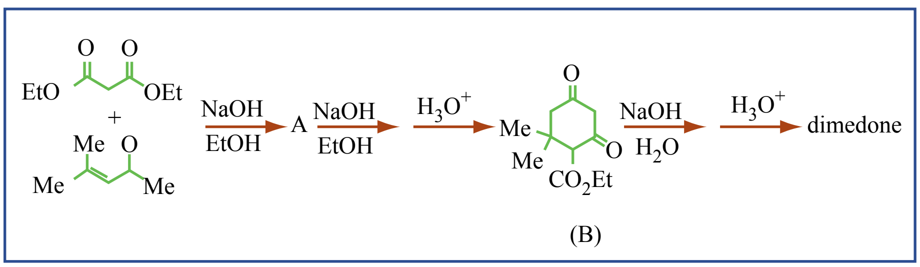

Figure by MIT OCW.

3. A biochemist, Sal Monella, has come to you to ask your assistance in testing a promising biosynthetic hypothesis. She wishes to have two samples of methylsuccinic acid specifically labeled with ^{14}C as shown below. The source of the isotope, for financial reasons, is the salt $Na^{14}CN$. Outline a synthesis that will accomplish this objective.

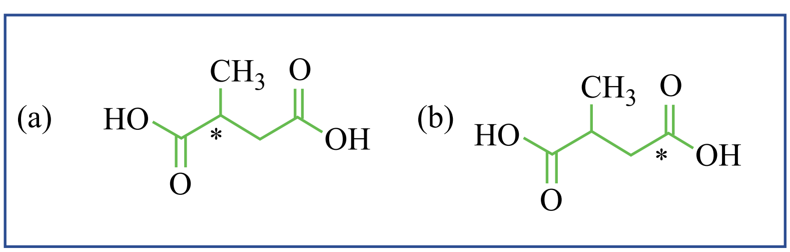

Figure by MIT OCW.

4. In early 1999, chemists from Tohoku Univerwsity in Japan reported that they had achieved the transformation shown below. In this equation, B: is a base strong enough to form enolate ions. Propose a reasonable mechanism for this transformation. (L 22.87)

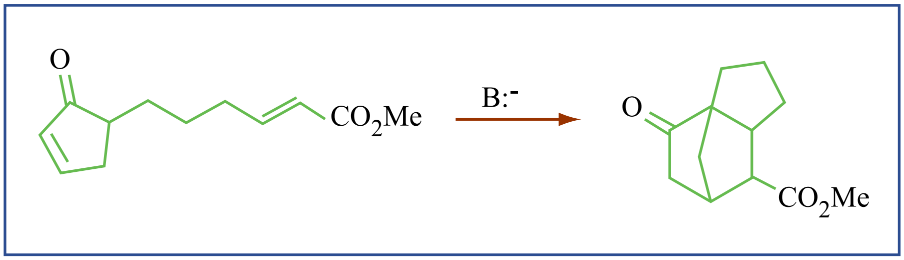

Figure by MIT OCW.

5. With the aid of three-dimensional drawings, provide a clear rationale for the products that are observed in the following transformations. Your rationale must include the mechanism for each transformation.

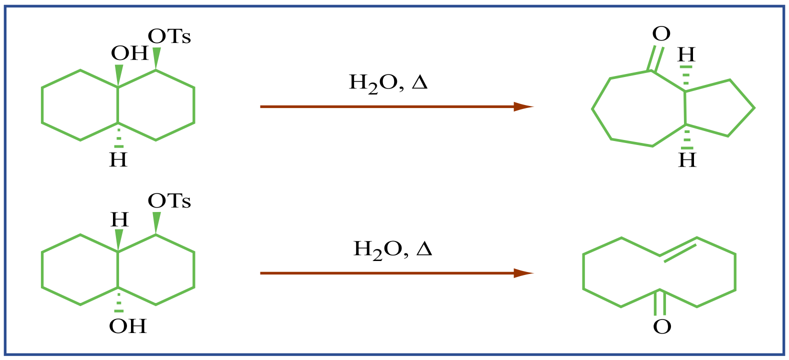

Figure by MIT OCW.

6. Please provide a detailed mechanism for the illustrated transformation.

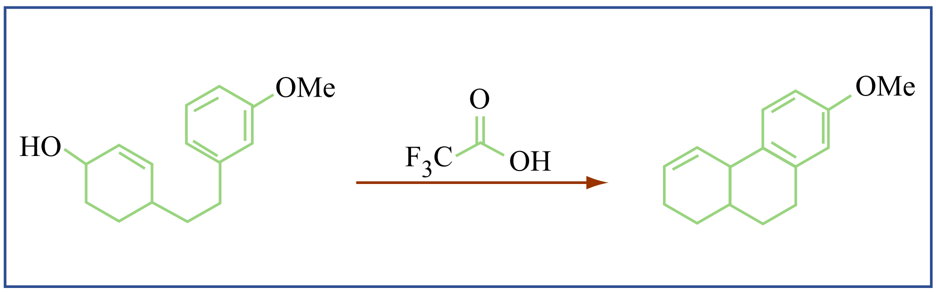

Figure by MIT OCW.

7. Please provide a detailed mechanism that accounts for the formation of all three of the observed products.

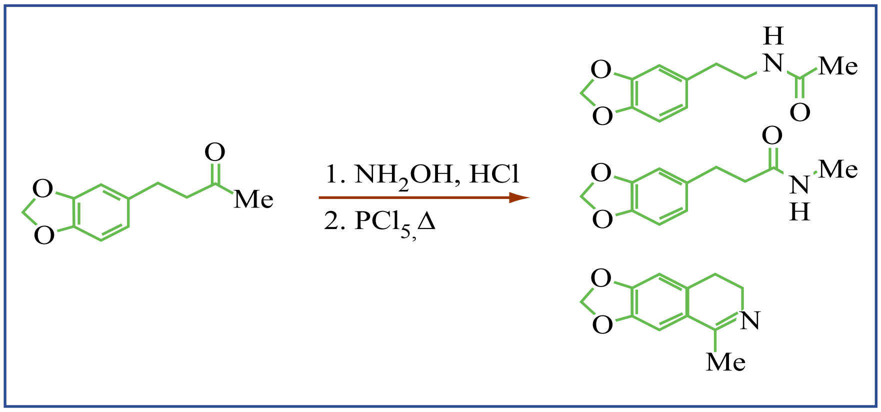

Figure by MIT OCW.

8. a). Please provide a rationale for the illustrated rate data.

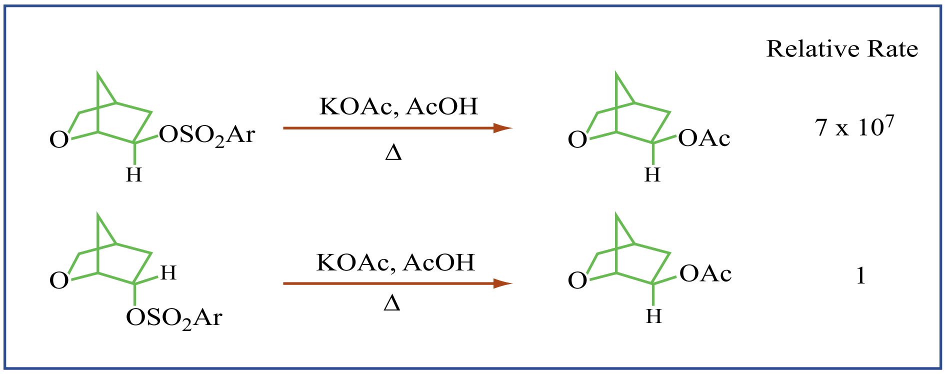

Figure by MIT OCW.

b). Please provide a mechanism to account for the formation of the products illustrated below. In addition, explain why no other stereoisomers are generated in the reaction.

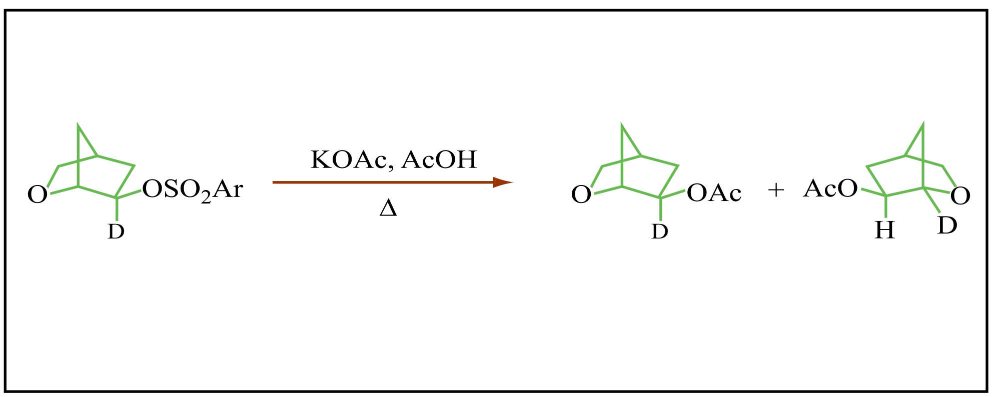

Figure by MIT OCW.

9. Please provide a detailed mechanism for the illustrated transformation.

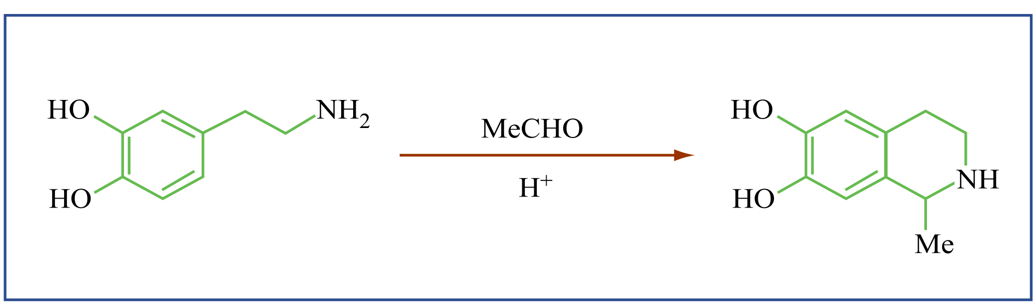

Figure by MIT OCW.

10. In the reaction illustrated below, the desired product from a simple Friedel-Crafts acylation (A) was not observed. Instead, and isomeric product (B) was generated through a more complex route that also involves Friedel-Crafts chemistry. Please provide a detailed mechanism for this unexpected process.

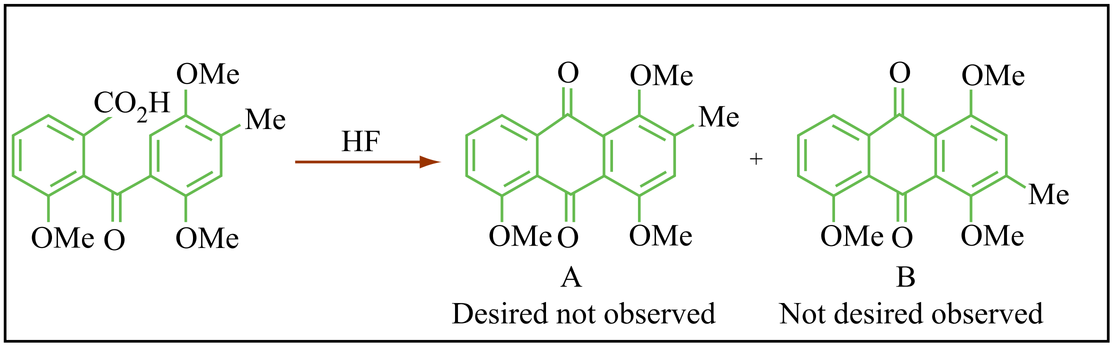

Figure by MIT OCW.

11. Provide the best mechanism. Please show all arrow pushing.

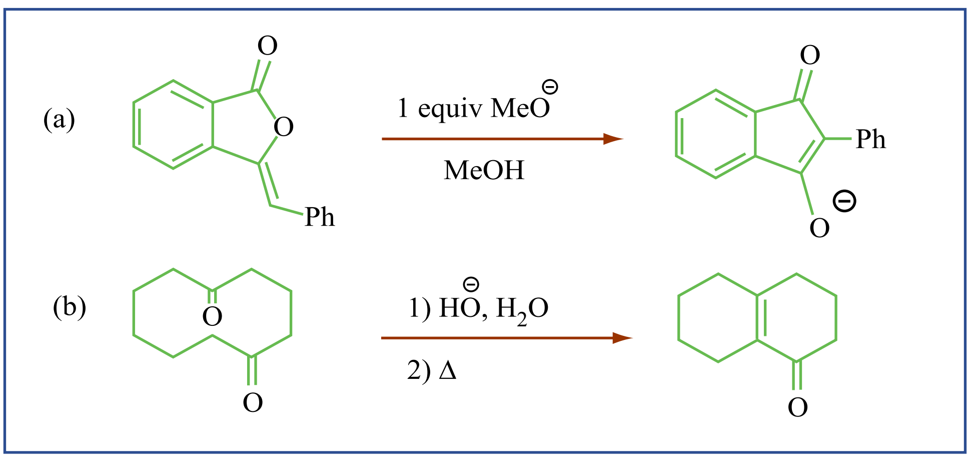

Figure by MIT OCW.

12. Propose a synthesis for each of the following compounds, starting with benzyl alcohol ($PhCH_2OH$) and with alcohol that contains three or fewer carbons.

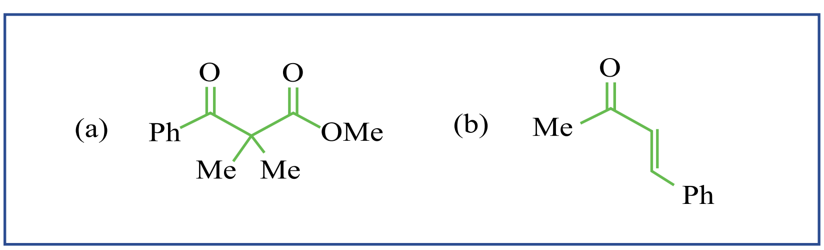

Figure by MIT OCW.

13. Provide a mechanism for the illustrated transformation that is consistent with the carbon-13 labeling results. Please show arrow pushing.

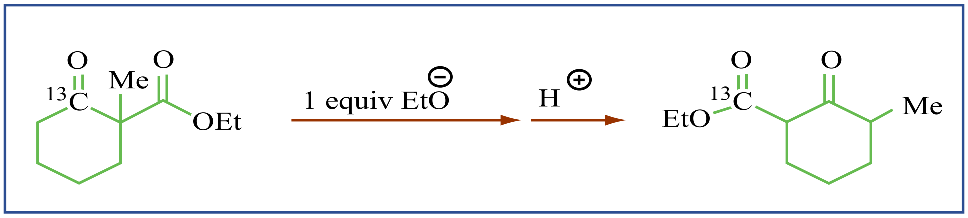

Figure by MIT OCW.

14. Provide a mechanism. Please show arrow pushing.

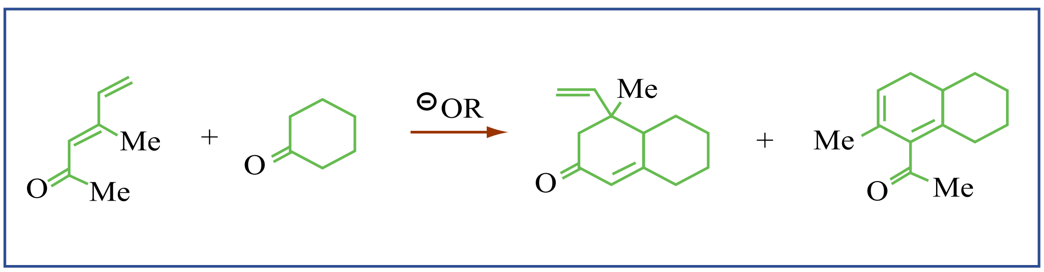

Figure by MIT OCW.

15. Propose a synthesis for the molecules on the right using the starting materials on the left and any one-carbon organic molecules.

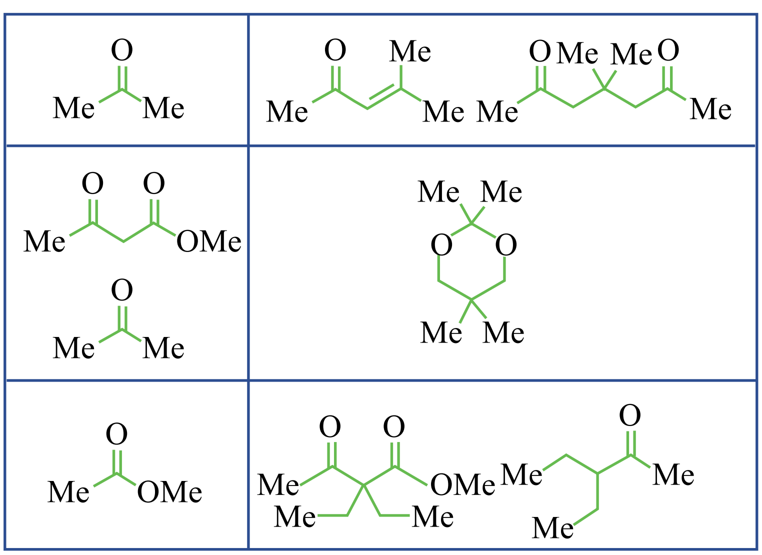

Figure by MIT OCW.

16. Provide a mechanism for the illustrated reaction. Please show arrow pushing.

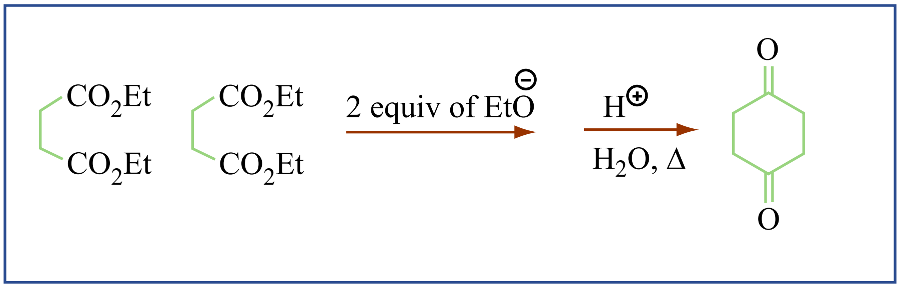

Figure by MIT OCW.

17. Provide a mechanism for the conversion of A to B and of B to C. Please show arrow pushing.

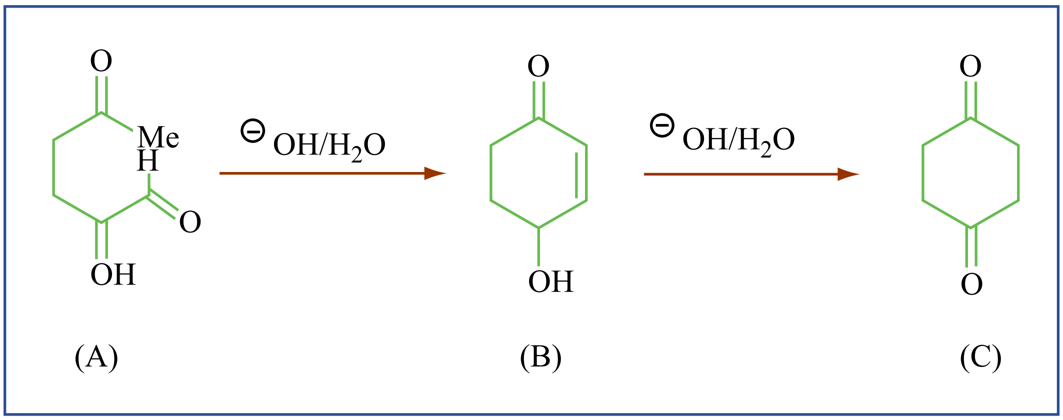

Figure by MIT OCW.

18. Provide a mechanism for the illustrated reaction. Please show arrow pushing.

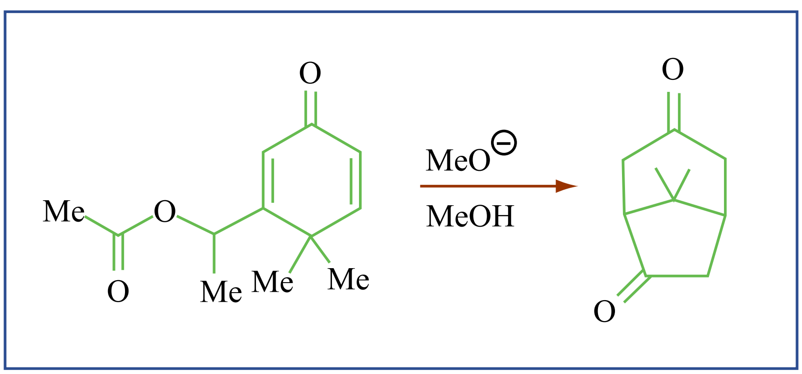

Figure by MIT OCW.

19. Provide the best mechanism. Please show all arrow pushing.

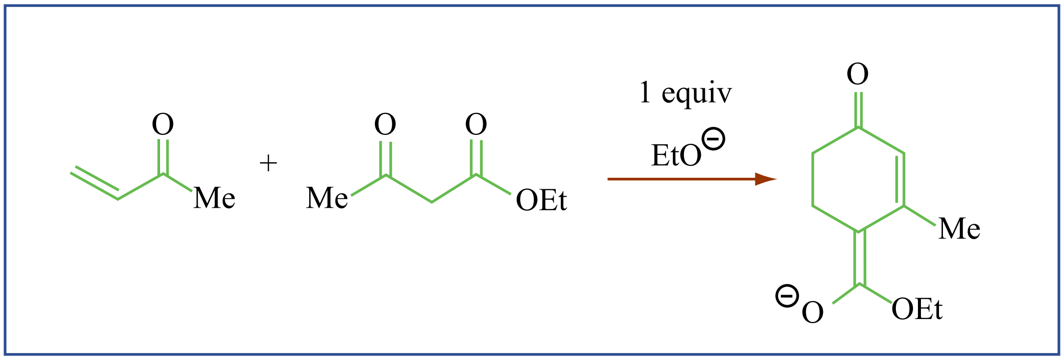

Figure by MIT OCW.

20. Provide the best mechanism for each of the reactions illustrated below. Hint: The mechanism for part (a) only requires three or four steps. Please show all arrow pushing.

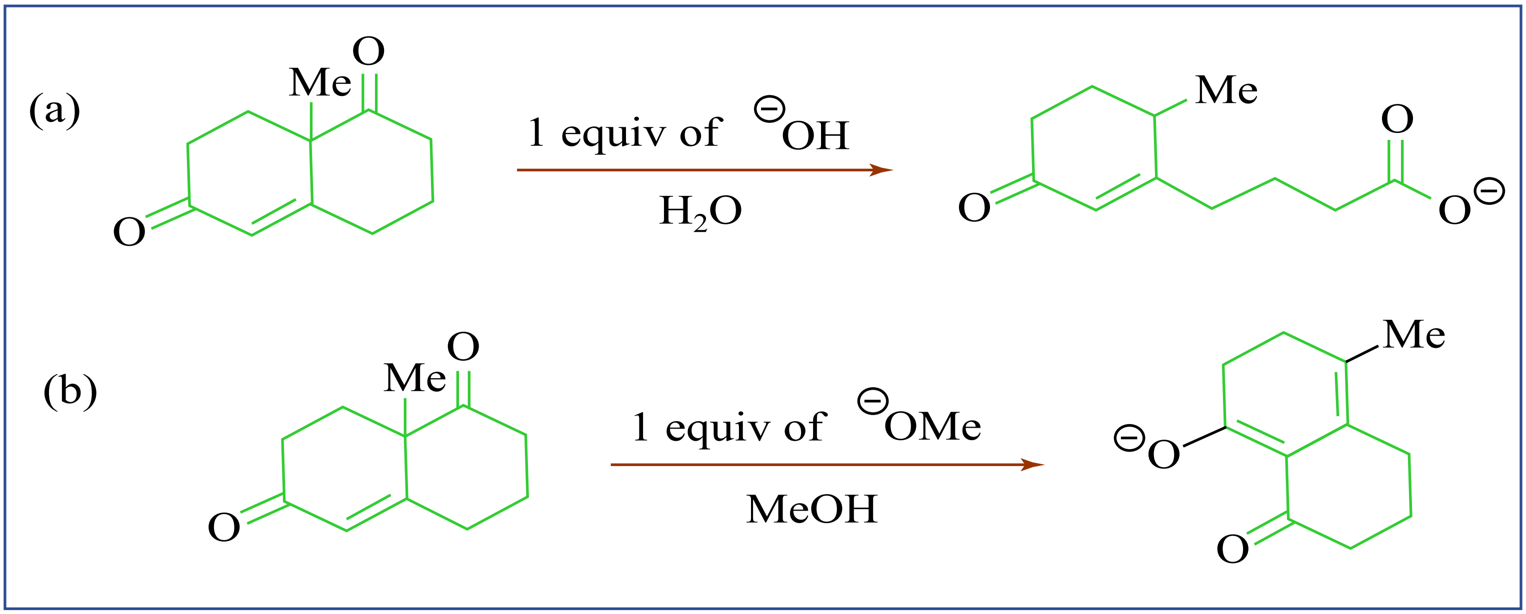

Figure by MIT OCW.

c). Succinctly explain why different pathways are observed under the different reaction conditions.

27. Diastereomers A and Bprovide different products upon diazotization. Please explain why only one product is generated selectively in each reaction. Your explanation should include three-dimensional structures (e.g., chair representations of cyclohexane rings) of the starting materials, intermediates, and products

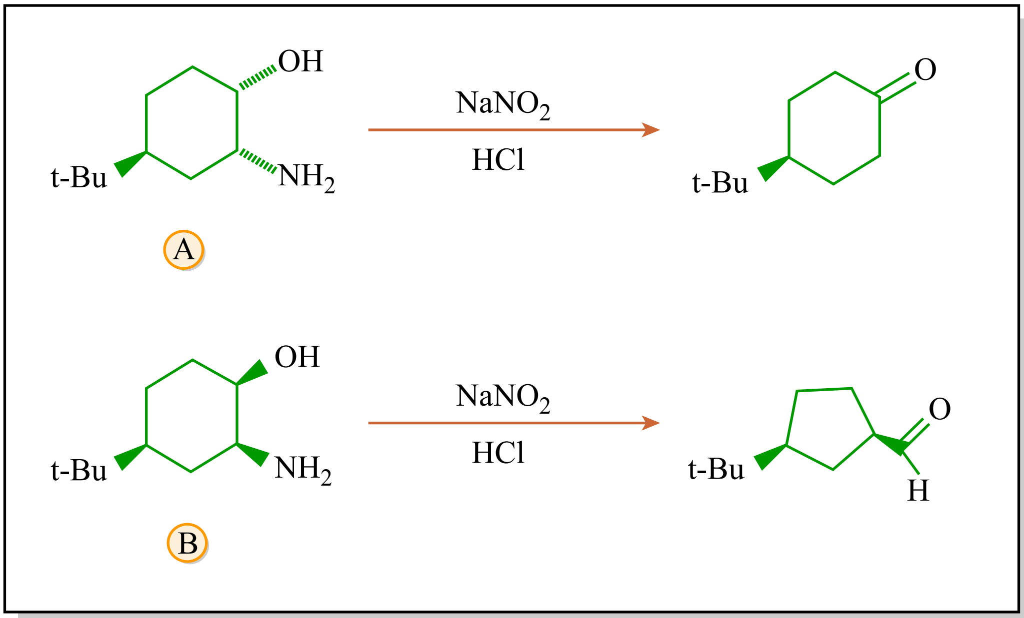

Figure by MIT OCW.