

EXAM #4 MORE PROBLEMS

DO THESE PROBLEMS BEFORE THE OTHER SET OF EXTRA PROBLEMS!

(they are more relevant to the exam material)

What to expect on Exam #4:

1. pK_a s of ketones, diketones, esters, etc.
2. ~3 Transformations – supply missing reagents
3. ~10 Transformations – supply missing product
4. ~2 Mechanisms
5. ~2 Synthesis

What NOT to expect on Exam #4:

1. Determine mechanism by crossover and stereochemical experiments (end of Friday's lecture)
2. Neighboring Group Participation – **Do not work through problems #8, 24 & 25 on the Extra Problem Set.**

1. Please provide a detailed mechanism for the following transformation. Show all arrow pushing.

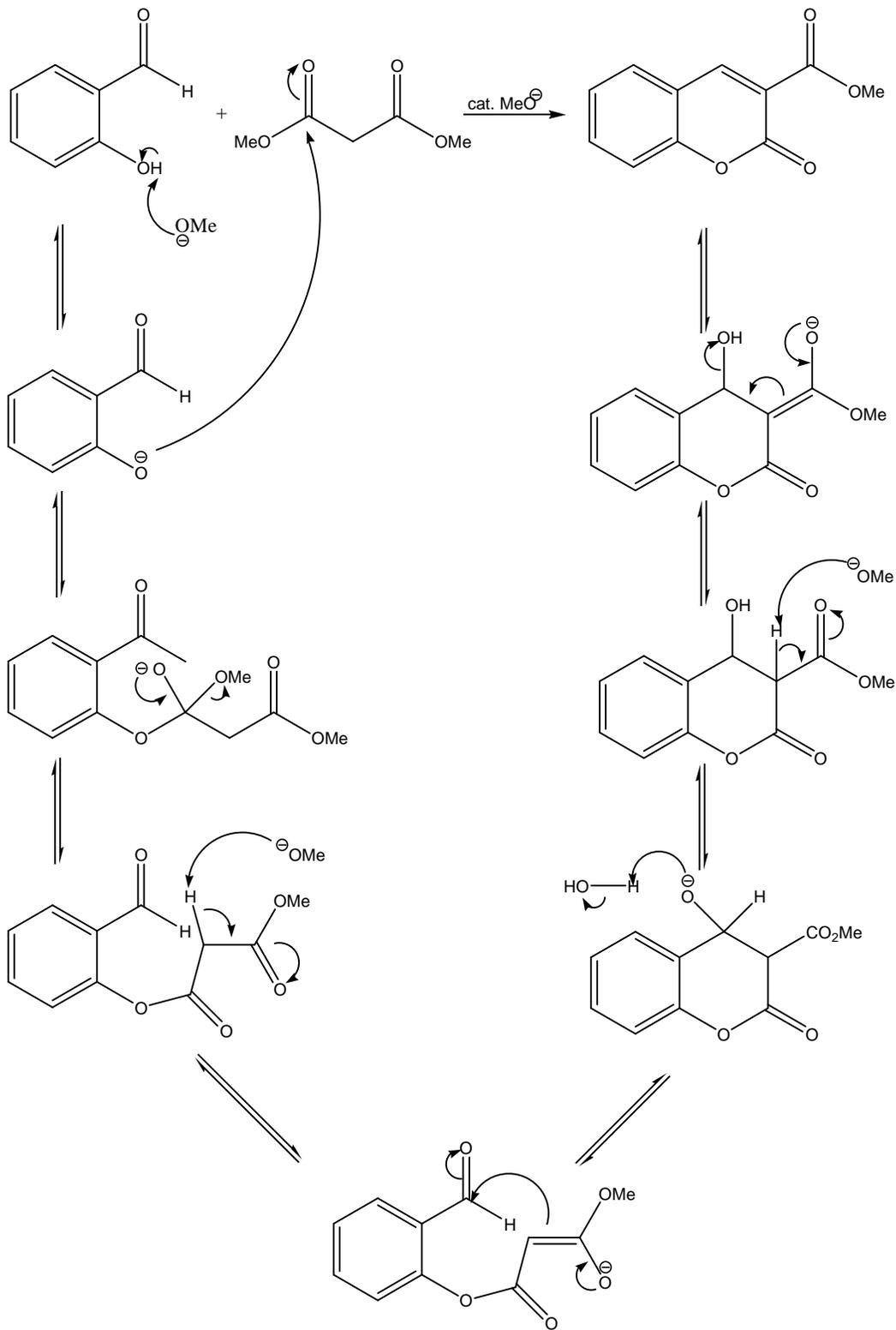


Figure by MIT OCW.

2. (10 points) Please provide a detailed mechanism for the following transformation. Show all arrow pushing.

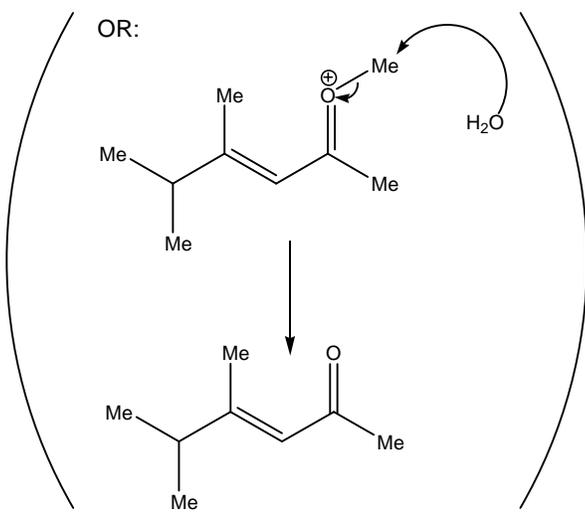
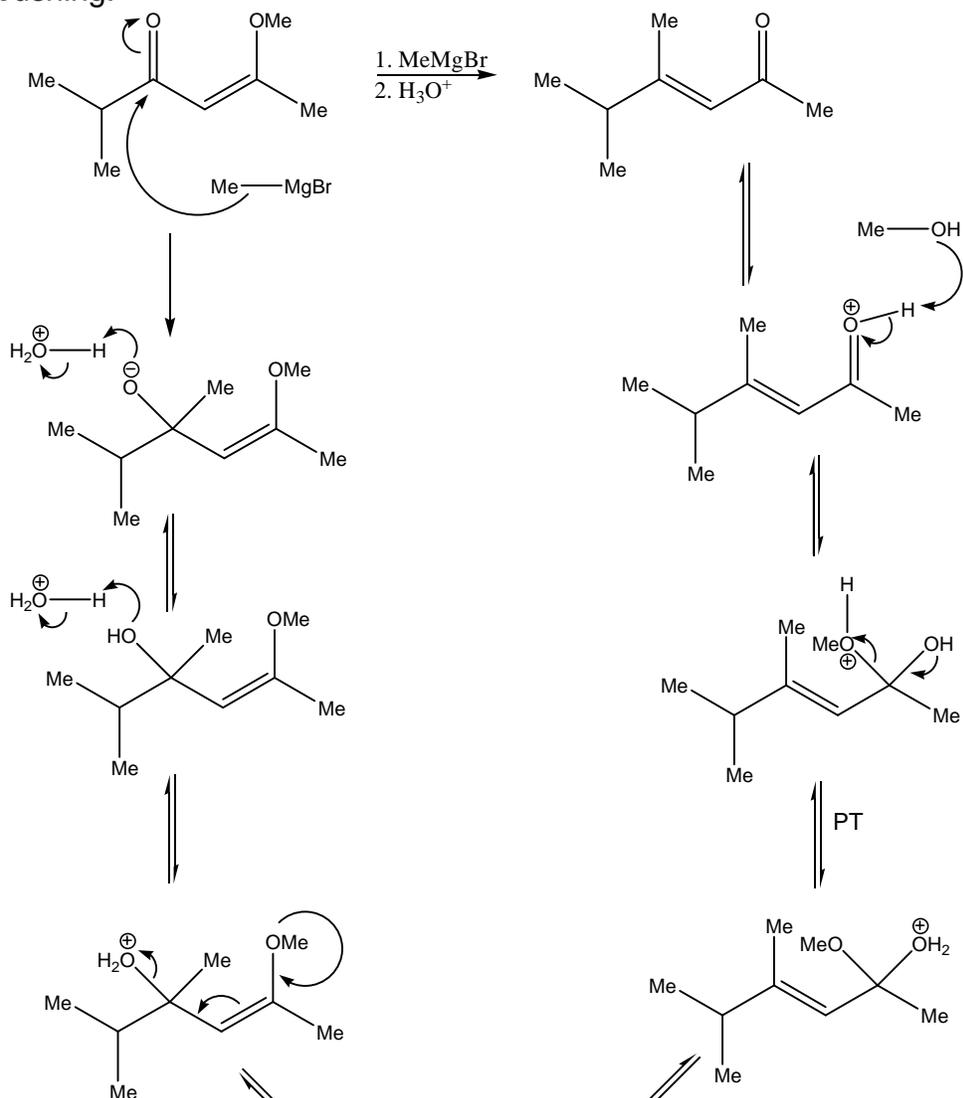


Figure by MIT OCW.

3. (10 points) Please provide a detailed mechanism for the following transformation. Show all arrow pushing. Hint: This mechanism is from problem set 6.

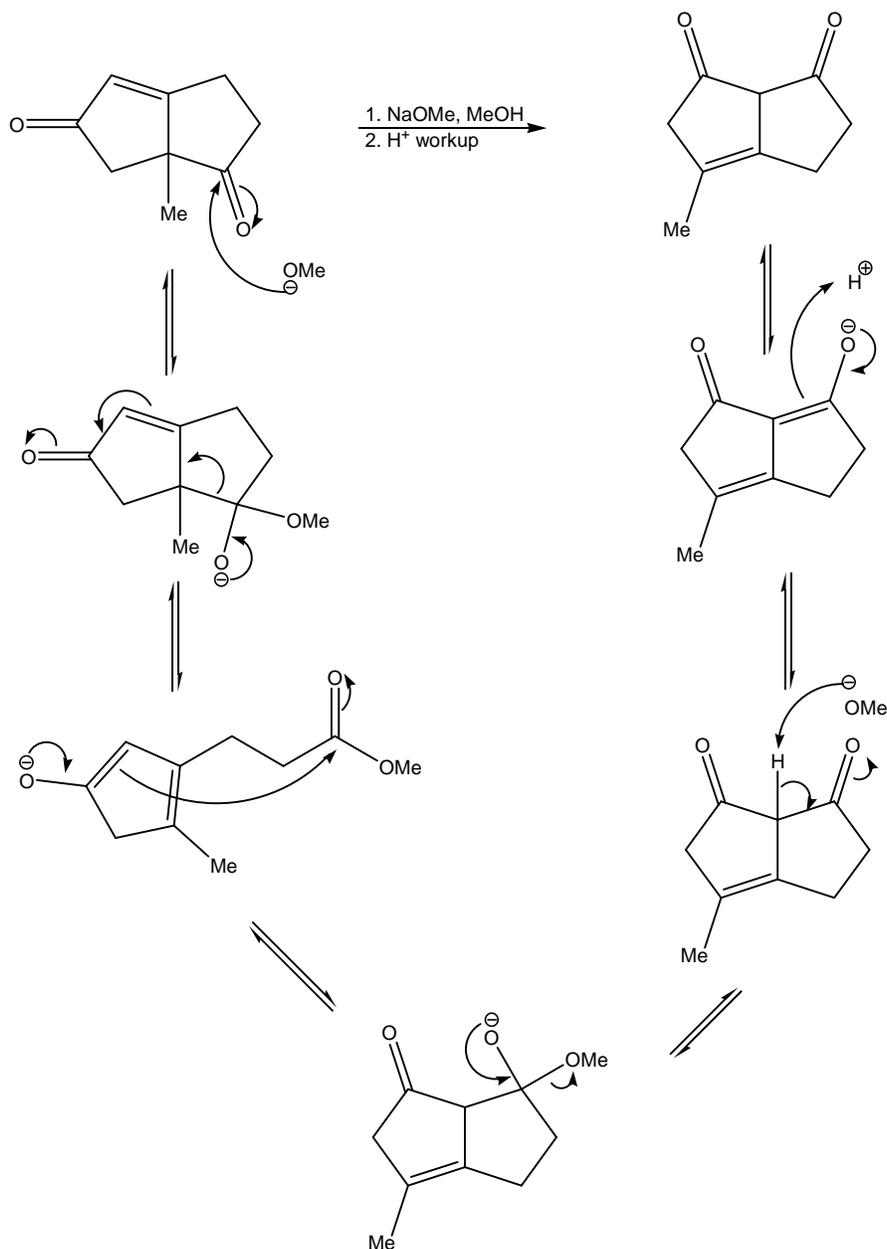
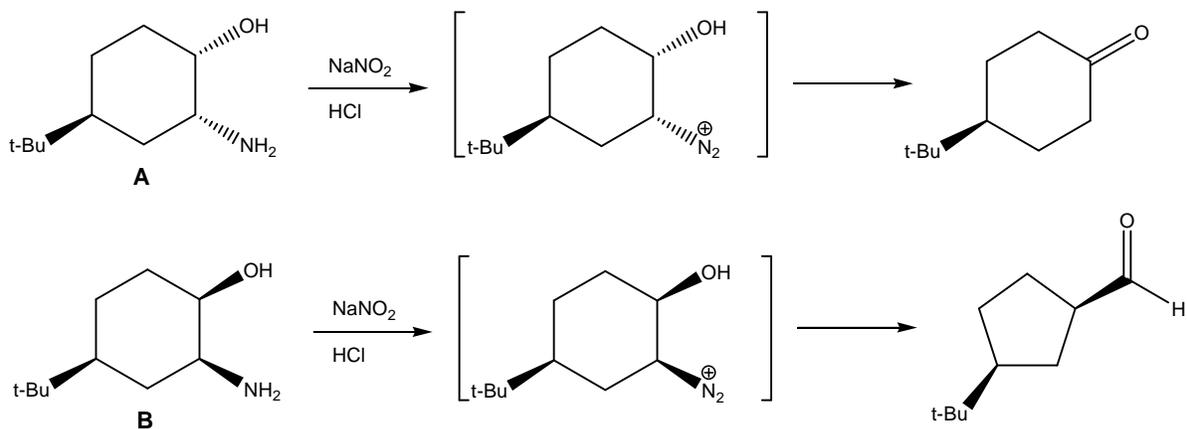
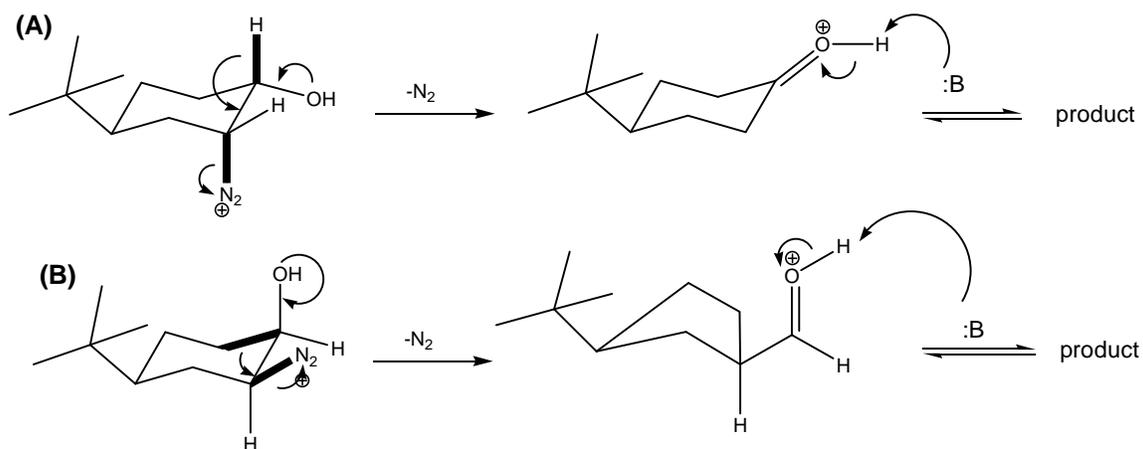


Figure by MIT OCW.

4. (10 points) Diastereomers **A** and **B** provide different products upon diazotization. Please explain why only one product is formed selectively in each reaction. Your explanation should include a **3-dimensional** mechanism for the formation of each product from the corresponding diazonium salt.



In the concerted Tiffeneau-Demjanov rearrangement, the migrating bond must be antiperiplanar to the leaving group.



(Bolded bonds are antiperiplanar)

Figure by MIT OCW.

5. Please provide a detailed mechanism for the following transformation. Show all arrow pushing.

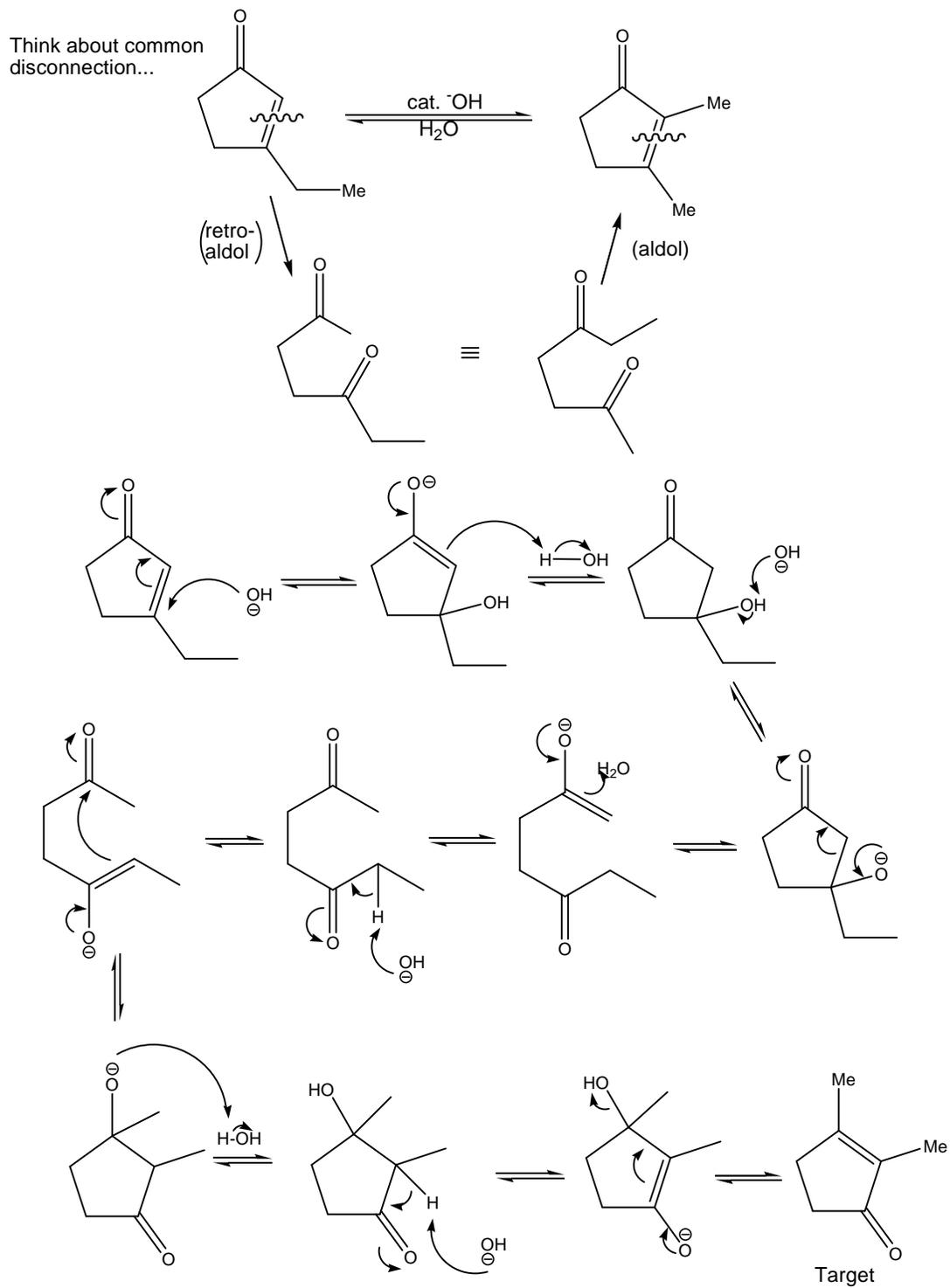


Figure by MIT OCW.

6. Please provide a detailed mechanism for the following transformation. Show all arrow pushing.

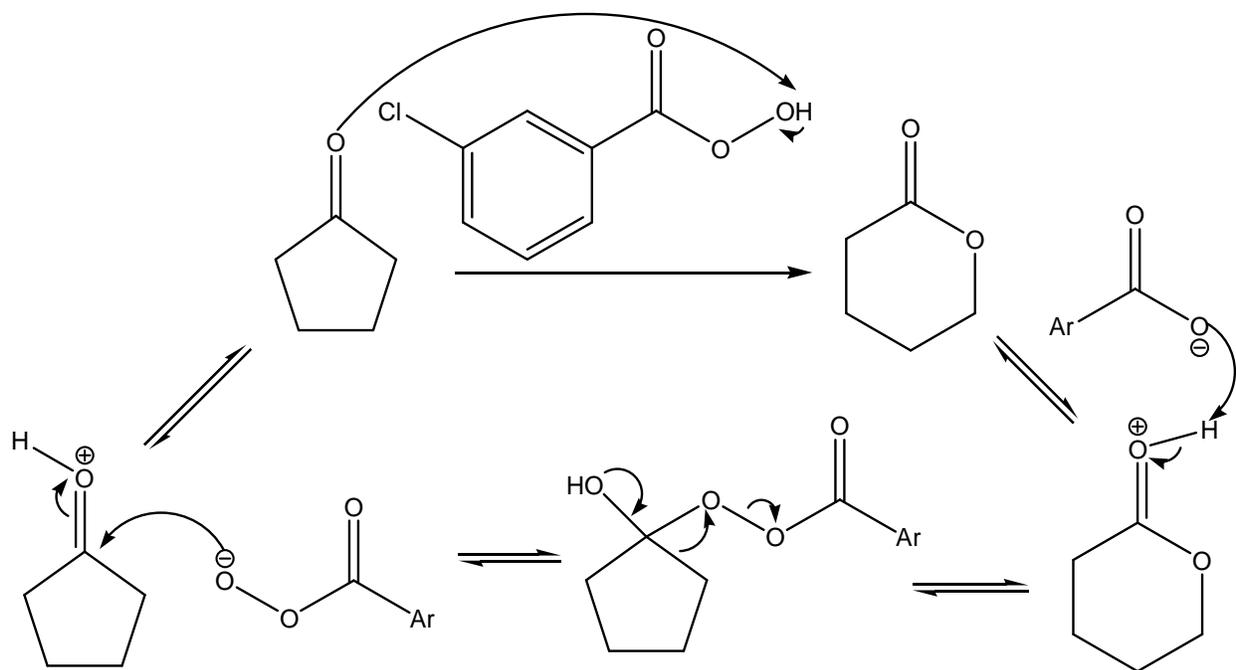


Figure by MIT OCW.

7. Please provide a synthesis of the indicated compound. All of the carbon atoms should be derived from methyl acetate.

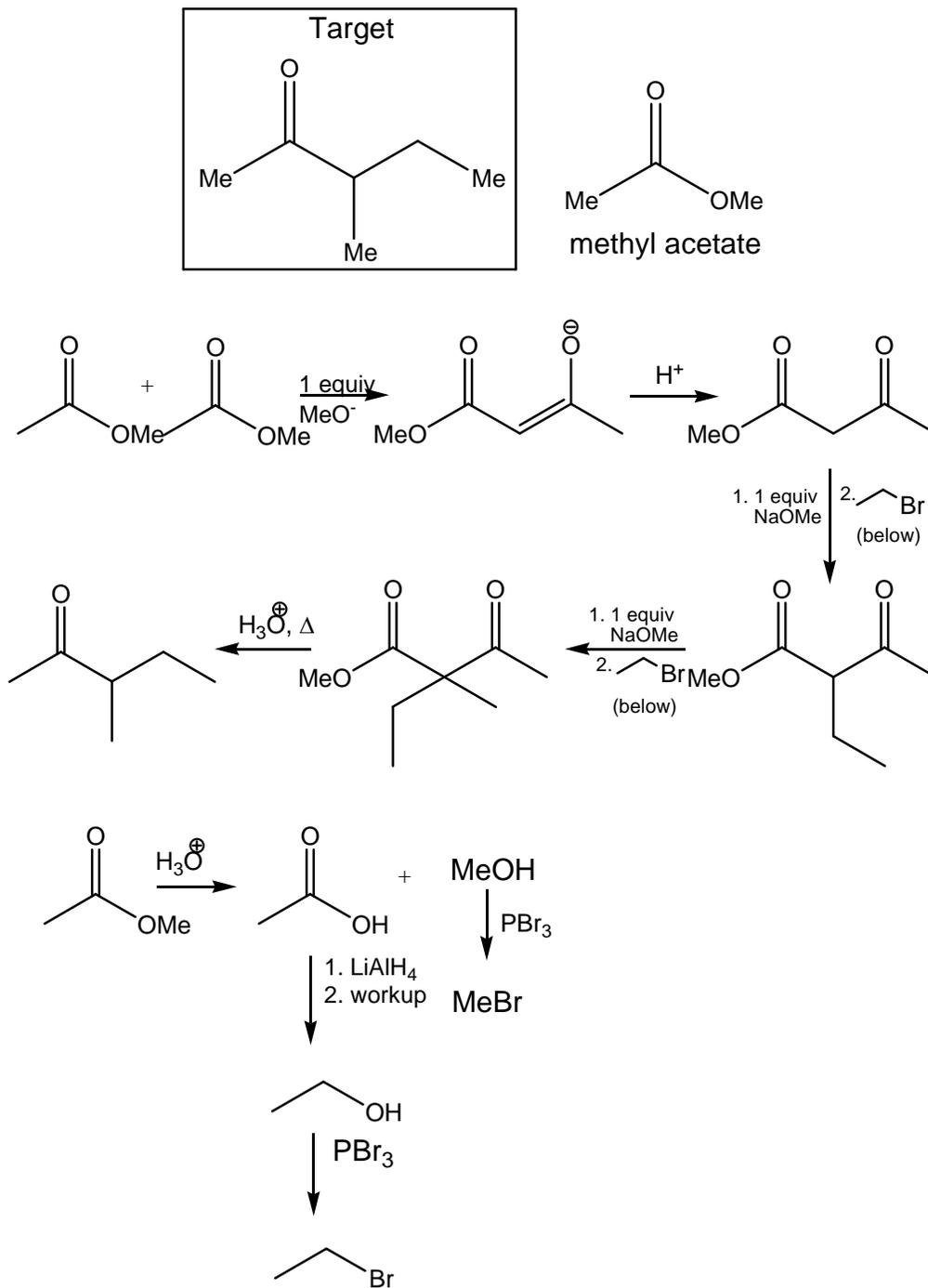
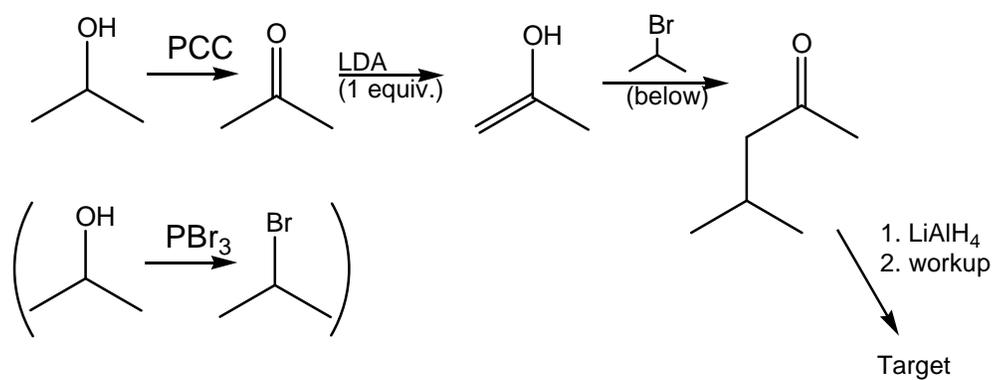
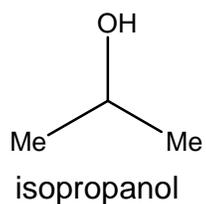
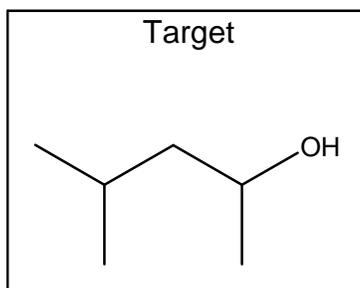


Figure by MIT OCW.

8. Please provide a synthesis of the indicated compound. All of the carbon atoms should be derived from isopropanol.



OR:

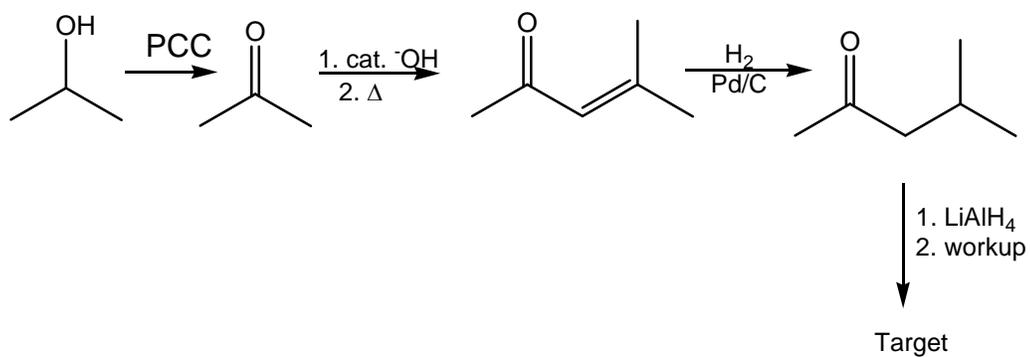


Figure by MIT OCW.

9. (12 points) Please provide a synthesis of the indicated compound. All of the carbon atoms should be derived from **methyl acetate**. You will receive partial credit for a complete retrosynthesis

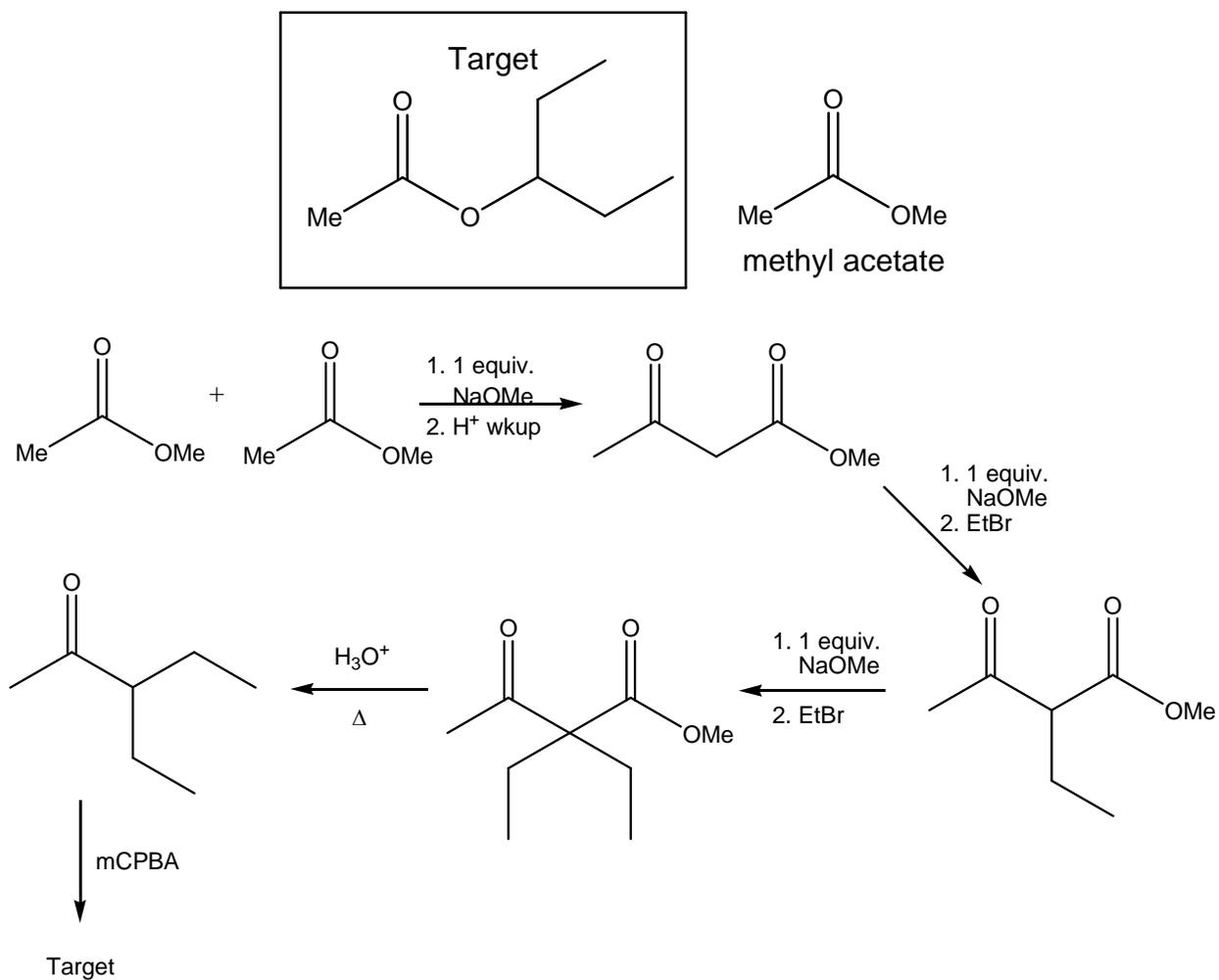


Figure by MIT OCW.

10. (12 points) Please provide a synthesis of the indicated compound. All of the carbon atoms should be derived from **dimethyl malonate** and **alcohols containing three or fewer carbons**. You will receive partial credit for a complete retrosynthesis.

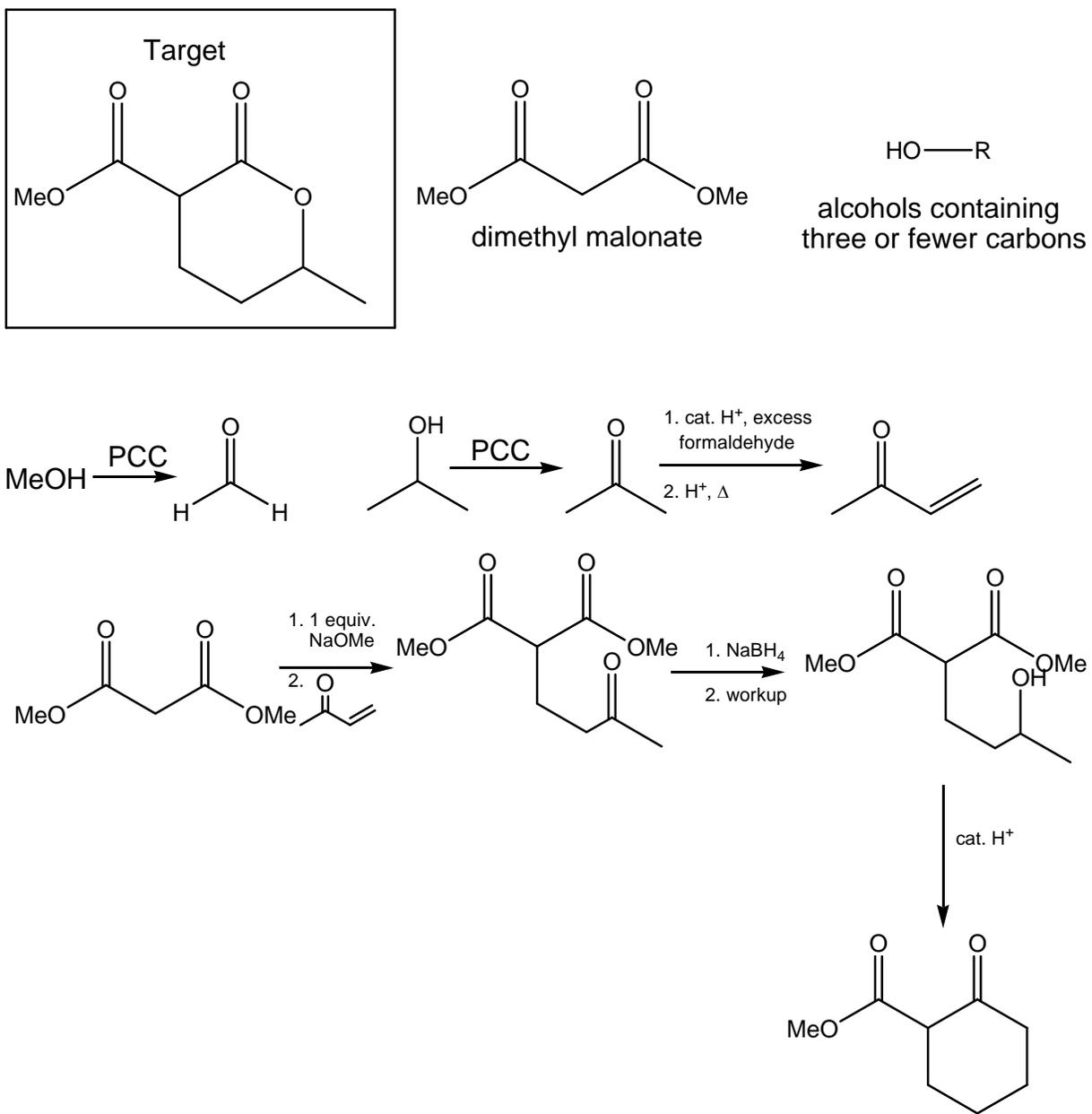


Figure by MIT OCW.