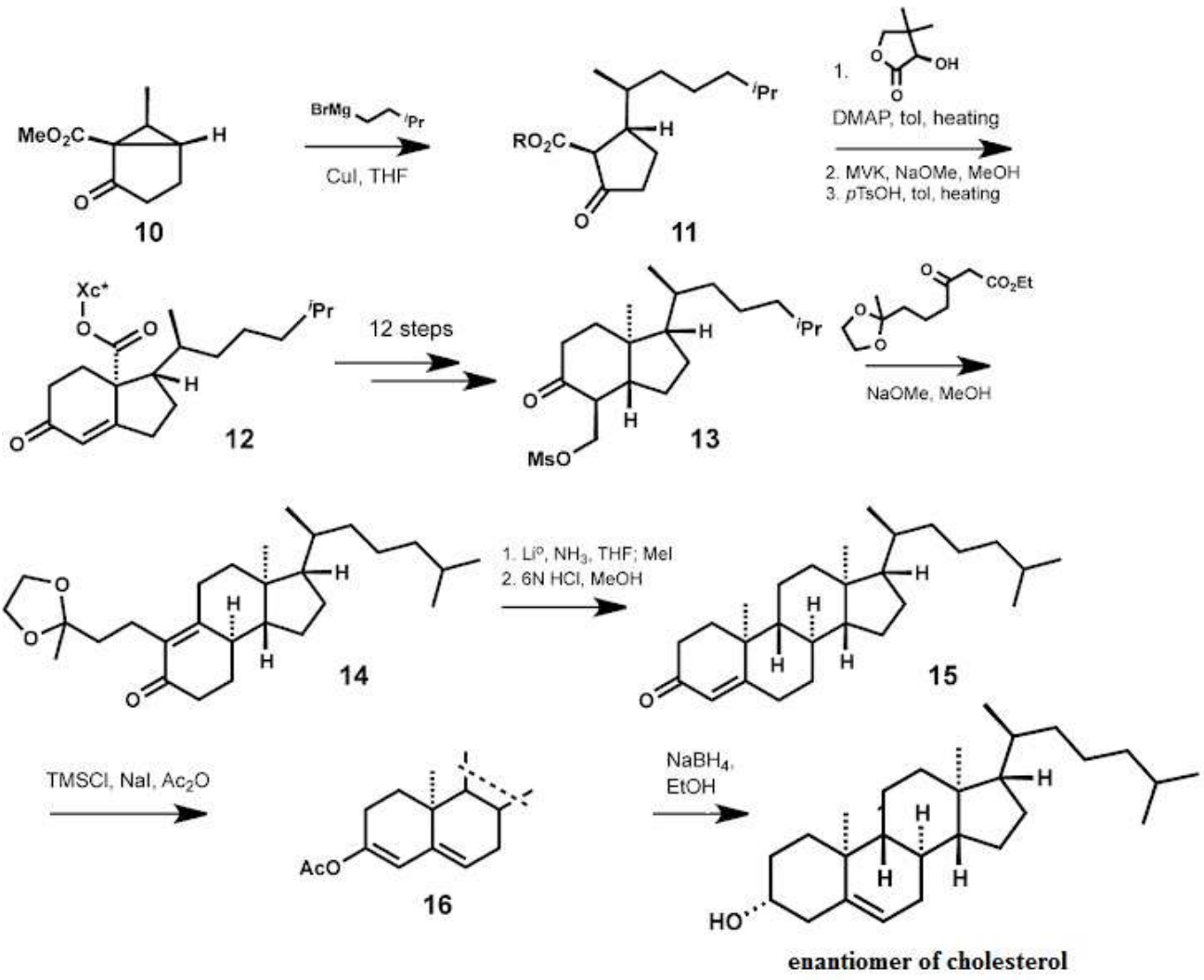
Name_____

NOTE: To receive credit, show your work.
If you feel strapped for time, try to at least *start* each problem before going on to the next.

PLEASE DO NOT OPEN THE EXAM UNTIL INSTRUCTED TO DO SO



Synthesis of the enantiomer of cholesterol
http://modernsteroid.blogspot.com/2012/02/enantiomeric-ent-steroids-and-bile.html

(12) 1. One of the most common bases used to form enolates in order to carry out alkylations is lithium diisopropylamide (LDA). Draw the structure of LDA and answer the questions below.

a. What makes LDA so popular? (What is its chief advantage over NaOH, for example.)

b. LDA is made in lab and used immediately. Briefly describe how that is done and why it is important to use it immediately. [Not asking for exact details, just what reagents are used and the basic procedure and care that must be taken to successfully make LDA.]

c. How is controlling the temperature of the reaction used to drive an alkylation to the desired product when using LDA?

(6) 2. Give a concrete (no "R" groups) example of:

a. a pair of tautomers

b. the azo compound ("azo dye") derived from 3-methoxyaniline and *p*-bromophenol

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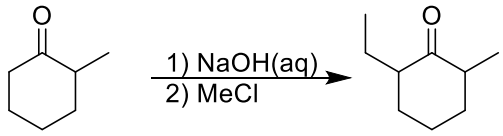
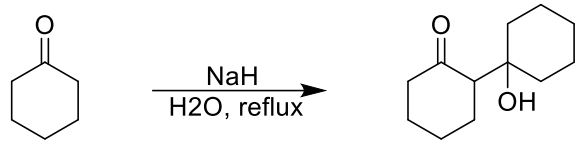
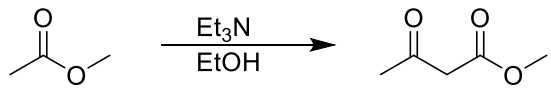
(9) 3. What are three major complications of enolate alkylations involving ketones?
[Don't waste too much time if you can only think of two. Come back later if you have time.]

(12) 4. None of the following reactions work. Briefly explain why. Suggest *simple* changes to the reagents or conditions that a chemist might reasonably try to get around the problem and get the indicated product in each case.

a. 

b. 

c. 

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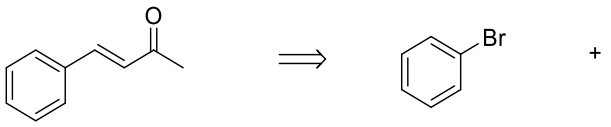
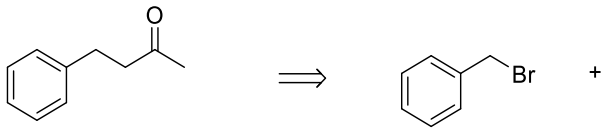
(16) 5. Show the *second* organic reactant that you would need to make indicated target in a single (overall) reaction – that is, a reaction that may involve two or more stages, such as adding base and then acid, but not two totally different reactions, such as oxidation and then alkylation. Your answer must be consistent with the given parameters. In each case show the reagents you would use.

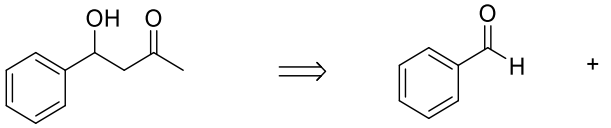
other compound reagents

a. 

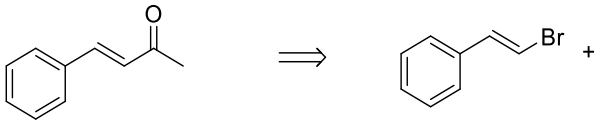
parameters: should be catalytic

b. 

parameters: should involve a dicarbonyl compound

c. 

parameters: should minimize further reaction

d. 

parameters: no contraints -- whatever works

(12) 6. Explain the mechanistic origin of…

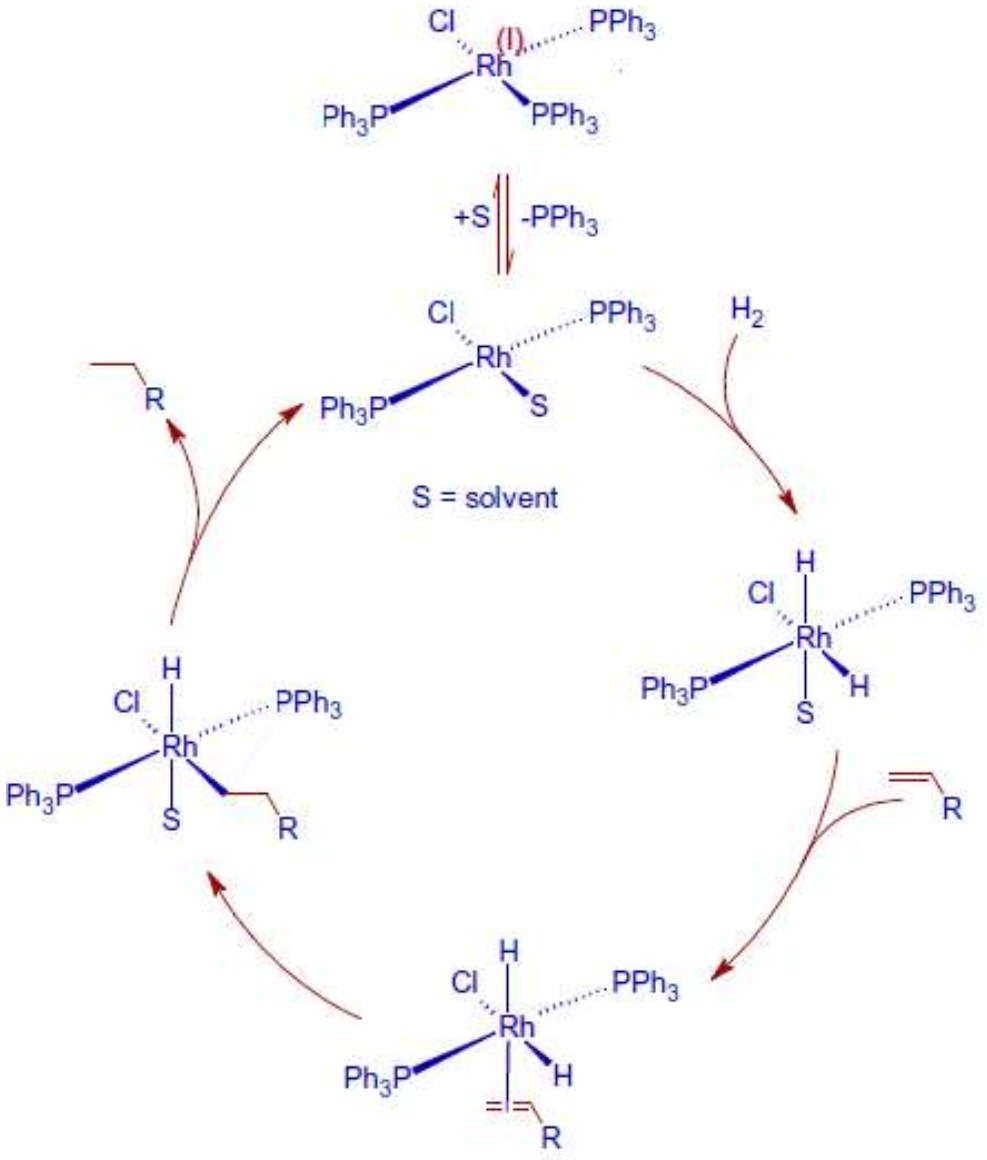
a. …the stereospecificity of the Suzuki reaction.

b. …the formation of small amounts of *Z* alkene in the Heck reaction

(20) 6. Shown below is a reaction mechanism using a rhodium catalyst you have probably not seen before.

a. What is the overall stoichiometric equation for this reaction?

b. Name each of the five steps in the mechanism using terms we have used in class and indicate the oxidation state of the rhodium atom all around the cycle.



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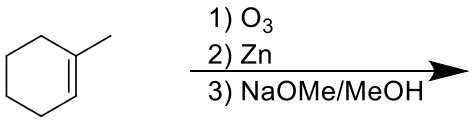
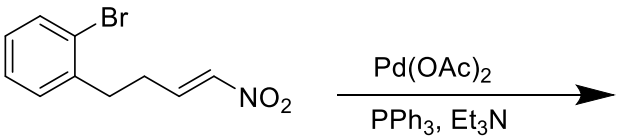
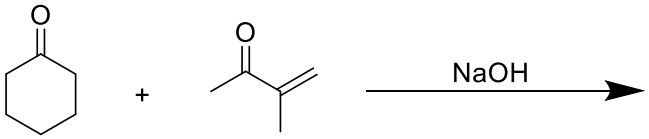
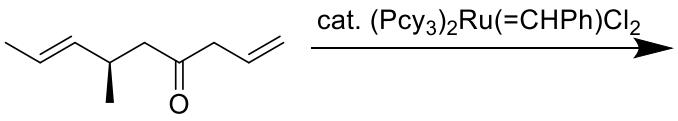
(16) 7. Suggest the major product in each case:

a) 

b) 

c) 

[IR shows no broad signals 3000-3500 cm^{-1}; 13C NMR has only one signal > 180 ppm]

d) 

PLEDGE: I pledge my honor that on this examination I have neither given nor received assistance not explicitly approved by the professor and that I have seen no dishonest work.

[ ] I intentionally did not sign the pledge. Signature_____