CHM 2120 – Assignment 8
ANSWERS

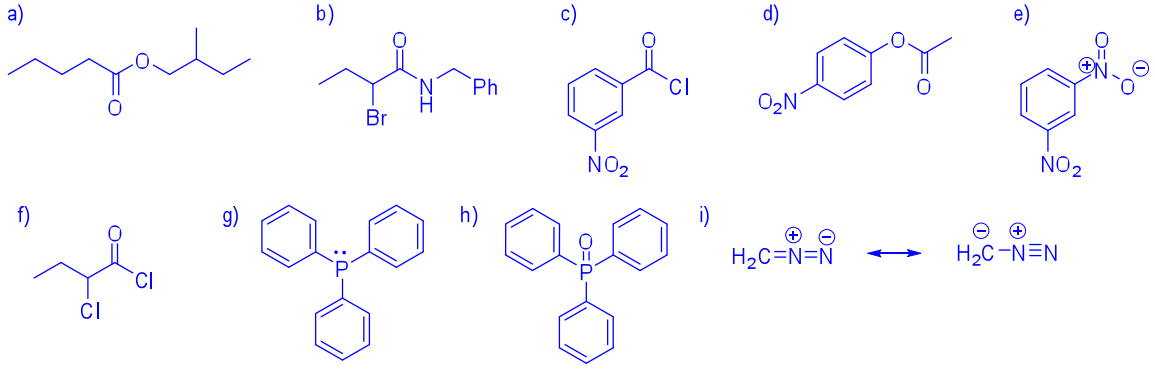
In this assignment:

- Esterification
- Saponification of esters
- Chemistry of carbonyl derivatives
- Synthesis of carbonyl compounds (via oxidation of alcohols, etc)

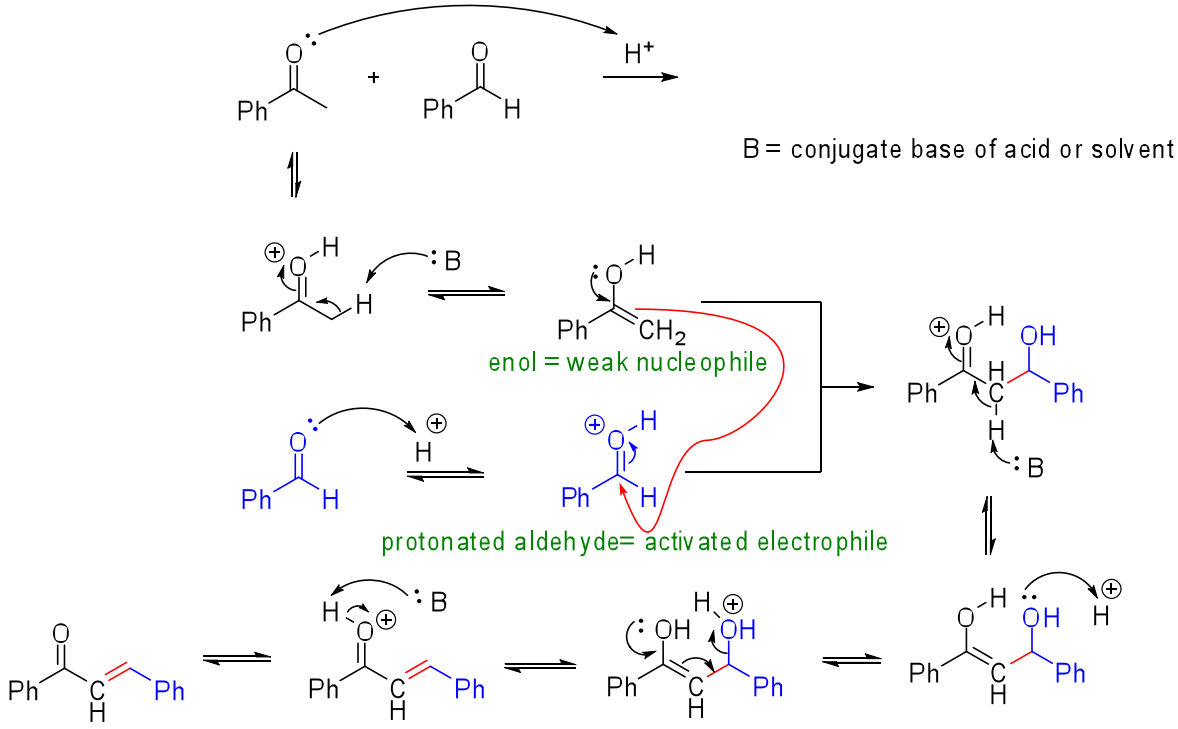
1. Give the IUPAC names or accepted trivial names for the following molecules:

a) 1,1-diphenylbutan-1-ol
b) butyl butanoate
c) 4-methylpentanoyl chloride
d) *N*,*N*-dimethyl-3-methylbenzamide
e) 3-methylbenzoyl chloride
f) methyl 4-hydroxy-3-methoxybenzoate
g) 3-methylbutyl (E)-but-2-enoate
h) sodium butanoate
i) phenyl acetate; phenyl ethanoate
j) 2-amino-5-phenylpentanoic acid
k) butanamide
l) *N*,*N*-dimethyl-3-hydroxybutanamide
m) 5-bromo-4-chloropentanoic acid
n) isopropyl pentanoate or 1-methylethyl pentanoate

2. Draw structures for
   a. 2-methylbutyl pentanoate
   b. *N*-benzyl-2-bromobutanamide
   c. 3-nitrobenzoyl chloride
   d. *p*-nitrophenyl acetate
   e. *meta*-dinitrobenzene
   f. 2-chlorobutanoyl chloride
   g. Triphenylphosphine
   h. Triphenylphosphine oxide
   i. Diazomethane,CH_2N_2 (the two most important resonance structures)

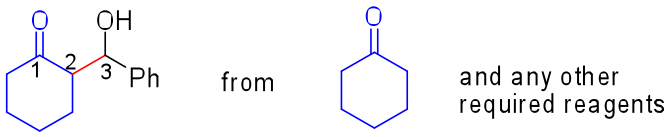


3. The aldol reaction can be accomplished using an acid catalyst. Give a mechanism for the following transformation:

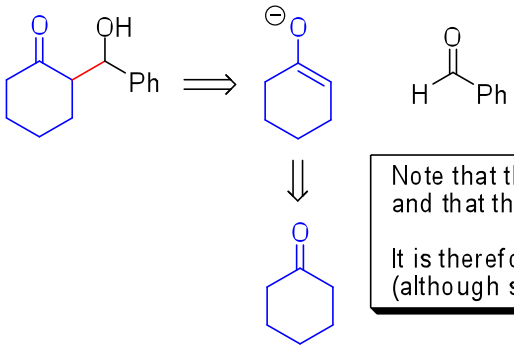


4. Propose a synthesis of the following compounds. A retrosynthetic analysis must also be included.

a.



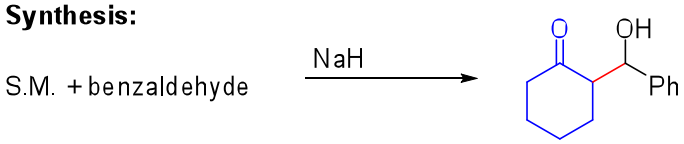
Identify the cyclohexanone ring present in starting material (S.M.) and product (P), then identify the new bond.
- The 1,3 relationship between the oxygens suggests that an aldol reaction would be appropriate



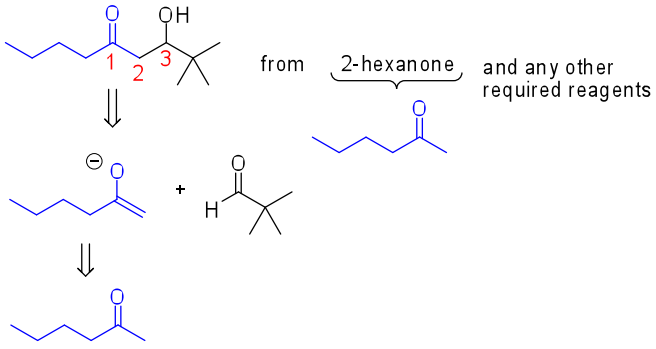
Note that the ketone contains only 1 type of alpha proton and that the aldehyde does not possess α-protons.

It is therefore not necessary to make the enolate separately (although still acceptable).

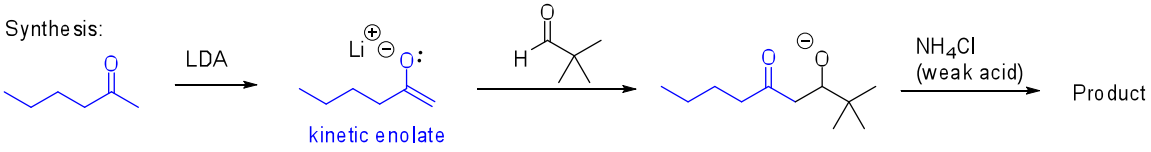
Synthesis:



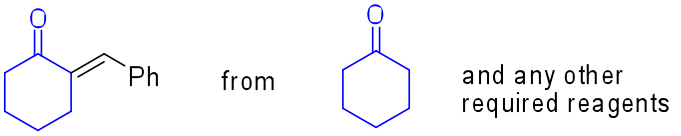
b.



*A 1,3-relationship suggests that an aldol reaction would be appropriate. The required starting material, in blue, has been mapped on to the product (this could also be done by circling or numbering the atoms in starting material and product)

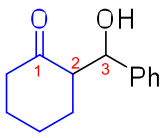


c. **(Question 4 continued)**

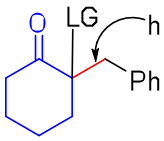


⇓ - Double bond made from elimination reaction, Wittig

Consider different possibilities:



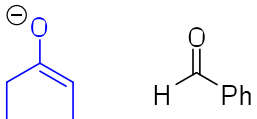
vs



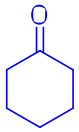
how to make the new C-C bond?
This route seems less direct than using an aldol reaction.

- 1,3 relationship allows for an aldol reaction--an excellent way to make new C-C bonds

⇓



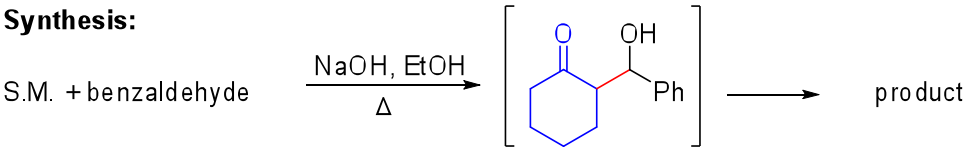
⇓



Note that the ketone contains only 1 type of alpha proton and that the aldehyde does not possess α-protons.

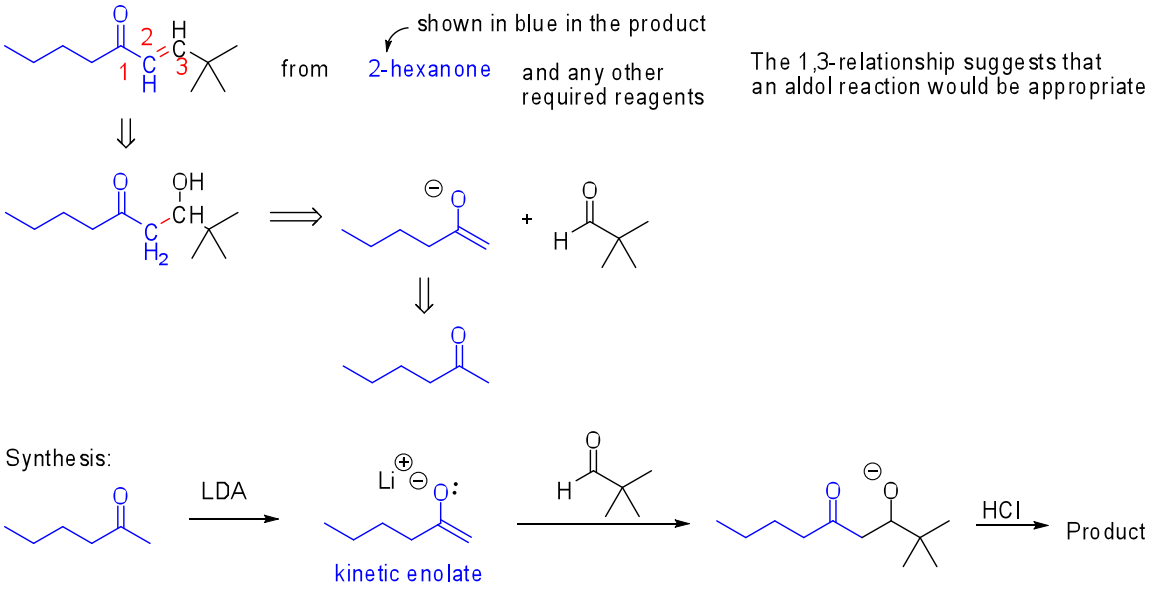
It is therefore not necessary to make the enolate separately (although still acceptable).

Synthesis:

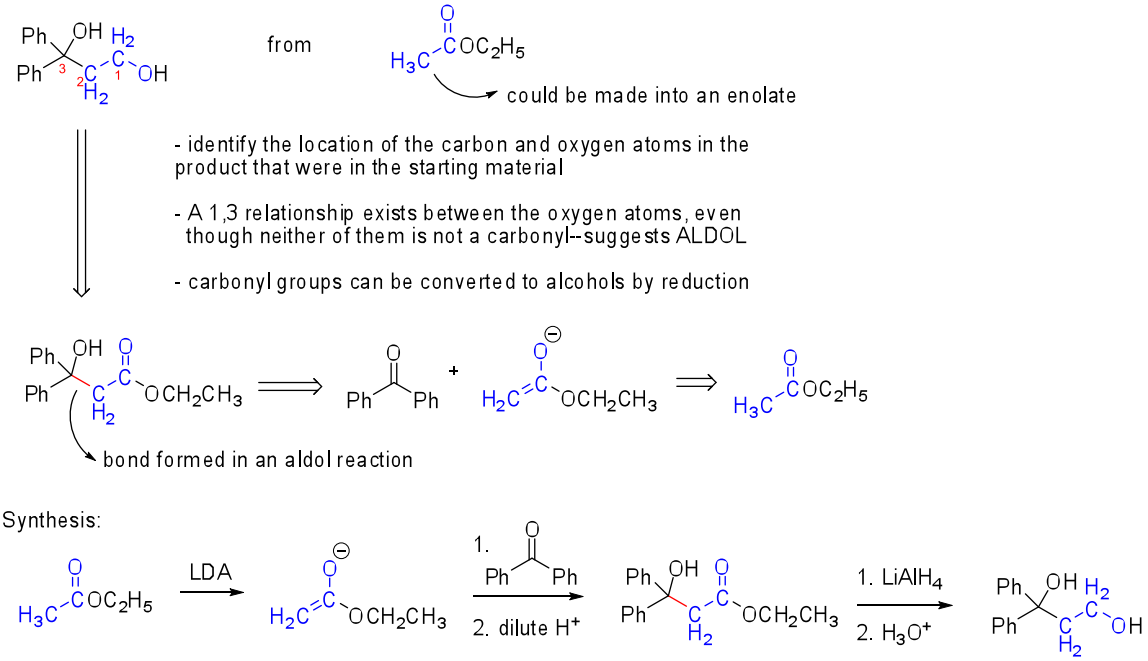


The square brackets indicate an intermediate that was not isolated

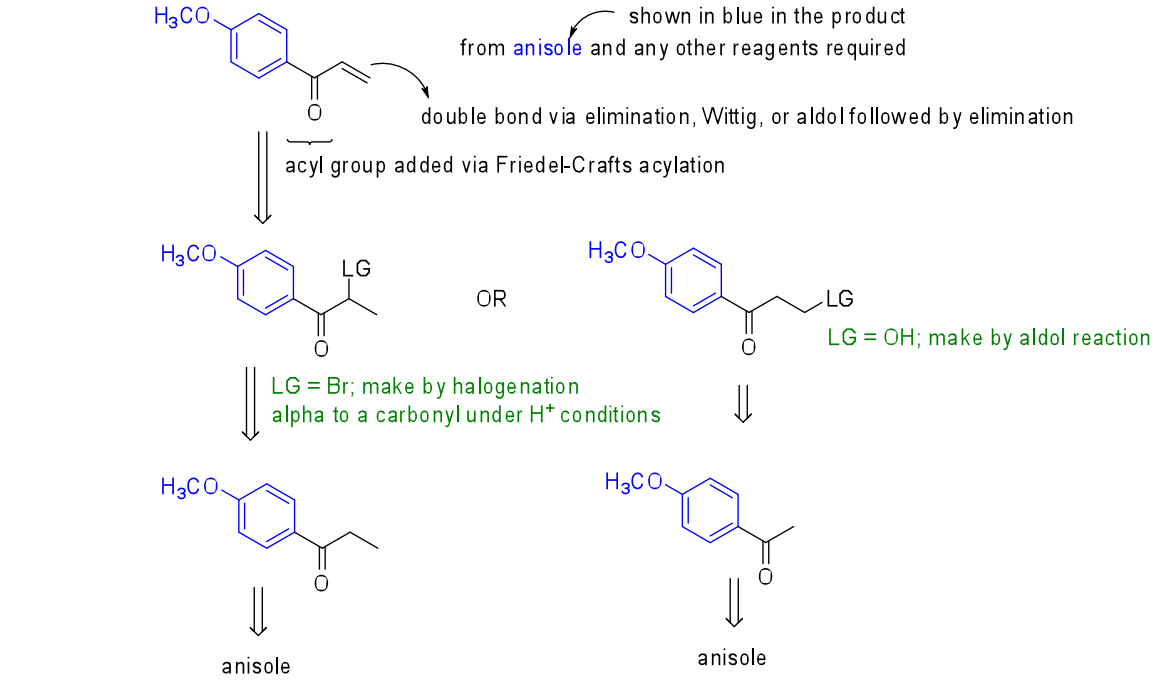
d. **(Question 4 continued)**



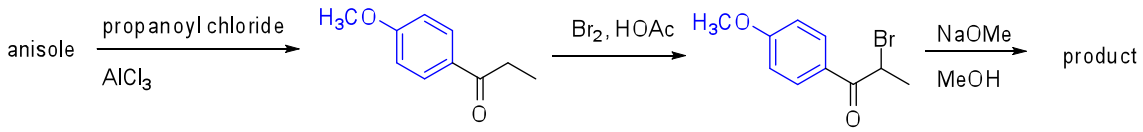
e.



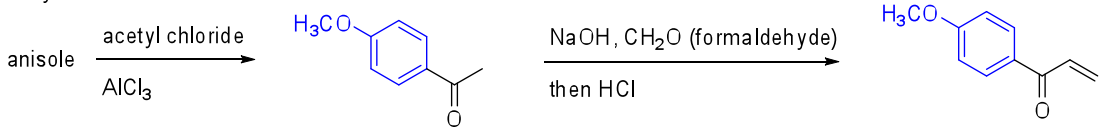
f. **(Question 4 continued)**



Synthesis A:

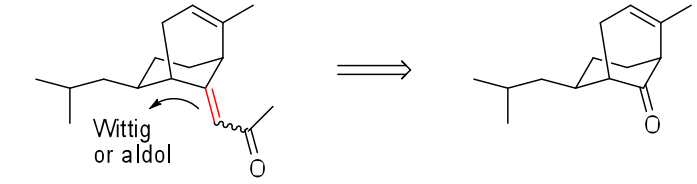


Synthesis B:

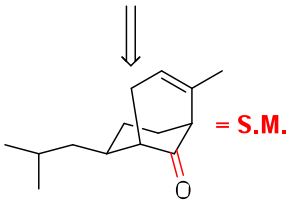


s

g. (**Question 4 continues**)



denotes a mixture of diastereomers



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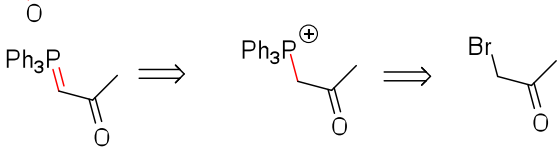
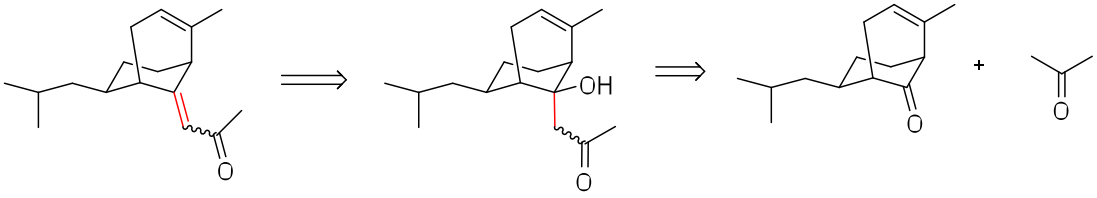
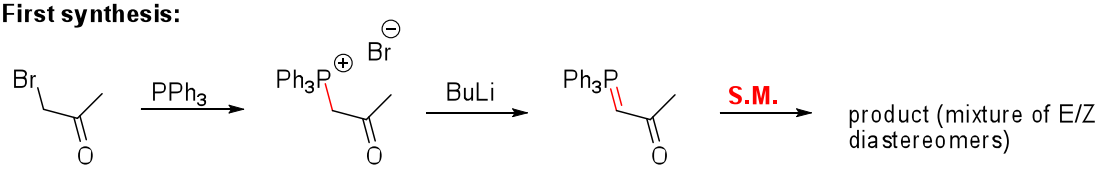


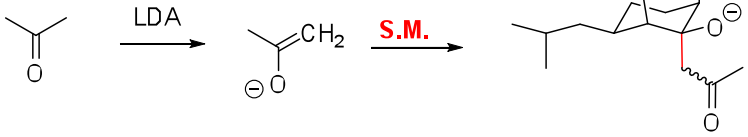


First synthesis:



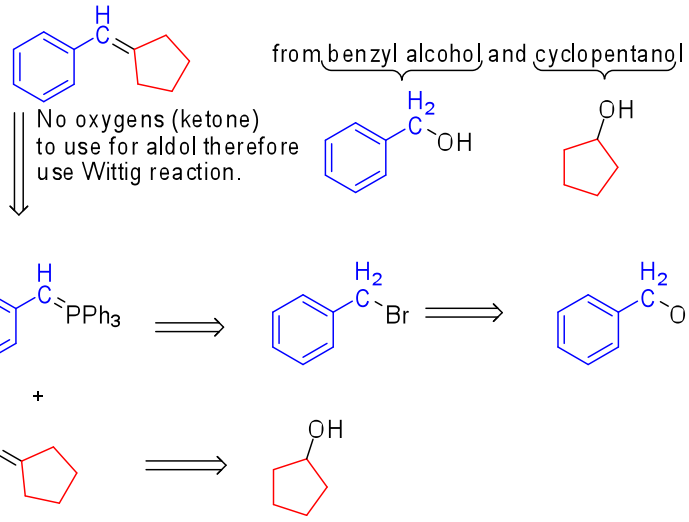
product (mixture of E/Z diastereomers)

Second synthesis:

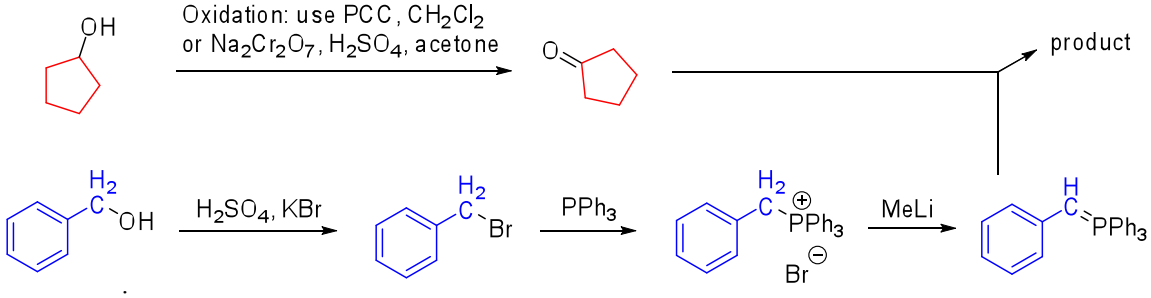


product (mixture of E/Z diastereomers)

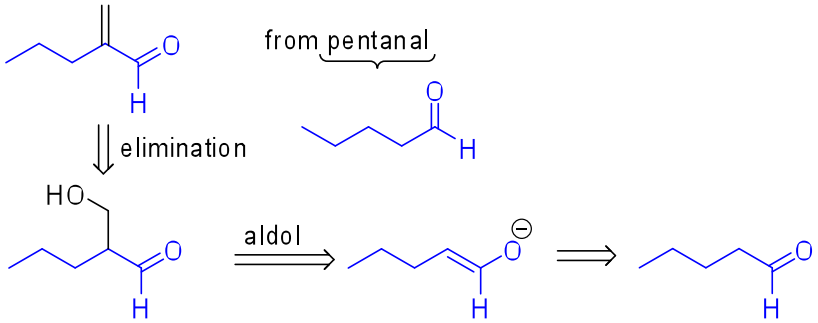
h. **(Question 4 continued)**



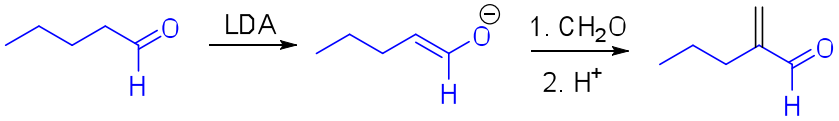
Synthesis:



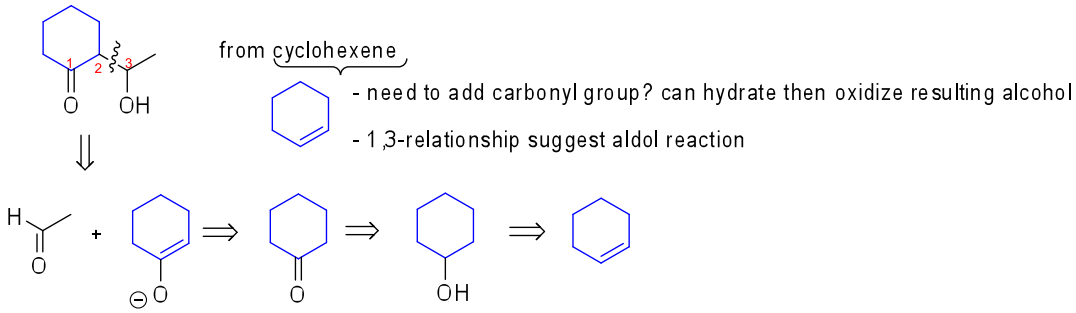
i.



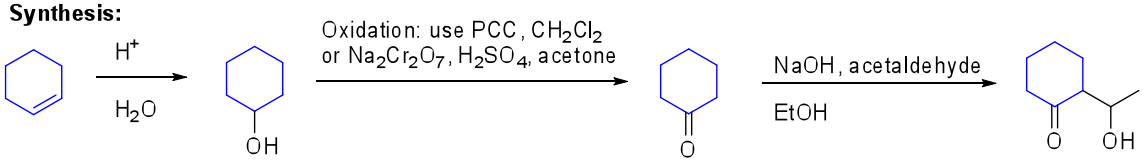
Synthesis:



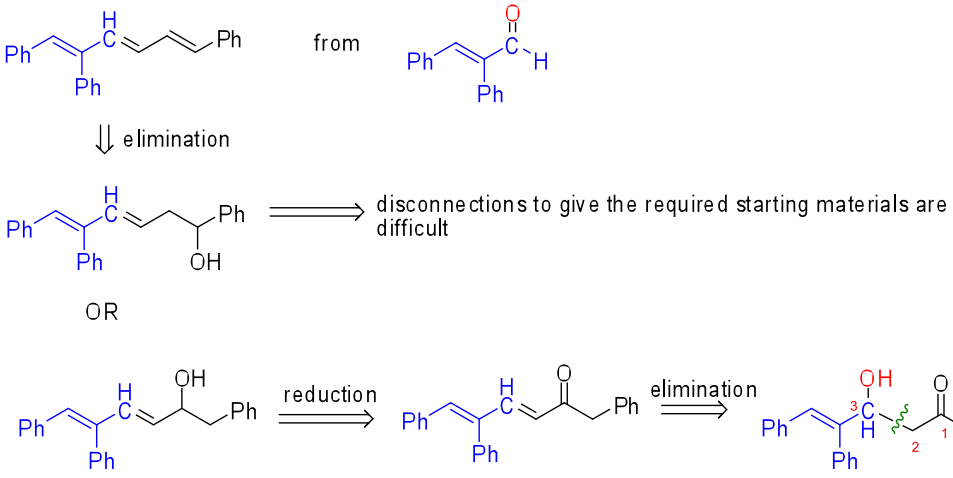
j. **(Question 4 continued)**



Synthesis:



k.



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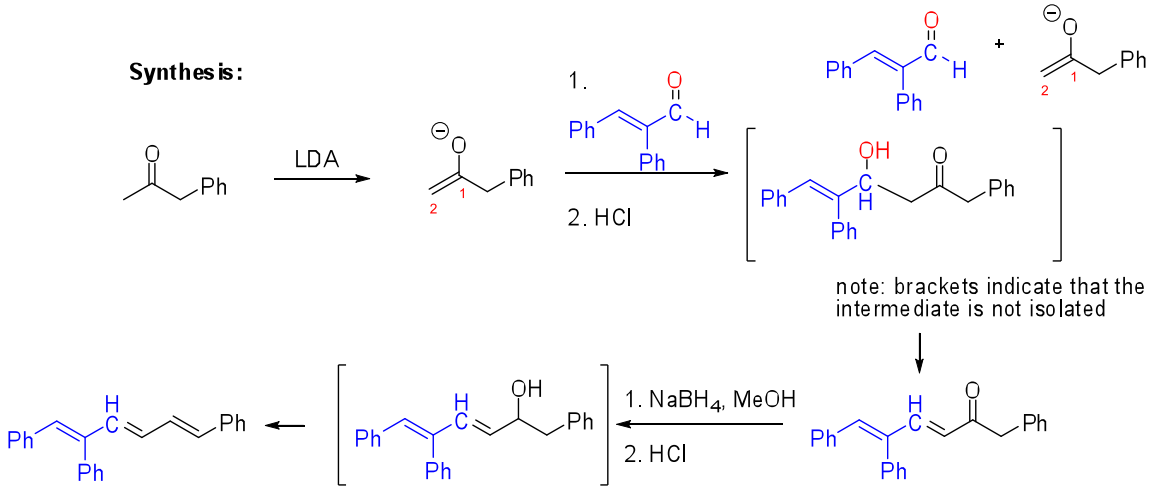
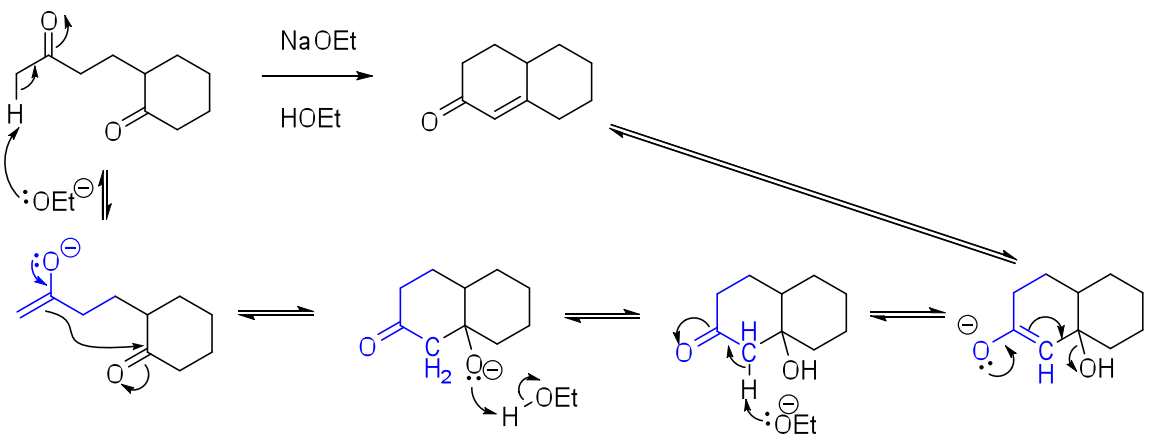
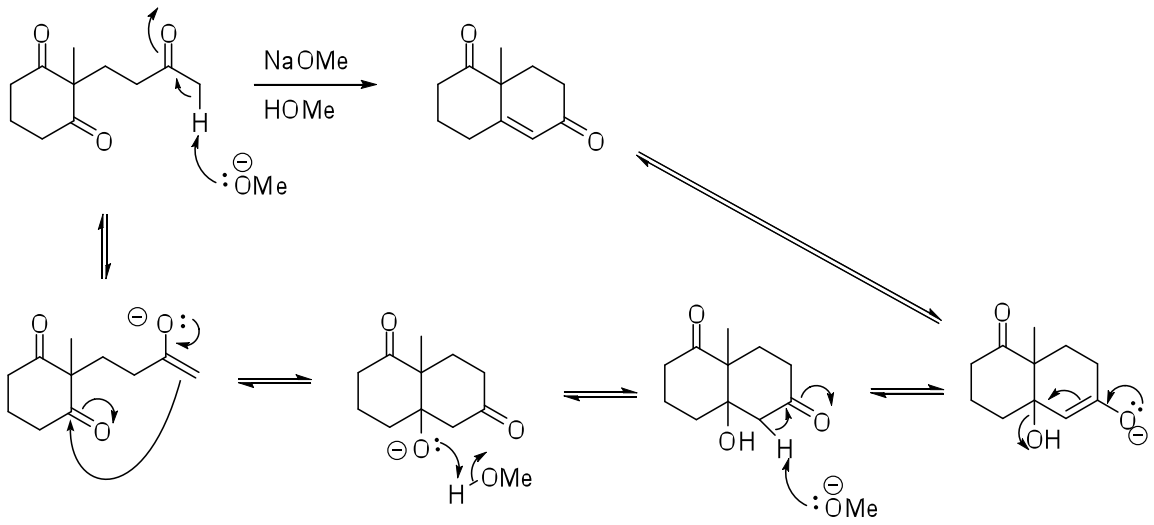


5. Provide a mechanism for the following transformation:

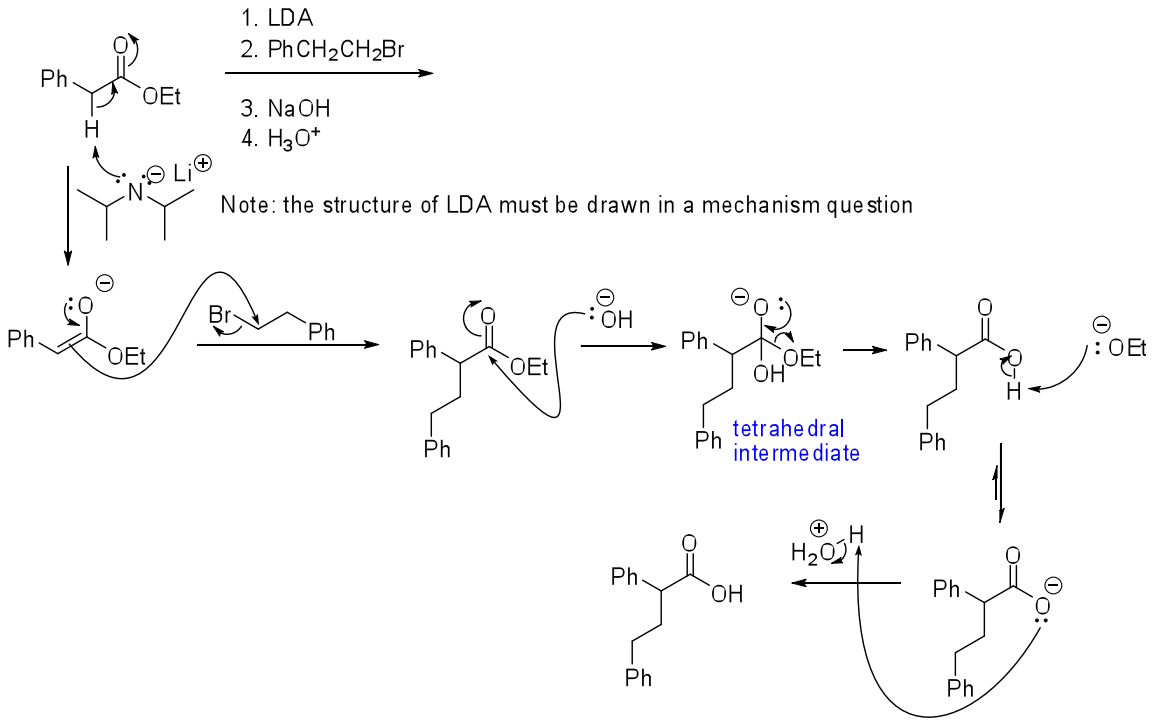
a.



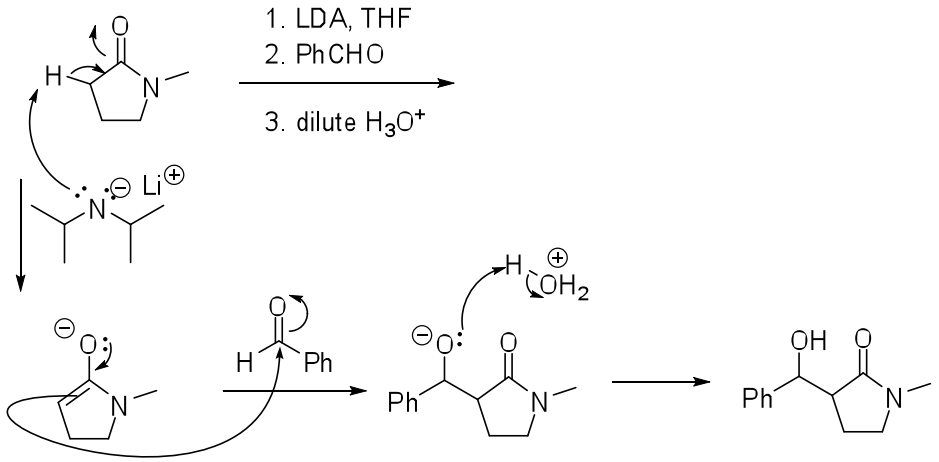
b.



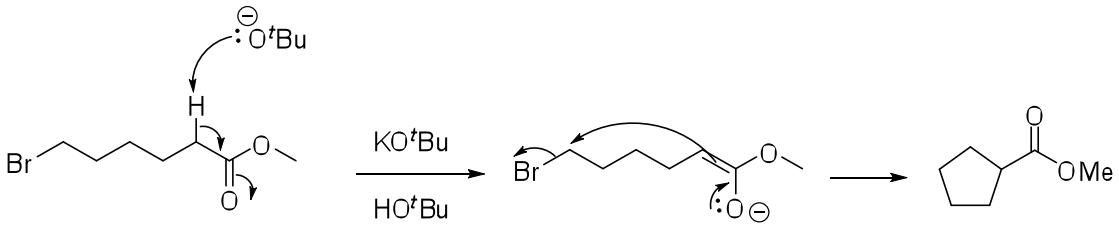
c. **(Question 5 continued)**



d.

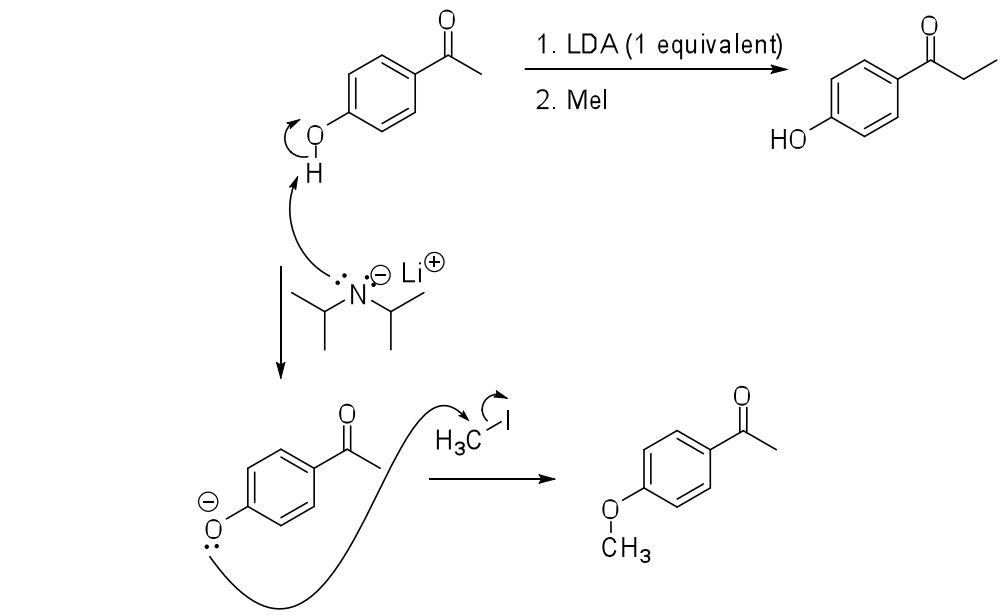


e.

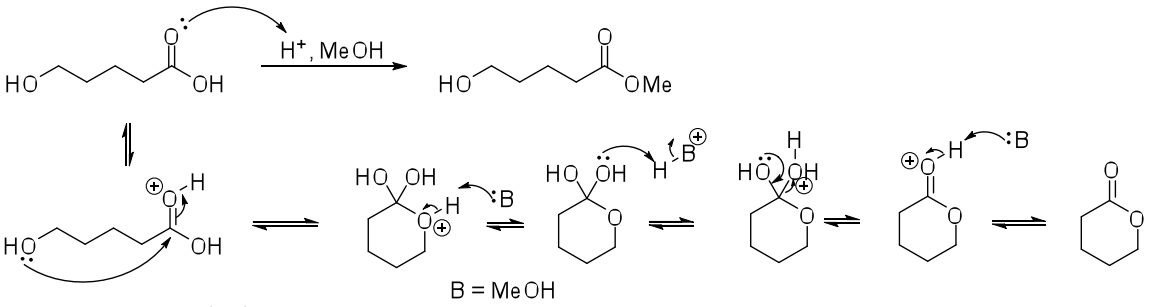


6. Why won't the following transformations work? Explain by showing the reaction that would happen instead.

a.

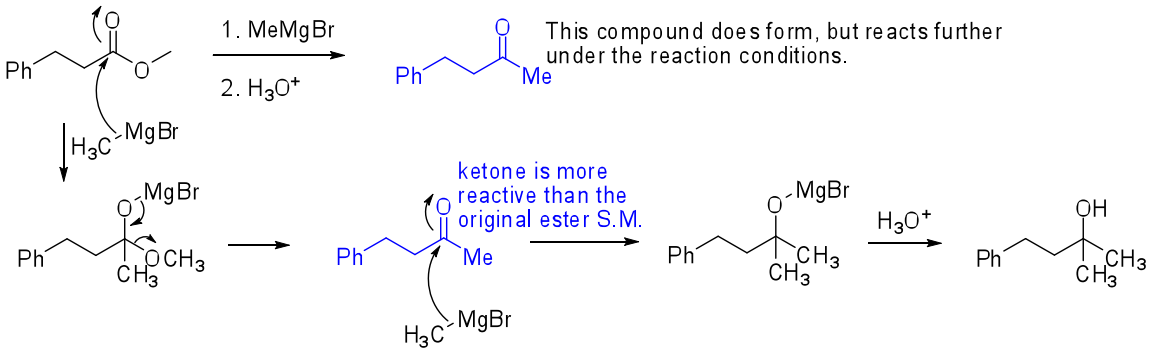


b.



Intramolecular cyclization to form a 6-membered ring is fast

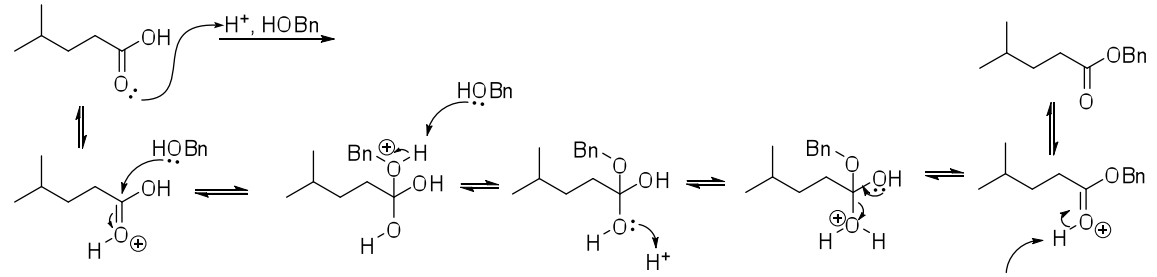
c.



This compound does form, but reacts further under the reaction conditions.

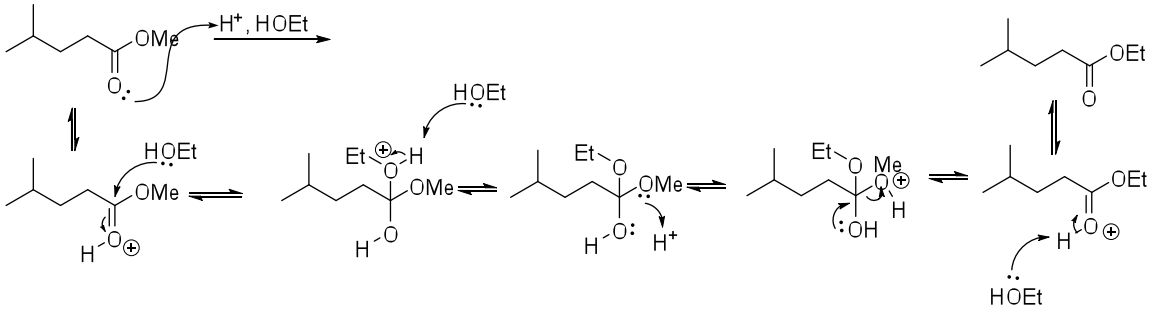
7. Provide a mechanism and the product for the following reactions:

a.

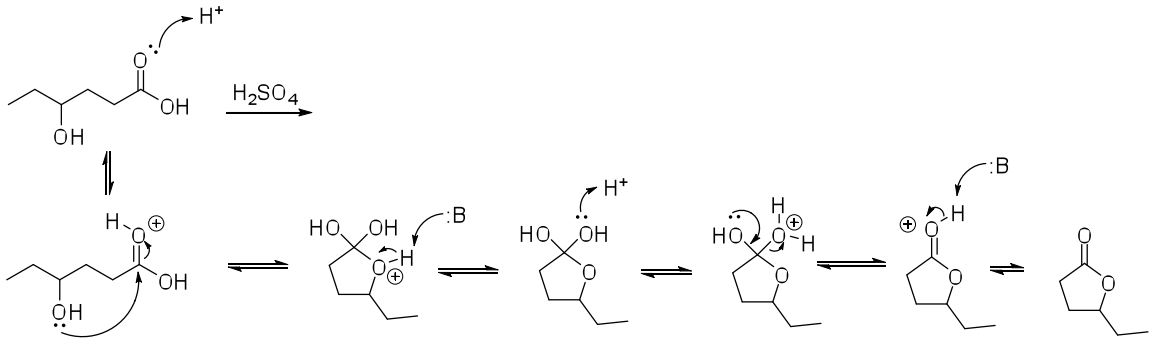


NOTE: Bn = $-CH_2Ph$

b.



c.



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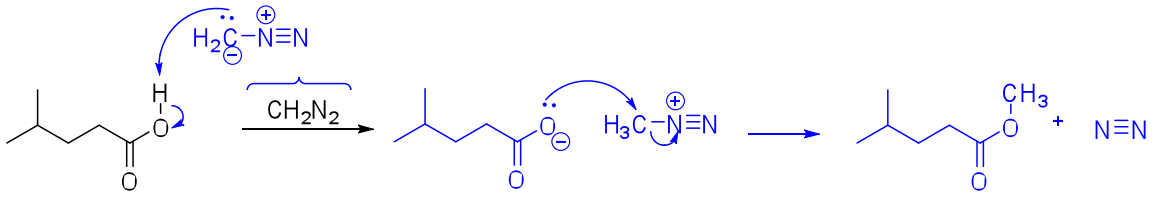
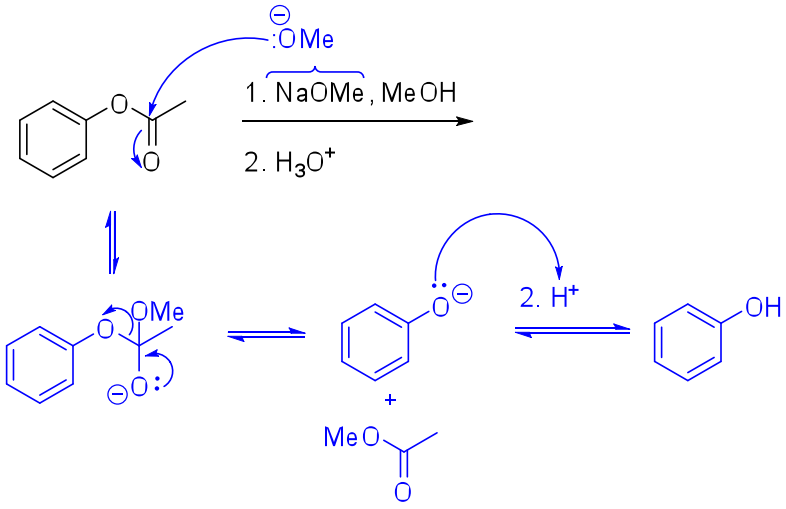


e. **(Question 7 continued)**



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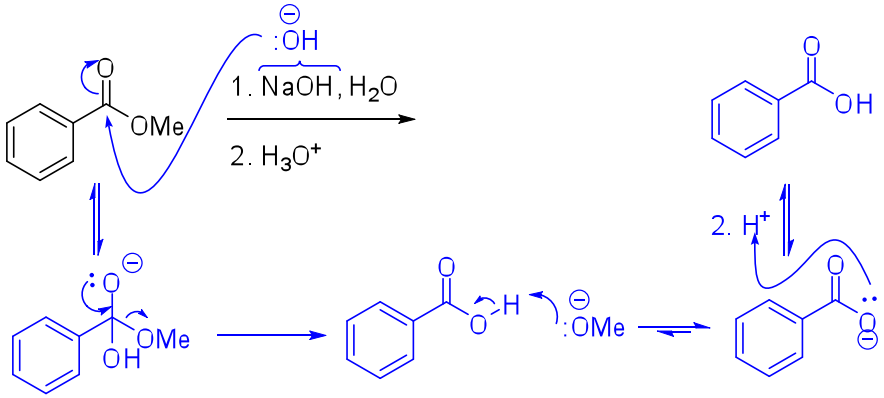
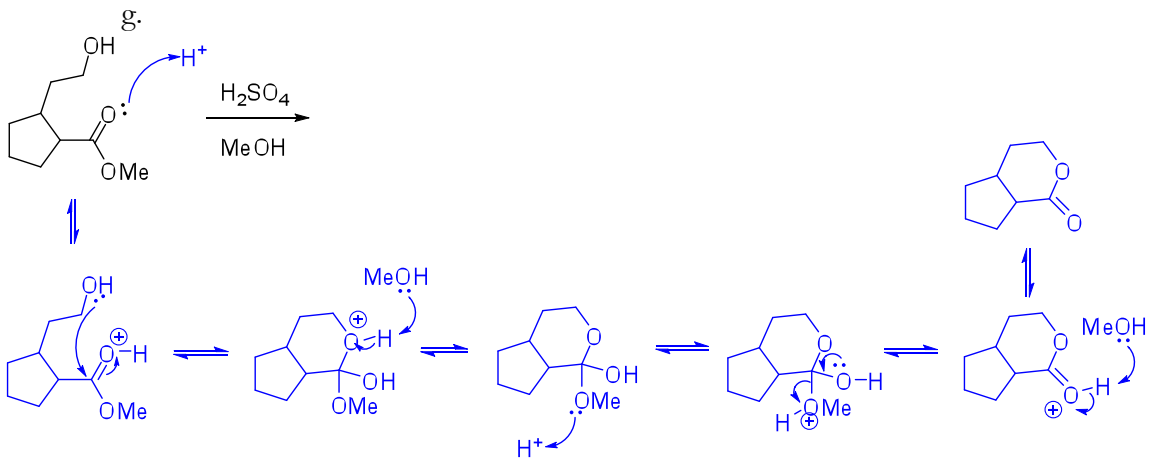
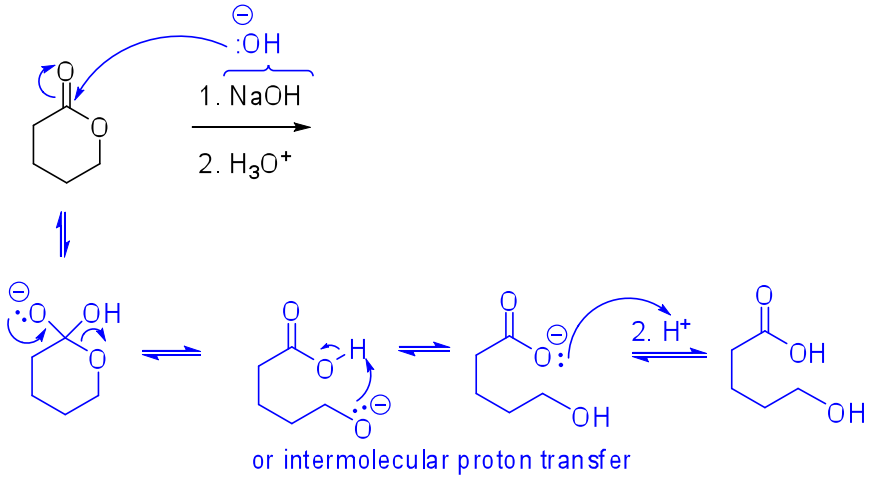


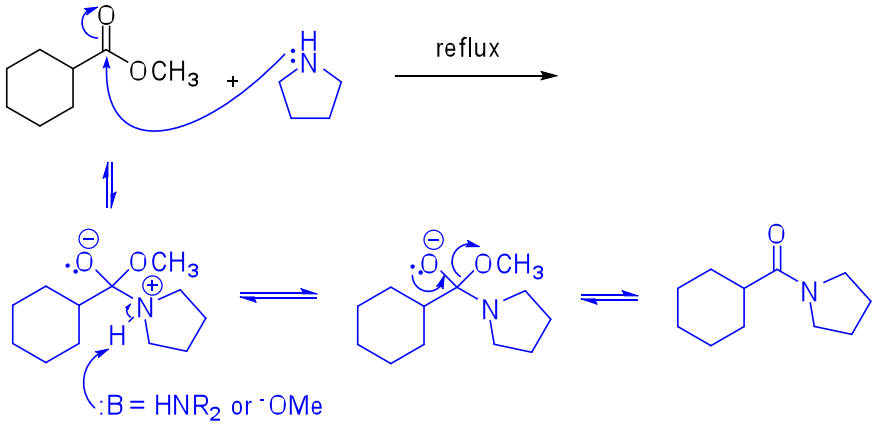
g.



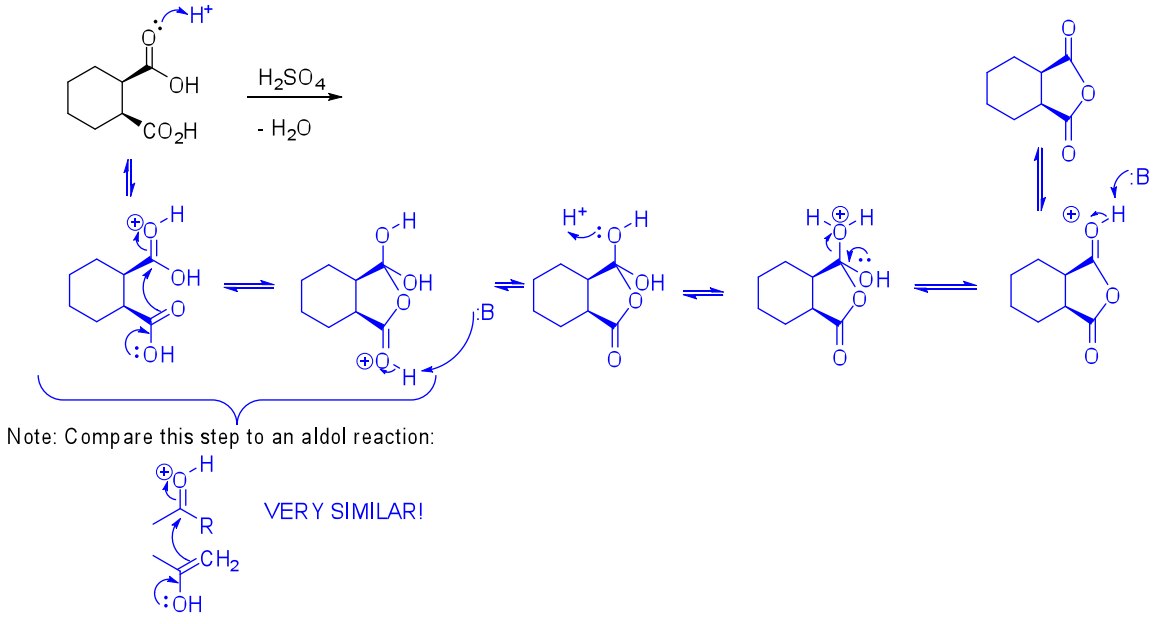
h. **(Question 7 continued)**



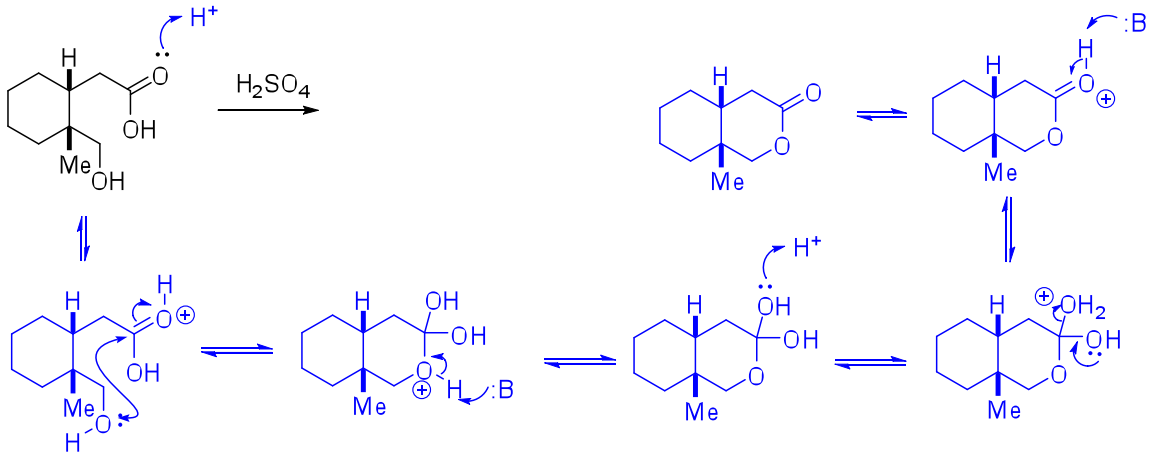
i.



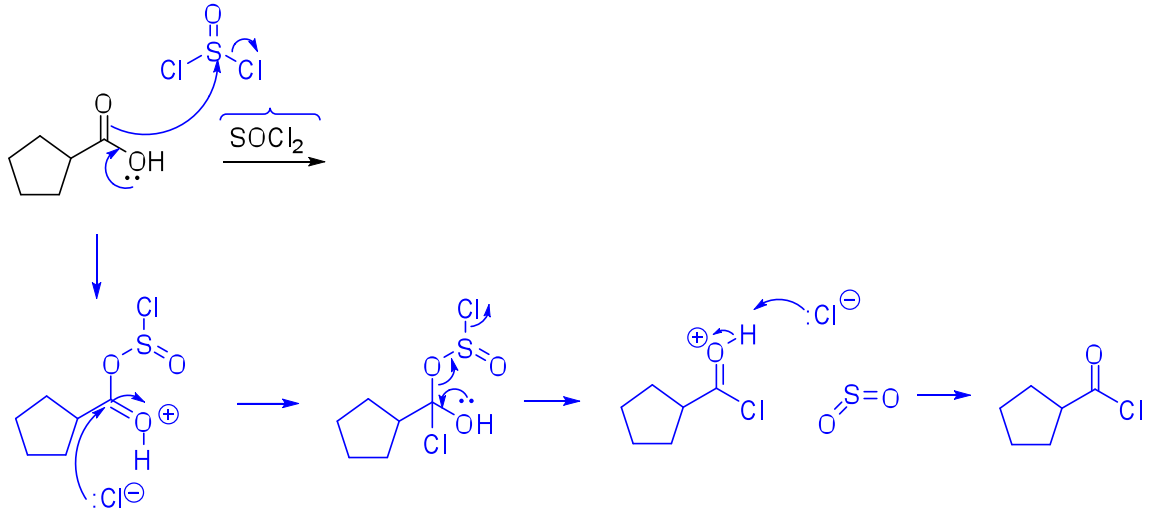
j.



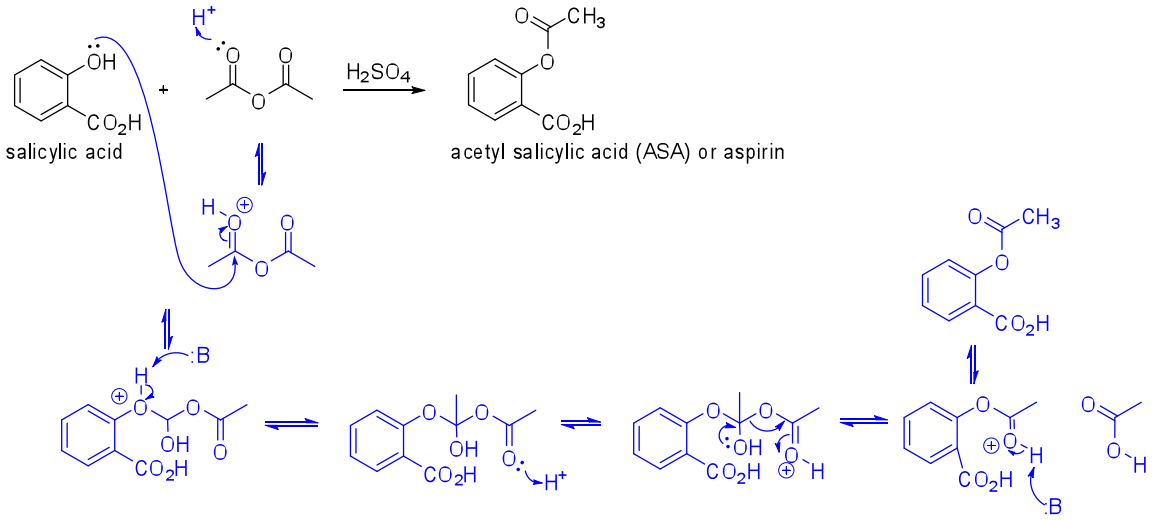
k. **(Question 7 continued)**



l.

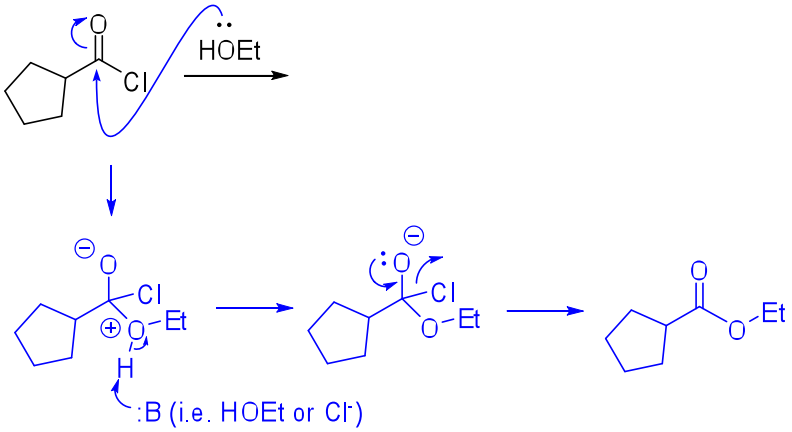


m.

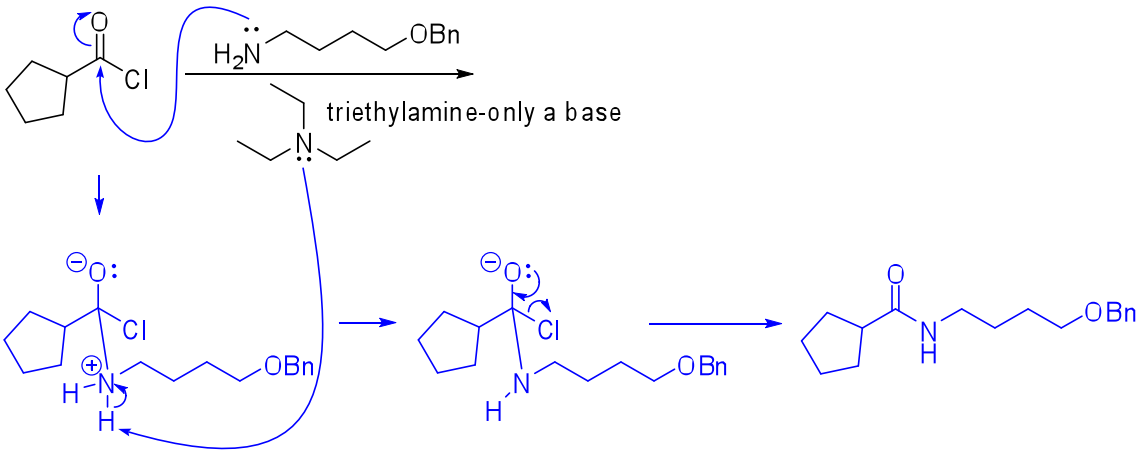


8. Give a mechanism and product for each of the following reactions:

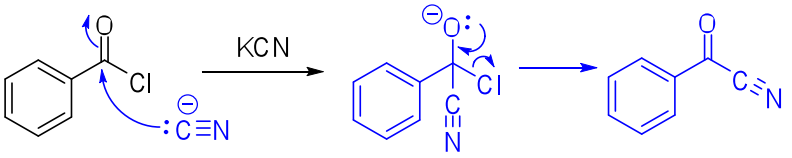
a.



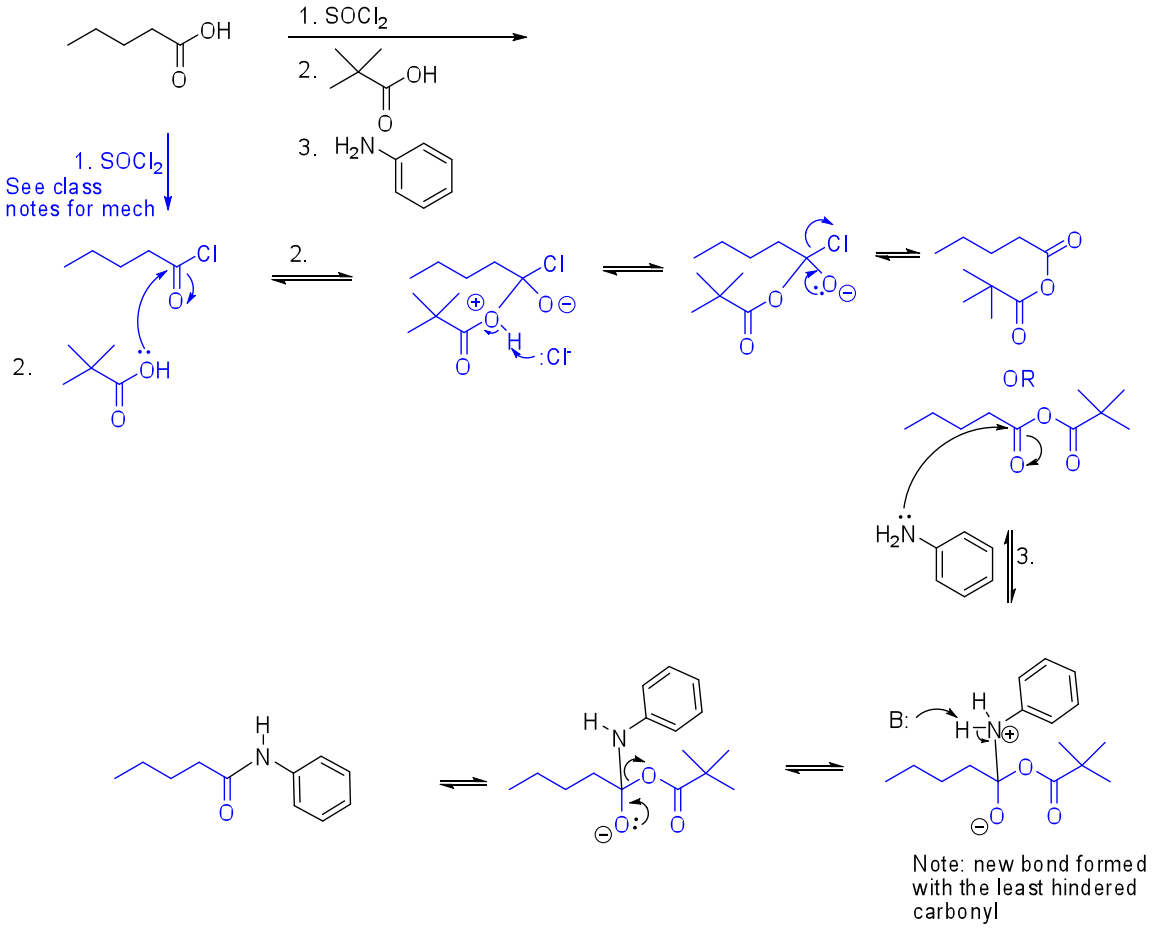
b.



c.

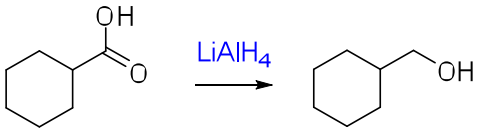


d. **(Question 8 continued)**

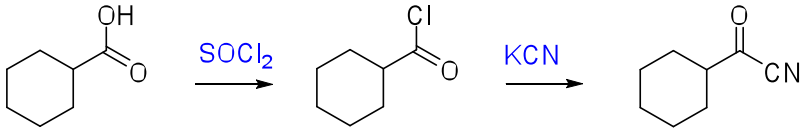


9. Fill in the reagents required to accomplish the following

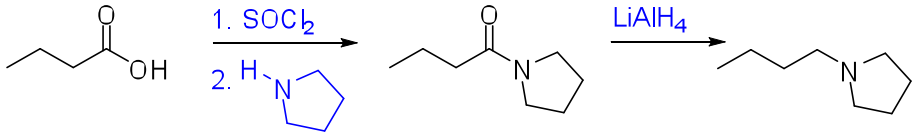
a.



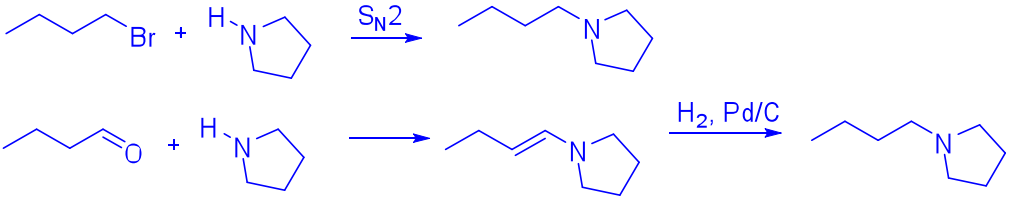
b.



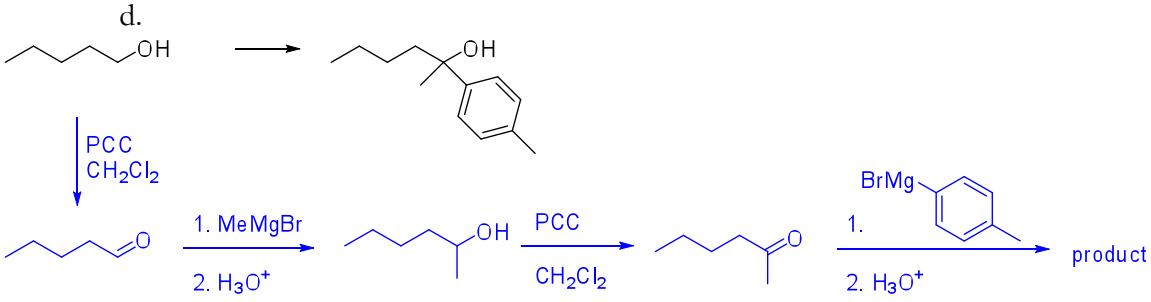
c.



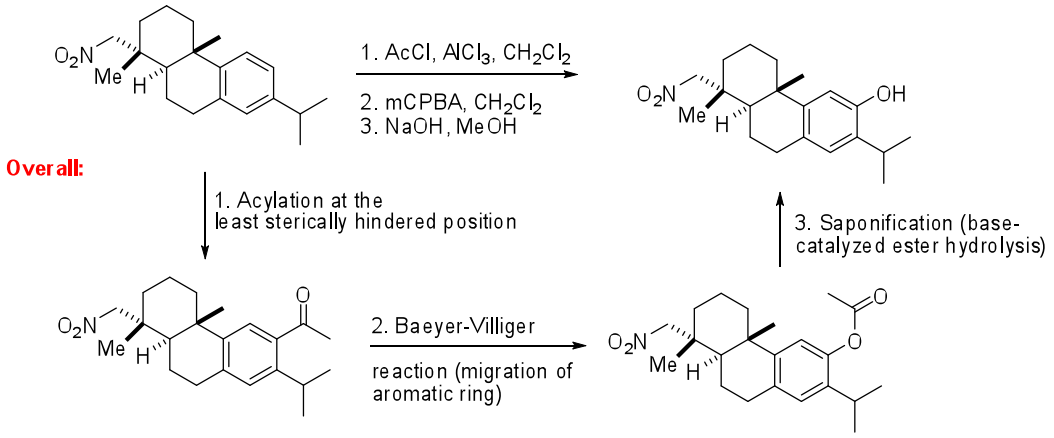
Suggest two other ways to synthesize the product shown in part c from starting materials containing only 4 carbons. The route can be completely different from the one used in part c.



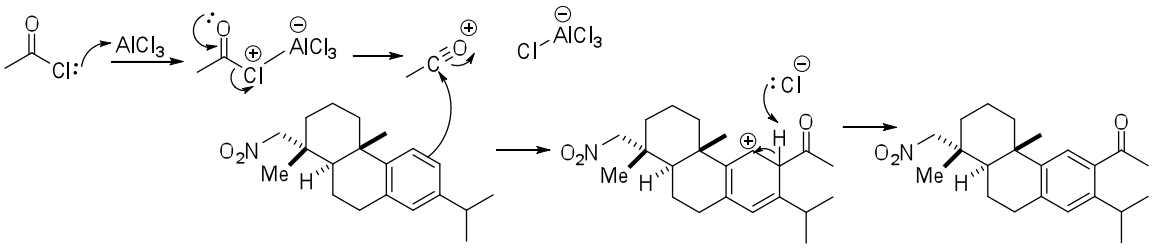
d.



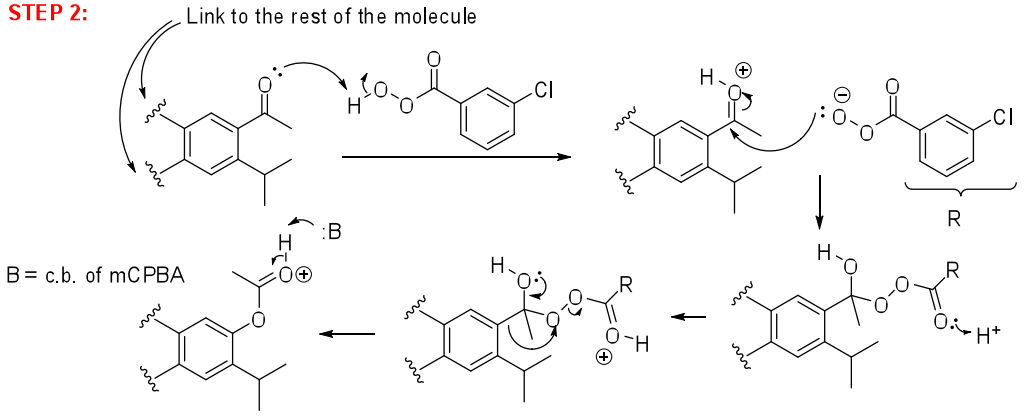
10. The following sequence brings together reactions from different parts of the course. Provide a mechanism for each step and give the structure of the final product.



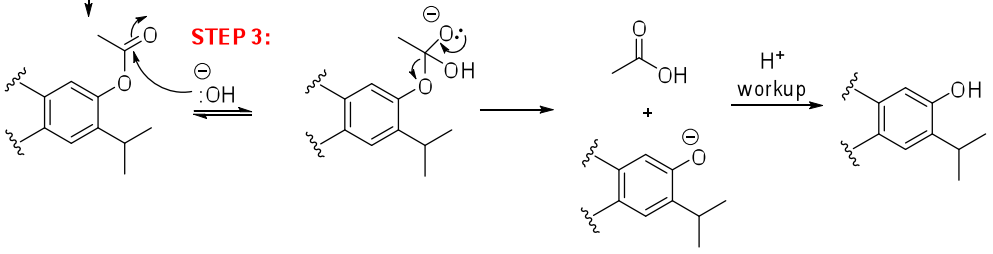
STEP 1:



STEP 2:

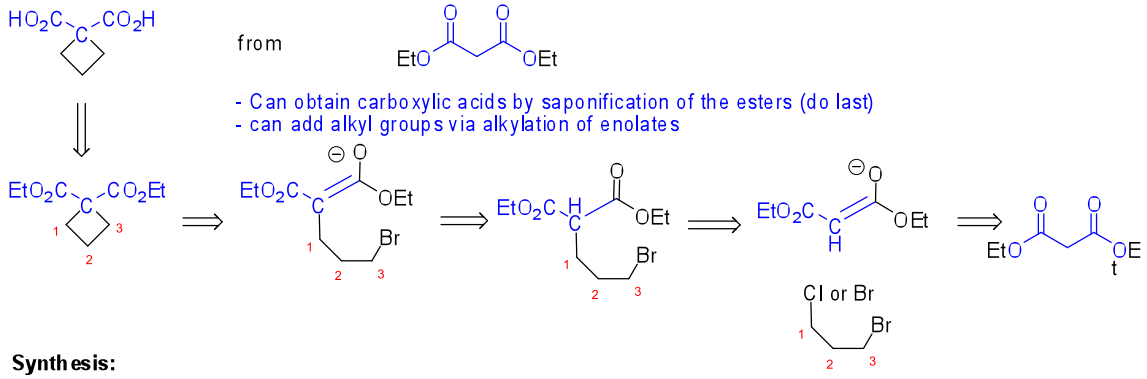


STEP 3:

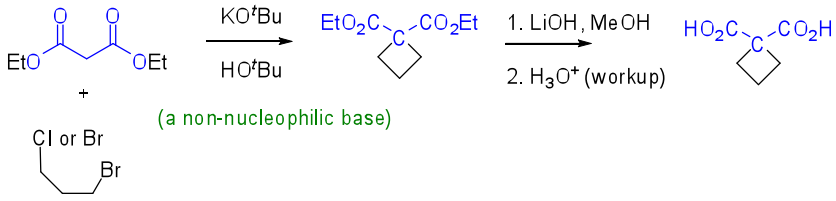


11. Propose a synthesis of the following compounds. A retrosynthetic analysis must be provided.

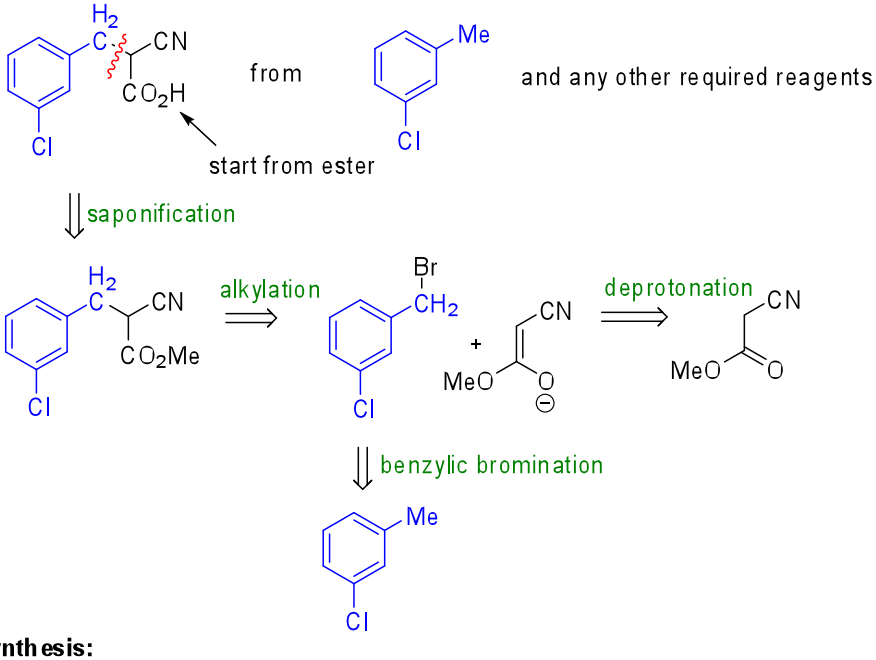
a.



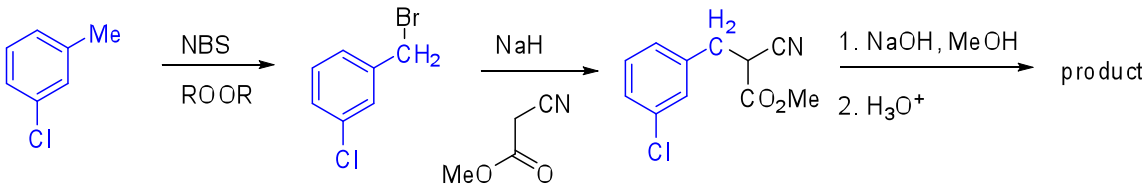
Synthesis:



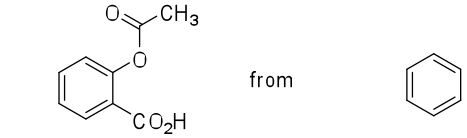
b. **Question 11 continues**



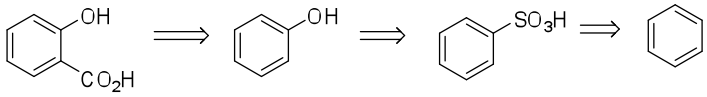
Synthesis:



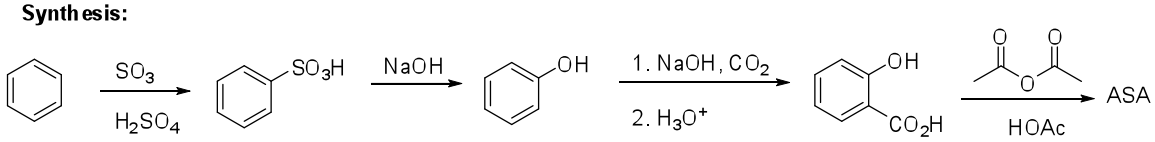
c. **(Question 11 continued)**



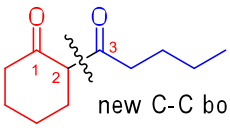
acetyl salicylic acid (ASA)
or aspirin



Synthesis:



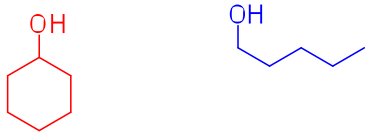
d.



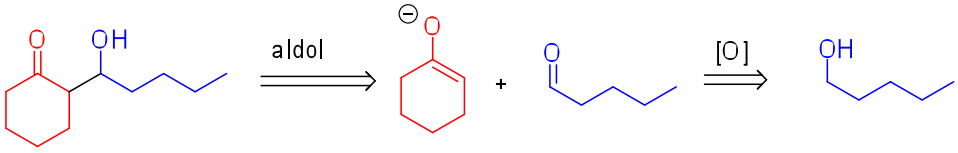
new C-C bond

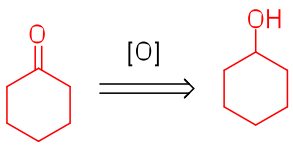
1,3-relationship suggests aldol reaction

from cyclohexanol and pentanol

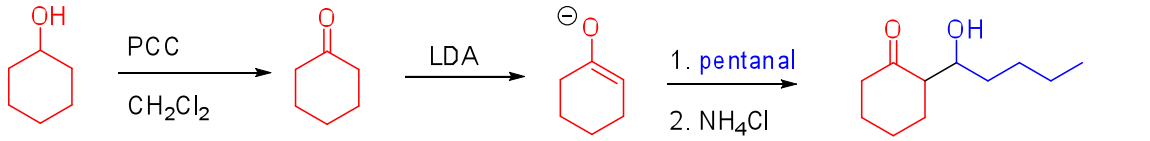


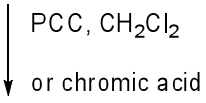
oxidation - [O]

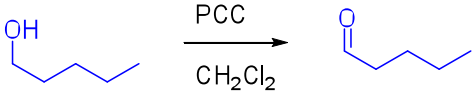




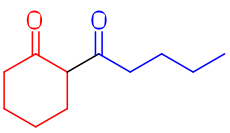
Synthesis:



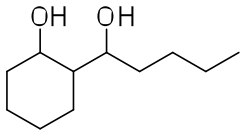




NOT chromic acid (why?)



e. **(Question 11 continued)**

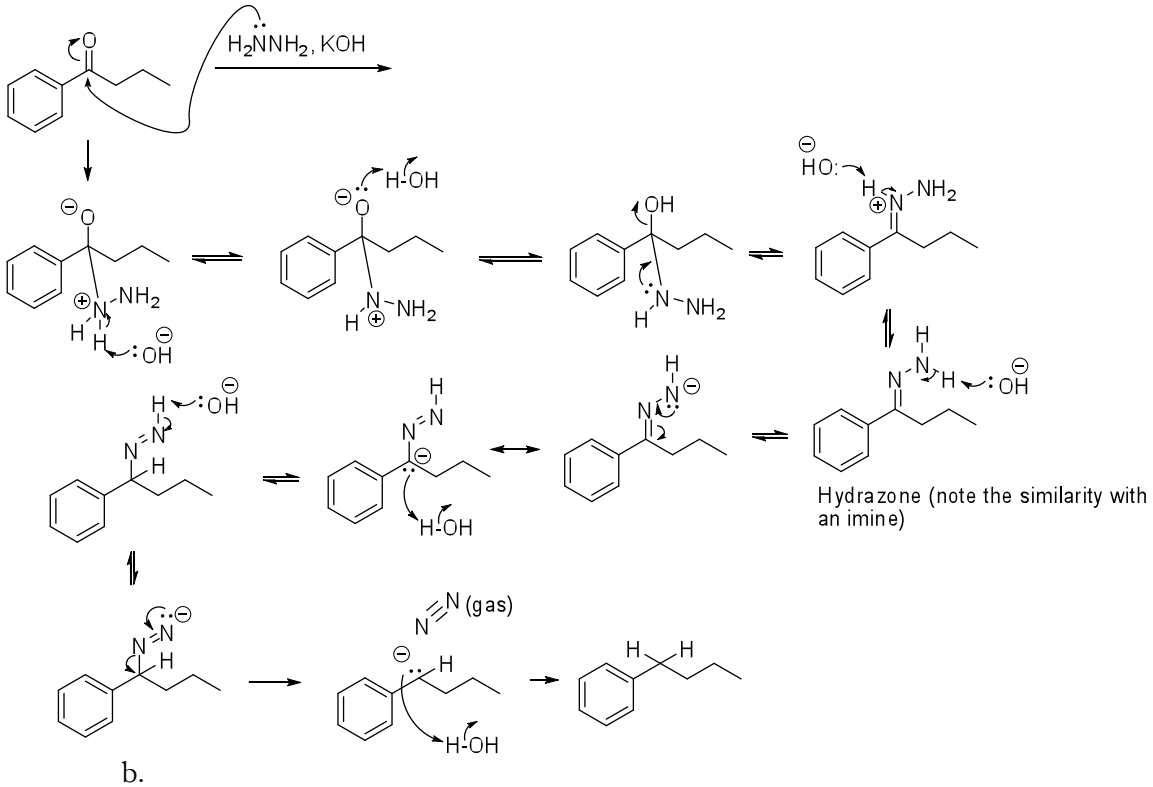


from cyclohexanol and pentanol

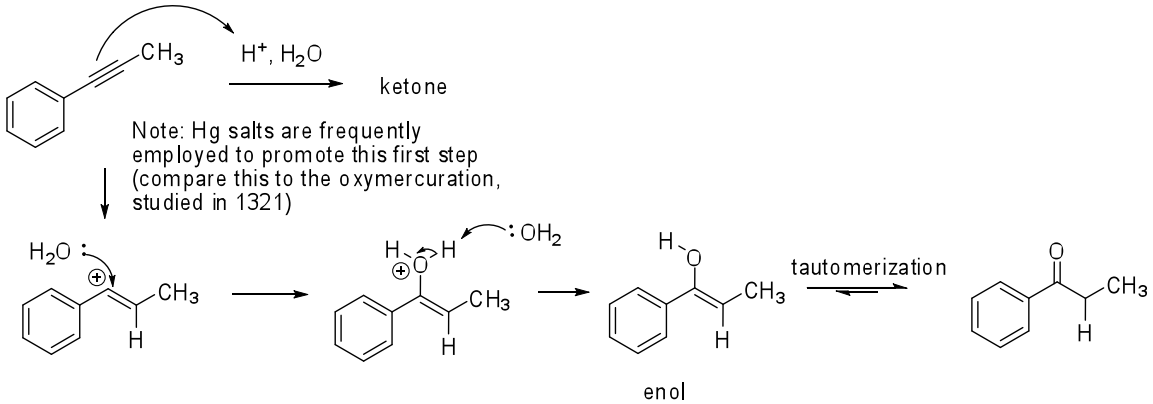
Same as above synthesis, except reduce the aldol product with $NaBH_4$ instead of oxidizing it.

12. Provide a mechanism and product for the following reactions:
Note: These mechanisms are closely related to reactions seen in class, although they are not quite identical to mechanisms studied in the course.

a.



b.



c. **(Question 12 continued)**