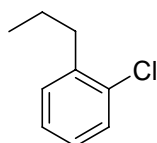
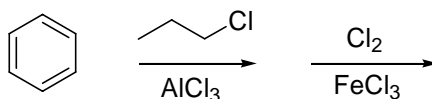
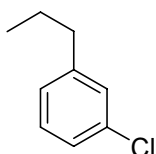


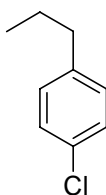
1. Predict the major product of the following reaction sequence.



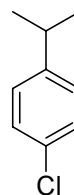
(a)



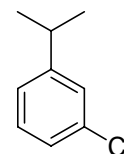
(b)



(c)

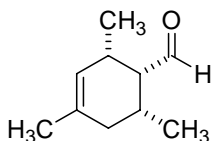
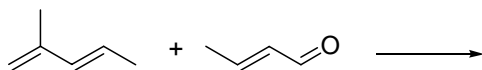


(d)

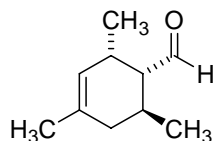


(e)

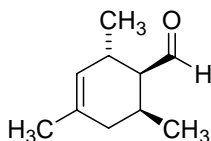
2. Predict the product of the following Diels Alder reaction.



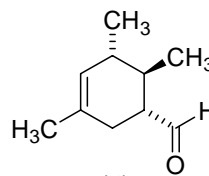
(a)



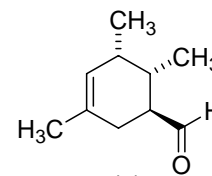
(b)



(c)

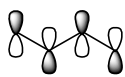


(d)

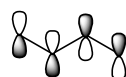


(e)

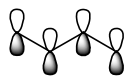
3. Consider the four π molecular orbitals of butadiene. Which of the following drawings does not properly represent one of the four π orbitals of butadiene?



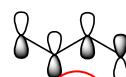
(a)



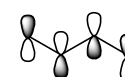
(b)



(c)

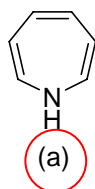


(d)

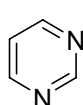


(e)

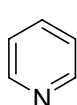
4. Which of the following compounds is not aromatic?



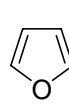
(a)



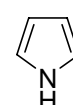
(b)



(c)

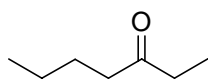
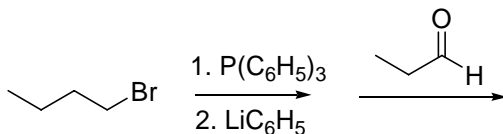


(d)

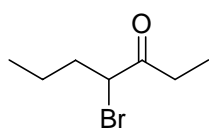


(e)

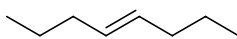
5. Predict the major product of the following reaction.



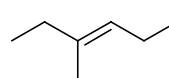
(a)



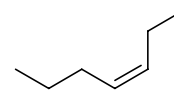
(b)



(c)

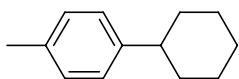
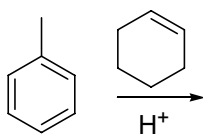


(d)

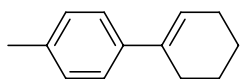


(e)

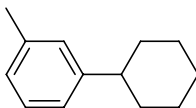
6. Predict the major product of the following reaction.



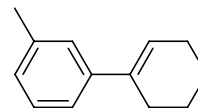
(a)



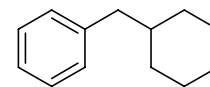
(b)



(c)

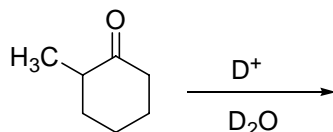


(d)

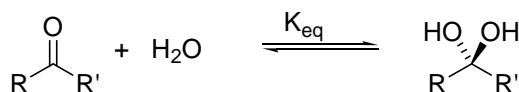


(e)

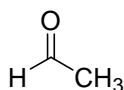
7. Predict the formula of the major product of the following reaction.

(a) $\text{C}_7\text{D}_7\text{H}_{11}\text{O}$ (b) $\text{C}_7\text{D}_2\text{H}_{10}\text{O}$ (c) $\text{C}_7\text{D}_3\text{H}_9\text{O}$ (d) $\text{C}_7\text{D}_5\text{H}_7\text{O}$ (e) $\text{C}_7\text{D}_9\text{H}_3\text{O}$

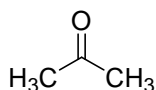
8. Which of the following compounds most readily forms a hydrate? In other words, which hydration reaction has the highest equilibrium constant?



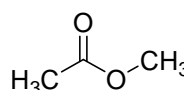
(a)



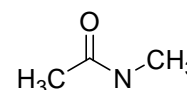
(b)



(c)

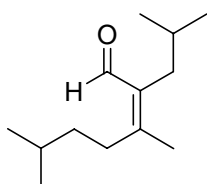
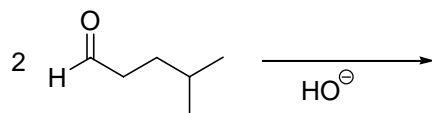


(d)

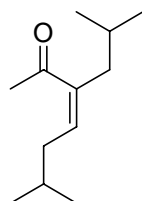


(e)

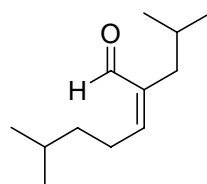
9. Predict the major product of the following aldol condensation.



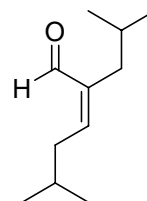
(a)



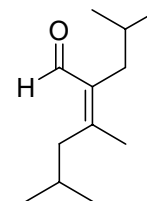
(b)



(c)

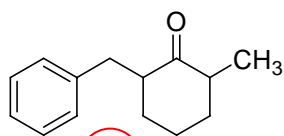
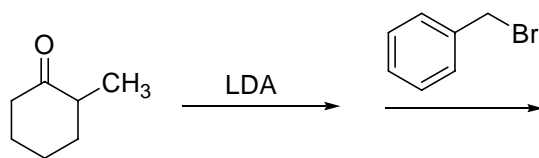


(d)

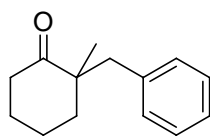


(e)

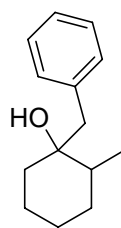
10. Predict the major product of the following reaction.



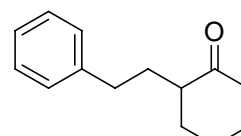
(a)



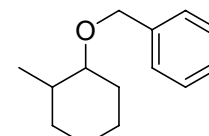
(b)



(c)

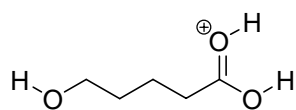
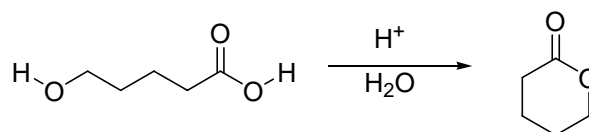


(d)

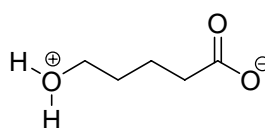


(e)

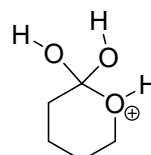
11. A student was asked to draw a mechanism for the acid catalyzed formation of a lactone. Which intermediate would not be found along a correct mechanistic pathway?



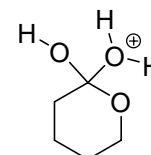
(a)



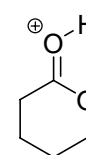
(b)



(c)

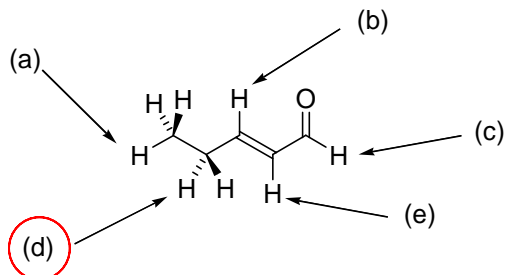


(d)

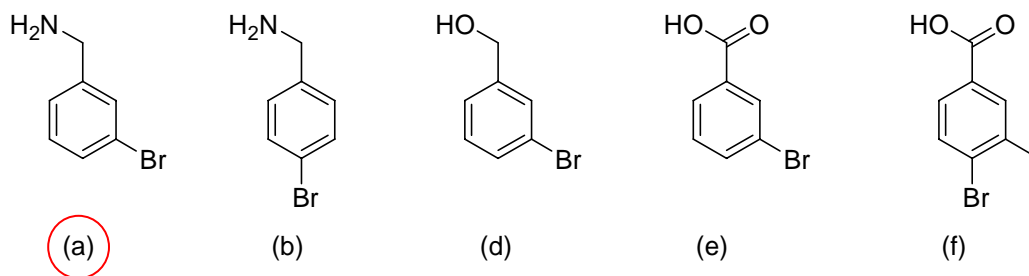
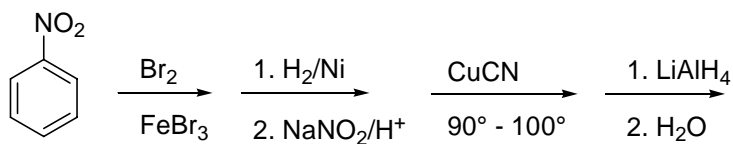


(e)

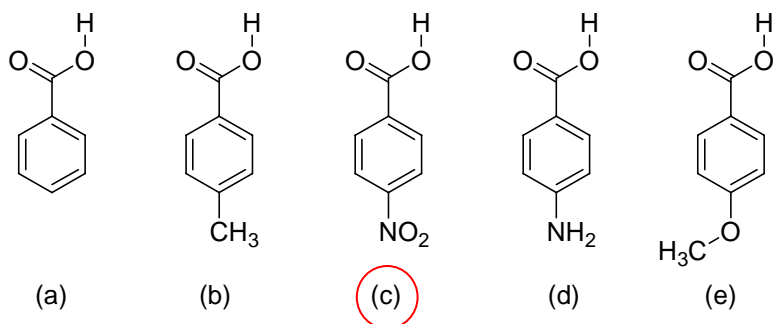
12. Which of the indicated hydrogen atoms of *E*-but-2-enal is the most acidic? (Lowest pK_a).



13. Predict the major product of the following reaction.

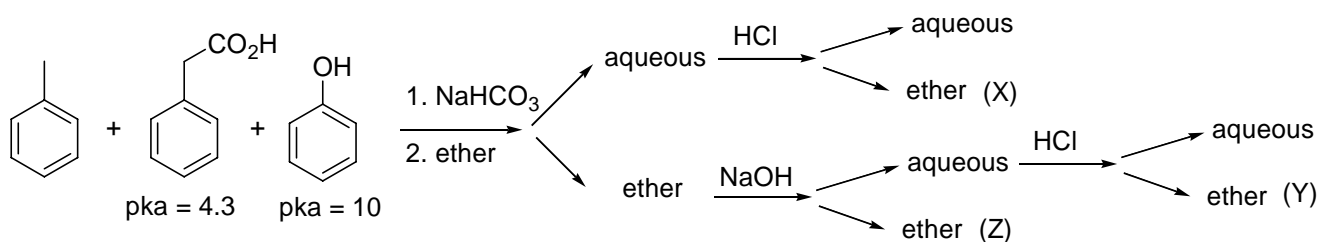


14. Which of the following compounds is the most acidic? (Lowest pK_a)



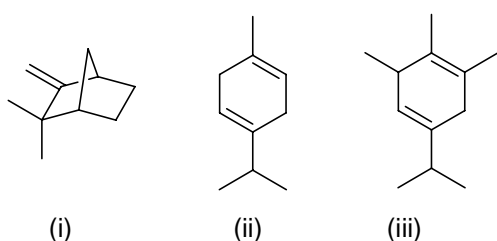
15. Which of the following statements about carbohydrates is false?
- In biological systems carbohydrates are used for energy storage.
 - Carbohydrates form an important structural component of plants.
 - In biological systems carbohydrates are used for molecular recognition and information.
 - Carbohydrates are lipid soluble.
 - Carbohydrates are polyalcohols of aldehydes or ketones.

16. Choose the answer that has the following compounds located correctly in the separation scheme.



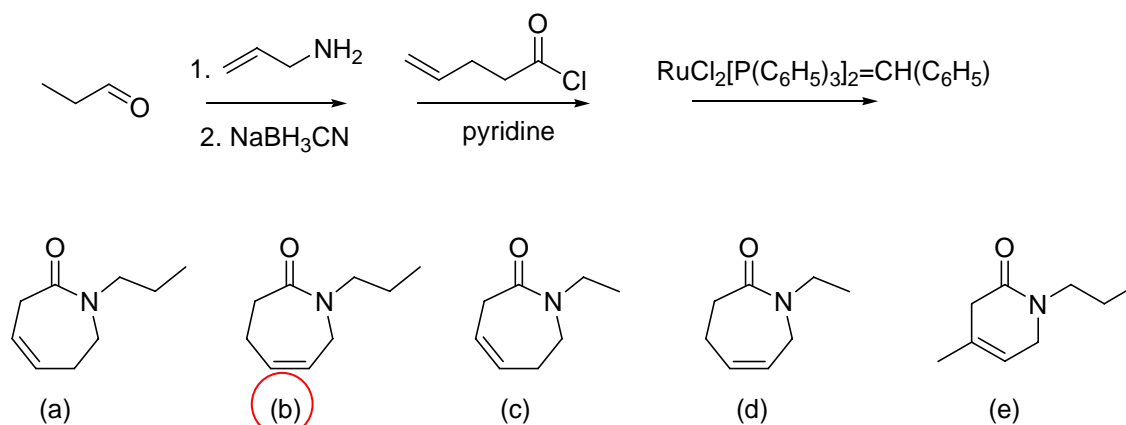
- toluene is in (Y); phenylacetic acid is in (Y); phenol is in (Z)
- toluene is in (Y); phenylacetic acid is in (X); phenol is in (Z)
- toluene is in (Z); phenylacetic acid is in (Y); phenol is in (X)
- toluene is in (Z); phenylacetic acid is in (X); phenol is in (Y)
- toluene is in (X); phenylacetic acid is in (Y); phenol is in (Z)

17. Which of the following compounds are terpenes and built up from isoprene units?



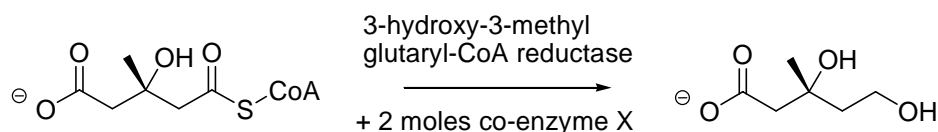
- Compounds i and ii are terpenes, iii is not.
- Compounds ii and iii are terpenes, i is not.
- Compounds i and iii are terpenes, ii is not.
- All three compounds are terpenes.
- None of the three compounds are terpenes.

18. Predict the major product of the following reaction sequence.



-
-
-
-
-

19. When we discussed the biosynthesis of cholesterol we began with the biosynthesis of an important intermediate called isopentenyl pyrophosphate. One important step along the pathway is shown below.



The reaction is enzyme catalyzed, but a co-enzyme is required. Which of the following compounds is co-enzyme X?

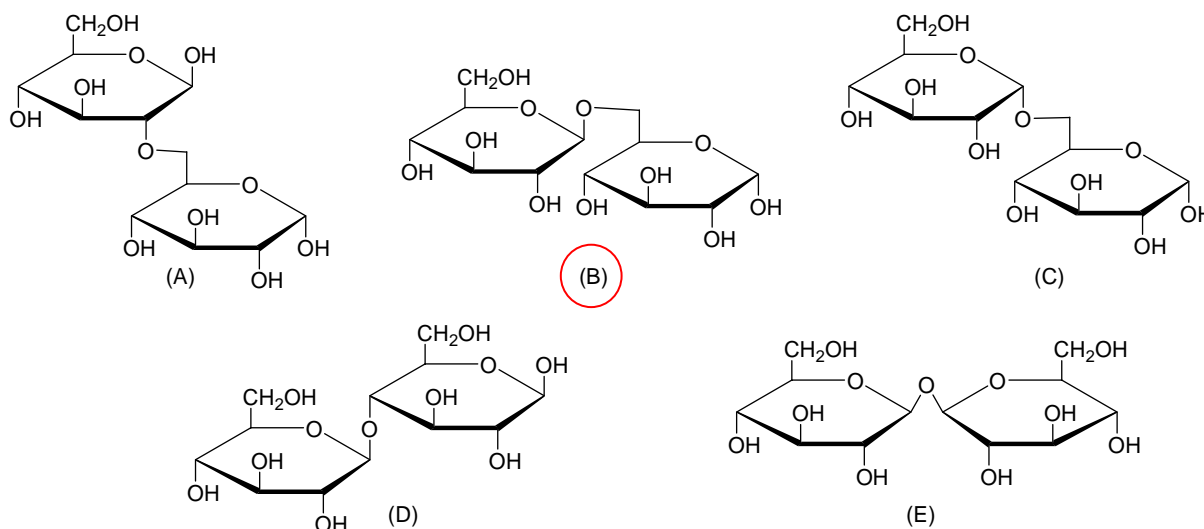
- (a) NAD^+ (b) NADH (c) H_2O (d) $\text{HP}_2\text{O}_5^{-3}$ (e) NADP^+

20. Gentiobiose is a disaccharide incorporated into the chemical structure of crocin, the chemical compound that gives saffron its color. Deduce the structure of gentiobiose from the following information.

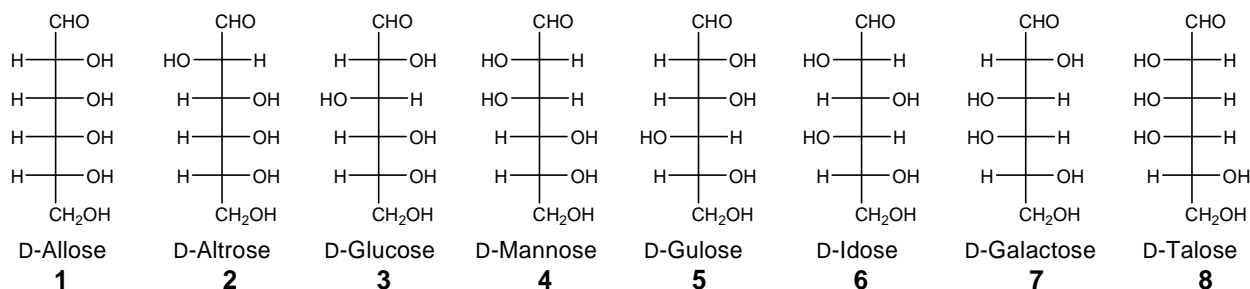
- i. Acid hydrolysis of gentiobiose yields only D-glucose.
- ii. Gentiobiose is hydrolyzed by β -glucosidase enzymes, but not by α -glucosidase enzymes.
- iii. Gentiobiose is a reducing sugar and reacts with sodium borohydride.
- iv. Methylation of gentiobiose followed by hydrolysis of the glycosidic bonds yields the two D-glucose derivatives shown below.



What is the structure of gentiobiose?

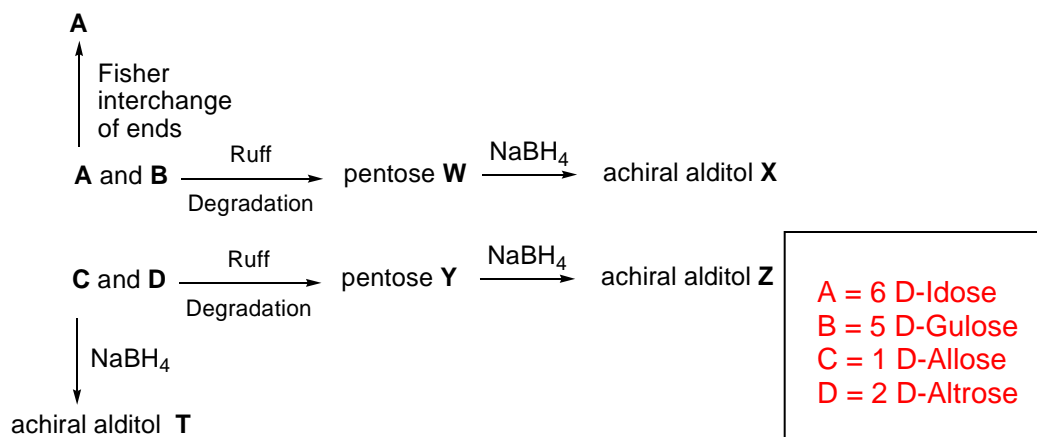


21. This problem is based upon the ideas used in the classic Fisher glucose proof. (12 points)



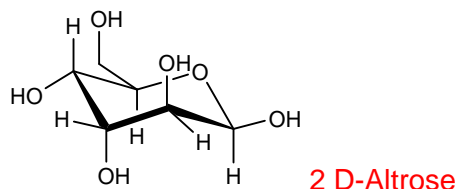
Suppose you had four unknown D-aldohexoses, compounds A, B, C and D. The following reactions were run to identify compounds.

- The Ruff degradation of a aldohexose removes the C-2 carbon and yields an aldopentose. The Ruff degradation of **A** and **B** gave the same pentose **W**. NaBH_4 reduction of pentose **W** gave an achiral alditol **X**.
- The Ruff degradation of **C** and **D** gave the same pentose **Y**. NaBH_4 reduction of pentose **Y** also gave an achiral alditol **Z**.
- NaBH_4 reduction of **C** gave an achiral alditol, **T**.
- Fisher developed a method for interchanging the ends of an aldohexose. Applying this procedure to aldohexose **A** gave back the same compound **A**.

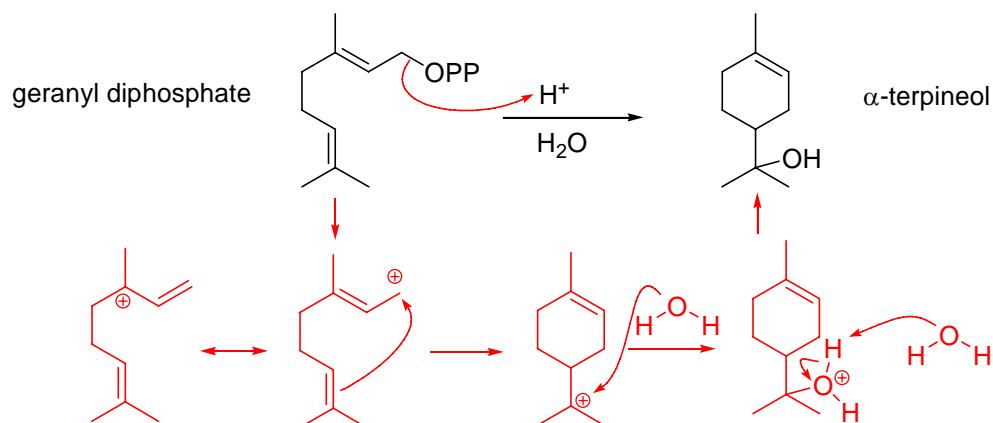


Identify the four compounds A, B, C and D. On the answer form fill in the blanks using the numbers given under the structure names in the figure at the top of this page.

22. Identify the following sugar. (Use the numbers given at the beginning of problem 21.) (6 points)

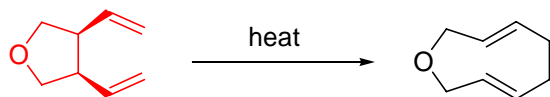


23. The compound geranyl diphosphate is the precursor in the biosynthetic pathway to various monoterpenes. Using the curved arrow formalism give a reaction mechanism showing the bond making and bond breaking in the acid catalyzed transformation of geranyl diphosphate into the compound α -terpineol. (10 points)

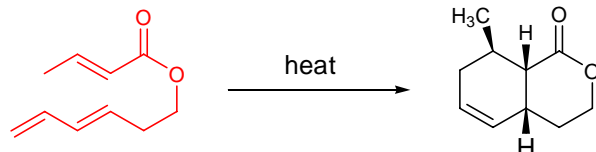


Complete the following pericyclic reactions by supplying the missing reactant. (5 points each)

24. .

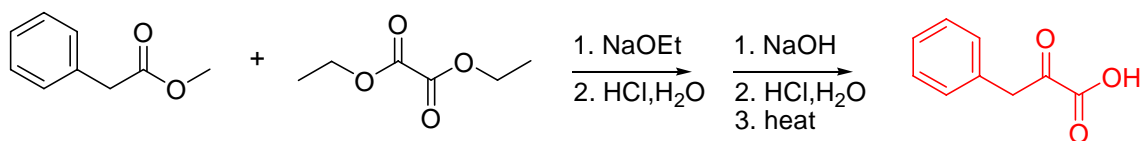


25.

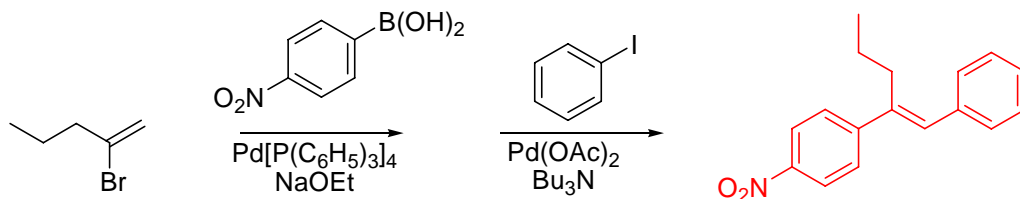


Predict the product of the following reaction sequences. (5 points each)

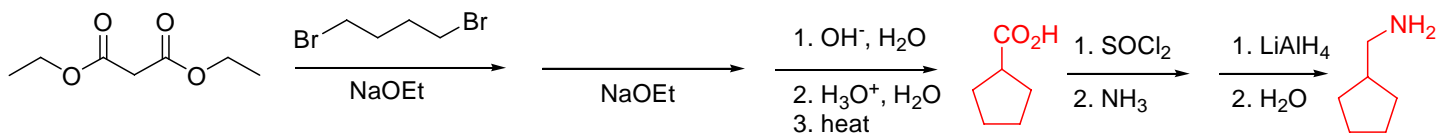
26.



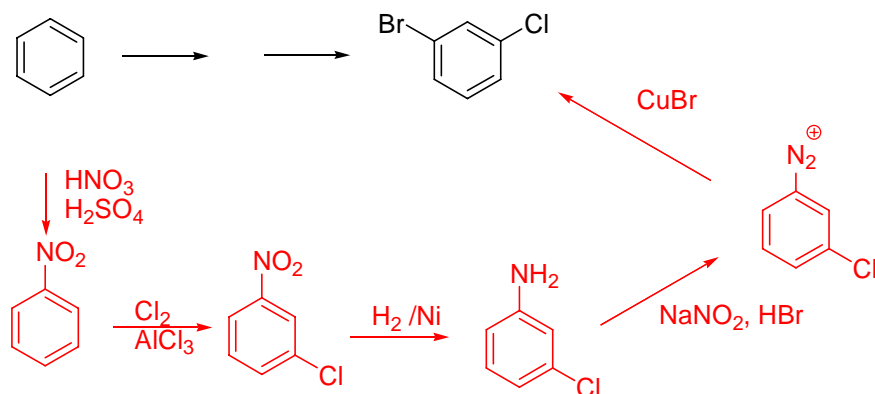
27.



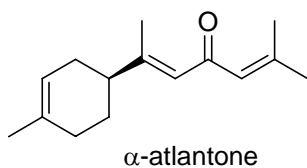
28. Complete the following malonic acid ester synthesis by identifying **A** and **B**. (10 points)



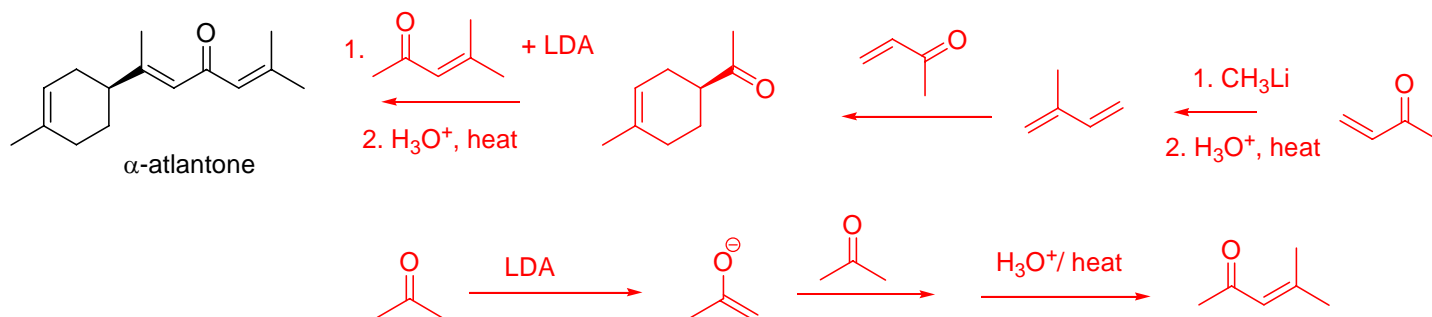
29. Complete the following synthesis (10 points)



30. The wood of the cedar tree, *Cedrus atlantica*, has a delightful fragrance. A major component of the fragrance is α -atlantone. (12 points)



Propose a racemic synthesis of α -atlantone. Your starting materials should be of four or fewer carbons.



Challenge Question.

The sesquiterpene *epi*-aristolochene can be isolated from tobacco plants. Its biosynthetic pathway starts with farnesyl pyrophosphate and includes another sesquiterpene, germacrene A as an intermediate. Using the curved arrow formalism give a reaction mechanism showing the bond making and bond breaking in these two acid catalyzed transformations.

