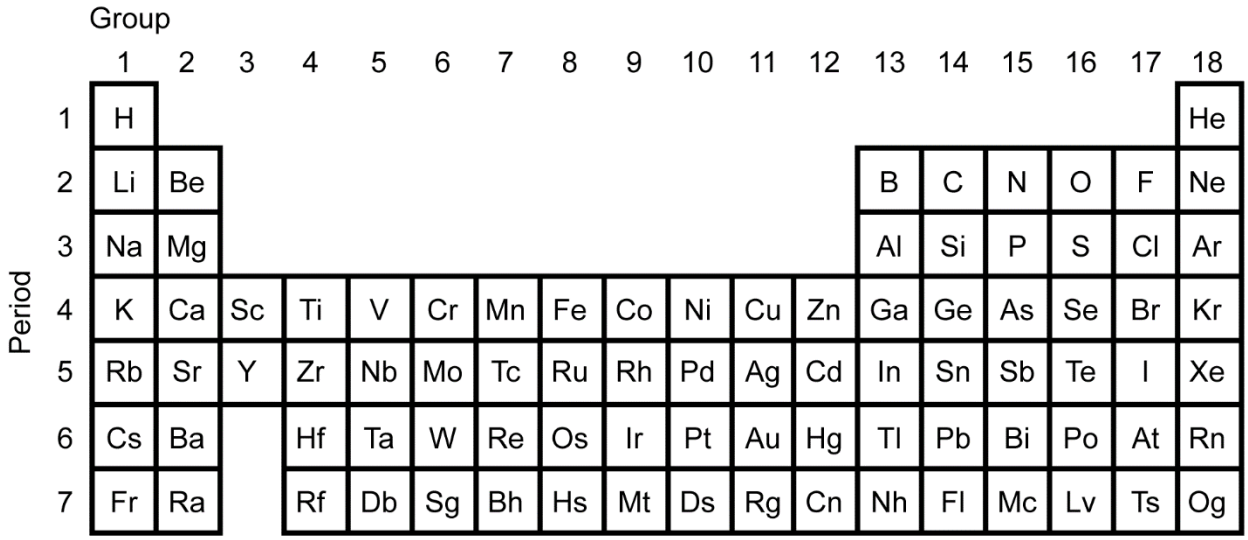
CHE 322 Organic Chemistry II

Final Exam Form 1

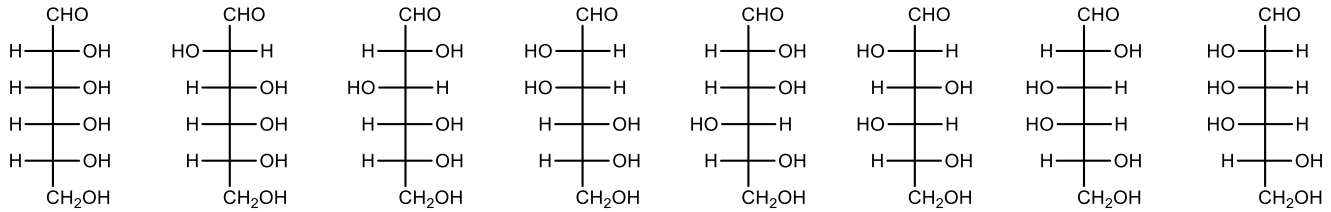
Thursday May 9, 2024

2:15 PM – 5:00 PM

1. Write your nine digit University ID number in the nine boxes provided and then bubble in each of the nine digits.
2. Print your name and sign your answer form using the spaces provided.
3. Questions 1 to 20 are multiple choice questions worth 5 points. Bubble your answers on the answer form. Questions 21-30 are short answer questions with points as indicated. Write out your answers in the indicated place on the answer form.



Stony Brook University



Effects of Substituents on Electrophilic Aromatic Substitution

Ortho-Para Directors

Strongly Activating

$-NH_2$ $-NHR$ $-NR_2$

$-OH$ $-O^-$

Moderately Activating

$-NHCOCH_3$ $-NHCOR$

$-OCH_3$ $-OR$

Weakly Activating

$-CH_3$ $-C_2H_5$ $-R$ $-C_6H_5$

Weakly Deactivating

$-F$ $-Cl$ $-Br$ $-I$

Meta Directors

Moderately Deactivating

$-C{\equiv}N$

$-SO_3H$

$-CO_2H$ $-CO_2R$

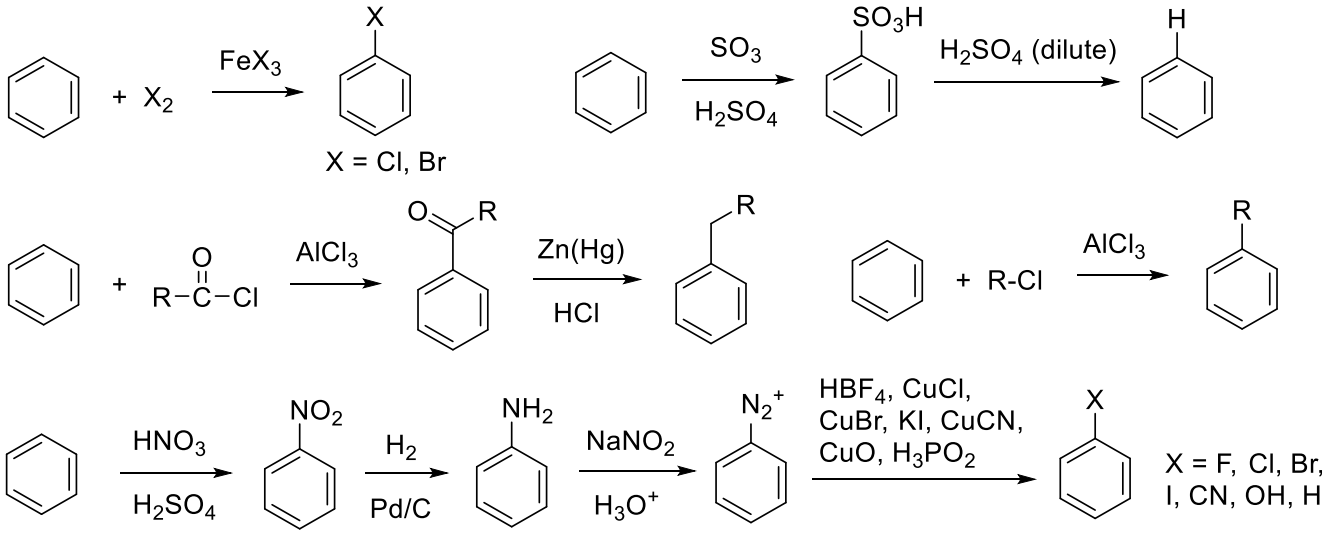
$-CHO$ $-COR$

Strongly Deactivating

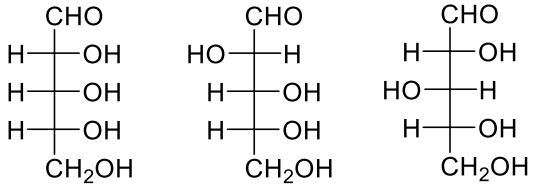
$-NO_2$

$-NH_3^+$ $-NR_3^+$

$-CF_3$ $-CCl_3$



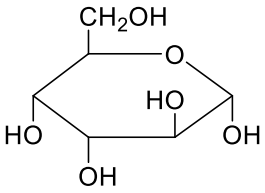
1. Which of the structures shown will form an achiral aldaric acid upon oxidation with nitric acid?

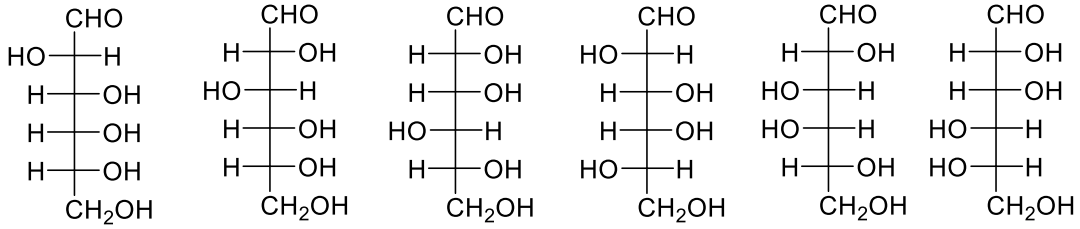


1 2 3

A. 1 only B. 2 only C. 3 only D. 1 and 2 E. 1 and 3 F. 2 and 3

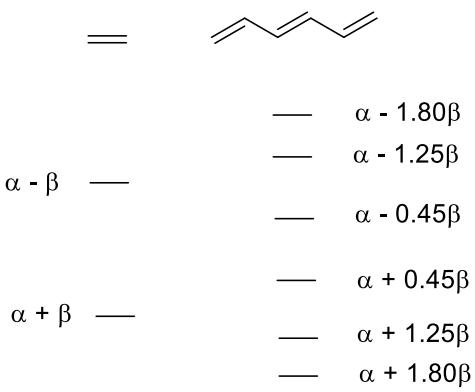
2. Which Fischer projection corresponds to the acyclic form of the sugar in the Haworth projection shown?





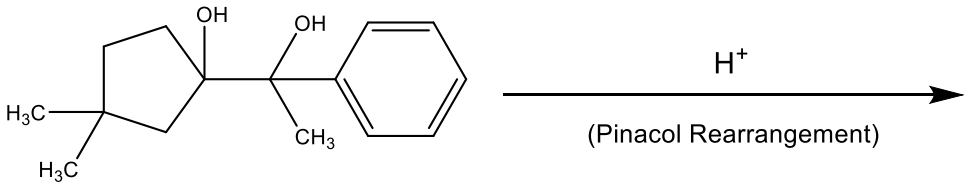
A B C D E F

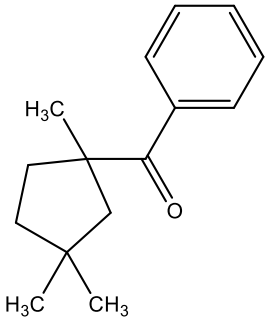
3. Shown are the Hückel π-molecular orbital energies for ethene and 1,3,5-hexatriene. Determine the delocalization energy for 1,3,5-hexatriene based on comparison to three ethene molecules. (Orbital energies are rounded so that you should not need or use a calculator.)



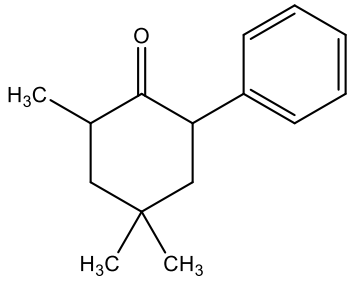
A. 0.45 β B. 1.0 β C. 1.25 β D. 1.8 β E. 2.0 β F. 3.0 β

4. Which of the following products will **NOT** be formed in a Pinacol Rearrangement of the following compound?

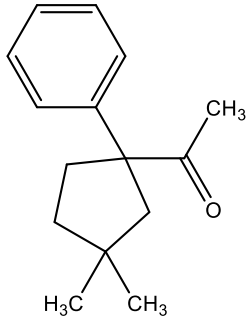




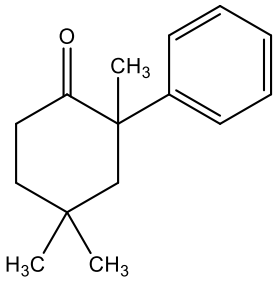
A



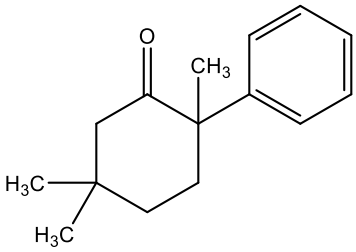
B



C

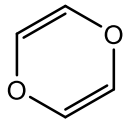


D

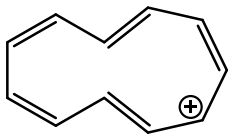


E

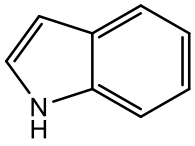
5. Which compound(s) is(are) aromatic?



1



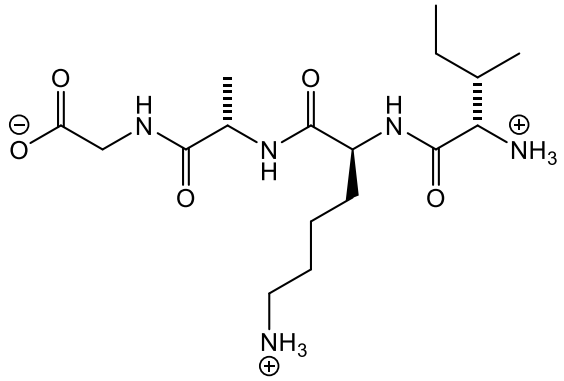
2



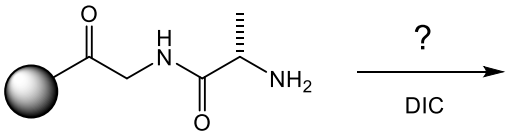
3

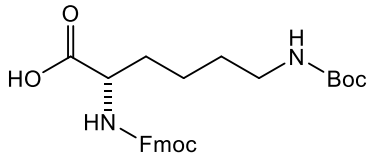
A. 1 only B. 2 only C. 3 only D. 1 and 2 E. 1 and 3 F. 2 and 3

6. The following short peptide was synthesized using solid-phase peptide synthesis.

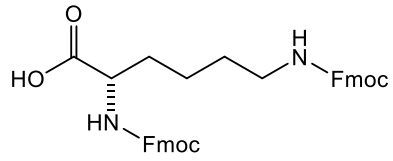


Choose the correct reagent for the coupling step shown of this peptide synthesis.

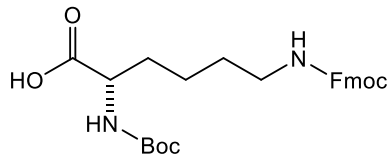




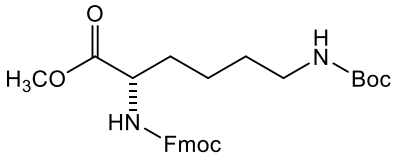
A



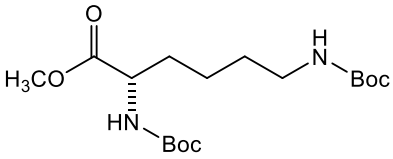
B



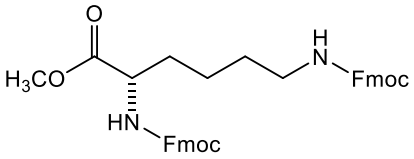
C



D

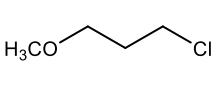


E

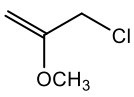


F

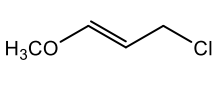
7. Select the order that has the following chlorides correctly arranged with respect to increasing reactivity in a solvolysis reaction.



1



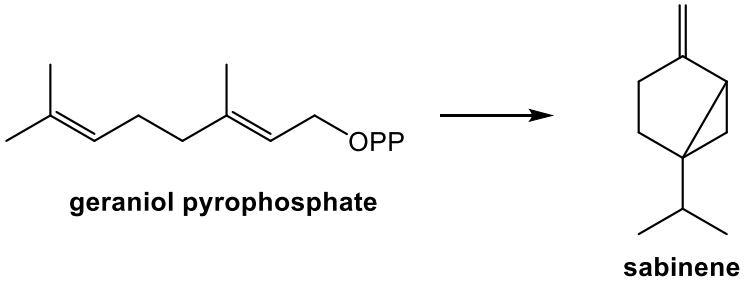
2



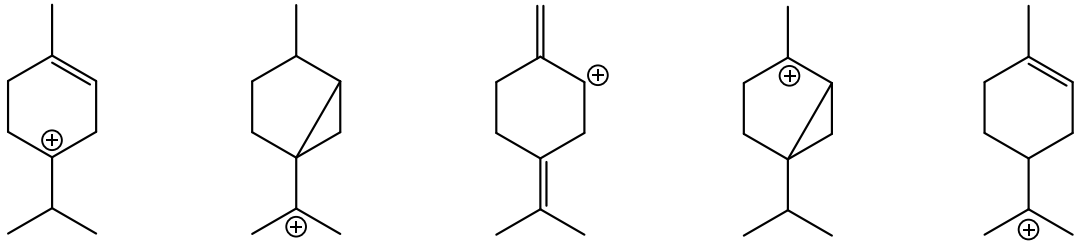
3

A **1 2 3** increasing reactivity → B **1 3 2** increasing reactivity → C **2 1 3** increasing reactivity → D **2 3 1** increasing reactivity → E **3 1 2** increasing reactivity → F **3 2 1** increasing reactivity

8. Which of the following are intermediates in the biosynthesis of sabinene from geraniol pyrophosphate?



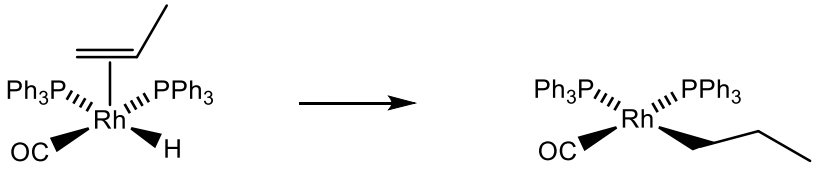
geraniol pyrophosphate **sabinene**



1 2 3 4 5

A. 2 and 5 B. 3 and 4 C. 3 and 5 D. 1, 2, 3 E. 1, 2, 4 F. 1, 4, 5

9. How would you classify the following mechanistic step?



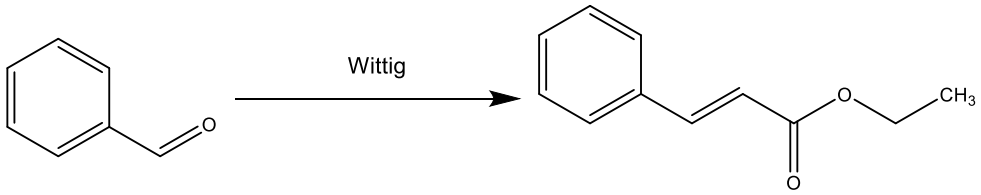
1 **2**

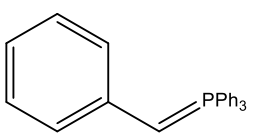
A. ligand association B. oxidation addition C. migratory insertion
D. ligand disassociation E. reductive elimination F. migratory deinsertion

10. What is the oxidation state of rhodium and the total valence electron count of intermediate **1** from the previous problem?

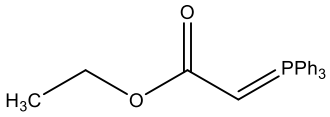
A. 0, 16 e^- B. 0, 18 e^- C. +1, 16 e^- D. +1, 18 e^- E. +2, 16 e^- F. +2, 18 e^-

11. Which of the following phosphorus ylides will be the ideal partner to synthesize the following product in a Wittig reaction?

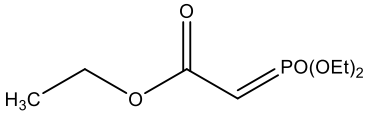




A



B



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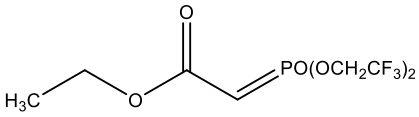
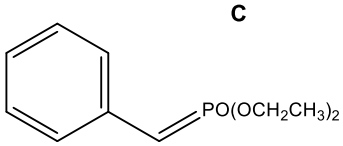
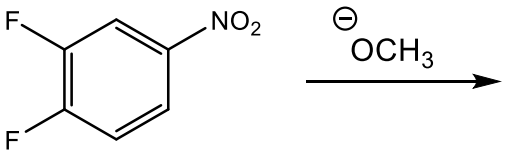


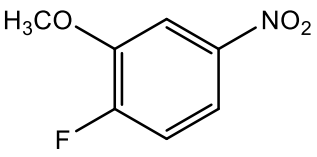
D



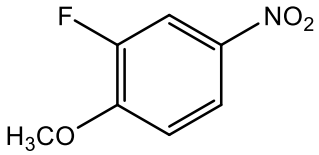
E

12. Choose the major product from the following nucleophilic aromatic substitution reaction that goes through an addition-elimination mechanism.

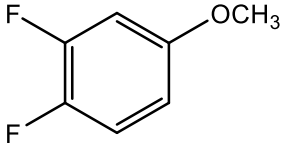




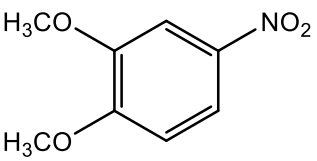
A



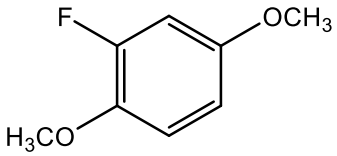
B



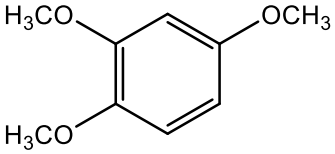
C



D

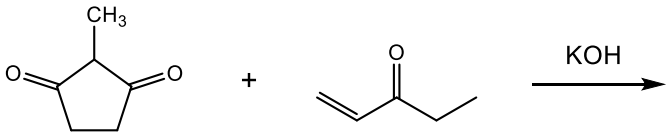


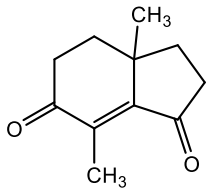
E



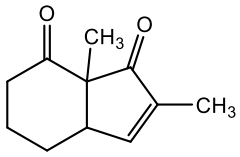
F

13. Select the major product of the following Robinson annulation.

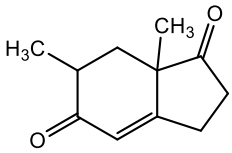




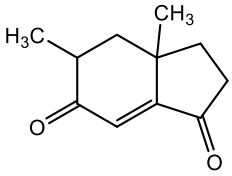
A



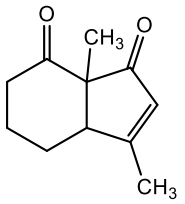
B



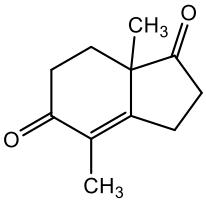
C



D

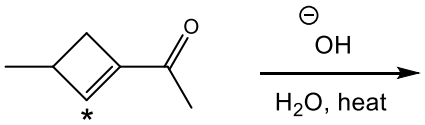


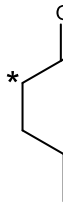
E



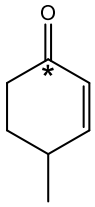
F

14. The following reaction undergoes a rearrangement that involves a retro aldol followed by an aldol condensation. Choose the correct product of this rearrangement. The asterisk denotes a radiolabeled carbon atom.

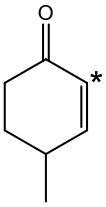




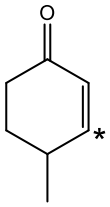
A



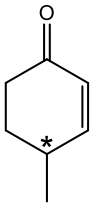
B



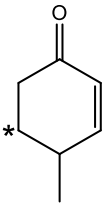
C



D

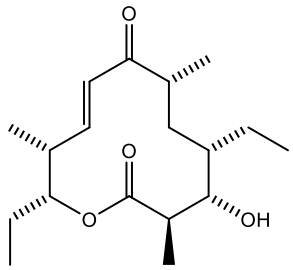


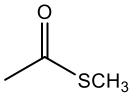
E



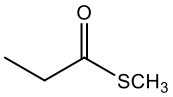
F

15. Which starter and extenders would be required for the biosynthesis of the following macrolide?

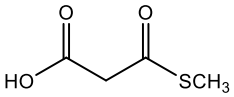




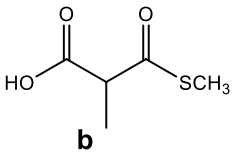
x



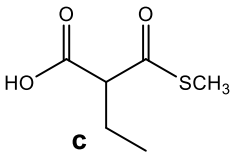
y



a



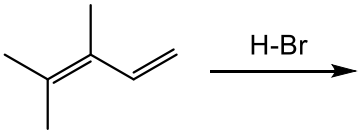
b

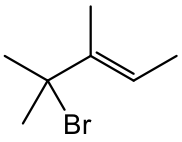


c

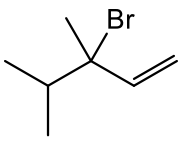
A. starter = **x**. extenders = one **a**, four **b**
B. starter = **x**. extenders = one **a**, two **b**, one **c**
C. starter = **x**. extenders = two **a**, two **b**, one **c**
D. starter = **y**. extenders = one **a**, four **b**
E. starter = **y**. extenders = one **a**, three **b**, one **c**
F. starter = **y**. extenders = one **a**, two **b**, two **c**

16. Select the two products of the following addition reaction.

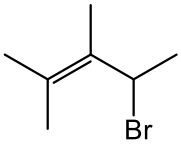




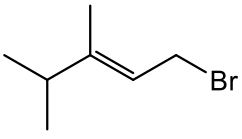
1



2



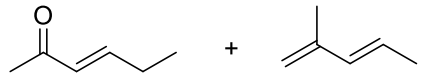
3

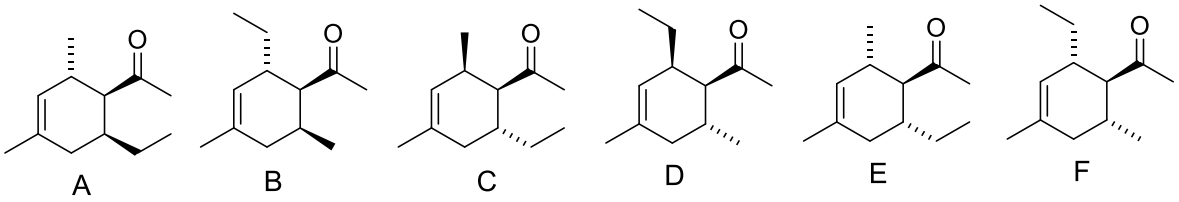


4

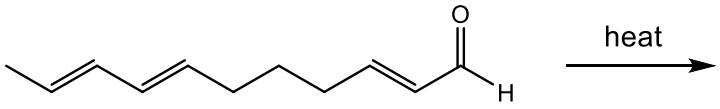
A. 1 and 2 B. 1 and 3 C. 1 and 4 D. 2 and 3 E. 2 and 4 F. 3 and 4

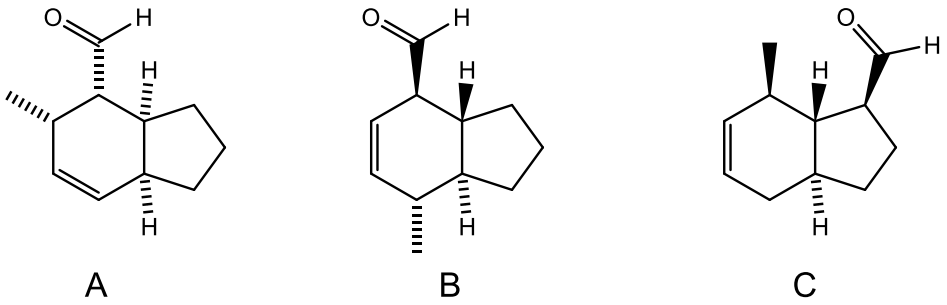
17. Predict the major product of the Diels-Alder reaction shown. (Each structure represents one enantiomer of a racemic mixture.)

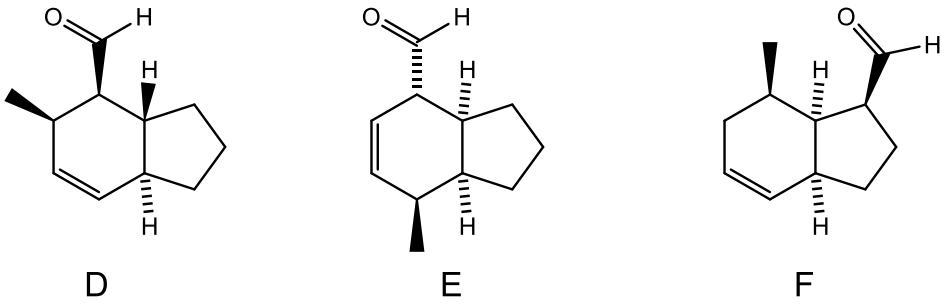




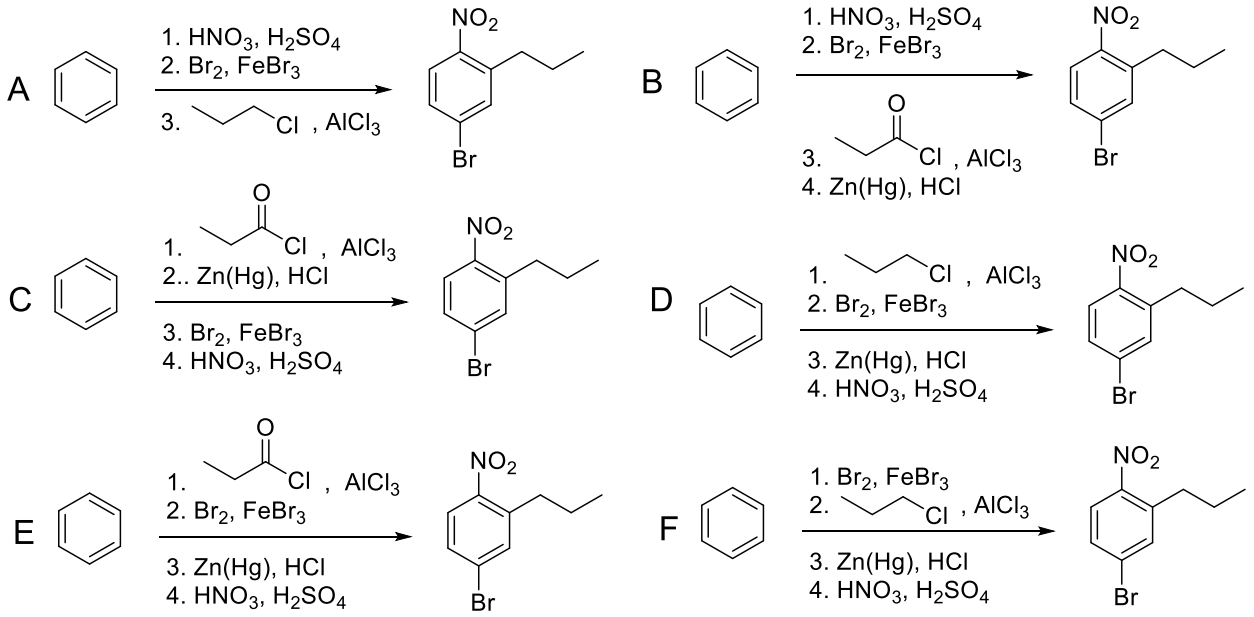
18. Choose the major product of the following intramolecular Diels-Alder reaction. The reaction will produce a racemic mixture, but only one enantiomer is shown in each choice. <u>Assume the endo product is the major product</u>.



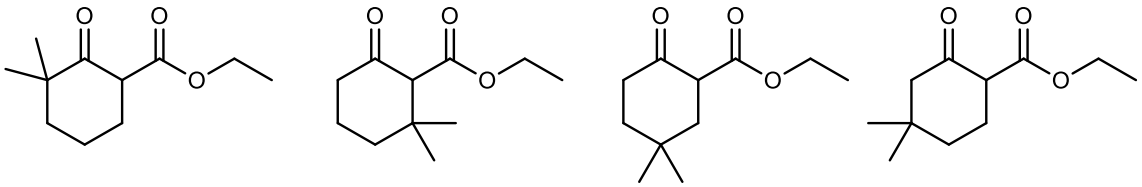




19. Choose the best method for making the product shown. The best answer is expected to form the product shown and one other major product.



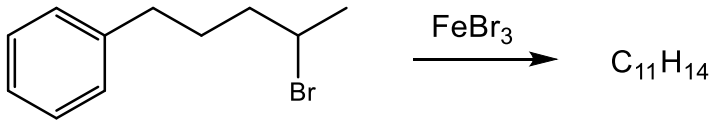
20. Which of the following Claisen products are derived from the same diester starting material.



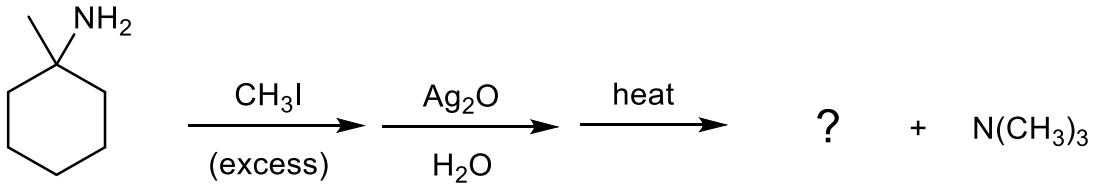
1 **2** **3** **4**

A. 1 + 2 B. 1 + 3 C. 1 + 4 D. 2 + 3 E. 2 + 4 F. 3 + 4

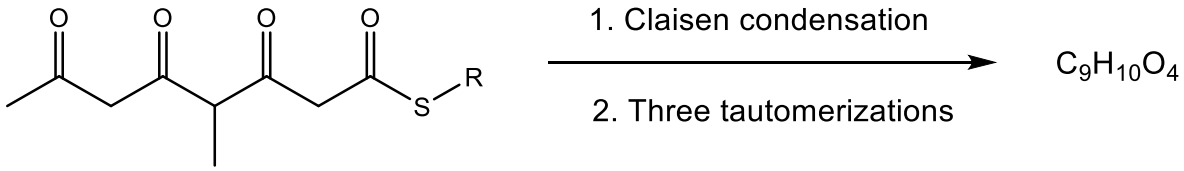
21. Draw the major product of the following Friedel-Crafts alkylation. 5 pts



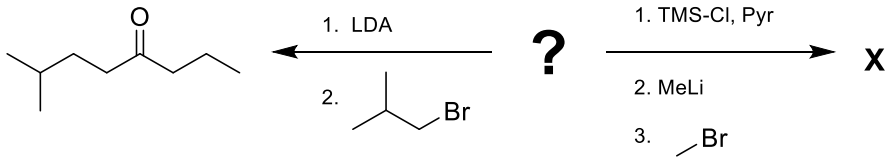
22. Draw the major product of the following Hofmann elimination. 5 pts



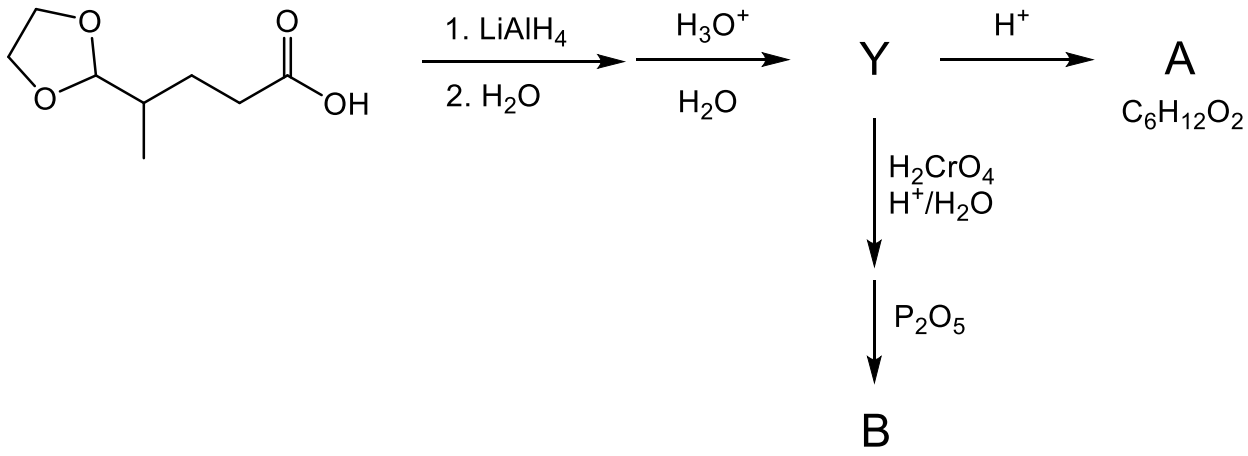
23. The biosynthetic pathway shown below leads to an aromatic compound. It starts with an enzymatic synthesis of the intermediate compound shown below and continues with a Claisen condensation followed by three enolizations. Draw the structure of the product. 5 pts



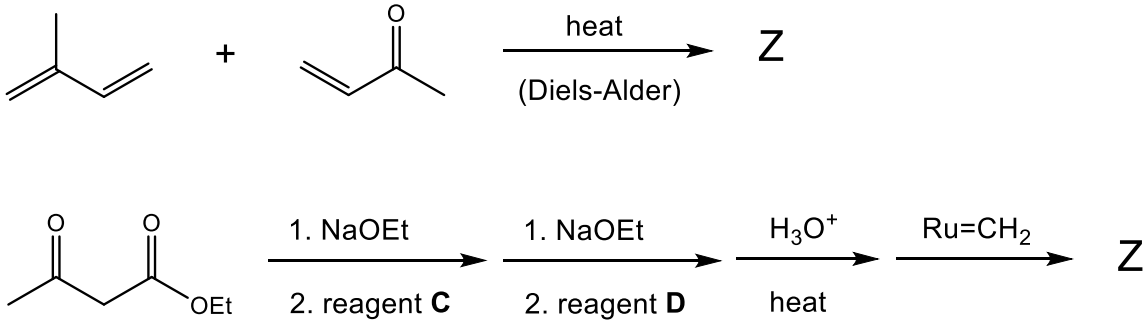
24. For the reaction scheme shown, provide the structure of the product **X**. 5 pts



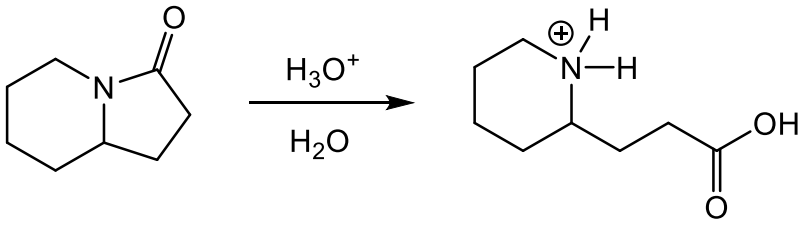
25. Based on the following scheme, determine, and draw the structures of compounds **A** and **B** only. 10 pts



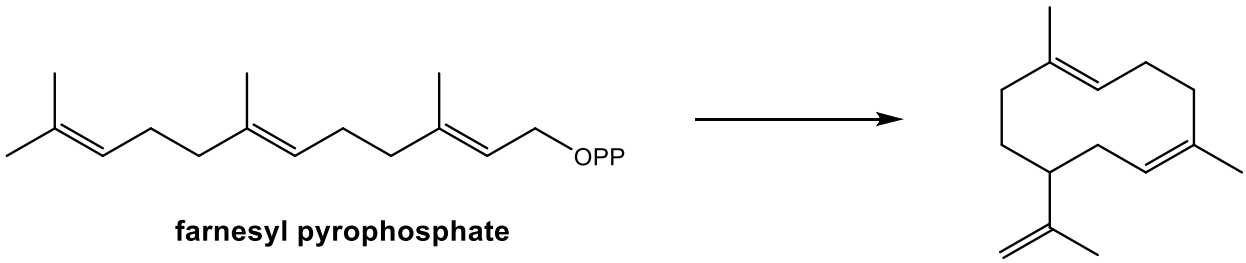
26. Below are shown two pathways to the same cyclic compound **Z**. Determine and draw the two bromide reagents **C** and **D** for the second pathway. 10 pts



27. Provide a curved arrow mechanism to illustrate all the bond breaking and bond making steps of the following hydrolysis. Show all intermediate structures. 10 pts



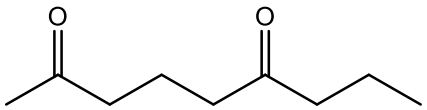
28. Helminthogermacrene is made from farnesyl pyrophosphate. Draw a curved arrow mechanism for the biosynthetic pathway of helminthogermacrene. HINT: redraw farnesyl pyrophosphate in the shape of the product to help you see which double bond attacks. 10 pts



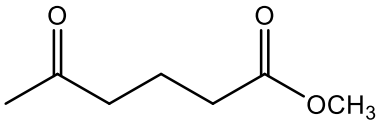
farnesyl pyrophosphate

helminthogermacrene

29. Propose a synthesis of the target compound from the starting material shown. You may use any reagents. 10 pts



target compound



starting material

30. Propose a synthesis of the following amine from benzene. You may use any other reagents. 10 pts