Dr. Steven Pedersen February 27, 2017

Chemistry 3B

Midterm 1

Student name: ANSWER KEY

Student ID: _____ (Also include your SID in the top left corner of each page)

Student signature: _____

Problem 1	_____	(19 pts)
Problem 2	_____	(36 pts)
Problem 3	_____	(32 pts)
Problem 4	_____	(12 pts)
Problem 5	_____	(12 pts)
Problem 6	_____	(14 pts)
Problem 7	_____	(8 pts)
Problem 8	_____	(17 pts)
Total Points	_____	(150 pts)

No Calculators Allowed
No Molecular Models Allowed
Be Sure Your Exam has 11 Pages

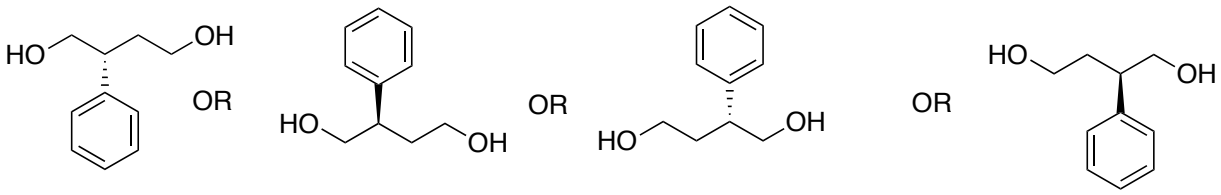
ALL ANSWERS MUST BE ON THE FRONT OF EACH PAGE. ANY ANSWERS ON THE BACK OF A PAGE WILL NOT BE CONSIDERED FOR GRADING.

1 H							2 He
3 Li	4 Be	5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca					35 Br	36 Kr
						53 I	54 Xe

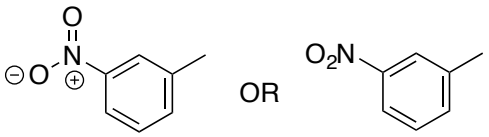
1. There will be NO partial credit for this problem. Avoid careless errors by checking over your answers. (19 pts)

A. Draw a structure for each of the following names. For cycloalkanes use flat rings.

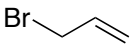
- *(R)*-2-phenyl-1,4-butanediol



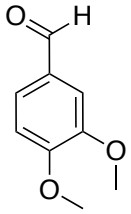
- *meta*-nitrotoluene



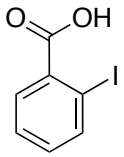
- allylbromide



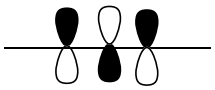
- 3,4-dimethoxybenzaldehyde



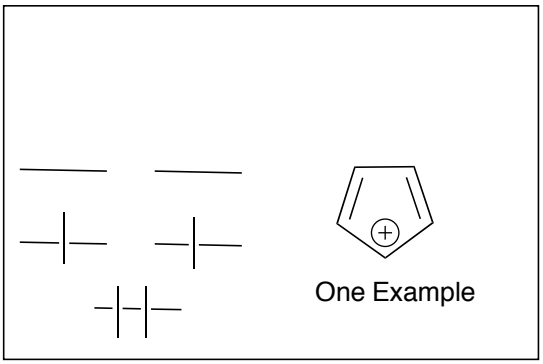
- *ortho*-iodobenzoic acid

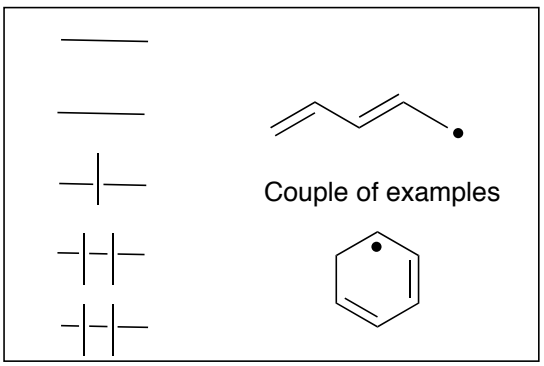


B. Draw the molecular orbital for the LUMO of allyl anion.

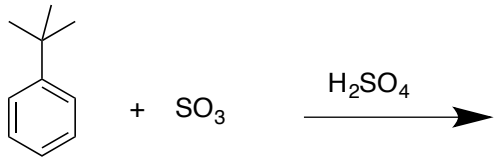


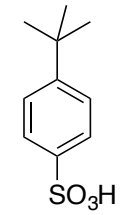
C. In each box below, provide a REAL example of a molecule that would have the π-energy level diagram shown.



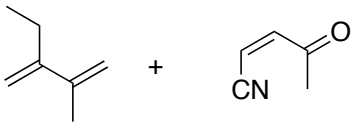


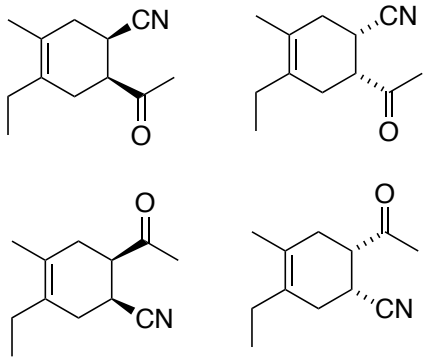
2. Predict all of the possible organic product(s) from the following reactions. Where relevant, show all stereoisomers. Pay particular attention to any information given in the product boxes. Each redundant or wrong answer within a box cancels one correct in the same box. (36 pts)



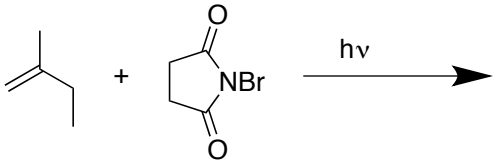


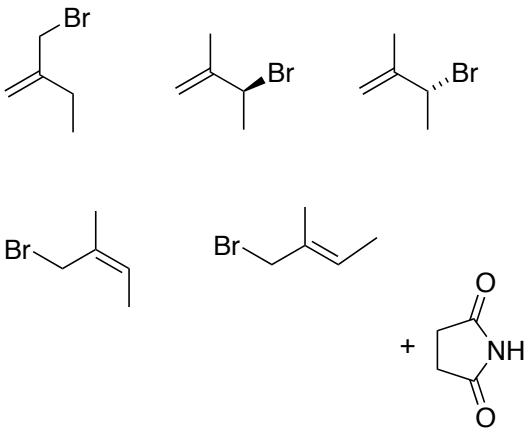
major product only





If you used wedges/dashes on the alkene carbons, you received no points.





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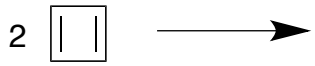
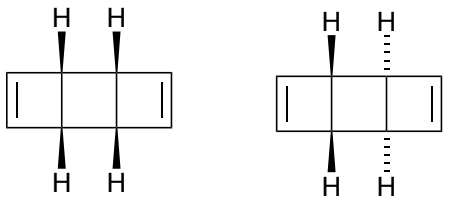
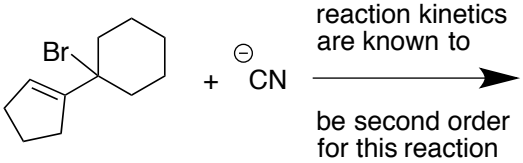
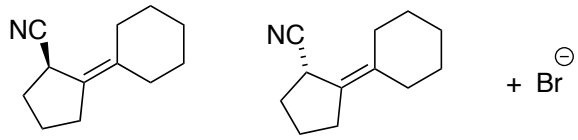


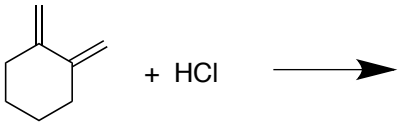


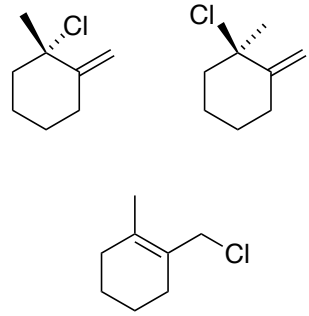
There were other ways of depicting these products, however if you did not clearly show how the two differed, you received no points.

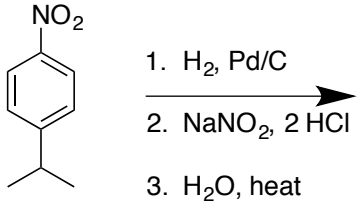
Two stereoisomers from 4 + 2 cycloaddition reactions

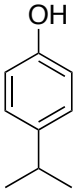




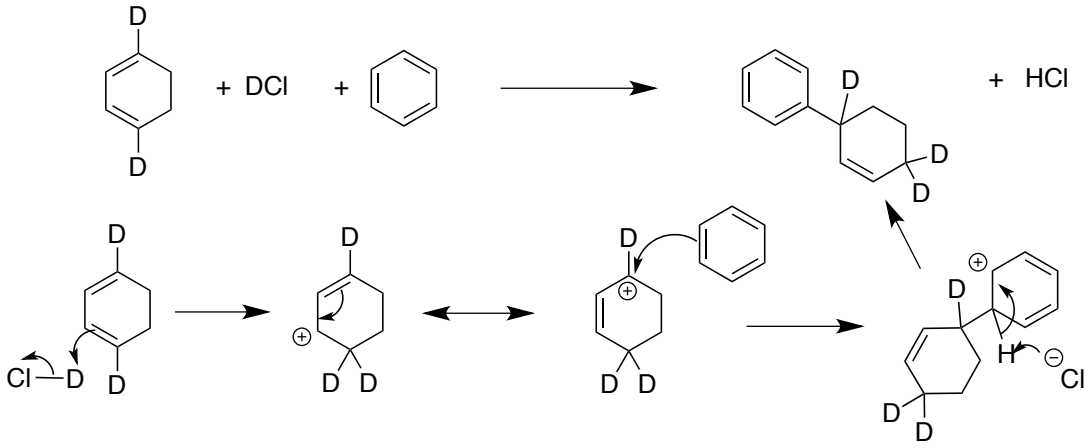


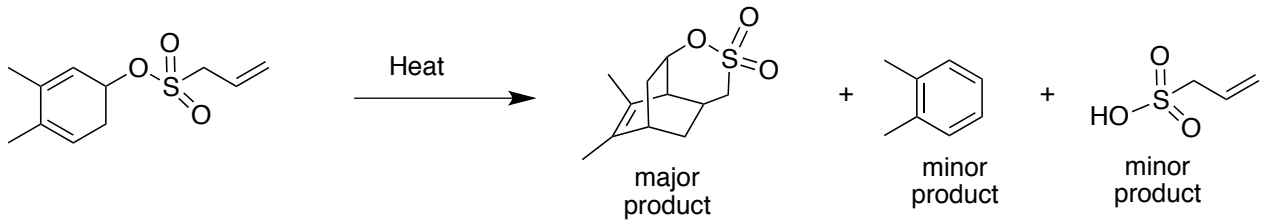






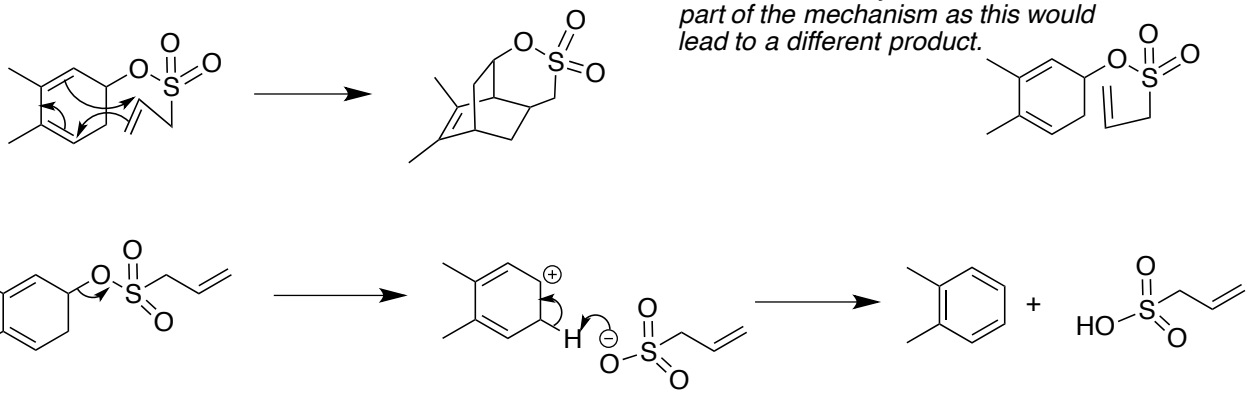
3. Write logical arrow-pushing mechanisms for the following reactions. Be sure that your mechanism accounts for all products shown. (32 pts)





Hint: The products might come from the same mechanism or different mechanisms.

Note, that on this mechanism if you wrote a 4 + 2 cycloadditon with the dienophile oriented as shown below, you received no credit for this part of the mechanism as this would lead to a different product.



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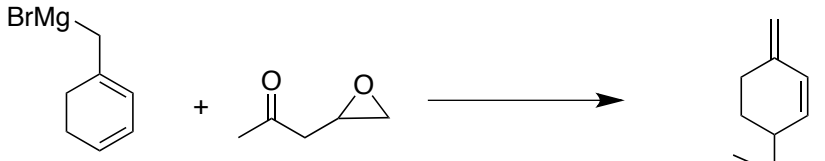
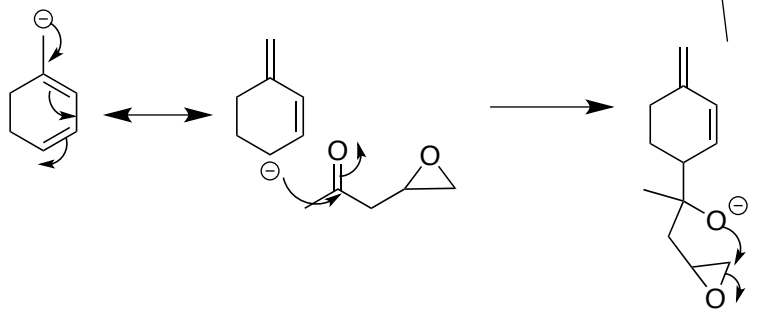
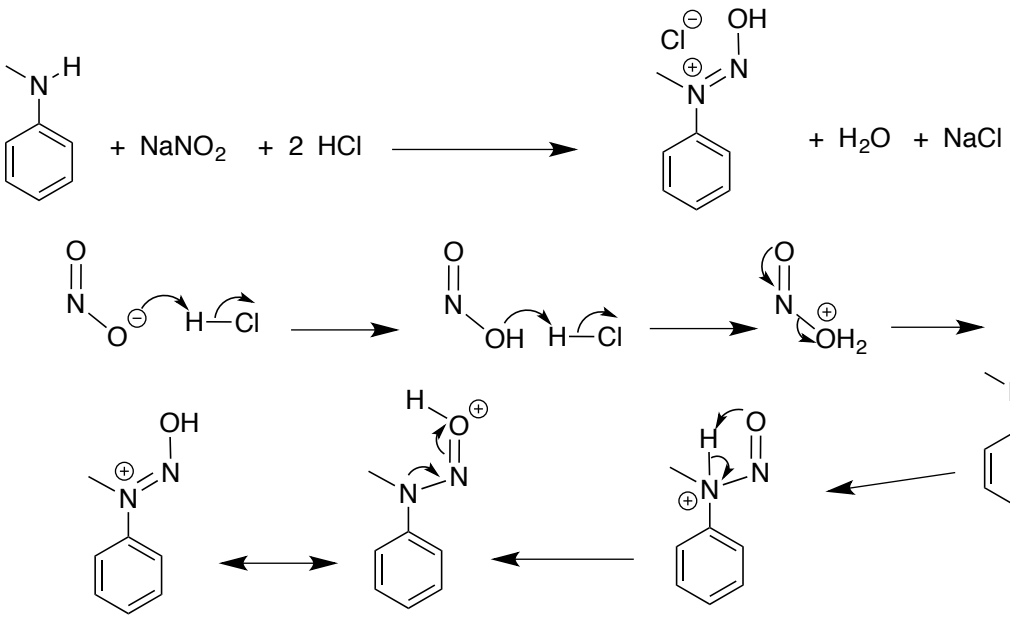


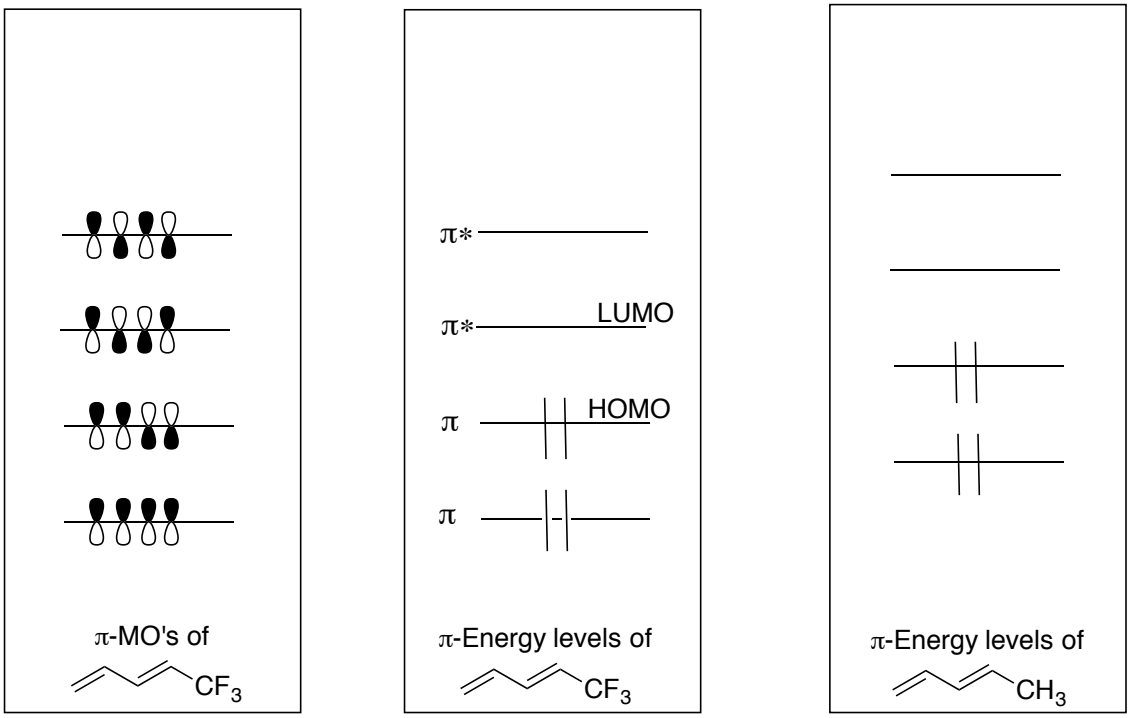
Hint: You do not need to show how the MgBr leaves the carbanion or attaches to the alkoxide.





4. (12 points)

A. In Box A below (labeled π-MO's) draw the molecular orbitals for the π-system of the diene shown in the box. In Box B below (labeled π-Energy Levels), draw the π–energy levels associated with the diene shown in Box A. In Box B also label each level as π, NB (non-bonding) or π * and then fill in the electrons and label the HOMO and LUMO.



Box A Box B Box C

B. In Box C above, draw in the π–energy levels for the diene shown and fill in the electrons. BE SURE TO CLEARLY SHOW THE π-ENERGY LEVELS OF THIS DIENE RELATIVE TO THE ONE IN BOX B. That is, if they are higher or lower in energy, then you must clearly show this. If they are the same energy as those in Box B, you must clearly show this also.

C. Explain why you drew the relative π–energy levels between Box B and Box C the way you did. If your answer to Part B is incorrect, you will receive no credit for Part C. Your answer must be kept within the space below.

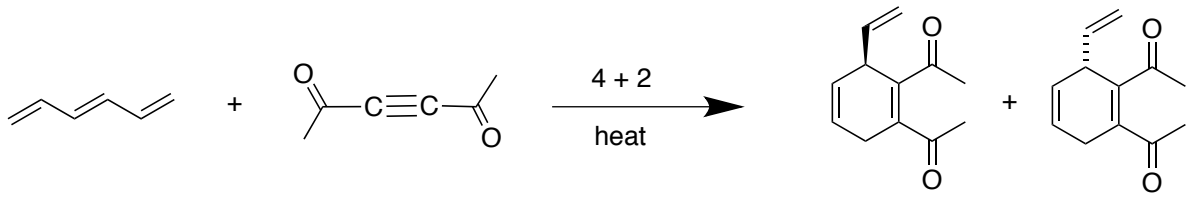
The energy levels in for the compound denoted in Box C are higher than those of the compound found in Box B because the methyl group (Box C) is electron donating relative to the CF_3 group on the compound in Box B. Electron donating groups will place more electron density on the diene, increasing Coulombic repulsions and raising overall energy levels.

5. (12 points)

A. Show the product(s) you might get from a 6 + 2 cycloaddition reaction between the two reactants shown below. Wrong answers cancel right answers.

This question was deleted and everyone in the class was awarded the original point value of this question, which was 3 points.

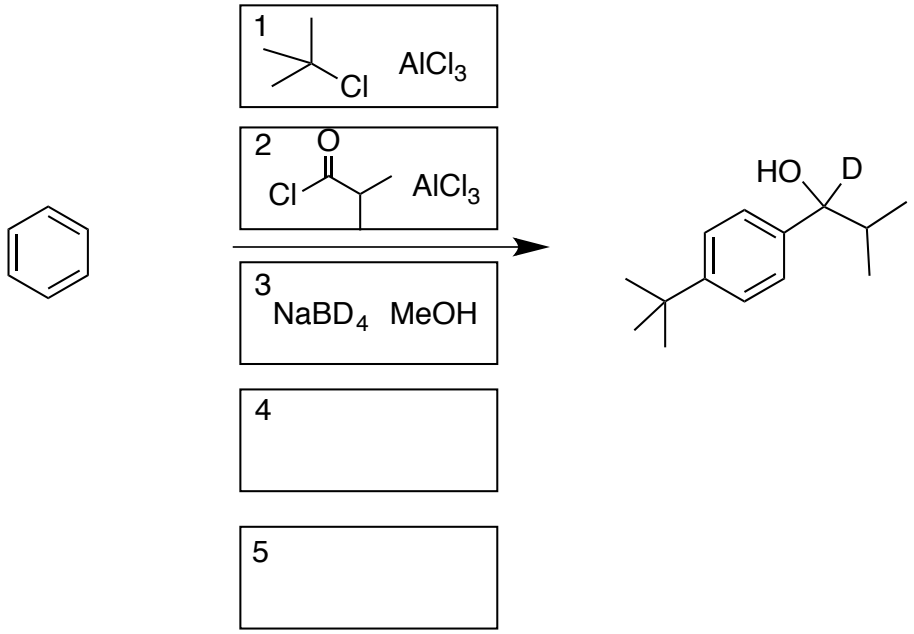
B. The 6 + 2 cycloaddition reaction shown above does not occur under thermal conditions. However these reactants will undergo a 4 + 2 cycloadditon reaction under thermal conditions. Show the product(s) from the reaction between these two reactants. Wrong and redundant answers cancel right answers.

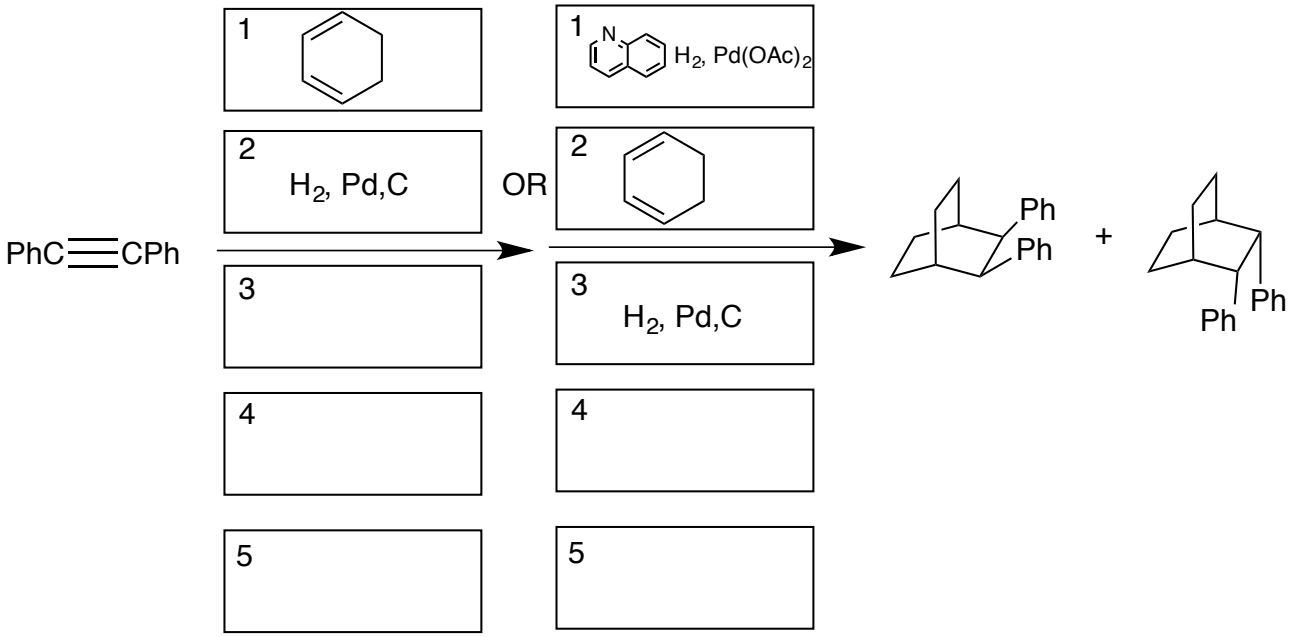


C. Even though the 6 + 2 cycloaddition reaction shown does not occur under thermal conditions, it is possible under another set of conditions. What are these conditions?

Photochemical Conditions

6. Provide the reagents and any other organic compounds necessary to synthesize the indicated product(s) from the starting material shown. For each problem, five boxes are provided in which to place each step of your synthesis. **No synthesis will require more than five steps. However, some or all, may require fewer than five steps.** (14 pts)

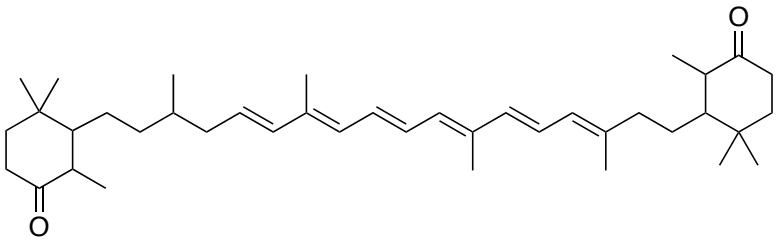




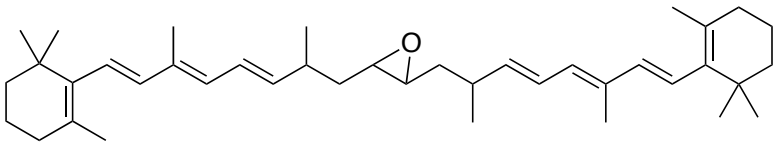
7. (8 points)

Only one of the following five derivatives of beta-carotene appears orange-red in color. The others are colorless. Circle the orange-red colored compound and briefly explain why it appears this way relative to the rest of the compounds. Make sure you include any relevant equations in your discussion. Keep your discussion within the box provided.

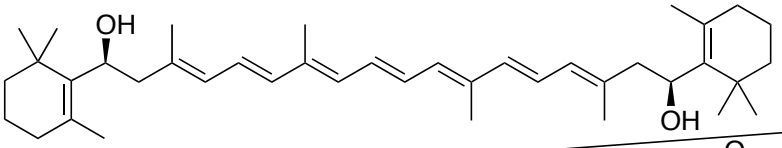
A



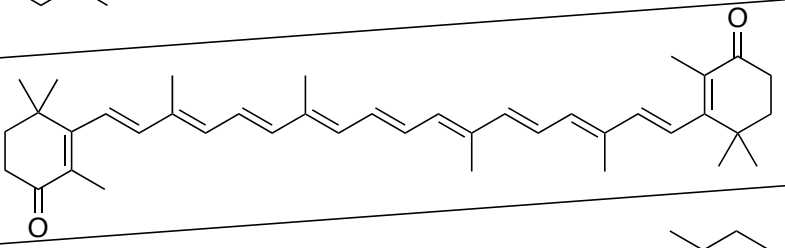
B



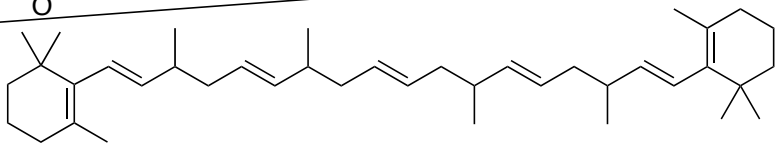
C



D



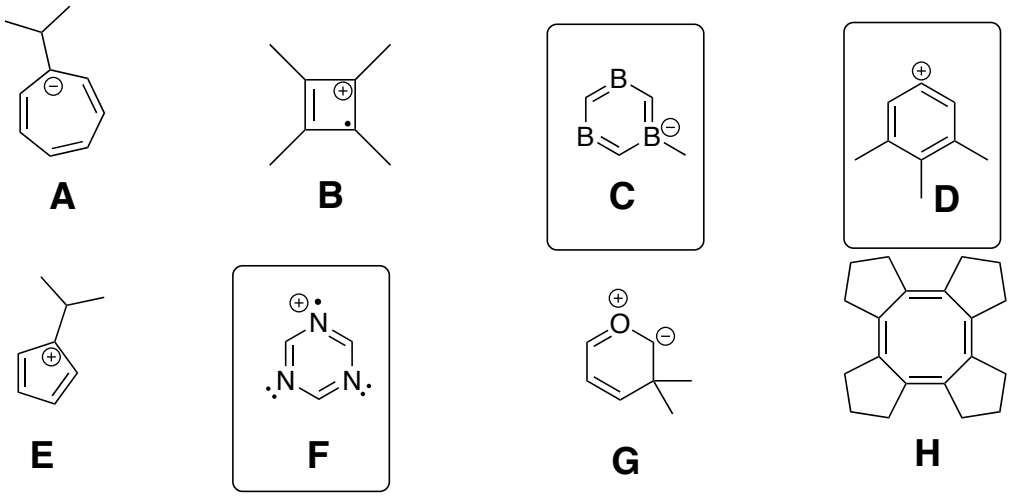
E



Compound D is the most conjugated molecule of the series with 13 double bonds in a row (i.e. 26 p-orbitals in a row). As the number of conjugated double bonds in a molecule increases, the distance separating each π-energy level decreases. This means that a π to π^* transition will require less energy which in turn means that a longer wavelength of light is required to promote this transition (E is inversely proportional to the wavelength, λ). Since only one compound in this series is colored and visible light has a lower energy and longer wavelength, this must be the orange-red colored compound.

8. (17 points)

A. Circle all of the aromatic compounds shown below. Wrong answers cancel right answers so don't guess.



B. When heated, one of the triene's below leads to Compound X via a 4 + 2 cycloaddition reaction. Circle the correct triene AND using mechanistic arrow-pushing show the RETRO 4 + 2 cycloaddition starting with Compound X. No points will be awarded for circling the correct triene and providing No or the Wrong mechanistic arrows. Hint: You should perform the Retro 4 + 2 first to help identify the correct triene.