

Organic Chemistry 2
First Examination
February 15/17, 2012
Prof. Malachowski

Name: Elena Delle Donne

The examination has eight questions on five pages. The point values for each question are found with the question. Partial credit will be given where appropriate.

Read each question carefully before answering. Be certain you understand everything the question is requesting. Do the easy questions first. If questions appear confusing or exceedingly complex, then you may need to rethink the question. Keep in mind the intended examination topics.

In organic chemistry, hand-drawn pictures convey specific information. Be sure the drawing you have made conveys the essential information required to answer the question. Don't forget to include lone pairs of electrons and formal charges when appropriate.

hydrogen 1 H 1.0079																				helium 2 He 4.0026									
lithium 3 Li 6.941	beryllium 4 Be 9.0122																				boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180			
sodium 11 Na 22.990	magnesium 12 Mg 24.305																				aluminum 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948			
potassium 19 K 39.098	calcium 20 Ca 40.078	scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80												
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29												
cesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 *	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]											
francium 87 Fr [223]	radium 88 Ra [226]	89-102 * *	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dundium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	unnilium 110 Uun [271]	ununium 111 Uuu [272]	unbibium 112 Uub [277]		ununquadium 114 Uuq [289]															

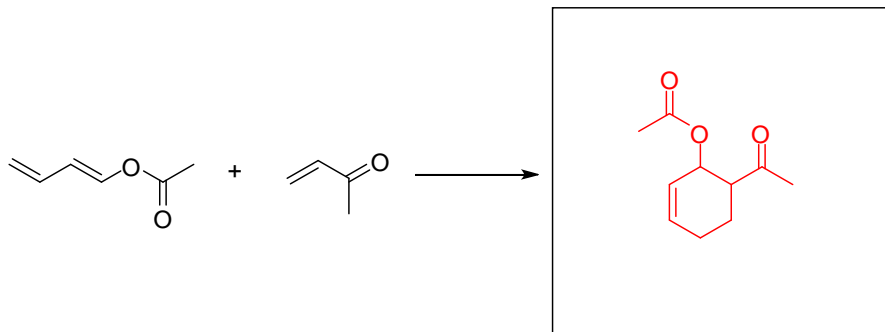
* Lanthanide series

lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

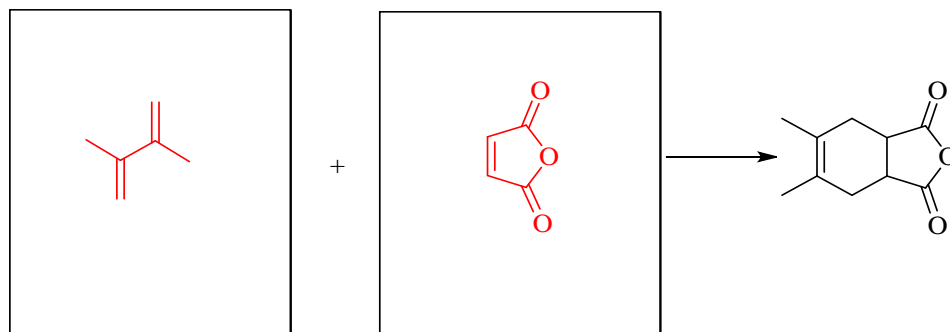
** Actinide series

1. Provide the necessary information, product(s) or starting materials, to complete the following reactions. (5 pts. each)

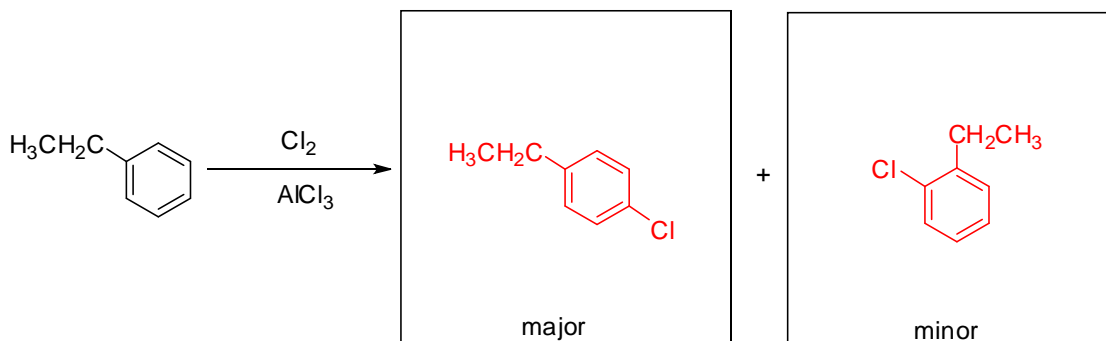
a)



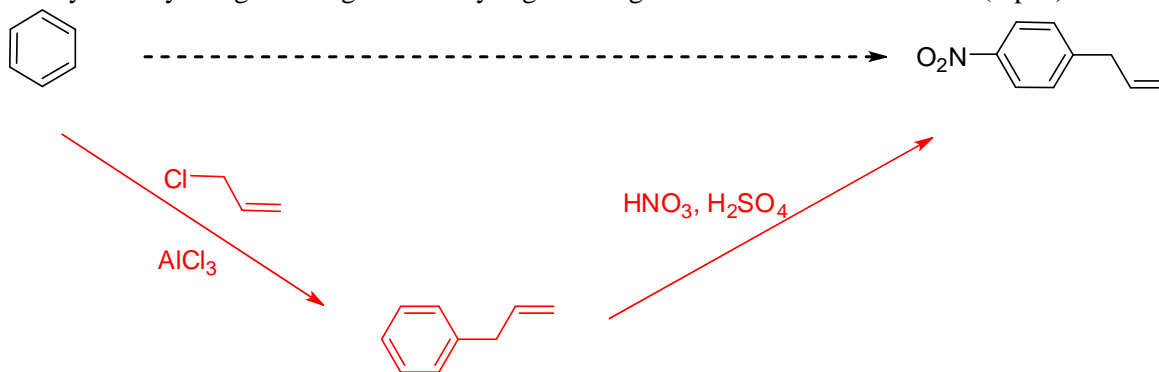
b)



c)

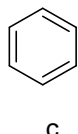
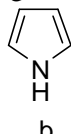
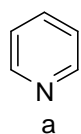


2. Suggest a series of reactions to take the starting material on the left to the product on the right. This will require two or three steps. You may use any inorganic reagent and any organic reagent of seven carbons or less. (6 pts.)

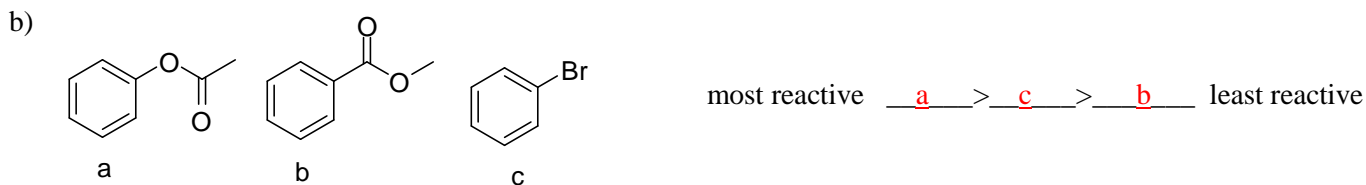


3. Rank the following structures in order of their reactivity in electrophilic aromatic substitution reactions. (3 pts. each)

a)

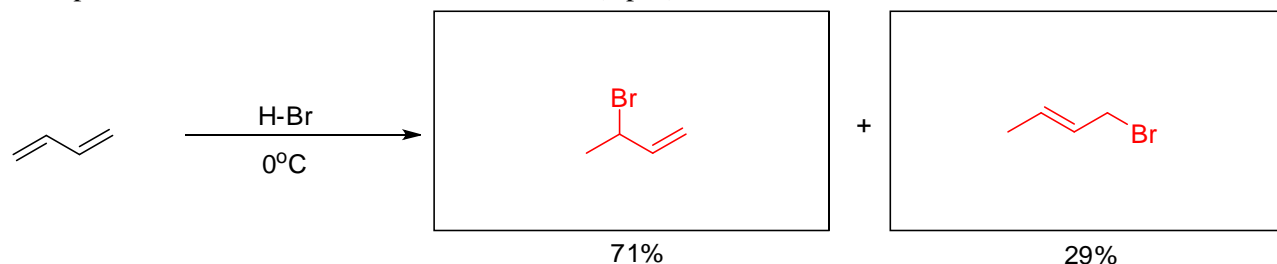


most reactive b > c > a least reactive

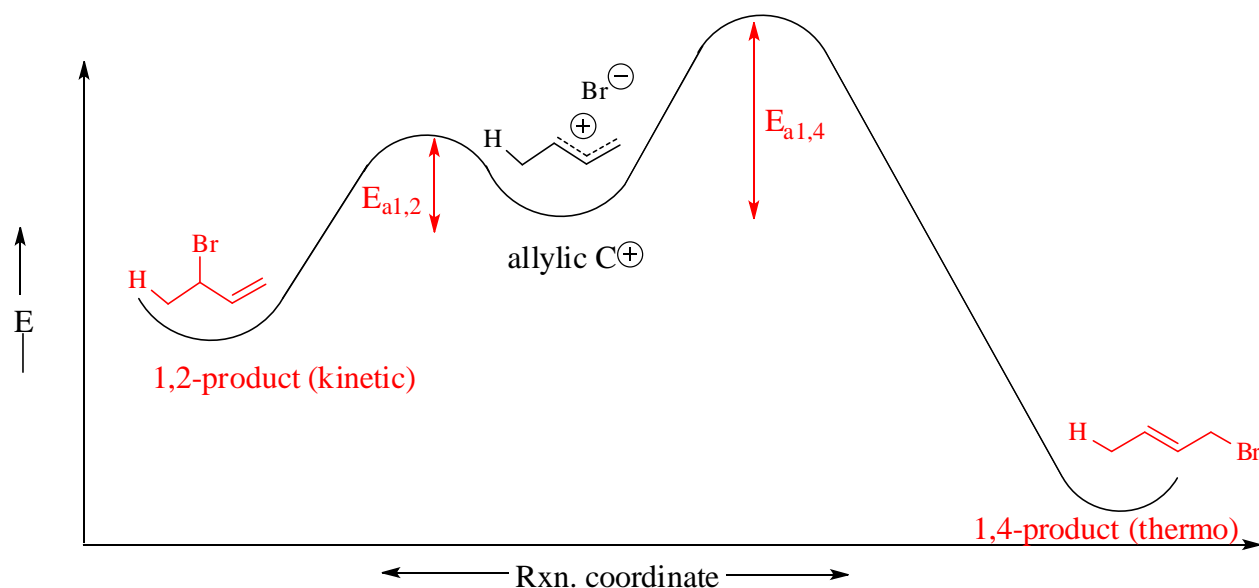


4. Answer the following questions about the reaction of 1,3-butadiene with HBr.

a) Draw the products of the reaction in the boxes below. (6 pts.)

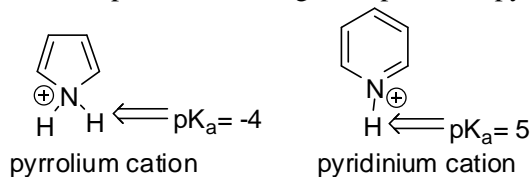


b) The energy diagram for the second step in the reaction is shown below. Label or place the following items on the diagram: energy of activation (E_a) for the 1,2-product; E_a for the 1,4-product; structure and location of the kinetic product; structure and location of the thermodynamic product. (9 pts.)



5. Multiple choice questions. (5 pts. each)

a. Which answer best explains the difference in pK_a for the designated proton in pyrrolium and pyridinium cation?



i) Pyrrole is a stronger conjugate acid than pyridine.

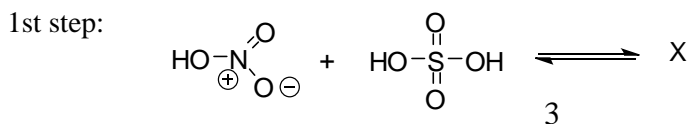
(ii) Pyrrole loses aromaticity when it protonates to form the pyrrolium cation.)

iii) Pyrrole is a more electron rich aromatic ring than pyridine.

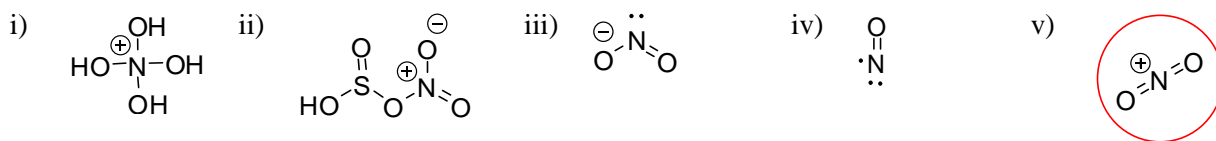
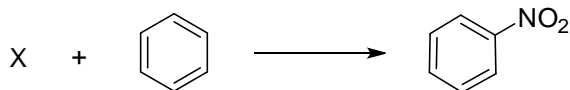
iv) Pyridinium cation distributes the cation charge around the ring better.

v) Pyridine has more stable molecular orbitals and a smaller HOMO-LUMO energy gap.

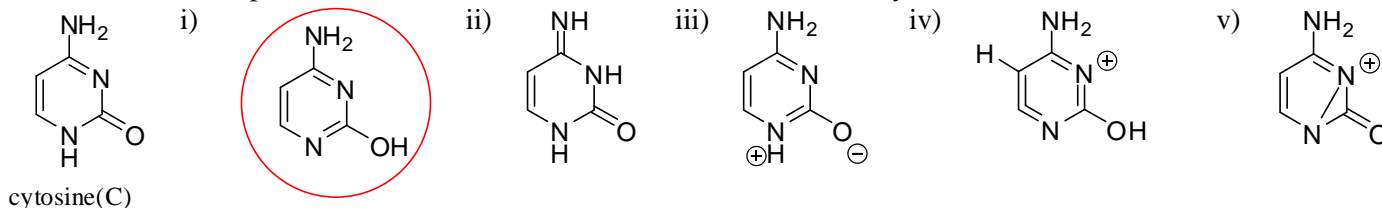
b. Circle the structure of the intermediate X that forms in the following reaction sequence.



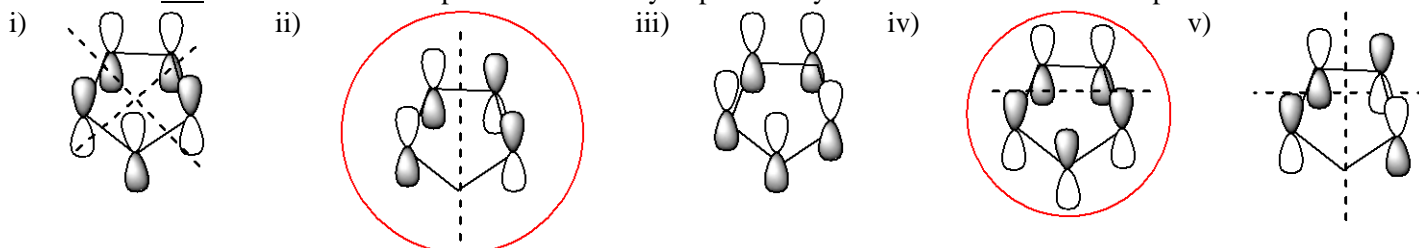
2nd step:



c. Which structure represents an aromatic tautomer or structural isomer of cytosine?

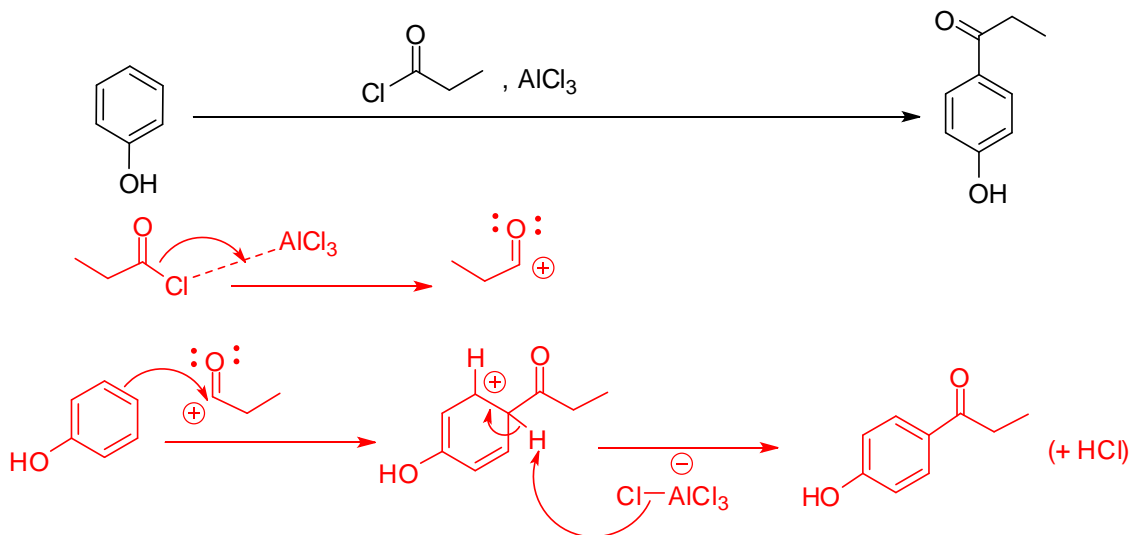


d. Circle the two molecular orbital representations of cyclopentadienyl anion shown below that represent HOMO orbitals.

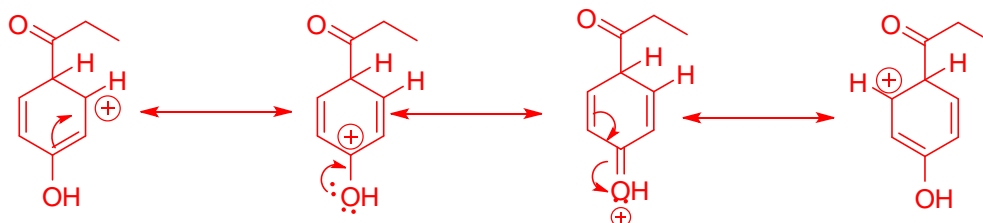


6. Provide the necessary information about the reaction shown below.

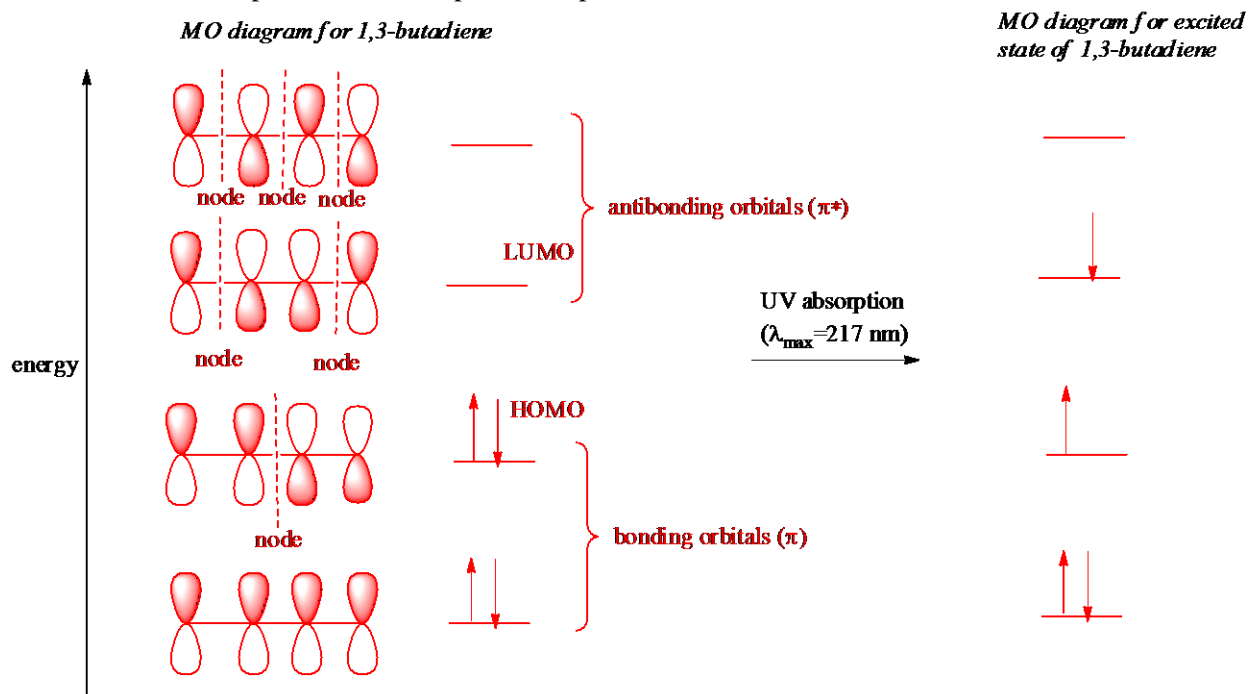
a) Draw the mechanism of the reaction. You do NOT need to include resonance structures. You should include all formal charges and curved electron flow arrows. (9 pts.)



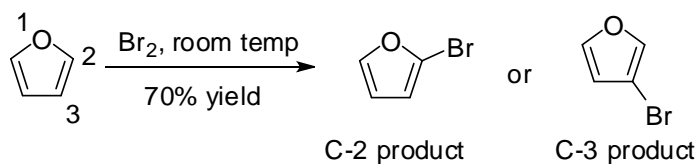
b) Show all the important resonance contributors of the key ring intermediate in the reaction. Be sure to include formal charges and curved electron flow arrows to indicate all electron movement. (6 pts.)



7. a) Draw the molecular orbital diagram for 1,3-butadiene in the space below. Include orbital phase and node information. Label the bonding and antibonding orbitals. Identify the HOMO and LUMO orbitals. (10 pts.)
 b) To the right of your diagram, show the effect of UV absorption at 217 nm. Draw the energy diagram for the excited state of 1,3-butadiene that results from this absorption. Assume the absorption is a π to π^* transition. You do not need to redraw the molecular orbital pictures with the phases. (3 pts.)

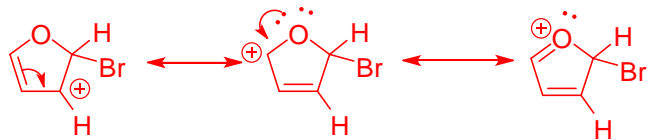


8. As shown below, the bromination of furan can in theory afford two possible products, the C-2 or the C-3 isomer. (10 pts.)

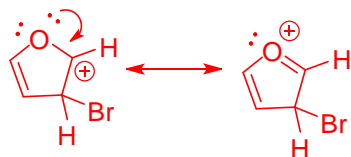


- a) Draw the carbocation intermediate for the reaction of both possible products. Draw all the important resonance forms for each carbocation intermediate. Be sure to include electron flow arrows, lone pairs and formal charges where appropriate.

C-2 isomer reaction:



C-3 isomer reaction:



- b) Which product is favored, the C-2 or C-3? Briefly explain why.

The C-2 product is favored since the carbocation intermediate has one extra important resonance contributor. This makes the path to the C-2 product lower energy and more favorable.

c) The bromination with furan occurs at room temperature, while that for benzene needs a Lewis acid catalyst and considerable heating. Circle the answer that best explains this reactivity difference.

i) Five member rings are always more electron rich than six member rings.

ii) Benzene has special stability from its aromatic system and furan is non-aromatic which is a more reactive state.

(iii) Furan has six π electrons controlled by 5 nuclei, while benzene has the same number of π electrons and one more nucleus.)

iv) The HOMO-LUMO gap for benzene is smaller which makes the pi electrons of benzene less stable.

v) Furan comes from the Latin word furfur which means bran and so it has the same explosive reactivity that too much bran in your diet can have.