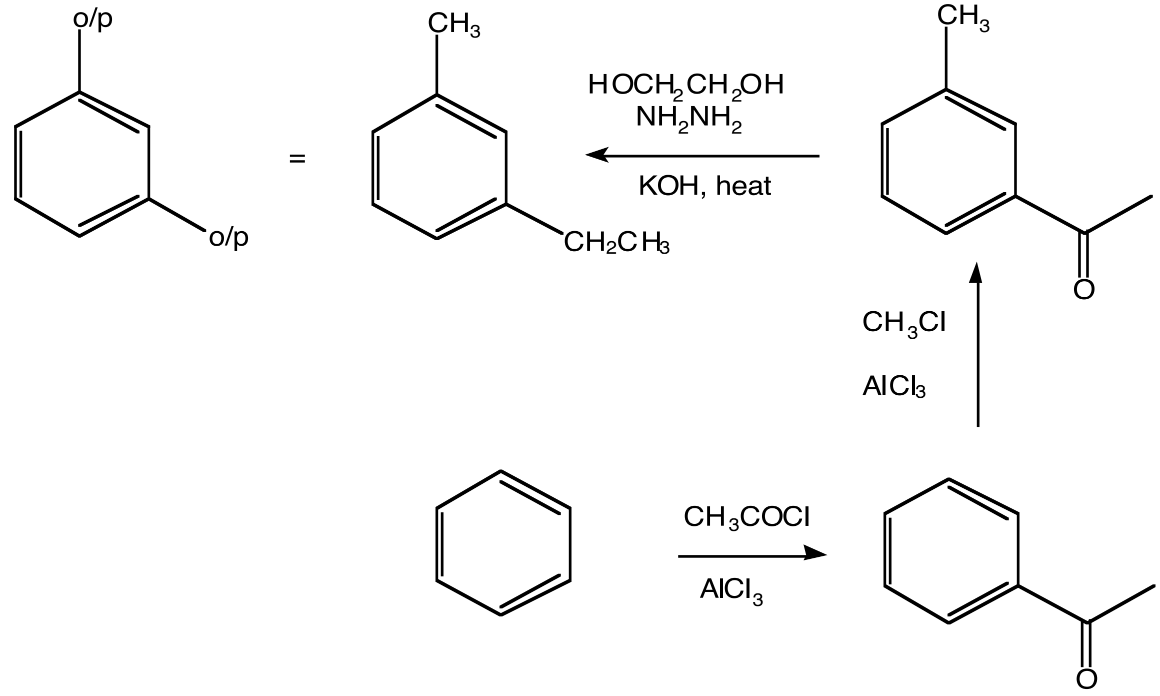
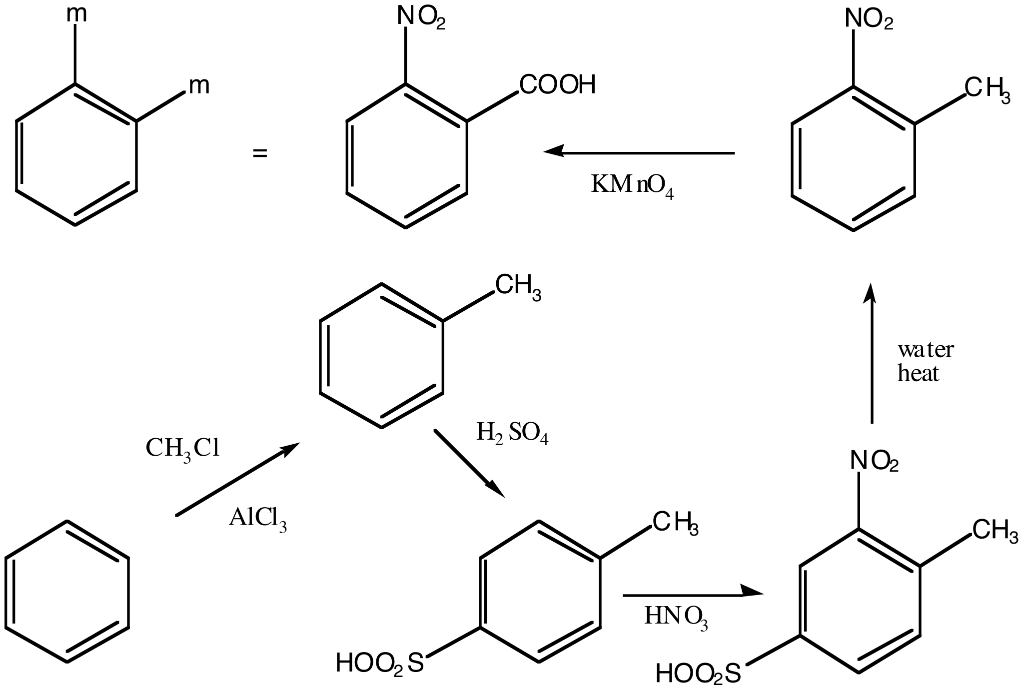
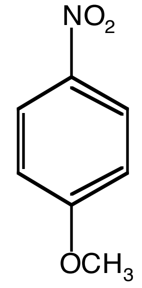
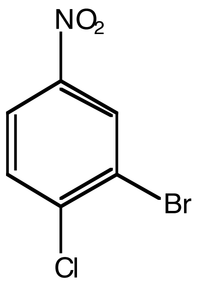
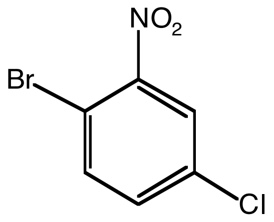
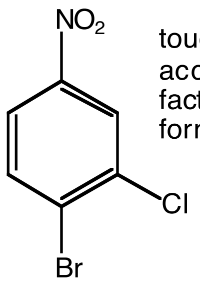
Answers to Hour Examination #1, Chemistry 302X - 2006

1. Neither of the following straightforward answers deserves a bonus. There are, of course, zillions of possible answers to this one.



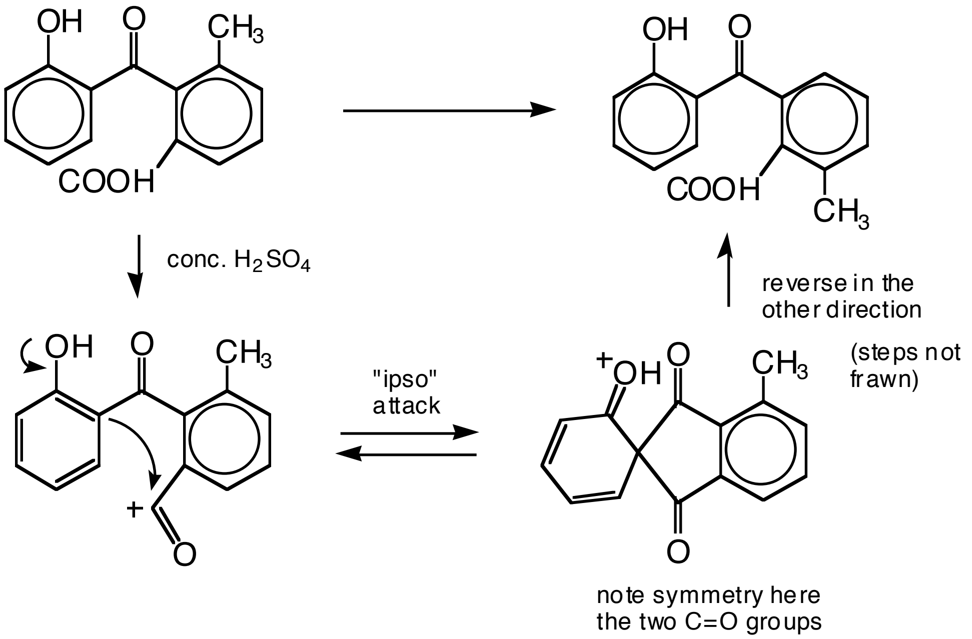


2.

	1	2
1,		no reaction (NO_2 can't stabilize the interrmediate if it is in the meta position)
2.	no reaction (no catalyst)	no reaction (no catalyst)
3.		  tough call - we wil accept either one -in fact only the first one is formed. Why?
4.	no reaction	no reaction

(no Friedel-Crafts on deactivated nitro compounds)

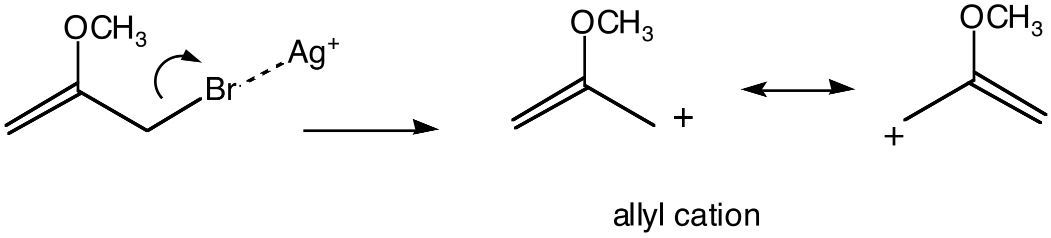
3. Such problems always ask you to find a way to make a symmetrical intermediate. The carbonyl groups have switched positions (the methyl “label” should tell you that). Here is one mechanism.



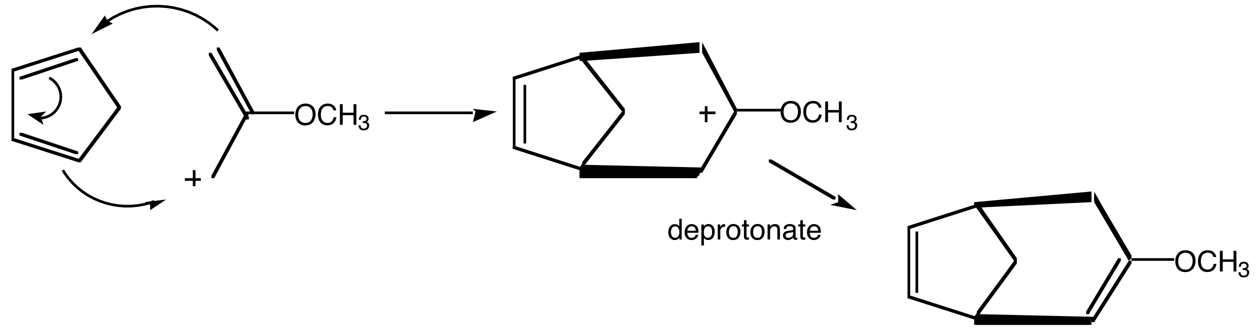
(steps not frawn)

note symmetry here the two C=O groups are now essentially equivalent

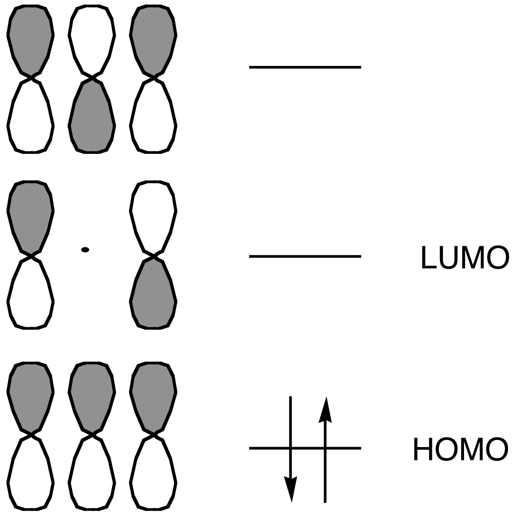
4. The silver ion assists ionization to give an allyl cation:

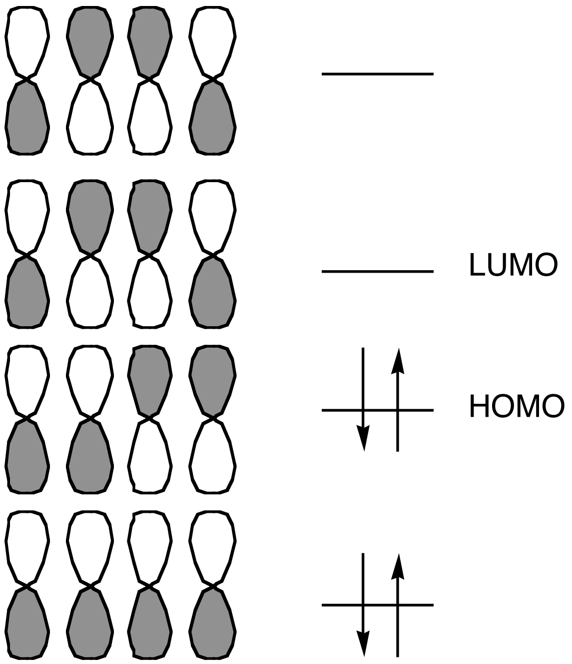


Cycloaddition with cyclopentadiene, essentially a masked Diels-Alder reaction, leads to the product, after a deprotonation.

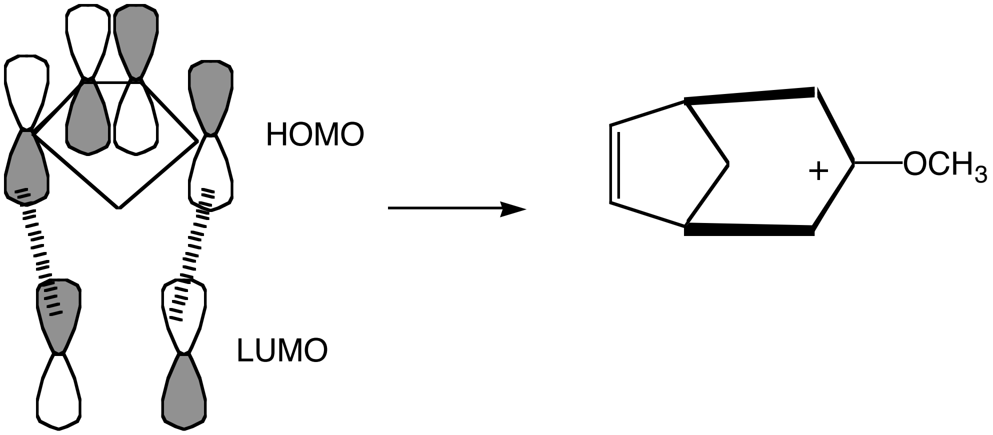


Here are the MOs involved:

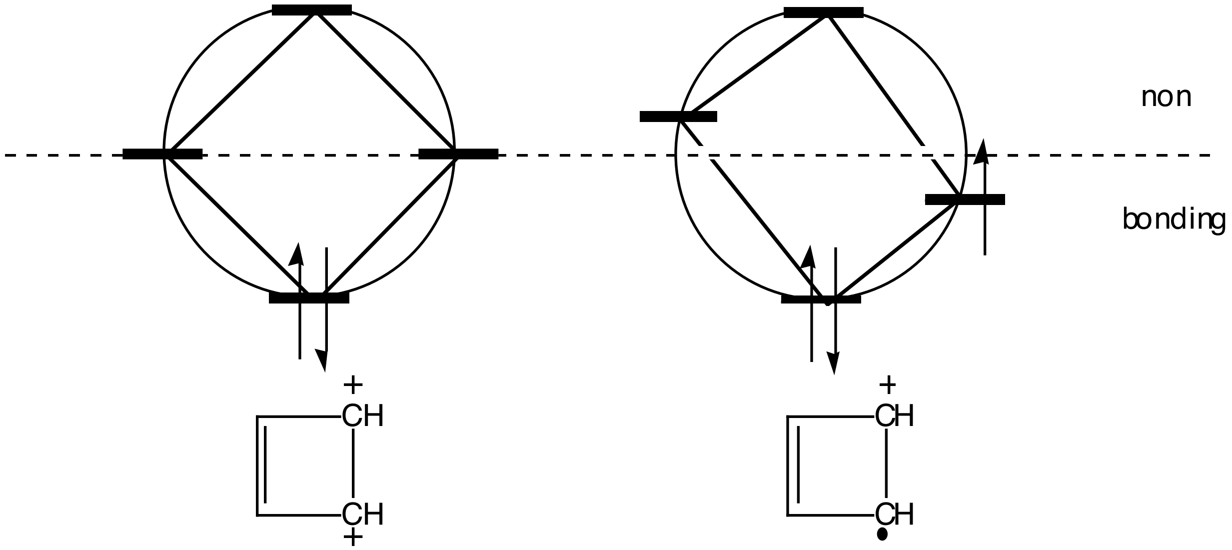




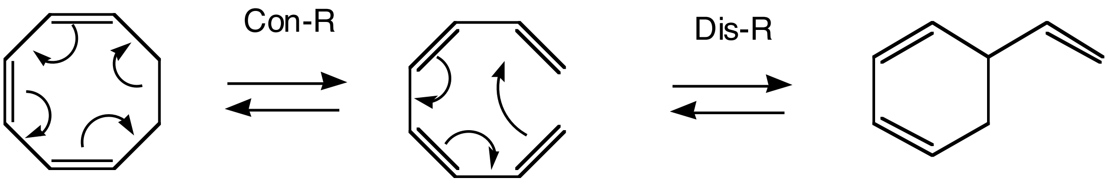
An orbital analysis (HOMO diene -LUMO dienophile) shows that a one-step, concerted thermal reaction is allowed.

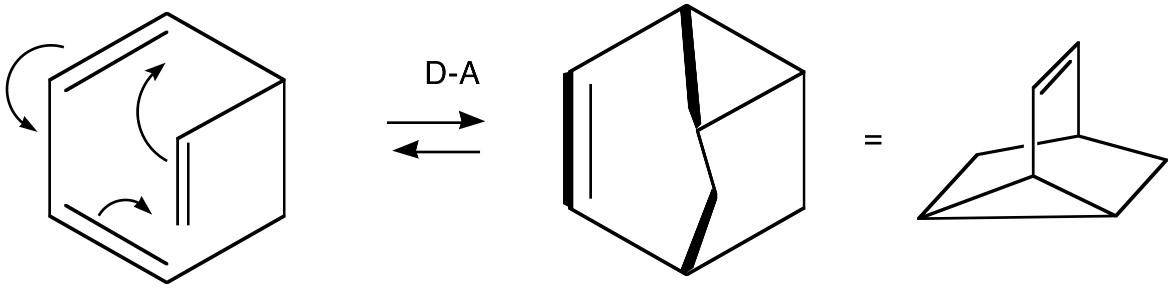


5. Both systems are cyclic, planar (or very close) and fully conjugated. The dication has only two pi electrons and they go, of course, into the lowest bonding MO. The other MOs are empty. If the three-electron system were square, one electron would have to be in a non-bonding porbital. In the rectangular system the third electron is in a bonding MO. So, it stretches the sigma bonds just a bit and becomes a rectangle. See Group Problems 16 and 17.

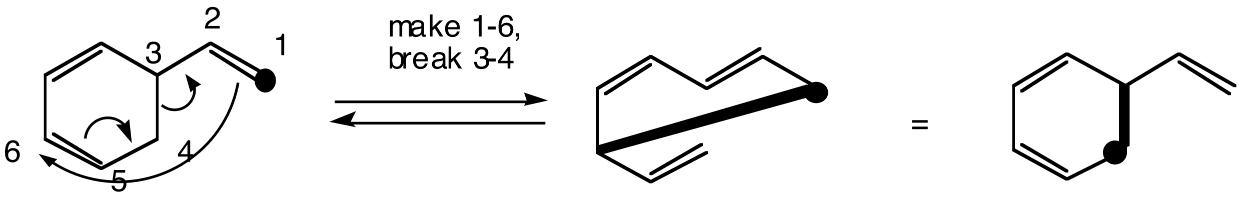


6a.





6b - One mechanism involves a Cope:



In the other mechanism, starting material simply opens to an octatetraene and recloses in the “other’ direction: