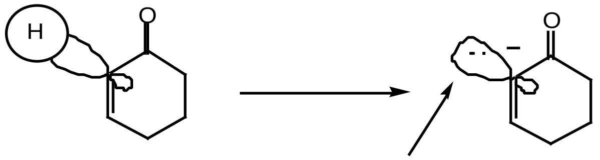
Answers to Chemistry 302X-302A Final Examination, 2005

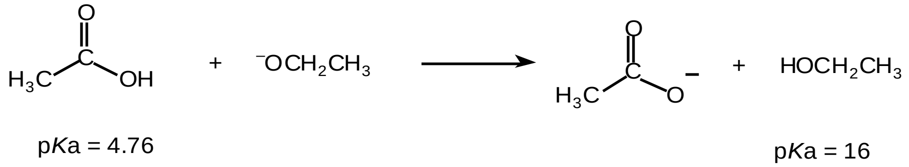
1.

(a)

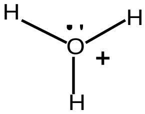


In the plane of the ring, does not overlap with the carbonyl pi bond- hence, no resonance stabilization, and no acidity of this hydrogen

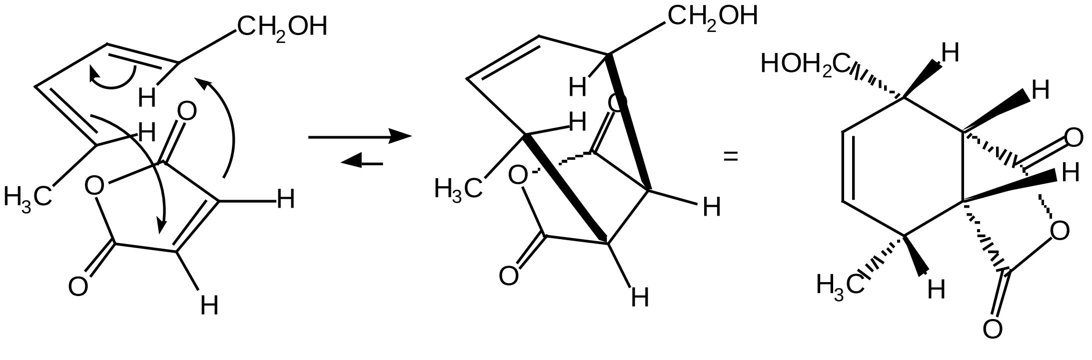
(b)



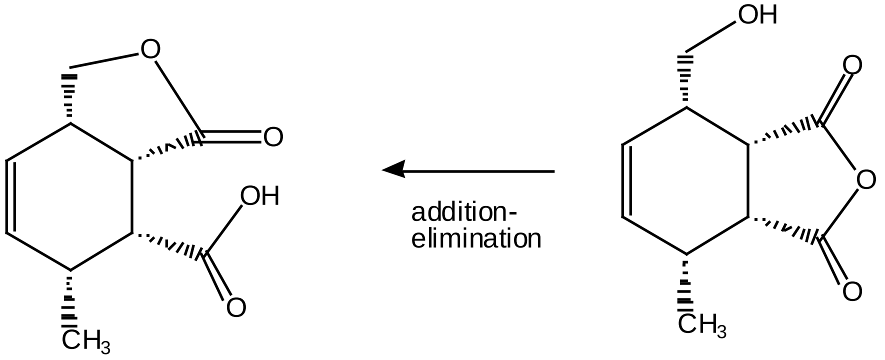
(c)



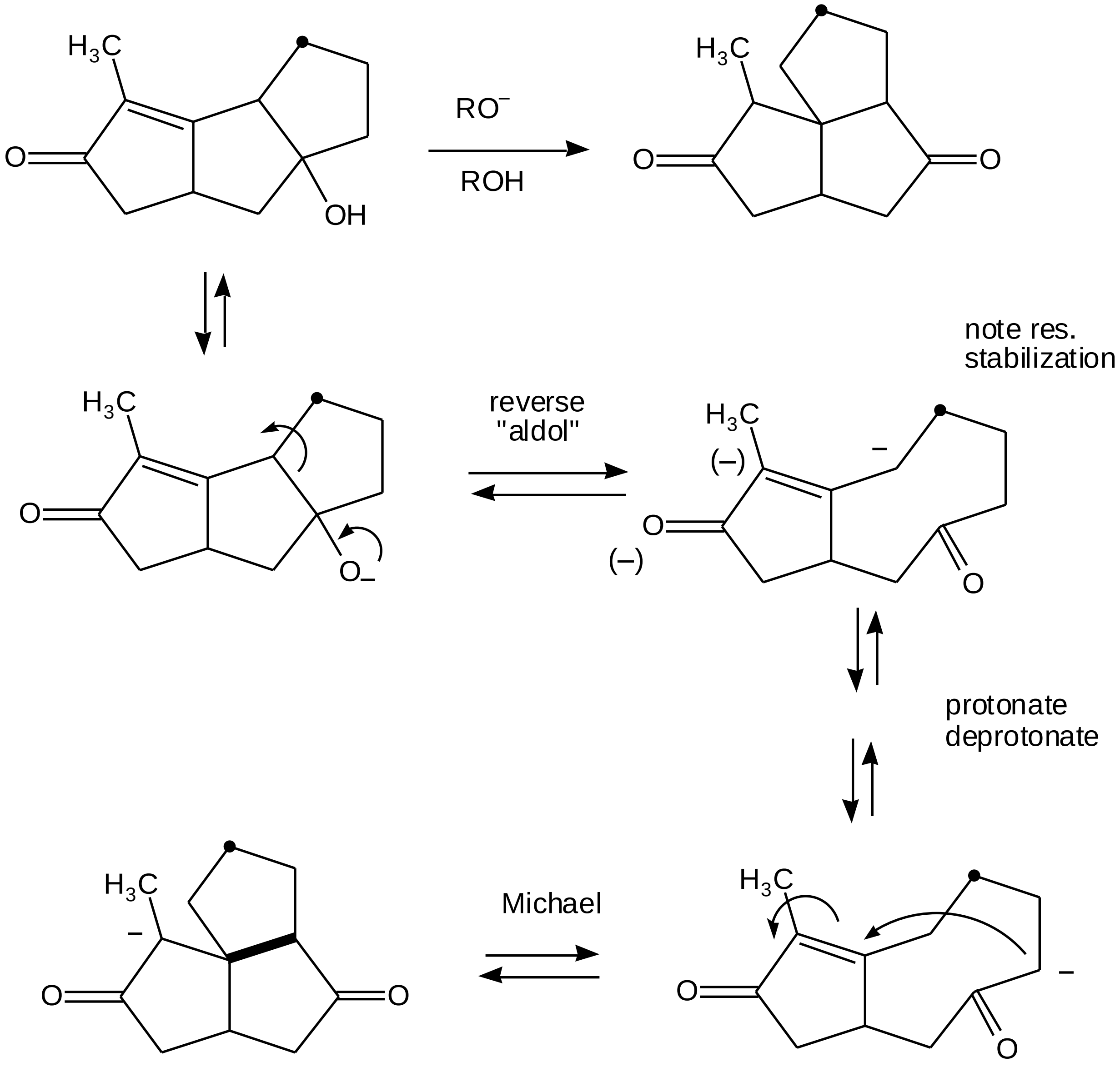
2.



note endo arrangement for Diels-Alder

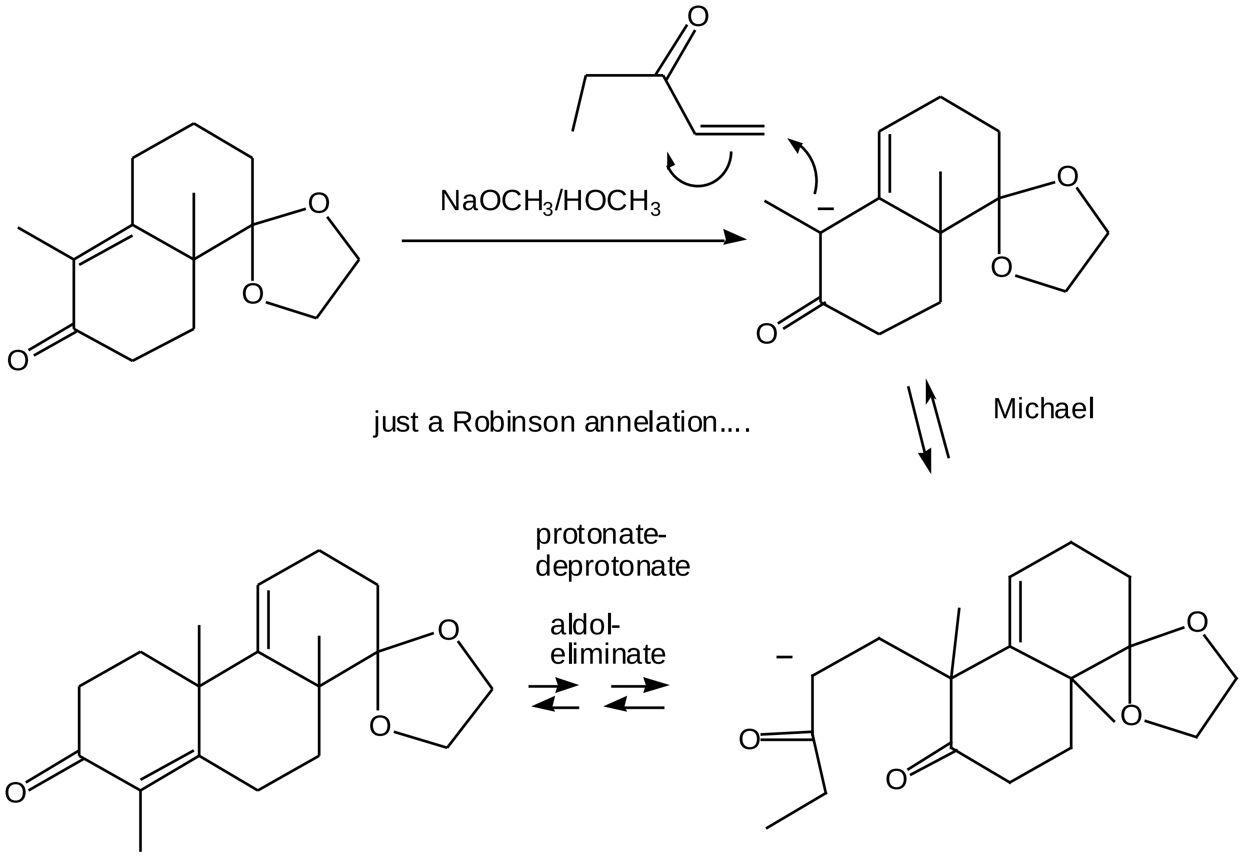


3.



protonate and you are done

4.



just a Robinson annelation....

5.

(a) First convert $PhCH_2CH_2OH$ into the corresponding acid ($KMnO_4$), then make the acid chloride with $SOCl_2$. Then do a Friedel-Crafts with $AlCl_3$

(b) Two equivalents of benzyllithium, followed by hydrolysis. Make benzyllithium from $PhCH_2OH$ (1. $SOCl_2$, 2. Li)

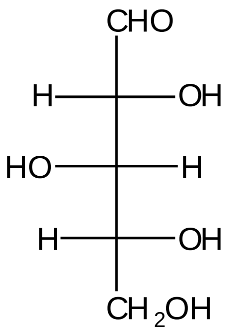
(c) Tricky - you cannot just add benzyllithium (why not?). Instead, hydrolyze to the acid and repeat (b).

(d) Do a sequence of bromination and eliminations (many ways possible) that eventually gets you to benzene. Repeat (a).

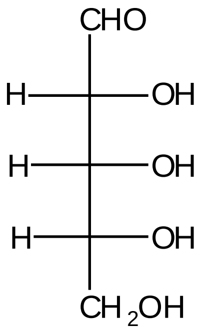
(e) Oxidize to the β-keto acid ($KMnO_4$) and watch it decarboxylate.

(f) Ozonize/oxidative workup to benzoic acid and repeat (b). There are many other ways.

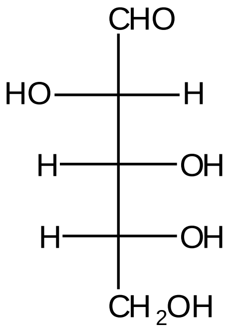
6. Here are the four possibilities:



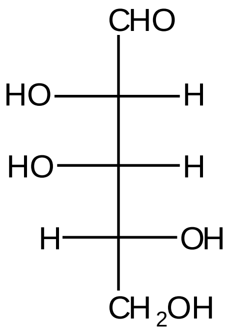
D-xylose



D-ribose



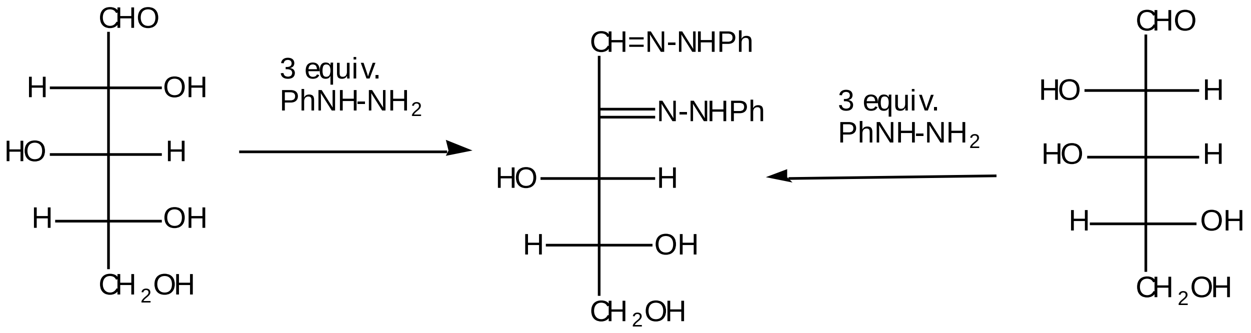
D-arabinose



D-lyxose

Here is one way to do it - there are many others.

(a) D-Xylose and D-lyxose give the same osazone, **X**. Thus, the structure of D-lyxose is known.

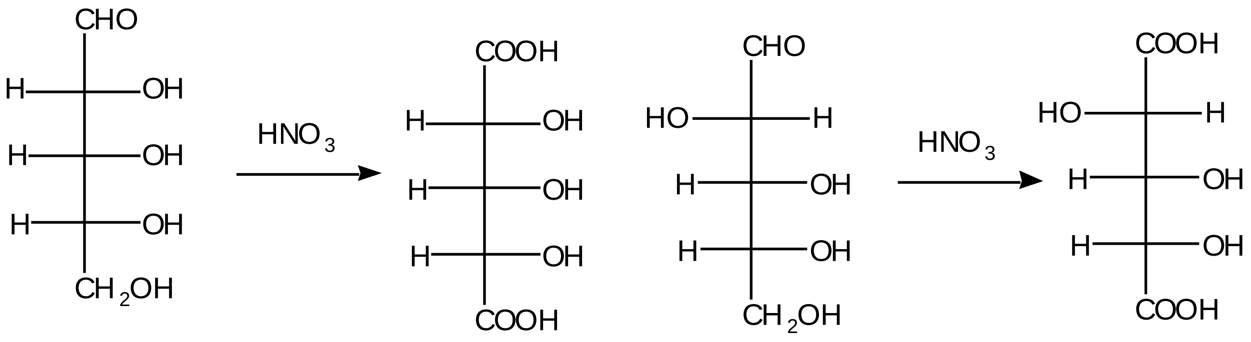


D-xylose

D-lyxose

X

(b) D-Ribose oxidizes to a meso diacid, whereas D-arabinose gives an optically active diacid.



D-ribose

meso

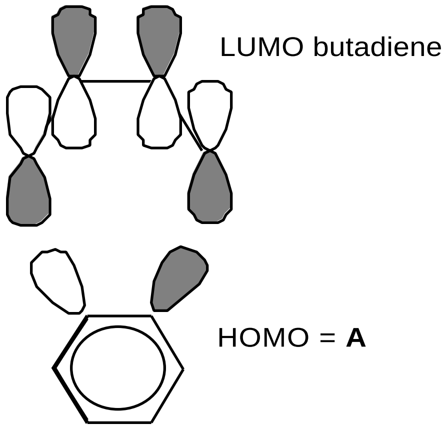
D-arabinose

optically active

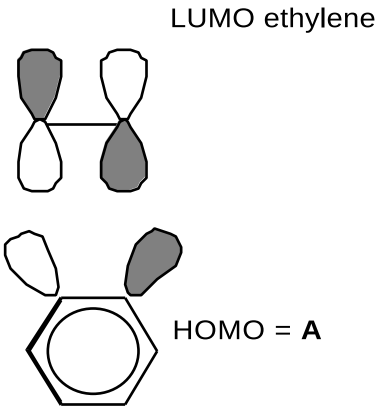
Done.

7. The point here is that for the “backward” HOMO and LUMO of **A** and **B**, the Woodward-Hoffmann rules will be reversed. The 2 + 4 reaction should be stepwise, and the 2 + 2 reaction concerted. A good answer demonstrates this notion with drawings such as these:

thermal 2 + 4 fails!

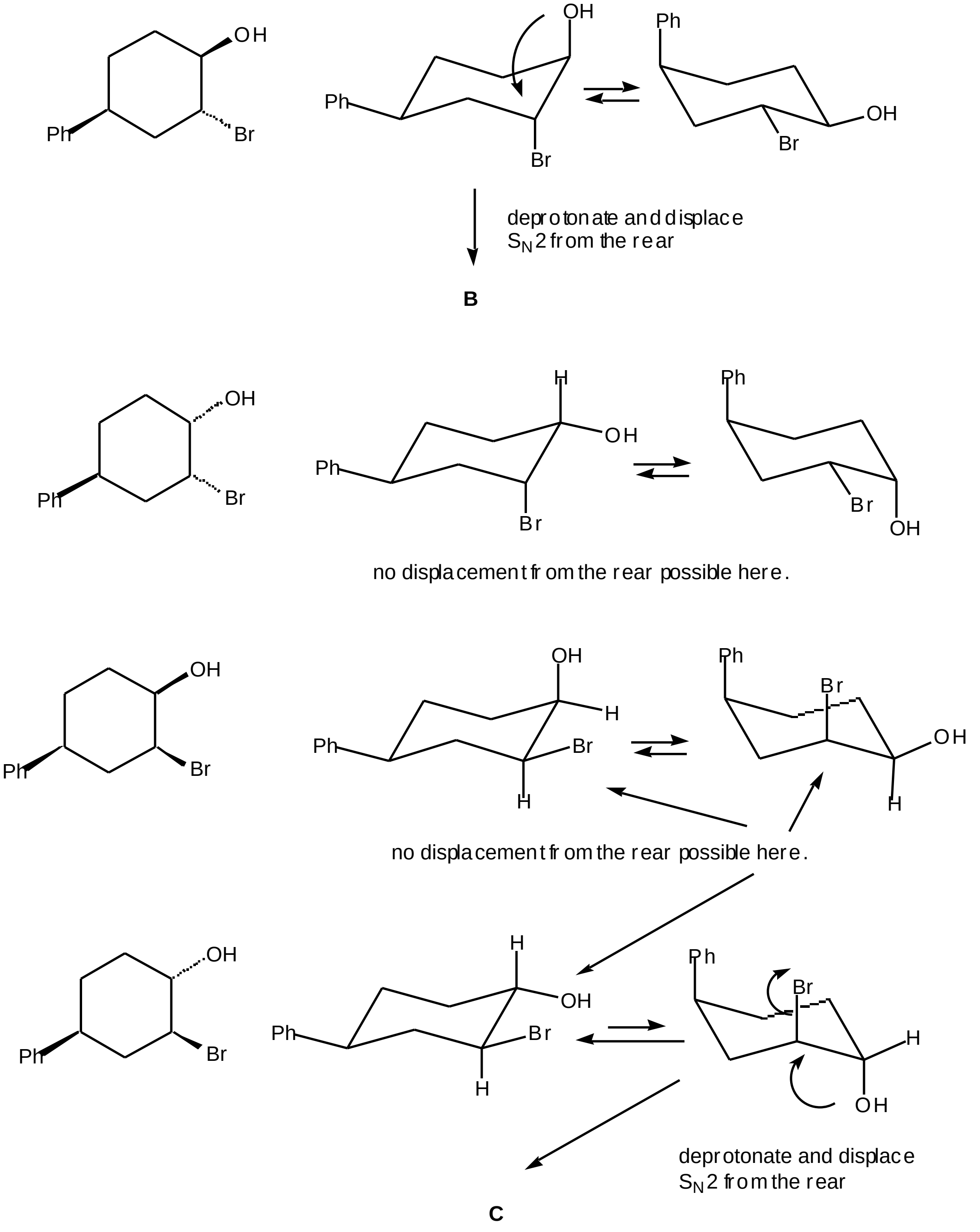


thermal 2 + 2 succeeds!



The experimental results are exactly the opposite,the 2 + 2 reaction is stepwise and the 2 + 4 reaction is concerted. Therefore, this weird HOMO/LUMO arrangement cannot be correct.

8.



deprotonate and displace
S_N2 from the rear

B

no displacement from the rear possible here.

no displacement from the rear possible here.

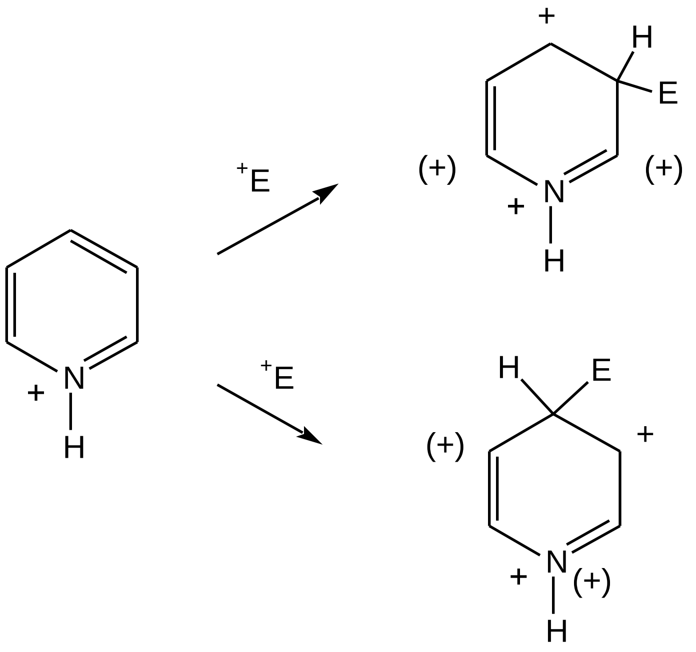
deprotonate and displace
S_N2 from the rear

C

Compound **B** is formed faster because **C** must come from a high energy, all-axial chair.

9.

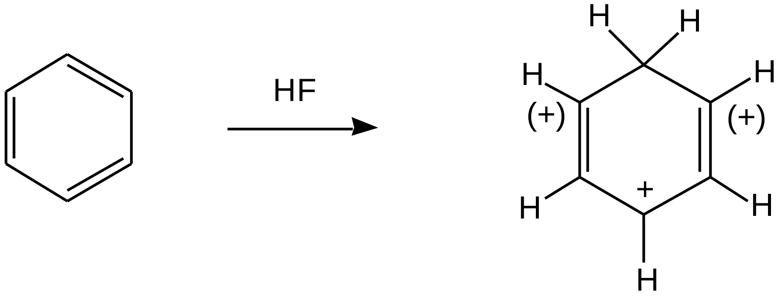
(a) Meta will be much better than para because it doesn't put two plus charges on N. Of course, any substitution by E^+ will be horrible, as the pyridinium ion is already positively charged, and it will substitute more slowly than benzene.



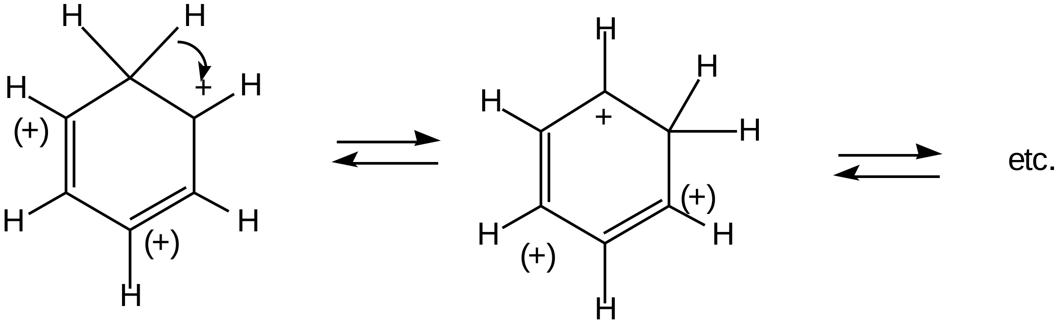
bad, but not as bad as ortho or para!

grim - ortho is similar

(b)
At lower temperature, the spectrum is static, and shows the expected 2:2:2:1 ratio for the cyclohexadienyl cation.

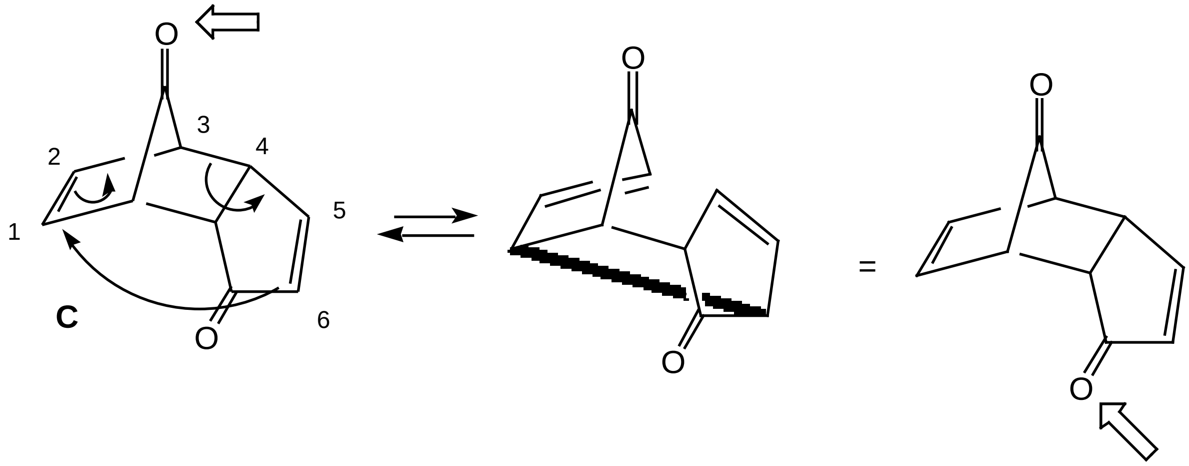


At higher temperature, a series of hydrogen (hydride or even H atom) shifts makes all hydrogens the same.



10. There is a Cope rearrangement that interconverts the two carbonyl groups:

(a)



(b) Diels-Alder-reverse Diels-Alder: