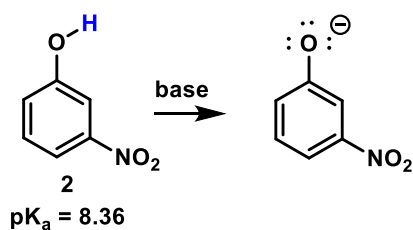
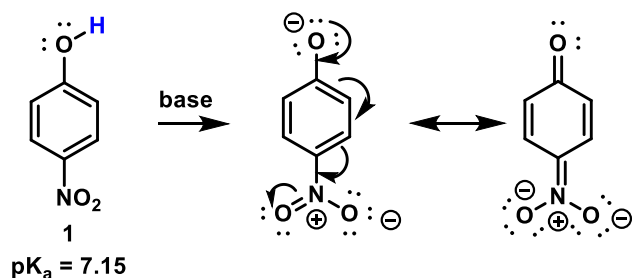


Homework 3 – 2017/04/11

1) 4-nitrophenol (**1**) has a pK_a of 7.15, while 3-nitrophenol (**2**) is slightly less acidic with a pK_a of 8.36. Can you think of a way to explain the experimental data?



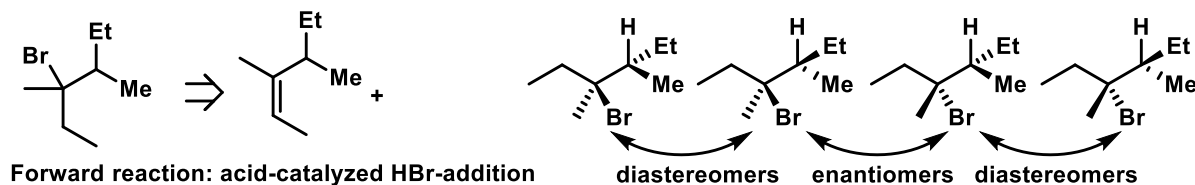
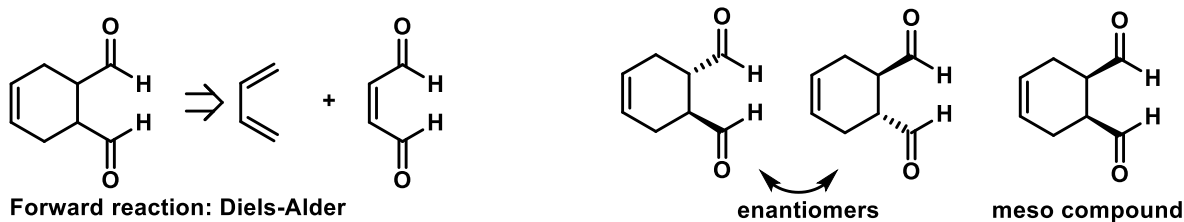
The increased acidity of a compound means that its *conjugate base* has increased stability.

Compare the conjugate bases of the two nitrophenols. For the more acidic one (i.e. the one with the lower pK_a), you can delocalize the negative charge formed on the O^- onto the nitro group. This is a stabilizing effect.

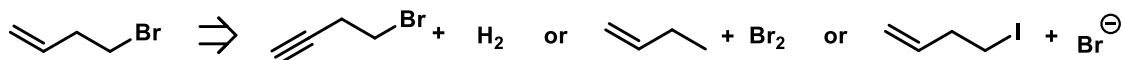
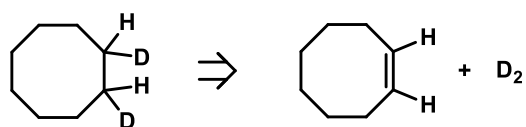
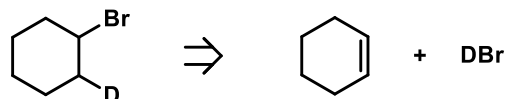
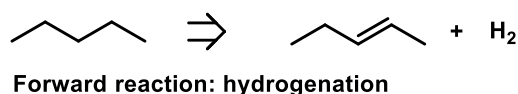
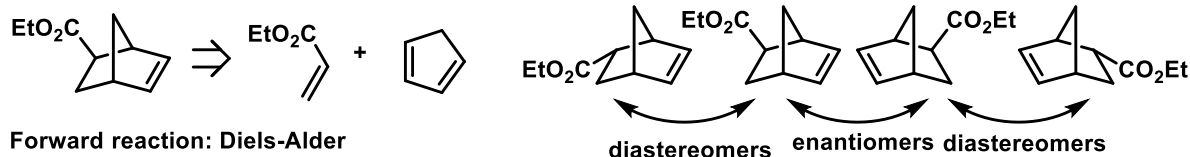
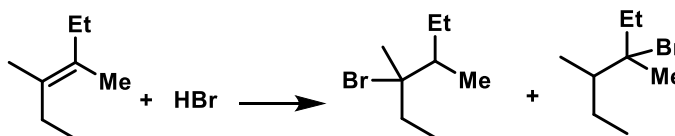
You cannot do a similar delocalization for the less acidic nitrophenol, which explains why this one is less keen on making the deprotonated species.

Note that both of these are more acidic than phenol. This is because the nitro group is more electron-withdrawing than H, so it helps to stabilize their conjugate bases compared to that of phenol.

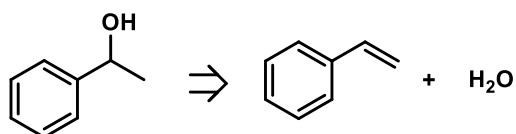
2) Suggest starting materials for the synthesis of the following compounds:



Note: this alkene would give you a mixture of products:

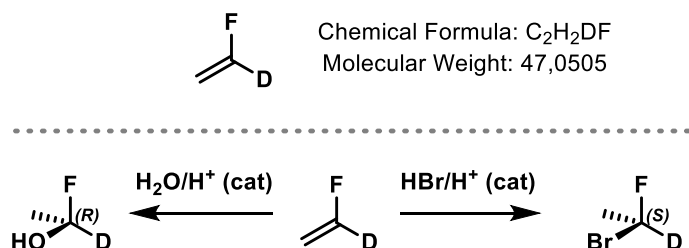


This one is not really straightforward. The first option (hydrogenation) might go all the way to the alkane (so you need to use Lindlar's catalyst, and monitor the reaction carefully). The second one might work if you succeed in doing it under strictly radical conditions, but you're most likely to get Br₂-addition to the double bond, too. The third one is really boring, but with a large excess of bromide salt (e.g. KBr), you should be able to kick out the iodine and push the equilibrium towards the product side.



3) Draw the alkene with the smallest molecular weight for which the addition of HBr will result in an *S*-product, while acid-catalyzed H₂O-addition will give the *R*-product.

I'm afraid this was a badly formulated question, not least because you have not discussed ways to make single enantiomers of products.



Anyway, the point was to realize that you needed to

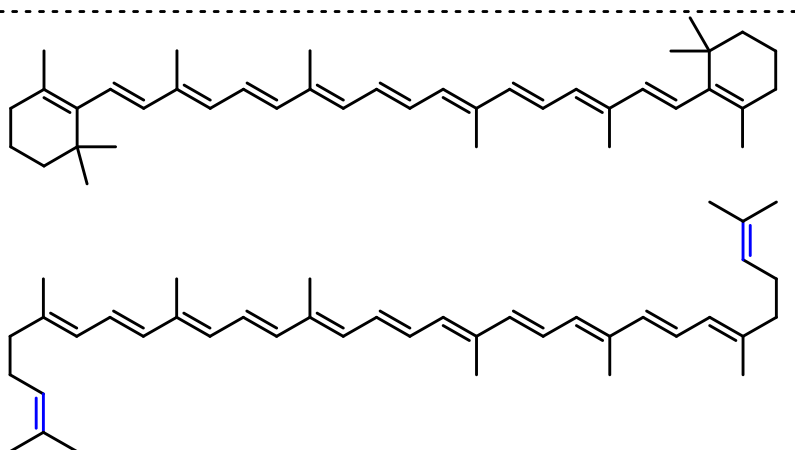
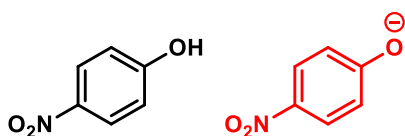
- 1) Make a small alkene (the smallest will have a H₂C= end)
- 2) Find the smallest possible group/atom that will be different from H (because you will add H-OH or H-Br, you cannot have H) → the next smallest is D (deuterium)
- 3) Find a group that is between OH and Br in priority. The smallest possible such is the atom straight after O, which is F.

Assuming you can take the same alkene, and add HBr or water with exactly the same mechanism to make the same single enantiomer (that is, the one where the OH/Br is poking out of the plane), this would give you an *R* product for one, and an *S* for the other.

Of course, the actual reaction would be freakishly difficult to do with such precision. But that is someone else's problem.

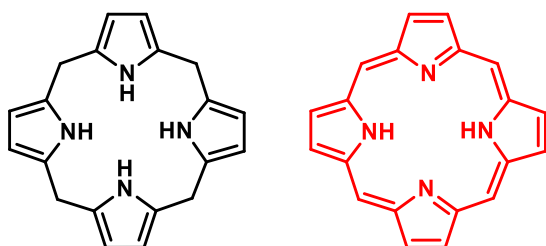
4) Which one of the pairs will have a longer absorption wavelength (λ_{max})?

Solution: the compounds highlighted in **red**, because they have more extended conjugation (i.e. longer double bond-single bond or lone pair alteration)



No obvious difference, the length of the conjugation is the same in both.

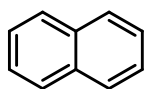
Note that the double bonds highlighted in **blue** are not conjugated to the rest.



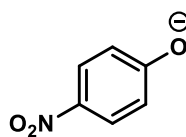
5) Which compounds will be blue, purple, yellow, red, or only absorb in the ultraviolet?
(Hint: putting the compounds in increasing λ_{\max} order first helps.)



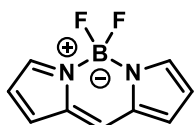
UV
pyrrole



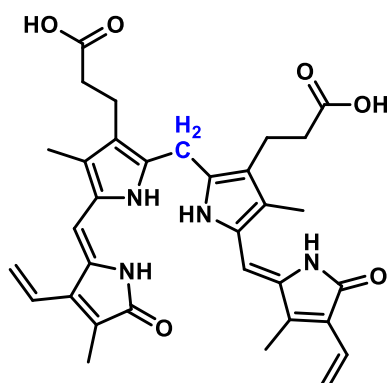
UV
naphthalene
used in mothballs



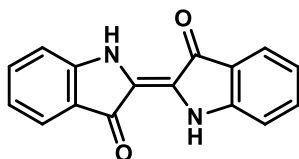
yellow
the colored product of a lot of enzyme assays



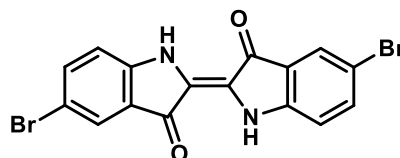
yellow
BODIPY, the core structure of
fluorescent compounds used in
biomolecule labelling



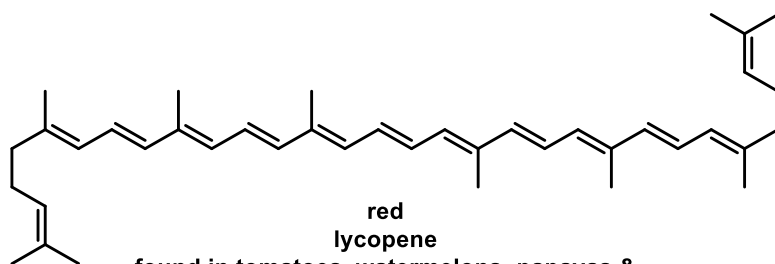
yellow
bilirubin
produced by heme degradation
(its the yellow color of bruises)
notice that the conjugation is broken
on the blue carbon, so while the
molecule is large, it is still yellow



blue
indigo
used to dye blue jeans



purple
Tyrian purple/imperial purple, produced by snails
used by e.g. the Romans to make posh robes



red
lycopene
found in tomatoes, watermelons, papayas &
asparagus (even if the latter is not red)

6) Identify the nucleophile, the electrophile, and draw in the curly arrows. What are the structures of the compounds **A** – **F**?

