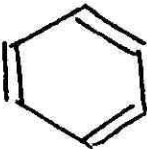
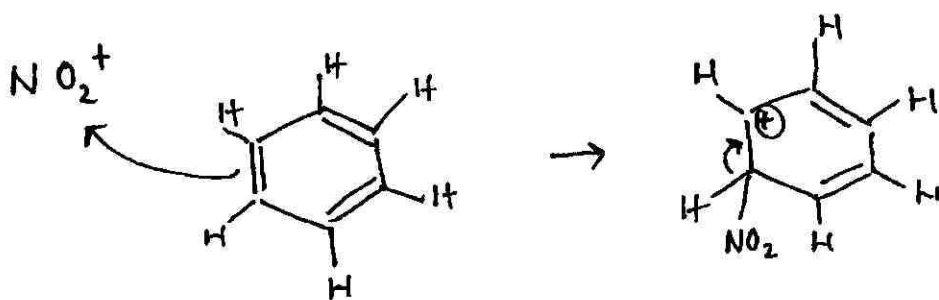


Lecture 27 Nitration and aromatic electrophilic substitution.

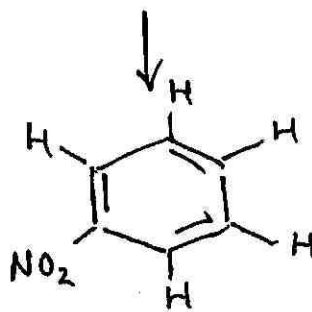
27.1

①  can act as a nucleophile.

A powerful electrophile is often a positively charged species. NO_2^+ is a powerful electrophile.

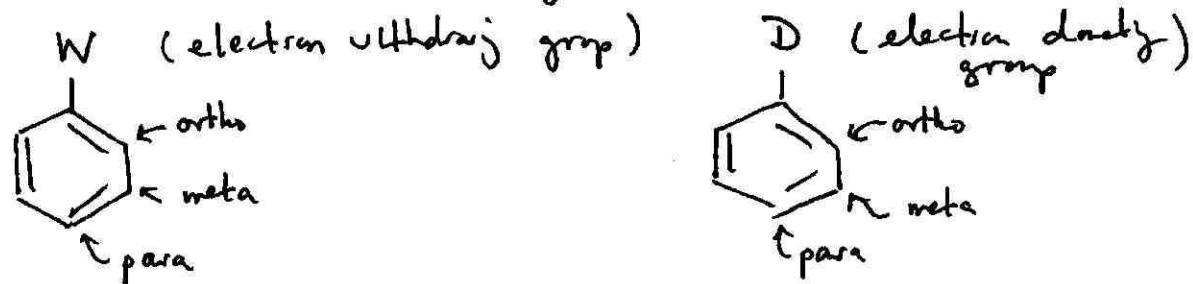


This reaction is called nitration. In it the aromatic ring acts as a nucleophile, the NO_2^+ as an electrophile and the reaction is termed an aromatic electrophilic substitution reaction (AES).



② One of the triumphs of late 19th century organic chemistry was working out the rules governing AES. In this lecture and the problem set we will find the MO basis of these rules.

③ The 19th century rules are as follows



Electron withdrawing groups deactivate the AES reaction. Substitution is at the meta site.

Electron donating groups activate the AES reaction. Substitution is at ortho or para site.

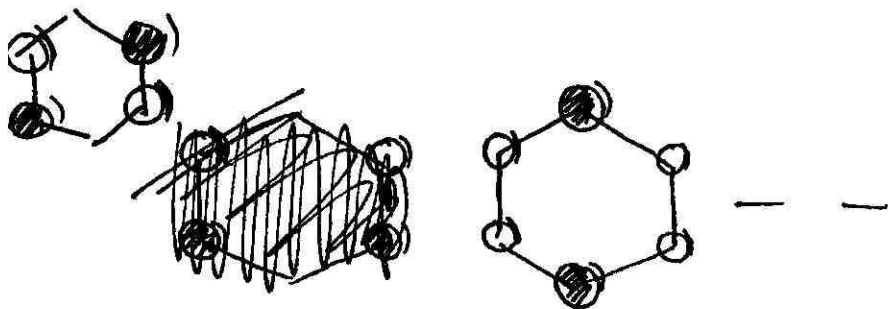
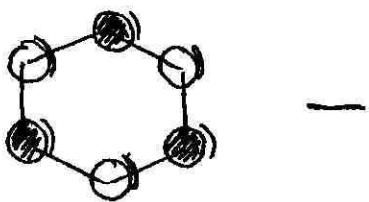
Silly mnemonic:
R o m p.
Around the Ring order is Ortho, Meta, Para.

④ We need to examine the HOMO of benzene ring as the ring acts as a nucleophile in this reaction.

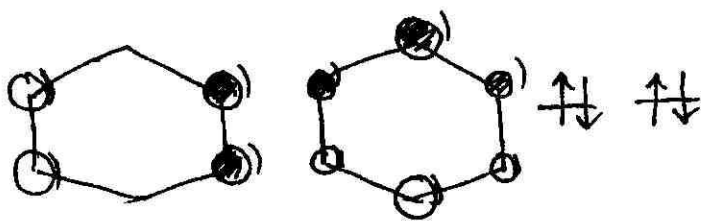
(i) First derive the MO diagram of benzene.

(ii) Find how HOMO change under affect of an electron donating group.

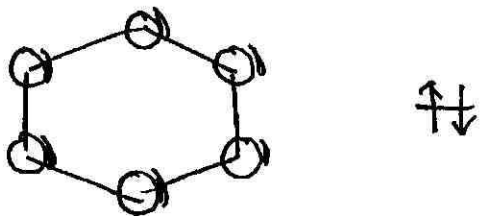
⑤ As we found in Problem Set 8, the π -MO's of an aromatic ring are:



$E \uparrow$



HOMO's



⑥ One point which was not clear, was the ordering of the energy of



To find the answer note both $\vec{\psi}_2$ and $\vec{\psi}_3$ are Hamiltonian eigenvectors.

$$H \vec{\psi}_2 = E_2 \vec{\psi}_2 \quad \text{and} \quad H \vec{\psi}_3 = E_3 \vec{\psi}_3$$

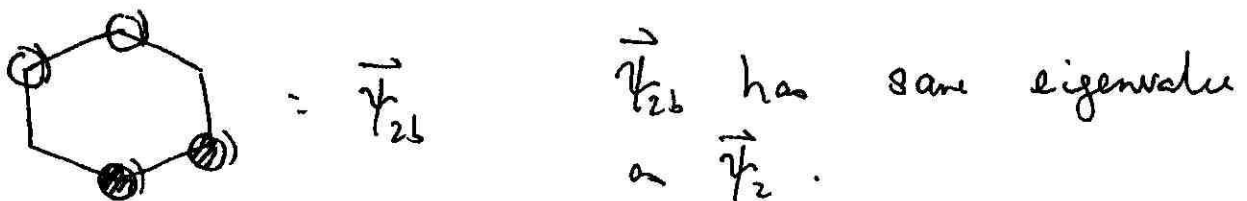
where E_2 and E_3 are their eigenvalues

⑦ Note if $\vec{\psi}_a$ and $\vec{\psi}_b$ are ^{energy} eigenvectors with the same eigenvalue $\Rightarrow \vec{\psi}_a + \vec{\psi}_b$ is also an eigenvector.

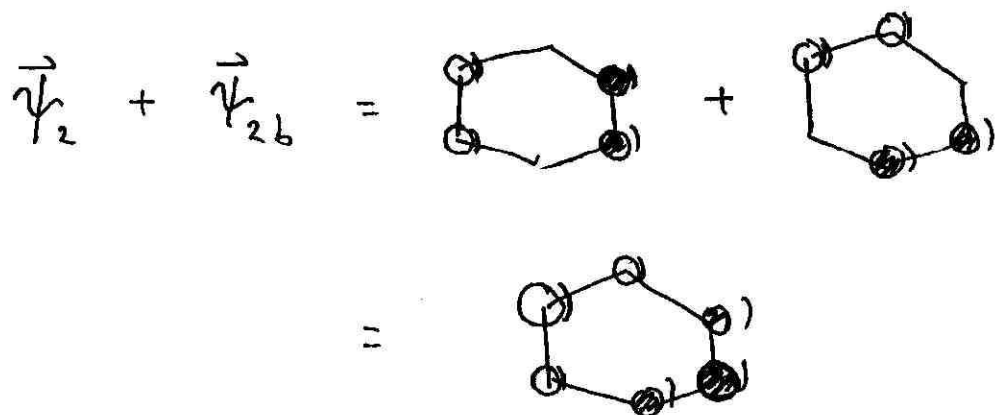
Reason

$$\begin{aligned} H(\vec{\psi}_a + \vec{\psi}_b) &= H\vec{\psi}_a + H\vec{\psi}_b \\ &= E\vec{\psi}_a + E\vec{\psi}_b \\ &= E(\vec{\psi}_a + \vec{\psi}_b) \end{aligned}$$

⑧ If $\vec{\psi}_2$ is an eigenvector, so is:



⑨ Let's now consider

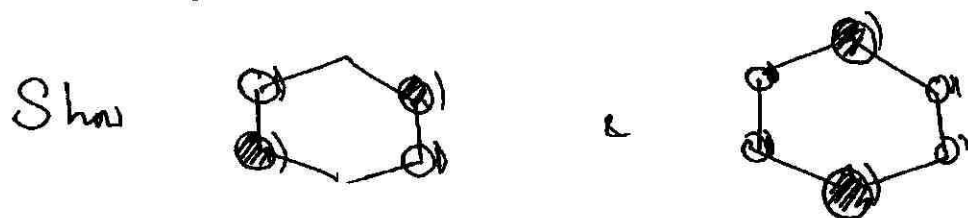


This is just a rotated version of $\vec{\psi}_3$.

$\therefore \vec{\psi}_3$ & $\vec{\psi}_2$ have the same energy eigenvalue.

⑩

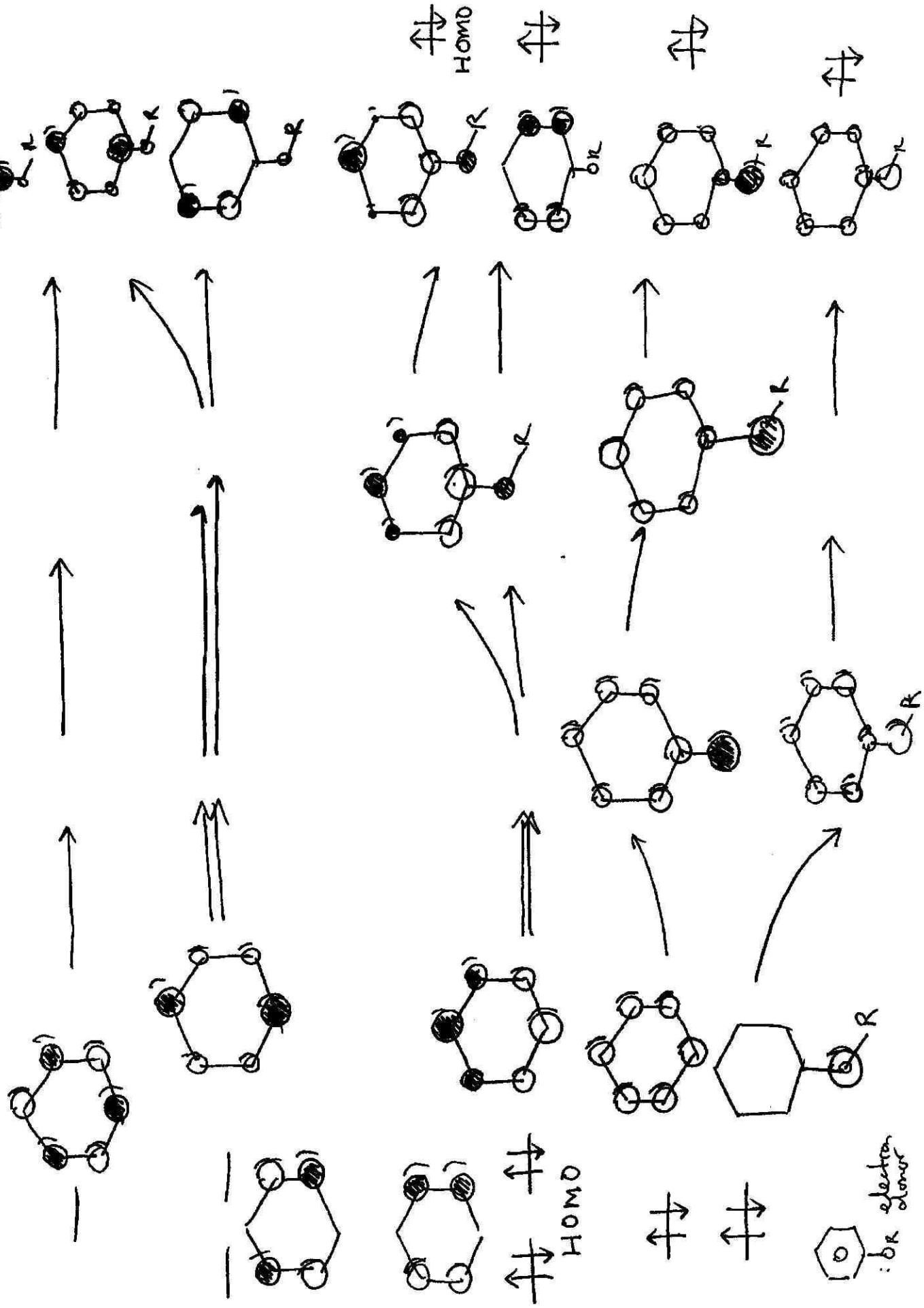
Exercise:



have the same energy eigenvalue.

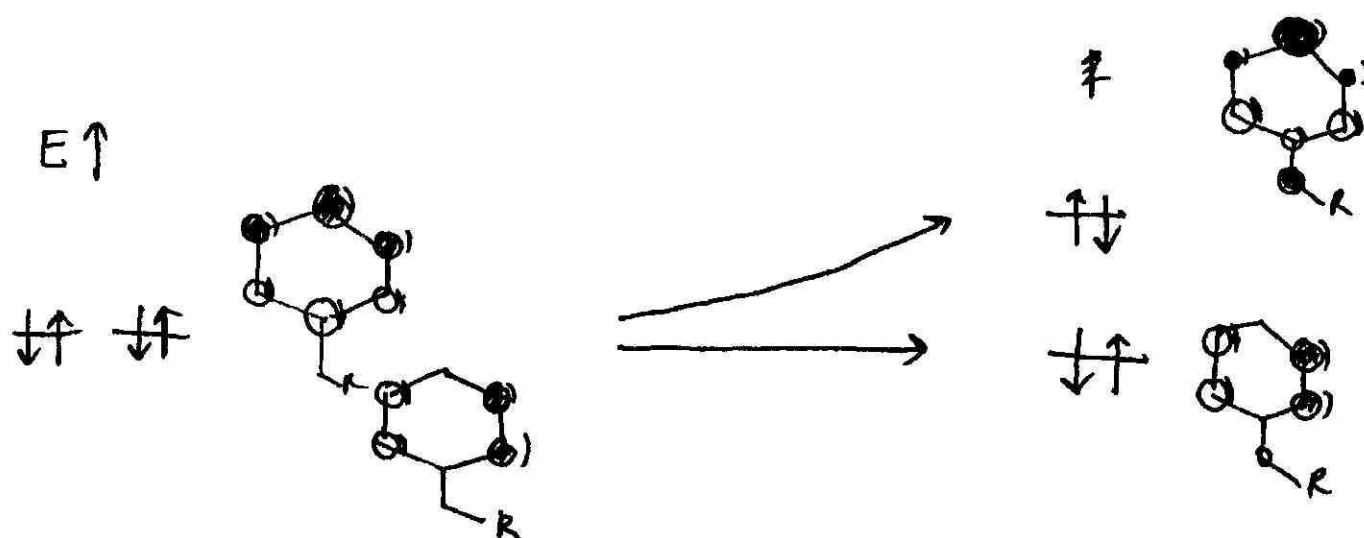
⑪ We now consider pair-wise MO diagram when an electron donating group ($-\ddot{O}R$) has been added.

Pairwise diagram to derive HOMO

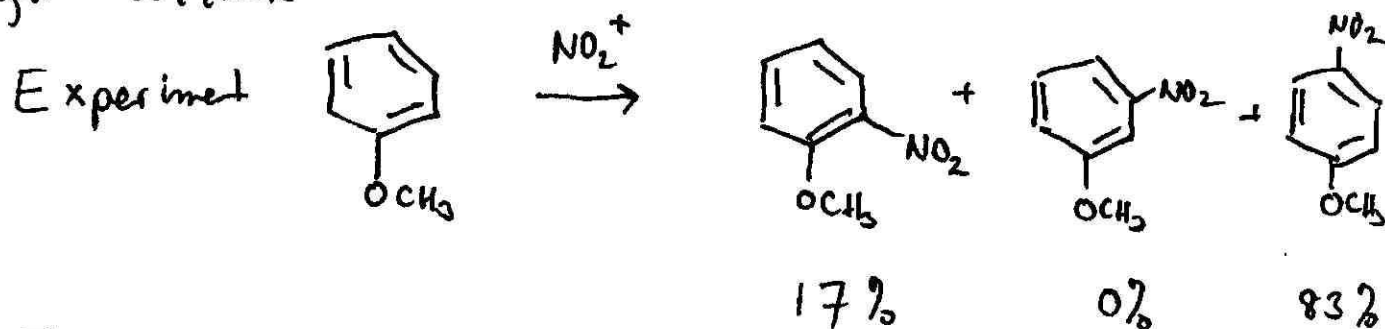


Note in the pairwise diagram to derive the HOMO we never even found the correct version of the most antibonding orbital.

Summarizing the situation for the HOMO

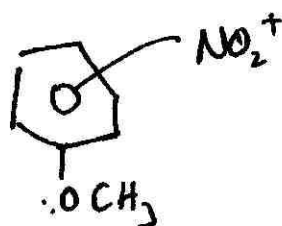


The HOMO's go up in energy and the ortho & para-sites become the dominant sites for attack



The rate of reaction for COc1ccccc1 is greater than for benzene.

The organic chemist's way of viewing the reaction is they would say $\overset{\ominus}{\text{O}}\text{CH}_3$ is electron donating. It stabilizes a cation intermediate.



\therefore reaction goes faster. To study chemistry I suggest you learn both views. But in my mind the MO theory is an explanation. The organic chemistry story is a rationalization.