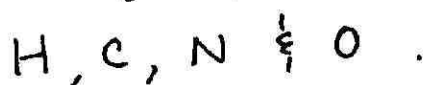


Lecture 25

① We now turn to organic chemistry, the chemistry of the 1st & 2nd row of the periodic table:

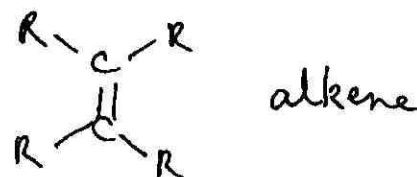
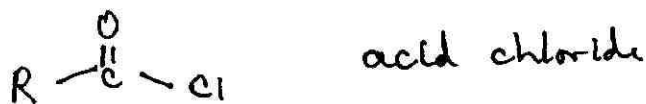
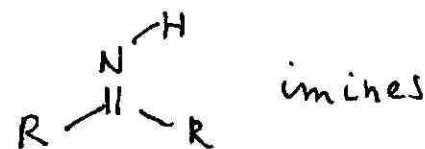
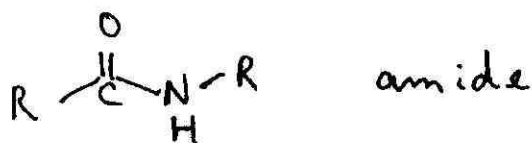
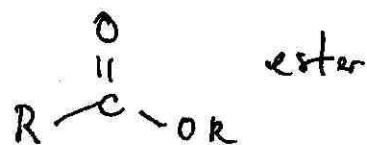
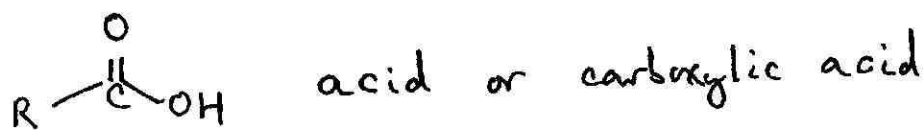
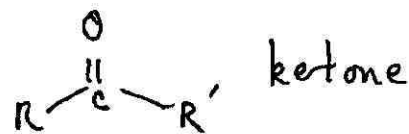
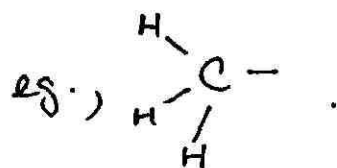


② The chemistry of these elements is often related to the π -orbitals of these systems (atoms doubly bonded to each other.)

③ For example one of the most common groups found in organic chemistry is the $R-\overset{O}{\parallel}C-Q$

$\overset{O}{\parallel}C$ is called a carbonyl.

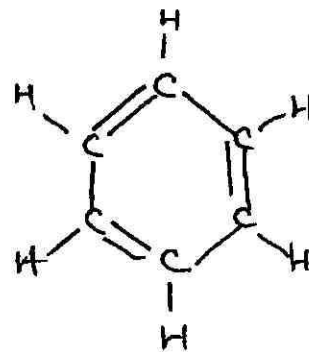
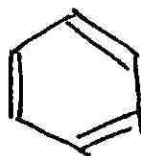
R- is a carbon piece



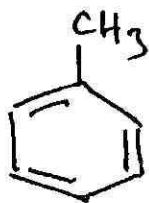
④ Another common example is the aromatic ring



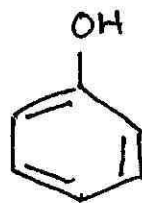
or



benzene



toluene



phenol



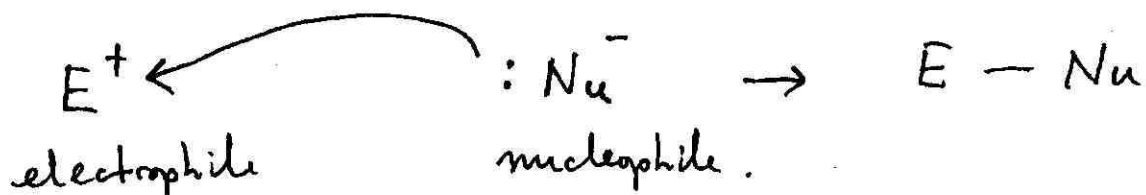
benzaldehyde

⑤ It turns out that understanding the π orbitals of these systems goes a long way to understanding the reactive chemistries of these organic molecules.

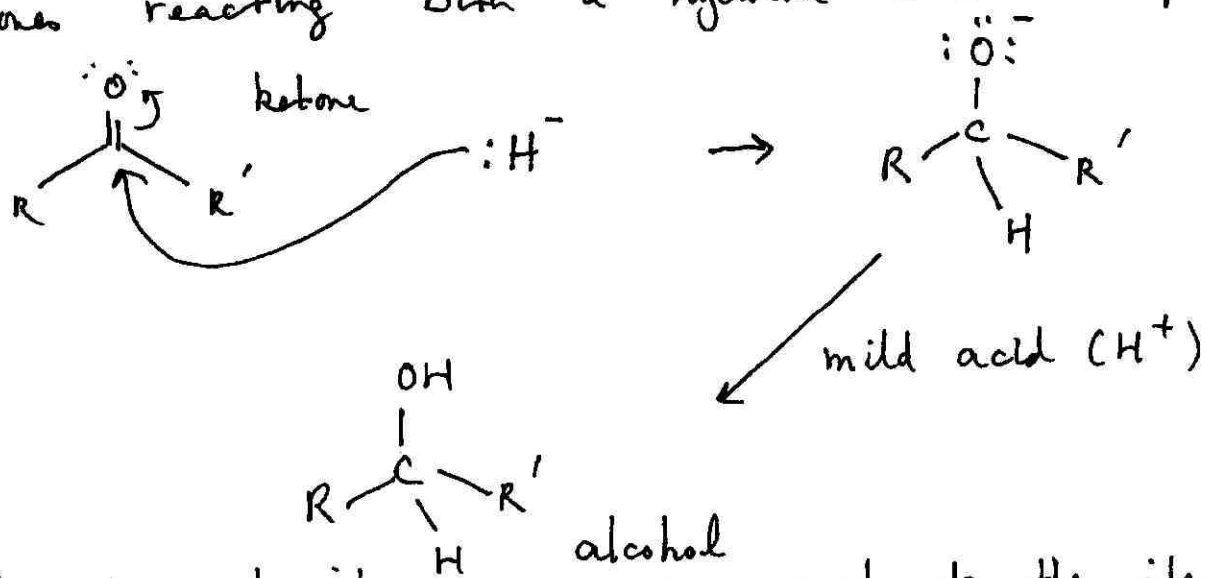
⑥ Historically, when organic chemistry was discovered, chemists did not know about MO theory. So next year when many of you study organic chemistry you will discover that the role of MO theory will be somewhat muted.

⑦ We will adopt the following format. First we will state organic chemistry in the form it is normally taught. Then we will show the connection with MO theory.

⑧ Organic chemists talk about electrophiles and nucleophiles. An electrophile is something looking for a pair of electrons, a nucleophile is something looking for an electrophile.



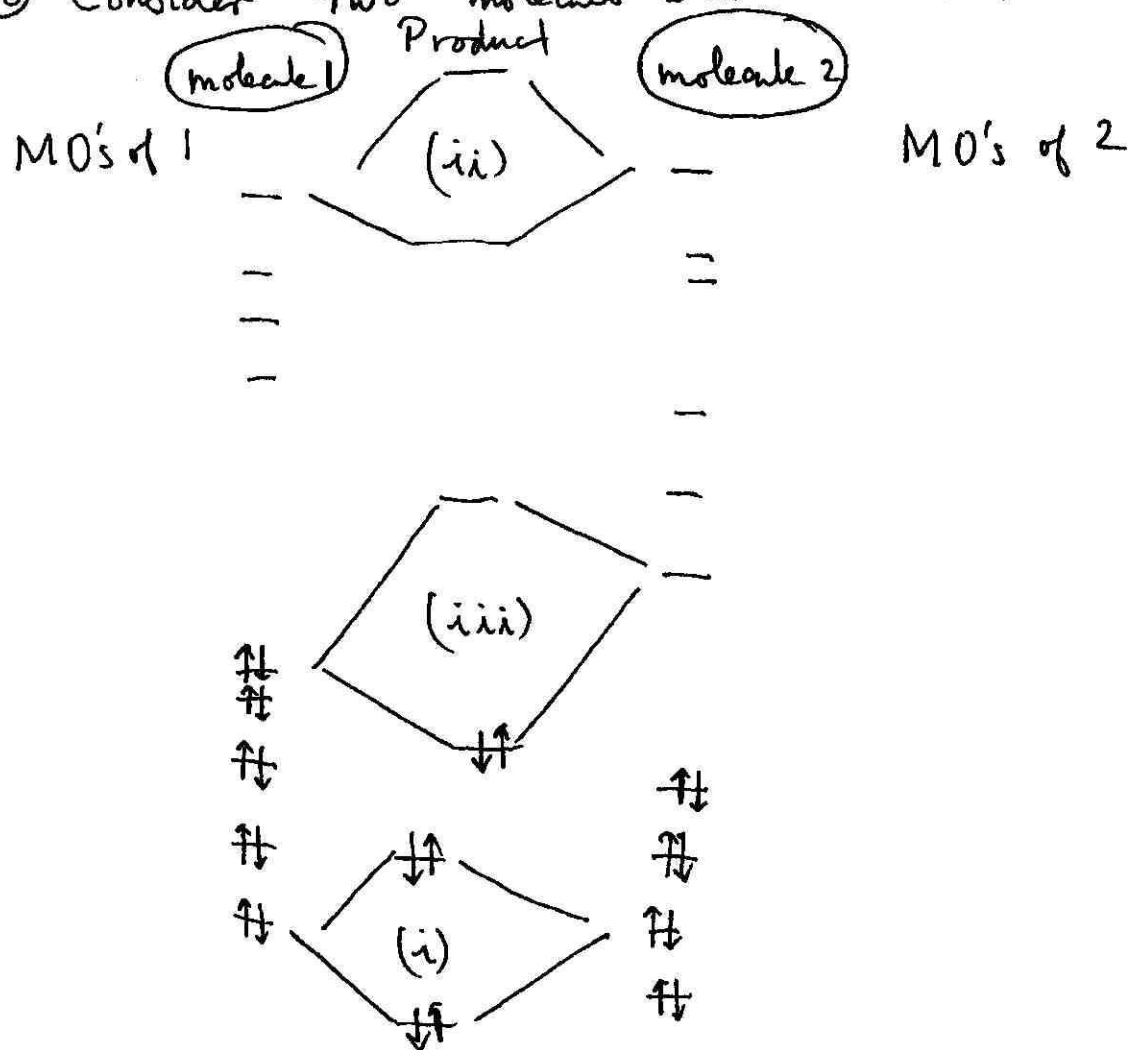
For example hydride, H^- is a nucleophile. Ketones reacting with a hydride are electrophile.



⑨ Organic chemists are very used to the idea of representing pairs of electrons as arrows.

Electrons are MO's, they are waves. They are not very much like arrows. The clue as to what the arrow means comes from MO theory.

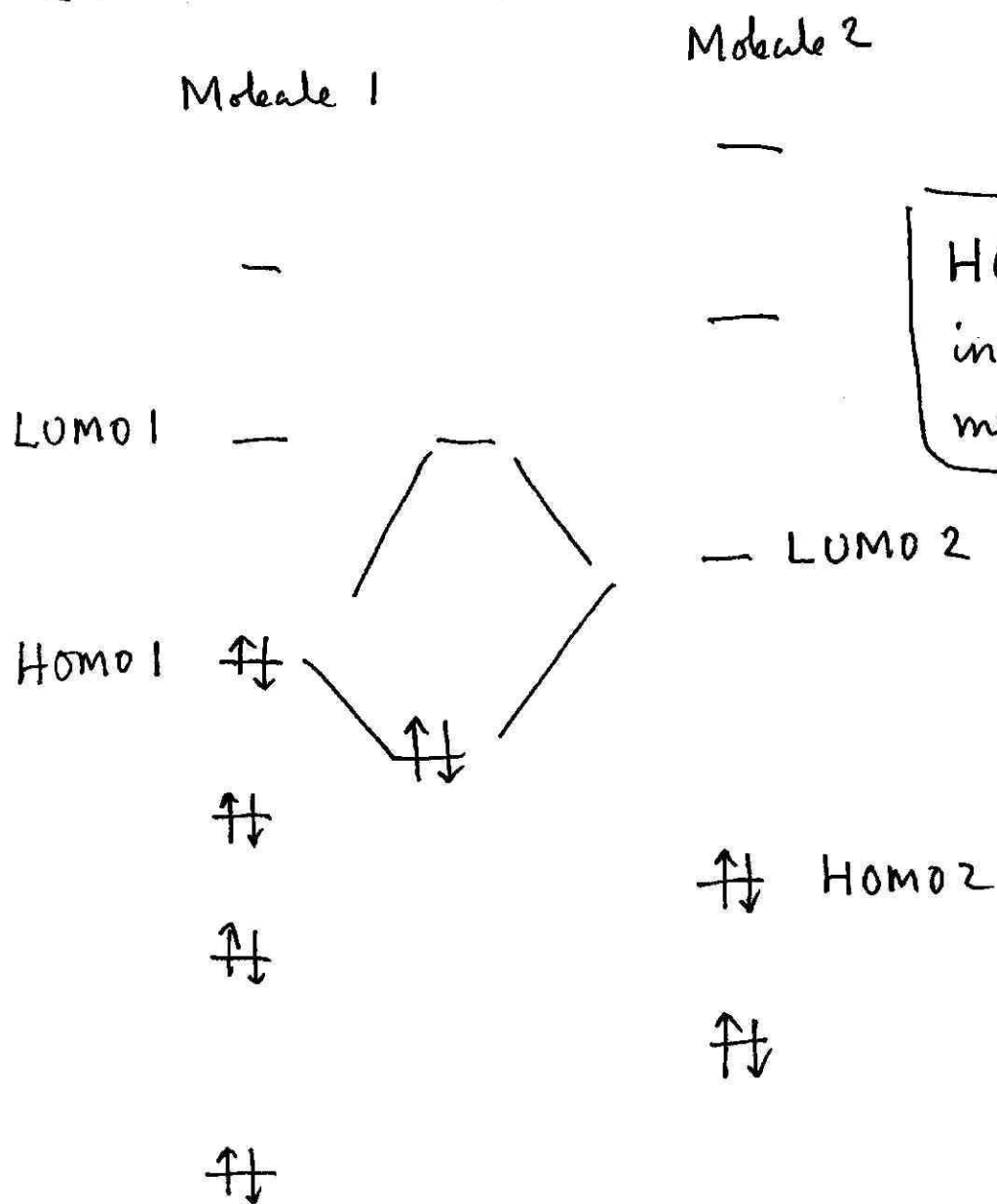
⑩ Consider two molecules which react :



We can envision 3 kinds of MO interaction.

- (i) Filled orbital of molecule 1 reacting with a filled orbital of molecule 2. As both orbitals are filled no net stabilization.
- (ii) Empty orbital of molecule 1 interacting with an empty orbital of molecule 2. As both orbitals are empty no net stabilization.
- (iii) Filled orbital of one molecule interacting with an empty orbital of other molecule. There is net stabilization.

① The stabilization is greatest for two orbitals which are initially close in energy [that's rule 3 for making MO diagram]

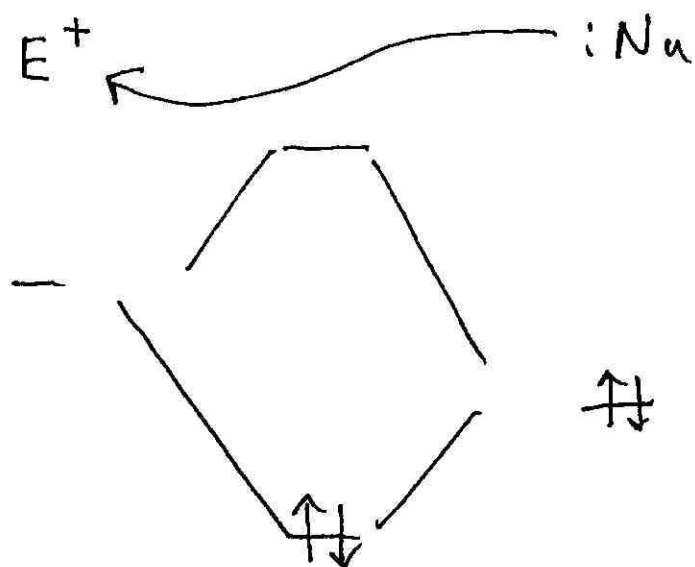


HOMO 1 to LUMO 2 interaction is the most important

LUMO = Lowest Unoccupied Molecular Orbital
 HOMO = Highest Occupied Molecular Orbital

(12)

A molecule with a high energy HOMO is a nucleophile. A molecule with a low energy LUMO is an electrophile.

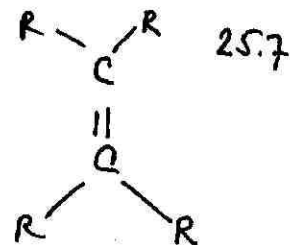


Consider H^- . The HOMO is a non-bonding orbital. $\therefore \text{H}^-$ has a high energy HOMO. It is a good nucleophile.

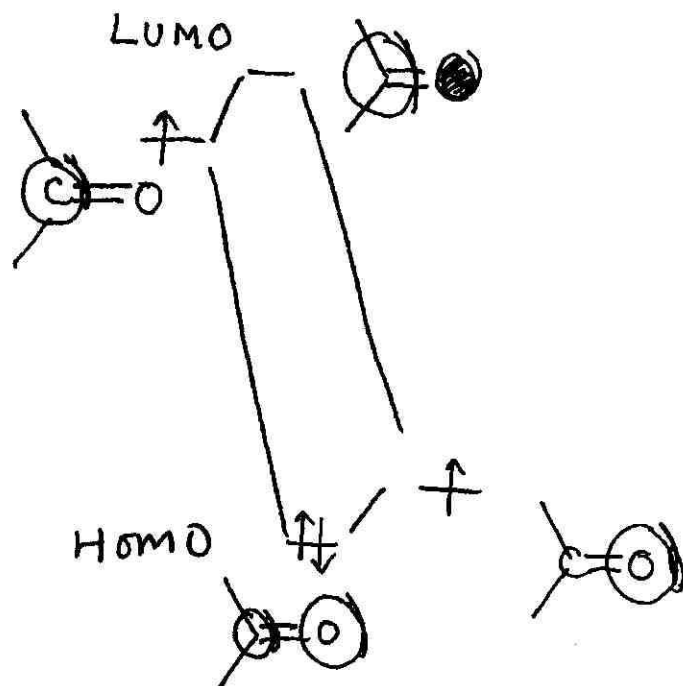
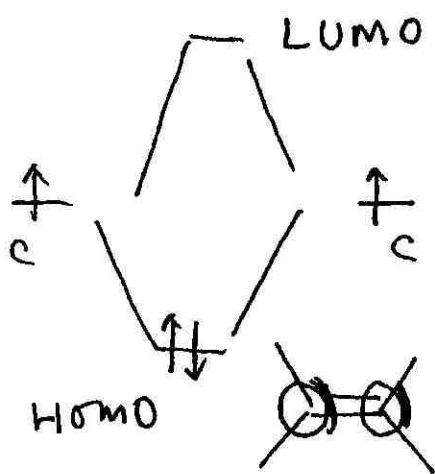
Let us now consider



vs.



These molecules have a LUMO which is a π -orbital.



LUMO of $\text{C}=\text{O}$ is lower in energy than $\text{C}=\text{C}$. \therefore Ketone is a better electrophile than an alkene. Also



is better than $\text{C}=\text{C}$:H^-
Why? (look at MO)