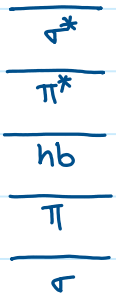
General Organic Chemistry

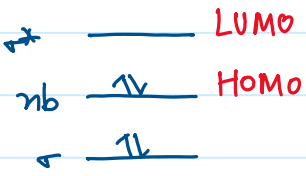
Molecular orbitals in organic Chemistry:-



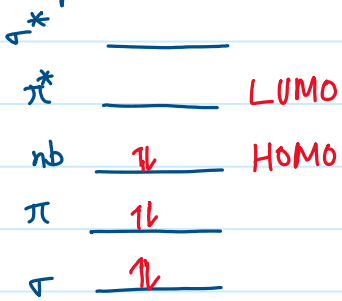
LUMO — Lowest unoccupied molecular orbital

HOMO — Highest occupied molecular orbital

For ex- $H_3C-\ddot{O}H$; in C–O bond, there is no π bond. But 'O' has lone pairs.



For example, in C=O bond



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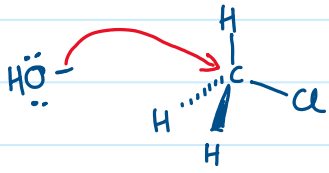
→ Electrons are always transferred from HOMO of one molecule to LUMO of another. For ex- in reaction shown below:-

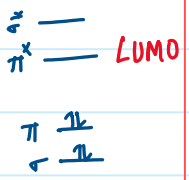


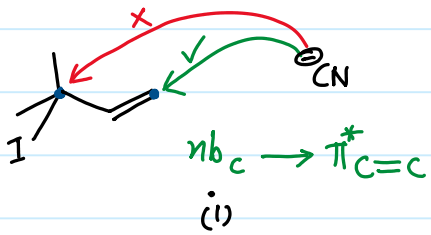
e⁻ are transferred from nb(p) orbitals of oxygen atom (HOMO) to σ* orbital of C–Cl bond. (LUMO)

→ HOMO: Highest energy level of atom/ion/molecule in which electrons are present.

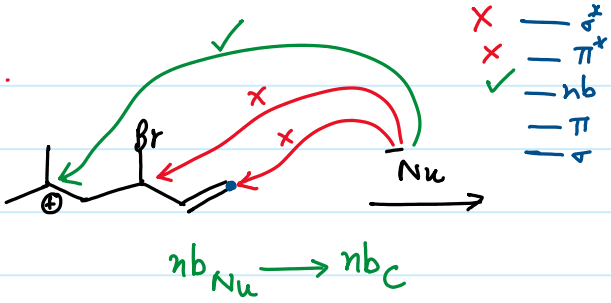
→ LUMO: Lowest energy level of atom/ion/molecule in which there are no electrons.

Que. Explain the flow of e^- in below transfers.





(i)



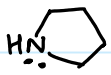
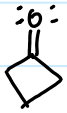
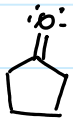
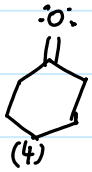
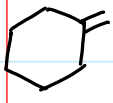
(ii)

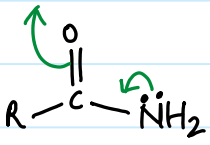
Donor ability/nucleophilicity :-

Ability of an electronic species to donate electrons from it's HOMO.

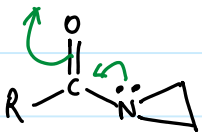
- energy levels of atom :- $s < p < d < f$
- energy levels of molecule :- $\sigma < \pi < nb < \pi^* < \sigma^*$
- energy levels of hybridized atom :- $p < sp < sp^2 < sp^3 < s$

Que. Predict donor ability

- (1) $\bar{C}H_3$ (sp^3) (2) $H\bar{C}{=}CH_2$ (sp^2) (3) $\bar{C}{\equiv}CH$ (sp) donor ability = 1 > 2 > 3 [Hybridization]
- (1) $\bar{C}H_3$ (2) $\bar{N}H_2$ donor ability = 1 > 2 [electronegativity]
- (1) $:NH_3$ (2) $:\bar{N}H_2$ donor ability = 2 > 1 [additional e^- charge]
-  (1)  (2)  (3) donor ability = 1 < 2 < 3 [s-character ∝ bond angle]
-  (1)  (2)  (3)  (4) donor ability = 4 > 3 > 2 > 1 [s-character ∝ bond angle]
- (1)  (2)  donor ability = 1 < 2 [bond angle ∝ s-character inside ring inside ring]
- (1)  (2)  donor ability = 2 < 1 [bond angle ∝ s-character outside ring outside ring]



(1)



(2)

donor ability :- 1 > 2

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lone pairs of N atom have more s-character in (2) due to a larger bond angle. Hence,

Factors affecting Nucleophilicity:-

1. Electronegativity:

donor ability $\propto \frac{1}{\text{electronegativity}}$

ex- $NH_3 > OH_2 > FH$

2. Size of donor atom:

donor ability $\propto$ atomic size

ex- $OH_2 < SH_2 < SeH_2 < TeH_2 < PoH_2$

3. Charge on donor atom:-

donor ability $\propto$ extra negative charge $\propto \frac{1}{\text{extra positive charge}}$

ex- $:OH_2 < :\bar{O}H < O^{2-}$;

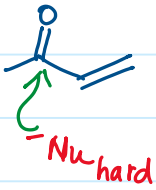
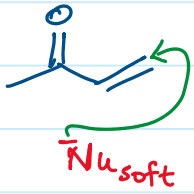
ex- $:O{=}C< \;>\; H{-}\overset{\oplus}{O}{=}C<$

4. Alpha α- effect :-

presence of a heteroatom adjacent to the donor atom increases the donor ability.

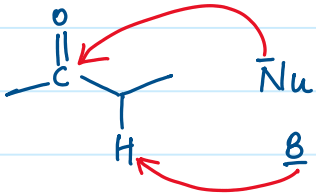
ex- $H_2\ddot{N}-\ddot{O}H$ > $H_2\ddot{N}-CH_3$

Hard & Soft Nucleophile :-

		Hard Nucleophile	Soft Nucleophile
(i)	Size	small	large
(ii)	– charge density	high	low
(iii)	electronegativity	high	low
(iv)	attack on α,β-unsaturated carbonyl		
(v)	examples	F^-, Cl^-, $\bar{O}H$, $\bar{N}H_2$	$\bar{S}H$, $\bar{P}H_2$, Br^-, I^-

Nucleophilicity & Basicity

Basicity is just nucleophilicity but for a proton.



* Some molecules/ions can act as base as well as nucleophile. For ex- $\bar{O}H$.
* A nucleophile RMgX ($\bar{R}$) can also act as a base if acidic hydrogen is present.

Electronic effects:

- Inductive effect
- Mesomeric effect
- Resonance effect
- Hyperconjugation
- Electromeric effect
- Cross conjugation

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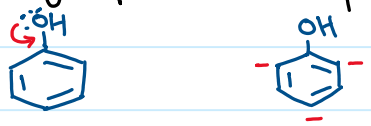
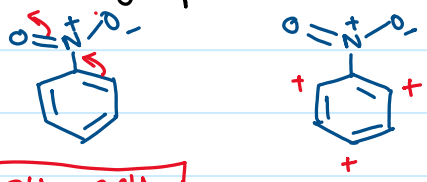
Directing Effects of groups:

1. -OH group is ortho & para directing by resonance (+M)

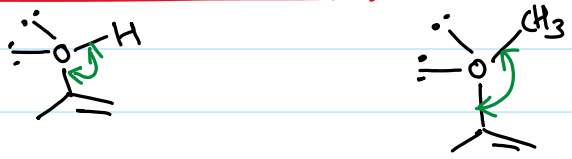


2. $-OCH_3$ group is ortho & para directing by resonance (+M)

3. $-NO_2$ group is meta directing by resonance (−M)



OH vs OCH_3



O atom in OCH_3 has more s-character because of more bond angle. Hence, donation of e^- is comparatively hard. So, OCH_3 is less directing as compared to OH group.