

Organic Chemistry B.Sc. Semester 1

“ATTACKING REAGENTS”

E-content by -

Siddhi Jaiswal

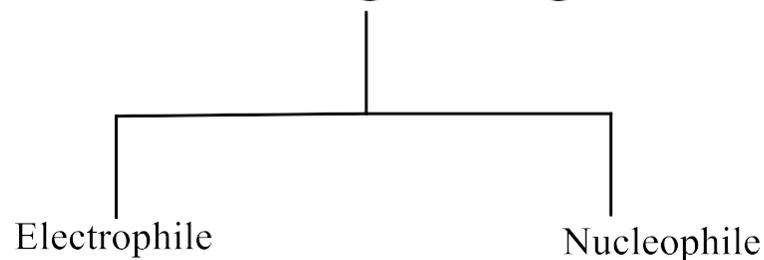
Assistant Professor

Department of Chemistry

Nari Shiksha Niketan P.G. College, Lucknow

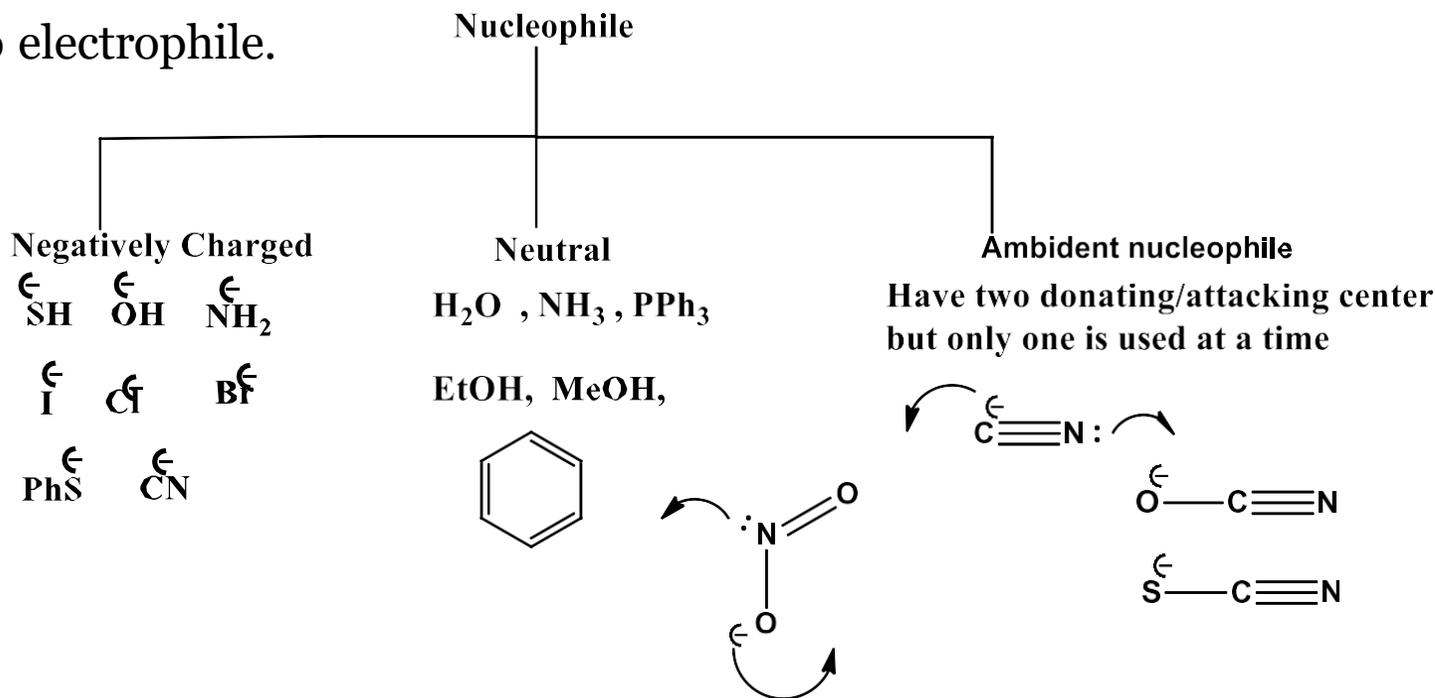
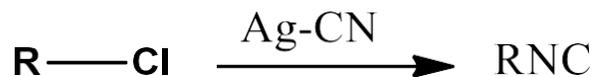
Email – dr.siddhichem@gmail.com

Attacking Reagents



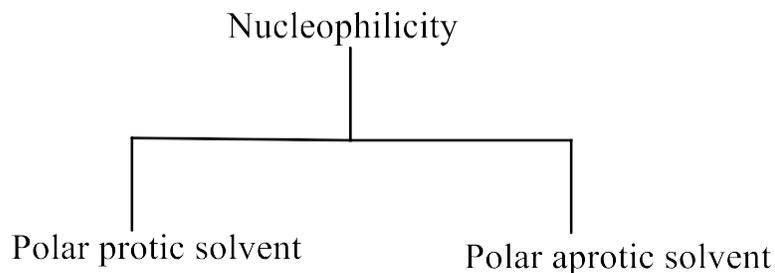
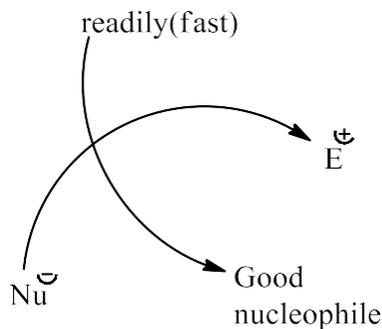
Nucleophiles and their Nucleophilicity:

- Nucleus loving species
- Nucleophile is a species having negative charge or lone pair of electrons and should be capable of donation its electron pair to electrophile.
- They are electron rich species.
- They acts as lewis bases.



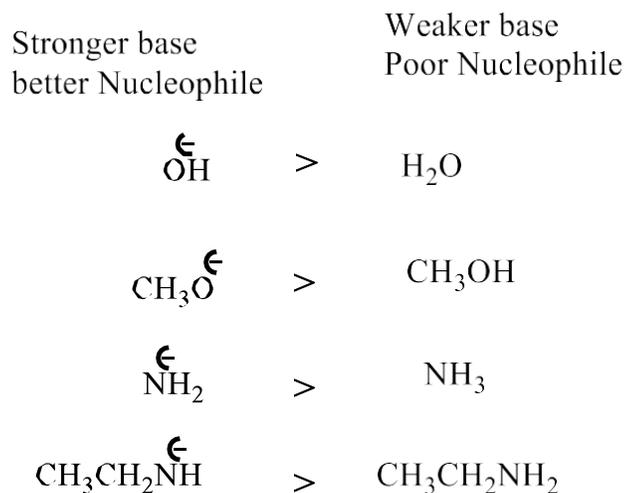
Nucleophilicity:

Measure of how readily a nucleophile is able to attack an electrophile, **determined by rate constant**



Factors affecting nucleophilicity in polar protic solvents:

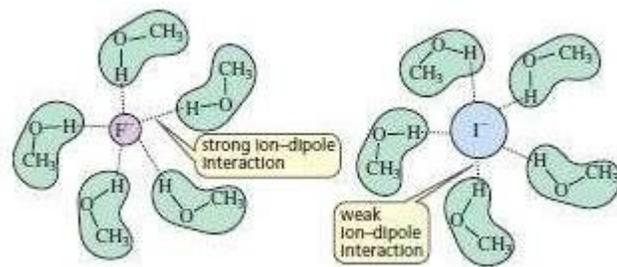
- i. Charge density: When attacking atoms (donor atoms) are same, then stronger the base better the nucleophile. Negatively charged species are stronger base and better nucleophile than corresponding neutral species.



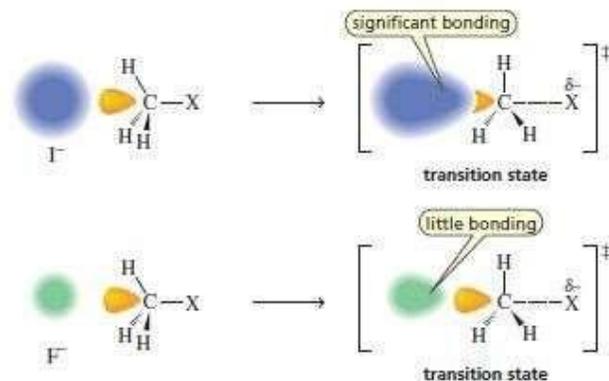
ii. Variation in group:

Solvation: greater the solvation, lesser the nucleophilicity.

Solvation \propto charge density. Extent of solvation : $F^- > Cl^- > Br^- > I^-$



Polarizability of atom: Greater the polarizability more free the electron cloud of that atom moves towards electrophile, more will be the nucleophilicity.



Order of Nucleophilicity:



Note :

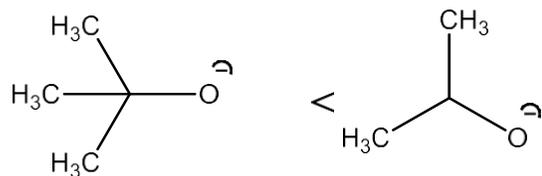


iii. Variation in Period:

- Same as basicity
- Inverse of E.N. of donar atom

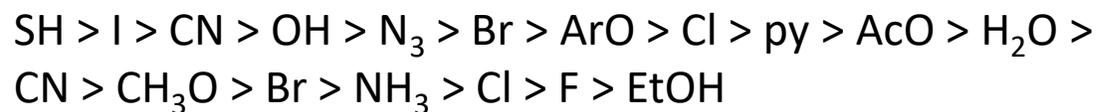
iv. Steric factor:

Greater the steric factor around the donar atom, lesser the nucleophilicity.



Note:

- overall nucleophilicity in polar protic solvent:

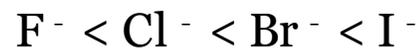


• Eg.

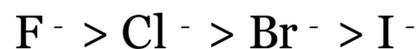


In Polar aprotic solvent :

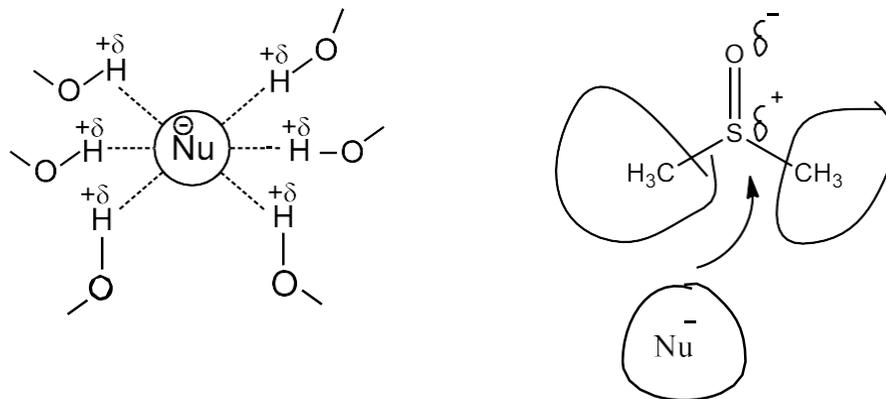
- It depends only on charge density and steric factors(no profound effect of solvation)
- In polar protic solvent large nucleophiles are good(because of poor solvation), and the halide ions show the following order



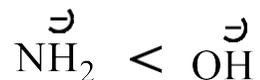
- In DMSO, the relative order of nucleophilicity of halide ions is



- This effect is related to the strength of the interaction between nucleophile and solvent molecules of polar protic solvent forms hydrogen bond to nucleophiles in the following manner :



e.g. In aprotic solvent



Note:

In case when donor/Nucleophilic atom is same, nucleophilicity is same as basicity.

- Nucleophilicity & Basicity :**

Nucleophilicity	Basicity
The tendency to give electron pair to an electron deficient atom other than proton is defined as nucleophilicity	Bases are the species which accept the proton or which donates l.p. of electron to proton
Nucleophilicity increases down the group	Basicity decreases down the group $\text{NH}_3 > \text{PH}_3$
Kinetic Parameter	Thermodynamic Parameter
Influenced by steric factors	Steric factors does not effect much the basicity
Decreases left to right in period	Decreases left to right in period

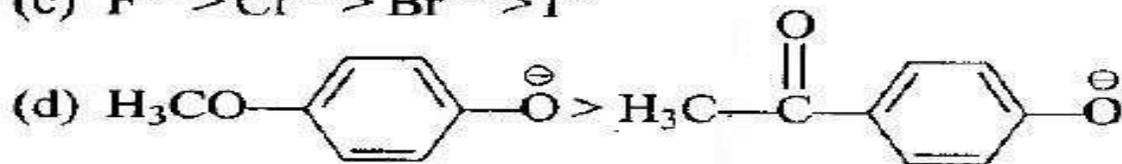
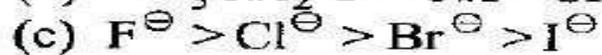
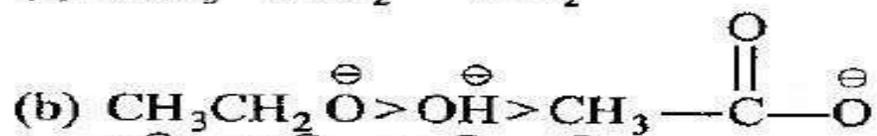
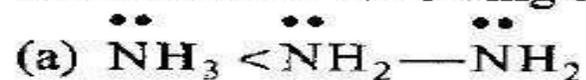
- α -Effect:**

Nucleophiles having another lone pair adjacent to them are better nucleophile.

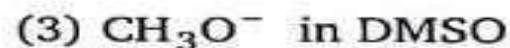
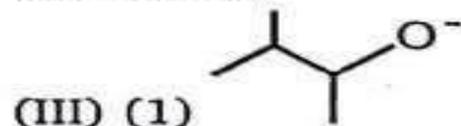
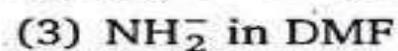
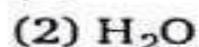
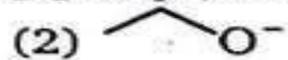
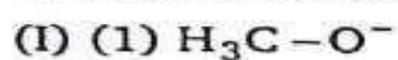


- Q1 Which is a better nucleophile?
- | | |
|--|---|
| a. Br^- or Cl^- in H_2O | e. HO^- or NH_2^- in H_2O |
| b. Br^- or Cl^- in DMSO | f. HO^- or NH_2^- in DMSO |
| c. CH_3O^- or CH_3OH in H_2O | g. I^- or Br^- in H_2O |
| d. CH_3O^- or CH_3OH in DMSO | h. I^- or Br^- in DMSO |

Q2. Which of the following are correct order of nucleophilicity in CH_3OH ?

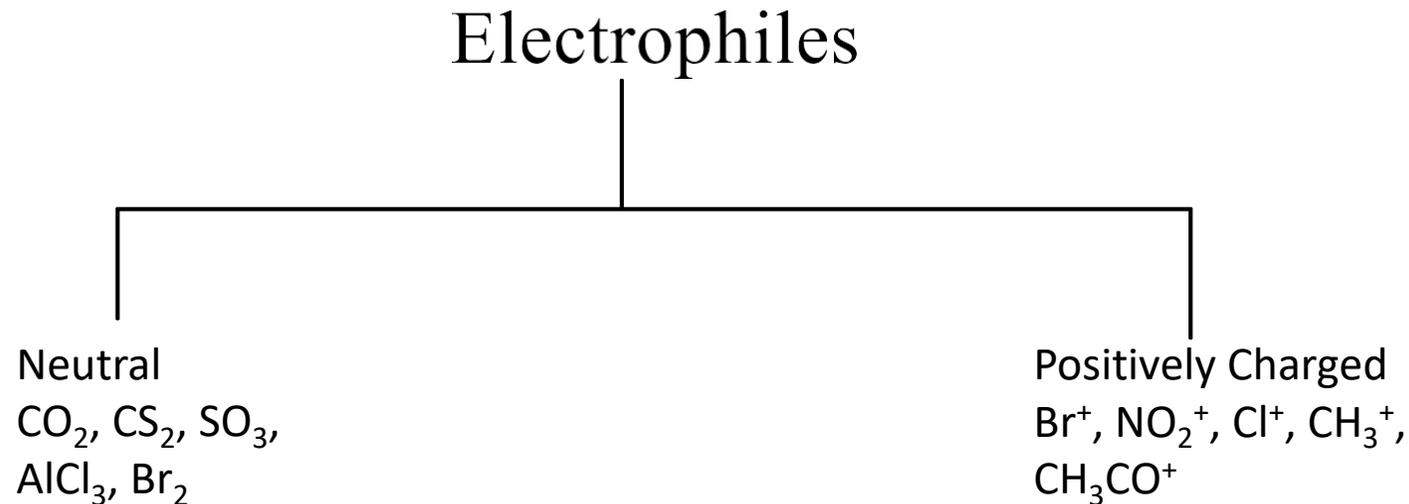


Q3 In each of the following groups, which is the strongest (best) nucleophile ?



Electrophile:

- Electron loving species
- Electrophiles are electron deficient species.
- They act as Lewis acids
- They should be having low-lying empty orbital

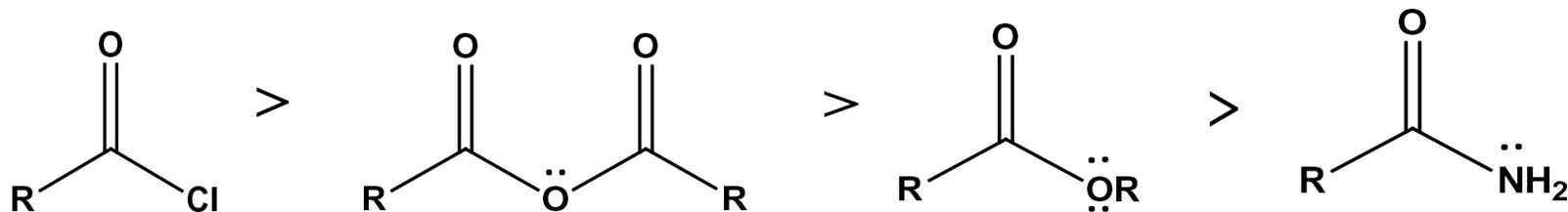
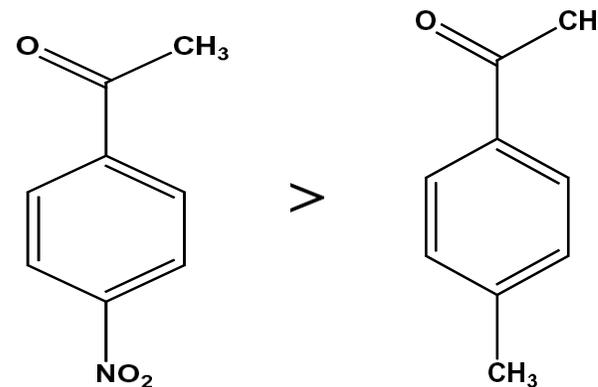
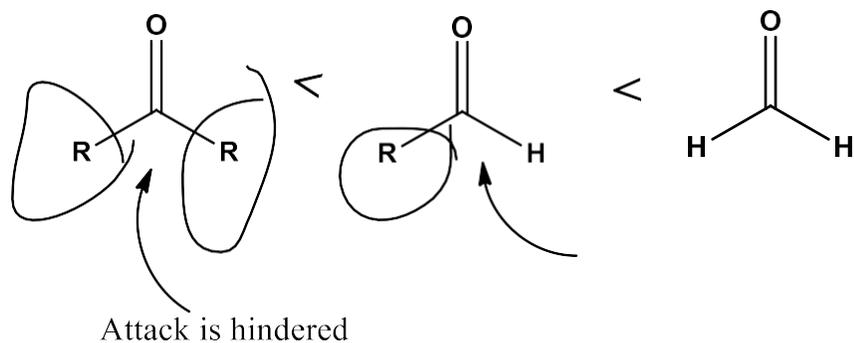


Electrophilicity:

- Measure of how readily an electrophile is able to accept an electron pair from a nucleophile.
- It depends upon two factors : \propto Electron deficiency

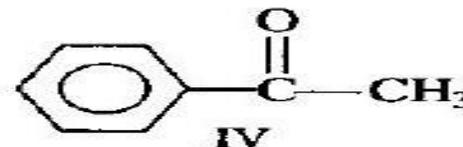
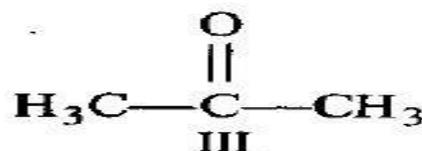
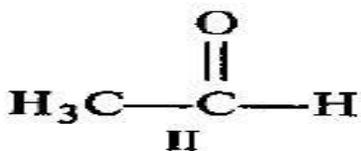
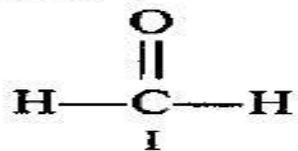
$$\propto \frac{1}{\text{steric factor}}$$

- Greater the electron deficiency, more will be the electrophilicity.
- Greater the steric factor around the electrophilic center, lesser will be electrophilicity



#Rate of nucleophilic addition on carbonyl \propto Electrophilicity of carbonyls

Q.1. Arrange the following compounds in decreasing order of nucleophilic addition reaction :



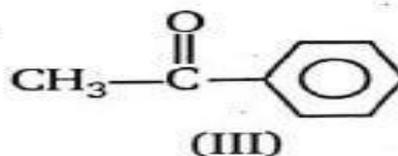
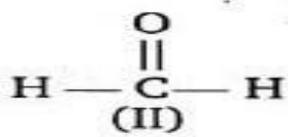
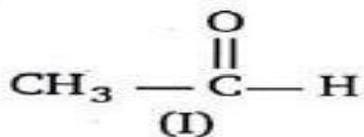
(a) $\text{II} > \text{IV} > \text{III} > \text{I}$

(c) $\text{IV} > \text{III} > \text{II} > \text{I}$

(b) $\text{I} > \text{II} > \text{III} > \text{IV}$

(d) $\text{II} > \text{III} > \text{IV} > \text{I}$

Q.2. Correct order of reactivity of following compounds towards Grignard reagent?



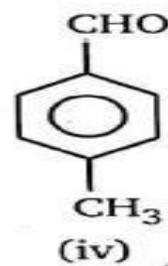
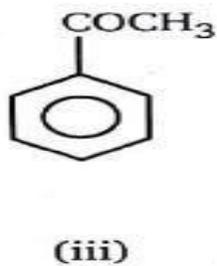
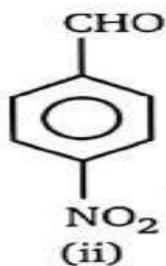
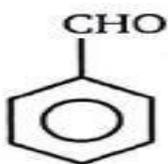
(a) $\text{I} > \text{II} > \text{III}$

(b) $\text{II} > \text{I} > \text{III}$

(c) $\text{II} > \text{III} > \text{I}$

(d) $\text{I} > \text{III} > \text{II}$

Q.3. Arrange the following carbonyl compounds in decreasing order of their reactivity in nucleophilic addition reaction.



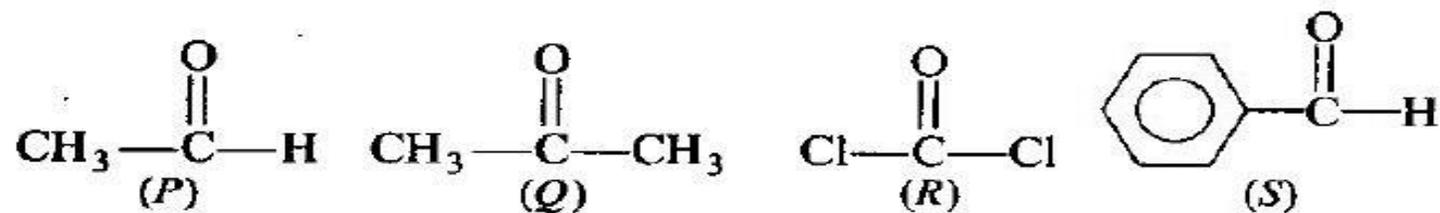
(a) $\text{ii} > \text{iii} > \text{i} > \text{iv}$

(c) $\text{iii} > \text{ii} > \text{i} > \text{iv}$

(b) $\text{ii} > \text{i} > \text{iv} > \text{iii}$

(d) $\text{iii} > \text{i} > \text{iv} > \text{ii}$

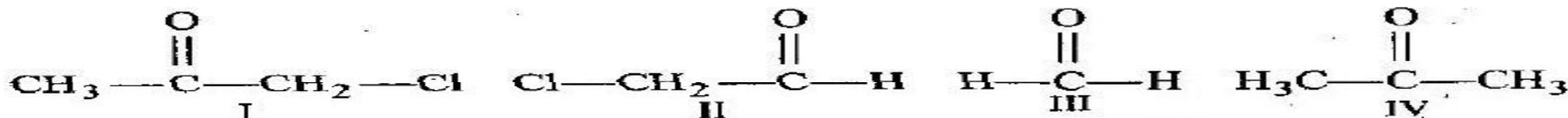
Q.4. Arrange the following compounds in decreasing order of nucleophilic addition reaction :



(a) $R > P > S > Q$
 (c) $Q > R > S > P$

(b) $P > Q > R > S$
 (d) $R > S > P > Q$

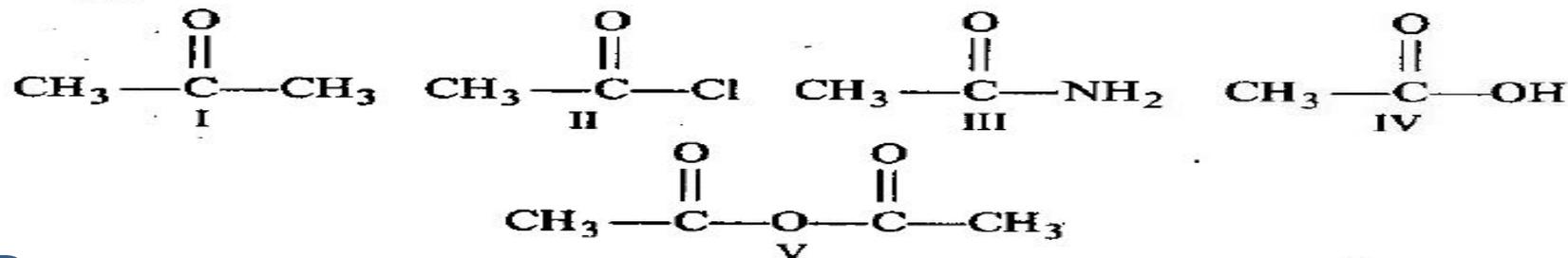
Q.5. Arrange the compounds in order of decreasing reactivity for nucleophilic addition reaction :



(a) $\text{I} > \text{IV} > \text{II} > \text{III}$
 (c) $\text{II} > \text{III} > \text{I} > \text{IV}$

(b) $\text{I} > \text{II} > \text{III} > \text{IV}$
 (d) $\text{II} > \text{I} > \text{III} > \text{IV}$

Q.6. Arrange the following compounds in decreasing order of nucleophilic addition reaction :



(a) $\text{II} > \text{V} > \text{I} > \text{IV} > \text{III}$
 (c) $\text{II} > \text{I} > \text{V} > \text{III} > \text{IV}$

(b) $\text{III} > \text{IV} > \text{I} > \text{V} > \text{II}$
 (d) $\text{IV} > \text{III} > \text{V} > \text{I} > \text{II}$