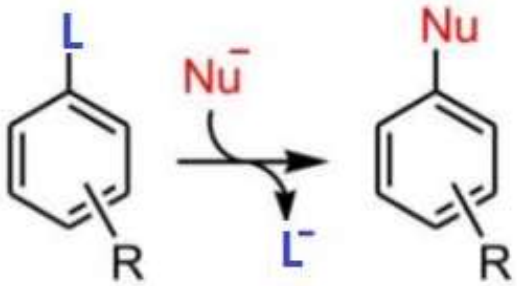
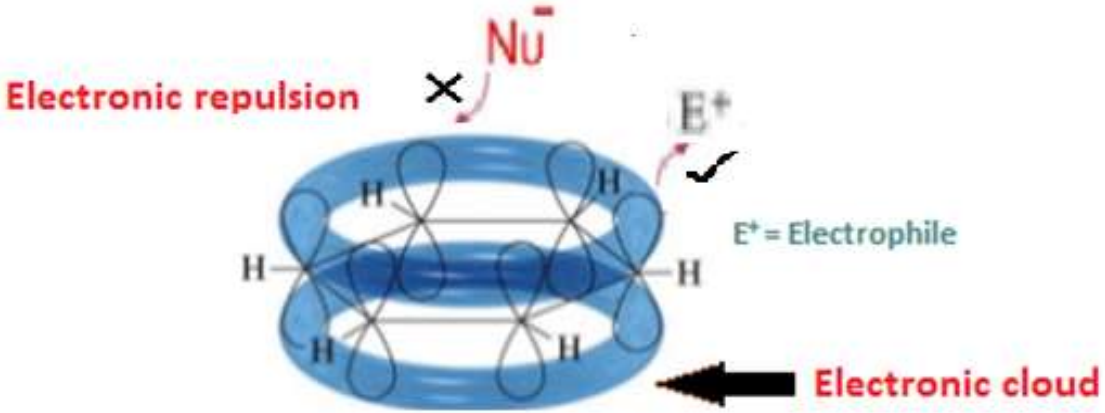
Nucleophilic Aromatic Substitution (S_NAr)

❖ *A nucleophilic aromatic substitution is a substitution reaction in which the nucleophile displaces a good leaving group on an aromatic ring.*



L = Leaving group (halogen etc.) Nu = nucleophile

Electrophilic Vs Nucleophilic Aromatic Subsitution



Nucleophile (electron rich species) attack is difficult on benzene ring due to repulsion by the delocalized π electron clouds.

Possible conditions for S_NAr

- *Properly substituted strong electron with-drawing group on the aromatic ring or electronegative hetero atom on the aromatic ring (pyridine).*
- *Very good leaving group.*
- *Drastic conditions like high temperature, pressure or strong nucleophile.*

Type of S_NAr reactions

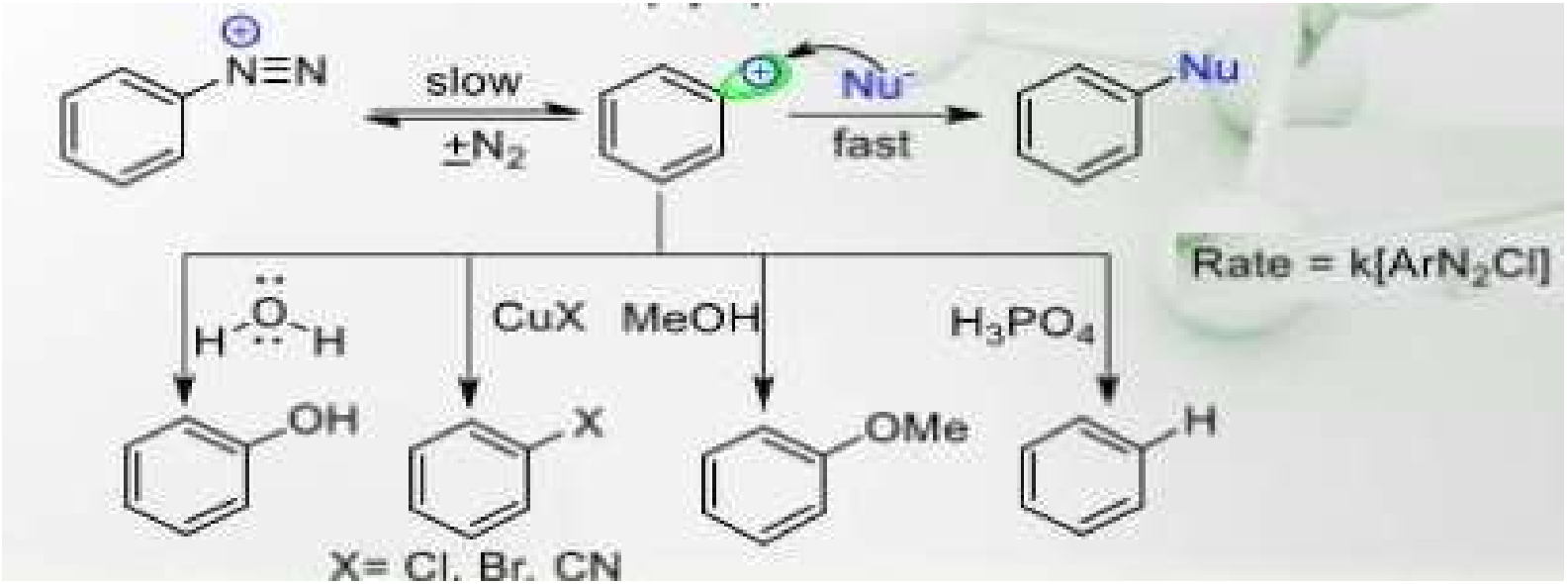
*Based on the mechanism involve in **S_NAr**, it is classified into three category*

- *Unimolecular via a carbenium ion intermediate (S_N1 aromatic).*
- *Bimolecular via intermediate complex anion (S_N2 aromatic).*
- *Elimination-addition via aryne intermediate.*

Unimolecular S_NAr

Aromatic S_N1 are very rare due to unstable carbocation formed at the sp^2 orbital.

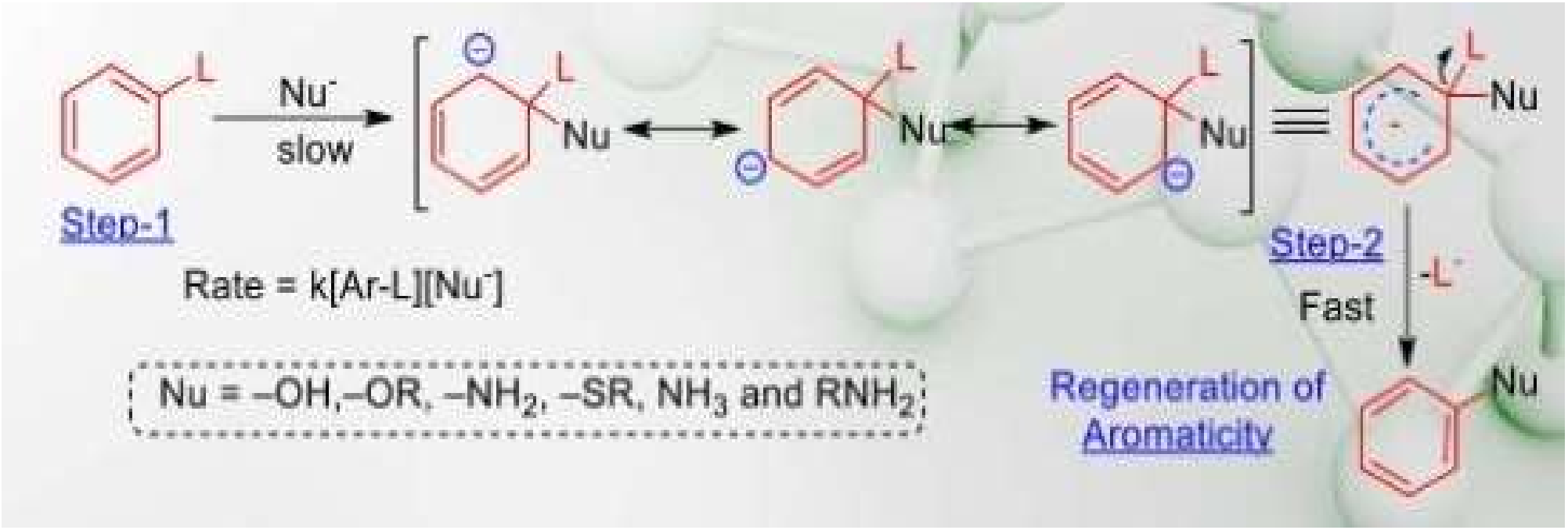
However diazonium compounds undergo aromatic S_N1 due to formation of highly stable N_2 molecule.



Bimolecular S_NAr

In aromatic compound, normal one step S_N2 is not possible as to attack the sp^2 carbon from the back, the nucleophile have to appear inside the benzene ring.

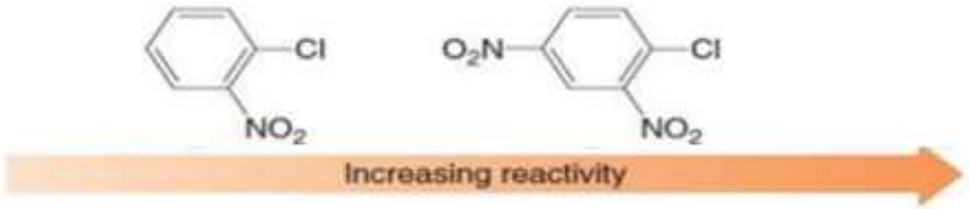
It follows a two step mechanism



❖ *The mechanism is also known as addition /elimination or intermediate complex mechanism*

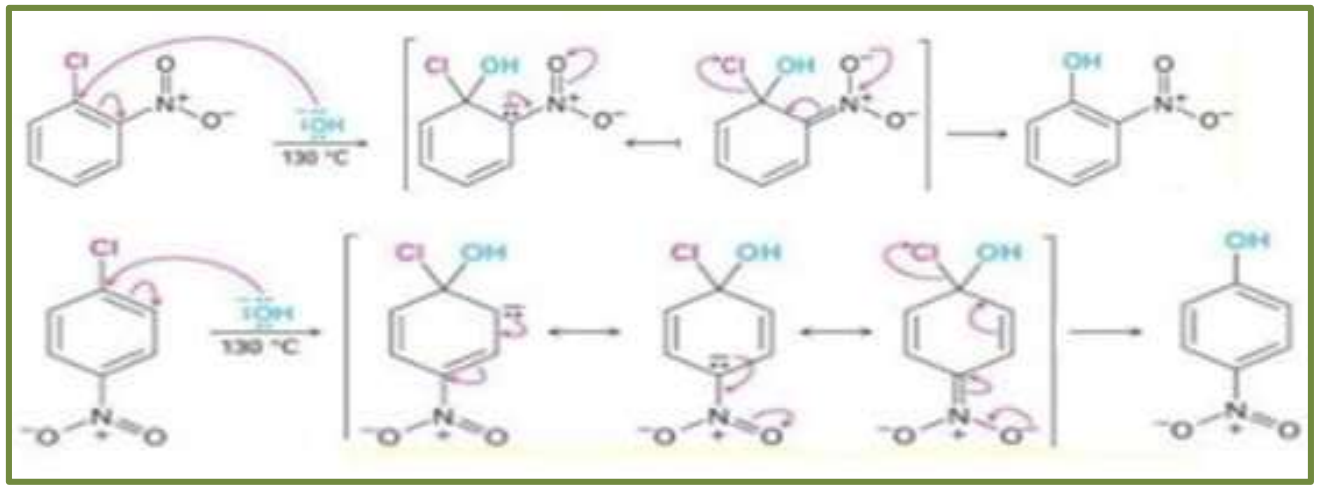
Effect of substrate structure on rate of bimolecular S_NAr

- *Electron withdrawing substituent will activate the ring (-I, -R) toward **S_NAr** by stabilizing the T.S and the intermediate carbanion formed in the RDS.*



- *-R group will activate the ring towards **S_NAr** only if it is present in o/p position.*

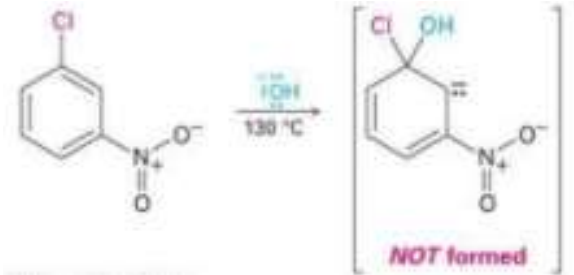
Ortho/Para NO_2 group



additional resonance stabilization

The negative charge is delocalized on the O atom of the NO_2 group.

Meta NO_2 group



The negative charge is never delocalized on the NO_2 group.