⇒ Types of organic reactions :-

⇒ Organic reaⁿ may be represented as -

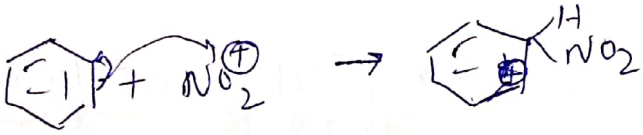
Substrate + attacking agent → [intermediate] → Product

Four types :- five.

1. Substitution or displacement reaⁿ.
2. addition reaⁿs.
3. Elimination reaⁿ.
4. Rearrangement.
5. Molecular Reaⁿ

1. Substitution reaⁿ :- In this type of reaⁿs an atom or group is replaced by another.

* The substituting species may be electrophile, nucleophile or free radical.



$$CH_3-CH_2-Br + \overset{\ominus}{O}H \rightarrow CH_3CH_2-OH + Br^{\ominus}$$

nucleophile

Chlorination of alkanes :-

$$CH_4 + Cl_2 \xrightarrow[\text{or } \Delta]{h\nu} CH_3Cl + \dots$$

* Chlorination of alkanes takes place either thermally or Photochemically and under either of these conditions the first step is breaking of Chlorine molecule.

Initiation - $Cl-Cl \xrightarrow[\text{or}\ \Delta]{h\nu} 2Cl^{\cdot}$

Propagation - $Cl^{\cdot} + H-CH_3 \longrightarrow HCl + {\cdot}CH_3$

$CH_3^{\cdot} + Cl-Cl \rightarrow CH_3Cl + Cl^{\cdot}$

Termination - $Cl^{\cdot} + Cl^{\cdot} \rightarrow Cl_2$

$CH_3^{\cdot} + {}^{\cdot}CH_3 \rightarrow CH_3-CH_3$

$CH_3^{\cdot} + {}^{\cdot}Cl \rightarrow CH_3Cl$

(1) Aliphatic Nucleophilic substitution :-

$$R-X + y^{\ominus} \rightarrow R-y + X^{\ominus}$$

(a) SN_2 mechanism – one step process, with no intermediate

(Substitutional Nucleophilic bimolecular)

$$y^{\ominus} + \text{>C}-X \rightarrow y\cdots C\cdots X \rightarrow y-C + X^{\ominus}$$

(Transition state)

(b) SN_1 mechanism – (Substitutional nucleophilic unimolecular)

$$R-X \underset{\text{fast}}{\overset{\text{slow}}{\rightleftharpoons}} R^{+} + X^{\ominus} \quad (\text{Carbonium ion process})$$

$$R^{+} + y \xrightarrow{\text{fast}} R-y$$

(a) $CH_3-Br + OH^{\ominus} \longrightarrow CH_2OH + Br^{\ominus}$

$$\text{Rate} = k[CH_2Br][OH^{\ominus}]$$

(b) $(CH_3)_2C-Br + OH^{\ominus} \rightarrow (CH_3)_2C-OH + Br^{\ominus}$

$$(CH_3)_3Br \xrightarrow{\text{slow}} (CH_3)_3C^{\oplus} + Cl^{\ominus}$$

$$(CH_3)_3-C^{\oplus} + OH^{\ominus} \xrightarrow{\text{fast}} CH_2-\underset{CH_3}{\overset{CH_3}{C}}-OH$$

(2). Neighbouring group Participation :-

(3).

(1) Aliphatic electrophilic substitution :-

eg. Friedel-Crafts alkylation of benzene with 1-Chloropropane

Free Radical :-

Types of organic rea^{n}s.

① Substitution or displacement rea^{n}
② Elimination rea^{n}
③ Addition rea^{n}
④ Rearrangement

① Substitution rea^{n}s → Aliphatic → Nucleophilic Subst^{n} ← S_N1 & S_N2
→ electrophilic substitution

Aromatic → Nucleophilic substitution
→ electrophilic substitution

Aliphatic Nucleophilic substitution :-

substrate — product.

Two types :- (I) S_N2 Mechanism or direct displacement process

$$:Nu^{\ominus} + R\text{-}L \longrightarrow (Nu \cdots R \cdots L)^{\ominus} \longrightarrow Nu\text{-}R + L^{\ominus}$$

transition state

(II) Carbonium ion process :-

$$R\text{-}L \rightarrow R^{+} + L^{\ominus}$$

$$R^{+} + :Nu^{\ominus} \rightarrow R\text{-}Nu$$

⇒ Nucleophilicity decreases on going from left to right in the Periodic table. This follows the increase in electronegativity from left to right. Thus high electronegativity is unfavourable ∴ due to tightly held electron.

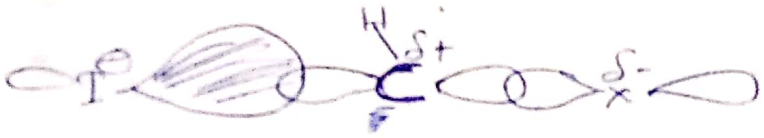
$OH^{\ominus} > F^{\ominus}$ $\quad NH_2 > H_2O$

* Nucleophilicity increases going down the periodic table:

$$I^- > Br^- > Cl^- > F^-$$

This order is the reverse of the basicity order of the halide ions:

$$F^- > Cl^- > Br^- > I^-$$



a "soft" (high-Polarizable) nucleophile.

a great deal of bonding between iodine and carbon in the transition state.

Fluoride is a "hard" (low Polarizability) nucleophile.

There is little bonding between fluorine and carbon in the transition state.

* increasing Polarizability improves nucleophile power.

Ex:

$$\xleftarrow[KOH]{\text{Alcoholic}} R\text{-}Br \xrightarrow[KOH]{\text{Alcoholic}}$$