Smiles rearrangement

In this video, we are going to learn

(1) What is Smiles rearrangement?

(2) Conditions for Smiles rearrangement

(3) Mechanism

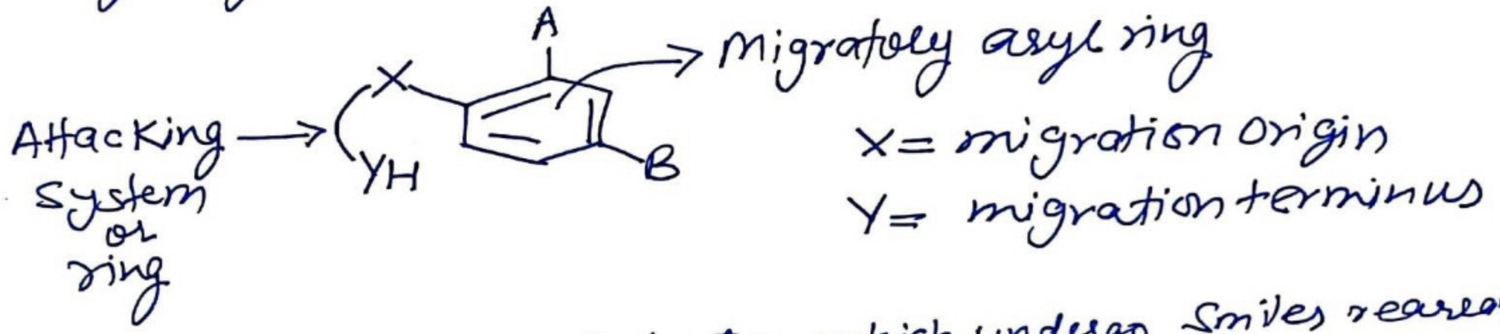
(4) Relevant examples

(5) Truce-Smiles rearrangement

Smiles Rearrangement

→ Intramolecular aromatic nucleophilic ~~substition~~ substitution reaction.

→ Given by organic compounds having general structure (X)



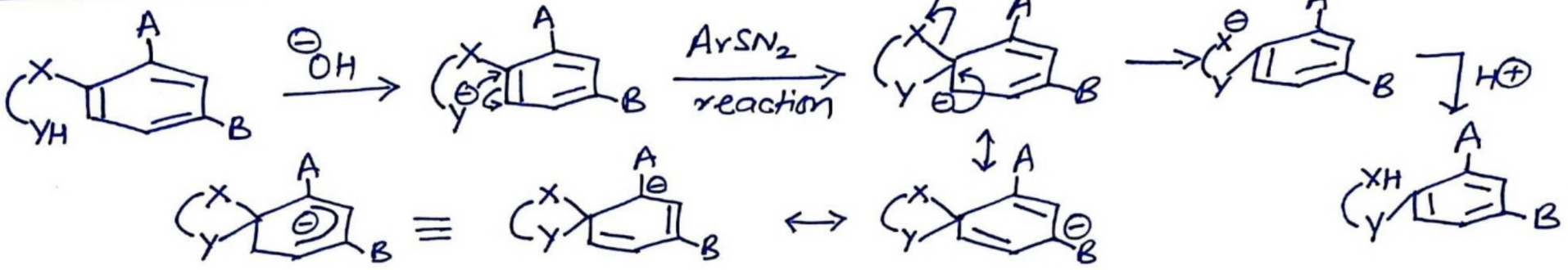
Essential conditions for the substrates which undergo Smiles rearrangement

(1) X must be good nucleophilic group as leaving group.
(X may be O, S, SO_2, SO, $-O-\overset{\oplus}{C}-$, etc.)

(2) YH must be sufficiently acidic to be deprotonated by $\overset{\ominus}{O}H$.
(YH may be OH, NH_2, NHR, SH, CONHAr etc.)

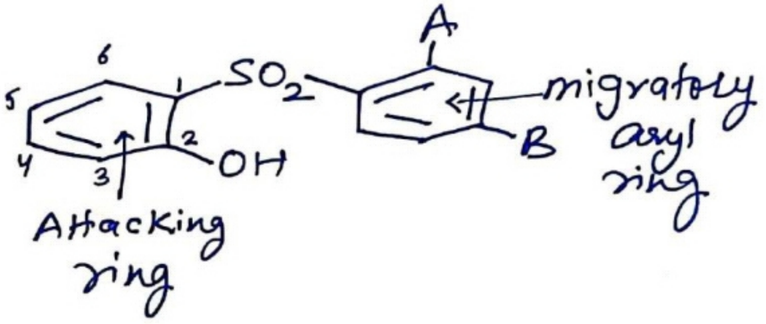
(3) A and/or B may be $-NO_2$, $-CNO_2$ $-CF_3$ group i.e., activating groups for nucleophilic substitution.

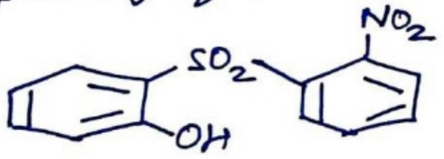
Mechanism

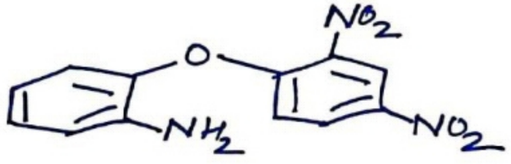


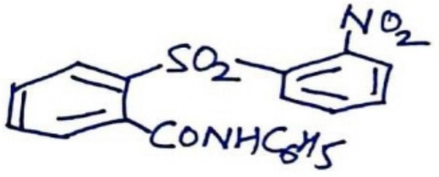
Cyclohexadienylide anion

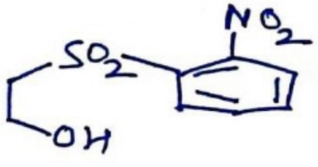
⇒ EWG at position-5 retards the rate of the Smile rearrangment ∵ such group reduce the nucleophilicity of $Y^{\ominus}$

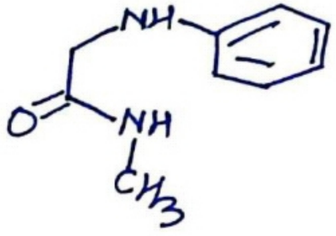


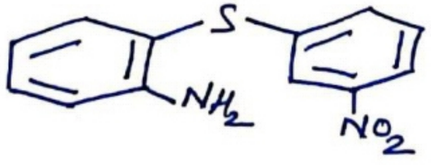


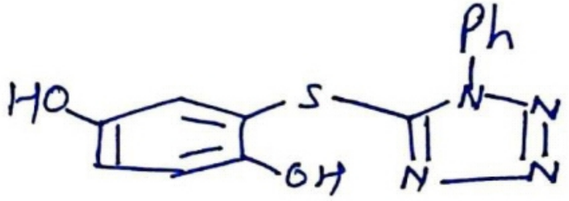




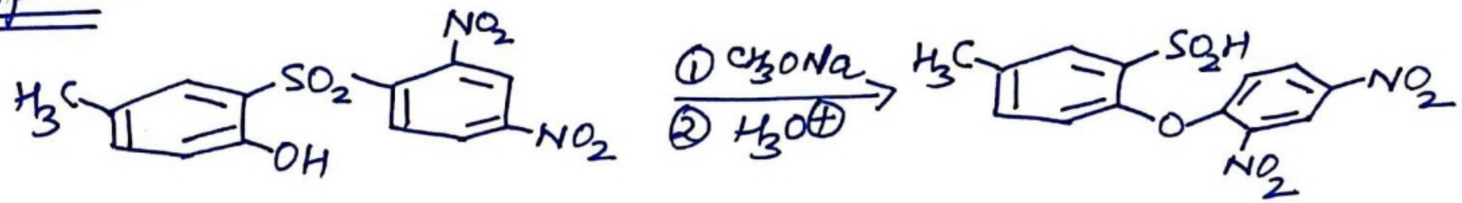


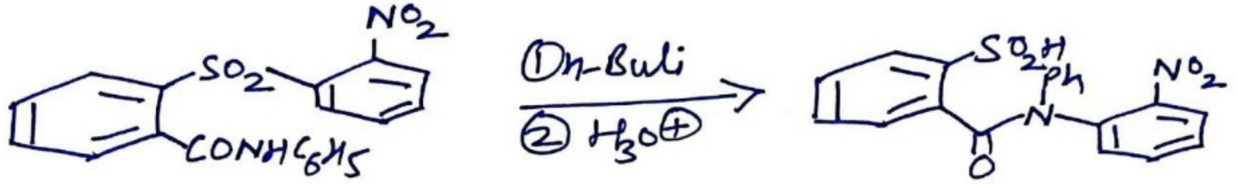


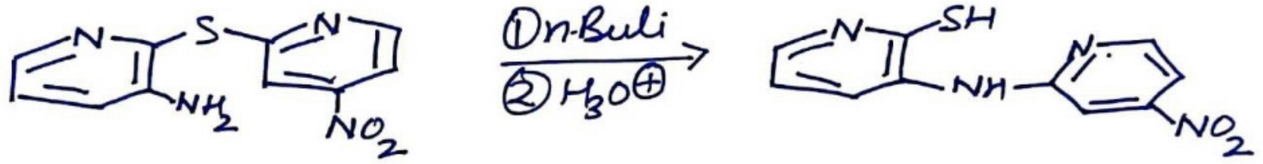


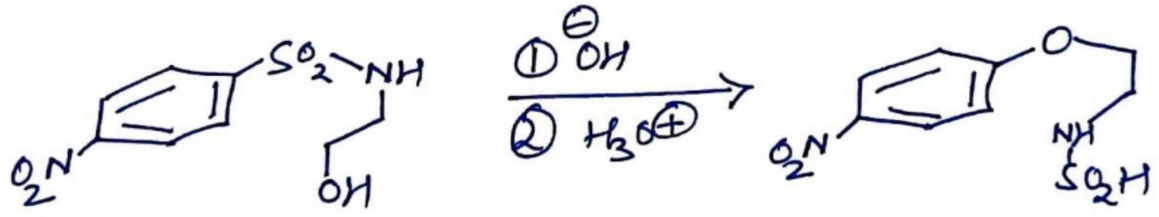


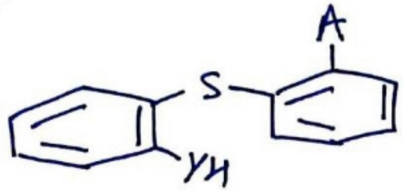
Examples :-

① 

② 

③ 

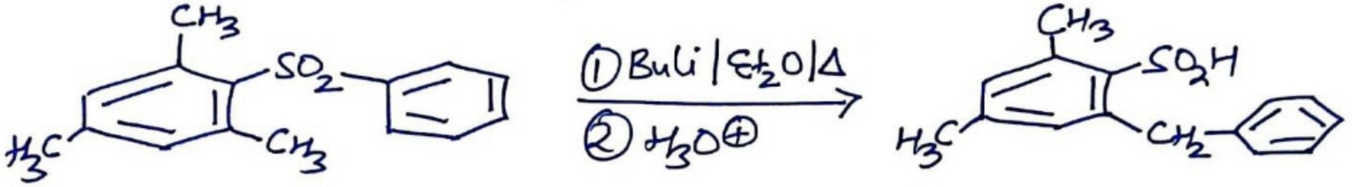
④ 



when, YH = CH_3

→ a strong Base like, RLi, PhLi is required

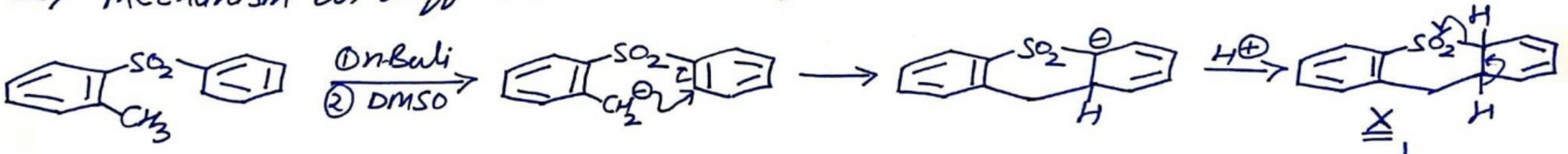
→ Rearrangment is known as Truce-Smiles rearrangment.



→ In the Truce-Smiles rearrangment the presence of EWG is not necessary on the migratory aryl group.

→ Mechanism is same when a strong base and non-protic solvents such as Et_2O and THF is used.

→ Mechanism is diffellent with strong base & protic solvent such as DMSO



→ Intermediate(X), dihydrothioxanthene-S-oxide has been isolated from reaction mixture.

→ This result confirms the mechanism.