

# INTERNAL NUCLEOPHILIC SUBSTITUTION REACTION ( $S_{Ni}$ )

**By**

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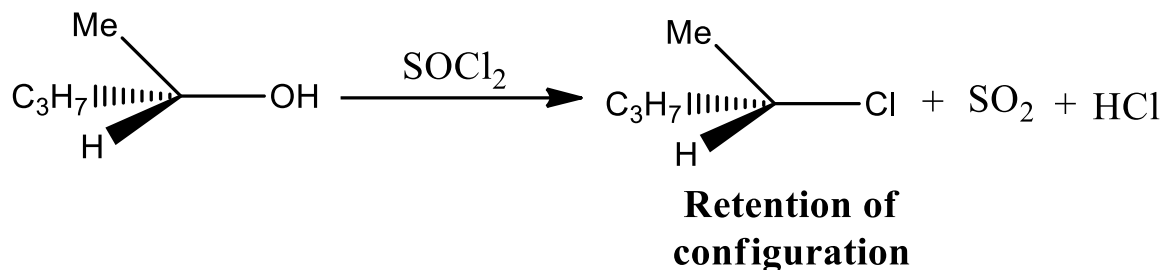


**Patna Women's College**

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# S<sub>N</sub>i: Internal Nucleophilic Substitution

- In S<sub>N</sub>i reaction, an internal nucleophilic attack from same side of leaving group occur with retention of configuration.



- In case of S<sub>N</sub>i reactions, the rate of the reaction is dependent on the concentration of both the alcohol and the thionyl chloride i.e 2<sup>nd</sup> order of reaction.

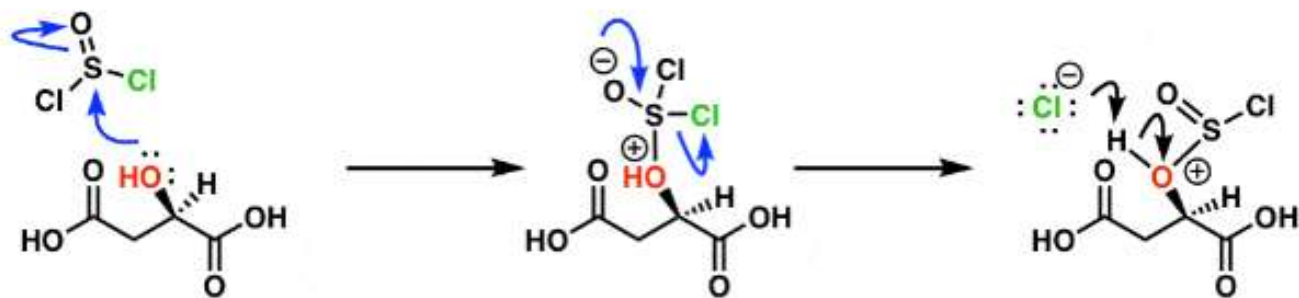
$$\text{Rate} = k [\text{R-OH}] [\text{SOCl}_2]$$

# Mechanism

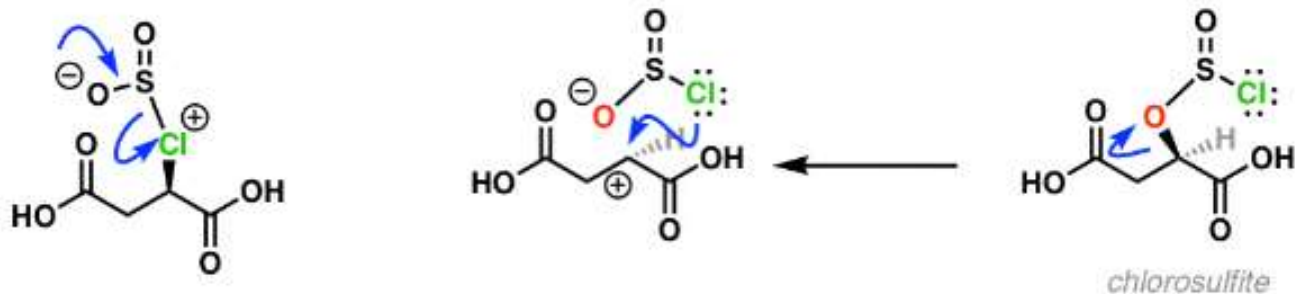
❖ Mechanism involves following steps:

- 1)  $\text{SOCl}_2$  coordinates to the alcohol, with loss of  $\text{HCl}$  and formation of a good leaving group (“chlorosulfite”).
- 2) The chlorosulfite leaving group can spontaneously depart, forming a carbocation, and when it does so, an “intimate ion pair” is formed, where the carbocation and negatively charged leaving group are held tightly together in space.
- 3) From chlorosulfite, the chlorine act as a nucleophile – attacking the carbocation on the same face from which it was expelled – and after expulsion of  $\text{SO}_2$ , we have formation of an alkyl chloride with retention of configuration.

# Mechanism



The alcohol attacks  $\text{SOCl}_2$  and after expulsion of  $\text{Cl}^-$  and deprotonation of O, a "chlorosulfite" is formed. The C-O bond breaks with expulsion of  $\text{Cl}^-$  forming  $\text{CO}_2$  and an "intimate" ion pair. Chloride then attacks the carbocation from the same face, resulting in "retention" of stereochemistry



# Adding both SOCl<sub>2</sub> AND Pyridine leads to Inversion via S<sub>N</sub>2 Mechanism

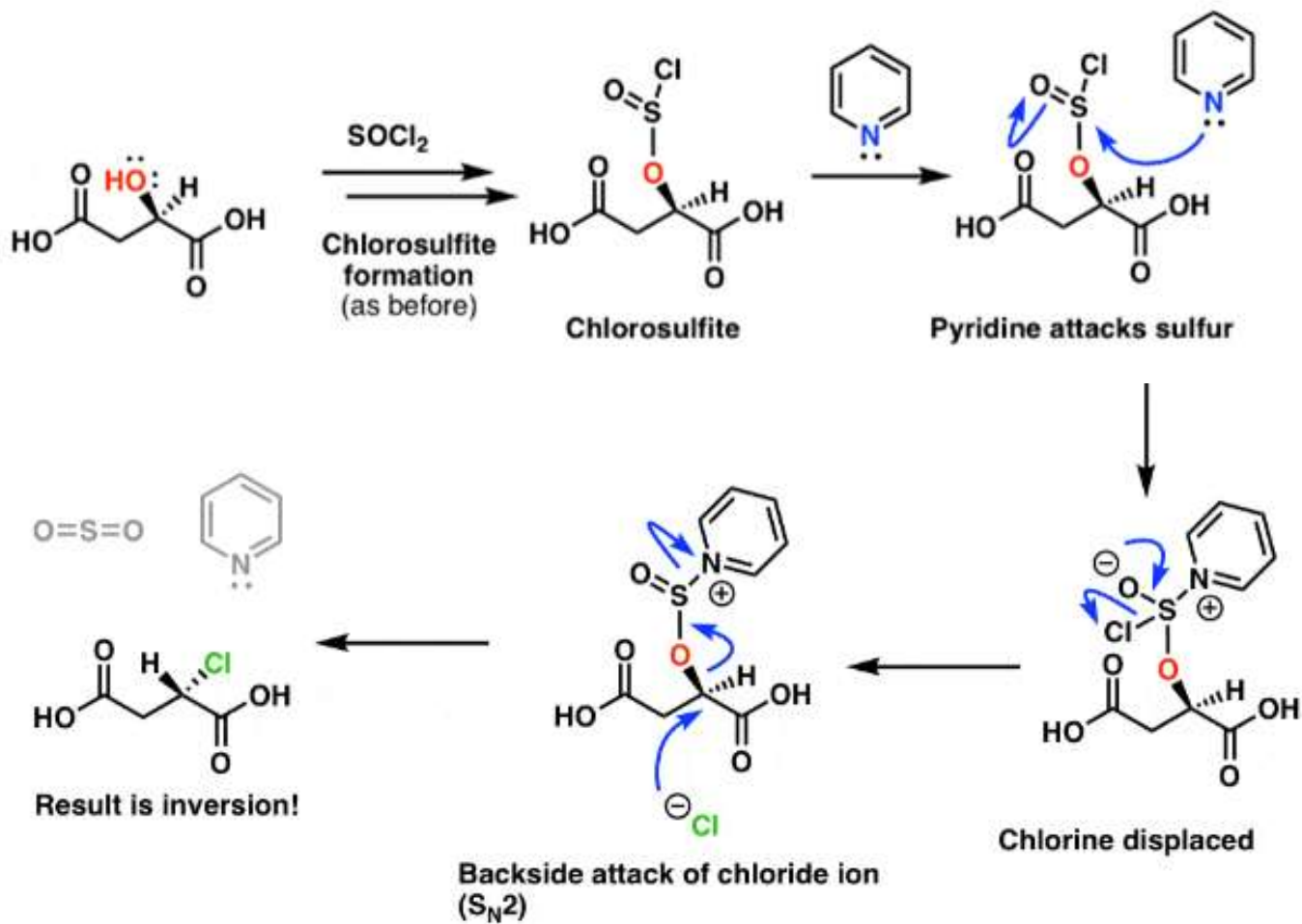
**Why?????????**

- Retention of stereochemistry with SOCl<sub>2</sub> alone but inversion with SOCl<sub>2</sub> **and pyridine.**
- But when pyridine is present, it can attack the chlorosulfite, displacing chloride ion and forming a charged intermediate (forming a carbocation). This chloride ion **attacks the carbon from the backside, leading to inversion of configuration and formation of a C-Cl bond.** The reaction changes from S<sub>N</sub>i to S<sub>N</sub>2.

**Why inversion this time? Because pyridine displaces chlorine from sulfur, and "internal return" from the leaving group cannot occur**

**The result is an S<sub>N</sub>2 reaction!**

# Mechanism



# SUMMARY

- ✓  $\text{SOCl}_2$  plus alcohol gives **retention** of configuration,
- ✓  $\text{SOCl}_2$  plus alcohol plus **pyridine** gives **inversion** of configuration ( $\text{S}_{\text{N}}2$ )

