# Quadrant II – Transcript and Related Materials

**Programme: Bachelor of Science (Third Year)**

**Subject: Chemistry**

**Course Code: CHC110**

**Course Title: Organic Chemistry (Section B)**

**Unit: Stereochemistry**

**Module Name: Substitution reactions : $S_N1$, $S_N2$ & $S_Ni$ reactions with Mechanisms – Part 2**

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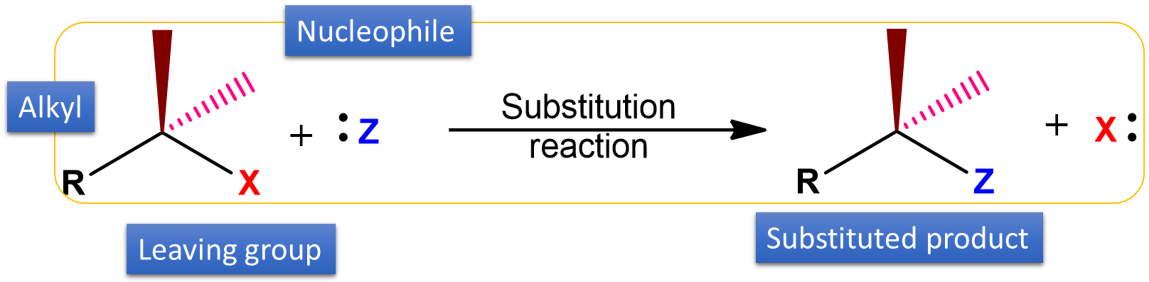
## Notes

### Types of Organic reactions

1. Addition reactions
2. Elimination reactions
3. **Substitution reactions**
4. Re-arrangement reactions
5. Pericyclic reactions

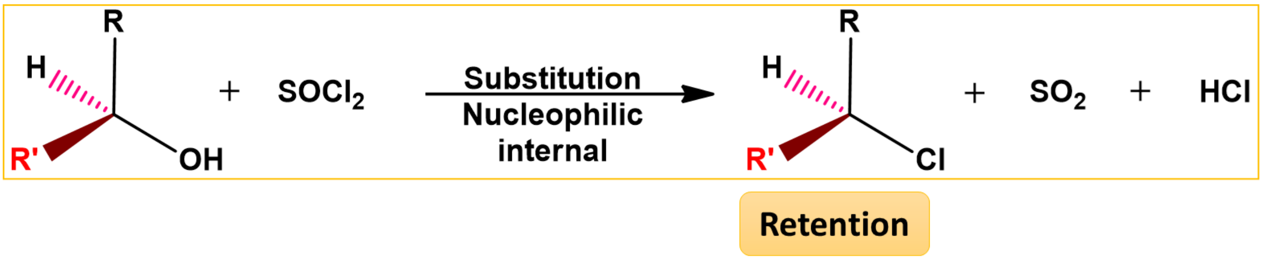
### Substitution Reaction

These are class of chemical reactions wherein a part of the reacting molecule (atom/ion/group) is replaced by another (atom/ion/group).



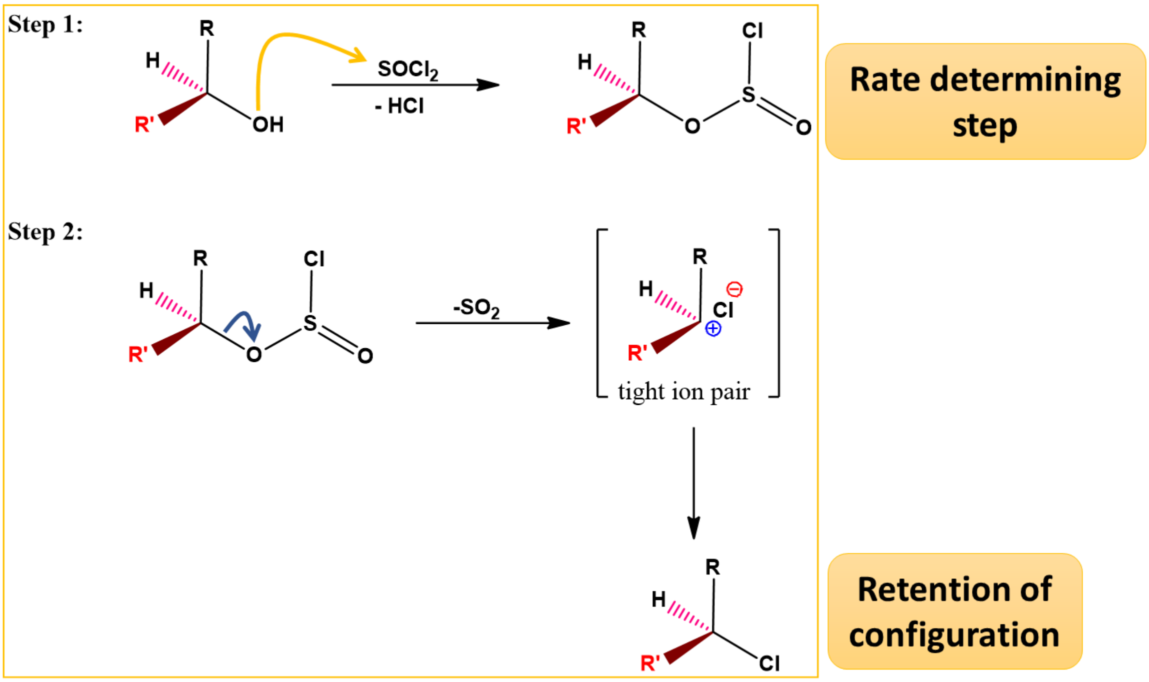
## Nucleophilic Substitution internal S$_{N}$i

Sometimes, nucleophilic substitution proceeds with retention of configuration, even where there is no possibility of a neighboring-group effect. In the S$_{N}$i mechanism (substitution nucleophilic internal), part of the leaving group attacks the substrate, detaching itself from the rest of the leaving group.



"S N" stands for nucleophilic substitution, and the “i" stands for internal. The name was introduced by Cowdrey et al. in 1937 to label nucleophilic reactions which occur with retention of configuration. Edward S. Lewis and Charles E. Boozer in 1952 also reported similar observations like Walden. Mechanistic and kinetic studies were reported much later by various researchers stating SNi reactions also proceed via two-step mechanism.

## Nucleophilic Substitution Unimolecular S$_{N}$i- Mechanism



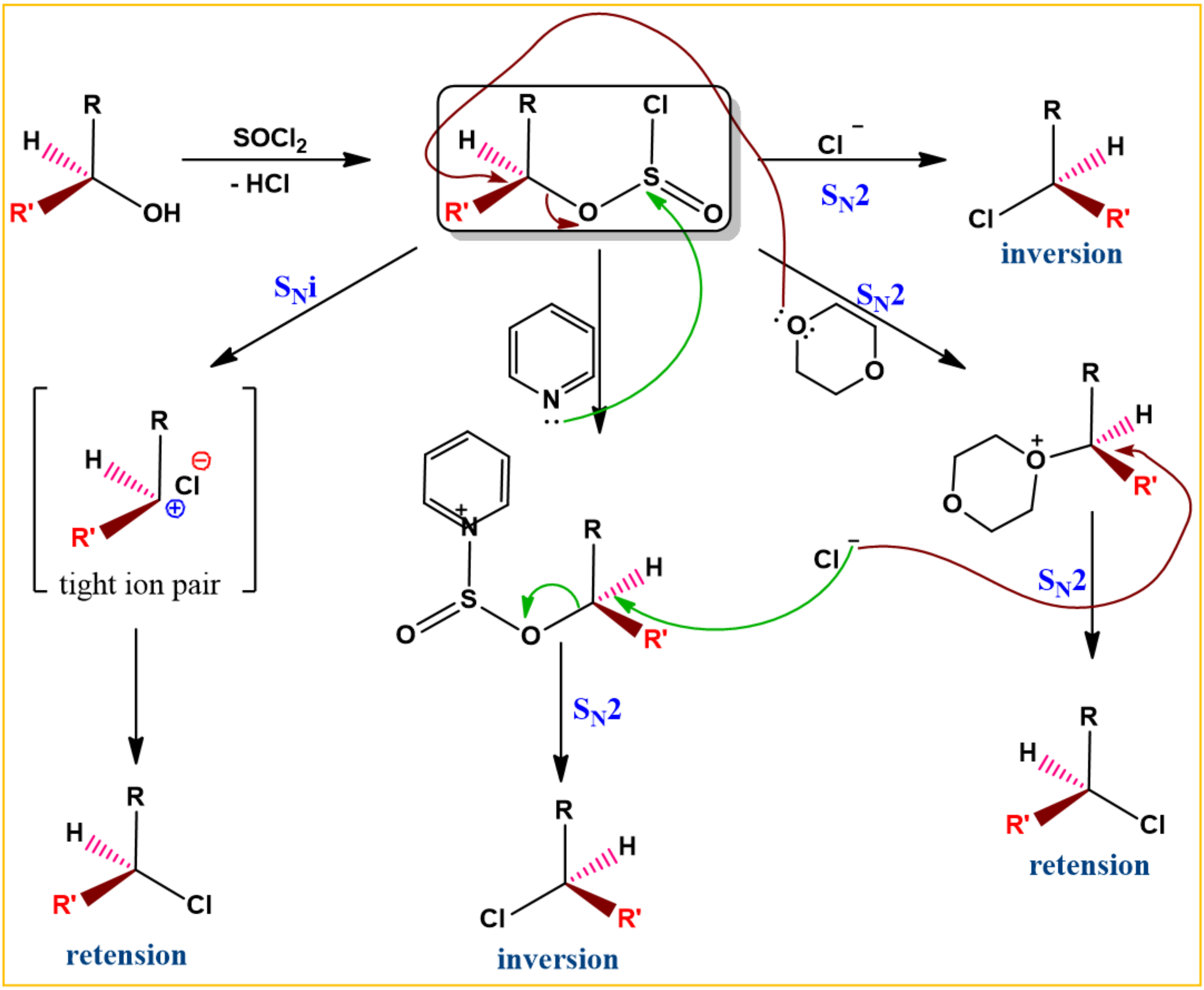
In the Mechanism, thionyl chloride first reacts with the alcohol to form an alkyl chlorosulfite, forming an intimate ion pair. The second step is the concerted loss of a sulfur dioxide molecule and its replacement by the chloride.

The difference between SN1 and SNi is that the ion pair is not completely dissociated, and therefore no real carbocation is formed, which else would lead to racemisation.

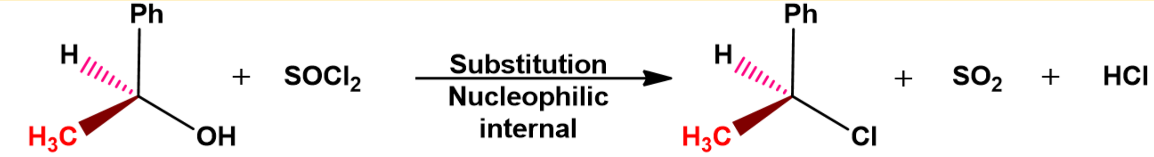
### Nucleophilic Substitution Unimolecular $S_Ni$- Solvent Effect

Carrying out the reaction in the presence of dioxane as the solvent also yields a product with retention of configuration. However, here retention arises due to two consecutive $S_N2$ reactions.

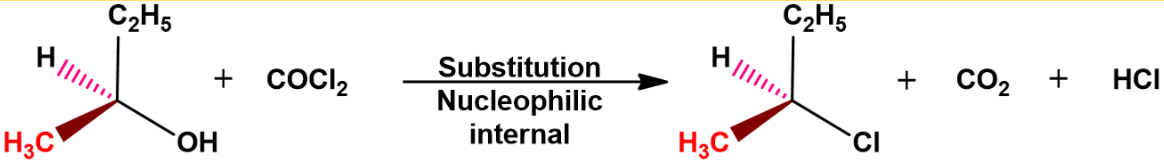
In the case of pyridine, the HCl gas released as a by product reacts with pyridine to form a salt C6H5NH+Cl-. Cl- being a good nucleophile attacks from the back side in a $S_N2$ fashion resulting in inversion of configuration.



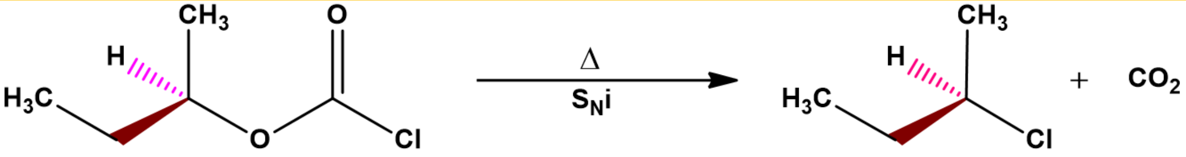
# Nucleophilic Substitution Internal $S_Ni$ - Examples



(*S*)-1-phenylethanol (*S*)-(1-chloroethyl)benzene



(*S*)-butan-2-ol (*S*)-2-chlorobutane



(*R*)-*sec*-butyl chloroformate (*R*)-2-chlorobutane