SN_i Mechanism:

→ Nu. Sub proceeds i retention of configuration, even without possibility of an NA effect.

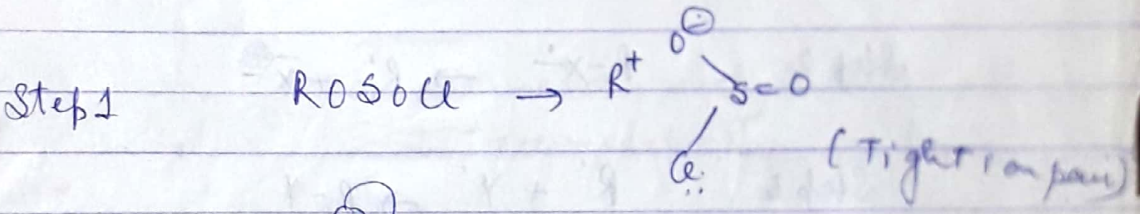
→ Here, part of leaving gp must be able to attack the substrate, detaching itself from rest of leaving gp in process.

→ I step = I step of SN^1 Rx (dissociation into an intimate ion pair).

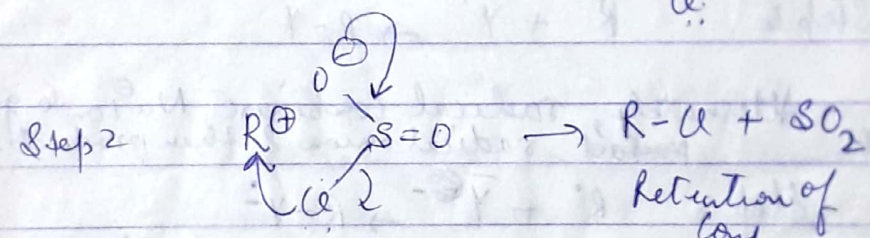
II step → part of leaving gp attacks from front since unable to get to rear. ∴ results in retention of conf.

$$ROH + SOCl_2 \rightarrow ROSOCl$$

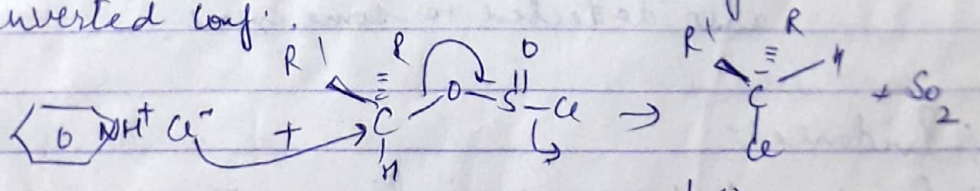
Step 1



Step 2



Evidence → Add^n of pyridine to mix. of alcohol and $SOCl_2$ results in formation of Rx ∴ inverted conf.



→ Very rare (SN_i)

II eg → $ROCOCl \rightarrow RCl + CO_2$

SET Mech:-
(Single e⁻ Transfer Mech)

→ In some $Nu^{\ominus}$ ~~Substitutions~~, there is involvement of radical or radical ions

→ I step → transfer of an e^- from $Nu^{\ominus}$ to substrate to yield radical anion.
→ Rad. ion then cleaves (step) 2 radical formed this way combine to give product (step 3).

Step 1 $R-X + \overline{Y}^{\ominus} \rightarrow R-X^{\cdot-} + Y^{\cdot}$

Step 2 $R-X^{\cdot-} \rightarrow R^{\cdot} + \overline{X}^{\ominus}$

Step 3 $R^{\cdot} + Y^{\cdot} \rightarrow R-Y$

or ~~Alternately~~, radical combines $Nu^{\ominus}$ ion to give radical anion & then product.

Step 2 $R^{\cdot} + \overline{Y}^{\ominus} \rightarrow R-Y^{\cdot-}$

Step 4 $R-Y^{\cdot-} + R-X \rightarrow R-Y + R-X^{\cdot-}$

→ ~~A~~ Racemization to some extent & inversion also detected to some extent.

→ Evidence:-
→ Finding of some racemization, Inversion can also take place in some SET process.

$$Y^{\ominus} + R-X \rightarrow \underbrace{[Y \cdot R-X^{\cdot-}]}_{\text{Solvent cage}} \rightarrow [Y \cdot R \cdot X^-] \text{ solvent cage} \downarrow Y-R + X^{\ominus}$$

Mixed SN^1 & SN^2 Rxs:-

→ Some Rxs are not characterized so easily by which mech they proceed.

→ There seems to be something in b'n, a mechanistic "border line" region

→ Two broad Theories to explain:-

a) I theory → Intermediate behaviour is caused by a mech. that is neither pure "SN1 nor "pure" SN^2 but some "in b'n" type.

b) II theory → No intermediate mech. & borderline behaviour is caused by simultaneous operation in same flask, of both SN^1 & SN^2 mech, i.e. some mol. by SN^1 & some by SN^2.

Acc. to Sneen (1st as intermediate mech. theory), all SN^1 & SN^2 Rxs. can be accomodated by one basic mechanism (ion pair mech.),

$$RX \overset{K_1}{\rightleftharpoons} R^+X^- \overset{K_2}{\rightleftharpoons} \text{Products}$$

Substrate, 1st ionizes to intermediate ion pair & is then converted to products.

In SN_1 (K_1) is rate determining

SN_2 (K_2) is " "

→ Borderline behaviour is found where rates of formation & destruction of ion pair are of same order of magnitude.