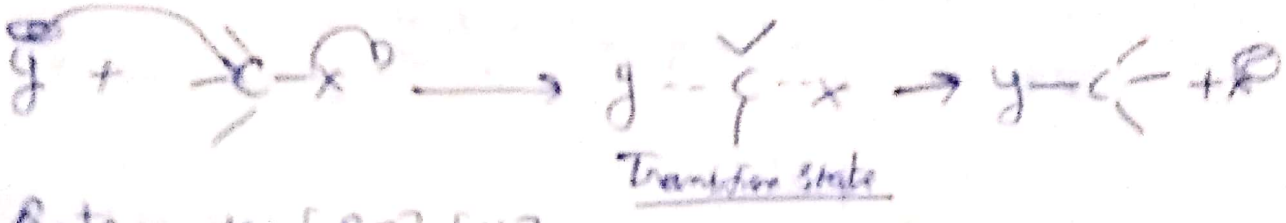
(1) The S_N2 Mechanism

* one step process with no intermediate



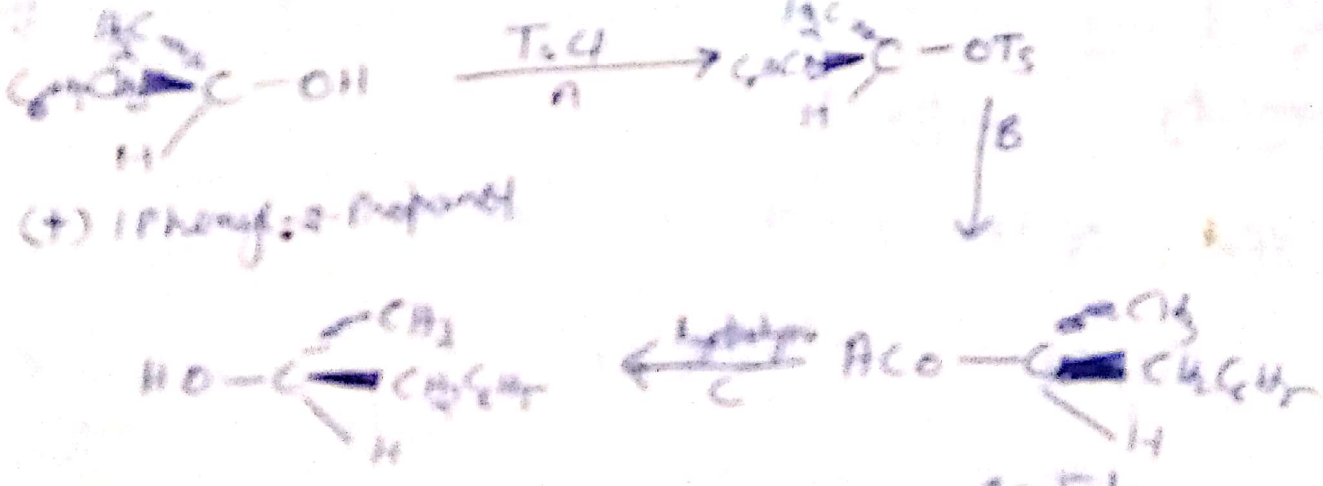
* Rate = $k[RX][Y]$

but if a large excess of nucleophile is present, for example if it is the solvent then Rxn will be bimolecular but the overall kinetics will be first order

$$Rate = k[RX]$$

* This mechanism predicts 'inversion of configuration' known as Walden inversion

* The experimental proof of Walden inversion was obtained by a series of reactions in which an optically active alcohol was converted into its enantiomer



(2) The S_N1 Mechanism

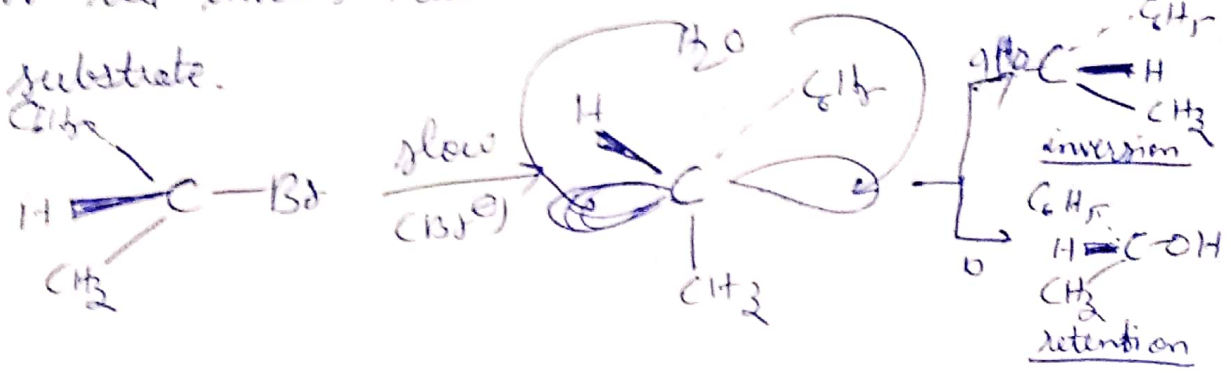
(1) two-step mechanism

(2) Step I $R-X \underset{\text{slow}}{\rightleftharpoons} R^+ + X^\ominus$

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

$$\text{Rate} = k[RX]$$

(3) S_N1 reaction involves racemisation of the optically active substrate.



* However, complete racemisation is uncommon. Usually the isomer having inverted configuration predominates over that with the same configuration.

Factors influencing the mechanism of Nucleophilic substitution reactions-

(1) Effect of the str of alkyl halide

CH_3Br	CH_3CH_2Br	$(CH_3)_2CHBr$	$(CH_3)_3C.Br$
S_N2	S_N2	$S_N2 + S_N1$	S_N1

Explanation (i) Inductive effect.

(ii) Hyperconjugation.

(iii) Steric effect.

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Effect of solvent :- * Hydrolysis of a halide in a polar solvent proceeds via SN1.

* More polar solvent is used greater are the chances of the reaction to proceed by the SN1 rather than the SN^2 mechanism.

The order of ionizing powers of more common solvents is -

$H_2O > HCOOH > CH_3OH > C_2H_5OH > CH_3COOH$

SET mechanisms :-

* In certain cases where nucleophilic substitutions occur, there is evidence that radicals and radical ions are actually involved.

First step :- transfer of an electron from the nucleophile to the substrate to form a radical anion.

$$R-X + :\ddot{Y}^{\ominus} \longrightarrow R-X^{\bullet} + Y\cdot$$

*[mechanism that begins this way is called SET (single electron transfer mechanism]

Step -2 → once formed, the radical ion cleaves.

$$R-X^{\ominus} \longrightarrow R^{\bullet} + X^{\ominus}$$

Step-3 →

$$R\cdot + Y^{\bullet} \rightarrow R-Y$$

or

$$R\cdot + :\ddot{Y}^{\ominus} \rightarrow R-Y^{\bullet-}$$

Step 4 →

$$R-Y^{\bullet\ominus} + R-X \rightarrow R-Y + R-X^{\ominus}$$

* The SET mechanism is chiefly found where

X = I, Br, NO_2

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* A closely related mechanism, the $S_{RN}1$ takes place with aromatic substrate. In that mechanism the initi

Free radicals with double bonds in this position are known to cyclize readily

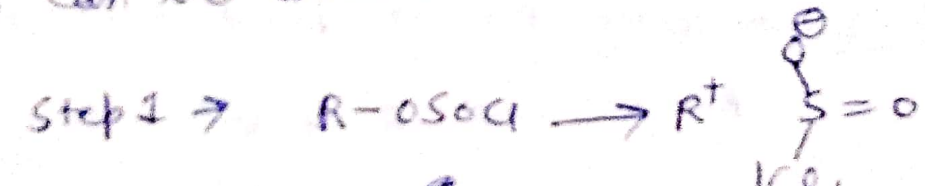
The SNi Mechanism:- (Substitution nucleophilic internal)

* In few rea^{n}s, nucleophilic substitution proceeds with retention of configuration, even where there is no possibility of a neighbouring group effect

e.g. → Rea^{n} of alcohols with thionyl chloride to give alkyl halides

$$ROH + SOCl_2 \longrightarrow ROSOCl$$ (these alkyl chloro sulfites can be isolated

mechanism- Step 1 →



Step 2 →

Evidence for this mechanism ① → addition of Pyridine to the mixture of alcohol and thionyl chloride results in the formation of alkyl halide with inverted configuration

* The SNi mechanism is Rare another → decomposition of ROCOCl (alkyl chloroformate)

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