

Neighboring Group Participation

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Summary of SN reactions

- ❖ In SN_2 reaction bond making and breaking occurs simultaneously while in SN_1 bond breaking occurs first.
- ❖ During SN_2 reaction, departure of LG is assisted by Nu- while in SN_1 , it is not.
- ❖ SN_2 is a 2nd order reaction while SN_1 is 1st order.
- ❖ In SN_2 inversion of configuration takes place while in SN_1 racemization occurs.

Neighboring Group Participation

There are some substitution reactions which are 1st order involving two successive $\text{S}_{\text{N}}2$ reactions.

These reactions are said to proceed through Neighboring Group Participation.

NGP reactions are characterized by

- enhanced rate and
- characteristic stereochemistry of retention of configuration

Neighbouring group participation (NGP)

(Also known as anchimeric assistance)

It is defined as the interaction of a reaction centre with a lone pair of electrons in an atom or the electrons present in a sigma bond or pi bond contained within the parent molecule but not conjugated with the reaction centre.

When NGP is in operation it is normal for the reaction rate to be increased. It is also possible for the stereochemistry of the reaction to be abnormal (or unexpected) when compared with a normal reaction.

Neighboring Group Participation

NGP can occur from.

- ❖ any group that have an unshared pair of electrons or
- ❖ a double bond

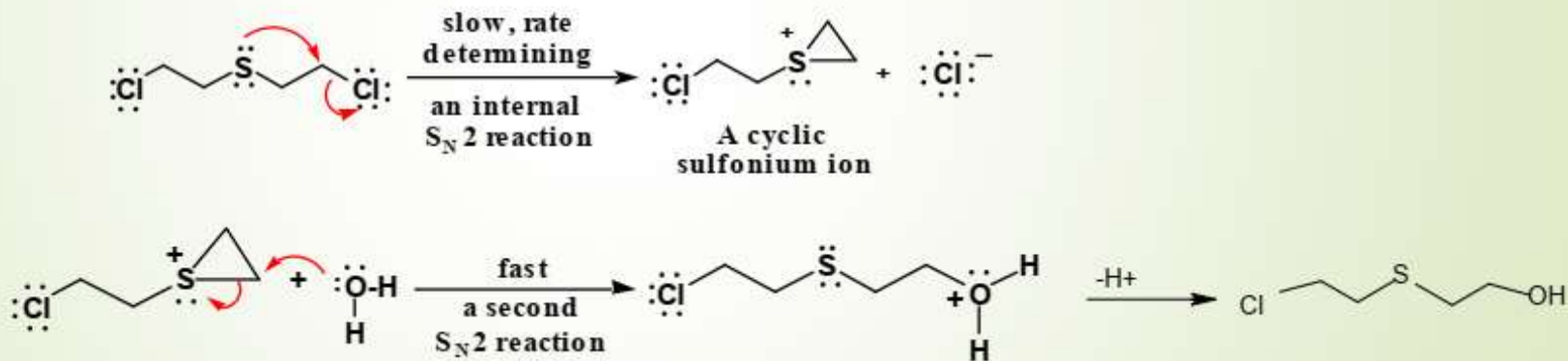
The electron density will accelerate the rate of departure of the leaving group

- ❖ New cyclic reaction intermediate
- ❖ Nucleophile must be in trans position to the leaving group

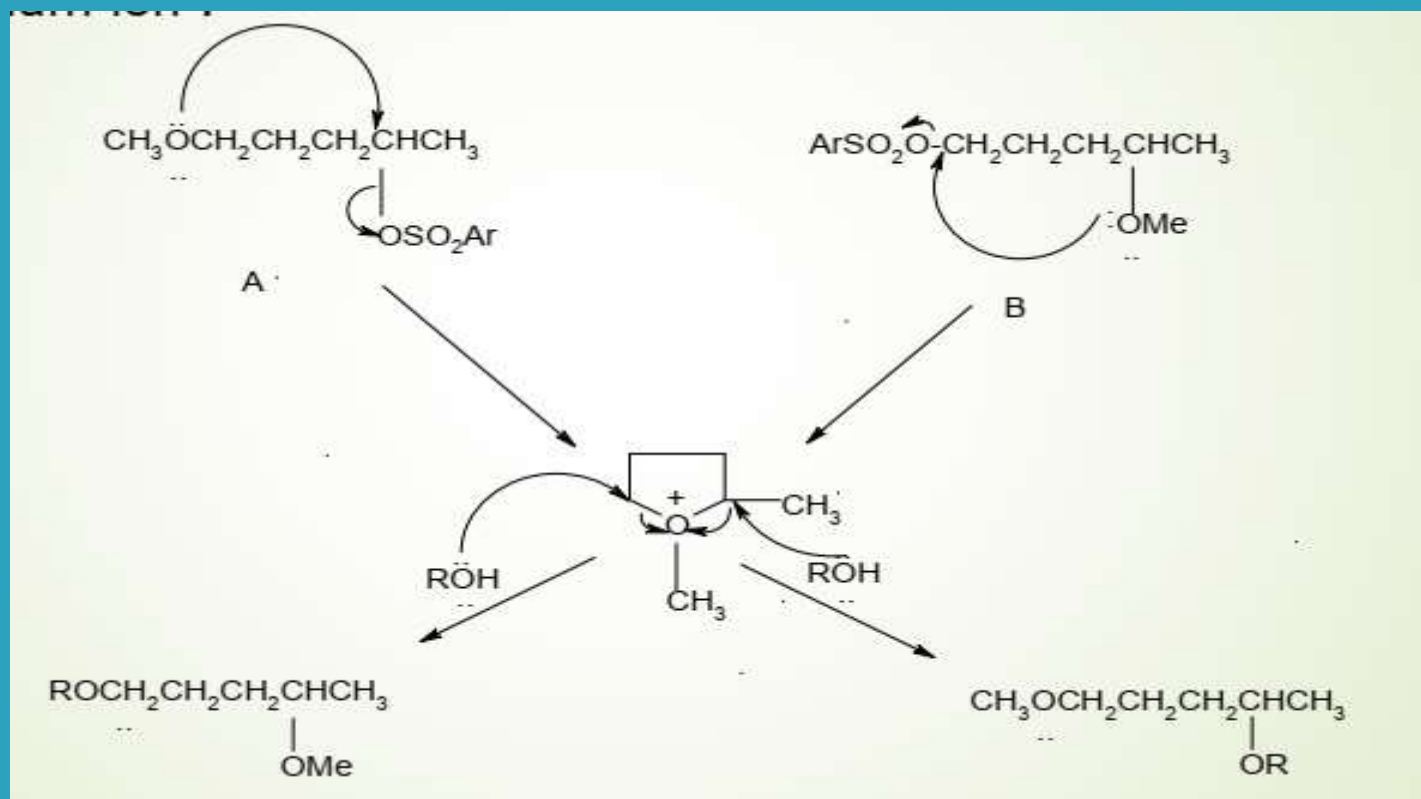
Mustard gas is β, β' -dichloroethylenesulphide is a primary halide which undergo hydrolysis rapidly in H_2O (a very poor nucleophile). This can not be explained on the basis of $\text{S}_{\text{N}}2$ mechanism



Mechanism :



Alkoxy group is a weak nucleophile but it can function as neighboring nucleophile. For example solvolysis of isomeric p-bromobenzenesulphonate ester A and B produce the identical product mixtures, indicating the involvement of common cyclic oxonium ion as an intermediate.



Solvolysis of chloroalkanol

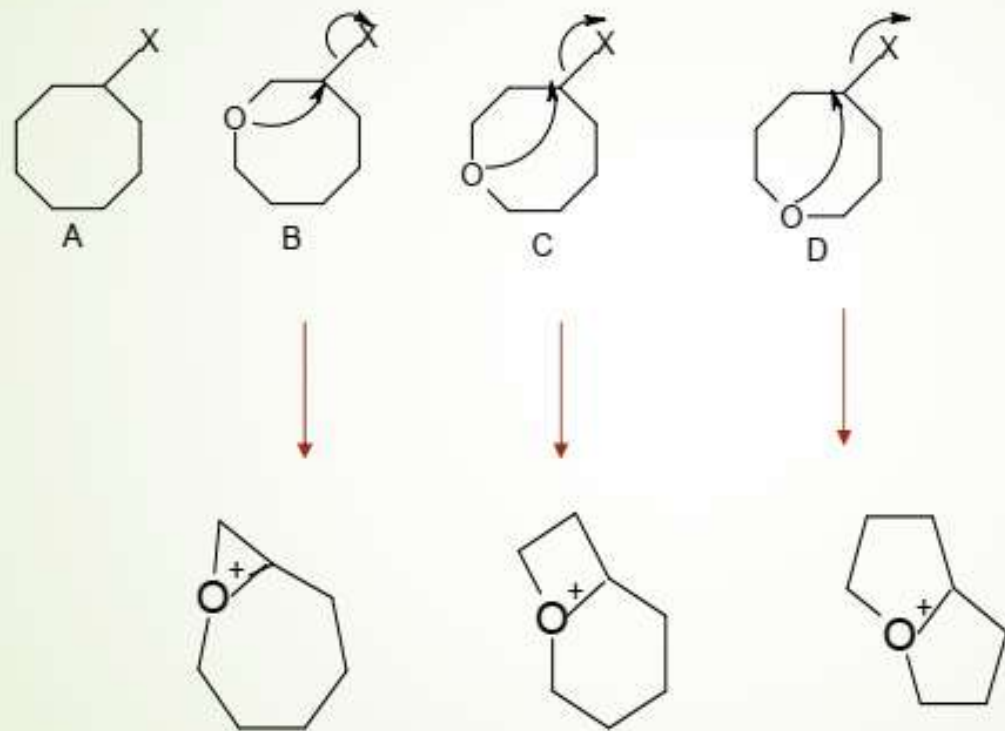
The hydroxy group in this case can act as an intermolecular nucleophile.

❖ NG Participation of oxygen in cyclic ether compounds.

❖ D reacts almost 4.84×10^4 times faster than A.

❖ NGP by lone pair of oxygen facilitate departure of LG.

❖ Formation of stable ring (5 member)



What groups facilitate NGP?

The following groups can facilitate NGP
COOR, COAr, OCOR, OR, OH, O⁻, NH₂,NHR,
NHCOR, SH, SR, I, Br, S⁻

The most likely NGP leads the formation of three, five, and six membered rings.

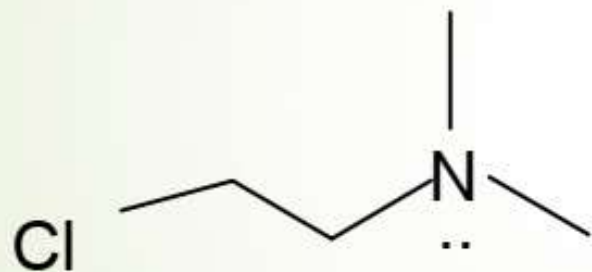
How to identify if a reaction is following NGP?

Kinetics: Reactions which follow NGP would be unimolecular and several fold faster than those without NGP.

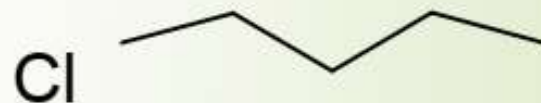
Stereochemistry: Reactions proceeding through NGP involve SN₂ reaction, so overall retention of configuration.

Practice Problems

1) Which will go faster and why?



or



2) Identify A and B in the following reaction



Summary

In general, any system that has a nucleophilic substituent situated properly for back side displacement of LG at another carbon atom can be expected to display NGP.

Reactions proceeding through NGP can be identified by their enhanced rate of reaction and characteristic stereo chemical outcome of retention of configuration