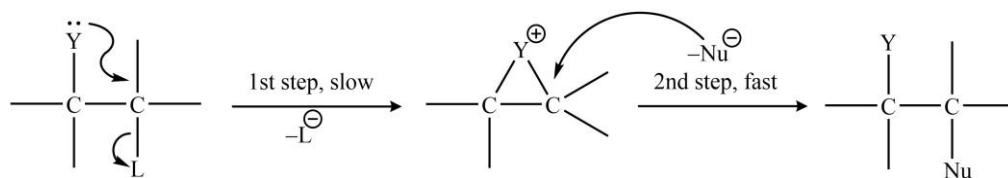


❖ The Neighbouring Group Mechanisms

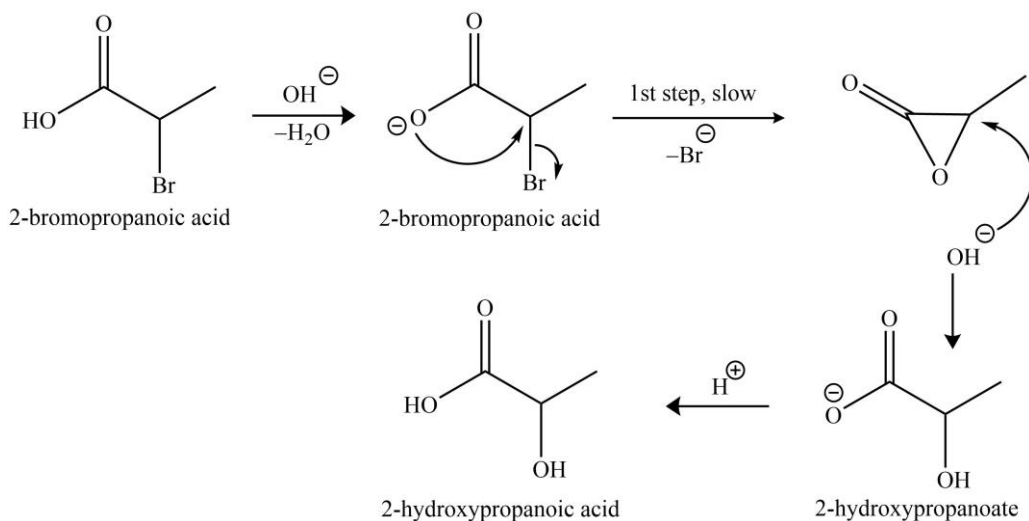
There are many nucleophilic substitution reactions that give rise to the same configuration (i.e., retention) instead of inversion or racemization. Also, the rate of reaction for such reactions is so high that we cannot rationalize them by simple nucleophilic substitutions. However, it has been observed that one feature that is common in these reactions is a group or atom at β -position to the leaving group. The mechanism responsible for such transformations is labeled as neighboring group participation and can be parted into two normal S_N2 consecutive steps. Now since the first S_N2 reaction gives inversion (neighboring group as the nucleophile), the subsequent S_N2 changes will revert the configuration to the original (neighboring group as leaving group).



The faster rate of reaction can be rationalized in terms of the ready availability of nucleophilic attack in the first step (rate-determining step). Furthermore, it should also be noted that the generation of the cyclic intermediate is a characteristic feature of the neighboring group participation. Some typical cases of neighboring group participation are discussed below.

➤ Reactions Involving Oxygen as Neighbouring Group

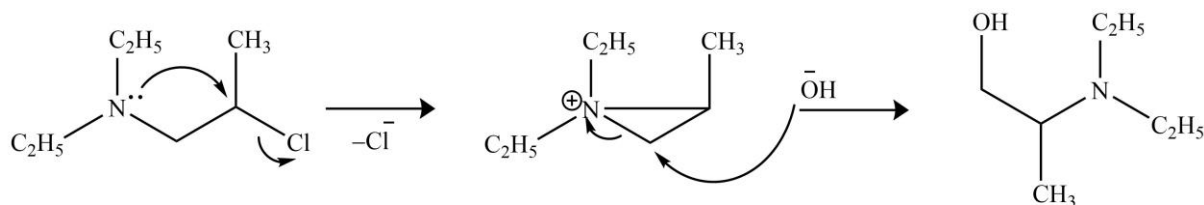
One of the most common examples of this type of neighboring group mechanism is the reaction of 2-bromopropanoic acid with a dilute solution of NaOH.



It is obvious from the above route that the configuration has remained the same (R)-lactate anion), unlike S_N2 where we would have obtained the (S)-lactate anion.

➤ **Reactions Involving Nitrogen as Neighbouring Group**

One of the most common examples of this type of neighboring group mechanism is the reaction of 2-chloro-*N,N*-diethylpropan-1-amine with a dilute solution of NaOH.

2-chloro-*N,N*-diethylpropan-1-amine

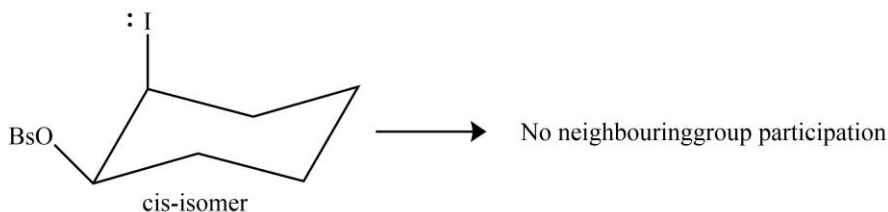
1,1-diethyl-2-methylaziridin-1-ium

2-(diethylamino)propan-1-ol

It is obvious from the above route that the configuration has remained the same, unlike S_N2 where we would have obtained the 1-(diethylamino) propan-2-ol.

➤ **Reactions Involving Halogen as Neighbouring Group**

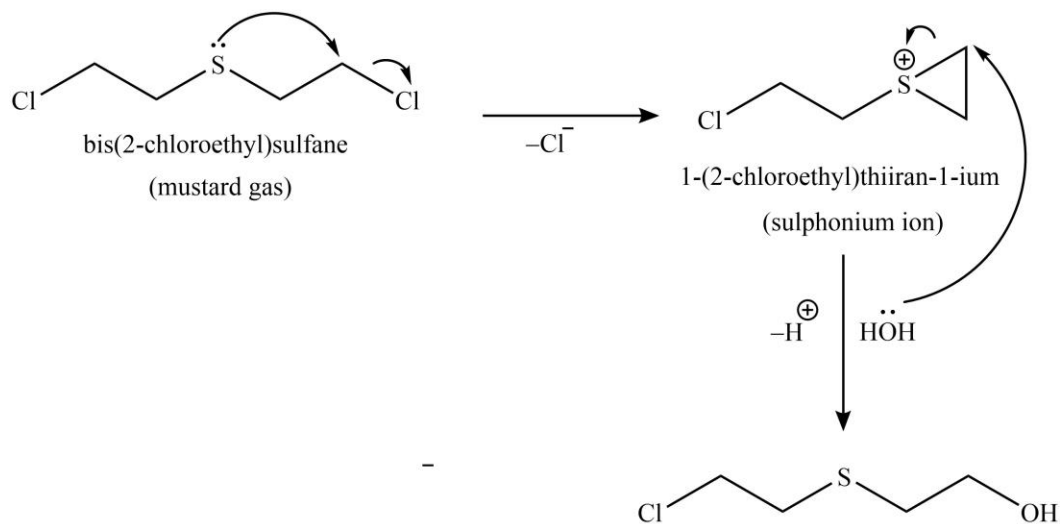
One of the most common examples of this type of neighboring group mechanism is the reaction involving the acetolysis of trans-2-iodocyclohexyl brosylate in which the configuration remains the same at the asymmetric center.



It is obvious from the above route that the configuration would have changed if the reaction had taken place via normal S_N2 , which is observed for cis isomer.

➤ **Reactions Involving Sulphur as Neighbouring Group**

One of the most common examples of this type of neighboring group mechanism is the reaction involving the hydrolysis of bis(2-chloroethyl) sulfane in which the configuration remains the same at the asymmetric center.



It is obvious from the above route that the configuration would have changed if the reaction had taken place via the normal $\text{S}_\text{N}2$ route.

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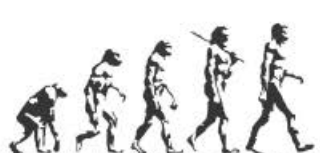
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A TEXTBOOK OF ORGANIC CHEMISTRY

Volume I

MANDEEP DALAL



First Edition

DALAL INSTITUTE

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