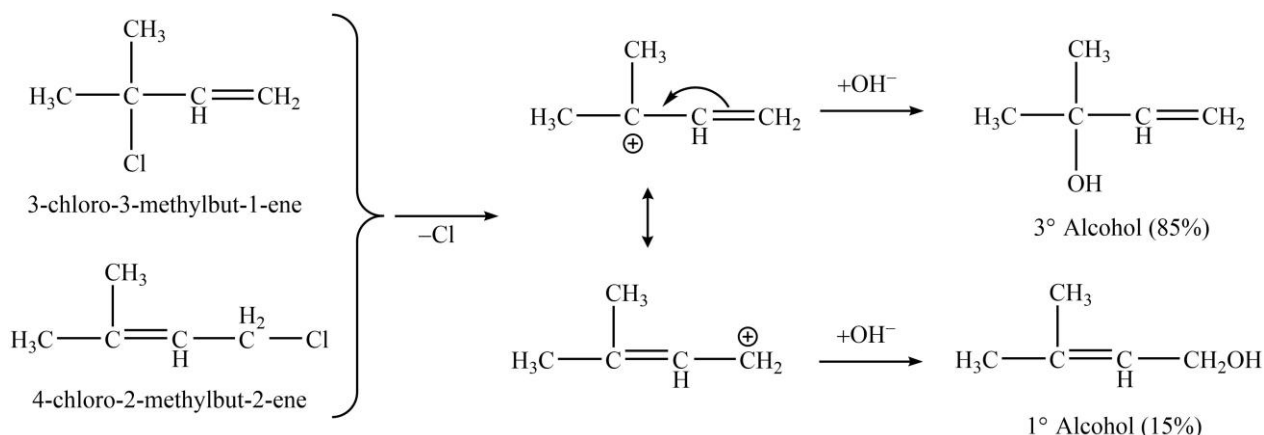


## ❖ Methods of Determining Mechanisms

The reaction mechanism of organic compounds can be determined via several individual routes; however, it is quite common to use multiple methods for confirmatory results. Some of the major methods to determine the organic reaction mechanism are given below.

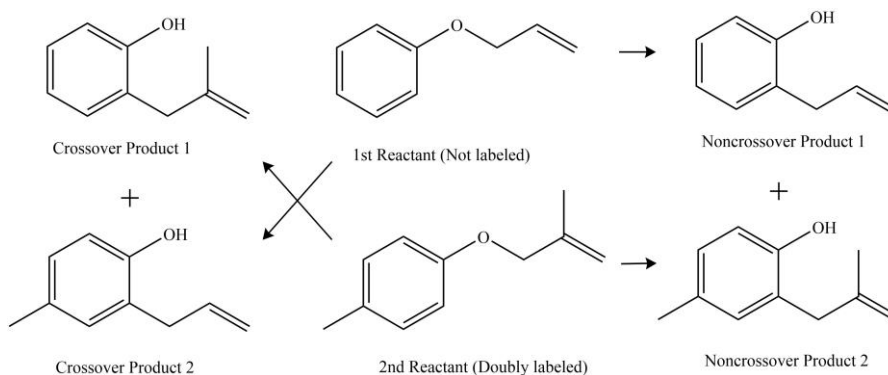
### ➤ 1. Product Identification

The proposed mechanism must account for all the products in the experimental reaction including by-products. Therefore, the theoretically proposed mechanisms are shortlisted depending upon the nature and number of the products. This can be illustrated by the hydrolysis of isomeric allyl chlorides. Since the hydrolysis of 3-chloro-3-methylbut-1-ene or 4-chloro-2-methylbut-2-ene give rise to 15% of primary alcohol and 85% tertiary alcohol in each case, a common intermediate must be proposed to rationalize the results.



### ➤ 2. Crossover Experiments

The crossover experiments are carried out to determine whether the reaction mechanism involves one step or two steps. To do so, a mixture of two similar but non-identical reactants is subjected to the reaction, and then the resulting products are investigated. Now because the migrating group needs to be free in a two-step process (intermolecular rearrangement), a mixture of the products corresponding to both reactants is expected (crossover products).



On the other hand, if the process is single-step (intramolecular rearrangement) we will not get any crossover products. This can be illustrated by the Claisen-rearrangement in which allyl aryl ethers are transformed into allyl phenols.

The concept underlying the crossover experiment is a basic one: provided that the labeling method chosen does not affect the way a reaction proceeds, a shift in the labeling as observed in the products can be attributed to the reaction mechanism. The most important limitation in crossover experiment design is therefore that the labeling does not affect the reaction mechanism itself.

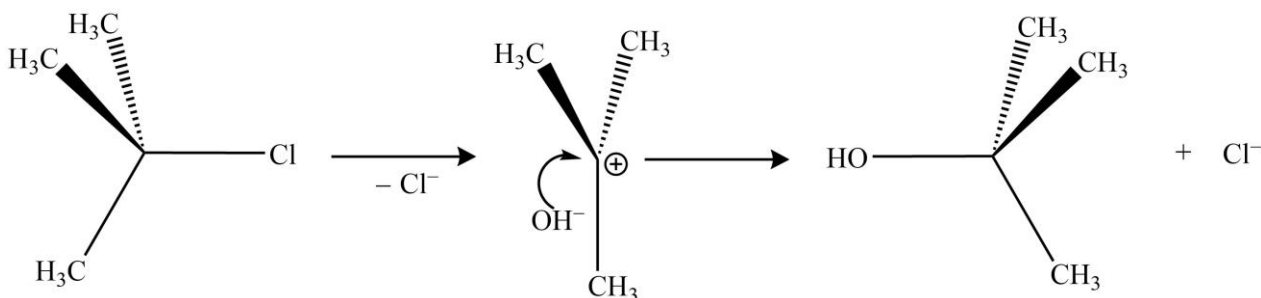
### ➤ 3. Isolation, Detection, and Trapping of Intermediates

Several organic reactions proceed via the generation of intermediates. If these intermediates are identified experimentally, the writing of a reasonable mechanism becomes very easy. These intermediates are usually detected by spectrophotometric methods directly; however, some unstable intermediates are first isolated by trapping them with reactive substrates.

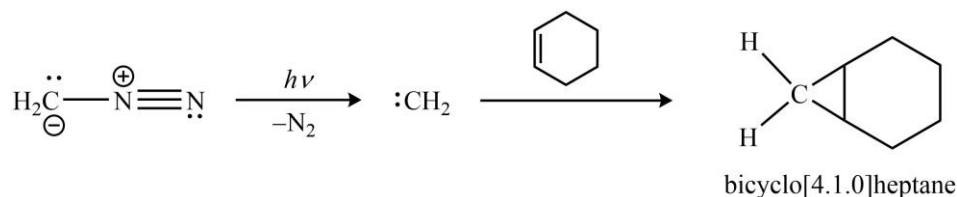
**i) Isolation:** In some cases, the isolation of an intermediate from the reaction mixture is possible either under mild conditions or by ending the reaction after some time. For instance, three intermediates can be isolated in the transformation of primary amides to primary amines (Hofmann rearrangement).



**ii) Detection:** If the intermediate formed in the course of the chemical reaction is very unstable, it is better to use spectrophotometric methods to detect them. For instance, the carbocation formed in the  $E_1$  and  $SN_1$  pathways can be detected via NMR spectroscopy confirming the route.



**iii) Trapping:** In some reactions, the intermediate formed is so unstable and short-lived that the conventional techniques cannot be used to identify them. In such cases, it is better to mix the reactant with a special reactive agent which can react with the intermediate to form detectable species. For instance, the formation of carbene during the decomposition of diazomethane can be detected by trapping them via cyclohexene.



#### ➤ 4. Isotopic Labelling

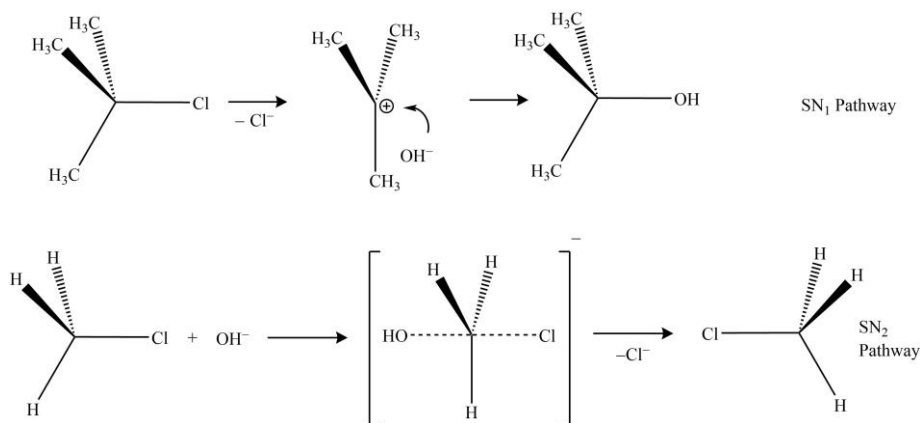
Isotopic labeling is a technique that is used to track the passage of reactants through a chemical reaction. The reactant is 'labeled' by displacing specific atoms by the corresponding isotope. The reactants are then permitted to undergo the chemical change, and the sites of the isotopes in the products are analyzed to find the sequence of the isotopes followed in the reaction mechanism. For instance, the mechanism of ester hydrolysis can be understood by replacing the normal water with  $\text{H}_2\text{O}^{18}$ .



It is obvious from the above reaction that it is the acyl-oxygen bond that gets broken rather than the alkyl-oxygen bond.

#### ➤ 5. Kinetic Studies

The kinetic of an organic reaction is very useful in identifying the correct reaction mechanism. The rate-determining step (slowest step) infers about the reaction route from the overall rate law. One of the most popular examples where the reaction kinetics has been found to be exceptionally useful to determine reaction mechanism aliphatic nucleophilic substitution.



For instance, the hydrolysis of methyl bromide follows second order kinetics i.e.

$$-\frac{d[\text{CH}_3\text{Br}]}{dt} = k[\text{CH}_3\text{Br}][\text{OH}^-] \quad (18)$$

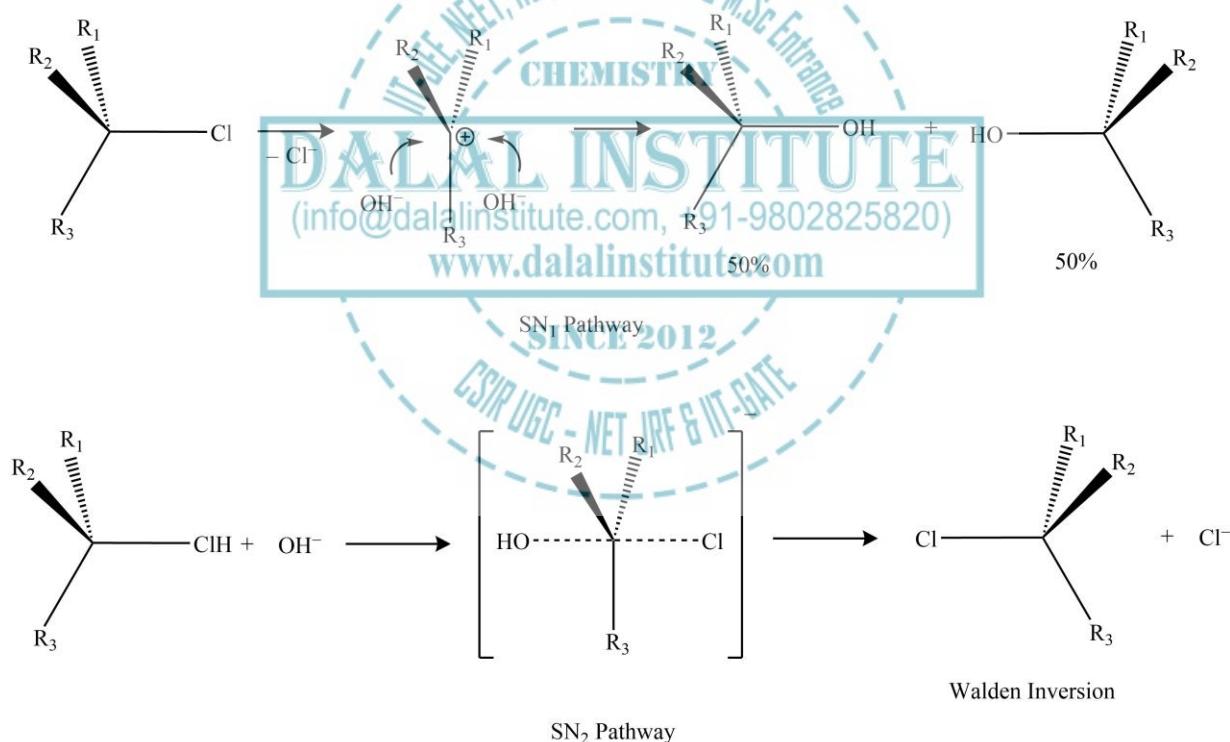
This is possible only if both reactants undergo a transition state instated of an intermediate. On the other hand, the hydrolysis of tert-butyl bromide follows first-order kinetics i.e.

$$-\frac{d[\text{CH}_3\text{Br}]}{dt} = k[(\text{CH}_3)_3\text{CBr}] \quad (19)$$

This is possible only if the substrate forms an intermediate instated transition state.

### ➤ 6. Stereochemical Analysis

In some cases, the stereochemistry of the reactants and products can also be used to identify the pathway of an organic reaction. For instance, the optical purity of the resulting product in aliphatic nucleophilic substitution in chiral compounds can infer whether it occurs via  $\text{S}_{\text{N}}1$  or  $\text{S}_{\text{N}}2$ .



The racemization of the product showed that the reaction has proceeded via a dissociative pathway where the attack on the two faces of the carbocation has happened. On the other hand, we get a mostly optically pure compound, which suggests that the reaction has proceeded via a dissociative pathway where the inversion has happened through a transition state.

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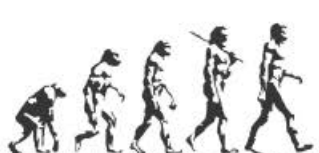
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# A TEXTBOOK OF ORGANIC CHEMISTRY

**Volume I**

**MANDEEP DALAL**



*First Edition*

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