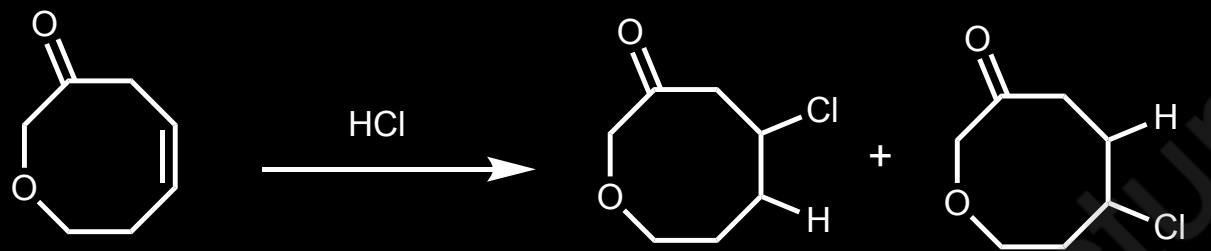
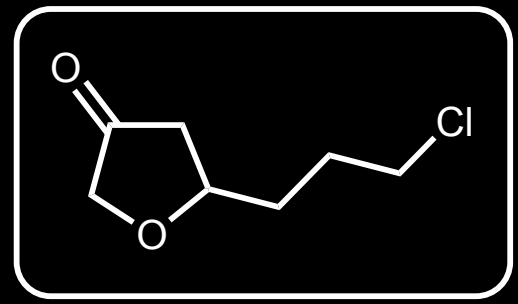
# Determination of Reaction Mechanism

## Organic Reaction

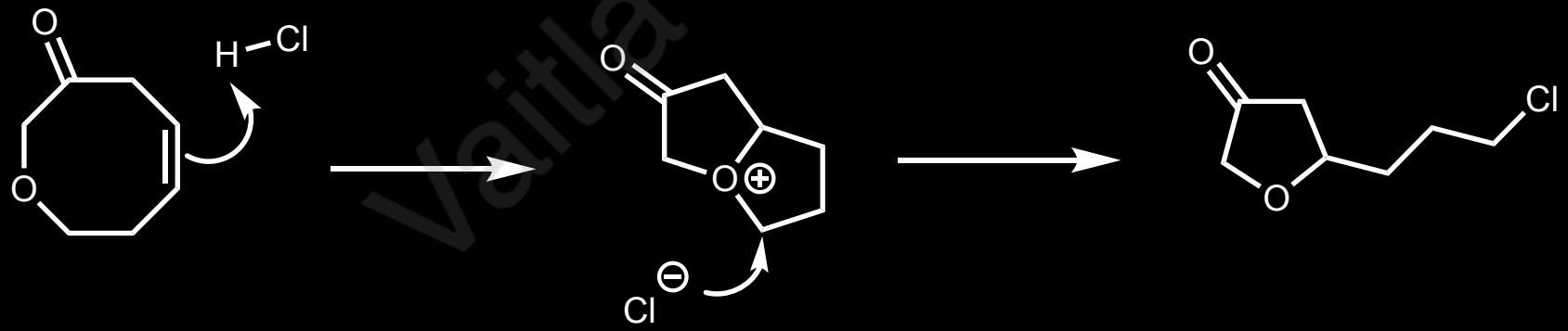
$$A + B \longrightarrow C$$




Expected Products




Observed Product



# Determination of Reaction Mechanism

New Organic Reaction

A + B ⟶ Product

- Questions:

What is the product?

What is the intermediate(s)?

How many steps are involved in this reaction?

How much time required to finish the reaction?

What reaction conditions are required to get the product?

What is the stability of the reagents and intermediates?

☆ Representing reactions by simple method

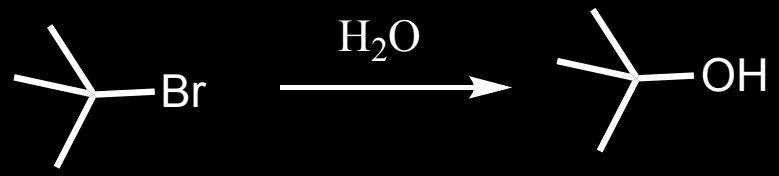
*What information you get?*

- *The reactants*
- *Reaction conditions*
- *Reaction mechanism---?.*

*What information you do not get?*

- *Stability of the reagents and steps involved*
- *How long does the reaction takes place*
- *How much product is formed.*

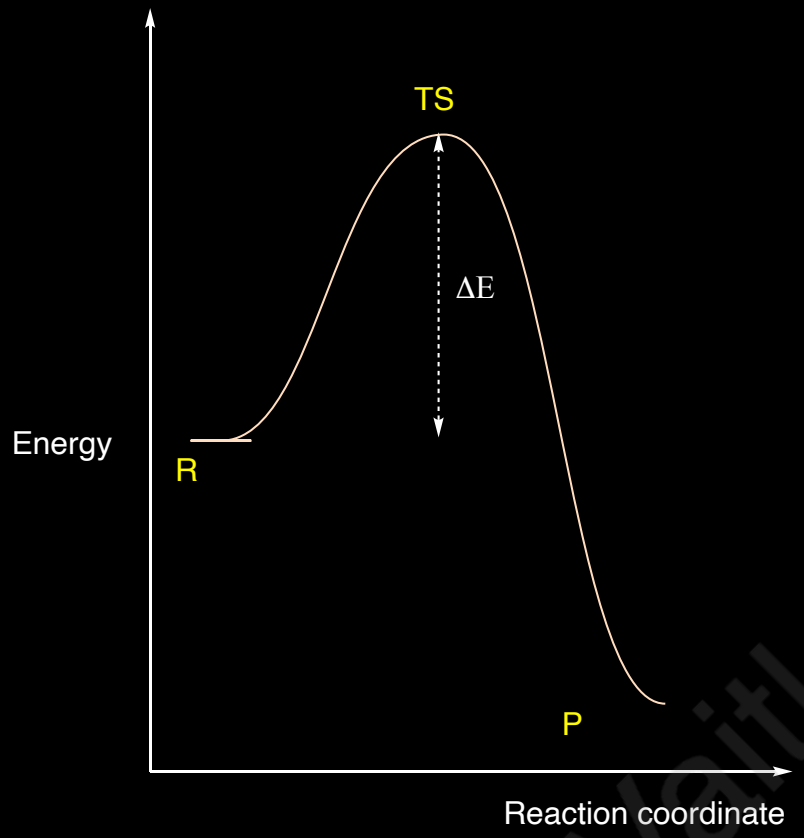
*$S_N1$ reaction*



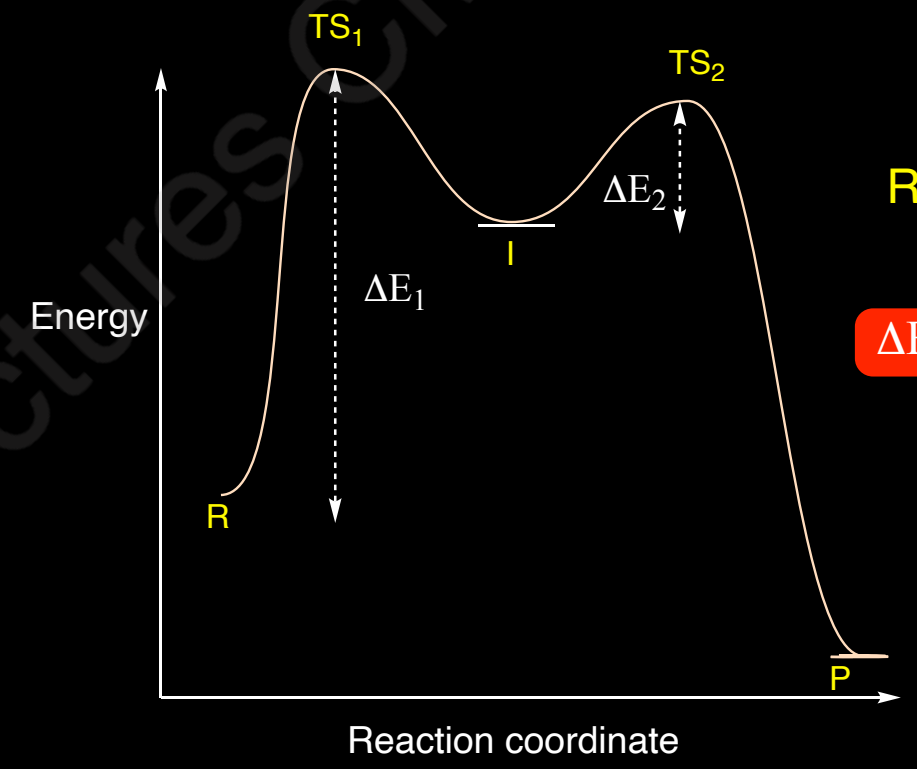
# Determination of Reaction Mechanism

☆ Another representation – Reaction coordinate diagram/Energy profile diagram

Theoretical representation of a single energetic pathway, along the reaction coordinate, as the reactants are transformed into products




R ⟶ P




R ⟶ I ⟶ P

$\Delta E_1 > \Delta E_2$

Step-1 is Rate determing step (RDS) or Slowest step

## ☆ Rate determining step (R.D.S)

# *Determination of Reaction Mechanism*

Kinetic Studies

Non-Kinetic methods

1) Product analysis or identificaiton of products

2) Detection of intermediates

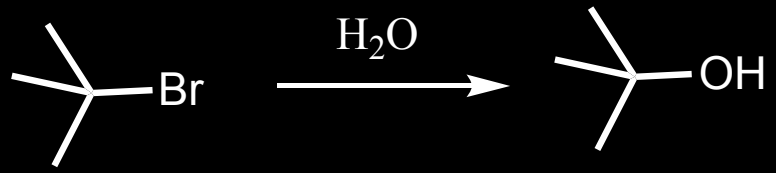
3) Trappng of intermediates

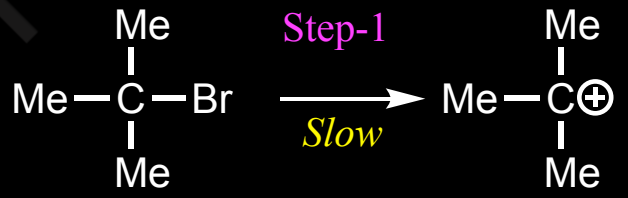
4) Isotopic labelling

5) Stereochemical studies

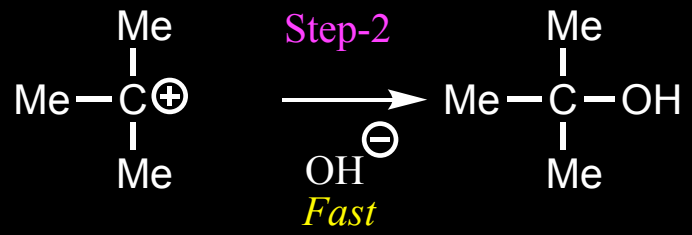
6) Isotopic effect

# Kinetic studies



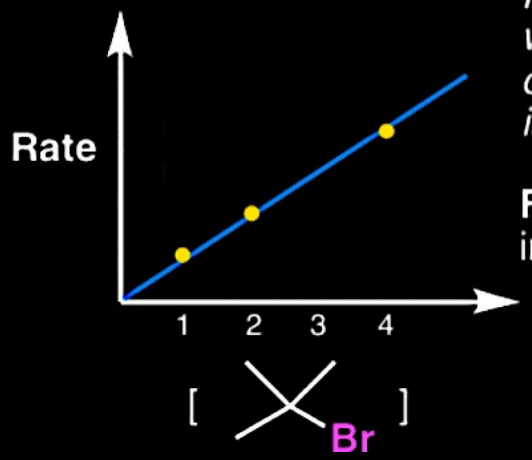




$$\text{Rate} = k\,[(CH_3)_3Br]$$



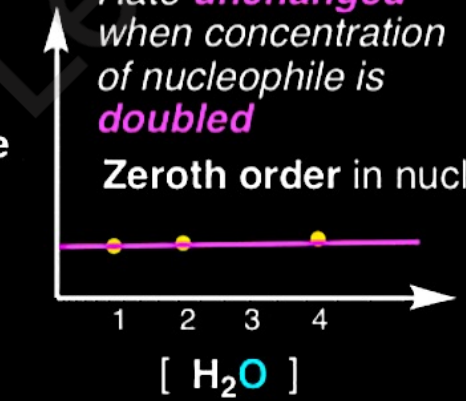

**Rate Law:**

**The rate of the reaction is only sensitive to the concentration of the substrate (and not the nucleophile)**

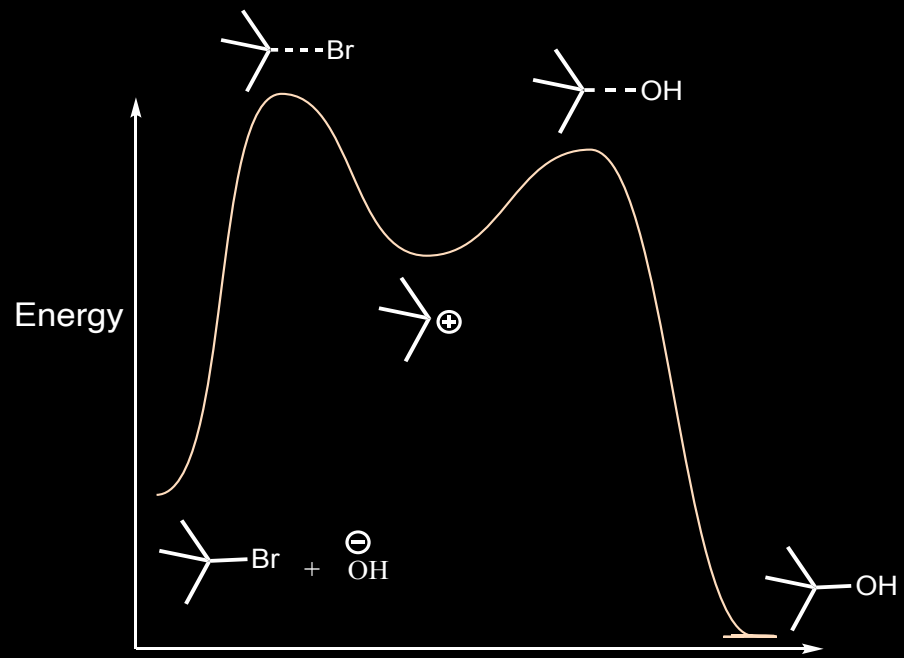

*Rate **doubles** when concentration of alkyl halide is **doubled***

**First order** in alkyl halide




*Rate **unchanged** when concentration of nucleophile is **doubled***

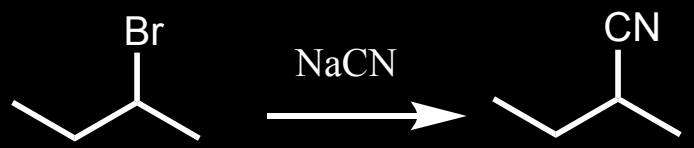
**Zeroth order** in nucleophile

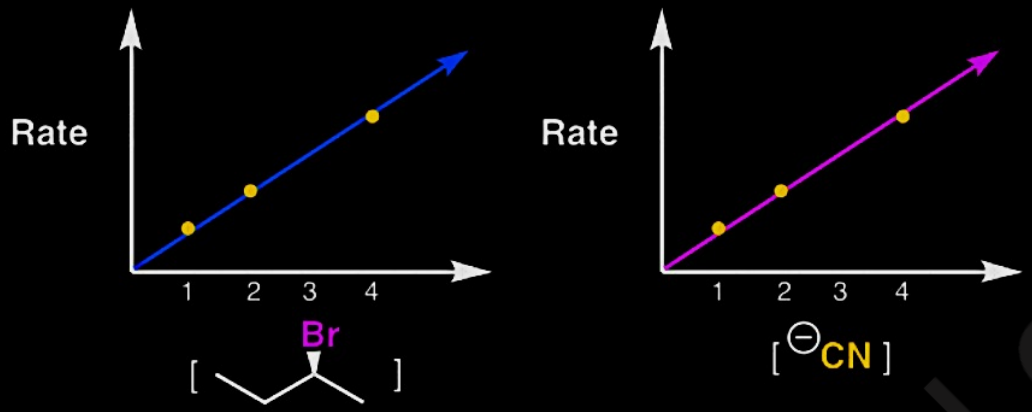


☆ Questions

# *Kinetic studies*

$S_N1$ or $S_N2$ ??

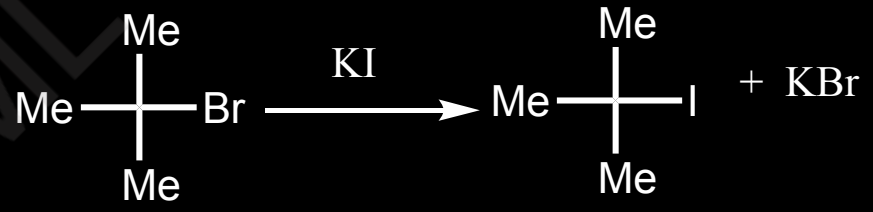



$Rate = k\,[(CH_3)_3Br]\,[NaCN]$

rate of the reaction is dependent on both the concentration of the nucleophile and that of the substrate. In other words, it's a second-order reaction. It is $S_N2$

$S_N1$ or $S_N2$ ??




| | $[C_4H_9Br]$ | [KI] | Rate |
|---|---|---|---|
| Run #1 | 1.0 M | 1.0 M | 1.0 |
| Run #2 | 2.0 M | 1.0 M | 2.0 |
| Run #3 | 2.0 M | 2.0 M | 2.0 |

Reaction rate is independent of KI.
Therefore, mechanism is $S_N1$.

## Non-Kinetic methods

1) Product analysis or identificaiton of products

2) Detection of intermediates

3) Trappng of intermediates

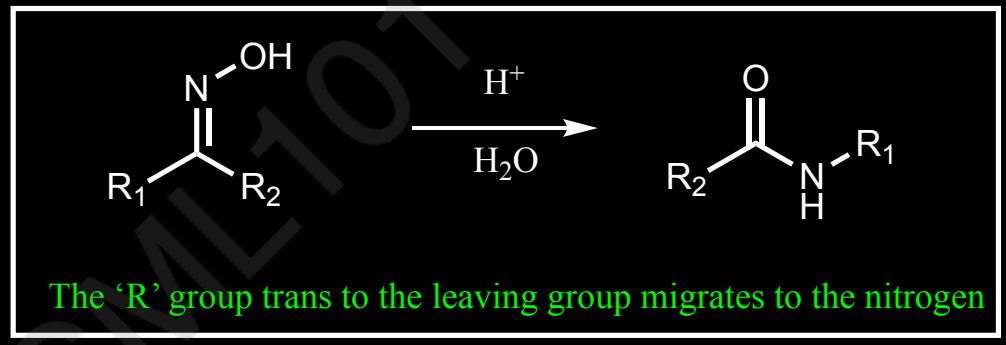
4) Isotopic labelling

5) Stereochemical studies

6) Isotopic effect

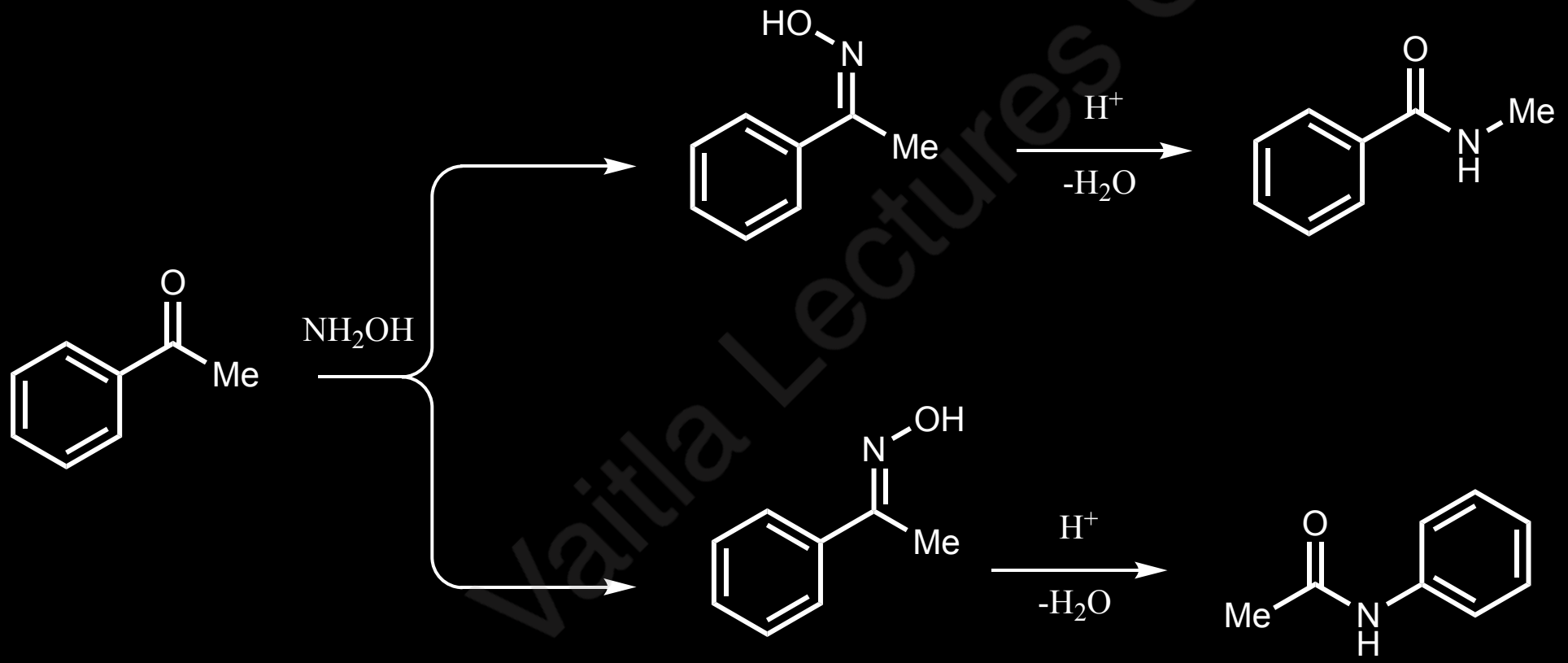
# Non-Kinetic Methods

☆ Product Analysis or identification of products

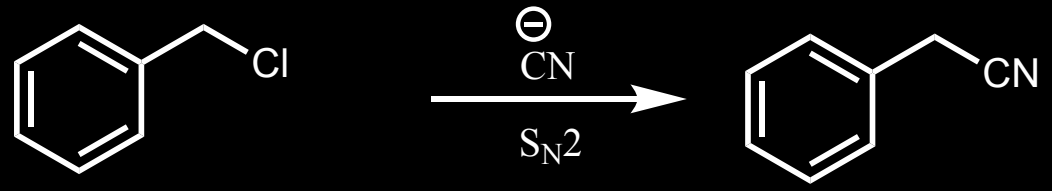


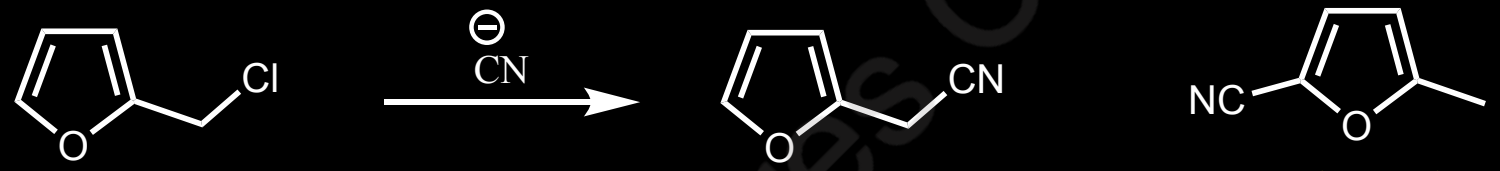

The 'R' group trans to the leaving group migrates to the nitrogen

☆ *Identify the intermediate structures?*



## ☆ Product Analysis or identification of products



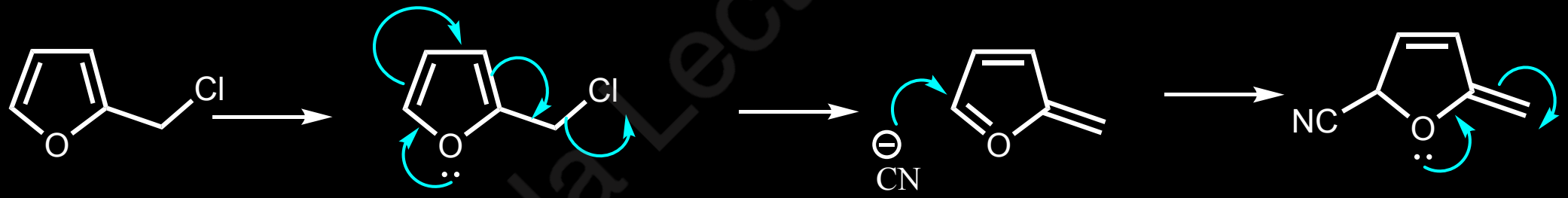



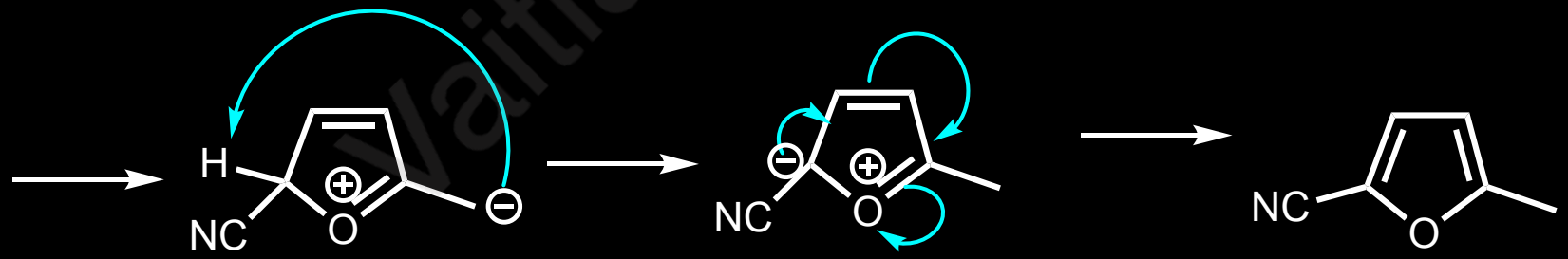

Expected




Observed

New mechanism!



## Non-Kinetic methods

1) Product analysis or identificaiton of products

2) Detection of intermediates

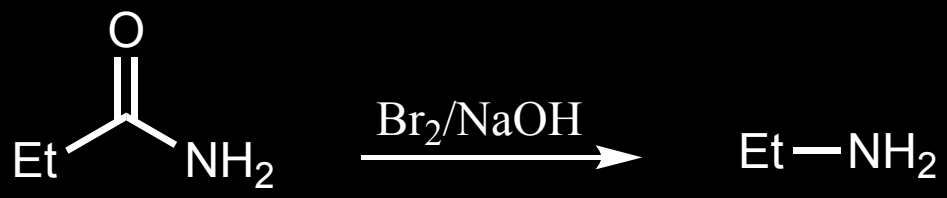
3) Trappng of intermediates

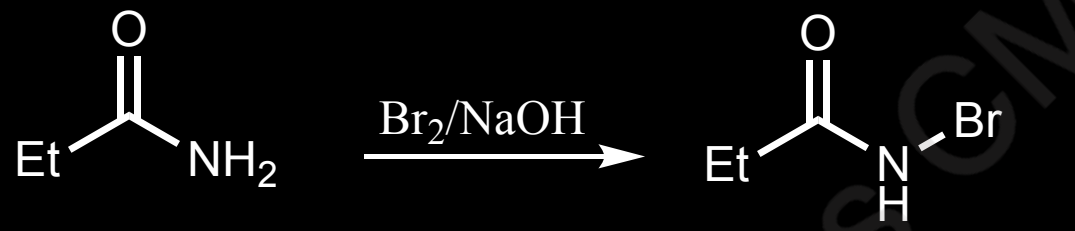
4) Isotopic labelling

5) Stereochemical studies

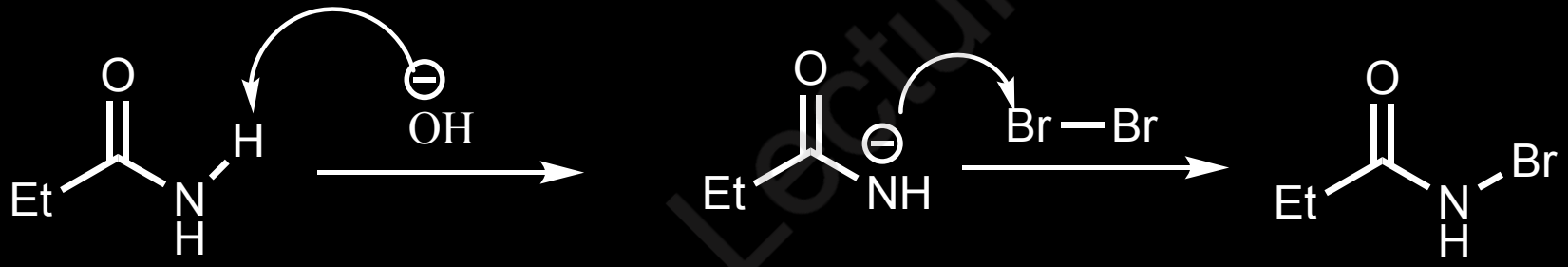
6) Isotopic effect

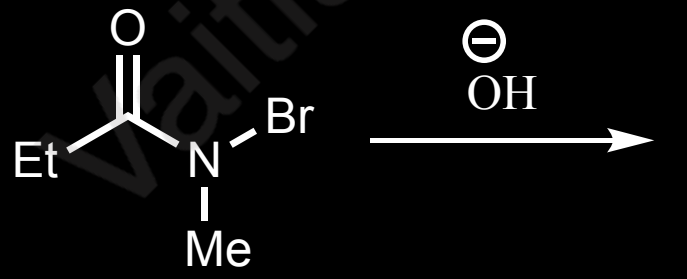
## ☆ Isolation of intermediate



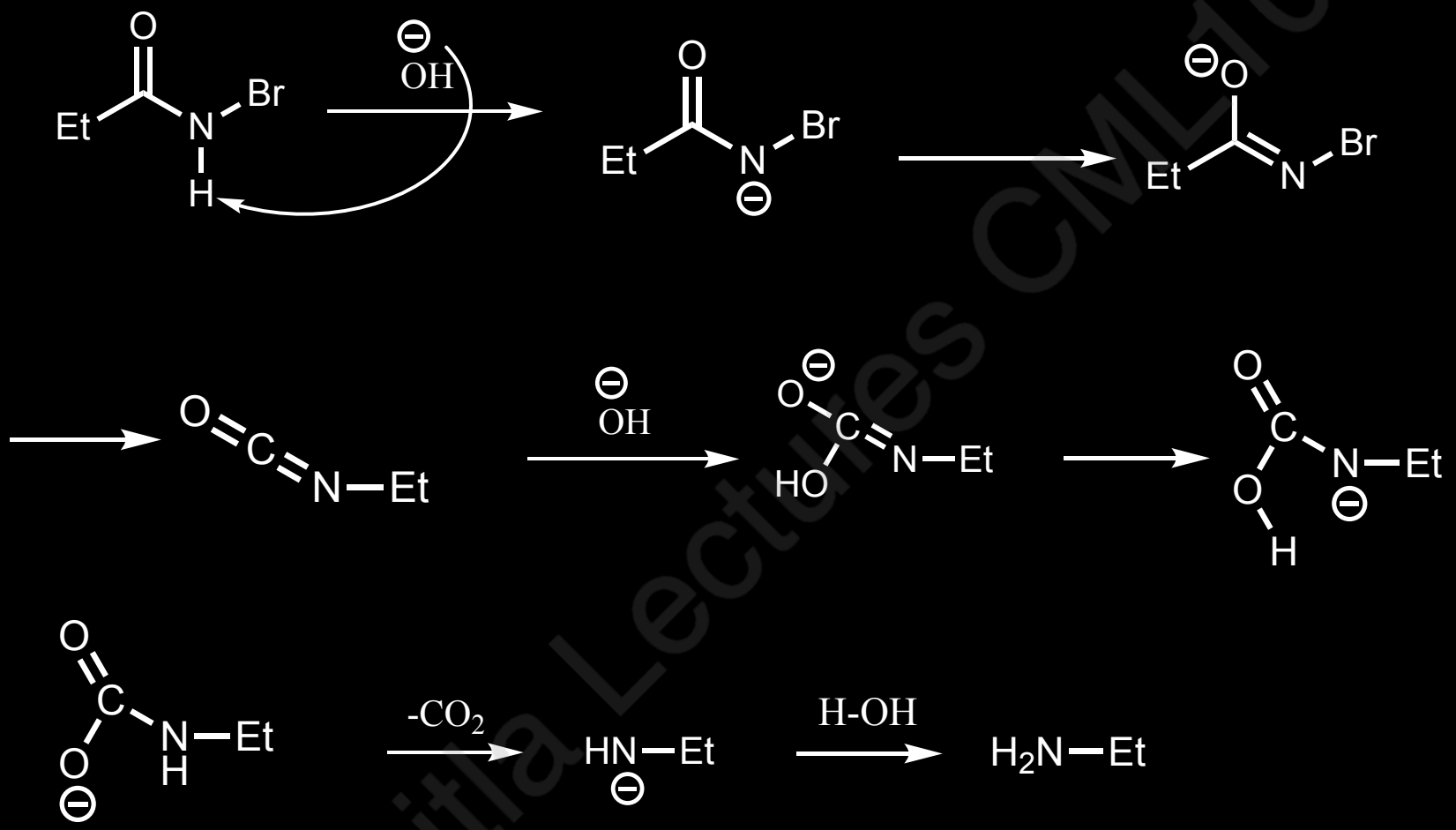

*isolable intermediate*




*No reaction*

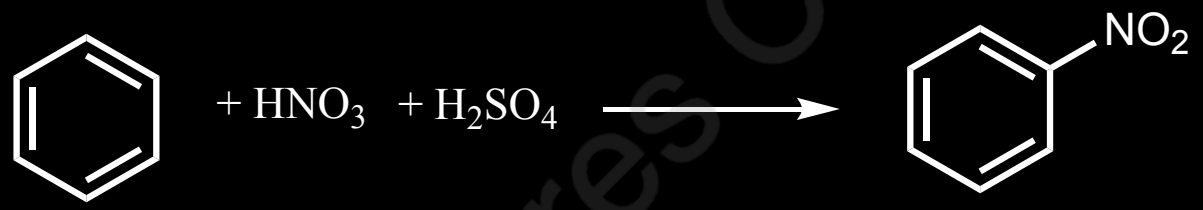
## ☆ Isolation of intermediate



## ☆ Detection of intermediate


*Intermediate unable to isolate*

Spectroscopic methods: IR, UV, NMR, ESR, Raman etc.





*Can be detected by Raman spectroscopy*

## Non-Kinetic methods

1) Product analysis or identificaiton of products

2) Detection of intermediates

3) Trappng of intermediates

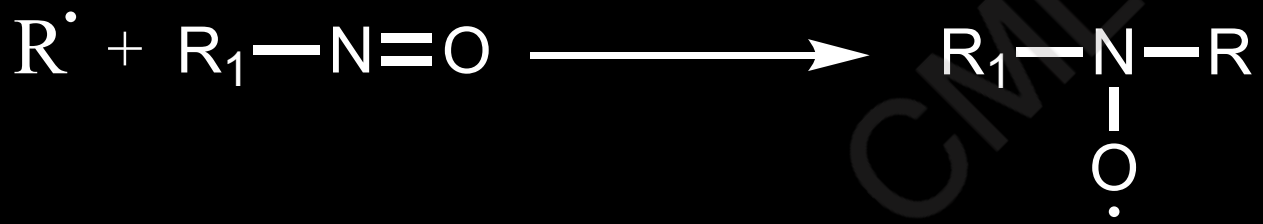
4) Isotopic labelling

5) Stereochemical studies

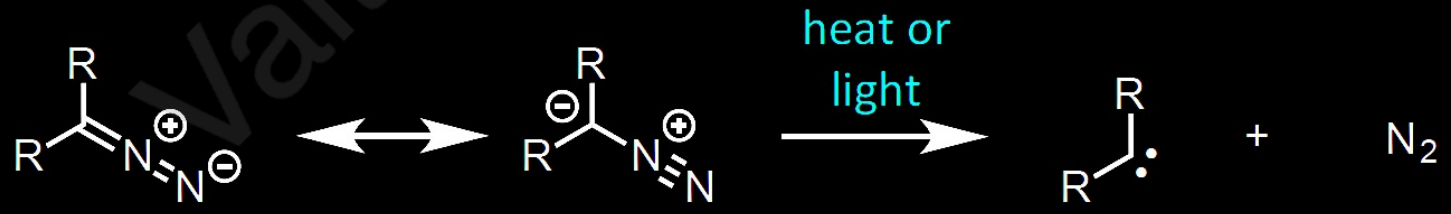
6) Isotopic effect

## ☆ Trapping of intermediate

### Trapping of free radical




### Trapping of Carbene

# Non-Kinetic methods

1) Product analysis or identificaiton of products

2) Detection of intermediates

3) Trappng of intermediates

4) Isotopic labelling

5) Stereochemical studies

6) Isotopic effect

## ☆ Isotopic labelling