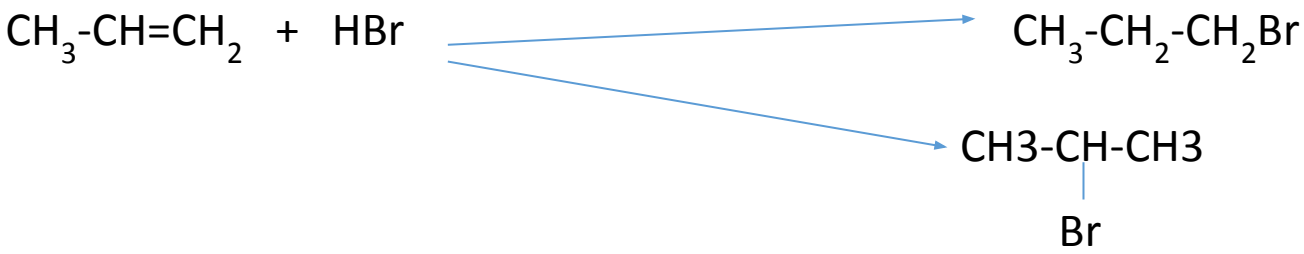
Unit V, **S9**

SLO-1: Cyclization

SLO-2: Ring opening reactions

**Dt. 04/01/2022**

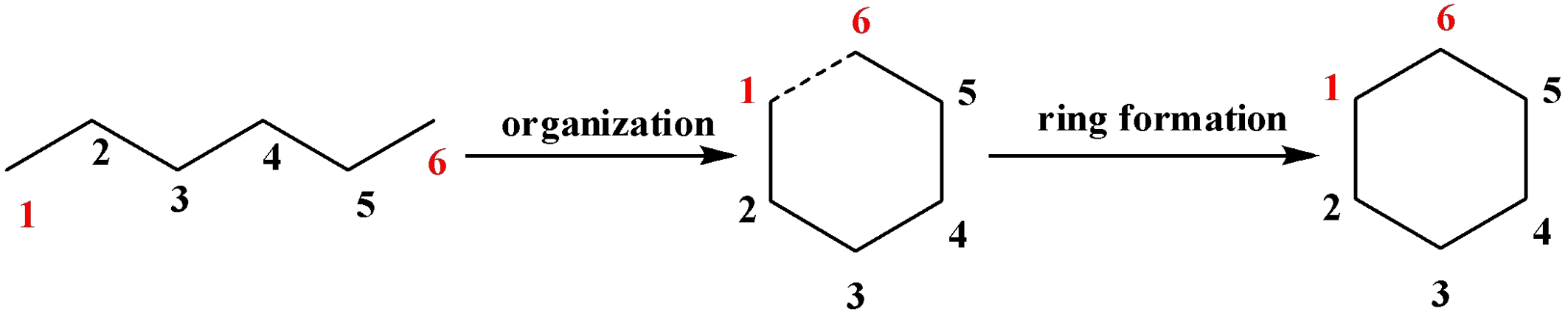
# Predict the major product of this following reaction?



# Cyclization

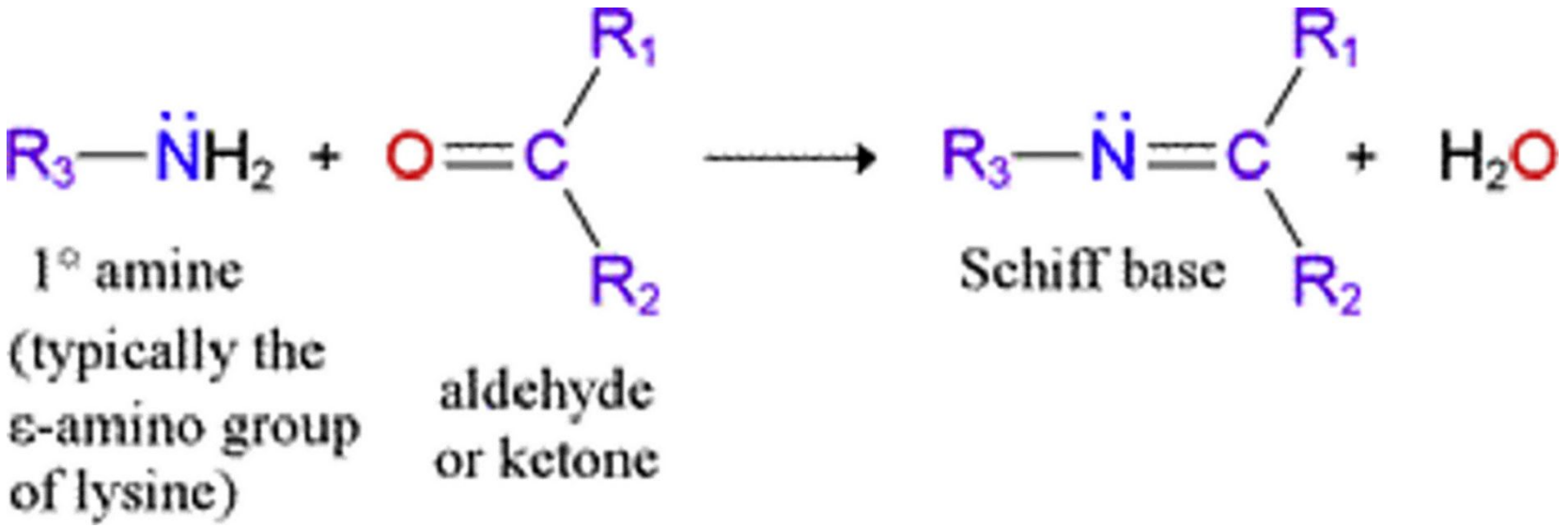
## Cyclization refers to the formation of a ring in a chemical compound

## Intramolecular reaction



# Condensation reaction

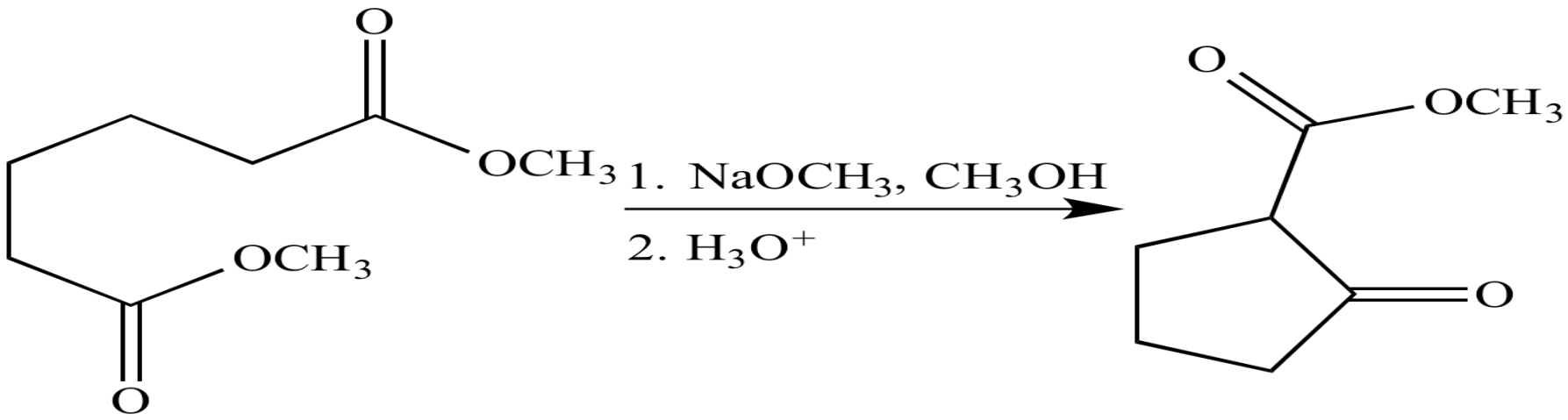
Condensation reaction is a reaction in which two molecules combine to form a larger molecule, producing a small molecule such as $H_2O$ as a by-product.



# Dieckmann Condensation

**It is an intramolecular Claisen condensation reaction.**

**Intramolecular Claisen reactions** occur when five- or six-membered rings can be formed. These are called the **Dieckmann condensation** where one *ester, of the same molecule,* serves as an electrophile and the other is deprotonated and acts as a nucleophile.

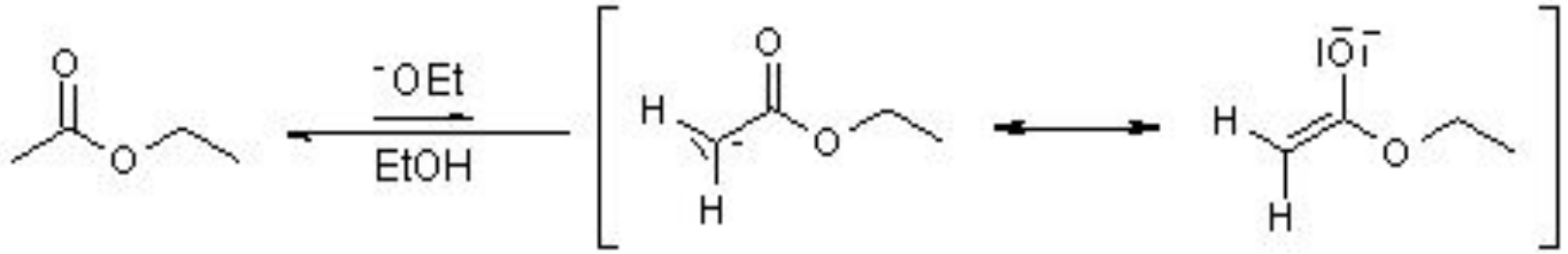


# Claisen Condensation

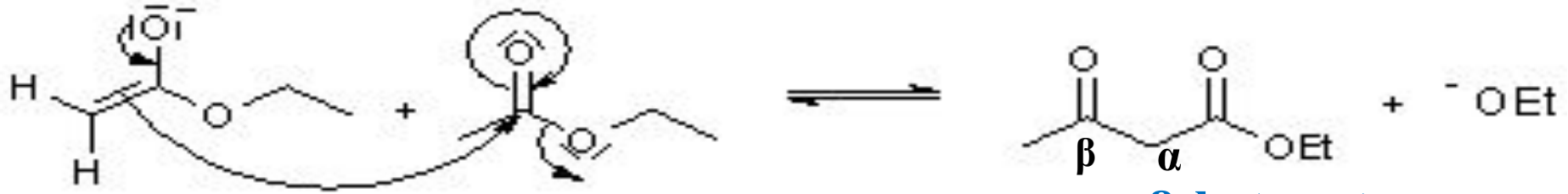
The Claisen Condensation between esters containing α-hydrogens, promoted by a base such as sodium ethoxide, affords β-ketoesters.

The driving force is the formation of the stabilized anion of the β-keto ester.

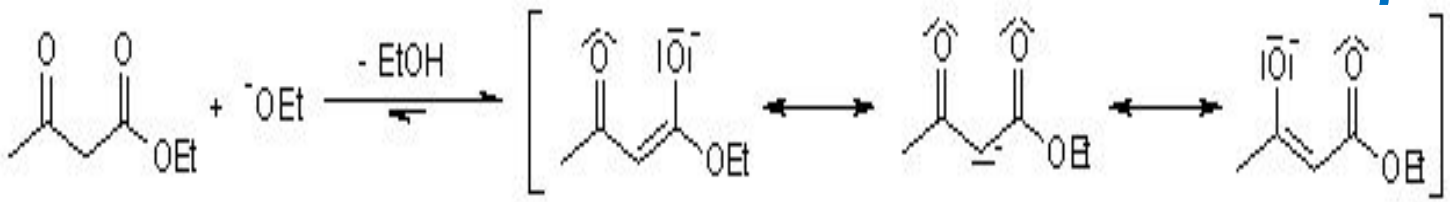
## 1st step: Deprotonation



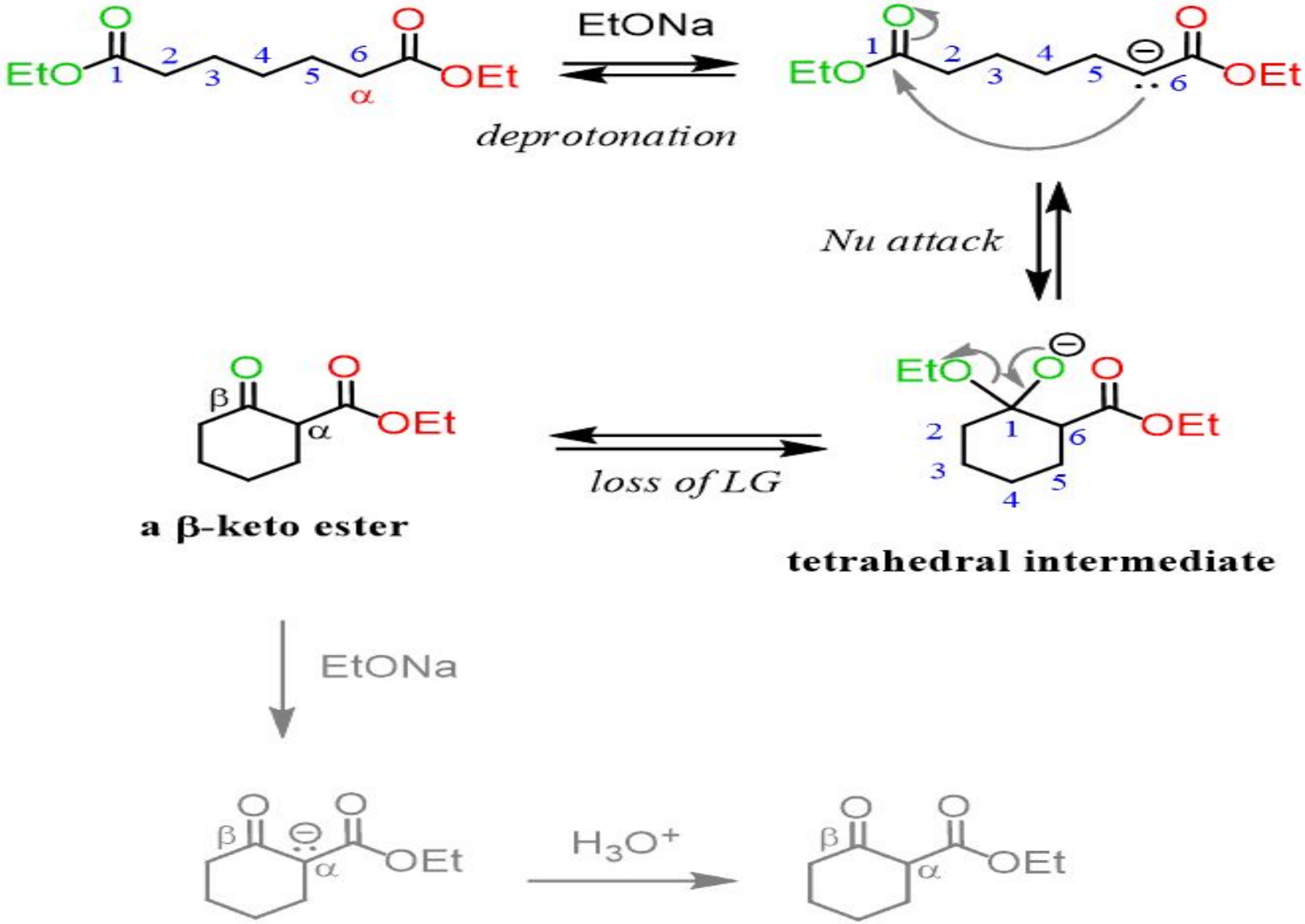

## 2nd step: Attack of nucleophile



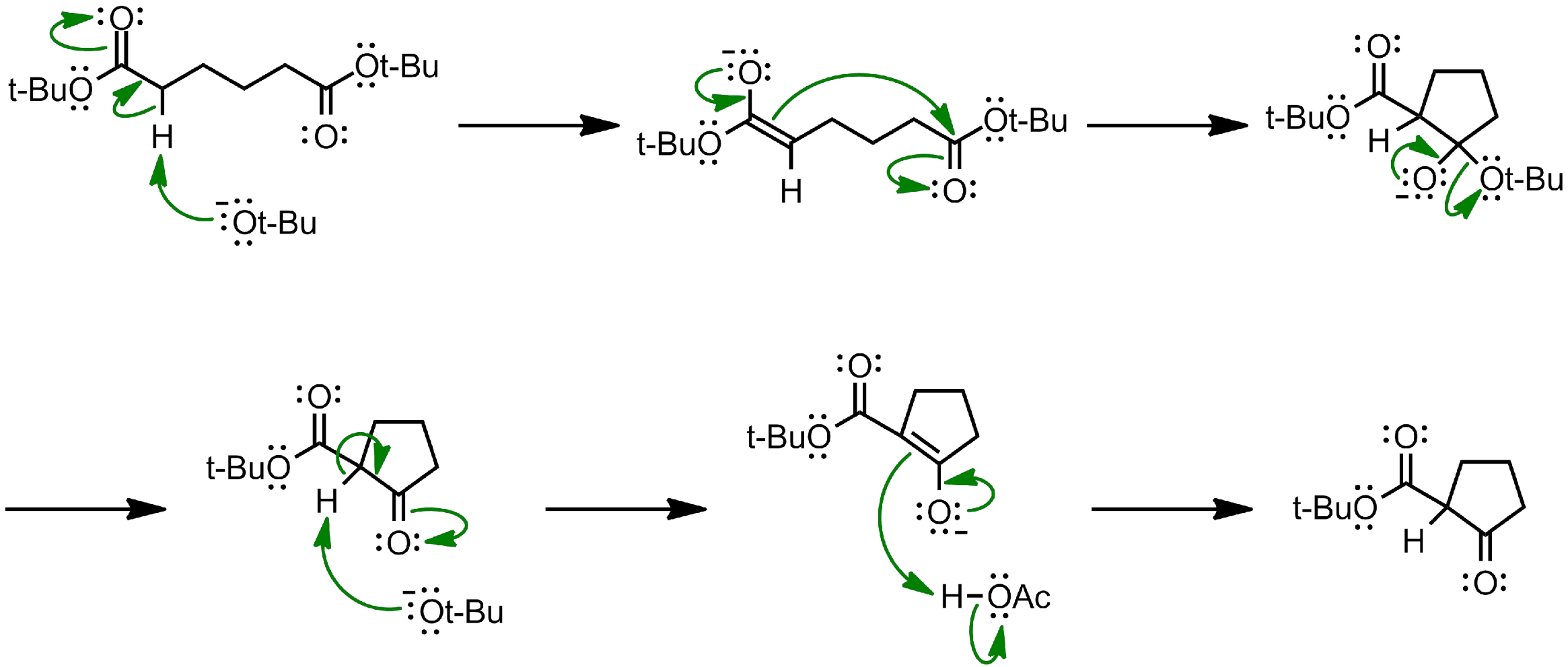

**β-keto ester**



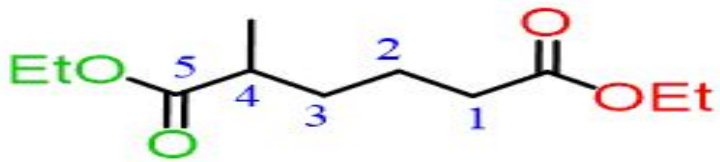
# The Mechanism of Dieckmann Condensation

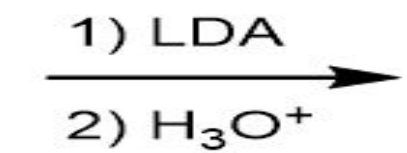


# Mechanism of Dieckmann Condensation



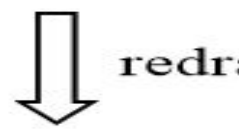
# Regioselective Dieckmann Condensation

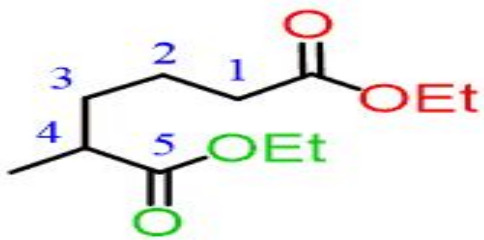


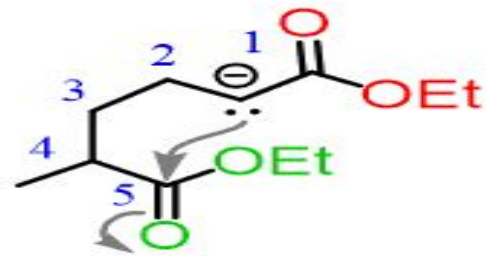

?

LDA = Lithium diisopropylamide
[(CH3)2CH]2NLi



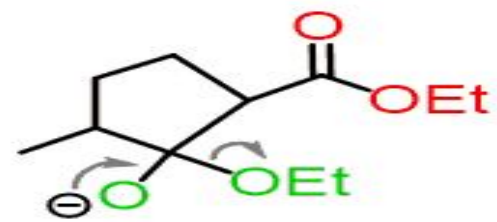





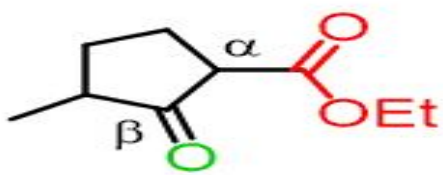



*Selective deprotonation of the less substituted α carbon*

*Nucleophilic attack*



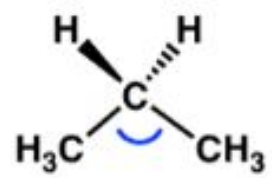

*Loss of the LG*



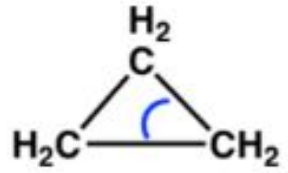

**a β-keto ester**

# Cyclopropane ring

**Cyclopropane has** large **ring strain** due to a mixture of angle **strain** and torsional **strain**



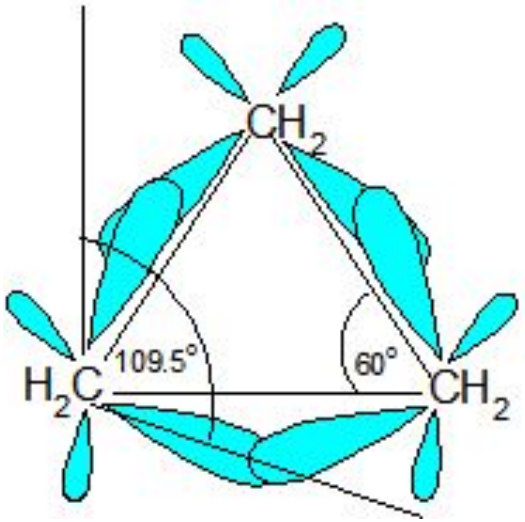

C–C–C bond angle 109.5°




interior bond angle 60°

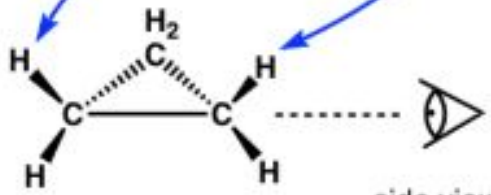
**(~ 49° less than ideal of 109°)**

**Orbital overlap**



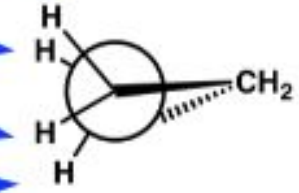

**Torsional Strain in Cyclopropane**


same as




side view

**note how hydrogens are eclipsed !**

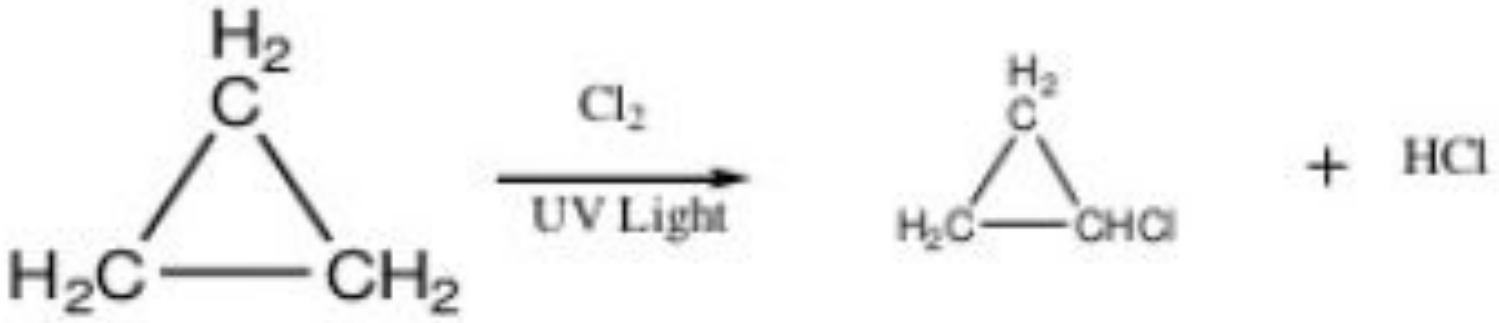


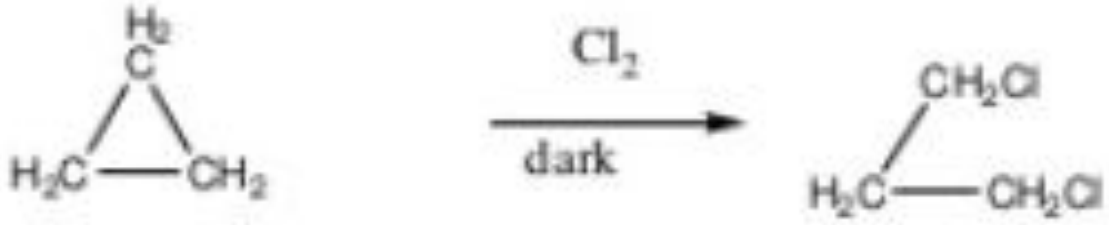

*Newman projection*

# Formation of cyclopropane ring

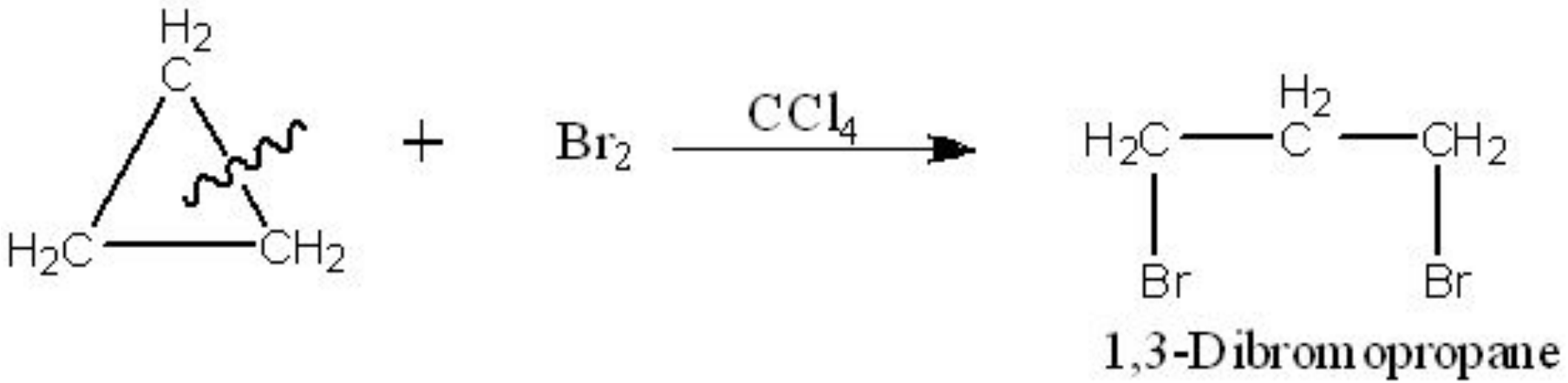
# Ring opening reactions

# Chlorination



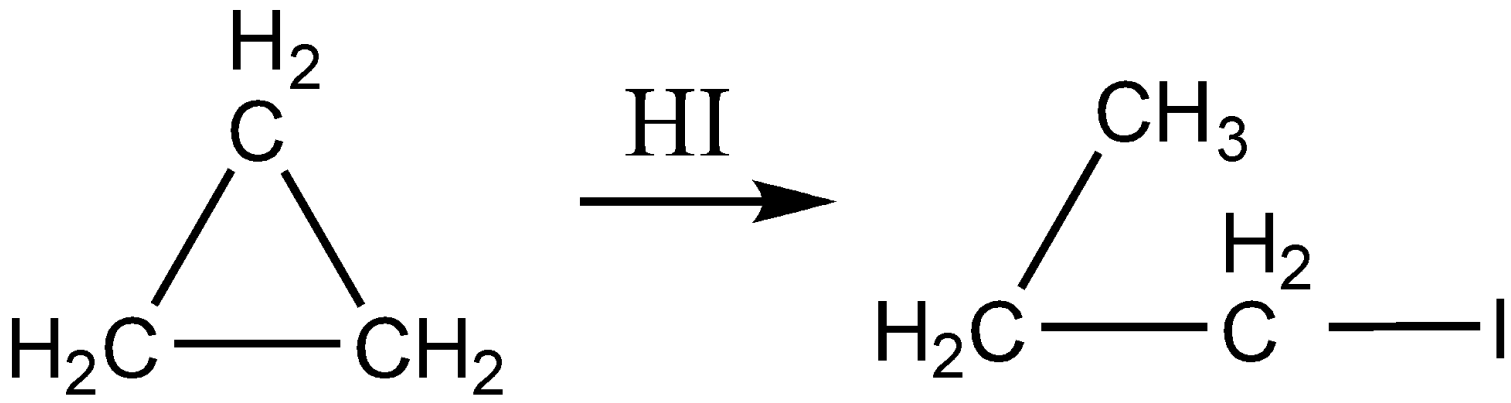



# Bromination

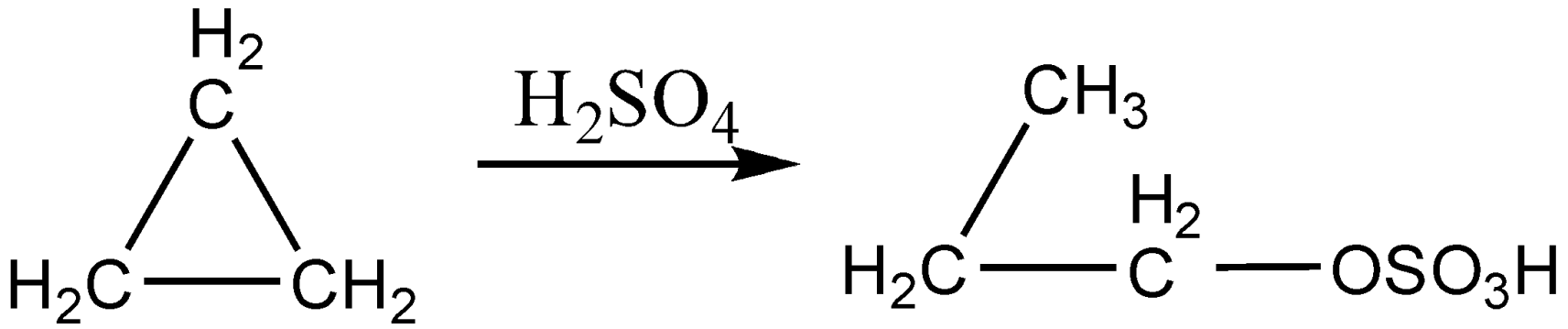



1,3-Dibromopropane

# Addition of HI (hydrogen iodide)



# Addition of sulfuric acid



# Reduction of Cycloalkane/ hydrogenation