

# **DAMIETTA UNIVERSITY**

## **CHEM-405: PERICYCLIC REACTIONS**

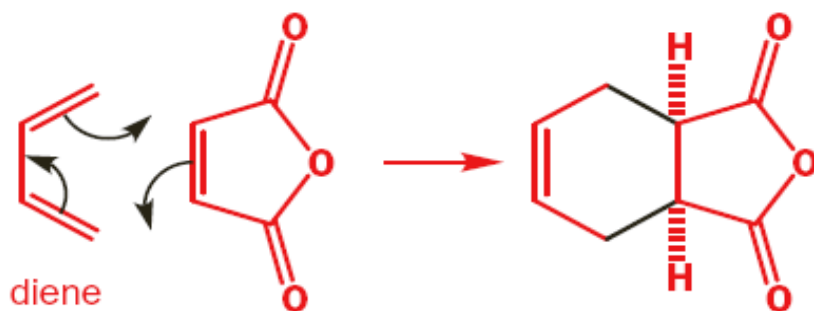
### **LECTURE 10**

**Dr Ali El-Agamey**

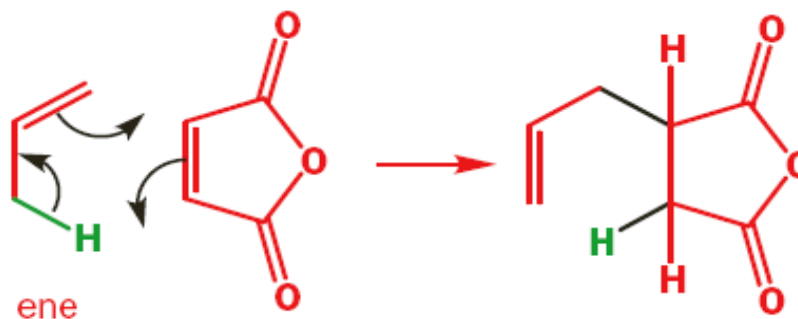
# Pericyclic Rearrangements

## Ene Reactions<sup>1</sup>

the Diels–Alder reaction

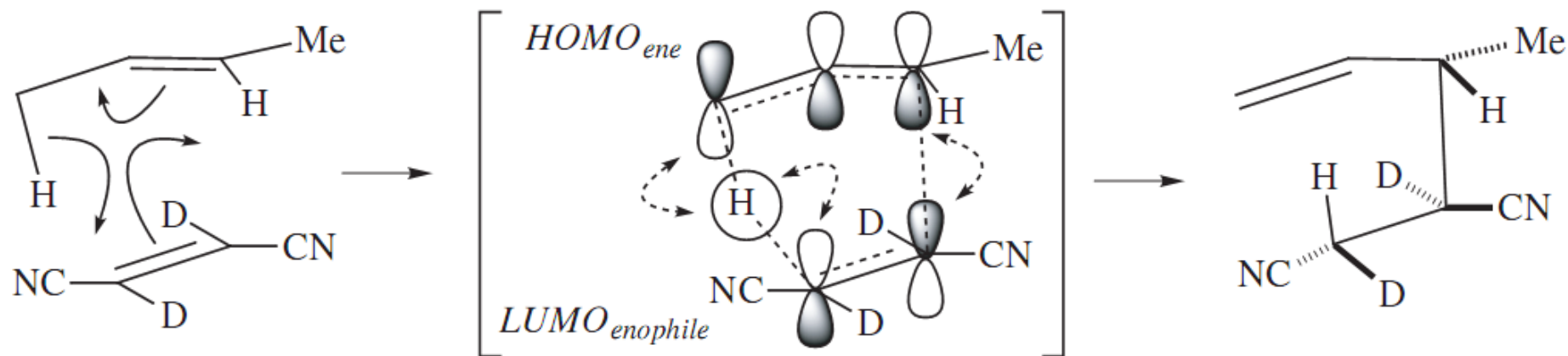


the Alder ene reaction



- The ene reaction shares some characteristics with both the Diels–Alder reaction and the [1,5] sigmatropic rearrangement.
- Like the Diels–Alder reaction:
  - The ene reaction is always a six-electron reaction
  - It has one four-electron component, **the ene**, and one two-electron component, **the enophile**. The two-electron component is a *pi* bond. The four-electron component consists of a *pi* bond and an allylic *sigma* bond.

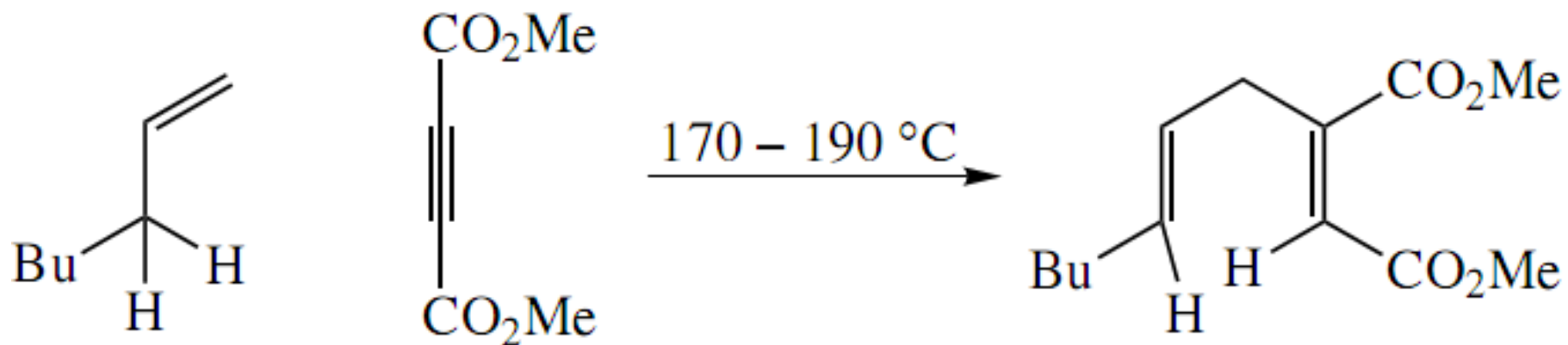
# Ene Reactions<sup>1</sup>



- The atom at the terminus of the *sigma* bond is **usually H**; the other five atoms involved in the ene reaction may be C or heteroatoms.
- Because the ene reaction involves **six electrons**, it is **suprafacial** with respect to all components.

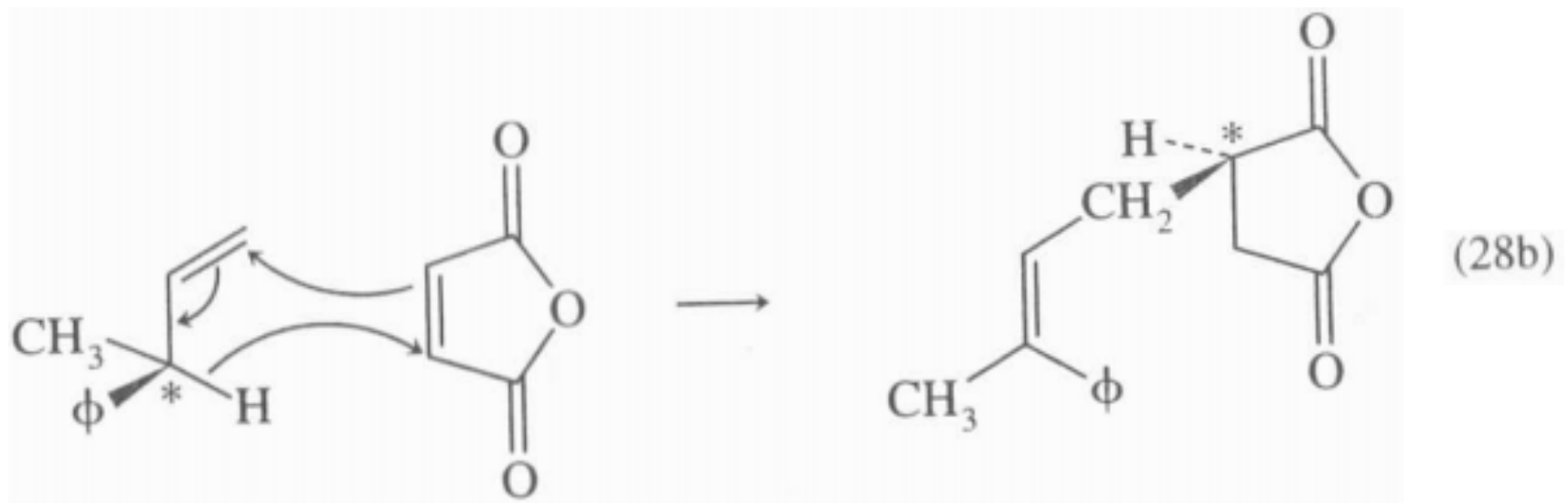
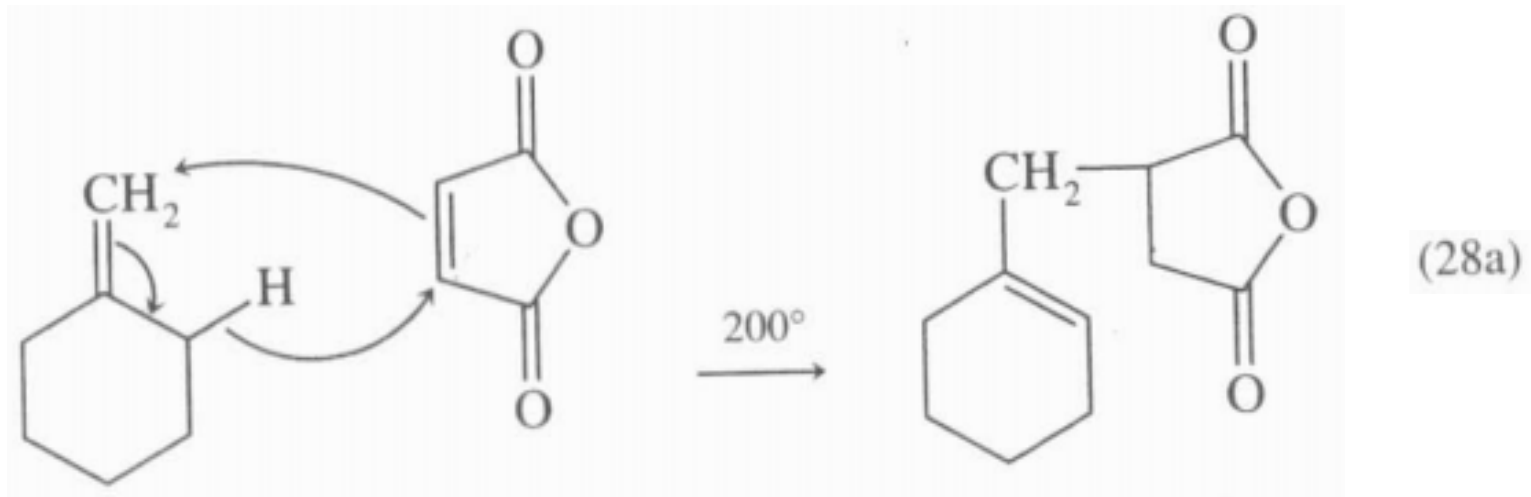
# Ene Reactions<sup>1</sup>

- The **suprafacial** reactivity of the enophile means that the two new bonds to the enophile form to the **same face**. When the enophile is an alkyne, the two new *sigma* bonds in the product **are cis** to one another.



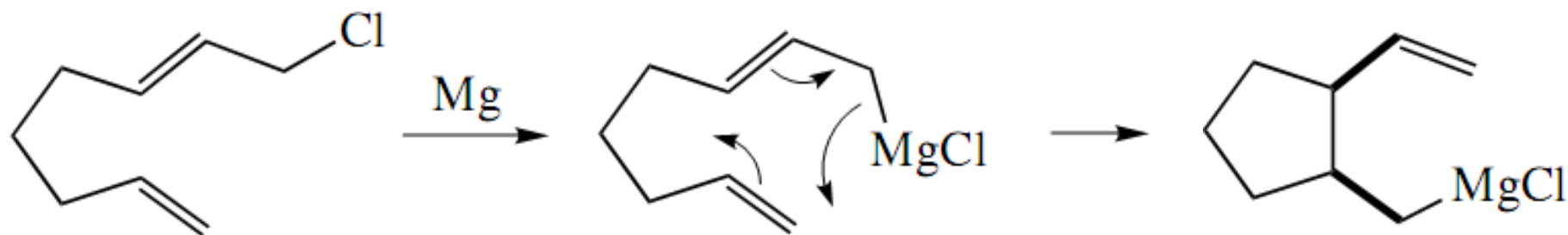
# Pericyclic Rearrangements

## Ene Reactions<sup>1</sup>



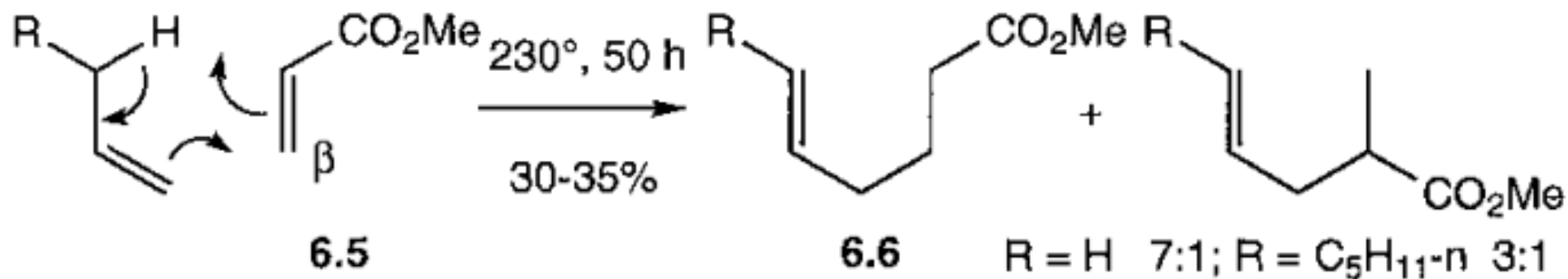
# Ene Reactions<sup>1</sup>

- Ene reactions involving five C atoms and one H usually **require very high temperatures (>200 °C)** to proceed. The reaction occurs at much lower temperature if the H atom is replaced with a **metal atom** in the *metalla-ene* reaction. The metal may be Mg, Pd, or another metal.



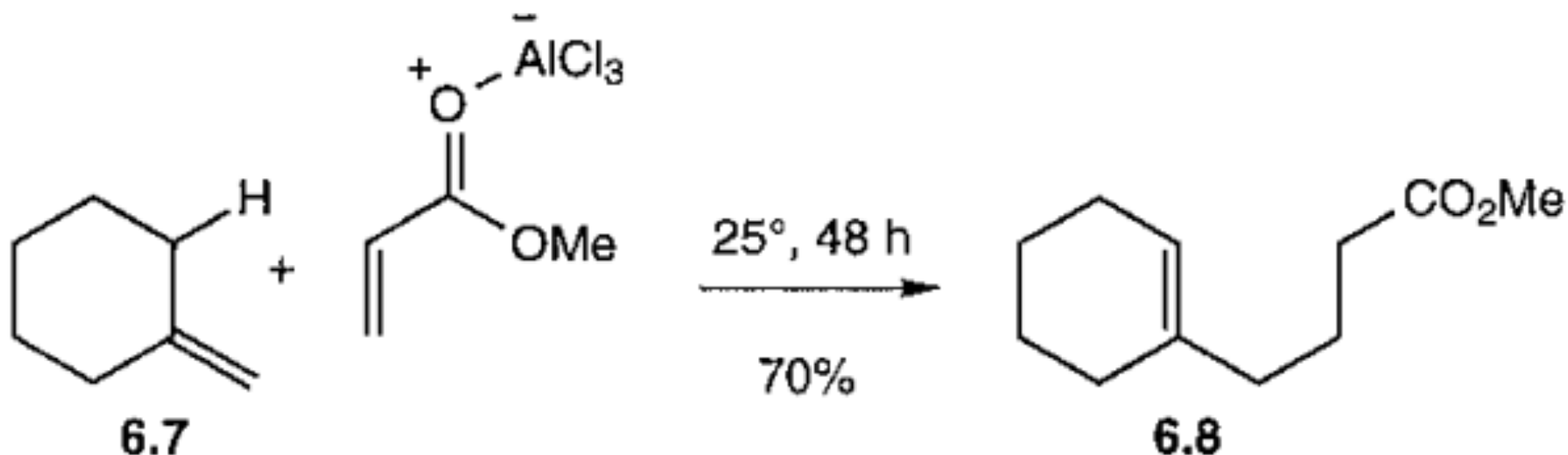
# Ene Reactions<sup>1</sup>

- As with Diels-Alder reactions, electron-withdrawing groups on the enophile and electron-donating groups on the ene **speed up** the reaction.
- The **regiochemistry** with an unsymmetrical enophile **6.5** is such that the major product **6.6** has the alkene carbon attacking the  $\beta$ -position of the enone system and the **hydrogen atom going to the  $\alpha$ -position**.



# Ene Reactions<sup>1</sup>

- **Lewis acid catalysis 6.7** → **6.8** has made the reaction much more amenable.<sup>1</sup>



- For most ordinary alkenes and enophiles, **Lewis acid catalysis** to make the enophile more electrophilic, **or an intramolecular reaction** (or both!), **is necessary for an efficient ene reaction.**<sup>2</sup>



# Pericyclic Rearrangements

## The Carbonyl Ene Reactions<sup>1</sup>

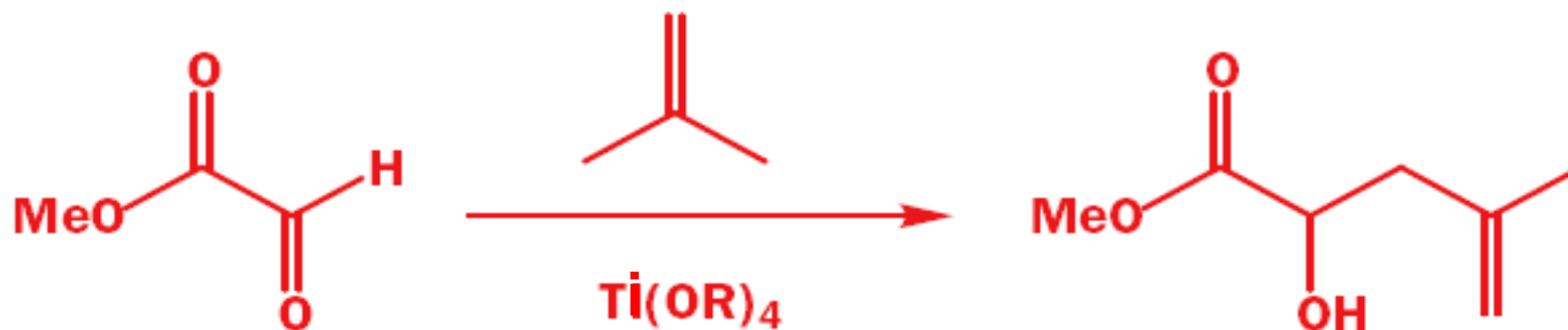
- **Carbonyl groups**, particularly in aldehydes, can act as “enophiles” in ene reactions. In these reactions, **allylic hydrogens** of alkenes are **transferred to carbonyl oxygens**, and the carbon atoms of the carbonyls react with the double bonds, converting the carbonyl groups to **alcohols**.<sup>1</sup>

the carbonyl ene reaction

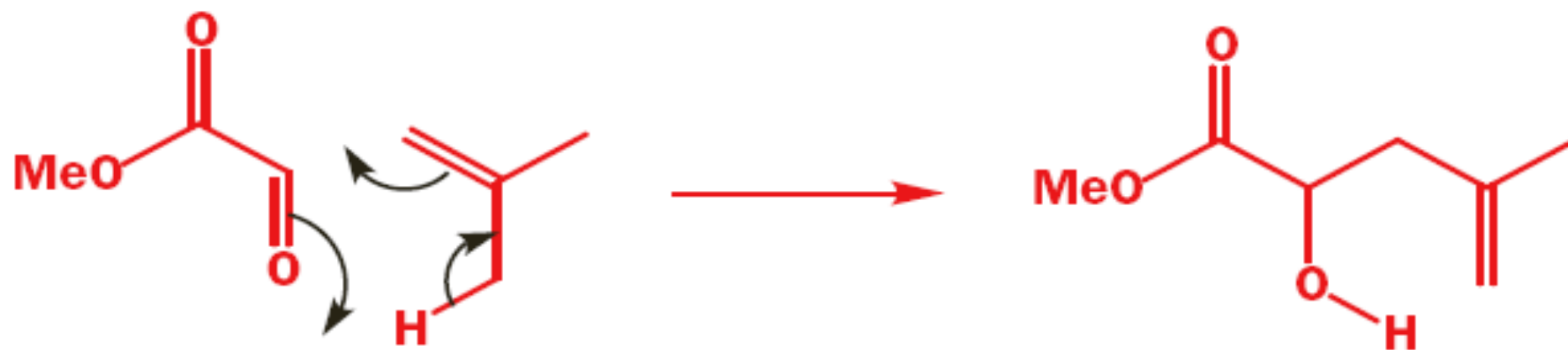


# The Carbonyl Ene Reactions<sup>1</sup>

- The important interaction is between the HOMO of the ene system and the LUMO of the carbonyl group—and a **Lewis-acid catalyst can lower the energy of the LUMO** still further.
- If there is a choice, the more electrophilic carbonyl group (the one with the lower LUMO) reacts.

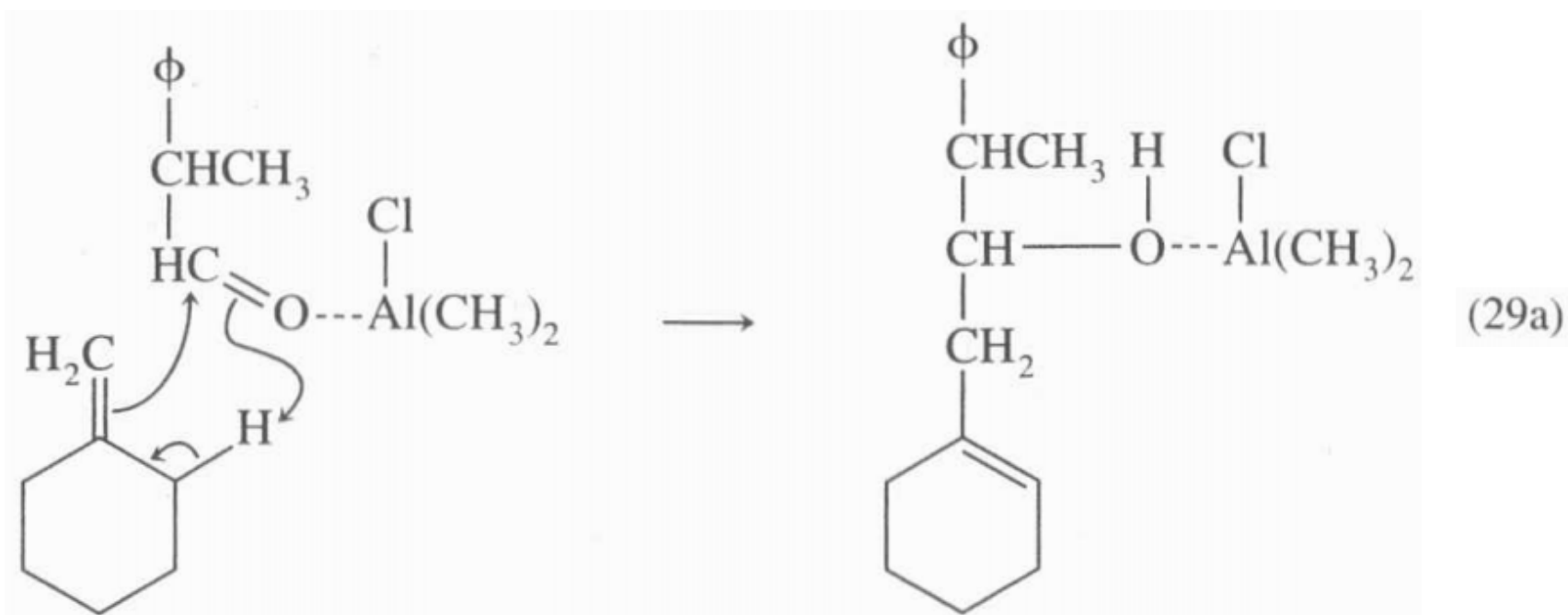


# The Carbonyl Ene Reactions<sup>1</sup>



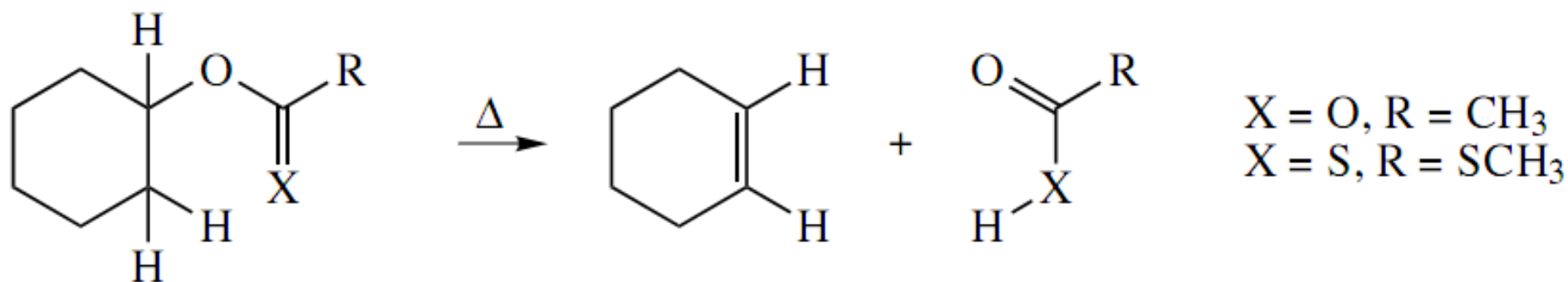
# The Carbonyl Ene Reactions<sup>1</sup>

- Ene reactions with carbonyl groups can be catalyzed by dimethylaluminum chloride as in **Eq. 29a**.



# Retro-Ene Reactions<sup>1</sup>

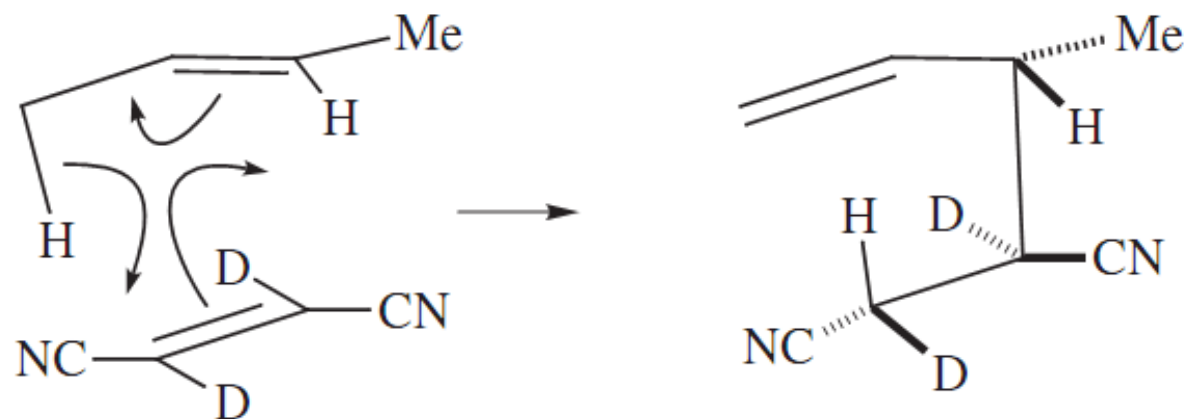
- A number of synthetically useful elimination reactions proceed thermally, with no base or acid required. These elimination reactions proceed through a **concerted retro-ene mechanism**. (The mechanism is sometimes called  $E_i$ .) The thermal elimination of acetic acid from alkyl acetates and the elimination of RSCOSH from alkyl xanthates (the **Chugaev reaction**) are **retro-ene reactions**.



- Retro-ene reactions are partly driven by the **gain in entropy**. (Entropic contributions to  $\Delta G^\circ$  are much **more important at the high temperatures** required for ene reactions.)

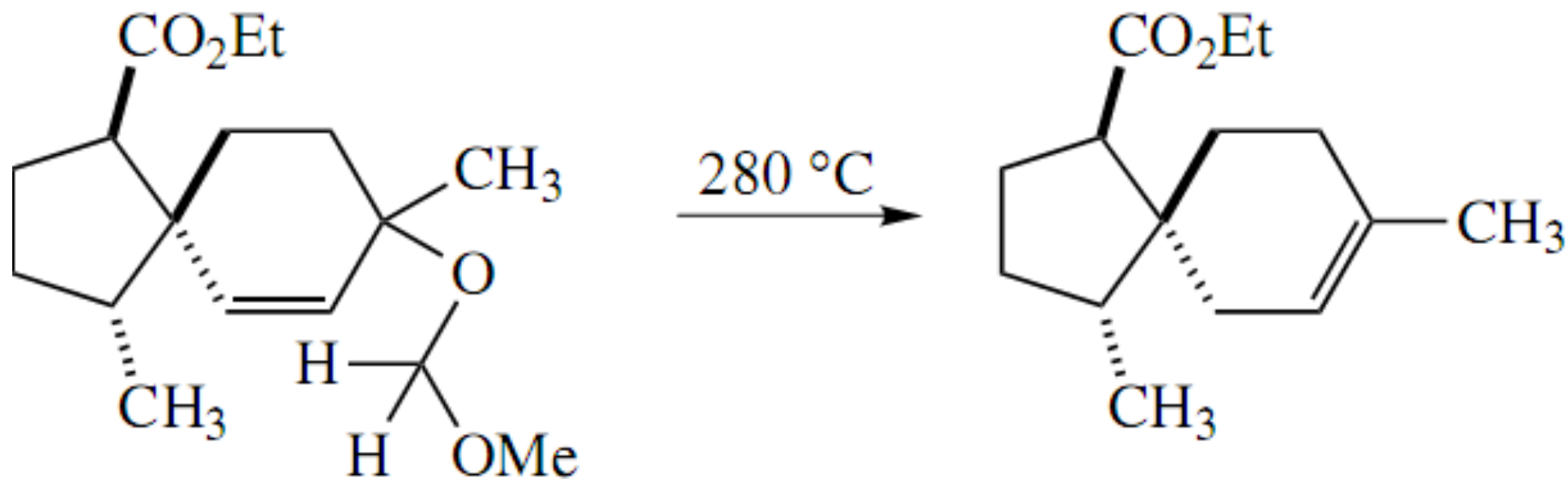
# Ene Reactions<sup>1</sup>

## ➤ Conclusions:



- **Ene reactions** make **one new *sigma* bond** at the expense of **one *pi* bond**, like electrocyclic reactions, but they are fairly easy to distinguish from electrocyclic reactions otherwise. **Look for allylic transposition of a double bond and transfer of an allylic H atom.**
- **In a retro-ene reaction**, a nonallylic H is transferred to an allylic position and **one new *pi* bond** at the expense of **one *sigma* bond**.

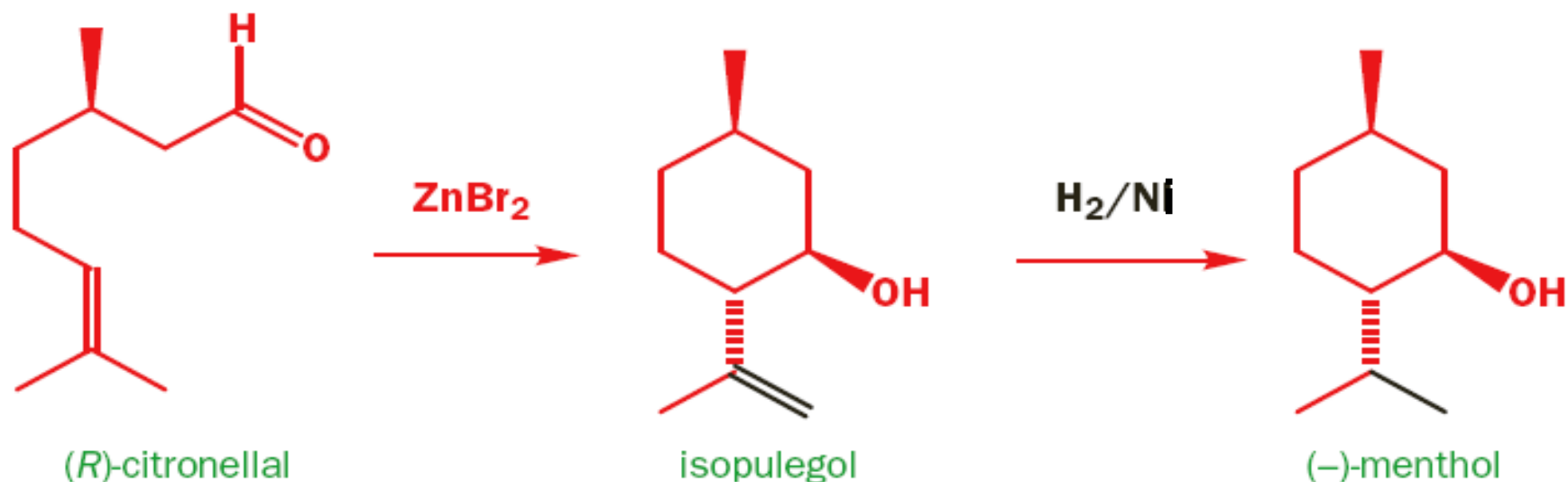
# Retro-Ene Reactions<sup>1</sup>



- **Homework:** Write the mechanism of the previous reaction and the structure of any other by-products?

# The Carbonyl Ene Reactions<sup>1</sup>

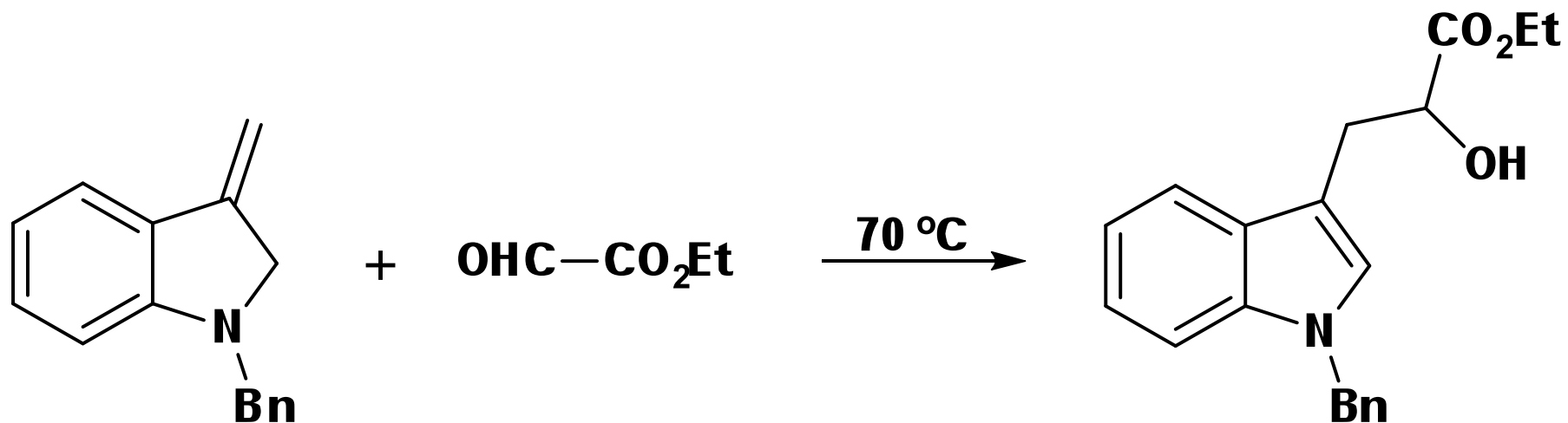
- One carbonyl ene reaction is of **commercial importance** as it is part of a process for the production of **menthol** used to give a **peppermint smell** and taste to many products. This is an **intramolecular ene reaction**.



- **Homework:** Write the mechanism of the first step reaction?



# The Carbonyl Ene Reactions<sup>1</sup>



- **Homework:** Write the mechanism of the previous reaction?