

**DAMIETTA  
UNIVERSITY**

**CHEM-405:  
PERICYCLIC REACTIONS**

**LECTURE 10**

**Dr Ali El-Agamey**

# LEARNING OUTCOMES

## LECTURE 10

### ➤ (1) Sigmatropic rearrangements

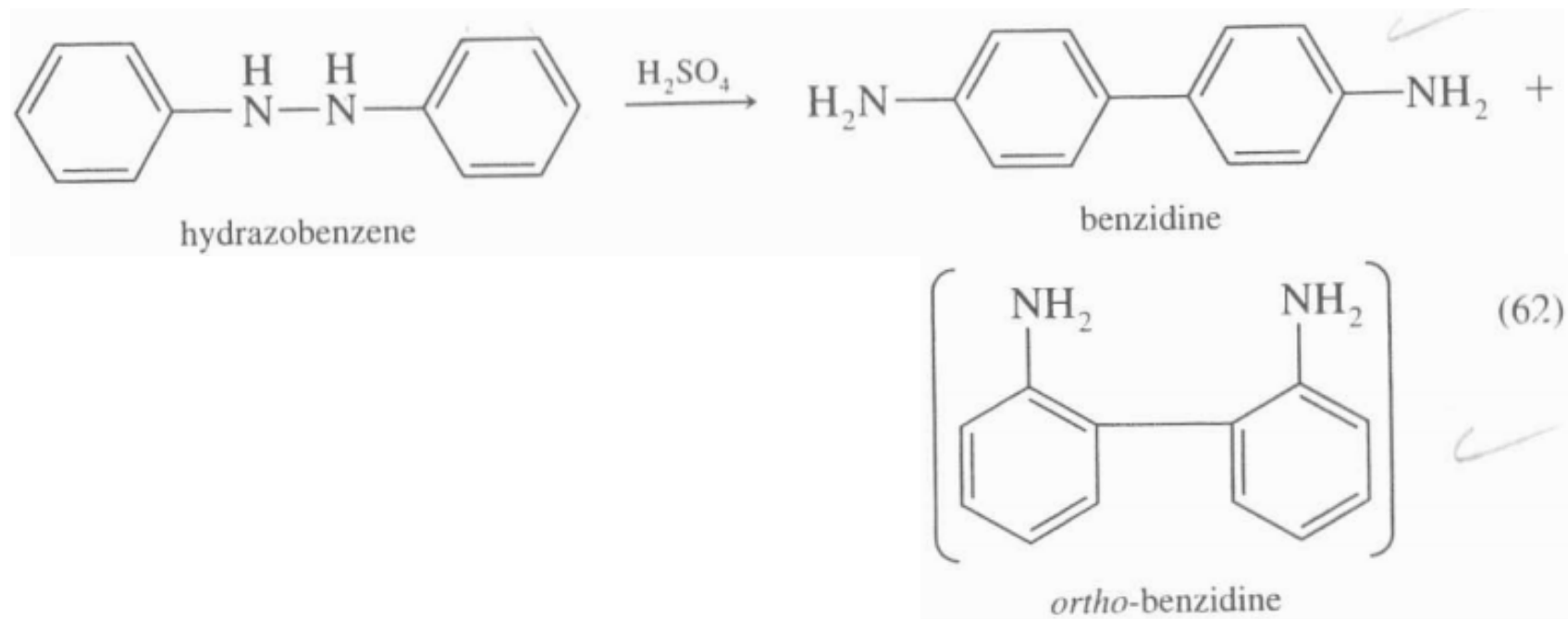
-Acid catalysis

- [2,3] sigmatropic rearrangements

# Sigmatropic Rearrangements

## Acid catalysis

- Some types of sigmatropic shifts were reported to occur **solely** as acid-catalyzed processes. The best known example is **benzidine rearrangements**.<sup>1</sup>

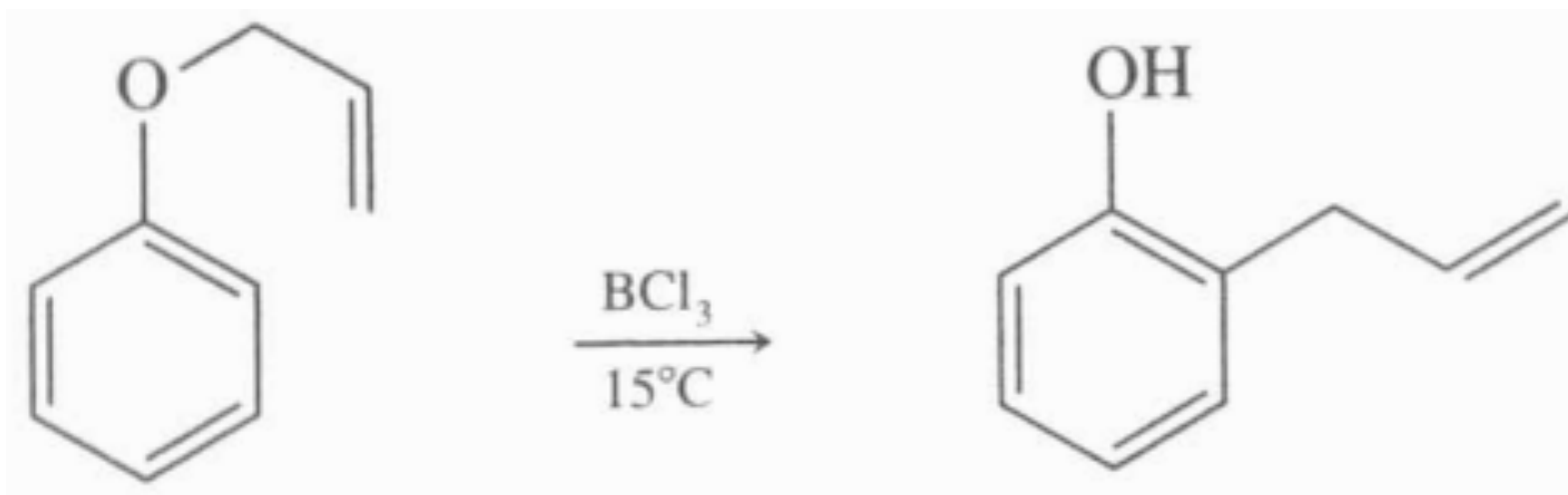


- **Homework:** Write the mechanism of the previous reaction?

# Sigmatropic Rearrangements

## Acid catalysis

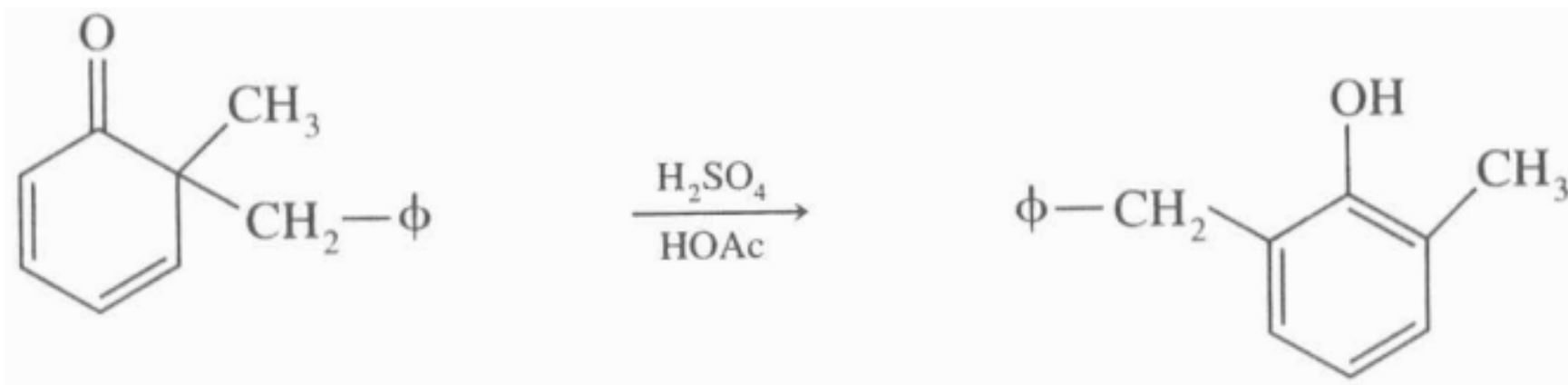
- Other examples : The addition of Lewis acid catalysts, e.g.  $\text{BCl}_3$ , **lowers** the temperatures necessary for **Claisen rearrangements** of allyl phenyl ethers **from about 200 °C to below RT.**



# Sigmatropic Rearrangements

## Acid catalysis

- **[1,5] shifts** of benzyl groups in cyclohexadienones, which **requires temperatures above 150 °C** in the absence of catalysis, **proceed at RT** when catalyzed by solutions of sulfuric acid in acetic acid.



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

# [m,n] Sigmatropic Rearrangements

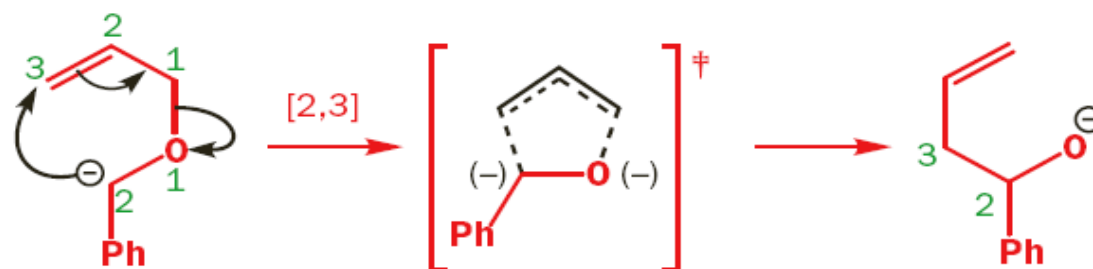
## [2,3] sigmatropic rearrangements:

- The [2,3]-sigmatropic rearrangement is a thermal isomerization reaction involving **six electrons** and a five-membered cyclic TS.<sup>1</sup>
- The [2,3] sigmatropic rearrangement of alloxycarbanions is known as the *Wittig rearrangement*.<sup>2</sup>



# [m,n] Sigmatropic Rearrangements

[2,3] sigmatropic rearrangements:

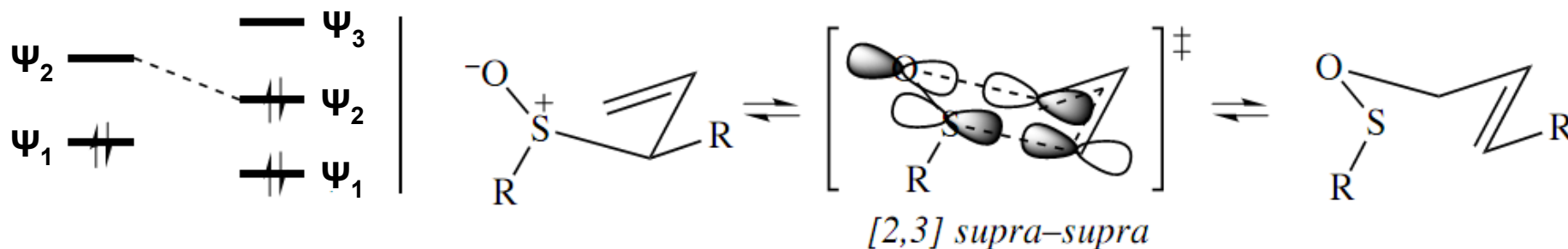


- The starting material is a benzyl allyl ether and undergoes [2,3]-sigmatropic rearrangement to make a new C–C sigma bond at the expense of a C–O sigma bond—a bad bargain this as the **C–O bond is stronger**.<sup>1</sup>
- The balance is tilted by the **greater stability of the oxyanion** in the product than of the **carbanion** in the starting material. The new bond has a 2,3 relationship to the old and the **TS is a five-membered ring**.<sup>1</sup>

# [m,n] Sigmatropic Rearrangements

## [2,3] sigmatropic rearrangements:

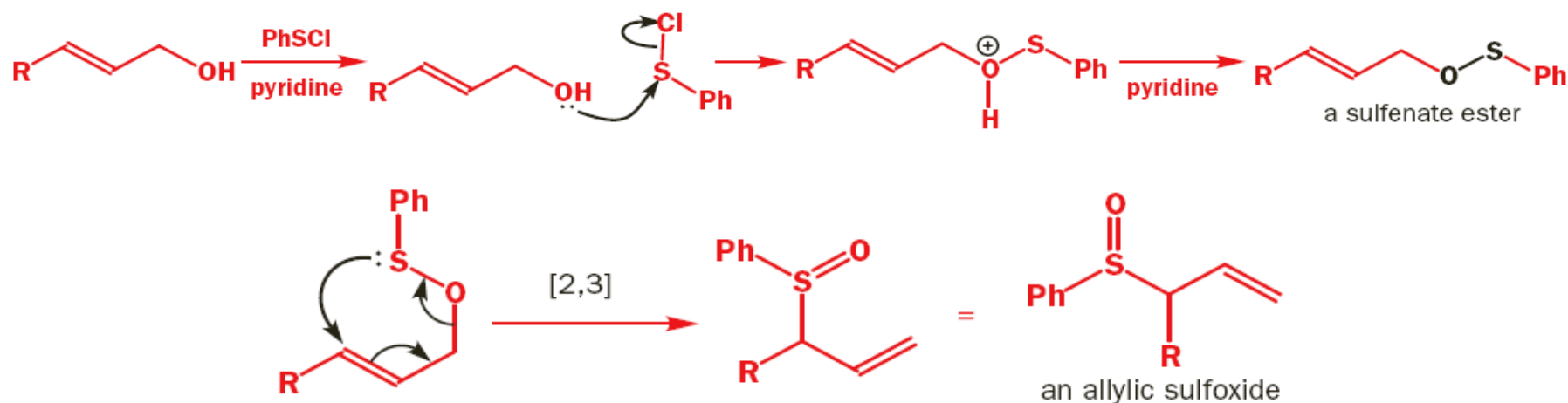
- The dominant FMO interaction in the TS of the [2,3] sigmatropic rearrangement is between  $\Psi_2$  of both components. The reaction proceeds **suprafacially** with respect to both components.<sup>1,2</sup>





# [m,n] Sigmatropic Rearrangements

[2,3] sigmatropic rearrangements:



- Reaction of an allylic alcohol with PhSCl gives an **unstable** sulfenate ester that rearranges on heating to an allylic sulfoxide by a [2,3]-sigmatropic rearrangement involving both O and S.<sup>1</sup>

# [m,n] Sigmatropic Rearrangements

[2,3] sigmatropic rearrangements:

- **The key** to identifying a [2,3] sigmatropic rearrangement is that **an allylic group migrates from a heteroatom to an adjacent atom** (which may be C or another heteroatom).<sup>1</sup>

# Questions

- **Homework:** Write the structure of **A** and the mechanism of the following reaction?

