

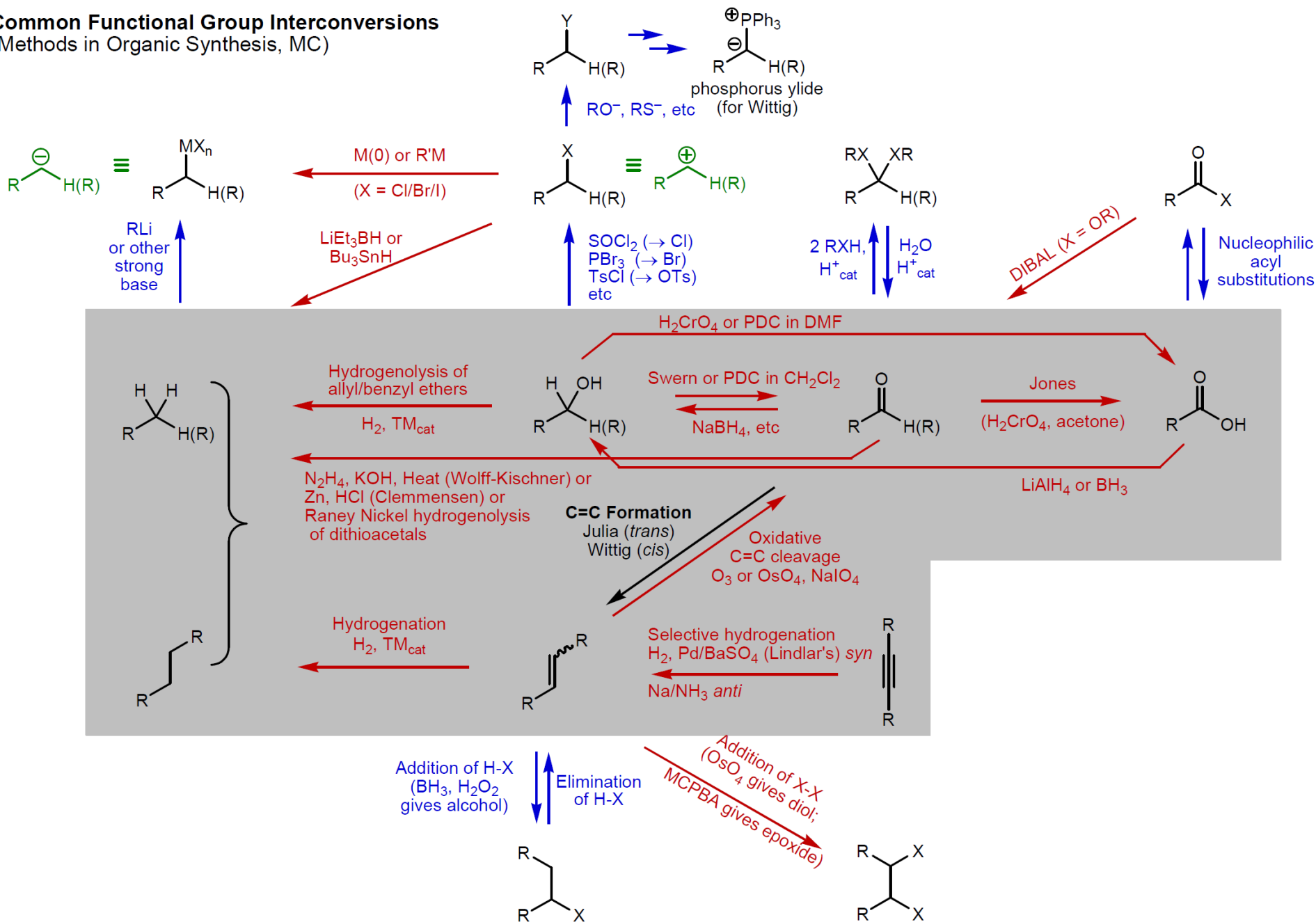
**University of Zagreb**  
**Faculty of Chemical Engineering and Technology**  
**Study programme Chemical and Environmental Technology**

# **FORMATION OF NEW C=C BOND**

**Prof. Marijana Hranjec, PhD**

**Academic year 2024/2025**

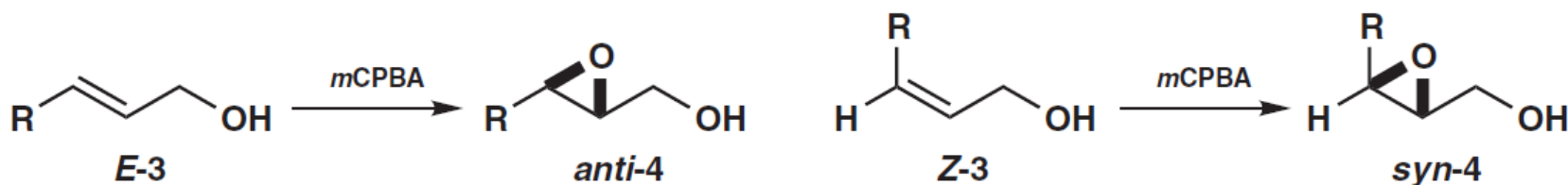
## Common Functional Group Interconversions (Methods in Organic Synthesis, MC)



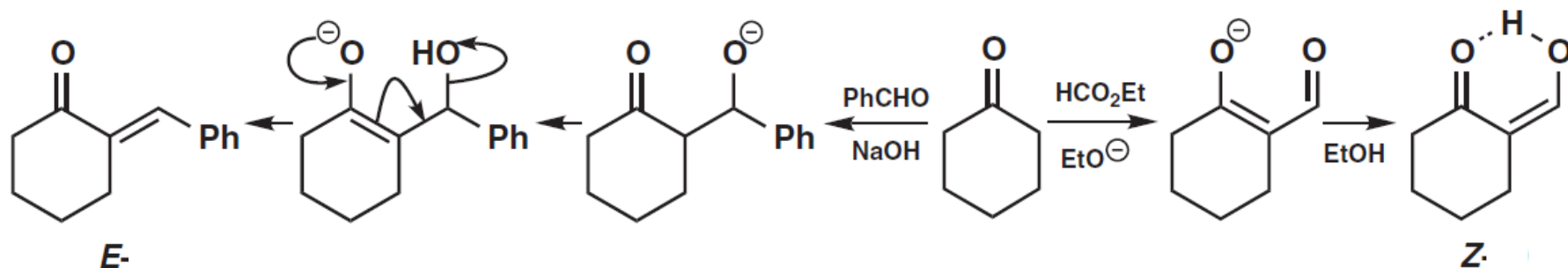
# 1. CREATION OF DOUBLE BONDS OF DEFINED STEREOCHEMISTRY

## Introduction

- ❖ The C = C bond in the allyl alcohol may be E or Z depending on the synthesis method



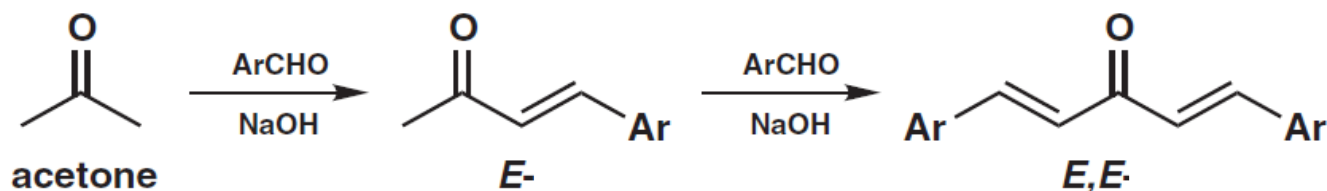
- ❖ in Claisen condensation of cyclohexanone with ethyl formate a more stable Z-enol ketoaldehyde is formed while in condensation with benzaldehyde an E-product is formed



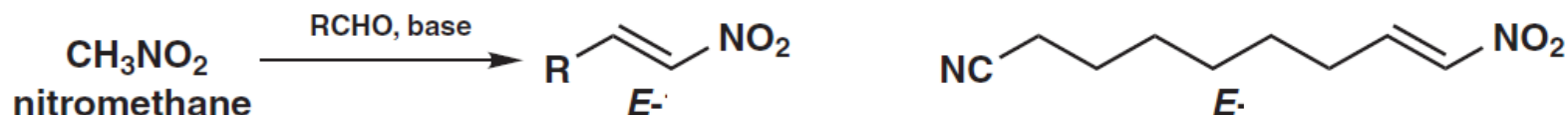
# 1. CREATION OF DOUBLE BONDS OF DEFINED STEREOCHEMISTRY

## Reactions yielding *E*-isomers

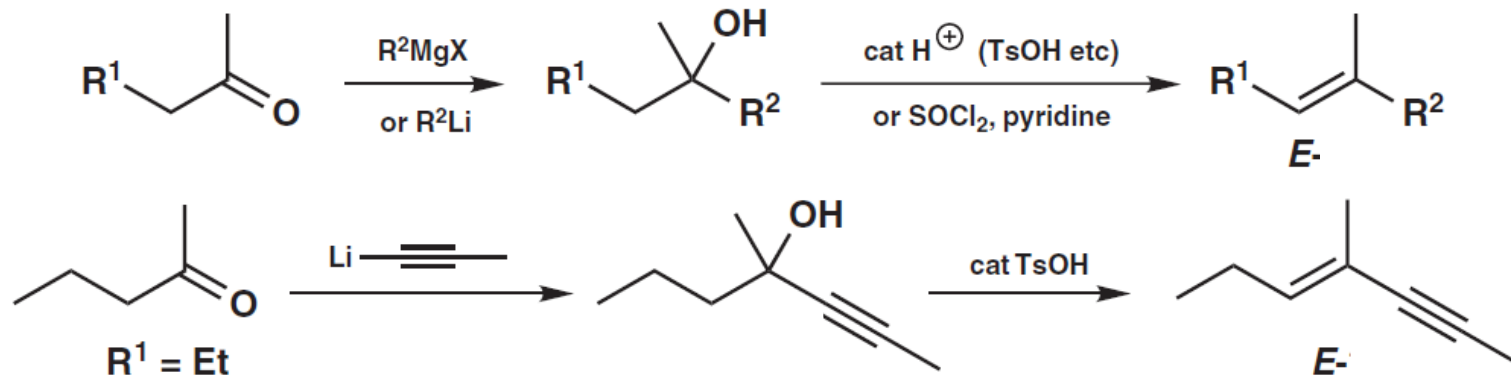
### 1. Aldol reactions followed by dehydration



### 2. Base-catalyzed condensation of nitromethane with aldehydes

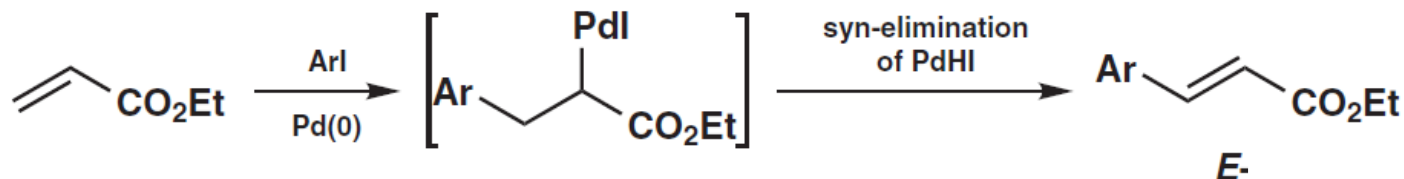


### 3. Dehydration of tertiary alcohols

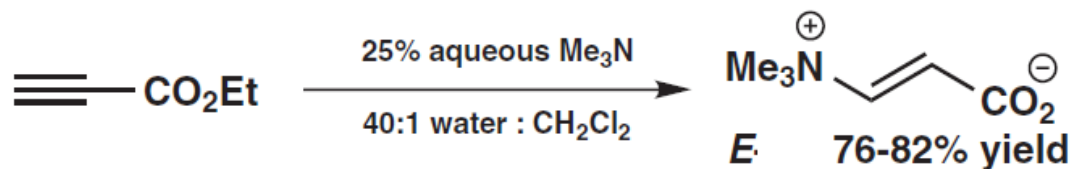


# 1. CREATION OF DOUBLE BONDS OF DEFINED STEREOCHEMISTRY

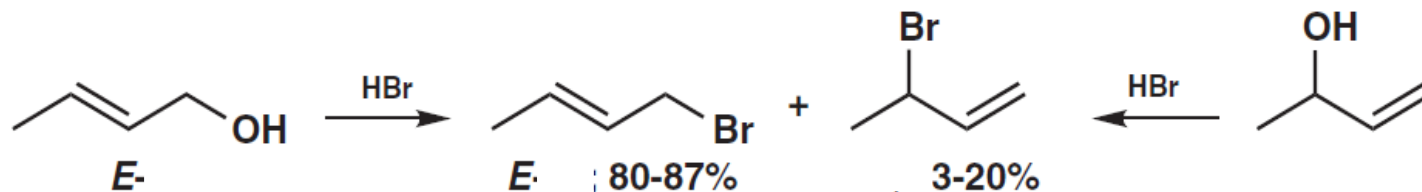
## 4. Heck reaction with $\alpha,\beta$ -unsaturated carbonyl compounds



## 5. Nucleophile addition on $\alpha,\beta$ -unsaturated alkynes

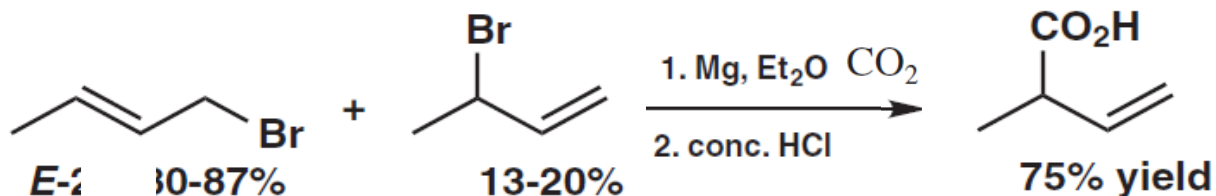
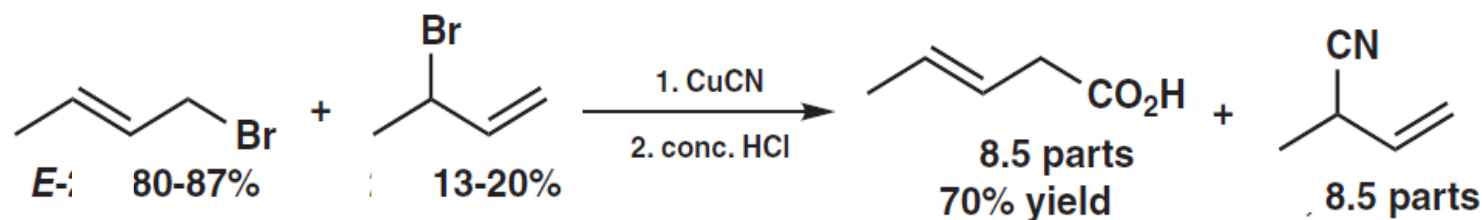


## 6. From allyl alcohols and allyl halides via allylic cation



# 1. CREATION OF DOUBLE BONDS OF DEFINED STEREOCHEMISTRY

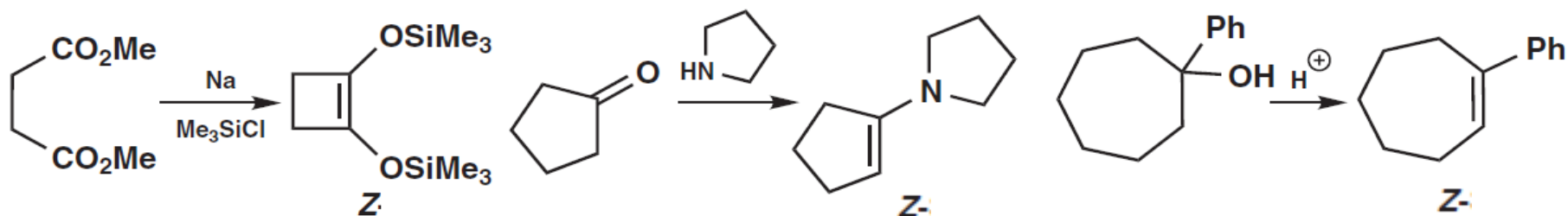
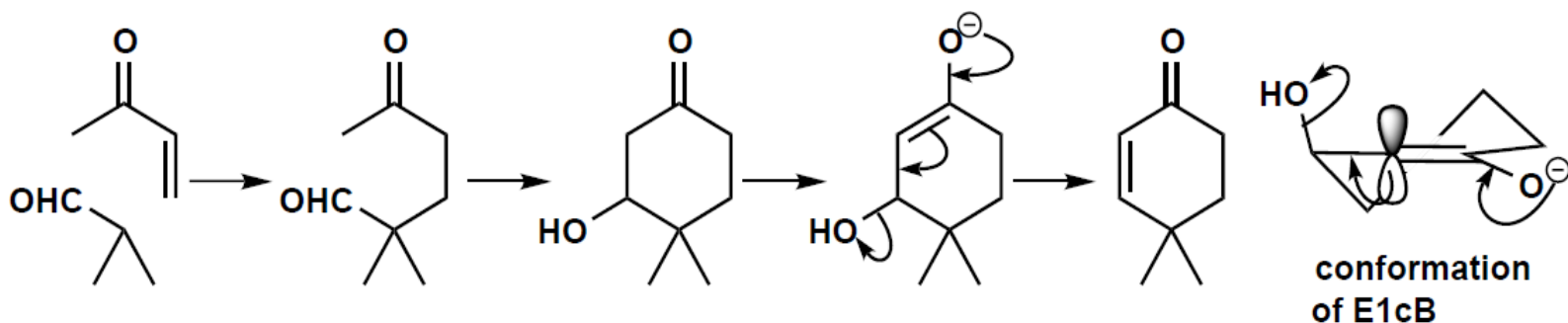
## 7. From organometal complexes of allyl halides



# 1. CREATION OF DOUBLE BONDS OF DEFINED STEREOCHEMISTRY

## 1. Only 1 alkene is formed: cyclic cis (*Z*) alkenes

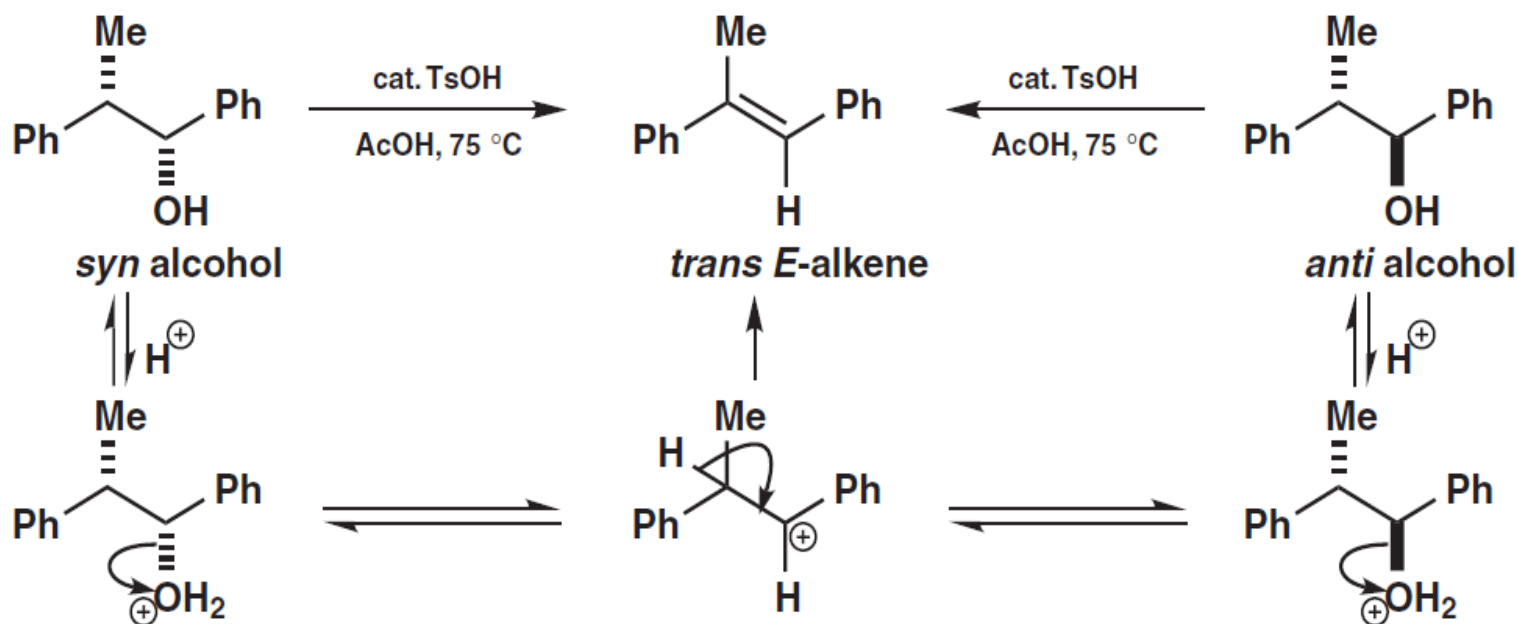
- ❖ alkenes in 3- to 7-membered rings are exclusively cis (*Z*) isomers; 8-membered rings may form trans (*E*) alkenes but are unstable; from the 12-membered rings further, trans (*E*) isomers are formed as more stable isomers



# 1. CREATION OF DOUBLE BONDS OF DEFINED STEREOCHEMISTRY

## 2. Two alkenes are in equilibrium and *trans* (*E*) is formed

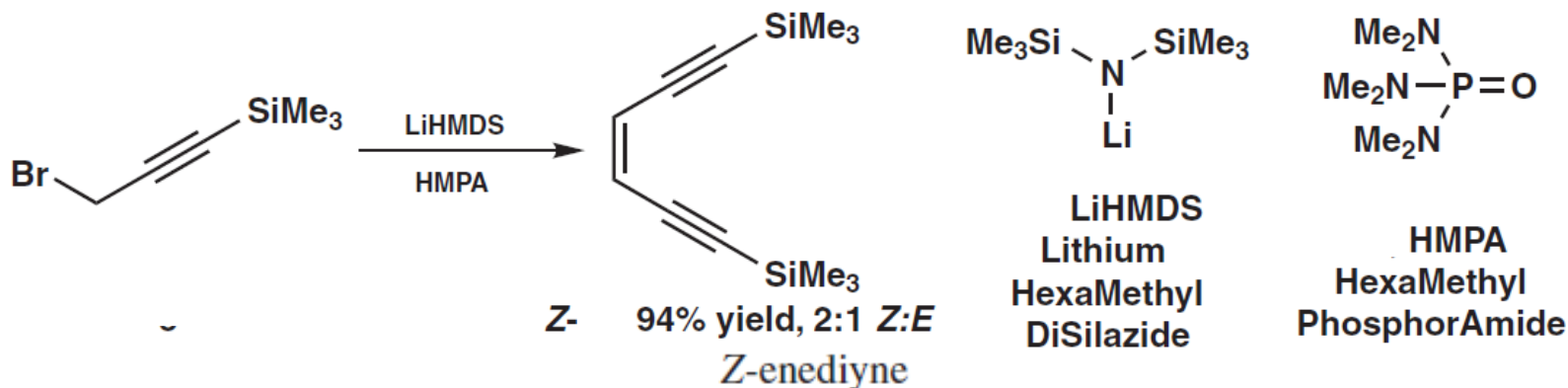
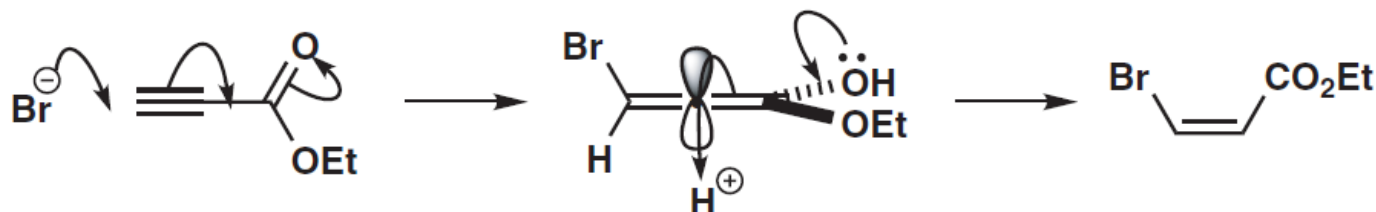
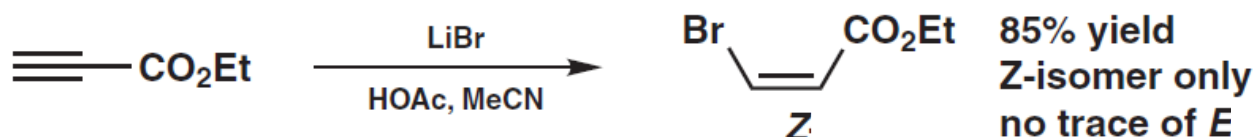
- ❖ in the reaction of both diastereomers of  $\sigma$ -alcohol with acid the same mixture of alkenes is formed in which the *trans* isomer dominates



# 1. CREATION OF DOUBLE BONDS OF DEFINED STEREOCHEMISTRY

## 3. *Cis* (*Z*) alken is formed stereoselective

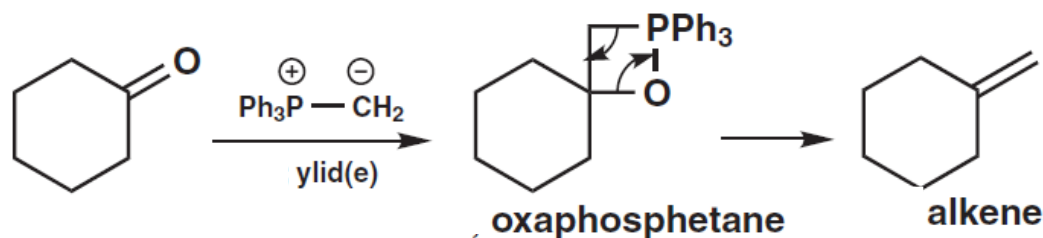
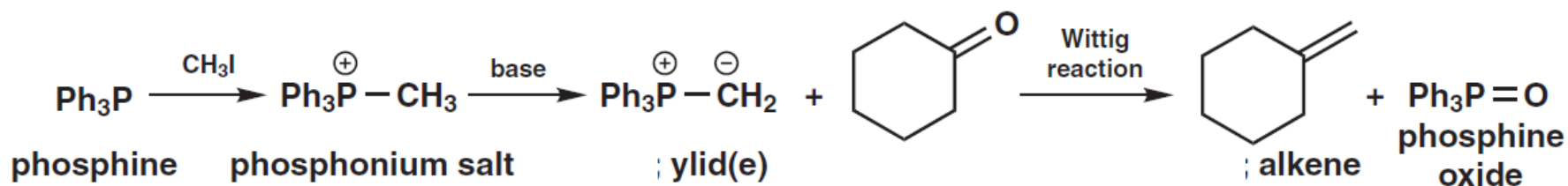
- ❖ Michael's alkyne addition
- ❖ there is no free rotation in the alene intermediate



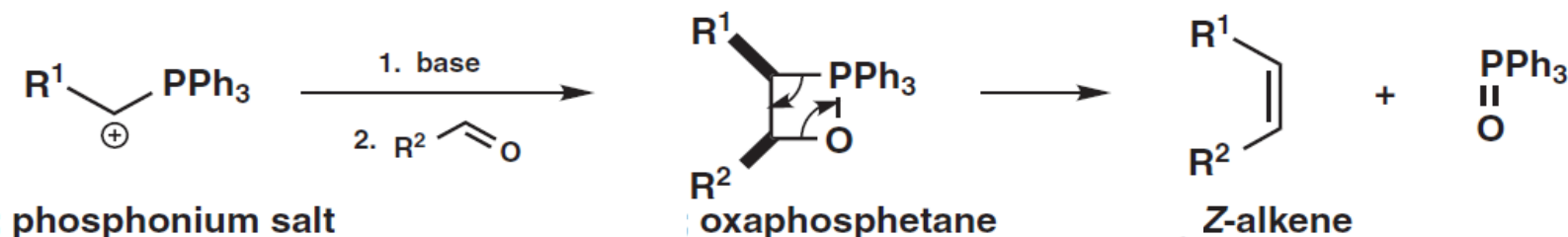
# 1. CREATION OF DOUBLE BONDS OF DEFINED STEREOCHEMISTRY

## Wittig reaction

- ❖ with aldol condensation and Diels-Alder reaction, one of the most important reactions in organic synthesis

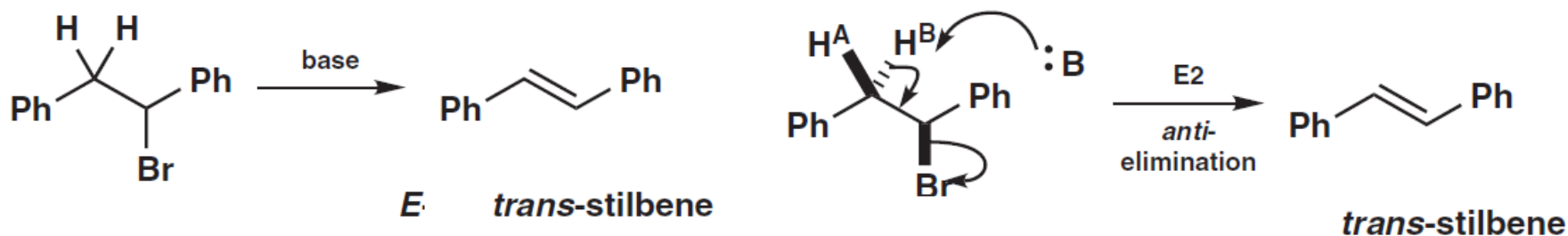


- ❖ the last stage of the Wittig reaction is stereospecific



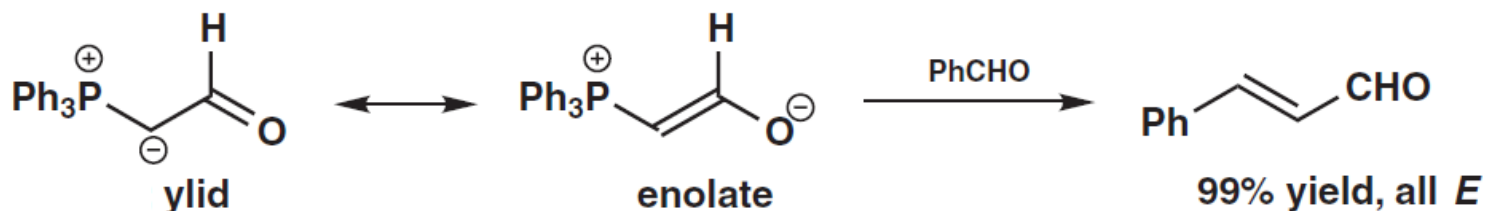
# 1. CREATION OF DOUBLE BONDS OF DEFINED STEREOCHEMISTRY

## 4. *Trans (E)* alkene is formed stereoselective E2 elimination reactions



## Trans selective Wittig reaction

- simple ylides show Z-selectivity while ylides in which the carbanion is stabilized except with the P<sup>+</sup> atom, and with some conjugate group, most often carbonyl, show E-selectivity

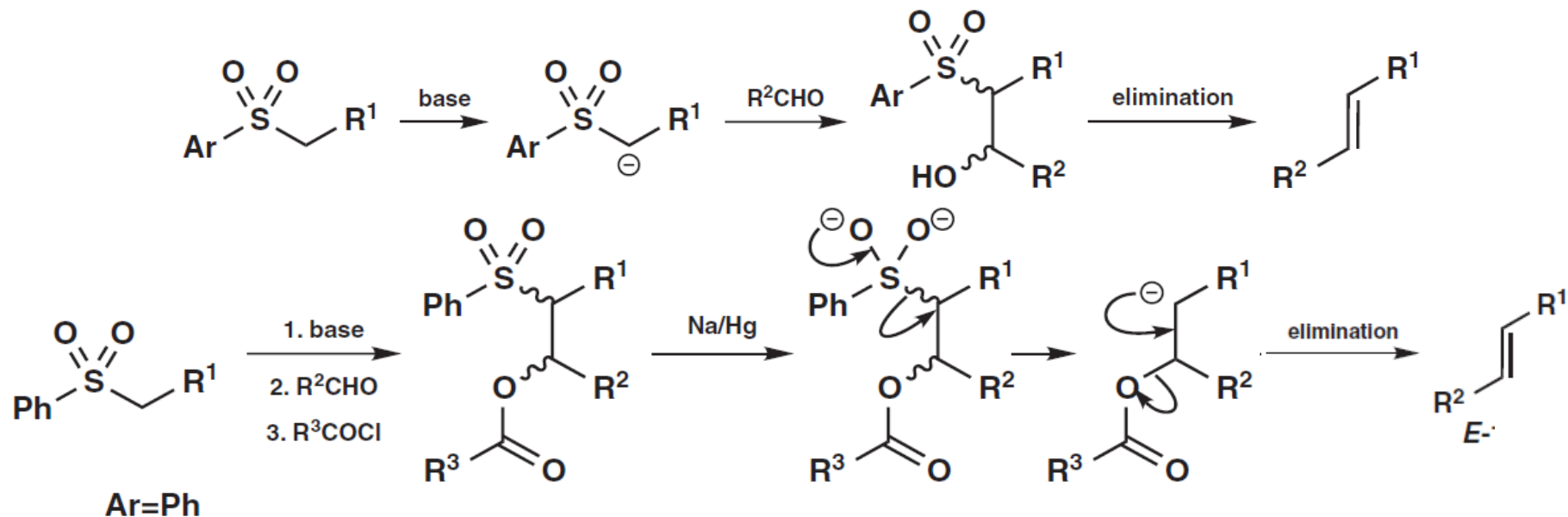


# 1. CREATION OF DOUBLE BONDS OF DEFINED STEREOCHEMISTRY

## Stereoselective methods for *E*-alkene:

### 1. "Julia" reaction

- ❖ similar to the Wittig reaction but sulfonium salts are used instead of the phosphonium salt
- ❖ the difference is in the stereoselective elimination step and both diastereomers of the intermediate give the same isomer in the case of straight-chain compounds
- ❖ elimination produces mostly the *E*-isomer and in the case of cyclic compounds the *Z*-isomer



# 1. CREATION OF DOUBLE BONDS OF DEFINED STEREOCHEMISTRY

## Interconversion of *E* i *Z* alkenes

### Photochemical isomerization in *Z*-isomer

- ❖ irradiated a more stable *E*-isomer at higher wavelengths produces a less stable *Z*-isomer

