

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

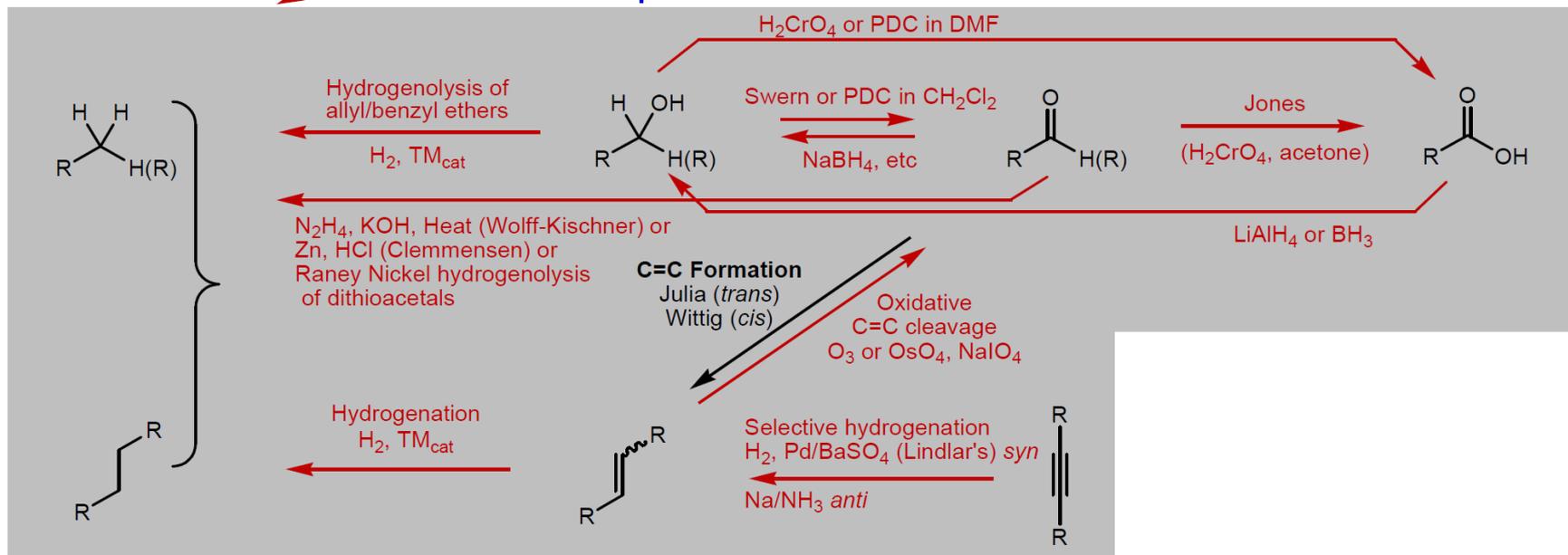
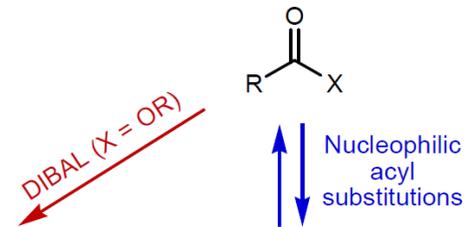
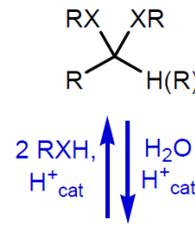
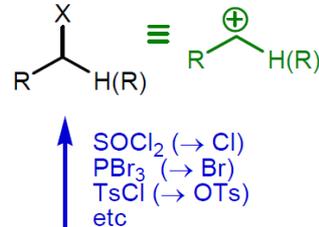
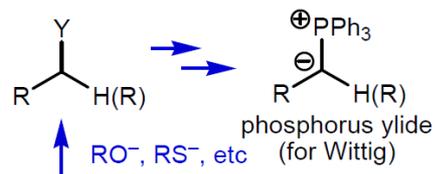
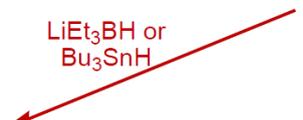
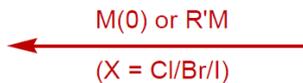
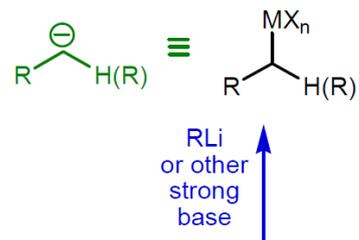
FORMATION OF NEW C=C BOND

Prof. Marijana Hranjec, PhD

Academic year 2024/2025

Common Functional Group Interconversions

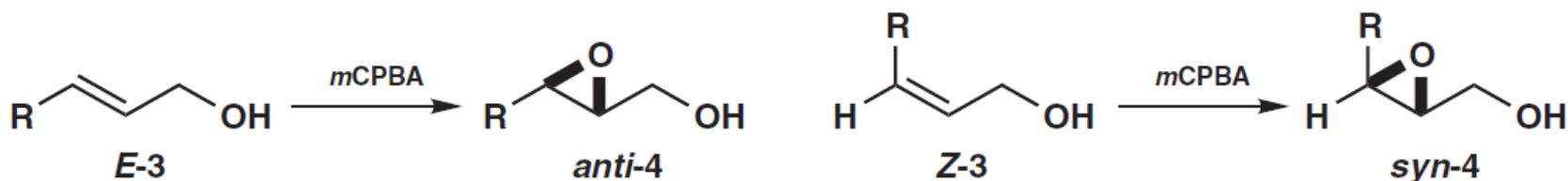
(Methods in Organic Synthesis, MC)



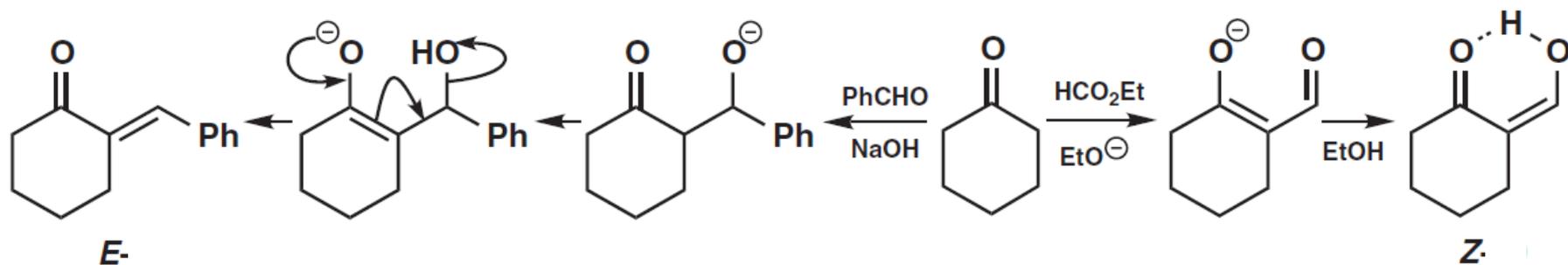
1. CREATION OF DOUBLE BONDS OF DEFINED STEREOCHEMISTRY

Introduction

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



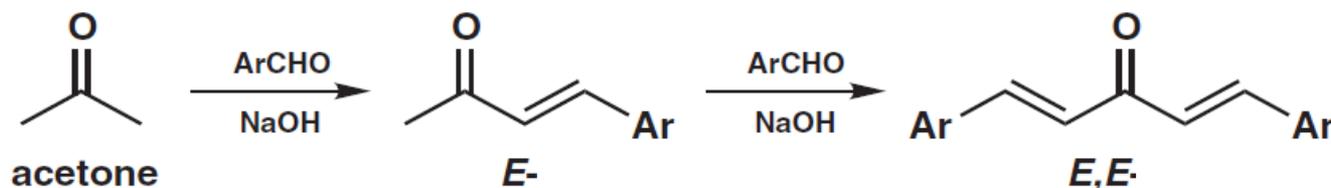
- ❖ in Claisen condensation of cyclohexanone with ethyl formate a more stable *Z*-enol ketoaldehyde is formed while in condensation with benzaldehyde an *E*-product is formed



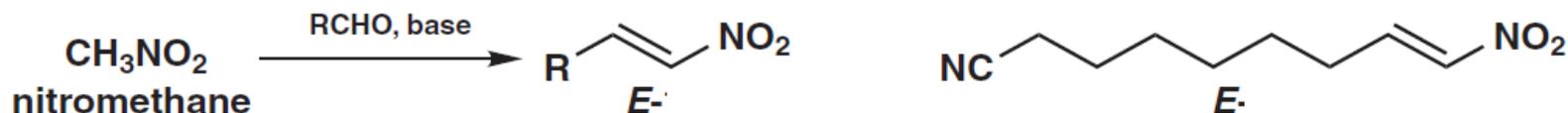
1. CREATION OF DOUBLE BONDS OF DEFINED STEREOCHEMISTRY

Reactions yielding *E*-isomers

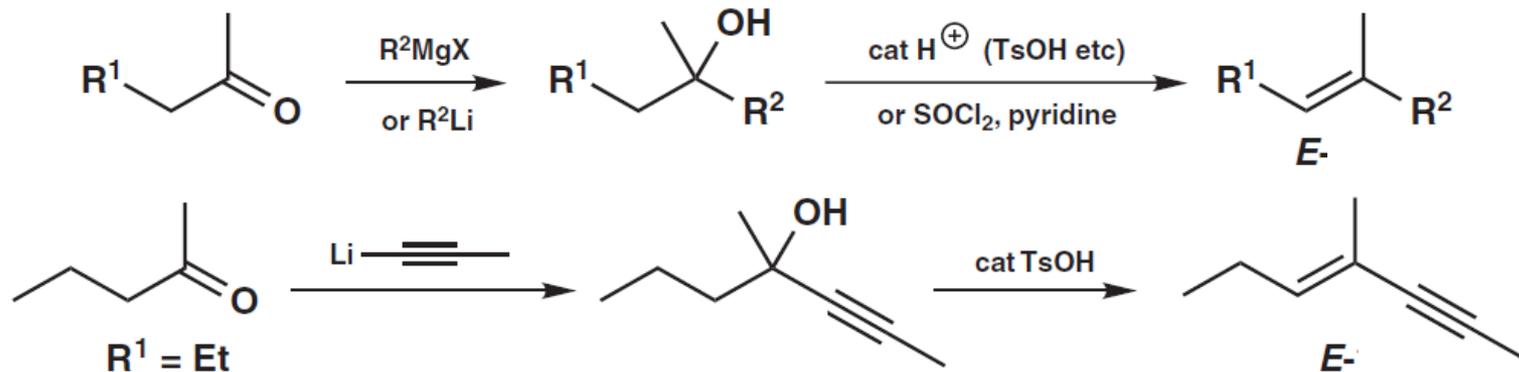
1. Aldol reactions followed by dehydration



2. Base-catalyzed condensation of nitromethane with aldehydes

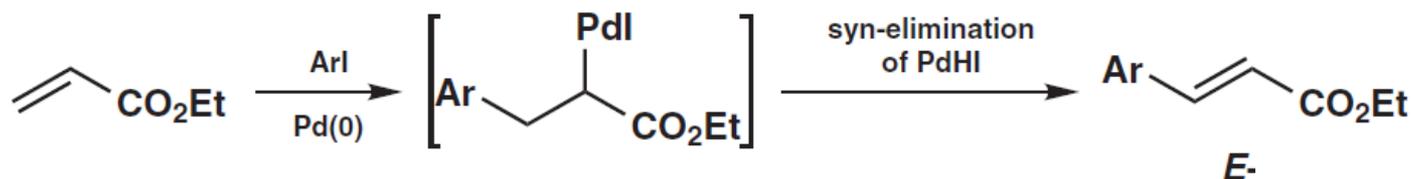


3. Dehydration of tertiary alcohols

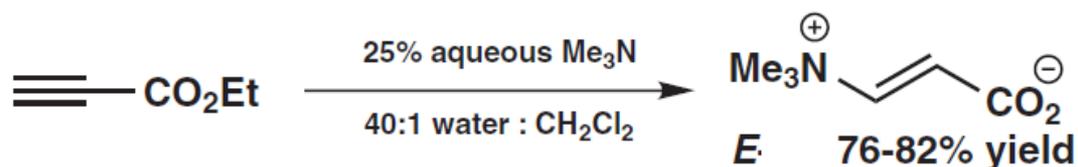


1. CREATION OF DOUBLE BONDS OF DEFINED STEREOCHEMISTRY

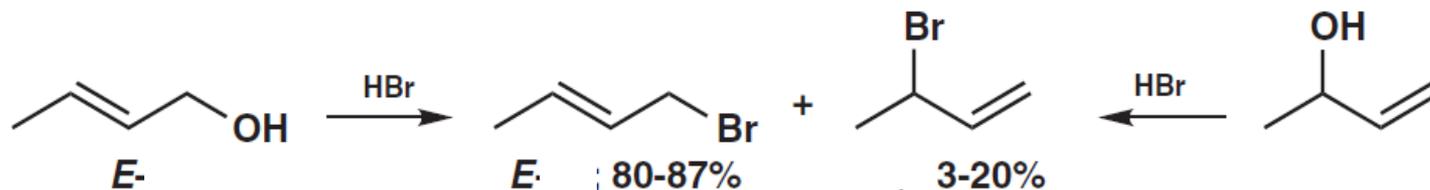
4. Heck reaction with α,β -unsaturated carbonyl compounds



5. Nucleophile addition on α,β -unsaturated alkynes

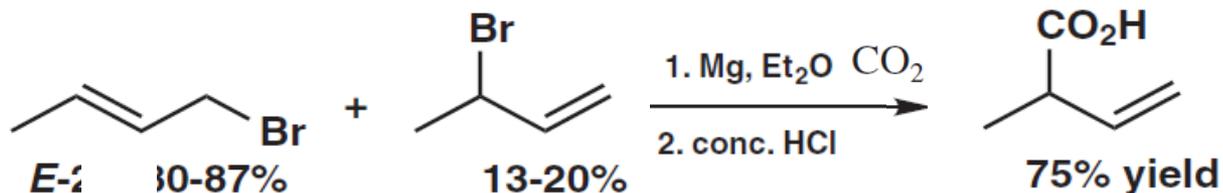
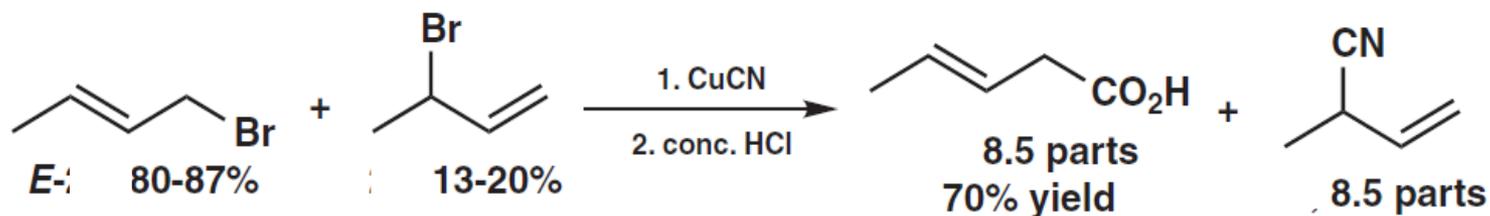


6. From allyl alcohols and allyl halides via allylic cation



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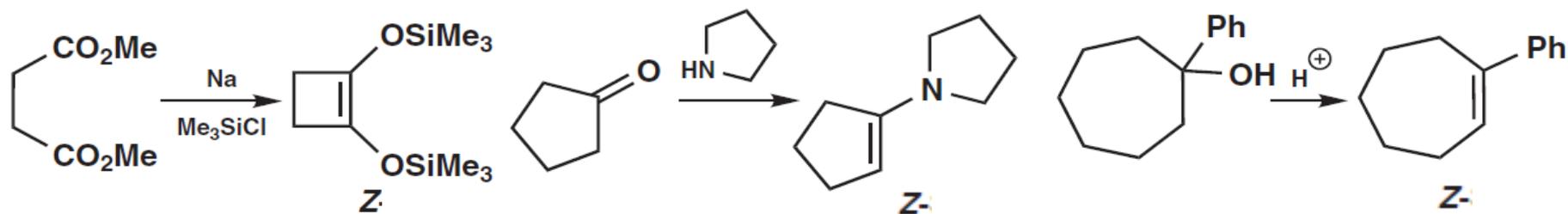
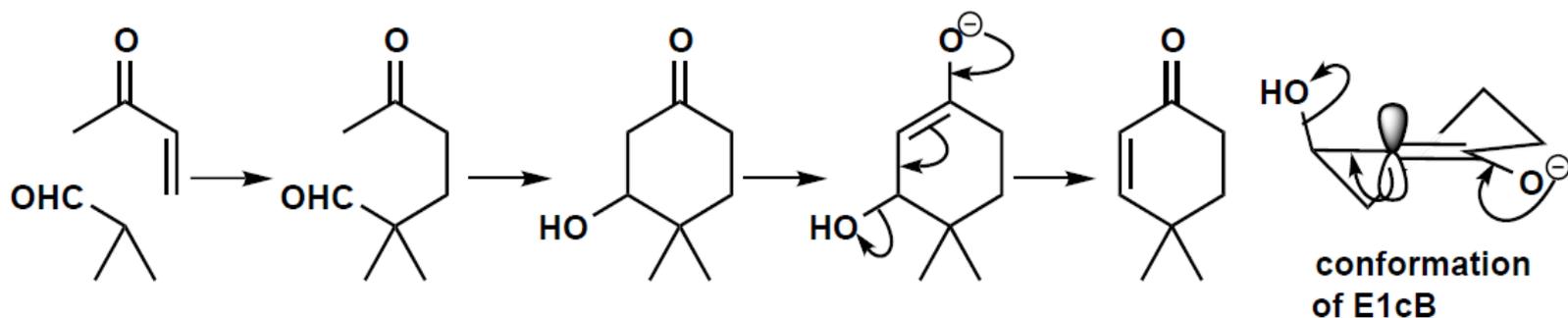
7. From organometal complexes of allyl halides



1. CREATION OF DOUBLE BONDS OF DEFINED STEREOCHEMISTRY

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

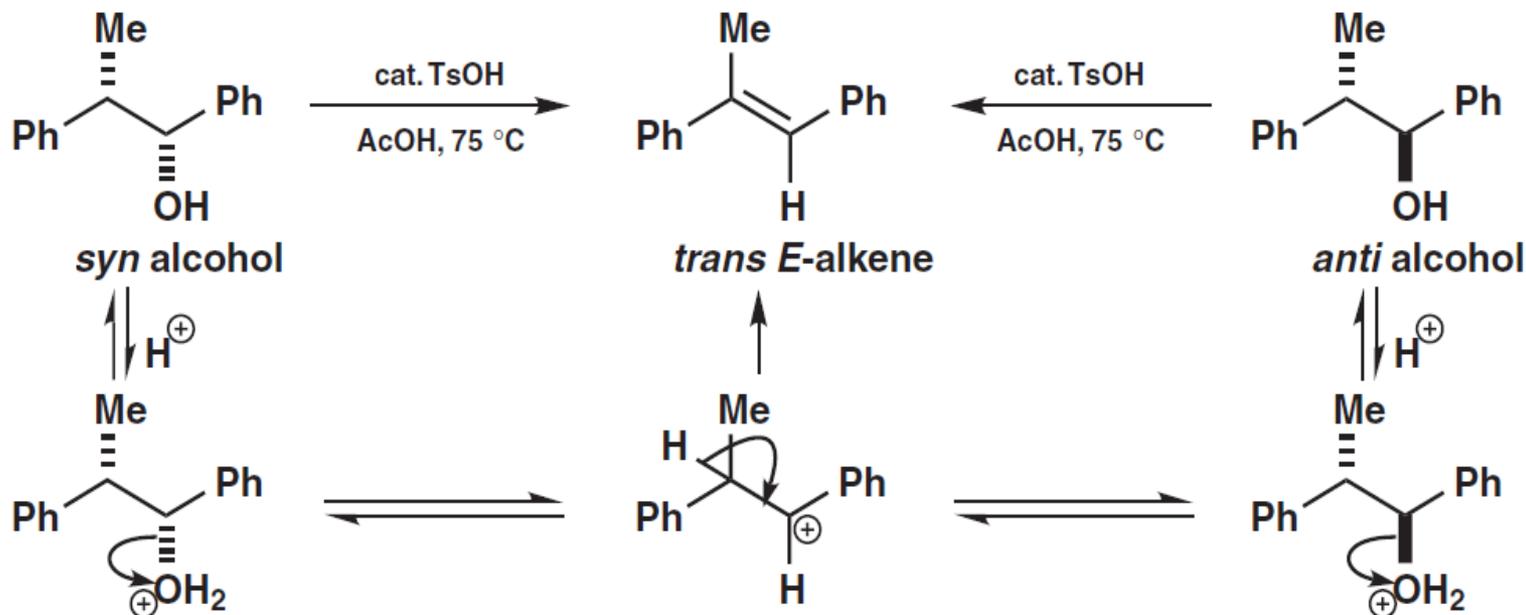
- ❖ alkenes in 3- to 7-membered rings are exclusively cis (*Z*) isomers; 8-membered rings may form trans (*E*) alkenes but are unstable; from the 12-membered rings further, trans (*E*) isomers are formed as more stable isomers



1. CREATION OF DOUBLE BONDS OF DEFINED STEREOCHEMISTRY

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

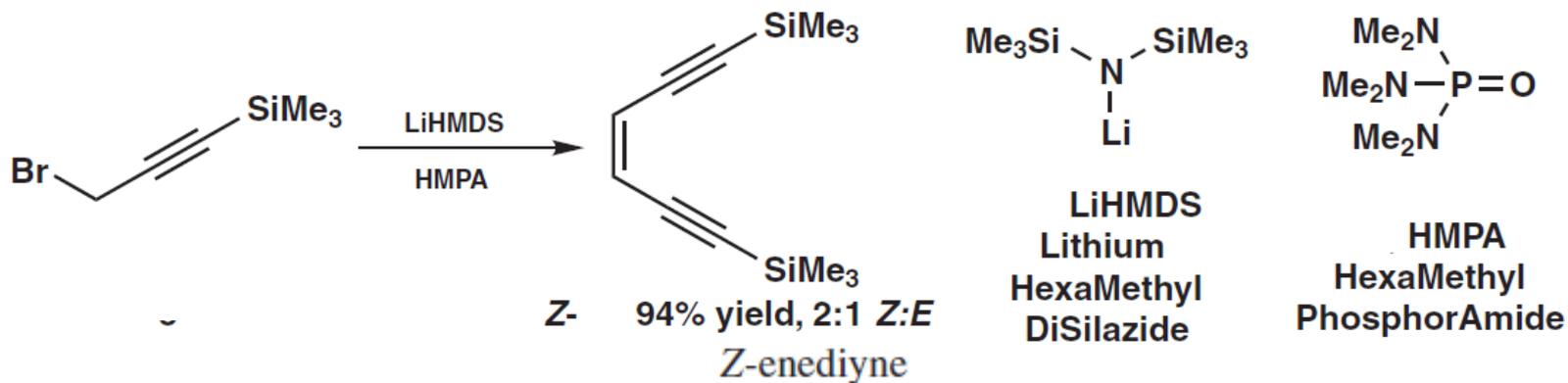
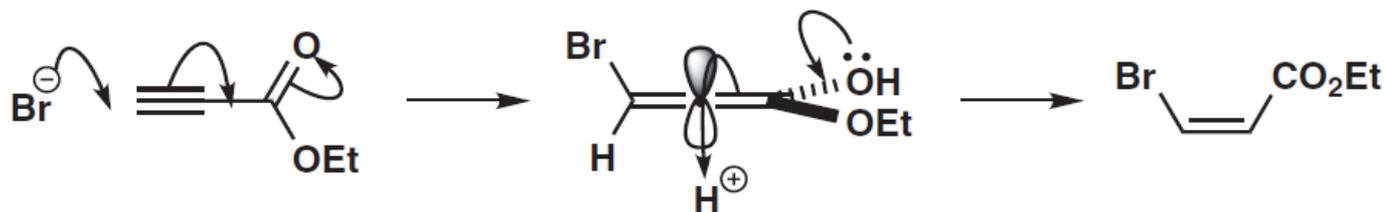
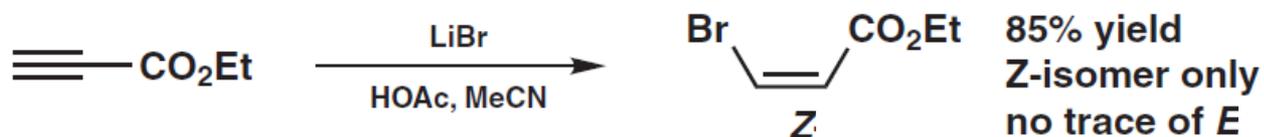
- ❖ in the reaction of both diastereomers of σ -alcohol with acid the same mixture of alkenes is formed in which the *trans* isomer dominates



1. CREATION OF DOUBLE BONDS OF DEFINED STEREOCHEMISTRY

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

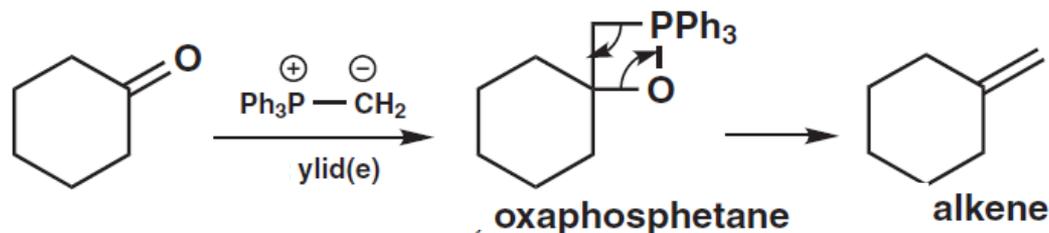
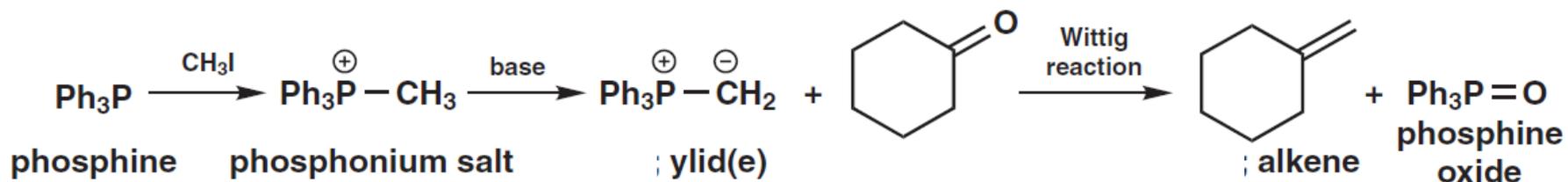
- ❖ Michael's alkyne addition
- ❖ there is no free rotation in the alene intermediate



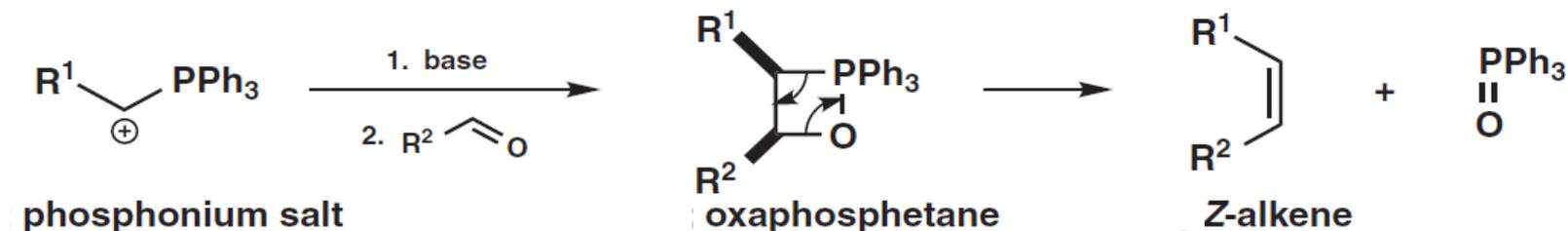
1. CREATION OF DOUBLE BONDS OF DEFINED STEREOCHEMISTRY

Wittig reaction

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



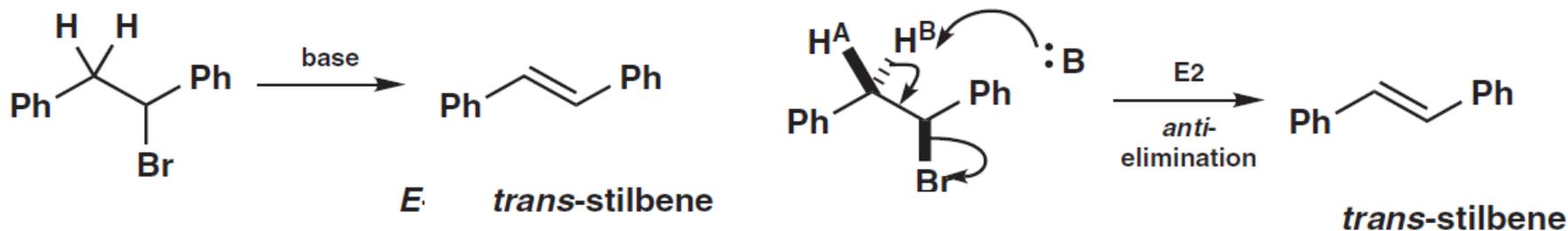
- ❖ the last stage of the Wittig reaction is stereospecific



1. CREATION OF DOUBLE BONDS OF DEFINED STEREOCHEMISTRY

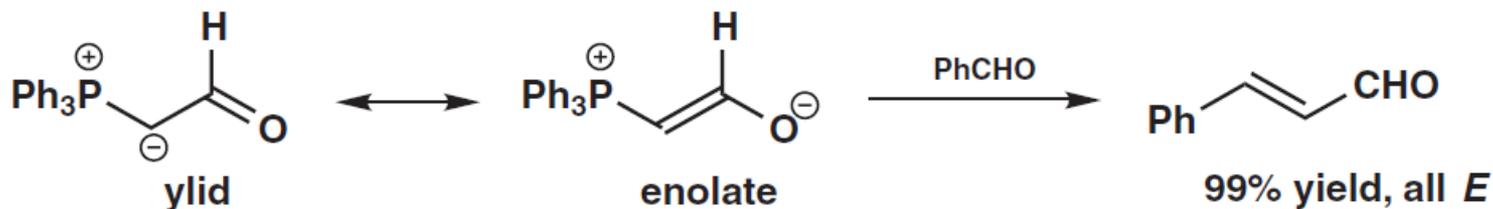
4. *Trans (E)* alkene is formed stereoselective

E2 elimination reactions



Trans selective Wittig reaction

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

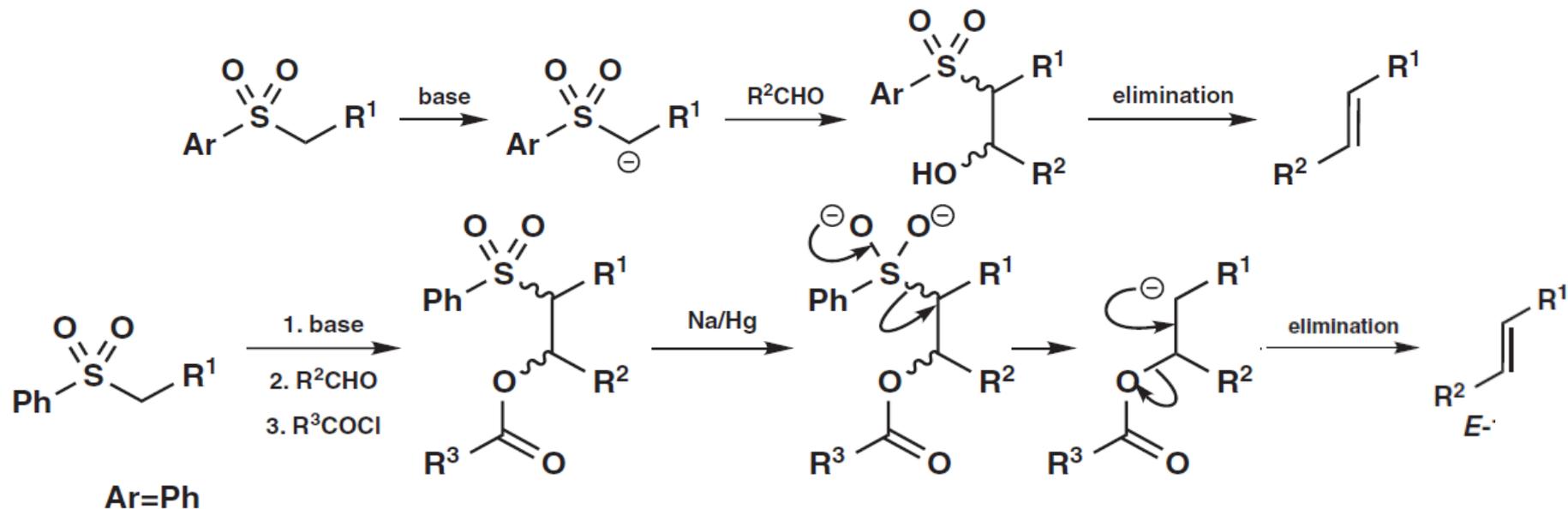


1. CREATION OF DOUBLE BONDS OF DEFINED STEREOCHEMISTRY

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

