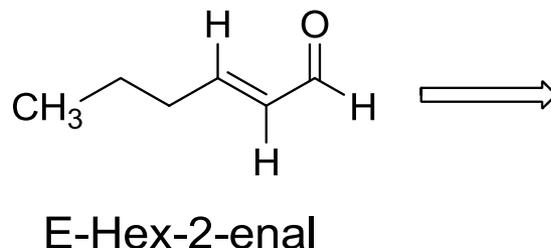


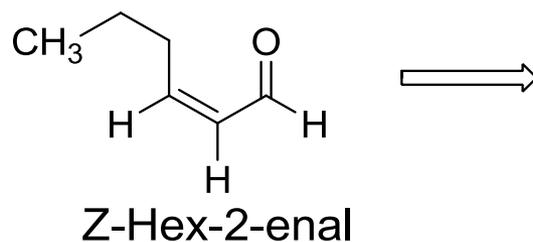
Stereospecific Synthesis of Alkenes

Stereospecific Synthesis of Alkenes

Motive for the Stereospecific Synthesis of Alkenes



Alarm pheromone of Myrmicine ants



(Insect repellent properties)

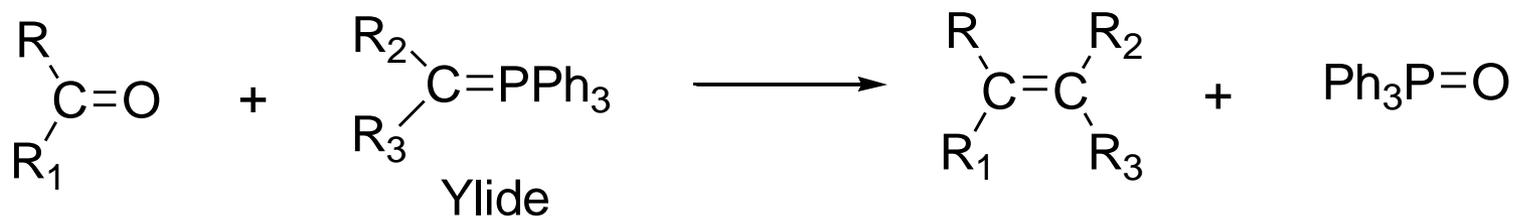


Aroma product of cabbages

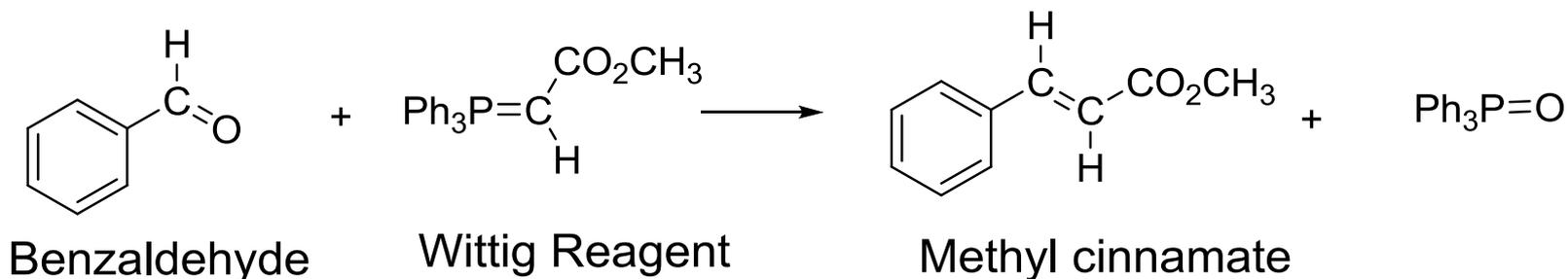
If an alkene is required for a specific application, it needs to be synthesized stereospecifically.

Synthesis of Alkenes

Recall the Wittig Reaction (SCH 202)



The Wittig reaction is a common method for the synthesis of alkenes from aldehydes or ketones.



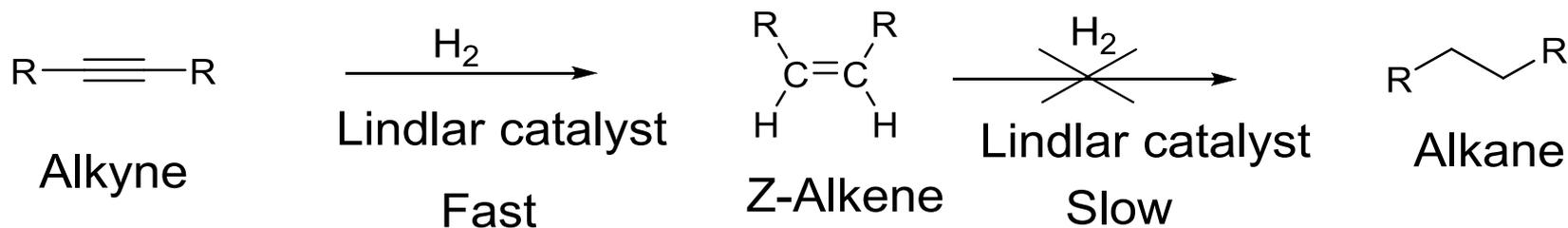
The synthetic disadvantage of the Wittig reaction is that it gives a mixture of E/Z-diastereomers of the alkene. Although one of the diastereomers may predominate in the mixture, the separation of the mixture is tedious.

Stereospecific Synthesis of Z-Alkenes

Catalytic Hydrogenation

Since E/Z diastereomers often have different bioactivities, it is essential that they be synthesized stereospecifically.

Partial Reduction of Alkynes to (Z)-Alkenes



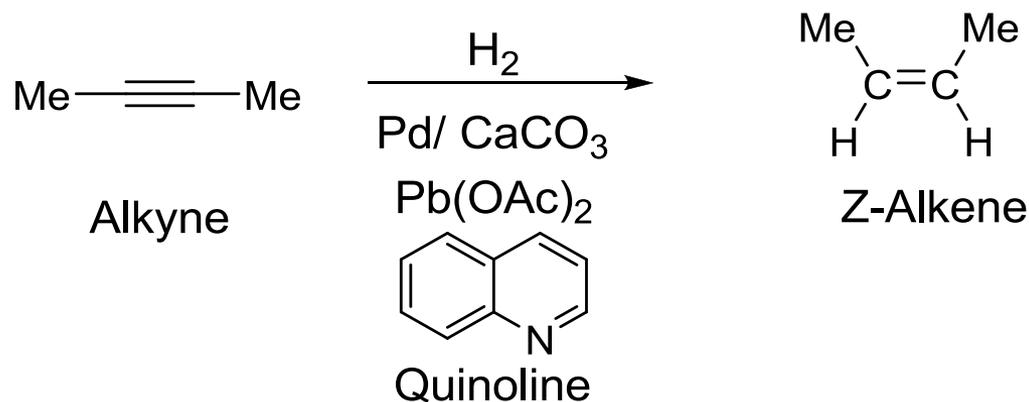
Since alkynes are more reactive to catalytic hydrogenation than alkenes, controlled/ selective reduction of alkynes to alkenes without over-reduction is possible by employing a poisoned palladium catalyst (Lindlar's catalyst).

Stereospecific Synthesis of Z-Alkenes

Catalytic Hydrogenation

Partial Reduction of Alkynes to (Z)-Alkenes

Lindlar's catalyst consists of 5% palladium on a calcium carbonate support poisoned with lead acetate and a small amount of quinoline.

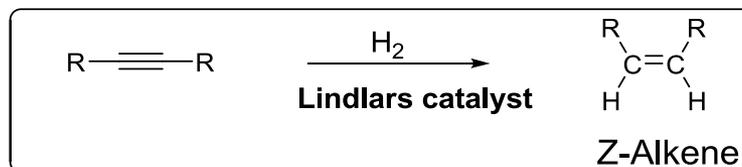


Lindlar catalyst

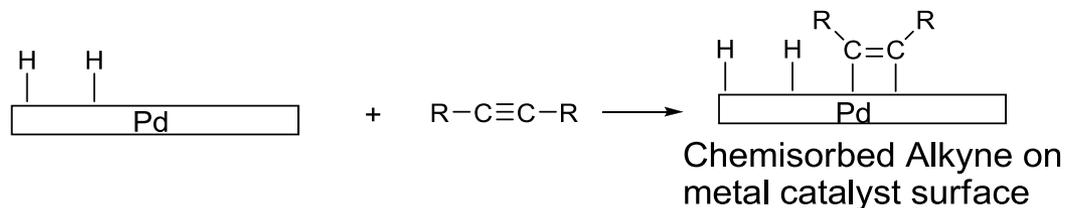
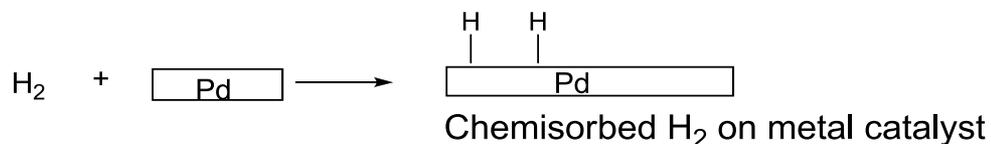
Due to environment concerns of the use of lead (Pb), other catalysts such as PdSO₄ poisoned with quinoline are found to be equally effective in this partial reduction.

Stereospecific Synthesis of Z-Alkenes

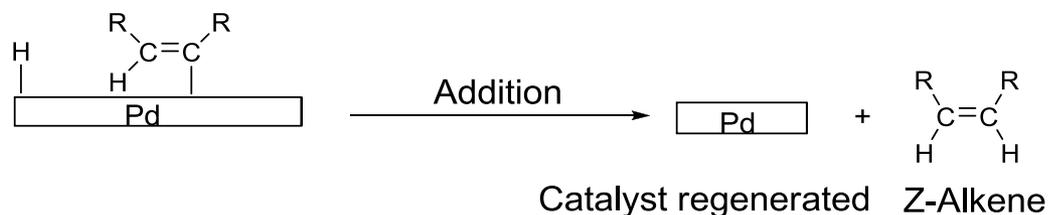
Catalytic Hydrogenation



Chemisorption of the hydrogen and the alkyne takes place first on a metal (Pd) surface



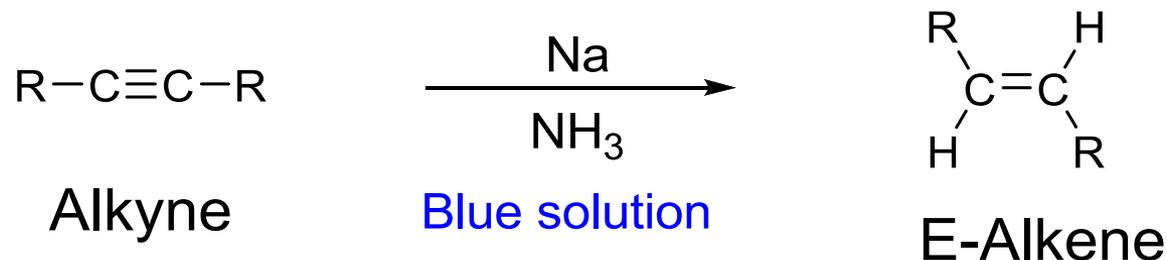
Chemisorbed Alkyne on metal catalyst surface



Stereospecific Synthesis of E-Alkenes

Dissolving Metal Reduction

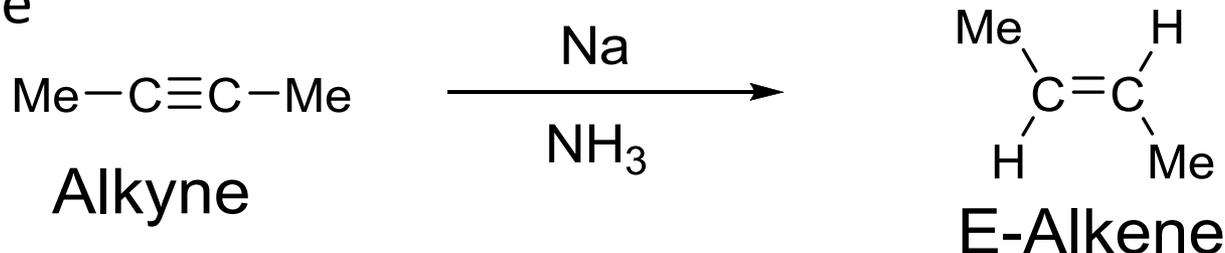
Partial Reduction of Alkynes to (E)-Alkenes



The reduction of alkynes under dissolving-metal conditions occurs through radical anion intermediates initiated by successive electron and proton-transfer processes.

Bright blue solutions of group 1 metals (Na or Li) in ammonia are used as the reducing mixture.

Example



Stereospecific Synthesis of E-Alkenes

Dissolving Metal Reduction

