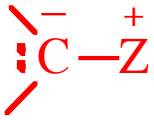
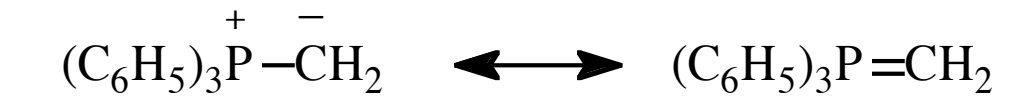
Ylides

Definition: Compounds in which a carbanion is directly bonded to a positively charged heteroatom.



where Z = N, P, As, Sb, S, Se

Structure and Nomenclature: Most ylides (except those containing nitrogen) can be represented by the following resonance forms:



triphenylphosphonium methylide

methylene triphenyl phosphorane

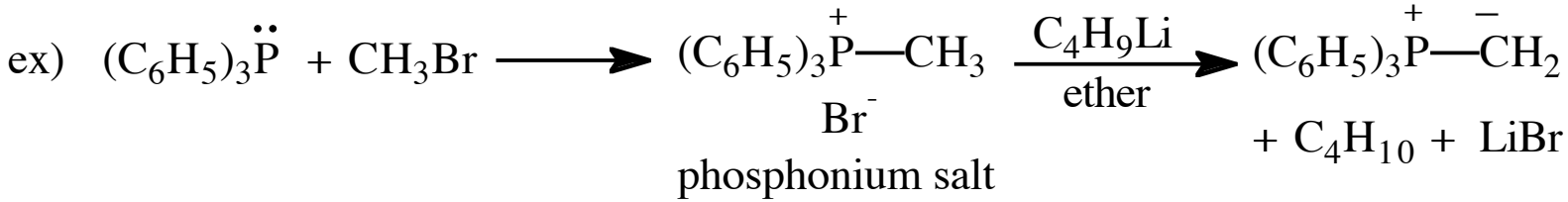
Stability and Reactivity:

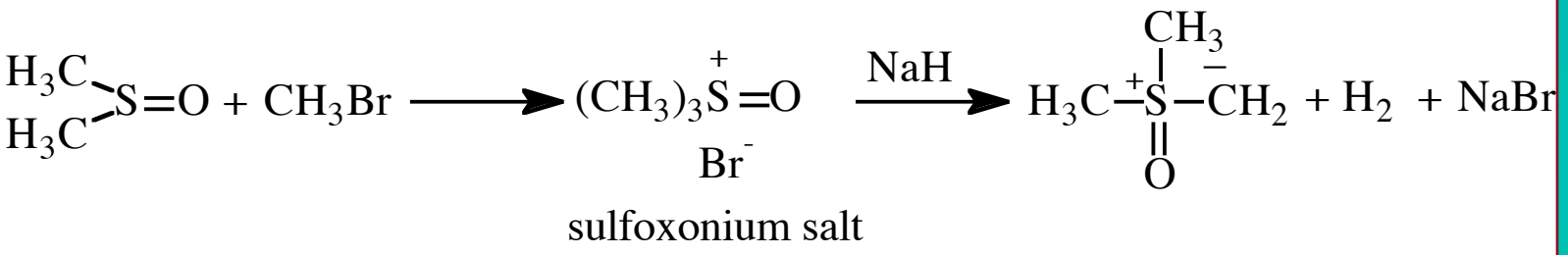
a) As the electron-donating ability of substituents bonded to the heteroatom increases, the stability of the ylide increases, and its reactivity decreases.

b) As the electron-withdrawing ability of substituents bonded to the carbanion carbon increases, the stability of the ylide increases, and its reactivity decreases.

Formation reactions of phosphorus ylides

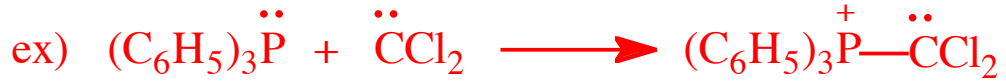
1. Proton abstraction from the corresponding "onium" salt by a strong base





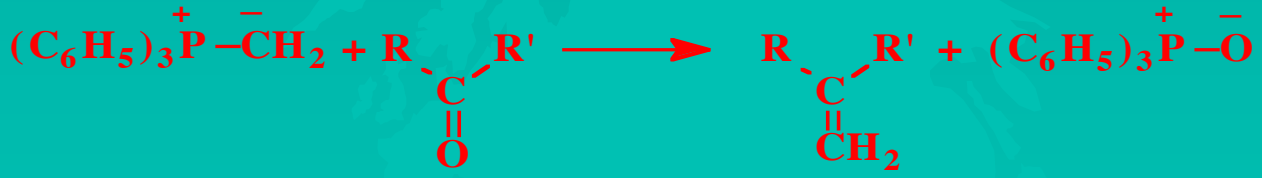
2. Addition of a carbanion to a vinyl "onium" salt

3. Addition of a carbene to a phosphine



Reactions of Phosphorus Ylides

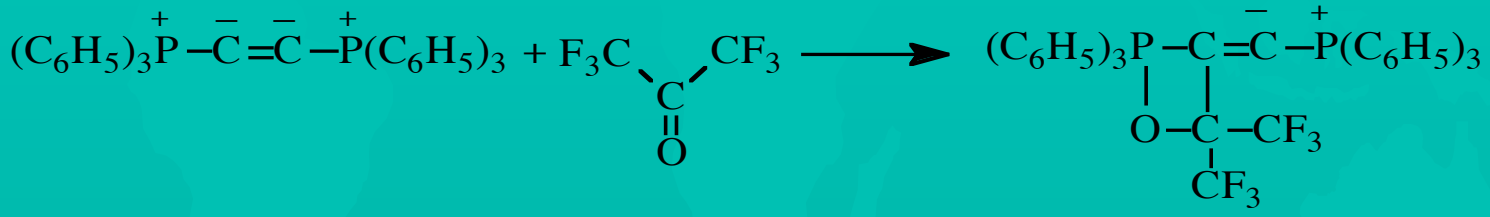
Wittig reaction:



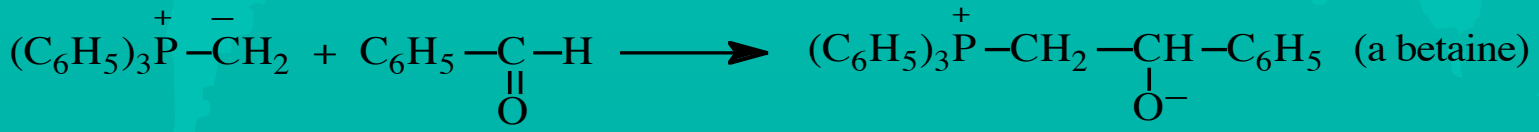
Facts pertinent to the mechanism of the Wittig reaction:

a) Electron-withdrawing groups on the carbanion carbon and electron-donating groups bonded to phosphorus retard the Wittig reaction.

b) The following observations have been made:

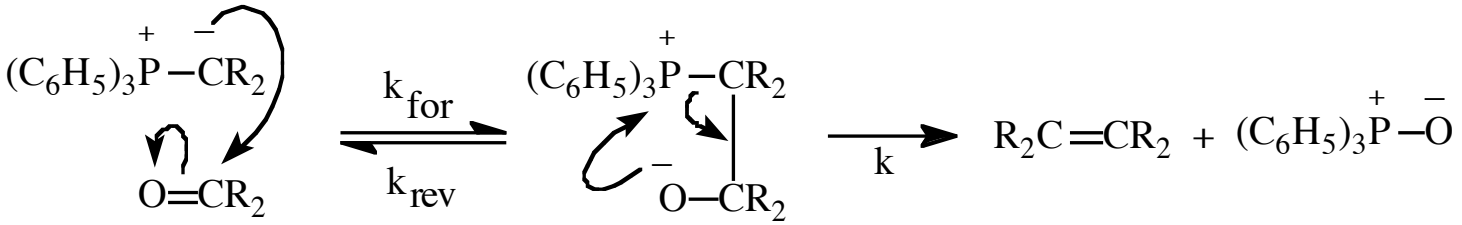


(has been isolated)



(has been isolated)

Wittig reaction: Accepted mechanism



a betaine

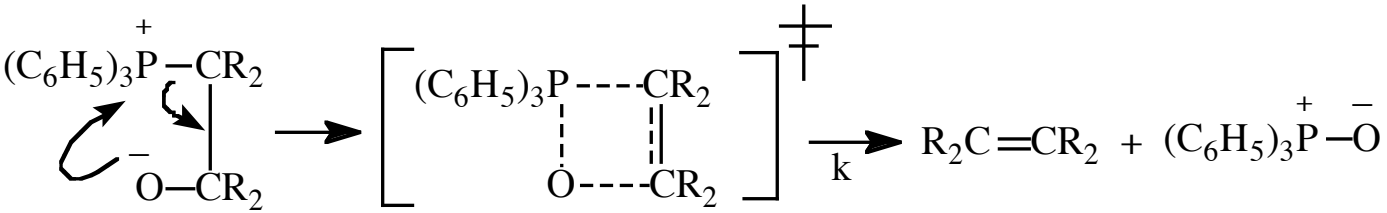
Rationale

a) With electron-withdrawing groups on the carbanion carbon, the nucleophilicity of the ylide is reduced and attack on the carbonyl carbon is retarded.

b) With electron-donating groups on phosphorus, phosphorus is less inclined to bond to the anionic oxygen atom and the betaine decomposes via k(reverse) instead of k.

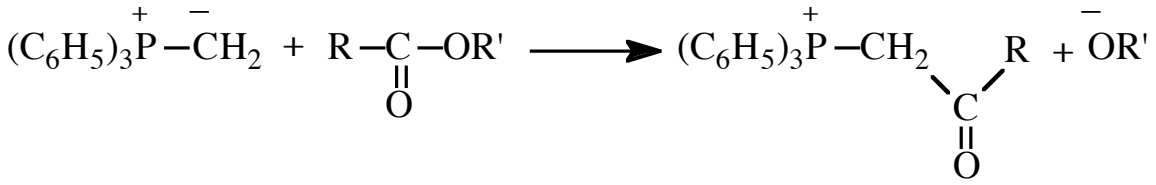
c) The isolation of a cyclic intermediate from the decomposition of betaine to products is consistent with the expected transition state for the change.

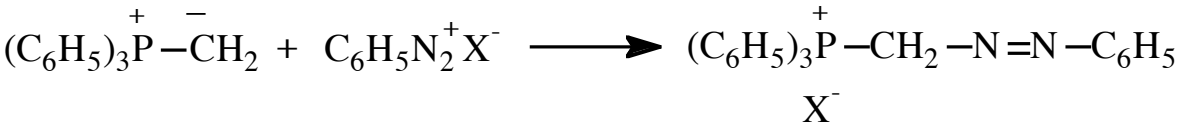
i.e.)

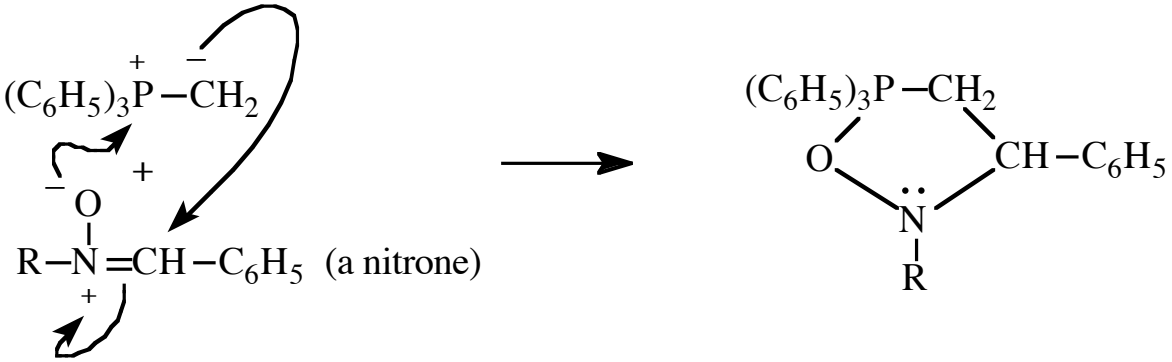


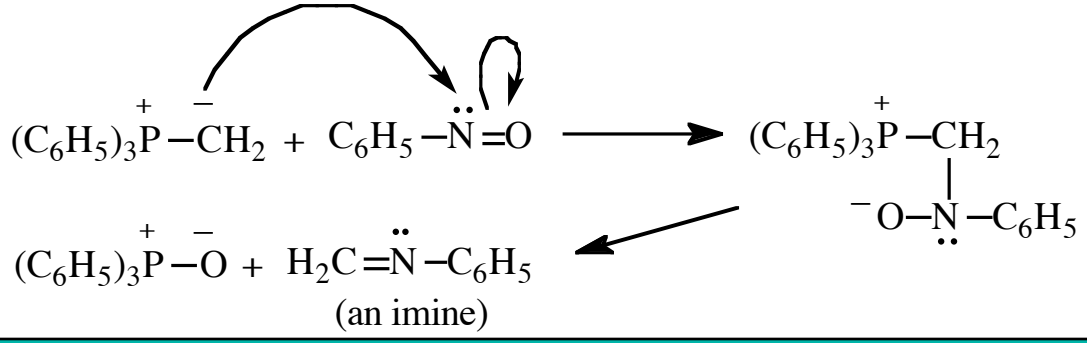
a betaine

Other Phosphorus Ylide Reactions

a) Acylation: 

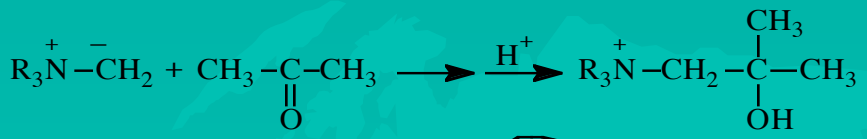
b) Coupling 

c) 1,3-Dipolar addition 

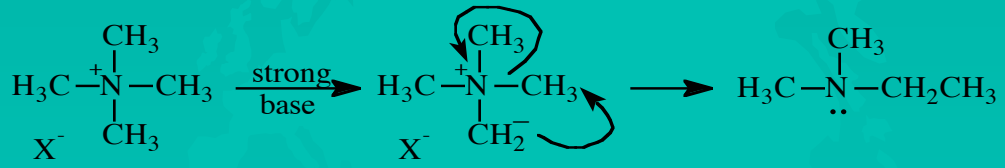
d) Reaction with a nitroso group 

Nitrogen Ylide Reactions

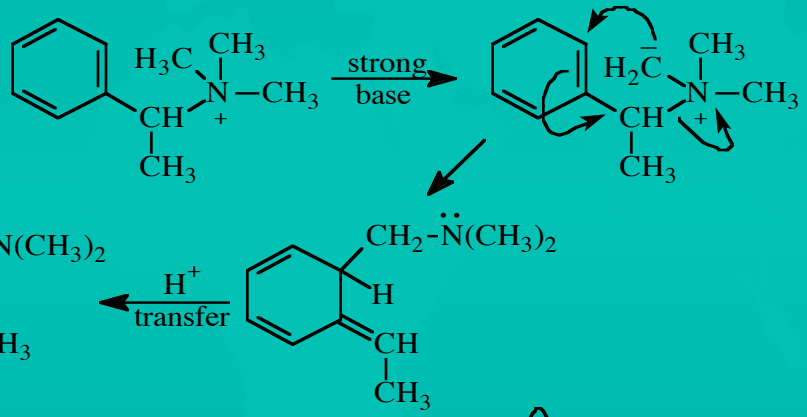
a) Reaction with a carbonyl group



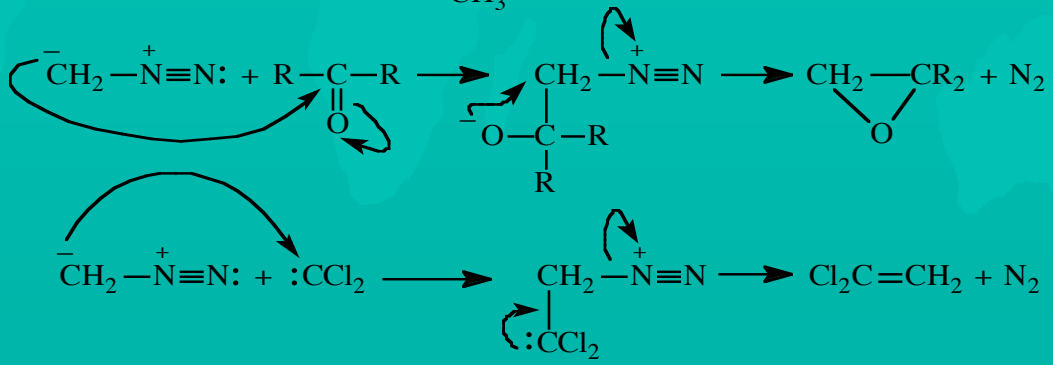
b) Stevens rearrangement



c) Sommelet rearrangement

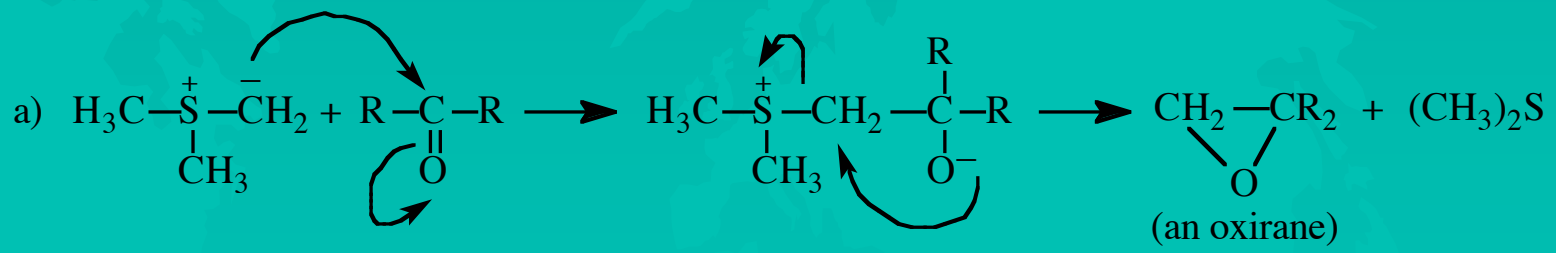


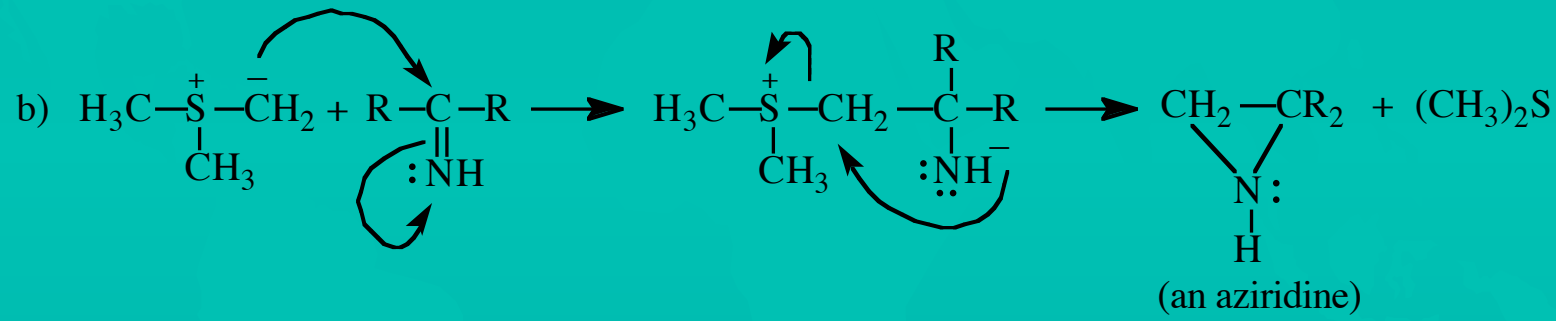
d) Reactions of diazo compounds

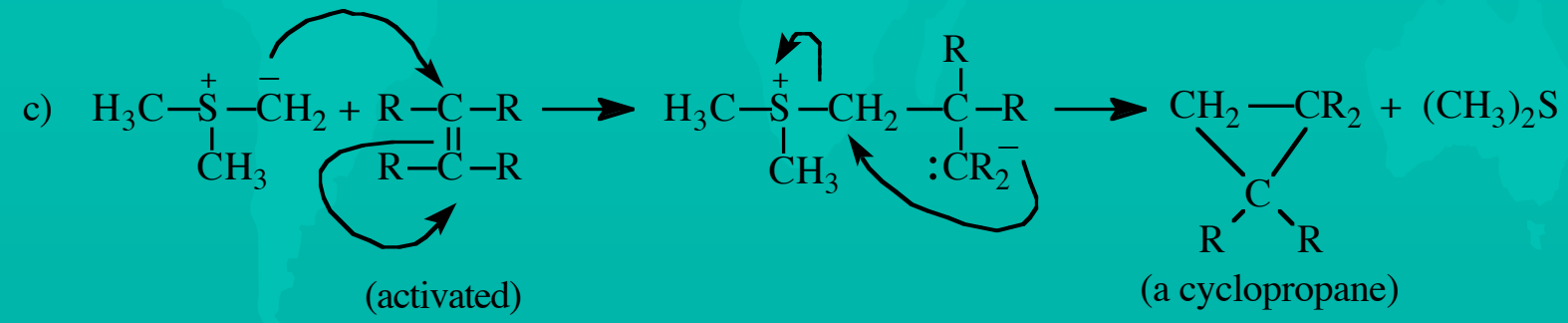


SULFUR YLIDES

Reactions with carbonyls, imines, and alkenes



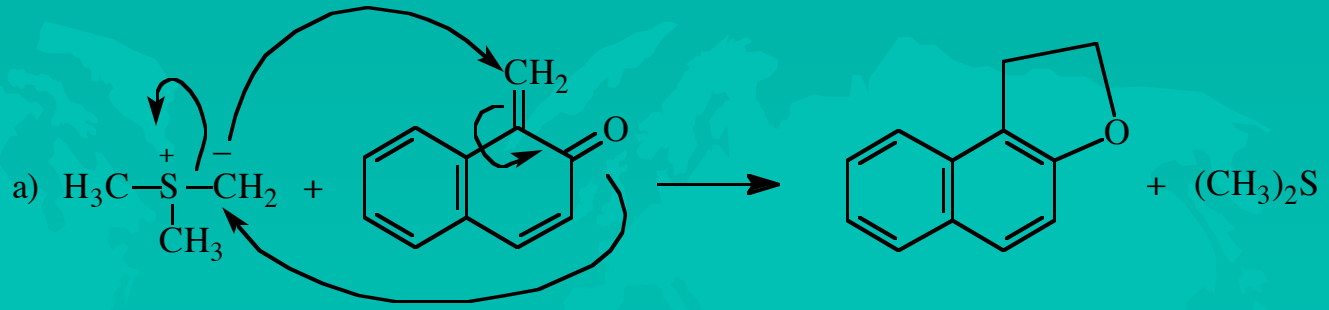




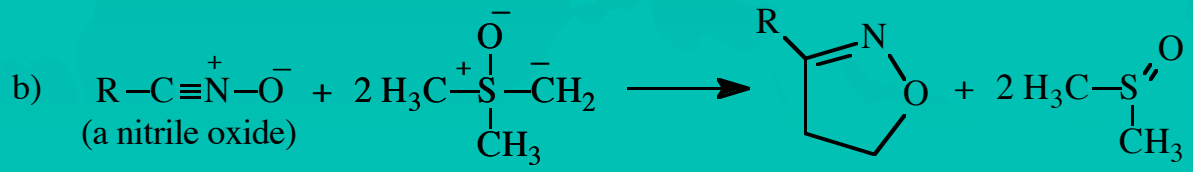
SULFUR YLIDES

Miscellaneous reactions

a)



b)



A Possible Pathway