REDOX NEUTRAL REACTIONS

Redox Disproportionation

- Cannizzaro Reaction
- Tishchenko Reaction
- Meerwein-Ponndorf-Verley/Oppenauer

Internal Redox Reactions

- Baylis-Hillman reaction
- Rauhut-Currier reaction
- Alkyne and Alkene Hydration
- Nef Reaction

Some Redox Neutral Rearrangements

- Pinacol Rearrangements
- Benzil rearrangement
- Favorskii rearrangement
- Payne rearrangement

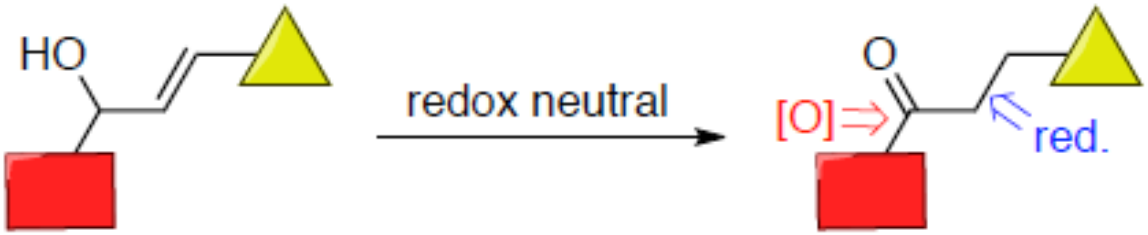
NHC-Catalyzed Reactions

- Benzoin Reactions
- The thiamine variant
- Stetter Reactions

Types of "Redox Neutral Organic Reactions"

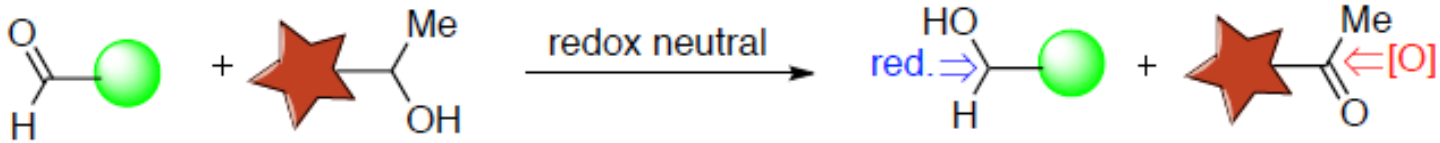
- Reactions with no external reducing or oxidizing agent

In this case, one part of the starting material is oxidized while the other is being reduced.

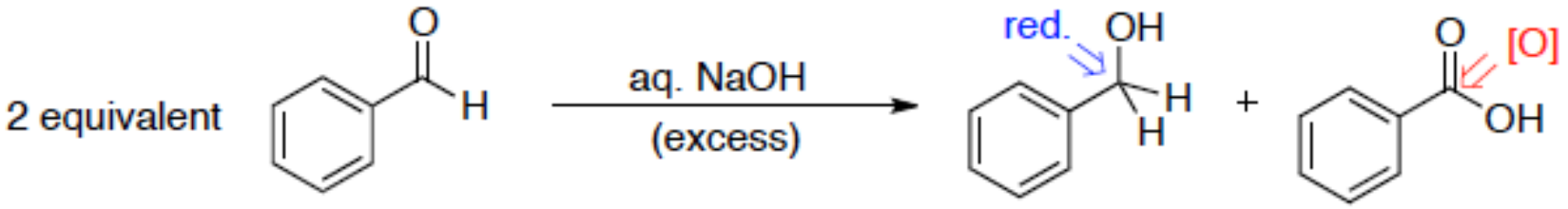


- "Redox Disproportionation"

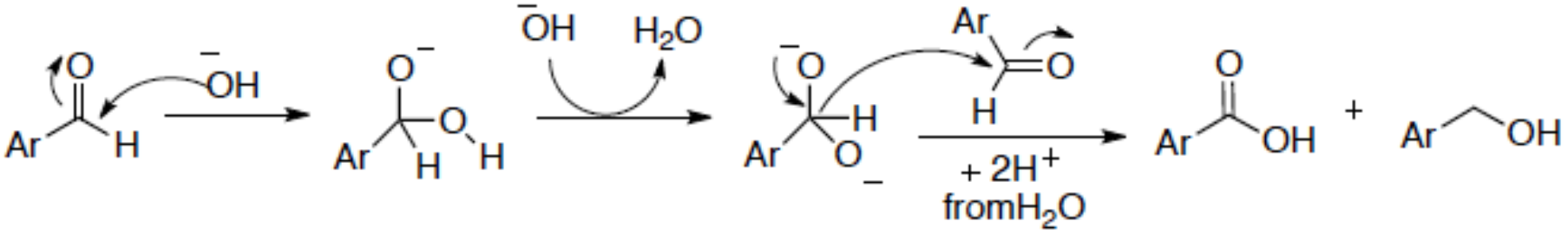
In this case, one starting material is oxidized while the other starting material is being reduced.

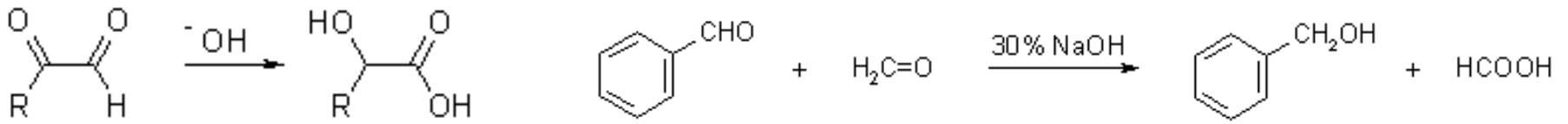


Cannizzaro Reaction



Mechanism

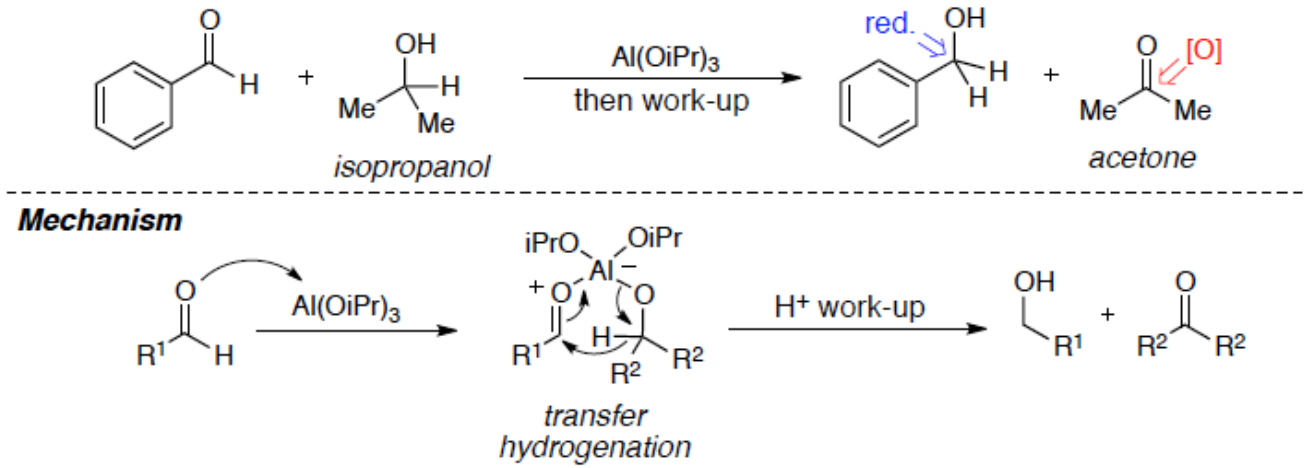




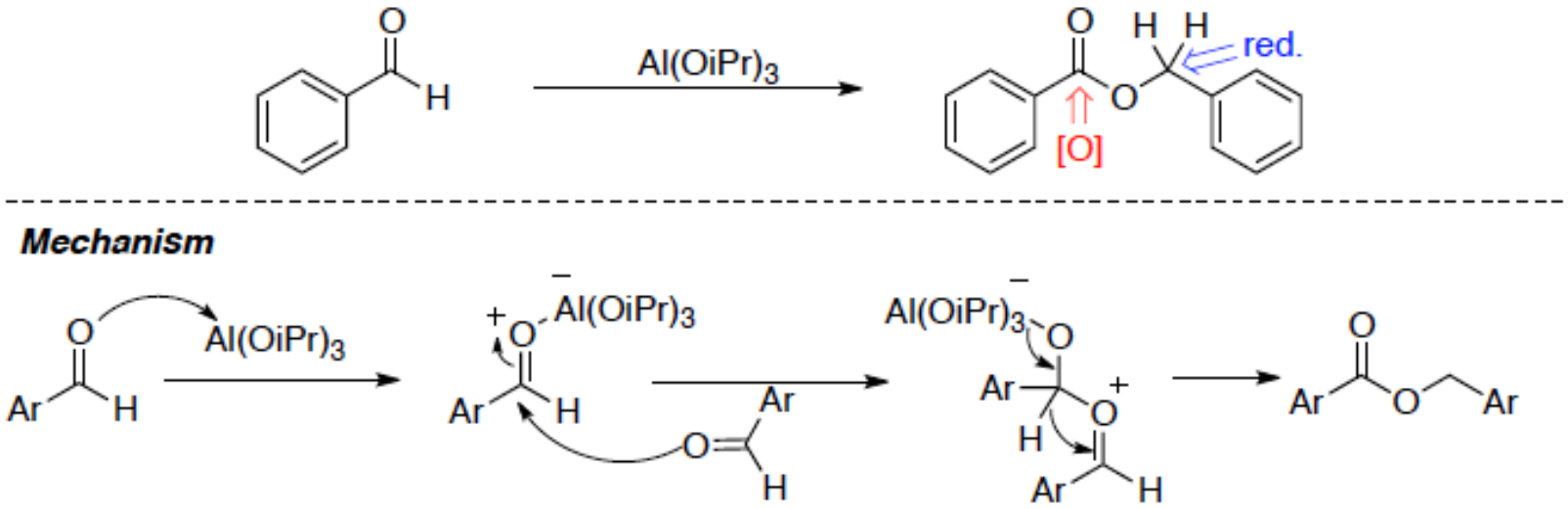
At the present time, various oxidizing and reducing agents can be used to carry out such conversions (with higher yields), so that today the Cannizzaro Reaction has limited synthetic utility except for the abovementioned conversion of α-keto aldehydes.

The Cannizzaro Reaction should be kept in mind as a source of potential side products when aldehydes are treated under basic conditions.

Meerwein-Ponndorf-Verley ***Reduction*** is the reverse reaction of Oppenauer ***Oxidation***

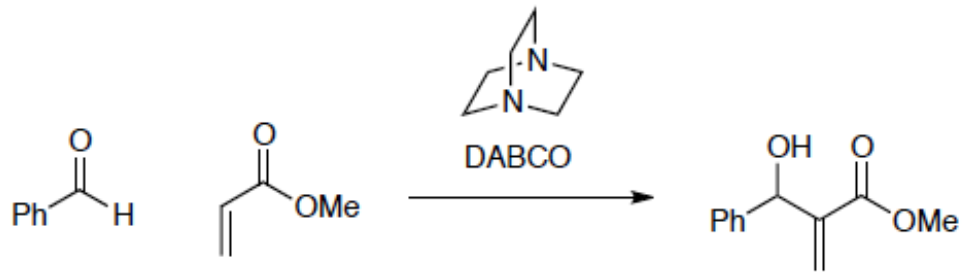


Tishchenko Reaction

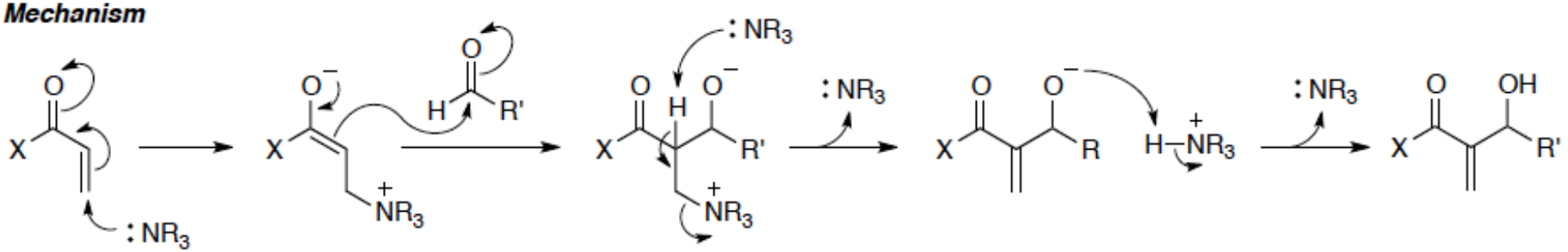


With nucleophilic catalysis

Baylis-Hillman reaction



Mechanism

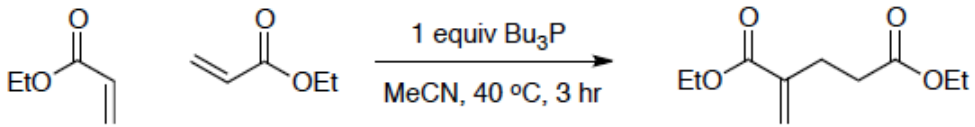


Anther good Nucleophile????
Another good electrophile????

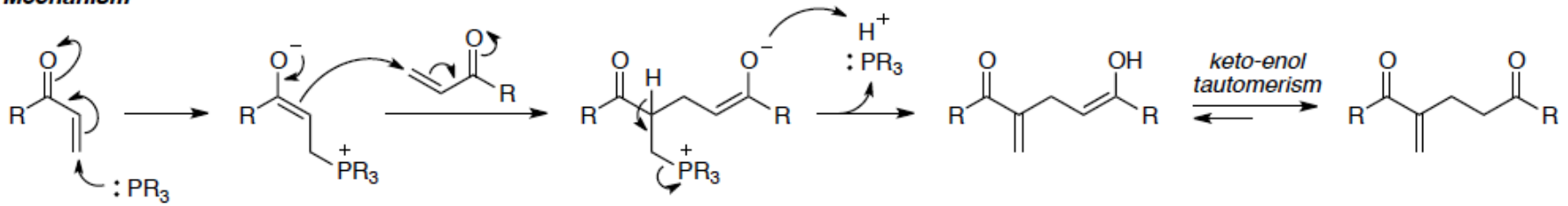
Enantioselective version???

Rauhut-Currier reaction (also called the vinylogous Morita–Baylis–Hillman reaction

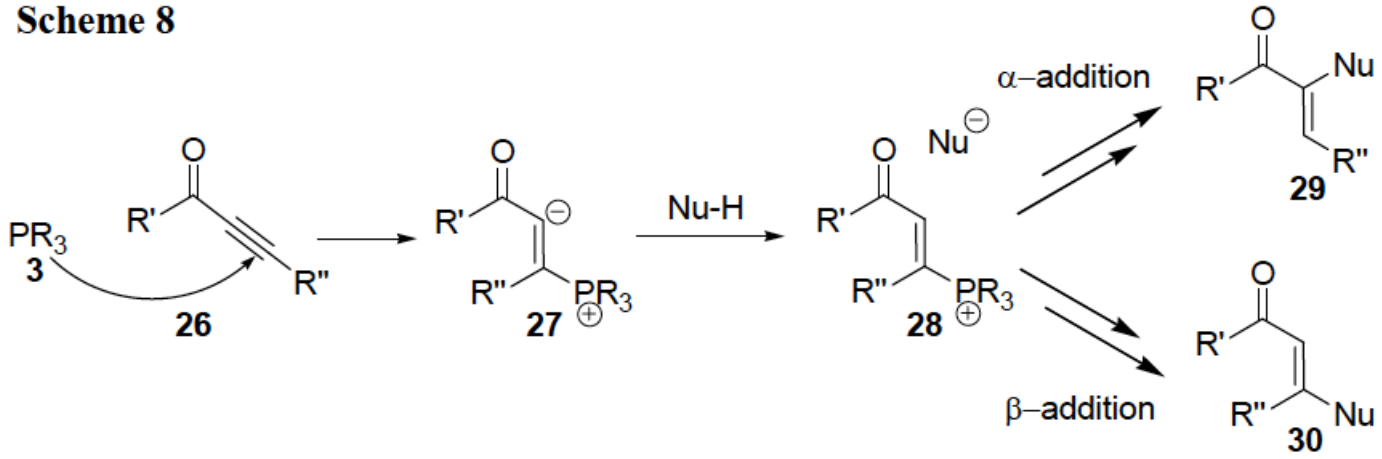
Phosphine-Triggered Reactions



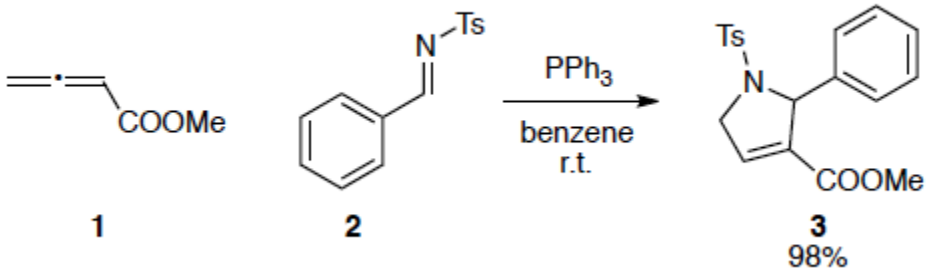
Mechanism



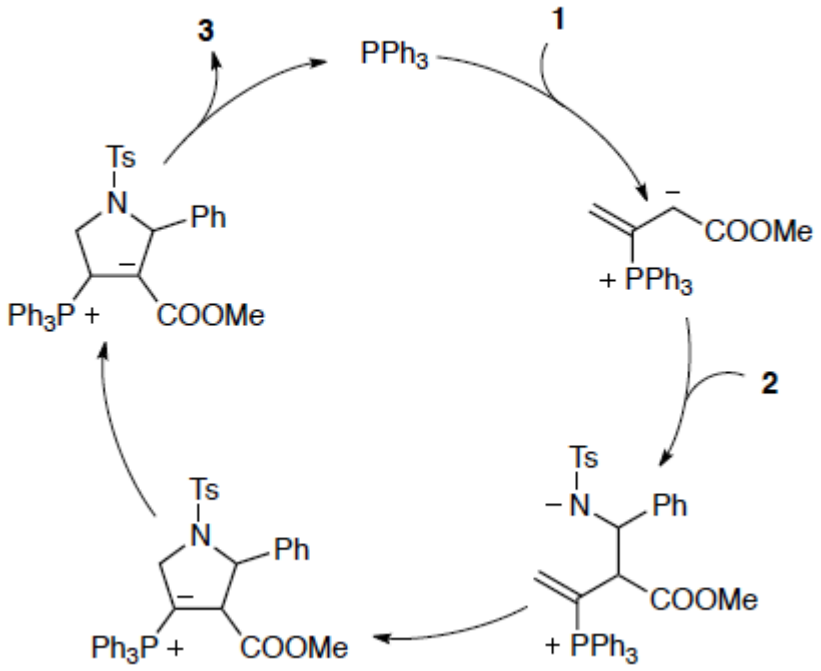
Scheme 8



PPh_3 catalyzed cycloaddition of *N*-Tosyl-substituted imines with allenes



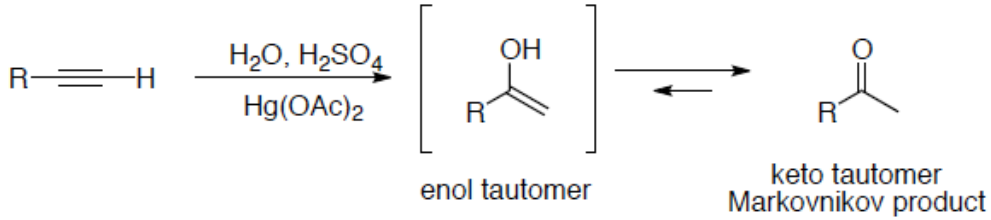
Mechanism



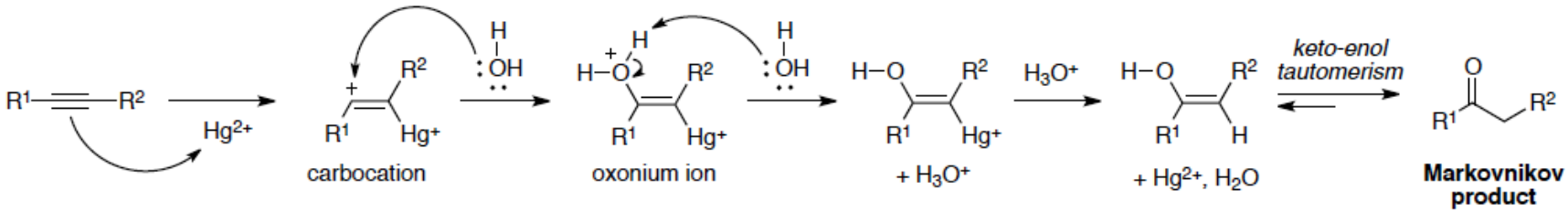
Alkyne and Alkene Hydration

Alkyne Hydration

- Mercuric ion-catalyzed hydration of alkynes goes with Markovnikov orientation.
- The Hg2+ salt acts as a catalyst to accelerate the rate of reaction; the nucleophile (e.g. H2O) will attack the most stabilized carbocation it formed.

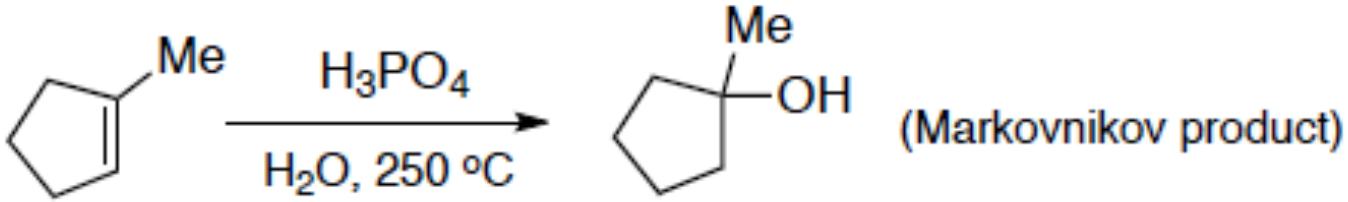


Mechanism

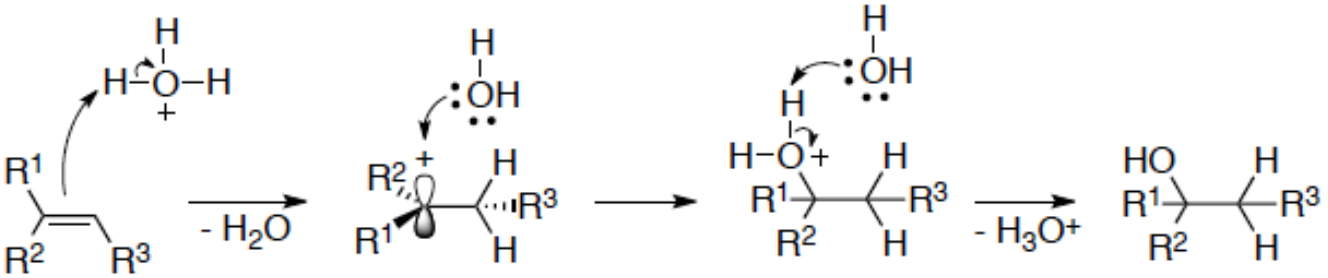


Regioselectivity???

Alkene Hydration

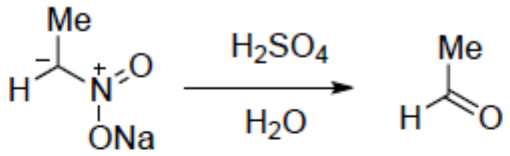


Mechanism

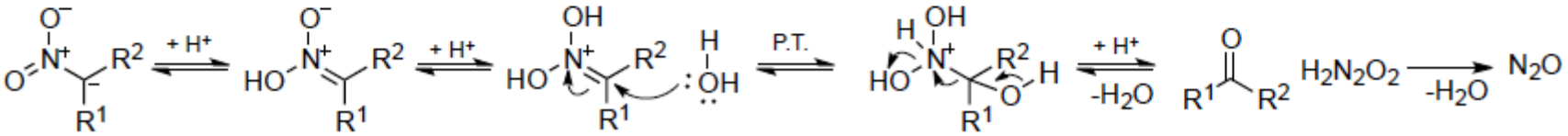


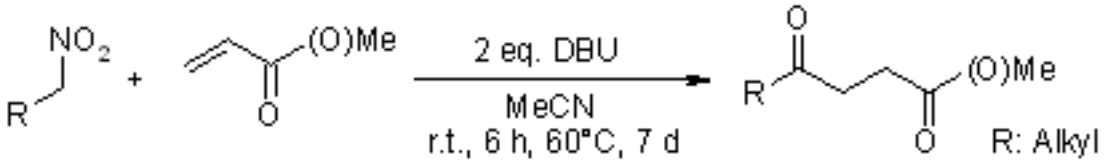
The orientation of hydration to alkenes with aqueous acid is followed by Markovnikov's rule

Nef Reaction



Mechanism





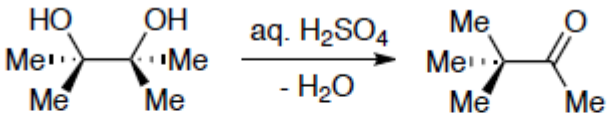
One-Pot Synthesis of γ-Diketones, γ-Keto Esters, and Conjugated Cyclopentenones from Nitroalkanes
R. Ballini, L . Barboni, G. Bosica, D. Fiorini, Synthesis, 2002, 2725-2728.

Rearrangements always redox neutral

Pinacol Rearrangements

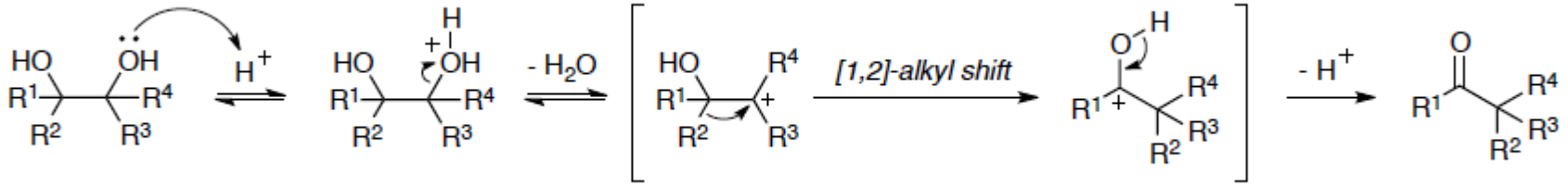
Pinacol to pinacolone

- The group that stabilizes a positive charge better migrates first.

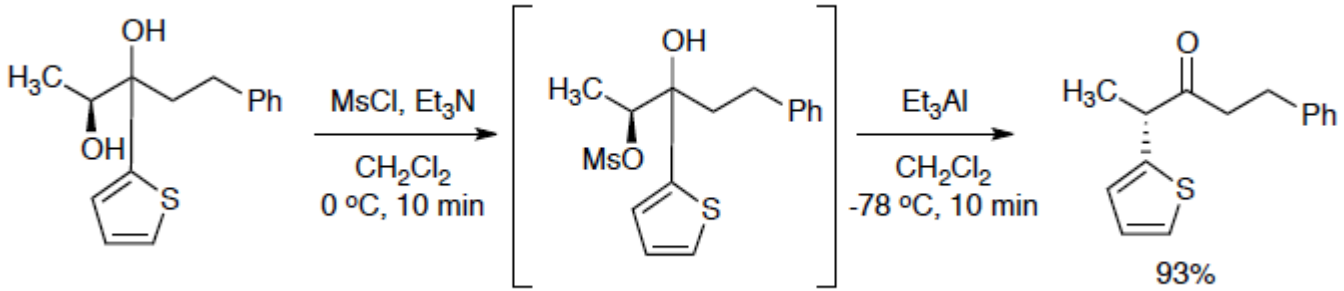


pinacol pnacolone

Mechanism

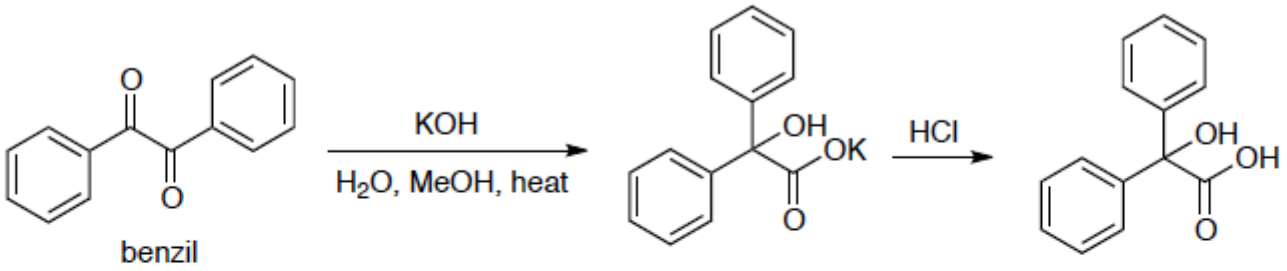


Stereospecific pinacol rearrangements

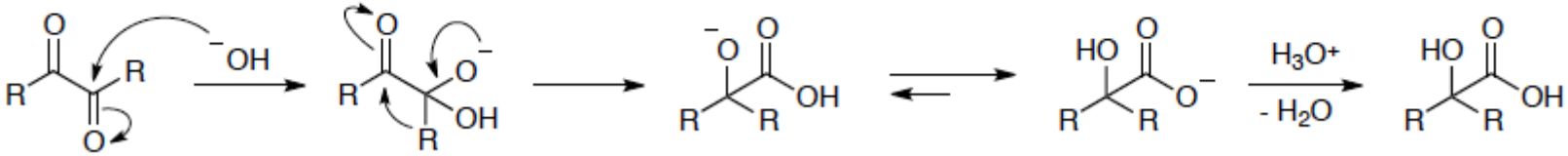


93%
99% e.e.

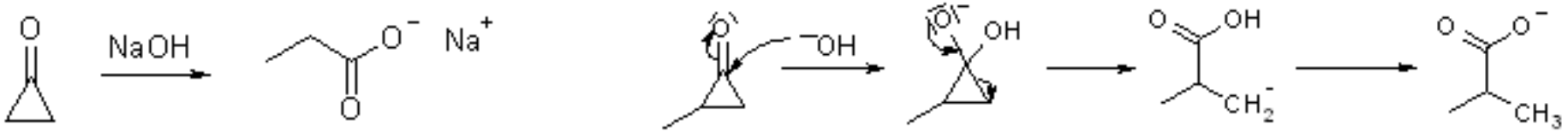
Benzil rearrangement (see Cannizzaro Reaction)

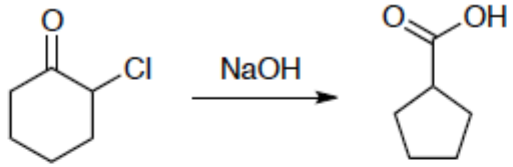


Mechanism

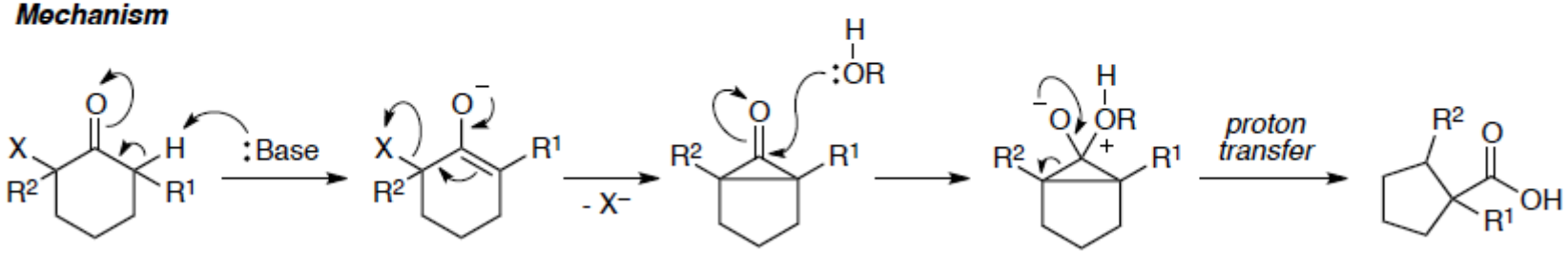


Favorskii rearrangement





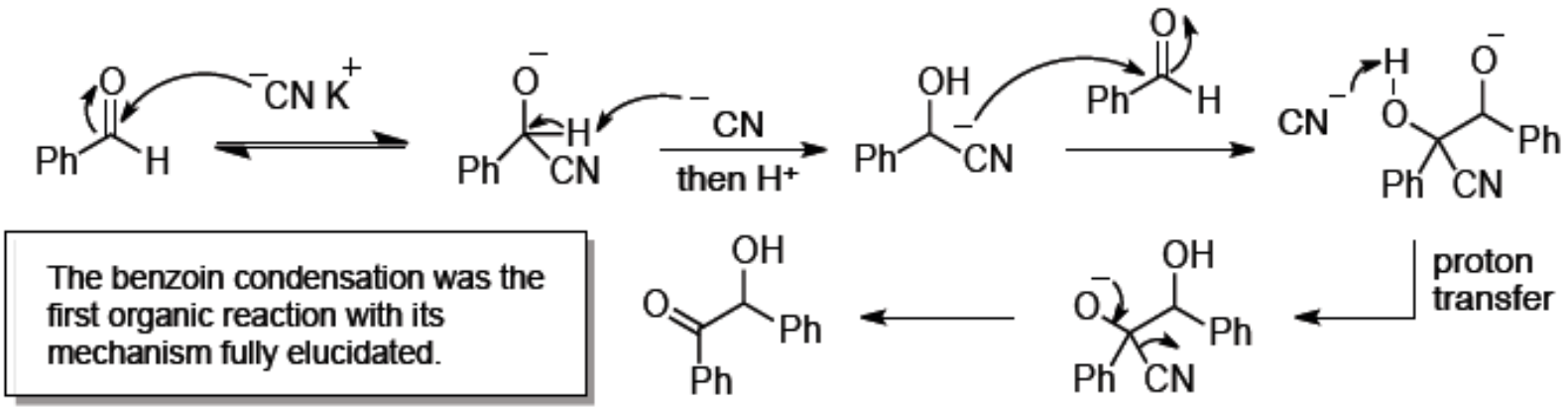
Mechanism



Benzoin Reactions

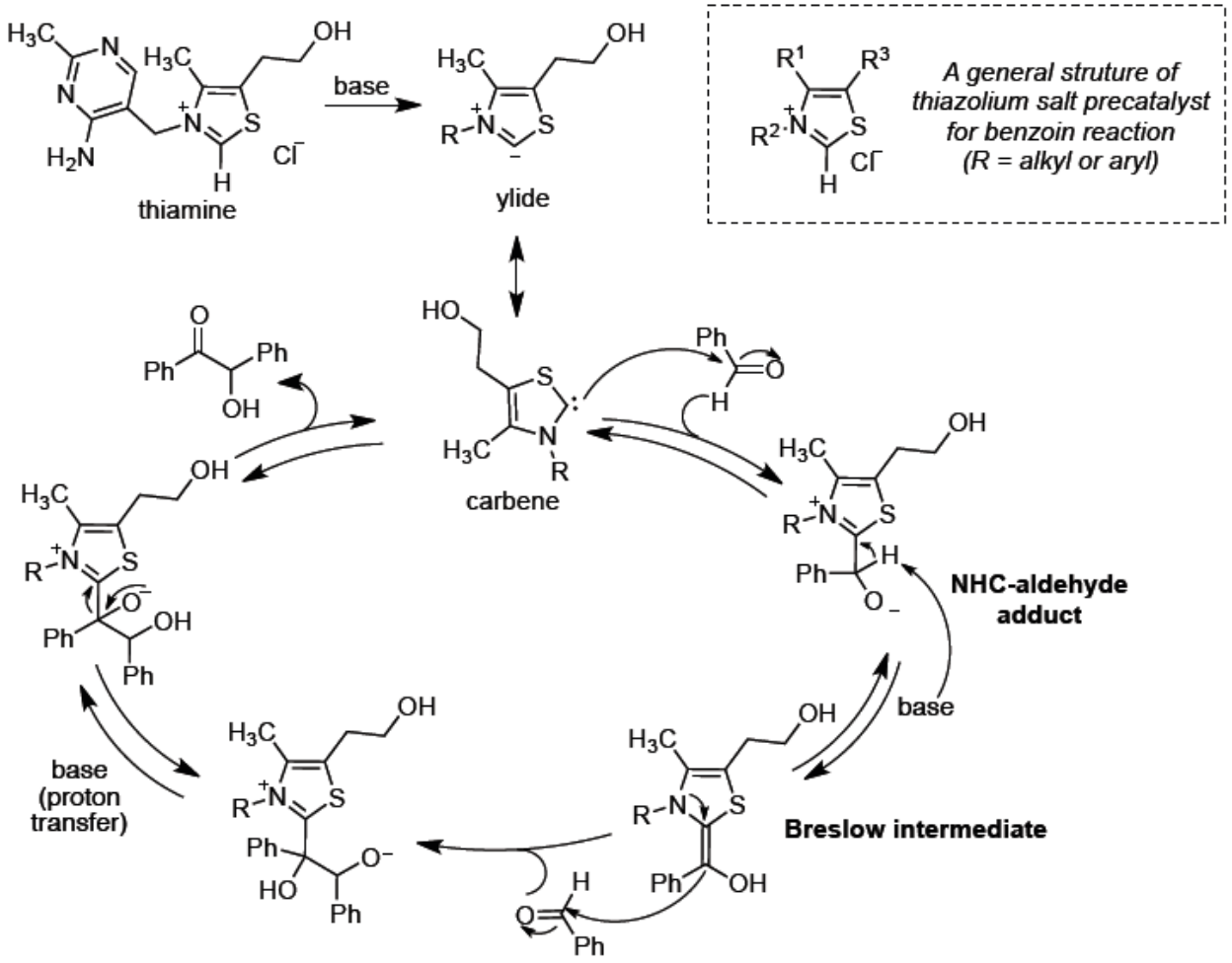
The Benzoin Condensation is a coupling reaction between two aldehydes that allows the preparation of α-hydroxyketones. The first methods were only suitable for the conversion of aromatic aldehydes.

Cyanide ion catalyzed benzoin condensation



The benzoin condensation was the first organic reaction with its mechanism fully elucidated.

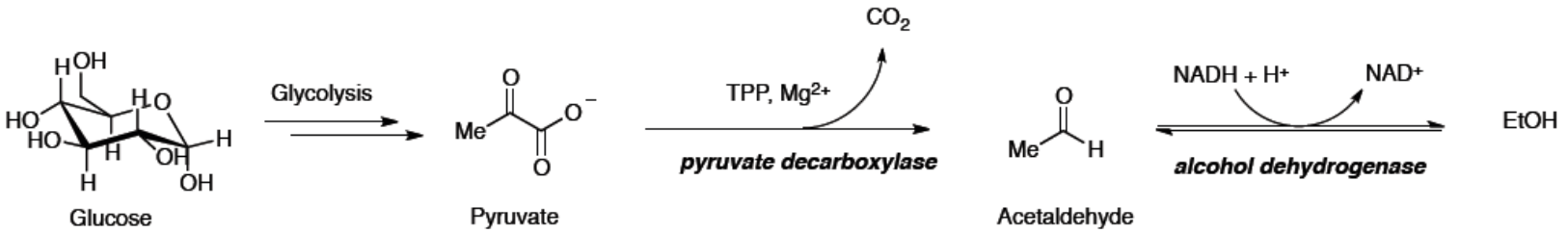
The thiamine variant:

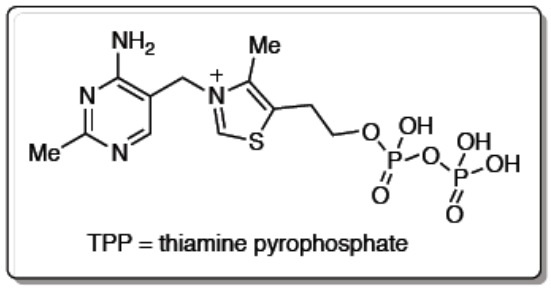


In the benzoin reaction (and many other NHC-catalyzed reactions), the aldehyde carbon undergoes a reversal in polarity from an electrophilic center to being a nucleophilic center. **This concept is termed "umpolung"**

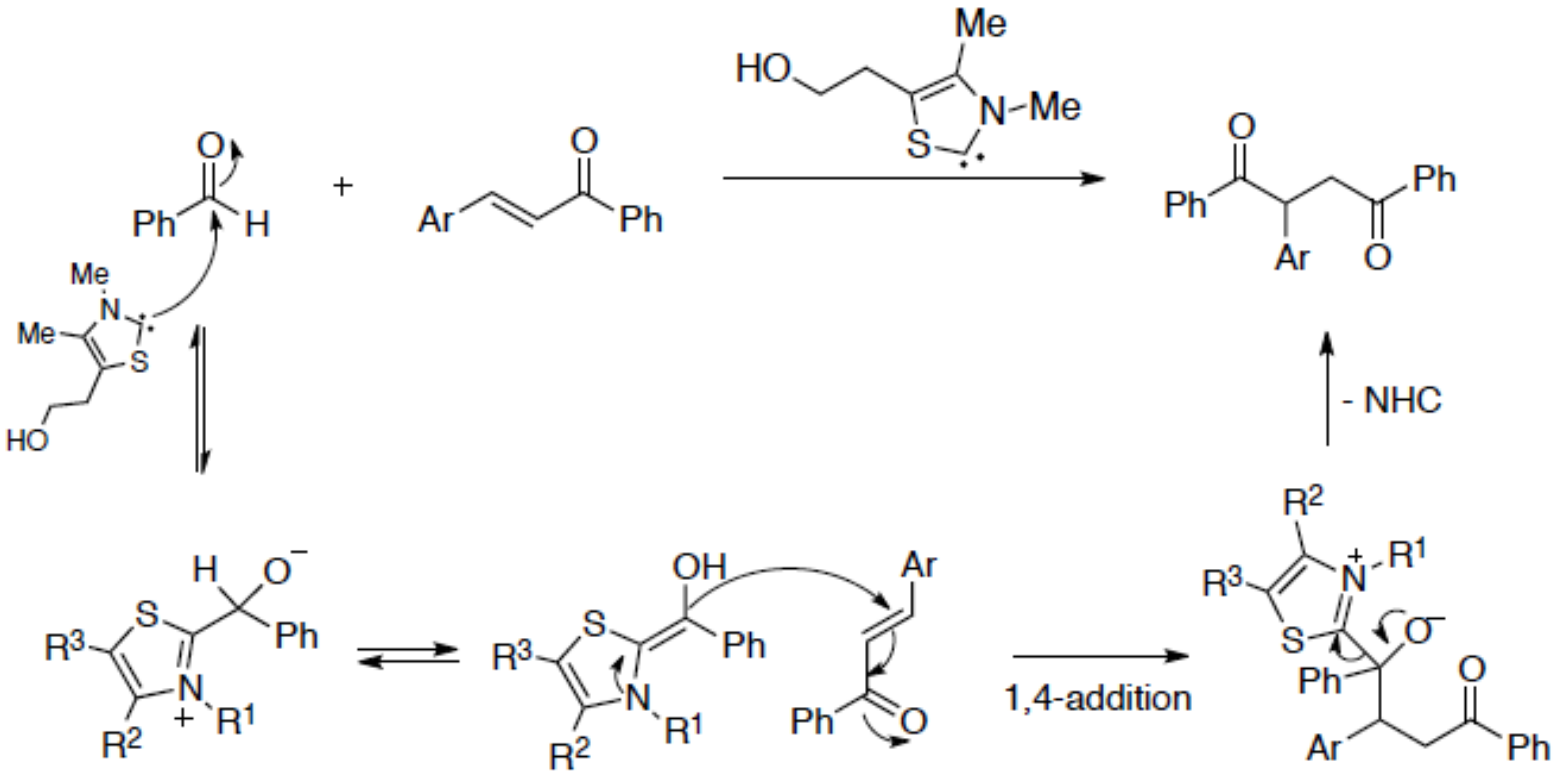
Biological counterparts

Carbenes play a central role in a number of biological processes. One of the most important examples is Vitamin B1 (Thiamine pyrophosphate), a coenzyme involved in many metabolic pathways. For instance, the enzyme *pyruvate decarboxylase* is assisted by TPP in catalyzing the transformation of pyruvate into acetaldehyde: a key step in the anaerobic fermentation… Think about it next time you'll have a drink!

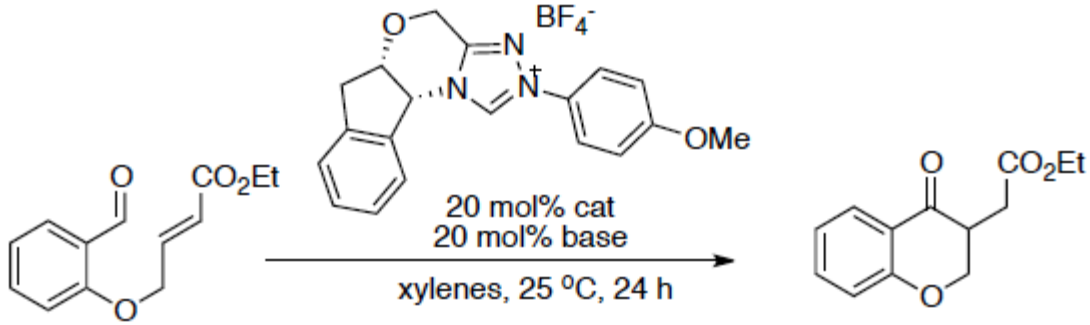




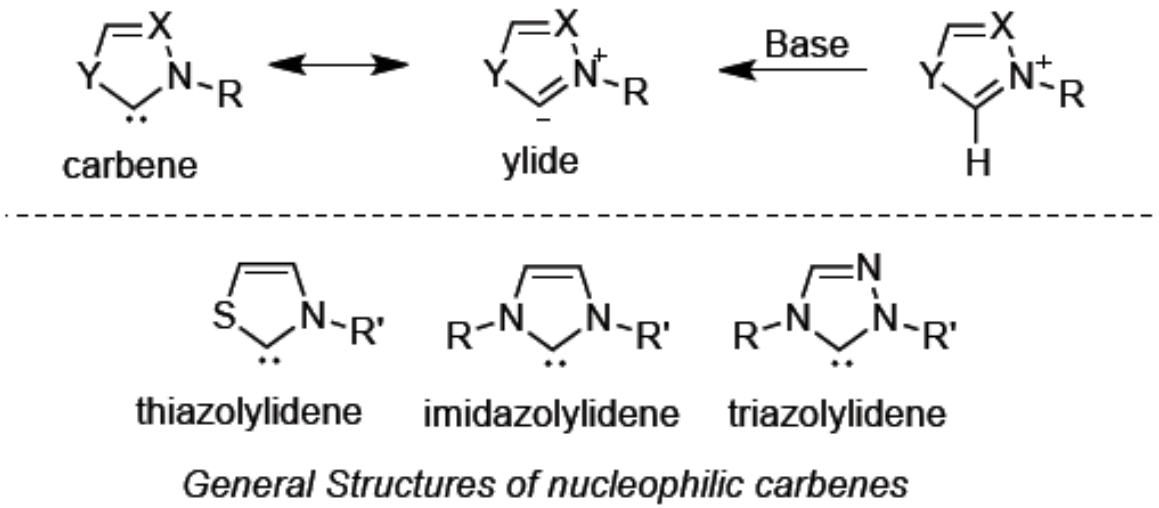
Stetter Reactions



The research program of Prof. Tom Rovis (Colorado State University) has established the current state of the art for Stetter reactions, especially the intramolecular variant:



NHC-Catalyzed Reactions



General Structures of nucleophilic carbenes

Unlike other carbene or carbenoid species which are high-energy intermediates, N-heterocyclic carbene is a stable singlet carbene. The lone pairs of the heteroatoms adjacent to the carbene carbon donate electron into the empty p-orbital of the carbene carbon. Additionally, the *N*-substitution provides kinetic stability.