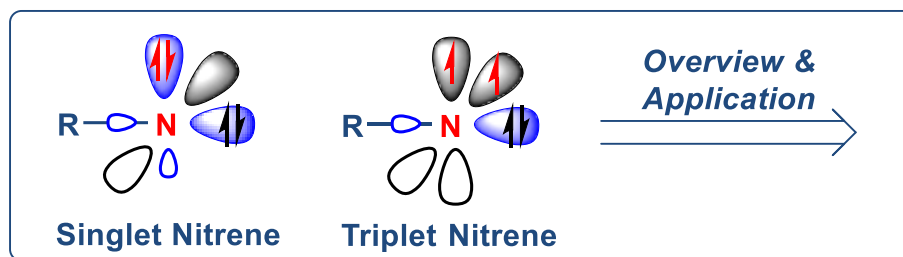




# Chemistry of Nitrenes



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Group-Meeting Presentation

09<sup>th</sup> Sep 2020

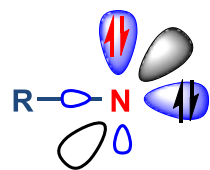
# Overview of Nitrenes



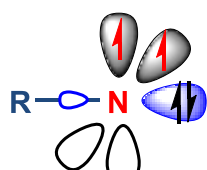
## What is Nitrene?

- Nitrenes are highly reactive neutral reaction intermediates.
- Electron deficient monovalent nitrogen species.
- Nitrogen atom surrounded by a sextet of electrons.

## Classification



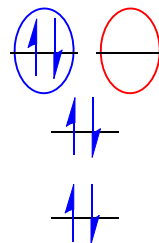
Singlet Nitrene  
 $sp^2$



Triplet Nitrene  
 $sp$

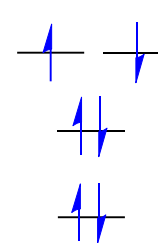
Singlet Nitrene

HOMO LUMO



Spin Paired

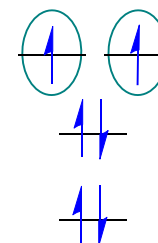
Unstable



Spin Paired

Triplet Nitrene

SOMO SOMO



Spin Unpaired

- **Singlet state:** Carbocation-like in nature, trigonal planar geometry.
- **Triplet state:** Diradical-like in nature, linear geometry.

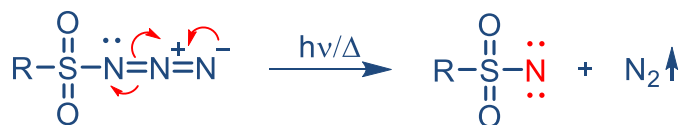
## Thermal or Photolytic decomposition of Azides



R = Alkyl, Aryl, H

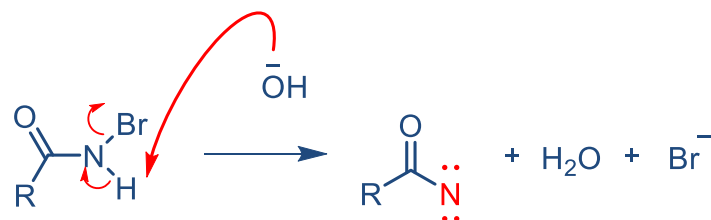


R = Alkyl, Aryl



R = Alkyl, Aryl

## Base catalyzed $\alpha$ -elimination

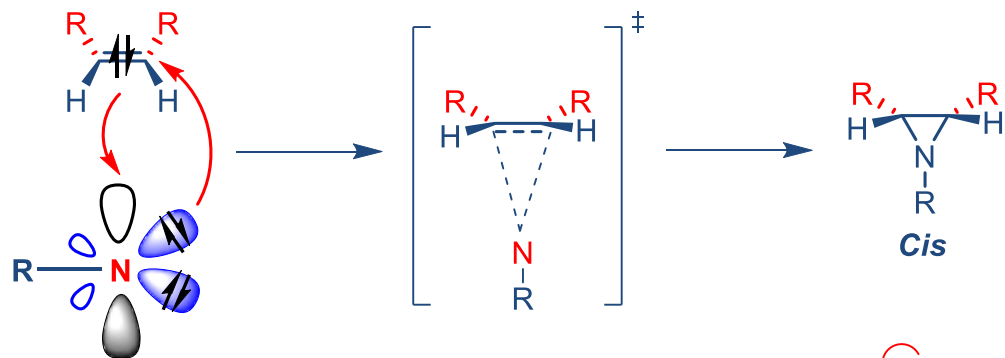


## Reduction of Nitro group



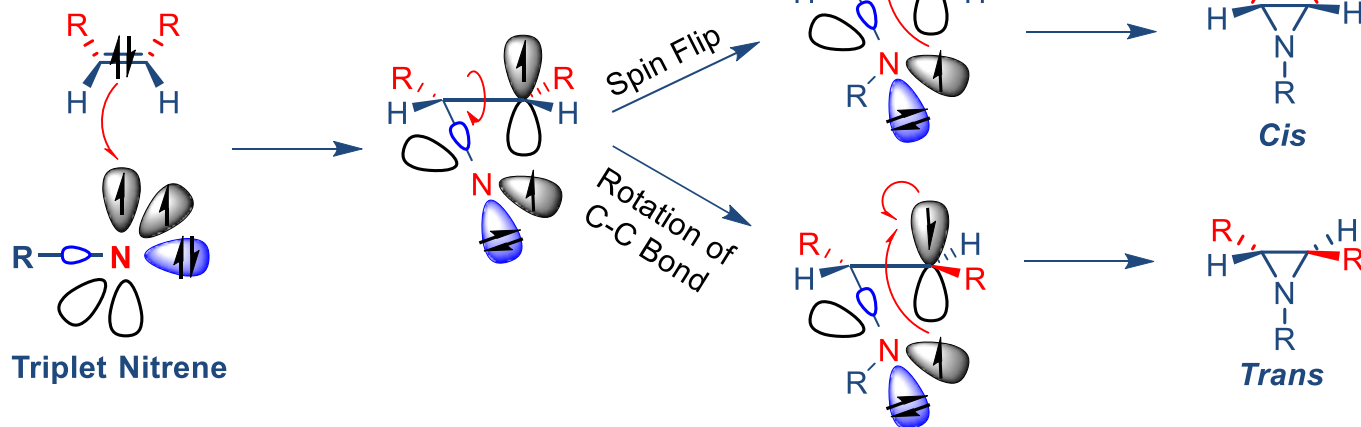
# Reaction of Nitrenes

## Cycloaddition



Singlet Nitrene

➤ One-step, **stereospecific** manner.

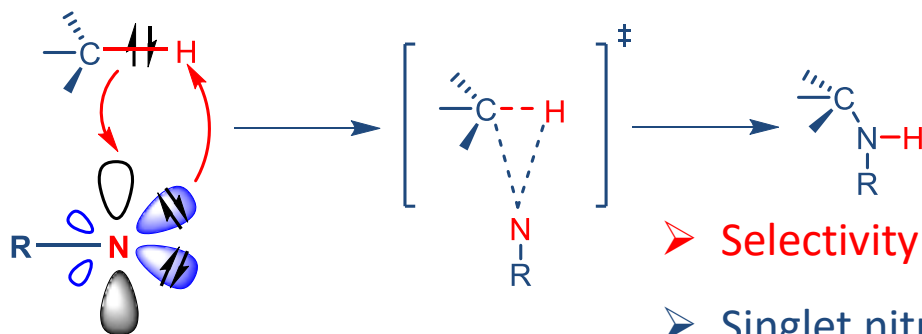


Triplet Nitrene

➤ Two-step, **non-stereospecific** manner.

# Reaction of Nitrenes

## C-H Insertion



Singlet Nitrene

- **Selectivity:** tertiary C-H > secondary C-H > primary C-H
- Singlet nitrenes insert into alkyl C-H bonds selectively with **retention** of configuration.
- Triplet nitrenes generally do not insert into alkyl C-H bonds.

## Rearrangement Reaction



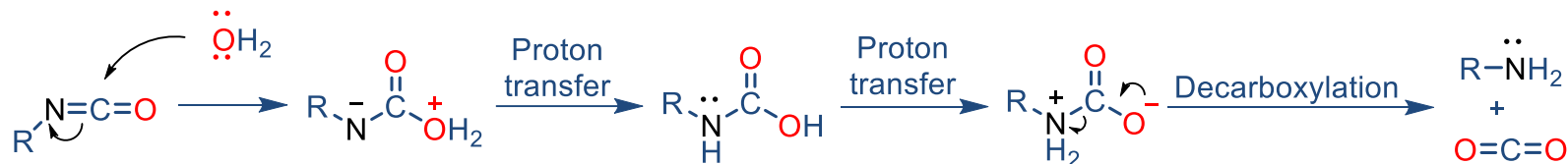
Acyl Nitrene

Alkyl Isocyanate

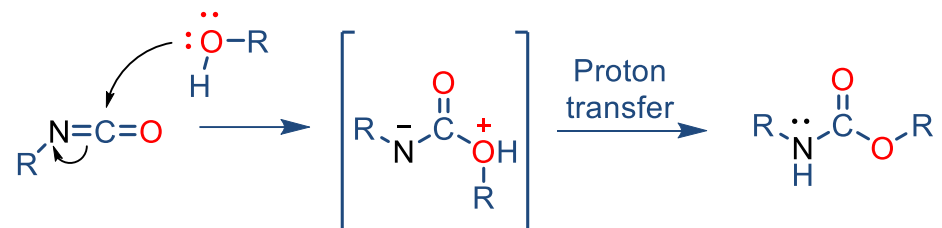
- Acyl nitrenes undergo skeletal rearrangement.
- Curtius and Hoffmann rearrangements.

## Transformation of Isocyanates

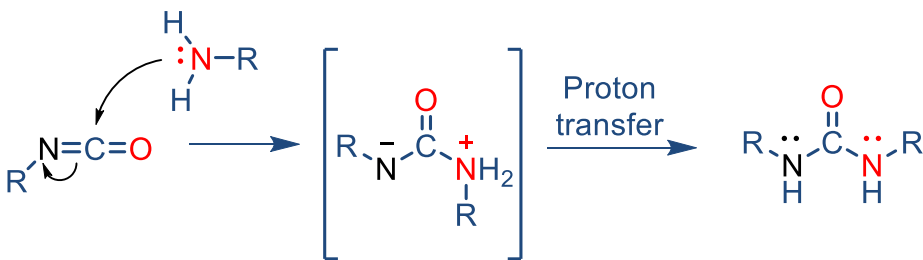
### 1. Addition of water to give carbamic acids (followed by decarboxylation)



### 2. Addition of alcohols to give carbamates



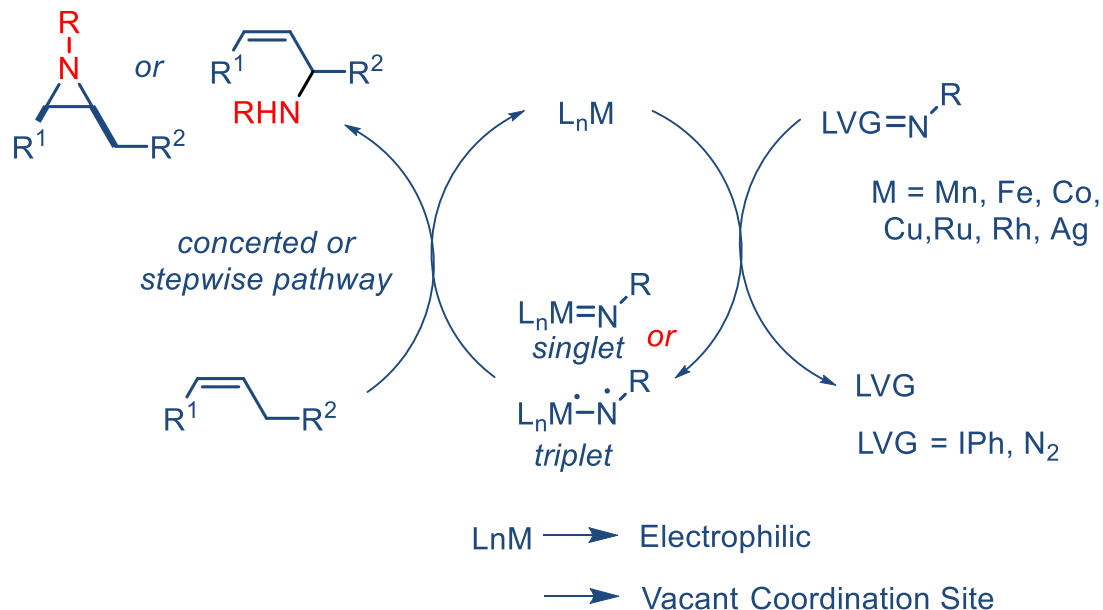
### 3. Addition of amines to give ureas



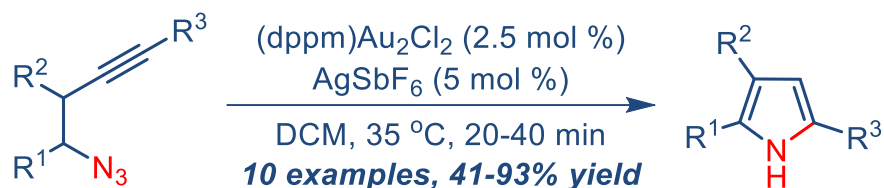
# Moderation of Reactivity



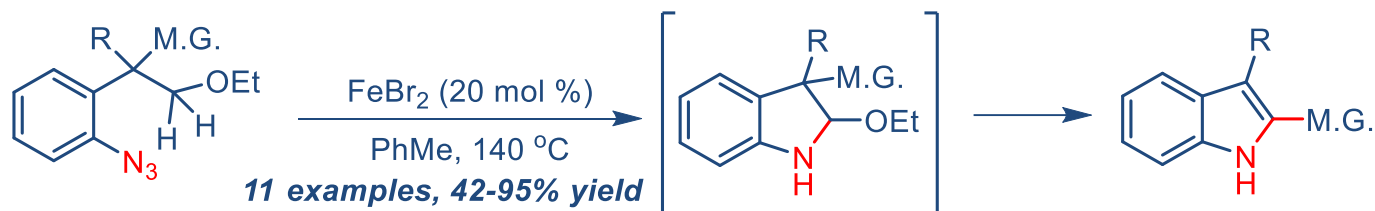
## General Mechanism



- Tune the reactivity of nitrene by changing **L**, **M**, **R**.
- Different species for 1. **addition reaction** 2. **insertion reaction** 3. **ylide formation** and more

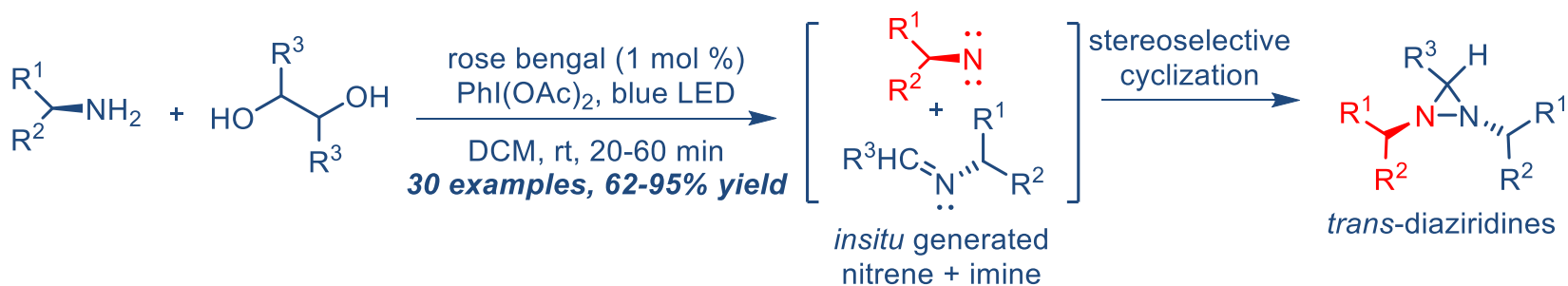


F. Dean Toste and co-workers, *J. Am. Chem. Soc.* **2005**, *127*, 11260-11261.



M.G. = Migrating Group

Tom G. Driver and co-workers, *J. Am. Chem. Soc.* **2013**, *135*, 620-623.



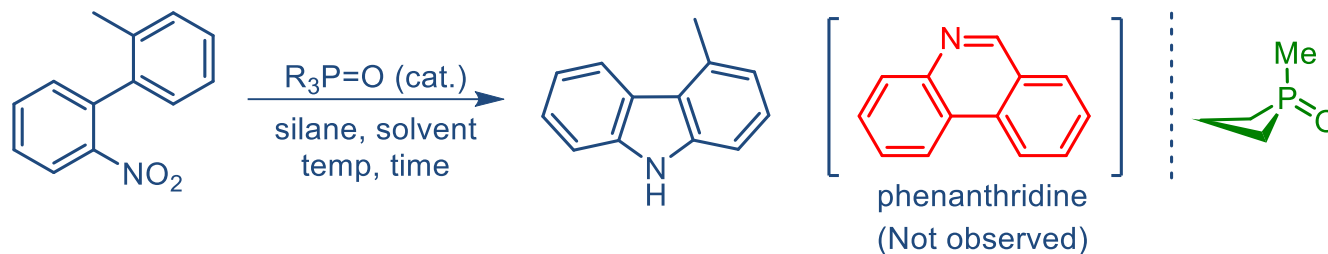
Dilip K. Maiti and co-workers, *Org. Lett.* **2017**, *19*, 5964-5967.



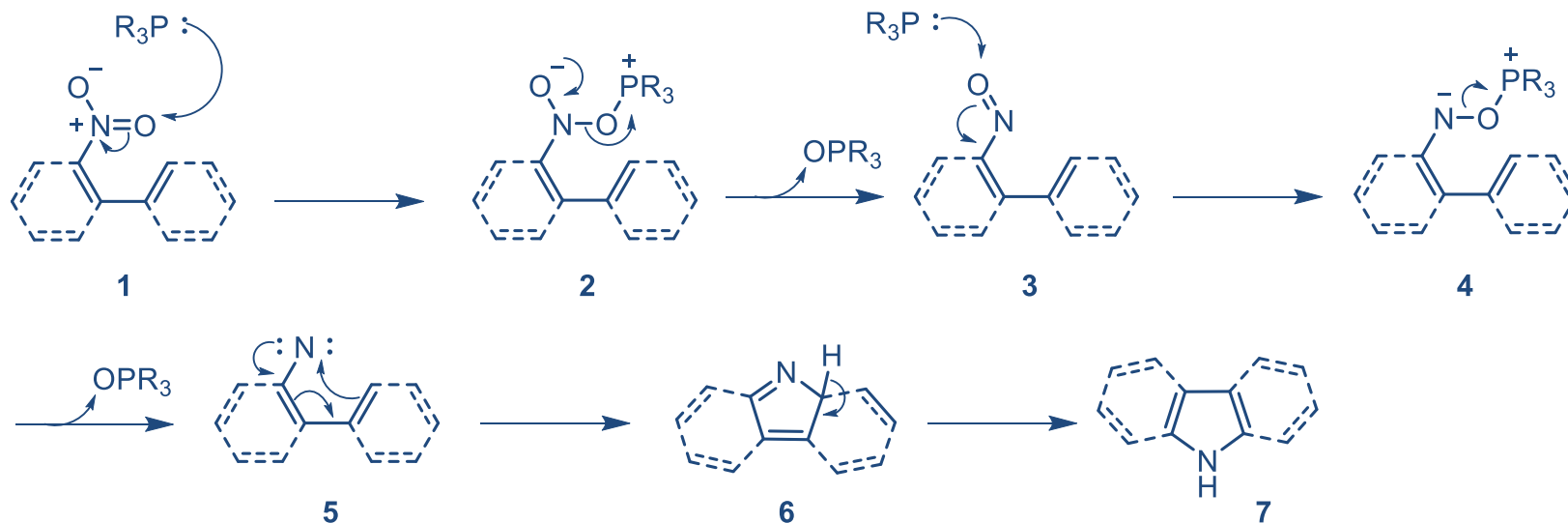
# Proposed Plan



## Reported Synthesis



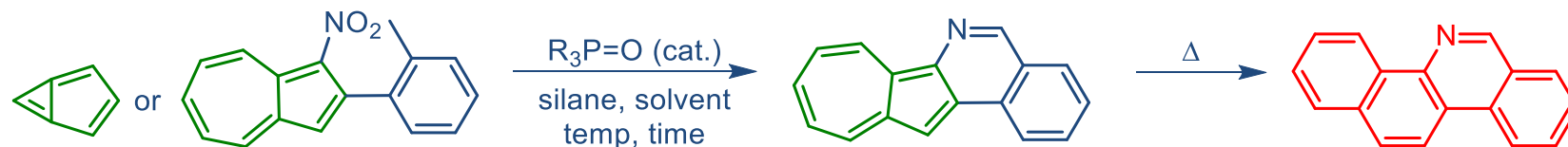
## General Mechanism



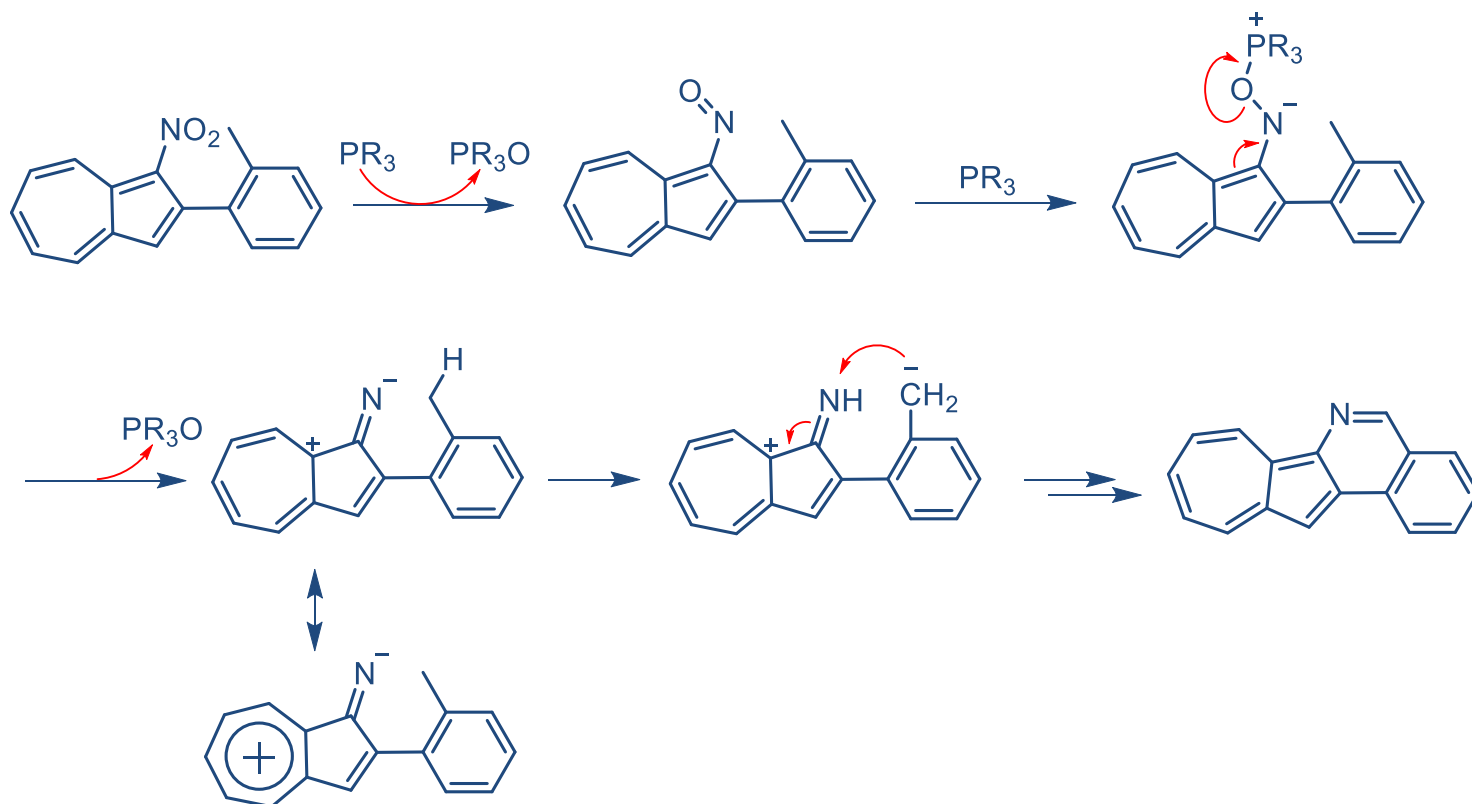
# Proposed Plan



## Hypothesis of Catalytic Cadogan on $sp^3$ C-H bond



## General Mechanism



# *Thank You*

*For Your Kind Attention.....*