

Dyotropic Reactions

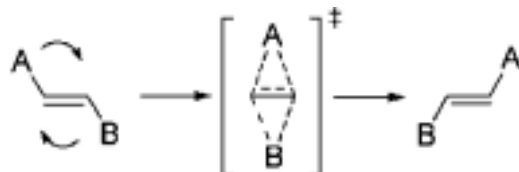
—Chen Peihao
2016-3-22

Abstract

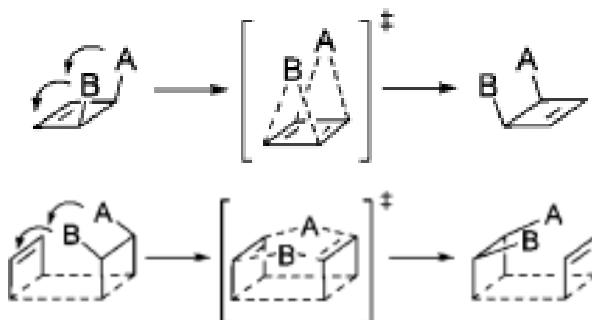
A dyotropic Reaction in organic chemistry is a type of organic reaction and more specifically a pericyclic valence isomerization in which **two sigma bonds simultaneously migrate intramolecularly**.

It was first described by **Manfred T. Reetz** in 1971.

Type I

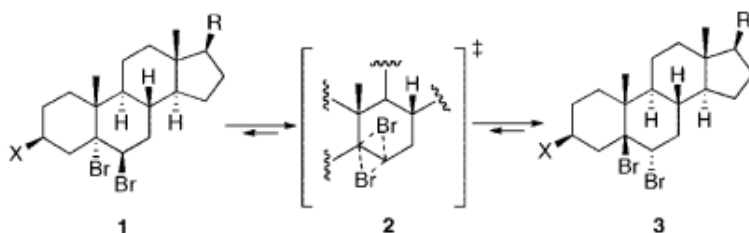


Type II



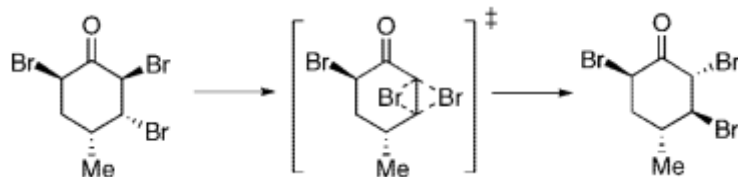
Type I Group 14 Elements

- C-C Bond as Stationary Framework

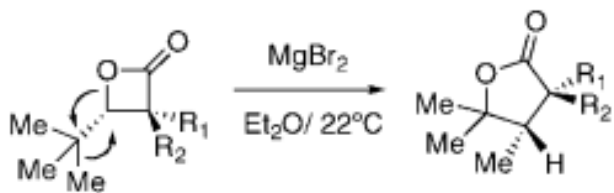


X = H, OH, OBz, Cl, Br
R = CH(CH₃)CHYCHYCHZCH(CH₃)₂ (Y=H, Br; Z=H, Et)

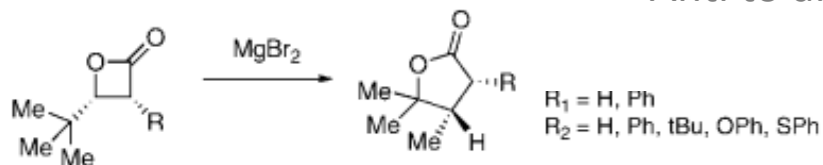
Firsted studied by Grob and Winstein



Showed coordinative mechanisms by Winstein and Barton

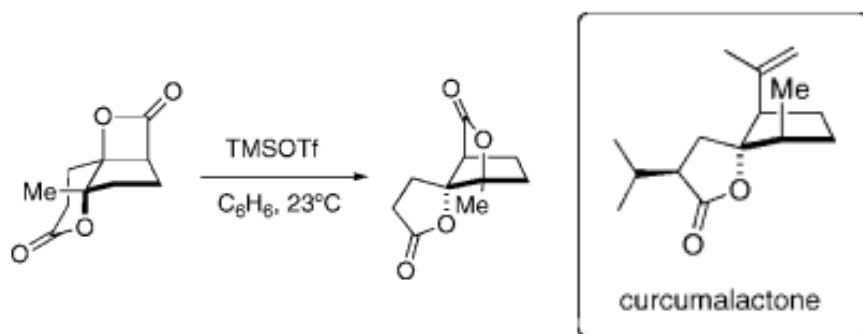


One of the most used types of I dyotropic reactions.
Anti to anti. Syn to syn.

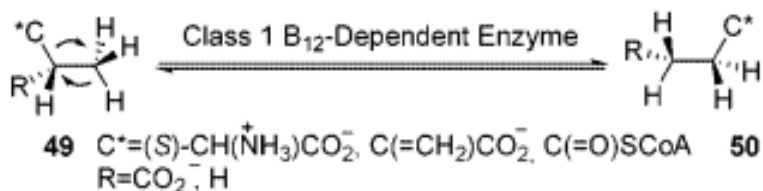


Type I Group 14 Elements

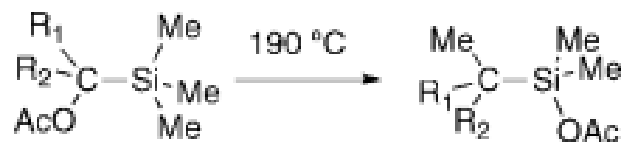
- C-C Bond as Stationary Framework**



Other Lewis acid



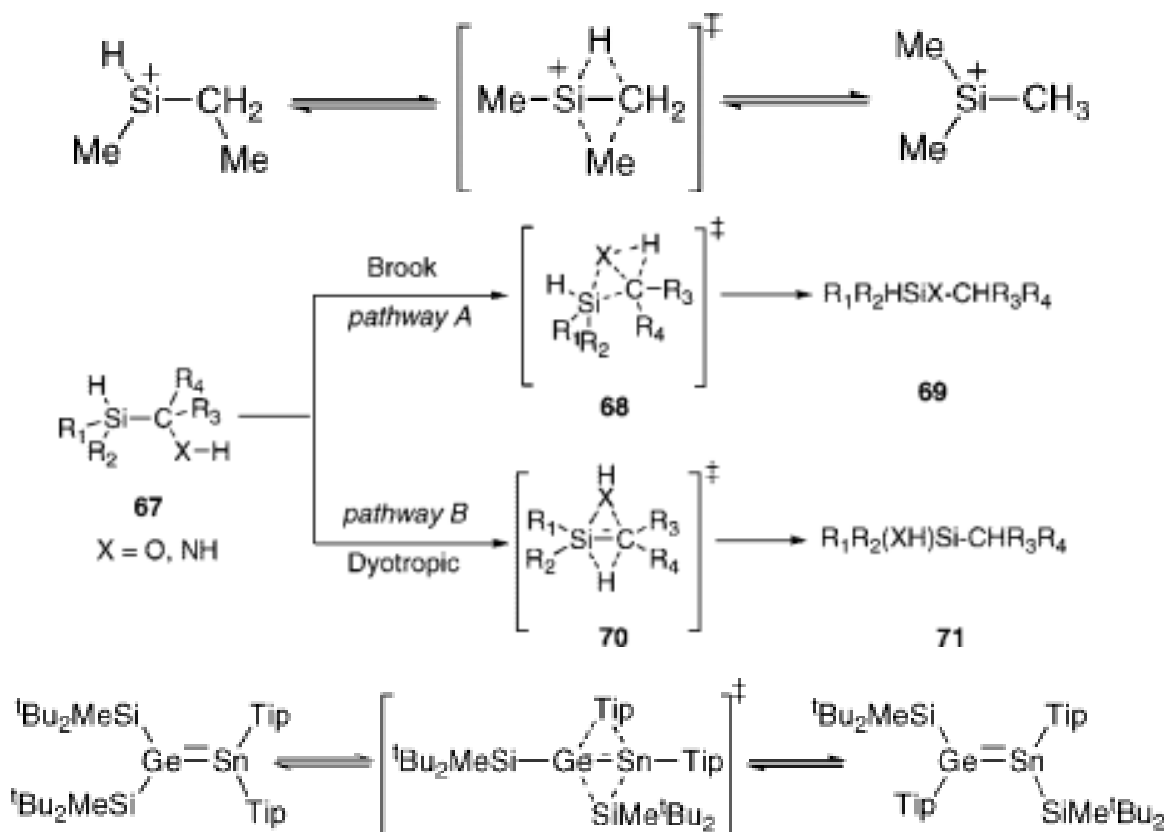
Catalyzed in biological systems



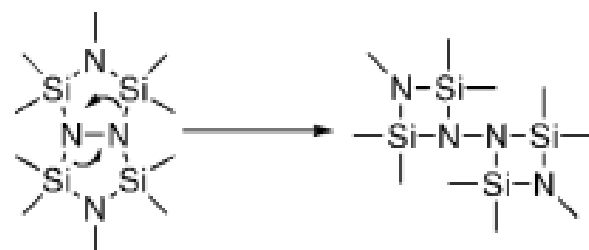
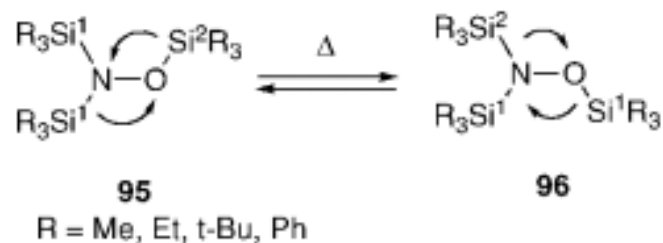
C-Si Bonds

Type I Group 14 Elements

- Silicon to Tin in the Static Scaffold**

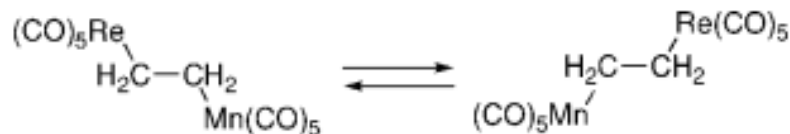


Type I Group 15-16 Elements

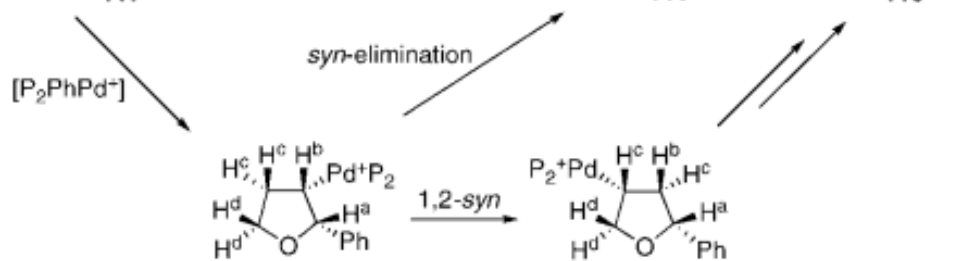
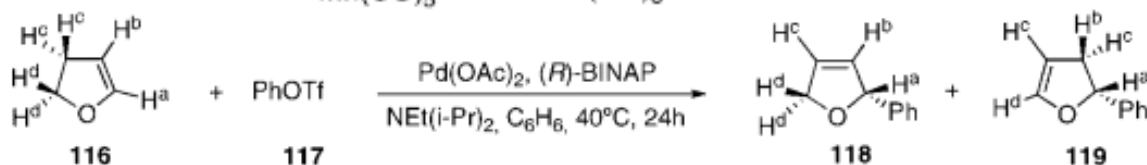


Type I Involving Transition Metals

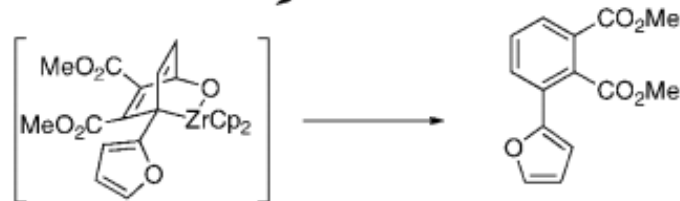
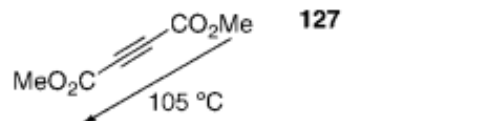
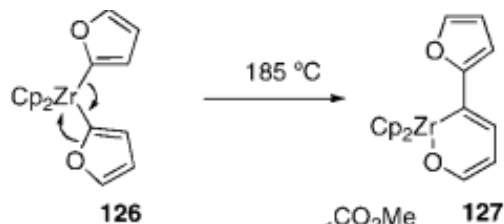
1



2

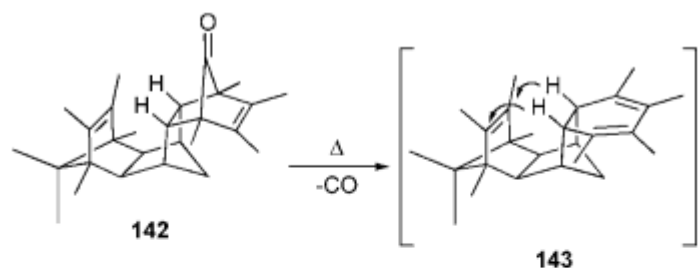


3

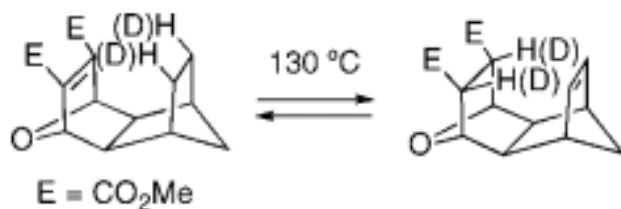
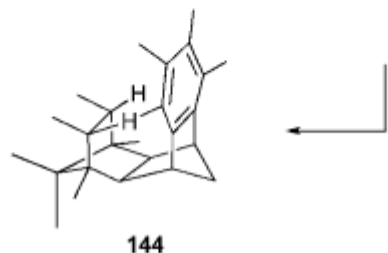


Type II Dyotropic Rearrangements

- **Thermal Reactions**

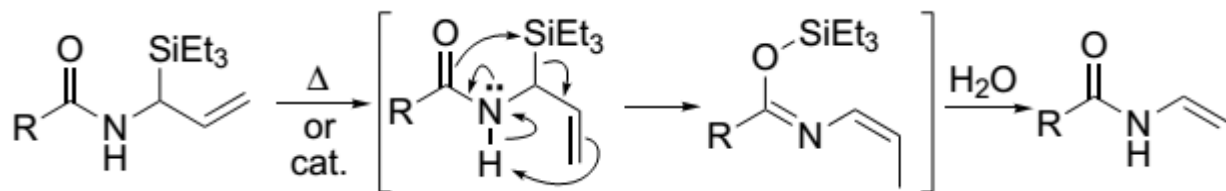
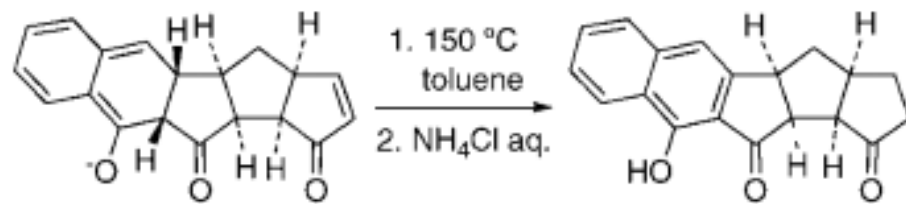
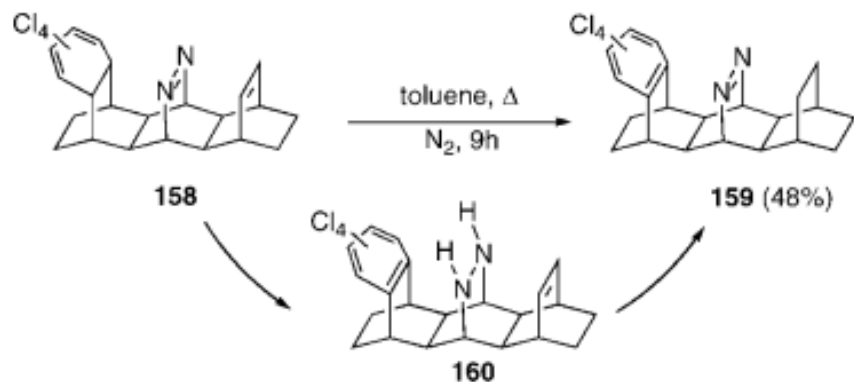


Defined by Woodward and Hoffmann
Thermal[$\sigma^2s+\sigma^2s+\pi^2s$] rearrangement



The rate constant of the rearrangement
is not affected by the concentration,
in agreement with the intramolecular
nature of the process.

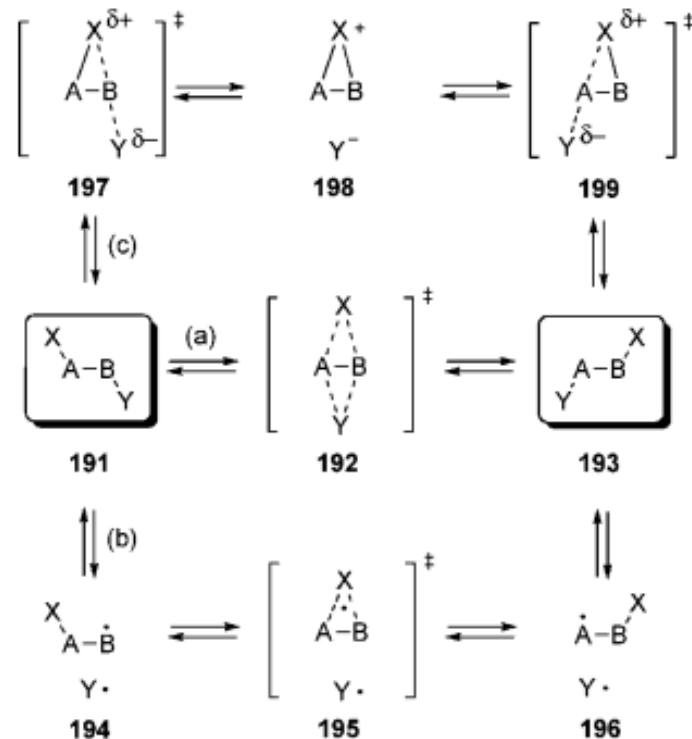
Type II Dyotropic Rearrangements



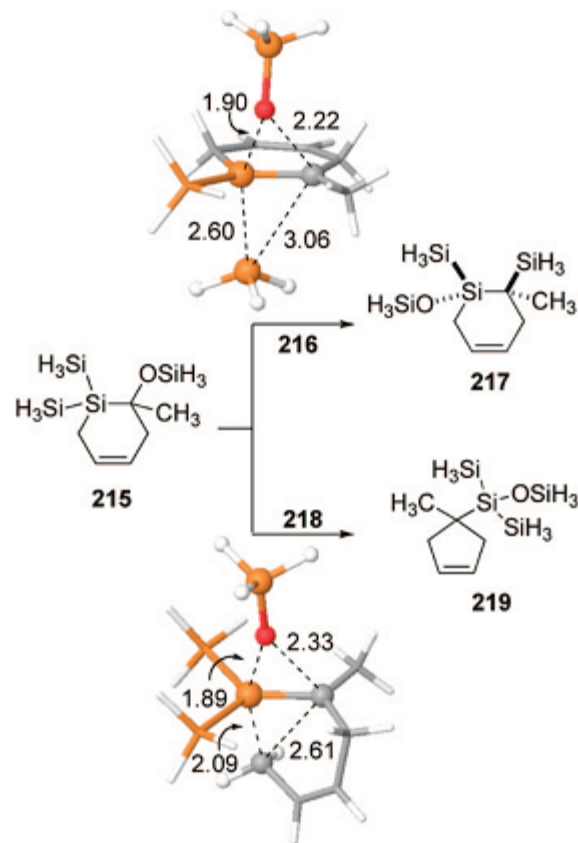
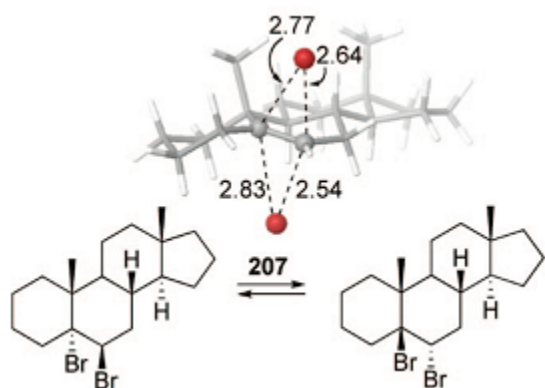
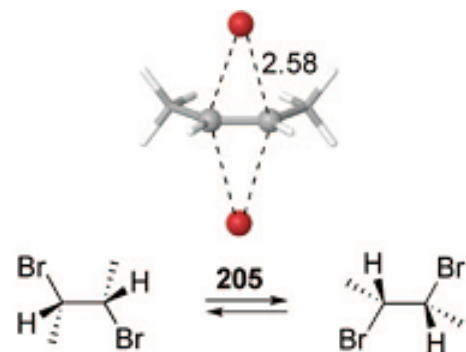
Reaction Mechanisms

- **Type I Dyotropic Processes**

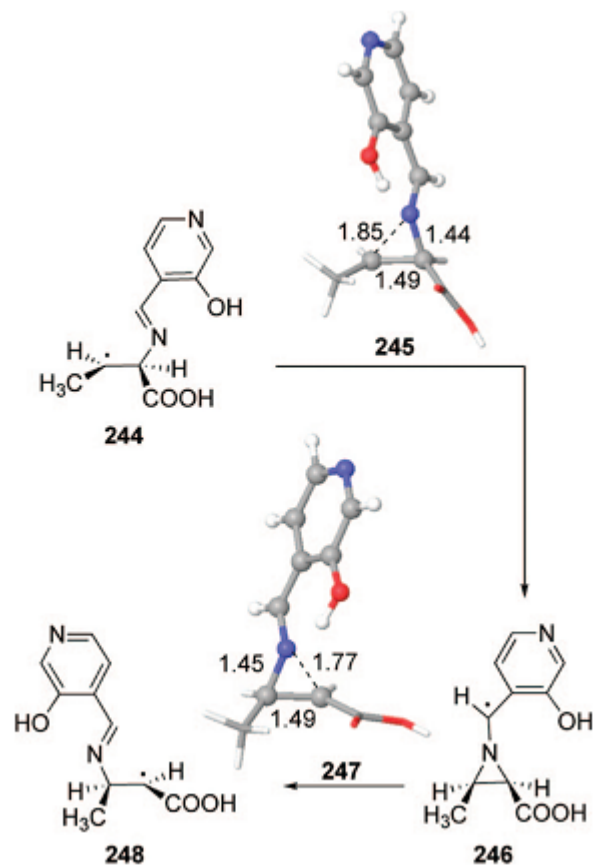
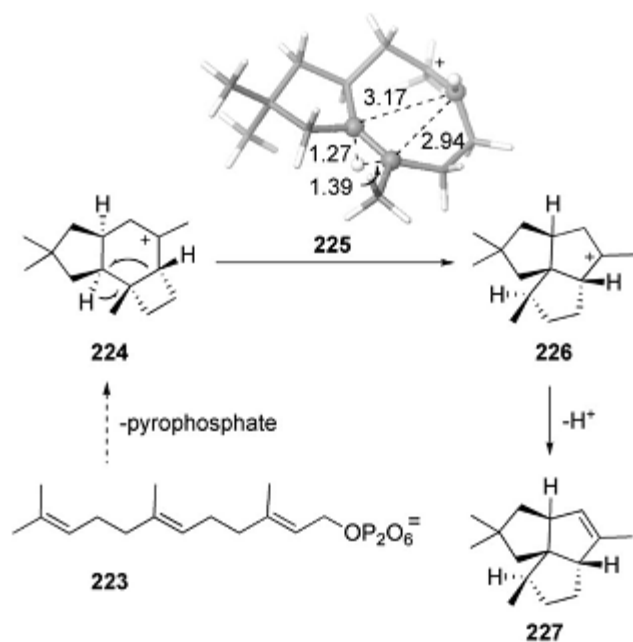
Strictly speaking, dyotropic reactions are concerted and take place via cyclic transition structures.



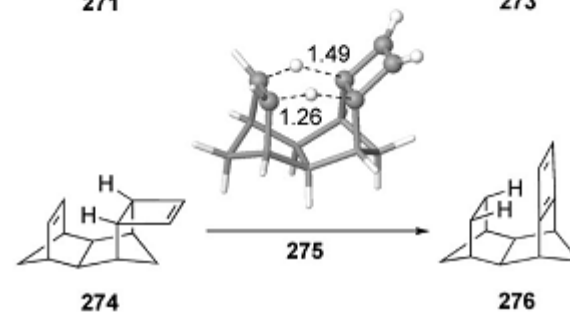
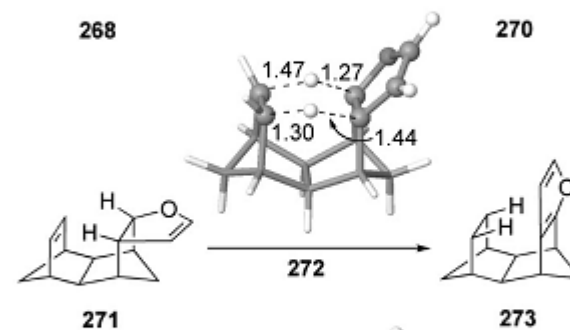
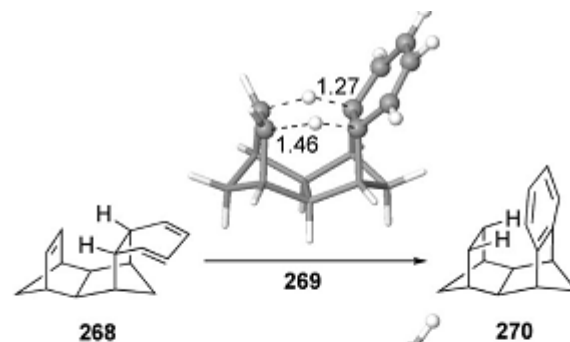
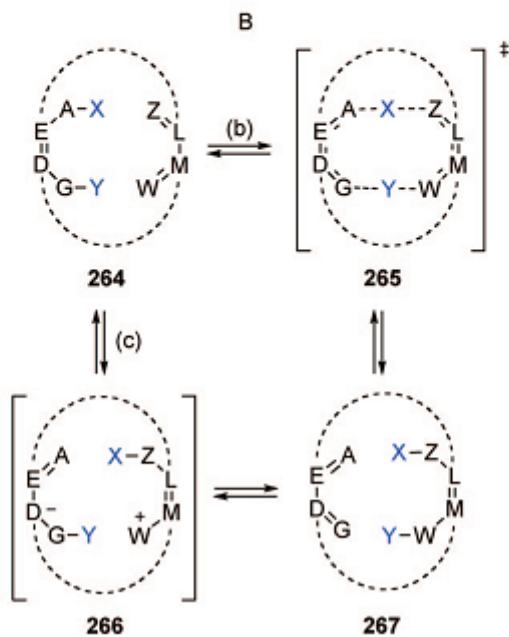
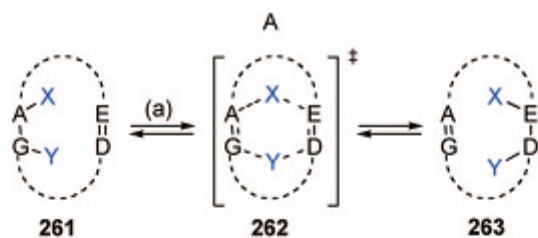
Type I Reaction Mechanisms



Type I Reaction Mechanisms

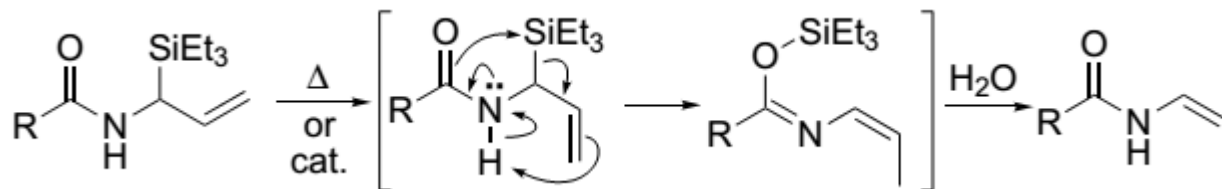
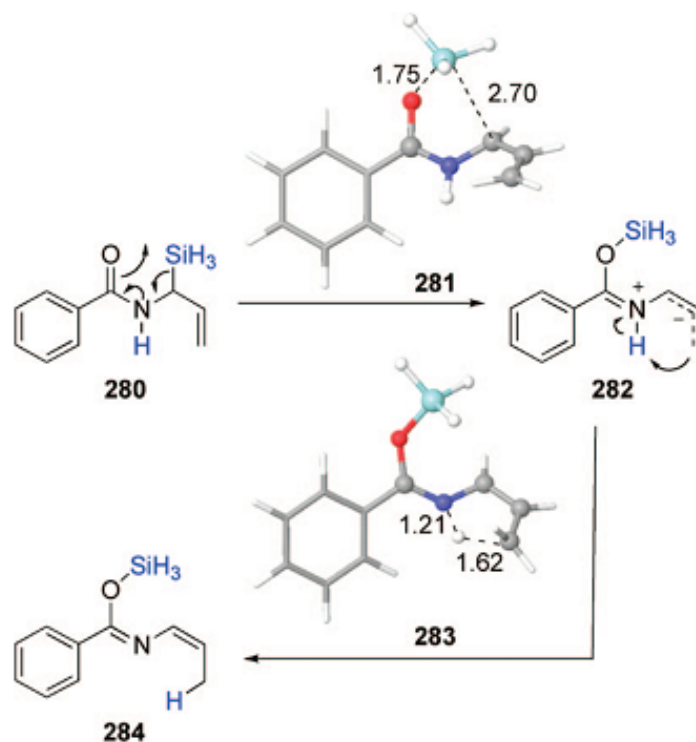


Type II Reaction Mechanisms

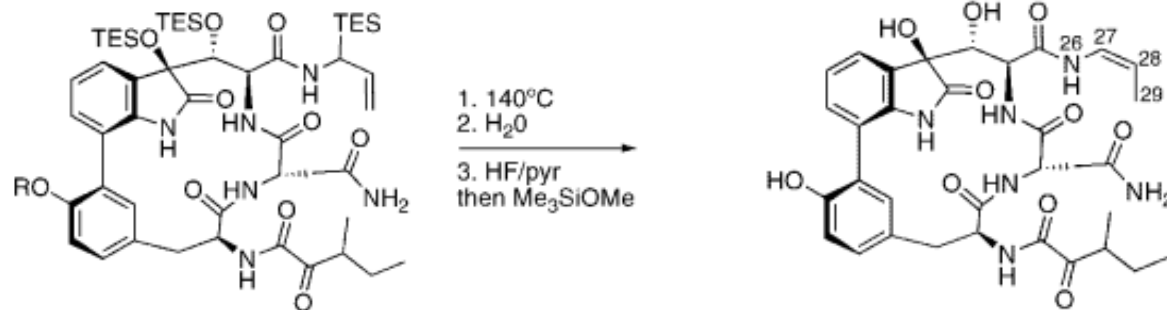


$[\sigma 2s + \sigma 2s + \pi 2s]$ Rearrangement

Type II Reaction Mechanisms

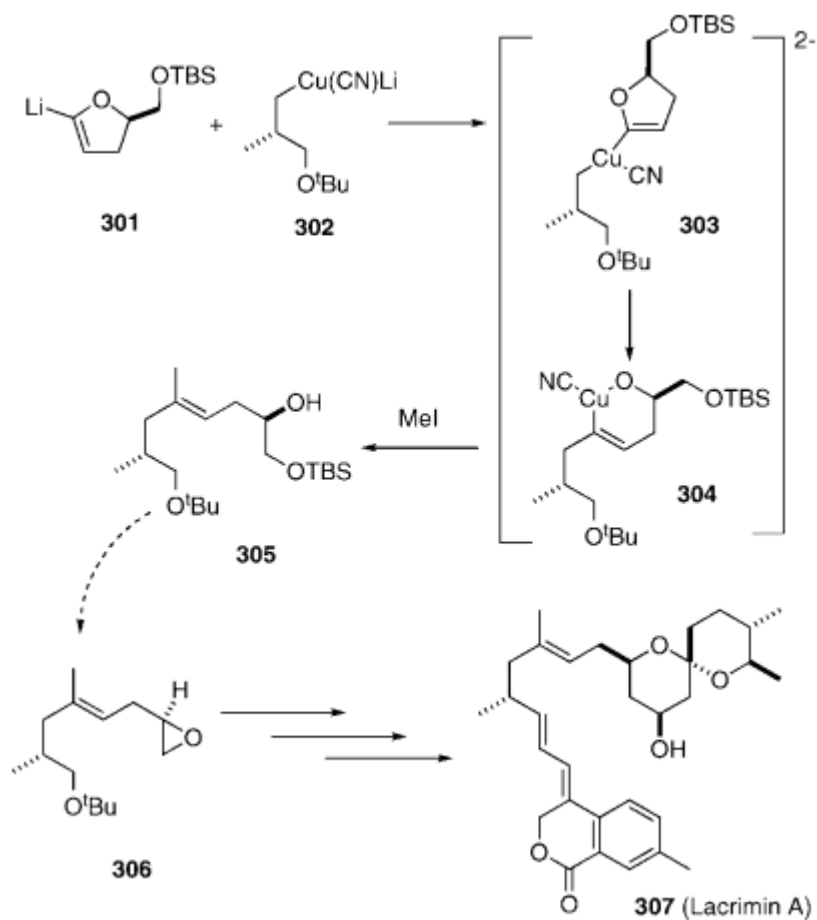


Applycation



—Samuel J. Danishefsky. *Angew. Chem. Int. Ed.* **2002**, 41

Application



Thanks