Dyotropic Reactions

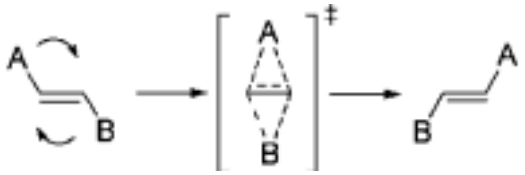
—Chen Peihao
2016-3-22

Abstract

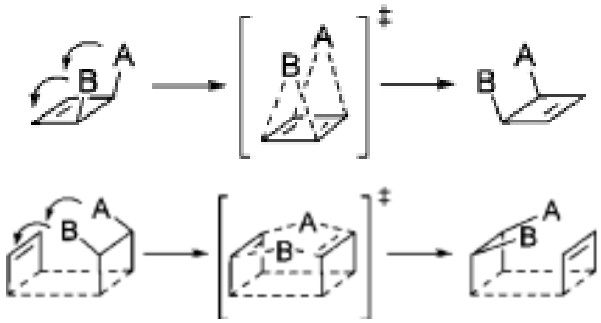
A dyotropic Reaction in organic chemistry is a type of organic reaction and more specifically a pericyclic valence isomerization in which two sigma bonds simultaneously migrate intramolecularly.

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

Type Ⅰ

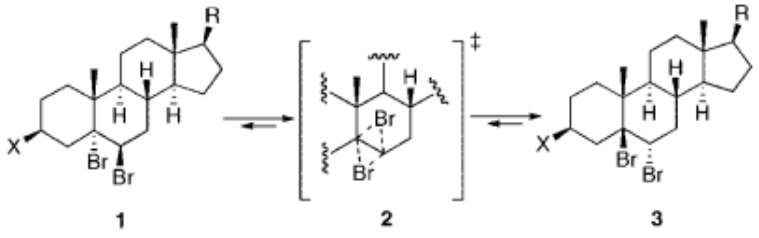


Type Ⅱ

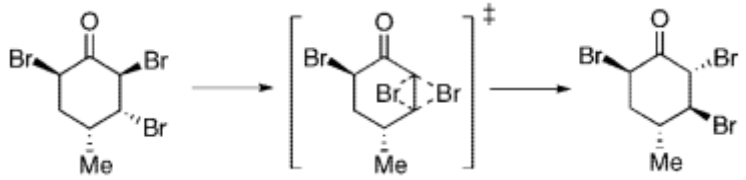


Type I Group 14 Elements

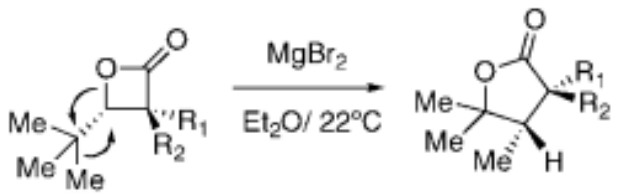
- **C-C Bond as Stationary Framework**



Firsted studied by Grob and Winstein



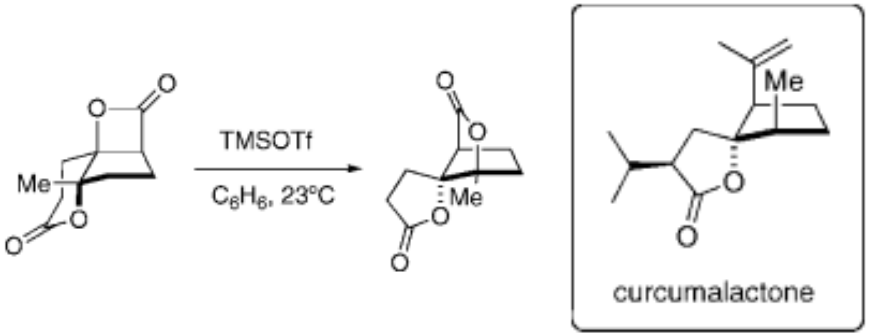
Showed coordinative mechanisms by Winstein and Barton



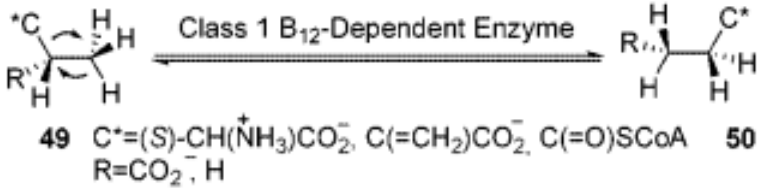
One of the most used types of I dyotropic reactions.
Anti to anti.Syn to syn.

Type Ⅰ Group 14 Elements

- **C-C Bond as Stationary Framework**



Other Lewis acid

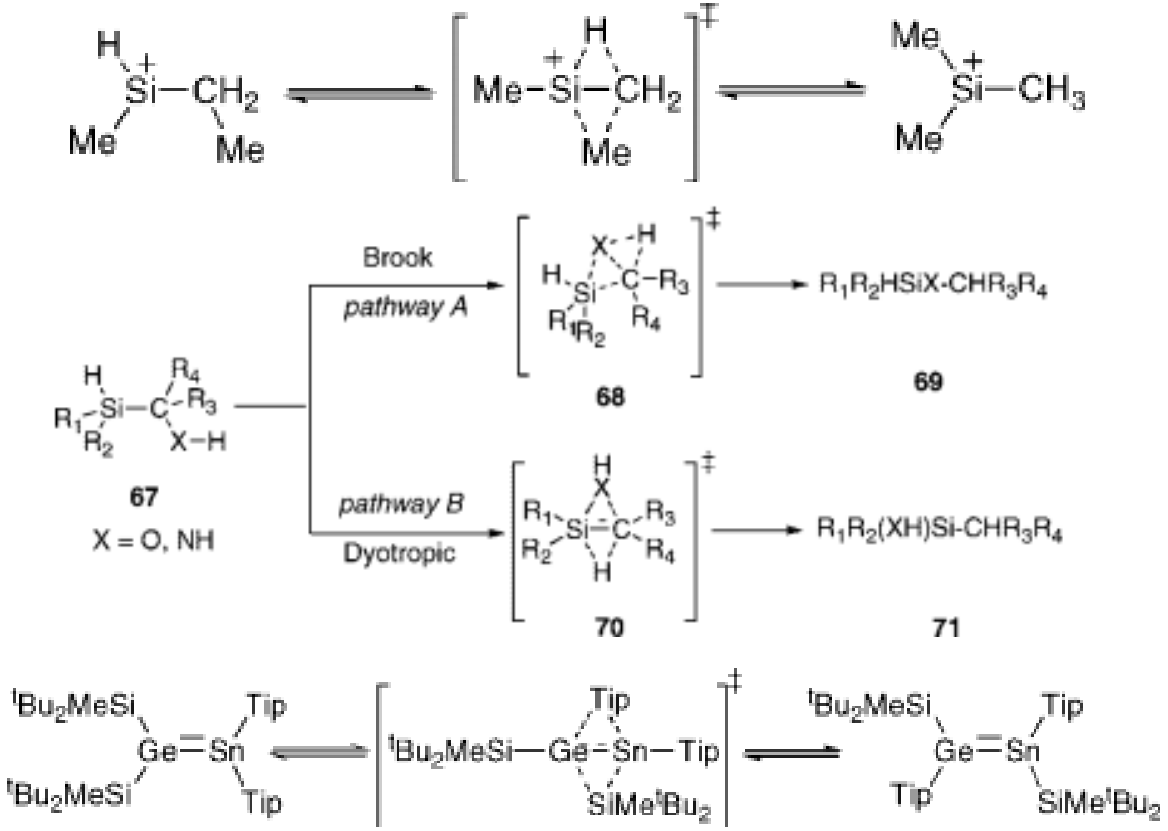


Catalyzed in biological systems

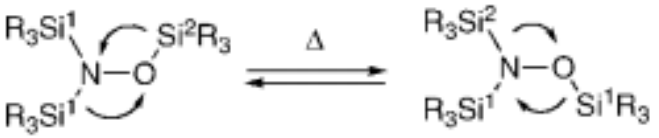
C-Si Bonds

Type Ⅰ Group 14 Elements

- **Silicon to Tin in the Static Scaffold**

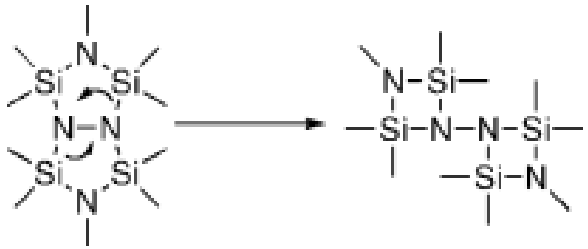


Type I Group 15-16 Elements



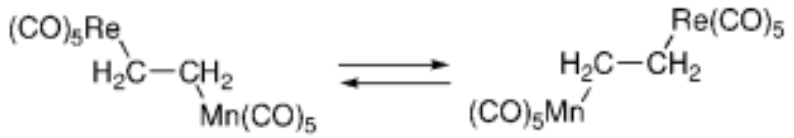
95 **96**

R = Me, Et, t-Bu, Ph

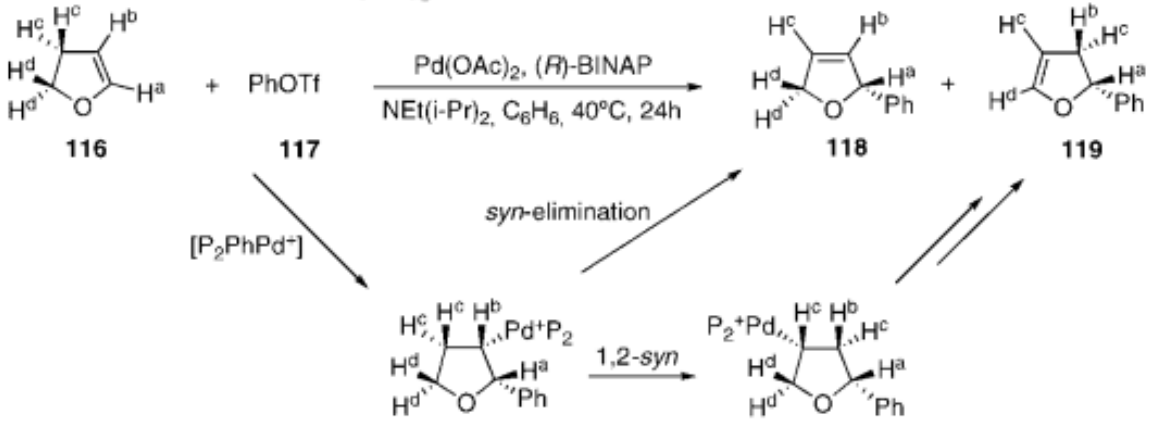


Type Ⅰ Involving Transition Metals

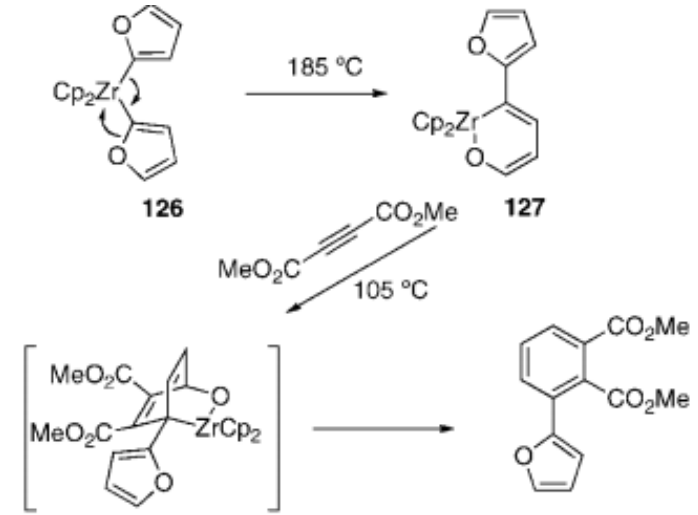
1



2

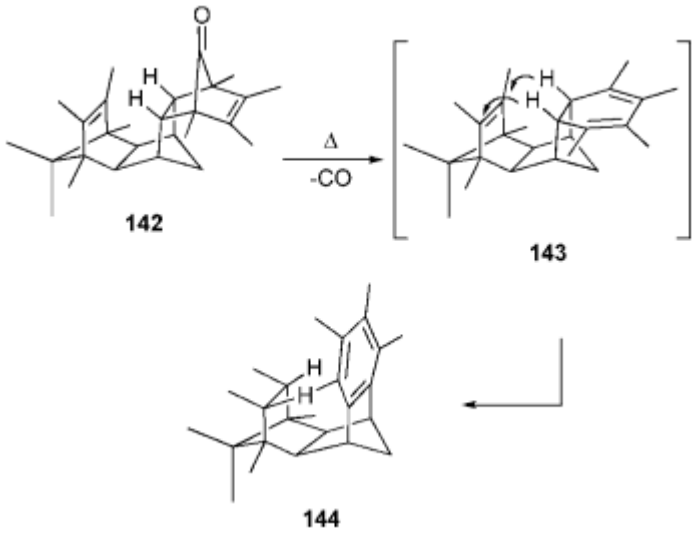


3

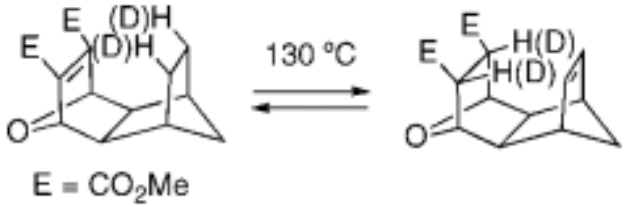


Type II Dyotropic Rearrangements

- **Thermal Reactions**

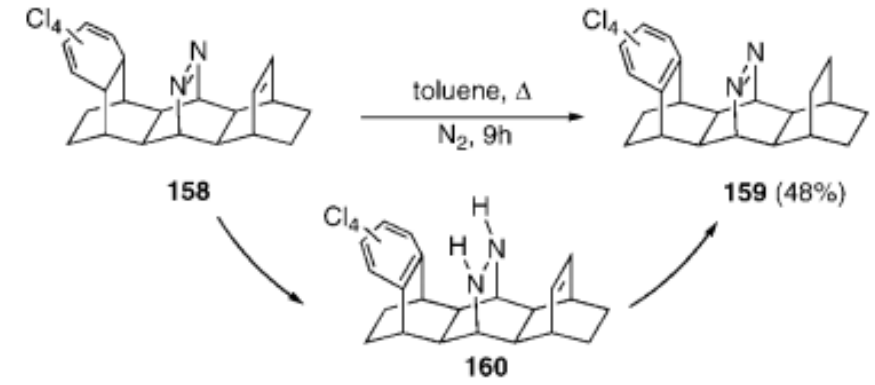


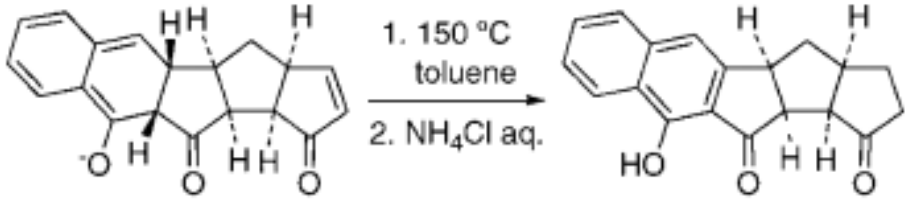
Defined by Woodward and Hoffmann
Thermal[σ2s+σ2s+π2s] rearrangement

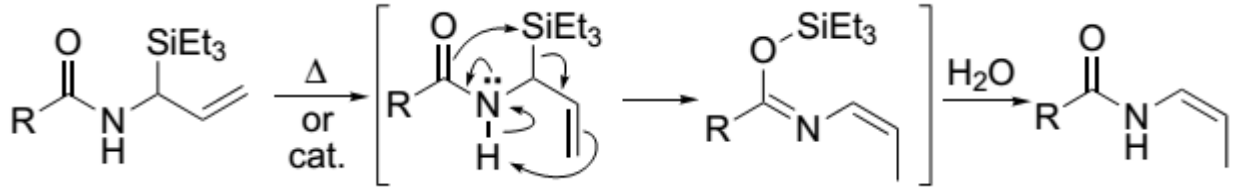


The rate constant of the rearrangement is not affected by the concentration, in agreement with the intramolecular nature of the process.

Type II Dyotropic Rearrangements



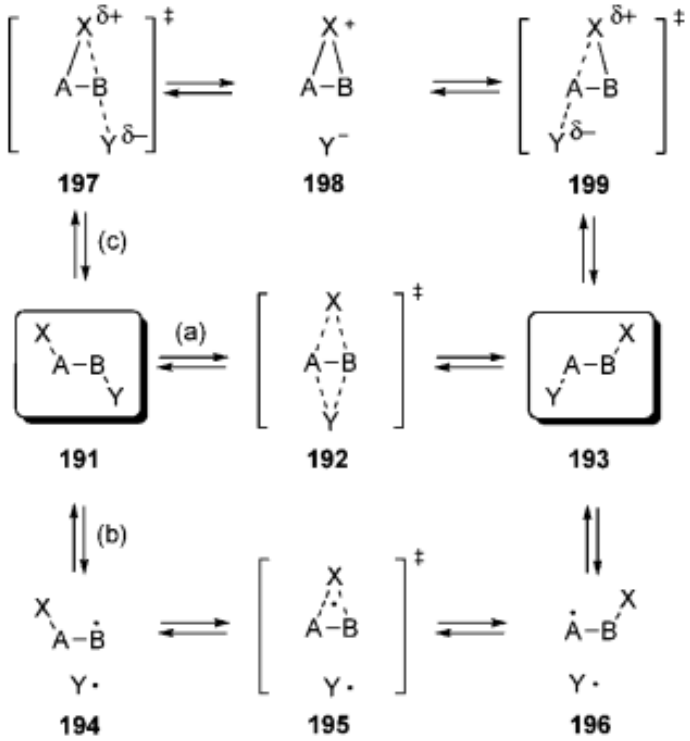




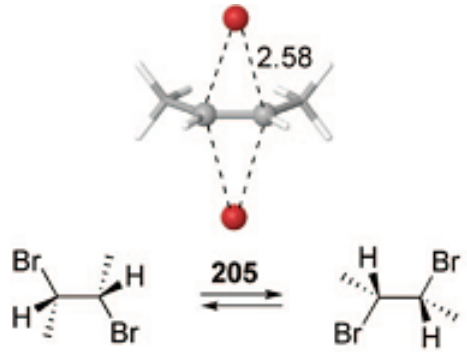
Reaction Mechanisms

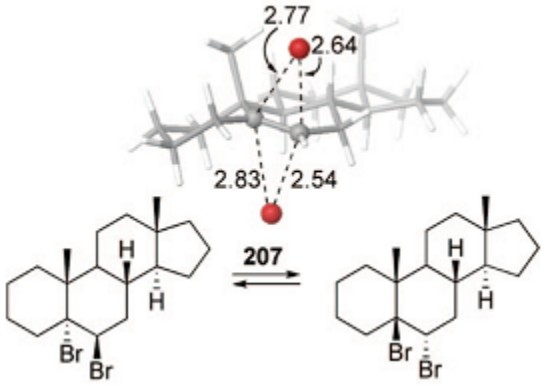
- **Type I Dyotropic Processes**

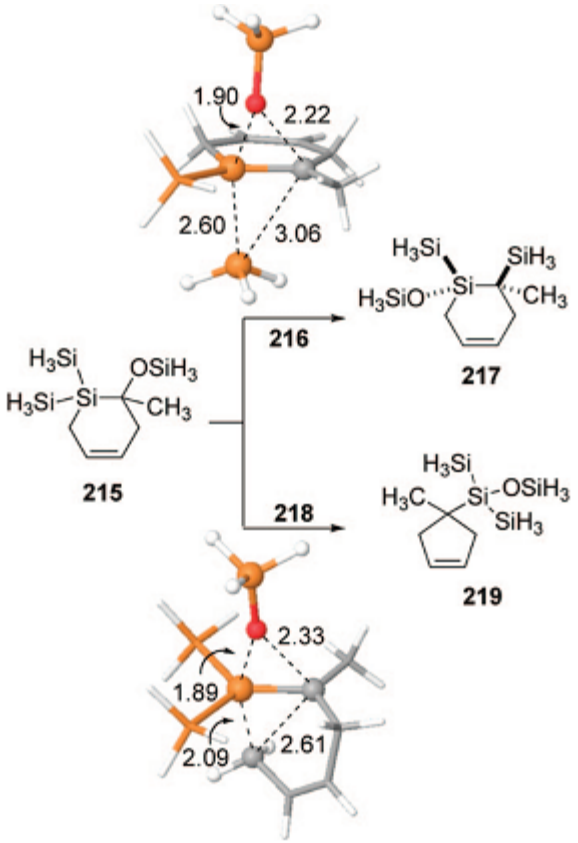
  Strictly speaking, dyotropic reactions are concerted and take place via cyclic transition structures.



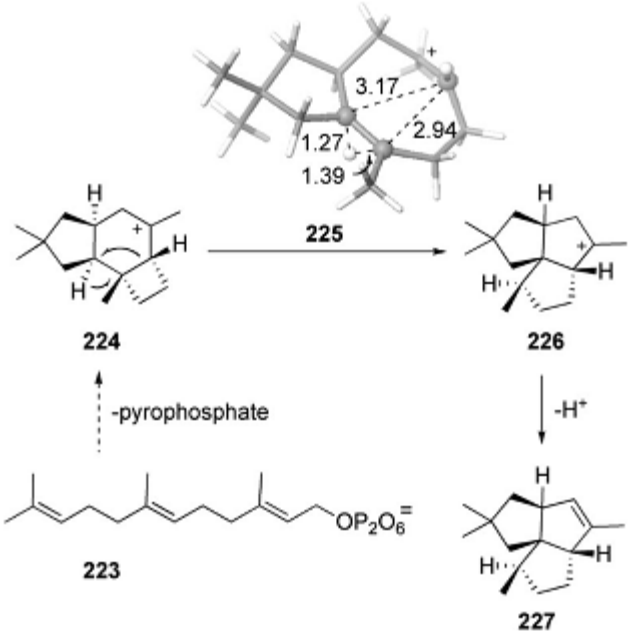
Type Ⅰ Reaction Mechanisms

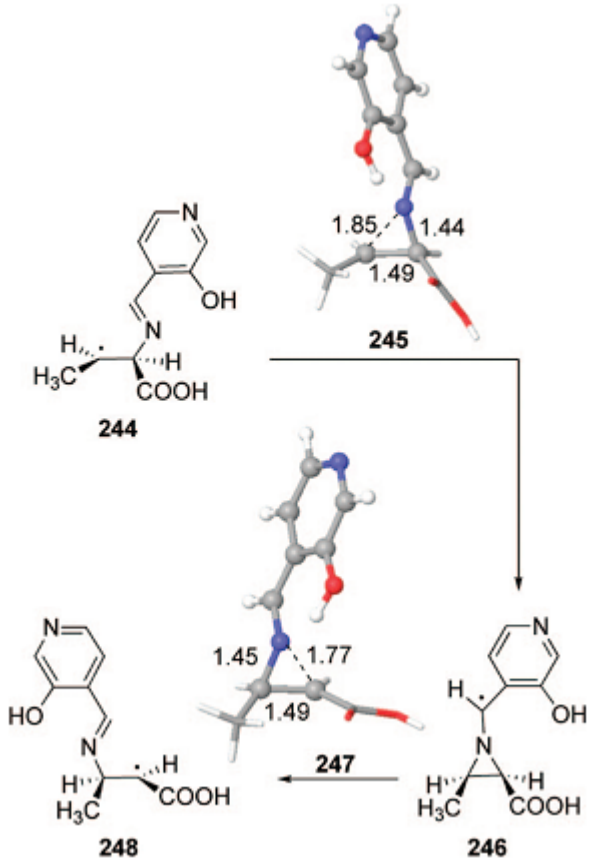




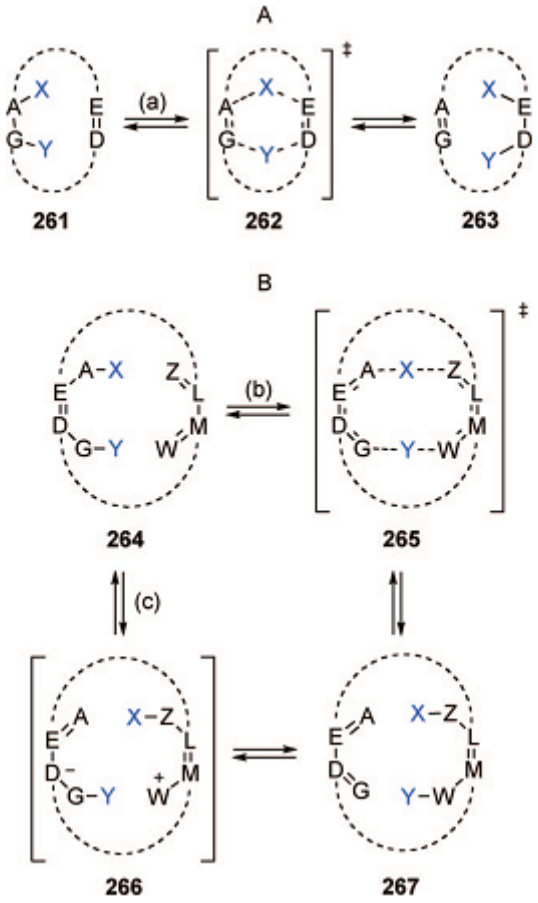


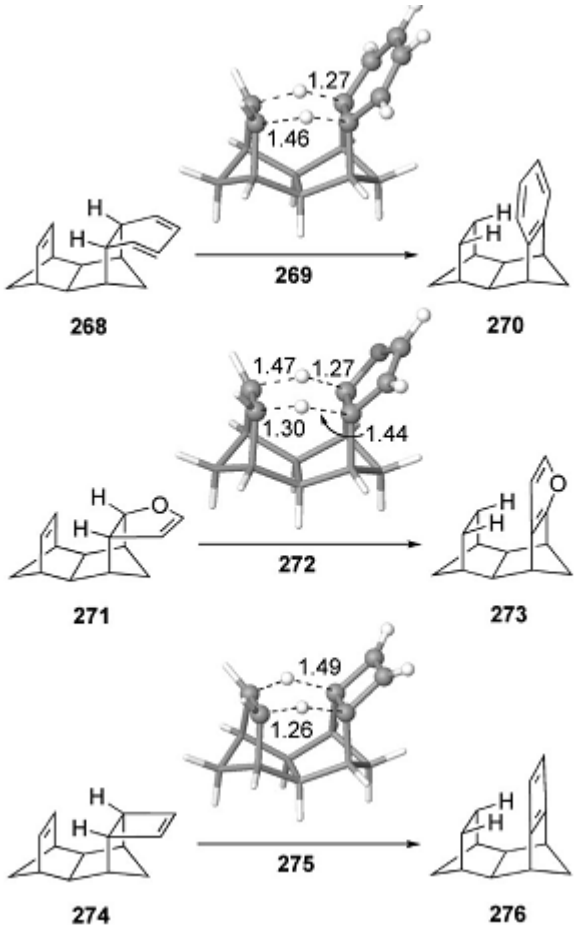
Type Ⅰ Reaction Mechanisms





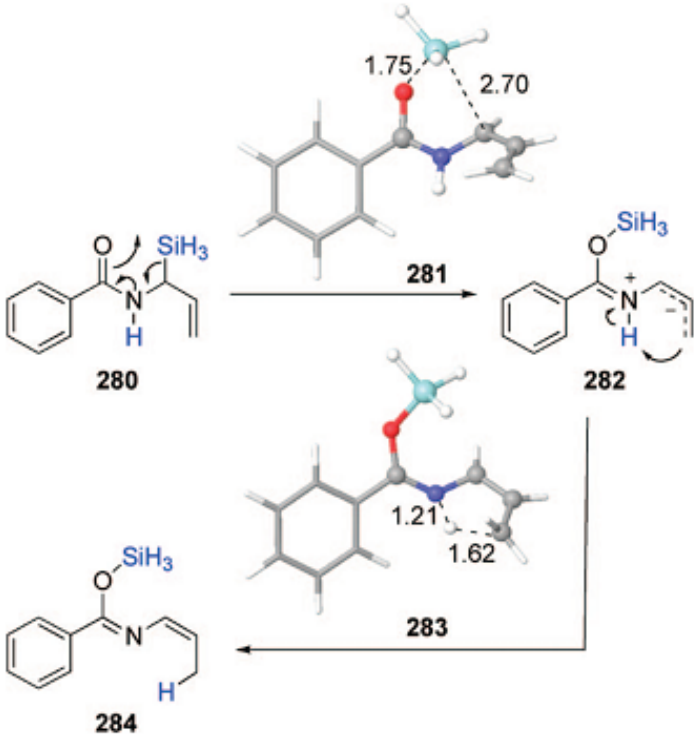
Type Ⅱ Reaction Mechanisms

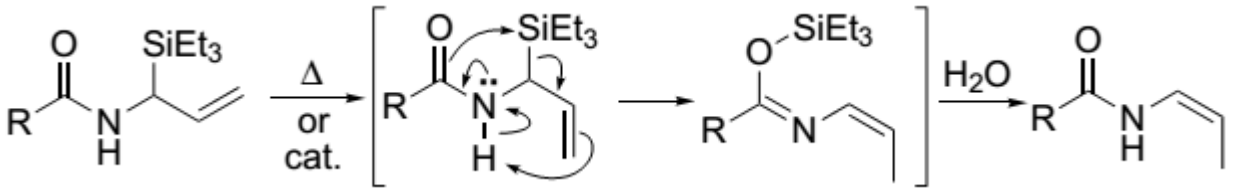




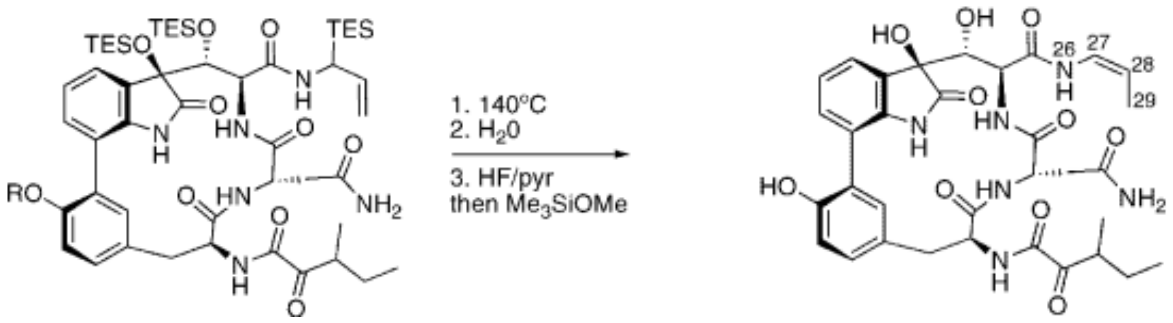
[σ2s+σ2s+π2s] Rearrangement

Type II Reaction Mechanisms



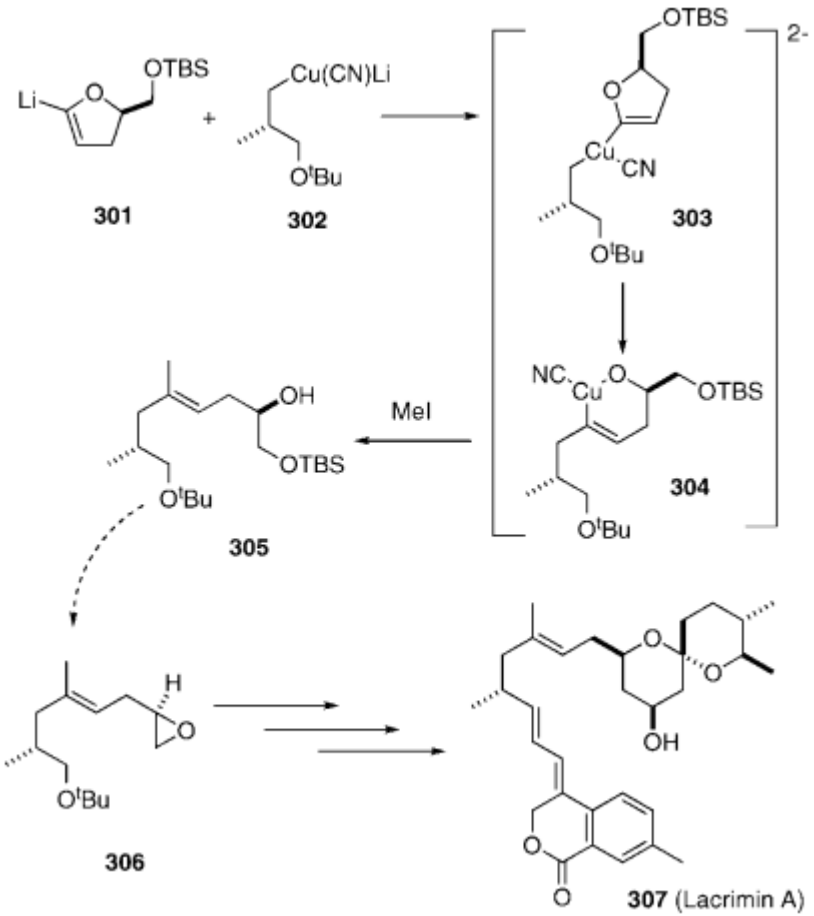


Applycation



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

Applycation



—Takle, A.; Kocienski, P. *Tetrahedron* **1990**, *46*, 4503

Thanks