

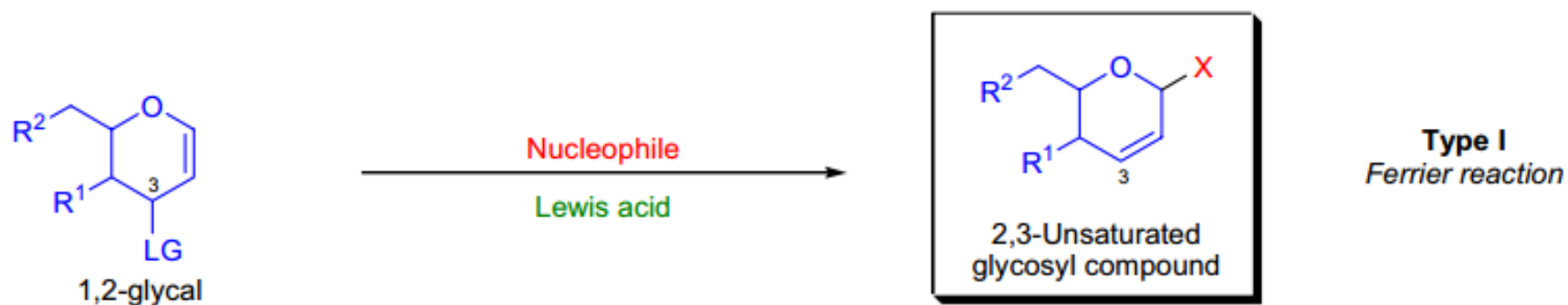
Ferrier reaction/rearrangement

Lirong Cai

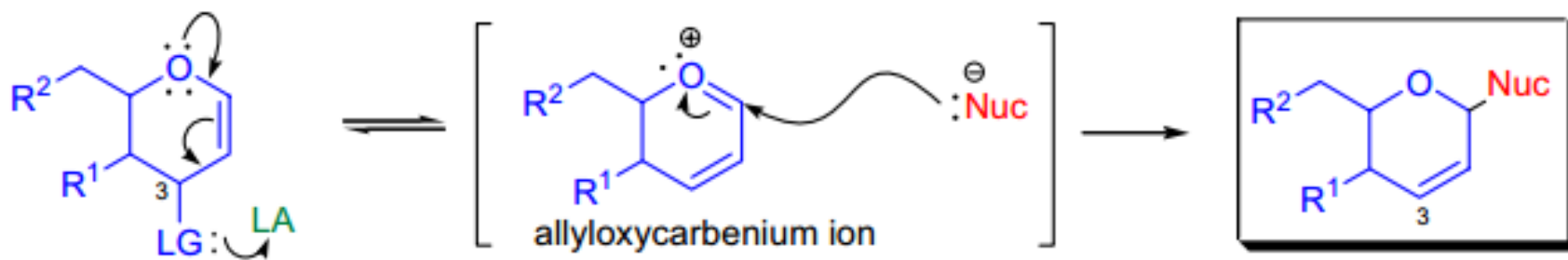
May 5th 2015

Ferrier reaction

- Type I ferrier reaction

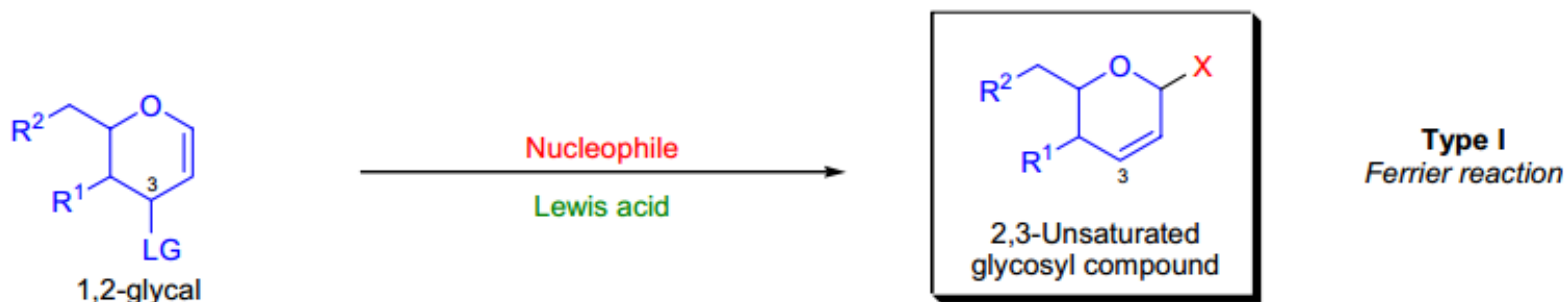


- Mechanism



Ferrier reaction

- Type I ferrier reaction

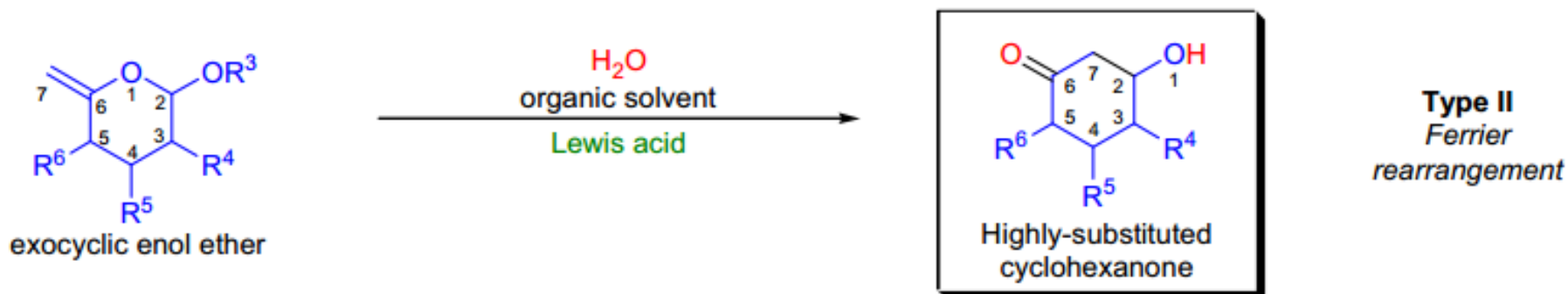


- Features

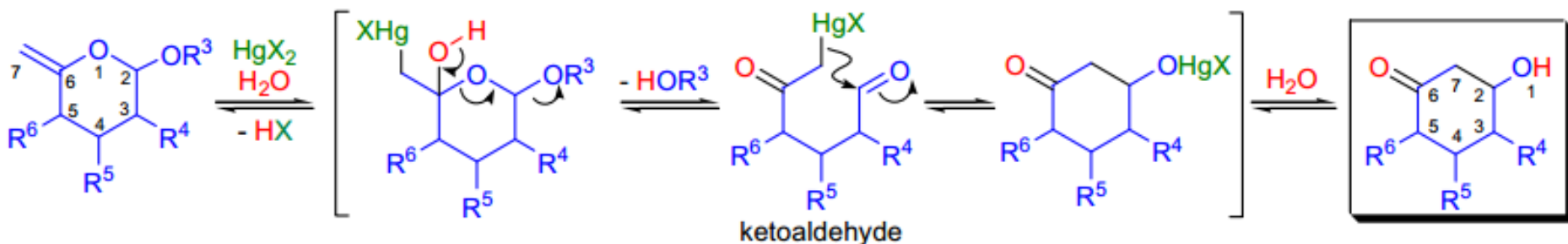
1. Substrates with good leaving groups, for example, acyloxy group, in 3-position can undergo the rearrangement upon heating in the presence of strong nucleophiles, even in the absence of a catalyst
2. Commonly used Lewis acids are BF₃.OEt₂, SnCl₄, I₂, FeCl₃, TMSOTf-AgClO₄
3. The hydroxyl group at C3 in the glycal can be activated under Mitsunobu reaction conditions without the use of a Lewis or protic acid
4. The stereochemistry of the 2,3-unsaturated glycosyl product at the anomeric center depends on the relative stereochemistry of the groups at C3 and C4 in the starting material, but the α -anomeric center is usually predominant

Ferrier rearrangement

- Type II ferrier rearrangement

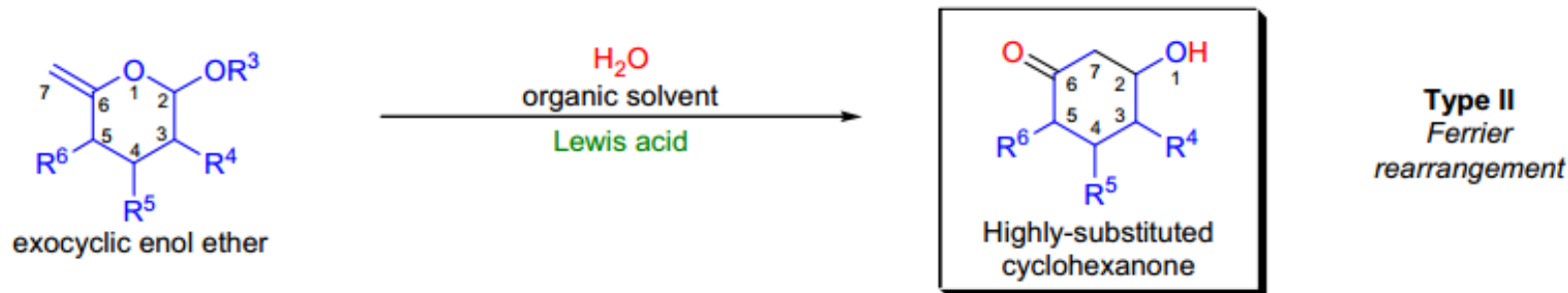


- Mechanism



Ferrier rearrangement

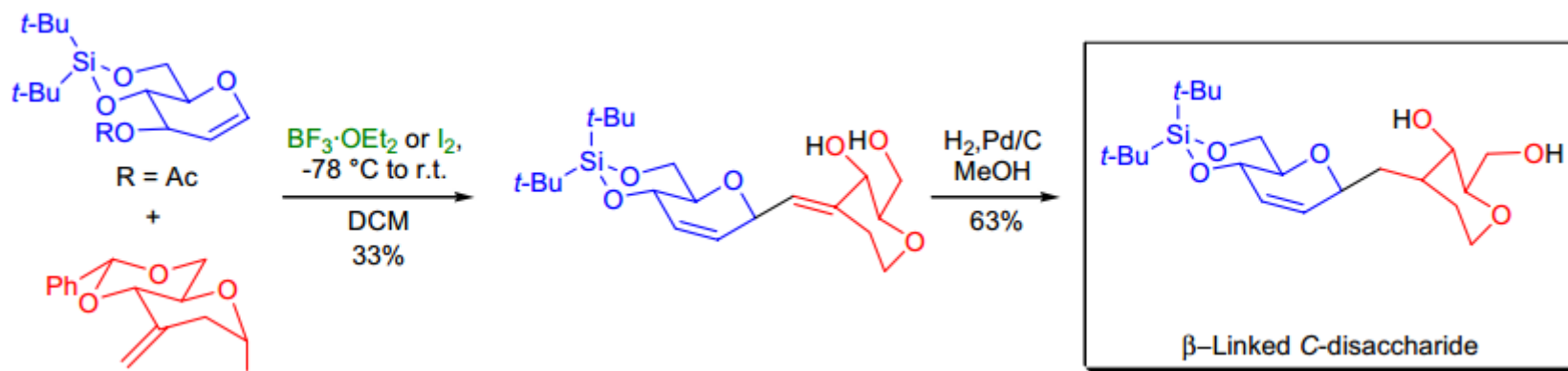
- Type II ferrier rearrangement



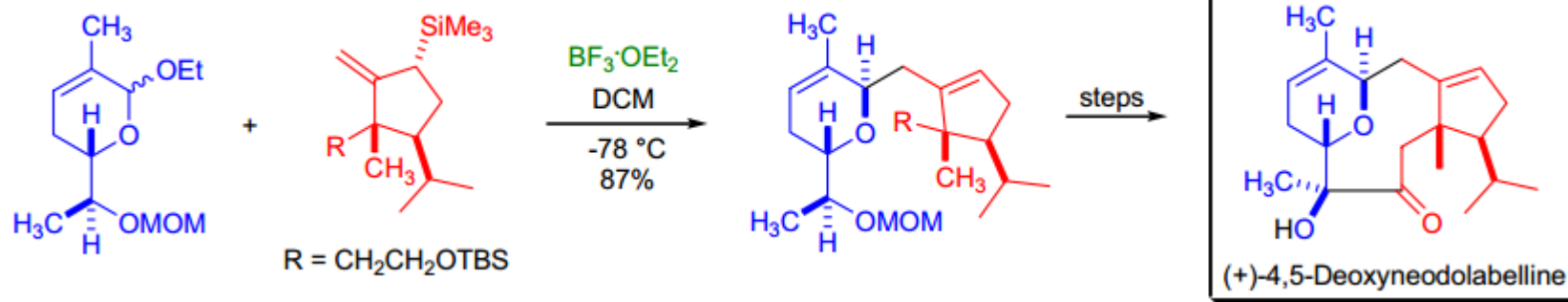
- Feature

1. The precursors are readily available from carbohydrates, so the synthesis of chiral, highly-substituted cyclohexanone derivatives is possible;
2. In most reactions, single diastereomers are isolated in high yield;
3. The Lewis acid can be used in catalytic amounts and complex targets having acid sensitive functionalities can be prepared.

Synthetic applications

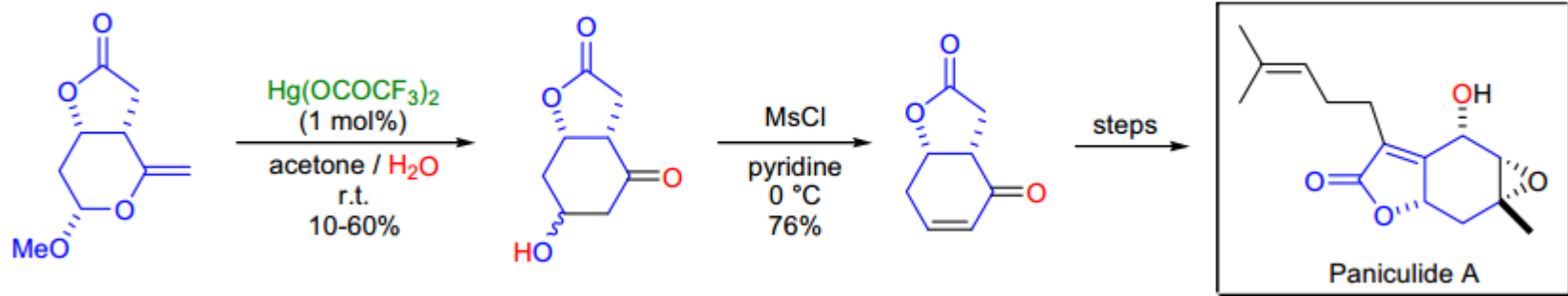


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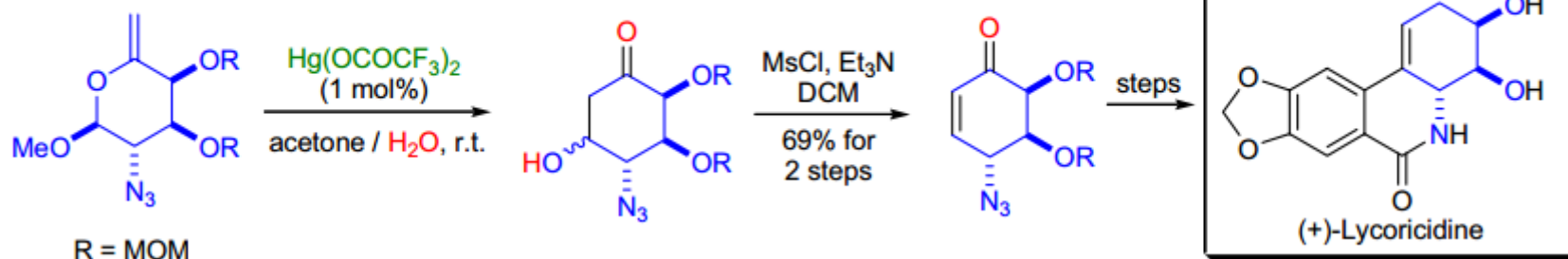


Williams, D. R. Heidebrecht, R. W., Jr. *J. Am. Chem. Soc.* **2003**, 125, 1843-1850.

Synthetic applications



Amano, S. *et al Tetrahedron* **1999**, 55, 3855-3870.



Chida, N., Ohtsuka, M., Ogawa, S. *J. Org. Chem.* **1993**, 58, 4441-4447.