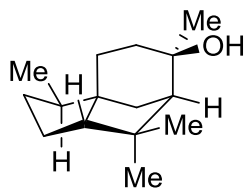


# Total Syntheses of (–)-Majucin and (–)-Jiadifenoxolane A, Complex Majucin-Type *Illicium* Sesquiterpenes

M. L. Condakes, K. Hung, S. J. Harwood, Thomas J. Maimone *JACS* **2017**, *139*, 17783–17786.



- 1)  $\text{PhI}(\text{OAc})_2$ ,  $\text{I}_2$ ,  $h\nu$   
then  $\text{Ac}_2\text{O}$ ,  $\text{H}_3\text{PO}_4$   
2)  $\text{BH}_3 \cdot \text{THF}$ ,  
then  $\text{CrO}_3 \cdot 2\text{pyr}$   
3)  $\text{NaBH}_4$

*Step 1: Name of the starting material?*

*Name and mechanism of this reaction?*

*(hint: without  $\text{Ac}_2\text{O}$ ,  $\text{H}_3\text{PO}_4$  a five-membered ring would be formed)*



- 4)  $\text{PhI}(\text{OAc})_2$ ,  $\text{I}_2$ ,  $h\nu$   
5)  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ ,  $\text{KBrO}_3$   
6)  $\text{SeO}_2$ , 4 Å MS  
then  $\text{K}_2\text{CO}_3$ ,  $\text{Me}_2\text{SO}_4$   
7) L-selectride  
then  $\text{KOH}/\text{MeOH}$

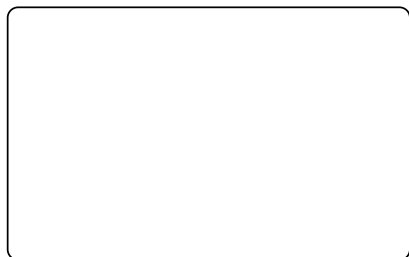
*Step 5: Please come up with a mechanism. What is the active species in this step?*

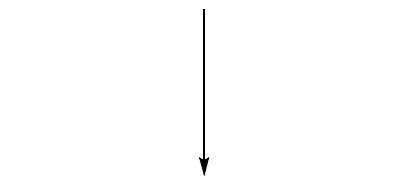
*(hint: triple oxidation occurs)*

*They also got 7% of a quadruple oxidized product. What is the structure of this side-product?*

*Step 6: hint: quadruple oxidation takes place*

*Step 7: hint: 3 transformations take place*





- 8) DMDO
- 9) PhCF<sub>3</sub>, MW, Δ
- 10) Me<sub>4</sub>NBH(OAc)<sub>3</sub>
- 11) TsOH·H<sub>2</sub>O, *n*-BuOH, Δ



(-)-majucin



(-)-jiadifenoxolane

- 12) LiHMDS, MoOPH
- 13) [Ru<sub>2</sub>(PEt<sub>3</sub>)<sub>6</sub>(OTf<sub>3</sub>)](OTf),  
*i*-PrOH
- 14) OsO<sub>4</sub>·TMEDA

- 15) MsCl, pyr

*Step 12: Structure of MoOPH ? Mechanism of this reaction ?*

*Step 13: hint: recently published paper by Hartwig in Nature Chemistry*

