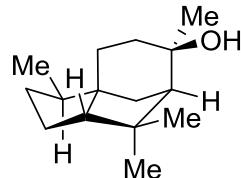
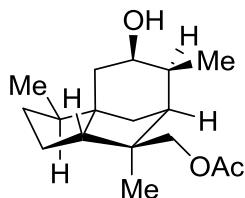


# Total Syntheses of (-)-Majucin and (-)-Jiadifenoxolane A, Complex Majucin-Type *Illicium* Sesquiterpenes

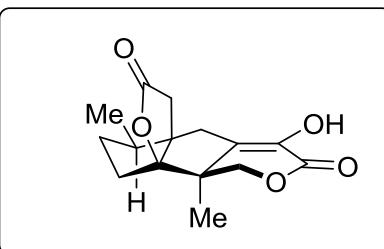
M. L. Condakes, K. Hung, S. J. Harwood, Thomas J. Maimone *JACS* 2017, 139, 17783–17786.



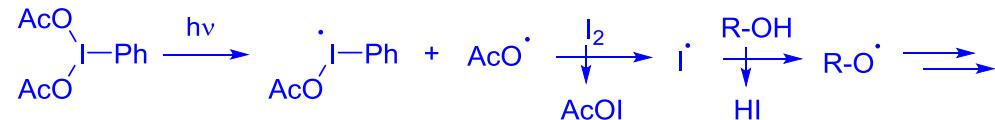
- 1)  $\text{PhI(OAc)}_2, \text{I}_2, \text{hv}$   
then  $\text{Ac}_2\text{O}, \text{H}_3\text{PO}_4$
- 2)  $\text{BH}_3\text{-THF}$ ,  
then  $\text{CrO}_3\text{-2pyr}$
- 3)  $\text{NaBH}_4$



- 4)  $\text{PhI(OAc)}_2, \text{I}_2, \text{hv}$
- 5)  $\text{RuCl}_3\text{-xH}_2\text{O}, \text{KBrO}_3$
- 6)  $\text{SeO}_2, 4 \text{ A MS}$   
then  $\text{K}_2\text{CO}_3, \text{Me}_2\text{SO}_4$
- 7) L-selectride  
then  $\text{KOH}/\text{MeOH}$



*Step 1:* Name of the starting material? (+)-cedrol  
Name and mechanism of this reaction? Suárez Oxidation  
(hint: without  $\text{Ac}_2\text{O}, \text{H}_3\text{PO}_4$  a five-membered ring would be formed)

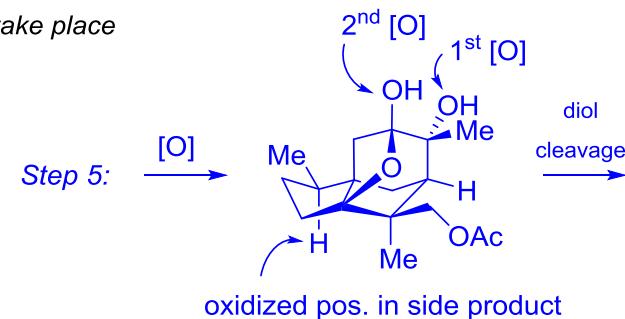


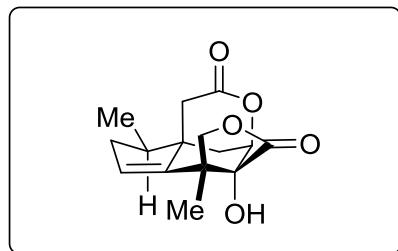
*Step 5:* Please come up with a mechanism. What is the active species in this step?  
(hint: triple oxidation occurs) *in situ generation of RuO4*

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





(-)majucin

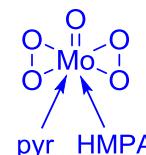
↓  
(-)-jiadifenoxolane

- 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

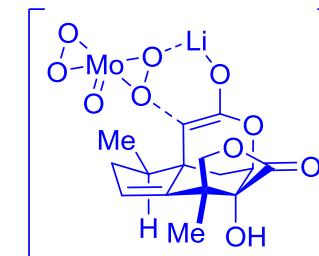
- 12) LiHMDS, MoOPH
- 13) [Ru<sub>2</sub>(PEt<sub>3</sub>)<sub>6</sub>(OTf)<sub>3</sub>][OTf], *i*-PrOH
- 14) OsO<sub>4</sub>·TMEDA

- 15) MsCl, pyr

*Step 12:*



via:



enolate-oxidation

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

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

