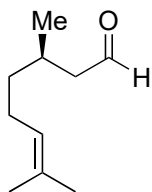
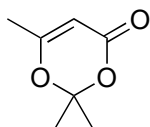
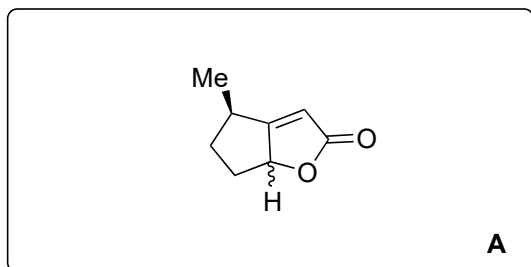


## Synthesis of (-)-11-O-Debenzoyltashironin: Neurotropic Sesquiterpenes cause Hyperexcitation

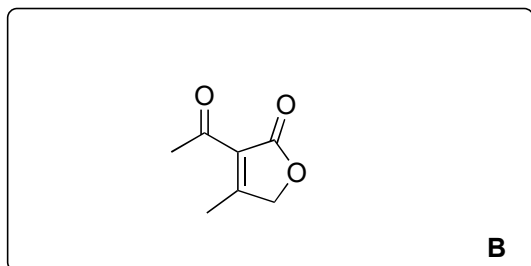
M. Ohtawa, M. J. Krambis, R. Cerne, J. M. Schkeryantz, J.M. Witkin,  
R. A. Shenvi *J. Am. Chem. Soc.*, **2017**, *139*, 9637-9644.



1-4



5-6



- 1)  $\text{Br}_2/(\text{PhO})_3\text{P}$   
 $\text{NEt}_3$
- 2)  $\text{KO}^t\text{-Bu}$
- 3)  $\text{O}_3$ , then DMS
- 4)  $\text{Mo}(\text{CO})_6$ , TBAB

- 5) Hydroxyacetone 120 °C
- 6) silica gel

Name of the starting material?

(+)-citronellal

Name 3 alternative reactions to achieve the transformation in 1) and 2)

e.g.

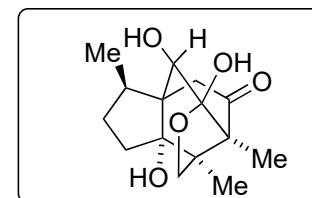
Corey-Fuchs

Seyferth Gilbert homologation

Ohira-Bestmann

Name of step 4?

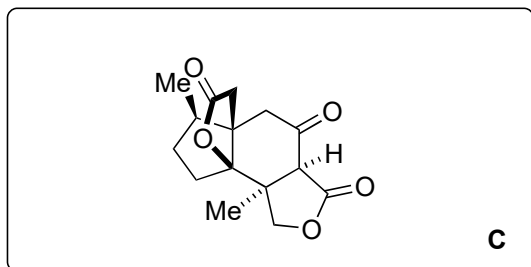
Hetero-Pauson-Khand reaction (hPK)



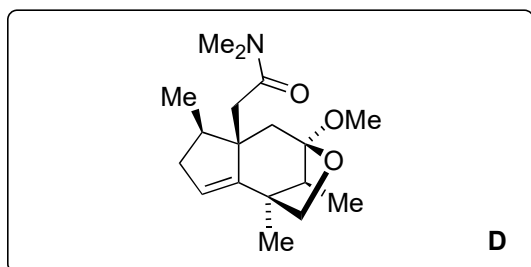
**A**



9



10-14



15-18

9) LDA, -78 °C,  
then **B**, -100 °C  
then Ti(*Oi*-Pr)<sub>4</sub>, LDA, 0 °C

10) MeI, K<sub>2</sub>CO<sub>3</sub>,  
11) NaOH, H<sup>+</sup>  
12) Me<sub>2</sub>NH, Me<sub>3</sub>Al  
13) TMSCl, NEt<sub>3</sub>  
then SOCl<sub>2</sub>  
14) H<sup>+</sup>, HC(OMe)<sub>3</sub>

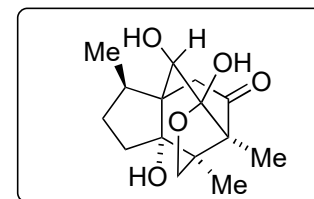
15) LiNMe<sub>2</sub>, HMPA  
then O<sub>2</sub>, P(OEt)<sub>3</sub>  
16) HCl  
17) Co(acac)<sub>2</sub>, PhSiH<sub>3</sub>, O<sub>2</sub>  
18) TsOH•H<sub>2</sub>O

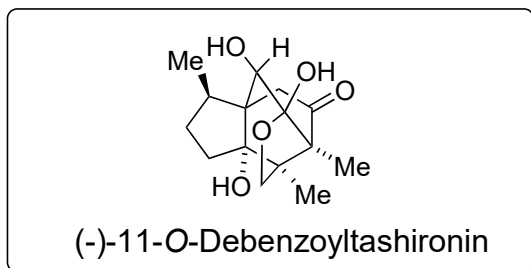
Draw the mechanism!

Which product is obtained upon acidic work up  
without the addition of Ti(*Oi*-Pr)<sub>4</sub> and additional  
LDA?

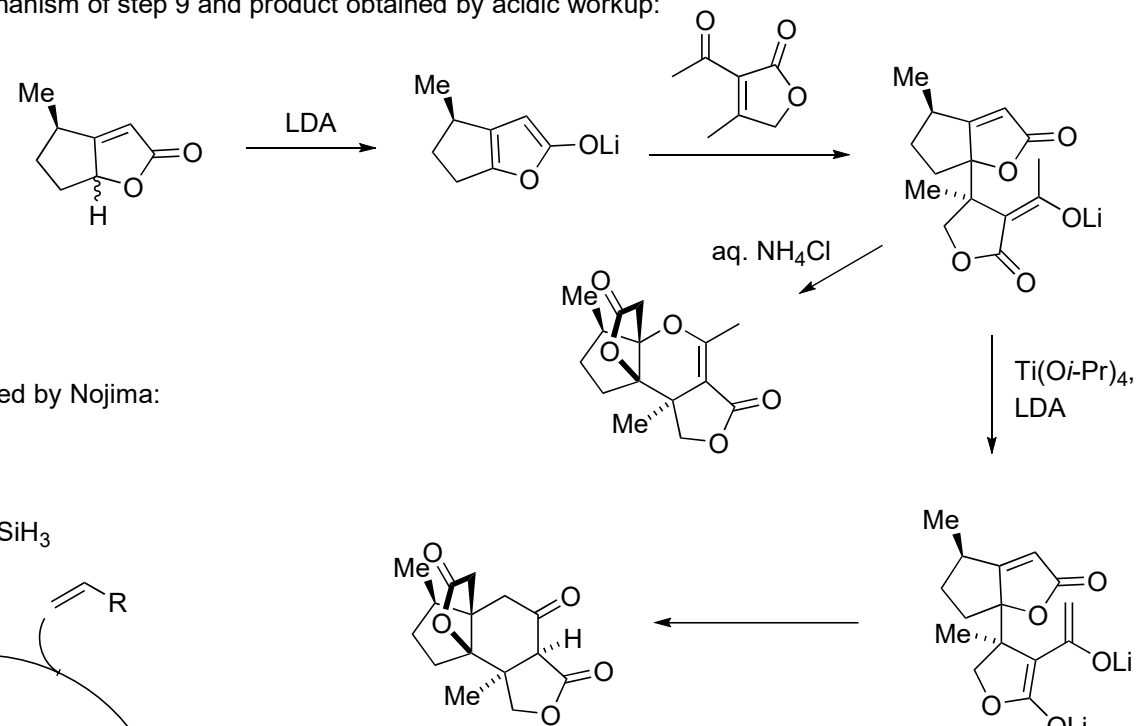
Name of step 17? Mukaiyama Hydration

Draw the mechanism!





Mechanism of step 9 and product obtained by acidic workup:



Mechanism of the Mukaiyama hydration as proposed by Nojima:

