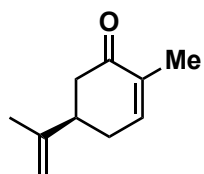


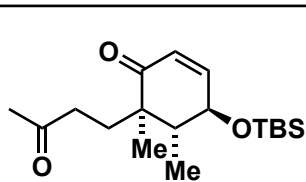
Total Synthesis of the Sesquiterpenoid Periconianone A Based on a Postulated Biogenesis

Raphael Liffert, Anthony Linden, and Karl Gademann

J. Am. Chem. Soc. **2017**, *139*, 16096–16099

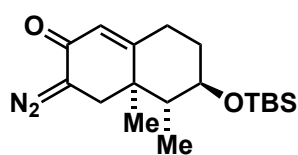


1-7



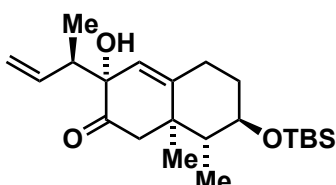
A

7-10



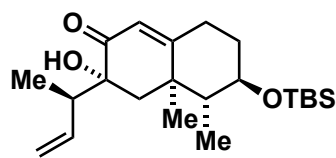
B

11



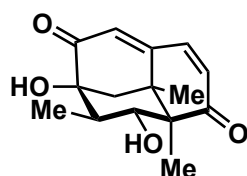
C

12



D


13-17



Periconianone A

- 1) FeCl_3 , MeMgBr , TMSCl
- 2) PhNO , AcOH
- 3) TBSCl , imid, DMAP
- 4) LiCl , CuI , MeMgBr , TMSCl
- 5) MVK , $\text{BF}_3 \cdot \text{Et}_2\text{O}$
- 6) O_3 , MeOH then $\text{Cu}(\text{OAc})_2$, FeSO_4

- 7) H_2 , Pd/C
- 8) NaOMe
- 9) LiHMDS , $\text{F}_3\text{C}(\text{CO})\text{OCH}_2\text{CF}_3$
- 10) MsN_3 , Et_3N

- 11) $\text{Rh}_2(\text{OAc})_4$, PhMe , 65°C 

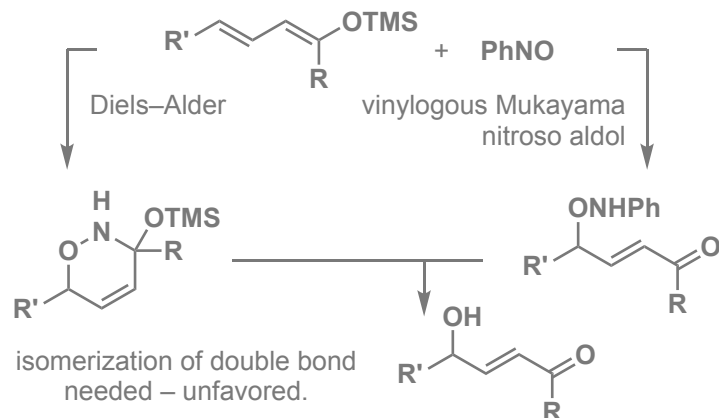
- 12) $\text{Ca}(\text{OMe})_2$, MeOH

- 13) HF (aq.)
- 14) DMP , NaHCO_3
- 15) O_3 , pyridine *then* PPh_3
- 16) diphenyl phosphate, 65°C
- 17) LiHMDS , PhSeCl *then* NaIO_4 (aq.)

Karasch reagent
JACS **1984**, *106*, 5759-5760.

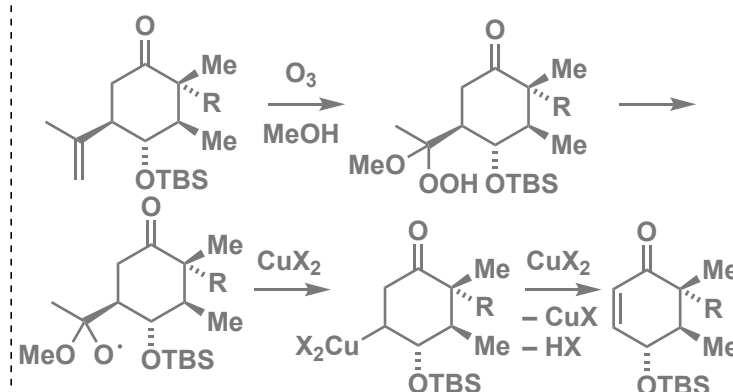
Step 1: Who invented this protocol?

Step 2: Come up with a mechanism.

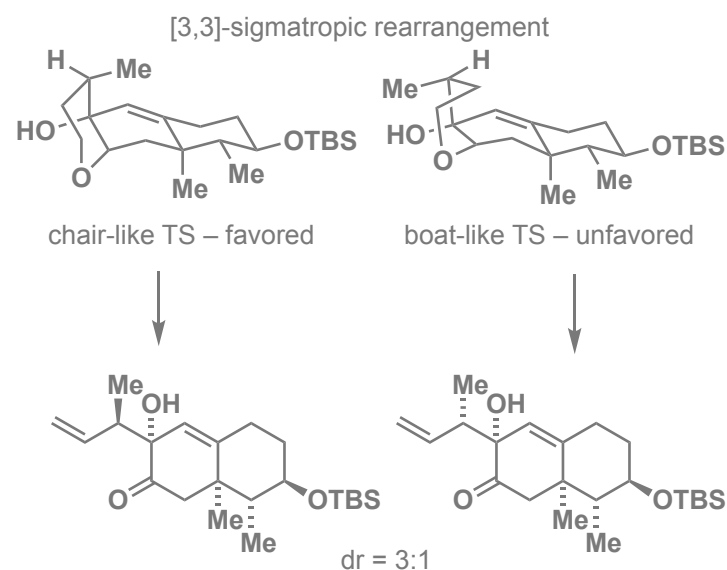


Step 6: Name this transformation.

Criegee Fragmentation, *JACS* **1980**, *102*, 6163–6165



Step 11: Classify this reaction and rationalize the stereochemical outcome.



Step 12: A rearrangement takes place.

Think about the driving force.

α -ketol-rearrangement
(acyloin rearrangement, formal [1,2]-allyl shift),
formation of the conjugated enone