Total Synthesis of Aplysiasecosterol A

Lu, Z., Zhang, X., Guo, Z., Chen, Y., Mu, T., Li, A.

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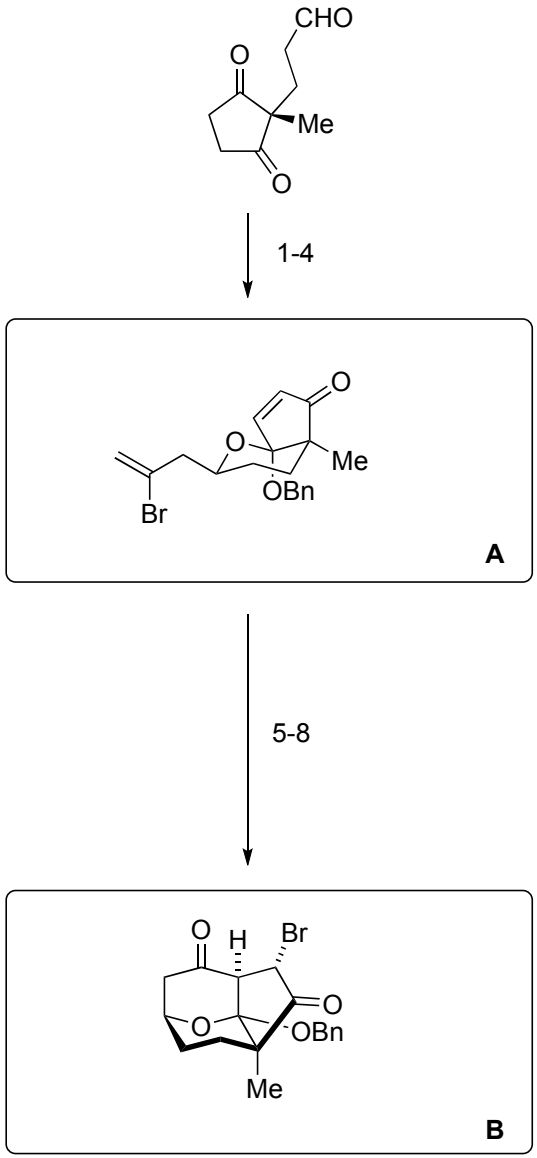
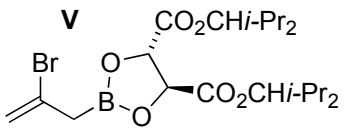
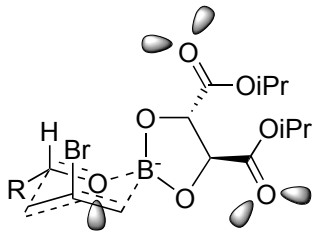




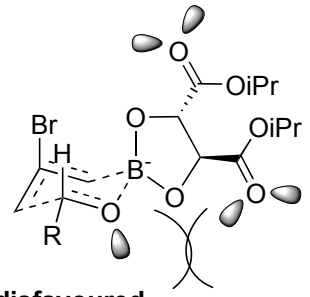
1) **V**
2) BnOH, MsOH
3) TMSOTf, NEt_3
4) IBX, MPO

Name of reaction 1, what is the reason for the stereochemical outcome?

Roush allylation



favoured

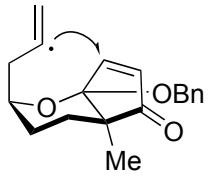


disfavoured

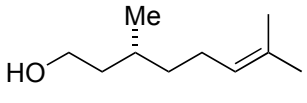
lone pair electronic repulsion

5) $(TMS)_3SiH$, ABCN, 100 ºC
6) KHMDS, TMSCl
7) NBS
8) O_3, SMe_2

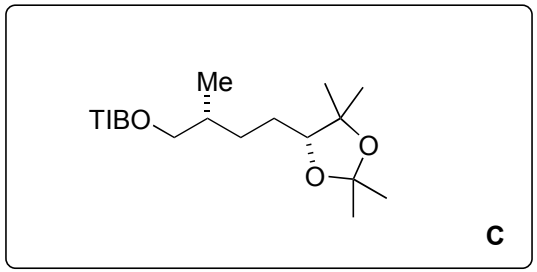
5: Why are ABCN and supersilane used instead of $HSnBu_3$ and AIBN?



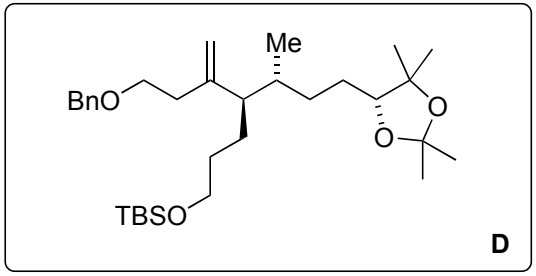
$(TMS)_3SiH$ is a weaker hydride donor, reacts slower than $HSnBu_3$ giving time to the sp_2 radical to react intramolecularly. ABCN is more stable than AIBN and allows for working at higher temperatures and longer time periods.

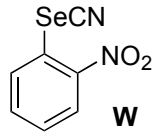


9-13

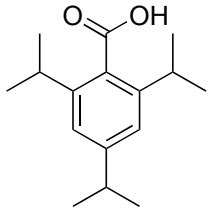


14-17





W



X

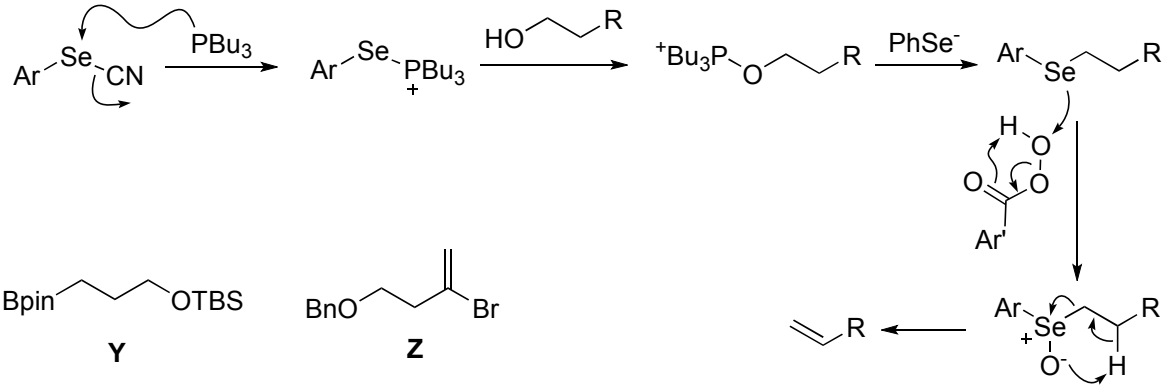
9) AD-mix-β, $MsNH_2$
10) acetone, TsOH
11) **W**, Bu_3P, *m*-CPBA
12) O_3, $NaBH_4$
13) **X**, PPh_3, DIAD

step 9: Name of the reaction?

Sharpless asymmetric dihydroxylation

step 11: Name and reaction mechanism

Grieco elimination



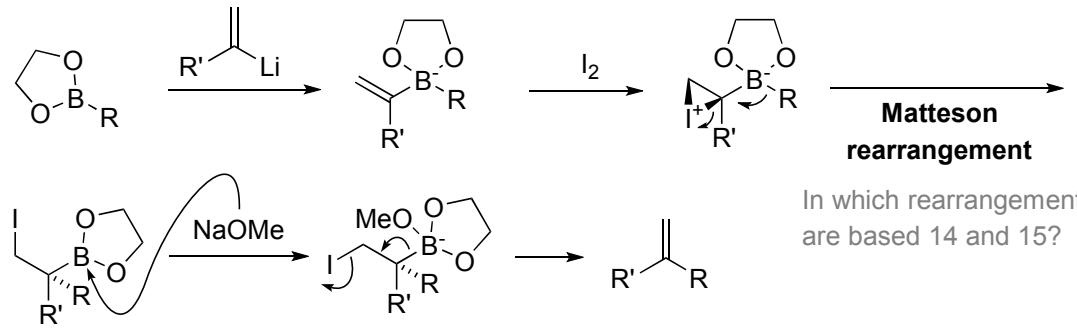
Y

Z

14) (+)-sparteine, *s*-BuLi, **Y**
15) **Z**, *t*-BuLi, NaOMe, I_2
16) TBAF, AcOH
17) DMP

step 15: draw the mechanism and provide reaction name

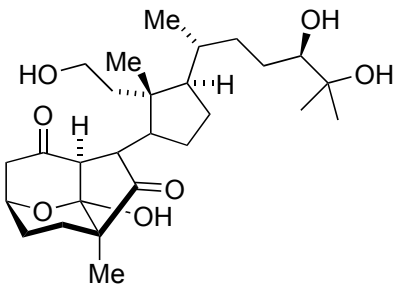
Zweifel-Evans-olefination



Matteson rearrangement

In which rearrangement are based 14 and 15?

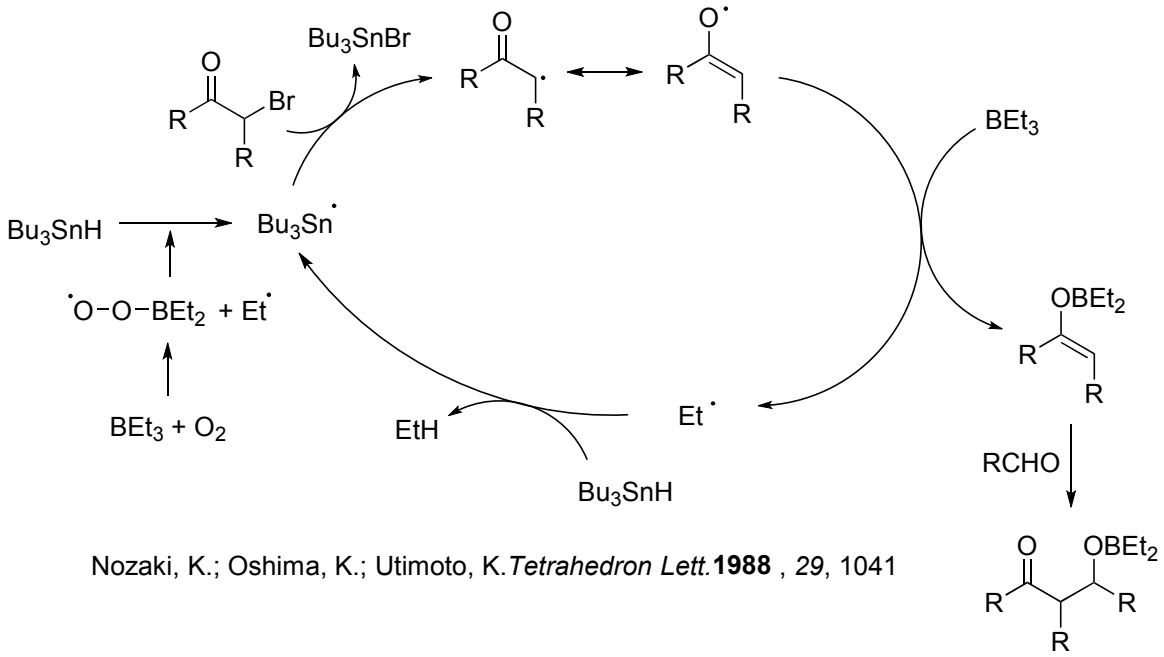
18-22



Aplysiasecosterol A

18) **B**, Et_3B, air, Bu_3SnH
19) Burgess reagent
20) $Fe(dpm)_3$, $Ph(i\text{-}PrO)SiH_2$
21) aq. $HClO_4$
22) $Pd(OH)_2/C$, H_2

step 18: draw the mechanism



Nozaki, K.; Oshima, K.; Utimoto, K.*Tetrahedron Lett.***1988** , *29*, 1041

step 20: reaction name

Shenvi hydrogenation
see *J. Am. Chem. Soc.,* **2014**, *136*, 1304–1307