Site-Specific Photochemical Desaturation Enables Divergent Syntheses of *Illicium* Sesquiterpenes

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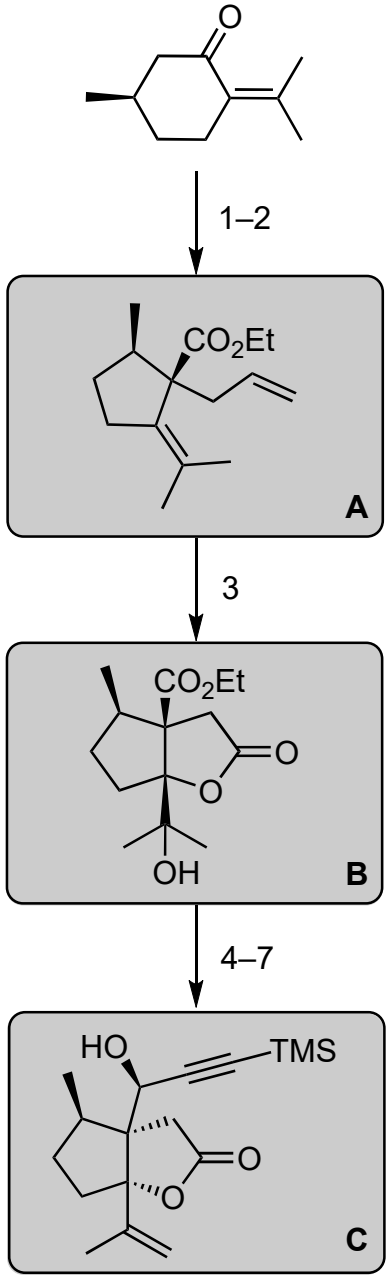
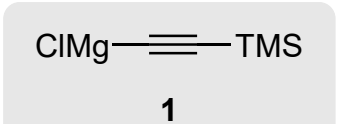
J. Am. Chem. Soc. **2021**, 143, 3256–3263.



1) Br_2, Et_2O;
then NaOEt
2) KHMDS, HMPA, allyl iodide, THF, –78 °C

3) *m*CPBA, $NaHCO_3$, MeCN, 0 °C;
then $RuCl_3$, $NaIO_4$, r.t.

4) $SOCl_2$, Et_3N, CH_2Cl_2, –78 °C
5) KHMDS; *then* $LiAlH_4$
6) DMP
7) **1**, THF, –78 °C to 23 °C



1

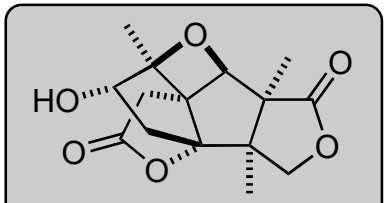
Name the starting material
(*R*)-pulegone

1) Please name the reaction and describe the mechanism.
Favorskii rearrangement

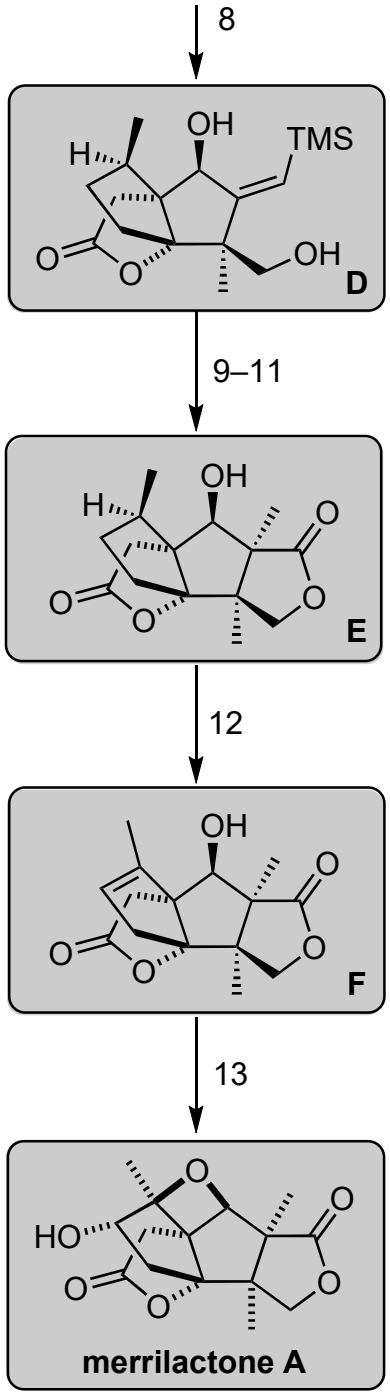
3) *hint*: a heterocycle is formed

5) *hint*: sneaky trick to ensure chemoselective reduction

7) Product obtained as single diastereomer; suggest which one and develop a rationale.



merrilactone A



8) $Pd(OAc)_2$, B_2pin_2, toluene/MeOH, 50 °C;
then H_2O_2, NaOH, THF, 0 °C

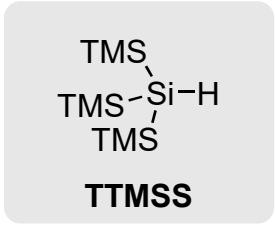
9) *p*-TsOH, MeCN, 23 °C
10) CDI, CH_2Cl_2, 23 °C;
then PhSeNa
11) TTMSS, AIBN, benzene, 80 °C

12) Ph_2CO, NBS, HFIP, violet LED

F is sometimes also referred to as *Danishefsky's intermediate*

13) *m*CPBA, EtOAc, 23 °C;
then *p*TsOH•H_2O, EtOAc/MeOH, 23 °C

8) *hint*:
(a) product chemical formular: $C_{17}H_{28}O_4Si$
(b) a carbocycle and a quaternary center are formed



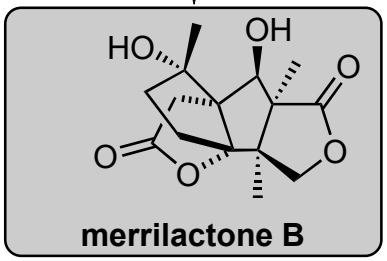
TTMSS

12) *hint*:
(a) look at the title
(b) the stereocenter that delivered the chiral information for the synthesis is planarized in this step

Additional:

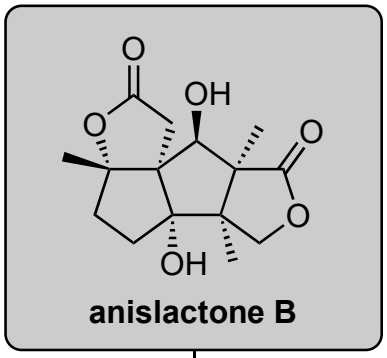
F

14



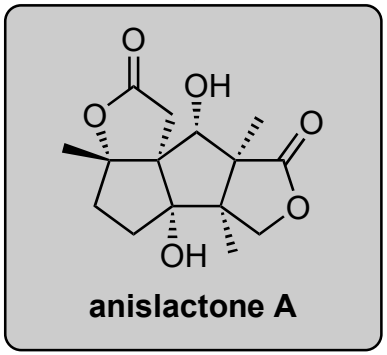
merrilactone B

15



anislactone B

16



anislactone A

14) $Ph(iPrO)SiH_2$, $Co(acac)_2$, O_2, THF, 23 °C

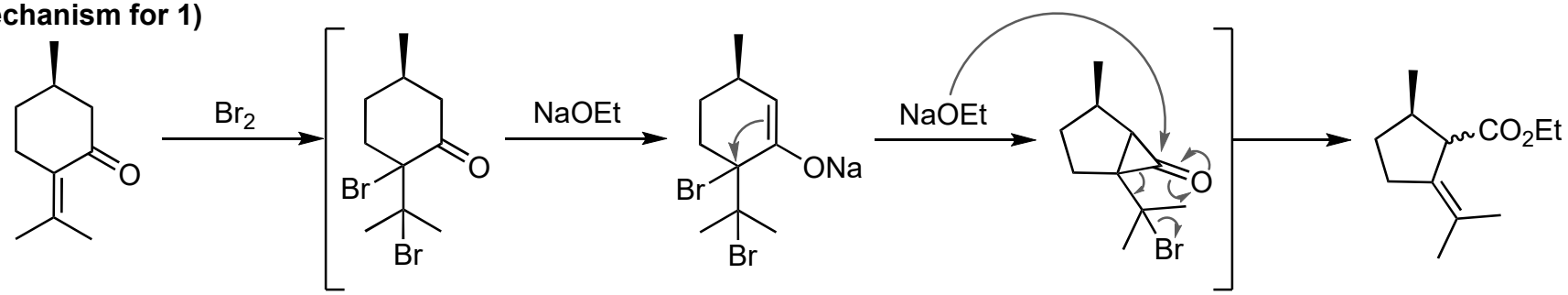
15) K_2CO_3, MeOH, 23 °C;
then HCl

16) K_2CO_3, MeOH, 23 °C;
then HCl

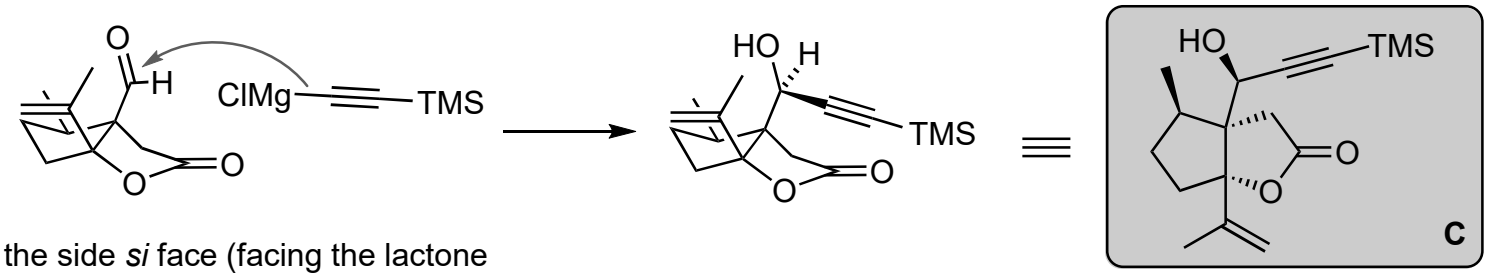
14) Name this reaction
Mukaiyama hydration

16) *hint*: epimerization

Mechanism for 1)



Potential stereochemical rationale for 7)



the side *si* face (facing the lactone ring) would be less congested in this reactive conformation

Plausible mechanistic pathways for 8)

J. Am. Chem. Soc. **2007**, *129*, 1874–1875.