Asymmetric Total Synthesis of Dankasterones A and B and Periconiastone A Through Radical Cyclization

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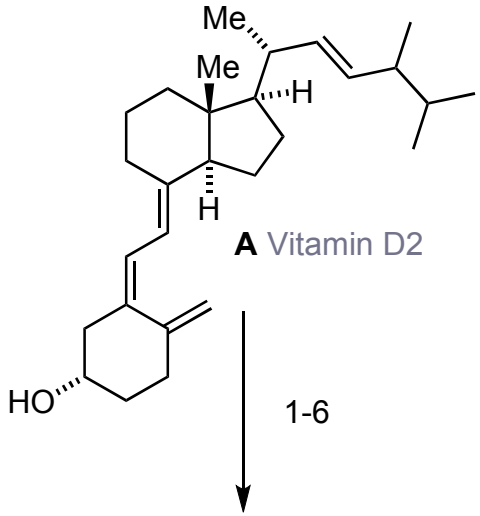
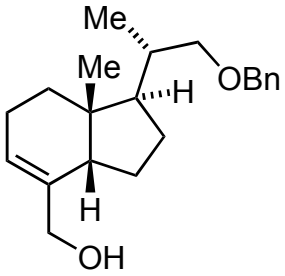


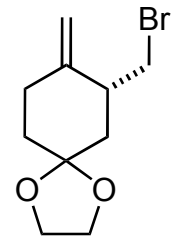
A Vitamin D2

1-6



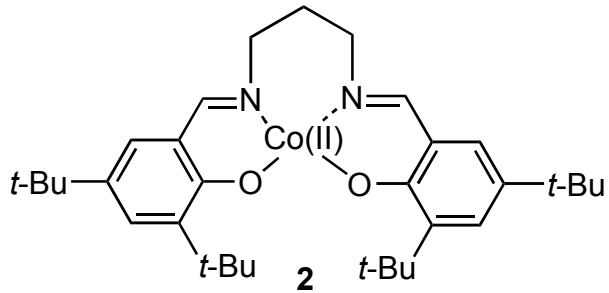
B

7-10



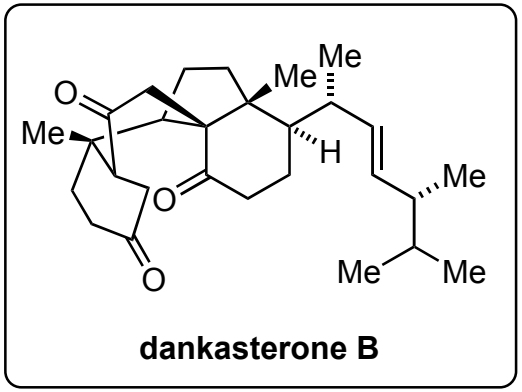
1

1) O_3, MeOH, pyridine, $NaBH_4$
2) BnBr (1 equiv.), NaH
3) DMP
4) NaH
5) LiHMDS, Comin's reagent
6) $Pd(PPh_3)_4$, Bu_3SnCH_2OH, LiCl
7) DMP
8) *t*-BuLi, **1**
9) DMP
10) **2**, $PhI(OAc)_2$, TMDSO, CF_3Ph, rt; *then* silica gel, DCM, air

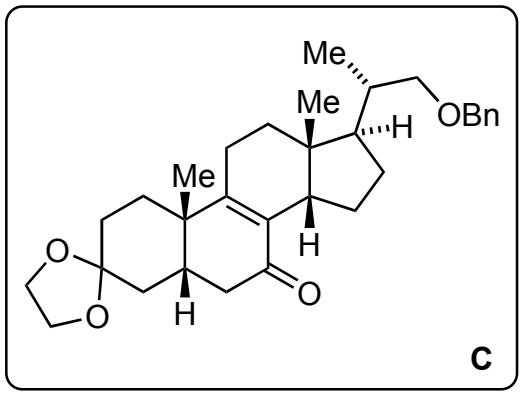


2

Comin's reagent



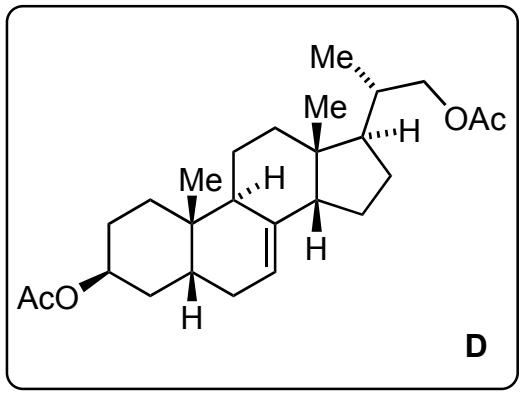
dankasterone B



11-17

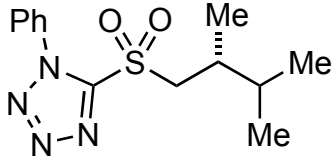
11) Li/NH_3
12) LAH
13) Ac_2O (1 equiv.), pyridine
14) $POCl_3$, pyridine
15) *p*-TsOH, acetone, H_2O
16) LAH
17) AcOH, DBAD, PPh_3

hint 11: one deprotection occurs as well.

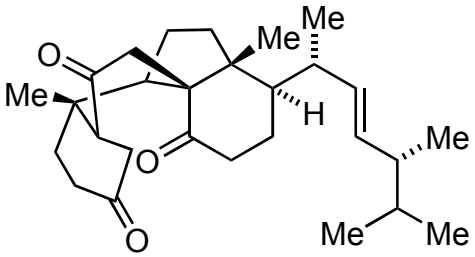


18-23

18) CrO_3, 3,5-DMP, 4A molsieves
19) $HClO_4$, EtOAc, O_2
20) $FeSO_4 \cdot H_2O$, THF, H_2O
21) K_2CO_3
22) DMP
23) LiHMDS, **3**



3



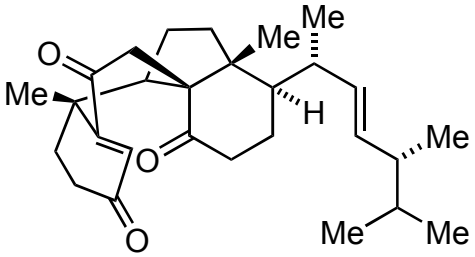
dankasterone B

24) PhI(OH)(OTs)

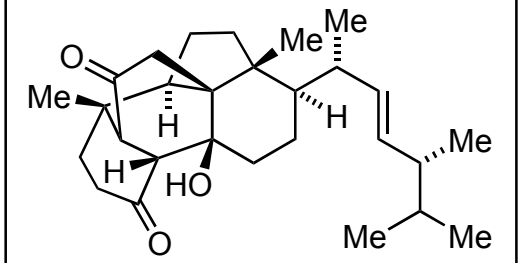
25) DBU, TMSOTf

24

25

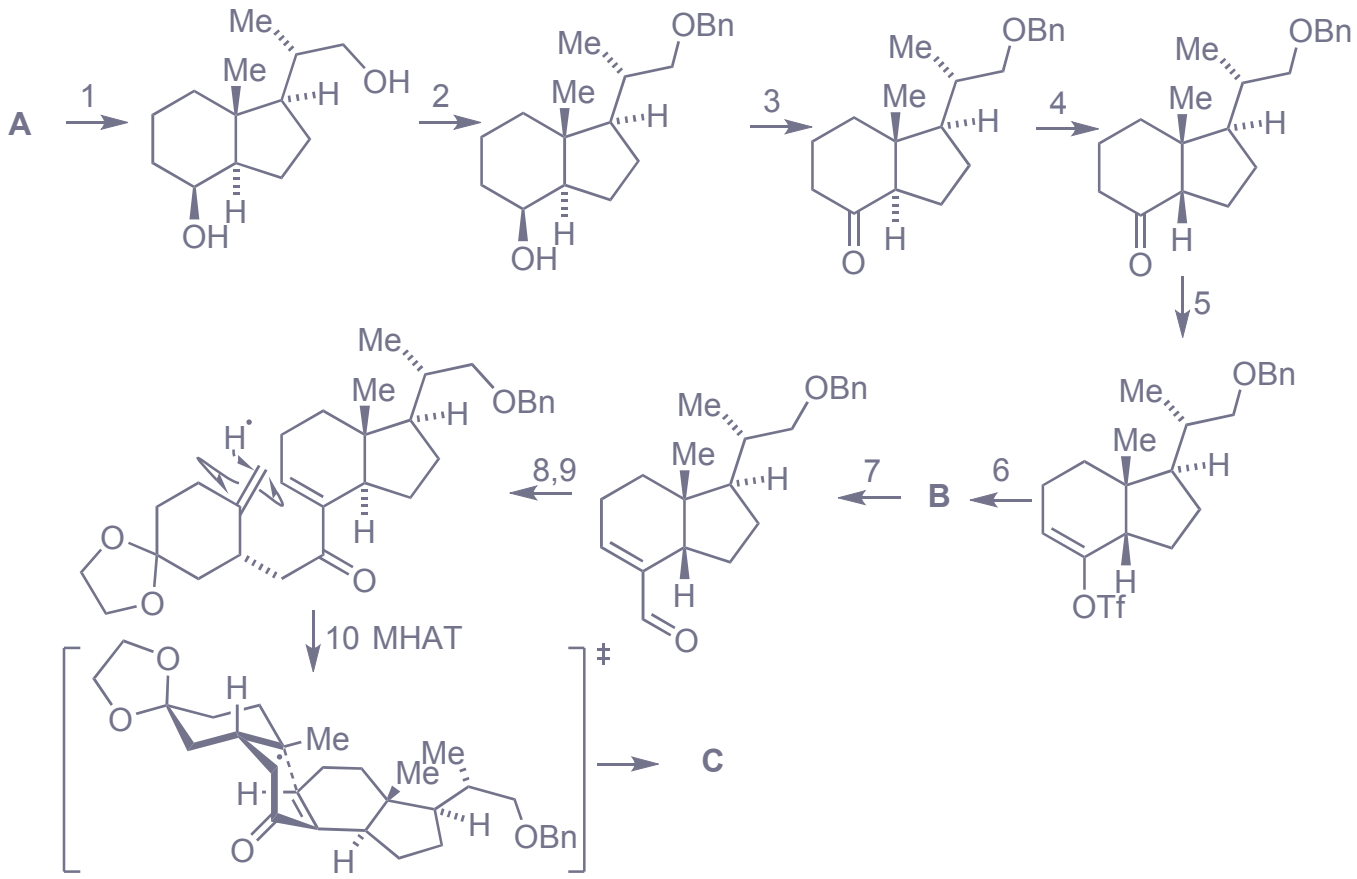


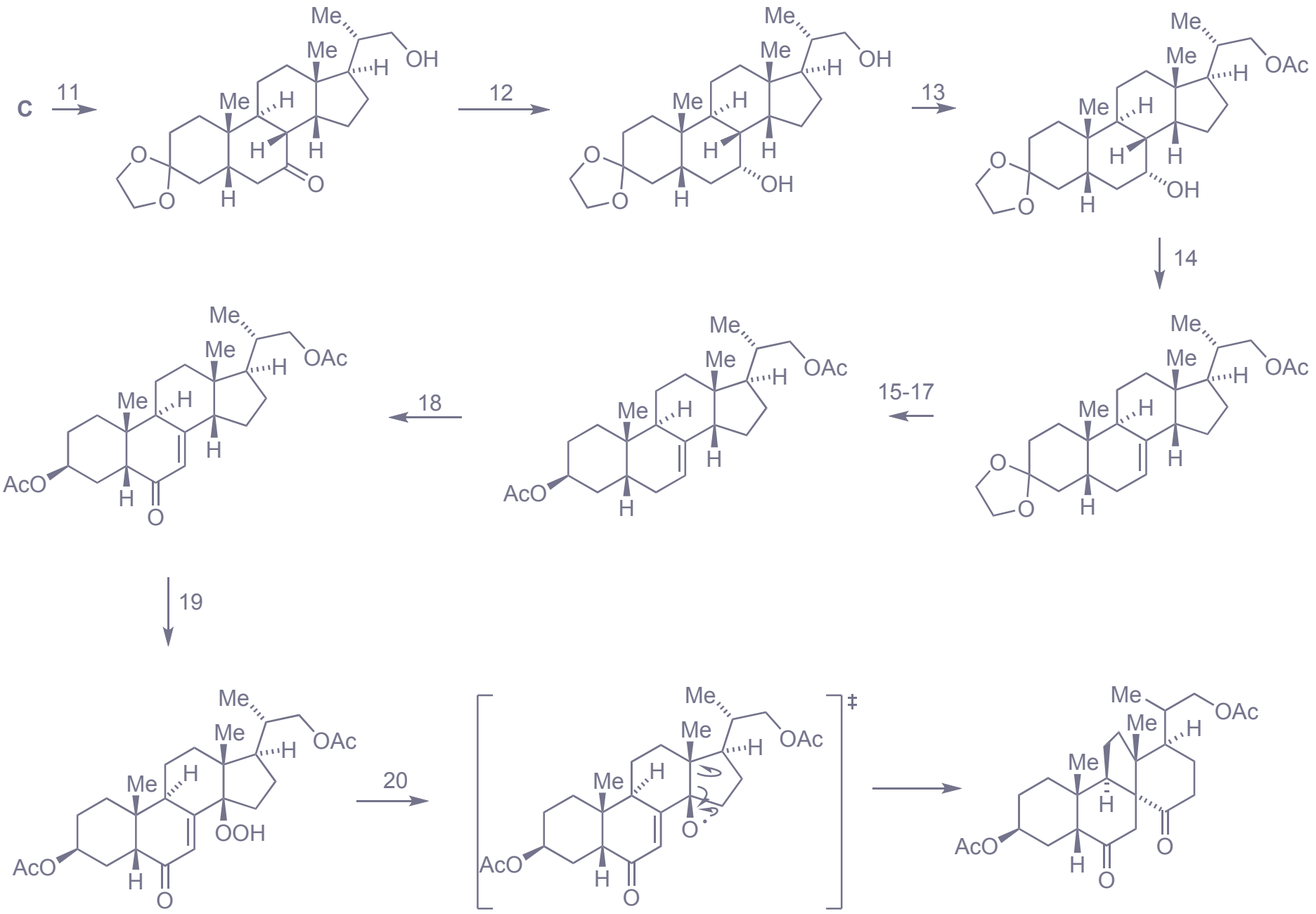
dankasterone A



periconiastone A

Answers:




C
11
12
13
14
15-17
18
19
20
Me
OH
OAc
AcO
OOH
O
H
‡