A 16-step synthesis of the isoryanodane diterpene (+)-perseanol

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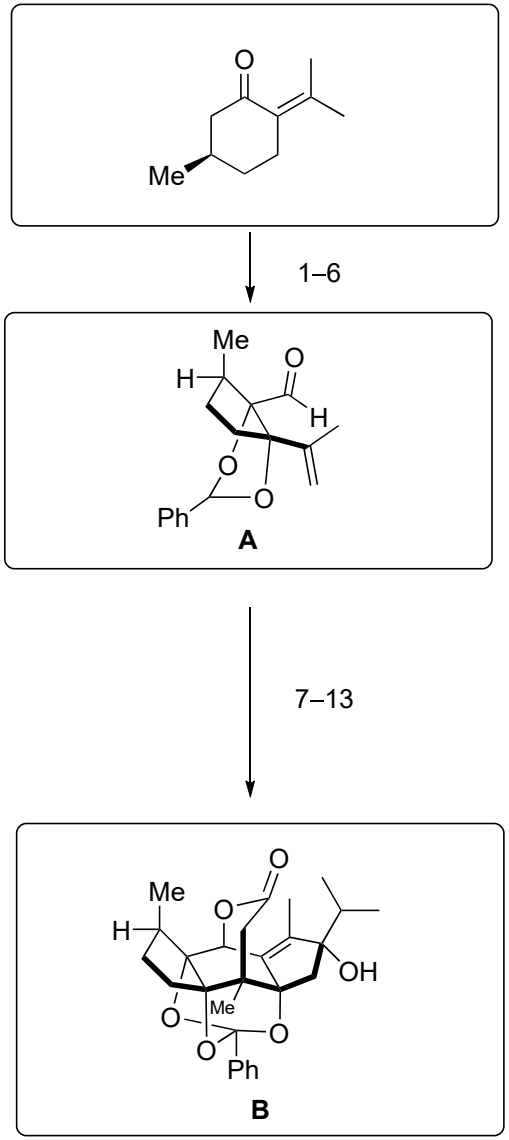
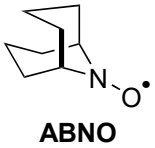
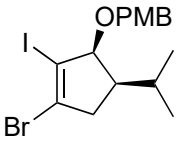


1) Br_2, $NaHCO_3$ *then* NaOMe, MeOH 55 °C
2) KHMDS then O_2, $P(OMe)_3$
3) m-CPBA
4) $Et_2Al(TMP)$
5) $PhCH(OMe)_2$, CSA, *then* DIBAL
6) $Cu(^{MeO}bpy)OTf$ (5 mol%), ABNO (1mol%), NMI (10 mol%), O_2



ABNO

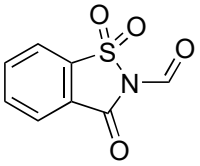


X

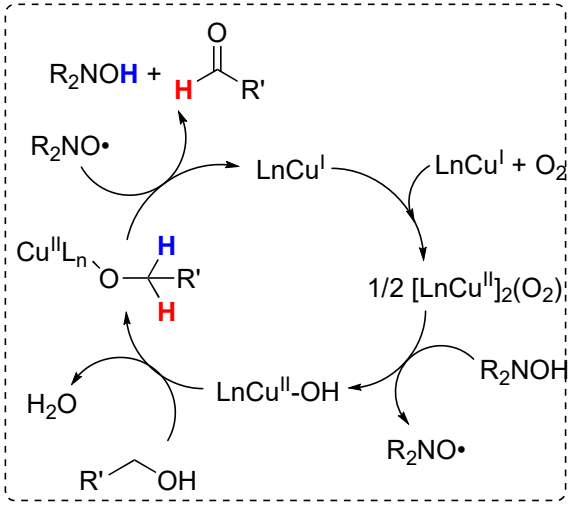
7) **X**, n-BuLi
8) $Pd(PPh_3)_4$ (50 mol%), **Y**, KF, NEt_3, 100 °C
9) DDQ
10) DMDO, Na_2SO_4
11) MeMgCl, $CeCl_3$·LiCl
12) TFA, 0°C
13) SeO_2

ad 1) Name of starting material? → **(R)-Pulegone**
Name reaction? → **Favorskii rearrangement**

ad 6) Please provide a mechanism for the transformation

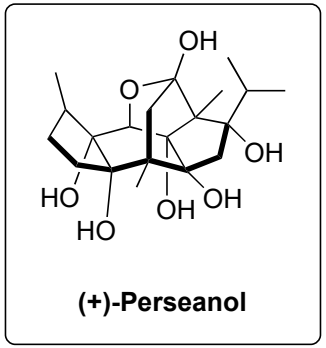


Y

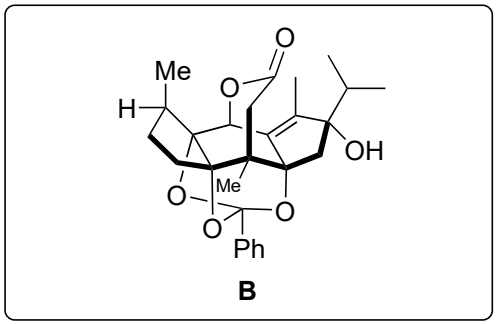


Hint: in step 8) two rings are closed

ad 13) Name reaction?
→ **Riley-Oxidation**

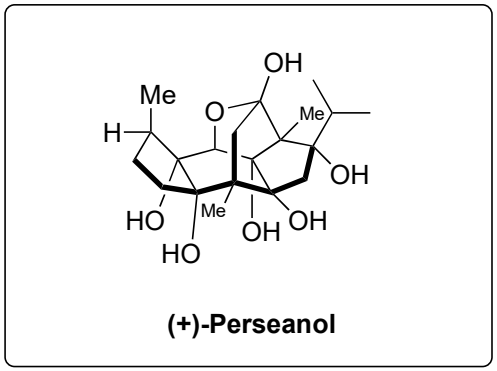


(+)-Perseanol



B

14–16



(+)-Perseanol

14) $VO(On\text{-}Pr)_3$, TBHP
15) LiPhNap
16) $Pd(OH)_2$, H_2

15) Propose a mechanism