13-Step Total Synthesis of Atropurpuran

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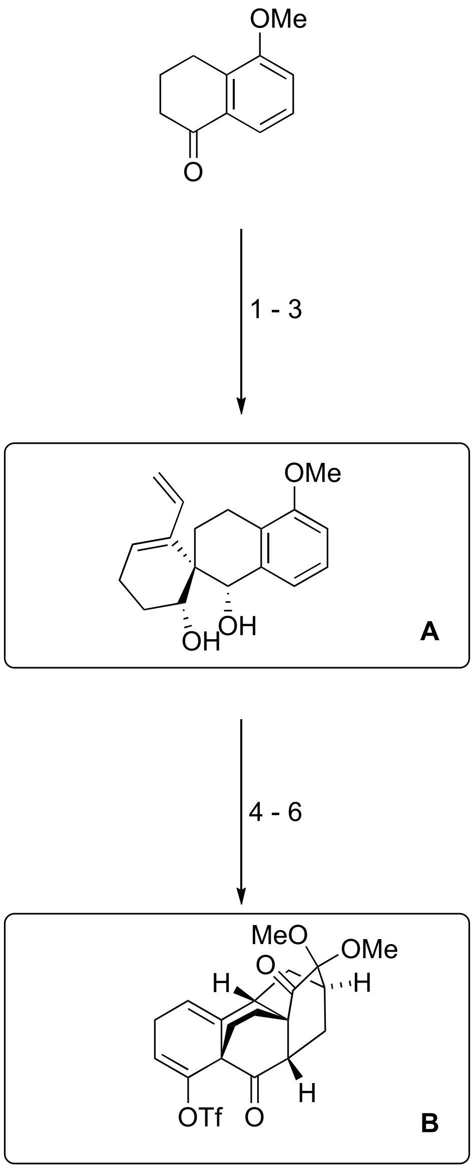
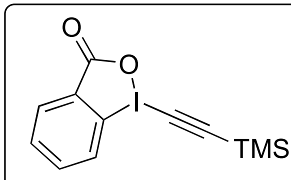
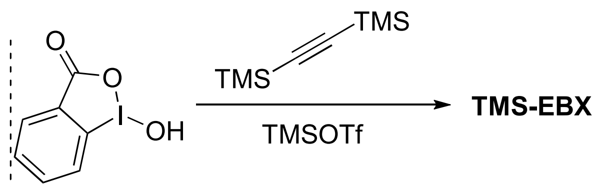


1) LHMDS, 4-pentenoylchlorid
2) TBAF, **TMS-EBX**
3) Grubbs **II**,
   then BBr_3
   then $AlCl_3$, $LiAlH_4$

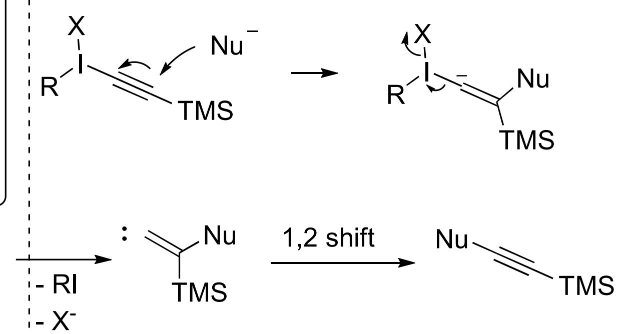


TMS-EBX or Waser's reagent

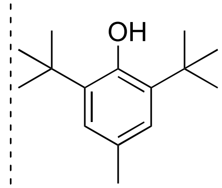
4) PIDA, MeOH
   then BHT, mesitylen 160 °C
5) Crabtree's catalyst
   then TPAP, NMO
6) KHMDS, $PhNTf_2$



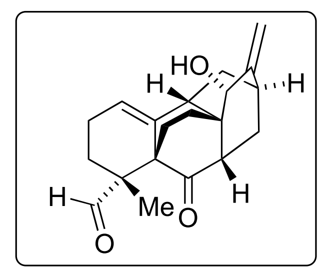
How would youe make TMS-EBX and come up with a reaction mechanism for step 2

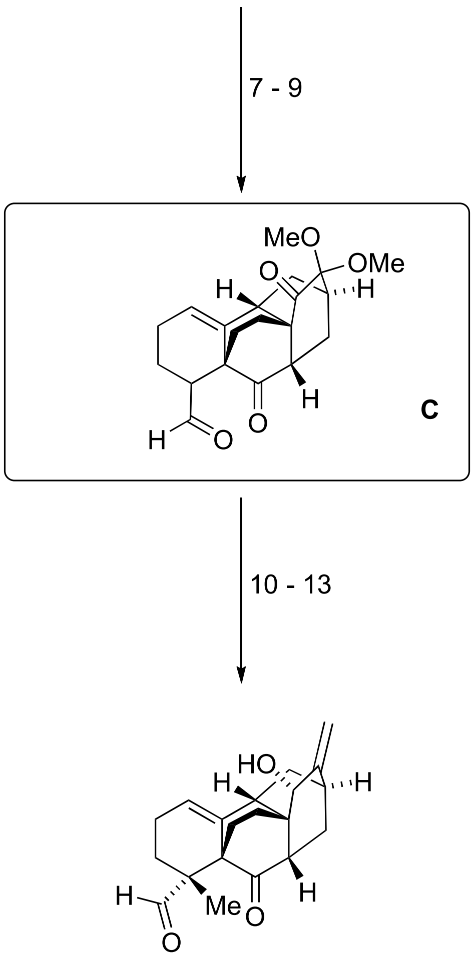


Structure and role of BHT?



radical inihibitor, supress polymerisation

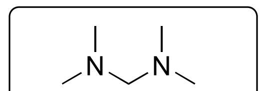




Atropurpuran

7) $Pd(PPh_3)_4$, CO, *n*Bu_3SnH
then DIBAL
8) TFAA, DMSO, NEt_3 [Note: work up with LiOH]
9) Crabtree's catalyst
then DMP

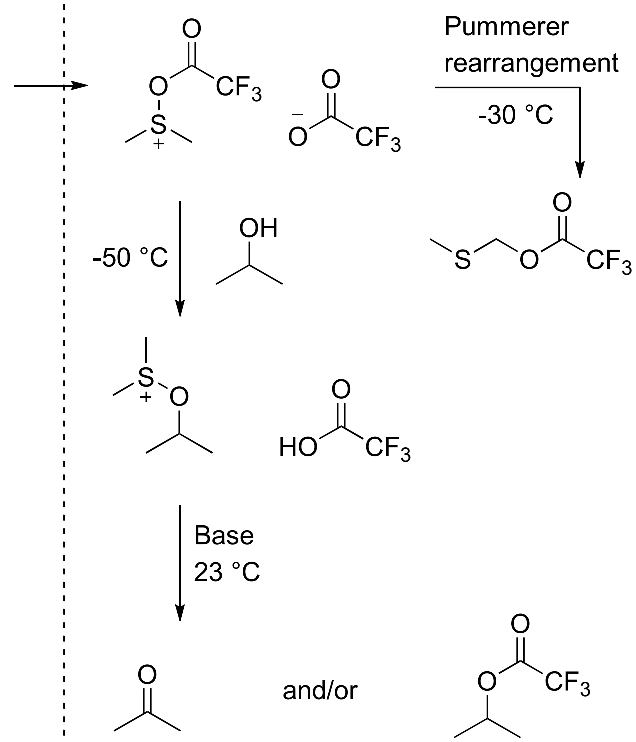
10) *t*BuOK, *t*BuOH, MeI [Note d.r. = 3:1]
11) SmI_2, MeOH
12) **TMMN**, Ac_2O
13) $NaBH(OMe)_3$



TMMN

Name the reaction in step 8) explain why these conditions are used. show shortly the mechanism with sidereactions

Omura–Sharma–Swern Oxidation
good for oxidations of sterically hindered alcohols, other alcohols form often the TFA-ester (here prim is protected with TFA, while sec alcohol is oxidized)



sterically hindered alcohols

less sterically hindered alcohols also formed when no base is added