An Efficient, Stereocontrolled, Total Synthesis of the Orchidaceae Alkaloid (±)-Dendrobine

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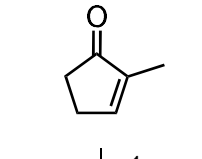
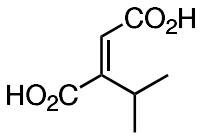
J. Am. Chem. Soc. 1992, *114*, 4089–4095.



1

A



2

B

A + B

3–6

C

1) $LiCH_2NC$, HMPA, THF, *then* TBSCl

How would you prepare the diacid?

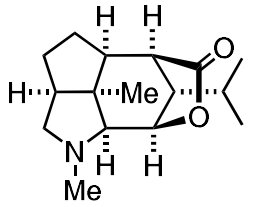
2) $SOCl_2$, CH_2OH

Hint: methanolysis at only one position

3) MS, CH_2Cl_2, reflux, *then* $AgBF_4$, DCE, –78 °C to –20 °C
4) MeOTf
5) $K[HB(O\textit{t}\text{-Bu})_3]$, –78 °C
6) SmI_2, THF, 25 °C

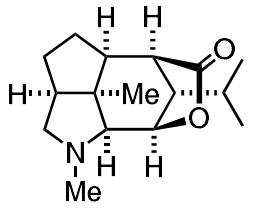
Step 3: Please provide a mechanism.

Step 6: A different main product is observed with HMPA at –78 °C, which?



(–)-dendrobine

7–12



(–)-dendrobine

7) $SOCl_2$, NEt_3, EtOAc, 0 °C to 25 °C
8) DBU, 1,4-dioxane, reflux
9) PtO_2, H_2, AcOH, 25 °C
10) $NaBH_4$, *i*-PrOH

Step 9: Hint: Two reactions occur.