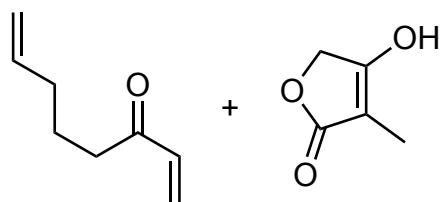


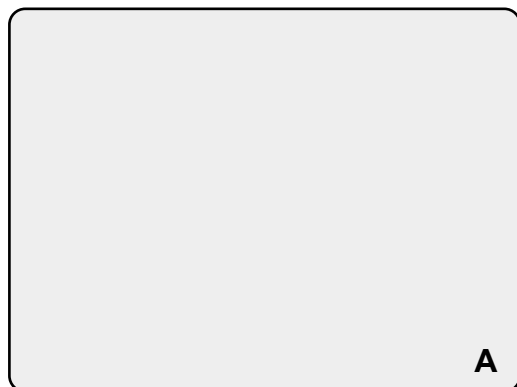
The First Total Synthesis of (±)-Saudin

Winkler, J. D.*; Doherty, E. M.

J. Am. Chem. Soc. **1999**, *121*, 7425 – 7426.



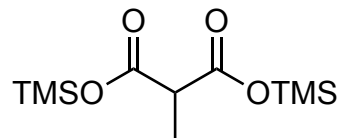
1–4



5–11

- 1) pyrrolidine, AcOH, THF
- 2) TMSI, HMDS, CH₂Cl₂, –20 °C (excess reagents)
- 3) O₃, MeOH *then* Me₂S *then* H⁺
- 4) BnOH, PPTS, benzene, reflux

- 5) KHMDS, 2-[*N,N*-bis(trifluoromethylsulfonyl)amino]-pyridine, THF, –78 °C
- 6) AlMe₃, LiCl, Pd(PPh₃)₄, THF
- 7) LiOH, MeOH
- 8) (COCl)₂, cat. DMF, CH₂Cl₂ *then* added to *n*-BuLi, **1**, THF, 0 °C *then* aq. NaHCO₃ *then* citric acid
- 9) (COCl)₂, benzene *then* Et₃N, Me₂CO, 95 °C
- 10) H₂, Pd/C
- 11) DMP

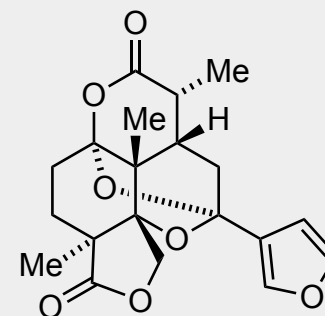


1

1) No H₂O is lost.

- 3) Hint: two alkenes are cleaved. Draw the mechanism. 3 bands in IR spectrum between 1780 – 1710 cm^{–1}.
- 4) Hint: a spirocycle is formed.

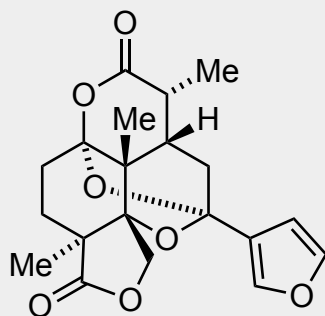
- 8) Role of DMF? Draw a mechanism.
- 8) Hint: product molecular formula: C₂₃H₂₈O₇
- 9) Hint: a heterocycle is formed.



(±)-Saudin

B

↓ 12–15



(±)-Saudin

- 12) Hg Hanovia lamp, pyrex filter,
9:1 CH₃CN:Me₂CO, 0 °C
- 13) *n*-BuLi, TMEDA *then* Tf₂O
- 14) (3-furyl)SnBu₃, LiCl, Pd(AsPh₃)₄
- 15) LiOH, MeOH, 65 °C
then PPTS, benzene, Dean-Stark, reflux

15) Provide a mechanism.