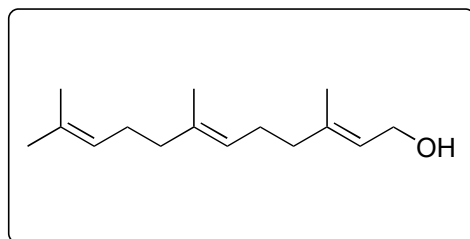


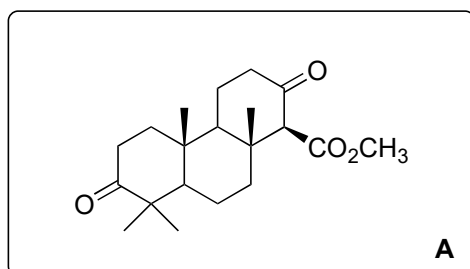
Synthesis of a limonoid, azadiradione

E. J. Corey, R. W. Hahl

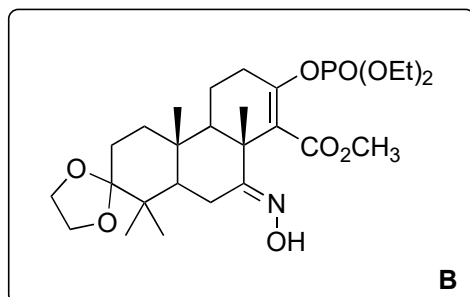
Tetrahedron Letters **1989**, *30*, 3023–3026.



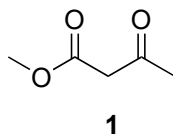
1–5



6–10

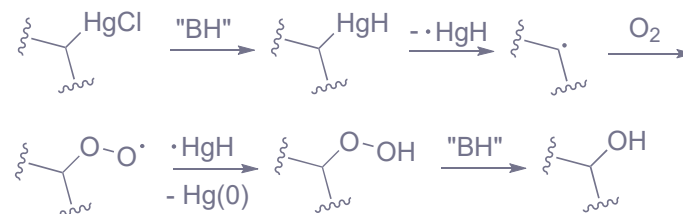


- 1) MsCl, Et₃N then LiBr
- 2) **1** (1.2 eq.), NaH (1.2 eq.)
then *n*-BuLi (1.2 eq.)
then substrate then P(OEt)₂Cl
- 3) Hg(OAc)₂, CH₃NO₂ then stir in NaCl (aq.)
- 4) NaBH₄ (3 eq.), O₂
- 5) CrO₃, aq. H₂SO₄

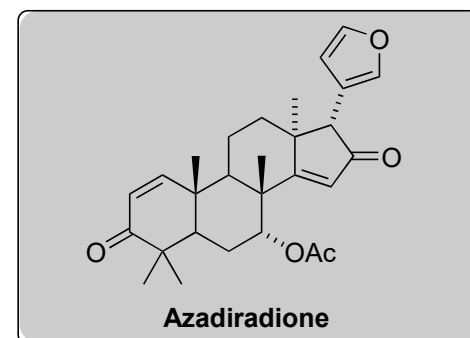


- 6) NaH, P(OEt)₂Cl (1 eq.)
- 7) ethylene glycol, PTSA
- 8) DIBAL
- 9) HO₃SONO
- 10) sunlamp, 50 °C

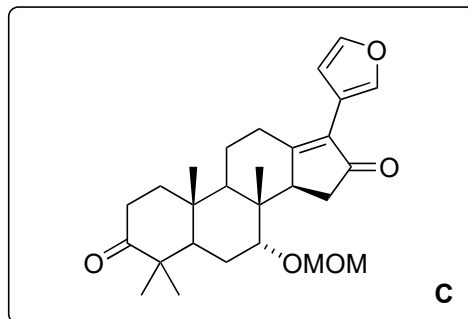
- 1) Name the starting material. *trans,trans*-Farnesol.
- 2) Hint: product has a phosphorous NMR shift around 140 ppm.
- 3) Hint: nitromethane is a solvent. A tricyclic system is formed.
- 4) Hint: oxidative demercuration. Can you propose a mechanism? See below.
- 5) Name of reagent? Jones reagent



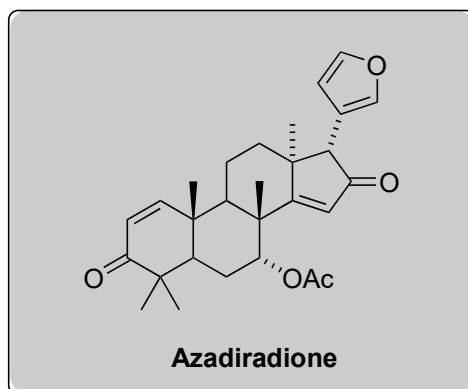
- 9) Hint: an alkyl nitrite is formed. *JACS* **1974**, *96*, 870.
- 10) Named reaction. Can you come up with a mechanism?
Barton Reaction



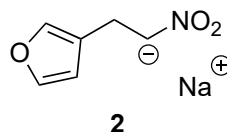
11–15



16–23

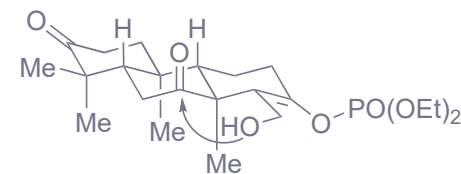


- 11) 1M HCl
- 12) $N(CH_3)_4BH(OAc)_3$, $-78\text{ }^\circ\text{C}$
- 13) **2**, EtOH, reflux *then* 12M HCl, $10\text{ }^\circ\text{C}$
- 14) NaOEt, EtOH, $70\text{ }^\circ\text{C}$
- 15) $BrCH_2OCH_3$, TBAI, DIPEA, $70\text{ }^\circ\text{C}$



- 16) L-selectride (excess)
- 17) BzOH, DEAD, PPh_3
then NaOH, EtOH
- 18) Zn/Ag, CH_2I_2 *then* substrate, $0\text{ }^\circ\text{C}$
- 19) DMP
- 20) Li, NH_3 , THF *then* DMP
- 21) LDA, PhSeBr
then 30% H_2O_2 in H_2O /pyridine
- 22) TMSBr, DCM
- 23) Ac_2O , DMAP

- 11) Hint: a hemiacetal is formed. Can you rationalize its diastereoselectivity? *see below*
- 12) Hint: selective hemiacetal reduction.
- 13) Name the two reactions occurring in this step. How would you prepare **2**? Michael and Nef reactions. **2** can be prepared through condensation of furan-3-carboxaldehyde and nitromethane followed by reduction with $NaBH_4$.



substrate-directed hemiacetal formation

- 17) Hint: selective reaction at C16 (according to IUPAC atom numbering for steroids). Name the reaction. Mitsunobu.
- 18) Name the reaction. Simmons-Smith reaction.