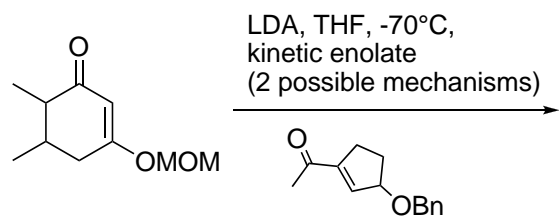


Denksport, Group-Seminar, **26.06.2008**, Harald Weinstabl

Gibbons, E.G.; **JACS**, **1982**, *104*, 1767-1769



A

tricycle

- 1.) Vinyl-lithium, THF/Et₂O, -40°C
- 2.) PCC, DCM (rearrangement)
- 3.) MeLi, THF, -93°C to -80°C
- 4.) MnO₂, DCM
- 5.) H₂, Pd/Al₂O₃, MgO,
Trimethylorthoformiat/EtOAc=25/1

B

mixture of epimers 3/1
(for the desired one)

- 1.) K₂CO₃, MeOH
- 2.) POCl₃, DMAP, Py/DCM
- 3.) CF₃CO₂H, DCM

C

tetracycle

- 1.) BuOOH, VO(acac)₂, benzene
- 2.) t-BuOK, t-BuOH/THF, -30°C
- 3.) KH, MOMCl
DMF/THF=3/5,5, -30°C to -20°C

D

- 1.) N-bromoacetamid,
MeOH/H₂O=3/1, NaOAc
- 2.) Zn-dust,
MeOH/AcOH=1/1, -20°C

E

tricycle

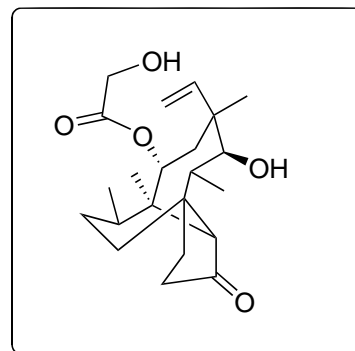
- 1.) DIBAL, 5eq., DCM
- 2.) MsCl, 5eq., DCM/pyr
(only one -OH reacts)
- 3.) LiAlH₄, 4eq., Et₂O, 0°C to 25°C
- 4.) PCC, DCM
- 5.) Na-wire, 5% Na/Hg, EtOH
- 6.) MOMBr, DIPEA, DCM (refl)

F

- 1.) O₃, MeOH/DCM, -78°C,
then P(OMe)₃
- 2.) 50eq, THF,
-35°C to -30°C
- 3.) 20% H₂SO₄(aq)/THF=1/2
- 4.) DIBAL, DCM, 0°C

G

- 1.) CuI, MeLi, n-Bu₃P⁺N(CH₃)PhI⁻, THF
("Murahashi's γ -alkylation")
- 2.) Li, NH₃ (liq.)
- 3.) PCC, DCM
- 4.) 3% HCl/EtOH
- 5.) AcOCH₂CO₂H, MsCl, DMAP, THF/Pyr
- 6.) 5% KOH/MeOH



(+/-)-pleuromutilin