Synthesis Challenge # 35

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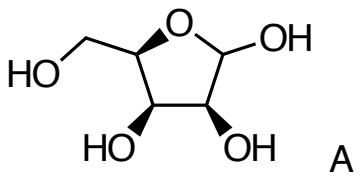


A

1-3

B

4-5

C

1) acetone H_2SO_4
2) Ohira-Bestmann reagent, K_2CO_3, MeOH
3) 2,2-DMP, PTSA, CH_2Cl_2

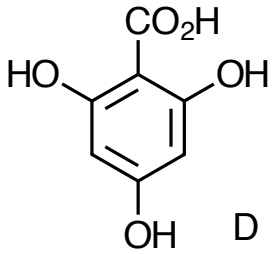
4) **I**, *n*BuLi, BF_3*OEt_2, THF –78°C
5) Raney-Ni, H_2, THF, rt

What is the name of compound A?
Is it D or L configured?

In step 1 only one regioisomer is formed. Why?
How do you prpeare the Ohira-Bestmann reagent?

I

How do you prepare **I** enantioselective?



D

12-16

E

C + E

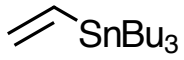
10-11

F

6) TFA, TFAA, acetone, rt
7) PPh_3, DIAD, MeOH, THF
8) Tf_2O, py, 0°C
9) **II**, $Pd(PPh_3)_4$, LiCl, PPh_3, DMF, rt

10) NaH, THF, 0°C to rt
11) dil. H_2SO_4, MeOH, 10°C

What is the name of the reaction in step 7)?
What is the role of LiCl in Step 9?



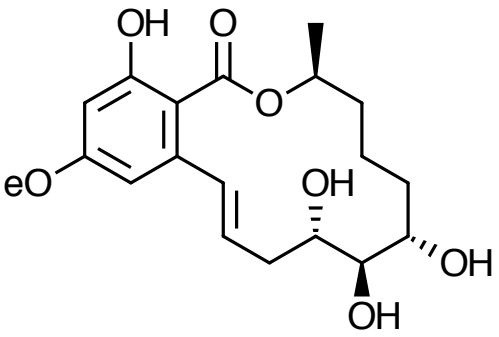
II

Hint: In step $_{10}$) only one acetonide is cleaved selectively. Possible explanations?

12-13

G

14-15



Paecilomycin F

12) $NaIO_4$, THF/water (3:1)
13) Zn, allyl bromide, THF/NH_4Cl

Please, explain the selectivety in step 13).

14) Hoveyda-Grubbs II, toluene, 70ºC
15) MeOH*HCl, 0ºC to rt

What is the structure of Hoveyda-Grubbs II?