Total Synthesis of (-)-5-Deoxyenterocin and Attempted Late-Stage Functionalization Reactions

Lilla Koser, Thorsten Bach*

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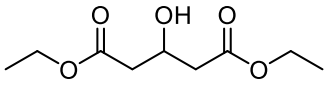
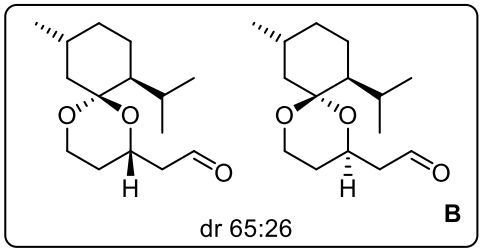


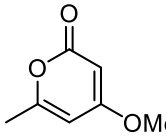
1, 2, 3

1) $LiAlH_4$ (2.54 eq.)
2) (-)-menthone (1.12 eq.), *p*TsOH (5mol%)
3) $(COCl)_2$ (1.11 equiv.), DMSO (2.20 eq.), NEt_3 (5.0 eq.)



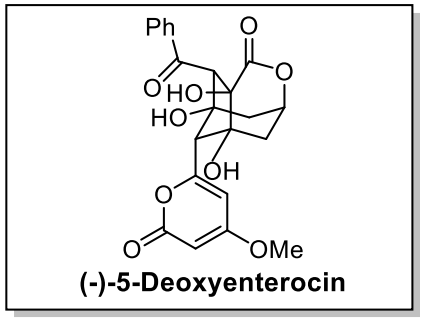
dr 65:26

B



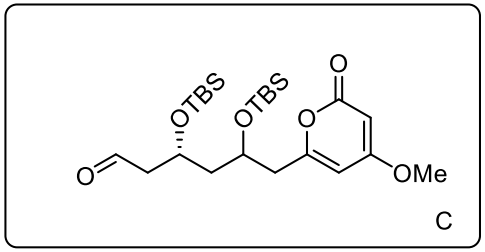
4, 5, 6, 7, 8

4) LiHMDS, then **B**
5) HCl (aq.), SiO_2
6) TBSCl (9.0 eq.), Im (15.0 eq.), DMAP (20 mol%)
7) PPTS (50 mol%)
8) $(COCl)_2$ (1.11 equiv.), DMSO (2.20 eq.), NEt_3 (5.0 eq.)



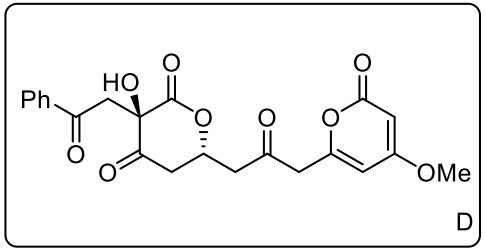
(-)-5-Deoxyenterocin

2) Why is the formation of the major isomer favored?
3) Name the Reaction draw a detailed Mechanism



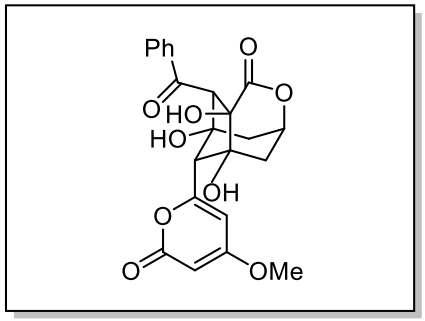
C

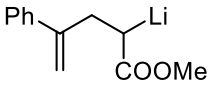
9, 10, 11,
12, 13, 14, 15



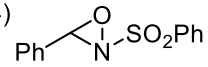
D

16



9) 

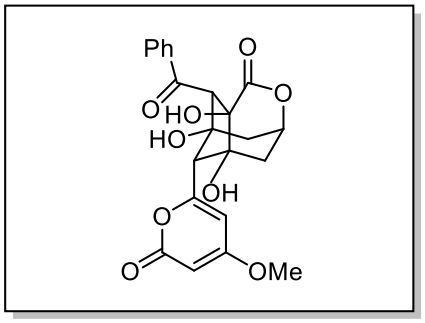
1., 4.0 eq.

10) OsO_4 (2 mol%), 2,6-lutidine (2.0 eq.), $NaIO_4$ (4.0 eq.)
11) DMP (2.0 eq.)
12) HF·pyr (excess)
13) NaOH
14) 

2., 2.0 eq.

15) DMP (1.25 eq.), $NaHCO_3$ (2.5 eq.)

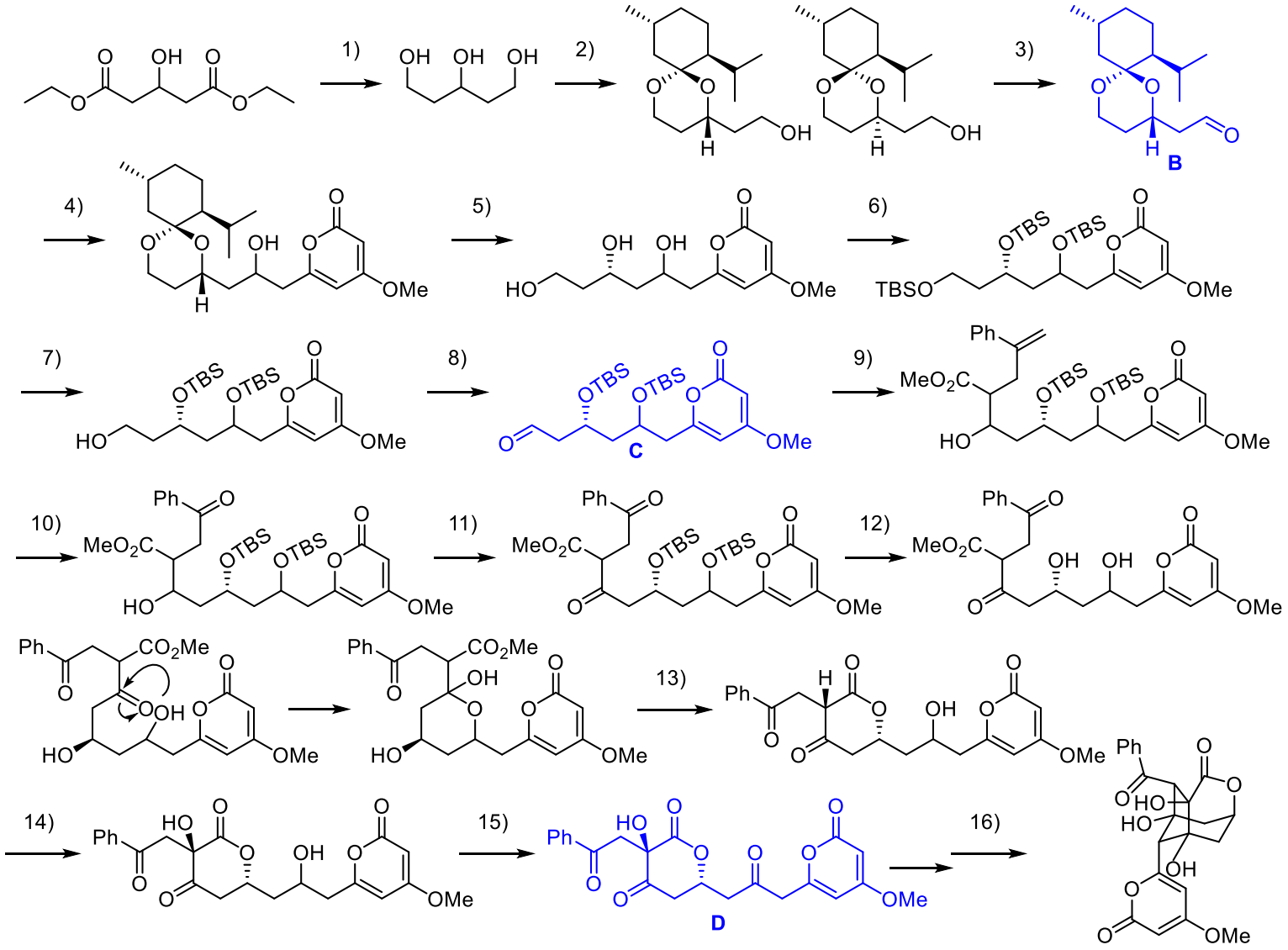
16) K_3PO_4



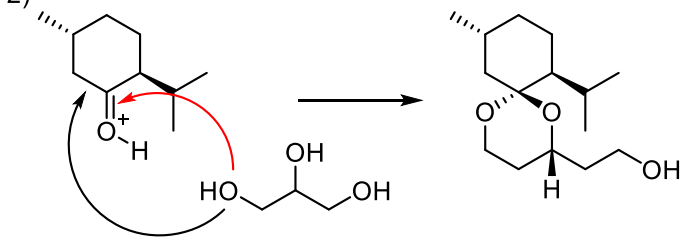
Draw the structure of DMP

12) Hint a first undesired 6-membered ring is formed
13) Hint the first 6 memberd ring is opened and transformed into a lactone
14) Draw a Mechanism, Name the reagent **2.**

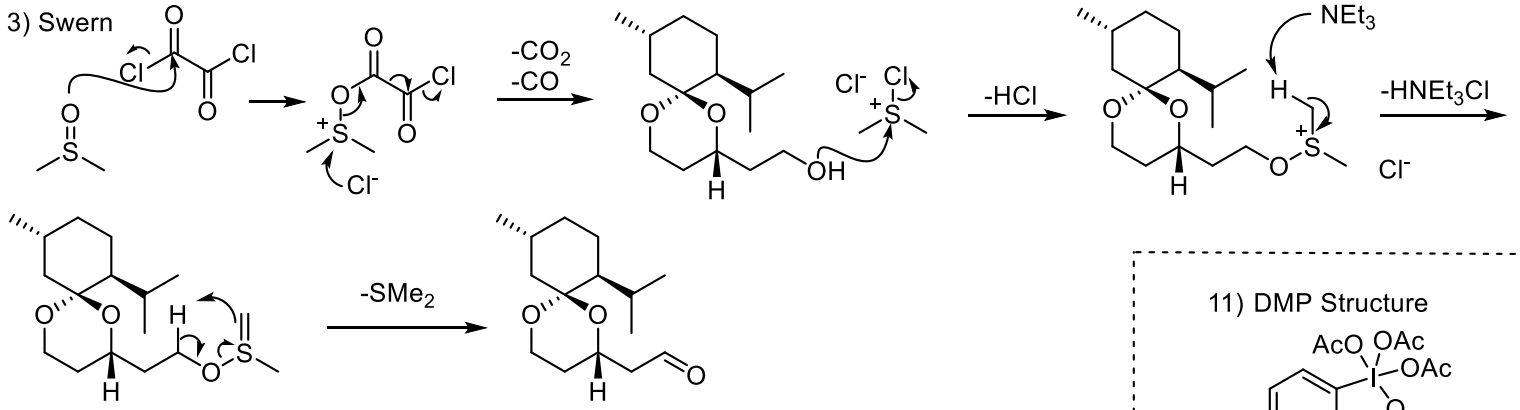
16) Hint 2 deprotonations occur.


1)
2)
3)
B
4)
5)
6)
7)
8)
C
9)
10)
11)
12)
13)
14)
15)
D
16)

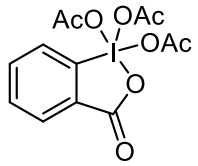
2)



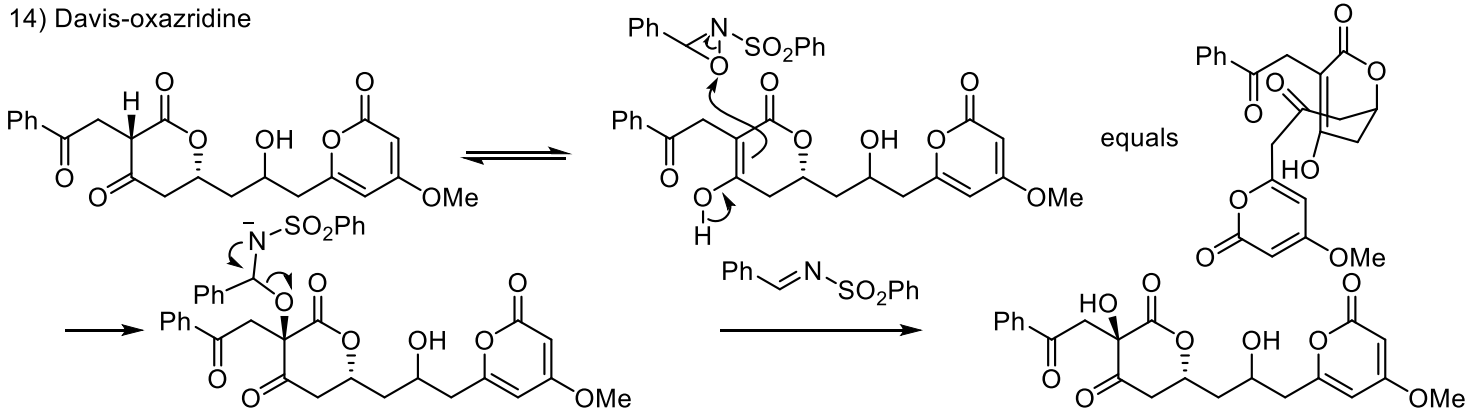
3) Swern

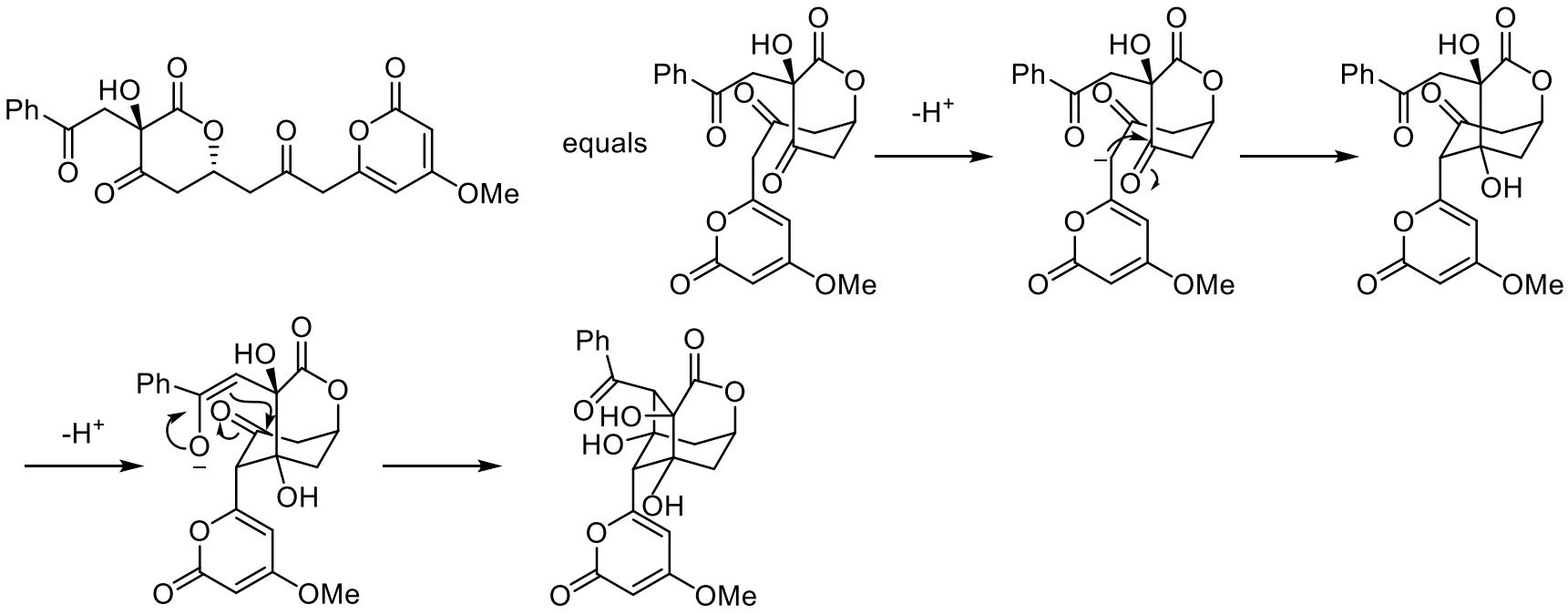


11) DMP Structure



14) Davis-oxazridine




Ph
HO
O
O
O
O
O
OMe
equals
-H+
OH
-H+