Total Synthesis of Rubriflordilactone B

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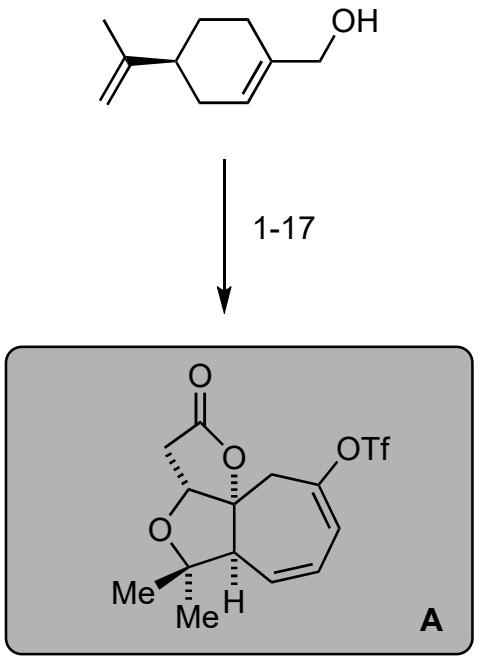
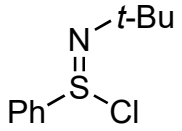


1) ZnI_2, $P(OEt)_3$, 140 °C
2) O_3, Me_2S, –78 °C, *then* aq. K_2CO_3, r.t.
3) LDA, **1**, –78 °C
4) L-Selectride, –78 °C
5) TMSCN, $AlEt_3$, r.t., *then* s.m., 80 °C, *then* aq. NaOH, r.t.
6) $Co(acac)_2$, $PhSiH_3$, O_2, 10 °C
7) aq. NaOH, 80 °C
8) $Ph_3P{=}CH_2$, –78 °C
9) KHMDS, **2**, *then* TESOTf, –78 °C



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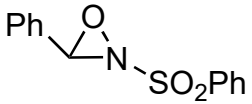


2

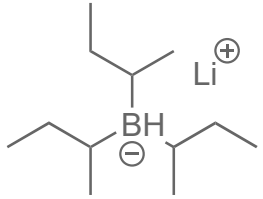
10) O_3, Me_2S, –78 °C
11) LiHMDS, $PhNTf_2$, –78 °C
12) $Sc(OTf)_2$, Ac_2O, r.t.
13) LiHMDS, –78 °C to 0 °C
14) Et_3SiH, $BF_3{\bullet}OEt_2$, 35 °C
15) NBS, BPO, 85 °C
16) $NaBH_4$, *o*-$NO_2C_6H_4SeCN$, r.t.
17) aq. H_2O_2 (30%), pyridine, r.t.

1) Name of starting material and reaction type ?
(–)-perillyl alcohol, Arbuzov-type reaction

2) Name of the reaction ?
intramolecular Horner-Wadsworth-Emmons olefination

3) Name of the reaction ?
Mukaiyama dehydrogenation

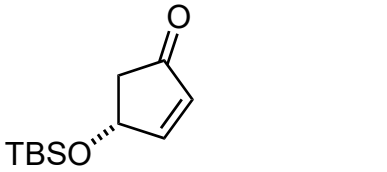
4) Structure of L-Selectride ?



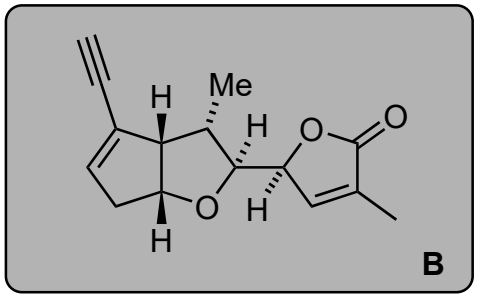
6) Name of the reaction ?
Mukaiyama hydration

9) Name of the reaction ?
Name of compound **2** ?
How would you prepare it ?
Rubottom/Davis oxidation
Davis oxaziridine

17) Name of the reaction ?
Grieco elimination

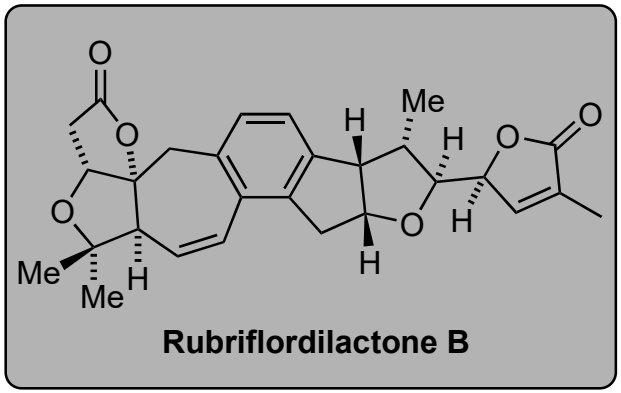


18-26



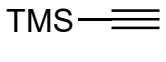
B

27-30



Rubriflordilactone B

18) I_2, K_2CO_3, 4-DMAP, r.t.
19) $NaBH_4$, $CeCl_3 \cdot 7\ H_2O$, –78 °C
20) CuI, Et_3N, $Pd(PPh_3)_2Cl_2$, **3**, r.t.
21) *o*-$NO_2C_6H_4OH$ (cat.), $EtC(OMe)_3$, 180 °C
22) TBAF, r.t.
23) LiTMP, –78 °C
24) DIBAL-H, –78 °C
25) **4**, DBU, LiCl, *then* s.m., 75 °C
26) TBSOTf, Et_3N, 0 °C,
then AcOH, TBAF, 0 °C



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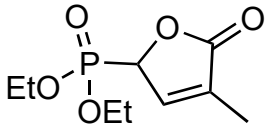

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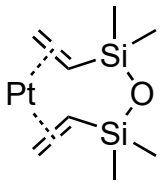
27) **A**, $Pd(PPh_3)_4$, CuI, LiCl, *i*Pr_2NEt, 70 °C
28) **5**, (3-pentyl-O)$SiMe_2H$, r.t.
29) 135 °C, *then* DDQ, r.t.
30) AgF, H_2O, r.t.



5

19) Name of the reaction ?
Luche reduction

20) Name of the reaction ?
Sonogashira coupling

21) Name and type of the reaction ?
Hint: γ,δ-unsatured ester formed
Johnson-Claisen rearrangement
[3,3]-sigmatropic rearrangement

22) *Note:* two epimers formed
23) *Note:* conversion of undesired epimer from 22) into desired product

25) Name of the reaction conditions?
Note: two epimers formed
Masamune-Roush conditions

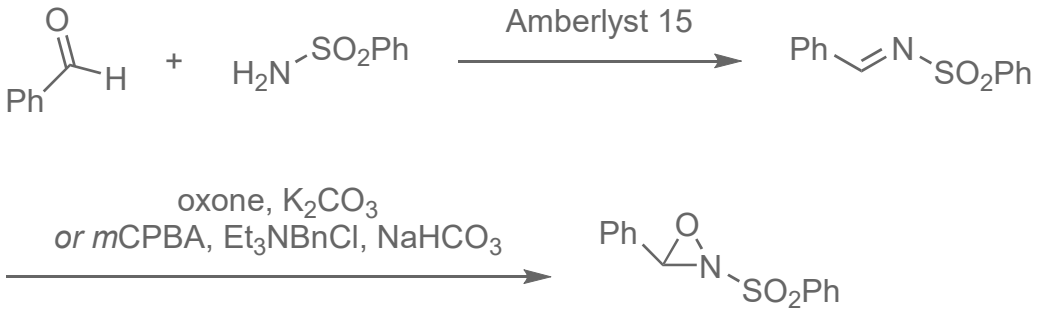
26) *Note:* conversion of undesired epimer from 25) into desired product

27) Name of the reaction ?
Sonogashira coupling

28) Name of compound **5** ?
Note: two regioisomers formed
Describe an alternative reaction.
Karsted catalyst
Hydrogenation with Lindlar catalyst

29) Classify the type of the reaction
6π-electrocyclization

Preparation of Davis oxaziridine



Lindlar hydrogenation