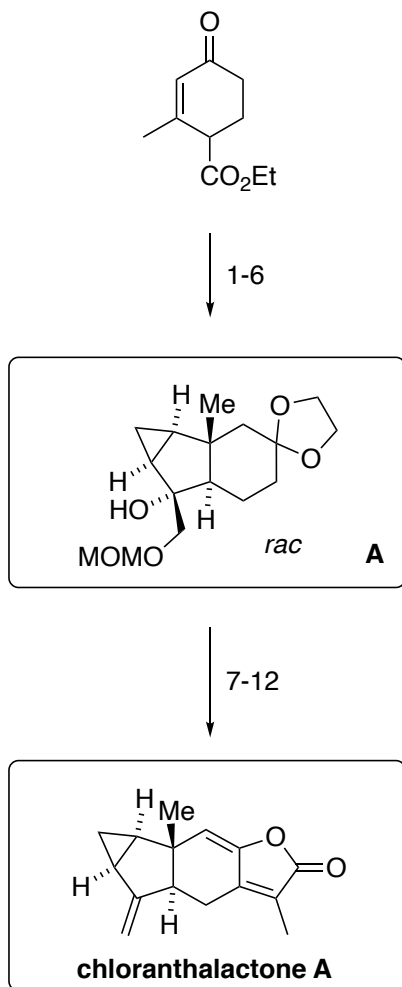


Total Synthesis of (±)-Chloranthalactone A

Yue, G.; Yang, L.; Yuan, C.; Jiang, X.; Liu, B.; *Org. Lett.* **2011**, *13*, 5406–5408.



- 1) vinylMgBr, CuBr · SMe₂
- 2) *p*-TsOH, ethylene glycol
- 3) HNMe(OMe) · HCl, *n*-BuLi, then substrate
- 4) *n*-Bu₃SnCH₂OMOM, *n*-BuLi, then substrate
- 5) CH₂Br₂, *n*-BuLi
- 6) LiTMP

- 7) aq. HCl
- 8) 1,1'-thiocarbonyldiimidazole
- 9) P(OMe)₃
- 10) ethyl pyruvate, LDA, ZnCl₂
- 11) *p*-TsOH, Ac₂O
- 12) DBU

Name of the starting material how would you make it? (at least 2 synthetic routes)

Hagemann's ester

step 5: Name the reaction, what could be an alternative reaction?

Matteson epoxidation

alternative: *Corey-Chaykovsky*

keystep 6: Name and classify the reaction, draw the transition state

Hodgson Cyclopropanation

type: *Cheletropic reaction*

(mechanism see below)

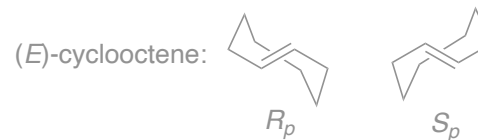
step 8/9: Name the reaction and propose a mechanism as well as an alternative name reaction.

Which famous 8-membered ring can be synthesized by this method?

Corey-Winter Elimination (mech. see below)

alternative: *Eastwood reaction*

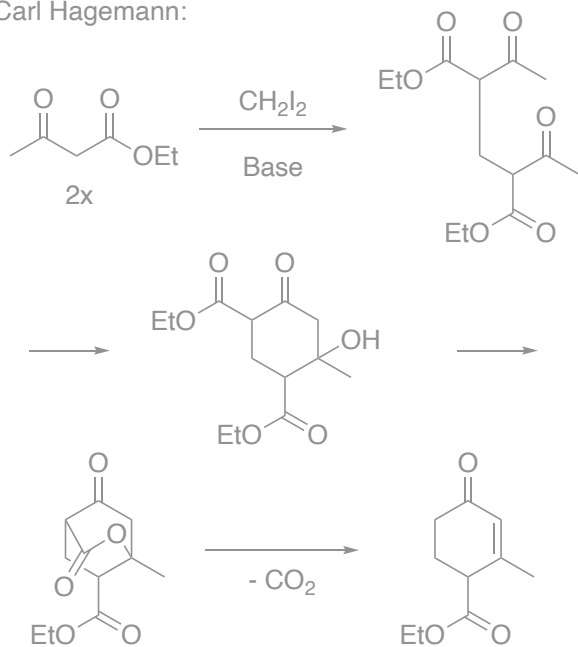
(OEt)₃CH, then AcOH)



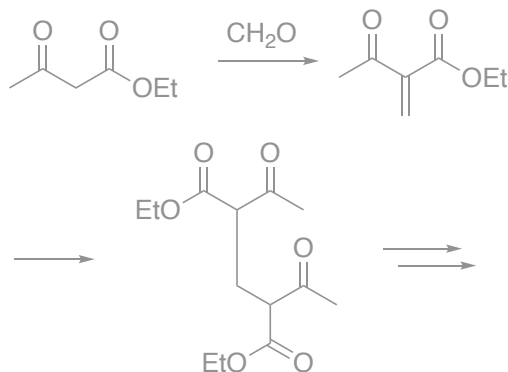
enantiomers

Hagemann's ester syntheses:

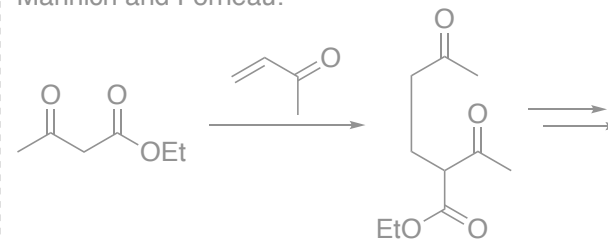
Carl Hagemann:



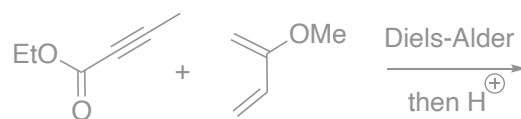
Emil Knoevenagel:



Mannich and Forneau:

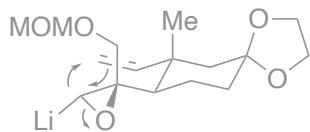


Newman and Lloyd:

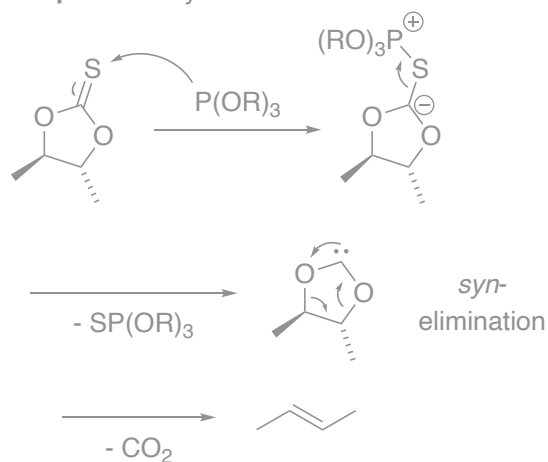


Step 6:

proposed mechanism
this paper



Step 9: Corey-Winter



alternatively, instead of a free carbene intermediate, the initial carbanion reacts with a second molecule of trimethylphosphite with concomitant cleavage of the sulfur-carbon bond. Elimination of the phosphorus stabilized carbanion gives the alkene, along with an acyl phosphite, which then decarboxylates.