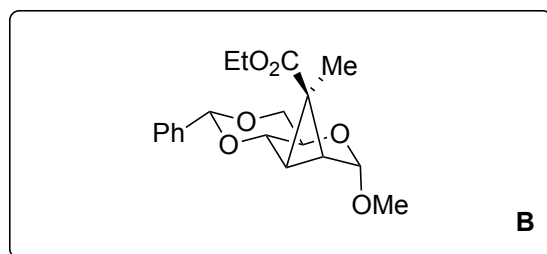
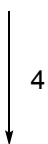
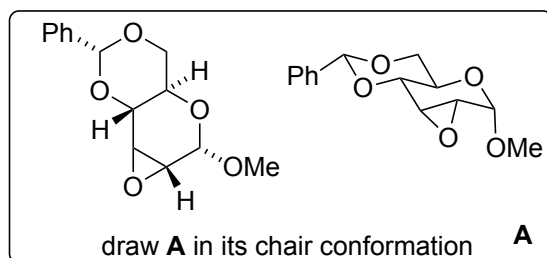
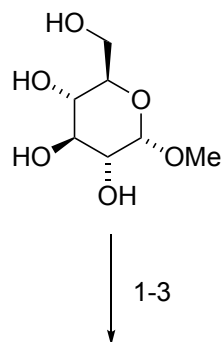


An Enantiospecific Route to (+)- and (-)-Chrysanthemum Dicarboxylic Acids

B. J. Fitzsimmons and B. Fraser-Reid

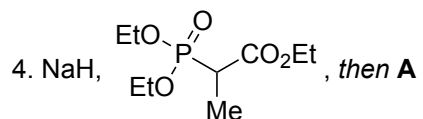
Tetrahedron **1984**, *40*, 1279-1287



1. *p*-TsOH, (MeO)₂CHPh
2. TsCl (excess), pyridine
3. NaOMe, MeOH/CH₂Cl₂

Preparation of **A**:

Can. J. Chem. **1982**, *60*, 327.



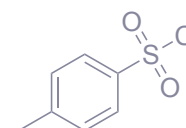
What is the name of the sugar starting material?

methyl glucopyranoside (glucose)

1. What is the name of the protecting group that is installed?

benzylidene

2. What is the structure of TsCl?



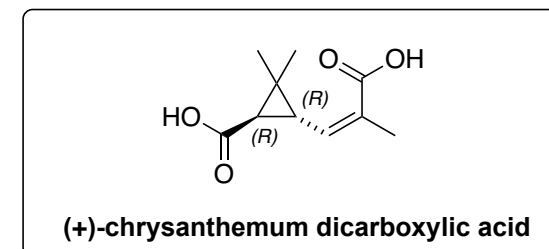
4. What is the name of this reaction?

Wadsworth-Emmons Cyclopropanation

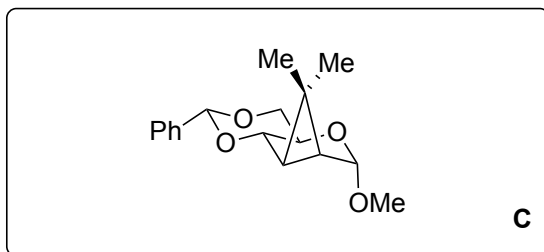
J. Am. Chem. Soc. **1962**, *84*, 3944.

Only one product is formed. Provide a mechanism and rationale for the formation of the product.

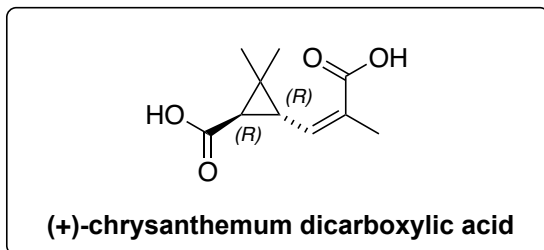
(Hint: think about orbitals) Ethoxide is not a leaving group.



5-7

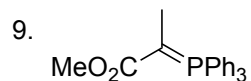


8-13



5. LiAlH_4
6. MeSO_2Cl
7. LiAlH_4

8. $\text{H}_2\text{O}/\text{dioxane}$, reflux



10. *p*-TsOH, MeOH
11. NaIO_4
12. NaOMe
13. $\text{Ag}_2\text{O}/\text{NaOH}$

8. How would you confirm the stereochemistry of the cyclopropane ring after this step?

The authors treated the resulting aldehyde with NaOMe to epimerize and compared the NMR signals of the aldehydic proton. The cis cyclopropane had $\delta = 9.45$ ppm and the trans cyclopropane had $\delta = 9.32$ ppm.

12. Hint: an epimerization occurs.
13. Hint: Ester is also hydrolyzed during this step.

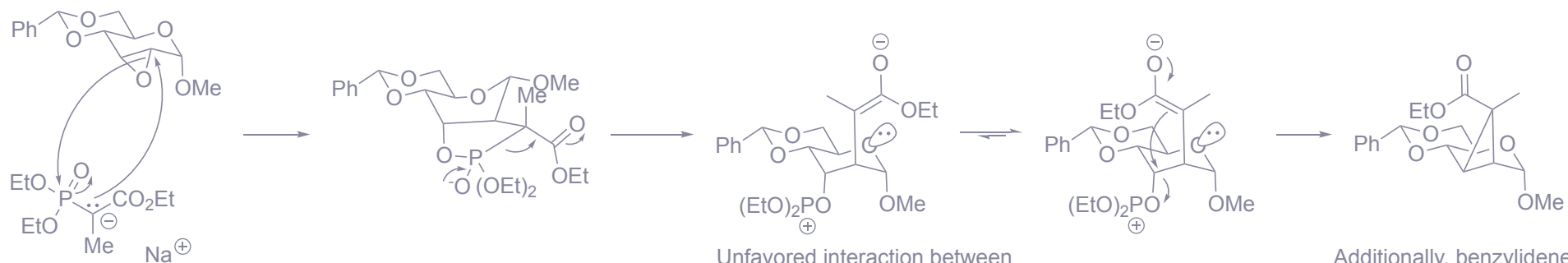
What is the name of this reagent?

Tollens Reagent

If you wanted to access the (–)-enantiomer, how would you do it from an intermediate in this synthesis?

Epimerize product after step 8 using NaOMe then follow steps 9-13, skipping step 12.

Step 4:



Unfavored interaction between enolate π electrons and p-orbital of ring Oxygen

Additionally, benzylidene restricts the flexibility of the system so only one product is formed