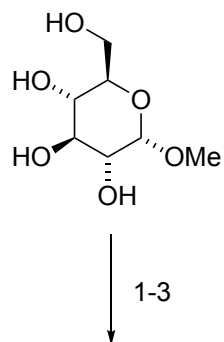


An Enantiospecific Route to (+)- and (-)-Chrysanthemum Dicarboxylic Acids

B. J. Fitzsimmons and B. Fraser-Reid

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



1-3

draw **A** in its chair conformation

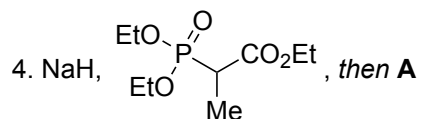
A

4

B

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

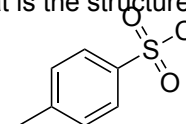
Preparation of **A**:



What is the name of the sugar starting material?

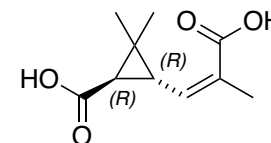
1. What is the name of the protecting group that is installed?

2. What is the structure of TsCl?



4. What is the name of this reaction?

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.

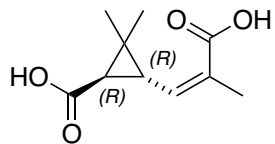


(+)-chrysanthemum dicarboxylic acid

5-7



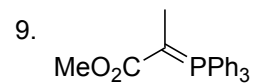
8-13



(+)-chrysanthemum dicarboxylic acid

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?

12. Hint: an epimerization occurs.
13. Hint: Ester is also hydrolyzed during this step.
What is the name of this reagent?

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