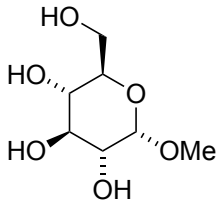
An Enantiospecific Route to (+)- and (–)-Chrysanthemum Dicarboxylic Acids

B. J. Fitzsimmons and B.Fraser-Reid

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



1-3

1. *p*-TsOH, $(MeO)_2CHPh$
2. TsCl (excess), pyridine
3. NaOMe, $MeOH/CH_2Cl_2$

What is the name of the sugar starting material?

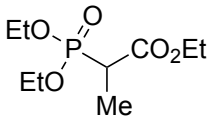
1. What is the name of the protecting group that is installed?

2. What is the structure of TsCl?

Preparation of **A:**

draw **A** in its chair conformation **A**

4

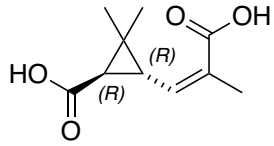
4. NaH, 

, *then* **A**

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: t*hink about orbitals) Ethoxide is not a leaving group.

B

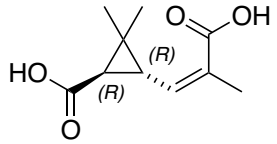


(+)-chrysanthemum dicarboxylic acid

5-7

C

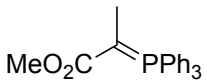
8-13



(+)-chrysanthemum dicarboxylic acid

5. $LiAlH_4$
6. $MeSO_2Cl$
7. $LiAlH_4$

8. H_2O/dioxane, reflux

9. 

10. *p*-TsOH, MeOH
11. $NaIO_4$
12. NaOMe
13. Ag_2O/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?