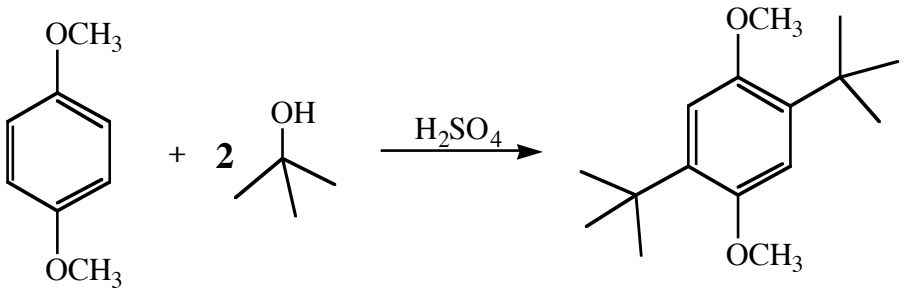
Friedel-Crafts Alkylation of 1,4-dimethoxybenzene



1,4-dimethoxybenzene

(hydroquinone dimethyl ether)

1,4-di-*t*-butyl-2,5-dimethoxybenzene

MW: 250.37 g/mole

mp: 104-105 °C

Introduction

The Friedel-Crafts Alkylation is a very useful reaction for adding alkyl groups to aromatic compounds. It is an example of an Electrophilic Aromatic Substitution reaction, and the classic reaction utilizes an alkyl chloride and $AlCl_3$ to generate an intermediate that has nearly a full positive charge on a carbon. However, there are many other ways to generate a carbocation, and these can also provide an effective way to add alkyl groups to an aromatic ring. Alkenes and alcohols can both react with strong acids to form carbocations. These are both reactions that we studied last semester. Carbonyl groups can also react with strong acids to create a carbon that has nearly a full positive charge on the carbon of the carbonyl group. All of these reactions involve creating a carbon with either a full positive charge or a very large δ+. Today we will be using an alcohol to generate our carbocation.

However, the Friedel-Crafts reaction has a number of limitations. It can only produce a product in good yield if the starting material is at least as reactive as benzene. If the benzene ring has deactivating groups attached, then little or no product is formed. Look at the groups attached to our starting material in this experiment. Is the ring activated or deactivated? Another problem with the Friedel-Crafts alkylation is that the product is more reactive than the starting material. Alkyl groups activate the ring, so addition of a second or third alkyl group is a faster reaction than the initial reaction. So poly-alkylated products are often obtained. Our product in this experiment has added two alkyl groups. Can you think of a reason why a third group is not added? A third issue to consider is the nature of the carbocation. As we learned last semester, carbocations are prone to rearrangement. Will the carbocation we generate in this experiment be stable, or will it undergo a rearrangement?

Despite these limitations, the Friedel-Crafts reaction is nevertheless a useful way of adding carbon groups to aromatic rings. We only need to exercise care in choosing our starting material, our desired product, and our intermediate carbocation.

Keep in mind that forming a carbocation is often quite easy and fast. The rate determining step in all Electrophilic Aromatic Substitution reactions is when the aromatic ring attacks the positive charge. This is always an uphill step, because the intermediate is no longer aromatic.

Experimental Procedure

In a 10-mL round-bottomed flask, place your small magnetic stirring bar and then dissolve 0.240 g of 1,4-dimethoxybenzene in 0.8 mL of concentrated acetic acid. You may have to warm the mixture slightly to dissolve all of the solid. Stirring the mixture slowly will help dissolve the solid. After the solid has dissolved, add 0.4 mL of *t*-butyl alcohol (you may have to warm the alcohol to melt it). Cool this mixture in an ice bath and then add 0.8 mL of concentrated sulfuric acid dropwise. Add the sulfuric acid slowly and stir the mixture during this addition.

After this addition is complete, you should have a significant amount of solid product, and you may have to manually stir the reaction with a stirring rod. Keep stirring the reaction, remove the ice bath, and allow the reaction to warm to room temperature. Once it has reached room temperature, stir it for another 10 minutes. At this point the reaction should be complete. Place the flask back in an ice bath to maximize crystal formation. **Very carefully** add a drop of water to the mixture (adding water to concentrated sulfuric acid is a very exothermic process!), and continue to add water dropwise until you have added 5 mL of water. Keep stirring the reaction during this addition. At this point you should have a great deal of solid. Filter the solid with suction using a Hirsch Funnel, and wash the solid with lots of ice cold water. Recrystallize your solid using the minimum amount of methanol. Remember the steps of a recrystallization: dissolve your solid in the minimum amount of boiling solvent, allow it to cool slowly to room temperature, then cool in an ice bath, and finally filter by suction. Wash your final crystals with ice cold methanol.

Allow your crystals to dry, and obtain an NMR, IR, and mp of your product.

Questions (these can just be included in your discussion)

1. What is the mechanism of this reaction?

2. Is this a good starting material for a Friedel-Crafts reaction? Why or why not?

3. Is our carbocation a good one for this reaction? Why or why not?

4. The starting material is very symmetrical, so there is only one place the first *t*-butyl group can go. Explain the regioselectivity of the addition of the second *t*-butyl group (why do you get only that product, and not other isomers?). Why don't we add a third *t*-butyl group? **This question is the most important one to answer in your discussion!**

5. How many peaks would you expect to see in a ^{13}C NMR of our product?