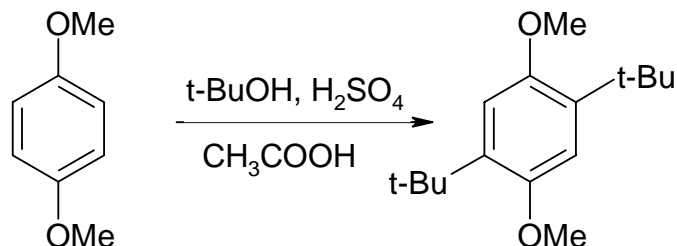


NOTES ON EXPERIMENT 4

Friedel-Crafts Alkylation of 1,4-Dimethoxybenzene (Chapter 29, Expt 4)



This reaction is another example of electrophilic aromatic substitution, similar to lab #3, except that this time we are using $t\text{Bu}^+$ rather than NO_2^+ as the electrophile. This is important, since the nitro group (once attached) acts as a *deactivating* group, making the attack of a second NO_2^+ much slower- therefore we can stop the reaction after only one nitro group has been added. However the *tert*-butyl group (an alkyl group) is *activating*, and this means that a second $t\text{Bu}^+$ will add more quickly than the first- this makes it hard to stop after only one *tert*-butyl group has been added. So why does it stop after only two in this case? If you make a model you will see that it is very hard to put two *tert*-butyl groups on neighboring carbons on the ring due to steric interactions- this makes the alkylation stop after two *tert*-butyl groups have been added in the particular reaction we are running. Note that the second *tert*-butyl group adds para to the first- you should understand why this is the case, bearing in mind the fact that the *tert*-butyl and the two methoxy groups are both activating groups.

Another difference from lab #3 is that this time we are using a ring that is *activated*, i.e., more reactive than is benzene itself. Whereas nitration can occur even in a strongly deactivated aromatic system such as methyl benzoate, alkylation cannot- methyl benzoate would not react in this reaction.

Experimental

- Prepare the ice/water bath (in a beaker) before you start the reaction.
- Carefully crush the 1,4-dimethoxybenzene in the tube before adding HOAc.
- Take care with both acids used, both are corrosive and cause severe burns.
- When cooling to crystallize be sure to add water dropwise with mixing.
- You should record mass and MP of both crude and pure product.
- We will be analyzing the product by TLC, but not IR. In your write-up, explain why the product has a higher R_f than the starting material.

Questions

From chapter 29, answer questions 4, 5 and 6. Note that #6 should refer to the IR, **not** the NMR. Also answer the following:

What differences would you expect to see between the starting material and the product of the reaction in the NMR spectrum? How could you use the NMR to show convincingly that you had the dialkylation product and not the monoalkylation product? [Hint: Also consider what the monoalkyl product would look on NMR.]