

8. S_N1: Substitution reaction of triphenylmethanol

M. Jones: S_N1 Chapter 7 (Section 7.7) pgs 305-312
Stability of trityl cation Chapter 14 (Section 14.12) pg 679

Background

In this experiment, you will perform two S_N1 (substitution nucleophilic unimolecular) reactions using triphenyl methanol as your substrate (R-L). The first one is the formation of the triphenylmethyl bromide from the reaction of triphenylmethanol with hydrobromic acid (Figure 1).

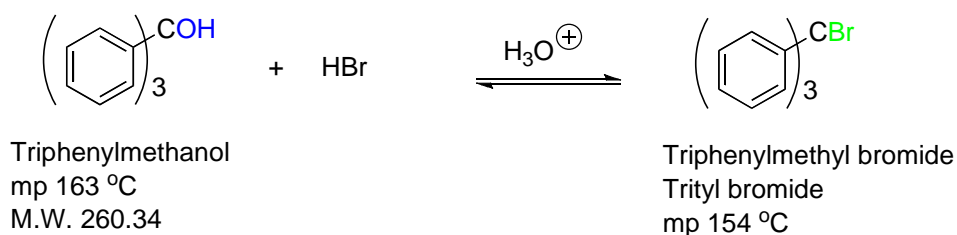


Figure 1. The overall reaction scheme for the formation of triphenylmethyl bromide.

The second reaction is the formation of an ether from the reaction of triphenylmethanol with methanol in acidic conditions (Figure 2).

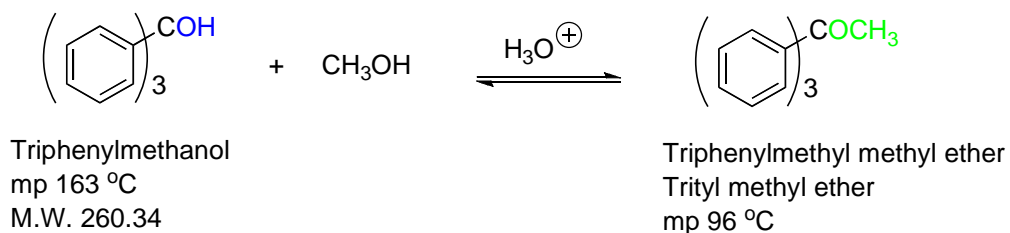
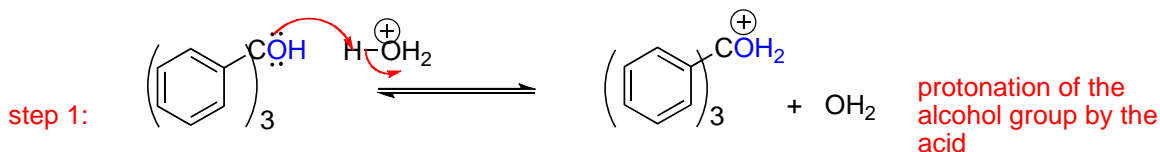


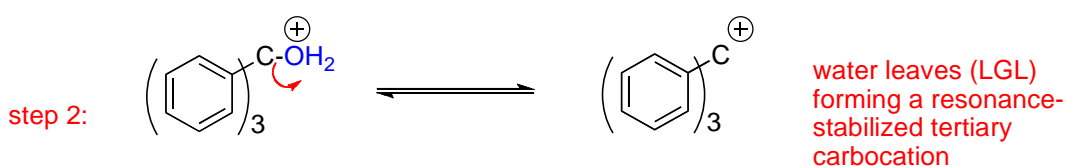
Figure 2. The overall reaction scheme for the formation of triphenylmethyl methyl ether.

The mechanisms for both reactions are very similar. The first thing to do is to identify the R-L and the Nu for the reaction. In this case the R-L is Ph₃C-OH, where the carbon of the C-L is tertiary. No S_N2 reaction can occur on a tertiary

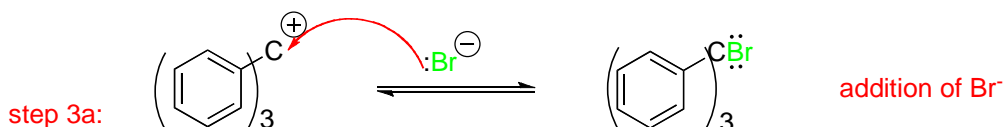
C-L. The nucleophile is then the methanol and bromide, respectively. So one of the initial steps in the reaction is that the leaving group leaves but in this case, we know that hydroxide is a poor leaving group. Therefore, the first step in this reaction is the protonation (addition of H^+ to the alcohol group), thus making a better leaving group, H_2O .



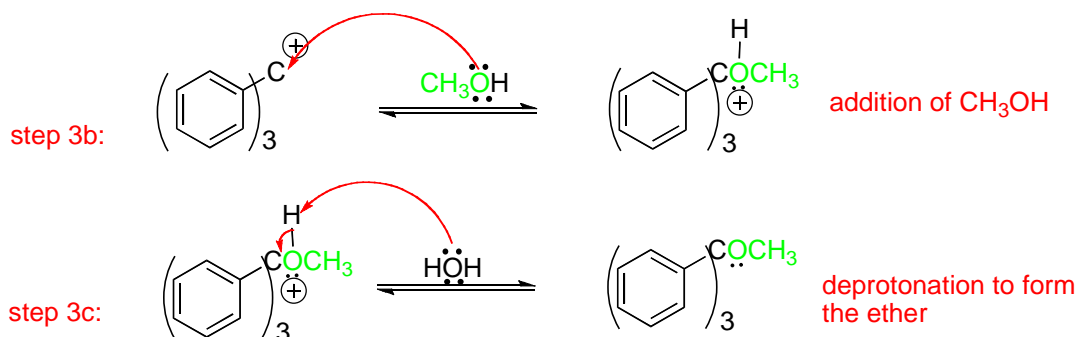
Then, the leaving group, water, departs leaving behind a carbocation. This cation is sp^2 -hybridized, extremely stable due to resonance stabilization of the positive charge throughout the three rings, which are propeller-shaped due to the steric bulk of the phenyl (benzene) groups.



The next step is the addition of the nucleophile. In the case of the bromide, the product is formed directly.



There is one more step for the addition of methanol. The intermediate has to be deprotonated in order to form the ether.



You can determine whether or not that you have your product by the comparison of melting points of your products and starting materials. You could also run a Beilstein test on your bromide using a copper wire and flame. If there is the halide present, there flame will appear to be blue-green due to the presence of copper bromide. In the case of copper chloride, the flame would be green, and blue in the presence of copper iodide. Finally, you could use IR spectroscopy to

determine whether or not you had starting material present. You will use at least one of these methods in the experiment today.

Tips:

- *Make sure to start experiment 1 by preparing your water bath and experiment 2 by cooling your methanol, which will save you some time.*
- *Be especially careful in the handling of concentrated sulfuric acid and hydrobromic acid (and less so for acetic acid).*
- *Record all measurements and color changes during the reactions.*

This procedure has been adapted from the microscale procedure described in *Macroscale and Microscale Organic Chemistry Experiments* by Kenneth L. Williamson.

Experiment

Before beginning these experiments, prepare a water bath by putting water into a beaker and start heating it to boiling (for part A). Also, add 1 mL of methanol and 5 mL of methanol to two separate reaction tubes and place both tubes into an ice-water bath (for part B).

A. Triphenylmethyl bromide.

Record all measurements and color changes. Weigh approximately 0.200 g of the triphenylmethanol (TPM) and place into a reaction tube. Using separate glass pipettes, add 4 mL of acetic acid and then 0.60 mL of hydrobromic acid (33% solution in acetic acid) to the same reaction tube. Then, heat the mixture for 5 minutes using the water bath (beaker with boiling water). After that time period, cool the reaction tube using an ice-water bath and collect the material using vacuum filtration. Wash the product using water (about ½ pipette full) and completely dry the product. Then, wash the product with hexanes (about ½ pipette full) and completely dry the product. Determine the weight of the crude product. Then, recrystallize the material from hexanes, which may take a little time so continue onto the next reaction.

Perform a Beilstein test to determine if your product contains bromine. This test is performed by heating a copper wire in the flame of a Bunsen burner until no additional coloration of the flame is noticed. Next, the copper wire is cooled by dipping it into a beaker of deionized water. Then, dip the copper wire into your sample and heat in the flame again. Record any color change you observe.

B. Triphenylmethyl methyl ether.

Record all measurements and color changes. Weigh approximately 0.200 g of the triphenylmethanol (TPM) and place into a reaction tube. Make sure to gently grind the TPM with a glass rod to help with solubility. Add 2.0 mL of concentrated sulfuric acid with a glass pipette to the reaction tube and stir the tube to help dissolve all of the TPM.

Transfer the acidic TPM mixture into the ice-cold 1 mL methanol reaction tube using a Pasteur pipette. You can use some of the methanol to help transfer all of the TPM solution from the first tube. If the yellowish orange color does not disappear after this addition, then put the reaction tube containing your acidic TPM and methanol mixture into the ice-water bath and add ½ pipette of methanol at a time from the ice-cold 5 mL tube until the color disappears (you probably won't use all of this!). You should also see crystals form. If no crystals have formed, gently scratch the side of the tube using a glass rod. Collect the crystals using vacuum filtration, wash the crystals with water, and squeeze the water from the crystals by putting the crystals between filter paper. Make sure your product is dry and then determine the weight of the crude material. Recrystallize the product from hot methanol and determine the product's melting point.