Glendale Community College  
Chemistry 106 Laboratory  
Experiment: Friedel-Crafts Alkylation  
(Synthesis of 1,4-di-t-butyl benzene)

Main Reaction:

\[
\begin{array}{c}
\text{AlCl}_3 \quad \text{(in situ)} \\
\end{array}
\]  

Figure 1: Equation for the main reaction.

Introduction:
Friedel-Crafts alkylation reactions belong to a large and synthetically useful family of chemical reactions called Electrophilic Aromatic Substitution (EAS) reactions. Similar to Nucleophilic Substitution (S_N) reactions, the net transformation in the EAS reactions is formation of a covalent bond between an electron-deficient species called Electrophile (in the case of EAS) and the substrate which is a phenyl ring. The difference however, lies in the fact that the substrate subjected to substitution is an aromatic ring, and not an aliphatic sp\(^3\) carbon. Naturally, the mechanism for these reactions is widely different from that of the Nucleophilic Substitution reactions. Figure 2 shows the general transformation described above:

Figure 2: General transformation during Electrophilic Aromatic Reactions

As seen in figure 2 above, an electrophile (E\(^+\)) covalently bonds to the aromatic ring displacing one of the aromatic hydrogens.

The specific reaction to be carried out during this experiment is shown in figure 1 above, where t-butyl benzene is the substrate, and t-butyl chloride is the source of the electrophile (t-butyl cation) generated in-situ with the electronic activation aid of aluminum chloride (the catalyst). Once initiated, the reaction releases large amounts of heat. Therefore it should be initiated and completed at a reduced temperature. This is physically possible by cooling the reaction flask in ice bath. As seen in figure 1, HCl(g) is formed as a byproduct. Therefore, the reaction should be carried out in a well-ventilated fume hood.

Your laboratory instructor will cover the reaction mechanism, during the discussion prior to the experiment.
Procedure:
a) Setting up the apparatus and the reactants: Place sufficient mass of 1.0mL of t-butyl chloride and 0.5mL of t-butylbenzene in a 25mL round-bottom flask equipped with a small magnetic stir bar and assembled together with a claisen head.

NOTE: Claisen head serves as a soft barrier between the dry conditions of the reaction and the potentially present outside moisture.

Assemble the reaction apparatus in a safely clamped manner inside a fume hood. Place the reaction flask in a small crystallizing dish, sitting on a magnetic stirrer. Place a small amount of ice and water, and stir the reaction mixture for about 10 minutes. While waiting for the reactants to cool to 0°C, weigh 0.05g of anhydrous aluminum chloride in a small dry test tube and cork it.

NOTE: Since AlCl$_3$ reacts rapidly with moisture; it may do so, even in the short amount of time it takes to weigh it into the test tube. Therefore, accurate measurement of this reagent will be difficult. Minimize your measurement time as much as you safely can.

Figure 2: Apparatus assembly for Friedel-Crafts alkylation reaction.

b) Performing the reaction: Once the reactants have been cooled to 0°C, carefully remove the Claisen head, and start adding the catalyst in small portions as it is stirred into the reaction flask.

NOTE: You will notice fizzing upon the addition of the catalyst as a sign of the reaction. Allow the fizzing to subside before adding more catalyst.

Once the entire aluminum chloride is added and the reaction is complete, re-assemble the Claisen head, and discontinue the cooling by removing the ice bath from the apparatus. Continue stirring for another 15 minutes for it to thaw to room temperature.

c) Work up: Remove the Claisen head, and slowly add 2mL of ice-cold water (de-ionized), and 2 mL of diethyl ether. You should see two distinct layers. Transfer the contents of the round-bottom flask into a small separatory funnel and separate the layers. Extract the aqueous layer with two additional 2mL portions of diethyl ether and combine it with the organic layer. Dry the organic layer with anhydrous sodium sulfate. Filter and separate the dry organic layer. Extract and filter the sodium sulfate matrix with a fresh 2mL portion of anhydrous diethyl ether and combine with the dried organic layer. Evaporate the solvent, and obtain the final product.

d) Product Analysis: The following analyses need to be performed on the final product:
   1. Measurement of mass; calculation of percent yield.
   2. Measurement of melting point, if solid.
   3. TLC analysis with a mixture of 50:50 hexane:ethyl acetate (by volume) used as the solvent system.
   4. IR spectroscopy.

e) To be included in laboratory report:
   1. Results and discussion from Product Analysis section above.
   2. Tabular prediction of $^1$H-NMR spectrum.