Benzene rings have as a characteristic feature a continuous ring-shaped cloud of electrons in their π orbitals. This cloud of electrons is attractive to electrophiles that may be in the vicinity. (Recall that an electrophile is any species that is electron-deficient.) If a sufficiently large difference exists between the electron supply of the ring and the electron deficiency of the electrophile, a reaction may occur. This process can be illustrated as shown below, where E represents the electrophile.

\[
\text{CH}_2\text{Cl}_2 + \text{E}^+ \rightarrow \text{CH}_2\text{Cl}_2\text{E}^+ \rightarrow \text{CH}_2\text{Cl}_2 + \text{H}^-\text{E}^+ 
\]

Other Resonance Structures

The ability of functional groups attached to the benzene ring to contribute electron density to or withdraw it from the ring π system influences the rate of attack of any given electrophile. Substituents that increase the electron density of the π system are activators of substitution since the rate of attack is accelerated. Activators include alkyl groups and directly attached oxygen and nitrogen atoms. The former activate by inductively donating electron density to the ring via hyperconjugation. Oxygen and nitrogen atoms directly attached to the ring activate via resonance that involves a nonbonding electron pair. Substituents that withdraw electron density from the ring π system are deactivators of substitution.

The nature of any substituent groups also influences the orientation of attack. An activator favors attack at positions that are ortho and para to it, while a deactivator favors meta attack (with one exception). Preferences for a given orientation of attack can be related to the degree to which the positively charged intermediate is stabilized (or destabilized) by the electronic nature of each of the attached substituent groups.

A very useful electrophilic aromatic substitution reaction was discovered around 1900 by Friedel and Crafts. These chemists found that if benzene or certain derivatives of benzene are mixed with an alkyl halide in the presence of a Lewis acid like AlCl₃, a reaction takes place with evolution of HCl gas. The benzene is found to have been substituted by the alkyl portion of the alkyl halide. Further study soon showed that acyl halides also react, producing aromatic ketones. Products from alkyl (but not acyl) halides showed evidence of rearrangement in some cases, revealing that a carbocation intermediate was involved. Rearrangement occurs as usual to give the most stable carbocation possible. Thus, if a 1° halide is used, the product will contain substantial quantities of 2° or possibly 3° substituents, but if the halide is 3°, no rearrangement is seen. The accepted mechanism for this reaction is shown below.

\[
\text{H}^+ + \text{AlCl}_4^- \rightarrow \text{HCl} (g) + \text{AlCl}_3 \]

The mechanism for acylation is similar, except that an acylium ion is the electrophile. Since this ion is resonance stabilized, there is no reason for it to rearrange, and so the product of an acylation doesn't show rearrangement of the substituent carbon skeleton.

One difficulty of Friedel-Crafts alkylation is that of multiple substitution (not shared by acylation). The reason is simple to understand. Once a benzene gains an alkyl substituent, it becomes more susceptible to electrophilic
attack because the substituent acts as an inductive electron donor. Thus the substituted benzene reacts faster than unsubstituted benzene. Multiple substitution can be minimized by using a large molar excess of benzene. In contrast, acylated benzenes are less reactive than benzene ones since the acyl group is electron withdrawing. In fact, Friedel-Crafts reactions are not possible on benzene rings that bear acyl substituents. Thus the reaction stops automatically at one acylation.

EXPERIMENTAL SECTION

**CAUTION:** Traces of H₂O destroy the Lewis acid character of AlCl₃ and release HCl fumes. Keep the stock bottle and your own supply tightly closed at all times. Benzene is toxic (known to cause certain kinds of leukemia). Pour it only in the hood and keep it away from your skin.

**Synthesis:** Find rubber stoppers suitable for a 125 mL vacuum flask and a medium size test tube. Use a soft flame to dry the vacuum flask and test tube. Immediately after taking the hot glass back to your desk, use your aspirator to draw air through the top of the vacuum flask and the test tube for a few seconds. This pulls out the water vapor inside. Obtain about one scoopula-end full of AlCl₃ from the stock bottle, put the powder in your dry test tube, and immediately stopper it (and close the stock bottle). After the glassware has cooled enough to handle, add to the flask 30 mL of dry benzene and 10 mL of tert-butyl chloride and stopper the flask. Set up the glassware as shown below. Use a discolored hose, glass funnel with stem, and a 600 mL beaker. Cool the flask in an ice/water bath. The inverted funnel should be clamped with a small 3-fingered clamp to a ring stand so that its lip just contacts the water surface (to maximize surface area of water within funnel area). Set up everything well inside your hood.

![Diagram of the setup](image)

Add about ¼ of the AlCl₃ through the main opening of the flask and swirl vigorously. Keep both the flask and the test tube stoppered between additions to avoid escape of HCl gas and to keep atmospheric moisture from destroying your catalyst. Initially, air bubbles will escape from under the funnel, but when HCl reaches the water it will all dissolve. A yellow color will form on the catalyst. Swirl the flask frequently, keeping it cool but also maintaining a good rate of bubbling. If the rate of bubbling slows, add another portion of catalyst. The reaction is over when the rate of bubbling becomes very slow even when a new portion of catalyst is added. Remove the flask from the ice bath and allow it to stand at room temperature for about 15 min.

Mix 15 mL worth of crushed ice and 40 mL of water. Working in your hood, add the water / ice solution to the flask, swirl it, and pour it into a separatory funnel. Shake and vent the separatory funnel as normal. Remove the aqueous layer (top or bottom?), and rinse the side-arm flask with about 50 mL of tap water. Add this to the separatory funnel. After shaking, recover the organic layer and wash it once with about 15 mL of 5% sodium bicarbonate to neutralize any acid that may have been carried over. Dry the organic layer over some anhydrous CaCl₂ by gently swirling it for about 5 minutes, then decant carefully into a dried 100 mL boiling flask.

**Purification:** Fractional distillation will be used to recover the tert-butylbenzene. Verify that the interior of all glassware needed is free of water before proceeding. Insulate the neck of the boiling flask with at least 6 rounds of paper before clamping it. Add a boiling chip and your dried product. Connect an Aldrich© Snyder fractionating column (first verifying the column has a Teflon sleeve on its bottom joint). Add the distillation head and finish assembly as usual (refer to your Grignard Reaction experiment notes for assistance). **Proper placement of the thermometer bulb is crucial; so are tightly connected glassware joints.** Insulate from the flask over the distilling head up to the water cooled condenser. Press the heating mantle firmly against the boiling flask to ensure good heat transfer. Adjust the variac to about 70 % of capacity until the temperature begins rising. Then turn the variac down to approx. 50 % of capacity (or whatever is needed to maintain a drip rate of ~2 drops/sec for
benzene). Collect benzene (b.p. about 80 °C) until the vapor temperature reaches ~110 °C (or schlieren lines appear), then switch to a weighed smaller round bottom flask to collect the product.

Note: The temperature will stay approx. 80 °C until most of the benzene is out, then may drop or vary. The drip rate will also slow down. At this time, increase your variac setting to about 90% of capacity. Eventually, the thermometer will shoot up to the expected b.p. Adjust variac to whatever is needed to maintain a drip rate of ~1 drop/sec for t-butylbenzene once it starts coming over.

Record the temperature at which most of the product distills. Turn off the heat when the temperature drops (or goes up) more than 8 °C from that at which most of the product distills.

Clean up: Recycle the benzene fraction into "benzene to be distilled" bottle, and after weighing the product, put the t-butylbenzene into “t-butylbenzene student prep” bottle. Pot residues go into the “mixed nonhalogenated organics” bottle. It may be necessary to boil a KOH or NaOH solution in your boiling flask to clean it – if so, do it in a big hood. Aqueous washes and water trap must be neutralized with solid NaHCO₃ before going down the drain. As always, do the first washes of all glassware in the sinks of the main hoods.

Your minor lab report should include all components described in the “How to Write a Strong Lab Report” general guidelines.

Some topics to consider including in your summary (concise):

- In your discussion of % yield, imagine that multiple substitutions somehow occurred during your experiment. Consider electron donating groups and their effects on the attack by a second substituent to find a plausible di-substituted side product; look up its boiling point to see if it is plausible that some may have formed, then been captured during distillation (at what point did you switch to the second collection flask?); and if this possibly happened, what direction is the resulting effect on the % yield?
- Comment on the theory of electrophilic aromatic substitution and electron donating/withdrawing groups as they relate to this experiment (and thus: how did procedural considerations, such as using an excess of benzene, or using a fractional distillation column, relate to the theory behind the experiment?)
- Comment on why you were not asked to characterize your compound by IR or qualitative chemical tests.
- Comment on the value of fractional distillation for separating liquid compounds compared to simple distillation.

Some useful resources for you as you prepare your minor lab report:

- Lab syllabus section “Sample Major Lab Report” – results and discussion sections
- “How to Write Strong Lab Report” document
- Instructors, TAs, and classmates (provided your work is your own and is cited where appropriate)