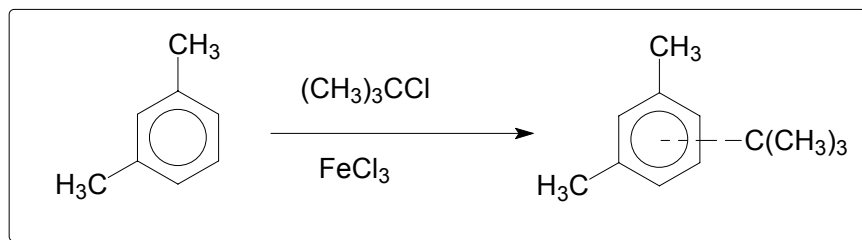


## Alkylation of *m*-Xylene: A Puzzle



Place 9 mL of *m*-xylene (1,3-dimethylbenzene) and 7.5 mL of t-butyl chloride (2-chloro-2-methylpropane) in a dry Erlenmeyer flask (50 mL). Place a cork in the flask and cool the mixture in an ice bath. Add a micro spinbar and then 0.6 g (600 mg) of iron(III) chloride (purple, free-flowing crystals when pure and dry). After a short induction period, the reaction will begin a vigorous evolution of hydrogen chloride. [Since you are working in a hood, we need not make arrangements to trap the HCl.]

After this vigorous part of the reaction is over, remove the ice bath and allow the reaction mixture to warm to room temperature. When bubbles of hydrogen chloride cease to be evolved or after 15 min, add 20 mL of water to the reaction mixture, mix well, and then transfer to a separatory funnel. Drain off the aqueous layer. Wash the organic layer using about 15 mL of saturated aqueous sodium carbonate solution (to remove any remaining HCl) and then with 15 mL of saturated sodium chloride solution. Transfer the organic layer to a clean Erlenmeyer flask and dry it with anhydrous calcium chloride pellets or granular anhydrous sodium sulfate.

From the boiling points of reactants and products in the table, decide which fraction to collect and analyze, and which to recycle as non-halogenated waste. Transfer the organic layer to a dry round-bottom flask, add a boiling chip, and arrange for distillation.

After distillation and collection of the fraction containing the product, analyze the residue by infrared spectroscopy, which is most easily done as a thin film between sodium chloride or silver chloride plates. From a correlation chart for the aromatic C-H out-of-plane bending modes, deduce the structure of the product. NMR spectra ( $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra) will be measured or

provided. We will also try to obtain mass spectra of your product(s). In your report, write a mechanism for this reaction that illustrates all the details of your conclusions. Discuss the structure of the product in terms of directive effects of substituents on the benzene ring, steric effects of substituents, and thermodynamic versus kinetic control of the reaction.

You will be given the results of molecular mechanics calculations on the three possible products to determine their relative steric energies or heats of formation. Do these calculations contribute to your conclusions?

Obtain the weight of collected product, and determine the percent yield of tri-substituted aromatic product.

### ***Cleaning Up***

Place any unused t-butyl chloride in the halogenated organic waste container and any unused xylene in the organic solvents container. Unused iron(III) chloride and wash solutions should be combined and neutralized with sodium bicarbonate solution, diluted with water, and flushed down the drain.