

Friedel-Crafts Alkylation: Synthesis of *p*-di-*t*-butylbenzene

Friedel-Crafts reactions, a type of electrophilic aromatic substitution (EAS), are an important class of C-C bond forming reactions. Friedel-Crafts alkylation involves the alkylation of an aromatic ring by an alkyl halide using a strong Lewis acid catalyst. Two commonly used Lewis acid catalysts are anhydrous aluminum chloride and ferric chloride.

In this reaction sequence the Lewis acid catalyst forms the carbocation first (Figure 1).

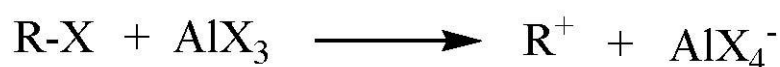


Figure 1: Generation of a carbocation by a Lewis Acid catalyst.

When the aromatic group is added the substitution occurs following the EAS mechanism shown in Figure 2. The alkyl group attaches at the position of the most stable carbocation formed. At this point the Lewis Acid catalyst is regenerated.

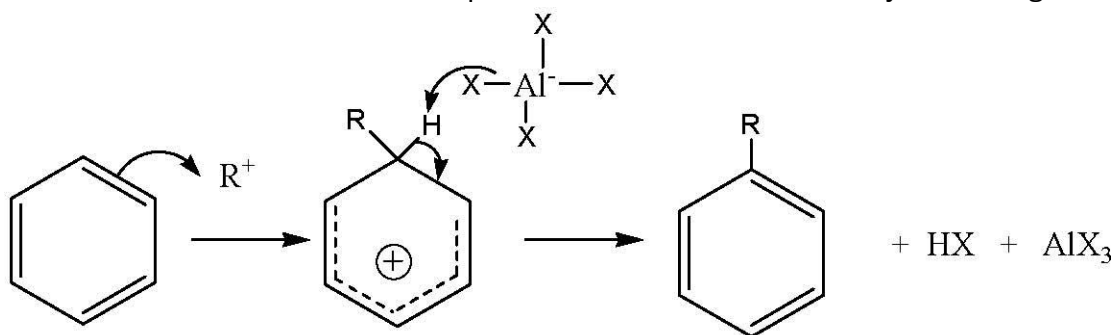


Figure 2: The mechanism of the Friedel Crafts alkylation.

This reaction has two major problems. Firstly, the product is more nucleophilic than the reactant due to the electron donating alkyl-chain, which leads to overalkylation of the molecule. Secondly, if the alkyl halide is not tertiary (or otherwise stabilized), carbocation will rearrange to the most stable carbocation available. These rearrangements occur through both hydride and alkyl shifts. Steric hindrance can be exploited to limit the number and relative position of alkylations. The use of tertiary halides limits carbocation rearrangement.

The reaction we will be doing today takes advantage of a tertiary halide to limit carbocation rearrangement and a sterically hindered aromatic compound to limit overalkylation. The overall reaction is shown in Figure 3.

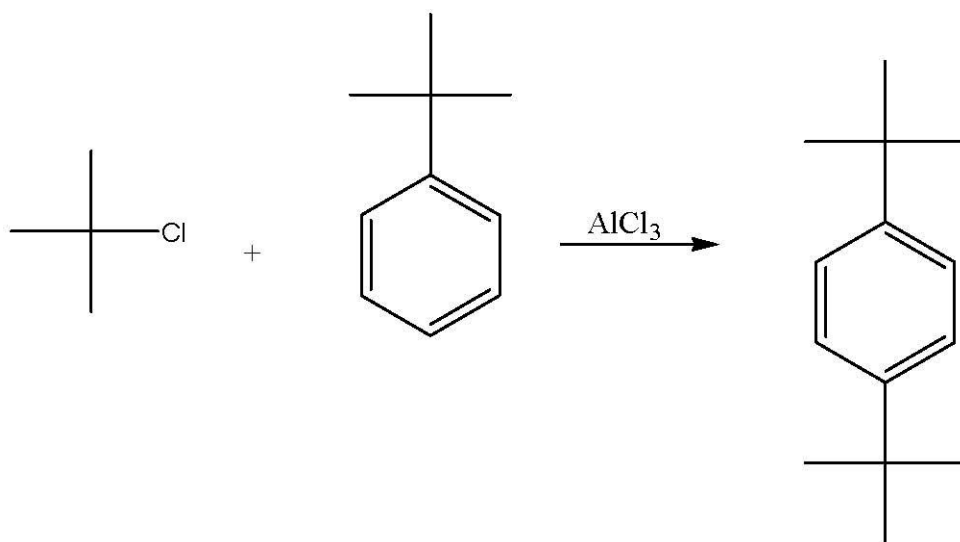


Figure 3: The Friedel Crafts alkylation of *t*-butylbenzene by *t*-butyl chloride in the presence of aluminum chloride.

*Note: The reaction should be performed inside a fume hood because HCl gas is produced in this reaction.

Procedure:

1. Place 1.0 mL of *t*-butyl chloride and 0.5 mL of *t*-butylbenzene in a 5 mL conical vial, equipped with a spin vane. This mixture should be cooled and stirred. Assemble such an apparatus by placing an ice bath, made with a small crystallizing dish, as the ice bath container, with the conical vial placed in it, over a stirring plate. Make sure the conical vial is securely clamped.
2. Weigh 0.05 grams of anhydrous aluminum chloride in a tared 1 dram vial and cap it. (Note: It may be difficult to weigh this material accurately because it reacts readily with moisture in the air. Therefore, it is critical to minimize the time it is exposed to open air. Have the vial tared beforehand, and weigh and transfer the material as quickly as possible.)
3. To the chilled reaction mixture, add the aluminum chloride in 3 portions, (This keeps the reaction from becoming too vigorous.) Upon each addition, recap the flask, and stir the mixture for 5 minutes until the reaction subsides. At the end of each 5-minute period, a white product should be visible.
4. After the aluminum chloride addition is complete, remove the reaction flask from the ice bath and allow it to warm to room temperature.

5. To the reaction mixture add 1 mL of ice-cold water (from the bath) and 2 mL of diethyl ether. Gently swirl the contents and separate the ether layer.
6. Extract the aqueous layer with two 1 mL portions of additional ether.
7. Dry the combined ether layers using anhydrous drying agent, filter the dried organic layer, and evaporate the solvent to obtain the product.
8. Measure the mass, the melting point, and obtain the IR spectrum of the product.

For your report:

1. Calculate the % Yield.
2. Predict the $^1\text{H-NMR}$ spectrum for the product.
3. Explain why this product is para-, not ortho-? Also, why is it not meta-?
4. Explain why there is no rearrangement of the t-butyl group.
5. Explain why there is no dialkylation.

Needed per student:

t-butyl chloride (1.0 mL)
t-butylbenzene (0.5 mL)
anhydrous aluminum chloride (0.05 g)
diethyl ether (3 mL)
magnesium sulfate