Although the aromatic ring is a π-system, its chemistry is quite different from that of a simple double or triple bond. Alkenes and alkynes undergo addition to the multiple bond when treated with most electrophilic reagents. Typical reactions include addition of HX (X = halogen), addition of X₂ (X = Cl or Br), acid-catalyzed addition of H₂O, hydroboration, etc. The process is usually exothermic since π-electrons become lower energy σ-electrons when the multiple bond is destroyed. However, the 6 π-electron system in an aromatic ring enjoys a special stability that makes addition reactions to the ring very difficult. Instead, the aromatic ring prefers to undergo substitution during which a hydrogen atom on the ring is replaced by another group thus preserving the aromatic nucleus in the product. The scope of this class of reaction is very broad. Although a wide range of electrophilic species and a variety of aromatic substrates are available, all of these reactions can be explained by a common mechanism shown at the top of Scheme 1. In the first step, the electrophile attacks the
electro-rich aromatic ring to generate a π-complex that collapses rapidly to the σ-complex. The σ-complex is a stabilized ( conjugated) carboxation that loses a proton (deprotonation) in the last step to restore the aromaticity in the final product.

If X = H in this equation, then the substrate is benzene and the product is a monosubstituted aromatic ring. However, if X is a substituent group on the aromatic substrate, then the product is a disubstituted benzene ring. Thus, there are three possible isomeric products from the reaction as shown by the green, red, and blue structures at the bottom of Scheme 1. These products arise from three different positions of attack by the electrophile on the aromatic ring. The route leading to the green product (1,2-disubstituted or ortho isomer) involves a σ-complex formed by electrophilic attack at either carbon 2 or carbon 6 of the substrate. The blue product (1,3-disubstituted or meta isomer) is formed by electrophilic attack at either carbon 3 or carbon 5 of the substrate; and the red product (1,4-disubstituted or para isomer) is the result of electrophilic attack at carbon 4. The group X on the substrate determines which isomer(s) will be produced as the major product(s) in the reaction. For example, if X is an electron-donating group, this can result in extra stabilization of the carboxation leading to formation of both the ortho and the para products ( i.e. , X is an ortho/ para director) . On the other hand, if X is an electron-withdrawing group, this can ( but not always) destabilize the cation leading to the ortho and para products and cause the meta isomer to the major product. These groups are called meta directors.

The electronic nature of the group X also has a dramatic impact on the reactivity of the ring. If X is electron withdrawing ( -NO₂, -CN, -SO₃H, carbonyl functions, etc.), the substrate becomes less reactive than benzene toward substitution. If X is electron donating ( alkyl, -OH, OCH₃, -NH₂, etc.), the substrate is more reactive than benzene.

The most common electrophiles for electrophilic aromatic substitution include carboxations, nitronium ( +NO₂), halonium ( C¹, Br¹), +SO₃H and acylum. Specific sets of reagents are used in the generation of each of these electrophiles. For example, carboxations can be produced by at least three familiar pathways. If a solution of isobutylene gas dissolved in benzene is treated with a very strong mineral acid such as sulfuric acid, the protonation of isobutylene gives the t-butyl carbocation.

This cation attacks the benzene ring and gives t-butylbenzene as the product. The famous Friedel-Crafts reaction uses t-butyl chloride and AlCl₃ to generate the same carbocation. Finally, t-butyl
alcohol with a strong acid is also a source of t-butyl carbocation via protonation of the oxygen and loss of water.

**PROBLEM SET – Electrophilic Aromatic Substitution**

1. What is the role of acetic acid in the electrophilic aromatic substitution reaction you did in the laboratory?

2. What is the structure of the most likely product from the reaction of methoxybenzene with an excess of t-butyl alcohol under the same conditions you used in the laboratory? What other products did you discount and why?

3. In the electrophilic aromatic substitution reaction you did in the laboratory, the substitution of the second t-butyl group on the ring is faster than the first substitution. Explain why this is true.