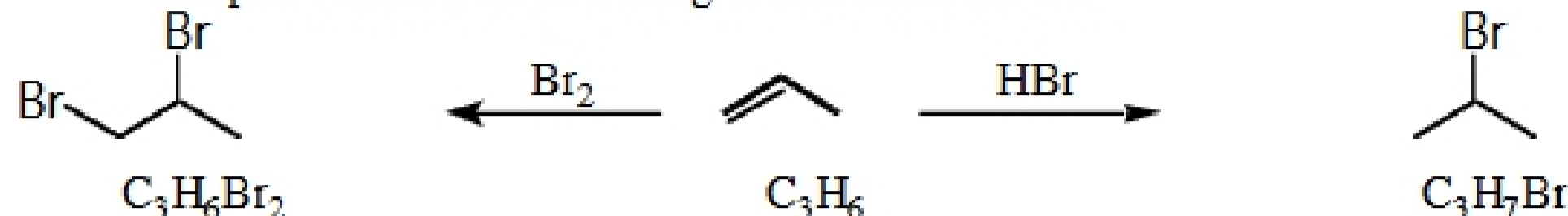


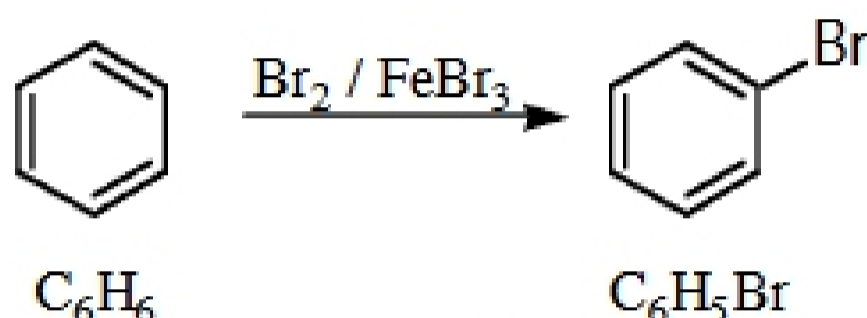
## Reactions of Aromatic Compounds

Simple alkenes tend to undergo addition reactions:



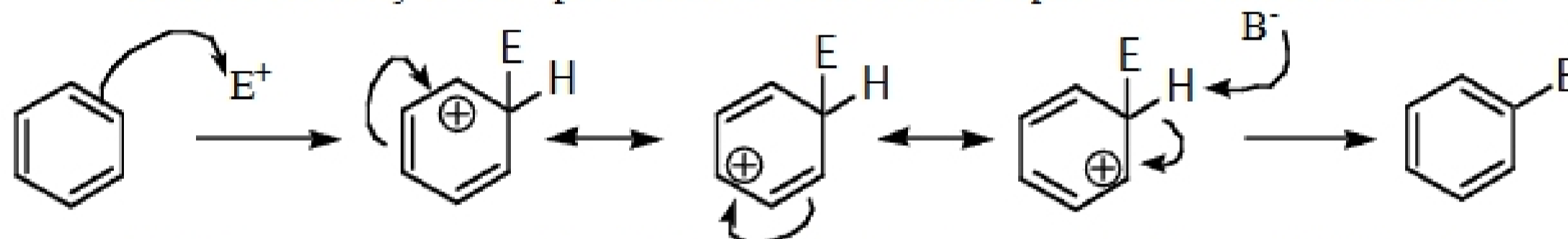
The elements of the reagent (HBr or Br<sub>2</sub>) are simply added to the starting material. This is called, unsurprisingly, and *addition* reaction.

Aromatic compounds do not react in this manner. A look at a simple aromatic bromination:



What we have done in this case is *substitute* a bromine for a hydrogen. Hence the term “aromatic substitution.” Because the benzene ring is quite electron-rich, it almost always behaves as the nucleophile in a reaction - which means that the substitution on benzene occurs by the addition of an electrophile -> electrophilic aromatic substitution.

There is basically one simple mechanism for all electrophilic aromatic substitutions:



The benzene acts as a nucleophile, attacking the electrophile with a pair of its  $\pi$ -electrons. This initial step destroys the aromaticity of the molecule! The resulting positive charge is delocalized over the *ortho* and *para* positions. The conjugate base of the initial electrophile then assists in removing the now-extraneous proton, and restores aromaticity. Because all electrophilic aromatic substitutions proceed in this way, the only thing that matters is the preparation of a “hot” electrophile.

Why a “hot” electrophile? As you can see, the first step of the reaction involves destroying aromaticity. In order to do this, there must be a significant energetic driving force. This driving force comes in the form of a very reactive (unhappy) electrophile.

How are such electrophiles generated?

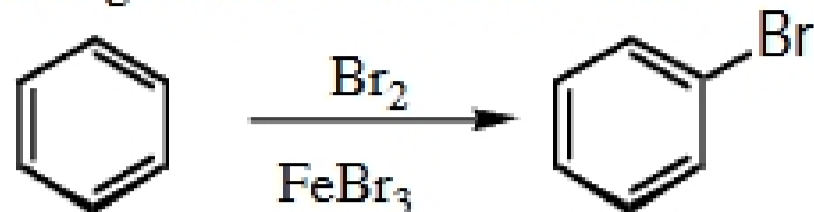
### Halogenation

As you can imagine, halogens bearing a positive charge are particularly reactive. I will focus on preparing halogen electrophiles from Br, Cl and I.

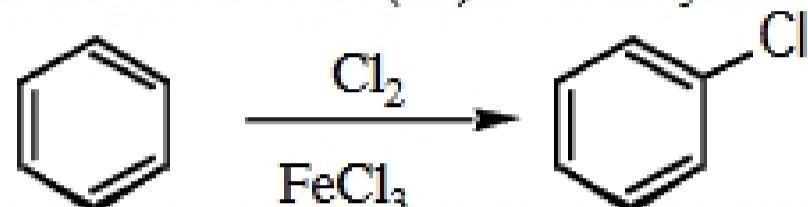
Bromine: Allowing bromine to react with iron metal first generates FeBr<sub>3</sub>, which then interacts with the remaining Br<sub>2</sub> to form a highly polarized system:



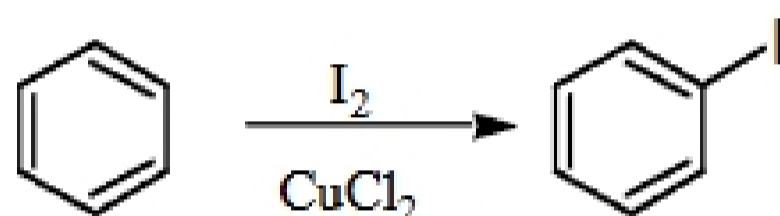
It is this highly polarized bromine that becomes a source of "Br<sup>+</sup>." The reaction proceeds by the mechanism shown above to give brominated benzene:



Chlorine: The same chemistry shown for bromine also works with chlorine to generate "Cl<sup>+</sup>." A mixture of benzene, chlorine and iron(III)chloride yields the chlorobenzene:

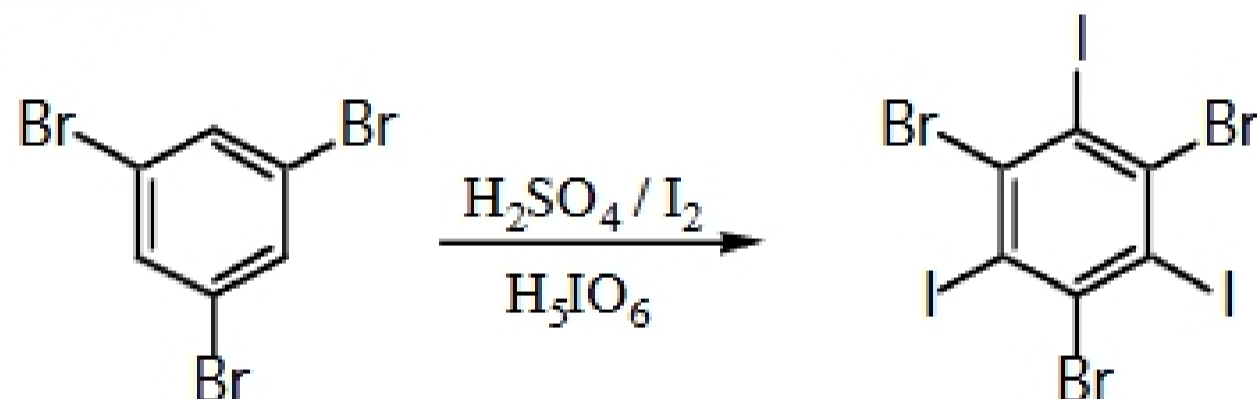


Iodine: It is a little more difficult to make iodine sufficiently electrophilic. For relatively activated compounds, where a mild source of "I<sup>+</sup>" is required, copper salts are often used as a catalyst:



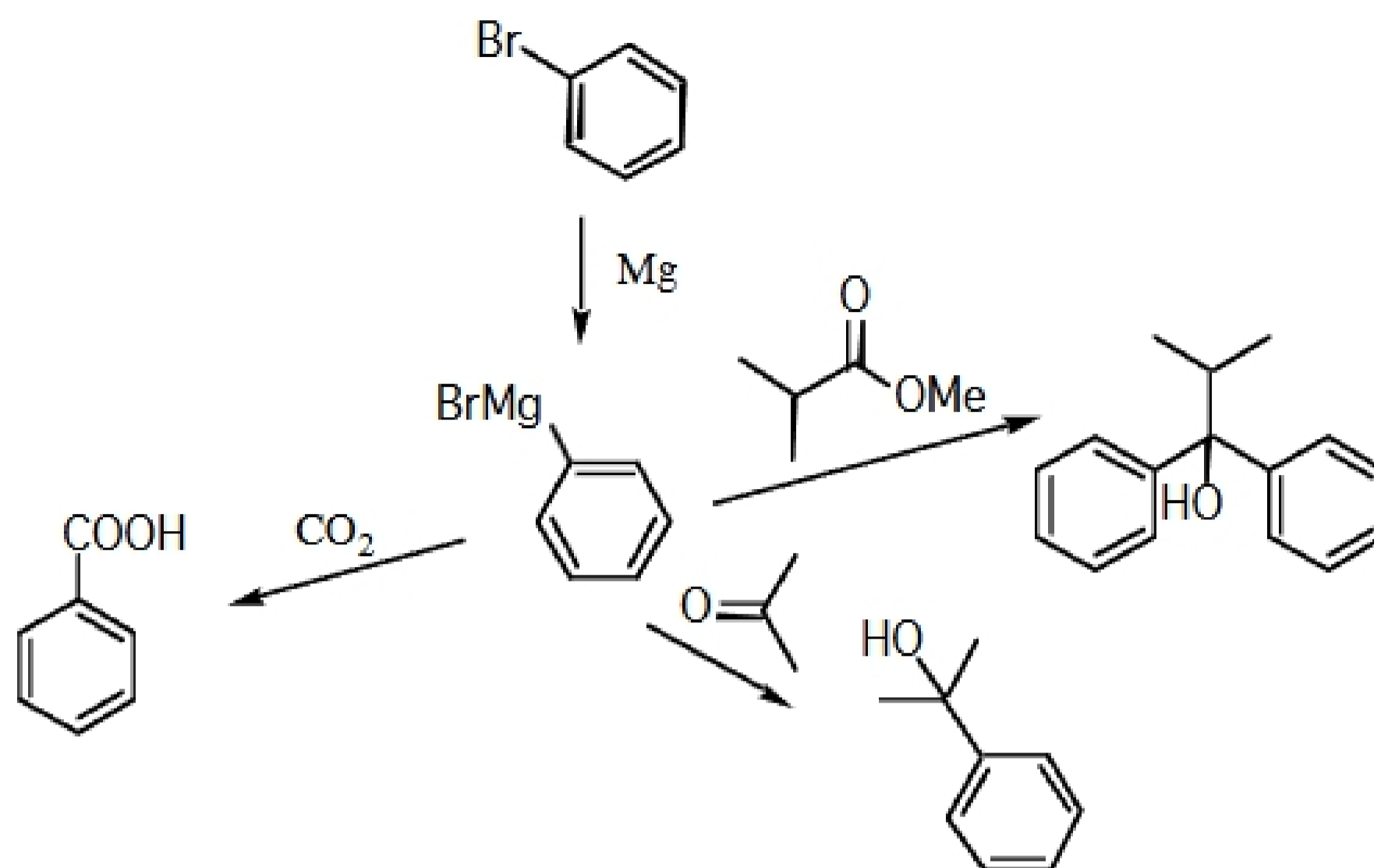
Reaction then proceeds by the standard mechanism, with I<sup>+</sup> as the electrophile, to give iodinated benzenes.

For more de-activated systems, or when more than one iodine needs to be added to the ring, a harsher reagent exists:



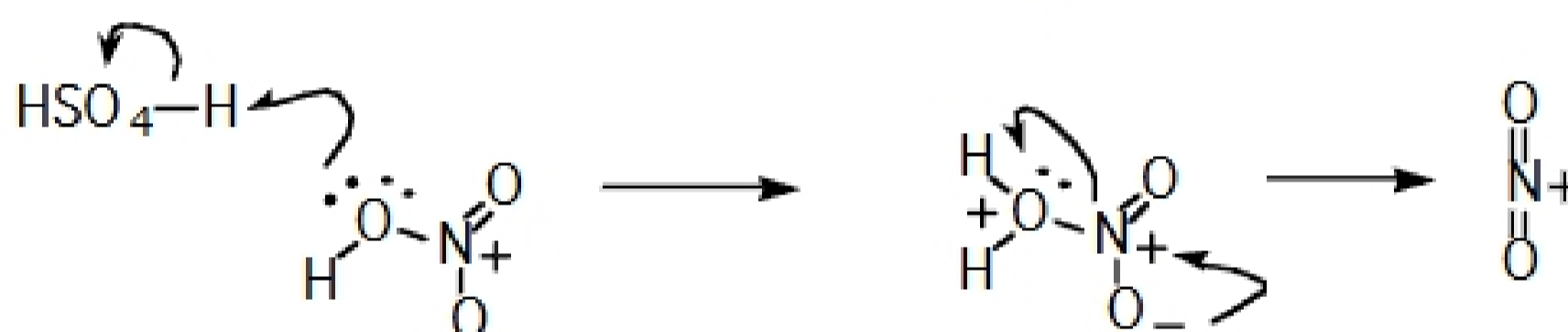
### Why?

You should always ask this question. What good are aromatic halides? The halogens are excellent synthetic "handles" – they can be easily converted into other functional groups. For example, bromobenzenes can be turned into Grignard reagents, and the reacted with aldehydes, ketones, etc....

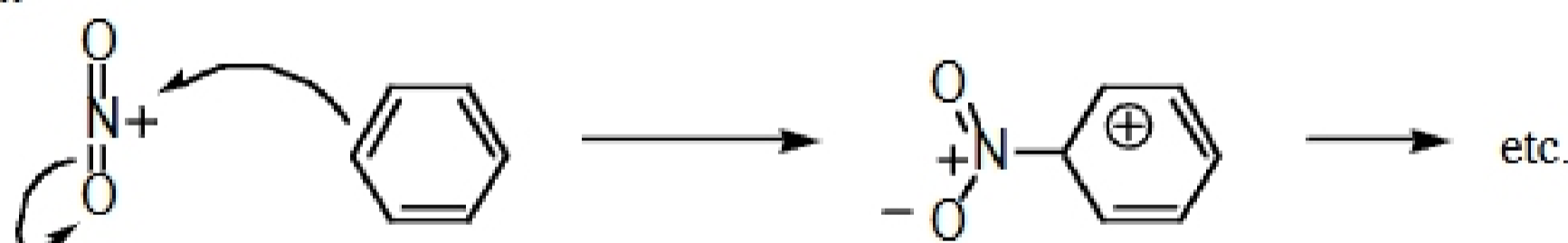


## NITRATION

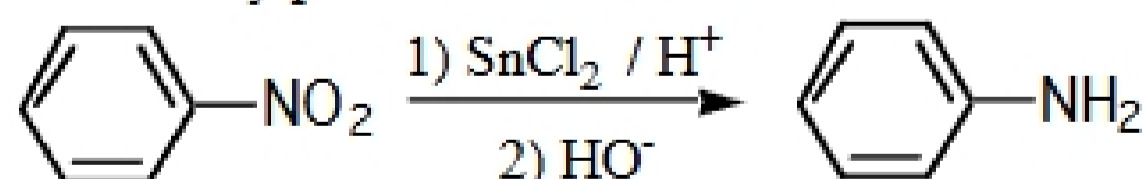
We can also make a highly electrophilic form of  $\text{NO}_2$ :



Which can then react with aromatic compounds via the standard mechanism to give nitrated aromatics...



**Why?** There are a couple of good reasons to nitrate things. The first is in the manufacture of explosives – highly nitrated organic molecules are frequently used as explosives (trinitrotoluene (TNT), nitroglycerine, etc.). The second reason is that nitro-groups are generally easy to reduce to amines. And since it is nearly impossible to make an amine electrophilic (in order to add it to an aromatic ring under electrophilic aromatic substitution conditions), aromatic nitro compounds are about the only precursors to aromatic amines:



## Sulfonation

Just as with nitration, it is easy to make a solution of highly electrophilic  $\text{SO}_3$ . This solution can be used to sulfonate aromatic compounds: