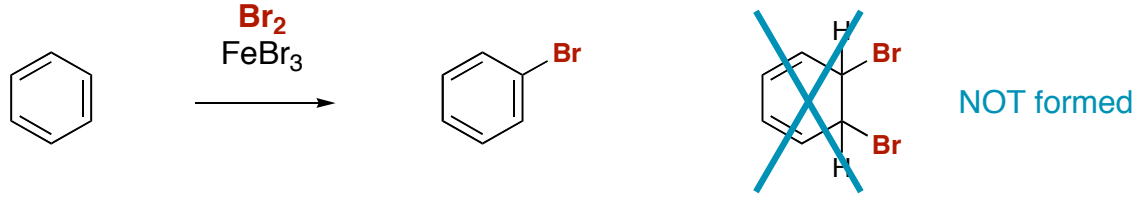
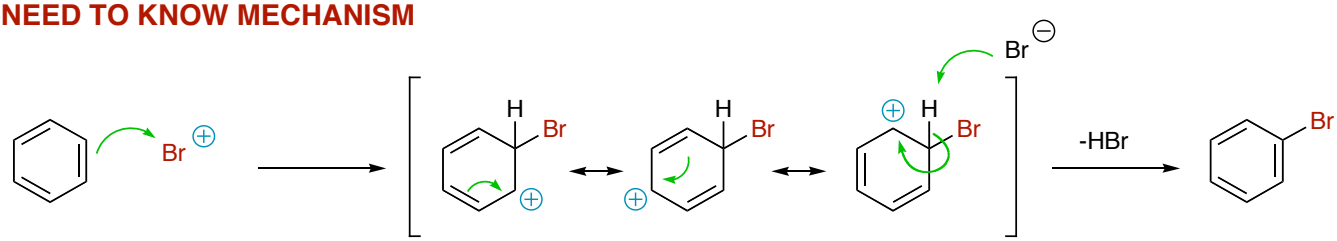
Chapter 16 - Chemistry of Benzene: Electrophilic Aromatic Substitution

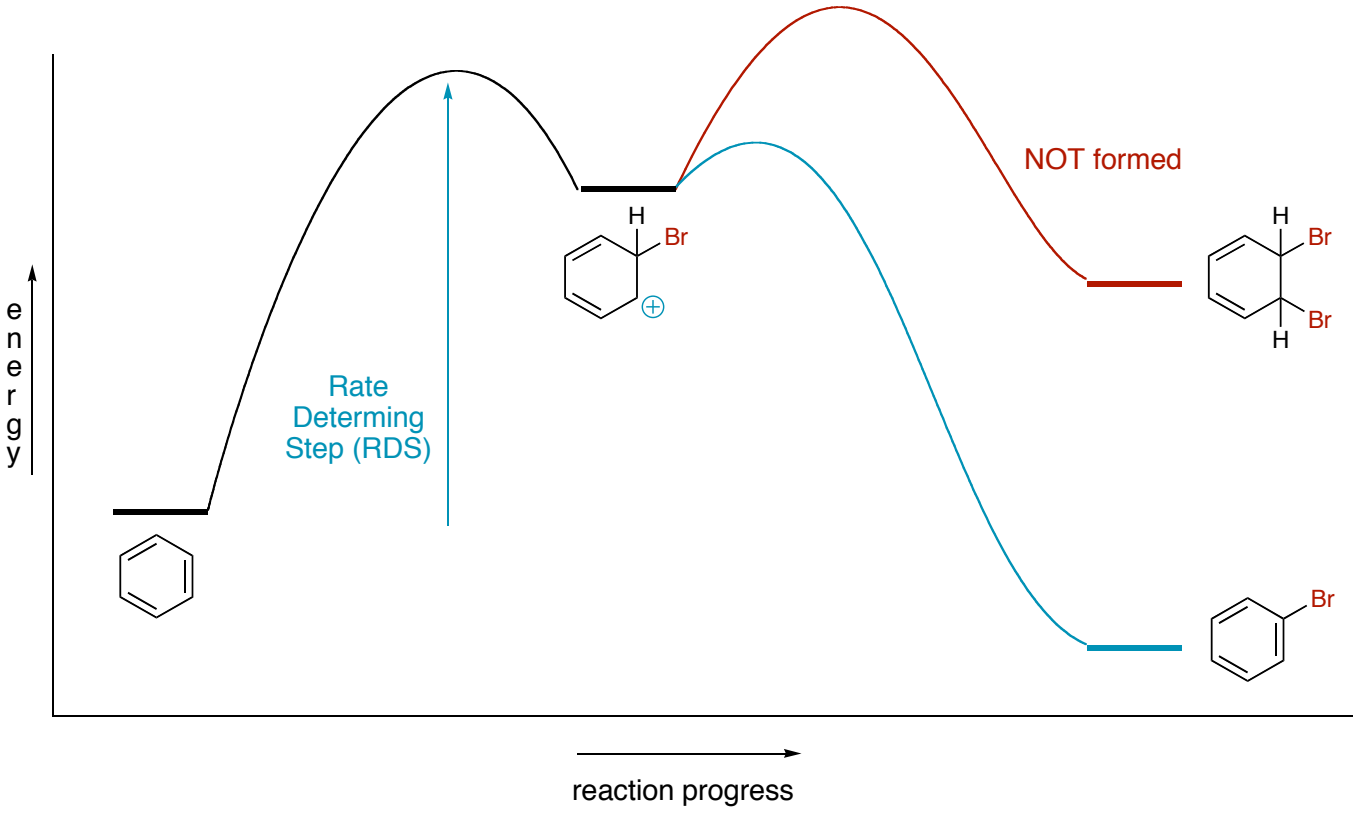
A stepwise mechanism

Aromatic rings do not react with electrophiles like typical double bonds. Although the first step is very similar, the second step is very different. An electrophile will add to form an intermediate carbocation (of which you can draw a number of resonance structures). Instead of a nucleophile adding to the carbocation, the intermediate will deprotonate to regenerate the stable aromatic ring. This is a much lower energy pathway than the addition product.

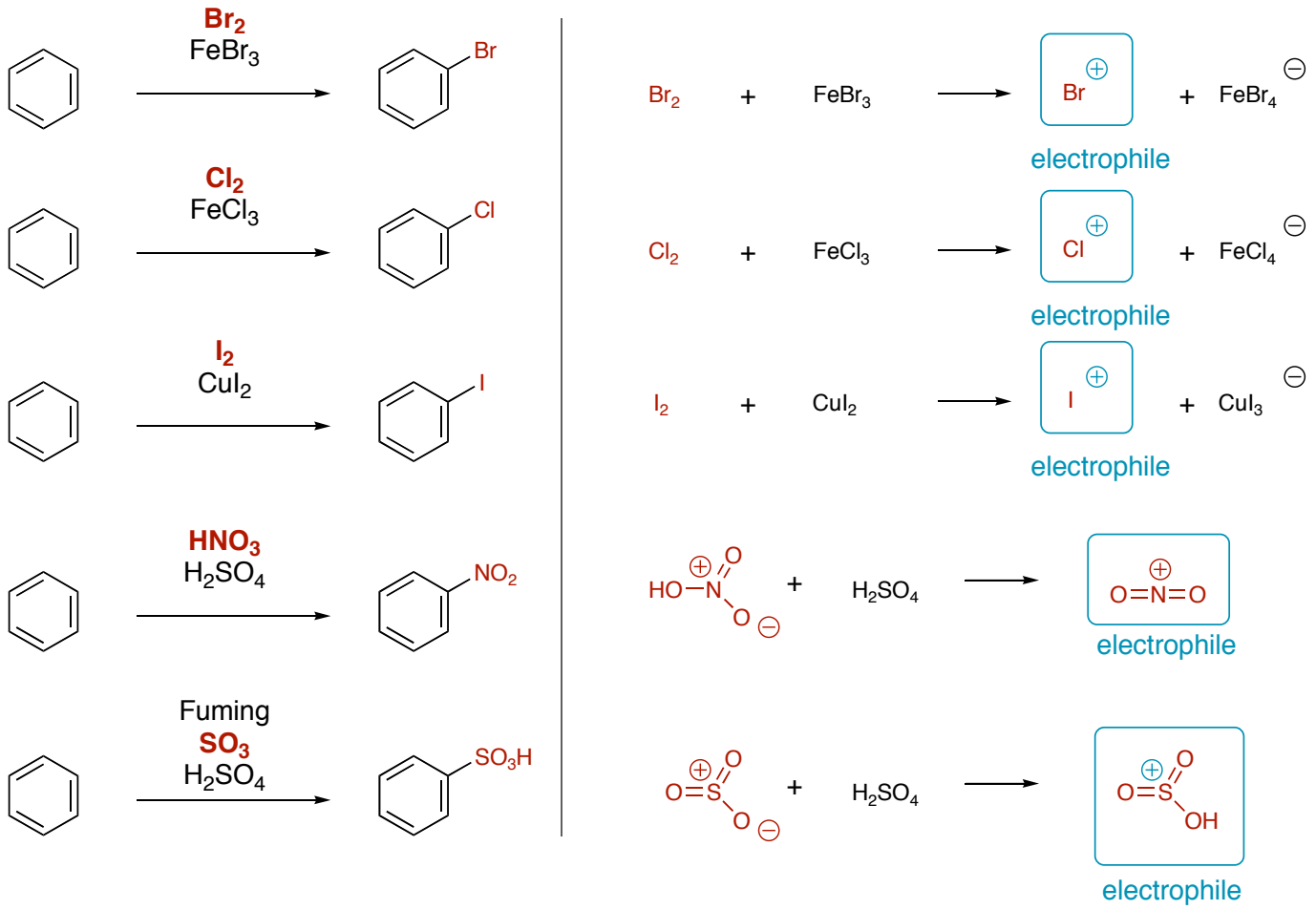


NEED TO KNOW MECHANISM



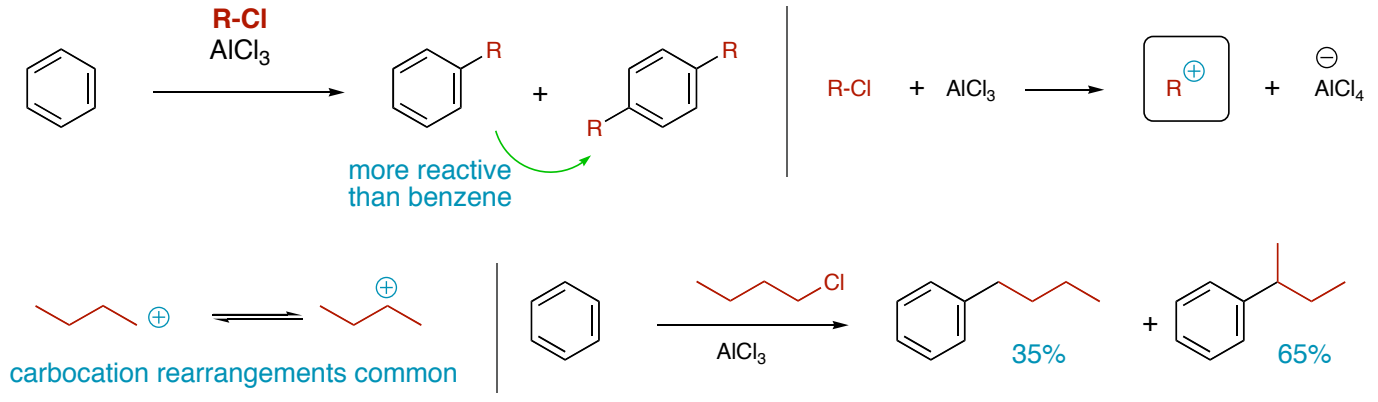


Electrophilic substitution will occur with many reactive electrophiles. Here is a list of some of the more common reagents for electrophilic aromatic substitution.



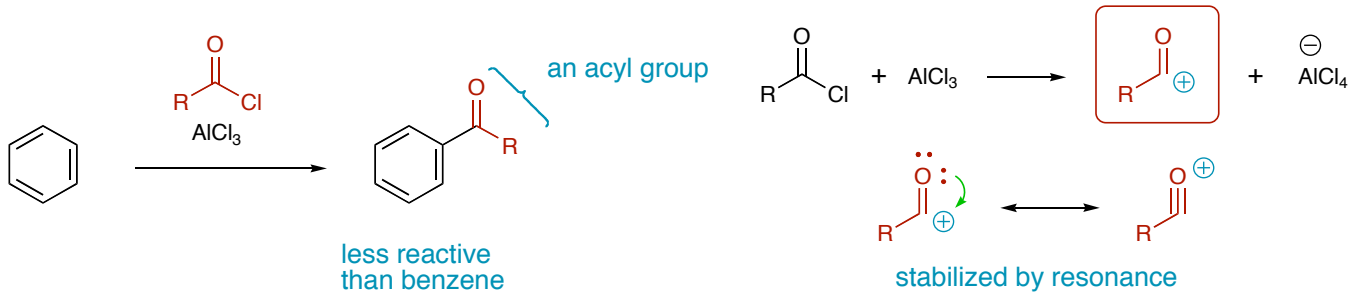
Friedel-Crafts Alkylation

Alkyl halides can be used to generate carbocations which will do substitution. There are two problems with this alkyation reaction. The products are more reactive than the starting material because alkyl groups are electron donating to the ring, so over reaction is common. Also, if possible, carbocations can undergo rearrangements affording a mixture of isomers in the products.



Friedel-Crafts Acylation

The reaction with acid chlorides solves both of the problems associated with alkylation reactions. The reactive acyl electrophile does not undergo rearrangements since it is the most stable cation, and the product is less reactive than benzene due to the electron withdrawing nature of the ketone. Thus, adding a second electrophile can be avoided.



Some notes about electrophilic aromatic substitution

Two step mechanism - E^+ addition followed by H^+ elimination

Reaction requires generation of very reactive electrophiles with strong Brønsted or Lewis acids.

X, NO_2. SO_3H, R, RCO can all be added to a benzene ring

OH and NH_2 cannot be directly added to a benzene ring

F-C Alkylation suffers from carbocation rearrangements and more than one addition

F-C Acylation solves the problems of the alkylation reaciton