

Electrophilic Attack On Benzene

from chapter(s) _____ in the recommended text

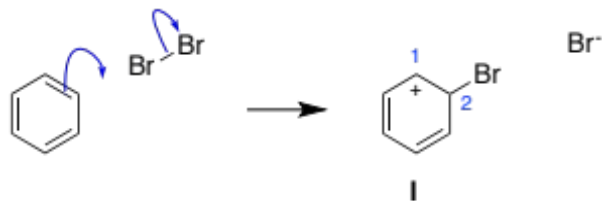
A. Introduction

B. Electrophilic Bromination Of Alkenes And Benzene Compared

First Step: Approach Of Electrophile

There *is not* a difference in the way electrons in Br_2 distribute when bromine approaches. This is called *polarization*.

Electrons *do* distribute in a similar way when bromine approaches benzene.



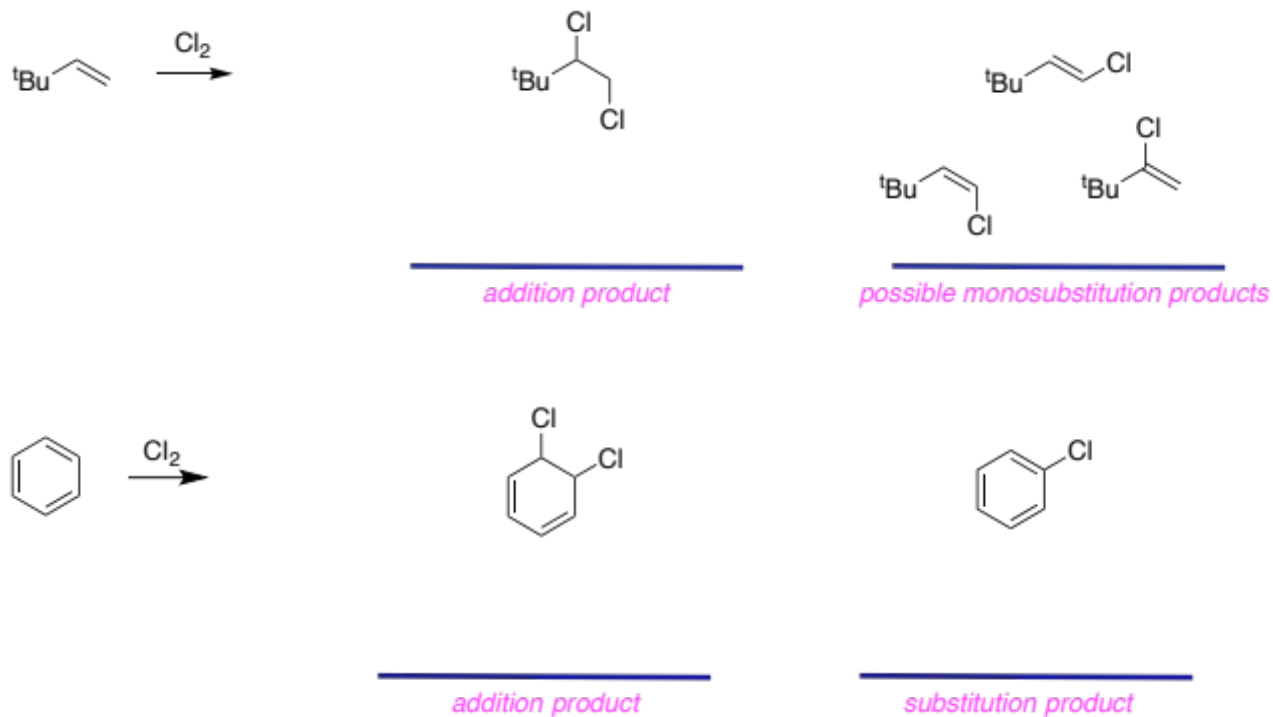
In the cationic intermediate I, there is **1** hydrogen atom on C^1 and **1** on C^2 .

Attack of bromine on ethene is *faster* than on benzene because for benzene *aromatic* stabilization is lost.

Second Step: Loss Of Positive Charge

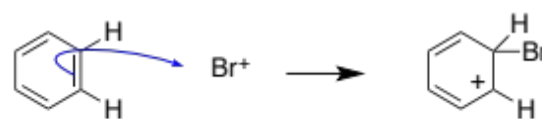
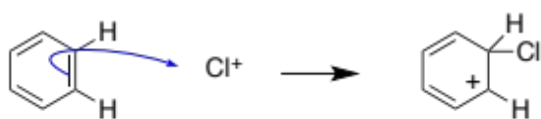
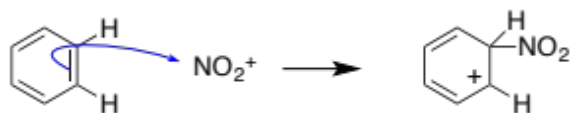
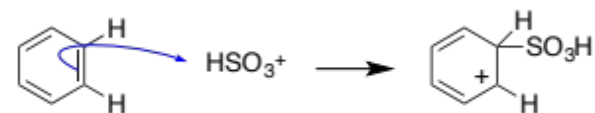
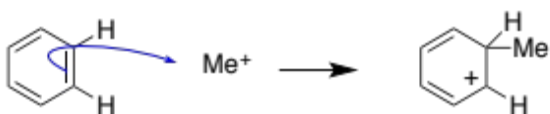
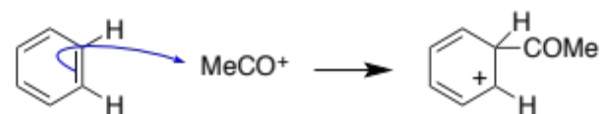
The second step in the reaction of bromine with benzene is loss of a *proton*.
 proceed differently because only benzene can regain *aromatic* stabilization in that second step.





The simplest electrophile to substitute H is a deuteron D⁺ (a *heavier* isotope of a proton). Electrophilic attack of a deuteron on benzene is *the same as* nucleophilic attack of benzene -electrons of benzene because it is electrostatically *attracted to*

The cationic *intermediate* formed in the step above is *non-aromatic*. Benzene *loses* aromatic stabilization when the deuteron adds, so this process is relatively *slow*.

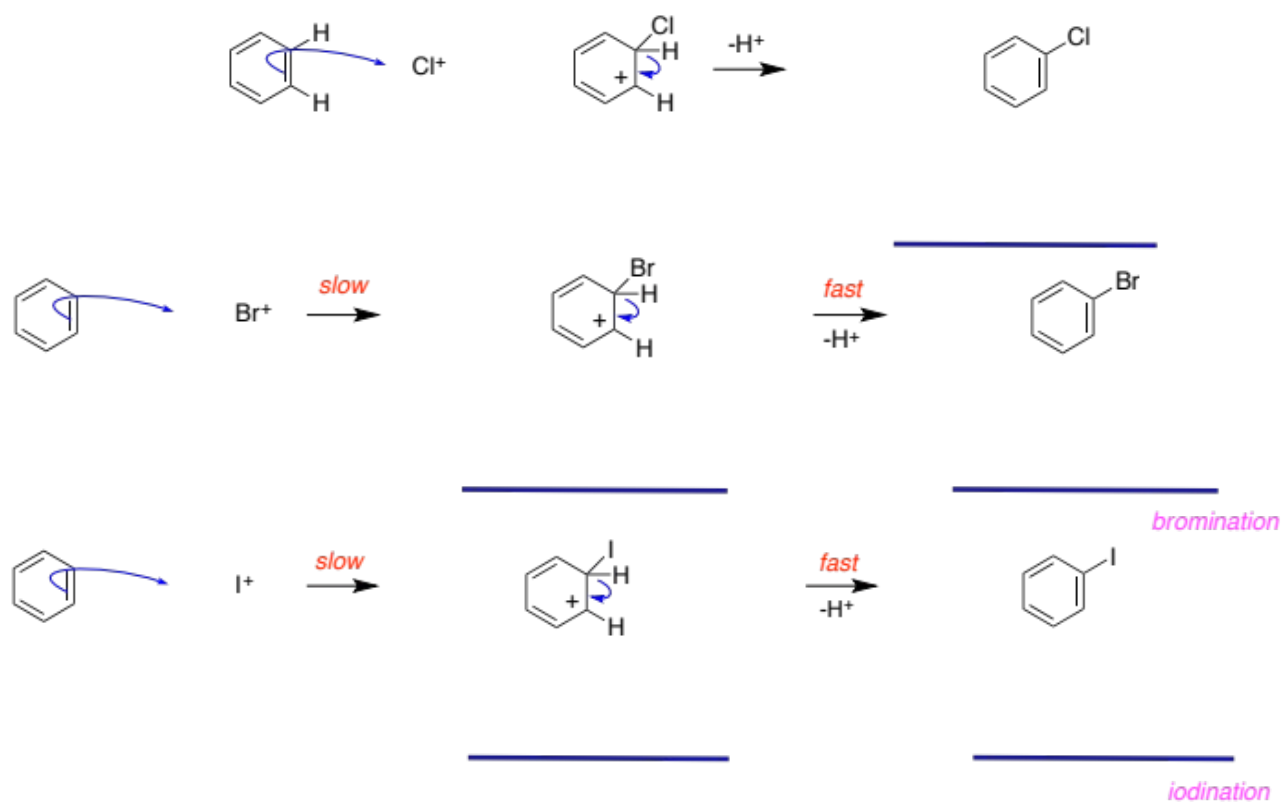
*Cl⁺**Br⁺**a nitronium ion, NO₂⁺**a sulfonium ion, HSO₃⁺**a methyl carbocation, Me⁺**an acylium ion, MeCO⁺*

Deuteron loss reforms benzene, hence addition of a deuteron to benzene is *reversible*.

C. Halogenation Of Benzene

Chlorine, bromine, and iodine are *insufficiently* electrophilic to react with benzene, but the X-X molecules can be polarized by a Lewis *acid* so that one atom has enhanced electrophilicity.

Iron tribromide and aluminum tribromides are Lewis *acid*.

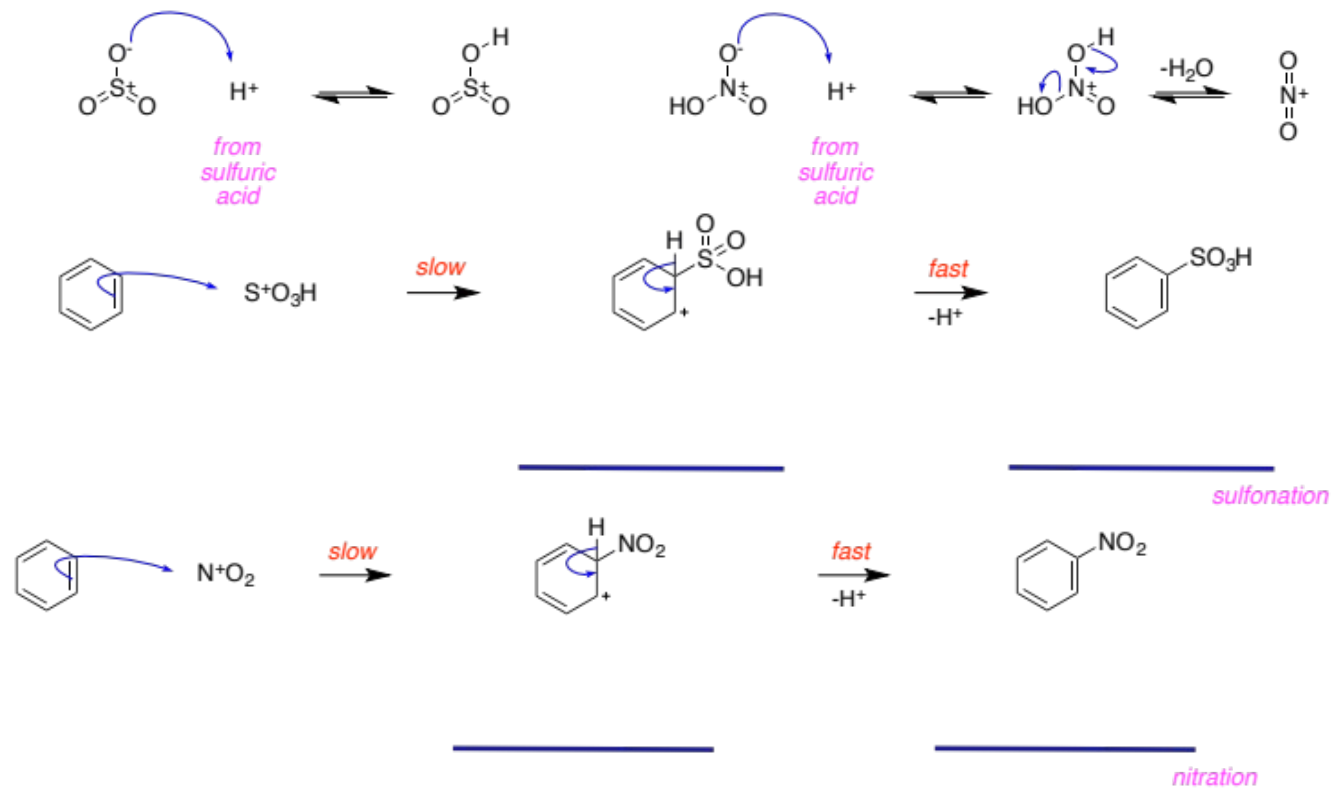


D. Sulfonation And Nitration Of Benzene

Sulfonium ions are formed by protonating sulfur trioxide; it takes *strong* acid, sulfuric

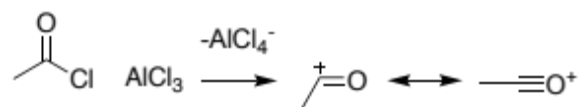
Solutions of SO_3 in sulfuric acid are called *fuming* acid or *oleum*.

Nitronium ions are made by *protonating* nitric acid with sulfuric acid, then loss of water.

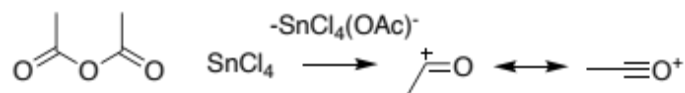


E. Acylation Of Benzene (Friedel-Crafts)

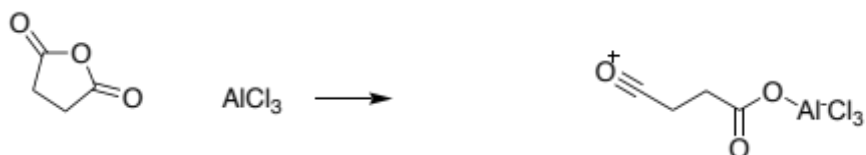
Electrophilic acylation reactions rely on generating *acylium ions*.



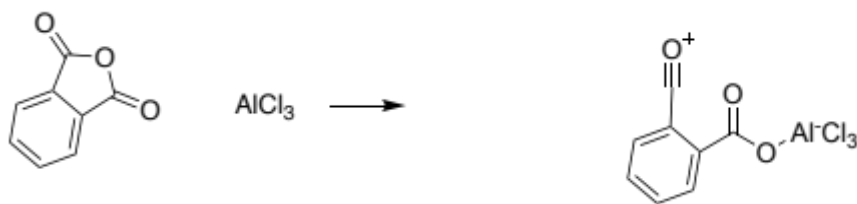
acylium



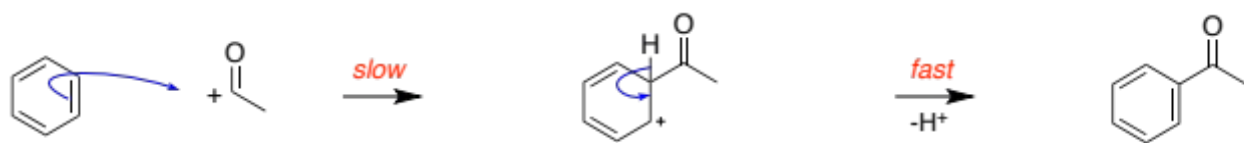
acylium



acylium



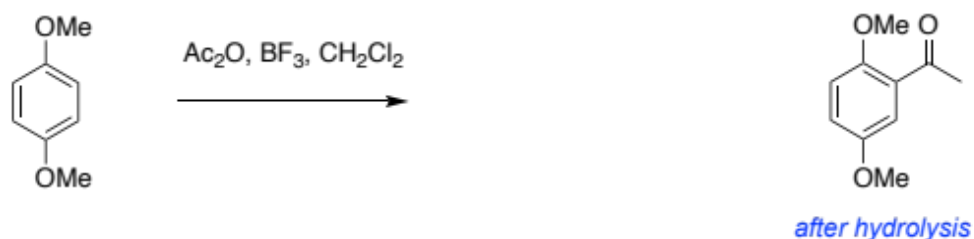
acylium



Products of electrophilic acylation reactions are *ketones*.

These products have *less* electron rich aromatic rings than the starting materials, and this explains why they *do not* tend to react with another acylium ion





It is conventional to show the products after hydrolysis.

In the last example, the carbon atoms on the aromatic ring that could react are all *equivalent*.

F. Alkylation (Friedel-Crafts)

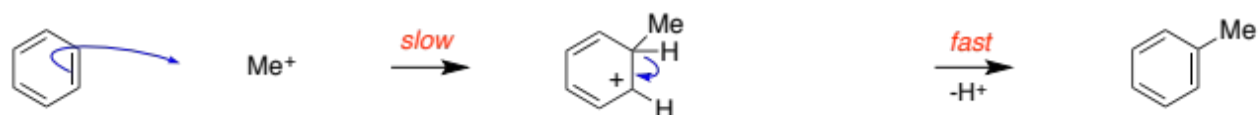
Electrophilic alkylation reactions proceed via *carbocations*.

Lewis *acids* combine with alkyl halides to give these reactive intermediates.



This mode of generation is most useful when the reactive intermediates *do not* rearrange before

simple symmetrical allyl, carbocations tend *not to be* vulnerable to rearrangement reactions, so rearrangement *is not* a concern



Products of electrophilic alkylation reactions are *alkylbenzenes*, these are *more* electron rich than the starting materials, hence *do* tend to add a second reactive intermediate; Friedel-Crafts alkylation reactions *are* therefore prone to deliver more than one alkyl group

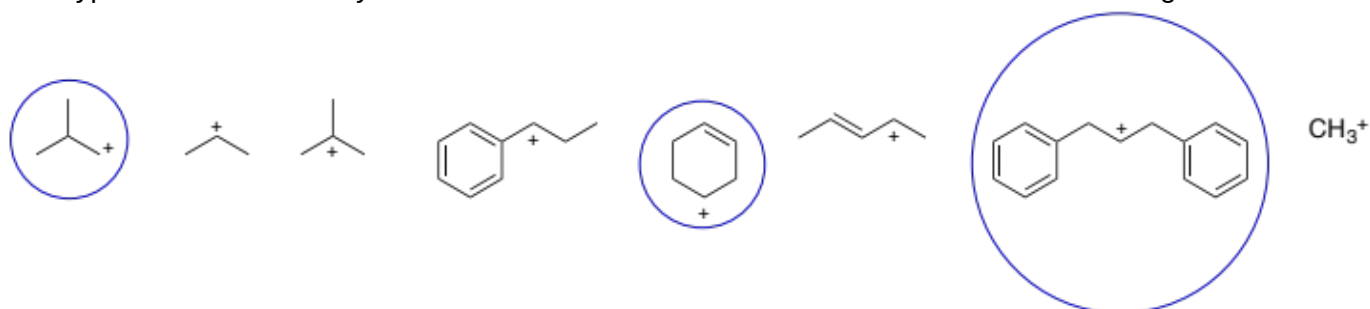
Carbocation Rearrangements Revisited

so this process can be referred to as a *hydride* shift.





This type of reaction is likely to occur if the carbocation formed is *more* stable than the original one.



hence carbocation stabilities *decrease* from tertiary, through secondary, to primary.

