The Golden Rules of Organic Chemistry

Your goal should be to understand, not memorize, the material presented in your organic chemistry course. The following principles should be learned as you begin your study of organic chemistry, then used as a solid foundation for building your understanding throughout the course. These simple ideas explain a great deal about the structures and properties of organic molecules, as well as the characteristic ways in which they react. Thoroughly understanding the following three key principles and related ideas will allow you to develop an intuitive feel for organic chemistry that avoids the necessity of resorting to the far less effective use of extensive memorization.

A. Predicting Structure and Bonding

1. In most stable molecules, all the atoms will have filled valence shells.

2. Five- and six-membered rings are the most stable.

3. There are two possible arrangements of four different groups around a tetrahedral atom.

B. Predicting Stability and Properties

4. The most important question in organic chemistry is "Where are the electrons?"

5. Delocalization of charge over a larger area is stabilizing.

6. Delocalization of unpaired electron density over a larger area is stabilizing.

7. Delocalization of pi electron density over a larger area is stabilizing.

C. Predicting Reactions

8. Reactions will occur if the products are more stable than the reactants and the energy barrier is low enough.

9. Functional groups react the same in different molecules.

10. A reaction mechanism describes the sequence of steps occurring during a reaction.

11. Most bond-making steps in reaction mechanisms involve nucleophiles reacting with electrophiles.

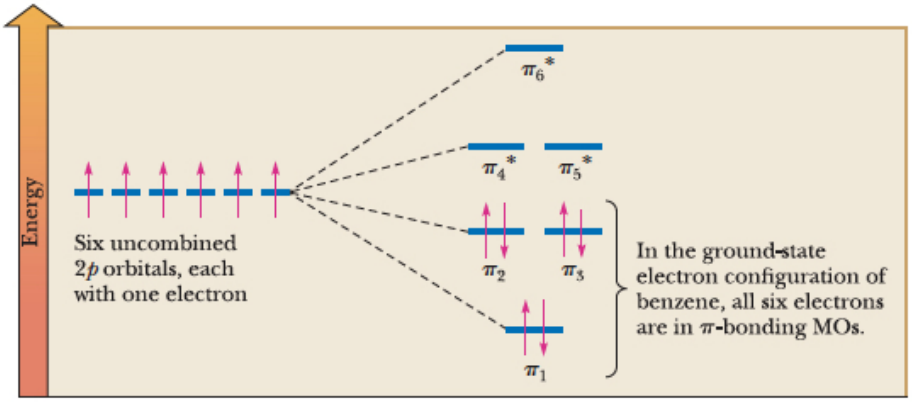


FIGURE 21.2 The molecular orbital representation of the π bonding in benzene.

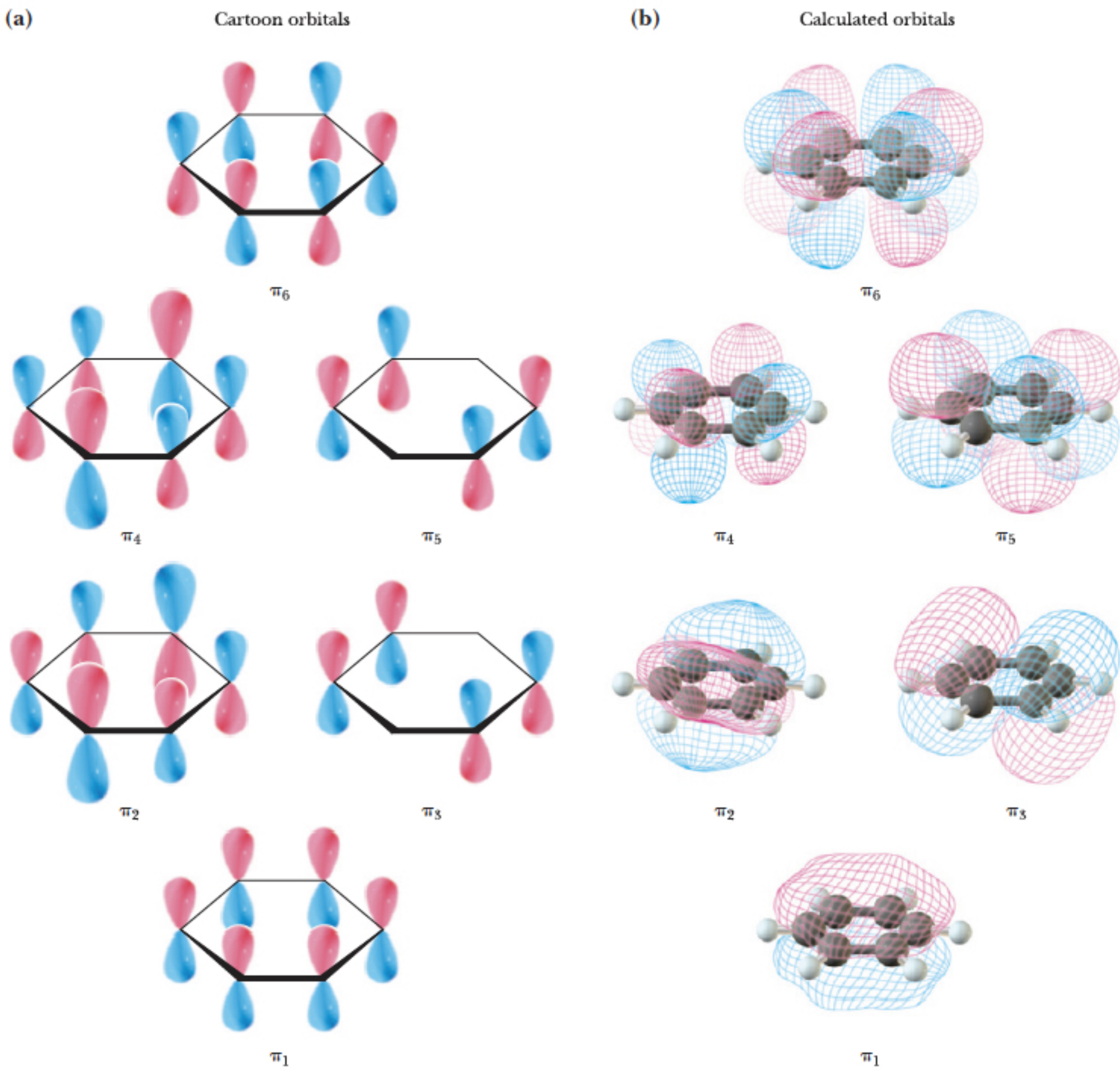


FIGURE 21.3 Orbitals for the π system of benzene. (a) Cartoon representations of the six calculated orbitals that chemists routinely draw. These pictures accentuate the fact that various combinations of parallel $2p$ orbitals lead to the π system of benzene. (b) Calculated orbitals. The three lowest in energy are occupied with electrons (see Figure 21.2). The lowest of these orbitals is the image most chemists use for the π system of benzene: a torus of electron density above and below the ring.

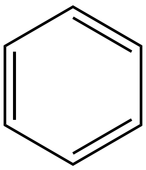
Hückel’s Aromaticity Criteria

1)

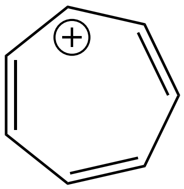
2)

3)

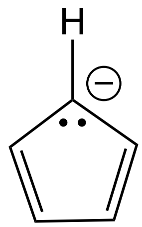
4)



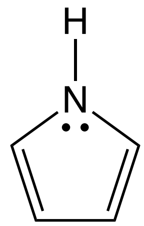
Benzene



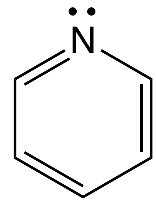
Tropylium Ion



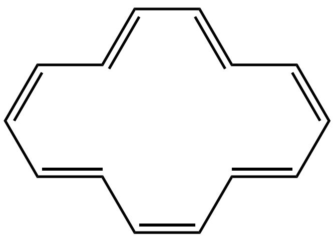
Cyclopentadienyl anion



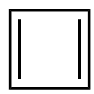
Pyrrole



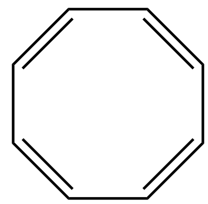
Pyridine



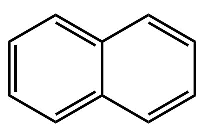
Annulene



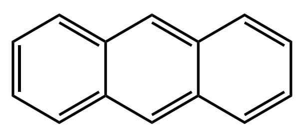
Cyclobutadiene



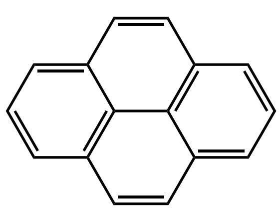
Cyclooctatetraene



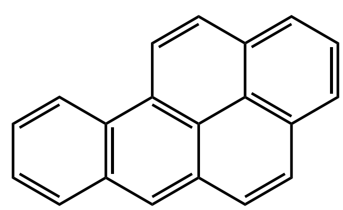
Naphtalene



Anthracene

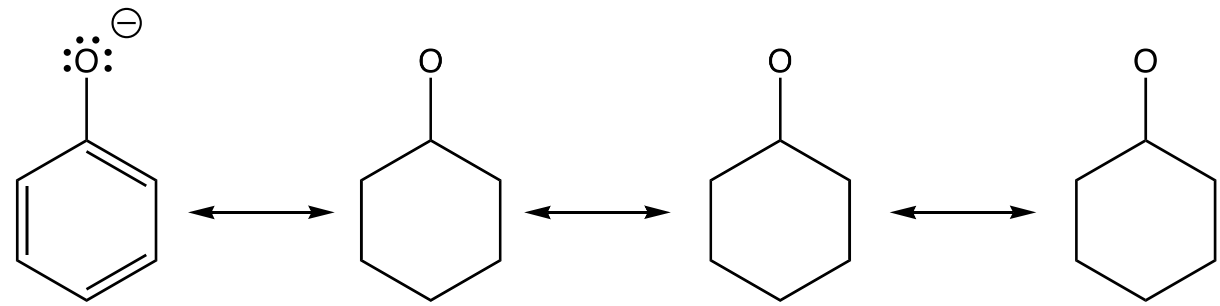


Pyrene

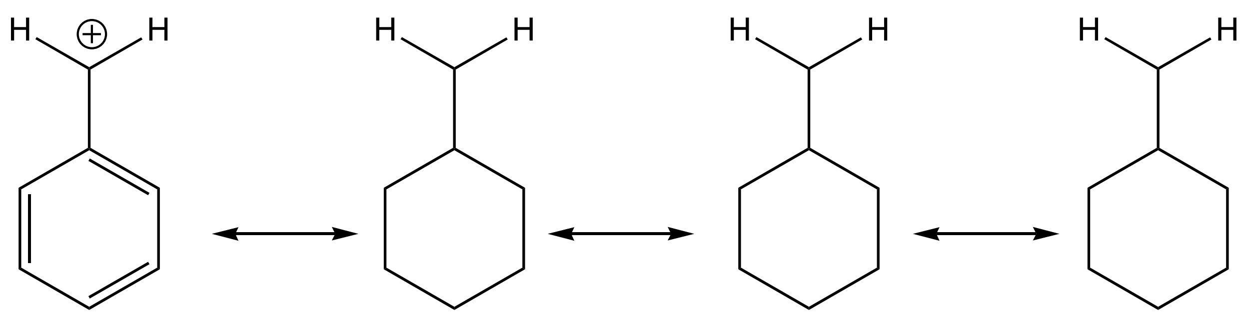


Benzo[α]pyrene

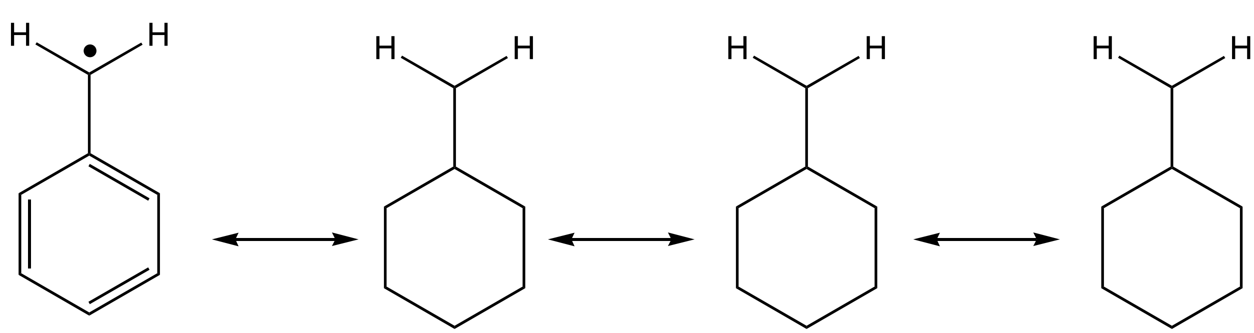
Aromatic resonance stabilization of charged species



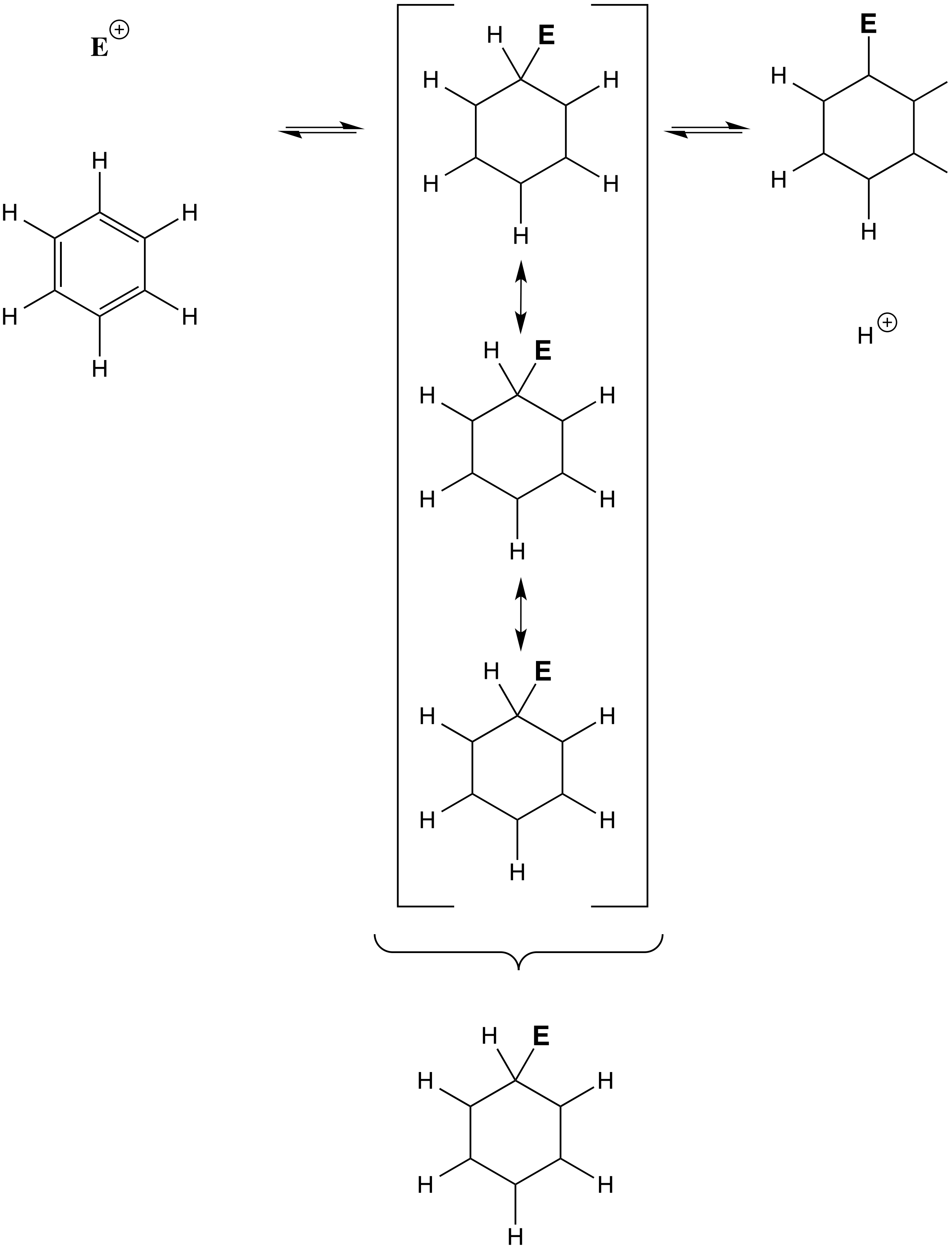
Phenoxide anion



Benzyl cation



Benzyl radical

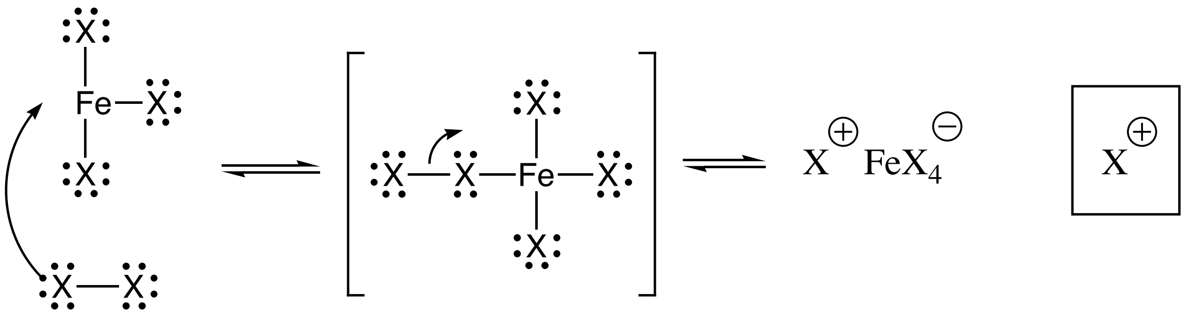


Reagents

Wicked strong electrophile

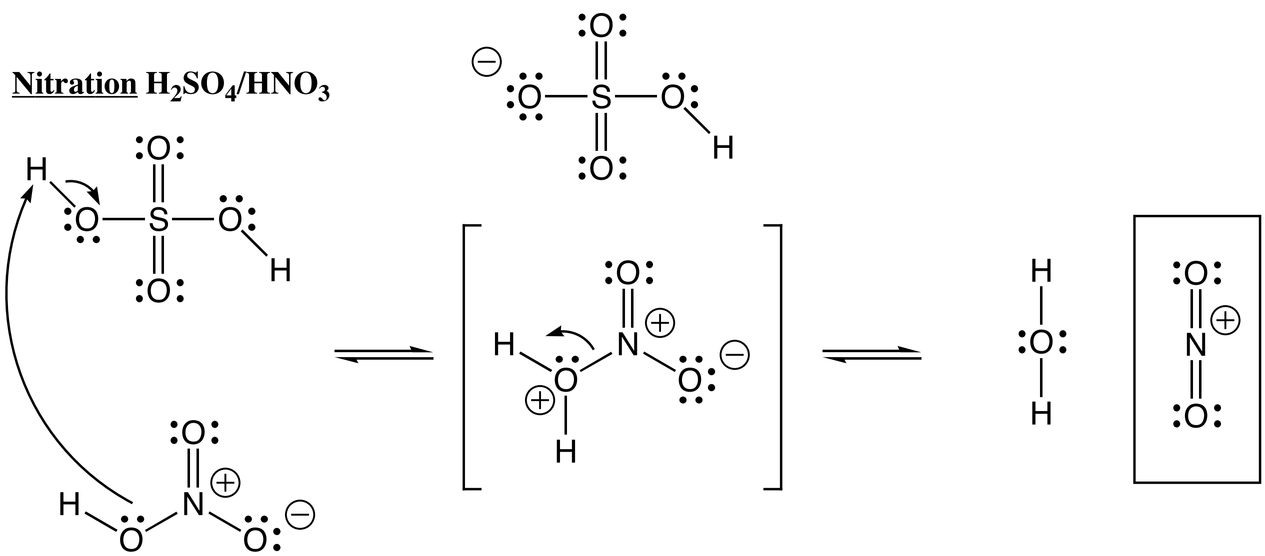
$E^{\oplus}$

Halogenation X_2, FeX_3

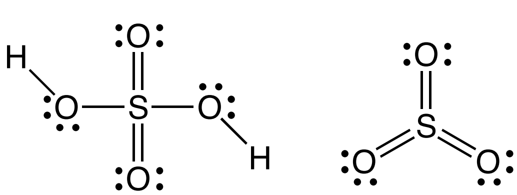


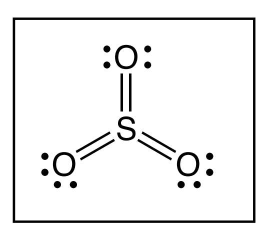
X = Br, Cl

Nitration H_2SO_4/HNO_3



Sulfonation H_2SO_4/SO_3





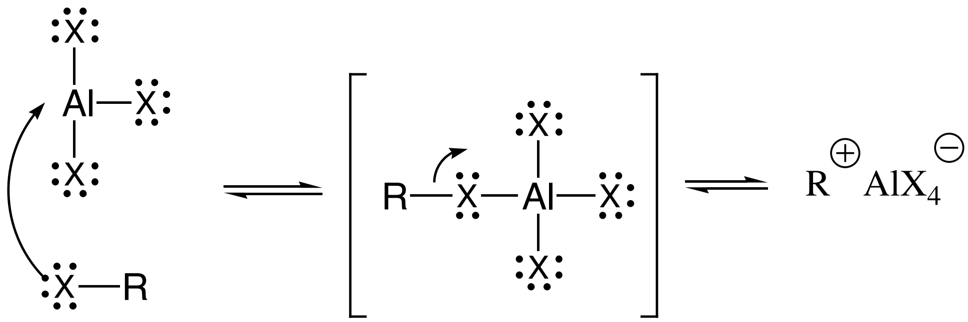
Fuming sulfuric acid contains both of the above reagents, the SO_3 is the important one

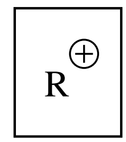
Reagents

Wicked strong electrophile

$E^{\oplus}$

Friedel-Crafts Alkylation **R-X, AlX_3**

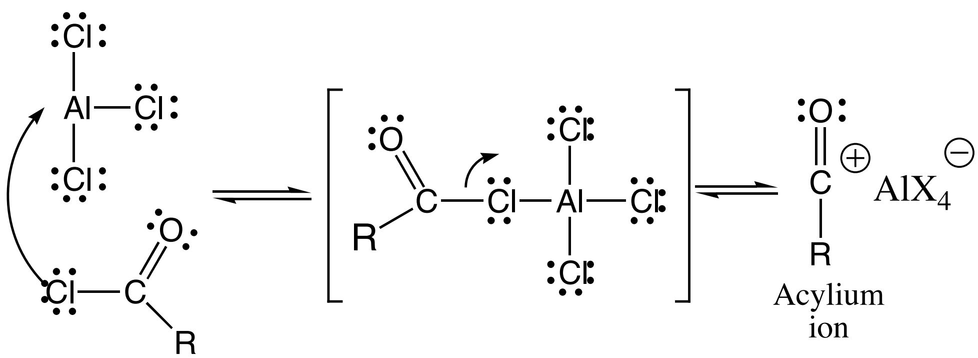


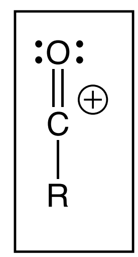


X = Br, Cl

Note this is a carbocation, so it will rearrange if it is a primary or a rearrangment-prone secondary cation

Friedel-Crafts Acylation **RCOCl, $AlCl_3$**





Other notes: 1) It is hard to stop the Friedel-Crafts alkylation after one alkyl group adds (because alkyl groups are "good", that is, activating), but it can be done. 2) Neither Friedel-Crafts reaction works if there is already an electron withdrawing (bad) group on the ring.