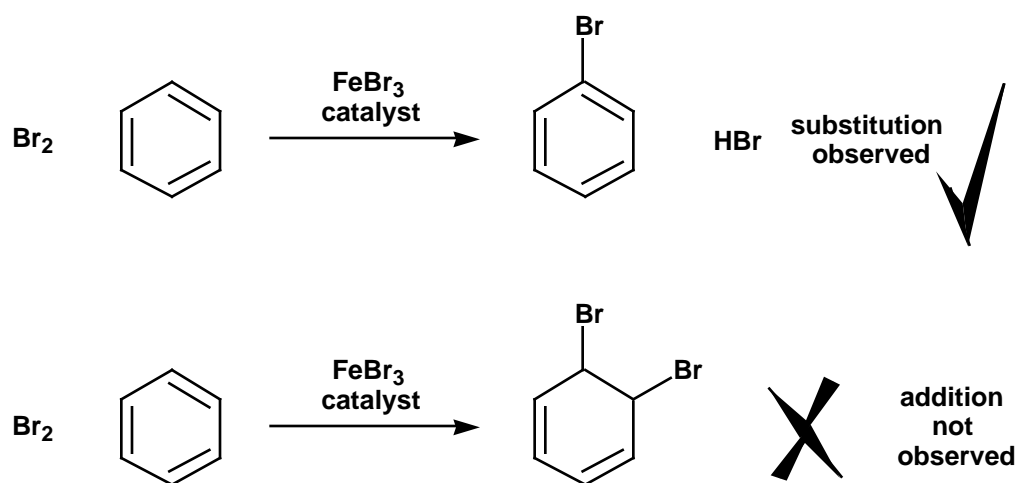


Text Related to Segment 15.07 ©2002 Claude E. Wintner

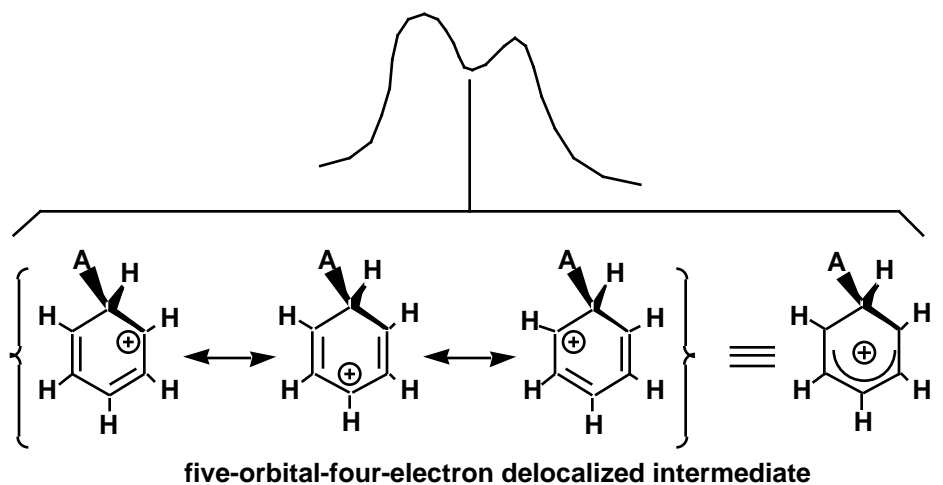
A special case of addition and elimination, amounting to overall substitution, occurs for systems possessing aromatic stability, the archetypal example being provided by benzene. Thus, bromine does not react with benzene to give the 1,2-dibromo addition product analogous to bromine addition products with alkenes. Instead bromobenzene, in which a bromine atom has been substituted for a hydrogen atom on the benzene nucleus, is the observed result:



in general, benzene reacts by substitution, not by addition

The reaction is relatively slow and requires catalysis, for example, by ferric ion. The determining factor here is the propensity of aromatic systems to retain their special delocalization — for benzene its 36 kcal/mole of "resonance energy." A related transformation produces nitrobenzene, to name just one more among many. All of these reactions share a common characteristic: they are initiated by acidic reagents which are strongly electron deficient, that is, electrophilic. We may abbreviate the entire class of reagents as A^+ reagents. Thus, the active reagent in the bromination is, effectively, Br^+ ; the active reagent in the nitration is the cationic species nitronium ion, $^+\text{NO}_2$. The initial step in the mechanism of what is termed

electrophilic aromatic substitution is the same as for addition to alkenes, that is, attack by the π system on the electrophile. In the case of bromination the catalyst serves, in effect, to weaken the Br—Br bond by providing a potent acceptor for bromide anion, as indicated in the figure:



mechanism of electrophilic aromatic substitution

Because the aromatic system is violated, the activation barrier for reaction is higher than it is for alkenes. Note, however, that the intermediate which is formed retains a good deal of delocalization as a five-orbital-four-electron system incorporating five of the original six trigonal sp^2 carbon atoms of benzene. The sixth

carbon atom becomes sp^3 in the intermediate. The conclusion of the reaction now could involve addition of an anion, but only at the cost of irrevocably giving up the aromaticity. Instead, a proton is lost, allowing aromaticity to be regained as the reaction is completed.

©2002 Claude E. Wintner