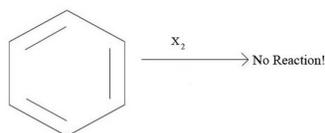


16.9: Halogenation

Halogenation is an example of electrophilic aromatic substitution. In electrophilic aromatic substitutions, a benzene is attacked by an electrophile which results in substitution of hydrogens. However, halogens are not electrophilic enough to break the aromaticity of benzenes, which require a catalyst to activate.

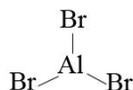
Activation of Halogen

(where X= Br or Cl, we will discuss further in detail later why other members of the halogen family Fluorine and Iodine are not used in halogenation of benzenes)

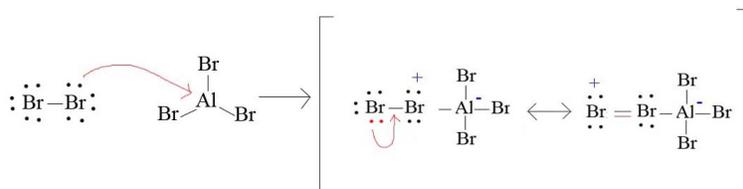


Hence, Halogen needs the help and aid of Lewis Acidic Catalysts to activate it to become a very strong electrophile. Examples of these activated halogens are Ferric Halides (FeX_3) Aluminum Halides (AlX_3) where X= Br or Cl. In the following examples, the halogen we will look at is Bromine.

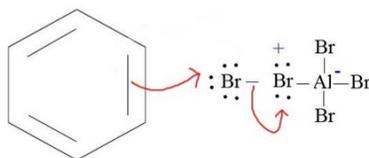
In the example of bromine, in order to make bromine electrophilic enough to react with benzene, we use the aid of an aluminum halide such as aluminum bromide.

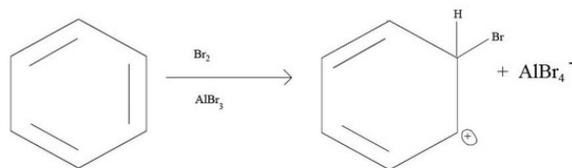


With aluminum bromide as a Lewis acid, we can mix Br_2 with $AlBr_3$ to give us Br^+ . The presence of Br^+ is a much better electrophile than Br_2 alone. Bromination is achieved with the help of $AlBr_3$ (Lewis acid catalysts) as it polarizes the Br-Br bond. The polarization causes the bromine atoms within the Br-Br bond to become more electrophilic. The presence of Br^+ compared to Br_2 alone is a much better electrophile that can then react with benzene.

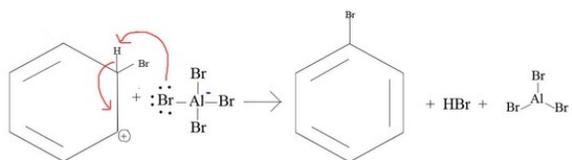


As the bromine has now become more electrophilic after activation of a catalyst, an electrophilic attack by the benzene occurs at the terminal bromine of $Br-Br-AlBr_3$. This allows the other bromine atom to leave with the $AlBr_3$ as a good leaving group, $AlBr_4^-$.





After the electrophilic attack of bromine to the benzene, the hydrogen on the same carbon as bromine substitutes the carbocation in which resulted from the attack. Hence it being an electrophilic aromatic SUBSTITUTION. Since the by-product aluminum tetrabromide is a strong nucleophile, it pulls of a proton from the Hydrogen on the same carbon as bromine.



In the end, AlBr_3 was not consumed by the reaction and is regenerated. It serves as our catalyst in the halogenation of benzenes.

Dissociation Energies of Halogens and its Effect on Halogenation of Benzenes

The electrophilic bromination of benzenes is an exothermic reaction. Considering the exothermic rates of aromatic halogenation decreasing down the periodic table in the Halogen family, Fluorination is the most exothermic and Iodination would be the least. Being so exothermic, a reaction of fluorine with benzene is explosive! For iodine, electrophilic iodination is generally endothermic, hence a reaction is often not possible. Similar to bromine, chlorination would require the aid of an activating presence such as Aluminium Chloride or Ferric Chloride. The mechanism of this reaction is the same as with Bromination of benzene.

Outside links

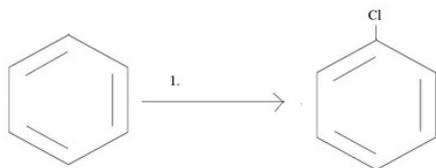
- <http://www.chemguide.co.uk/mechanism...ogeneration.html>
- http://en.wikipedia.org/wiki/Electro...c_halogenation

References

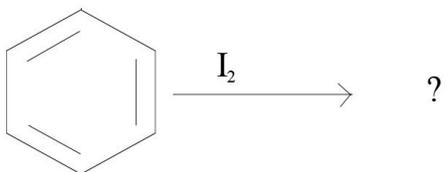
1. Vollhardt, Peter, and Neil Shore. Organic Chemistry: Structure and Function. 5th Edition. New York: W.H. Freeman and Company, 2007.

Problems

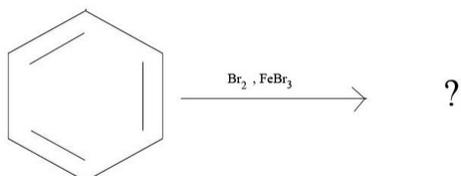
1. What reagents would you need to get the given product?



2. What product would result from the given reagents?



3. What is the major product given the reagents below?



4. Draw the formatin of Cl^+ from $AlCl_3$ and Cl_2

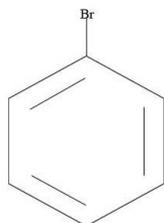
5. Draw the mechanism of the reaction between Cl^+ and a benzene.

Solutions

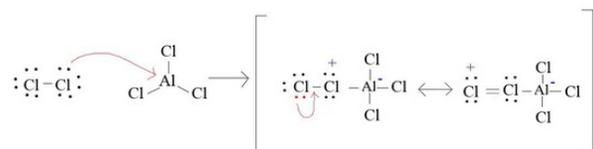
1. Cl_2 and $AlCl_3$ or Cl_2 and $FeCl_3$

2. No Reaction

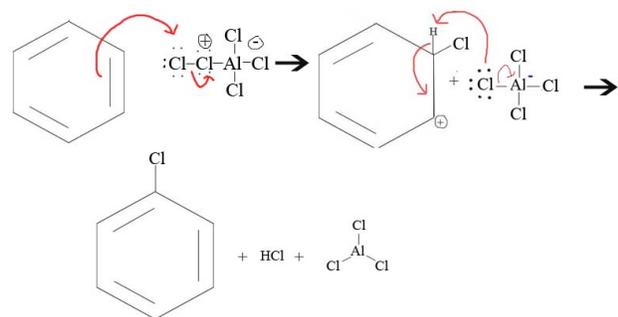
3.



4.



5.



Contributors

- Catherine Nguyen

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