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# Electrophilic bromination of benzene

Objectives After completing this section, you should be able to write the detailed mechanism for bromination reaction with benzene in the presence of a suitable catalyst. Drawing resonance contributors for carbocation forming during bromination reaction with benzene. Compare the reaction that takes place between Bromine and Benzene and the reaction that takes place between Bromine and Alkene. Draw an energy diagram for bromination reaction with benzene. Identify the reagents needed to bring about aromatic bromination. Write an equation to represent aromatic bromination. The mechanism for electrophilic substitution reactions of benzene is the key to understanding the electrophilic aromatic replacement. You will see similar equations written for nitration, sulfonation, acid, etc., with the main difference being the identity of the electrophile in any case. Note that the intermediate carbocation formed has a series of forms of resonance. Furthermore, it is possible to review section 8.2 to satisfy the lens 3. The halogenation is an example of aromatic electrophilic replacement. In aromatic electrophilic substitutions, a benzene is attacked by an electrophile that translates into a replacement of hydrogen. However, halogens are not electrophilic enough to break benzene's aromaticity, which requires a catalyst to activate. A two-phase mechanism has been proposed for these electrophilic replacement reactions. In the first, slow or rate-determining, step the electrophile forms a sigma bond to the benzene ring, generating a positively charged intermediate, the arenium ion. In the second, fast step, a proton is removed from this intermediate, producing a substituted benzene ring. The following illustration in four parts shows this mechanism for the bromination reaction. Also, an animated diagram can be seen. Preliminary phase: formation of the bromine molecule. Step 1: the electrophile attacks the benzene ring, forming a sigma bond to the benzene ring, producing a positively charged arenium ion intermediate. Step 2: a proton is removed from this intermediate, producing a substituted benzene ring. This mechanism for electrophilic aromatic replacement should be considered in the context with other mechanisms involving carbocation intermediates. These include SN1 and E1 reactions of alkyl halides and Brønsted acid addition reactions of alkenes. To sum up, when forming the carbocation intermediates you can expect that you can expect it to react further from one or more of the following ways: 1. Cation may react with a nucleophile to give a replacement or an addition product. 2. Cation can transfer a proton to a base, giving a double-bonded product. 3. Cation can reorganize to a more stable carbocation, then react in mode #1 or #2. The SN1 and E1 reactions are respective examples of the first two reaction modes. The second phase of the mechanism proceeds from the first mode, and one of these three reactions can exhibit molecular rearrangement if an initial unstable carbocation is formed. The arenium ion intermediate in the aromatic electrophilic substitution (arenium ion) is stabilized with the delocalization of the charge (resonance) so that it is not subject to reorganization. In principle it could react with both modes 1 or 2, but the energy advantage of the reform of an aromatic ring leads to the exclusive reaction in mode 2 (i.e. loss of proton). Exercise 1 What reagents should you have to produce the specified product? Answer Cl2 and AlCl3 or Cl2 and FeCl3

EXERCISE 2 Which product would result from the indicated reagents? Answer No reaction

EXERCISE 3 What is the main product given the reagents below? Answer Exercise 4 Draw the formation of Cl+ from AlCl3 and Cl2. Exercise Response 5 Draw the reaction mechanism between Cl+ and a benzene. Answer 6 contributors and attributes

Arenation is an example of an electrophilic aromatic replacement. In aromatic electrophilic substitution a benzene is attacked by an electrophile that results in hydrogen substitution. However, halogens are not enough electrophiles to break the aromaticity of benzenes, which requires a catalyst to activate. (where X = Br or Cl, we will discuss later because other members of the halogen family are not used in benzene arenation) Halogens are not enough reactive on their own to react with an aromatic ring. Halogens need a Lewis acid catalyst to activate them to become a very strong electrophile. Examples of these active halogens are ferric halogens (FeX3) and aluminum halogens (AlX3) where X = Br or Cl. In order to make the electrophile strong enough to react with the benzene, we use the help of an aluminum halogen as aluminum bromide. With aluminum bromide such as Lewis acid, we can mix Br2 with AlBr3 to give us Br+. Br+ is a much better electrophile than Br2 alone. Bromination is achieved with the help of AlBr3 (catalyst Lewis acid) as it polarizes the Br-Br bond. Polarization causes polarization to cause bromine atoms within the Br-Br bond to become more electrophilic. The presence of Br+ compared to Br2 alone is a much better electrophile that can therefore react with benzene. Since the bromine became more electrophilic after activation with a catalyst, an electrophilic attack from the benzene occurs at the terminal bromine of Br-Br-AlBr3. This allows the other bromine atom to leave with AlBr3 as a good leaving group, AlBr4-. After the electrophilic attack of bromine to benzene, hydrogen on the same carbon as bromine replaces the carbocation in which it comes from the attack. Therefore is an aromatic substitution electrophilic. Since the tetrabromide in aluminum by-product is a strong nucleophile, it pulls a proton from hydrogen on the same carbon as bromine. At the end, it was not consumed by the reaction and is regenerated. It serves as a catalyst in benzene arenation. Electrophilic arenation of benzenes is an exothermic reaction. Considering the exothermic rates of aromatic arenation that decrease the periodic table of the halogen family, fluorination is the most exothermic and iodine would be the minimum. Being so exothermic, a fluorine reaction with benzene is explosive! For iodine, electrophilic iodine is generally endothermic, so a reaction is not often possible. Similarly to bromine, chlorination would require the help of an activating presence such as aluminum chloride or ferric chloride. The mechanism of this reaction is the same as benzene bromination. Vollhardt, Peter and in the shore. Organic chemistry: structure and function. 5th edition. New York: W.H. Freeman and company, 2007. 2. Which product would be translated from data reagents? 3. What is the main product given the reagents below? 4. Draw the Cl+ reaction mechanism from AlCl3 and Cl2 5. Draw the mechanism of reaction between Cl+ and benzene. 1. Cl2 and AlCl3 or Cl2 and FeCl3 2. No reaction 3. 4. 5. Catherine Nguyen Layne A. Morsch - University of the Illinois Springfield Springfield Springfield the electrophilic bromination and chlorination of benzene requires

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