

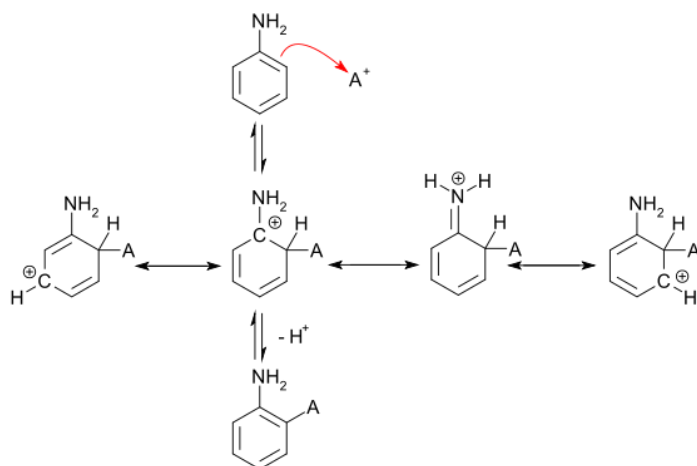
Question #72512, Chemistry / Organic Chemistry

Explain in detail the electrophilic aromatic substitution reaction of aryl amine

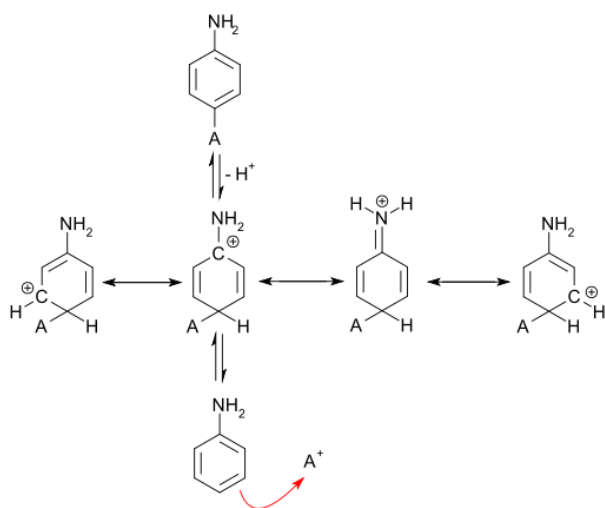
Solution:

Electrophilic aromatic substitution is an organic reaction in which an atom that is attached to an aromatic system (usually hydrogen) is replaced by an electrophile. In terms of the reaction mechanism, the aromatic ring attacks the electrophile. This step leads to the formation of a positively charged cyclohexadienyl cation, also known as an arenium ion. Groups with unshared pairs of electrons, such as the amino group of aniline, are strongly activating and ortho/para-directing by resonance. Such activating groups donate those unshared electrons to the pi system, creating a negative charge on the ortho and para positions. These positions are thus the most reactive towards an electron-poor electrophile. The highest electron density is located on both ortho and para positions, although this increased reactivity might be offset by steric hindrance between substituent and electrophile. The final result of the electrophilic aromatic substitution might thus be hard to predict, and it is usually only established by doing the reaction and determining the ratio of ortho versus para substitution. In addition to the increased nucleophilic nature of the original ring, when the electrophile attacks the ortho and para positions of aniline, the nitrogen atom can donate electron density to the pi system (forming an iminium ion), giving four resonance structures (as opposed to three in the basic reaction). This substantially enhances the stability of the cationic intermediate.

Mexanism of orto-substitution:



Mexanism of para-substitution:



When the electrophile attacks the meta position, the nitrogen atom cannot donate electron density to the pi system, giving only three resonance contributors. This reasoning is consistent with low yields of meta-substituted product.

Mexanism of meta-substitution:

