

The Influence of a Grignard Reagent on Acyl Group Addition to Bipyrrole

Fiona Evans, Jason M. Keith

Department of Chemistry, Colgate University, Hamilton, NY

Porphyrins are cyclic molecules that contain four pyrrole groups, with various substituents and connections, and can serve as important metal ion transporters in nature. In an organic synthesis to produce a porphyrin called N-confused corrole, an acetyl chloride was added in excess to bipyrrole in the presence of the Grignard reagent ethylmagnesium bromide. Because of an understanding of conjugation, experimenters expected a particular diacyl product (Figure 1), but did not observe the formation of that product. DFT energy calculations of all possible isomers of products and reactants were performed using a 6-311+G basis set and a B3LYP functional. These calculations revealed that the symmetric diacyl product should have the lowest energy (Figure 2) and the Grignard reagent could provide an energy lowering effect if it is bound the nitrogen atoms of the bipyrrole system. Transition state calculations using DFT have also been performed on the lowest energy isomers of the system, which have indicated the mechanism of the reaction. During the addition of the acetyl chloride, the chlorine atom gets pushed away from the acetyl carbon as it approaches the biphenyl system and the chloride ion is lost to form a tetrahedral intermediate. Next, the chloride ion removes the hydrogen atom from the tetrahedral carbon, leading to somewhat planar product. Energy calculations for the transition states, using DFT, are still being performed to determine if kinetic or thermodynamic control is the determining factor in the formation of the diacyl product. Additionally, NMR calculations using both DFT and HF methods are being performed to determine if experimental NMR spectra are being interpreted correctly.

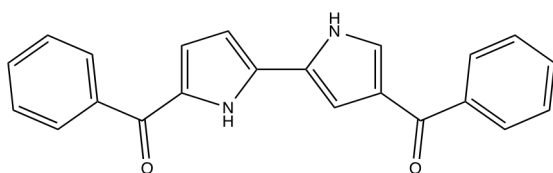


Figure 1. Expected diacyl product.

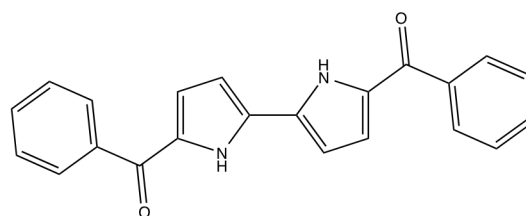


Figure 2. Diacyl product with the lowest calculated energy.