

Fries Rearrangement of Aryl Formates Promoted by BCl_3 . Mechanistic Evidence from ^{11}B NMR Spectra and DFT Calculations*

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The Fries rearrangement of model aryl formate esters, promoted by boron trichloride, has been investigated by means of NMR spectroscopy (both experimental and computational) and by DFT calculations. Firstly, the ^{11}B NMR chemical shifts of a series of model boron compounds have been predicted by GIAO-B3LYP/6-31G(d,p) calculations, in order to make predictions of the chemical shifts of transient reaction intermediates observable by ^{11}B NMR. Such ^{11}B spectra for the reaction of two esters (phenyl and 3-methoxyphenyl formates) have been obtained, and are found to follow different patterns which can be rationalized on the basis of computed chemical shifts. Secondly, DFT calculations (B3LYP/6-31G(d,p) level) have been employed to investigate several mechanistic pathways of the rearrangement of phenyl formate. It is found that the pathways leading to the lowest activation energies are those in which formyl chloride is generated from a complex between phenyl formate and BCl_3 , which then acts as the formylating agent.

Key words: Fries Rearrangement, Reaction Mechanisms, Electrophilic Reactions,
DFT Calculations, ^{11}B NMR