Negative Ion Rearrangements
in the Gas Phase

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Doctor of Philosophy

by

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Abstract

In this thesis the investigation of rearrangements known to proceed in solution were examined in the gas phase. Where possible the results obtained in solution are indicated in the text and in this way the behaviour of the compounds in condensed phase and the gas phase may be directly compared.

In solution there are many factors influencing the course of a reaction. The term "intrinsic" reactivity is often applied to reactions occurring in the gas phase. In the introduction, this concept is dealt with to demonstrate the influence of the solvent and counter ions which are seldom considered when dealing with anionic chemistry. In this way, the unique insight that the study of gas phase ion chemistry provides is highlighted.

The systems chosen for study have been carefully selected. In solution there are significant differences in the behaviour of the systems. The Wittig rearrangement was chosen because the mechanism is believed to involve a dissociated intermediate, the Smiles rearrangement involves nucleophilic attack at the ipso position of the aromatic ring, and the Benzilic Acid rearrangement was studied because in solution chelation of a metal ion is important to effect nucleophilic addition of the base.