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1-Phosphonoalkylium ions as reactive intermediates in heterolytic carbon-heteroatom bond cleavage reactions

Carbenium ions are common intermediates in the reactions of organic compounds. They are mainly formed in heterolytic carbon-heteroatom bond cleavage reactions of halogenoalkanes, oxonium salts, ammonium salts and diazonium salts. The influence of neighboring groups on the reactivity of carbenium ions has been extensively described in the chemical literature. However, there is no information neither about carbenium ions containing a neighboring phosphonic group (1-phosphonoalkylium ions), nor any reactions involving these ions. For these reasons, I have chosen reactions of 1-phosphonoalkylium ions as the subject of my dissertation.

The aim of the study was to investigate whether 1-phosphonoalkylium ions are formed in reactions analogous to reactions in which alkyl ions are intermediates. I have described synthesis of precursors and investigation of heterolytic carbon-heteroatom bond cleavage reactions of following compounds:

- 1) N,N-dialkyl-N-(1-phosphonoalkyl)ammonium salts and N,N,N-trialkyl-N-(1-phosphonoalkyl)ammonium salts,
- 2) 1-phosphonoalkanediazonium salts,
- 3) 1-phosphonoalkyloxonium salts.

I have not observed a C-N bond cleavage reactions that could suggest the participation of the 1-phosphonoalkylium ions in the reactions of N,N-dialkyl-N-(1-phosphonoalkyl)ammonium salts, which are formed *in situ* as a result of the protonation of 1-[bis(phosphonomethyl)amino]alkylphosphonic acids, 1-[alkyl(phosphonomethyl)amino]alkylphosphonic acids and 1-(dialkylamino)alkylphosphonic acids. These compounds undergo concurrent phosphonic group protonation, which results in C-P bond cleavage reaction.

Quaternary ammonium salts with neighboring phosphonic group – N,N,N-trialkyl-N-(1-phosphonoalkyl)-ammonium salts – are stable in acidic media. Unlike quaternary ammonium salts without a phosphonic group, most of the tested N,N,N-trialkyl-N-(1-phosphonoalkyl)ammonium salts are also stable in the alkaline solutions. However, the reaction products of some quaternary salts allow for postulation of the presence of 1-phosphonoalkylium ions as intermediates.

In the reactions of 1-phosphonoalkanediazonium salts, which are generated in reactions of 1-aminoalkylphosphonic acids with HNO₂, reaction products (nucleophile addition products, elimination products and rearranged products) clearly prove the intermediacy of 1-phosphonoalkylium ions.

1-Phosphonoalkyloxonium salts, which are formed as the result of the protonation of 1-hydroxyalkylphosphonic acids, are relatively stable in hydrochloric acid, Lucas reagent (ZnCl₂/HCl), hydrobromic acid, as well as with sulfuric (VI) acid. However, some of the reaction products of the 1-hydroxyalkylphosphonic acids allow to postulate the intermediacy of 1-phosphonoalkylium ions. These compounds undergo concurrent phosphonic group protonation, which results in C-P bond cleavage reaction.

My research proves that 1-phosphonoalkylium ions are formed in many reactions. However, phosphonic group does not stabilize carbenium ions, nor does it force specific direction of reaction. The remaining substituents have the greatest influence on the stability and direction of the reaction of 1-phosphonoalkylium ions. The poor reactivity of many compounds containing phosphonic group in the 1-position may be explained by the high stereoelectronic hindrance of the phosphonic group.