Abstract

1-Haloalkynes are an important class of precursors widely used in organic synthesis. The potential of 1-haloalkynes as versatile reagents stems from the fact that these molecules exhibit both electrophilic and nucleophilic properties. Numerous literature reports indicate that these compounds are commonly used as building blocks in coupling reactions carried out both under catalytic and non-catalytic conditions.

The primary goal of this research was to perform oxidative addition reactions as well as coupling reactions of 1-haloacetylenes and various molecules possessing high nucleophilicity parameter, isolation of the resulting derivatives and their characterization. A solvent-free method was adopted with grinding of the reagents (in a mortar or ball mill) on a solid substrate.

As a result, a series of azulene species containing ethynyl or polyyne chain was obtained. The derivatives were obtained by direct C-H alkynylation of azulenes under mild conditions without the use of a solvent and a reaction catalyst. In addition, by changing the stoichiometry of the reaction, it was shown that it is possible to isolate the double addition products of azulene for the most reactive 1-haloalkynes. Finally, to demonstrate the usefulness of compounds with the $(C\equiv C)_2$ fragment as substrates for further chemical modifications, azulene derivatives containing thiophene rings were obtained. Particular attention was given to the characteristics of the obtained derivatives. All compounds were fully characterized by NMR methods (^{1}H, ^{13}C), UV-Vis, IR and HRMS(ESI). Five compounds have also been characterized with use of X-ray single crystal diffraction techniques.

In the next step, alkyne precursors were used to carry out the inverse Sonogashira coupling with pentafulvenes and other aromatic compounds (including heterocyclic compounds). As a result, three ethynyl derivatives of fulvenes and one fulvene with $(C\equiv C)_2$ fragment were obtained. Spectroscopic and structural properties of the resulting derivatives were explored in detail using NMR, IR and HRMS(ESI).

In the thrust, a series of reactions between 1-haloalkynes and iridium precursor $(PPh_3)_2Ir(CO)Cl$ (are not discussed in the dissertiation since my contribution to this project was relatively small and hard “to be isolated”) as well as ester end-group and aromatic amines and indoline was

carried out, resulting in two known ketoamides. Next, the inverse Sonogashira coupling reactions between 1-haloakynes and heterocyclic compounds were tested. Various reaction media and grinding methods (ball mill or mortar) were tried.