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Hydrothiolation reactions as an alternative to hydrosilylation in the synthesis of organosilicon compounds

Summary

Silicon compounds are very popular and find applications in science, industry, and everyday life. The special properties and wide range of applications of organosilicon compounds result from the simultaneous presence of organic and inorganic groups in their structure. Hydrosilylation is one of the most important methods for obtaining organosilicon derivatives. Hydrosilylation involves the addition of organic and inorganic silicon hydrides to carbon-carbon multiple bonds, as well as to carbon-heteroatom bonds such as carbon-oxygen, carbon-nitrogen, and also nitrogen-nitrogen, and nitrogen-oxygen. Unfortunately, the synthesis in most cases is conducted in the presence of the catalysts based on expensive noble metals, which are often sensitive to oxygen and moisture. In the presence of impurities, such as sulfur, poisoning can occur, leading to catalyst deactivation.

The hydrothiolation reaction (thiol-ene addition reaction) involves the addition of thiols to a carbon-carbon multiple bond, resulting primarily in a product that does not follow Markovnikov's rule. The hydrothiolation is classified as a "click" reaction. It is characterized by simple reaction conditions, readily available substrates, high selectivity, and yield. Synthesis is often conducted at room temperature, and it is not necessary to conduct the synthesis under an inert gas atmosphere. This process usually does not require the use of expensive noble metal catalysts. Therefore, hydrothiolation seems to be an alternative to the classic hydrosilylation reaction, which is used to obtain organosilicon derivatives.

The primary goal of this work was to develop an effective method for the synthesis of organosilicon derivatives based on the hydrothiolation reaction (thiol-ene) and determine whether it could be an alternative to the classic hydrosilylation process.

The study compared the initiation of the hydrothiolation reaction based on (i) a free radical mechanism (generating radicals thermally or via UV radiation) and (ii) a catalytic mechanism involving catalysts such as phosphines and bases. Activity tests were conducted on the initiators for the hydrothiolation reaction. Among other things, the study examined whether the location of the thiol group on the organosilicon compound or on the organic compound could affect the reaction rate and efficiency. As a result, a number of organosilicon derivatives terminated with various functional groups were obtained. All obtained compounds were characterized using spectroscopic methods. Additionally, the application potential of the selected derivatives was examined. Some of the compounds were used to modify the surface of

cotton fabrics to impart hydrophobic properties. The hydrothiolation reaction was used both to synthesize the derivatives and to conduct the thiol-ene reaction on the fabric surface. SEM-EDS and WCA analyses confirmed that the resulting fabrics were hydrophobic both before and after washing, confirming that the cotton samples were permanently modified and retained their hydrophobic properties. The possibility of synthesizing polar organosilicon derivatives via the hydrothiolation reaction was also investigated. Hydrosilylation of this group of compounds often results in competitive processes, and these reactions are often non-selective. The application potential of the synthesized compounds was examined by applying the products to microscope slides and examining the WCA angle. All derivatives exhibited hydrophilic properties.

As a result of the conducted studies, a number of organosilicon derivatives were synthesized via both the free-radical-initiated hydrothiolation reaction and the thiol-Michael addition reaction. All derivatives were characterized using spectroscopic methods. The hydrothiolation reaction is suitable for the direct synthesis of organosilicon derivatives and can also be used for the rapid modification of cotton fabrics. The presented studies confirm that hydrothiolation is an efficient method for obtaining a wide range of organosilicon derivatives and can provide an alternative to the classical hydrosilylation reaction, which typically produces silicon compounds.