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ADDITION OF SULFENYL CHLORIDES TO OLEFINS: GENERAL MECHANISM, SYNTHETIC DEVELOPMENT

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ADDITION OF SULFENYL CHLORIDES TO OLEFINS: GENERAL MECHANISM, SYNTHETIC DEVELOPMENT.

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A generally accepted mechanism of sulfenyl chloride addition to the double bond which included the intermediate of episulfonium type. was revised $^{1-3}$. It was shown that (1) episulfonium ions are certainly NOT intermediates in usual conditions of the addition, and (2) various types of intermediates with various degrees of dissociation of S-C1 bond actually take part in the process, depending on the conditions. Starting from this point, a new method for increasing the effective electrophilicity of weak electrophiles through the addition of strong electrolytes has been developed. For example, the addition of the LiClo, leads to the strong increase of effective electrophilicity of these reagents which, in turn, leads to (1) formation of rearranged products, and (2) incorporation of external nucleophile and new reactions of mixed 1,2-addition. Examples of homoallylic, trans-annular and Wagner-Meerwein rearrangements are discussed, as well as the scope and limitation of this method, its synthetic utility, and extension to other classes of sulfur-containing electrophiles and substrates (aromatic and cyclopropane hydrocarbons, etc.).

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