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作品名稱 **New approach to the synthesis of functionalized fluoroalkenes**

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НОВЫЙ МЕТОД СИНТЕЗА
ФУНКЦИОНАЛИЗИРОВАННЫХ ФТОРАЛКЕНОВ
Раскрытие цикла
Изомеризация
Реакции с нуклеофилами
Планы
УЧАСТНИК

Abstract

Fluorine has a big influence on physical, chemical and biological properties of organic structures. Organofluorine compounds are widely used in modern medical chemistry to develop new drugs. Insertion of fluorine atom into organic molecules can improve their reactivity in biological systems, increase their metabolic stability, lipophilicity and permeability through membranes. As a consequence, in recent years, the percentage of drugs containing one or more fluorine atoms has increased rapidly up to 40%. The fluoroallylic fragment is also able to change properties of bioactive molecules. Its introduction into such structures as inhibitors of histonedeacetylase, inhibitors of matrix metalloproteinase, asparagine, glutamine, etc. increases their biological activity and electronic properties.

We propose a new method for the synthesis of functionalized fluoroalkenes, based on the generation of fluoroallyl nucleophiles from silyl- and boronyl-substituted fluorocyclopropanes and their further usage in the allylation of carbonyl compounds or their derivatives.

Due to the fact that the cyclopropanation of alkenyl boronates is not possible under conditions of alkaline dehydrohalogenation of dibromofluoromethane, we have developed a new method for the preparation of silyl- and boronyl-substituted cyclopropanes, which consist of carbene cyclopropanation of multiple C=C bonds by sodium dibromofluoroacetate catalyzed by (IPr)AgCl. The new method is effective for the cyclopropanation of not only boronyl- and silyl-substituted olefins, but also for low-reactivity alkenes, such as monoalkyl substituted alkenes, allyl alcohol ethers and α,β-unsaturated carbonyl compounds.

The conditions for isomerization of silyl- and boronyl-substituted

fluorohalocyclopropanes in the presence of catalytic amounts of copper (I) bromide in acetonitrile was selected. It was shown that the regioselectivity of the process is determined by the thermodynamic control. Thus, the formation of fluorovinylsilanes or fluorovinylboranes in the isomerization of α-silyl- or α-boronyl-gem-bromofluorophenylcyclopropanes and fluoroallylsilanes upon isomerization of β-silyl-gem-bromofluorophenylcyclopropanes was observed.

Thus, new types of fluorinated reagents were obtained that are not previously described in the literature (...)

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Fluorination reaction is critical for small drug pharmaceutical industry because many important drugs are originated from fluorine-analogs of nature ingredients. The students herein introduce a new synthetic approach to synthesize fluoroalkenes. These molecules can be utilized as synthons for more attractive drug precursors or analogs. The students also comprehensively studied all the necessary elements for development of a useful organic synthetic method. In particular, the utilization of silver-carbene enhanced the reaction yield dramatically. Moreover, many different functional groups can be tolerated as substrates. Therefore, a widely applicable method was developed. The presentation is also well-organized and the results are fascinating.