

The use of unusual radical precursors in reactions with electrophiles

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Development of organic chemistry is driven by continuous introduction of new synthetic tools to the accessible methodologies. The requirements set by modern chemistry are high and include high functional group tolerance, lack of protecting groups, selectivity, use of non-toxic reagents and catalysts, mild reaction conditions and low costs. The methods based on radical reactions frequently respond to these needs. Identifying new radical precursors and planning non-standard synthetic pathways are necessary to enable their involvement in creating organic structures unknown before.

One of the promising groups of the potential radical precursors are small cyclic and polycyclic molecules. Their high strain energy contributes to unusual reactivity, which may be used to create extremely valuable products.

The aim of this work was to develop new methods for the generation of alkyl radicals from unusual precursors and their use in reactions with electrophiles.

In the first part of this work, I used electrophilic bicyclo[1.1.0]butanes as the precursors of cyclobutyl radicals generated in the reaction catalyzed by vitamin B₁₂ derivative. Combining this transformation with another, Ni-based catalytic cycle enabled reaction with electrophiles – aryl iodides.

In the second part of my studies, I investigated donor-acceptor cyclopropanes in the role of radical precursors. Using vitamin B₁₂ as the catalyst facilitated generating of the radical on donor-substituted carbon. This resulted in reversal of regioselectivity in the reaction with electrophilic olefins.

In the last part of this work I exploited aldehydes in the role of alkyl radical precursors. Using benzothiazoline as the activating group enabled reaction of an aldehyde with an electrophilic olefin.