1,2-ZWITTERIONIC Ga COMPLEXES OF METHYLIDENEMALONATES AND THEIR REACTIONS WITH ACETYLENES

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Donor-acceptor cyclopropanes (DACs) are a broad class of substituted three-membered carbocycles. They are known for their capability to undergo small ring opening to act as 1,3-zwitterionic synthons. Our group developed a quiet different type of reactivity of DAC – the use of 2-arylcyclopropane-1,1-dicarboxylates (ACDC, 1) as sources for generation of 1,2-zwitterions 3 in the presence of GaCl3 [1]. We also examined the methylidenemalonates 2 as a simpler substrates for generation of 1,2-zwitterionic synthons 4 [2]. Complexes obtained were identified by NMR spectra.

Now we demonstrate a new approach for using ACDC and methylidenemalonates 2 in reactions with acetylenes in the presence of GaCl3. As a result, we have been developed a new strategy for assembly of substituted indenes 5, (3-haloallyl)malonates 6, dihydronaphtalenes 7 and lactones 8. All processes were very selective: the reactions between the complex 4 and arylalkylacetylenes occurs by a formation of indenes 5 with selective location of aryl and alkyl groups in structure; in case vinyl halides 6 the assembly of a molecule involving ACDC, acetylenes and GaX3 proceeded with selective trans-functionalization. The reactivity of the 1,2-zwitterionic complex 3 in reactions with arylacetylenes occurs according to the type of [4+2]-annulation to form the dihydronaphthalene scaffold 7. The reaction between 1,2-zwitterionic complexes 3,4 and propyn halides occurs with the selective formation of the lactone 8 as trans-isomer. As the result all discovered processes proceed with a high regio- and diastereoselectivity and good yields of products obtained.

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