NOVEL CAGE COMPOUNDS FROM THE REACTION OF THIAZOLIUM N-METHYLIDE WITH METHYLENECYCLOPROPENE

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Thiazolium N-dicyanomethylide and N-phenacylide reacted with methylenecyclopropenes bearing a carbonyl group at the 4-position to give cage compounds in quantitative yields. Thus, 3-(2,3-diphenyl-2-cyclopropenylidene)-2,4-pentanedione, 2-benzoyl-2-(2,3-diphenyl-2-cyclopropenylidene)-acetonitrile, and ethyl 2-cyano-2-(2,3-diphenyl-2-cyclopropenylidene)acetate cycloadded, across their endocyclic double bonds, to the thiazolium ylides in a highly stereo- and regioselective manner to form the intermediary endo [3 + 2] cycloadducts which then underwent an intramolecular 6π electrocyclic reaction leading to the cage compounds.

On the other hand, such methylenecyclopropenes bearing an aryl group at the 4-position as 2-phenyl-2-(2,3-diphenyl-2-cyclopropenylidene)acetonitrile and 10-(2,3-diphenyl-2-cyclopropenylidene)-9-anthrone gave similar cage compounds also in excellent yields. Interestingly the former methylenecyclopropene isolated a thermally unstable endo [3 + 2] cycloadduct to thiazolium N-phenacylide, which, when heated, cyclized into two isomeric cage compounds. The formation of isomers will have resulted from a non-stereo selective 1,3-hydrogen shift of the initial cycloadduct.

Although the reaction of thiazolium N-dicyanomethylide with 2-(2,3-diphenyl-2-cyclopropenylidene)propanedinitrile in tetrahydrofuran yielded neither a cycloadduct nor a cage compound under various reaction conditions, the same reaction in alcohols afforded similar cage compounds incorporated with the alcohols.