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A PROMISING CLASS OF REAGENT(SYNTHON) FOR CYCLOADDITION REAGENT DESIGN AND STUDY OF 1,4-DITHIINS

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The frontier molecular orbital(FMO) concept has been succesfully applied to the development of the new reagents with a high reactivity and selectivity. As a continuation of our studies on the frontier-controlled pericyclic reactions, we have synthesized various 1,4-dithiin derivatives(4-8) and investigated their reactivities in cycloaddition reactions.

According to the cyclic conjugation theory, the conjugation mode of 1,4-dithiin is discontinuous and the induction of the electron-withdrawing groups onto the C=C double bonds will cause a lowering of the LUMO energy level. Therefore such 1,4-dithiins(4-8) are expected to have a high reactivity in the reactions with the electron-rich dienes.

Thus, the 1,4-dithiin(6) reacted with cyclopentadiene to give a high yield of 1:1- or 1:2-adducts depending on the reaction conditions. Reactions with polycyclic aromatic compounds such as anthracene and acridine were also investigated. The results are classified into four types as follows: (1) only charge transfer(CT) complexes are formed; (2) 1:1 adducts are formed via CT-complexes; (3) 1:1 adducts are directly formed ; (4) neither CT-complexes nor 1:1 adducts are formed. The structures of the adducts and CT-complexes are determined on the basis of spectroscopic data.

The reaction mechanism is studied in detail by carrying out the kinetic study and the structure-reactivity relationships are clarified.