

REAGENT DESIGN AND STUDY OF 1,4-DITHIIN AS PROMISING CLASS OF REAGNETS (SYNTHONS)
FOR CYCLOADDITION. THE DIELS-ALDER REACTIONS WITH ANTHRACENE DERIVATIVES VIA
CHARGE-TRANSFER COMPLEXES

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Contrary to the previous notion, 1,4-dithiin and derivatives are suggested to readily take on a planar structure based on MO calculations and on the cyclic conjugation theory. Cycloaddition reactions of 1,4-dithiin-tetracarboxylic N,N'-dimethyldiimide and dianhydride with various anthracene derivatives have been investigated. These derivatives react smoothly with electron-rich anthracenes via charge-transfer complexes to give Diels-Alder adducts in high yields. In contrast, the diimide reacts slowly with electron-deficient 9-anthraldehyde to afford an adduct, without passing through charge-transfer complex. The reaction of diimide with acridine gives a stable 1:1 complex, which does not change further to give an adduct. Kinetic study of these reactions clarified the remarkable effects of substituents, reagent concentration, and solvents. The mechanisms of these reactions are discussed on the basis of kinetic observations and in terms of the frontier molecular orbital theory.