PERICYCLIC REACTION OF OXEPIN

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The cycloaddition reaction of heteropine has received attention in the past decade. Interestingly, all cycloaddition reactions of oxepin(1) proceed via benzene oxide and no example is yet known in which seven-membered ring acts as either a 4π or 6π donor. We now wish to report the cycloadditivity and periselectivity of 1 with cyclopentadienones(2a-c) on the basis of the frontier-controlled donor-acceptor interaction theory.

(1) When a solution containing a large exess of 1 and 2,5-dimethoxycarbonyl-3,4-diphenylcyclopentadienone(2a) in benzene was stirred at room temperature for 1 day, two crystalline 1:1 adducts [exo[6+4]π cycloadduct(3a) and endo[2+4]π cycloadduct(4a)] were afforded. 4a was converted to 6a by refluxing in benzene for 3 days.

(2) When a solution of a large exess of 1 and 2,3,4,5-tetraphenylcyclopentadienone (2b) in benzene was refluxed for 3 days, two crystalline 1:1 adducts [syn-endo[4+2]π cycloadduct(7b) and anti-endo[4+2]π cycloadduct(5b)] were afforded. The precursor of 7b will be considered 3b or 8b, that is different from the pathway of 4b to 5b.

(3) When a solution containing a large exess of 1,3-diphenyl-1,3-bisdiazo-2-propanone, which is the precursor of 2,5-diphenyl-3,4-diazacyclopentadienone(2c), in benzene was stirred at room temperature for 1 day, a crystalline 1:1 adduct [anti-endo[4+2]π cycloadduct(5c)] was afforded. When 5a was solved in $CDCl_3$, 5c was converted to 6c slowly. Although the rearrangement product 6c was unsuccesful to isolate at present stage, the eqilibrium was observed in the ratios of 5:1 at room temparature after 3h and 1:1 at 55°C by ^{1}H-NMR inspection.