PERI- AND REGIOSELECTIVITY OF 1H-AZEPINE TO PHENCYCLONE

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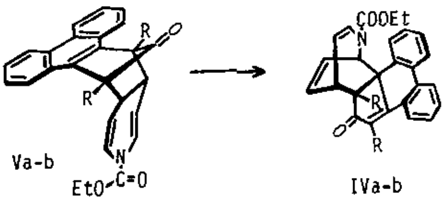
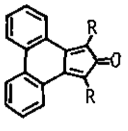
To clarify the peri- and regiochemistry in pericyclic reaction of cyclopentadienones and seven membered ring unsaturated polyenes, 1H-azepine, we have previously elucidated the molecular structures of the endo[4+2] and exo[6+4] cycloadducts[1] and proposed the possibility of the direct path in formation reaction of the anti-endo[4+2] adduct on the basis of consideration of the aromaticity of the primary endo[2+4] cycloadduct. However, we successfully isolated the endo[2+4] cycloadducts (Va-b) of phencyclone derivatives (IIa-b)(4π) and N-ethoxycarbonylazepine (NEA)(I)(2π) which readily isomerized to anti-endo[4+2] cycloadducts (IVa-b). Therefore, we have examined the kinetics of the rearrangements of Va and Vb, and discussed the formation mechanisms for the cycloaddition reaction of several cyclopentadienones (IIa-d) with NEA.

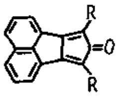
The Cope rearrangement showed a first order process with relatively low sensitivity to the ionizing power of the medium indicating that it proceeds by a mechanism which involves very little change in charge separation between the ground state and the transition state. The rearrangement rate of V to IV was effected by the change of 2,5-substituents of cyclopentadienones. As pointed out by Fukui et al.,[2] these results can be explained in terms of the three-system interaction theory which involves the interaction among the HOMO's of the two π bonds and the LUMO of the σ bond. Then, the total energies between two molecules were calculated by treatments with perturbation theory (CNDO/2 MO method) assuming the two components might approach with molecular angles in 60° to show the endo[2+4] adduct being favored over the anti endo[4+2] adduct by 0.52 eV/mole. The calculation of the stabilization energies also suggested the favor for the endo[2+4] adduct formation.



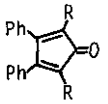
Va-b
IVa-b



IIa: R=C_6H_5
(Phencyclone)
IIb: R=p-ClC_6H_4



IIc: R=C_2H_5(EAC)
IId: R=$COOC_2H_5$
(ECAC)



IIe: R=$COOCH_3$(CPC)
IIf: R=CH_3(MPC)

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1) K. Harano, T. Ban, M. Yasuda and K. Kanematsu, Tetrahedron Letters, 4037, 1978; idem, ibid, 1599, 1979.

2) S. Inagaki, H. Fujimoto and K. Fukui, J. Am. Chem. Soc., 98, 4693(1976).