REACTIVITY OF 1H-AZEPINE IN PERICYCLIC REACTION: X-RAY CRYSTALLOGRAPHIC STUDY OF THE CYCLOADDUCTS

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In connection with the studies on molecular design by cycloaddition reactions, the reactions of N-ethoxycarbonylazepine(I) with phencyclone(IIa), 2,5-dimethoxycarbonyl-3,4-diphenylcyclopentadienone(IIb) and 3,4-diaza-2,5-diphenylcyclopentadienone(IIc) were investigated. It was of interest to examine reactivity and regio-, peri- and stereoselectivity of these related compounds for the cycloadditions; e.g. controlling factors over the modes of cycloadditions needed clarification.

With IIa, I added as 1,4-diene to give a single anti endo[4+2]π adduct(IIIa) in nearly quantitative yield. Similarly, the reaction of I with IIc gave anti endo[4+2]π adduct(IIIc) in 42% yield. On the other hand, the reaction of I with IIb gave anti endo[4+2]π(IIIb) and exo[6+4]π adduct(IVb) in 20 and 80% yields, respectively. To the best of our knowledge, IVb is the first example in cycloaddition reaction of I with dienes.

The structual elucidations of these adducts were mainly accomplished by X-ray crystallographic study. Crystals of IIIa are monoclinic, space group $P2_1/n$ with a=15.119(10), b=14.532(6), c=13.042(10)Å, β=91.40(6)°. Those of IVb are monoclinic, space group $P2_1/c$, with a=16.447(6), b=9.933(4), c=16.331(6)Å and β=100.053(3)°. Those of IIIc are triclinic, space group $P\bar{1}$, with a=12.503(5), b=9.172(3), c=9.920(3)Å, α=105.46(3), β=81.74(3), γ=72.80(3)°. The molecular structures were solved by a direct method using the MULTAN series of programs. They were refined by least squares calculations to R values of 0.068, 0.098 and 0.052, respectively. The structure of IIIb was determined by comparison of the NMR spectral data with that of IIIc.

From the observation described above, the following conclusions can be deduced: 1) With cyclopentadienones(II), I behaves 4π component by the dominant interaction of the HOMO of I, and the LUMO of II, showing the high degree of regiospecificity. This behavior is discussed in terms of dipole-dipole interaction between I and II. 2) Anti endo[4+2]π adducts might be formed not through sigmatropic rearrangement of endo[4+2]π adduct(V) in which IIa added as 4π component but through direct cycloaddition reaction of IIa(2π) with I(4π) because the destruction of aromaticity in V seemed to be energetically unfavorable. 3) With respect to the regiochemistry of endo[4+2]π adduct, two regioisomers may be derived from the independent pathway and the interconversion of these isomers cannot be allowed in the thermal condition. Syn endo[4+2]π adduct may be indirectly formed from sigmatropic rearrangements of exo[6+4]π cycloadduct.