

AN MO INVESTIGATION OF THE FORMATION OF endo-[6 + 4]- π ADDUCT
FROM ISOBENZOFURAN AND 6,6-DIMETHYLFULVENE

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According to well known Hoffmann-Woodward rule, the concerted thermal cycloaddition reaction between 6π and 4π systems should occur with the exo-fashion. After accumulations, to date, of considerable examples which verified the theoretical prediction, a few of the exceptional endo-[6 + 4] π adduct formations has been however observed. Since the [6 + 4] π adducts are always possible to be derived, at least in a formal sense, after symmetry-allowed sigmatropic rearrangements of the initially formed cycloadducts, like endo-[2 + 4] π adducts, it should not be regarded as the genuine adducts unless certain evidences on the cycloaddition were provided. In fact, there are some observations on the formation of the [6 + 4] π adducts from the other modes of cycloadducts by rearrangements. As previously reported, the reaction of isobenzofuran with 6,6-dimethylfulvene afforded the endo-[6 + 4] π adduct. Since the conjugated system of dimethylfulvene is not linear, the overlappings of the π -electron system to govern the stereoselectivity may not be sufficient unlike as other typical 6π addends, but still the product formation has been thoroughly controlled to show an inverted endo-selectivity. Therefore, we have carried out the investigations to understand the cycloaddition process by means of the extended Hückel MO treatment; the results obtained therefrom will be described herein.

First of all, peri-selectivity of the reaction of two components, isobenzofuran and 6,6-dimethylfulvene, was deduced from the HOMO and LUMO interactions to show the endo-[6 + 4] π addition being favored. Thus, the endo-adduct seems to be a primary adduct, but not a rearrangement product of undetectable precursor. Then, the stabilization energies for the reaction was calculated by treatments with perturbation theory assuming the two components might approach with the geometry of parallel in each other to show again the endo-adduct being favored over the exo-isomer by 2.9 kcal/mole. The overlap integrals between two molecules in certain stereochemical geometries also deduced the parallel results; in cases of approach with molecular angles in 60° for endo-addition and 20° for exo-addition, the calculation suggested the favor for the endo-adduct formation.

Therefore, the endo-addition process in the present example has been supported by MO evidences.