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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 genuin 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 controled 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.