MOLECULAR DESIGN BY CYCLOADDITION REACTIONS WITH OXABENZONORBORNADIENE

Tadashi Sasaki, Ken Kanematsu, Masayuki Uchide, Kenji Hayakawa, and Kinji Iizuka
Institute of Applied Organic Chemistry, Faculty of Engineering, Nagoya University, Chikusa, Nagoya

The dienophilicity and dipolarophilicity of oxabenzonorbornadiene(1) are expected to be increased by ring strain and futher by the orbital participation of the n-electrons of the proximate oxygen atom.

The nature of (1) was studied by performing MO calculations and by investigating cycloadditions to some ene-compounds, dipolar compounds, and dienes.

The thermal cycloaddition reactions of (1) with ene-compounds such as diethyl azodicarboxylate(2), 4-phenyl-1,2,4-triazoline-3,5-dione(3), and chlorocyanoacetylene(4) gave the concerted 1,4-cycloadduct(5), 1:1 adduct(7) and (10) which might be proceeded via stepwise cycloaddition through a dipolar intermadiate followed by the Wagner-Meerwine rearrangement, and 1,2-cycloadduct(9), respectively.

The reactions of (1) with some dipolar compounds such as phenylglyoxylonitrile oxide(11), 1-methylpyridinium-3-olate(13), ethyl azidoformate, and phenyl azide gave the corresponding 1:1 adducts. Similar treatments of (1) with benzenesulphonyl and tosyl azide afforded only imine derivatives.

Reaction of (1) with 6,6-dimethylfuluvene yielded a mixture of isomeric 1:1 and 1:2 adducts. The reactions of (1) with tropone and tropolone gave rise to the $[4+2]\pi$ *endo,exo*-(22a), and *exo,exo*-(24b) cycloadducts, respectively, in relatively high yield. However, attempted reaction of (1) with cycloheptatriene to give a bicyclo[3,2,2]nona-2,6-diene skeleton is unsuccessful. This is probably because (1) is an electron-rich dienophile and reacts preferentially with more electron-deficient dienes in inverse Diels-Alder reactions.

Thus, a ready chemical transformation of bicyclo[3,2,2]nona-3,6-dien-2-one into the bicyclo[3,2,2]nona-2,6-diene skeleton is attempted.

The dimethyl carboxamide(27c) which was easily prepared from the photoinduced reaction of (22a) in the presence of dimethylamine was converted into compound(30) containing the bicyclo[3,2,2]nona-2,6-diene skeleton, by Hofmann degradation, followed by Cope rearrangement.