

MOLECULAR DESIGN BY CYCLOADDITION REACTIONS

WITH OXABENZONORBORNADIENE

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The dienophilicity and dipolarophilicity of oxabenzonorbornadiene(1) are expected to be increased by ring strain and further 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 chlorocynoacetylene(4) gave the concerted 1,4-cycloadduct(5), 1:1 adduct(7) and (10) which might be proceeded via stepwise cycloaddition through a dipolar intermediate followed by the Wagner-Meerwein 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-dimethylfulvene 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.