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Studies of Bridged Benzoheterocycles. I. Cycloaddition of Oxabenzonorbornadiene to Azo- and Acetylenic Compounds.

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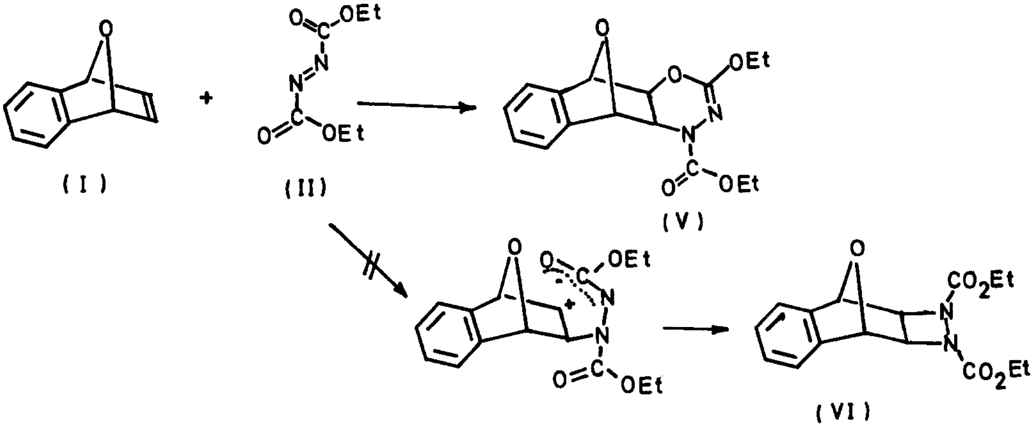
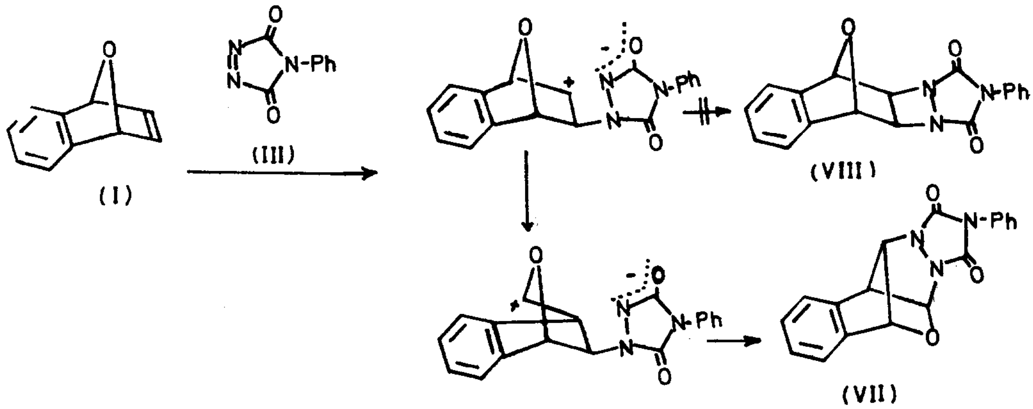
The nature of the benzonorbornadienyl skeleton is a subject of current interest.[1)] However, no systematic study has been reported on the cycloaddition reactions of the benzonorbornenyl compounds.[2)] Our purpose of this work is to characterize the products of a variety of the addition reactions of such bridged oxabenzonorbornadiene (1,4-dihydro-1,4-endoxynaphthalene) (I), effective dienophiles or dipolarophiles,[3)] since the dienophilicity of compound (I) might be increased by the ring strain, and further by the orbital participation of the n-electrons of the proximate oxygen atom.

We now wish to describe the thermal cycloaddition reactions of oxabenzonorbornadiene to versatile ene-components such as diethyl azidoformate (II), 4-phenyl-1,2,4-triazoline-3,5-dione (III), and chlorocyanoacetylene (IV). Reaction of I with diethyl azidoformate (II) in refluxing benzene afforded a 1:1 adduct (V) (m.p. 117-119°, $C_{16}H_{18}N_2O_5$) in 30% yield. The NMR spectrum revealed less symmetrical structure of the adduct from the chemical shifts of the two pairs of non-equivalent ethoxycarbonyl protons [τ 5.74(2H, q), 5.82 (2H, q), 8.64 (3H, t) and 8.68 (3H, t)], and two protons between dihydrofuran and dihydro-1,3,4-oxadiazine rings [τ 5.38(1H, d, J= 6.5 Hz and τ 5.99 (1H, d, J= 6.5 Hz)]. In addition, a singlet signal due to the oxygen bridgehead protons at τ 4.63 (2H) indicated both the dihedral angles between the oxygen bridgehead and the center bridge protons being approximately 90°. Thus, the structure was assigned as exo-1,4-cycloadduct, and the symmetrical adduct (VI) can be ruled out. Surprisingly the orbital symmetry-allowed concerted 1,4-cycloaddition ($\pi_s^4 + \pi_s^2$) of azodiformate to I can completely overcome the dis-concerted 1,2-cycloaddition.



Similar treatment of I with III at room temperature gave a 1:1 adduct (VII) (m.p. 162-164°, $C_{18}H_{13}N_3O_3$) in 8% yield. The NMR spectrum showed signals of phenyl protons at τ 2.6 (m, 9H), two protons as each singlet at τ 4.40 and 4.57, and two protons as each doublets at τ 5.50 and 5.62 with the coupling constants of 2.4 Hz. The IR spectrum exhibited absorptions at 1790 and 1715 cm^{-1} due to the triazoline-dione moiety.4) Thus, the assumable symmetrical structure (VIII) could be ruled out and assigned to VII. The formation of VII might be proceeded via stepwise cycloaddition through a dipolar intermediate followed by the Wagner-Meerwein rearrangement since the concerted $\pi_s^2 + \pi_s^2$ diazetidine formation is forbidden by the Woodward-Hoffmann rules5) even using a cis-locked azodicarbonyl compound.



Reaction of I with IV in benzene in a sealed tube at 90-100° gave 51% yield of a mixture of X and XI. The NMR spectrum is shown in Figure 1. From the ratio of the integrated areas for each peak at τ 4.87 and 6.98 (each singlet) attributable to the bridgehead protons of X, and those at τ 4.49 and 4.62 (each singlet), and τ 5.94 and 6.87 (each doublet, J= 7.0 Hz) due to the bridgehead protons of XI, the product distribution of X to XI was 16:1.

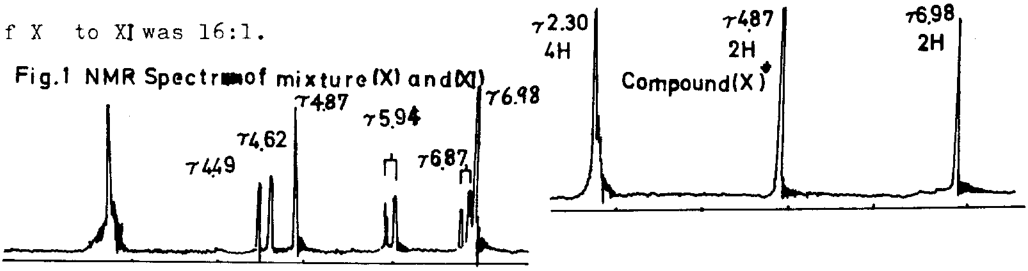
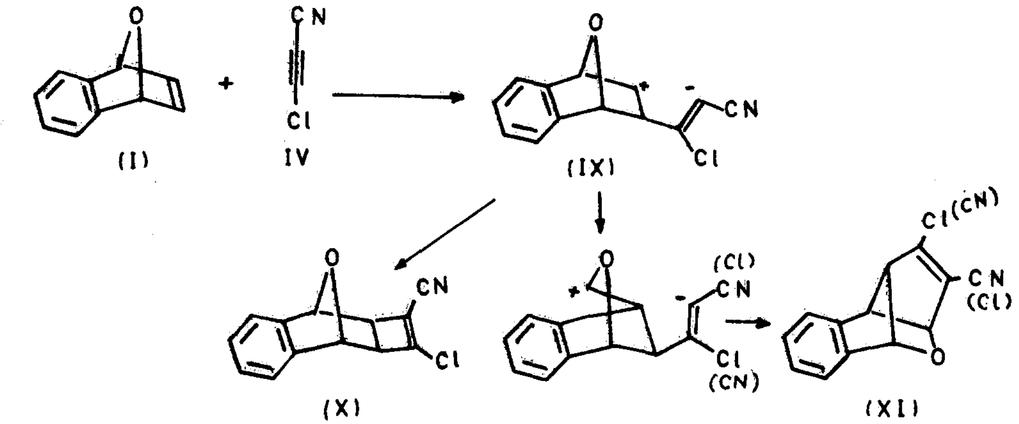


Fig.1 NMR Spectrum of mixture (X) and (XI)

The major product (X)* was isolated from the reaction mixture by column chromatography [m.p. 154-155°, IR 2250 (C≡N) and 1620 (C=C) cm^{-1}, $C_{13}H_8NOCl$], while the isomeric minor product (XI) could not be separated by column chromatography or by repeated recrystallization. Interestingly, the formations of X and XI could be interpreted as the result of the step-wise 1,2-cycloaddition fashion and by the Wagner-Meerwein type rearrangement *via* the dipolar intermediate (IX), in which the rearranged product formation in the cycloaddition reactions seems to be the first case in the series of the benzoheterocycles.



References

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