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ELECTROPHILIC ADDITION TO BICYCLO[6.1.0]NONATRIENE

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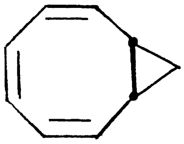
Reaction of *cis*-bicyclo[6.1.0]nonatriene with an IN_3 solution, a mixture of iodine azide and sodium azide, gave a *cis*-bisazide in quantitative yield. The mechanism of the reaction is discussed on the bishomotropylium cation or cyclopentadienyl cation intermediate proposed.

Recently, considerable interest has been shown in the mechanism of the thermal[1)] and photochemical[2)] reorganization of *cis*-bicyclo[6.1.0]nona-2,4,6-triene (1) based on orbital symmetry consideration, and intricate interconversion have been observed to occur between 1,2,3, and 4, etc; some cycloaddition reactions of 1 have been reported.[3)] By contrast, electrophilic additions to 1 have been little scrutinized.[4)]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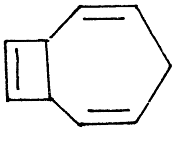
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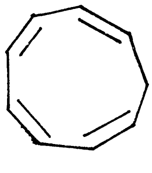
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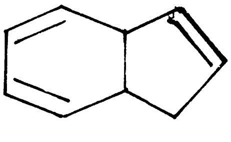
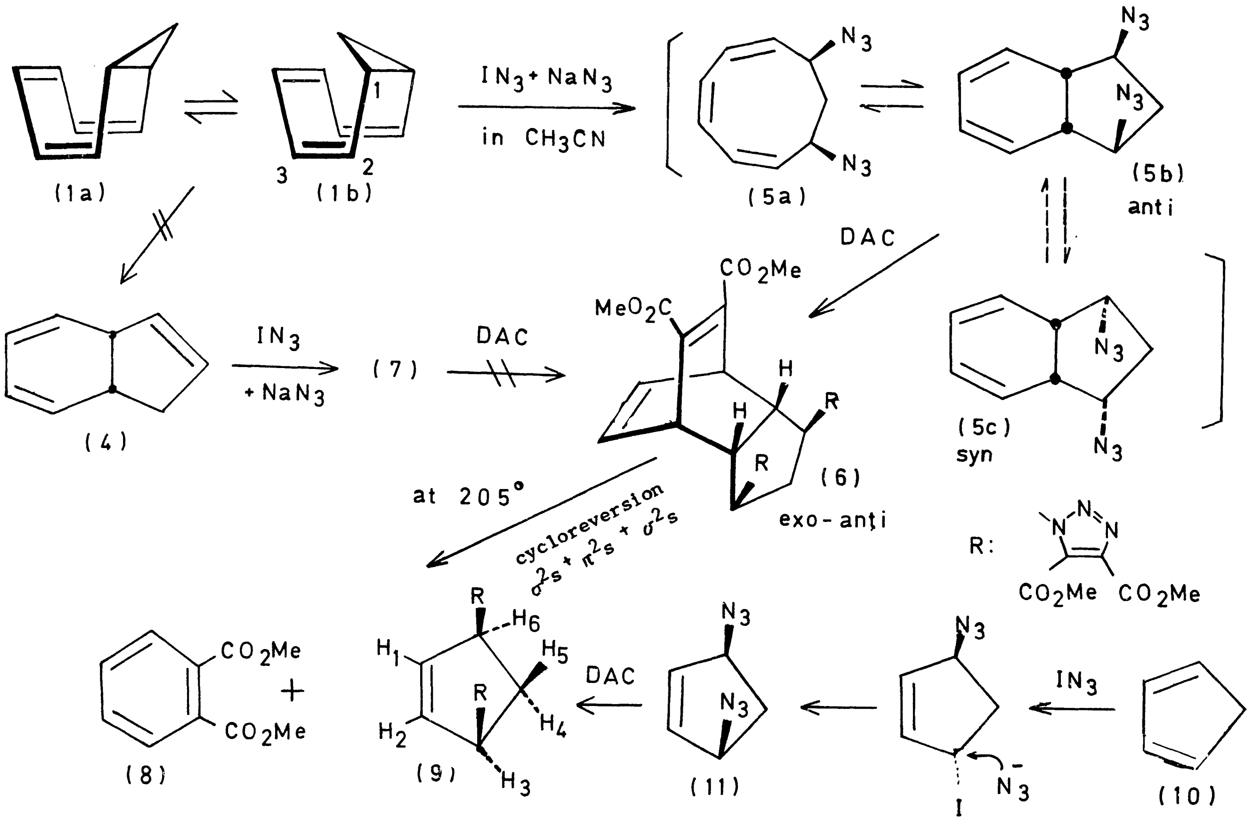
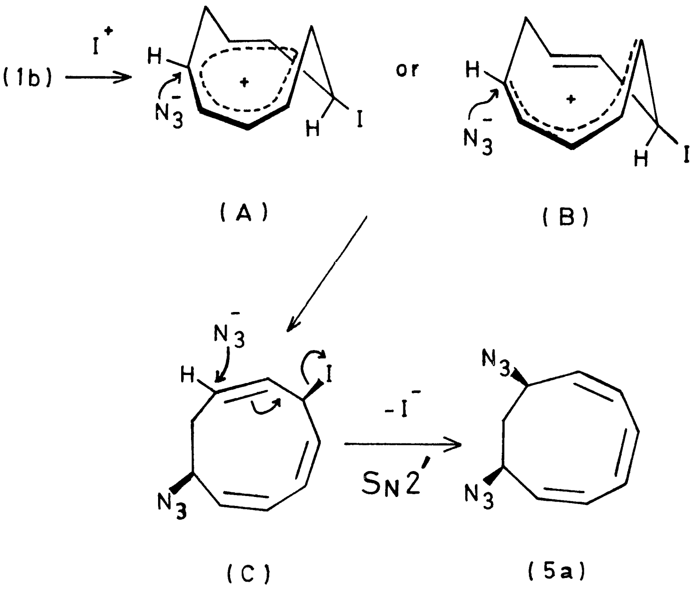

(4)

As an extension of our previous work,[5)] we have investigated the electrophilic addition reaction of 1 with an IN_3 solution.

The reaction of 1 with an IN_3 solution prepared *in situ* from excess sodium azide and iodine monochloride in acetonitrile afforded an oily compound (5) in quantitative yield. The compound (5) showed a strong azido absorption at 2100 cm^{-1} in the ir spectrum and no cyclopropane ring protons by the nmr spectrum. The structure determination of 5 was based on that of its 1,3-dipolar cycloadduct; treatment of 5 with dimethyl acetylenedicarboxylate gave crystalline compound (6), mp 215-217°C, $C_{27}H_{28}N_6O_{12}$, suggesting of Diels-Alder cycloadduct of bis-triazolo compound. The nmr spectrum[τ 3.20 (2H, t, J= 3.8 Hz), 5.15 (2H, m), 6.00 (6H, s, 2 CO_2CH_3), 6.05 (6H, s, 2 CO_2CH_3), 6.30 (6H, s, 2 CO_2CH_3), 6.0-6.8 (5H, complex multiplets), 7.32 (1H, dt, J= -14.6 and 7.3 Hz)] suggested the structure of the adduct (6). For further structural elucidation, the pyrolysis of the adduct (6) was carried out at 205°C in a sealed tube and gave a mixture of dimethyl phthalate (8) and bis-triazolo derivative (9), mp 148-150°C, $C_{17}H_{18}N_6O_8$; compound (9) was assigned as the *cis*-3,5-bistriazolocyclopent-1-ene from the nmr spectrum; it displayed two equivalent vinyl protons (H_1 and H_2) as a singlet at τ 3.62, two equivalent methine protons (H_3 and H_6) as a double doublet ($J_{3,4}= J_{6,4}=$ 7.5 Hz and $J_{3,5}= J_{6,5}=$ 6.8 Hz) at τ 3.75, two methyl protons of two methoxycarbonyl groups as two singlet patterns at τ 6.00 and 6.08, the one of the methylene protons (H_4) as a double triplet ($J_{4,5}=$ -13.6 Hz and $J_{4,3}= J_{4,6}=$ 7.5 Hz) at τ 6.50, and the other (H_5) as double triplet ($J_{5,4}=$ -13.6 Hz and $J_{5,3}= J_{5,6}=$ 6.8 Hz) at τ 7.36. On the other hand, similar treatment of cyclopentadiene (10) and the IN_3 solution gave an oily compound (11), which was converted to a cycloadduct (9) with DAC; the nmr spectrum was completely identical those of the product (9) prepared from the pyrolysis of 6. Although the stereochemistry of 6 was not clearly revealed by the nmr data, it was tentatively assigned the *exo-anti*-configuration (6) by consideration of the steric effect; that is to say, the configuration of 5b was more favorable than that of 5c because of the steric interaction between two azido functions and the vinyl hydrogens.



On the other hand, similar treatment of bicyclo[4.3.0]nona-2,4,7-triene (4)1) with the IN$_3$ solution under the same conditions as described above gave a labile 1:1 adduct (7). Compound (7) exhibited a strong azido absorption at 2100 cm^{-1} in the ir spectrum and gave a positive Beilstein halogen test, but could not afford the 1,3-dipolar cycloadduct (6) to DAC and only intractable materials were obtained. Thus, the formation of the bisazide (5) through the pathway of 1 to 4 followed by addition to the IN$_3$ solution might be excluded at least. Although the mechanisms for the stereospecific formation of bisazide (5) is not clear at present stage, one possible mechanism involving the *bishomotropylium cation*6) or the *cyclopentadienyl cation* intermediate could be considered for the formation of the bisazide (5); initial IN$_3$ addition to compound (1) could be expected to lead to the intermediacy (C) *via* the cationic intermediates [(A) or (B)] followed by S$_N$2' reaction with the azido ion to give 5a as illustrated in the following scheme.



In these connections, recently, Paquette *et al*4c) reported that the reaction pathway in the cycloaddition reaction of 1 with tetracyanoethylene or chlorosulfonyl isocyanate involved electrophilic attack of the reagent at C-3 of the less bicyclononatriene tub conformation (1b) and the generation of *trans*-1,3-bishomotropylium ion or pentadienyl cation is followed by the C-C bond formation affording uniquely a *trans*-fused cyclobutane ring.

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