MOLECULAR DESIGN BY CYCLOADDITION REACTIONS. XIII.[1] CYCLOADDITION OF 1,3-DIPHENYLISOBENZOFURAN WITH *CIS*-BICYCLO[6.1.0]NONA-2,4,6-TRIENE

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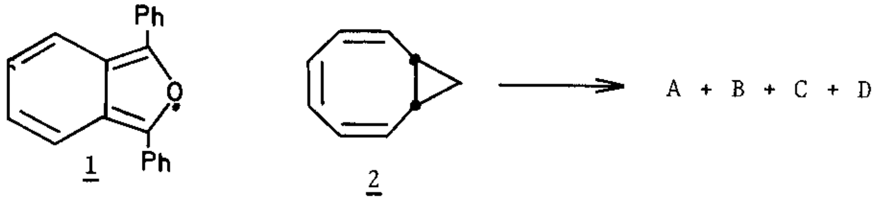
Cycloaddition reaction of 1,3-diphenylisobenzofuran with *cis*-bicyclo[6.1.0]nona-2,4,6-triene gave four 1:1 adducts. The structural elucidation of major products was accomplished by spectral evidences and chemical properties. Possible mechanism for the reaction is also discussed.

1,3-Diphenylisobenzofuran (1) has proved to be useful as a trapping agent for highly reactive and non-isolable intermediates such as benzyne,[2] *trans*-cycloheptene,[3] and benzocyclobutadienes.[4] However, attempts to effect the thermal reactions of 1 with medium-sized ring unsaturated compounds such as cycloheptatriene, tropone, and cyclooctatetraene were unsuccessful in our experiments.[5]

In the course of our studies on the cycloaddition reactions of cyclic conjugated trienes with various heterodienes,[1] we report here the cycloaddition reaction of 1 with *cis*-bicyclo[6.1.0]nona-2,4,6-triene (2) for the purpose of trapping of any common key intermediate, *i.e.*, the cyclobutene intermediate (3), since considerable interest has been shown in the mechanism of the facile thermal reorganization of 2 to *cis*-dihydroindene (4).[6,7]

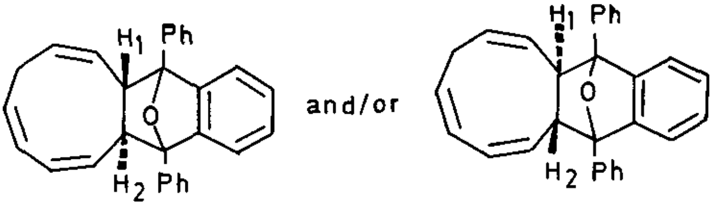
Treatment of 1 with an equimolar amount of 2 in boiling benzene led to four 1:1 adducts: (A), 40%, colorless crystals, mp 140-142°, (B), 30%, colorless plates, mp 188-191°, (C), 10%, colorless plates, mp 145-150° (decomp.), and (D), 5%, colorless needles, mp 130-135° (decomp.). Major products (A) and (B) were thermally stable under more drastic conditions. Catalytic hydrogenation (Pd/C or PtO_2) of compounds (A) or (B) gave complex mixtures of partially hydrogenated products by nmr inspections, which could not be separated. By contrast, thermal decomposition of minor products (C) and (D) easily proceeded at their melting points to give starting material (1).



The uv spectra of the adducts (A) and (B) in ethanol reveal a shoulder at 220 nm (log ε 4.34) and 221 nm (log ε 4.35) together with absorptions originated from aromatic rings, respectively, which suggest the presence of a conjugated diene in an eight or nine-membered ring.[8] The 100 MHz spectrum of major product (A) taken in $CDCl_3$ shows signals at δ 2.30-2.85 (m, 3H), 3.04 (dd, J=10.0 and 4.0, 1H), 5.13 (t, J=10.0 Hz, 1H), 5.32-6.10 (m, 5H), and 7.05-7.80 (m, 14H). The spectrum of compound (B) exhibits signals at δ 2.40-2.60 (m, 2H), 2.90 (q, J=10.5 Hz, 1H), 3.30 (t, br.,

$J=4.0$ Hz, 1H), 5.30-6.00 (m, 6H), and 7.00-7.80 (m, 14H). The presence of six olefinic and four aliphatic protons in the presence of compounds (A) and (B) firmly implicated a monocyclic hydrocarbon segment. Besides, significant observations in the spectra are concerned with the magnitude of the vicinal coupling ($J_{1,2}=4.0$ Hz) indicating clearly its *trans*-configuration.[9]

Assignments of these signals and coupling constants in compounds (A) and (B) were confirmed by spin-decoupling experiments. From these results, compounds (A) and (B) are proposed to be *trans*-fused cyclononatriene derivatives (5).[10]



On the other hand, the presence of four olefinic and six aliphatic protons in the spectra of minor products (C) and (D) implicated a bicyclic hydrocarbon segment. These substances also isolated by the reaction of compound (4) with 1 at 80°. From these results, compounds (C) and (D) are decided to be 1:1 adducts of 1 and 4, but not 1 and 3. However, it is difficult to determine their structures at present, because of the complexity of their nmr signals.

$$\underline{1} + \underline{4} \longrightarrow \mathrm{C} + \mathrm{D}$$

As described above, the reaction of 1 with 2 gave readily *trans*-fused cyclononatriene derivatives in total yields of 70%. By contrast, Paquette and coworkers[11] reported that the electrophilic addition of 2 with tetracyanoethylene or chlorosulfonyl isocyanate gave *trans*-fused cyclononatriene derivatives *via* transient of dipolar *trans*-1,3-bishomotropylium ions. While, mechanism of the cycloaddition reaction of 1 with various olefins has been discussed; compound (1) is not only expected to react as a diene, but also as a 1,3-dipolar (a carbonyl ylids system).[12] Although the reaction of the cycloaddition of 1 with 2 might proceed *via* the cationic intermediate, the formation of compounds (A) and (B) could rather be considered to be the [4+2] cycloaddition of 2 with highly reactive intermediate, *cis*[2], *trans*, *cis*-cyclononatetraene,[6] since the reaction of 1 with 2 could not proceed below the reorganizing temperature of 2 to 4.

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