

MOLECULAR DESIGN BY CYCLOADDITION REACTIONS. X.¹ PHOTOCHEMICAL
CROSS CYCLOADDITION OF 1,3-DIPHENYLISOBENZOFURAN TO CYCLOHEPTATRIENE

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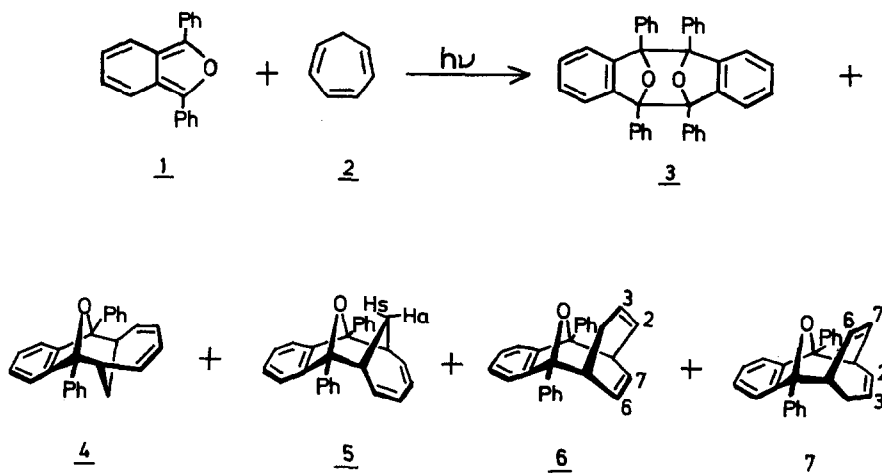
A considerable interest has been shown in the singlet state complexes, especially as the intermediates of the photocycloadditions.²

1,3-Diphenylisobenzofuran has been known to be a strong fluorescent compound³ and converted to the dimer by exposure to sunlight.⁴ It is surprising that there is little study on the photochemical cross addition of 1,3-diphenylisobenzofuran (1), compared with a large number of its thermal cycloadditions.⁵

In the course of our studies on the cycloaddition reactions of cyclic conjugated trienes,⁶ we report here the first example on the cross photocycloaddition of 1 to cycloheptatriene (2).

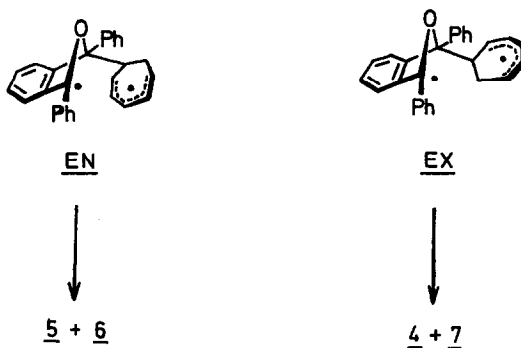
Irradiation of 1 and excess 2 in ethanol with a 100-W Hg lamp through a Pyrex filter yielded four 1:1 adducts 4 - 7⁷ besides a known photodimer (3) of 1 after the immediate disappearance of the strong fluorescence. Compound 4 (*exo*[6+4]cycloadduct) was isolated in 16% yield: mp 181-183°; uv max (ethanol) 248 nm (ϵ 3700); ir (KBr) 1000, 990, and 740 cm^{-1} ; nmr (CDCl_3) δ 1.98 (m, 2, CH_2), 3.11 (t, 2, $J = 6.0$ Hz, $\text{C}=\text{C}-\text{CH}\times 2$), 5.78 (m, 4, $\text{CH}=\text{CH}\times 2$), 7.02 (m, 4, ArH), and 7.45 ppm (m, 10, ArH). Catalytic hydrogenation of 4 gave a tetrahydro derivative 8, mp 241-243°. Compound 5 (*endo*[6+4]cycloadduct) was isolated in 20% yield: mp 250-252°; uv max (ethanol) 260 nm (ϵ 5500); ir (KBr) 1000, 750, and 700 cm^{-1} ; nmr (CDCl_3) δ 1.30 (dd, 1, $J = 12.0$ and 2.0 Hz, *anti*-CH), 2.82 (ddd, 1, $J = 12.0$, 6.5, and 4.5 Hz, *syn*-CH), 3.53 (t, 2, $J = 6.5$ Hz, $\text{C}=\text{C}-\text{CH}\times 2$),

5.13 (5-line pattern, 2, =CH-CH=),⁸ 6.05 (m, 2, C=CH₂), 6.63 (m, 4, ArH), and 7.50 ppm (m, 10, ArH). The *syn*-proton at the bridge is remarkably deshielded by the oxygen bridge.⁹ Catalytic hydrogenation of 5 gave a tetrahydro derivative 9, mp 233-235°. Compound 6 (*endo*[4+4]cycloadduct) was isolated in 14% yield: mp 180-182°; uv max (ethanol) 260 (ε 1700) and 274 nm (ε 1100); ir (KBr) 1020, 750, and 700 cm⁻¹; nmr (CDCl₃) δ 2.30 (m, 2, C=CCH₂), 3.08 (m, 1, C=CCH), 3.50 (m, 1, (C=C)₂CH), 5.39 (ddd, 1, J = 9.5, 7.5, and 2.0 Hz, H-2), 5.66 (ddd, 1, J = 9.5, 4.5, and 3.0 Hz, H-3), 5.68 (ddd, 1, J = 9.0, 6.0, and 2.0 Hz, H-6), 5.79 (ddd, 1, J = 9.0, 7.0, and 2.0 Hz, H-7),¹⁰ and 7.35 ppm (m, 14, ArH). Catalytic hydrogenation of 6 gave a tetrahydro derivative 10, mp 188-189°. Compound 7 (*exo*[4+4]cycloadduct) was isolated in 4% yield: mp 161-163°; uv max (ethanol) 260 (ε 1100) and 278 nm (ε 800); ir (KBr) 1000, 750, and 690 cm⁻¹; nmr (CDCl₃) δ 2.31 (m, 2, C=CCH₂), 3.39 (m, 1, C=CCH), 3.82 (m, 1, (C=C)₂CH), 5.21 (ddd, 1, J = 10.0, 4.5, and 3.0 Hz, H-3), 5.38 (ddd, 1, J = 10.0, 7.5, and 2.0 Hz, H-2), 5.81 (ddd, 1, J = 9.0, 7.5, and 2.0 Hz, H-6), 5.97 (ddd, 1, J = 9.0, 7.0, and 2.0 Hz, H-7),¹⁰ and 7.30 ppm (m, 14, ArH).



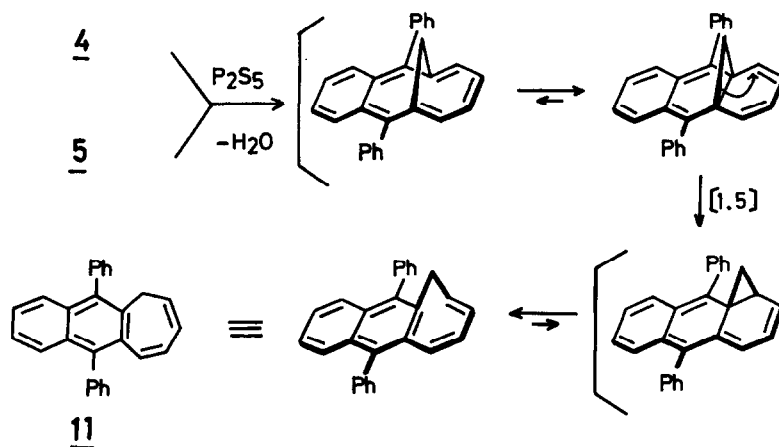
Prolonged irradiation of each adduct under the same conditions resulted in no changes suggesting no interconversions of these adducts. While the possi-

bility of the concerted [4+4] cycloaddition cannot be omitted, such results are readily understandable in terms of a two-step mechanism. Consideration of two possible geometries of the singlet biradical intermediates (EX and EN)^{2b} that might arise in the reaction leads to the conclusion that intermediate EX can produce either 4 or 7 by a least-motion process and that intermediate EN can produce either 5 or 6.



No formation of [4+2] adducts is presumed to be as a result of an energetically unfavored ring closure. This behavior is similar to that which we recently observed in the photochemical reaction of 2 with anthracene.⁶ Sensitized irradiation (benzophenone in benzene) sharply retarded the appearance of the adducts (4-7). Furthermore, the fluorescence of 1 was efficiently quenched by 2; the Stern-Volmer plot for the fluorescence quenching of 1 by 2 in ethanol showed the straight line, from which $K_q\tau_s$ was calculated to be 3.94 M^{-1} . Thus, it seems plausible that some of the photochemical reactions could be initiated by the singlet exciplex formation between 1 and 2 followed by the stepwise σ -bond formation. Finally, dehydration of 4 or 5 by P_2S_5 or polyphosphoric acid gave a skeletal rearranged product (11): mp 194-195°; uv max (ethanol) 260 (ϵ 16900), 274 (sh, ϵ 14300), and 318 nm (ϵ 11650); ir (KBr) 3020, 760, 740, and 690 cm^{-1} ; nmr (CDCl_3) δ 2.86 (d, 2, $J = 6.0 \text{ Hz}$, $\text{C}=\text{CCH}_2$), 5.83 (m, 1, $\text{C}=\text{CH}$), 6.10 (m, 1, $\text{C}=\text{CH}$), 6.72 (dd, 1, $J = 11.0$ and 2.0 Hz , $\text{C}=\text{CH}$), 7.02 (m, 1, $\text{C}=\text{CH}$), and 7.23 ppm (m, 14, ArH).¹¹ Interestingly, the formation of compound 11 might proceed through initial dehydration of 4 or 5 to give an intermediacy of a benzo-methano[10]annulene followed by a valence-bond

isomerization, which then rearranges by a thermal [1,5] shift to 11.¹²



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