Photochemical and Thermal Cycloaddition Reactions of 1,3-Diphenylisobenzofuran with Cycloheptatriene[1]

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Abstract: Irradiations (Pyrex, >290 nm) of 1,3-diphenylisobenzofuran (**1**) with a large excess of cycloheptatriene (**2**) gave a mixture of formal [6 + 4] and [4 + 4] adducts with exo and endo configurations (**4**, **5**, and **6**, **7**) together with a known photodimer (**3**). Similar irradiations in air-saturated solvents gave a photooxidation product [1,2-dibenzoylbenzene (**8**)] besides all above products. The formation mechanisms for these products were also investigated. Remarkable solvent effects for the reactions were observed in polar and nonpolar solvents by the presence and absence of oxygen. The formation of the [4 + 4] adducts may proceed by a concerted manner *via* an exciplex intermediate in π–π^* singlet state. On the other hand, the [6 + 4] adducts are thought to arise from the excited π–π^* triplet state of **1** indicating a stepwise mechanism. In contrast, the thermal reaction of **1** with **2** afforded a mixture of endo [4 + 2] and exo [6 + 4] adducts by way of a concerted mechanism.

It is well known that conjugated dienes quench the fluorescence of aromatic hydrocarbons *via* exciplex formation,[2-5] and that some cycloaddition reactions follow as deactivating processes.[6-11] Recently, we have reported similar behavior of some cyclic trienes: cycloheptatriene efficiently quenched the fluorescence of anthracene followed by the cycloaddition reactions to give [6 + 4] and [4 + 4] cycloadducts. These adducts were considered to be formed *via* a common exciplex intermediate.[12] A question, whether these observations on the cyclic triene are general or not, led us to examine other systems.

1,3-Diphenylisobenzofuran, a highly fluorescent compound,[13] has been known for a long time to convert to the dimer on exposure to sunlight.[14] It is surprising, however, that there is little study on the photochemical crossaddition of 1,3-diphenylisobenzofuran compared with a large number of its thermal cycloadditions,[15] while the nature of the excited states has been elucidated by study of the photooxidation reaction.[16,17]

As one of our studies on the cycloaddition reactions of cyclic conjugated trienes,[18] we have investigated the photochemical and thermal cycloaddition reactions of 1,3-diphenylisobenzofuran with cycloheptatriene. These results are discussed in detail in this paper in comparison with the previous work[12a] and with additional data that we have obtained.[12b]

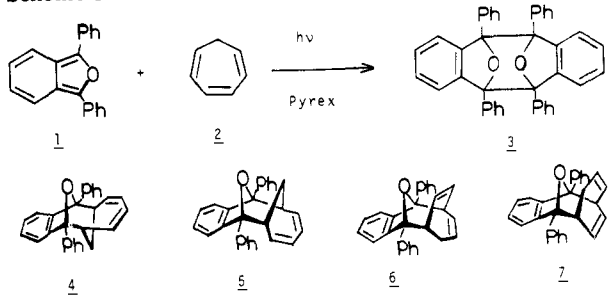
Results

Photochemical Cycloaddition Reactions. When a solution of 1,3-diphenylisobenzofuran (**1**) and a large excess of cycloheptatriene (**2**) in ethanol was irradiated with a high-pressure mercury lamp (100-W) in a Pyrex vessel at room temperature, the fluorescent color of **1** was immediately discharged. After removal of the known photodimer **3**[14] (35%) which precipitated during the irradiation, careful chromatography of the photolysis mixture on silica gel gave four adducts,[19] **4** (11.5%), **5** (14.5%), **6** (3.6%), and **7** (10%), together with 1,2-dibenzoylbenzene (**8**, 21%) (a photooxidation product).[16,17]

Similar irradiation in benzene gave the same photoproducts but in the different ratio (**3**, 26%; **4**, 5.5%; **5**, 9.5%; **6**, 7%; **7**, 11.5%; and **8**, 37%), and no other 1:1 adducts were detectable by thin-layer chromatography[19] and nmr spectroscopy.

The structural assignments were made on the basis of elemental analyses and spectroscopic data. The mass spectrum of each adduct displayed a molecular ion peak at *m/e* 362 and prominent fragments at *m/e* 270 (1,3-diphenylisobenzofuran, base peak) and 91 (tropylium ion) originating

Scheme I

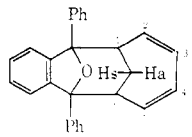
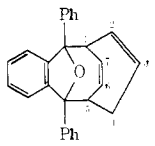
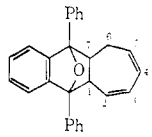


from a cycloreversion fragmentation. The uv spectra suggested the similarities in the structures of **4** and **5** and of **6** and **7** (see Experimental Section). The nmr spectra which permitted the eventual assignments of the structures are summarized in Table I.

The highly symmetrical structures of **4** and **5** were suggested by the presence of two equivalent allylic methine protons at δ 3.11 (t) and 3.53 (t), respectively. The downfield shift of the syn bridged methylene proton (H_s-7) of **5** at δ 2.82 compared with the anti methylene proton (H_a-7) at δ 1.30 was attributable to the anisotropic deshielding effect of the oxygen bridge.[20,21] A large difference in the chemical shifts of the methylene bridge protons has been observed in the nmr spectrum of a 1:1 adduct of 1,3-diphenylisobenzofuran with norbornadiene.[22] Such an effect was not observed, however, for the adduct **4**, and two methylene protons appeared at δ 1.98 (2 H, m).[22] These characteristic differences allow ready identification of two stereoisomers. Additionally, catalytic hydrogenations of **4** and **5** gave tetrahydro derivatives **9** and **10**, respectively, and the nmr spectra were also suggestive of highly symmetrical structures. The similar deshielding effect of the oxygen bridge was observed only for **10** (see Experimental Section). Thus, the former two adducts were concluded to be exo [6 + 4] (**4**) and endo [6 + 4] cycloadducts (**5**), which are not allowed to arise in a concerted fashion from an excited state by orbital symmetry theory.[23]

The nmr spectrum showed two kinds of bridgehead methine protons for **6** at δ 3.39 (H-5, allylic) and 3.82 (H-1, bisallylic) and for **7** at δ 3.08 and 3.50, suggesting that the structures lacked an element of symmetry. The olefinic protons of **6** and **7** were readily assigned by comparison with those of previously reported cycloheptatriene and anthracene adducts,[12,24] and these spectral features were completely compatible with [4 + 4] adducts. The downfield shift ($\Delta\delta$ *ca.* 0.3 ppm) of the methine proton signals of **6** compared with the corresponding signals of **7** was attribut-

Table I. Nmr Data of the Adducts

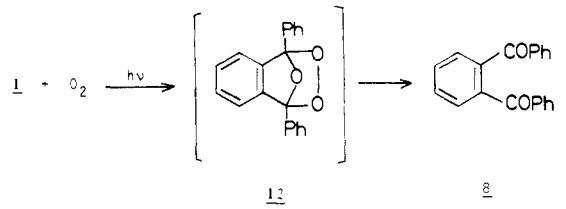
Structure	Compd	Chemical shifts, δ (J in hertz) Methylene H	Methine H	Olefinic H	Aromatic H
	**4** (exo)	1.98 (m, 2 H, H_a, H_s)	3.11 (t, 2 H, J = 6.0, H_1, H_6)	5.78 (m, 4 H, H_2, H_3, H_4, H_5)	7.02 (m, 4 H) 7.45 (m, 10 H)
	5 (endo)	1.30 (dd, 1 H, J = 12.0, 2.0, H_a) 2.82 (ddd, 1 H, J = 12.0, 6.5, 4.5, H_s)	3.53 (t, 2 H, J = 6.5, H_1, H_6)	5.13 (5-line pattern, 2 H, H_3, H_4) 6.05 (m, 2 H, H_2, H_5)	6.63 (m, 4 H) 6.63 (m, 4 H) 7.50 (m, 10 H)
	**6** (exo)	2.31 (m, 2 H, H_4)	3.39 (m, 1 H, H_5) 3.82 (m, 1 H, H_1)	5.21 (ddd, 1 H, J = 10.0, 4.5, 3.0, H_3) 5.38 (ddd, 1 H, J = 10.0, 7.5, 2.0, H_2) 5.81 (ddd, 1 H, J = 9.0, 7.5, 2.0, H_6) 5.97 (ddd, 1 H, J = 9.0, 7.0, 2.0, H_7)	7.30 (m, 14 H)
	7 (endo)	2.30 (m, 2 H, H_4)	3.08 (m, 1 H, H_5) 3.50 (m, 1 H, H_1)	5.39 (ddd, 1 H, J = 9.5, 7.5, 2.5, H_2) 5.66 (ddd, 1 H, J = 9.5, 4.5, 3.0, H_3) 5.68 (ddd, 1 H, J = 9.0, 6.0, 2.0, H_6) 5.79 (ddd, 1 H, J = 9.0, 7.0, 2.0, H_7)	7.35 (m, 14 H)
	**13** (endo)	1.33 (m, 1 H, H_{6e}) 2.33 (m, 1 H, H_{6e})	3.63 (td, 1 H, J = 10.5, 2.5, H_7) 3.88 (dd, 1 H, J = 10.5, 1.0, H_1)	5.92 (m, 4 H, H_2, H_3, H_4, H_5)	7.33 (m, 14 H)

able to the position of the hydrogens of **6** in the closer distance from the oxygen bridge,[20-22] which was to be expected for the exo isomer by molecular models. Thus, the latter two adducts were concluded to be exo [4 + 4] (**6**) and endo [4 + 4] cycloadducts (**7**).

Control experiments showed that no interconversions of the adducts **4–7** took place under similar reaction conditions. Both [4 + 4] adducts **6** and **7** were photostable and were unchanged after similar irradiation but for much longer time. However, [6 + 4] adducts **4** and **5** were gradually converted by prolonged irradiations to a mixture of several unknown photoproducts,[25] from which no [6 + 4] adducts were detected by nmr inspection (<3%).

1,2-Dibenzoylbenzene (**8**) was considered to arise from 1,4-cycloaddition of oxygen dissolved in the solution to **1**[16,17,26] (Scheme II). Actually, the photooxidation product

Scheme II



8 was exclusively obtained when a solution of **1** and excess **2** in ethanol was irradiated under oxygen.

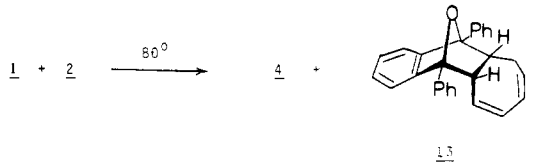
To avoid the formation of **8**, similar irradiations were carried out in various solvents under argon stream. The results are summarized in Table II.

Most significantly, the irradiation of **1** and **2** in benzene solution under argon resulted in a remarkable decrease in the formation of not only **8** but also of **4** and **5**, when compared with that of **6** and **7**. In contrast, the [6 + 4] adducts were formed together with the [4 + 4] adducts by irradiating **1** and **2** in ethanol even under argon. These striking effects of solvents are discussed later.

All adducts obtained as above apparently arose from the photochemically induced reaction. No reactions occurred when solutions of **1** and **2** in benzene were allowed to stand in the dark at the irradiation temperature for 20 hr. When the solutions were heated at 80° for 15 hr, a quite different type of adduct was obtained (*vide infra*).

Thermal Cycloaddition Reaction and Chemical Conversions of the Adducts. When **1** and a large excess of **2** were heated in benzene in a sealed tube for 15 hr at 80°, most of **1** was consumed. Careful chromatography of the reaction mixture on silica gel gave **4** (10%), **13** (20%), and several minor products[27] (Scheme III).

Scheme III



Compound **4** was identical in all respects with the photochemically formed exo [6 + 4] adduct. The nature of **13** as a 1:1 adduct was apparent from the elemental analysis and mass spectrum [*m/e* 362 (M^+), 270 (base peak), and 91]; the fragmentation pattern was similar to those of photoadducts **4–7**. The [4 + 2] nature of **13** was shown by its unsymmetrical nmr feature (Table I) and by its catalytic hydrogenation which gave a tetrahydro derivative **14** after uptake of 2 equiv of hydrogen. The methine protons at δ 3.63 (H-1) and 3.88 (H-7) were remarkably deshielded relative to the cycloheptatriene-anthracene adduct **15** (δ 2.03 and

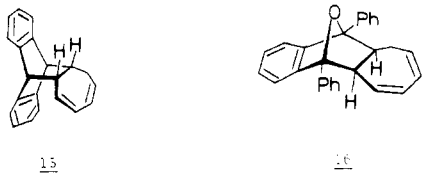


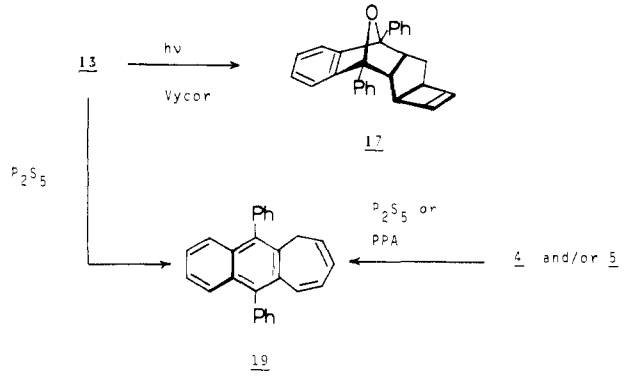
Table II. Solvent Dependence for Formations of [6 + 4] and [4 + 4] Cycloadducts[a]

Solvent[b]	Catalyst	Product ratios[c] of adducts [6 + 4] : [4 + 4]	
EtOH	None	1.1	1.0
	O_2	1.9	1.0
	Azulene	0.2	1.0
	Eosine	0.3	1.0
C_6H_6	None	0.5	1.0
	O_2	0.8	1.0
AcOEt	O_2	1.2	1.0
Cyclohexane	None	0.4	1.0
Chloroform	None	1.3	1.0
Methylene chloride	None	1.3	1.0

[a] Irradiations were carried out at room temperature for 2 hr. [b] 50 ml, 0.003 *M* in **1** and 0.03 *M* in **2**. [c] Photodimer **3** was always obtained in about 40% yield. Furthermore, in the presence of oxygen, 1,2-dibenzoylbenzene (**8**) was also isolated in about 30% yield.

2.73). The exo isomer **16** could not show such an anisotropic deshielding effect because of the anti position of the methine protons to the oxygen bridge.

Scheme IV

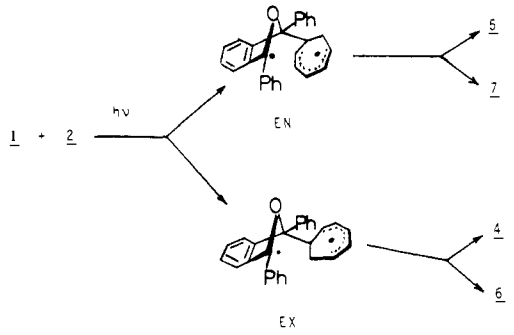


Thus, the new adduct was concluded to be a symmetry-allowed endo [4 + 2] adduct **13**. Further structure elucidation of **13** was also accomplished by the chemical conversions. Irradiation of **13** in benzene with a high-pressure mercury lamp (100-W) through a Vycor filter for 3 hr gave a new isomer **17** in 73% yield[28] (Scheme IV). The structural assignment for **17** was made on the basis of the spectroscopic data. The mass spectrum showed a molecular ion peak at *m/e* 362 with the base peak and at *m/e* 270 (1,3-diphenylisobenzofuran). The 100-MHz nmr spectrum ($CDCl_3$) exhibited signals at δ 1.38 (ddd, 1 H, H_e-6, J = 13.0, 10.0, and 4.0 Hz), 1.89 (ddd, 1 H, H_a-6, J = 13.0, 10.0, and 2.0 Hz), 2.54 (dd, 1 H, H-5, J = 10.0 and 2.0 Hz), 3.02 (d, 1 H, H-2, J = 2.0 Hz), 3.36 (dd, 1 H, H-1, J = 10.0 and 2.0 Hz), 3.94 (td, 1 H, H-7, J = 10.0 and 4.0 Hz), 5.97 (d, 1 H, H-4, J = 2.4 Hz), 6.10 (d, 1 H, H-3, J = 2.4 Hz) and 7.04 (m, 14 H, aromatic). The deshielding effect of the oxygen bridge was observed by the nmr for the methine protons (H-1 and H-7).[29] Catalytic hydrogenation of **17** yielded a dihydro derivative **18** after uptake of 1 equiv of hydrogen. On the other hand, treatment of **13** with phosphorus pentasulfide gave a dehydrated product **19** in 76% yield. The structure of **19** was determined on the spectral evidence (see Experimental Section).[30] Interestingly, compound **19** was also obtained as only one isolable product by dehydration of **4** or **5** with phosphorus pentasulfide or polyphosphoric acid.[12b]

Discussion

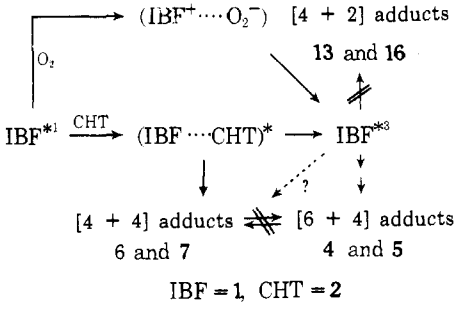
The photochemical cycloaddition reaction of **1** and **2** in ethanol led to the formation of [6 + 4] (**4** and **5**) and [4 + 4] cycloadducts (**6** and **7**). All these adducts were formed early in the photolysis, and the product ratio was found to be unchanged. Furthermore no interconversions of each adduct were observed when the pure isolated samples were irradiated under the same conditions. These results are very similar to those which we recently obtained in the photochemical reaction of **2** with anthracene.[12a] In a preliminary report,[12b] we considered that the reactions might proceed similarly in a two-step mechanism *via* common biradical intermediates, which have two possible geometries (EX and EN) as shown in Scheme V. However this mechanism can-

Scheme V



not explain the striking effects of oxygen and solvents as can be seen in Table II. On the basis of spectroscopic and kinetic data, Olmsted and Akashah have reported that the fluorescence quantum yield of 1,3-diphenylisobenzofuran (**1**) is sensibly unity (ϕ_f = 0.96) in the absence of oxygen, and hence the unimolecular internal conversion and intersystem crossing are negligible.[17] However, in air-saturated solutions, oxygen quenching of the singlet (fluorescence quenching, ϕ_q = 0.12) induced the photooxidation reaction and the intersystem crossing involving no energy transfer to oxygen.[31] Thus, the charge-transfer complex is suggested to be involved in that process[17,32] (see Scheme VI).

Scheme VI



Therefore, the decrease in the ratio of [6 + 4] adducts to [4 + 4] adducts (**4** + **5**/**6** + **7**) in oxygen-free benzene solution compared with that in air-saturated benzene solution suggests that [6 + 4] adducts might arise from the triplet state of **1** in contrast to the formation of [4 + 4] adducts from the singlet state. This is also supported by increase in the total yields of **4** and **5** contrary to decrease in those of **6** and **7** in the heavy-atom solvents (Table II).[33,34]

To obtain further evidence for this postulation, we carried out the quenching experiments using azulene (E_T = ~42 kcal mol^{-1}) which is known to quench the triplet state of **1**[17,35] and anthracene[34] at a diffusion-controlled rate. When a solution of **1** (0.003 *M*), **2** (0.18 *M*), and azulene (0.03 *M*) in ethanol was irradiated under argon stream, only [6 + 4] adducts were quenched; **4** + **5**/**6** + **7** = 0.2 (1.1 when azulene was not used). The reaction was similarly quenched by eosine (E_T = 43 kcal mol^{-1}); **4** + **5**/**6** + **7** = 0.3. By contrast, the photochemical reaction of anthracene with **2** was not affected by azulene,[36] suggesting a different mechanism.

The fluorescence of **1** was readily quenched by **2** with $K_q\tau_s$ of 6.0 ± 0.5 M^{-1} in benzene, which was calculated from the Stern–Volmer plot. Therefore, exciplex formation is involved in the cycloaddition process as is known in other systems.[6-12]

All these observations are most reasonably understood in terms of the mechanism as shown in Scheme VI, which is composed of both singlet and triplet substrate reactions.

The [4 + 4] cycloaddition is a symmetry-allowed process and may occur in a concerted fashion from the singlet exciplex, although the possibility of the stepwise formation *via* a short-lived singlet biradical intermediate cannot be completely excluded. On the contrary, the [6 + 4] cycloaddition which is symmetry forbidden may arise in a stepwise manner from the triplet state. In this event, however, the possibility of the formation of [4 + 4] adducts from the triplet state by a stepwise mechanism cannot be excluded.[33] The 1,6-ring closure of the resulting biradical is presumably favored in the thermodynamic sense.[37] Similarly, it would seem that the thermal [4 + 2] adducts **13** and **16** might be formed in the photochemical reactions through the triplet states.[38] However, no formation of photochemical [4 + 2] adducts may be attributable to the steric hindrance to bond rotation in the intermediacy of the biradical, which is a similar result to that of the reaction of anthracene with **2**.[12]

Additionally, it seems likely that the intersystem crossing is also induced in the fluorescence quenching process of **1** with **2**, since the [6 + 4] adducts are formed even in the absence of oxygen as shown in Table II. In air-saturated solvents, therefore, the triplet state of **1** must be a composite of that induced by the exciplex formation and oxygen quenching (oxygen perturbation).[32] Indeed, photooxidation product **8** was also obtained as suggested by previous work.[17]

The product distribution is also affected by the polarity of a solvent (Table II). The formation of [6 + 4] adducts is more favorable in a polar solvent than in a nonpolar solvent. Recently, it has been established experimentally that both the lowest singlet and triplet excited states of isobenzofurans are π–π^* in nature, insignificantly perturbed by any nearby n–π^* state.[17,39] From this fact, any polarity effect would not be expected. In this connection, Hammond and coworkers have suggested that the exciplex (DQ)* could be formulated as $D^*Q \leftrightarrow DQ^* \leftrightarrow D^+Q^- \leftrightarrow D^-Q^+$.[2,3] Then, it is suggested from the above postulation that the intersystem crossing in the absence of oxygen might occur *via* a somewhat polar exciplex, and its contribution will dominate in a polar solvent.[2]

On the other hand, the thermal reaction of **1** with **2** gave exo [6 + 4] (**4**) and endo [4 + 2] cycloadducts (**13**). Both reactions are symmetry-allowed processes,[23] and the secondary orbital interactions would lead to the [6 + 4] and [4 + 2] cycloadditions to the exo and endo adducts, respectively. Under the reaction conditions, isolated pure products, **4** and **13**, were stable, and no interconversions were observed; both adducts were exclusively cycloreversed to **1** and **2** after melting (by tlc inspection). Furthermore, the cycloaddition reaction was unaffected by change of the solvents. Thus, it is reasonably concluded that the thermal adducts are formed in a competition between concerted [6 + 4] and [4 + 2] cycloadditions. Such a phenomenon is well known for thermal reaction in conjugated polyene systems.[18,40,41] The preference for the [4 + 2] adduct over the [6 + 4] adduct is presumably a result of steric hindrance in the transition states.[42]

Experimental Section

Melting points are uncorrected. Microanalyses were performed with a Perkin-Elmer 240 elemental analyzer. Uv spectra were determined with a JASCO ORD-UV-5 spectrometer. Nmr spectra were taken with JEOL C-60-XL spectrometer and with a Varian A-60 recording spectrometer, with tetramethylsilane as internal standard. Ir spectra were taken with a JASCO-IR-S spectrophotometer. Mass spectra were obtained with a Hitachi RMU-D double-focusing spectrometer operating at an ionization potential of 70 eV. The solid samples were ionized by electron bombardment after sublimation directly into the electron beam at 100–150°.

Photochemical Cycloaddition Reaction of 1,3-Diphenylisobenzofuran (1) with Cycloheptatriene (2). (1) A solution of 0.5 g of **1** and 20 g of **2** in 100 ml of ethanol was irradiated for 2 hr with a 100-W high-pressure mercury lamp (Ushio UM-102) fitted with a Pyrex filter at room temperature. After the precipitated isobenzofuran dimer **3** (170 mg, 35%) was filtered off, the solvent was removed under reduced pressure. The residual solid was chromatographed on a silica gel column. The first fractions using benzene–*n*-hexane (1:7) gave 75 mg (11.5%) of adduct **4** as colorless prisms: mp 181–183° (ethanol); ir (KBr) 3020, 1600, 1300, 1000, 990, and 740 cm^{-1}; uv (ethanol) λ_{max} 248 nm (ϵ 3700); mass *m/e* 362 (parent), 270 (base peak), and 91. *Anal.* Calcd for $C_{27}H_{22}O$: C, 89.47; H, 6.12. Found: C, 89.73; H, 6.35. The second fractions using benzene–*n*-hexane (1:5) gave 95 mg (14.5%) of adduct **5** as colorless needles: mp 250–252° (ethanol); ir (KBr) 3000, 1600, 1000, 750, 700 cm^{-1}; uv (ethanol) λ_{max} 260 nm (ϵ 5500); mass *m/e* 362 (parent), 270 (base peak), and 91. *Anal.* Calcd for $C_{27}H_{22}O$: C, 89.47; H, 6.12. Found: C, 89.19; H, 6.29. The third fractions using benzene–*n*-hexane (1:3) gave 65 mg (10%) of adduct **7** as colorless needles: mp 180–182° (ethanol); ir (KBr) 3020, 1600, 1450, 1020, 750, and 700 cm^{-1}; uv (ethanol) λ_{max} 260 nm (ϵ 1700) and 274 (1100); mass *m/e* 362 (parent), 270 (base peak), and 91. *Anal.* Calcd for $C_{27}H_{22}O$: C, 89.47; H, 6.12. Found: C, 89.30; H, 6.30. The fourth fractions using benzene–*n*-hexane (1:2) gave 25 mg (3.6%) of adduct **6** as colorless prisms: mp 161–163° (ethanol); ir (KBr) 2920, 1600, 1450, 1000, 750, and 690 cm^{-1}; uv (ethanol) λ_{max} 260 nm (ϵ 1100) and 278 (800); mass *m/e* 362 (parent), 270 (base), and 91. *Anal.* Calcd for $C_{27}H_{22}O$: C, 89.47; H, 6.12. Found: C, 89.55; H, 6.20. The fifth fractions using benzene gave 110 mg (21%) of 1,2-dibenzoylbenzene **8**: mp 150–151° (lit.[16,17] mp 148°).

(2) A solution of 1.0 g of **1** and 30 g of **2** in 100 ml of benzene was irradiated for 2 hr under the same condition as described above. After the precipitated dimer **3** (260 mg, 26%) was filtered off, the solvent was removed, and the solid residue was chromatographed to give 55 mg (4.1%) of **4**, 95 mg (6.6%) of **5**, 70 mg (4.9%) of **6**, 115 mg (8.0%) of **7**, and 390 mg (37%) of **8**.

(3) With the use of various solvents, a solution of **1** (0.003 *M*) and **2** (0.03 *M*) in 50 ml of a solvent was prepared. Then the solution was degassed with argon and irradiated for 2 hr through a Pyrex filter under argon stream. After the precipitated dimer **3** was filtered off, the products were isolated by preparative thin-layer chromatography. The results were summarized in Table II.

(4) A solution of **1** (0.003 *M*), **2** (0.03 *M*), and azulene (0.03 *M*) or eosine (0.03 *M*) in 50 ml of ethanol was prepared. The solution was then degassed with argon and irradiated under the same condition as described above. The results were given in Table II.

Fluorescence Quenching. Fluorescence intensities were measured with an Hitachi MPF-2A fluorescence photometer, using an excitation wavelength of 410 nm. A sample (3 ml) containing 2.46 × 10^{-6} *M* diphenylisobenzofuran (**1**) and varying concentrations of cycloheptatriene (**2**) in benzene were placed in a quartz cell. The intensities were measured three times for each cell, and an average value for each sample was used. Thus, $K_q\tau_s$ was calculated to be 6.0 ± 0.5 M^{-1}.

Hydrogenation of Adduct 4. A solution of 30 mg (0.083 mmol) of **4** in 30 ml of ethanol was hydrogenated over 50 mg of 10% Pd/C at atmospheric pressure until 2 equiv (3.7 ml) of hydrogen was consumed. The catalyst was removed by filtration, and the filtrate was concentrated under reduced pressure. Recrystallization from ethanol gave 30 mg (99%) of tetrahydro derivative **9** as colorless prisms: mp 241–243°; ir (KBr) 1000, 750, and 700 cm^{-1}; nmr ($CDCl_3$) δ 1.10–1.78 (m, 10 H), 2.44 (m, 2 H), and 7.05–7.65 (m, 14 H). *Anal.* Calcd for $C_{27}H_{26}O$: C, 88.48; H, 7.15. Found: C, 88.35; H, 7.21.

Hydrogenation of Adduct 5. A solution of 20 mg (0.055 mmol) of **5** in 30 ml of ethanol was hydrogenated over 30 mg of 10% Pd/C at atmospheric pressure until 2 equiv (2.5 ml) of hydrogen was consumed. Work-up as described above gave 20 mg (99%) of tet-

rahydro derivative **10** as colorless needles: mp 233–235° (ethanol); ir (KBr) 1010, 750, and 700 cm^{-1}; nmr ($CDCl_3$) δ 1.21–1.85 (m, 9 H), 2.50 (m, 1 H), 2.83 (m, 2 H), and 6.76–7.65 (m, 14 H). *Anal.* Calcd for $C_{27}H_{26}O$: C, 88.48; H, 7.15. Found: C, 88.35; H, 7.21.

Hydrogenation of Adduct 7. A solution of 40 mg (0.11 mmol) of **7** in 50 ml of ethanol was hydrogenated over 50 mg of 10% Pd/C at atmospheric pressure until 2 equiv (4.9 ml) of hydrogen was consumed. Work-up as described above gave 30 mg (74%) of tetrahydro derivative **11** as colorless needles: mp 188–189° (ethanol); ir (KBr) 1020, 760, and 690 cm^{-1}; nmr ($CDCl_3$) δ 1.30–2.05 (m, 10 H), 2.35–3.00 (m, 2H), and 7.02–7.78 (m, 14 H). *Anal.* Calcd for $C_{27}H_{26}O$: C, 88.48; H, 7.15. Found: C, 88.50; H, 7.27.

Thermal Cycloaddition Reaction of 1 with 2. A solution of 0.958 g of **1** and 15 g of **2** in 20 ml of benzene was heated at 80° under argon in a sealed tube for 24 hr. The solution was then concentrated under reduced pressure and chromatographed on a silica gel column using *n*-hexane–benzene (3:1). The first fractions gave 130 mg (10%) of **4.** The second fractions using *n*-hexane–benzene (2:1) gave 280 mg of **13** as colorless prisms: mp 152–154°; uv λ_{max} (EtOH) 245 nm (ϵ 4900); ir (KBr) 1005, 755, and 695 cm^{-1}. *Anal.* Calcd for $C_{27}H_{22}O$: C, 89.47; H, 6.12. Found: C, 89.48; H, 6.44.

Hydrogenation of Adduct 13. A solution of 30 mg of **13** in 30 ml of ethanol was hydrogenated over 50 mg of 10% Pd/C at atmospheric pressure until 2 equiv (3.7 ml) of hydrogen was consumed. The catalyst was removed by filtration, and the filtrate was concentrated under reduced pressure. Recrystallization from ethanol gave 30 mg (99%) of tetrahydro derivative **14** as colorless prisms: mp 189–192°; ir (KBr) 1450, 1000, 975, 965, 745, and 700 cm^{-1}; mass *m/e* 362 (parent), 270, and 91; nmr ($CDCl_3$) δ 0.94–2.04 (m, 10 H), 3.04 (m, 2 H), and 7.45 (m, 14 H). *Anal.* Calcd for $C_{27}H_{26}O$: C, 88.38; H, 7.15. Found: C, 88.33; H, 7.25.

Irradiation of 13. A solution of 150 mg of **13** in 50 ml of benzene was irradiated for 3 hr with a 100-W high-pressure mercury lamp (Ushio UM-102) fitted with a Vycor filter under argon. The solvent was removed under reduced pressure. Chromatography on a silica gel column using benzene–*n*-hexane (1:3) and recrystallization from ethanol gave 110 mg (73%) of the valence tautomer **17** as colorless needles: mp 148–150°; ir (KBr) 1445, 990, 775, and 690 cm^{-1}; nmr ($CDCl_3$) at 100 MHz δ 1.38 (ddd, 1 H, J = 13.0, 10.0, and 4.0 Hz), 1.89 (ddd, 1 H, J = 13.0, 10.0, and 2.0 Hz), 2.54 (dd, 1 H, J = 10.0 and 2.0 Hz), 3.02 (d, 1 H, J = 2.0 Hz), 3.36 (dd, 1 H, J = 10.0 and 2.0 Hz), 3.94 (td, 1 H, J = 10.0 and 4.0 Hz), 5.97 (d, 1 H, J = 2.4 Hz), 6.10 (d, 1 H, J = 2.4 Hz), 7.04 (m, 14 H). *Anal.* Calcd for $C_{27}H_{22}O$: C, 89.47; H, 6.12. Found: C, 89.58; H, 6.25. Similar irradiation of 150 mg of **13** in 50 ml of benzene for 12 hr under the same conditions as described above through a Pyrex filter resulted in the recovery of the unreacted starting material.

Hydrogenation of Compound 17. A solution of 30 mg (0.083 mmol) of **17** in 30 ml of ethanol was hydrogenated over 30 mg of 10% Pd/C at atmospheric pressure until 1 equiv (1.86 ml) of hydrogen was consumed. The catalyst was filtered off, and the filtrate was concentrated under reduced pressure. Recrystallization from ethanol gave 23 mg (76%) of the dihydro derivative **18** as colorless prisms: mp 159–160°; ir (KBr) 1490, 1450, 750, and 695 cm^{-1}; nmr ($CDCl_3$) δ 1.21–2.31 (m, 6 H), 2.70 (m, 2 H), 3.42 (m, 1 H), 4.14 (m, 1 H), and 6.89–7.41 (m, 14 H). *Anal.* Calcd for $C_{27}H_{24}O$: C, 88.97; H, 6.64. Found: C, 88.90; H, 6.60.

Dehydration of the Adducts. (1) A solution of 0.4 g of **13** and 6 g of phosphorus pentasulfide in 50 ml of carbon disulfide was stirred for 7 hr at room temperature. After removal of the solvent, the residual solid was extracted with benzene. Chromatography on a silica gel column using *n*-hexane gave 290 mg (76%) of **19** as colorless needles: mp 194–195° (ethanol); ir (KBr) 1380, 760, 740, and 690 cm^{-1}; uv (ethanol) λ_{max} 260 nm (ϵ 16,900), 274 (14,300), and 318 (11,650); nmr ($CDCl_3$) δ 2.86 (d, 2 H, J = 6.0 Hz), 5.83 (m, 1 H), 6.10 (m, 1 H), 6.72 (dd, 1 H, J = 11.0 and 2.0 Hz), 7.02 (m, 1 H), and 7.23 (m, 14 H). *Anal.* Calcd for $C_{27}H_{20}$: C, 94.15; H, 5.85. Found: C, 93.89; H, 6.11. (2) Similar dehydration of 100 mg of **4** with 2.0 g of phosphorus pentasulfide in 30 ml of carbon disulfide gave 60 mg (63%) of **19**. (3) Similar dehydration of 90 mg of **5** with 2.0 g of phosphorus pentasulfide in 30-ml of carbon disulfide gave 10 mg (12%) of **19.** (4) A mixture of 30 mg of **4** and 3 g of polyphosphoric acid was heated on a steam bath for 2 days with occasional stirring. The mixture was cooled, and then added to ice–water (20 ml). Extraction with chloroform followed by chromatography on a silica gel column using *n*-hexane gave 15 mg (52%) of **19.**

Acknowledgment. The authors wish to thank Professor T. Goto of the Faculty of Agriculture, Nagoya University, for measurement of fluorescence spectroscopy.

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(36) A solution of anthracene (3.0×10^{-3} *M*), **2** (5.6×10^{-2} *M*), and azulene (2.8×10^{-2} *M*) in ethanol was irradiated by a high-pressure mercury lamp (100-W) (Ushio UM-102) through a Pyrex filter under argon. The photolysis mixture was analyzed by nmr spectroscopy, and the same results as those of the direct irradiation were obtained (see ref 12a).
(37) It must be in enthalpic differences due to bond angle strain, torsional strain, and/or nonbonded interactions; unsymmetrical structures **6** and **7** are generally favored for the ring closure because of their greater entropy. In the case under consideration, **4** and **5** are symmetrical, while **6** and **7** are chiral and exist as enantiomeric pairs. Thus, **6** and **7** should be favored by *RT* ln 2 over **4** and **5** if only symmetry is considered. We are indebted to a referee for pointing out this possibility to us.
(38) A referee suggests the unlikely possibility that **13** might be converted to **4, 5, 6,** and/or **7** when irradiated in the presence of 1,3-diphenylisobenzofuran through a Pyrex filter. However, no reactions occurred even under the above condition.

(39) 1,3-Diphenylisobenzothiophen has shown the similar photochemical behavior. The fluorescence of 1,3-diphenylisobenzothiophen was readily quenched by **2** ($K_q\tau_s = 3.3 \pm 0.3\ M^{-1}$ in ethanol), and the adduct formation was observed. The detailed results will be reported at a later date.
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Thermal Rearrangements of (Substituted allyl)dialkyl-2*H*-pyrroles

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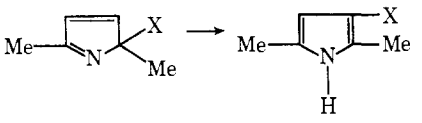
Abstract: The thermal behavior of simple substituted 2*H*-pyrroles, which are contained in tetrahydrocorrin systems and are intermediates in trialkylpyrrole isomerizations, was examined to elucidate possible competitive [1,5] and [3,3] sigmatropic rearrangement paths. The major path followed in the rearrangement of (substituted allyl)dialkyl-2*H*-pyrroles depends upon the substitution pattern of the migrating allyl group. Crotyl substituents migrate by a [1,5] shift (without inversion) from the 2- to the 3-position of the ring. On the other hand, the α-methylallyl group migrates by competitive [3,3] shifts (with inversion): migration from the 2- to the 5-position and migration from the 2- to the 4-position. Of the two migrations, the former is the more rapid. The transition state in the more rapid migration presumably possesses the more stable 2*H*-pyrrole configuration as compared with the latter path which contains the less stable 3*H*-pyrrole configuration.

N-(Substituted allyl)pyrroles undergo thermal isomerization involving competitive [1,5] and [3,3] sigmatropic shifts of the allyl group.[1] When the 2- and 5-positions of the pyrrole ring are substituted with alkyl groups, allylic migration to the 3-position of the pyrrole ring occurs with both inversion and noninversion of the allyl substituent. The N- to 3-migration without inversion suggests that this competitive rearrangement path proceeds by consecutive [1,5] shifts involving 2*H*-pyrrole intermediates. Evidence for the participation of such 2*H*-pyrrole intermediates in the thermal isomerization of other trisubstituted pyrroles has been reported,[2] and it has been found that these 2*H*-pyrrole species (2-benzyl-2,5-dimethyl-2*H*-pyrrole) undergo a facile isomerization to the corresponding 3-isomer (3-benzyl-2,5-dimethylpyrrole).[3] An investigation of possible competitive [1,5] and [3,3] sigmatropic shifts of allyl groups in the nickel tetrahydrocorrin system (contains a 2*H*-pyrrole species) by Grigg and coworkers[4] showed that the 3-methyl-2-butenyl group migrated without inversion. However, because of low conversions (*ca.* 2%) it was not possible to exclude other competing paths. In order to elucidate the migration modes of substituted allyl groups in 2*H*-pyrrole systems, we have investigated the pyrolytic behavior of (substituted allyl)dialkyl-2*H*-pyrroles.

Results and Discussion

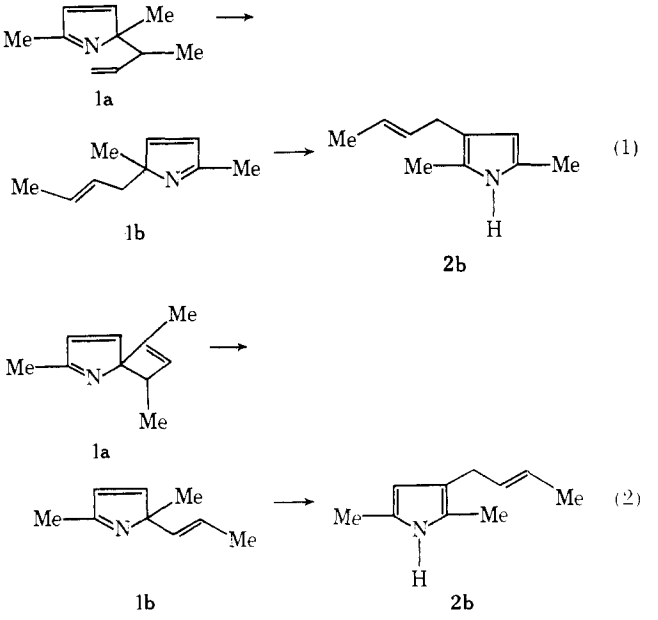
Initial pyrolyses with 2-α-methylallyl- (**1a**) and 2-crotyl-2,5-dimethyl-2*H*-pyrrole (**1b**) at 180° showed that the major (*ca.* 90%) thermolysis product in either experiment was 3-crotyl-2,5-dimethylpyrrole (**2b**). While these results



1 2

a, X = α-methylallyl; b, X = *trans*-crotyl; c, X = *cis*-crotyl

suggested that, as one possibility, the 2-methylallyl group migrated from the 2- to 3-position with inversion, such 2- to 3-migrations with inversion were considered to be unlikely in the pyrolysis of 2-α-methylallylpyrrole.[1] In addition, nmr studies of the isomerization of 2-crotyl-2,5-dimethyl-2*H*-pyrrole (**1b**) at 100° indicated that the compound rearranged predominately to the 3-crotyl compound (without inversion), while, on the other hand, the pyrolysis of 2-α-methylallyl-2,5-dimethyl-2*H*-pyrrole (**1a**) produced initially a 2-crotyl-2,5-dimethyl-2*H*-pyrrole (**1b**) which on further heating was converted to the 3-crotyl-2,5-dimethylpyrrole (**2b**). The formation of the 3-crotyl isomer in the latter experiment conceivably could have arisen from one or from combinations of the following paths: an across-the-ring migration of the α-methylallyl substituent from the 2- to 5-position with inversion followed by a shift of the crotyl group to the 4-position without inversion (eq 1); an inversion of the α-methylallyl substituent at the 2-position followed by a 2 to 3 shift of the crotyl group (eq 2); or an



1a 1b 2b (1)

1a 1b 2b (2)