Photochemical Codimerization of Benzofurans

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The photochemical codimerization of benzofuran with 2-substituted benzofurans has been examined. Irradiation of benzofuran with 2-(3-pyridyl)benzofuran or 2-phenylbenzofuran resulted in formation of the head-to-tail syn and anti cyclobutane codimers as main products. On the other hand, benzofuran with methyl benzofuran-2-carboxylate on irradiation gave the head-to-head syn codimer in addition to one homodimer of methyl benzofuran-2-carboxylate and two carbonyl compounds. It is suggested that the former proceeds via the excited singlet of benzofuran and the latter involves the excited singlet of methyl benzofuran-2-carboxylate.

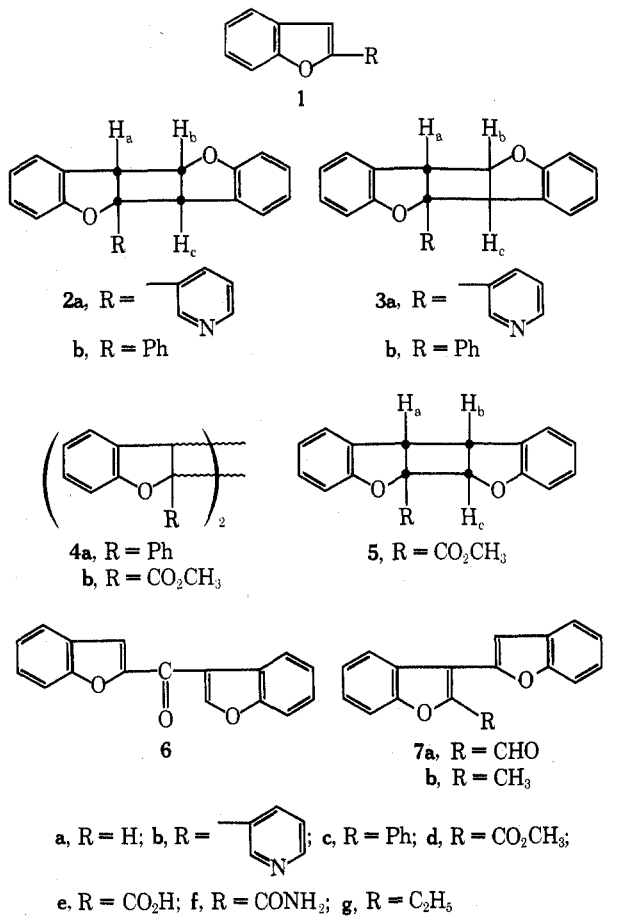
The connection between orientation and multiplicity of excited states in photoinduced dimerizations has attracted a great deal of attention.[1] With regard to the photochemistry of benzofurans, several examples including homodimerization in the presence of triplet sensitizers and addition reactions with carbonyl compounds and dimethylmaleic anhydride have been reported in the literature.[2-7] However, there has been no report on the photoreaction from the excited singlet of benzofurans. In this paper we would like to describe photoinduced codimerization of benzofuran with 2-substituted benzofurans, in which singlet excited states of benzofurans are involved.[8]

Results and Discussion

All photochemical reactions described herein were carried out with a 350-W high-pressure mercury lamp in a nitrogen atmosphere. The products were isolated by chromatography over silica gel, and the structures were determined by analytical and spectroscopic data.

Irradiation of an acetonitrile solution of benzofuran (**1a**) and 2-(3-pyridyl)benzofuran (**1b**), derived from photoreaction of **1a** with 3-iodopyridine, gave two codimers **2a** and **3a** in good yields. The stereochemistry of these codimers is assigned mainly on the basis of their NMR spectra. The 100-MHz NMR spectrum of **2a** (CCl_4) showed three cyclobutane protons at δ 4.48 (J = 6.0 and 3.8 Hz, H_a or H_c), 4.59 (J = 6.5 and 3.8 Hz, H_a or H_c), and 5.54 (J = 6.5 and 6.0 Hz, H_b). The large two coupling constants of J_{ab} and J_{bc} suggest that these three protons have a cis orientation. Furthermore, the observed strong upfield shift of the aromatic protons of the two benzofuran moieties can be attributed to long-range shielding by the π electrons of the aromatic rings. Thus, **2a** was identified as the head-to-tail syn codimer. The large long-range coupling constant (J_{ac}) observed in **2a** relative to that in the literature (0.5–2.0 Hz) may be due to mutual repulsion of the two benzofuran moieties which results in a conformation permitting effective coupling through the cyclobutane ring.[9] The NMR spectrum of **3a** (CCl_4) contained signals of three methine protons at δ 4.40 (J = 1.7 and <1.0 Hz, H_a), 4.57 (J = 6.5 and <1.0 Hz, H_c), and 5.06 (J = 6.5 and 1.7 Hz, H_b). In addition, the aromatic protons of the pyridine ring and one phenyl ring were shifted upfield from their normal positions. Thus, **3a** was assigned as the head-to-tail anti codimer. Pyrolysis of **2a** and **3a** at 220–240° in a degassed Pyrex tube leads in both cases to **1a** and **1b**.

Irradiation of a solution of **1a** and 2-phenylbenzofuran (**1c**) in acetonitrile through Pyrex glass afforded two codimers **2b** and **3b** and one homodimer **4a** as main products.[10] The stereochemistry of **2b** and **3b**, in analogy with **2a** and **3a**, is assigned mainly on the basis of their NMR spectra. The NMR spectrum of **2b** ($CDCl_3$) showed three methine protons at δ 4.43 (J = 6.2 and 4.0 Hz, H_a or H_c), 4.46 (J = 7.6 and 4.0 Hz, H_a or H_c), and 5.49 (J = 7.6 and 6.2 Hz, H_b), eight aromatic protons of the two benzofuran moieties at δ 6.2–7.1, and five aromatic protons at δ 7.3–7.6. The NMR spectrum of **3b** ($CDCl_3$) contained signals of three cyclobutane protons at δ 4.40 (J = 2.0 and 1.0 Hz, H_a), 4.46 (J = 7.0 and 1.0 Hz, H_c), and 5.10 (J = 7.0 and 2.0 Hz, H_b), and aromatic protons of the phenyl group and one of the two benzofuran moieties at higher field than the normal positions. These NMR spectra suggest that **2b** is the head-to-tail syn codimer and **3b** is the head-to-tail anti codimer. Pyrolysis of **2b** and **3b** at 220–240° gave **1a** and **1c** in quantitative yield.



Irradiation of an acetonitrile solution of **1a** and methyl benzofuran-2-carboxylate (**1d**) through Pyrex glass mainly gave a homodimer **4b**,[11] a codimer **5**, a ketone **6**,[12] and an aldehyde **7a**.[12] None of the other possible homodimers and codimers was detectable. **5** was identified as the head-to-head syn codimer on the basis of its NMR spectrum ($CDCl_3$): three methine protons at δ 4.42 (J = 8.0 and 6.5 Hz, H_b), 4.49 (J = 8.0 and 3.8 Hz, H_a), and 5.63 (J = 6.5 and 3.8 Hz, H_c) as an ABX spectrum, one methyl group at δ

3.80, and eight aromatic protons with the strong upfield shift at δ 6.6–7.0. Evidence for the structure **7a** has been obtained by the Wolff–Kishner reduction of **7a** to **7b**.

Solutions of **1a** and other 2-substituted benzofurans (**1e–g**) were also irradiated, but no detectable amount of cyclobutane dimers was obtained.

In order to try to clarify the excited state which is involved in these photocodimerization reactions, sensitization and quenching experiments were carried out. When an acetonitrile solution of **1a** (0.2 *M*) and **1c** (0.05 *M*) was irradiated through an *n*-hexane solution of naphthalene which cut out wavelengths shorter than 320 nm and assured absorption of **1c** alone, only **4a** was obtained as a main product. Irradiation (366 nm) of a solution in the presence of acetophenone (0.1 *M*) or benzophenone (0.1 *M*) as triplet sensitizers gave no detectable amount of codimers **2b** and **3b**. Furthermore, the formation of **2b** and **3b** was not quenched by 1,3-pentadiene (0.1 *M*), known as a triplet quencher. Similar results were obtained in the case of codimerization of **1a** with **1b**. These results suggest that the codimerization of **1a** with **1b** or **1c** proceeds via the excited singlet **1a**. The photocodimerization of **1a** and **1d** was also examined. When an acetonitrile solution of **1a** and **1d** was irradiated with 313-nm radiation, absorbed only by **1d**, the same products as obtained in the case of irradiation through Pyrex glass were mainly formed. The formation of these compounds was neither photosensitized by triplet sensitizer (acetophenone or benzophenone) nor quenched by 1,3-pentadiene. These results indicate that **5** is formed via addition of the excited singlet **1d** to the ground state **1a**, which contrasts with the case of the codimerization of **1a** with **1b** or **1c**.

With regard to the photochemical codimerization of **1a** with 2-substituted benzofurans, our present results indicate that the reactions obviously depend upon the benzofurans used, and two kinds of codimerization exist. One case is the codimerization of the excited singlet **1a** with the ground state of aryl-substituted benzofurans **1b** and **1c**, which leads to the head-to-tail syn and anti codimers. The other is the codimerization of the excited singlet **1d** with the ground state **1a**, which gives the head-to-head syn codimer. At the present state, it is difficult to state clearly the correlation between the orientation of addition and multiplicity of the excited states in the photodimerization of benzofurans. However, in view of the high substrate and orientational selectivity noted in these experimental results, it might be reasonable to consider that the reactions involve initial formation of a π complex between the excited singlet of one molecule and the ground state of another.[13]

Experimental Section

Melting points are uncorrected. Nuclear magnetic resonance spectra were determined on a JEOL JNM JS-100 spectrometer using tetramethylsilane as a internal standard. Mass spectra were performed on a Hitachi Perkin-Elmer RMF-60 mass spectrometer. Infrared spectra were obtained on a Japan Spectroscopic DS-402G infrared spectrophotometer with samples prepared as KBr pellets.

Photoreaction of 3-Iodopyridine with Benzofuran (1a). A solution of 3-iodopyridine (4.1 g, 20 mmol) and **1a** (9.5 g, 80 mmol) in acetonitrile (180 ml) was prepared in a Pyrex doughnut-type vessel. The solution was flushed with nitrogen for several minutes before being irradiated. Irradiation was carried out using a 350-W high-pressure mercury lamp in a quartz immersion well with water-cooled jacket at room temperature for 48 hr. After removal of solvent in vacuo, the residue was dissolved in diethyl ether and washed with a diluted NH_4OH solution. Evaporation of diethyl ether and recovery of unreacted **1a** and 3-iodopyridine (2.24 g) in vacuo afforded a crude product mixture (1.7 g). Chromatography on a column of silica gel (Merck) with benzene–diethyl ether (10:1) as eluent gave four fractions. The first fraction afforded **3a** (910 mg, 32% on the basis of consumed 3-iodopyridine) as colorless needles: mp 150° (from benzene); *m/e* 313 (M^+), 195, 166, 139, and 118; ir (KBr) 1592, 1480, 1460, 1420, 1235, 1004, 905, 763, 752, and 712 cm^{-1}; NMR (CCl_4) δ 4.40 (1 H, dd, *J* = 1.7 and <1.0 Hz), 4.57 (1 H, dd, *J* = 6.5 and <1.0 Hz), 5.06 (1 H, dd, *J* = 6.5 and 1.7 Hz), 6.40–6.68 (2 H, m), 6.12–6.72 (5 H, m), 7.20 (1 H, dd, *J* = 8.0 and 1.8 Hz), 7.27 (1 H, dd, *J* = 8.0 and 1.8 Hz), 7.35 (1 H, dt, *J* = 7.0 and 1.7 Hz), 8.31 (1 H, dd, *J* = 4.5 and 1.7 Hz), and 8.40 (1 H, d, *J* = 1.7 Hz).

Anal. Calcd for $C_{21}H_{15}NO_2$: C, 80.49; H, 4.83; N, 4.47. Found: C, 80.39; H, 4.59; N, 4.18.

The second fraction from the column gave **1b** (90 mg, 5%) as colorless needles: mp 78° (from benzene); *m/e* 195 (M^+), 166, and 139; ir (KBr) 1578, 1445, 1253, 1163, 1110, 915, 797, 746, and 700 cm^{-1}; NMR (CCl_4) δ 7.03 (1 H, s), 7.12–7.36 (2 H, m), 7.27 (1 H, dd, *J* = 7.5 and 4.2 Hz), 7.44 (1 H, d, *J* = 8.0 Hz), 7.48 (1 H, d, *J* = 8.0 Hz), 8.03 (1 H, dt, *J* = 7.5 and 1.8 Hz), 8.46 (1 H, dt, *J* = 4.2 and 1.8 Hz), and 9.00 (1 H, d, *J* = 1.8 Hz).

Anal. Calcd for $C_{13}H_9NO$: C, 79.98; H, 4.65, N, 7.17. Found: C, 79.92; H, 4.51; N, 7.20.

The third fraction gave a mixture of pyridylbenzofuran isomers (90 mg, 5%): bp 120–130° (6 mmHg) (bath temperature); *m/e* 195 (M^+), 166, and 139. The NMR spectrum (CCl_4) of the mixture showed one major component (~85%): δ 6.84 (1 H, dd, *J* = 2.2 and 1.0 Hz), 7.28 (1 H, dd, *J* = 7.8 and 4.5 Hz), 7.18–7.34 (3 H, m, AB part of the ABX system), 7.39 (1 H, dt, *J* = 7.8 and 1.0 Hz, X part of the ABX system), 7.61 (1 H, d, *J* = 2.2 Hz), 7.80 (1 H, dt, *J* = 7.5 and 1.8 Hz), 8.51 (1 H, dd, *J* = 4.5 and 1.8 Hz), and 8.76 (1 H, d, *J* = 1.8 Hz). These NMR signals are probably attributed to 4-(3-pyridyl)benzofuran. Repeated recrystallizations of the HCl salt of the mixture from methanol–water afforded a white solid, mp 104°.

The fourth fraction gave **2a** (600 mg, 21%): mp 113° (from benzene); *m/e* 313 (M^+), 195, 166, 139, and 118; ir (KBr) 1592, 1480, 1460, 1235, 1062, 880, 752, and 712 cm^{-1}; NMR (CCl_4) δ 4.44 (1 H, dd, *J* = 6.0 and 3.8 Hz), 4.59 (1 H, dd, *J* = 6.5 and 3.8 Hz), 5.54 (1 H, dd, *J* = 6.5 and 6.0 Hz), 6.31 (1 H, dd, *J* = 8.0 and 1.5 Hz), 6.35 (1 H, dd, *J* = 8.0 and 1.5 Hz), 6.64 (1 H, dd, *J* = 8.0 and 7.0 Hz), 6.82 (2 H, dd, *J* = 8.0 and 7.0 Hz), 7.00 (1 H, dd, *J* = 7.0 and 1.5 Hz), 7.05 (1 H, dd, *J* = 7.0 and 1.5 Hz), 7.26 (1 H, dd, *J* = 7.5 and 4.5 Hz), 7.84 (1 H, dt, *J* = 7.5 and 1.8 Hz), 8.52 (1 H, dd, *J* = 4.5 and 1.8 Hz), and 8.81 (1 H, d, *J* = 1.8 Hz).

Anal. Calcd for $C_{21}H_{15}NO_2$: C, 80.49; H, 4.83; N, 4.47. Found: C, 80.39; H, 4.57; N, 4.29.

Pyrolysis of **2a** (310 mg, 1 mmol) at 220–240° in a degassed Pyrex tube for 30 min, distillation of **1a**, and sublimation at 90–100° (6 mmHg) gave **1b** (190 mg). Similarly, pyrolysis of **3a** at 220–240° afforded **1b** quantitatively.

Photoreaction of 1a and 2-(3-Pyridyl)benzofuran (1b). A solution of **1a** (240 mg, 2 mmol) and **1b** (100 mg, 0.5 mmol) in acetonitrile (100 ml) was irradiated in a Pyrex vessel for 12 hr using a 350-W high-pressure mercury lamp. After removal of the solvent and **1a** in vacuo, sublimation of the residue at 150–160° (0.2 mmHg) gave 280 mg of a mixture of the codimer **2a, 3a**. The ratio of the codimers was determined by an NMR spectrum of the mixture (**2a: 3a** = 2:3).

Photoreaction of 1a and 2-Phenylbenzofuran (1c). A solution of **1a** (2.43 g, 20 mmol) and **1c** (1.0 g, 5.2 mmol) in acetonitrile (180 ml) in a Pyrex vessel was irradiated for 70 hr. During this time, colorless needles of **4a** (270 mg, 14% based on consumed **1c**) separated from the solution: mp 287–288°; *m/e* 388 (M^+), 194, and 165; NMR (Me_2SO-D_6) δ 5.04 (2 H, s), 6.64 (2 H, m), 7.00 (2 H, m), 7.10–7.55 (10 H, m).

Anal. Calcd for $C_{28}H_{20}O_2$: C, 86.57; H, 5.19. Found: C, 86.60; H, 5.10.

Evaporation of the filtrate to dryness and distillation of unreacted **1a** in vacuo gave a crude solid (1.26 g). Chromatography on a column of silica gel with *n*-hexane–benzene (6:1) as eluent gave three fractions. The first fraction gave **1c** (40 mg, 2 mmol). The second fraction afforded **3b** (1.06 g, 68%): mp 153–154° (from benzene); *m/e* 312 (M^+), 194, and 165; ir (KBr) 1594, 1480, 1460, 1245, 1002, 900, 745, and 700 cm^{-1}; NMR ($CDCl_3$) δ 4.40 (1 H, dd, *J* = 2.0 and 1.0 Hz), 4.60 (1 H, dd, *J* = 7.0 and 1.0 Hz), 5.11 (1 H, dd, *J* = 7.0 and 2.0 Hz), 6.56 (1 H, m), 6.74–7.06 (4 H, m), and 7.08–7.42 (7 H, m).

Anal. Calcd for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16. Found: C, 84.90; H, 5.43.

The third fraction gave **2b** (190 mg, 12%): mp 130° (from diethyl ether); *m/e* 312 (M^+), 194, and 165; ir (KBr) 1586, 1570, 1455, 1220, 1060, 870, 793, 745, and 695 cm^{-1}; NMR ($CDCl_3$) δ 4.43 (1 H,

dd, J = 6.2 and 4.0 Hz), 4.64 (1 H, dd, J = 7.6 and 4.0 Hz), 5.49 (1 H, dd, J = 7.6 and 6.2 Hz), 6.40 (2 H, d, J = 7.5 Hz), 6.68 (2 H, d, J = 6.7 Hz), 7.11 (2 H, d, J = 6.7 Hz), and 7.24–7.68 (5 H, m).

Anal. Calcd for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16. Found: C, 84.90; H, 5.43.

Photoreaction of 1a with Methyl Benzofuran-2-carboxylate (1d). A solution of **1a** (4.37 g, 37 mmol) and **1d** (1.6 g, 91 mmol) in acetonitrile (180 ml) was irradiated in a Pyrex vessel for 62 hr. After removal of solvent and unreacted **1a** in vacuo, chromatography of the residue on a column of silica gel gave five fractions. The first fraction (*n*-hexane–benzene, 10:1, as eluent) afforded **1d** (450 mg, 2.5 mmol). The second fraction (*n*-hexane–benzene, 10:1, as eluent) yielded **7a** (240 mg, 14%): mp 202–203° (from *n*-hexane–benzene); *m/e* 262 (M^+), 234, 205, and 176; ir (KBr) 1662, 1615, 1385, 1340, 1166, 1113, 1077, 876, 815, and 755 cm^{-1}; NMR ($CDCl_3$) δ 7.20–7.70 (7 H, m). 7.50 (1 H, s), 8.28 (1 H, m), and 10.88 (1 H, s).

Anal. Calcd for $C_{17}H_{10}O_3$: C, 77.85; H, 3.84. Found: C, 77.66; H, 3.59.

The third fraction (*n*-hexane–benzene, 10:1, as eluent) gave **6** (290 mg, 17%): mp 157–158° (from benzene); *m/e* 262 (M^+), 245, 234, 205, 145, and 117; ir (KBr) 1662, 1620, 1387, 1340, 1164, 1110, 1075, 870, 810, and 750 cm^{-1}; NMR ($CDCl_3$) δ 7.30–7.80 (7, H, m), 7.62 (1 H, s), 8.35 (1 H, m), and 8.84 (1 H, s).

Anal. Calcd for $C_{17}H_{10}O_3$: C, 77.85; H, 3.84. Found: C, 77.60; H, 3.59.

The fourth fraction (benzene as eluent) afforded **5** (540 mg, 28%): mp 99° (from benzene–diethyl ether); *m/e* 294 (M^+), 176, 145, 118, and 89; ir (KBr) 1750, 1476, 1460, 1232, 1126, 835, 755, and 742 cm^{-1}; NMR ($CDCl_3$) δ 3.80 (3 H, s), AB part of the ABX spectrum at 4.42 (J = 8.0 and 6.6 Hz) and 4.49 (J = 8.0 and 3.8 Hz), X part of the ABX spectrum at 5.63 (1 H, dd, J = 6.6 and 3.8 Hz), and 6.4–7.0 (8 H, m).

Anal. Calcd for $C_{18}H_{14}O_4$: C, 73.46; H, 4.80. Found: C, 73.18; H, 4.77.

The fifth fraction (diethyl ether as eluent) yielded **4b** (160 mg, 7%): mp 166° (from benzene–diethyl ether); *m/e* 352 (M^+), 176, 145, 118, and 89; ir (KBr) 1765, 1730, 1476, 1460, 1430, 1230, 1130, 1075, 1042, 1025, 982, 845, and 750 cm^{-1}; NMR ($CDCl_3$) δ 3.80 (6 H, s), 4.68 (3 H, s), and 6.5–7.0 (8 H, m).

Anal. Calcd for $C_{20}H_{16}O_6$: C, 68.18; H, 4.58. Found: C, 68.29; H, 4.38.

Wolff–Kishner Reduction of 7a. A mixture of **7a** (20 mg, 0.077 mmol), potassium hydroxide (50 mg), 90% hydrazine hydrate (50 mg), and diethylene glycol (5 ml) was heated to reflux for 1 hr. After refluxing, water was removed and refluxing was continued for an additional 2 hr. The mixture was then cooled and extracted with benzene. Evaporation of the dried solution and sublimation of the residue at 100–110° (6 mmHg) gave **7b** (17 mg, 88%): mp 126–127° (from *n*-hexane); *m/e* 248 (M^+); NMR (CCl_4) δ 2.60 (3 H, s), 7.04 (1 H, s), 7.10–7.30 (4 H, m), and 7.30–7.60 (4 H, m).

Anal. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87. Found: C, 82.40, H, 4.90.

Registry No.—**1a,** 271-89-6; **1b,** 7035-06-5; **1c,** 1839-72-1; **1d,** 1646-27-1; **2a,** 52437-49-7; **2b,** 57237-76-0; **3a,** 52169-67-2; **3b,** 57287-76-0; **4a,** 57237-77-1; **4b,** 57237-78-2; **5,** 57237-79-3; **6,** 57237-80-6; **7a,** 57237-81-7; **7b,** 57237-82-8; 3-iodopyridine, 1120-90-7; 4-(3-pyridyl)benzofuran, 57237-83-9.

References and Notes

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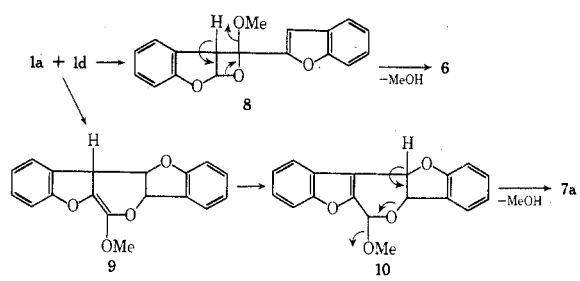
(9) L. M. Jackman and S. Sternhell, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed, Pergamon Press, Oxford, 1969, p 334.
(10) The decrease in the yield of **2b** and the increase in the yield of **3b** were observed as irradiation time increased. Irradiations of **2b** and **3b** in acetonitrile through Pyrex glass resulted in formation of **1a** and **1c.** Thus, the observed variation in the ratio of **2b:3b** is probably due to the effective photodecomposition of **2b** relative to that of **3b.**
(11) The stereochemistry of **4b,** as well as that of **4a,** has not yet been established. However, **4b** is assigned as one of two possible syn dimers on the basis of its NMR spectrum, in which the strong upfield shift of the aromatic protons was observed. The formation of only one of four possible homodimers from **1d** shown in our present experiments contrasts with the results of the triplet sensitized homodimerization of **1d,** in which three isomers were obtained.[4]
(12) The formation of **6** can be envisaged as occurring via an oxetane intermediate **8** followed by elimination of MeOH. Similarly, a plausible pathway for the formation of **7a** is as follows: 1,4 cycloaddition of **1d** to **1a** followed by aromatization affords an acetal intermediate **10** that may readily lose MeOH to give **7a.**



(13) The possibility of the ground state charge-transfer complex between these benzofurans should be excluded by absorption studies in which no charge-transfer band was observed. In our preliminary mechanistic studies, we found that the fluorescence of **1a** (in cyclohexane) is completely quenched by **1c** (10^{-3} *M*) at room temperature. However, no new emission suggesting the existence of an exciplex has been observed.

Intramolecular Reorganization of Some Unsaturated 2*H*-Azirines[1]

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The thermal and photochemical expansion reactions of several unsaturated 2*H*-azirines have been examined. The azirines undergo thermal rearrangement by rupture of the C–N single bond to give a butadienyl nitrene which undergoes cyclization followed by a [1,5]-sigmatropic migration and subsequent tautomerization. The butadienyl nitrene was also found to insert into a neighboring allylic methyl group and the nitrene could also be trapped when the thermolysis was carried out in the presence of tris(dimethylamino)phosphine. The azirine derivatives were found to undergo photochemical reorganization via transient nitrile ylide intermediates which can be trapped with external dipolarophiles.

Previous papers from this laboratory have established that arylazirines undergo irreversible ring opening on electronic excitation to give nitrile ylides as reactive intermediates.[2-6] These species can be intercepted with a variety of