Scheme I will not compete with hydrolysis of the amide bond (path b). Suggestions that acid catalyzed N–O bond heterolysis of *N*-hydroxy-*N*-arylamides may be important in vivo processes[1a,6c] must be viewed with suspicion in view of these results.

Acknowledgment. This work was supported, in part, by a grant from the National Institutes of General Medical Sciences (Grant GM 38449-01). The support of the Faculty Research Council of Miami University is also acknowledged.

Supplementary Material Available: Table II, pseudo-first-order rate constants for the hydrolysis of **1a–d** in dilute HCl (1 page). Ordering information is given on any current masthead page.

A Desirable Route to Heterodimers of 1,4-Dihalobenzenes and Anthracene and Their Photoproperties and Thermal Properties

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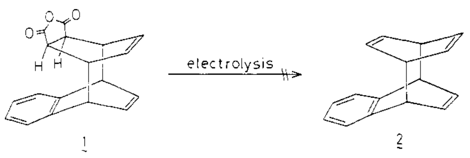
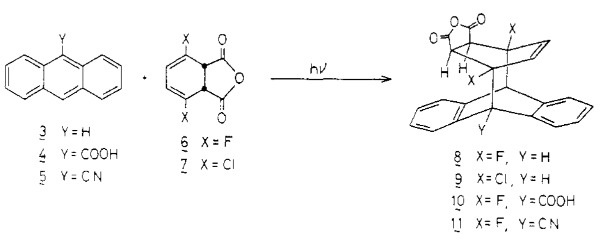
Electronic oxidative bisdecarboxylation of photoadducts of 2,5-dihalo-1,2-dihydrophthalic anhydride and anthracene gave the corresponding energy-rich heterodimers **12** and **13**. The quantum yields of the formation of the excited anthracene from **12** and **13** by the irradiation of 280-nm light were 0.65 and 0.25, respectively. We assumed that the heterodimers of **12** and **13** form biradicaloid intermediates during thermal retro [$4\pi s + 4\pi s$] cycloaddition and consumed their stored energy without any visible light. However, we observed emission light from 340 to 460 nm through a glass filter and the formation of anthracene using Nd-YAG laser IR light (1.06 μm) by the multiphoton absorption, when fine powders of **12** and **13** were used.

Heterodimers of arenes are a group of important energy-rich molecules. Although benzene[1c] and condensed aromatic hydrocarbons, such as anthracene[1a] and naphthalene,[1b] undergo photodimerization, the synthesis of these energy-rich heterodimers has not been accomplished by photocycloaddition of benzenes and other arenes. A few heterodimers have been synthesized by an application of photocycloaddition of substituted 1,3-cyclohexadienes to arenes followed by conversion of substituents to an olefinic bond using carefully controlled methods.[2] A desirable and economical route to heterodimers is direct oxidative bisdecarboxylation of photocycloadducts of 1,2-dihydrophthalic anhydrides and arenes. However, when the diacid derived from **1** was subjected to electronic oxidative bisdecarboxylation directly under a variety of conditions, the expected heterodimer **2** was not detected among the products (Scheme I).[3] Now we have overcome this difficulty by the introduction of halogen atoms on the bridgehead of [$4\pi s + 4\pi s$] photoadducts (**8** and **9**). Thus we report here the synthesis and photoconversion to excited anthracene through the adiabatic process of heterodimers **12** and **13**. The kinetic behavior of thermal retro [$4\pi s + 4\pi s$] cycloaddition of these heterodimers was also studied. This study presents an analysis of the chemiluminescent and dark reaction pathways for these thermal

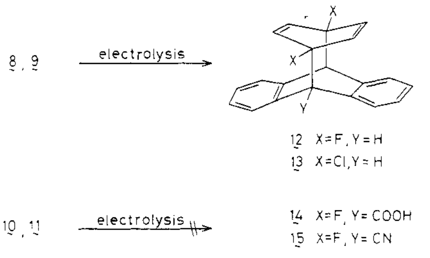
Scheme I



Scheme II



Scheme III



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(1) (a) Mustafa, A. *Chem. Rev.* **1952**, *51*, 1. Laird, T. *Chem. Ind. (London)* **1978**, 186. (b) Teitei, T.; Wells, D.; Sasse, W. H. F. *Tetrahedron Lett.* **1974**, 367. Blank, N. E.; Haenel, M. W. *Chem. Ber.* **1981**, *114*, 1520. (c) Kushner, A. S. *Tetrahedron Lett.* **1971**, 3275. Higuchi, H.; Takatsu, K.; Otsubo, T.; Sakata, Y.; Misumi, S. *Ibid.* **1982**, 671.

(2) (a) Yang, N. C.; Chen, P. J. *J. Am. Chem. Soc.* **1984**, *106*, 7310. (b) Yang, N. C.; Yang, X. Q. *Ibid.* **1987**, *109*, 3804.

(3) Mark, K. T.; Srinivasachar, K.; Yang, N. C. *J. Chem. Soc., Chem. Commun.* **1979**, 1038.

Table I. The Kinetic Activation Parameters for the Thermal Dissociation of 12, 13, and 16 and the Quantum Yields of the Photoreaction of 12, 13, and 16

	thermolysis		
compd	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$\Phi_{AN}{}^{*}$[a]
12	28.3 ± 1.2	1.0	0.69
13	26.8 ± 0.3	5.3	0.39
16[b]	33.0 ± 0.9[b]	16.4[b]	0.80[b]

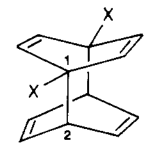
[a] Reference 11. [b] Reference 2.

retro [4πs + 4πs] cycloadditions.

The reaction route for the synthesis of the heterodimers is shown in Schemes II and III. The first important stage of the synthesis is the photocycloaddition of anthracenes and *cis*-dihalo-1,2-dihydrophthalic anhydrides **6** and **7**. Normally, one obtains both [4πs + 4πs] and [4πs + 2πs] cycloadducts in the photocycloaddition reactions.[4] However, only the [4πs + 4πs] cycloaddition products **6–9** were observed in this study. These adducts (**6–9**) may be key intermediates for the synthesis of heterodimers **12–15**. The second important stage is the electrooxidative bisdecarboxylation of photoadducts **9–11**. Usually the corresponding free diacids were used for the electrooxidative bisdecarboxylation;[3] however, even the acid anhydrides **8** and **9** were available for the bisdecarboxylation in this case. Technically the addition of *n*-hexane to the reaction system is very important because the two-layered system protects these heterodimers from further oxidative electrolysis to 1,4-dihalobenzenes and anthracene. We failed to synthesize **14** and **15** by $Pb(OAc)_4$ or electrooxidative bisdecarboxylation.

The UV spectra of **12** and **13** exhibit a similar absorption pattern to that of **16**, suggesting that they have the same *o*-xylene-like chromophore.[2a] In the NMR spectrum of **12** in $CDCl_3$, the pattern of chemical shifts is almost the same as that of protons in **13**; however, the coupling pattern is not the same as that of protons in **13** because of the large coupling (27.8 Hz) of fluorines on the bridgeheads with the protons on both double bonds and the other bridgeheads (4.20 ppm). On the other hand, the mass spectrum of **12** has a small molecular ion peak at *m/e* 292, while **13** has no molecular ion peak.[6] On electron impact, **13** easily loses HCl and gives the corresponding ion peak at *m/e* 288, while both **12** and **13** lose anthracene radical cation as a base peak. We had an interest in the unsymmetrical substituent effect that the introduction of fluorine atoms on the bridgeheads may destabilize this heterodimer system more than the introduction of chlorine atoms in the heterodimer system as in the case of the thermal ring opening reaction of 1-halo-substituted bicyclo[2.2.0](1-halo-Dewar benzene).[7] The kinetic activation parameters for the thermal dissociation of **12** and **13** to anthracene and the corresponding 1,4-dihalobenzene were collected and are summarized in Table I. When we compared these parameters with those of **16**, we could not conclude that the introduction of fluorine atoms destabilized the system as we expected. CNDO-3 calculation of benzene dimers suggests that the introduction of fluorine atoms on the bridgehead stabilizes the bridge C–C bonds as shown in Table II.[8]

Table II. The Results of CNDO-3 Calculation of Substituted Benzene Dimers



X	C_1–C_2 bond length, Å	ΔH_f, kcal/mol	IP, eV	dipole moment, D
F	1.5842	30.13532	9.2096	1.2531
Cl	1.5991	122.58188	9.2442	1.5639
H	1.5918	132.94821	8.8635	0.0013

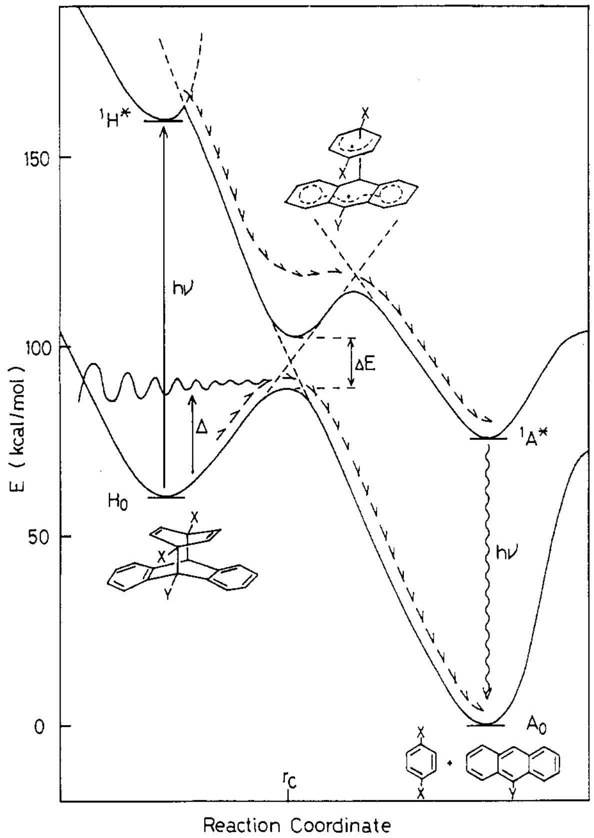
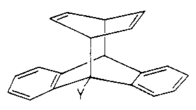


Figure 1. A schematic diagram of the reaction coordinate of thermolysis and photolysis of heterodimers. H_0 = heterodimers in the ground state. $^1H^*$ = heterodimers in the excited singlet state. A_0 = anthracene in the ground state. $^1A^*$ = anthracene in the excited singlet state.



16 Y = H
17 Y = COOH

It is of interest to test the possibility of chemiluminescent reaction using this energy-rich system. Recently, N. C. Yang et al. tested this possibility by using **16** and **17**.[2] Thermal reaction of **17** gave the excited 9-anthronic acid through a polarized intermediate **19**. By comparison, **12**

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[4] (a) Kimura, M.; Nukada, K.; Satake, K.; Morosawa, S. *J. Chem. Soc., Perkin Trans. 1* **1986**, 885. (b) Kimura, M.; Sagara, S.; Morosawa, S. *J. Org. Chem.* **1982**, *47*, 4344. (c) Yang, N. C.; Libman, J.; Savitzky, M. F. *J. Am. Chem. Soc.* **1975**, *97*, 5006. Jpn. Kokai Tokkyo Koho 87-22734.

[5] Radlick, P.; Klem, R.; Spurlock, S.; Smis, J. J.; van Tamelen, E. E.; Whitesides, T. *Tetrahedron Lett.* **1968**, 5117. Westberg, H. H.; Dauben, H. J., Jr. *Ibid.* **1968**, 5123.

[6] The electron impact of **12** and **13** gave the ion of anthracene as the base peak by retro [4πs + 4πs] cycloaddition.

[7] Breslow, R.; Napierski, J.; Schmidt, A. H. *J. Am. Chem. Soc.* **1972**, *94*, 5906. Lechtken, P.; Breslow, R.; Schmidt, A. H.; Turro, N. J. *Ibid.* **1973**, *95*, 3025.

[8] The laser experiments were performed at The Johns Hopkins University.

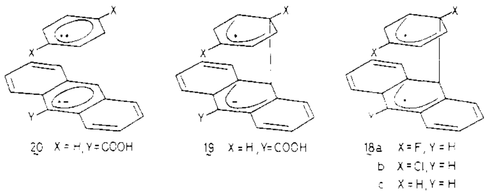

Figure 2. Biradical intermediate 18, ionic intermediate 19, and CT transition state 20.

and 13 have halogen atoms on the bridgeheads; these heavy atoms may help to give excited triplet anthracene by enhancing the efficiency of intersystem crossing.[7] Unfortunately, we could not observe emissions by heating solutions of 12 or 13 in xylene with or without fluorescer (rubrene, dibromoanthracene, or diphenylanthracene). If the concerted retro [4πs + 4πs] reaction of the heterodimers is prohibited by the conservation of orbital symmetry, then an efficient crossing (<100 cm^{-1}) between the ground and an excited surface for the chemiluminescence is to be expected.[9] However, these heterodimers are not chemiluminescent. A plausible explanation derives from a lack of an effective surface crossing for geometries near the critical point (r_c in Figure 1). We assumed a stepwise bridge C–C bond cleavage for the reaction. As the reaction proceeds, one of the C–C bonds cleaves to form biradicaloid intermediate 18. From the calculation of HMOs of **18a–d**, **18d** should be stabilized by electron transfer to form the more stable ionic structure **19** (Figure 2). The formation of biradical intermediate **18** should be the more energy consuming pathway. We may conclude that a stepwise C–C bond cleavage for **18a–c** would consume almost all energy stored in the system without any visible light emission; however, ionic intermediate **19** may reach at the CT transition state (**20**) to the excited anthracene (Figure 2). From this observation we can draw a picture of the image of the ground and excited energy surfaces for the reaction of heterodimers as shown in Figure 1. We show two more interesting phenomena in the energy surfaces.

When **12** and **13** were irradiated at 280 nm, very efficient fluorescent emission from anthracene was observed as shown in Figure 3. This means that there is a smooth energy surface in the excited states between the excited heterodimer and the excited anthracene, and an adiabatic photoreaction occurred efficiently. We observed emission light when fine powders of **12** and **13** were used between 340 and 460 nm through a glass filter and the formation of anthracene using Nd-YAG laser IR light (1.06 μm, 26.9 kcal/mol).[8] We conclude that the dissociation of the heterodimers by the multiphoton absorption promotes the heterodimers to the excited energy surface. The energy gap at r_c should be small enough to jump to the excited surface through the electron transfer intermediates for **18d**. However, there is a larger energy gap at r_c for **18a–c**. When we checked the HMO levels of intermediates at r_c using model intermediates constructed from diphenylmethyl and pentadienyl radicals, we found that the COOH substituent can stabilize the ionic intermediate as shown in Figure 4.[12]

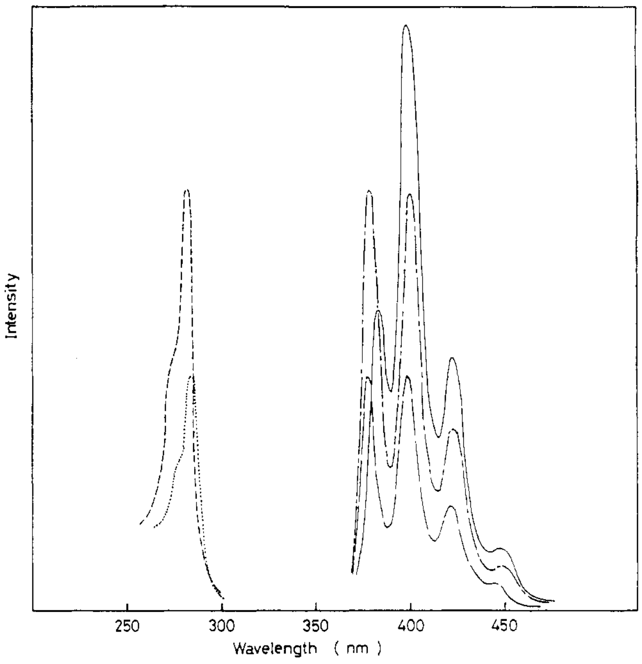

Figure 3. The emission spectra from **12** (–·–) and **13** (– – –) through an adiabatic pathway, the excitation spectrum of the emission from **12** (- - -) and **13** (···) at 400 nm, and the fluorescence of anthracene (—). These emission spectra are observed by the irradiation of UV light at 280 nm using hexane solutions with the same absorbancy at 280 nm as each other.

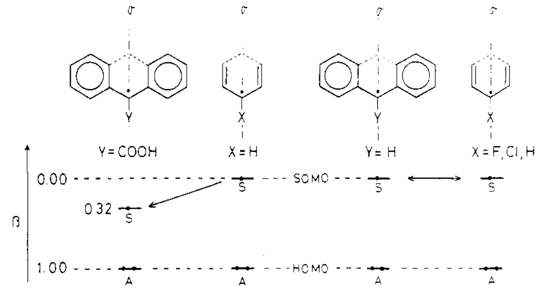

Figure 4. HMO energy levels (β units) of HOMO and SOMO for the diphenylmethyl and pentadienyl radicals which are π systems for the intermediates at r_c in Figure 1. Coulomb and exchange integral parameters for the HMO calculation are selected from ref 11. σ = the symmetry mirror plane. A = antisymmetric orbital with respect to reflection through the plane. S = symmetric orbital with respect to reflection through the plane.

As suggested here, the ionic intermediate is an important key for introducing the reaction into the chemiluminescent pathway. It is noteworthy that the spin–orbit coupling of the reaction system consisting of aromatic hydrocarbons is too small to send them to the triplet excited anthracene, and even the heterodimer with heavy atoms (**13**) does not give off light.

In the case of the heterodimer with COOH (**17**), we can rationalize the formation of the excited anthracene as follows. The ground-state energy surface of H_0 may correlate to a charge-transfer state of 9-anthracenecarboxylic acid anion and benzene cation (**20**) as an energetically favorable route. The electron transfer from the anion radical to the cation radical produces the corresponding excited anthracene.[3] As shown here, the systems of **12** and **13** also form a biradicaloid (**18**) intermediate; however, this intermediate can not produce the corresponding excited anthracene (A*) and ground-state benzene because the formation of A* would be a more energy consuming route than that of **17** giving the corresponding anthracene in the ground state.

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(9) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978; p 156.

(10) One of the authors (Fukazawa) calculated these results of CNDO-3.

(11) In our evaluation of the relative quantum yields of photolysis of 12 and 13, we followed the method by Berlman, and each area under their fluorescence curves was compared to the area under the fluorescence curve for anthracene (6 × 10^{-4} M). Berlman, I. B. *Handbook of Fluorescence Spectra of Aromatic Molecules*; Academic: New York, 1965; p 14.

(12) Purcell, W. P.; Singer, J. A. *J. Chem. Eng. Data* **1967**, *12*, 253.

Experimental Section

General Procedures. Melting points were measured with a Yanagimoto micro melting point apparatus, and these were uncorrected. The ^1H NMR spectra were taken on a JEOL JNMPX 60 spectrometer with tetramethylsilane as internal standard. The IR spectra were recorded on a JASCO IRA-1 spectrometer. The UV spectra were recorded on a Hitachi Model 200-10 spectrometer. The fluorescent spectra were recorded on a Hitachi Perkin-Elmer spectrometer. Mass spectra were obtained on a JEOL JMS-D 300 mass spectrometer.

Materials. 3,6-Dichlorophthalic anhydride was prepared in 33% yield from phthalic anhydride by the method of Villiger,[13] mp 186–189 °C (lit. mp 190–191 °C). 3,6-Difluorophthalic anhydride was prepared in 29% yield by the method of Heller et al.,[14] mp 208–210 °C (lit. mp 212 °C). 3,6-Dichloro-1,2-dihydrophthalic acid was prepared in 37% yield by the method of Breslow et al.,[7] mp 212–214 °C (lit. mp 212–214 °C). *cis*-3,6-Dichloro-1,2-dihydrophthalic anhydride (**7**) was prepared as follows. To 5 mL of acetic anhydride was added 3,6-dichloro-1,2-dihydrophthalic acid (12.9 g), and the solution was heated at 98–100 °C for 10 min. The yellow solution formed was cooled, and acetic anhydride was removed under reduced pressure. The residue was solidified, giving *cis*-3,6-dichloro-1,2-dihydrophthalic anhydride (11.5 g), which was used for photoreaction with anthracenes without further purification: mp 86–88 °C (lit. mp 87–89 °C);[7] ^1H NMR ($CDCl_3$) 6.19 (s, 2 H), 4.21 ppm (s, 2 H). 3,6-Difluoro-1,2-dihydrophthalic acid was prepared by the method of McDonald et al.:[15] yield 92%; ^1H NMR ($CDCl_3$) 9.47 (br s, 2 H), 3.93 ppm (t, 2 H); IR (Nujol) ν_{max} 3440, 2900, 720, 1640 cm^{-1}. Anal. Calcd for $C_8H_6F_2O_4$: C, 47.07; H, 2.96. Found: C, 47.36; H, 3.15. *cis*-3,6-Difluoro-1,2-dihydrophthalic anhydride (**6**) was prepared by the method applied for the synthesis of 3,6-dichloro-1,2-dihydrophthalic anhydride: yield 90%; mp 99–103 °C; ^1H NMR ($CDCl_3$) 5.65 (t, 2 H), 4.35 ppm (t, 2 H); IR (Nujol) ν_{max} 1865, 1770 cm^{-1}; UV λ_{max} 265 nm (log ϵ 3.44). Anal. Calcd for $C_8H_4F_2O_3$: C, 51.63; H, 2.17. Found: C, 51.82; H, 2.2.

Photoadduct 8. A solution of anthracene (2.2 g, 12 mmol) and *cis*-3,6-difluoro-1,2-dihydrophthalic anhydride (**6**) (5.0 g, 25 mmol) in benzene (110 mL) was irradiated with a Ushio 100 Hg high-pressure lamp through a Pyrex filter for 37 h under an atmosphere of nitrogen. The solvent was evaporated under reduced pressure, and the residue was chromatographed on silica gel with benzene elution to give **8** (1.6 g, 36%): colorless needles (from ethanol); mp 164.5–166 °C; ^1H NMR ($CDCl_3$) 6.92 (s, 2 H), 6.55 (m, 2 H), 6.00 (m, 2 H), 4.14 (d, 2 H), 3.54 (s, 2 H), 2.38 ppm (s, 6 H); IR (Nujol) ν_{max} 1852, 1780, 1755 cm^{-1}; UV (EtOH) λ_{max} 208 (log ϵ 4.65), 278 nm (3.27). Anal. Calcd for $C_{22}H_{14}F_2O_3$: C, 72.52; H, 3.87. Found: C, 72.31; H, 3.95.

Photoadduct 9. This was prepared by the method of preparation of **8**: 40% yield; colorless prisms (ethyl acetate); mp 229–230 °C; ^1H NMR ($CDCl_3$) 7.28 (m, 8 H), 5.52 (s, 2 H), 4.29 (s, 2 H), 3.26 ppm (s, 2 H); IR (Nujol) ν_{max} 1845, 1780 cm^{-1}; UV (EtOH) λ_{max} 272 (log ϵ 2.85), 281 nm (2.91). Anal. Calcd for $C_{22}H_{14}O_3Cl_2$: C, 66.52; H, 3.55. Found: C, 66.41; H, 3.44.

Photoadduct 11. This was prepared by the method of preparation of **8**: 11% yield; colorless crystals; mp 208.5–209.5 °C; ^1H NMR ($CDCl_3$) 7.37 (m, 8 H), 5.64 (m, 2 H), 4.56 (d, 1 H), 3.81 ppm (s, 2 H); IR (Nujol) ν_{max} 2240, 1844, 1768 cm^{-1}; UV (EtOH) λ_{max} 277 (log ϵ 2.56), 215 nm (4.38). Anal. Calcd for $C_{23}H_{13}O_3NF_2$: C, 70.95; H, 3.37; N, 3.60. Found: C, 70.82; H, 3.33; N, 3.30.

Photoadduct 10. This was prepared by the method of preparation of **8**: yield 12%; colorless crystals; mp 189.5–190 °C; ^1H NMR ($CDCl_3$ + DMSO-d_6) 7.20 (m, 8 H), 5.48 (m, 2 H), 4.46 (d, 1 H), 3.36 (q, 2 H); IR (Nujol) ν_{max} 3020, 1856, 1780, 1721 cm^{-1}; UV (EtOH) λ_{max} 215 (log ϵ 4.02), 266 (2.76, sh), 278 nm (2.56, sh). Anal. Calcd for $C_{23}H_{14}F_2O_5$: C, 67.65; H, 3.46. Found: C, 67.52; H, 3.41.

Heterodimer 12. Compound **8** (130 mg, 0.34 mmol) was dissolved in 80% aqueous pyridine (6.3 mL) and triethylamine (100 μL). *n*-Hexane (13 mL) was added to the solution in order to extract products during the reaction. This stirred mixture, cooled with an ice water bath, was electrolyzed by using two platinum-plate electrodes (width, 2 mm) with a current of 100 mA for 12 h (44.8 mF). The reaction mixture was extracted with *n*-hexane and after the usual workup gave **12** (11.2 mg) in 11.2% yield: colorless plates; mp 198–200 °C; ^1H NMR (CCl_4) 7.30 (m, 8 H), 5.73 (sex., 4 H), 4.22 ppm (d, 2 H); UV (cyclohexane) λ_{max} 218 (log ϵ 4.47), 275 (3.17), 286 nm (3.39).

Heterodimer 13. This was prepared by the method of preparation of **12**: yield 8.9%; colorless prisms; mp 128–129 °C; ^1H NMR ($CDCl_3$) 4.52 (s, 2 H), 5.23 (s, 4 H), 7.12 (m, 8 H); UV (*n*-hexane) λ_{max} 286 (log ϵ 3.41), 277 nm (3.19). Anal. Calcd for $C_{20}H_{14}Cl_2$: C, 73.86; H, 4.34. Found: C, 73.67; H, 4.51.

Multiphoton Experiment. The experimental apparatus consists of a Quantel International Q-switched Nd-Yag laser, series YG 580. The laser has an output energy of approximately 0.2 J/pulse at 1.064 μm with a width of 15 ns. The laser beam was sent to the sample cell. The cell is made of quartz. Neutral density filters were used to control the intensity of the incident beam, and narrow band-pass filters were used to ensure that only the 1.064-μm radiation reached the sample and only the light between 340 and 460 nm (Corning 9-57 glass filter) reached the detectors (window for the fluorescence of anthracene). An RCA 2022 phototube with S-1 surface was used to detect the emission from the powder of **12** or **13**. A total of 10^{15} and 2×10^{14} photons were detected from **12** and **13**, respectively. Only anthracene was confirmed as a product by the measurement of the UV spectrum and TLC (silica gel, benzene:ethyl acetate = 10:1) of the reaction mixture in benzene. We assigned the source of the photons as anthracene.

Acknowledgment. This investigation was partially supported by a grant-in-aid for scientific research from the Ministry of Education in Japan, Science and Culture (No 58540136) and by the Air Force Office of Scientific Research under Grant No. AFOSR 84-0363 to purchase the laser system. M.K. thanks Professor Kazuyoshi Kawazu (Okayama University) for the mass measurements of **12** and **13** and Professor N. C. Yang (Chicago University) and Professor E. H. White (Johns Hopkins University) for their encouragement.

Registry No. **3**, 120-12-7; **4**, 723-62-6; **5**, 1210-12-4; **6**, 109350-23-4; **6** (acid), 115307-04-5; **7**, 37602-42-9; **7** (acid), 49578-24-7; **8**, 115318-64-4; **9**, 115307-05-6; **10**, 115307-06-7; **11**, 115307-07-8; **12**, 109350-26-7; **13**, 115307-08-9.

Supplementary Material Available: UV and ^1H NMR data for **12** and **13** (2 pages). Ordering information is given on any current masthead page.

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[15] McDonald, R. N.; Reineke, C. E. *J. Org. Chem.* **1967**, *32*, 6034.