October, 1985] © *1985 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 58, 2863—2869 (1985)* 2863

Photochemical Electron-transfer Reactions of Biphenyl-2,2′-dicarboximide and Naphthalene-1,8-dicarboximide with Olefin. Dependence of the Reaction Course on the Structure of the Aromatic Imide[1)]

Yasuo Kubo,* Takeo Araki, and Kazuhiro Maruyama†
Department of Chemistry, Faculty of Science, Shimane University, Matsue, Shimane 690
†*Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606*

(Received May 16, 1985)

Photoreactions of *N*-methylbiphenyl-2,2′-dicarboximide and *N*-ethylnaphthalene-1,8-dicarboximide (**2**) with 1,1-diphenylethylene (**3**) in methanol gave methanol-incorporated 1 : 1 : 1-adduct (**7**) and 2,2-diphenylethyl methyl ether (**6**), an anti-Markovnikov adduct of methanol to **3**. The ratio of the two types of products largely depends on the structure of the aromatic imides. Probably the spin densities of the radical anions of the aromatic imides seem to play an important role to determine the reaction courses after the photochemical electron-transfer process. Similar results were obtained in the photoreaction of *N*-(2-phenylallyl) aromatic imides; elimination induced by methanol-incorporation *vs.* *anti*-Markovnikov addition of methanol. Photoreactions of *N*-(*trans*-3-phenylallyl) aromatic imides in methanol gave methanol-incorporated *O*-cyclized products (**20** and **27**) and *C*-cyclized products (**21** and **28**). A tentative mechanism for the *O*-cyclization is proposed; *i.e.*, intramolecular electron transfer followed by *anti*-Markovnikov addition of methanol to the radical cation of the double bond moiety, nucleophilic attack of the aromatic imide radical anion moiety, secondary electron-transfer, and then polar addition of methanol.

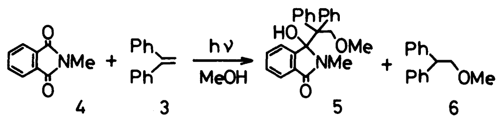
Recently, photoreactions involving electron-transfer process have received much attention from synthetic and mechanistic aspects in organic photochemistry.[2)] Numerous photo-reactions between electron-donor (D) and electron-acceptor (A) molecules have been studied in view of ion radical intermediate.[3)] For example, nucleophiles such as methanol can add to photochemically generated cation radicals of olefins.[4)] However, factors which control the reaction courses after the photochemical electron-transfer between D and A molecules, seem to be not always clear. Little systematic investigation has been known in this field.

In the course of studies on the photochemistry of imides,[5)] we and other groups have found in the photoreactions of phthalimide-olefin systems a variety of alcohol(solvent)-incorporated intermolecular addition[6)] and intramolecular cyclization products,[7)] which seem to occur *via* electron-transfer process. However, the imides employed in the previous investigations have been confined to phthalimides, and little information has been reported on the effects of arene structures of arenedicarboximides (aromatic imides).[8)] Our studies have been focused on the effects of extended π-conjugation system in the arene structure.[9)]

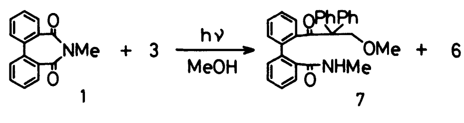
Here we report the results of intermolecular photoreactions of *N*-methylbiphenyl-2,2′-dicarboximide (**1**) and *N*-ethylnaphthalene-1,8-dicarboximide (**2**) with 1,1-diphenylethylene (**3**), and intramolecular photoreactions of *N*-(2- and 3-phenylallyl)biphenyl-2,2′- and naphthalene-1,8-dicarboximides in methanol, comparing with those of the phthalimide derivatives. The results indicate that the structure of the aromatic imide play an important role to determine the reaction courses after the photochemical electron-transfer process.

Results

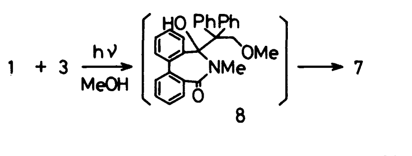
Intermolecular Photoreactions of Aromatic Imides with 3 in Methanol. Photoreaction of *N*-methylphthalimide (**4**) (9.9 mM, 1 mM$=1\times10^{-3}$ mol dm^{-3}) with **3** (12 mM) under N_2 for 5 h gave methanol-incorporated adduct (**5**) (44%) and 2,2-diphenylethyl methyl ether (**6**) (12% based on used **4**) together with recovered **4** (36%) (Eq. 1) as previously reported.[6a,d)] Irradiation of **1** and **3** in similar conditions gave **7** (31%) and **6** (44%) together with recovered **1** (58%) (Eq. 2). The product (**7**) is probably derived from a primary adduct (**8**) by 1,3-hydrogen migration which is the familiar reaction in the imide photochemistry (Eq. 3).[10)] Irradiation of **2** and **3** in similar conditions gave **6** (70%) together with recovered **2** (93%) (Eq. 4). In Eq. 4, **2** acts as a



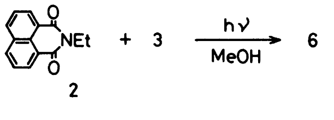
(1)



(2)



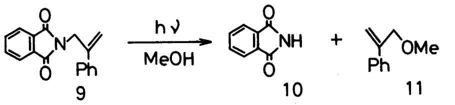
(3)



(4)

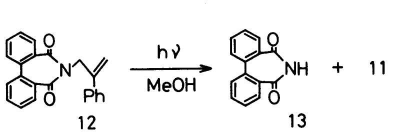
typical electron-transfer photosensitizer for the *anti*-Markovnikov addition of methanol to **3**.[4)] The results of the intermolecular reaction show that the yields of the methanol-incorporated adducts (**5** and **7**) decreases, and at the same time the yield of **6** increases, with extension of the conjugated aromatic π-system of the aromatic imide.

Intramolecular Photoreactions of N-*(2-Phenylallyl) Aromatic Imides in Methanol.* Photoreaction of *N*-(2-phenylallyl)phthalimide (**9**) (0.6 mM) in methanol was reported to give methanol-incorporated elimination products, phthalimide (**10**) (30%) and 3-methoxy-2-phenyl-1-propene (**11**) (30%) (Eq. 5).[7a)]

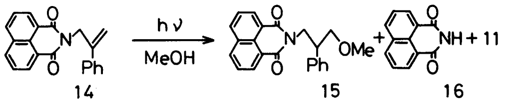


(5)

Irradiation of *N*-(2-phenylallyl)biphenyl-2,2′-dicarboximide (**12**) (0.4 mM) in methanol similarly gave biphenyl-2,2′-dicarboximide (**13**) (25%) and **11** (25%) (Eq. 6). Irradiation of *N*-(2-phenylallyl)naphthalene-1,8-dicarboximide (**14**) (0.5 mM) in methanol gave an *anti*-Markovnikov adduct of methanol (**15**) (27%), naphthalene-1,8-dicarboximide (**16**) (20%), and **11** (22%) (Eq. 7). Thus, the electron-transfer photosensitized addition of methanol was observed only in the reaction of **14** which had the most extended aromatic π-system.

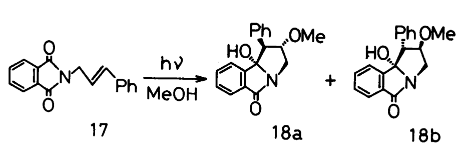


(6)



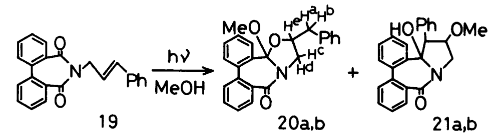
(7)

Intramolecular Photoreactions of N-*(*trans-*3-Phenylallyl) Aromatic Imides in Methanol.* Photoreaction of *N*-(*trans*-3-phenylallyl)phthalimide (**17**) (5 mM) in methanol was reported to give methanol-incorporated *C*-cyclized products [**18a** (68%) and **18b** (17%)] (Eq. 8).[7a,e)]



(8)

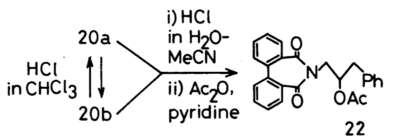
Irradiation of *N*-(*trans*-3-phenylallyl)biphenyl-2,2′-dicarboximide (**19**) (3.3 mM) in methanol gave a mixture of two groups of products; *i.e.*, two stereoisomers of methanol-incorporated *O*-cyclized products [**20a** (30%) and **20b** (5%)], and two stereoisomers of methanol-incorporated *C*-cyclized products [**21a** (21%) and **21b** (17%)] (Eq. 9). The isomers were isolated by chromatography.



(9)

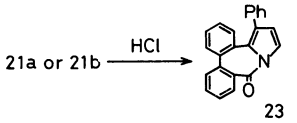
The structures of **20a** and **20b** were assigned on the basis of the spectral data and chemical manipulations outlined below. Combination of the ^{1}H and ^{13}C NMR multiplicity and chemical shifts, and the IR data gave rise to at least four characteristic common features in the structures of **20a** and **20b**. Namely, (i) one amide group [**20a**: IR-1640 cm^{-1}: ^{13}C NMR δ=165.1 (s), **20b**: IR-1628 cm^{-1}: ^{13}C NMR δ=165.1 (s)], but no hydroxyl group (IR), is present. (ii) The benzyl moiety is directly bonded to a ring system and characterized by having the triplet carbon [**20a**: δ=39.6 (t), **20b**: δ=39.3 (t)], and the nonequivalent methylene protons (H^a and H^b). (iii) One quaternary carbon atom [**20a**: δ=108.8 (s), **20b**: δ=109.5 (s)] corresponds reasonably to the acetal carbon [arom-*C*(OMe)(O-)N] adjacent to an aromatic system. (iv) Protons in the methoxyl group [**20a**: δ=2.83 (s), **20b**: δ=2.90 (s)] are strongly shielded by the biphenyl group.

As expected from the acetal structures, **20a** and **20b** were found to be highly sensitive to acid. Thus, on treatment with hydrochloric acid in chloroform, both of pure **20a** and **20b** were converted to an equilibrium mixture of **20a**:**20b**=0.63:1, probably *via* a stable tertiary carbonium ion intermediate. In addition, treatment of a mixture of **20a** and **20b** (6:1) with hydrochloric acid in acetonitrile–water (4/1 volume ratio) followed by acetylation with acetic anhydride and pyridine gave an imide (**22**) (70%) (Eq. 10).



(10)

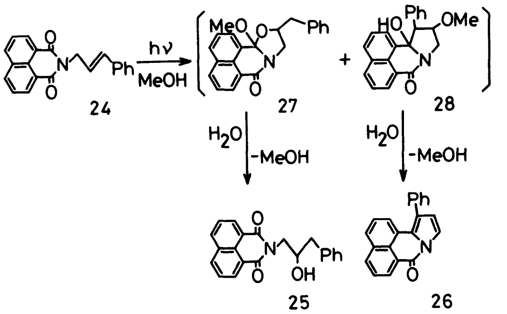
The structures of **21a** and **21b** were deduced from the similarity of the spectral data to those of **18a** and **18b**.[7a)] As expected, an elimination product (**23**) was formed quantitatively from each of **21a** and **21b** upon treatment with hydrochloric acid in chloroform (Eq. 11).



(11)

Photoreaction of **19** (3.3 mM) in 50 ml of methanol-d_1 (>99%) was carried out to examine the deuterium incorporation in **21a**. The ^{1}H NMR spectrum of the isolated **21a** showed that the integration of H^a and H^b signals was reduced to 55±5% compared with those of the other signals, although the ratio of the integration of H^a to that of H^b could not be determined because of the considerable overlapping of these signals. The result indicates almost quantitative one-deuterium incorporation at the benzylic position (H^a and H^b) of **21a**.

Irradiation of *N*-(*trans*-3-phenylallyl)naphthalene-1,8-dicarboximide (**24**) (3.5 mM) in methanol followed by chromatographic (SiO_2) separation gave **25** (58%) and **26** (trace) (Scheme 1). That the products **25** and **26** were not observed in the reaction mixture immediately after the photolysis suggested the isolated products were derived from primary products during the separation. The primary products could not be obtained probably due to their instability. However, the primary photoproducts are presumed to be methanol-incorporated *O*-cyclized products (**27**) for **25**, and methanol-incorporated *C*-cyclized products (**28**) for **26**, respectively, in view of the results obtained in the photolysis of **19**.



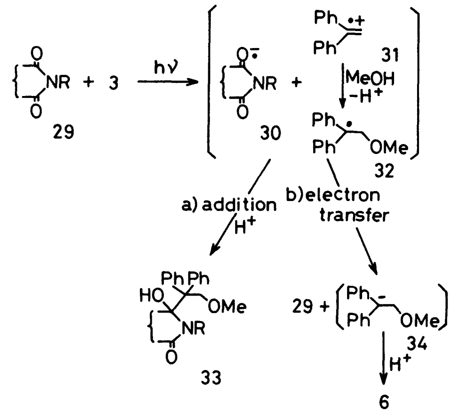
Scheme 1.

Triplet Photosensitization of 19. The photocyclization of **19** (styryl moiety, E_T=59.8 kcal mol^{-1})[11] was not sensitized by benzophenone (E_T=69.2 kcal mol^{-1})[12] as a triplet sensitizer. The benzophenone sensitization in methanol gave only an equilibrium mixture of **19** and the *cis* isomer (0.4:0.6). The result seems to indicate that the photocyclization of **19** directly occurs from the singlet excited state of the aromatic imide moiety.

Discussion

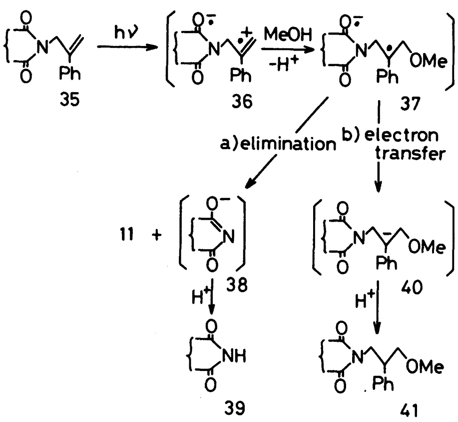
Mechanism on the Intermolecular Photoreactions of Aromatic Imides with 3 and Intramolecular Photoreactions of N-*(2-Phenylallyl) Aromatic Imides.* Photoreaction of *N*-methylnaphthalene-1,8-dicarboximide and **3** in benzene, a nonpolar solvent, was reported to give a cyclobutane.[9a] In benzene no photoreaction of **1** and **3** was observed even on the prolonged irradiation. However, in methanol the distinct mode of photoreactions was observed as described above.

A reasonable mechanism for the intermolecular photoreactions of **1**, **2**, and **4** with **3** is shown in Scheme 2, where **1**, **2**, and **4** are denoted as **29**. The singlet excited state of the imides readily undergoes one-electron reduction through interaction with the electron-rich olefin **3** to give **30** and **31**. The cation radicals **31** are captured by methanol to give **32**. Whether the methanol-incorporated addition to the imide carbonyl group or the *anti*-Markovnikov addition of methanol to **3** predominates is controlled at this stage by the relative rate of bond formation between **30** and **32** to generate the coupling products **33** (path a) *vs.* electron-transfer from **30** to **32** to produce an alkyl anion (**34**) (path b). The results of photoreaction of **1**, **2**, and **4** with **3** suggest the path b is more efficient than the path a in the photoreaction of imide which has the more extended aromatic π-system.



Scheme 2.

A mechanism for the intramolecular photoreactions of **9**, **12**, and **14** is shown in Scheme 3, where **9**, **12**, and **14** are denoted as **35**. Whether the elimination induced by methanol-incorporation or the *anti*-Markovnikov addition of methanol to the olefinic moiety predominates is also controlled by the relative rate of bond cleavage of the 1,4-biradical (**37**) to generate the elimination products (**11** and **39**) (path a) *vs.* the intramolecular electron transfer within **37** to produce an alkyl anion (**40**). The results suggest that the path b can compete with the path a only in the photoreaction of imide **14** which has the most extended aromatic π-system.



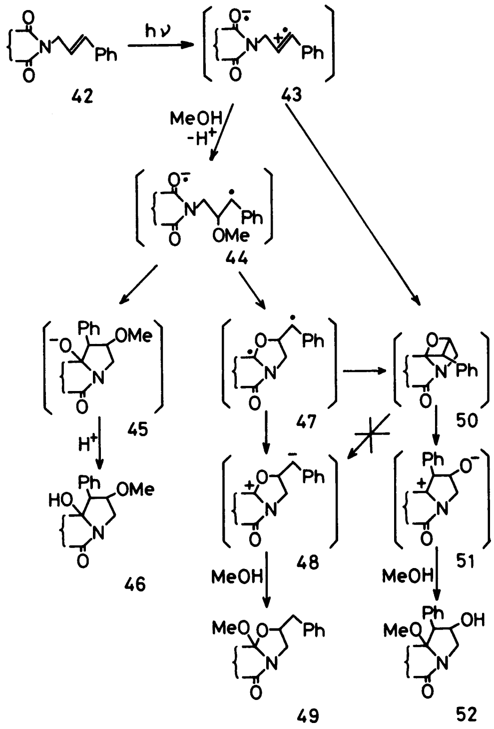
Scheme 3.

The alternative of the path a or the path b in the both photoreactions might be due to the ability of the radical anion of the imide moiety to serve as a reducing agent in reduction of the alkyl radical moiety in path b.[13] The relative reduction potentials of the imide moiety can be used to estimate the energetics and, thus, the rate for the electron transfer processes. However, the one-electron reduction potential of phthalimide (**10**) ($E_{1/2}=-1.47$ V)[14] is somewhat lower than that of naphthalene-1,8-dicarboximide (**16**) ($E_{1/2}=-1.25$ V).[14] Thus, the electron-transfer from the radical anion of naphthalene-1,8-dicarboximide moiety to the alkyl radical moiety (path b) would be expected to be less competitive with the path a than for the case of the corresponding phthalimide moiety, inconsistently with the results.

The alternative of the path a or the path b may be due to the ability of the radical anion of the imide moiety to serve as a radical reactant with the alkyl radical moiety in path a. In the case the relative spin densities of the radical anion of imide moieties can be used to estimate the rate for the radical reaction processes. In accord with the results, the calculated spin density (McLachlan method) at the carbonyl carbon of the radical anion of **10** (0.174) was reported to be considerably larger than that of **16** (0.067).[14] Consequently, whether the reaction proceeds by the path a or the path b seems to mainly depend on the ability of the radical anion of the imide moiety to serve as a radical reactant with the alkyl radical moiety in path a, which is reflected in the relative spin densities of the radical anion of the aromatic imide.

Mechanism on the Intramolecular Photoreactions of N-(trans-*3-Phenylallyl) Aromatic Imides.* The two types of products, *O*-cyclized and *C*-cyclized products, were obtained in the photoreaction of **19** and **24**. Especially, the *O*-cyclization seems to be novel in the photochemistry of the carbonyl compounds.

A possible mechanistic scheme for the intramolecular photo-reaction of **17**, **19**, and **24** is shown in Scheme 4, where **17**, **19**, and **24** are denoted as **42**. The initial step is photoinduced intramolecular electron-transfer from the electron-donating double bond to the excited imide moiety to form an intermediate (**43**), in analogy with the cases of the other systems. Successive anti-Markovnikov addition of methanol to the radical cation moiety results in the formation of **44**. The divergent behavior of these systems stems from the variable reactivity of the intermediate (**44**). From the intermediate, intramolecular coupling (cyclization) of the aromatic imide radical anion moiety and alkyl radical moiety (**44**→**45**), followed by protonation (**45**→**46**), gives *C*-cyclized products (**46**).[7a)] Alternatively, intramolecular nucleophilic attack of the aromatic imide radical anion moiety accompanying elimination of methoxide ion (**44**→**47**), followed by intramolecular electron transfer (**47**→**48**) and polar addition of methanol (**48**→**49**), results in the formation of the *O*-cyclized products (**49**). One deuterium incorporation at the benzylic position of **21a** in the photoreaction in methanol-d_1 supports the presence of the zwitter-ionic precursor (**48**). Whether the intramolecular coupling (radical reaction) (**44**→**45**) or the nucleophilic attack (**44**→**47**) predominates seems to depend on the ability of the radical anion of the imide moiety to serve as a radical reactant with the alkyl radical moiety, which is reflected in the relative spin densities of the radical anion of the aromatic imide, in analogy with the cases of the intermolecular photoreaction and the intramolecular photo-reaction of *N*-(2-phenylallyl) aromatic imides.



Scheme 4.

Another mechanism for the *O*-cyclization of **42**, involving intramolecular oxetane formation might be considered, as the oxetane formation was sometimes reported in photoreactions of aromatic imides and olefins.[9b,15] However, heterolytic cleavage of the oxetane (**50**) derived from **43** or **47** was expected to occur at the C–O bond to give the more stable zwitter ion (**51**), rather than at the C–C bond of the oxetane ring to give **48**. Thus, the mechanism involving the oxetane formation could not rationalize the observed structures of the products. Furthermore, the expected methanol-adduct (**52**) from **51** was not observed in the photoreaction.

In conclusion, this work demonstrates that the structure of the aromatic imide (electron acceptor) play an important role to determine the reaction course after the photochemical electron transfer between the aromatic imide and the olefin (electron donor). These results are also of interest in terms of the effect of the geometrical situation between the acceptor and the donor on the reaction course after the electron-transfer process.

Experimental

The mps were measured by a Yanagimoto micromelting point apparatus, and are uncorrected. ^{1}H NMR spectra were determined on a JEOL JNM-MH-100 spectrometer in $CDCl_3$ solution. IR spectra were obtained with a Hitachi 260-50 spectrophotometer. Mass spectra were measured on a JEOL JMS-DX-300 apparatus. Microanalyses were performed on a Yanagimoto CHN corder MT-2. UV irradiation was carried out with an Eikosha PIH 300-W high-pressure Hg-lamp through Pyrex filter under N_2 at ambient temperature. Column chromatography was done on Wakogel C-200 (silica gel, 74—149 μ). HPLC analyses were performed on a Hitachi 635 A apparatus.

Materials. *N*-Methylbiphenyl-2,2′-dicarboximide (**1**) and *N*-ethylnaphthalene-1,8-dicarboximide (**2**)[16] were prepared by the reaction of the corresponding anhydride and amine.

1: Mp 167—169 °C; ^{1}H NMR δ=3.51 (s, 3H, NMe), 7.4—8.0 (m, 8H, Arom H); IR (KBr) 1695 (imide), 1658 (imide), 1606, 1352, 1322, 740 cm^{-1}. Found: C, 75.89; H, 4.82; N, 5.96%. Calcd for $C_{15}H_{11}NO_2$: C, 75.93; H, 4.67; N, 5.90%.

The imides (**12**, **14**, **19**, and **24**) were prepared by the reaction of the corresponding imide and halide in an analogous manner as described in the preparation of *N*-alkenylphthalimides.[7a)]

N-*(2-Phenylallyl)biphenyl-2,2′-dicarboximide (12)*: From the reaction of **13** and 3-bromo-2-phenyl-1-propene,[17)] 60% based on the bromide; mp 95—97 °C (from ethanol): ^{1}H NMRδ=5.01 (s, 1H, C=CH_2), 5.11 (s, 2H, NCH_2), 5.29 (s, 1H, C=CH_2), 7.2—8.0 (m, 13H, arom H); IR (KBr) 1688 (imide), 1640 (imide), 1358, 1238, 736 cm^{-1}. Found: C, 81.50; H, 5.20; N, 4.08%. Calcd for $C_{23}H_{17}NO_2$: C, 81.39; H, 5.05; N, 4.13%.

N-*(2-Phenylallyl)naphthalene-1,8-dicarboximide (14)*: From the reaction of **16** and 3-bromo-2-phenyl-1-propene, 53% based on the bromide; mp 181—183 °C (from ethanol); ^{1}H NMR δ=4.97 (s, 1H, C=CH_2), 5.19 (s, 2H, NCH_2), 5.32 (s, 1H, C=CH_2), 7.2—7.7 (m, 5H, Ph), 7.74 (t, 2H, arom H), 8.23 (d, 2H, arom H), 8.63 (d, 2H, arom H); IR (KBr) 1698 (imide), 1658 (imide), 1348, 1236, 782 cm^{-1}. Found: C 80.58; H, 4.96; N, 4.50%. Calcd for $C_{21}H_{15}NO_2$: C, 80.49; H, 4.83; N, 4.47%.

N-*(*trans*-3-Phenylallyl)biphenyl-2,2′-dicarboximide (19)*: From the reaction of **13** and cinnamyl chloride,[18)] 80% based on the chloride; mp 155—157 °C (from ethanol); ^{1}H NMR δ=4.81 (d, *J*=6 Hz, 2H, NCH_2), 6.28 (dt, *J*=6, 16 Hz, 1H, CH_2CH=C), 6.66 (d, *J*=16 Hz, 1H, PhC*H*=C), 7.1—8.0 (m, 13H, arom H); IR (KBr) 1702 (imide), 1662 (imide), 1340, 1328, 746 cm^{-1}. Found: C, 81.63; H, 5.26; N, 4.16%. Calcd for $C_{23}H_{17}NO_2$: C, 81.39; H, 5.05; N, 4.13%.

N-*(*trans*-3-Phenylallyl)naphthalene-1,8-dicarboximide (24)*: From the reaction of **16** and cinnamyl chloride, 75% based on the chloride; mp 149—151 °C (from ethanol); ^{1}H NMR δ=4.93 (d, *J*=6 Hz, 2H, NCH_2), 6.37 (dt, *J*=6, 16 Hz, 1H, CH_2CH=C), 6.76 (d, *J*=16 Hz, 1H, PhC*H*=C), 7.0—7.5 (m, 5H, Ph), 7.72 (t, 2H, arom H), 8.18 (d, 2H, arom H), 8.58 (d, 2H, arom H); IR (KBr) 1704 (imide), 1670 (imide), 1388, 1340, 1242, 786 cm^{-1}. Found: C, 80.27; H, 5.02; N, 4.41%. Calcd for $C_{21}H_{15}NO_2$: C, 80.49; H, 4.83; N, 4.47%.

1,1-Diphenylethylene (**3**) was a commercial sample from Tokyo Chemical Industry.

Intermolecular Photoreactions of Aromatic Imides with 3. Solutions of aromatic imide (**1** and **2**) (9.9 mM) and **3** (12 mM) in 20 cm^3 of methanol were irradiated for 5 h. After evaporation of the solvent, the residue was subjected to chromatography to give the products. 2,2-Diphenylethyl methyl ether (**6**) was identical with a sample prepared by irradiation of *p*-dicyanobenzene, **3**, and phenanthrene (sensitizer) in methanol.[4a)] On the other hand, the irradiated methanol solutions were analyzed by HPLC and ^{1}H NMR measurements with an internal standard to determine the yields of the products.

N-*Methyl-2′-(2,2-diphenyl-3-methoxy-1-oxopropyl)biphenyl-2-carboxamide (7)*: Mp 156—158 °C; ^{1}H NMR δ=2.49 (d, *J*=4 Hz, 3H, NH*Me*, these signals were changed to s by shaking with D_2O), 3.14 (s, 3H, OMe), 4.23 and 4.37 (ABq, *J*=19 Hz, 2H, C*H*$_2$OMe), 6.9—7.9 (m, 19H, arom H+NH); IR (KBr) 3370 (NH), 1672 (amide and ketone), 1542, 1232, 758, 702 cm^{-1}. Found: C, 80.31; H, 6.00; N, 3.15%; M$^+$, 449. Calcd for $C_{30}H_{27}NO_3$: C, 80.15; H, 6.05; N, 3.12%; M, 449.

Intramolecular Photoreactions of N-*(2-Phenylallyl) Aromatic Imides.* Solutions of *N*-(2-phenylallyl) aromatic imides (**12** and **14**) in 400 cm^3 of methanol were irradiated for 5 h. After evaporation of the solvent, the residue was subjected to chromatography to give the products. 3-Methoxy-2-phenyl-1-propene (**11**) was identical with an authentic sample.[19)] Biphenyl-2,2′-dicarboximide (**13**) was identical with an authentic sample.[20)] Naphthalene-1,8-dicarboximide (**16**) was also identical with a commercial sample from Nakarai Chemical Industry. On the other hand, the irradiated methanol solutions were analyzed by HPLC and ^{1}H NMR measurements with an internal standard to determine the yields of the products.

N-*(3-Methoxy-2-phenylpropyl)naphthalene-1,8-dicarboximide (15)*: Mp 115—117 °C; ^{1}H NMR δ=3.21 (s, 3H, OMe), 3.5—3.8 [m, 3H, PhC(*H*)C*H*$_2$OMe], 4.36 (dd, *J*=7, 12 Hz, 1H, NCH_2), 4.58 (dd, *J*=6, 12 Hz, 1H, NCH_2), 7.1—7.5 (m, 5H, Ph), 7.71 (t, 2H, arom H), 8.17 (d, 2H, arom H), 8.57 (d, 2H, arom H); IR (KBr) 1709 (imide), 1678 (imide), 1602, 1354, 1248, 802 cm^{-1}. Found: C, 76.41; H, 5.81; N, 3.97% M$^+$, 345. Calcd for $C_{22}H_{19}NO_3$: C, 76.50; H, 5.55; N, 4.06%; M, 345.

Intramolecular Photo-reaction of 19. A solution of **19** in 400 cm^3 of methanol was irradiated for 5 h. After evaporation of the solvent, the residue was subjected to chromatography to give the products. On the other hand, the irradiated methanol solution was analyzed by HPLC and ^{1}H NMR measurement with an internal standard to determine the yields of the products.

*6-Benzyl-4*b*-methoxy-6,7-dihydro-4*bH,9H*-dibenz-[3′,4′:5′,6′]-azepino[2,1-*b*]oxazol-9-one Isomer A (20a)*: Mp 156—158 °C; ^{1}H NMR δ=2.83 (s, 3H, OMe), 2.95 (dd, *J*=6.1, 13.5 Hz, 1H, H^a), 3.27 (dd, *J*=6.4, 13.5 Hz, 1H, H^b), 3.42 (dd, *J*=9.6, 11.2 Hz, 1H, H^c), 4.19 (dd, *J*=5.9, 11.2 Hz, 1H, H^d), 4.5—5.0 (m, 1H, H^e), 7.1—8.1 (m, 13H, arom H); ^{13}C NMR δ=39.6 (t, *C*H$_2$Ph), 50.8 (q, OMe), 50.9 (t, NCH_2), 76.1 (d, OCH), 108.8 [s, Ph*C*(OMe)(O–)N], 125.1, 126.9, 127.7, 128.2, 128.4, 128.6, 129.2, 129.5, 129.7, 129.8, 129.9, 130.3, 130.9, 132.9, 135.7, 136.4, 137.3, 137.6 (18C, arom C), 165.1 (amide); IR (KBr) 1640 (amide), 1455, 1408, 1079, 1045, 742 cm^{-1}. Found: C, 77.62; H, 5.97; N, 3.68% M$^+$, 371. Calcd for $C_{24}H_{21}NO_3$: C, 77.60; H, 5.70; N, 3.77%; M, 371.

Isomer B (20b): Mp 150—152 °C; ^{1}H NMR δ=2.90 (s, 3H, OMe), 3.06 (dd, *J*=6.6, 13.9 Hz, 1H, H^a), 3.27 (dd, *J*=6.0, 13.9 Hz, 1H, H^b), 3.57 (dd, *J*=9.2, 11.0 Hz, 1H, H^c), 4.03 (dd, *J*=5.9, 11.0 Hz, 1H, H^d), 4.3—4.7 (m, 1H, H^e), 7.1—8.1 (m, 13H, arom H); ^{13}C NMR δ=39.3 (t, CH_2Ph), 49.7 (q, OMe), 50.5 (t, NCH_2), 75.6 (d, OCH), 109.5 [s, PhC(OMe)(O–)N], 123.0, 125.2, 127.0, 127.5, 128.0, 128.5, 128.7, 128.9, 129.2, 129.5, 129.9, 130.7, 131.4, 131.8, 136.0, 136.2, 138.0, 138.4 (18C, arom C), 165.1 (amide); IR (KBr) 1628 (amide), 1458, 1419, 1122, 742 cm^{-1}. Found: C, 77.86; H, 5.91; N, 3.82%; M$^+$, 371. Calcd for $C_{24}H_{21}NO_3$: C, 77.60; H, 5.70; N, 3.77% M, 371.

4b-Hydroxy-6-methoxy-5-phenyl-4b,5,6,7-tetrahydro-9H-dibenzo[c,e]pyrrolo[1,2-a]azepin-9-one Isomer A (21a): Mp 191—192.5 °C; ^{1}H NMR δ=3.51 (s, 3H, OMe), 3.86 (dd, J=4, 13 Hz, 1H), 4.2 (br s, 1H, OH), 4.24 (dd, J=7, 13 Hz, 1H), 4.28 (d, J=3 Hz, 1H), 4.2—4.5 (m, 1H), 6.9—7.0 (m, 2H, arom H), 7.1—7.6 (m, 9H, arom H), 7.9—8.1 (m, 1H, arom H); IR (KBr) 3280 (OH), 1640 (amide), 1460, 1420, 1130, 755, 713 cm^{-1}. Found: C, 77.46; H, 5.62; N, 3.80%; M$^+$, 371. Calcd for $C_{24}H_{21}NO_3$: C, 77.60; H, 5.70; N, 3.77%; M, 371.

Isomer B (21b): Mp 213—215 °C; ^{1}H NMR δ=2.8 (br s, 1H, OH), 3.26 (s, 3H, OMe), 3.34 (d, J=10 Hz, 1H), 4.2—4.4 (m, 1H), 4.5—4.7 (m, 1H), 7.1—8.0 (m, 13H, arom H); IR (KBr) 3280 (OH), 1610 (amide), 1455, 1416, 1108, 743, 708 cm^{-1}. Found: C, 77.87; H, 5.50; N, 3.85%; M$^+$, 371. Calcd for $C_{24}H_{21}NO_3$: C, 77.60; H, 5.70; N, 3.77%; M, 371.

*Acid Isomerization and Degradation of **20a** and **20b**.* To a solution of 30 mg of **20a** in 10 cm^3 of chloroform was added a few drops of hydrochloric acid. After 1 d, the solution was washed with water and dried. Then, after evaporation of the solvent, the residue was examined by measurement of ^{1}H NMR spectrum with an internal standard to contain a mixture of **20a** and **20b** (the isomer ratio was 0.63:1, the total yield was 78%). A similar result was obtained starting from 15 mg of **20b**.

To a solution of 30 mg of a mixture of **20a** and **20b** (6:1) in 30 cm^3 of acetonitrile–water (4/1 volume ratio) added a few drops of hydrochloric acid. After 1 d, the solvent was evaporated and the residue was subjected to chromatography to give an alcohol. ^{1}H NMR spectrum of the alcohol could not be obtained due to the low solubility in $CDCl_3$. Thus, the alcohol was converted to its acetate (**22**) (70% based on **20a**+**20b**) by acetic anhydride and pyridine.

N-(2-Acetoxy-3-phenylpropyl)biphenyl-2,2′-dicarboximide (22): Mp 117—120 °C; ^{1}H NMR δ=2.44 (s, 3H, OAc), 2.7—2.8 (m, 2H, CH_2Ph), 3.51 (dd, J=6, 14 Hz, 1H, NCH_2), 4.34 (dd, J=3, 14 Hz, 1H, NCH_2), 5.5—5.7 (m, 1H, CHOAc), 6.9—7.7 (m, 12H, arom H), 8.2 (dd, J=2, 7 Hz, 1H, arom H); IR (KBr) 1740 (ester), 1700 (imide), 1655 (imide), 1338, 1242, 1035, 744 cm^{-1}. Found: C, 74.91; H, 5.59; N, 3.48%; M$^+$, 399. Calcd for $C_{25}H_{21}NO_4$: C, 75.17; H, 5.30; N, 3.51%; M, 399.

*Acid Degradation of **21a** and **21b**.* To a solution of 30 mg of **21a** in 10 cm^3 of chloroform was added a few drops of hydrochloric acid. After 1 d, the solution was washed with water and dried. Then, after evaporation of the solvent, chromatography of the residue gave 22 mg (85%) of **23**. A similar result was obtained starting from 30 mg of **21b** (yield 76%).

5-Phenyl-9H-dibenzo[c,e]pyrrolo[1,2-a]azepin-9-one (23): Mp 169—171.5 °C; ^{1}H NMR δ=6.58 (d, J=3 Hz, 1H), 7.0—7.9 (m, 13H, arom H), 8.07 (d, 1H, arom H); IR (KBr) 1708 (amide), 1364, 1340, 704, 753 cm^{-1}. Found: C, 86.13; H, 4.62; N, 4.36%; M$^+$, 321. Calcd for $C_{23}H_{15}NO$: C, 85.96; H, 4.71; N, 4.36%; M, 321.

*Intramolecular Photoreaction of **24**.* A solution of **24** in 400 cm^3 of methanol was irradiated for 5 h. After evaporation of the solvent, the residue was subjected to chromatography to give **25** and **26**. The primary photoproducts could not be obtained probably due to the instability on the separation. Chromatography on aluminium oxide also gave **25** and **26**. The ^{1}H NMR spectrum of the irradiation mixture revealed that the **25** and **26** were not the primary products, and the primary products showed mainly two methoxy singlets at δ=2.84 and 3.02 (intensity ratio 4:1).

N-(2-Hydroxy-3-phenylpropyl)naphthalene-1,8-dicarboximide (25): Mp 148—150 °C; ^{1}H NMR δ=2.5—2.7 (br s, 1H, OH), 2.8—3.0 (m, 2H, CH_2Ph), 4.2—4.4 (m, 3H, NCH_2CHOH), 7.1—7.4 (m, 5H, Ph), 7.67 (t, 2H, arom H), 8.14 (d, 2H, arom H), 8.51 (d, 2H, arom H); IR (KBr) 3500 (OH), 1702 (imide), 1644 (imide), 1592, 1236, 782 cm^{-1}. Found: C 76.10; H, 4.99; N, 4.31%; M$^+$, 331. Calcd for $C_{21}H_{17}NO_3$: C, 76.12; H, 5.17; N, 4.23%; M, 331. Its acetate: mp 117—120 °C; ^{1}H NMR δ=1.81 (s, 3H, OAc), 3.02 (d, J=7 Hz, 2H, CH_2Ph), 4.23 (dd, J=3, 13 Hz, 1H, NCH_2), 4.59 (dd, J=9, 13 Hz, 1H, NCH_2), 5.6—5.8 (m, 1H, CHOAc), 7.0—7.4 (m, 5H, Ph), 7.67 (t, 2H, arom H), 8.14 (d, 2H, arom H), 8.53 (d, 2H, arom H); IR (KBr) 1732 (ester), 1703 (imide), 1672 (imide), 1596, 1341, 1243, 786 cm^{-1}. Found: C, 73.84; H, 5.29; N, 3.72%; M$^+$, 373. Calcd for $C_{23}H_{19}NO_4$: C, 73.98; H, 5.13; N, 3.75%; M, 373.

11-Phenyl-7H-benzo[de]pyrrolo[2,1-a]isoquinolin-7-one (26): Mp 171—173 °C; ^{1}H NMR δ=6.49 (d, J=4 Hz, 1H), 7.1—8.0 (m, 10H, arom H), 8.13 (d, J=7 Hz, 1H, arom H), 8.69 (d, J=7 Hz, 1H, arom H); IR (KBr) 1715 (amide), 1590, 1321, 785 cm^{-1}. Found: C, 85.47; H, 4.30; N, 4.77%; M$^+$, 295. Calcd for $C_{21}H_{13}NO$: C, 85.40; H, 4.44; N, 4.74%; M, 295.

*Triplet Photosensitization of **19**.* The photoreaction of **19** (3.3 mM) in the presence of benzophenone (30 mM) was carried out with light of >340 nm (filter: Pyrex and aq 5,7-dimethyl-1,4-diazacyclohepta-4,7-dienium perchlorate[21]) in methanol. The irradiated methanol solution was analyzed by HPLC with an internal standard to determine the yields of the products. The *cis* isomer of **19** was obtained by the repeated recrystallization (ethanol) of the irradiated mixture.

N-(cis-3-Phenylallyl)biphenyl-2,2′-dicarboximide: Mp 136—138 °C; ^{1}H NMR δ=4.98 (dd, J=2, 7 Hz, 2H, NCH_2), 5.65 (dt, J=7, 12 Hz, 1H, NCH_2CH=C), 6.58 (dt, J=2, 12 Hz, 1H, C=CHPh), 7.2—8.0 (m, 13H, arom H); IR (KBr) 1692 (imide), 1658 (imide), 1360, 1342, 1318, 738 cm^{-1}. Found: C, 81.11; H, 5.10; N, 4.05%. Calcd for $C_{23}H_{17}NO_2$: C, 81.39; H, 5.05; N, 4.13%.

The authors wish to express their thanks to Mrs. Yukimi Kinuta and Mr. Tetsufumi Misawa for their experimental assistance. The present work was partially supported by a Grant-in-Aid for Scientific Research No. 574199 from the Ministry of Education, Science and Culture.

References

1) Y. Kubo, T. Araki, and K. Maruyama, Symposium on Photochemistry, Kanazawa, October 1982, Abstr., No IA213.

2) P. S. Mariano, *Acc. Chem. Res.*, **16**, 130 (1983); S. L. Mattes and S. Farid, *ibid.*, **15**, 80 (1980); R. S. Caldwell and D. Creed, *ibid.*, **13**, 45 (1980); F. D. Lewis, *ibid.*, **12**, 152 (1979).

3) K. Mizuno, M. Ishii, and Y. Otsuji, *J. Am. Chem. Soc.*, **103**, 5570 (1981); D. S. Steichen and C. S. Foote, *ibid.*, **103**, 1855 (1981); D. R. Arnold, R. M. Borg, and A. Albini, *J. Chem.*

Soc., Chem. Commun., **1981**, 138.

4) a) T. Majima, C. Pac, A. Nakasone, and H. Sakurai, *J. Am. Chem. Soc.*, **103**, 4499 (1981); b) V. R. Rao and S. S. Hixson, *ibid.*, **101**, 6458 (1979); c) A. J. Maroulis and D. R. Arnold, *Synthesis*, **1979**, 819; d) A. J. Maroulis, Y. Shigemitsu, and D. R. Arnold, *J. Am. Chem. Soc.*, **100**, 535 (1978).

5) For reviews see: P. H. Mazzocchi, "Organic Photochemistry," ed by A. Padwa, Marcel Dekker, New York (1981), Vol. 5, p. 421; Y. Kanaoka, *Acc. Chem. Res.*, **11**, 407 (1978).

6) a) K. Maruyama and Y. Kubo, *J. Org. Chem.*, **51**, 1426 (1985); b) P. H. Mazzocchi and F. Khachik, *Tetrahedron Lett.*, **22**, 4189 (1981); c) P. H. Mazzocchi, S. Minamikawa, and P. Wilson, *ibid.*, **1978**, 4361; d) K. Maruyama and Y. Kubo, *Chem. Lett.*, **1978**, 851.

7) a) K. Maruyama and Y. Kubo, *J. Org. Chem.*, **46**, 3612 (1981); b) H. Hayashi, S. Nagakura, Y. Kubo, and K. Maruyama, *Chem. Phys. Lett.*, **72**, 291, (1980); c) M. Machida, K. Oda, K. Maruyama, Y. Kubo, and Y. Kanaoka, *Heterocycles*, **14**, 779 (1980); d) K. Maruyama, and Y. Kubo, *J. Am. Chem. Soc.*, **100**, 7772 (1978); e) K. Maruyama, Y. Kubo, M. Machida, K. Oda, Y. Kanaoka, and K. Fukuyama, *J. Org. Chem.*, **43**, 2303 (1978).

8) P. H. Mazzocchi, C. Somich, and C. Ammon, *Tetrahedron Lett.*, **25**, 3551 (1984).

9) a) Y. Kubo, T. Araki, and K. Maruyama, *Chem. Lett.*, **1984**, 1909; b) Y. Kubo, S. Tojo, M. Suto, R. Toda, and T. Araki, *ibid.*, **1984**, 2075.

10) Y. Kanaoka, Y. Migita, K. Koyama, Y. Sato, H. Nakai, and T. Mizoguchi, *Tetrahedron Lett.*, **1973**, 1193; P. H. Mazzocchi, M. J. Bowen, and N. K. Narian, *J. Am. Chem. Soc.*, **99**, 7063 (1977).

11) D. O. Cowan and A. A. Baum, *J. Am. Chem. Soc.*, **92**, 2153 (1970).

12) S. L. Murov, "Handbook of Photochemistry," Marcel Dekker, New York, (1973), p. 3.

13) J. L. Stavinoha and P. S. Mariano, *J. Am. Chem. Soc.*, **103**, 3136 (1981).

14) R. E. Sioda and W. S. Koski, *J. Am. Chem. Soc.*, **89**, 475 (1967).

15) M. Machida, H. Takeuchi, and Y. Kanaoka, *Tetrahedron Lett.*, **23**, 4981 (1982); P. H. Mazzocchi, L. Klingler, M. Edwards, P. Wilson, and D. Shook, *ibid.*, **24**, 143 (1983).

16) Jaubert, *Ber.*, **28**, 362 (1895) ("Beilsteins Handbuch der Organischen Chemie," **21**, p. 527).

17) J. S. McConaghy, Jr. and W. Lwowski, *J. Am. Chem. Soc.*, **89**, 2357 (1967).

18) T. Posner, *Ber.*, **26**, 1858 (1893).

19) M. G. Baldwin and S. F. Reed, Jr., *J. Polym. Sci., Polym. Chem. Ed.*, **6**, 2627 (1968).

20) H. W. Underwood, Jr. and L. A. Clough, *J. Am. Chem. Soc.*, **51**, 583 (1929).

21) K. Kasha, *J. Opt. Soc. Am.*, **38**, 929 (1948).