Photochemistry of N-(2-Alkenyl)phthalimides. Photoinduced Cyclization and Elimination Reactions

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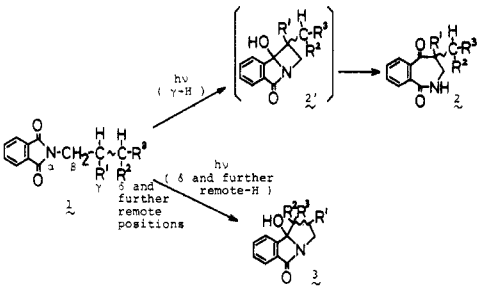
The photochemical reactions of *N*-(2-alkenyl)phthalimides **4a–f** were examined. Irradiation of a solution of **4a,b,d,f** in methanol yielded a mixture of the methanol-incorporated cyclization products **5a + 6a, 13a–d, 15a + 16a**, and **23 + 24**, respectively. Chemical and spectroscopic evidence for the structures of the products is presented. Photolysis of methanol solutions of *trans*-**4d** or *cis*-**4d** resulted in cis–trans isomerization to attain an equilibration ratio of *trans*-**4d**/*cis*-**4d** of 85–90/15–10, together with the cyclization to **15a** and **16a**. Irradiation of a methanol solution of **4e** yielded a mixture of the methanol-incorporated elimination products **21** and **22**. No photoreaction of **4c** was observed in methanol. In acetonitrile, **4a–f** showed no change upon irradiation, with the exception of *trans*-**4d** and *cis*-**4d**. The latter two underwent cis–trans isomerization under the same conditions. Possible reaction paths are proposed, i.e., an intramolecular electron transfer from olefinic double bond to the singlet excited state of phthalimide moiety followed by successive anti-Markovnikov addition of methanol and ring formation to give the final product.

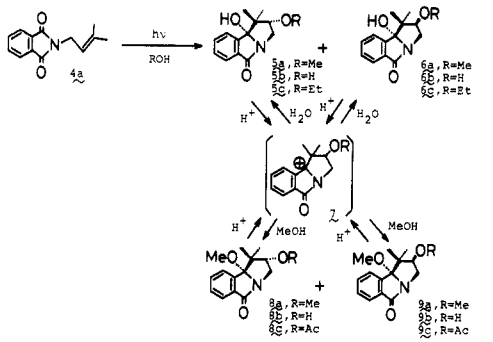
In recent years a number of reports on the photochemistry of imides have been published: for example, (a) oxetane formation,[1] (b) α-cleavage reaction,[2] (c) hydrogen abstraction.[3] Especially a wide variety of N-substituted phthalimides **1** such as *N*-alkyl-,[4] *N*-cycloalkyl-,[5] *N*-alkoxyalkyl-,[6] *N*-arylalkyl-,[7] *N*-alkylaryl-,[8] *N*-aminoalkyl-,[9] and *N*-[(alkylthio)alkyl]-substituted[10] phthalimides undergo photochemical intramolecular hydrogen abstraction reactions to give 3,4-benzo-6,7-dihydroazepine-2,5-diones **2** (via γ-hydrogen abstraction) and cyclization products **3** (via δ-hydrogen and further remote hydrogen abstraction; see Scheme I).

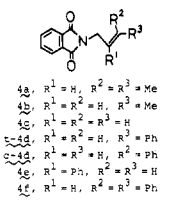
Previously we published a short paper on a new type of photocyclization of N-substituted phthalimides, that is, solvent-incorporated cyclization of *N*-(2-alkenyl)phthalimides.[11] This paper contains full details of the investigations. *N*-(2-Alkenyl)phthalimides **4a–f** were prepared, and their photochemical reactions were examined in a variety of solvents.

Scheme I



Scheme II





Results and Discussion

Irradiation of 4a. A methanol solution of **4a** (5 mM) was irradiated under a nitrogen atmosphere with a high-pressure Hg lamp at ambient temperature for approximately 5 h. At this stage, the starting material had almost disappeared. The products were considerably photostable

(1) (a) K. Maruyama and Y. Kubo, *J. Org. Chem.*, **42**, 3215 (1977); (b) K. Maruyama and Y. Kubo, *Chem. Lett.*, 769 (1978); (c) K. Maruyama, T. Ogawa, and Y. Kubo, *ibid.*, 1107 (1978); (d) Y. Kanaoka, K. Yoshida, and Y. Hatanaka, *J. Org. Chem.*, **44**, 664 (1979).

(2) (a) R. O. Kan and R. L. Furey, *Tetrahedron Lett.*, 2573 (1966); (b) D. W. Jones and G. Kneen, *J. Chem. Soc., Chem. Commun.*, 1038 (1972); (c) J. A. Schutyser and F. C. De Schryver, *Chem. Ind. (London)*, **3**, 465 (1972); (d) Y. Kanaoka, T. Tsuji, and K. Itoh, K. Koyama, *Chem. Pharm. Bull.*, **21**, 455 (1973); (e) Y. Katsuhara, H. Maruyama, Y. Shigemitsu, and Y. Odaira, *Tetrahedron Lett.*, 1323 (1973); (f) G. Scharf and B. Fuchs, *J. Chem. Soc., Chem. Commun.*, 244 (1975); (g) J. A. Schutyser and F. C. De Schryver, *Tetrahedron*, **32**, 251 (1976); (h) Y. Kanaoka, H. Okajima, and Y. Hatanaka, *Heterocycles*, **8**, 339 (1977); (i) K. Maruyama, T. Ishitoku, and Y. Kubo, *J. Am. Chem. Soc.*, **101**, 3670 (1979); (j) Y. Kanaoka, H. Okajima, and Y. Hatanaka, J. Org. Chem., **44**, 1749 (1979); (k) P. H. Mazzocchi, W. Jameson, T. Nishiyama, and A. DeCamp, *Tetrahedron Lett.*, 989 (1980).

(3) (a) Y. Kanaoka, *Yuki Gosei Kagaku Kyokaishi*, **33**, 949 (1975); (b) Y. Kanaoka, *Acc. Chem. Res.*, **11**, 407 (1978), and references cited therein; (c) M. Tanabe, R. L. Dehn and R. R. Bramhall, *J. Agric. Food Chem.*, **22**, 54 (1974); (d) H. J. Roth and D. Schwarz, *Arch. Pharm. (Weinhein, Ger.)*, **309**, 52 (1976); (e) H. J. Roth and G. Hundeshagen, *ibid.*, **309**, 58 (1976).

(4) Y. Kanaoka, Y. Migita, K. Koyama, Y. Sato, H. Nakai, and T. Mizoguchi, *Tetrahedron Lett.*, 1193 (1973).

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(6) H. Nakai, Y. Sato, H. Ogiwara, T. Mizoguchi, and Y. Kanaoka, *Heterocycles*, **2**, 621 (1974).

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(8) M. Terashima, K. Koyama, and Y. Kanaoka, *Chem. Pharm. Bull.*, **26**, 630 (1978).

(9) (a) H. J. Roth and D. Schwarz, *Arch. Pharm. (Weinheim, Ger.)*, **308**, 218 (1975); (b) H. J. Roth and D. Schwarz, *ibid.*, **308**, 631 (1975); (c) H. J. Roth, D. Schwarz, and G. Hundeshagen, *ibid.*, **309**, 48 (1976); (d) M. Machida, H. Takeuchi, and Y. Kanaoka, *Heterocycles*, **7**, 273 (1977); (e) J. D. Coyle and G. L. Newport, *Tetrahedron Lett.*, 899 (1977); (f) J. D. Coyle, G. L. Newport, and A. Harriman, *J. Chem. Soc., Perkin Trans. 2*, 133 (1978).

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(11) K. Maruyama, Y. Kubo, M. Machida, K. Oda, Y. Kanaoka, and K. Fukuyama, *J. Org. Chem.*, **43**, 2303 (1978).

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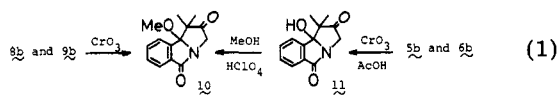
on prolonged irradiation. Chromatography gave the two stereoisomeric products **5a** (41%) and **6a** (41%). Progress of the photoreaction was followed by ^1H NMR spectroscopy. A portion of the reaction mixture was subjected to inspection at different times. No other products or intermediates were detectable, and the isomer ratio of **5a**/**6a** was kept constant during the course of the reaction. On the basis of the mass spectra and the elemental analyses, the composition of the products **5a** and **6a** was determined as $C_{14}H_{17}NO_3$, the starting imide plus MeOH. The structure of the products **5a** and **6a** was assigned as 1,1-dimethyl-9b-hydroxy-2-methoxy-1,2,3,9b-tetrahydro-5*H*-pyrrolo[2,1-*a*]isoindol-5-one on the basis of the IR and ^1H NMR spectra and the chemical manipulations outlined below. The IR spectra (KBr disk) of **5a** and **6a** showed respectively amide carbonyl bands at 1685 and 1680 cm^{-1}, as well as a characteristic bands due to the hydroxy group at 3400 and 3250 cm^{-1}. The ^1H NMR spectra of **5a** and **6a** both showed three kinds of methyl singlets due to the two methyl protons and one methoxy proton, signals of a three-spin system due to H^1, H^2, and H^3, a singlet due to the hydroxy proton (the singlet was disappeared by shaking with a drop of D_2O), and low-field multiplet signals due to the aromatic protons. Both of the products **5a** and **6a** were resistant to acetylation by acetic anhydride–pyridine and to chromic acid oxidation. When a $CDCl_3$ solution of **5a** mixed with a drop of D_2O was allowed to stand for a long time at room temperature, isomerization from **5a** to **6a** was observed, and an equilibrium ratio of **5a**/**6a** of 2:1 was achieved. Under the similar conditions, a part of **6a** isomerized to **5a** to give an equilibrated mixture. The isomerization could probably occur via a common stable tertiary carbonium ion **7** catalyzed by a trace of DCl. In actuality, on treatment with a trace amount of perchloric acid in methanol, each of **5a** and **6a** was converted to an equilibrium mixture of the methyl ethers **8a** and **9a** (3:1; see Scheme II).

When a solution of **4a** (5 mM) in water–acetonitrile (1/8 v/v) was irradiated, the corresponding water-incorporated cyclization products **5b** and **6b** were obtained in a yield of 70% (1:1 **5b**/**6b**). A mixture of the products **5b** and **6b** was converted to an equilibrium mixture of the monomethyl ethers **8b** and **9b** (1:3) by being treated with methanol in the presence of a trace amount of perchloric acid. Alcohols **8b** and **9b** were easily acetylated by acetic anhydride–pyridine to give **8c** and **9c**, respectively, and they were oxidized by Jones oxidation to give ketone **10**. Ketone **10** was also obtained by the reverse manipulation, i.e., initial oxidation of **5b** and **6b** followed by successive hydrolysis and methylation (see eq 1).



(1)

The stereochemistry of the compounds **5**, **6**, **8**, and **9** was assigned by their IR and ^1H NMR spectra. The IR spectra of **5c** and **6c** in dilute carbon tetrachloride solutions are shown in Figure 1. The spectra of **5c** showed a single amide carbonyl band at 1715 cm^{-1} and a single hydroxy band at 3490 cm^{-1}, presumably due to the intramolecular hydrogen bonding with ether group [–OH···O(Et)–]. No band shift was observed on with concentrating the solution. On the contrary, the spectra of **6c** showed two amide carbonyl bands at 1715 and 1695 cm^{-1} and two hydroxy bands at 3580 and 3300 cm^{-1}. The absorption bands centered at 3580 and 1715 cm^{-1} predominated with dilution of the solution. Therefore, the bands at 3580 and 1715 cm^{-1} were assigned to free OH and C=O, and the bands

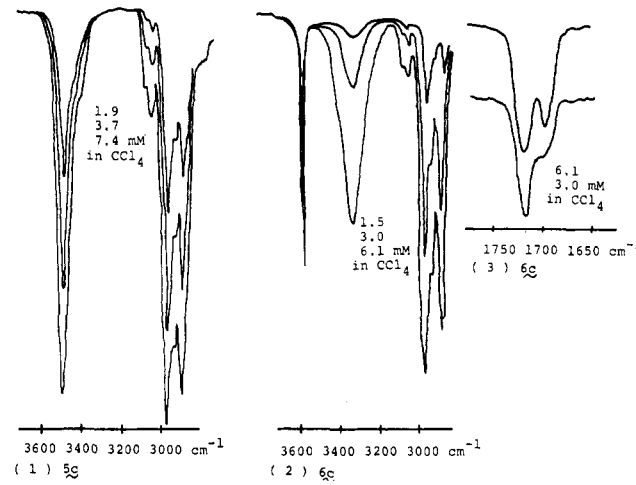


Figure 1. Infrared spectra of **5c** and **6c**.

at 3300 and 1695 cm^{-1} to intermolecular hydrogen bonded OH and C=O (>C=O···HO–). These results support the stereochemistry of the compounds **5** and **6**.

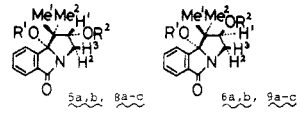
The ^1H NMR data of **5**, **6**, **8**, and **9** are summarized in Table I. ^1H NMR spectra of these compounds showed the presence of two kinds of *C*-methyl groups. The *endo*-methyl (Me^1) signals appeared at δ 0.28–0.47 and the *exo*-methyl (Me^2) signals at δ 1.25–1.42. The differences between the chemical shifts of the *endo*-methyl signals and those of the *exo*-methyl signals in each compounds were in the region of 0.78–1.08 ppm. The ^1H NMR spectrum of **12**, possessing a related structure, was reported to show the *endo*-methyl signal at δ 0.50 and the *exo*-methyl signal at δ 1.18 in $CDCl_3$.[12] The anisotropic shielding effect of

12

the phenyl ring is probably responsible for the difference of the chemical shift of the two methyl groups. The OR^1 methoxy protons showed the signals at δ 2.89–3.02 in **8a–c** and **9a–c**. The higher field shift of the OR^1 methoxy signals could reflect a possible shielding effect of the phenyl ring. Thus, for the isomer **5** or **8**, the higher field shift of the methine (H^1) signals compared to those of the corresponding isomers **6** or **9** (shift for **6a** minus shift for **5a** = 0.3 ppm, **6b** – **5b** = 0.58 ppm **9a** – **8a** = 0.69 ppm **9b** – **8b** = 0.6 ppm **9c** – **8c** = 0.30 ppm) may be explicable in terms of the same anisotropic effect seen for the *C*-methyl groups. In the ^1H NMR spectra of **5b** and **6b** the assignment of the H^1 signals was easily carried out on the basis of the observed coupling between the H^1 and OR^2 hydroxy protons. The coupling disappeared on addition of a drop of D_2O to the solution. In the ^1H NMR spectra of **8c** and **9c** the H^1 protons showed lower field signals at δ 5.17 and 5.47 compared with those of **8a,b** and **9a,b** due to the presence of the acetoxy groups. Furthermore, a characteristic coupling pattern of the three spin system (H^1, H^2, H^3) was observed in the ^1H NMR spectra of the series of the compounds. The geminal coupling constants between H^2 and H^3 were 11–13 Hz in all the compounds. In the series of **5a–c** and **8a–c**, the vicinal coupling constants between H^1 and H^2 were 0–2 Hz, and those between H^1 and H^3 were 5–7 Hz. On the other hand, the vicinal coupling constants between H^1 and H^2 in the series of **6a–c** and **9a–c** were 8 Hz, and those between H^1 and H^3 were also 8 Hz. Ap-

(12) M. Suzuki, H. Hart, E. Dunkelblum, and W. Li, *J. Am. Chem. Soc.*, **99**, 5083 (1977).

Table I. ^{1}H NMR Spectral Data[a] of 5a,b, 6a,b, 8a–c, and 9a–c



compd (R^1, R^2)	chemical shift,[b] δ				
	H^1 (1 H)	H^2 (1 H), H^3 (1 H)	R^1, R^2	Me^1 (s, 3 H), Me^2 (s, 3 H)	arom H (m, 4 H)
5a (H, Me)	3.5–3.9 (m, 3 H)		4.51 (s, 1 H, OH), 3.48 (s, 3 H, OMe)	0.42, 1.42	7.3–7.9
5a (H, Me)[c]	3.91 (d, J = 5)	3.98 (d, J = 13), 4.54 (dd, J = 5, 13)			
6a (H, Me)	4.37 (t, J = 8)	3.27 (dd, J = 8, 11), 3.62 (dd, J = 8, 11)	3.07 (s, 1 H, OH), 3.43 (s, 3 H, OMe)	0.32, 1.40	7.3–7.8
5b (H, H)[d]	4.20 (dd, J = 5, 7)	3.33 (d, J = 12), 3.89 (dd, J = 5, 12)	5.42 (s, 1 H, OH), 4.71 (d, J = 7, 1 H, OH)	0.35, 1.42	7.4–7.8
6b (H, H)[d]	4.78 (m, J = 7, 8, 8)[e]	3.19 (dd, J = 8, 11), 3.58 (dd, J = 8, 11)	5.26 (s, 1 H, OH), 4.44 (d, J = 7, 1 H, OH)	0.28, 1.34	7.4–7.8
8a (Me, Me)	3.63 (dd, J = 2, 6)	3.28 (dd, J = 2, 12), 4.12 (dd, J = 6, 12)	2.96 (s, 3 H, OMe), 3.40 (s, 3 H, OMe)	0.41, 1.36	7.3–7.8
9a (Me, Me)	4.32 (t, J = 8)	3.41 (dd, J = 8, 11), 3.70 (dd, J = 8, 11)	2.90 (s, 3 H, OMe), 3.44 (s, 3 H, OMe)	0.34, 1.36	7.3–7.9
8b (Me, H)	3.8–4.1 (m, 3 H)[f]	3.24 (d, J = 12)	3.02 (s, 3 H, OMe)	0.38 1.35	7.3–7.9
9b (Me, H)	4.68 (t, J = 8)	3.35 (dd, J = 8, 11), 3.59 (dd, J = 8, 11)	2.89 (s, 3 H, OMe), 3.94 (s, 1 H, OH)	0.32, 1.30	7.3–7.9
8c (Me, Ac)	5.17 (dd, J = 2, 7)	3.13 (dd, J = 2, 12), 4.22 (dd, J = 7, 12)	2.97 (s, 3 H, OMe), 2.12 (s, 3 H, OAc)	0.47, 1.25	7.3–7.9
9c (Me, Ac)	5.47 (t, J = 8)	3.34 (dd, J = 8, 12), 3.74 (dd, J = 8, 12)	2.95 (s, 3 H, OMe), 2.07 (s, 3 H, OAc)	0.40, 1.30	7.3–7.9

[a] Spectra were determined with a JEOL PS-100 (100 MHz). [b] Chemical shifts are relative to Me_4Si in $CDCl_3$; J values are in hertz; s = singlet, d = doublet, t = triplet, dd = doublet of doublet. [c] In the presence of Eu(fod) (shift reagent); **5a**/Eu(fod) molar ratio of 1:0.06. [d] Solvent CD_3COCD_3. [e] The coupling constants were estimated from the other signals (H^2, H^3, and OH). [f] In these signals H^1, OH, and H^2 were included.

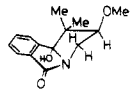
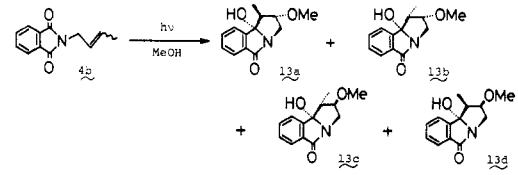


Figure 2. "Envelope" conformation of **6a**.

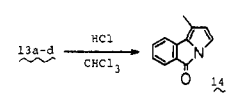
plying the Karplus relation to this system,[13] we may be able to explain the observed coupling constants of the series of the compounds in terms of an "envelope" conformation in which one of the carbon atom (H^1–C–OR^2) is puckered out to the exoside of the plane of the other four atoms in the ring (Figure 2). This "envelope" conformation seems to be sterically more stable than another envelope conformation in which one of the carbon atoms (H^1–C–OR^2) is puckered out to the endo side. Examination of the envelope molecular model predicts that the dihedral angles of ∠(H^1–H^2) and ∠(H^1–H^3) in the series of compounds **5a–c** and **8a–c** are 85° and 35°, with coupling constants J(H^1–H^2) = 0.4 Hz and J(H^1–H^3) = 6.0 Hz. These values are all in a good agreement with the observed coupling constants J(H^1–H^2) = 0–2 Hz and J(H^1–H^3) = 5–7 Hz, respectively. Similarly, the dihedral angles of ∠(H^1–H^2) and ∠(H^1–H^3) in the series of compounds **6a–c** and **9a–c** are predicted to be 35° and 155°, together with their coupling constants of J(H^1–H^2) = 6.0 Hz and J(H^1–H^3) = 8.1 Hz consistent with the observed coupling constants J(H^1–H^2) = 8 Hz and J(H^1–H^3) = 8 Hz, respectively.

Irradiation of an ethanol solution of **4a** (5 mM) gave the corresponding products **5c** (20%) and **6c** (20%) accompanied by the recovery of **4a** (45%). Treated with a trace of hydrochloric acid in chloroform, each of **5c** or **6c** gave an equilibrium mixture of **5c** and **6c** in the ratio 2.5:1. However, on irradiation of **4a** in isopropyl alcohol (5 mM) for 15 h, the starting imide **4a** was only recovered in 85% yield without any other products. Photolysis of **4a** in ethyl acetate, acetone, acetonitrile, and benzene (5 mM) for about 10 h also resulted in recovery of the starting material in amounts of 80–90%.

Irradiation of 4b. A methanol solution of **4b** (5 mM) was irradiated (7 h) to give four products. By fractional recrystallization and repeated chromatography, three products, **13a–c**, were isolated in nearly pure form, but product **13d** was obtained contaminated with **13c**. The isolated total yield of the four products was 75%, and the isomer ratio was roughly 4:1:5:2 **13a**/**13b**/**13c**/**13d** on the basis of the ^{1}H NMR spectrum and HPLC analysis (eq 2).



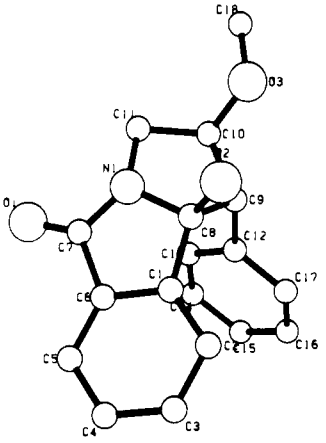
(2)



(3)

The four products corresponded to all of the possible stereoisomers of the methanol-incorporated cyclization products on the basis of the ^{1}H NMR, IR, and mass spectra and elemental analyses. Furthermore, on treatment with a trace of hydrochloric acid in chloroform, a mixture of **13a–d** was converted to **14** (eq 3). The structure of **14** was supported by the spectral data and elemental analysis. The stereochemistry of the C^1-methyl groups of **13a–d** was

(13) The Karplus rule have been applied to conformational analyses of five-membered heterocyclic compounds. For example see: (a) R. U. Lemieux, J. D. Stevens, and R. R. Fraser, *Can. J. Chem.*, **40**, 1955 (1962); (b) L. D. Hall, *Chem. Ind.* (London), 950 (1963); (c) R. J. Abraham and W. A. Thomas, *J. Chem. Soc.*, 3739 (1964).



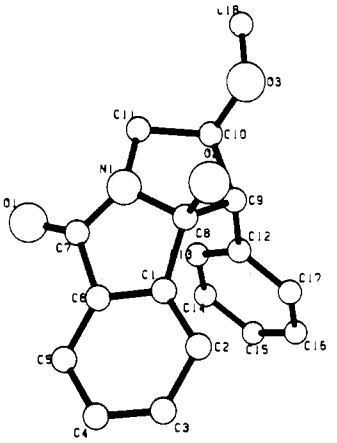
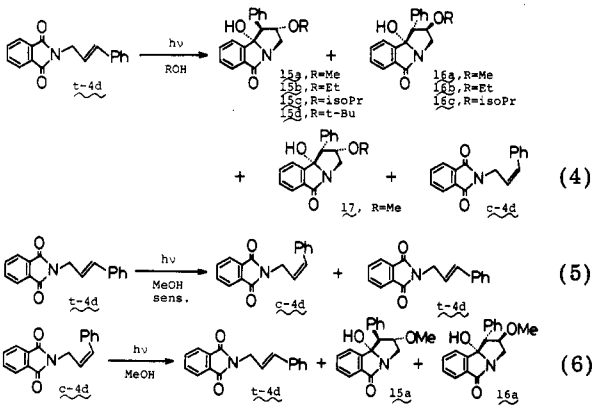


Figure 3. Stereoscopic view of **15a**.

easily determined by the chemical shifts of the methyl protons and the C^1 methine protons (HCMe). The C^1-methyl protons of **13a** and **13d** appeared at δ 0.41 as doublets and the C^1 methine protons appeared at δ 2.5–2.9 as multiplets. Therefore, **13a** and **13d** have *endo*-C^1-methyl groups. On the other hand, the C^1-methyl protons and C^1 methine protons of **13b** and **13c** appeared at δ 1.37 and 1.5–1.9, respectively, indicating the presence of *exo*-C^1-methyl groups in their structures. The stereochemistry of the C^2-methoxy groups of **13a–d** was assigned as follows. In the pair of compounds **13b** and **13c**, the methoxy signal of **13c** and the C^2 methine signals of **13b** appeared at slightly higher fields compared with those of the other. The ^{1}H NMR spectrum of **13c** showed J = 7 and 8 Hz between the C^2 methine proton (HCOMe) and the C^3 methylene protons, in agreement with dihedral angles of approximately 35° and 155° as described in the cases of photoproducts of **4a**. The IR spectra of **13a** and **13b** in carbon tetrachloride solution showed absorption bands centered at 3480 and 3490 cm^{-1}, respectively, assigned to intramolecular hydrogen bonded hydroxy group (–OH···O(Me)–].

Irradiation of 4c. A methanol solution of **4c** (5 mM) was irradiated for about 15 h to give mainly the recovered imide **4c** (73%) and no corresponding methanol-incorporated products, except with a few minor products.

Irradiation of *trans*- and *cis*-4d. A methanol solution of *trans*-**4d** (5 mM) was irradiated for about 5 h. Chromatography gave **15a** (54%), **16a** (15 %), and a trace of **17** (eq 4–6). The reaction was followed by ^{1}H NMR



(4)

(5)

(6)

spectroscopy and revealed that in the course of the reaction less than 10% of the cis isomer (*cis*-**4d**) was formed compared to the amount of trans isomer (*trans*-**4d**). When other alcohols (ethanol, isopropyl alcohol, *tert*-butyl alcohol) were used as the solvent, the corresponding alcohol-incorporated cyclization products **15b–d** and **16a–c** were obtained similarly. These results are summarized in Table II. The products **15a** and **16a** were found to be very sensitive to acid. On being treated with a drop of hydrochloric acid in chloroform, **15a** and **16a** were changed to **18** (eq 7). The reaction was followed by ^{1}H NMR spectroscopy at room temperature. In a $CDCl_3$ solution containing equivalent weights of **15a** and **16a**, **16a** disappeared faster than **15a**. After being refluxed in acetic anhydride and sodium acetate for 0.5 h, **15a–d** were easily dehydrated to give the corresponding **19a–d**. The isomer **16a** also gave **19a** in the same way. The dehydrated product **19a** was also converted to **18** in the presence of an acid catalyst. On the other hand, **15a** was oxidized by chromic acid in acetic acid to give **20a** (eq 8). Oxidative C–C bond

Table II. Photocyclization of *trans*-*N*-(3-Phenylallyl)phthalimide (*trans*-4d) in Alcohols[a]

	R,	alcohols	irradiation time, h	isolated yields,[b] % 15	16
a,	Me,	methanol	5	54	15
b,	Et,	ethanol	5	62	16
c,	*i*-Pr,	isopropyl alcohol	10	50	7
d,	*t*-Bu,	*tert*-butyl alcohol	15	55	*c*

[a] The alcohol solution of *trans*-**4d** (5 mM) was irradiated with an Hg lamp. [b] Yields were based on the starting imide, *trans*-**4d**, used. [c] Not isolated in a pure form.

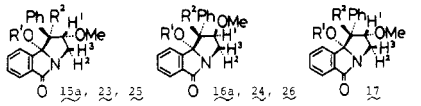
(7)

(8)

cleavage reactions of tertiary alcohols in chromic acid oxidation are well-known processes.[14] The dehydrated products **19a** and **19b** were also oxidized to **20a** and **20b**, respectively. On the contrary, minor photoproduct **16a** was resistant to the oxidation under the same conditions. The structures of these products, **15–20**, were assigned by means of ^{1}H NMR, IR, and mass spectra and elemental analyses. The structure and the stereochemistry of **15a**

(14) (a) L. F. Fieser and J. Szmuszkovicz, *J. Am. Chem. Soc.*, **70**, 3352 (1948); (b) J. G. Burr, Jr., *ibid.*, **75**, 1990 (1953).

Table III. ^{1}H NMR Spectral Data of 15a, 16a, and 23-26



compd (R^1, R^2)	chemical shift,[a] δ				
	H^1 (1 H)	H^2, H^3	R^2 (1 H)	R^1, OMe	arom H
15a (H, H)	4.3-4.5 (m, 2 H)	3.5-3.9 (m, 2 H)		4.20 (s, 1 H, OH), 3.41 (s, 3 H, OMe)	6.6-6.9 (m, 2 H), 7.0-7.1 (m, 3 H), 7.2-7.4 (m, 3 H), 7.5-7.7 (m, 1 H)
15a (H, H)[b]	4.4-4.6 (m, J = 2, 2, 7)[c]	3.90 (dd, J = 2, 13, 1 H), 4.85 (dd, J = 7, 13, 1 H)	4.05 (d, J = 2)		
16a (H, H)	4.7-5.1 (m, J = 6, 7, 9)[c]	3.50 (dd, J = 6, 11, 1 H), 3.78 (dd, J = 7, 11, 1 H)	2.78 (d, J = 9)	3.18 (s, 3 H, OMe), 3.64 (s, 1 H, OH)	6.8-7.0 (m, 1 H), 7.1-7.6 (m, 8 H)
17 (H, H)	4.46 (ddd, J = 1, 4, 4)	3.75 (dd, J = 1, 13, 1 H), 3.95 (dd, J = 4, 13, 1 H)	2.77 (d, J = 4)	3.41 (s, 3 H, OMe), 4.67 (s, 1 H, OH)	6.9-7.8 (m, 9 H)
23 (H, Ph)	5.02 (d, J = 5)	3.83 (d, J = 14, 1 H), 4.60 (dd, J = 5, 14, 1 H)	*d*	3.35 (s, 3 H, OMe), 5.20 (s, 1 H, OH)	6.6-7.0 (m, 5 H), 7.1-8.1 (m, 9 H)
24 (H, Ph)	5.19 (t, J = 7)	3.83 (d, J = 7, 2 H)	*d*	3.48 (s, 3 H, OMe), 4.18 (s, 1 H, OH)	6.6-7.0 (m, 5 H), 7.1-8.1 (m, 9 H)
25 (Me, Ph)	4.96 (dd, J = 1, 7)	3.63 (dd, J = 1, 13, 1 H), 4.82 (dd, J = 7, 13, 1 H)	*d*	3.16 (s, 3 H, OMe), 3.38 (s, 3 H, OMe)	6.5-7.0 (m, 5 H), 7.1-7.9 (m, 9 H)
26 (Me, Ph)	5.10 (dd, J = 7, 8)	3.92 (dd, J = 8, 12, 1 H), 4.22 (dd, J = 7, 12, 1 H)	*d*	3.02 (s, 3 H, OMe), 3.54 (s, 3 H, OMe)	6.6-7.0 (m, 5 H), 7.1-7.9 (m, 9 H)

[a] Solvent $CDCl_3$; J values are given in hertz. [b] In the presence of Eu(fod) (shift reagent); **15a**/Eu(fod) molar ratio of 1.0.02. [c] The coupling constants were estimated from the other signals (H^2, H^3, and R^2). [d] The corresponding phenyl protons were included under in aromatic H.

were confirmed by X-ray diffraction analysis. As can be seen from the stereoscopic view in Figure 3, the structure of **15a** possesses the C^1-*endo*-phenyl group and C^1-*exo*-methoxy group. The ^{1}H NMR data of **15a**, **16a**, and **17** are summarized in Table III. The assignment of the signals was easily performed by inspecting the coupling patterns. The R^2 = H proton of **16a** and **17** showed a higher chemical shift (δ 2.78 and 2.77) as compared with that of **15a** (δ ~3.8). In the ^{1}H NMR spectra of **15a–d**, C^1-phenyl protons showed characteristic signals; i.e., two protons, probably two ortho protons, appeared at a higher field, δ 6.6–6.9. The anisotropic shielding effect of the fixed phenyl ring to the eclipsed C^1-phenyl group is probably responsible for the higher field shift. No such the effect was observed in the ^{1}H NMR spectra of **16a** and **17**. Therefore, **16a** has the C^1-*exo*-phenyl group, and **17** has the C^1-*endo*-phenyl group. The difference in the chemical reactivity between **15a** and **16a** toward the acid dehydration and the chromic acid oxidation may be explainable in terms of their stereochemistry. The stereochemistry of methoxy group of **16a** can be assigned by the chemical shift and the coupling constant of the C^2 methine proton (H^1). The H^1 proton of **16a** showed lower field signals at δ 4.7–5.1 compared with those at δ 4.3–4.6 for **15a** and those at δ 4.46 for **17**. The ^{1}H NMR spectrum of **15a** in the presence of a small amount of a shift reagent (**15a**/Eu(FOD)[15] molar ratio of 1:0.02) showed $J(H^1–H^2)$ = 2 Hz, $J(H^1–H^3)$ = 7 Hz, and $J(H^1–R^2)$ = 2 Hz, in agreement with dihedral angles of approximately 85°, 35°, and 85°, respectively, predicted from examination of the "envelope" conformation of a molecular model. On the other hand, the ^{1}H NMR spectrum of **16a** showed $J(H^1–H^2)$ = 6 Hz, $J(H^1–H^3)$ = 7 Hz, and $J(H^1–R^2)$ = 9 Hz, in agreement with the respective dihedral angles about 35°, 155°, and 155°. These values are easily predictable from examination of the molecular model of **16a** which has an *endo*-methoxy group. In the same way, the ^{1}H NMR spectrum of **17** showed $J(H^1–H^2)$ = 1 Hz, $J(H^1–H^3)$ = 4 Hz, and $J(H^1–R^2)$ = 4 Hz, in agreement with the predicted values of their diehedral angles of approximately 85°, 35°, and 35°, respectively.

The IR spectra of **15b** and **17** in carbon tetrachloride solutions showed the presence of intramolecular hydrogen bonding [–OH···O(R)–]; i.e., **15b** and **17** have a C^2-*exo*-alkoxy group.

The presence of a triplet quencher (penta-1,3-diene, 1 mol/L) in the photoreaction of *trans*-**4d** in methanol did not significantly affect the rate of formation of the products. On the other hand, triplet photosensitization by 0.1 mol/L of benzophenone or acetophenone in methanol resulted in isomerization around the double bond of *trans*-**4d** to give a 1:1 mixture of *trans*-**4d** and *cis*-**4d**. In these cases no cyclization products such as **15a** or **16a** were obtained.

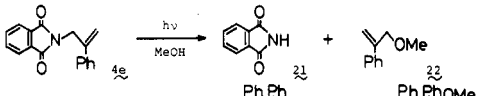
We further examined the photolysis of *cis*-**4d**. Irradiation of *cis*-**4d** (5 mM) in methanol resulted in facile isomerization to the *trans*-**4d** and formation of the identical cyclization products, **15a** and **16a** (eq 6). At a low conversion of *cis*-**4d** (5% conversion), the ratio of the products was 10:1.0:1.0–0.9 *trans*-**4d**/**15a**/**16a**. As the ratio of the cyclization products **15a** and **16a** was somewhat different from that initiated from *trans*-**4d**, the products **15a** and **16a** seem to be directly formed from the singlet excited state of **cis-4d**. On prolonged irradiation, the ratio of *cis*-**4d** to *trans*-**4d** reached to a constant value, 10–15:85–90.

For the photolyses in acetonitrile, cis–trans isomerization of **4d** was also observed. Irradiation of *trans*-**4d** or *cis*-**4d** in acetonitrile (2 mM) gave an equilibrium mixture of

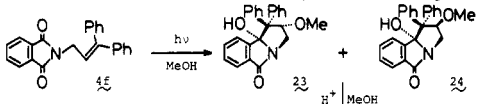
(15) Tris[(heptafluorobutanoyl)pivaloylmethanato]europium.

trans-**4d** to *cis*-**4d** of 10–15:85–90. No other products were isolated.

Irradiation of 4e. Prolonged irradiation of **4e** (5 mM) in methanol gave a complex mixture of products. At a low conversion of **4e**, we obtained phthalimide (**21**) and 2-phenylallyl ether (**22**) as main products, together with the recovery of the starting material (eq 9). The amounts of



(9)



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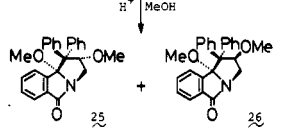


(11)

each were 18%, 14%, and 68%, respectively. However, no methanol-incorporated cyclization product was produced. Phthalimide (**21**) was identical with an authentic sample. The ether **22** was also indentical with an authentic sample synthesized by the method of Baldwin and Reed.[16]

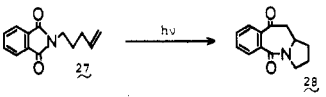
Irradiation of **4e** (5 mM) in acetonitrile for 10 h resulted in no reaction of the starting material.

Irradiation of 4f. Irradiation of **4f** (2 mM) in methanol for around 10 h gave the corresponding methanol-incorpporated cyclization products **23** (27%) and **24** (54%) (eq 10). These photoproducts were converted to an equilibrium mixture of the methyl ethers **25** and **26** (1:0.9) by treatment with a trace amount of perchloric acid in methanol (eq 11). ^{1}H NMR spectra of these products **23–26** are summarized in Table III. The stereochemical assignments of these compounds were straightforward, as shown below. The ^{1}H NMR spectra showed $J(H^1–H^2)$ = 0–1 Hz and $J(H^1–H^3)$ = 5–7 Hz in **23** and **25** and $J(H^1–H^2)$ = $J(H^1–H^3)$ = 7–8 Hz in **24** and **26** in agreement with dihedral angles of approximately $\angle(H^1–H^2)$ = 85° and $\angle(H^1–H^3)$ = 35° in **22** and **24** and $\angle(H^1–H^2)$ = 35° and $\angle(H^1–H^3)$ = 155° in **23** and **25**, respectively, consistent with the prediction from examination of the "envelope" conformation of a molecular model. The IR spectrum of **23** in carbon tetrachloride solution showed an absorption bands centered at 3440 cm^{-1}, which was assigned to the intramolecular hydrogen bonded hydroxy group [–OH···O(Me)–].

Emphasis should be made here that though the substituents varied over wide ranges, the ^{1}H NMR data (chemical shifts and coupling constants) of the photocyclization products showed characteristic features explainable in terms of the "envelope" conformation model.

Reaction Mechanism. Several examples of photoreactions of imides with olefins are known. We reported that the photolyses of alicyclic imides (for example *N*-methylsuccinimide and *N*-methylglutarimide) and alkyl-substituted olefins (for example isobutylene) in acetonitrile gave oxetanes in good yields.[1b,c] Oxetane formation is the most common process in the photolysis of alicyclic imides with olefins, illustrating its normal $n\pi^*$ carbonyl photoreactivity. Since the initial step of oxetane formation is the oxygen atom attack of $n\pi^*$-excited carbonyl systems at the double bonds, the most favorable position via a six-membered transition state for intramolecular oxetane formation is the γ,δ-double bond, which corresponds to *N*-2-alkenyl imide systems.[1a] Photolysis of *N*-allylsuccinimide in methanol in actuality gave products mainly via intramolecular oxetanes, whereas irradiation of *N*-(3-butenyl)- and *N*-(4-pentenyl)succinimide in methanol afforded γ-hydrogen abstraction products as the main products.[1b]

On the other hand, photoreactions of phthalimides with olefins are quite different from those of alicyclic imides with olefins. We reported that the photolysis of *N*-methylphthalimide with isobutylene in acetonitrile gave 3,4-benzo-6,7-dihydro-1,6,6-trimethylazepine-2,5-dione as a main isolated product.[1b,d] Mazzocchi and his co-workers reported that on irradiation *N*-methylphthalimide also reacted with certain dienes[17] and olefins in acetonitrile.[18] They insisted that the photoaddition of *N*-methylphthalimide to *cis*- and *trans*-2-butene was stereospecific through a concerted $_\pi2 + _\sigma2$ process.[18a] In the intramolecular photoreactions of *N*-(4-alkenyl)- and *N*-(5-alkenyl)phthalimides, we found that this type of reaction actually proceeded in limited members of the *N*-alkenylphthalimides.[1b] For example, photolysis of *N*-(4-pentenyl)phthalimide (**27**) in acetonitrile gave **28** in a good yield (eq 12). This peculiar preference of the *N*-4-alkenyl



(12)

double bond for the intramolecular cyclization reaction could be explained by taking into account the initial attack of imide N atom on the double bond via a five-membered transition state. On the contrary, intramolecular photocyclizations of *N*-(2-alkenyl)phthalimides do not proceed in acetonitrile, with exception of the cis–trans isomerization. However, in alcohols, *N*-(2-alkenyl)phthalimides gave solvent-incorporated intramolecular cyclization products (Scheme II and eq 2, 4, 6, and 10). This interesting solvent dependency of the reactions is worthy of comment.

In the case of **4d**, the phthalimide moiety, i.e., *N*-methylphthalimide ($E_s \approx 80$ kcal/mol, E_t = 68.5 kcal/mol[9f]), may have a lower excited singlet energy and a higher excited triplet energy than those of the β-methyl styryl moiety; i.e., for β-methylstyrene $E_s > 95$ kcal/mol, and E_t = 59.8 kcal/mol.[19] Even in those situations, **4d** underwent in methanol the same type of photocyclization as observed in the case of **4a**, in which the phthalimide moiety had obviously lower singlet and triplet energys than those of the aliphatic double bond moiety. In addition, the triplet-sensitized reactions of **4d** with acetophenone (E_s = 78.7 kcal/mol, E_t = 74.1 kcal/mol)[20] or benzophenone (E_s = 74.4 kcal/mol, E_t = 69.2 kcal/mol)[20] resulted only in cis–trans isomerization to give a 1:1 mixture of *trans*-**4d** and *cis*-**4d** and no solvent-incorporated cyclization products. From these results, we can conclude that the solvent-incorporated cyclization reactions of *N*-(2-alkenyl)phthalimides occur directly from the singlet excited state of the phthalimide moiety.[21–23] Similarly, photoisomerization

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

(17) P. H. Mazzocchi, M. J. Bowen, and N. K, Narain, *J. Am. Chem. Soc.*, 99, 7063 (1977).

(18) (a) P. H. Mazzocchi, S. Minamikawa, and M. J. Bowen, *J. Org. Chem.*, 43, 3079 (1978); (b) P. H. Mazzocchi, S. Minamikawa, and P. Wilson, *Tetrahedron Lett.*, 4361 (1678); (c) P. H. Mazzocchi, S. Minamikawa, and P. Wilson, *J. Org. Chem.*, 44, 1186 (1979).

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

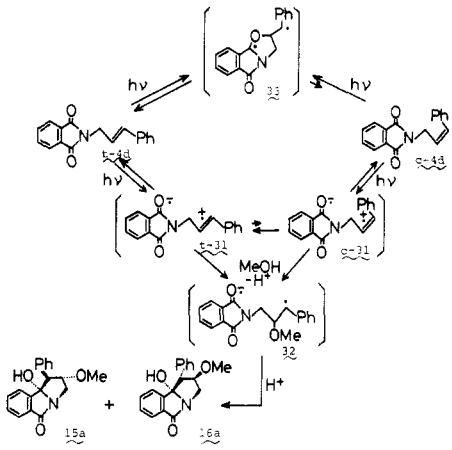
(20) S. L. Murov, "Handbook of Photochemistry", Marcel Dekker, New York, 1973.

(21) It was reported that the triplet excitation energy of phthalimide was completely transfered to a intramolecular acceptor (naphthalene). See: D. E. Breen, R. A. Keller, *J. Am. Chem. Soc.*, 90, 1935 (1968).

(22) No clear evidence of charge-transfer complex formation in the UV spectra of 4a–f was observed.

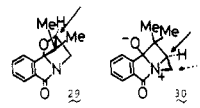
(23) The character of the singlet excited state of phthalimides is not so clear.[9f]

Scheme III



of **4d**, displacing the cis–trans equilibrium to trans, must be caused via a biradical intermediate directly produced from the excited singlet state of the phthalimide moiety.

Possible other mechanisms for these solvent-incorporated cyclization reactions of *N*-(2-alkenyl)phthalimides involving the intermediates of oxetane **29**[18c] or switterionic azetidine **30**[18] via [2 + 2] cycloaddition of the double bond to a C=O or O=CN< chromophore could not rationalize the observed stereochemistry of the products. If, in the photoreaction of **4a**, for example, the reaction resulted from the nucleophilic attack of methanol on **29** or **30**, formation of a single product would be required, which is inconsistent with our results.



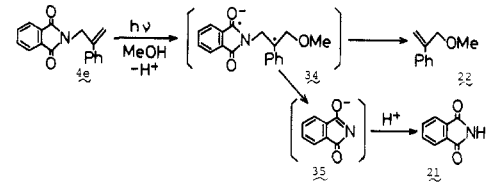
The structural and stereochemical features of those reactions appear nicely to be rationalized by using electron transfer mechanism presented in Scheme III. The photoreaction of **4d** in methanol is representative.

Initial step of the solvent-incorporated photocycloaddition reaction is an electron transfer from the double bond to the singlet excited phthalimide group. The free-energy change associated with the electron transfer can be roughly estimated by using eq 13.[24] In this

$$\Delta G = 23.06[E(\mathrm{D}/\mathrm{D}^+) - E(\mathrm{A}^-/\mathrm{A}) - C] - \Delta E_{0,0} \quad (13)$$

equation $E(\mathrm{D}/\mathrm{D}^+)$ is the oxidation potential of the donor (in volts), $E(\mathrm{A}^-/\mathrm{A})$ is the reduction potential of the acceptor (in volts), $\Delta E_{0,0}$ is the energy of the excited species (kcal/mol), and C is the "coulombic attraction term". Since the contribution of the term C may be estimated to be small and same for compounds **4a–c**, it can be neglected in discussing their relative reactivity. The equation can be applied to the phthalimides **4a–c**. The reduction potential for *N*-methylphthalimide was determined as −1.36 V (in 0.5 M Et_4NClO_4/acetonitrile; cyclic voltammetry with a platinum electrode vs. Ag/0.01 M $AgClO_4$). For the other values we have used the following oxidation potentials: 2-methyl-2-butene,[18b] +1.79 V; 2-butene,[25] +2.26 V; propene,[25] +2.84 V (in 0.14 M Et_4NBF_4/acetonitrile vs. Ag/0.01 M $AgClO_4$). The singlet energy of *N*-methylphthalimide is ~80 kcal/mol.[9f] With these data, one calculates ΔG = −7.5 kcal/mol for the intramolecular electron transfer of **4a**, ΔG = +3.5 kcal/mol for that of **4b**, and ΔG = +11.5 kcal/mol for that of **4c**. Though the absolute magnitudes of these values are certainly ill-defined, it seems reasonable to conclude that the intramolecular electron transfer in methanol would be possible for **4a** and **4b** from the point of view of the free-energy change but would be impossible for **4c**, consistent with our results.

Scheme IV



Furthermore, irradiation of **4a** gave the solvent-incorporated cyclization products only in methanol or in ethanol but not in isopropyl alcohol. On the other hand, irradiation of **4d** gave the cyclization products in all three alcohols. These solvent effects can be reasonably explained in terms of the solvent polarity; i.e., the *N*-(2-alkenyl)phthalimides possessing the higher oxidation potential would need more polar solvents to induce photochemical intramolecular electron transfer.

After the photochemical electron transfer (*trans*-**4d** → *trans*-**31**, Scheme III), methanol attack on radial cation *trans*-**31** in "anti-Markovnikov fashion" is expected[26] to form more stable radical **32**. Since protonation of the radical anion in methanol seems to be unfavorable,[27] cyclization of **32** followed by protonation is most probable to give products **15a** and **16a**. The mechanism involving the radical species **32** successfully interprets the regiochemical and the stereochemical features of the reactions as well as the formation of identical photoproducts derived from *trans*- or *cis*-**4d**.

The photochemical methanol-incorporated cyclization of *trans*-**4d** and *cis*-**4d** was accompanied by the cis–trans isomerization of the double bond to attain an 85–90:15–10 equiliblium mixture of *trans*-**4d** and *cis*-**4d**. Because the triplet state of the β-methylstyrene moiety gave a photoequilibration of 1:1 *trans*-**4d**/*cis*-**4d**, the cis–trans isomerization seems to be directly caused by the singlet excited state of phthalimide moiety: i.e., the mechanism presumably involves reversible formation of singlet biradicals rather than the formation of the triplet state of the double bond via intra- or intermolecular energy transfer.[21] We are still left with the following two mechanistic candidates: i.e., (a) the isomerization occurs via radical cation of the double bond (*trans*-**4d** ⇄ *trans*-**31** ⇄ *cis*-**31** ⇄ *cis*-**4d**, Scheme III); (b) the isomerization occurs via biradical intermediates like **33** (*trans*-**4d** ⇄ **33** ⇄ *cis*-**4d**, Scheme III).[18,28]

In addition to the photochemical solvent-incorporated cyclization reactions, we also found a photochemical solvent-incorporated elimination reaction in the case of **4e**. Starting from **4e** (Scheme IV), one can expect methanol to attack the radical cation, resulting in the formation of the more stable radical **34**. The intermediate **34** possesses an analogous structure to the well-known 1,4-biradical intermediates postulated in the Norrish Type II elimination reaction of carbonyl compounds.[29] Therefore, it is

(24) D. Rehm and A. Weller, *Isr. J. Chem.*, 8, 259 (1970).
(25) M. Fleischmann and D. Pletcher, *Tetrahedron Lett.*, 6255 (1968).
(26) A. J. Maroulis, Y. Shigemitsu, and D. R. Arnold, *J. Am. Chem. Soc.*, **100**, 535 (1978), and references cited therein.
(27) O. R. Brown, S. Fletcher, and J. A. Harrison, *J. Electroanal. Chem. Interfacial Electrochem.*, **57**, 351 (1974).
(28) For a discussion of the mechanism of cis–trans isomerization via a singlet biradical, see S. R. Kurowsky and H. Morrison, *J. Am. Chem. Soc.*, **94**, 507 (1972).
(29) P. J. Wagner, *Acc. Chem. Res.*, 4, 1681 (1971).

reasonable to consider that **34** cleaves to give **22** and **35**. The latter will finally give **21**.

In conclusion, emphasis on the generality of the solvent-incorporated addition of a double bond to a phthalimide carbonyl system should be made.[30] We have already reported the corresponding photoaddition in the reactions of *N*-(3-alkenyl)phthlimides to form new five- and six-membered-ring systems[31] and of *N*-alkenylphthalimides with a more remote alkenyl double bond to attain medium-sized cyclic to macrocyclic compounds.[32] A similar mechanism will be true for the intermolecular reactions of phthalimides with various olefins.[33]

Experimental Section

Melting points were measured with a Yanagimoto micromelting-point apparatus and are uncorrected. ^{1}H NMR spectra were taken with a JEOL PS-100 spectrometer (100 MHz) with Me_4Si as an internal standard. IR spectra were recorded with a JASCO IR-G spectrophotometer. UV spectra were taken with a Shimadzu UV-200 spectrophotometer. Mass spectra were recorded with a Hitachi M-52 mass spectrometer. Microanalyses were performed by the Microanalytical Laboratory of Kyoto University, Kyoto, Japan. UV irradiation was carried out with an Eikosha PIH 300 (300 W) high-pressure mercury lamp through quartz at ambient temperature.

Preparation of *N*-(2-Alkenyl)phthalimides 4a–f. *N*-(3-Methyl-2-butenyl)phthalimide [**4a**; mp 102.0–105 °C (lit. mp 100 °C)] was prepared by the method of Späth and Spitzy.[34] *N*-(2-Butenyl)phthalimide [**4b**; mp 77.5–79.5 °C (lit. mp 75.2–5.8 °C)] was prepared by the method of Roberts and Mazur.[35] *N*-Allylphthalimide [**4c**; mp 74–72 °C (lit. mp 70–71 °C)] was prepared by the method of Neumann.[36] *trans*-*N*-(3-Phenylallyl)phthalimide [*trans*-**4d**; mp 158.0–159 °C (lit. mp 153 °C)] was prepared by the method of Posner.[37]

cis-*N*-(3-Phenylallyl)phthalimide (*cis*-**4d**) was prepared as follows. A solution of 8 g of *trans*-**4d** and 2 g of benzophenone in 400 mL of benzene was irradiated with an Hg lamp. After 3 h, the solvent was evaporated, and the residue was dissolved in 100 mL of ethanol with heating. After the mixture was cooled and the precipitated crystals, which were mainly composed of *trans*-**4d**, were filtered off, the filtrate was concentrated to 50 mL. The plates of *cis*-**4d** crystallized on standing. The crystals were purified by recrystallization from ethanol. The yield of *cis*-**4d** was 1.5 g (19%, based on *trans*-**4d**); mp 109.0–110 °C (lit. mp 110–111 °C).[38]

N-(2-Phenylallyl)phthalimide [**4e**; mp 126–127 °C (lit. mp 123–124 °C)] was prepared by the method of McConaghy and Lwowski.[39]

N-(3,3-Diphenylallyl)phthalimide (**4f**) was prepared as follows. A solution of 15 g (83 mmol) of 1,1-diphenyl-1-propene, which was prepared by the method of Baker and Holdsworth,[40] and 17.8 g (0.1 mol) of *N*-bromosuccinimide (NBS) in 100 mL of carbon tetrachloride was refluxed in 12 h. After the mixture was cooled and the succinimide filtered off the filtrate was evaporated. A solution of the residue and 22.3 g (0.12 mol) of potassium phthalimide in 100 mL of dimethylformamide was heated at 80 °C for 2 h. The mixture was poured in 200 mL of water and extracted with chloroform. The extracts were washed successively with 1 N potassium hydroxide, water, 0.5 N hydrochloric acid, and again with water. The chloroform solution was dried over magnesium sulfate, and the solvent was evaporated. The residual crude **4f** was purified by column chromatography on silica gel (Wakogel C-200) and by recrystallization from ethanol. The yield of **4f** was 13 g (46%, based on 1,1-diphenyl-1-propene): mp 126–128 °C; ^{1}H NMR ($CDCl_3$) δ 4.35 (d, J = 7 Hz, 2 H), 6.02 (t, J = 7 Hz, 1 H), 7.0–7.5 (m, 10 H), 7.5–7.9 (m, 4 H). Anal. Calcd for $C_{23}H_{17}NO_2$: C, 81.39; H, 5.05; N, 4.13. Found: C, 81.39; H, 5.10; N, 4.10.

Irradiation of 4a in Methanol. A solution of 430 mg (2 mmol) of **4a** in 400 mL of methanol was placed in a photolysis cell equipped with a gas-inlet tube and a water-cooled quartz immersion well. The solution was deoxygenated by passing a stream of nitrogen through the solution. The solution was irradiated with an Hg lamp. After 5 h, column chromatography over 45 g of silica gel (Wakogel C-200) eluted with ether gave **5a** and **6a** in yields of 41% and 41%, respectively.

1,1-Dimethyl-9bα-hydroxy-2α-methoxy-1,2,3,9b-tetrahydro-5*H*-pyrrolo[2,1-*a*]isoindol-5-one (**5a**): mp 98–99 °C (from hexane); IR (KBr) 3400 (OH), 1685 (amide), 1386, 1372, 1368, 1098, 1072, 770, 704 cm^{-1}; mass spectrum (20 eV), *m/e* (relative intensity) 247 (M^+, 2), 232 (7), 229 (7), 216 (20), 215 (M^+ – MeOH, 100), 200 (62), 161 (20), 160 (60). Anal. Calcd for $C_{14}H_{17}NO_3$: C, 67.99; H, 6.93; N, 5.66. Found: C, 68.02; H, 7.18; N, 5.50.

1,1-Dimethyl-9bα-hydroxy-2β-methoxy-1,2,3,9b-tetrahydro-5*H*-pyrrolo[2,1-*a*]isoindol-5-one (**6a**): mp 200–201 °C (from benzene–hexane); IR (KBr) 3250 (OH), 1680 (amide), 1380, 1368, 1171, 76 cm^{-1}; mass spectrum, *m/e* (relative intensity) 247 (M^+, 1), 232 (8), 229 (6), 216 (16), 215 (M^+ – MeOH, 100), 200 (67), 161 (25), 160 (58). Anal. Calcd for $C_{14}H_{17}NO_3$: C, 67.99; H, 6.93; N, 5.66. Found: C, 67.78; H, 6.87; N, 5.57.

Methyl Etherification of 5a and 6a. To a solution of **5a** (150 mg) in 30 mL of methanol was added 1 drop of perchloric acid (60%). After 1 day the solution was poured into 50 mL of saturated sodium hydrogen carbonate solution and extracted with chloroform. The extracts were washed with water and dried over magnesium sulfate. After evaporation, column chromatography gave **8a** and **9a** in yields of 65% and 22%, respectively.

On similar treatment, **6a** also gave **8a** and **9a** in a 3:1 ratio (82% total yield).

2α,9bα-Dimethoxy-1,1-dimethyl-1,2,3,9b-tetrahydro-5*H*-pyrrolo[2,1-*a*]isoindol-5-one (**8a**): mp 89.5–90.0 °C (from hexane); IR (KBr) 1708 (amide), 1463, 1356, 1325, 1108, 1074, 762 cm^{-1}; mass spectrum, *m/e* (relative intensity) 261 (M^+, 15), 247 (15), 246 (100), 214 (49), 175 (46), 160 (88). Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 69.11; H, 7.37; N, 5.35.

2β,9bα-Dimethoxy-1,1-dimethyl-1,2,3,9b-tetrahydro-5*H*-pyrrolo[2,1-*a*]isoindol-5-one (**9a**): mp 98.0–99.0 °C (from hexane); IR (KBr) 1700 (amide), 1462, 1360, 1103, 1082, 766 cm^{-1}; mass spectrum, *m/e* (relative intensity) 261 (M^+, 18), 247 (18), 246 (100), 214 (47), 175 (43), 160 (88). Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 68.84; H, 7.31; N, 5.33.

Irradiation of 4a in Water–Acetonitrile. A solution of 430 mg (2 mmol) of **4a** in 400 mL of water–acetonitrile (1/8 v/v) was irradiated for 10 h. Chromatography of the reaction mixture gave **5b** (100 mg, 21%) and **6b** (100 mg, 21%), together with recovered imide **4a** (170 mg, 40%).

2α,9bα-Dihydroxy-1,1-dimethyl-1,2,3,9b-tetrahydro-5*H*-pyrrolo[2,1-*a*]isoindol-5-one (**5b**): mp 172–174 °C; IR (KBr) 3475, 3135 (OH), 1678 (amide), 1464, 1382, 1073, 763, 698 cm^{-1}; mass spectrum, *m/e* (relative intensity) 216 (9), 215 (53), 200 (13), 187 (55), 186 (100), 172 (20), 158 (16), 145 (18). Anal. Calcd for $C_{13}H_{15}NO_3$: C, 66.93; H, 6.48; N, 6.01. Found: C, 66.81; H, 6.45; N, 5.98.

2β,9bα-Dihydroxy-1,1-dimethyl-1,2,3,9b-tetrahydro-5*H*-pyrrolo[2,1-*a*]isoindol-5-one (**6b**): mp 179.0–181.0 °C; IR (KBr) 3310 (br OH), 1685 (amide), 1375, 1088, 1068, 758, 658 cm^{-1}; mass spectrum, *m/e* (relative intensity) 216 (10), 215 (57), 200 (21), 187 (55), 186 (100), 172 (28), 160 (28), 1587 (17), 145 (17). Anal. Calcd for $C_{13}H_{15}NO_3$: C, 66.93; H, 6.48; N, 6.01. Found: C, 66.97; H, 6.47; N, 5.93.

Monomethyl Etherification of 5b and 6b. A mixture of **5b** and **6b** (230 mg) was converted to the monomethyl ethers **8b** and **9b** [1:3 ratio from the ^{1}H NMR spectra; yield, 178 mg (73%) of

(30) Similar methanol-incorporated addition of the olefins to iminium salts was reported. See P. S. Mariano, J. L. Stavinoha, G. Pêpe, and E. F. Meyer, Jr., *J. Am. Chem. Soc.*, **100**, 7114 (1978).
(31) M. Machida, K. Oda, K. Maruyama, Y. Kubo, and Y. Kanaoka, *Heterocycles*, **14**, 779 (1980).
(32) K. Maruyama and Y. Kubo, *J. Am. Chem. Soc.*, **100**, 7772 (1978).
(33) K. Maruyama and Y. Kubo, *Chem. Lett.*, 851 (1978).
(34) E. Späth and W. Spitzy, *Chem. Ber.*, **58**, 2276 (1925).
(35) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **72**, 2509 (1951).
(36) A. Neumann, *Chem. Ber.*, **23**, 999 (1890).
(37) T. Posner, *Chem. Ber.*, **26**, 1857 (1893).
(38) R. P. Mull (CIBA Ltd.), Belgian Patent 655403; *Chem. Absr.*, **64**, 17481*b* (1966).
(39) J. S. McConaghy, Jr., and W. Lwowski, *J. Am. Chem. Soc.*, **89**, 2357 (1967).
(40) J. W. Baker and J. B. Holdsworth, *J. Chem. Soc.*, 728 (1945).

8b + 9b] in a manner similar to that described for methyl etherification of **5a** and **6a**. The monomethyl ethers **8b** and **9b** were each separated by column chromatography with elution with chloroform.

1,1-Dimethyl-2α-hydroxy-9bα-methoxy-1,2,3,9b-tetrahydro-5*H*-pyrrolo[2,1-*a*]isoindol-5-one (**8b**): oil; IR (neat) 3470 (OH), 1700 (amide), 1466, 1362, 1082 cm^{-1}; mass spectrum, *m/e* (relative intensity) 232 (26), 216 (36), 215 (80), 200 (68), 161 (24), 160 (100), 148 (26), 58 (27), 43 (34). Anal. Calcd for $C_{14}H_{17}NO_3$: C, 67.99; H, 6.93; N, 5.66. Found: C, 68.21; H, 6.76; N, 5.62.

1,1-Dimethyl-2β-hydroxy-9bα-methoxy-1,2,3,9b-tetrahydro-5*H*-pyrrolo[2,1-*a*]isoindol-5-one (**9b**): oil; IR (neat) 3380 (OH), 1685 (amide), 1467, 1371, 1070 cm^{-1}; mass spectrum, *m/e* (relative intensity) 232 (24), 216 (30), 215 (94), 200 (66), 161 (18), 160 (100), 148 (24), 58 (24), 43 (36). Anal. Calcd for $C_{14}H_{17}NO_3$: C, 67.99; H, 6.93; N, 5.66. Found: C, 67.86; H, 6.82; N, 5.60.

Acetylation of 8b and 9b. A solution of 200 mg of **8b** in 1 mL of acetic anhydride and 10 mL of pyridine was heated at 60 °C for 2 h. After cooling, the solution was poured into 20 mL of cold water and the mixture extracted with 30 mL of chloroform. The extract was washed with saturated sodium hydrogen carbonate solution and cold water. The solution was dried over magnesium sulfate. After evaporation of the solvent, the residue was purified by column chromatography to give 120 mg (50%) of **8c**. In a similar way, 400 mg of **9b** was converted to the acetate **9c** in a yield of 280 mg (60%).

2α-Acetoxy-1,1-dimethyl-9bα-hydroxy-1,2,3,9b-tetrahydro-5*H*-pyrrolo[2,1-*a*]isoindol-5-one (**8c**): oil; IR (neat) 1735 (sh, ester), 1705 (amide), 1466, 1364, 1240, 1088, 1065 cm^{-1}; mass spectrum, *m/e* (relative intensity) 289 (20), 275 (10), 274 (85), 258 (10), 232 (60), 215 (20), 214 (100), 175 (30), 163 (93), 161 (50), 148 (10). Anal. Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.49; H, 6.60; N, 4.86.

2β-Acetoxy-1,1-dimethyl-9bα-hydroxy-1,2,3,9b-tetrahydro-5*H*-pyrrolo[2,1-*a*]isoindol-5-one (**9c**): oil; IR (neat) 1736 (ester), 1708 (amide), 1466, 1360, 1230 cm^{-1}; mass spectrum, *m/e* (relative intensity) 289 (25), 275 (17), 274 (87), 258 (17), 232 (58), 215 (22), 214 (100), 175 (30), 163 (93), 161 (67), 148 (25). Anal. Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.70; H, 6.68; N, 4.79.

Oxidation of 8b and 9b. To a cold solution of 500 mg of a mixture of **8b** and **9b** in 50 mL of acetone was added rapidly with stirring 1 mL of standard chromic trioxide reagent (a solution of 2.7 g of chromium trioxide in 2 mL of concentrated sulfuric acid diluted with water to a volume of 10 mL was used). After 10 min the solution was neutralized with sodium hydrogen carbonate solution and extracted with 50 mL of chloroform. The extract was washed with sodium carbonate solution and water. The chloroform solution was dried over magnesium sulfate. After evaporation of the solvent, the residue was purified by column chromatography to give 250 mg (50%) of **10**.

1,9b-Dihydro-1,1-dimethyl-9b-methoxy-5*H*-pyrrolo[2,1-*a*]isoindol-2(3*H*),5-dione (**10**): mp 114–116 °C (from benzene–hexane); ^1H NMR ($CDCl_3$) δ 0.49 (s, 3 H, *endo*-Me), 1.37 (s, 3 H, *exo*-Me), 2.99 (s, 3 H, OMe), 3.58 and 4.39 (AB q, *J* = 17 Hz, 2 H, methylene), 7.4–8.0 (m, 4 H, aromatic H); IR (KBr) 1755 (keto), 1698 (amide), 1458, 1430, 1365, 1090, 1070 cm^{-1}; mass spectrum, *m/e* (relative intensity) 246 (15), 245 (M^+, 77), 231 (15), 230 (100), 202 (16), 186 (16), 186 (16), 175 (18), 160 (68). Anal. Calcd for $C_{14}H_{15}NO_3$: C, 68.55; H, 6.16; N, 5.71. Found: C, 68.32; H, 6.14; N, 5.69.

Oxidation of 5b and 6b to 11 and Methyl Etherification of 11. To a solution of 200 mg of a mixture of **5b** and **6b** in 5 mL of acetic acid was added with stirring a solution of 200 mg of chromic trioxide in 5 mL of acetic acid. The solution was kept over night at room temperature. The solution was poured into 50 mL of water and extracted with chloroform. The extract was washed with saturated sodium hydrogen carbonate solution and finally with water. The chloroform solution was dried over magnesium sulfate, and the solvent was evaporated. The residue was purified by column chromatography to give 143 mg (72%) of **11**.

1,9b-Dihydro-1,1-dimethyl-9b-hydroxy-5*H*-pyrrolo[2,1-*a*]isoindol-2(3*H*),5-dione (**11**): mp 200–202 °C (from benzene); ^1H NMR ($CDCl_3$) δ 0.44 (s, 3 H, *endo*-Me), 1.40 (s, 3 H, *exo*-Me), 3.45 and 4.13 (AB q, *J* = 20 Hz, 2 H, methylene), 4.0 (s, 1 H, OH), 7.3–7.9 (m, 4 H, aromatic H); IR (KBr) 3280 (OH), 1765 (keto), 1688 (amide), 1413, 1400, 1162 cm^{-1}; mass spectrum, *m/e* (relative intensity) 232 (17), 231 (M^+, 100), 213 (24), 185 (17), 174 (26), 161 (29), 160 (30), 159 (26), 148 (57), 84 (100), 71 (40), 69 (24). Anal. Calcd for $C_{13}H_{13}NO_3$: C, 67.52; H, 5.67; N, 6.06. Found: C, 67.28; H, 5.65; N, 6.05.

The alcohol **11** (100 mg) was converted to the methyl ether **10** (92 mg, 87%) in a manner similar to that described for the methyl etherification of **5a** and **6a**.

Irradiation of 4a in Ethanol. 1,1-Dimethyl-2α-ethoxy-9bα-hydroxy-1,2,3,9b-tetrahydro-5*H*-pyrrolo[2,1-*a*]isoindol-5-one (**5c**): mp 70.0–71.5 °C (from hexane); ^1H NMR ($CDCl_3$) δ 0.39 (s, 3 H, *endo*-Me), 1.25 (t, *J* = 7 Hz, 3 H, OCH_2CH_3), 1.38 (s, 3 H, *exo*-Me), 3.3–3.9 (m, 5 H, methylene, methine, OCH_2CH_3), 4.64 (s, 1 H, OH), 7.3–7.7 (m, 4 H, aromatic H); IR (KBr) 3370 (OH), 1676 (amide), 1464, 1384, 1106, 1074, 766 cm^{-1}; mass spectrum, *m/e* (relative intensity) 261 (M^+, 1), 246 (16), 243 (17), 216 (15), 215 (100), 200 (67), 184 (15), 161 (19), 160 (60). Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 68.69; H, 7.55; N, 5.25.

1,1-Dimethyl-2β-ethoxy-9bα-hydroxy-1,2,3,9b-tetrahydro-5*H*-pyrrolo[2,1-*a*]isoindol-5-one (**6c**): mp 174.5–175.5 °C (from benzene–hexane); ^1H NMR ($CDCl_3$) δ 0.29 (s, 3 H, *endo*-Me), 1.18 (t, *J* = 7 Hz, 3 H, OCH_2CH_3), 1.37 (s, 3 H, *exo*-Me), 3.14 (dd, *J* = 8, 11 Hz, 1 H of methylene), 3.3–3.9 (m, 4 H, 1 H of methylene, OH, OCH_2CH_3), 4.36 (t, *J* = 8 Hz, 1 H, methine), 7.2–7.6 (m, 4 H, aromatic H); IR (KBr) 3220 (OH), 1672 (amide), 1466, 1380, 1122, 1075, 758 cm^{-1}; mass spectrum, *m/e* (relative intensity) 261 (M^+, 1), 246 (20), 243 (26), 216 (24), 215 (100), 200 (70), 184 (17), 161 (26), 160 (61). Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 69.06; H, 7.25; N, 5.43.

Irradiation of 4b in Methanol. 9bα-Hydroxy-2α-methoxy-1β-methyl-1,2,3,9b-tetrahydro-5*H*-pyrrolo[2,1-*a*]isoindol-5-one (**13a**): mp 80–83 °C (from benzene–hexane); ^1H NMR ($CDCl_3$) δ 0.41 (d, *J* = 7 Hz, 3 H, *endo*-Me), 2.67 (br q, 1 H, exo-C^1 methine HCMe), 3.47 (s, 3 H, OMe), 3.4–4.1 (m, 3 H, C^2 methine HCOMe, methylene), 4.60 (s, 1 H, OH), 7.3–7.9 (m, 4 H, aromatic H); IR (KBr) 3240 (OH), 1670 (amide), 1378, 1104, 1060, 764 cm^{-1}; mass spectrum *m/e* (relative intensity) 201 (M^+ – MeOH, 9), 184 (17), 183 (100), 182 (66), 154 (9). Anal. Calcd for $C_{13}H_{15}NO_3$: C, 66.93; H, 6.48; N, 6.01. Found: C, 66.87; H, 6.51; N, 5.83.

9bα-Hydroxy-2α-methoxy-1α-methyl-1,2,3,9b-tetrahydro-5*H*-pyrrolo[2,1-*a*]isoindol-5-one (**13b**): mp 149–152 °C (from ethanol); ^1H NMR ($CDCl_3$) δ 1.37 (d, *J* = 6 Hz, 3 H, *exo*-Me), 1.6–1.9 (m, 1 H, endo-C^1 methine), 3.46 (s, 3 H, OMe), 3.5–3.9 (m, 2 H, methylene), 4.0–4.2 (m, 1 H, C^2 methine), 4.30 (s, 1 H, OH), 7.3–7.9 (m, 4 H, aromatic H); IR (KBr) 3385 (OH), 1682 (amide), 1403, 1091, 1068, 974, 768 cm^{-1}; mass spectrum, *m/e* (relative intensity) 201 (M^+ – MeOH, 5), 183 (100), 182 (75), 154 (15). Anal. Calcd for $C_{13}H_{15}NO_3$: C, 66.93; H, 6.48; N, 6.01. Found: C, 67.02; H, 6.43; N, 6.11.

9bα-Hydroxy-2β-methoxy-1α-methyl-1,2,3,9b-tetrahydro-5*H*-pyrrolo[2,1-*a*]isoindol-5-one (**13c**): mp 113–116 °C (from benzene–hexane); ^1H NMR ($CDCl_3$) δ 1.37 (d, *J* = 6 Hz, 3 H, *exo*-Me), 1.5–1.8 (m, 1 H, endo-C^1 methine), 3.38 (s, 3 H, OMe), 3.4 (dd, *J* = 8, 12 Hz, 1 H, 1 H of methylene), 3.58 (s, 1 H, OH), 3.60 (dd, *J* = 7, 12 Hz, 1 H, 1 H of methylene), 4.1–4.4 (m, 1 H, C^2 methine), 7.3–7.7 (m, 4 H, aromatic H); IR (KBr) 3220 (OH), 1678 (amide), 1390, 1156, 1090, 765 cm^{-1}; mass spectrum, *m/e* (relative intensity) 201 (M^+ – MeOH, 12), 183 (100), 182 (72), 154 (12). Anal. Calcd for $C_{13}H_{15}NO_3$: C, 66.93; H, 6.48; N, 6.01. Found: C, 67.21; H, 6.53; N, 5.84.

9bα-Hydroxy-2β-methoxy-1β-methyl-1,2,3,9b-tetrahydro-5*H*-pyrrolo[2,1-*a*]isoindol-5-one (**13d**): partial ^1H NMR spectrum ($CDCl_3$) δ 0.41 (d, *J* = 7 Hz, *endo*-Me), 2.5–2.9 (m, 1 H, exo-C^1 methine), 3.32 (s, OMe).

Acid Degradation of 13a–d. To a solution of a mixture of **13a–d** (200 mg) in 20 mL of chloroform was added 1 drop of hydrochloric acid. After 1 day, the chloroform solution was washed with sodium hydrogen carbonate and water and dried over magnesium sulfate. After evaporation, chromatography gave 50 mg (32%) of **14**.

1-Methyl-5*H*-pyrrolo[2,1-*a*]isoindol-5-one (**14**): orange crystals; mp 69.0–70.0 °C (from hexane); ^1H NMR ($CDCl_3$) δ 2.18 (s, 3 H, Me), 5.93 (d, *J* = 3 Hz, 1 H, C^2 methine), 8.88 (d, *J* = 3 Hz, 1 H, C^3 methine), 6.9–7.7 (m, 4 H, aromatic H); IR (KBr) 1730 (amide), 1388, 1298, 762, 690 cm^{-1}; mass spectrum *m/e* (relative intensity)

184 (16), 183 (M^+, 100), 182 (64), 160 (12). Anal. Calcd for $C_{12}H_9NO$: C, 78.67; H, 4.98; N, 7.65. Found: C, 78.87; H, 4.91; N, 7.61.

Irradiation of *trans*-4d and *cis*-4d in Various Solvents. A methanol solution of *trans*-**4d** was irradiated to give **15a** and **16a** in 54% and 15% isolated yields together with a trace of **17** (mp 142–144 °C). Photolyses of *trans*-**4d** in other alcohols (ethanol, isorpopyl alcohol, *tert*-butyl alcohol) gave the corresponding products **15b–d** and **16b,c**. The yields are summarized in Table II. The other results were shown in the text. Using either a quartz or a Pyrex filter on irradiation gave the same result.

9bα-Hydroxy-2α-methoxy-1β-phenyl-1,2,3,9b-tetrahydro-5*H*-pyrrolo[2,1-*a*]isoindol-5-one (**15a**): mp 162–164 °C (from ethanol–ether); IR (KBr) 3317 (OH), 1677 (amide), 1377, 1088, 1057 cm^{-1}; mass spectrum, *m/e* (relative intensity) 277 ($M^+ - H_2O$, 8), 264 (9), 263 (10), 247 (9), 246 (36), 245 (100), 148 (30), 116 (51). Anal. Calcd for $C_{18}H_{17}NO_3$: C, 73.20; H, 5.80; N, 4.74. Found: C, 73.46; H, 5.65; N, 4.85.

9bα-Hydroxy-2β-methoxy-1α-phenyl-1,2,3,9b-tetrahydro-5*H*-pyrrolo[2,1-*a*]isoindol-5-one (**16a**): mp 189–91 °C (from ethanol–ether); IR (KBr) 3220 (OH), 1668 (amide), 1385, 1115, 1098 cm^{-1}; mass spectrum, *m/e* (relative intensity) 277 ($M^+ - H_2O$, 12), 263 (25), 247 (20), 246 (56), 245 (100), 148 (42), 116 (56). Anal. Calcd for $C_{18}H_{17}NO_3$: C, 73.20; H, 5.80; N, 4.74. Found: C, 73.31; H, 5.86; N, 4.72.

2α-Ethoxy-9bα-hydroxy-1β-phenyl-1,2,3,9b-tetrahydro-5*H*-pyrrolo[2,1-*a*]isoindol-5-one (**15b**): mp 130–132.5 °C (from benzene–hexane); ^1H NMR ($CDCl_3$) δ 1.26 (t, J = 7 Hz, 3 H, OCH_2CH_3), 3.4–3.9 (m, 4 H, C^1 methine, OCH_2CH_3, 1 H of methylene), 4.2–4.5 (m, 2 H, C^2 methine, 1 H of methylene), 4.63 (s, 1 H, OH), 6.6–6.9 (m, 2 H, aromatic H), 6.9–7.6 (m, 7 H, aromatic H); IR (KBr) 3280 (OH), 1675 (amide), 1382, 1092, 1063 cm^{-1}; mass spectrum, *m/e* (relative intensity) 309 (M^+, trace), 307 (1), 263 (3), 246 (21), 245 (100), 116 (6). Anal. Calcd for $C_{19}H_{19}NO_3$: C, 73.76; H, 6.19; N, 4.53. Found: C, 73.48; H, 6.14; N, 4.58.

2β-Ethoxy-9bα-hydroxy-1α-phenyl-1,2,3,9b-tetrahydro-5*H*-pyrrolo[2,1-*a*]isoindol-5-one (**16b**): mp 176–178 °C (from benzene–hexane); ^1H NMR ($CDCl_3$) δ 1.04 (t, J = 7 Hz, 3 H, OCH_2CH_3), 2.84 (d, J = 9 Hz, 1 H, C^1 methine), 3.36 (qd, J = 1, 7 Hz, 2 H, OCH_2CH_3), 3.38 (s, 1 H, OH), 3.60 and 3.84 (2 dd, J = 7, 12 Hz, 2 H, methylene), 4.9–5.3 (m, 1 H, C^2 methine), 6.9–7.1 (m, 1 H, aromatic H), 7.3–7.7 (m, 8 H, aromatic H); IR (KBr) 3170 (OH), 1660 (amide), 1371, 1110, 1088, cm^{-1}; mass spectrum *m/e* (relative intensity) 291 ($M^+ - H_2O$, 10), 263 (30), 247 (10), 246 (42), 245 (100), 148 (38), 116 (54). Anal. Calcd for $C_{19}H_{19}NO_3$: C, 73.76; H, 6.19; N, 4.53. Found: C, 73.98; H, 6.13; N, 4.45.

9bα-Hydroxy-2α-isopropoxy-1β-phenyl-1,2,3,9b-tetrahydro-5*H*-pyrrolo[2,1-*a*]isoindol-5-one (**15c**): mp 119–121 °C (from benzene–hexane); ^1H NMR ($CDCl_3$) δ 1.23 (d, J = 6 Hz, 6 H, $OCHMe_2$), 3.5–4.0 (m, 3 H, C^1 methine, $OCHMe_2$, 1 H of methylene), 4.2–4.7 (m, 3 H, OH, C^2 methine, 1 H of methylene), 6.6–6.9 (m, 2 H, aromatic H), 6.9–7.6 (m, 7 H, aromatic H); IR (KBr) 3315 (OH), 1658 (amide), 1328, 1247, 1120, 1052; mass spectrum, *m/e* (relative intensity) 263 (3), 246 (24), 245 (100), 117 (4), 116 (5). Anal. Calcd for $C_{20}H_{21}NO_3$: C, 74.28; H, 6.55; N, 4.33. Found: C, 74.04; H, 6.78; N, 4.52.

9bα-Hydroxy-2β-isopropoxy-1α-phenyl-1,2,3,9b-tetrahydro-5*H*-pyrrolo[2,1-*a*]isoindol-5-one (**16c**): mp 161–164 °C (from benzene–hexane): ^1H NMR ($CDCl_3$) δ 0.93 and 1.08 (2 d, J = 6 Hz, 6 H, $OCHMe_2$), 2.79 (d, J = 8 Hz, 1 H, C^1 methine), 3.3–4.0 (m, 4 H, OH, $OCHMe_2$, methylene), 4.9–5.3 (m, 1 H, C^2 methine), 6.9–7.1 (m, 1 H, aromatic H), 7.2–7.7 (m, 8 H, aromatic H); IR (KBr) 3280 (OH), 1674 (amide), 1465, 1380, 1119, 1084, 688 cm^{-1}; mass spectrum, *m/e* (relative intensity) 305 (20), 263 (40), 247 (24), 246 (64), 245 (100), 160 (24), 148 (40), 116 (56). Anal. Calcd for $C_{20}H_{21}NO_3$: C, 74.28; H, 6.55; N, 4.33. Found: C, 74.21; H, 6.72; N, 4.25.

2α-*tert*-Butoxy-9bα-hydroxy-1β-phenyl-1,2,3,9b-tetrahydro-5*H*-pyrrolo[2,1-*a*]isoindol-5-one (**15d**): mp 151–153.5 °C (from benzene–hexane); ^1H NMR ($CDCl_3$) δ 1.22 (s, 9 H, *t*-Bu), 3.52 (dd, J = 2, 12 Hz, 1 H, 1 H of methylene), 3.62 (d, J = 2 Hz, 1 H, C^1 methine), 4.34 (dd, J = 7, 12 Hz, 1 H, 1 H of methylene), 4.4–4.6 (m , 1 H, C^1 methine), 4.64 (s, 1 H, OH), 6.6–6.9 (m, 2 H, aromatic H), 6.9–7.6 (m, 7 H, aromatic H); IR (KBr) 3300 (OH), 1662 (amide), 1302, 1234, 1185, 1053 cm^{-1}; mass spectrum, *m/e* (relative intensity) 319 (1), 263 (3), 246 (20), 245 (100), 217 (5), 216 (6). Anal. Calcd for $C_{21}H_{23}NO_3$: C, 74.75; H, 6.87; N, 4.15. Found: C, 74.95; H, 6.95; N, 4.20.

The precise description of the X-ray diffraction analysis of **15a** will be presented elsewhere by Keiichi Fukuyama (Tottori University) in the near future.

The quenching examination was carried out as follows. Methanol solutions A (5 mM *trans*-**4d**) and B (5 mM *trans*-**4d** and 1 M penta-1,3-diene) were prepared in Pyrex test tubes, which were degassed by bubbling argon through them, and then irradiated in parallel with an Hg lamp. Product concentrations were determined by HPLC analysis with a UV (254 nm) detector. The results are shown in the text.

Sensitized reactions were performed as follows. A methanol solution of 2 mmol of *trans*-**4d** and 40 mmol each of benzophenone and acetophenone was irradiated with >340 nm light by using an Hg lamp placed in a Pyrex jacket equipped with a solution filter (aqueous solution of 2,7-dimethyl-3,6-diazacyclohepta-2,6-diene perchlorate, 0.20 g/L). The reaction was followed by inspecting the ^1H NMR spectra and the high-pressure liquid chromatogram. The results are shown in the text.

Dehydration of 15a–d and 16a–c. A solution of 200 mg of **15a–d** and **16a–c** and 20 mg of sodium acetate in 10 mL of acetic anhydride was refluxed for 0.5 h. The cooled solution was poured into 50 mL of water, neutralized with sodium hydrogen carbonate solution, and extrated with chloroform. The extract was washed with sodium hydrogen carbonate and water and dried. After evaporation of the solvent, chromatography of the residue gave a dehydrated products **16a–d**.

2,3-Dihydro-2-methoxy-1-phenyl-5*H*-pyrrolo[2,1-*a*]isoindol-5-one (**19a**): 72% from **15a** and 73% from **16a**; pale yellow needles; mp 164–166.5 (from methanol); ^1H NMR ($CDCl_3$) δ 3.39 (s, 3 H, OMe), 4.09 (d, J = 5 Hz, 2 H, methylene), 5.41 (t, J = 5 Hz, 1 H, methine), 7.3–8.1 (m, 9 H, aromatic H); IR (KBr) 1680 (amide), 1408, 1089, 1079, 1042 cm^{-1}; mass spectrum, *m/e* (relative intensity) 277 (M^+, 1), 246 (20), 245 (100), 217 (5), 216 (6), 189 (3). Anal. Calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 77.75; H, 5.34; N, 5.02.

2,3-Dihydro-2-ethoxy-1-phenyl-5*H*-pyrrolo[2,1-*a*]isoindol-5-one (**19b**): 70% from a mixture of **15b** and **16b**; mp 100–103.5 °C (from ethanol); ^1H NMR ($CDCl_3$) δ 1.24 (t, J = 7 Hz, 3 H, OCH_2CH_3), 3.5–3.8 (m, 2 H, OCH_2CH_3), 4.05 (dd, J = 6, 15 Hz, 1 H, 1 H of methylene), 4.21 (dd, J = 4, 15 Hz, 1 H, 1 H of methylene), 5.44 (dd, J = 4, 6 Hz, 1 H, methine), 7.3–8.1 (m, 9 H, aromatic H); IR (KBr) 1689 (amide), 1417, 1105, 1095, 767, 690 cm^{-1}; mass spectrum, *m/e* (relative intensity) 246 (22), 245 (100), 217 (4), 216 (4). Anal. Calcd for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.55; H, 5.84; N, 4.55.

2,3-Dihydro-2-isopropoxy-1-phenyl-5*H*-pyrrolo[2,1-*a*]isoindol-5-one (**19c**): 62% from a mixture of **15c** and **16c**; mp 107.5–108.5 °C (from methanol); ^1H NMR ($CDCl_3$) δ 1.21 (d, J = 6 Hz, 6 H, $OCHMe_2$), 3.6–4.3 (m, 3 H, $OCHMe_2$, methylene), 5.33 (dd, J = 3, 7 Hz, 1 H, methine), 7.2–8.0 (m, 9 H, aromatic H); IR (KBr) 1680 (amide), 1402, 1136, 1126, 771, 692 cm^{-1}; mass spectrum, *m/e* (relative intensity) 246 (20), 245 (100), 217 (4), 216 (5). Anal. Calcd for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.86; H, 6.19; N, 4.49.

2-*tert*-Butoxy-2,3-dihydro-1-phenyl-5*H*-pyrrolo[2,1-*a*]isoindol-5-one (**19d**): 55% from **15d**; mp 131–132 °C (from methanol); ^1H NMR ($CDCl_3$) δ 1.25 (s, 9 H, *t*-Bu), 3.89 (dd, J = 4, 13 Hz, 1 H, 1 H of methylene), 4.24 (dd, J = 7, 13 Hz, 1 H, 1 H of methylene), 5.52 (dd, J = 4, 7 Hz, 1 H, methine), 7.3–8.0 (m, 9 H, aromatic H); IR (KBr) 1685 (amide), 1408, 1390, 1194, 758, 682 cm^{-1}; mass spectrum, *m/e* (relative intensity) 319 (M^+, 9), 263 (10), 262 (10), 246 (40), 245 (100). Anal. Calcd for $C_{21}H_{21}NO_2$: C, 78.97; H, 6.63; N, 4.39. Found: C, 79.12; H, 6.71; N, 4.53.

Acid Degradation of 15a, 16a, and 19a. To a solution of 100 mg of **15a**, **16a**, or **18a** in 10 mL of chloroform was added 1 drop of hydrochloric acid. After 1 day, the solution was washed with sodium hydrogen carbonate and water and dried. After evaporation, chromatography gave 80%, 85%, and 93% of **18**, respectively.

1-Phenyl-5*H*-pyrrolo[2,1-*a*]isoindol-5-one (**18**): orange crystals; mp 113–115 °C (from hexane); ^1H NMR ($CDCl_3$) δ 6.26 (d, J = 4 Hz, 1 H, C^2 methine), 7.01 (d, J = 4 Hz, 1 H, C^3 methine), 7.1–7.7 (m, 9 H); IR (KBr) 1720 (amide), 1601, 1380, 1210 cm^{-1}; mass

spectrum, m/e (relative intensity) 246 (20), 245 (100), 217 (7), 216 (7). Anal. Calcd for $C_{17}H_{11}NO$: C, 83.24; H, 4.52; N, 5.71. Found: C, 83.03; H, 4.41; N, 5.96.

Oxidation of 15a, 16a, and 19a,b. To a solution of 200 mg of **15a** in 10 mL of acetic acid was added with stirring a solution of 230 mg of chromic trioxide in 10 mL of acetic acid. The solution was refluxed for 2 h and then poured into a 50 mL of water. The solution was extracted with chloroform. The extract was washed with sodium hydrogen carbonate solution and finally with water. The solution was dried, and the solvent was evaporated. The residue was purified by column chromatography to give 159 mg (76%) of **20a**.

N-(2-Methoxy-3-oxo-3-phenylpropyl)phthalimide (**20a**): mp 135–136 °C (from methanol); ^{1}H NMR ($CDCl_3$) δ 3.36 (s, 3 H, OMe), 3.98 (dd, J = 5, 14 Hz, 1 H, 1 H of methylene), 4.23 (dd, J = 8, 14 Hz, 1 H, 1 H of methylene), 5.05 (dd, J = 5, 8 Hz, 1 H, methine), 7.3–7.9 (m, 7 H, aromatic H), 8.0–8.3 (m, 2 H, aromatic H); IR (KBr) 1773, 1708 (imide), 1695 (keto), 1422, 1401, 1366, 1124 cm^{-1}; mass spectrum, m/e (relative intensity) 309 (M^+, 2), 277 (2), 205 (14), 204 (100), 160 (9), 147 (7), 105 (19). Anal. Calcd for $C_{18}H_{15}NO_4$: C, 69.89; H, 4.89; N, 4.53. Found: C, 69.64; H, 4.65; N, 4.55.

A solution of 200 mg of **16a** and 230 mg of chromic trioxide in 20 mL of acetic acid was refluxed for 2 h, resulting in the recovery of the starting material **16a** (65%) together with a trace of **20a**.

In a similar procedure, **19a** and **19b** were oxidized by a slight excess of chromic trioxide in acetic acid with refluxing for 2 h to give **20a** (50%) plus phthalimide **21** (30%) and **20b** (30%) plus **21** (30%), respectively.

N-(2-Ethoxy-3-oxo-3-phenylpropyl)phthalimide (**20b**): mp 100–101 °C (from hexane); ^{1}H NMR ($CDCl_3$) δ 1.09 (t, J = 7 Hz, 3 H, OCH_2CH_3), 3.43 and 3.58 (2 q, J = 7 Hz, 2 H, OCH_2CH_3), 3.98 (dd, J = 6, 14 Hz, 1 H, 1 H of methylene), 4.22 (dd, J = 8, 14 Hz, 1 H, 1 H of methylene), 5.05 (dd, J = 6, 8 Hz, 1 H, methine), 7.3–7.9 (m, 7 H, aromatic H), 8.0–8.3 (m, 2 H, aromatic H); IR (KBr) 1775, 1706 (imide), 1695 (keto), 1422, 1396, 1367, 1139, 720 cm^{-1}; mass spectrum m/e (relative intensity) 277 (6), 218 (100), 190 (51), 147 (43), 132 (34), 105 (57). Anal. Calcd for $C_{19}H_{17}NO_4$: C, 70.57; H, 5.30; N, 4.33. Found: C, 70.63; H, 5.24; N, 4.19.

Irradiation of 4f in Methanol. A solution of 679 mg (2 mmol) of **4f** in 400 mL of methanol was irradiated for about 10 h. Chromatography gave **23** (200 mg, 27%) and **24** (400 mg, 54%).

1,1-Diphenyl-9bα-hydroxy-2α-methoxy-1,2,3,9b-tetrahydro-5*H*-pyrrolo[2,1-*a*]isoindol-5-one (**23**): mp 213–215 °C (from benzene–hexane); IR (KBr) 3405 (OH), 1696 (amide), 1465, 1347, 1114, 1087 cm^{-1}; mass spectrum, m/e 371 (M^+, 3), 370 (6), 369 (15), 353 (36), 339 (17), 337 (14), 308 (18), 192 (100). Anal. Calcd for $C_{24}H_{21}NO_3$: C, 77.60; H, 5.70; N, 3.77. Found: C, 77.71; H, 5.81; N, 3.70.

1,1-Diphenyl-9bα-hydroxy-2β-methoxy-1,2,3,9b-tetrahydro-5*H*-pyrrolo[2,1-*a*]isoindol-5-one (**24**): mp 219–221 °C (from benzene–hexane); IR (KBr) 3265 (OH), 1682 (amide), 1467, 1418, 1112, 1064, 692 cm^{-1}; mass spectrum m/e (relative intensity) 271 (M^+, 1), 370 (4), 369 (12), 353 (39), 339 (12), 337 (13), 308 (17), 245 (16), 193 (17), 192 (100). Anal. Calcd for $C_{24}H_{21}NO_3$: C, 77.60; H, 5.70; N, 3.77. Found: C, 77.68; H, 5.72; N, 3.81.

Methyl Etherification of 23 and 24. To a solution of 150 mg of a mixture of **23** and **24** in 30 mL of methanol was added 1 drop of perchloric acid (60%). After 1 day the solution was poured into 50 mL of saturated sodium hydrogen carbonate solution and extracted with chloroform. The extract was washed with water and dried. Chromatography gave **25** (45%) and **26** (41%).

2α,9bα-Dimethoxy-1,1-diphenyl-1,2,3,9b-tetrahydro-5*H*-pyrrolo[2,1-*a*]isoindol-5-one (**25**): mp 214–216 °C (from benzene–hexane); IR (KBr), 1701 (amide), 1462, 1368, 1010, 1082 cm^{-1}; mass spectrum, m/e (relative intensity) 385 (M^+, 23), 370 (31), 353 (100), 308 (42), 210 (29), 192 (46), 175 (62), 160 (27). Anal. Calcd for $C_{25}H_{23}NO_3$: C, 77.90; H, 6.01; N, 3.63. Found: C, 78.20; H, 5.98; N, 3.64.

2β,9bα-Dimethoxy-1,1-diphenyl-1,2,3,9b-tetrahydro-5*H*-pyrrolo[2,1-*a*]isoindol-5-one (**26**): mp 182–184 °C (from benzene–hexane); IR (KBr) 1695 (amide), 1462, 1380, 1105, 1076, 1051 cm^{-1}; mass spectrum, m/e (relative intensity) 385 (M^+, 22), 354 (39), 353 (100), 338 (28), 322 (21), 308 (45), 210 (22), 192 (35), 175 (48), 160 (22). Anal. Calcd for $C_{25}H_{23}NO_3$: C, 77.90; H, 6.01; N, 3.63. Found: C, 78.16; H, 6.20; N, 3.55.

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Registry No. 4a, 15936-45-5; **4b**, 66784-19-8; **4c**, 5428-09-1; (*Z*)-**4d**, 4335-61-9; (*E*)-**4d**, 17480-07-8; **4e**, 16307-59-8; **4f**, 74483-71-9; **5a**, 66784-05-2; **5b**, 66784-08-5; **5c**, 78127-64-7; **6a**, 66784-06-3; **6b**, 66784-09-6; **6c**, 78127-65-8; **8a**, 66891-34-7; **8b**, 66840-64-0; **8c**, 78127-66-9; **9a**, 66784-07-4; **9b**, 66784-10-9; **9c**, 78127-67-0; **10**, 66784-11-0; **11**, 66784-12-1; **13a**, 78184-50-6; **13b**, 78184-51-7; **13c**, 78184-52-8; **13d**, 78184-53-9; **14**, 78127-68-1; **15a**, 74410-44-9; **15b**, 78127-69-2; **15c**, 78185-50-9; **15d**, 78127-70-5; **16a**, 66784-14-3; **16b**, 78184-54-0; **16c**, 78127-71-6; **17**, 78184-55-1; **18**, 66784-15-4; **19a**, 66840-65-1; **19b**, 78127-72-7; **19c**, 78127-73-8; **19d**, 78127-74-9; **20a**, 66784-16-5; **20b**, 78127-75-0; **23**, 74372-24-0; **24**, 74372-23-9; **25**, 78127-76-1; **26**, 78127-77-2; 1,1-diphenyl-1-propene, 778-66-5; *N*-bromosuccinimide, 128-08-5.