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Effect of 3- and 4-Methyl Substituents on the Photocyclization of *N*-(3-Alkenyl)phthalimides: Synthesis of Pyrroloisoindoles and Pyridoisoindoles[1)]

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Photolysis of *N*-(3-alkenyl)phthalimides **2** in methanol gave tetrahydro-5*H*-pyrrolo[2,1-*a*]isoindol-5-ones **3** and/or tetrahydropyrido[2,1-*a*]isoindol-6(2*H*)-ones **4** depending on the degree of substitution at the olefin carbons of **2**. Electron transfer followed by the anti-Markownikoff addition of methanol is proposed as a possible pathway.

Keywords——*N*-(3-alkenyl)phthalimide; photocyclization; pyrroloisoindole; pyridoisoindole; electron transfer; anti-Markownikoff addition

Recently there has been a great deal of interest in the photochemistry of imides,[2,3)] and cyclic imides have been shown to undergo a variety of photoreactions common to carbonyl compounds, including inter- and intramolecular photoaddition of alkenes. In the previous papers[4,5)] we reported that photolysis of *N*-substituted phthalimides possessing an alkenyl group in their *N*-alkyl side chain gave rise to nitrogen heterocycles such as pyrroloisoindole and pyridoisoindole derivatives. During studies on the synthetic scope of these reactions, we found that *N*-(3-alkenyl)phthalimides undergo photocyclization, giving several pyrroloisoindole and pyridoisoindole derivatives depending on the number of methyl substituents on the alkenyl carbons.[5)] The present report is a full account of this work, including the results of a detailed study of the stereochemistry of these heterocyclic photoproducts.

The required haloalkenes **1** were obtained by the procedures described in the experimental section. *N*-(3-Alkenyl)phthalimides **2** were prepared in moderate yields by the reaction of potassium phthalimide with appropriate 1-halo-3-alkenes (**1**) in dimethylformamide at 80 °C as listed in Table I.

A typical irradiation of **2** was carried out in 10 mM methanol solution for 1 h. As listed in Table II, all of the *N*-(3-alkenyl)phthalimides **2a**—**f** cyclized smoothly to give major products **3** and/or **4**, as a mixture of stereoisomers in the cases of **3b**—**d** and **4e**, **f**, mostly in good combined yield after silica gel column chromatography (Chart 1, Table II). Compound **3a-i** was obtained as a sole product from **2a**. The structural and stereochemical assignments of these photoproducts **3** and **4** were based on their spectroscopic and chemical data (Table III).

In the infrared (IR) spectra of the photoproducts **3** and **4**, the bands in the regions of 3150—3500 and 1670—1710 cm^{-1} indicated the presence of the cyclol and lactam moieties, respectively.[6)] In the mass spectra of **3** and **4**, the molecular ion peaks of the corresponding substrate **2** plus methanol ($M^+ + MeOH$) appeared, suggesting the ring closure of **2** with incorporation of a methanol molecule. In the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectra of **3** and **4**, the peaks due to the alkenyl carbons which were present in **2** no longer appeared, and new singlet peaks appeared at 89—99 ppm, indicating the presence of a tertiary carbon (marked* in Chart 1) substituted by a hydroxyl group. The chemical shifts of

TABLE I. Preparation of the *N*-(3-Alkenyl)phthalimides

Halo alkene	Phthal-imide	Yield (%)	mp[a] (°C)	Formula	Analysis (%) Calcd (Found)		
					C	H	N
1a	**2a**	85	51—52 (51.1—51.5)[b]				
1b	**2b**	88	51—52 (51—53)[c]				
1c	**2c**	88	58.5—60	$C_{13}H_{13}NO_2$	72.54 (72.38	6.09 6.11	6.51 6.48)
1d	**2d**	79	48—49.5	$C_{14}H_{15}NO_2$	73.34 (73.25	6.59 6.45	6.11 6.09)
1e	**2e**	92	33—35	$C_{14}H_{15}NO_2$	73.34 (73.08	6.59 6.42	6.11 5.96)
1f	**2f**	82	32—33	$C_{15}H_{17}NO_2$	74.05 (74.25	7.04 7.22	5.76 5.56)

a) Recrystallized from ethanol.
b) See ref. 13.
c) N. J. Leonard, S. M. Hecht, F. Skoog, and R. Y. Schmitz, *Proc. Natl. Acad. Sci. U.S.A.*, **59**, 15 (1968).

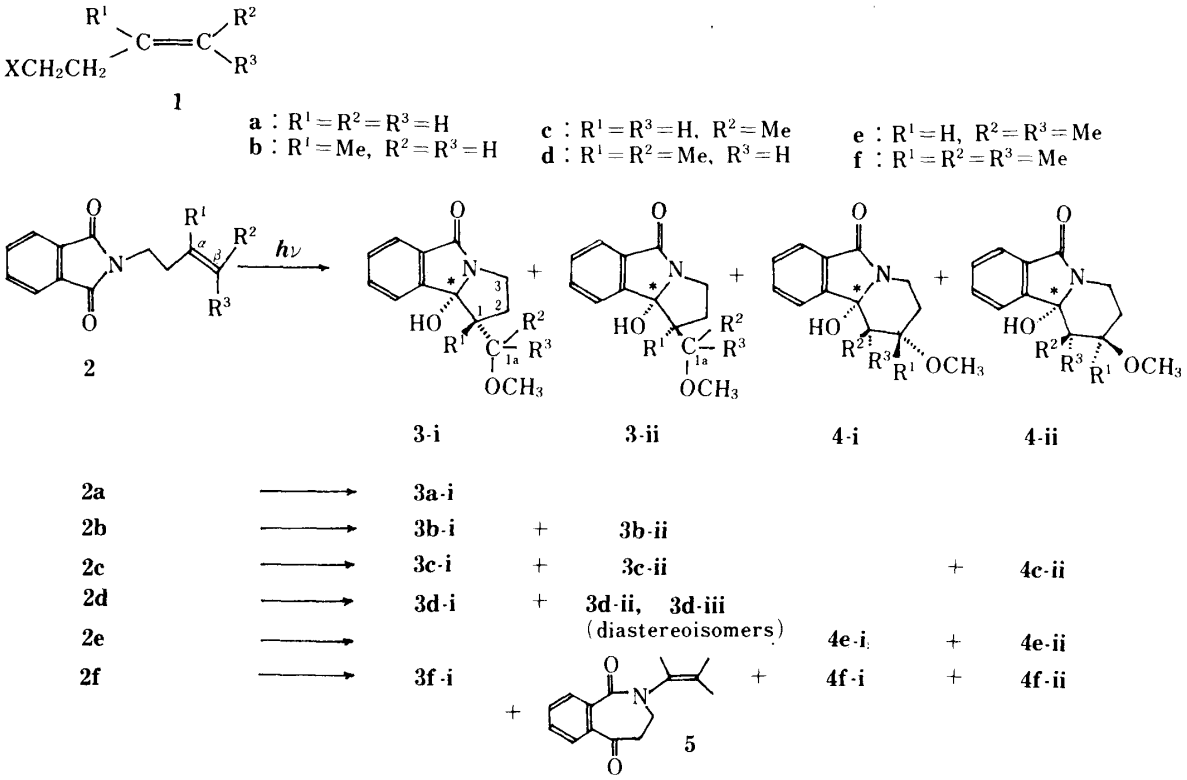


Chart 1

the carbonyl carbon in the lactam and the tertiary carbon (*) showed distinct differences between the series of pyrroloisoindoles **3** and pyridoisoindoles **4** (Table IV). On the basis of these ^{13}C-NMR data, the structures of **3** and **4** can be easily assigned, and this information may find a general use in the structural determination of new compounds with analogous carbon skeletons. The structure of 3,4-dihydro-2-(1,2-dimethyl-2-propenyl)-1*H*-2-benz-

TABLE II. Photoproducts from **2**

Substrate	Product	mp (°C)	Yield (%)	Appearance (Recryst. solvent)	Formula	Analysis (%) Calcd (Found) C	H	N
2a	**3a-i**	150—152	9	Colorless prisms	$C_{13}H_{15}NO_3$	66.93 (66.96	6.48 6.33	6.01 6.08)
2b	**3b-i**	156—158.5	52	Colorless plates (Benzene)	$C_{14}H_{17}NO_3$	67.99 (68.22	6.93 6.81	5.66 5.78)
	3b-ii	162—163	31	Colorless columns (Benzene–*n*-hexane)	$C_{14}H_{17}NO_3$	67.99 (67.84	6.93 6.85	5.66 5.36)
2c	**3c-i**	164—164.5	18	Colorless columns (Benzene)	$C_{14}H_{17}NO_3$	67.99 (67.98	6.93 6.86	5.66 5.84)
	3c-ii	168.5—170	14	Colorless needles (Benzene–*n*-hexane)	$C_{14}H_{17}NO_3$	67.99 (68.11	6.93 6.97	5.66 5.58)
	4c-ii	161—163.5	39	Colorless needles (Benzene–*n*-hexane)	$C_{14}H_{17}NO_3$	67.99 (68.22	6.93 6.81	5.66 5.78)
2d	**3d-i**	168—170.5	17	Colorless needles (Benzene–*n*-hexane)	$C_{15}H_{19}NO_3$	68.94 (68.88	7.33 7.26	5.36 5.27)
	3d-ii	177—179	27	Colorless needles (Benzene)	$C_{15}H_{19}NO_3$	68.94 (68.98	7.33 7.37	5.36 5.41)
	3d-iii	159—162	19	Colorless plates (*n*-Hexane)	$C_{15}H_{19}NO_3$	68.94 (68.99	7.33 7.31	5.36 5.28)
2e	**4e-i**	111—112	41	Colorless needles (Benzene)	$C_{15}H_{19}NO_3$	68.94 (68.88	7.33 7.26	5.36 5.27)
	4e-ii	198—200	43	Colorless needles (*n*-Hexane)	$C_{15}H_{19}NO_3$	68.94 (68.98	7.33 7.37	5.36 5.41)
2f	**3f-i**	99.5—101	11	Colorless needles (*n*-Hexane)	$C_{16}H_{21}NO_3$	69.79 (69.73	7.69 7.69	5.09 5.20)
	4f-i	154—156	20	Colorless needles (Benzene)	$C_{16}H_{21}NO_3$	69.79 (69.76	7.69 7.45	5.09 5.12)
	4f-ii	117—119	9	Colorless plates (*n*-Hexane)	$C_{16}H_{21}NO_3$	69.79 (69.72	7.69 7.58	5.09 5.01)
	5	108—110	23	Colorless needles (*n*-Hexane)	$C_{15}H_{17}NO_2$	74.05 (74.00	7.04 7.24	5.76 5.56)
2c	**6c**	184—186	28	Colorless plates (Benzene)	$C_{13}H_{15}NO_3$	66.93 (66.88	6.48 6.35	6.01 5.92)
2e	**6e-i**	180—182	35	Colorless plates (Benzene)	$C_{14}H_{17}NO_3$	67.99 (68.22	6.93 6.81	5.66 5.78)
	6e-ii	245—258	26	Colorless needles (Benzene)	$C_{14}H_{17}NO_3$	67.99 (67.98	6.93 6.84	5.66 5.66)
2f	**6f-i**	182—184	12	Colorless plates (Benzene)	$C_{15}H_{19}NO_3$	68.94 (68.88	7.33 7.21	5.36 5.30)
	6f-ii	238—240	11	Colorless plates (Benzene)	$C_{15}H_{19}NO_3$	68.94 (68.92	7.33 7.10	5.36 5.15)
2e	**11e**	117—119	36	Colorless needles (Benzene)	$C_{14}H_{15}NO_2$	73.34 (73.12	6.59 6.42	6.11 6.40)

azepine-1,5(2*H*)-dione **5** was determined based on the IR, and ^{1}H- and ^{13}C-NMR spectra. Thus, the IR spectrum of **5** showed carbonyl (1710 cm^{-1}) and amide carbonyl (1680 cm^{-1}) absorptions. The ^{13}C-NMR spectrum showed peaks due to carbonyl, amide

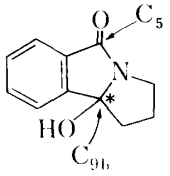
TABLE III. Spectral Data for Photoproducts

	IR (cm^{-1})		MS (M^+, M^+-18)			^{1}H-NMR (in $CDCl_3$, δ)
3a-i	3350	1690	233	215		1.8—2.2 (1H, m, –C<u>H</u>–CH_2), 2.2—2.4 (2H, m, N–CH_2–C<u>H</u>$_2$), 3.1—4.0 (4H, m), 3.4 (3H, s, –OCH_3), 4.3 (1H, s, OH), 7.3—7.8 (4H, m, aromatic H)
3b-i	3230	1670	247			0.5 (3H, s, C–Me), 1.7—2.1 (2H, m, N–CH_2–C<u>H</u>$_2$), 2.2—2.7 (2H, m, –C<u>H</u>$_2$–OMe), 3.2—3.8 (2H, m, N–CH_2), 3.5 (3H, s, –OMe), 4.1 (1H, s, OH), 7.3—7.7 (4H, m, aromatic H)
3b-ii	3350	1690	247			1.3 (3H, s, –C–Me), 2.3 (2H, m, N–CH_2C<u>H</u>$_2$), 2.6 (2H, m, –C<u>H</u>$_2$OMe), 2.8 (3H, s, –OMe), 3.0—3.8 (2H, m, N–CH_2), 4.0 (1H, s, OH), 7.2—7.4 (4H, m, aromatic H)
3c-i	3250	1690			229 (M^+-18)	1.2 (3H, d $J=6$ Hz, –CH–<u>Me</u>), 1.5—2.0 (1H, m, –C<u>H</u>–CH–OMe), 2.0—2.4 (2H, m, N–CH_2C<u>H</u>$_2$) 3.1—3.5 (2H, m, N–CH_2), 3.5 (3H, s, OMe), 3.7 (1H, m, –C<u>H</u>–OMe), 3.8 (1H, s, OH), 7.2—7.8 (4H, m, aromatic H)
3c-ii	3250	1690			229 (M^+-18)	0.3 (3H, d $J=7$ Hz, –CH–<u>Me</u>), 1.2—1.6 (1H, m, –C<u>H</u>–CH–OMe), 1.5—2.0 (2H, m, N–CH_2C<u>H</u>$_2$) 2.7—2.9 (1H, m, –C<u>H</u>–OMe), 3.4 (3H, s, OMe), 2.8—3.2 and 3.8—4.1 (2H, m, N–CH_2), 4.3 (1H, s, OH), 7.2—7.8 (4H, m, aromatic H)
4c-ii	3250	1660			229 (M^+-18)	1.0—1.5 (2H, m, N–CH_2C<u>H</u>$_2$), 1.3 (3H, s, –CH–Me), 1.9—2.3 (1H, m, –CH–Me), 3.4 (3H, s, OMe), 3.5 (1H, m, –C<u>H</u>–OMe), 2.7—3.1 and 3.8—4.1 (2H, m, N–CH_2), 4.5 (1H, s, OH), 7.2—7.8 (4H, m, aromatic H)
3d-i	3150	1690	261			0.3 (3H, s, C–Me), 1.3 (3H, d $J=6$ Hz, –CH–<u>Me</u>), 1.8—2.2 (2H, m, N–CH_2C<u>H</u>$_2$), 3.5 (3H, s, OMe), 2.6—3.5 and 3.3—3.7 (2H, m, N–CH_2), 3.8 (1H, q $J=6$ Hz, –C<u>H</u>–OMe), 6.4 (1H, s, OH), 7.3—7.8 (4H, m, aromatic H)
3d-ii	3250	1670	261			1.0 (3H, d $J=6$ Hz, –CH–<u>Me</u>), 1.3 (3H, s, –C–Me), 2.2 (3H, s, OMe), 1.9—2.5 (2H, m, N–CH_2C<u>H</u>$_2$), 2.4 (1H, q $J=6$ Hz, –C<u>H</u>–OMe), 3.1—3.5 (2H, m, N–CH_2), 3.5 (1H, s, OH), 7.3—7.7 (4H, m, aromatic H)
3d-iii	3320	1680	261			0.9 (3H, d $J=6$ Hz, –CH–<u>Me</u>), 1.3 (3H, s, –C–Me), 2.4 (3H, s, OMe), 2.1—2.6 (2H, m, N–CH_2C<u>H</u>$_2$), 2.7 (1H, q $J=6$ Hz, –C<u>H</u>–Me), 3.1 (1H, s, OH), 3.0—3.7 (2H, m, N–CH_2), 7.2—7.8 (4H, m, aromatic H)
4e-i	3290	1670		261	229 (M^+-32)	0.5 (3H, s, C–Me), 1.5 (3H, s, C–Me), 1.9 (2H, m), 3.0—3.5 and 4.0—4.5 (3H, m), 3.5 (3H, s, OMe). 5.7 (1H, s, OH), 7.3—8.0 (4H, s, aromatic H)
4e-ii	3410	1685		261	229 (M^+-32)	0.3 (3H, s, C–Me), 1.5 (3H, s, C–Me), 1.8 (2H, m), 2.7—4.1 (3H, m), 3.4 (3H, s, OMe), 4.3 (1H, s, OH), 7.2—7.7 (4H, m, aromatic H)

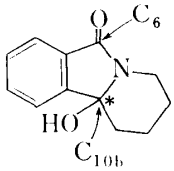
TABLE III. continued.

	IR (cm^{-1})		MS (M^+, M^+-18)		^{1}H-NMR (in $CDCl_3$, δ)
3f-i	3250	1690	275		0.6 (3H, s, C–Me), 1.3 (3H, s, C–Me), 1.7 (3H, s, C–Me), 1.7—2.1 (2H, m, N–$CH_2C\underline{H}_2$) 3.5 (3H, s, OMe), 3.0—3.9 (2H, m, N–CH_2), 7.2 (1H, s, OH), 7.3—7.9 (4H, m, aromatic H)
4f-i	3300	1680	275		0.5 (3H, s, C–Me), 1.4 (3H, s, C–Me), 1.7 (4H, s, C–Me), 1.6—2.8 (2H, m, N–$CH_2C\underline{H}_2$) 3.2 (3H, s, OMe), 3.4 (1H, s, OH), 2.8—3.2 and 3.9—4.3 (2H, m, N–CH_2), 7.2—7.7 (4H, m, aromatic H)
4f-ii	3500	1710	275		0.5 (3H, s, C–Me), 1.2 (3H, s, C–Me), 1.5 (3H, s, C–Me), 1.6—2.1 (2H, m, N–$CH_2C\underline{H}_2$) 2.8 (3H, s, OMe), 2.9—3.3 and 4.1—4.3 (2H, m, N–CH_2), 4.9 (1H, s, OH), 7.4—8.0 (4H, m, aromatic H)
5	1710	1680	243		2.2 (6H, s, 2 × Me), 2.4 (3H, s, C–Me), 2.9 (2H, t $J=8$ Hz, N–$CH_2C\underline{H}_2$), 4.3 (2H, t $J=8$ Hz, N–CH_2), 7.3—8.0 (4H, m, aromatic H)
6e-i	3250	1690		229 (M^+-18)	0.35 (3H, s, Me), 1.45 (3H, s, Me), 1.75 (2H, m), 3.35 and 4.10 (2H, m, N–CH_2), 3.70 (1H, m, methine), 3.4 (1H, m, OH), 6.5 (1H, m, OH), 7.4—7.8 (4H, m)
6e-ii	3250	1670		229 (M^+-18)	0.25 (3H, s, Me), 1.35 (3H, s, Me), 1.60 (m, 2H), 2.7—4.2 (m, 3H), 3.3 (1H, s, OH), 6.15 (1H, s, OH), 7.4—7.7 (4H, m)
7e-i		1700	333		0.7 (3H, s, Me), 1.45 (3H, s, Me), 2.10 (2H, m), 3.10 and 4.35 (2H, m, N–CH_2), 4.15 (1H, m, methine), 7.2—7.9 (9H, m)
11e	1710	1680	229		1.8 (6H, s, 2 × Me), 3.4—4.2 (3H, m, NH–CH_2–CH), 5.0—5.4 (1H, m, vinyl H) 7.6—8.1 (5H, m, aromatic H + NH)
6c	3250	1690		215 (M^+-18)	0.3 (3H, s, Me), 1.6—1.8 (m, 3H), 3.6 (m, 1H), 3.4—4.1 (2H, m, N–CH_2), 3.6 (1H, s, OH), 6.8 (1H, s, OH), 7.4—7.8 (4H, m, aromatic H)
6f-i	3250	1690		243 (M^+-18)	0.3 (3H, s, Me), 1.6 (3H, s, Me), 1.7 (3H, s, Me), 1.6—1.8 (2H, m), 3.2—4.0 (2H, m, N–CH_2), 3.6 (1H, s, OH), 5.2 (1H, s, OH), 7.4—7.8 (4H, m, aromatic H)
6f-ii	3250	1670		243 (M^+-18)	0.3 (3H, s, Me), 1.6 (3H, s, Me), 1.7 (3H, s, Me), 1.6—1.8 (2H, m), 3.0—3.6 (2H, m, N–CH_2), 3.6 (1H, s, OH), 6.8 (1H, s, OH), 7.4—7.9 (4H, m, aromatic H)

TABLE IV. ^{13}C-NMR Data for **3** and **4**



Pyrroloisoindoles (**3**)



Pyridoisoindoles (**4**)

Product	Chemical shift (ppm from TMS)		Product	Chemical shift (ppm from TMS)	
	C_5	C_{9b}		C_6	C_{10b}
3a-i	170	97	**4c-ii**	165	89
3b-i	170	98	**4e-i**	165	92
3b-ii	171	99	**4e-ii**	165	90
3c-i	170	98	**4f-i**	165	89
3c-ii	169	96	**4f-ii**	165	89
3d-i	169	99	**6c**	165	89
3d-ii	170	98	**6f-i**	165	92
3d-iii	170	98	**6f-ii**	165	89
3f-i	170	98			

carbonyl, and tetrasubstituted alkenyl carbons at 206, 168, 132, and 129 ppm, respectively. In the ^{1}H-NMR spectrum, two triplet peaks appeared at 2.9 and 4.3 ppm (J=8 Hz), indicating the presence of a methylene–methylene bond (–CH_2CH_2–). In the pyrroloisoindole derivatives (**3b—d**) the configurations of the hydroxyl group at the benzylic position and the substituents at C_1 were confirmed on the basis of the ^{1}H-NMR spectra of the substituents by considering the anisotropic shielding effects of the phenyl ring. For example, the signal of the C_1-methyl protons appeared at 0.5 and 1.3 ppm for **3b-i** and **3b-ii**, respectively. For **3c-i** and **3c-ii**, the C-methyl protons on the C_1-substituent appeared as doublets at 1.2 and 0.3 ppm, respectively. In **3d-i**, the C_1-methyl showed an upfield shift from 1.3 to 0.3 ppm compared with those of the corresponding stereoisomers (**3d-ii** and **3d-iii**), which have the same configuration at the C_1-substituents but not at the C_{1a}-carbon of the C_1-substituent ($C_{1a}(R^2, R^3)OCH_3$). On standing in deuterochloroform, compound **3d-i** was easily converted to **3d-iii**, which is presumably the diastereoisomers of **3d-ii**. Although the stereoisomer of **3f-i** was not isolated, the C_1-methyl of **3f-i** also showed an upfield shift at 0.6 ppm. Thus, in a series of pyrroloisoindoles **3** the presence of C_1-substituents showing such a high field shift due to the anisotropic effect of the phenyl ring indicates the *trans* configuration of the hydroxyl group and the substituent.

To obtain stereochemical information, **2e** and **2f** were irradiated in acetonitrile–water. The diol compounds **6** thus obtained were then converted to their cyclic esters (**7e-i**, **f-i**): Reaction of **6e-i** and **6f-i** with phenylboric acid in benzene easily led to the cyclic phenylboronates **7e-i** and **7f-i**,[7] respectively, in high yields, but the esters **7** were not obtained from **6e-ii** and **6f-ii**. The fact that **6e-i** and **6f-i** react smoothly with phenylboric acid to form the cyclic boronates definitely supports the *cis* configuration of two hydroxyl groups in **6e-i** and **6f-i** (Chart 2). Upon irradiation of **2c** in acetonitrile–water, three 1,3-diols including **6c** were obtained homogeneously. The failure of the formation of the cyclic ester **7** in the reaction of **6c** with phenylboric acid suggests the *trans* configuration of the two hydroxyl groups. The stereochemistry of **4c-ii** was assigned based on the similarity of the ^{1}H-NMR spectra of **6c** and **4c-ii**. Attempts to prepare other cyclic derivatives of the *cis* diol with acetone and 2,2-

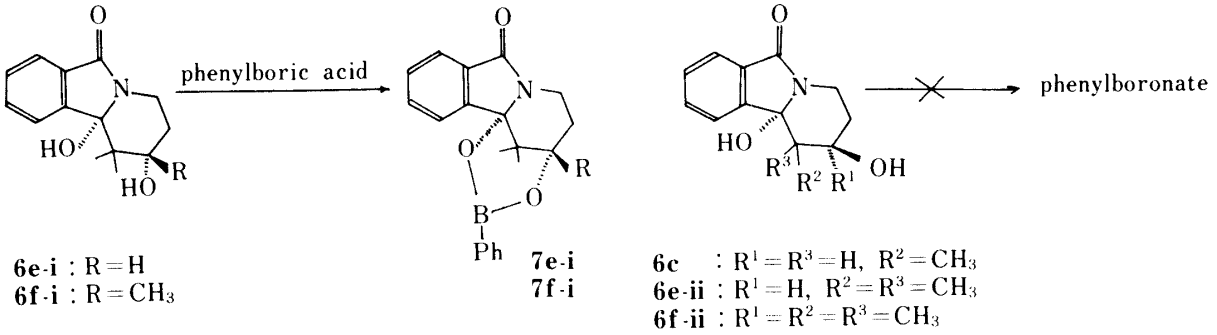


Chart 2

dimethoxypropane were unsuccessful.

As shown in Chart 1, the stereochemistries of **4e-i** and **4e-ii** were assigned by analogy with **6e-i** and **6e-ii**, in which the configurations of the two hydroxyl groups are *cis* and *trans*, respectively, based on comparison of the ^{1}H-NMR spectra. Similarly, the configurations of **4f-i** and **4f-ii** were correlated with those of **4e-i** and **4e-ii** on the basis of their ^{1}H-NMR spectra.

It is worth noting that such a small variation in the substrate (**2**) structure as the existence of a methyl group profoundly influences the reaction site, resulting in predominant formation of either the pyrroloisoindoles **3** or pyridoisoindoles **4** (Chart 1).

In the photoaddition reactions of imides with olefins, Mazzocchi *et al.*[3,8] proposed two competing processes, in which electron transfer (k_{ET}) competes with the addition reaction (k_{CN}) to the imide C(O)–N bond. Very recently we have found that the Paterno–Büchi reaction (k_{PB}) takes place in phthalimide photoaddition to give the imide-oxetane.[9] Thus, the general aspects of the photoaddition of aromatic cyclic imides with alkenes may now be outlined as shown in Chart 3. The electron transfer from the alkene to the imide generates a radical cation

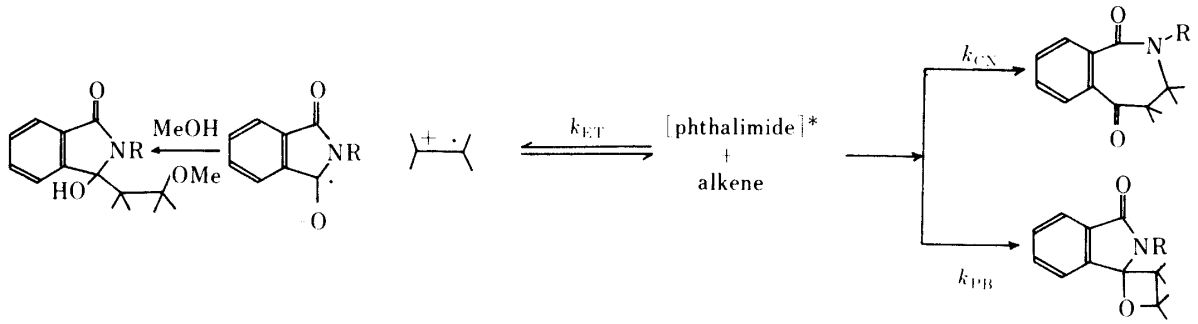


Chart 3

in competition with the addition (k_{CN}) and the Paterno–Büchi reaction (k_{PB}), giving the benzazepinedione and the oxetane, respectively. In fact, the sensitivity of the addition process to alkene ionization potential is considered to be due to the electron transfer quenching of the phthalimide excited state by the alkene.[3] In addition, the pathways are strongly dependent on the reaction media employed. Irradiation of alkenes in an alcoholic solvent frequently induces photochemical behavior which involves nucleophilic trapping of a reactive intermediate by the solvent.[10] Thus, the radical cation (**8**),[4,11] generated on excitation, can be trapped by anti-Markownikoff addition in methanol to form a more stabilized biradical intermediate (**9** and **10**) (Chart 4). With the reactants in which the C_α atom is more substituted, the biradical (**9**) may be formed and then give rise to the products **3**, while with reactants having more substituents at the C_β atom, the preferred biradical (**10**) leads to **4**. When the C_α and C_β atoms

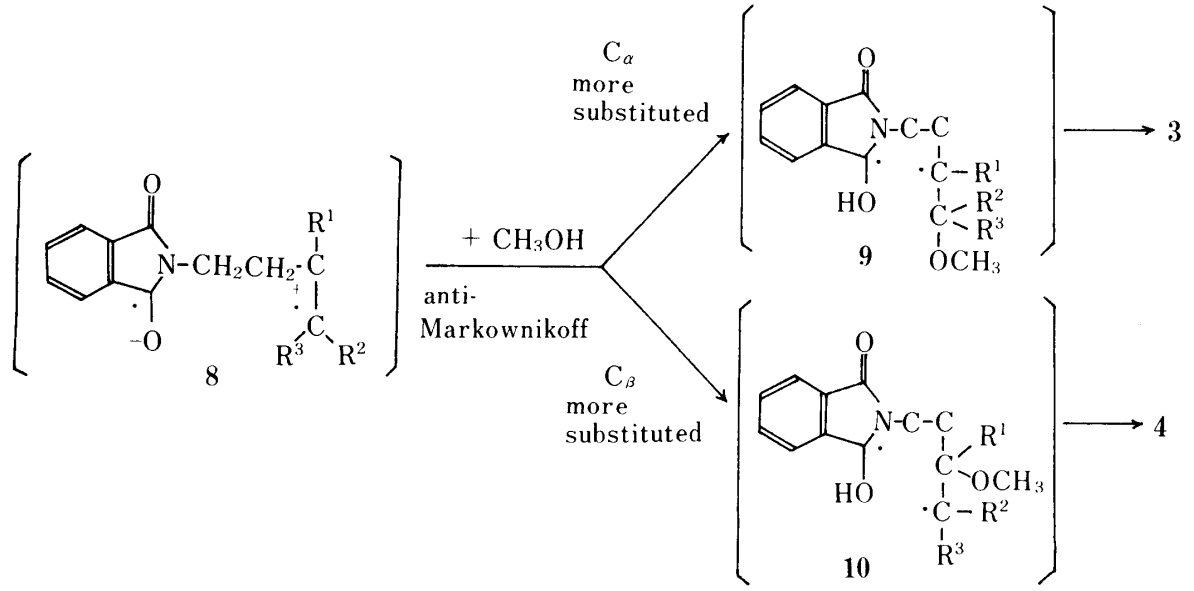
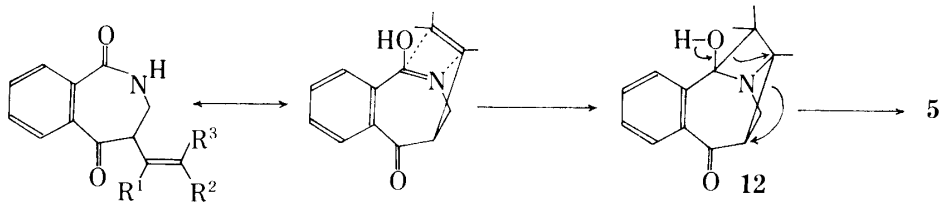


Chart 4

are substituted to an equal extent as in the case of **2c** and **2f**, both products were indeed formed. Upon photolysis in methanol, **2e** gave **4**, whereas in acetonitrile **2e** gave only benzazepinedione **11e**.

Interestingly, irradiation of **2f** gave four products, **3f-i**, **4f-i**, **4f-ii**, and **5**. The formation of **5** could be tentatively explained by considering a secondary intramolecular photoaddition of the alkenyl group to the initially formed benzazepinedione **11** by way of an intermediate **12**, but the mechanism is still uncertain (Chart 5).



11e : $R^1=H$, $R^2=R^3=Me$
11f : $R^1=R^2=R^3=Me$

Chart 5

The formation of either **3** or **4** in the photocyclization of *N*-(3-alkenyl)phthalimides **2** depends on the degree of substitution at the alkenyl carbons (α,β) (Chart 4). This substitution dependency strongly suggests that the photocyclization is initiated by electron transfer from the alkene in the side chain to the imide, followed by the anti-Markownikoff addition of methanol. Except in the case of a fully substituted alkene (**2f**) in which the addition (k_{CN}) occurred to give the benzazepinedione, the above electron transfer pathway provides a reasonable interpretation for the product distributions.

Experimental

All melting points were determined on a Yamato melting point apparatus (model MP-21) and are uncorrected. IR spectra were recorded on a Shimadzu IR-400 spectrometer. NMR spectra were taken on a Hitachi R-40 spectrometer and a JEOL-FX 60 spectrometer. Chemical shifts are reported in parts per million (δ) relative to

tetramethylsilane (TMS, 0.0 ppm) as a internal standard. The abbreviations used are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Mass spectra (MS) were determined with a gas chromatograph-mass spectrometer (Shimadzu-LKB 9000) with a direct inlet system.

Irradiations of phthalimide derivatives in methanol (10 mM) were conducted using a 500 W high-pressure mercury lamp and a water-cooled quartz immersion well (Eikosha PIH-500) at room temperature. Stirring of the reaction mixture was effected by the introduction of a stream of nitrogen at the bottom of the outer jacket. All column chromatography was conducted using silica gel (Merck, Kieselgel 60, 70—230 mesh).

4-Chloro-1-butene (1a)——3-Buten-1-ol (bp 111—112 °C, lit.[12] bp 113.5 °C) prepared from vinylacetic acid was treated with $SOCl_2$ to give **1a**, bp 72—74 °C (lit.[13] bp 75 °C).

4-Chloro-2-methyl-1-butene (1b)——The Grignard reagent prepared from methallyl chloride and magnesium was allowed to react with paraformaldehyde in dry ether to afford 3-methyl-3-buten-1-ol (bp 123—125 °C, lit.[14] bp 125—135 °C) which was refluxed with $SOCl_2$ to give **1b**, bp 99—101 °C (lit.[14] bp 101—102.7 °C).

(*E*)-5-Bromo-2-pentene (1c)——Methyl cyclopropyl ketone obtained from 1-acetyl-γ-butyrolactone following the reported procedure[15] was reduced with $LiAlH_4$ in tetrahydrofuran to give cyclopropyl methylcarbinol, bp 117—119 °C (lit.[16] bp 119 °C). The carbinol was hydrolyzed with 48% HBr to afford **1c**, bp 123—125 °C (lit.[17] bp 125—126 °C).

(*E*)-5-Bromo-3-methyl-2-pentene (1d)——Methyl-1-methylcyclopropyl ketone was obtained from 1-methyl-1-acetyl-γ-butyrolactone, which was prepared from 1-acetyl-γ-butyrolactone and CH_3I. The ketone was reduced and hydrolyzed to **1d**, bp 148—151 °C (lit.[18] bp 148—150 °C).

5-Bromo-2-methyl-2-pentene (1e)——The bromide (**1e**) was prepared from 1-acetyl-γ-butyrolactone according to the method of Manjarrez, bp 48—50 °C (12 mmHg) (lit.[15] bp 90—92 °C (100 mmHg)).

5-Bromo-2,3-dimethyl-2-pentene (1f)——Dimethyl-(1-methyl cyclopropyl)carbinol was prepared from methyl-1-methylcyclopropyl ketone and the Grignard reagent CH_3MgI, and hydrolyzed with 48% HBr to give **1f**, bp 54—55.5 °C (14 mmHg) (lit.[19] bp 50—51 °C (10 mmHg)).

General Procedure for *N*-(3-Alkenyl)phthalimide Derivatives——A mixture of potassium phthalimide (0.02 mol) and the 1-halo-3-alkene derivative (**1**) (0.02 mol) in 30 ml of dimethylformamide was stirred at 80 °C for 3 h and then at room temperature for 3 h. The reaction mixture was poured into ice-water and the solid product was collected on a filter funnel. The phthalimide derivatives were recrystallized from ethanol. The melting points of these imides are listed in Table I.

Irradiation of 2: General Procedure, Irradiation of *N*-(3,4-Dimethyl-3-pentenyl)phthalimide (2e)——A solution of **2e** (1.216 g; 5 mmol) in MeOH was irradiated for 1 h. The solvent was removed *in vacuo* and the residue was chromatographed on 120 g of silica gel using a mixture of chloroform–ethyl acetate (30 : 1; v/v). Chromatography of the products gave four compounds, **5**, **4f-ii**, **3f**, and **4f-i** in the order of separation.

3a-i, 1,2,3,9b-tetrahydro-9b-hydroxy-(methoxymethyl)-5*H*-pyrrolo[2,1-*a*]isoindol-5-one; **3b-i**, *cis*-1,2,3,9b-tetrahydro-9b-hydroxy-1-(methoxymethyl)-1-methyl-5*H*-pyrrolo[2,1-*a*]isoindol-5-one; **3b-ii**, *trans*-1,2,3,9b-tetrahydro-9b-hydroxy-1-(methoxymethyl)-1-methyl-5*H*-pyrrolo[2,1-*a*]isoindol-5-one; **3c-i**, *cis*-1,2,3,9b-tetrahydro-9b-hydroxy-1-(1-methoxyethyl)-5*H*-pyrrolo[2,1-*a*]isoindol-5-one; **3c-ii**, *trans*-1,2,3,9b-tetrahydro-9b-hydroxy-1-(1-methoxyethyl)-5*H*-pyrrolo[2,1-*a*]isoindol-5-one; **3d-i**, *cis*-1,2,3,9b-tetrahydro-9b-hydroxy-1-(1-methoxyethyl)-1-methyl-5*H*-pyrrolo[2,1-*a*]isoindol-5-one; **3d-ii**, **3d-iii**, *trans*-1,2,3,9b-tetrahydro-9b-hydroxy-1-(1-methoxyethyl)-1-methyl-5*H*-pyrrolo[2,1-*a*]isoindol-5-one; **3f-i**, *cis*-1,2,3,9b-tetrahydro-9b-hydroxy-1-(1-methoxy-1-methylethyl)-1-methyl-5*H*-pyrrolo[2,1-*a*]isoindol-5-one; **4c-ii**, *trans*-1,3,4,10b-tetrahydro-10b-hydroxy-2-methoxy-1-methylpyrido[2,1-*a*]isoindol-6(2*H*)-one; **4e-i**, *cis*-1,3,4,10b-tetrahydro-10b-hydroxy-2-methoxy-1,1-dimethylpyrido[2,1-*a*]isoindol-6(2*H*)-one; **4e-ii**, *trans*-1,3,4,10b-tetrahydro-10b-hydroxy-2-methoxy-1,1-dimethylpyrido[2,1-*a*]isoindol-6(2*H*)-one; **4f-i**, *cis*-1,3,4,10b-tetrahydro-10b-hydroxy-2-methoxy-1,1,2-trimethylpyrido[2,1-*a*]isoindol-6(2*H*)-one; **4f-ii**, *trans*-1,3,4,10b-tetrahydro-10b-hydroxy-2-methoxy-1,1,2-trimethylpyrido[2,1-*a*]isoindol-6(2*H*)-one; **5**, 3,4-dihydro-2-(1,2-dimethyl-2-propenyl)-1*H*-2-benzazepine-1,5(2*H*)-dione.

Irradiation of *N*-(4-Methyl-3-pentenyl)phthalimide 2e in Acetonitrile–Water——Irradiation of **2e** (10 mM) in acetonitrile–water (8 : 1) was carried out in a manner similar to that described above. The crude photolysate was chromatographed on 80 g of silica gel, and elution with chloroform–ethyl acetate (4 : 1) gave the diol compounds **6e-i** and **6e-ii**.

Reaction of 6e-i with Phenylboric Acid——A mixture of 50 mg (0.2 mmol) of **6e-i** and 24 mg (0.2 mmol) of phenylboric acid in 10 ml of benzene was refluxed for 30 min. The solvent was removed *in vacuo*, and the residue was recrystallized from ethanol to give 52 mg of **7e-i** as colorless needles: mp 161—163 °C; MS *m/e*: 333 (M^+), 315 ($M^+ - 18$); IR (KBr): 1700 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 0.70 (s, 3H, Me), 1.45 (s, 3H, Me), 2.10 (m, 2H), 3.10 and 4.35 (m, 2H, NCH_2), 4.15 (m, 1H, methine), 7.2—7.9 (m, 9H). *Anal.* Calcd for $C_{20}H_{20}BNO_3$: C, 72.09; H, 6.05; N, 4.20. Found: C, 71.85; H, 6.09; N, 3.90.

7f-i: colorless needles; mp 182—183 °C; MS *m/e*: 347 (M^+), 329 ($M^+ - 18$); IR (KBr): 1700 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 0.80 (s, 3H, Me), 1.30 (s, 3H, Me), 1.45 (s, 3H, Me), 3.20 and 4.20 (m, 2H, NCH_2), 7.2—7.9 (m, 9H). *Anal.* Calcd for $C_{21}H_{22}BNO_3$: C, 72.85; H, 6.70; N, 4.05. Found: C, 72.70; H, 6.72; N, 4.12.

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