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Intramolecular Photoreactions of Phthalimide–Alkene Systems. Oxetane Formation of *N*-(ω-Indol-3-ylalkyl)phthalimides[1)]

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Upon irradiation in acetone, *N*-(ω-indol-3-ylalkyl)phthalimides (**1**, $n=2-5$) underwent intramolecular Paterno–Büchi reaction to give oxeto[2,3-*b*]indoles or their ring-opening products. However, *N*-(ω-indol-2-ylalkyl)phthalimides (**9**, $n=2, 3$) yielded not the oxetane, but the *N*-deacetylated compounds.

Keywords——intramolecular photocyclization; indolylalkylphthalimide; oxeto-indole; iso-indolone; Paterno–Büchi reaction; imide-oxetane; photoreaction

There are remarkable differences between the photochemical behavior of alicyclic imides and that of aromatic imides (*i.e.*, phthalimides).[2)] In photoreactions with alkenes, alicyclic imides efficiently undergo inter-[3)] and intramolecular[4)] Paterno–Büchi reaction (oxetane formation), whereas phthalimides undergo competitively the photoaddition (k_{CN}) to the C(=O)–N bond (benzazepinedione formation)[5)] in a concerted process, the photoreduction and the photocyclization (*e.g.*, isoindole formation)[6)] by an initial electron transfer process (k_{ET}) proposed previously,[7)] and not oxetane formation. Recently possible participation of the Paterno–Büchi reaction in the phthalimide systems has been reported,[5b)] but none of the Paterno–Büchi products (oxetanes) were isolated. Therefore attempts to detect oxetane formation are of continuing interest in the photochemistry of the imide–alkene system. In previous papers, we have reported the first examples of efficient inter-[8)] and intramolecular[9)] oxetane formation (k_{PB}) in phthalimide–indole systems (Chart 1). Independently Mazzocchi and Klingler also reported the isolation of the Paterno–Büchi product obtained intermolecularly.[10)] The present report presents full details of further research on the intramolecular photoreaction of the imide–indole systems.

A series of *N*-(ω-indol-3-ylalkyl)phthalimides (**1** and **9**) was prepared by the procedures described in the experimental section. Melting points and analytical data of these imides (**1**

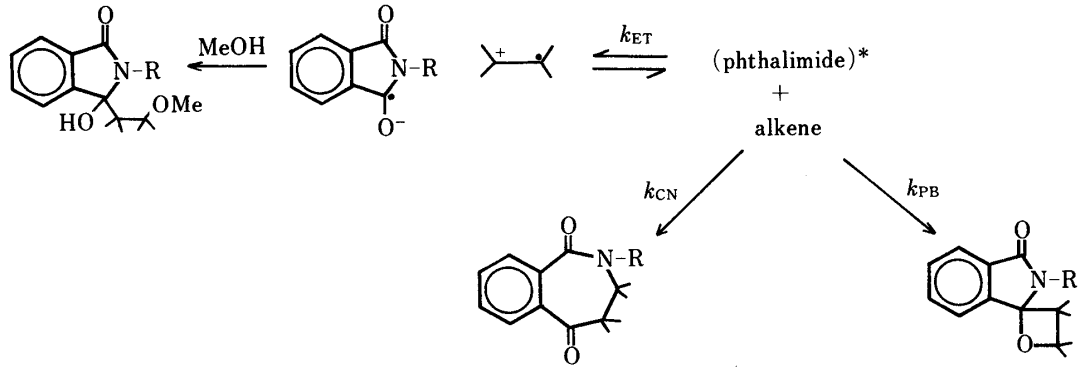
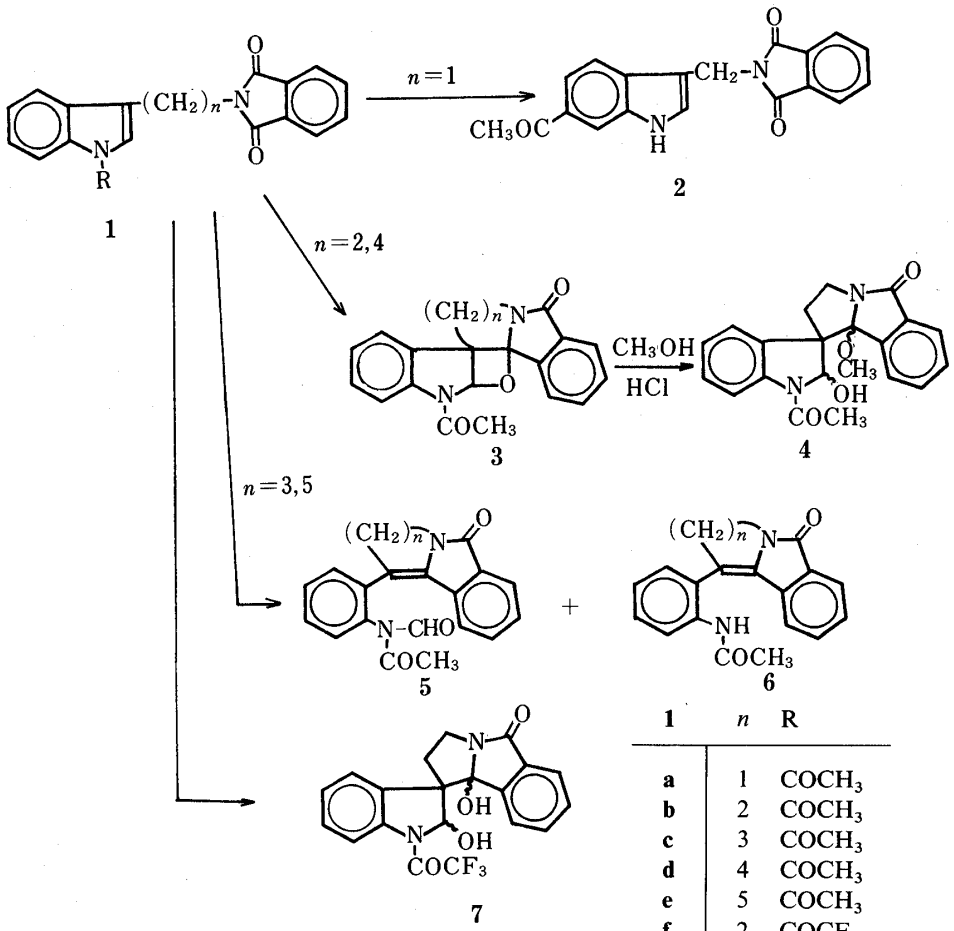


Chart 1

TABLE I. Preparation of *N*-[ω-(Indolyl)alkyl]phthalimides (**1** and **9**)

	n	R	mp °C (Solvent)	IR (Nujol) cm^{-1}	MS *m/z* (M^+)	Formula	Analysis (%) Calcd (Found) C	H	N
1a	1	$COCH_3$	200—200.5 (Acetone)	1770, 1705,	318	$C_{19}H_{14}N_2O_3$	71.69 (71.74	4.43 4.37	8.80 8.94)
1b	2	$COCH_3$	197—198 ($CHCl_3$)	1765, 1700, 1680	322	$C_{20}H_{16}N_2O_3$	72.28 (72.10	4.85 4.79	8.43 8.25)
1c	3	$COCH_3$	134—136 (Acetone)	1775, 1725, 1705	346	$C_{21}H_{18}N_2O_3$	72.82 (72.86	5.24 5.17	8.09 8.28)
1d	4	$COCH_3$	109—110.5 (EtOH)	1765, 1700	360	$C_{22}H_{20}N_2O_3$	73.31 (73.35	5.59 5.49	7.77 7.85)
1e	5	$COCH_3$	82—84 (Benzene–Et_2O)	1765, 1705, 1675	374	$C_{23}H_{22}N_2O_3$	73.78 (73.49	5.92 5.98	7.48 7.51)
1f	2	$COCF_3$	172—172.5 (AcOEt)	1770, 1720, 1705	386	$C_{20}H_{13}F_3N_2O_3$	62.18 (62.19	3.39 3.33	7.25 7.17)
1g	2	CH_3	177—179 (AcOEt)	1760, 1705,	304	$C_{19}H_{16}N_2O_2$	74.98 (74.98	5.30 5.13	9.21 9.19)
9a	2	$COCH_3$	183—184 (AcOEt–acetone)	1770, 1710, 1700	332	$C_{20}H_{16}N_2O_3$	72.28 (72.39	4.85 4.75	8.43 8.60)
9b	3	$COCH_3$	121—122.5 (EtOH)	1760, 1710, 1700	346	$C_{21}H_{18}N_2O_3$	72.82 (72.80	5.24 5.08	8.09 8.03)



1	*n*	R
a	1	$COCH_3$
b	2	$COCH_3$
c	3	$COCH_3$
d	4	$COCH_3$
e	5	$COCH_3$
f	2	$COCF_3$
g	2	CH_3

Chart 2

TABLE II. Photolysis of **1** and **9**

Substrate	*n*	React. time (h)	Product	Yield (%) (**1** or **9**)[a]	mp (°C)	Appearance (Solvent)	Formula	Analysis (%) Calcd (Found) C	H	N
1a	1	50	**2**	18 (36)	248.5—249.5	Colorless needles (AcOEt–hexane)	$C_{19}H_{14}N_2O_3$	71.69 (71.63	4.43 4.26	8.80 8.78)
1b	2	12.5	**3b**	27 (—)	181—182	Colorless columns (CH_3CN)	$C_{20}H_{16}N_2O_3$	72.28 (72.10	4.85 4.80	8.43 8.24)
1b	2	9	**4**	38 (32)	195—196.5	Colorless prisms (EtOH)	$C_{21}H_{20}N_2O_4$	69.21 (69.08	5.53 5.36	7.69 7.51)
1c	3	8	**5c**	34 (28)	161—162	Pale yellow prisms (Benzene–Et_2O)	$C_{21}H_{18}N_2O_3$	72.82 (72.75	5.24 5.22	8.09 8.12)
			6c	3	238.5—240	Colorless prisms (AcOEt–benzene)	$C_{20}H_{18}N_2O_2$	75.45 (75.32	5.70 5.66	8.80 8.78)
1d	4	6	**3d**	69 (19)	187.5—188.5	Colorless prisms (Benzene–Et_2O)	$C_{22}H_{20}N_2O_3$	73.31 (73.34	5.59 5.50	7.77 7.83)
1e	5	4	**5e**	28 (19)	200—200.5	Colorless prisms (Benzene–Et_2O)	$C_{23}H_{22}N_2O_3$	73.78 (73.90	5.92 6.02	7.48 7.42)
			6e	6	271.5—272.5	Colorless prisms (Benzene–Et_2O)	$C_{22}H_{22}N_2O_2$	76.27 (76.22	6.40 6.32	8.09 8.03)
1f	2	7	**7**	52 (—)	178—179	Colorless powder (Acetone–hexane)	$C_{20}H_{15}F_3N_2O_4$	59.40 (59.58	3.74 3.69	6.93 6.94)
1g	2	28	—	— (98)						
9a	2	14	**10a**	26 (17)	217.5—218.5	Colorless needles (Acetone–hexane)	$C_{20}H_{16}N_2O_3$	72.28 (72.22	4.85 4.71	8.43 8.30)
			11a	8	227—228	Yellow prisms (Acetone)				
9b	3	12.5	**10b**	12 (15)	193—194	Colorless needles (AcOEt–hexane)	$C_{21}H_{18}N_2O_3$	72.82 (72.85	5.24 5.38	8.09 8.25)
			11b	7	155—156	Yellow plates (AcOEt–hexane)	$C_{19}H_{16}N_2O_2$	74.98 (74.89	5.30 5.15	9.21 9.13)

a) Recovery (%) of unchanged substrate.

and **9**) are listed in Table I. Photolyses of **1** and **9** were carried out in acetone (10 mM) with a 500 W high-pressure mercury lamp through a Pyrex filter under a nitrogen atmosphere at room temperature. The results are collected in Table II.

As shown in Chart 2, photolysis of **1a** ($n=1$) resulted only in rearrangement of an acetyl group onto the benzene ring to give the 6-acetylindole derivative (**2**) in a poor yield, and unchanged **1a** was recovered in 36% yield even after prolonged irradiation (50 h). In the photolysis of **1b** ($n=2$), the oxetane (**3b**) was obtained in 27% yield after fractional recrystallization. The oxetane **3b** was easily decomposed to uncharacterized compounds during silica gel column chromatography. On treatment with methanolic hydrochloric acid, the isolated oxetane **3b** was quantitatively converted to a spiro compound (**4**) through fission of the oxetane ring by acid catalysis. Similarly, upon irradiation of **1b** for 9 h followed by treatment of the photolysate with methanolic hydrochloric acid, the spiro compound **4** was obtained in 38% yield together with recovery of **1b** in 32% yield. In the case of **1d** ($n=4$), the oxetane (**3d**) was obtained in 69% yield even after column chromatography. However, upon treatment with a catalytic amount of *p*-toluenesulfonic acid in acetone, both the oxetanes **3b** and **3d** were easily decomposed to the original substrates **1b** and **1d**, respectively. In addition, irradiation of the oxetane **3d** in acetone for 2 h also gave the original imide **1d** and unchanged **3d** in 28 and 56% yields, respectively. It is likely that the photochemical formation and

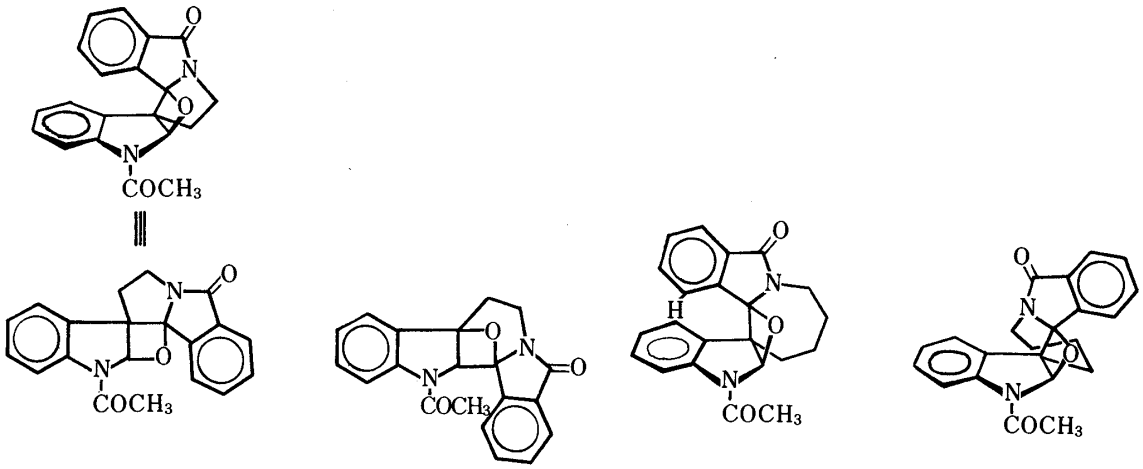
TABLE III. Spectral Data for Photoproducts

Compound	IR (Nujol) cm^{-1}	MS (M^+) m/z	^{1}H-NMR ($CDCl_3$) δ, ppm	^{13}C-NMR ($CDCl_3$) (OFR) δ, ppm
2[a]	3310, 1765, 1715, 1660	318	2.57 (3H, s, $COCH_3$), 4.88 (2H, s, C–CH_2–N), 7.5—7.9 (8H, m, aromatic H and NH), 7.93 (1H, s, aromatic H)	26.6, 32.4, 110.4, 112.7, 118.1, 118.9, 123.0, 129.5, 130.5, 131.5, 134.4, 135.3, 167.7, 197.4
3b	1705, 1670	332	2.35 (3H, s, $COCH_3$), 2.3—2.6 (2H, m, C–CH_2CH_2–N), 3.6—4.0, 4.4—4.7 (2H, m, C–CH_2CH_2–N), 6.40 (1H, s, N–CH–O), 6.6—6.8 (2H, m, aromatic H), 6.90 (1H, t, J=6.5 Hz, aromatic H), 7.0—7.8 (4H, m, aromatic H), 8.28 (1H, d, J=8.4 Hz, aromatic H)	23.8 (q), 32.9 (t), 42.2 (t), 62.9 (s), 92.4 (d), 109.1 (s), 117.4 (d), 123.0 (d), 123.5 (d), 124.5 (d), 130.0 (d), 131.0 (d), 132.5 (s), 133.0 (d), 139.4 (s), 144.4 (s), 168.7 (s), 169.3 (s)
4[a]	3220, 1718, 1640	364	1.7—2.0 (1H, m, C–CH_2CH_2–N), 2.37 (3H, s, $COCH_3$), 2.88 (3H, s, OCH_3), 2.8—3.6 (3H, m, C–CH_2CH_2–N), 5.7—5.9 (1H, m, N–CH–O), 6.02 (1H, d, J=7.5 Hz, aromatic H), 6.63 (1H, t, J=7.5 Hz, aromatic H), 7.02 (1H, t, J=7.5 Hz, aromatic H), 7.4—7.8 (4H, m, aromatic H), 7.92 (1H, d, J=7.5 Hz, aromatic H)	23.5 (q), 40.1 (t), 40.5 (t), 49.8 (q), 60.6 (s), 90.1 (d), 103.0 (s), 117.0 (d), 122.7 (d), 123.3 (d), 124.0 (d), 125.1 (d), 128.5 (d), 130.4 (d), 130.8 (s), 133.1 (d), 134.9 (s), 140.5 (s), 141.1 (s), 169.7 (s)
5c	1725, 1690, 1655	346	1.7—2.6 (7H, m, C–$(CH_2)_2$–CH_2–N and $COCH_3$), 3.82 (2H, t, J=6 Hz, C–CH_2–N), 6.5—7.9 (8H, m, aromatic H), 9.0—9.5 (1H, m, CHO)	21.5 (t), 24.1 (q), 29.3 (t), 38.2 (t), 162.4 (d), 165.6 (s), 172.2 (s)
6c	3290, 1675, 1600	318	1.98 (3H, s, $COCH_3$), 2.0—2.3 (2H, m, C–CH_2CH_2–N), 2.4—2.7 (2H, m, C–CH_2–$(CH_2)_2$–N), 3.8—4.0 (2H, m, C–CH_2–N), 6.4—6.6 (1H, m, aromatic H), 7.0—7.8 (7H, m, aromatic H and NH), 8.0—8.3 (1H, m, aromatic H)	21.8 (t), 24.2 (q), 29.8 (t), 38.2 (t), 117.2 (s), 122.2 (d), 122.7 (d), 123.0 (s), 125.0 (d), 128.8 (d), 129.1 (d), 129.4 (d), 129.9 (s), 131.5 (d), 132.2 (s), 134.0 (s), 135.6 (s), 165.5 (s), 168.9 (s)
3d	1710, 1685	360	1.5—2.3 (6H, m, C–$(CH_2)_3$–CH_2–N), 2.40 (3H, s, $COCH_3$), 3.2—3.7, 4.2—4.6 (2H, m, C–CH_2–N), 5.97 (1H, d, J=8.7 Hz, aromatic H), 6.52 (1H, d, J=7.5 Hz, aromatic H), 6.62 (1H, s, N–CH–O), 6.8—7.5 (4H, m, aromatic H), 7.61 (1H, d, J=7.5 Hz, aromatic H), 8.1—8.4 (1H, m, aromatic H)	23.8 (q), 26.4 (t), 30.0 (t), 32.5 (t), 39.6 (t), 63.9 (s), 90.5 (d), 103.3 (s), 117.2 (d), 122.5 (d), 124.3 (d), 124.4 (d), 124.9 (d), 129.6 (d), 130.1 (d), 131.1 (s), 131.3 (d), 133.5 (s), 141.1 (s), 142.2 (s), 166.5 (s), 169.1 (s)
5e	1675, 1605	374	1.4—2.6 (7H, m), 2.9—3.4 (1H, m), 3.8—4.3 (1H, m), 4.3—4.7 (1H, m), 6.21 (1H, d, J=7.8 Hz, aromatic H), 7.0—7.9 (7H, m, aromatic H), 9.0—9.3 (1H, m, CHO)	21.5 (t), 24.5 (q), 27.4 (t), 28.8 (t), 32.2 (t), 39.8 (t), 118.9, 122.9, 124.2, 128.5, 129.4, 129.7, 129.9, 130.8, 131.8, 134.3, 135.3, 137.1 (s), 142.0 (s), 162.4 (d), 167.2 (s), 172.1 (s)
6e	3250, 1670	346	1.6—2.1 (6H, m, C–$(CH_2)_3$–CH_2–N), 2.14 (3H, s, $COCH_3$), 2.3—2.7, 3.0—3.5, 3.6—4.0, 4.1—4.5 (4H, m), 6.09 (1H, d, J=7.5 Hz, aromatic H), 6.9—8.3 (8H, m, aromatic H and NH)	22.0 (t), 24.4 (q), 26.8 (t), 29.0 (t), 32.9 (t), 39.6 (t), 119.2, 122.9, 123.3, 124.5, 125.1, 128.5, 129.0, 129.2, 129.8, 131.8, 133.7, 135.4 (s), 137.0 (s), 167.2 (s), 168.9 (s)
7[a]	3550, 3500, 2260, 1700 (sh), 1680	386 (M^+-18)	2.3—2.7 (1H, m), 2.9—3.3 (1H, m), 3.25 (1H, s, OH), 3.4—3.7 (1H, m), 3.8—4.3 (1H, m), 6.3—6.5 (1H, m, N–CH–OH), 6.6—7.4 (8H, m, aromatic H and OH), 7.65 (1H, d, J=7.8 Hz, aromatic H)	33.4 (t), 61.3 (s), 86.7 (d), 97.1 (s), 106.3 (s), 116.7 (d), 120.8 (d), 122.1 (d), 123.3 (d), 125.8 (d), 128.3 (d), 129.4 (d), 131.9 (d), 132.7 (s), 133.9 (s), 139.2 (s), 143.9 (s), 167.6 (s)
10a	3340, 1770, 1700	332	2.64 (3H, s, $COCH_3$), 3.62 (2H, t, J=6 Hz, C–CH_2–CH_2–N), 4.14 (2H, t, J=6 Hz, C–CH_2–N), 7.1—7.5 (3H, m, aromatic H), 7.5—8.0 (5H, m, aromatic H), 9.4—9.7 (1H, m, NH)	27.0, 30.7, 36.8, 111.5, 120.3, 120.7, 121.1, 121.7, 122.9, 126.2, 131.6, 134.2, 134.9, 144.1, 167.4, 193.2
10b	3260, 1760, 1700	346	2.0—2.3 (2H, m, C–CH_2–CH_2–N), 2.65 (3H, s, $COCH_3$), 3.13 (2H, t, J=6 Hz, C–CH_2–$(CH_2)_2$–N), 3.70 (2H, t, J=6 Hz, C–CH_2–N), 7.1—8.0 (9H, m, aromatic H and NH)	25.1 (t), 28.0 (t), 31.4 (q), 37.0 (t), 111.6 (d), 120.6 (d), 121.9 (d), 122.3 (d), 123.5 (d), 125.0 (s), 126.9 (s), 132.0 (s), 134.3 (d), 134.9 (s), 147.0 (s), 169.3 (s), 194.5 (s)

OFR, off-resonance. *a*) Dimethyl sulfoxide-d_6.

decomposition of the oxetanes **3b** and **3d** were reversible.

Structural assignments of the photoproducts were made on the basis of spectral and analytical data (Table III). The mass spectrum (MS) of **2** showed the molecular ion peak at *m/z* 318 corresponding to the molecular weight of **1a**. The infrared (IR) spectrum of **2** indicated the presence of a carbonyl group (1660 cm^{-1}) conjugated with an aromatic ring, imide carbonyls (1715 and 1765 cm^{-1}) as well as those of **1a**, and N–H (3310 cm^{-1}). In the proton nuclear magnetic resonance (^{1}H-NMR) spectrum of **2**, a singlet appeared at 7.93 ppm in the aromatic proton region, suggestive of the rearrangement of an acetyl group on the 6-position of the indole ring as described later. The mass spectrum of the oxetane **3b** showed the molecular ion peak at *m/z* 332 corresponding to the molecular weight of **1b**. In the IR spectrum of **3b**, the bands at 1670 and 1705 cm^{-1} indicated amide and lactam absorptions (assignments may be interchanged). In the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum of **3b**, a singlet and a doublet newly appeared at 62.9 and 92.4 ppm, respectively, instead of peaks due to olefinic carbons (2- and 3-positions) in the indole ring, suggesting oxetane formation between the imide carbonyl and the olefinic carbons in the pyrrole ring. In the oxetane formation, two regioisomers **3b**-i and **3b**-ii are possible as shown in Chart 3. In the ^{1}H-NMR spectrum of **3b**, a singlet peak appeared at 6.40 ppm, indicating the presence of a methine proton, whose chemical shift value is close to that (6.20 ppm) of the methine proton adjacent to the nitrogen and oxygen atoms in the previously reported oxeto[2,3-*b*]indole system.[11] Further, the presence of this methine was also supported by the appearance of the doublet at lower field (92.4 ppm) in the ^{13}C-NMR spectrum. Therefore, the regioisomer of **3b** was determined to be **3b**-i. The stereochemistry of **3b**-i was confirmed on the basis of the ^{1}H-NMR spectrum, in which a multiplet and a triplet due to aromatic protons of the isoindolone moiety showed upfield shifts at 6.6—7.0 ppm, indicating that the two benzene rings are close to each other. This shift is explained by considering the anisotropic effects of the benzene rings on each other. Likewise, the structure of **3d** was confirmed to be **3d**-i on the basis of the analogy with the spectral data of **3b**. In the ^{1}H-NMR spectrum of **3d**, a doublet with the coupling constant of 8.7 Hz showed an abnormal upfield shift at 5.97 ppm compared with that of aromatic protons, and the signal was assigned to be an aromatic proton of the isoindolone moiety as illustrated in Chart 3. Another possible stereoisomer (**3d**-ii) of **3d** was excluded based on this anisotropic effect, as well as its unfavorable conformation due to the short methylene chain length ($n=4$) between the indoline and the isoindolone moieties (Chart 3). The structure of **4** was also determined on the basis of the spectral data, although the stereochemistry is not clear yet. The mass spectrum showed the molecular ion peak at *m/z* 364.



3b-i **3b**-ii **3d**-i **3d**-ii

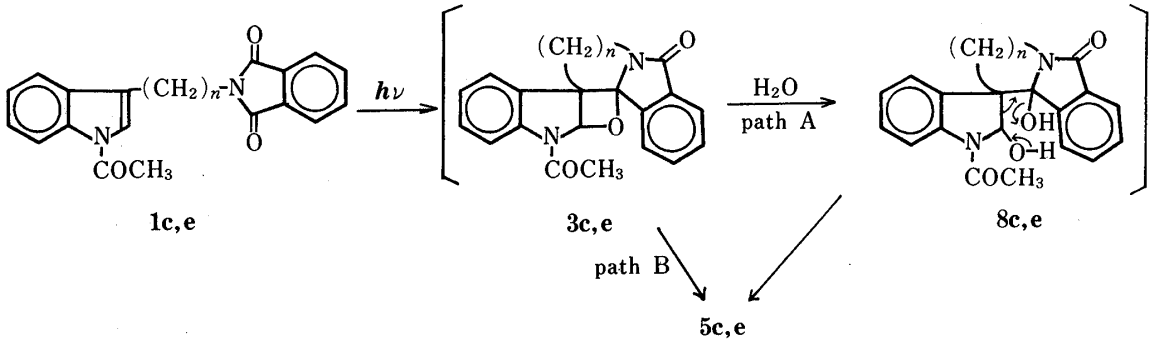
Chart 3

In the ^{1}H-NMR spectrum of **4**, a doublet-like signal at 5.7—5.9 ppm coalesced into a singlet at 5.8 ppm on adding deuterium oxide, indicating the presence of a methine substituted with a hydroxy group. In addition, the presence of the methine was supported by means of the decoupling technique in ^{1}H-NMR spectroscopy. The ^{13}C-NMR spectrum of **4** showed peaks due to a spiro-carbon, a methine carbon adjacent to a nitrogen atom and a hydroxy group, and a quaternary carbon with a methoxy group, at 60.6 (s), 90.1 (d), and 103.0 (s) ppm, respectively.

By contrast, upon irradiation under similar conditions **1c** ($n=3$) and **1e** ($n=5$) gave tricyclic isoindolones (**5c** and **5e**, respectively), accompanied with small amounts of **6c** and **6e**, which are deformylation products from **5c**, **e**. The tricyclic isoindolones (**5c**, **e**) may arise either from initially formed imide-oxetanes (**3c**, **e**) by hydrolysis of the oxetane ring followed by subsequent ring opening of the indoline ring (**8c**, **e**) (path A), or directly from the imide-oxetane (**3c**, **e**) (path B) as illustrated in Chart 4. In fact, irradiation of the *N*-trifluoroacetyl derivative (**1f**), the analogue of **1b**, also afforded in 52% yield a similar spiro-diol (**7**), which arose from the initially formed imide-oxetane (Chart 2). As previously described, when the imide-oxetane (**3b** or **3d**) was treated with *p*-toluenesulfonic acid the original imide was regenerated. In such a case, appearance of a polar species observed on thin layer chromatography suggested the possibility of formation of a diol, which would lead to the original imide. This assumption was supported by the isolation of the diol compound (such as **7**). In addition, as reported in a previous paper,[3] an imide-oxetane gives, on treatment with an acid catalyst, a ring-opened product, which probably arises from a diol intermediate. From these results, path A through the diols (**8c**, **e**) seems likely for the formation of **5c**, **e**, although path B involving a concerted ring opening of the oxetane could not be excluded. Thus, the ease of fission of the oxetane ring seems to be influenced by the length of the methylene chain between the indole and phthalimide moieties and the properties of the *N*-substituent on the indoline ring, although the reasons are not clear yet.

The ^{1}H- and ^{13}C-NMR spectra of **5c**, **e** showed a peak at 9.0—9.5 ppm and a doublet at 162.4 ppm, respectively, indicating the presence of a formyl group. In addition, the ^{13}C-NMR spectra showed two singlets at 165.6—167.2 and 172.1—172.2 ppm due to the carbonyls of an acetyl and a lactam. The structure of **7** was determined on the basis of the spectral data although the stereochemistry is not clear yet. The ^{1}H-NMR spectrum showed peaks due to two hydroxy groups, which disappeared on addition of deuterium oxide. A doublet-like signal at 6.3—6.5 ppm due to a methine proton coalesced into a singlet at 6.4 ppm on addition of deuterium oxide. The ^{13}C-NMR spectrum of **7** was analogous with that of **4**: a spiro-carbon (61.3 ppm, s), the methine with a hydroxy group (86.7 ppm, d), and a quaternary carbon with a hydroxy group (97.1 ppm, s).

Although irradiation of enamine analogues such as *N*-methylindole (**1g**) was similarly examined, it resulted in quantitative recovery of the starting material even after 28 h. As a



1c,e **3c,e** **8c,e** **5c,e**

Chart 4

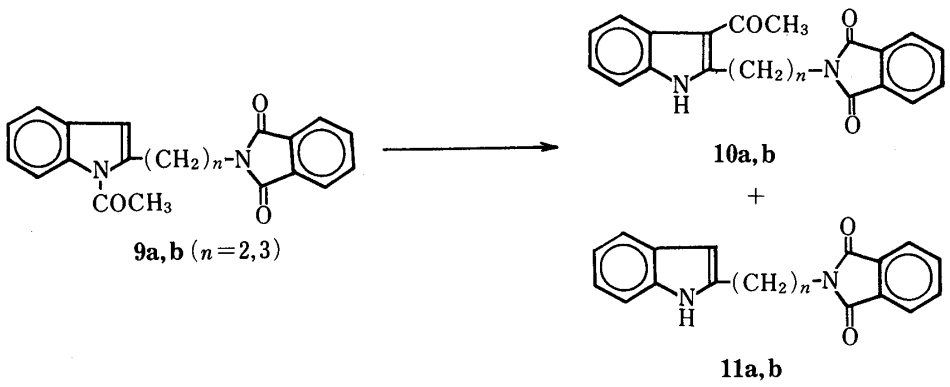


Chart 5

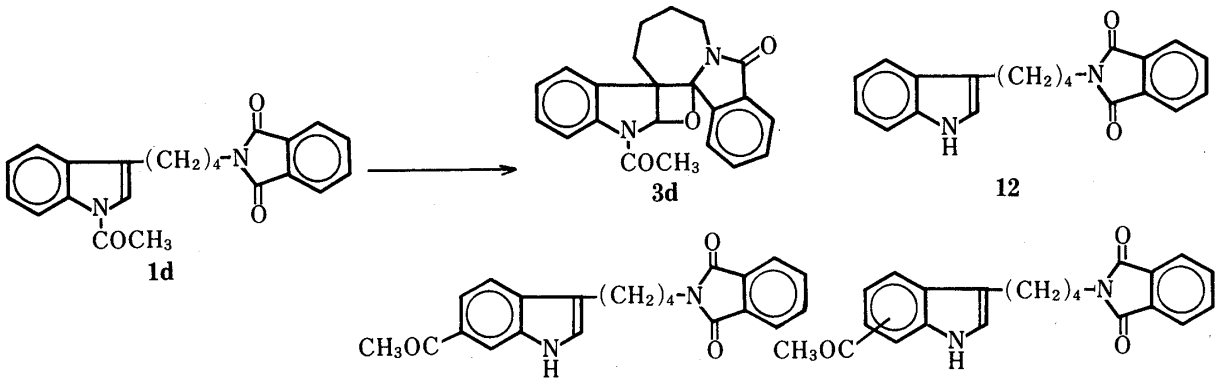


Chart 6

structural variation of indole–phthalimide systems, 2-substituted indoles (**9a, b**) were irradiated under similar conditions. The substrates **9a, b** underwent *N*-acetyl fission to give rearranged 3-acetylindole derivatives (**10a, b**) and *N*-deacetylated products (**11a, b**), whose structures were assigned on the basis of spectral data (Chart 5).

Next, in order to gain further information on the formation of imide-oxetanes, **1d** was selected as a substrate, and photolysis was carried out in various solvents. The results are listed in Table IV. Upon irradiation in benzene, the oxetane **3d** was obtained, accompanied with a deacetylated indole (**12**), 6-acetylindole (**13**) and another acetylindole (**14**) in moderate yields. In a protic solvent, methanol, no oxetane was obtained, whereas two acetylindoles (**13** and **14**) and the deacetylated indole **12** were isolated. In the case of a mixed solution of ethanol and hexane (1 : 3, v/v), a similar product distribution was observed to that in the case of benzene solution, except for the oxetane formation. The structure of the 6-acetylindole (**13**) was determined on the basis of spectral data. The ^{1}H-NMR spectrum showed a singlet at 7.93 ppm, indicating the presence of a proton on the 7-position of the indole ring. The position of the acetyl substituent in the acetylindole **14** could not be completely confirmed by spectroscopy, but was inferred to be the 4-position from the reported evidence, that the ease of rearrangement of 1-substituted indoles decreases in the order of positional reactivity of the indole molecule as $3>6>4>2$.[12]

The excited state involved in the oxetane formation process in acetone or benzene was suggested to be a triplet state from the solvent effect in this study. Further, in order to obtain evidence for the triplet state, photolyses were carried out in the absence and presence of benzophenone as a sensitizer in acetonitrile. As expected, in the presence of benzophenone the yield of the oxetane dramatically increased to 58% even after 2 h, whereas deacetylation

TABLE IV. Photolysis of **1d** in Various Solvents

Solvent	Reaction time (h)	Yield (%) of product				Recovery of **1d**
		3d	**12**	**13**	**14**	
Acetone	6	69	—	—	—	19
Benzene	6.2	23	18	12	15	14
MeOH	18	—	21	16	5	Trace
EtOH–hexane (1 : 3, v/v)	4.5	6	15	8	10	35
CH_3CN	6	5	27	—	7	13
CH_3CN[a)]	2	58	2	—	—	7

a) In the presence of benzophenone (0.5 mol).

decreased, suggesting that the oxetane formation is occurring from the triplet state. This observation is consistent with the evidence that the oxetane arises from the lowest triplet state in the photoreaction of *N*-methylphthalimide with 2,3-dimethyl-2-butene.[10a)]

From many studies reported by Mazzocchi *et al.*,[5,7,10)] Maruyama *et al.*,[4,13)] and our group,[6)] it has become increasingly clear that the characteristic feature of the photoadditions of phthalimides with alkenes is associated with the electron transfer process. Mazzocchi *et al.* discussed the competition of the addition (k_{CN}) and electron transfer (k_{ET}) in terms of the ionization potentials and using a form of the Weller equation,[7a,14)] and the Paterno–Büchi reaction (k_{PB}) from the triplet state of *N*-methylphthalimide and 2,3-dimethyl-2-butene, which leads to the corresponding oxetane in a poor yield.[10)] The occurrence of the Paterno–Büchi reaction (k_{PB}) in the phthalimide photoaddition has now been verified by effectively trapping the imide-oxetane using the *N*-acylindole group, as a good Paterno–Büchi acceptor. However, it is difficult to elucidate the reason why the phthalimide–*N*-acetylindole system undergoes the Paterno–Büchi reaction as compared with the phthalimide–indene system (involving an electron transfer process) and other imide systems.[6a)] The process of the oxetane formation competes with deacetylation processes, including the rearrangement, probably depending on solvent polarity. The quantum yield of the formation of the oxetane **3d** (k_{PB}) in acetone is 0.045, of the same order as for the intramolecular formation of benzazepinedione (k_{CN}) reported by Mazzocchi *et al.*[5a)] Therefore, the formation of the oxetane in this imide system is a relatively efficient photoreaction, when acetone is used as a triplet sensitizer.

In conclusion, the photolysis of *N*-(ω-indol-3-ylalkyl)phthalimides is the first example of oxetane formation of an aromatic imide carbonyl in the Paterno–Büchi reaction. The photocycloaddition of the phthalimide system having an *N*-acetylindole moiety would provide a simple synthetic route to imide-oxetanes which may lead to interesting complex heterocyclic ring systems. In addition, *N*-acetylindoles can serve as the Paterno–Büchi acceptor even in the case of the phthalimide system having a flexible long chain as a link to a nonconjugated bichromophore such as in **1e**. The possibility of such a remote Paterno–Büchi reaction ($n > 5$) is currently under study.

Experimental

All melting points were determined on a Yamato melting point apparatus (model MP-21) and are uncorrected. Infrared spectra were recorded on a Shimadzu IR-400 spectrometer and a JASCO A-102 spectrometer. Nuclear magnetic resonance spectra were taken on a Hitachi R-40 spectrometer and JEOL-FX 60 and 90Q spectrometers. Chemical shifts are reported in parts per million (δ) relative to tetramethylsilane (TMS, 0.0 ppm) as an internal standard. The abbreviations used are as follows: s, singlet; d, doublet; t, triplet; m, multiplet. Mass spectra were determined with a JEOL JMS-QH-100 gas chromatograph-mass spectrometer with a direct inlet system.

Irradiations of substrates 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).

***N*-[(*N'*-Acetylindol-3-yl)methyl]phthalimide (1a)**——CH_3I (14.2 g, 0.1 mol) was added to a solution of gramine (3.48 g, 20 mmol) in tetrahydrofuran (THF) at 0 °C over 2 h. After stirring of the reaction mixture at room temperature for 1 h, the solvent was removed *in vacuo*. The residue was heated with potassium phthalimide (3.70 g, 20 mmol) in dimethylformamide (DMF) at 150 °C for 5 h. After removal of the solvent the residue was chromatographed on a silica gel column to give *N*-(indol-3-ylmethyl)phthalimide (3.10 g, 56%), which was recrystallized from acetone to give colorless prisms, mp 179.5—180.5 °C (lit.,[15] mp 182—183 °C). Next a solution of the resulting phthalimide (1.79 g, 6.5 mmol) and acetic anhydride (3 ml, 32 mmol) in DMF (6 ml) was refluxed in the presence of K_2CO_3 (449 mg, 3.25 mmol) for 30 min, and the reaction mixture was poured into ice-water, extracted with $CHCl_3$ and dried over Na_2SO_4. After removal of the solvent, the residue was recrystallized from acetone to give **1a** (1.87 g) in 91% yield.

***N*-[2-(*N'*-Acetylindol-3-yl)ethyl]phthalimide (1b)**——*N*-[2-(Indol-3-yl)ethyl]phthalimide was prepared by fusion of tryptamine and phthalic anhydride in a usual manner. Yellow columns, mp 165—166.5 °C from acetone (lit.,[16] mp 164 °C). The resulting phthalimide was acetylated with acetic anhydride to give **1b** by the method described above.

***N*-[3-(*N'*-Acetylindol-3-yl)propyl]phthalimide (1c)**——$(C_6H_5)_3P$ (7.86 g, 30 mmol) was added portionwise to an ice-cooled solution of 3-(3-hydroxypropyl)indole[17] (4.73 g, 27 mmol) and CBr_4 (9.96 g, 30 mmol), and the mixture was stirred at room temperature for 2 h. The resulting precipitate ($(C_6H_5)_3PO$) was filtered off, and then the mother liquor was concentrated and chromatographed. Yield 5.84 g (91%). A solution of the resulting 3-(3-bromopropyl)indole (2.86 g, 12 mmol) and potassium phthalimide (2.22 g, 12 mmol) in DMF was refluxed for 2 h, and worked up in a similar manner to that described above (2.74 g, 75%). Recrystallization from AcOEt gave *N*-(3-indol-3-ylpropyl)phthalimide as yellow prisms, mp 127—128.5 °C (lit.,[18] mp 131—132 °C). The title compound **1c** was obtained by acetylation of *N*-(3-indol-3-ylpropyl)phthalimide with acetic anhydride.

***N*-[4-(*N'*-Acetylindol-3-yl)butyl]phthalimide (1d)**——*N*-[4-(Indol-3-yl)butyl]phthalimide was prepared from potassium phthalimide and 3-(4-bromobutyl)indole, which was itself prepared from 3-(4-hydroxybutyl)indole[19] and CBr_4 in a similar manner to that described above. Recrystallization from benzene–hexane gave yellow prisms of mp 121.5—122.5 °C. MS *m/z*: 360 (M^+). IR (Nujol) cm^{-1}: 3350, 1760, 1700. ^{1}H-NMR ($CDCl_3$) δ: 1.6—2.0 (4H, m, C–(CH_2)$_2$–CH_2–N), 2.6—3.0 (2H, m, CH_2–(CH_2)$_3$–N), 3.6—3.9 (2H, m, CH_2–N), 6.8—7.4 (4H, m, aromatic H), 7.4—7.8 (5H, m, aromatic H), 7.8—8.0 (1H, m, NH). *Anal.* Calcd for $C_{20}H_{18}N_2O_2$: C, 75.45; H, 5.70; N, 8.80. Found: C, 75.64; H, 5.76; N, 8.84. The resulting phthalimide was treated with acetic anhydride to give **1d**.

***N*-[5-(*N'*-Acetylindol-3-yl)pentyl]phthalimide (1e)**——A solution of 3-(4-cyanobutyl)indole[20] (4.0 g, 20 mmol) in ether (60 ml) was added dropwise to a stirred suspension of $LiAlH_4$ (3.0 g, 80 mmol) in dry ether (80 ml) at 0 °C. The mixture was refluxed for 2 h, 10% NaOH aqueous solution (10 ml) was added, and the whole was stirred for 10 min. The resulting inorganic salt was filtered off, and the filtrate was dried over Na_2SO_4 and evaporated to dryness. 3-(5-Aminopentyl)indole was obtained as colorless crystals of mp 60—62 °C. Yield 4.0 g (99%). MS *m/z*: 202 (M^+). IR (Nujol) cm^{-1}: 3350. The resulting aminopentylindole (3.6 g, 18 mmol) was dissolved in $CHCl_3$. To this solution, phthalic anhydride (2.7 g, 18 mmol) was added, and the solvent was again removed. The residue was fused at 160 °C to give *N*-[5-(indol-3-yl)pentyl]phthalimide (5.6 g, 93%), which was recrystallized from AcOEt to give yellow prisms, mp 133.5—135 °C. MS *m/z*: 374 (M^+). IR (Nujol) cm^{-1}: 3420, 1770, 1695. ^{1}H-NMR ($CDCl_3$) δ: 1.2—2.0 (6H, m, CH_2–(CH_2)$_3$–CH_2–N), 2.6—2.9 (2H, m, CH_2–(CH_2)$_4$–N), 3.5—3.8 (2H, m, CH_2–N), 6.8—7.4 (4H, m, aromatic H), 7.4—8.0 (6H, m, aromatic H and NH). *Anal.* Calcd for $C_{21}H_{20}N_2O_2$: C, 75.88; H, 6.07; N, 8.43. Found: C, 76.16; H, 6.04; N, 8.50. The resulting phthalimide was acetylated with acetic anhydride to give **1e** according to the method described for **1a**.

***N*-[2-(*N'*-Trifluoroacetylindol-3-yl)ethyl]phthalimide (1f)**——*N*-[2-(Indol-3-yl)ethyl]phthalimide (7.25 g, 25 mmol) in DMF was treated with trifluoroacetic anhydride (14.9 g, 70 mmol) in the presence of K_2CO_3 (1.73 g, 12.5 mmol) at room temperature for 1 h. The reaction mixture was poured into ice-water, and extracted with AcOEt. The extract was washed with brine, dried over Na_2SO_4, and evaporated. The resulting product was recrystallized from AcOEt to give **1f** (5.78 g, 60%).

***N*-[2-(*N'*-Methylindol-3-yl)ethyl]phthalimide (1g)**——A solution of *N*-[2-(indol-3-yl)ethyl]phthalimide (2.90 g, 10 mmol) in THF (30 ml) was added dropwise to a stirred suspension of KH (480 mg, 12 mmol) in THF at 0 °C. The reaction mixture was stirred for 30 min, then CH_3I (1 ml, 16 mmol) was added under cooling, and the mixture was stirred at room temperature for 1 h. After removal of the solvent, the residue was treated with $CHCl_3$ and water. The organic layer was dried over Na_2SO_4, and evaporated. The resulting product was recrystallized from AcOEt to give **1g** (2.75 g, 90%).

***N*-[2-(*N'*-Acetylindol-2-yl)ethyl]phthalimide (9a)**——A mixture of 2-(2-aminoethyl)indole[21] (1.80 g, 11.3 mmol) and phthalic anhydride (1.67 g, 11.3 mmol) was fused at 160—170 °C for 20 min. Recrystallization from acetone gave *N*-[2-(indol-2-yl)ethyl]phthalimide as pale yellow prisms (2.40 g, 73%), mp 227—228 °C. MS *m/z*: 290 (M^+). IR

(Nujol) cm^{-1}: 3350, 1760, 1705. ^{1}H-NMR ($CDCl_3$) δ: 3.15 (2H, t, J=7.2 Hz, $C\underline{H}_2CH_2$–N), 4.02 (2H, t, J=7.2 Hz, CH_2–N), 6.28 (1H, m, N–C=CH), 6.9—7.9 (8H, m, aromatic H), 8.1—8.4 (1H, m, NH). The resulting phthalimide was acetylated to give **9a** according to the method described for **1a**.

***N*-[3-(*N'*-Acetylindol-2-yl)propyl]phthalimide (9b)**——*N*-[3-(Indol-2-yl)propyl]phthalimide was prepared by a modification of Yonemitsu *et al.*'s method.[22] 5-(4-Phthalimidobutyryl) Meldrum's acid was prepared from Meldrum's acid and phthalimidobutyric acid. A solution of the acyl Meldrum's acid and phenylhydroxylamine oxalate in acetonitrile was refluxed for 30 min. After work-up in a usual manner, the corresponding acylacetylphenylhydroxylamine was obtained and purified by silica gel column chromatography. Next, the resulting acylacetylphenylhydroxylamine in xylene was refluxed for 6 h. After removal of the solvent, the residue was subjected to silica gel column chromatography, giving a 2-substituted indole derivative. Recrystallization from AcOEt–hexane gave *N*-[3-(indol-2-yl)propyl]phthalimide as yellow plates, mp 155—156 °C. MS *m/z*: 304 (M^+). IR (Nujol) cm^{-1}: 3350, 1760, 1705. ^{1}H-NMR ($CDCl_3$) δ: 1.9—2.3 (2H, m, $CH_2C\underline{H}_2CH_2$–N), 2.75 (2H, t, J=7.2 Hz, $C\underline{H}_2$–$(CH_2)_2$–N), 3.75 (2H, t, J=6 Hz, CH_2–N), 6.20 (1H, m, N–C=C$\underline{H}$–), 6.9—7.9 (8H, m, aromatic H), 8.4—8.7 (1H, m, NH). *Anal.* Calcd for $C_{19}H_{16}N_2O_2$: C, 74.98; H, 5.30; N, 9.21. Found: C, 74.89; H, 5.15; N, 9.13. The resulting phthalimide was acetylated with acetic anhydride to give **9b**.

Irradiation of 1 and 9: General Procedure——A solution of **1** or **9** (10 mM) in acetone was irradiated with a 500 W high-pressure mercury lamp through Pyrex glass at room temperature. After removal of the solvent *in vacuo*, the residue was subjected to silica gel column chromatography for **1a**, **d**, **f**, **g**, **9a** and **9b**, and to silica gel thin layer chromatography for **1c**, **e**. The solvent systems used were as follows: **1a**, AcOEt : hexane = 1 : 2 v/v; **1c**, **9b**, AcOEt : hexane = 1 : 1 v/v; **1d**, AcOEt : hexane = 3 : 2 v/v; **1e**, AcOEt : hexane = 4 : 3 v/v; **1f**, CH_2Cl_2 : Et_2O = 3 : 1 v/v; **1g**, AcOEt : hexane = 2 : 1 v/v; **9a**, acetone : hexane = 1 : 2 v/v. In the case of **1b**, after removal of the solvent, acetone was added to the residue, and the resulting precipitate was collected on a filter funnel. Fractional recrystallization from CH_3CN gave only **3b**.

Reaction of 3b in the Presence of Hydrochloric Acid——A solution of **3b** (62 mg, 0.19 mmol) in MeOH (4 ml) was stirred in the presence of one drop of 33% HCl–MeOH at room temperature for 1 h. The resulting precipitate was collected by filtration (68 mg, quantitatively) and recrystallized to give **4**.

Irradiation of 1b Followed by Ring-Opening Reaction of the Oxetane——A solution of **1b** (664 mg, 2 mmol) in acetone (10 mM) was irradiated in a similar manner to that described above. After removal of the solvent, the residue was dissolved in MeOH (50 ml). The solution was treated with three drops of 33% HCl–MeOH, and stirred at room temperature for 30 min. The solvent was removed, and the residue was subjected to column chromatography on silica gel; elution with AcOEt–hexane (1 : 1, v/v) gave **4** (227 mg, 38%) and unchanged **1b** (210 mg, 32%).

Reaction of the Oxetanes 3b, d with *p*-Toluenesulfonic Acid——A solution of the oxetane **3b** (66 mg, 0.2 mol) and *p*-toluenesulfonic acid monohydrate (3 mg) in acetone (4 ml) was stirred at room temperature overnight. The product (**1b**) was obtained in 83% yield (55 mg). Similarly, **3d** was converted to **1d** in 86% yield.

Conversion of 3d to 1d by Photolysis——A solution of **3d** (360 mg, 1 mmol) in acetone (100 ml) was irradiated with a 500 W high-pressure mercury lamp through Pyrex glass at room temperature for 2 h under a nitrogen atmosphere. After removal of the solvent, the residue was subjected to column chromatography on silica gel, and elution with AcOEt–hexane (1 : 1, v/v) gave the phthalimide **1d** (100 mg, 28%) and the unchanged oxetane **3d** (202 mg, 56%).

Irradiation of 1d in Various Solvents——Irradiation of **1d** was carried out in MeOH (6.7 mM), CH_3CN (10 mM), benzene (10 mM) or EtOH–hexane (1 : 3, v/v, 10 mM), under similar conditions to those described above. After removal of the solvent, the residue was subjected to column chromatography on silica gel, and elution with AcOEt–hexane (1 : 2, v/v) gave the products **3d**, **12**, **13** and **14**. Compounds **3d** and **12** were characterized as described above.

Compound **13**: Yellow prisms, mp 150—151 °C (from benzene–Et_2O). MS *m/z*: 360 (M^+). IR (Nujol) cm^{-1}: 3370, 1760, 1700, 1655. ^{1}H-NMR ($CDCl_3$) δ: 1.5—2.0 (4H, m, CH_2–$(C\underline{H}_2)_2$–CH_2–N), 2.60 (3H, s, $COCH_3$), 2.5—3.0 (2H, m, $C\underline{H}_2$–$(CH_2)_3$–N), 3.5—3.9 (2H, m, CH_2–N), 7.0—7.9 (7H, m, aromatic H), 7.93 (1H, s, aromatic H), 8.3—8.6 (1H, m, NH). *Anal.* Calcd for $C_{22}H_{20}N_2O_3$: C, 73.31; H, 5.59; N, 7.77. Found: C, 73.21; H, 5.60; N, 7.87.

Compound **14**: Pale yellow prisms, mp 166—167 °C (AcOEt–hexane). MS *m/z*: 360 (M^+). IR (Nujol) cm^{-1}: 3360, 1770, 1710, 1635. ^{1}H-NMR ($CDCl_3$) δ: 1.6—2.0 (4H, m, CH_2–$(C\underline{H}_2)_2$–CH_2–N), 2.57 (3H, s, $COCH_3$), 3.0—3.3 (2H, m, $C\underline{H}_2$–$(CH_2)_3$–N), 3.6—3.9 (2H, m, CH_2–N), 6.9—7.9 (8H, m, aromatic H), 8.8—9.1 (1H, m, NH). *Anal.* Calcd for $C_{22}H_{20}N_2O_3$: C, 73.31; H, 5.59; N, 7.77. Found: C, 73.35; H, 5.59; N, 7.88.

Irradiation of 1d in the Presence of Benzophenone——A solution of **1d** (720 mg, 2 mmol) in CH_3CN (200 ml) was irradiated in the presence of benzophenone (182 mg, 1 mmol) for 2 h under similar conditions to those described above. After removal of the solvent, the residue was subjected to column chromatography on silica gel, and elution with AcOEt–hexane (1 : 2, v/v) gave the oxetane **3d** (420 mg, 58%), deacetylated indole **12** (15 mg, 2%), unchanged **1d** (51 mg, 7%), and benzophenone (117 mg, 64% recovered yield).

Quantum Yield for Oxetane Formation (3d)——Acetone solutions of **1d** (10 mM) in four Pyrex test tubes were degassed with four freeze-pump-thaw cycles and sealed. Similarly, four 0.012 M potassium ferrioxalate actinometers were prepared. Quantum yields were measured relative to the actinometers with parallel irradiation of the samples on a merry-go-round apparatus under the same conditions for 2, 4, 6, and 8 min. A filter solution containing potassium

chromate aqueous solution (0.27 g/l) and sodium carbonate aqueous solution (1 g/l) was used to isolate the 313 nm region. Yields for **3d** formation were determined by ultraviolet absorption spectroscopy, taking the molecular coefficient of **3d** to be 16300 at 245 nm.

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