Intramolecular Photoreactions of Phthalimide-Alkene Systems. Macrocyclic Synthesis through the Remote Paterno–Büchi Reaction of Phthalimide with Indole Derivatives[1)]

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Received April 30, 1993; accepted August 21, 1993

Upon irradiation, phthalimide-indole in bichromophoric systems underwent intramolecularly remote Paterno–Büchi reaction to give oxeto[2,3-*b*]indole derivatives containing macrocycles, in competition with Norrish type II reaction.

Keywords remote photocyclization; indolylalkylphthalimide; oxeto-indole; Paterno–Büchi reaction; intramolecular photocyclization; nonconjugated bichromophore

As part of a continuing study of the photochemistry of imide carbonyl systems, we have investigated macrocyclic syntheses using the remote photocyclization of nonconjugated bichromophoric systems, in which phthalimides efficiently serve as a good electron acceptor in an electron donor–acceptor pair system.[2–5)] These remote photocyclization processes, however, are limited to the case of Norrish type II reaction, and little is known about remote photocyclization *via* a process of [2+2]cycloaddition in this phthalimide system.

Recently, we have reported the first example of efficient oxetane formation through [2+2]photocycloaddition (Paterno–Büchi reaction) in phthalimide-indole systems, *i.e.*, intermolecular reaction in an *N*-methylphthalimide-*N*-acetylindole system[6)] and intramolecular reaction in an *N*-[ω-(*N'*-acetylindol-3-yl)alkyl]phthalimide system.[7)] In these systems it was found that oxetane formation occurred regio- and stereoselectively, suggesting possible involvement of a stacking interaction between the phthalimide (electron acceptor) and indole derivative (electron donor). As a logical extension of this reaction, we examined macrocycle synthesis through the remote Paterno–Büchi reaction in an electron donor–acceptor pair system, in which nonconjugated bichromophores are separated by a carbon chain.

Since *N*-acetyl-1,2,3,4-tetrahydrocarbazole was previously shown to be a good oxetane-forming partner,[6)] a phthalimide system having a tetrahydrocarbazole in the *N*-alkyl side chain was selected as a bichromophoric substrate. A series of phthalimide-*N*-acylindole bichromophoric systems (**1a**—**h**, **3**, **6**, **10**, **12**) were prepared by the methods described in the experimental section. Melting points and analytical data of these imides (**1a**—**h**, **3**, **6**, **10**, **12**) are listed in Table I.

Photoreactions of **1a**—**h**, **3**, **6**, **10**, **12** were carried out in acetone (5—10 mM) with a 500 W or 1 kW high-pressure mercury lamp through a Pyrex filter under a nitrogen atmosphere. The reaction was monitored by following the disappearance of the starting material on thin layer chromatography. The results are collected in Table II.

As shown in Chart 1, irradiation of **1a** and **1b** ($n=5$, 6) gave ring-expanded ketolactams **2a** and **2b** in 6 and 11% yields, respectively, but none of the expected remote Paterno–Büchi products were obtained. The ring opening to ketolactams can be explained on the basis of the general pattern of imide chemistry,[2,8)] that is, the Norrish type II reaction occurs at the allylic position (1-position) of tetrahydrocarbazole, to give isoindolol, followed by ring opening of pyrrolidone leading to ketolactams (**2**) with ring expansion by a retro-transannular reaction. That Paterno–Büchi reaction did not take place seems to reflect an unfavorable conformation due to the short methylene chain length between the phthalimide and the carbazole moieties.[9)] The structures of **2a**, **b** were assigned on the basis of the elemental analysis and spectral data. The mass spectra (MS) of **2a** and **2b** showed the molecular ion peaks at m/z 414 and 428 corresponding to the molecular weights of **1a** and **1b**, respectively. The infrared (IR) spectra of **2a**, **b** suggested the presence of two amides (CONH and CO-N) and/or one ketone at 3350—3400 (NH), 1680—1685, and 1635—1665 cm^{-1}. In addition, the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectra of **2a**, **b** supported the presence of the two amide groups [170.7—171.2 (s) and 173.6—174.4 ppm (s)] and the ketone [197.2—197.9 ppm (s)]. With regard to the structures of **2a**, **b**, two regioisomers **2a**, **b**-i and **2a**, **b**-ii are possible, as shown in Chart 1. Although in the ^{1}H-NMR spectra of **2a**, **b**, the signal at 5.3 ppm (1H, br t) showed the presence of the allylic methine proton, the regiochemical structure (**2**-i or **2**-ii) could not be completely assigned. To clarify the structure, the ^{1}H-detected heteronuclear multiple bond connectivity (HMBC) spectrum of **2b** was measured (Fig. 1). The C-1 proton signal (H-1) at δ 5.3 ppm (1H, br t), which was coupled with the signals of carbons at C-2 [28.5 (t)], C-3 [19.4 (t)], C-4a [122.4 (s)] and C-9a [133.9 (s)] of the tetrahydrocarbazole moiety, was correlated to the carbonyl carbon of ketone at C-25 [197.2 (s)] and the quaternary carbon at C-24 [132.7 (s) or δ 139.3 (s)] of the benzene moiety. Further, the carbonyl carbon at C-25 which was connected with the tetrahydrocarbazole moiety was also coupled with the benzene proton at 8.08 (H-23). On the other hand, the C-4 methylene proton signals at (H-4) δ 2.5—2.9 ($\underline{2H}$+1H, m), which were coupled with the carbons at C-2, C-3, C-4a and C-9a, were also correlated to the ^{13}C-NMR signal at δ 131.1 (s) assigned to the carbon at the C-4b position. Therefore, the structure

TABLE I. Physical Properties and Spectral Data for Phthalimide Derivatives **1a**—**h**, **3**, **6**, **10** and **12**

Compd.	mp (°C) (Recrystn. solvent)[a]	IR $\nu_{\max}^{\mathrm{Nujol}}$ (cm^{-1})	MS (m/z) M^+	^{1}H-NMR ($CDCl_3$) δ ppm	Formula	Analysis (%) Calcd (Found) C	H	N
1a	130—132.5 (EA–H)	1770, 1720, 1675	414	1.3—2.2 (10H, m), 2.5—2.9 (2H, m), 2.8—3.2 (4H, m), 3.71 (2H, t, $J=7$ Hz, N–CH_2), 7.2—7.6 (3H, m, ArH), 7.7—8.2 (5H, m, ArH)	$C_{26}H_{26}N_2O_3$	75.34 (75.37	6.32 6.33	6.76 6.70)
1b	122—124 (EA–H)	1770, 1705, 1690	428	1.2—2.1 (12H, m), 2.5—2.8 (2H, m), 2.7—3.2 (4H, m), 3.5—3.9 (2H, m, N–CH_2), 7.0—7.4 (3H, m, ArH), 7.5—8.0 (5H, m, ArH)	$C_{27}H_{28}N_2O_3$	75.67 (75.77	6.59 6.66	6.54 6.66)
1c	114—115 (EA–H)	1770, 1705, 1680	442	1.2—2.2 (14H, m), 2.4—2.8 (2H, m), 2.6—3.2 (4H, m), 3.68 (2H, t, $J=7$ Hz, N–CH_2), 7.1—7.5 (3H, m, ArH), 7.5—8.2 (5H, m, ArH)	$C_{28}H_{30}N_2O_3$	75.99 (76.16	6.83 6.93	6.33 6.42)
1d	94—96 (EA–H)	1770, 1720, 1690	456	1.1—2.1 (16H, m), 2.5—3.1 (6H, m), 3.5—3.8 (2H, m, N–CH_2), 7.0—7.4 (3H, m, ArH), 7.5—8.0 (5H, m, ArH)	$C_{29}H_{32}N_2O_3$	76.29 (76.47	7.07 7.11	6.14 6.21)
1e	82—84 (EA–H)	1765, 1715	484	1.2—2.0 (20H, m), 2.5—2.8 (2H, m), 2.8—3.2 (4H, m), 3.68 (2H, t, $J=7$ Hz, N–CH_2), 7.2—7.5 (3H, m, ArH), 7.6—8.2 (5H, m, ArH)	$C_{31}H_{36}N_2O_3$	76.83 (76.66	7.49 7.60	5.78 5.87)
1f	Semisolid	1770, 1705[b]	498	1.1—1.5 (12H, m), 1.5—2.1 (10H, m), 2.6—3.2 (6H, m), 3.67 (2H, t, $J=7$ Hz, N–CH_2), 7.1—7.6 (3H, m, ArH), 7.6—8.0 (5H, m, ArH)	$C_{32}H_{38}N_2O_3$	498.28822[c] (498.28896)		
1g	Oil	1770, 1700[b]	472	1.5—2.8 (12H, m), 2.8—3.2 (4H, m), 3.73 (2H, t, $J=7$ Hz, N–CH_2), 4.08 (2H, t, $J=6$ Hz, O–CH_2), 7.1—7.4 (3H, m, ArH), 7.5—7.8 (4H, m, ArH), 7.8—8.1 (1H, m, ArH)	$C_{28}H_{28}N_2O_5$	472.19978[c] (472.20058)		
1h	56—57.5 (H)	1770, 1720, 1705	584	1.1—2.8 (28H, m), 2.8—3.2 (4H, m), 3.5—3.8 (2H, m, N–CH_2), 3.8—4.2 (2H, m, O–CH_2), 7.0—7.4 (3H, m, ArH), 7.4—8.1 (5H, m, ArH)	$C_{36}H_{44}N_2O_5$	73.94 (73.79	7.59 7.71	4.79 4.97)
3	109 (EA–H)	1760, 1695	388	1.1—2.1 (8H, m), 2.62 (3H, s, CH_3), 2.97 (2H, t, $J=7$ Hz, $COCH_2$–), 3.69 (2H, t, $J=7$ Hz, N–CH_2–), 6.34 (1H, s, =CH–), 7.0—7.6 (3H, m, ArH), 7.6—8.0 (5H, m, ArH)	$C_{24}H_{24}N_2O_3$	74.20 (74.00	6.23 6.24	7.21 7.13)
6	101—102 (EA–H)	1770, 1690	388	1.2—2.0 (8H, m), 2.28 (3H, d, $J=1.3$ Hz, CH_3), 2.86 (2H, t, $J=7$ Hz, $COCH_2$–), 3.70 (2H, t, $J=7$ Hz, N–CH_2–), 7.2—7.6 (4H, m, ArH), 7.8—8.0 (4H, m, ArH), 8.5—8.7 (1H, m, ArH)	$C_{24}H_{24}N_2O_3$	74.20 (74.40	6.23 6.27	7.21 7.29)
10	Oil	1765, 1715 (sh)[b] 1700	544	1.1—1.8 (18H, m), 1.8—2.2 (2H, m), 2.2—2.5 (2H, m), 2.56 (3H, s, $COCH_3$), 2.5—2.9 (2H, m), 3.5—3.8 (2H, m, N–CH_2), 3.9—4.2 (2H, m, O–CH_2), 7.1—7.4 (3H, m, ArH), 7.4—7.9 (5H, m, ArH), 8.2—8.5 (1H, m, ArH)	$C_{33}H_{40}N_2O_5$	544.29367[c] (544.29259)		
12	86—87 (EA–H)	1765, 1750, 1700	502	1.1—1.9 (16H, m), 2.39 (2H, t, $J=7$ Hz, CO–CH_2), 2.79 (3H, s, $COCH_3$), 3.67 (2H, t, $J=7$ Hz, N–CH_2), 5.48 (2H, d, $J=1$ Hz, CH_2–OCO), 6.67 (1H, d, $J=1$ Hz, C=C–H), 7.2—7.4 (2H, m, ArH), 7.5—8.0 (6H, m, ArH)	$C_{30}H_{34}N_2O_5$	71.69 (71.50	6.82 6.88	5.57 5.59)

a) Solvents for recrystallization: EA, ethyl acetate; H, hexane. *b*) Measured neat. *c*) Determined by high-resolution mass spectrometry (HR-MS). Upper figure, calcd for M^+; lower figure, found.

of **2b** was assigned as **2b**-i. In addition, in the photoreaction of the 2- and 3-methylindole derivatives (**3** and **6**) as a model reaction, only 2-methylindole (**3**) in acetone gave isoindolol **4**, accompanied with the oxetane derivative (**5**). However, in the case of 3-methylindole **6**, the photoreaction gave no isoindolol, but provided a small amount of the oxetane compound (**7**) along with a complex photolysate. From these results, the regioisomers of **2a** and **2b** were assigned as **2a**-i and **2b**-i, respectively, although the stereochemistry was not clarified.

Next, photoreactions of a series of bichromophoric system having a longer chain ($n=7$, 8, 10) were examined. The imides **1c**—**e** underwent [2+2]cycloaddition, as expected, to give polycyclic oxetanes (**8c**—**e**) in moderate yields together with isoindolols (**9c**—**e**), which arise from the Norrish type II reaction (Chart 2). Interestingly, the yields for the formation of the oxetanes **8c**—**e** increased with increase of the number of methylene units, whereas the yields for the formation of **9c**—**e** decreased. The structures of **8c**—**e** were determined on the basis of the spectral and analytical data. The ^{13}C-NMR spectra of **8c**—**e** showed two singlet peaks at 168.4—169.8 and 174.3—174.5 ppm, suggesting the presence of two amide groups. Although the formation of four regio- and stereoisomeric oxetanes (i—iv) is possible, the regioisomers iii and iv were excluded on the basis of the ^{13}C-NMR spectra by comparison with that of the oxeto[2,3-*b*]indole system[6] reported previously. That is, as shown in the oxeto[2,3-*b*]indole structure (Chart 2), the signals of two quaternary carbons adjacent to both the nitrogen and the oxygen atoms appear at 102.7—103.6 and 94.5—100.0 ppm, respectively. Similarly, in the spectra of **8c**—**e** two

TABLE II. Photoreaction of Phthalimide Derivatives (**1a**—**h**, **3**, **6**, **10**) and Physical Properties for Photoproducts (**2a**, **2b**, **4**, **5**, **7**, **8c**—**h**, **9c**—**e**, **9g**, **9h** and **11**)

Compd.	n	Irradiation time (h)	Product	Yield (%)	mp (°C)	Appearance (Solvent)[a]	IR ν_{max}^{Nujol} (cm^{-1})	MS (m/z) (M$^+$)	Formula	Analysis (%) Calcd (Found)			Maximum ring size
										C	H	N	
1a	5	2.6	**2a**	6	247—249	Colorless prisms (C–H)	3400, 1680, 1665	414	$C_{26}H_{26}N_2O_3$	75.34 (75.37	6.32 6.33	6.76 6.70)	
1b	6	2.5	**2b**	11	217—218.5	Colorless needles (C–H)	3350, 1685, 1635	428	$C_{27}H_{28}N_2O_3$	75.67 (75.71	6.59 6.62	6.54 6.40)	
1c	7	2.3	**8c**	7	163—165	Colorless prisms (EA–H)	1705, 1670	442	$C_{28}H_{30}N_2O_3$	75.99 (75.97	6.83 6.90	6.33 6.17)	13
			9c	17	195—197	Colorless needles (EA–H)	3280, 1690, 1670	442 424 (M$^+-18$)	$C_{28}H_{30}N_2O_3$	75.99 (76.16	6.83 6.86	6.33 6.44)	
1d	8	3.0	**8d**	12	177—179.5	Colorless needles (EA–H)	1700, 1660	456	$C_{29}H_{32}N_2O_3$	76.29 (76.25	7.07 7.17	6.14 6.09)	14
			9d	14	200—201	Colorless prisms (EA–H)	3350, 1700, 1675	456 438 (M$^+-18$)	$C_{29}H_{32}N_2O_3$	76.29 (76.22	7.07 7.12	6.14 6.14)	
1e	10	1.7	**8e**	37	190—193	Colorless needles (EA–H)	1710, 1665	484	$C_{31}H_{36}N_2O_3$	76.83 (76.65	7.49 7.58	5.78 5.68)	16
			9e	11	224—226	Colorless needles (EA–H)	3510, 1710, 1685	484 466 (M$^+-18$)	$C_{31}H_{36}N_2O_3$	76.83 (76.87	7.49 7.65	5.78 5.82)	
1f	10	2.8	**8f**	53	220—222.5	Colorless needles (EA–H)	1710, 1660	498	$C_{32}H_{38}N_2O_3$	77.07 (76.95	7.68 7.84	5.62 5.84)	16
1g	3	5.0	**8g**	24	194—196	Colorless prisms (EA–H)	1725, 1705, 1645	472	$C_{28}H_{28}N_2O_5$	71.17 (70.91	5.97 5.98	5.93 6.11)	14
			9g	11	216—218	Colorless needles (EA–H)	3390, 1735, 1700, 1680	472 454 (M$^+-18$)	$C_{28}H_{28}N_2O_5$	71.17 (70.91	5.97 6.21	5.93 5.86)	
1h	11	0.8	**8h**	59	140.5—142	Colorless plates (B–H)	1740, 1700, 1670	584	$C_{36}H_{44}N_2O_5$	73.94 (74.05	7.59 7.56	4.79 4.94)	22
			9h	Trace	176—178	Colorless prisms (ET–IPE)	3000, 1730, 1700, 1670	584 566 (M$^+-18$)	$C_{36}H_{44}N_2O_5$	584.3250[b] (584.3272)			
3		1[c]	**4**	7	205—208	Colorless needles (EA–H)	3300, 1680, 1660	388 370 (M$^+-18$)	$C_{24}H_{24}N_2O_3$	74.20 (73.97	6.23 6.20	7.21 7.05)	
			5	12	179—181	Colorless prisms (EA–H)	1700, 1665	388	$C_{24}H_{24}N_2O_3$	74.20 (74.14	6.23 6.25	7.21 7.07)	
6		7.5[c]	**7**	7	238—242	Colorless prisms (EA–MC)	1700, 1670	388	$C_{24}H_{24}N_2O_3$	388.1787[b] (388.1811)			
10		6.5[c]	**11**	28	158—160	Colorless prisms (MC–IP)	1715 (sh), 1700, 1680	544	$C_{33}H_{40}N_2O_5$	72.75 (72.74	7.41 7.48	5.15 5.19)	19

a) Solvents for recrystallization: C, chloroform; H, hexane; EA, ethyl acetate; ET, ethanol; IPE, diisopropyl ether; MC, methylene chloride; B, benzene. *b*) Determined by HR-MS. *c*) A 1 kW high-pressure mercury lamp was used.

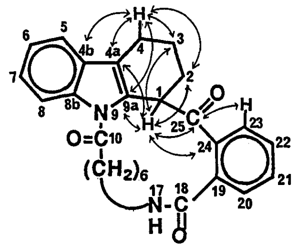

Fig. 1. C–H Long-Range Correlations in the HMBC Spectrum of **2b**

singlets appeared at 97.8—98.8, and 103.0—104.1 ppm, respectively, indicating that regioselective cycloaddition had occurred between one carbonyl of the imide moiety and the carbon–carbon double bond of the 4a- and 9a-positions in the carbazole moiety. The stereoisomers **8c**—**e**-ii were also excluded on the basis of ^{1}H-NMR spectra, in which signals due to certain aromatic protons showed upfield shift in comparison with those of substrates **1c**—**e**, indicating that the two benzene rings are close to each other. Thus, the structures of **8c**—**e** were confirmed to be **8c**—**e**-i, spectral data of which are analogous to that of the precedent described previously.[6] Further, the structural assignments for **9c**—**e**, were based on the following data. In the IR spectra of **9c**—**e** the bands in the regions of 3280—3510 and 1670—1710 cm^{-1} indicated the presence of the isoindolol and two lactam moieties, respectively. In the ^{13}C-NMR spectra, **9c**—**e** showed peaks due to two amide carbonyls and a quaternary carbon adjacent to a nitrogen and an oxygen atom at 167.6—168.1, 176.6—177.4 and 92.8—93.4 ppm, respectively. The ^{1}H-NMR spectra of **9c**—**e** showed the anisotropic effects of benzene rings in analogy with those of **8c**—**e**, indicating that two benzene rings are close to each other. From this result, the structure of **9** was considered to be **9**-i or **9**-ii. In the ^{1}H-NMR spectra of **9c**—**e**, although the signal attributable to the allylic methine proton was observed at 4.2—4.4 ppm (1H, m), it was difficult to discriminate the C-1 and C-4 methine protons. Therefore, in order to confirm the regiochemical structure of **9**, the HMBC spectrum of **9c** was measured (Fig. 2). The C-1 proton signal (H-1) at δ 4.32 ppm (1H, br t), which was coupled with the signals of carbons at C-2 [24.3 (t)], C-3 [18.8 (t)], C-4a [121.1 (s)] and C-9a [130.0 (s)] of the indole moiety, was also correlated to the quaternary carbons at C-24 and C-23a [92.8 (s) and δ 145.0 (s), respectively] of the isoindolol moiety. On the other hand, the C-4 methylene proton signals (H-4) at δ 2.1—2.3 ($1\underline{H}+1H$, m) and 2.4—2.6 (1H, m), which were coupled with the carbons at C-2, C-3, C-4a and C-9a, were also correlated to the ^{13}C-NMR signal at δ 127.4 (s) assigned to the carbon at the C-4b position. If hydrogen abstraction

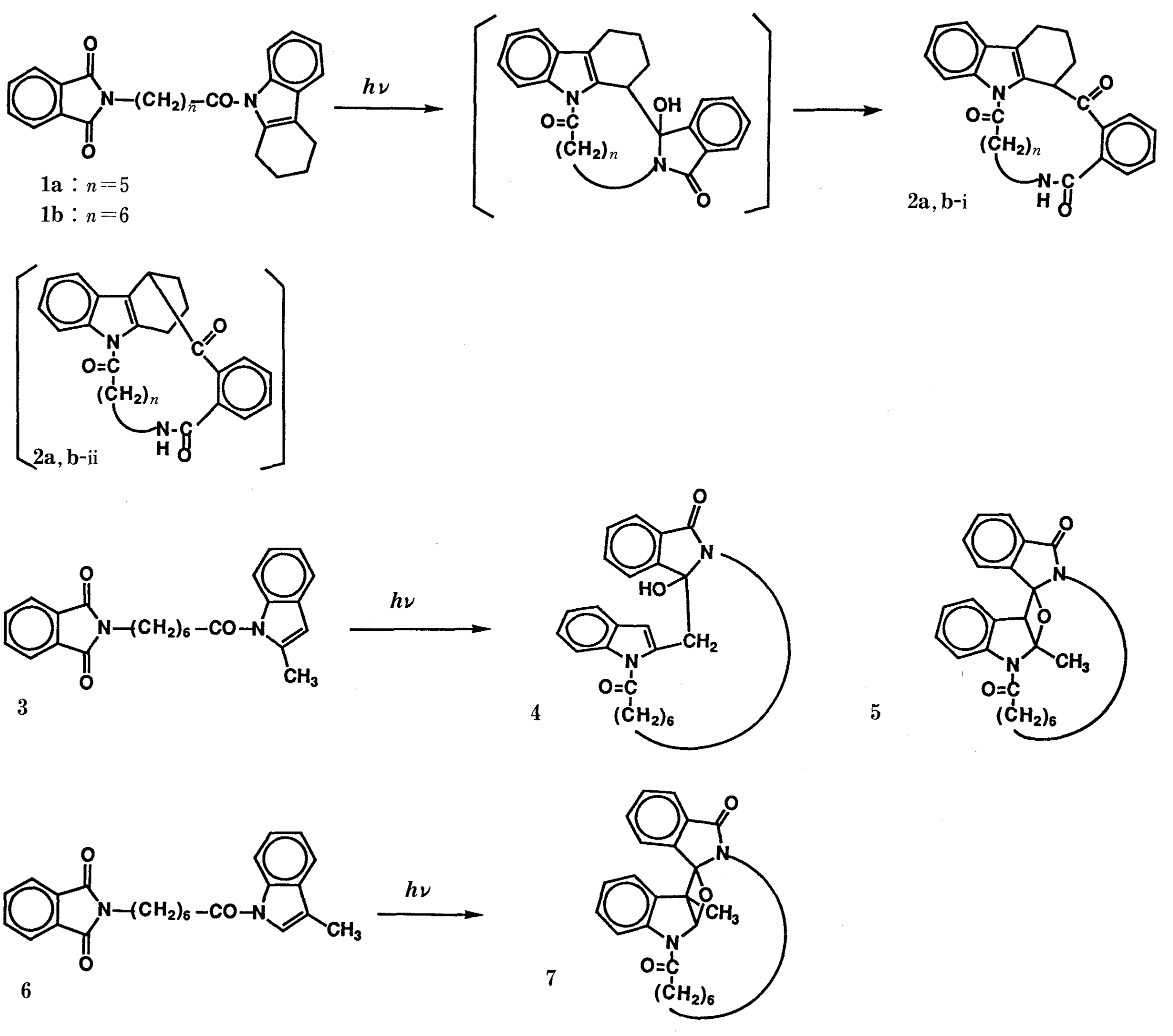

Chart 1

occurred at the C-4 position, the C-4 proton signal should be correlated to the ^{13}C-NMR signals of five quaternary carbons (C-4a, C-4b, C-9a, C-24, C-23a) and two methylene carbons (C-2 and C-3), but no such correlation was observed in the HMBC spectrum of **9c** (Fig. 2). Therefore, the structure of **9c** was assigned as **9c**-i. The structures of **9d** and **9e** were also determined to be **9d**-i and **9e**-i by analogy with the spectral data for **9c**.

In addition, photoreaction of **1f**, having a fused seven-membered ring as a homologue of tetrahydrocarbazole (**1e**, $n=10$), was examined. Upon irradiation, **1f** gave exclusively the Paterno–Büchi oxetane (**8f**) in 53% yield.

Further, in order to examine the possibility of forming larger sized rings, an ester bond as a connecting portion between phthalimide and tetrahydrocarbazole was adopted in the *N*-alkyl side chain in this system. Upon irradiation of **1g** ($n=3$), the oxetane **8g** (14-membered ring) was obtained in 24% yield, accompanied with a small amount of the isoindolol compound (**9g**). Further, on irradiation of **1h** ($n=11$) having a longer chain, the remote Paterno–Büchi reaction occurred most efficiently, affording the 22-membered macrocyclic compound **8h** in 59% yield.

Moreover, to examine the scope and limitations of this macrocyclic synthesis, photolysis of 3-substituted (**10**) and 2-substituted (**12**) indole derivatives having an ester bond in the side chain was investigated. In the photoreaction of **10**, the oxetane **11** involving a 19-membered ring was obtained in 28% yield together with unchanged **10** (20%). However, photolysis of the 2-substituted indole **12** yielded a complex photolysate, and isolable products were not obtained. It was difficult to clarify the difference of photochemical behavior between **10** and **12** (Chart 3). The structure **11** was assigned on the basis of analytical and spectral data. The ^{1}H-NMR and ^{13}C-NMR spectra of **11** were analogous to those of oxetoindole described previously.[6,7]

In conclusion, as seen in the cases of **1c**—**h**, the phthalimide-carbazole system underwent the remote Paterno–Büchi reaction, although competition between the Norrish type II reaction and Paterno–Büchi reaction was observed, depending on the chain length by which the nonconjugated bichromophores are separated. When $n \geqq 7$, the ratio of the Paterno–Büchi reaction to hydrogen abstraction reaction (**8**/**9**) increased with increase of the methylene chain length. This suggests that Paterno–Büchi reaction occurred much more efficiently than hydrogen abstraction in the case of the system without the restriction due to the short methylene chain. Indeed, in the in-

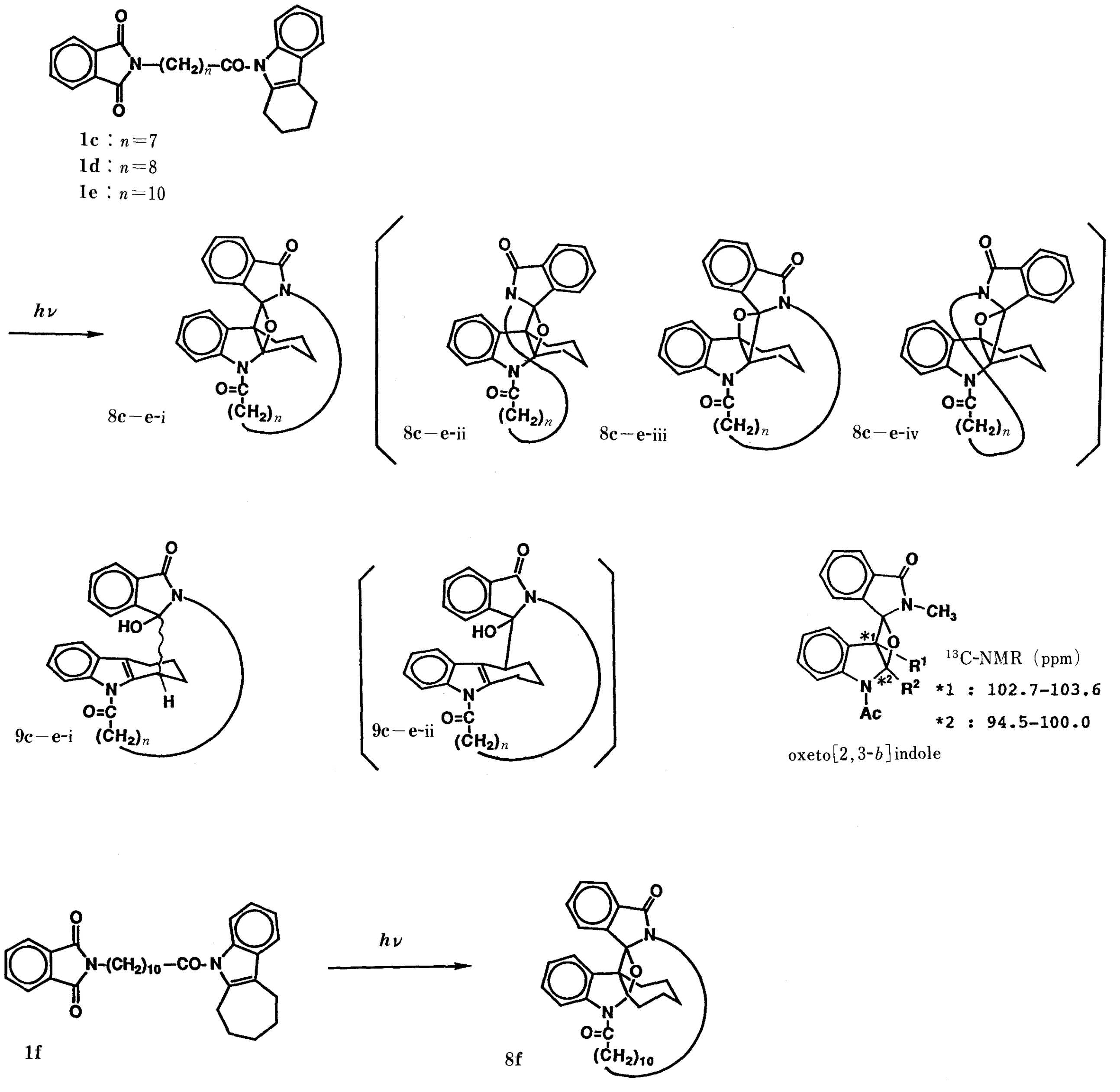

Chart 2

termolecular photoreaction of the *N*-methylphthalimide-*N*-acyl-tetrahydrocarbazole system, only the Paterno–Büchi reaction proceeds.[6] These results would suggest a stacking interaction, such as an excited complex, between the aromatic rings of the phthalimide (a good electron acceptor) and the indole derivatives **1**, **10** (good electron donors), although spectroscopic evidence has not yet been obtained. Thus, there seems to be no critical limitation in the synthesis of larger-sized macrocycles than the 22-membered ring (**8h**) with regard to photocyclization of phthalimide-tetrahydrocarbazole systems. The occurrence of the Paterno–Büchi reaction in the phthalimide systems has now been verified by trapping the imide oxetanes (up to 22-membered rings), showing that the working hypothesis of "photolysis of donor–acceptor systems" may be applicable not only for the hydrogen abstraction reaction (Norrish type II reaction), but also for the Paterno–Büchi reacton in the phthalimide systems.

Experimental

All melting points were determined on a Yamato melting point apparatus (model MP-21) and are uncorrected. Infrared (IR) spectra were recorded on a JASCO A-102 spectrometer. Nuclear magnetic resonance (NMR) spectra were taken on JEOL FX-90Q and JEOL JNM-EX 400 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: br, broad; s, singlet; d, doublet; t, triplet; q, quartet, m, multiplet. Mass spectra were determined with a JEOL JMS-QH-100 gas chromatograph-mass spectrometer with a direct inlet system and high-resolution MS (HR-MS) spectra were recorded using a JEOL JMS-DX 303 mass spectrometer.

Irradiations of substrates were conducted using 500 W and 1 kW high-pressure mercury lamps and a water-cooled quartz immersion well (Eikosha PIH-500 and Eikosha EHB-W-1000) 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,

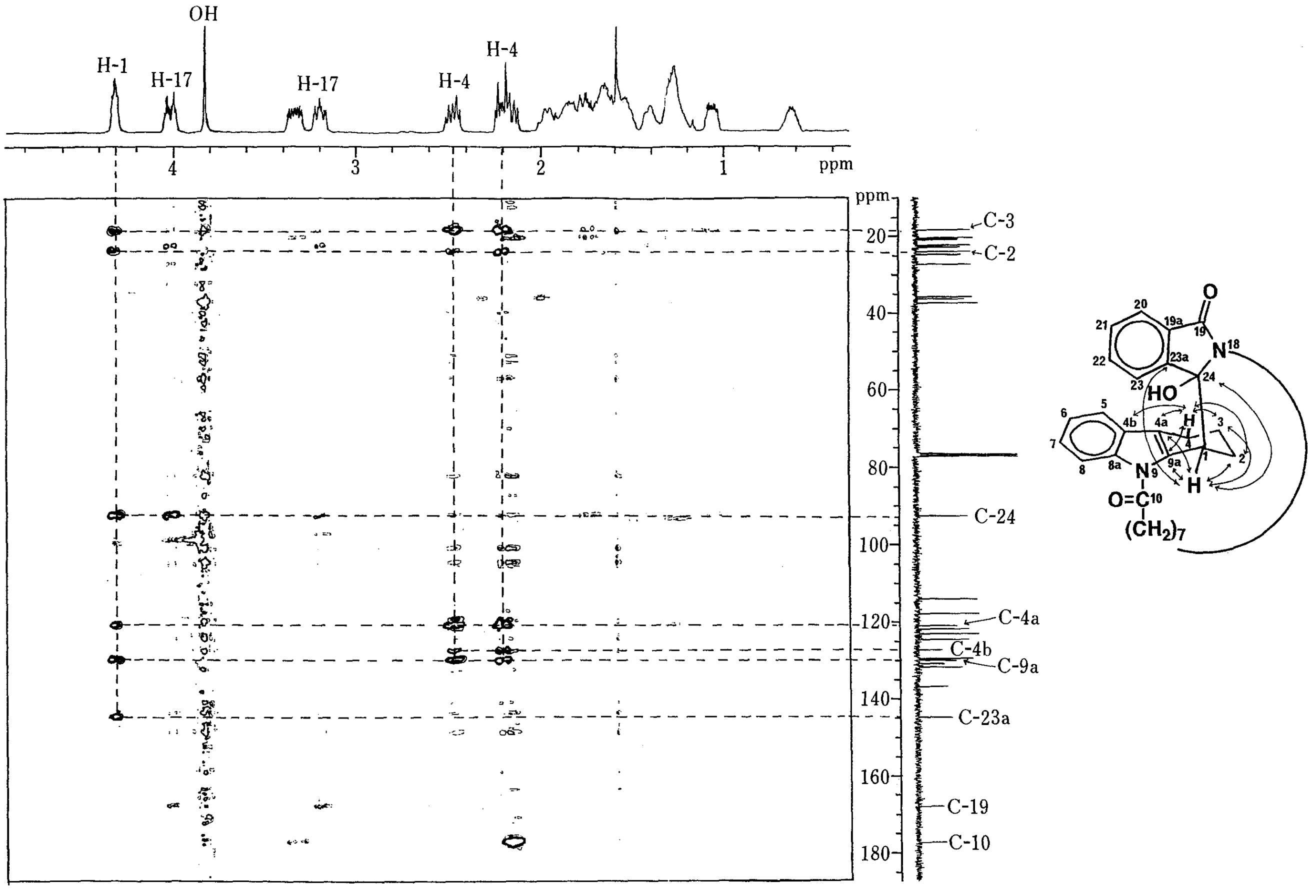

Fig. 2. HMBC Spectrum of **9c** in $CDCl_3$

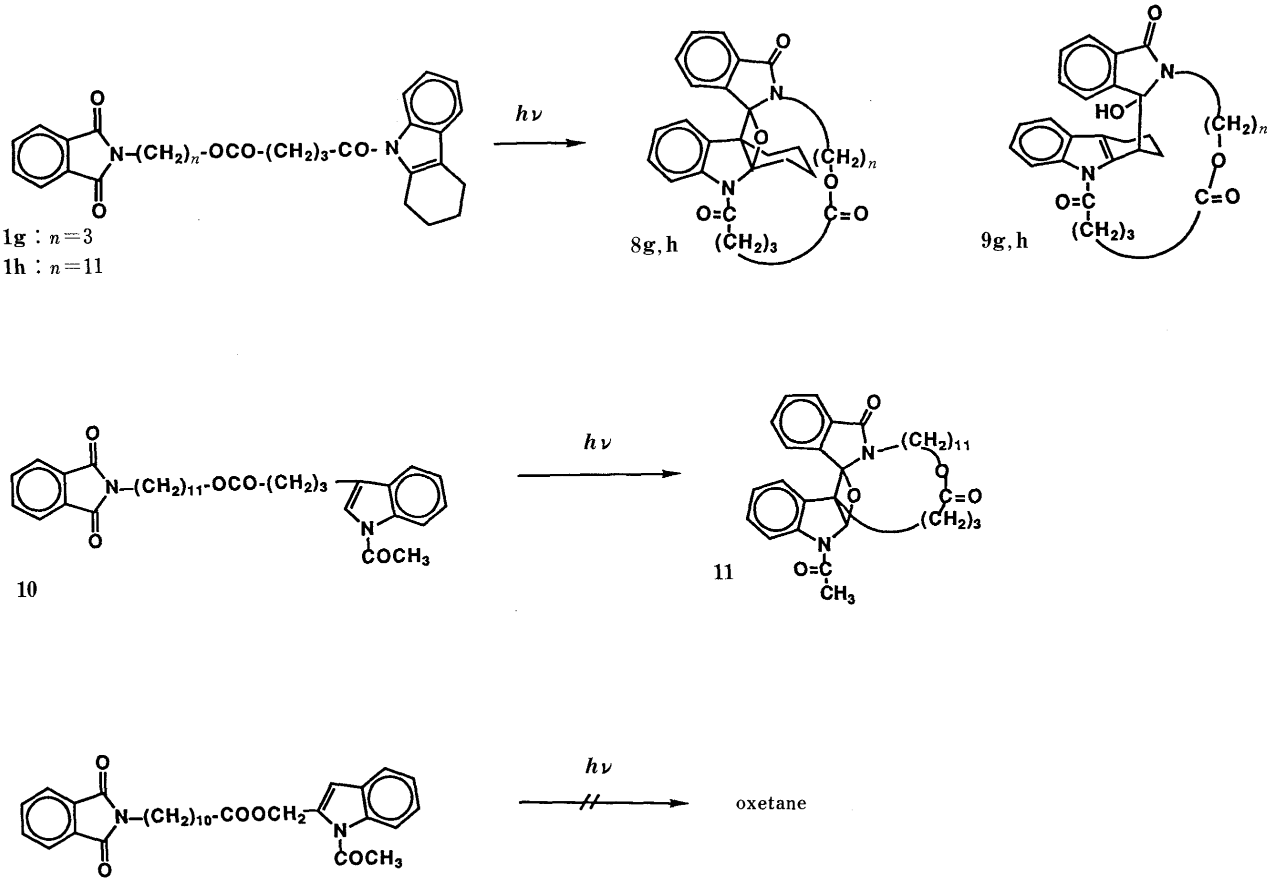

Chart 3

Table III. NMR Spectral Data for the Photoproducts **2a**, **2b**, **4**, **5**, **7**, **8c**—**h**, **9c**—**e**, **9g**, **9h** and **11**

Compd.	^{1}H-NMR (CDCl$_3$) δ	^{13}C-NMR (CDCl$_3$) δ
2a[a]	1.2—1.4 (1H, m), 1.4—1.7 (3H, m), 1.7—1.8 (1H, m), 1.8—2.1 (3H, m), 2.1—2.3 (1H, m), 2.3—2.5 (1H, m), 2.6—2.9 (3H, m), 3.0—3.2 (1H, m), 3.3—3.5 (1H, m), 3.6—3.8 (1H, m), 5.3 (1H, br t, –CH–), 5.8—6.0 (1H, m, NH), 7.2—7.4 (2H, m, ArH), 7.4—7.7 (5H, m, ArH), 8.0—8.1 (1H, m, ArH)	19.8 (t), 21.1 (t), 23.2 (t), 24.4 (t), 26.0 (t), 29.4 (t), 37.4 (t), 39.6 (t), 45.7 (d), 114.6 (d), 119.0 (d), 122.4 (s), 123.3 (d), 124.4 (d), 128.5 (d), 129.0 (d), 129.9 (s), 131.1 (s), 132.3 (d), 133.9 (s), 134.8 (s), 139.1 (s), 170.7 (s), 174.4 (s), 197.9 (s)
2b[a]	1.2—2.0 (10H, m), 2.1—2.3 (2H, m), 2.6—2.9 (3H, m), 3.3—3.5 (3H, m), 5.3 (1H, br t, –CH–), 5.6—5.8 (1H, m, NH), 7.2—7.4 (2H, m, ArH), 7.4—7.7 (5H, m, ArH), 8.08 (1H, d, $J=7$ Hz, ArH)	19.4 (t), 21.1 (t), 24.0 (t), 25.0 (t), 26.0 (t), 26.2 (t), 28.5 (t), 38.0 (t), 38.5 (t), 44.9 (d), 114.6 (d), 118.9 (d), 122.4 (s), 123.1 (d), 124.3 (d), 129.1 (d) × 2, 129.5 (d), 131.1 (s), 132.5 (d), 132.7 (s), 133.9 (s), 134.8 (s), 139.3 (s), 171.2 (s), 173.6 (s), 197.2 (s)
4[a]	0.5—0.7 (1H, m), 1.0—1.3 (2H, m), 1.4—1.6 (2H, m), 1.6—1.9 (2H, m), 2.0—2.2 (1H, m), 2.9—3.3 (4H, m), 3.75 and 4.25 (2H, ABq, $J=17$ Hz, =C–C$\underline{\mathrm{H}}_2$–COH), 4.10 (1H, s, OH), 5.03 (1H, s, =CH–), 7.0—7.8 (8H, m, ArH)	23.8 (t), 24.4 (t), 25.5 (t), 26.3 (t), 33.7 (t), 37.9 (t), 39.6 (t), 90.9 (s), 108.3 (d), 113.0 (d), 120.9 (d), 122.3 (d), 122.5 (d), 123.4 (d), 123.5 (d), 129.1 (s), 130.0 (d), 131.8 (s), 132.5 (d), 133.9 (s), 134.9 (s), 147.3 (s), 168.6 (s), 176.0 (s)
5[a]	0.8—1.0 (1H, m), 1.0—1.1 (1H, m), 1.1—1.3 (1H, m), 1.4—1.6 (2H, m), 1.7—1.9 (2H, m), 2.1—2.3 (1H, m), 2.21 (3H, s, CH$_3$), 2.4—2.5 (1H, m), 2.6—2.7 (1H, m), 3.0—3.1 (1H, m), 3.3—3.4 (1H, m), 4.68 (1H, s, PhCH–), 6.9—7.1 (2H, m, ArH), 7.3—7.4 (1H, m, ArH), 7.5—7.6 (1H, m, ArH), 7.7—7.8 (1H, m, ArH), 7.8—8.0 (2H, m, ArH), 8.23 (1H, d, $J=8$ Hz, ArH)	21.2 (t), 24.3 (t), 26.1 (q), 26.5 (t), 27.1 (t), 34.0 (t), 38.0 (t), 58.9 (d), 96.1 (s), 96.7 (s), 115.6 (d), 121.7 (d), 123.2 (d), 124.6 (d), 125.7 (d), 130.0 (d), 130.4 (d), 130.6 (s), 132.7 (d), 145.4 (s), 145.9 (s), 167.2 (s), 174.6 (s)
7[a]	1.4—2.2 (8H, m), 1.57 (3H, s, CH$_3$), 2.6—2.8 (2H, m), 3.5—3.6 (1H, m), 4.1—4.2 (1H, m), 6.02 (1H, d, $J=7$ Hz, ArH), 6.49 (1H, s, N–CH–O), 6.56 (1H, d, $J=7$ Hz, ArH), 7.02 (1H, t, $J=7$ Hz, ArH), 7.13 (1H, t, $J=7$ Hz, ArH), 7.3—7.5 (2H, m, ArH), 7.71 (1H, d, $J=7$ Hz, ArH), 8.39 (1H, d, $J=8$ Hz, ArH)	17.3 (q), 24.4 (t), 26.2 (t), 28.4 (t), 28.8 (t), 35.8 (t), 42.2 (t), 59.8 (s), 93.6 (d), 104.1 (s), 117.5 (d), 122.6 (d), 124.4 (d) × 2, 125.6 (d), 129.8 (d), 130.3 (d), 131.2 (d), 131.6 (s), 133.1 (s), 141.0 (s), 142.6 (s), 167.4 (s), 171.1 (s)
8c	0.4—3.1 (20H, m), 3.6—4.3 (2H, m), 6.2—6.6 (2H, m, ArH), 6.7—7.4 (4H, m, ArH), 7.60 (1H, d, $J=7$ Hz, ArH), 8.02 (1H, d, $J=8$ Hz, ArH)	17.9 (t), 18.6 (t), 22.7 (t), 23.5 (t), 23.9 (t), 26.1 (t), 27.5 (t), 32.6 (t), 35.7 (t), 40.9 (t), 61.6 (s), 97.8 (s), 103.0 (s), 118.0 (d), 122.8 (d), 123.2 (d), 124.5 (d), 124.8 (d), 129.5 (d), 129.7 (d), 131.3 (s), 131.5 (d), 143.7 (s), 146.3 (s), 169.8 (s), 174.5 (s)
9c[a]	0.5—0.7 (1H, m), 1.0—1.1 (1H, m), 1.1—2.0 (12H, m), 2.1—2.3 (2H, m), 2.4—2.6 (1H, m), 3.1—3.3 (1H, m), 3.3—3.4 (1H, m), 3.82 (1H, s, OH), 3.9—4.1 (1H, m), 4.32 (1H, br t), 5.93 (1H, d, $J=8$ Hz, ArH), 6.97 (1H, t, $J=8$ Hz, ArH), 7.1—7.3 (3H, m, ArH), 7.34 (1H, d, $J=7$ Hz, ArH), 7.56 (1H, m, ArH), 7.73 (1H, d, $J=7$ Hz, ArH)	18.8 (t), 20.8 (t), 21.0 (t), 22.7 (t), 23.1 (t), 24.3 (t), 25.0 (t), 27.7 (t), 36.2 (t), 36.7 (t), 37.8 (d), 92.8 (s), 114.2 (d), 118.1 (d), 121.1 (s), 122.0 (d), 123.3 (d) × 2, 124.7 (d), 127.4 (s), 129.8 (d), 130.0 (s), 131.1 (s), 131.9 (d), 137.0 (s), 145.0 (s), 168.1 (s), 177.4 (s)
8d	0.8—2.6 (20H, m), 2.6—3.1 (2H, m), 3.5—4.0 (1H, m), 4.2—4.7 (1H, m), 6.4—6.6 (2H, m, ArH), 6.7—7.4 (4H, m, ArH), 7.5—7.7 (1H, m), 8.0—8.2 (1H, m, ArH)	18.5 (t), 18.8 (t), 24.3 (t), 24.9 (t), 26.1 (t), 26.4 (t), 26.6 (t), 33.5 (t), 35.6 (t), 43.6 (t), 62.0 (s), 98.2 (s), 103.6 (s), 118.1 (d), 122.9 (s), 123.5 (d), 123.9 (d), 124.9 (d), 129.4 (d), 129.7 (d), 130.6 (s), 131.2 (d), 131.7 (d), 143.0 (s), 146.4 (s), 168.9 (s), 174.5 (s)
9d	0.2—0.7 (1H, m), 1.0—2.2 (15H, m), 2.3—2.9 (3H, m), 3.1—4.0 (3H, m), 4.2—4.4 (1H, m), 4.52 (1H, s, OH), 6.33 (1H, d, $J=7$ Hz, ArH), 7.0—7.6 (5H, m, ArH), 7.65 (1H, d, $J=7$ Hz, ArH), 7.8—8.1 (1H, m, ArH)	17.8 (t), 20.1 (t), 22.9 (t), 24.2 (t), 24.6 (t), 25.9 (t), 26.2 (t), 37.1 (t), 38.3 (d), 39.2 (t), 93.4 (s), 114.6 (d), 118.1 (d), 121.3 (s), 122.3 (d), 123.1 (d), 123.3 (d), 124.8 (d), 128.1 (s), 129.6 (d), 130.9 (s), 131.5 (d), 131.7 (s), 136.9 (s), 145.4 (s), 167.6 (s), 176.6 (s)
8e	0.6—3.1 (26H, m), 3.6—4.0 (1H, m), 4.2—4.6 (1H, m), 6.40 (2H, d, $J=8$ Hz, ArH), 6.7—7.4 (4H, m, ArH), 7.58 (1H, d, $J=8$ Hz, ArH), 8.22 (1H, d, $J=8$ Hz, ArH)	18.2 (t), 18.4 (t), 23.5 (t), 24.8 (t), 24.9 (t), 27.0 (t), 27.3 (t), 27.5 (t), 27.6 (t), 27.8 (t), 33.6 (t), 36.1 (t), 42.0 (t), 61.3 (s), 98.8 (s), 104.1 (s), 117.2 (d), 122.8 (d), 123.1 (d), 124.1 (d), 124.9 (d), 129.5 (d), 129.6 (d), 130.2 (s), 131.7 (d), 143.4 (s), 146.1 (s), 168.4 (s), 174.3 (s)
9e	0.1—0.5 (1H, m), 0.9—2.6 (21H, m), 3.0—3.3 (2H, m), 3.4—3.9 (2H, m), 3.5—3.9 (1H, m, OH), 4.2—4.4 (1H, m), 6.8—7.0 (1H, m, ArH), 7.2—7.9 (7H, m, ArH)	16.9 (t), 19.5 (t), 22.9 (t), 24.9 (t), 25.3 (t), 25.8 (t), 26.2 (t), 26.4 (t), 26.8 (t), 27.4 (t), 37.8 (t), 38.8 (d), 39.1 (t), 93.3 (s), 115.3 (d), 119.2 (d), 121.6 (s), 123.1 (d), 123.5 (d), 123.7 (d), 124.6 (d), 129.4 (d), 130.8 (s), 131.2 (d), 132.3 (s), 134.0 (s), 136.0 (s), 146.4 (s), 167.8 (s), 177.1 (s)
8f	0.5—3.1 (28H, m), 3.6—4.0 (1H, m), 4.2—4.6 (1H, m), 6.2—6.5 (2H, m, ArH), 6.7—7.4 (4H, m, ArH), 7.60 (1H, d, $J=8$ Hz, ArH), 8.25 (1H, d, $J=8$ Hz, ArH)	23.4 (t), 24.4 (t), 24.8 (t), 25.7 (t), 26.9 (t), 27.2 (t), 27.5 (t), 28.5 (t), 31.1 (t), 36.1 (t), 37.6 (t), 42.5 (t), 67.1 (s), 101.4 (s), 103.6 (s), 117.4 (d), 122.8, 123.1, 123.7, 124.8, 129.3, 129.6, 130.5 (s), 130.7, 131.4, 143.4 (s), 146.5 (s), 168.4 (s), 174.5 (s)
8g	1.5—3.0 (14H, m), 3.5—3.9 (4H, m), 4.4—4.8 (2H, m), 6.4—6.7 (2H, m, ArH), 6.7—7.4 (4H, m, ArH), 7.6—7.8 (1H, m, ArH), 8.00 (1H, d, $J=8$ Hz, ArH)	19.0 (t), 21.7 (t), 24.5 (t), 27.2 (t), 32.4 (t), 33.9 (t), 41.3 (t), 61.9 (t), 64.3 (t), 98.0 (s), 103.5 (s), 118.7 (d), 123.1 (d), 123.4 (d), 123.7 (d), 125.2 (d), 129.3 (d), 129.6 (d), 130.6, 131.0, 131.8 (d), 143.0 (s), 145.9 (s), 169.0 (s), 174.3 (s)
9g	0.2—0.8 (1H, m), 1.1—1.5 (2H, m), 1.5—3.0 (10H, m), 3.2—3.7 (1H, m), 3.75 (1H, s, OH), 3.7—4.5 (5H, m), 6.25 (1H, d, $J=7$ Hz, ArH), 7.1—7.6 (5H, m, ArH), 7.6—7.8 (1H, m, ArH), 8.1—8.3 (1H, m, ArH)	17.9 (t), 20.3 (t) × 2, 24.3 (t), 28.8 (t), 33.5 (t), 35.1 (t), 37.7 (d), 39.0 (t), 62.2 (t), 93.2 (s), 115.1 (d), 118.0 (d), 121.6 (s), 122.5 (d), 123.1 (d), 123.4 (d), 125.0 (d), 127.9 (s), 129.7 (d), 130.3 (s), 131.3 (s), 131.7 (d), 137.2 (s), 145.4 (s), 167.7 (s), 173.9 (s), 175.1 (s)
8h	1.1—2.9 (32H, m), 3.5—4.3 (4H, m), 6.3—6.5 (2H, m, ArH), 6.7—7.3 (4H, m, ArH), 7.57 (1H, d, $J=8$ Hz, ArH), 8.22 (1H, d, $J=8$ Hz, ArH)	17.9 (t), 18.5 (t), 20.5 (t), 24.8 (t), 25.1 (t), 26.4 (t), 27.4 (t), 27.9 (t), 28.3 (t), 32.9 (t), 33.3 (t), 35.5 (t), 43.1 (t), 60.9 (t), 64.0 (t), 98.5 (s), 103.4 (s), 116.9 (d), 122.4 (d), 123.2 (d), 124.0 (d), 124.8 (d), 129.4 (d), 129.6 (d), 130.4 (s), 131.4 (d), 143.3 (s), 145.8 (s), 168.0 (s), 172.6 (s), 173.1 (s)
9h[a]	0.1—0.3 (1H, m), 1.2—2.6 (27H, m), 3.1—3.5 (3H, m), 3.7—3.9 (1H, m), 4.1—4.3 (2H, m, OCH$_2$–), 4.5 (1H, br s, =C–CH–), 6.57 (1H, d, $J=7$ Hz, ArH), 6.71 (1H, s, OH), 7.25 (1H, t, $J=7$ Hz, ArH), 7.3—7.5 (4H, m, ArH), 7.71 (1H, d, $J=8$ Hz, ArH), 7.76 (1H, d, $J=7$ Hz)	16.7 (t), 19.8 (t), 20.8 (t), 24.9 (t), 25.4 (t), 26.6 (t), 28.1 (t), 28.2 (t), 28.3 (t), 28.4 (t), 28.5 (t), 28.7 (t), 34.2 (t), 38.8 (t), 38.9 (d), 64.4 (t), 93.4 (s), 115.8 (d), 119.2 (d), 122.6 (s), 123.1 (d), 123.4 (d), 123.8 (d), 124.9 (d), 129.4 (d), 130.8 (s), 131.3 (d), 132.2 (s), 134.4 (s), 136.1 (s), 146.1 (s), 167.7 (s), 172.8 (s), 175.8 (s)
11	1.0—2.3 (24H, m), 2.44 (3H, s, COCH$_3$), 3.4—4.4 (4H, m), 5.96 (1H, d, $J=7$ Hz, ArH), 6.51 (1H, d, $J=7$ Hz, ArH), 6.72 (1H, s), N–CH–O), 6.9—7.5 (4H, m, ArH), 7.69 (1H, d, $J=7$ Hz, ArH), 8.38 (1H, d, $J=8$ Hz, ArH)	19.7 (t), 23.8 (q), 24.1 (t), 25.8 (t), 26.6 (t), 27.0 (t), 27.4 (t), 28.3 (t), 28.8 (t), 29.5 (t), 32.8 (t), 42.9 (t), 63.8 (s), 64.3 (t), 93.2 (d), 104.2 (s), 117.8 (d), 122.6 (d), 124.4 (d), 125.9 (d), 129.9 (d), 130.2 (d), 130.7 (s), 131.1 (d), 131.7 (d), 141.4 (s), 143.8 (s), 167.8 (s), 169.0 (s), 173.3 (s)

a) Taken on a JEOL FX-400 spectrometer.

70—230 mesh).

N-[6-(1,3-Dihydro-1,3-dioxo-2H-isoindol-2-yl)hexanoyl]-1,2,3,4-tetrahydro-9H-carbazole (1a) A solution of 1,2,3,4-tetrahydrocarbazole (4.30 g, 25 mmol) in dimethylformamide (DMF) (30 ml) was added dropwise to a stirred suspension of KH (1.20 g, 30 mmol) in DMF (100 ml) at -30 °C. The mixture was stirred for 1.5 h, then 6-phthalimidohexanoyl chloride {prepared from 6-phthalimidohexanoic acid [6-(1,3-dihydro-1,3-dioxo-2H-isoindol-2-yl)hexanoic acid][10] (6.52 g, 25 mmol) and thionyl chloride (11.90 g, 100 mmol) in dry benzene (60 ml)} in DMF (20 ml) were added dropwise to the reaction mixture at -40—-50 °C. The reaction mixture was slowly warmed to room temperature, then poured into saturated NH_4Cl solution, and the aqueous mixture was extracted with $CHCl_3$. The $CHCl_3$ extracts were washed with brine, dried over $MgSO_4$, and evaporated. The residue was purified by column chromatography on silica gel using AcOEt–hexane (1 : 4, v/v) as the eluant to give **1a** (7.08 g, 68%). Melting points and analytical data of phthalimide derivatives (**1a**—**h**, **3**, **6**, **10** and **12**) are listed in Table I.

N-[7-(1,3-Dihydro-1,3-dioxo-2H-isoindol-2-yl)heptanoyl]-1,2,3,4-tetrahydro-9H-carbazole (1b) i) Diethyl malonate (16.00 g, 100 mmol) was added to an ice-cooled suspension of 55% NaH (2.18 g, 50 mmol) in dry DMF (30 ml) and the mixture was stirred for 30 min. 1,5-Dibromopentane (23.00 g, 100 mmol) was added at -30 °C, then the reaction mixture was slowly warmed to room temperature, and stirred overnight. Water was added to the reaction mixture, and the product was extracted with Et_2O. The organic layer was washed with brine and dried over $MgSO_4$. After evaporation of the solvent *in vacuo*, distillation of the oily residue gave 5-bromopentylmalonic acid diethyl ester (10.20 g, 66%). $bp_{0.9}$ 157—162 °C (lit.[11] bp_3 159—161 °C).

ii) A mixture of the resulting 5-bromopentylmalonic acid diethyl ester (3.63 g, 11.7 mmol) and potassium phthalimide (2.17 g, 11.7 mmol) in DMF (20 ml) was warmed at 80—90 °C for 1 h. The reaction mixture was diluted with water and extracted with AcOEt. The organic layer was washed with brine, dried ($MgSO_4$) and concentrated. Chromatography on silica gel with AcOEt–hexane (1 : 3, v/v) as the eluent gave 5-phthalimidopentylmalonic acid diethyl ester (3.35 g, 76%), mp 29.5—32 °C.

iii) Aqueous 5 N NaOH (20 ml) was added dropwise to a stirred solution of the above malonate (8.00 g, 21 mmol) in dioxane (20 ml), and the mixture was refluxed for 2 h. After removal of the dioxane, concentrated HCl (8.5 ml) was added to the residue, then the water layer was siphoned off, and the oil obtained was heated at 180 °C for 12 min to give the decarboxylated product [7-phthalimidoheptanoic acid, 4.88 g, 84%, mp 112.5—114 °C, (lit.[12] 113—114 °C)]. Next, the title compound was prepared according to the procedure described for **1a**. The product **1b** was purified by column chromatography on silica gel (CH_2Cl_2–hexane, v/v). Yield, 81%.

N-[8-(1,3-Dihydro-1,3-dioxo-2H-isoindol-2-yl)octanoyl]-1,2,3,4-tetrahydro-9H-carbazole (1c) Compound **1c** was obtained by the same method as described for the preparation of **1b**, but with 1,6-dibromohexane in place of 1,5-dibromopentane. 6-Bromohexyl malonic acid diethyl ester: bp_1 167 °C (lit.[11] bp_3 164 °C). 8-Phthalimidooctanoic acid: mp 90—91 °C (lit.[13] mp 89—90 °C). The title compound was purified by column chromatography on silica gel (CH_2Cl_2–hexane, 2 : 1, v/v). Yield, 78%.

N-[9-(1,3-Dihydro-1,3-dioxo-2H-isoindol-2-yl)nonanoyl]-1,2,3,4-tetrahydro-9H-carbazole (1d) Compound **1d** was obtained by the same method as described for the preparation of **1b**, but with 1,7-dibromoheptane in place of 1,5-dibromopentane. 7-Bromoheptyl malonic acid diethyl ester: bp_2 170—173 °C (lit.[14] bp_1 187 °C). 9-Phthalimidononanoic acid: mp 89—91 °C (lit.[12] mp 91—92.5 °C). The product **1d** was purified by column chromatography (CH_2Cl_2–hexane, 2 : 1, v/v). Yield, 60%.

N-[11-(1,3-Dihydro-1,3-dioxo-2H-isoindol-2-yl)undecanoyl]-1,2,3,4-tetrahydro-9H-carbazole (1e) i) A mixture of 11-bromoundecanoic acid (7.95 g, 30 mmol) and thionyl chloride (11.00 g, 92 mmol) in benzene (60 ml) was refluxed for 7.5 h. The mixture was concentrated to yield the corresponding acid chloride, which was used for the next reaction without purification.

ii) A solution of 1,2,3,4-tetrahydrocarbazole (3.80 g, 22.2 mmol) in tetrahydrofuran (THF) (20 ml) was added dropwise under an N_2 atmosphere to an ice-cooled stirred suspension of KH (1.00 g, 25 mmol) in THF (60 ml). The mixture was stirred at the same temperature for 30 min, then a solution of the resulting acid chloride in THF (5 ml) was added to it, and the whole was stirred at room temperature for 1 h. The mixture was diluted with water and extracted with AcOEt. The extract was washed with brine, dried ($MgSO_4$) and evaporated. The residue was chromatographed on silica gel with acetone–hexane (1 : 10, v/v) to give N-(11-bromoundecanoyl)-1,2,3,4-tetrahydro-9H-carbazole as a solid (4.00 g, 43%). Recrystallization from AcOEt–hexane afforded colorless prisms, mp 66—67 °C. IR (Nujol): 1685 cm^{-1}. ^1H-NMR ($CDCl_3$) δ: 1.1—1.6 (12H, m), 1.6—2.1 (8H, m), 2.5—2.8 (2H, m), 2.8—3.2 (4H, m), 3.41 (2H, t, $J=7$ Hz, $-CH_2Br$), 7.2—7.5 (3H, m, ArH), 7.9—8.1 (1H, m, ArH). MS m/z: 417 (M^+-1), 419 (M^++1). *Anal.* Calcd for $C_{23}H_{32}BrNO$: C, 66.02; H, 7.71; N, 3.35. Found: C, 66.08; H, 7.71; N, 3.30.

iii) A mixture of the resulting bromide (2.51 g, 6.0 mmol) and potassium phthalimide (1.22 g, 6.6 mol) in DMF (60 ml) was stirred at 80—90 °C for 1 h. The reaction mixture was poured into water and extracted with AcOEt. The extract was washed with brine, dried ($MgSO_4$) and evaporated. The residue was chromatographed on silica gel using AcOEt–hexane (1 : 5, v/v) as the eluant to give **1e** (2.64 g, 91%).

N-[11-(1,3-Dihydro-1,3-dioxo-2H-isoindol-2-yl)undecanoyl]-5,6,7,8,-9,10-hexahydrocyclohept[*b*]indole (1f) Compound **1f** was obtained by the same method as described for the preparation of **1e**, but with 2,3-cycloheptenoindole[15] in place of 1,2,3,4-tetrahydrocarbazole. N-(11-Bromoundecanoyl)-2,3-cycloheptenoindole: mp 59—60 °C. IR (Nujol): 1675 cm^{-1}. ^1H-NMR ($CDCl_3$) δ: 1.1—1.6 (12H, m), 1.6—2.2 (10H, m), 2.6—3.3 (6H, m), 3.40 (2H, t, $J=7$ Hz, $-CH_2Br$), 7.2—7.6 (3H, m, ArH), 7.7—8.0 (1H, m, ArH). *Anal.* Calcd for $C_{24}H_{34}BrNO$: C, 66.66; H, 7.93; N, 3.24. Found: C, 66.54; H, 7.95; N, 3.32. The product **1f** was purified by column chromatography (acetone : hexane = 1 : 5). Yield, 93%.

3′-(1,3-Dihydro-1,3-dioxo-2H-isoindol-2-yl)propyl 5-Oxo-5-(1,2,3,4-tetrahydro-9H-carbazol-9-yl)pentanoate (1g) i) A solution of 1,2,3,4-tetrahydrocarbazole (8.55 g, 50 mmol) in DMF (30 ml) was added dropwise under an N_2 atmosphere to a stirred suspension of KH (2.40 g, 60 mmol) in DMF (120 ml) at -30—-40 °C. The mixture was stirred at room temperature for 30 min, then a solution of glutaric anhydride (5.70 g, 50 mmol) in DMF (50 ml) was added to it at -30—-40 °C. The reaction mixture was slowly warmed to room temperature, and stirred at room temperature for 30 min. The mixture was diluted with water, neutralized to pH 7.0 with concentrated HCl, and then extracted with $CHCl_3$. The extract was washed with brine and dried ($MgSO_4$). Solvents ($CHCl_3$ and DMF) were evaporated off, and the residue was chromatographed on silica gel (AcOEt–hexane, 1 : 1, v/v) to give 5-oxo-5-(1,2,3,4-tetrahydro-9H-carbazol-9-yl)pentanoic acid (4.80 g, 34%). Colorless needles, mp 167.5—169 °C (EtOH). IR (Nujol): 2700, 1695, 1680 cm^{-1}. ^1H-NMR ($CDCl_3$) δ: 1.7—2.0 (4H, m), 2.0—2.3 (2H, m), 2.4—2.8 (4H, m), 2.8—3.2 (4H, m), 7.0—7.4 (3H, m, ArH), 7.8—8.1 (1H, m, ArH). *Anal.* Calcd for $C_{17}H_{19}NO_3$: C, 71.56; H, 6.71; N, 4.91. Found: C, 71.39; H, 6.70; N, 4.85.

ii) A mixture of the resulting carbazole derivative (1.73 g, 6 mmol) and N,N'-dicyclohexylcarbodiimide (DCC, 1.23 g, 6 mmol) in dry CH_2Cl_2 (20 ml) was stirred at room temperature for 5 min, then N-(3-hydroxypropyl)phthalimide[16] (1.23 g, 6 mmol) and 4-pyrrolidinopyridine (90 mg, 0.6 mmol) were added, and the stirring was continued for 1 h. After removal of precipitated urea by filtration, the mother liquor was concentrated and subjected to column chromatography (AcOEt–hexane, 1 : 1, v/v) to give **1g** (2.74 g, 97%).

11-(1,3-Dihydro-1,3-dioxo-2H-isoindol-2-yl)undecyl 5-Oxo-5-(1,2,3,4-tetrahydro-9H-carbazol-9-yl)pentanoate (1h) Compound **1h** was obtained by the same method as described for the preparation of **1g**, but with N-(11-hydroxyundecyl)phthalimide[17] in place of N-(3-hydroxypropyl)phthalimide. The product **1h** was purified by column chromatography (AcOEt–hexane, 1 : 5, v/v). Yield, 78%.

N-[7-(1,3-Dihydro-1,3-dioxo-2H-isoindol-2-yl)heptanoyl]-2-methyl-1H-indole (3) Compound **3** was obtained by the same method as described for the preparation of **1b**, but with 2-methylindole in place of 1,2,3,4-tetrahydrocarbazole. The product **3** was purified by column chromatography (AcOEt–hexane, 1 : 4, v/v). Yield, 47%.

N-[7-(1,3-Dihydro-1,3-dioxo-2H-isoindol-2-yl)heptanoyl]-3-methyl-1H-indole (6) Compound **6** was obtained by the same method as described for the preparation of **1b**, but with 3-methylindole in place of 1,2,3,4-tetrahydrocarbazole. The product **6** was purified by column chromatography (AcOEt–hexane, 1 : 5, v/v). Yield, 68%.

11-(1,3-Dihydro-1,3-dioxo-2H-isoindol-2-yl)undecyl 4-(N-Acetyl-1H-indol-3-yl)butanoate (10) Compound **10** was prepared from 4-(1H-indol-3-yl)butyric acid (3.05 g, 15 mmol), N-(11-hydroxyundecyl)phthalimide (4.76 g, 15 mmol) and DCC (3.09 g, 15 mmol) in the presence of 4-pyrrolidinopyridine (222 mg, 1.5 mmol) according to the esterification procedure described for the preparation of **1g**. The crude product was purified by column chromatography (AcOEt–hexane, 1 : 3, v/v) to give 11-(1,3-dihydro-1,3-dioxo-2*H*-isoindol-2-yl)undecyl 4-(1*H*-indol-3-yl)butanoate. Yield, 91%; pale yellow oil. IR (neat): 3380, 1765, 1715 (sh) and 1700 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 1.1—1.9 (18H, m), 1.9—2.2 (2H, m), 2.2—2.5 (2H, m), 2.78 (2H, t, $J=7$ Hz), 3.5—3.8 (2H, m, N–CH$_2$–), 4.00 (2H, t, $J=6$ Hz, OCH$_2$–), 6.8—7.4 (4H, m, ArH), 7.4—7.9 (5H, m, ArH), 7.9—8.2 (1H, m, NH). High resolution MS (HR-MS) *m/z*: Calcd for $C_{31}H_{38}N_2O_4$: 502.2831 (M$^+$). Found: 502.2821.

Next, the ester (6.51 g, 13 mmol) was refluxed with acetic anhydride (10 ml) in the presence of K_2CO_3 (897 mg, 6.5 mmol) in DMF (20 ml) for 1 h. The reaction mixture was poured into ice-water, and extracted with AcOEt, then the organic layer was washed with brine, dried over Na_2SO_4 and evaporated. The residue was subjected to column chromatography (hexane–acetone, 3 : 1, v/v) to give **10** (6.46 g, 91%). Yield, 91%.

(*N*-Acetyl-1*H*-indol-2-yl)methyl 11-(1,3-Dihydro-1,3-dioxo-2*H*-isoindol-2-yl)undecanoate (12) 2-Hydroxymethylindole$^{18)}$ (4.26 g, 29 mmol) was acylated with 11-bromoundecanoic acid (7.68 g, 29 mmol) in the presence of DCC (6.58 g, 32 mmol) and 4-pyrrolidinopyridine (450 mg, 2.9 mmol) to give (1*H*-indol-2-yl)methyl 11-bromoundecanoate (10.9 g, 95%) according to the esterification procedure described for the preparation of **1g**, mp 63—64 °C. IR (Nujol): 3350, 1700 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 0.9—2.0 (16H, m), 2.35 (2H, t, $J=7$ Hz, CH$_2$CO), 3.39 (2H, t, $J=7$ Hz, CH$_2$Br), 5.22 (2H, s, CH$_2$OCO), 6.4—6.6 (1H, m, ArH), 7.0—7.4 (3H, m, ArH), 7.5—7.7 (1H, m, ArH), 8.4—8.7 (1H, m, NH). Next, a mixture of the resulting ester (7.50 g, 19 mmol) and potassium phthalimide (3.50 g, 19 mmol) in DMF (100 ml) was warmed at 90—100 °C for 1 h, giving (1*H*-indol-2-yl)methyl 11-(1,3-dihydro-1,3-dioxo-2*H*-isoindol-2-yl)undecanoate (7.25 g, 83%), mp 106—108 °C. IR (Nujol): 3350, 1770, 1720 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 1.0—2.0 (16H, m), 2.1—2.5 (2H, m), 3.67 (2H, t, $J=7$ Hz, N–CH$_2$), 5.22 (2H, s, CH$_2$OCO), 6.4—6.6 (1H, br s, C=CH), 6.9—8.0 (8H, m, ArH), 8.5—8.9 (1H, m, NH). The resulting phthalimide derivative was acetylated according to the method described for the preparation of **10**. The product **12** was purified by column chromatography (AcOEt–hexane, 1 : 3, v/v). Yield, 87%.

Photoreactions of 1a—h, 3, 6, 10 and 12 General Procedure: A solution of an indole derivative (**1a**—**g**, **3**, **6**, **10**, **12**, 10 mM, and **1h**, 5 mM) in acetone was irradiated with a 500 W high-pressure mercury lamp through a Pyrex filter at room temperature. After removal of the solvent *in vacuo*, the residue was subjected to silica gel column chromatography. The solvent systems used were as follows: **2a**, **b**, AcOEt : hexane = 2 : 1, v/v; **8c**, **9c**, **8g**, **9g**, AcOEt : hexane = 1 : 2, v/v; **8d**, **9d**, **8h**, **9h**, **11**, AcOEt : hexane = 1 : 3, v/v; **8e**, **9e**, **8f**, AcOEt : hexane = 1 : 5, v/v; **4**, **5**, **7**, AcOEt : hexane = 2 : 3, v/v.

Acknowledgement We are indebted to Mrs. H. Mukai and Miss S. Mikami for technical assistance in some of the experiments.

References

1) *a*) Photochemistry of the Phthalimide System, XLIV. Part XLIII, Y. Sato, H. Nakai, M. Wada, T. Mizoguchi, Y. Hatanaka, Y. Kanaoka, *Chem. Pharm. Bull.*, **40**, 3174 (1992); *b*) Photoinduced Reactions CXXII. Part CXXI: ref. 1*a*).
2) Y. Kanaoka, *Acc. Chem. Res.*, **11**, 407 (1978).
3) *a*) Y. Sato, H. Nakai, T. Mizoguchi, Y. Hatanaka, Y. Kanaoka, *J. Am. Chem. Soc.*, **98**, 2349 (1976); *b*) M. Wada, H. Nakai, K. Aoe, K. Kotera, Y. Sato, Y. Hatanaka, Y. Kanaoka, *Tetrahedron*, **39**, 1273 (1983).
4) M. Machida, H. Takechi, Y. Kanaoka, *Chem. Pharm. Bull.*, **30**, 1579 (1982).
5) M. Machida, K. Oda, Y. Kanaoka, *Tetrahedron*, **41**, 4995 (1985).
6) H. Takechi, M. Machida, Y. Kanaoka, *Chem. Pharm. Bull.*, **36**, 3770 (1988).
7) H. Takechi, M. Machida, Y. Kanaoka, *Chem. Pharm. Bull.*, **36**, 2853 (1988).
8) H. Takechi, M. Machida, Y. Kanaoka, *Justus Liebigs Ann. Chem.*, **1986**, 859.
9) K. Oda, E. Yoshida, K. Ohno, M. Machida, Y. Kanaoka, *Chem. Pharm. Bull.*, **37**, 642 (1986).
10) N. Ž. Stanaćev, M. Proštenik, *Arhiv Kem.*, **27**, 203 (1955) [*Chem. Abstr.*, **50**, 11985*e* (1956)].
11) F. S-Legagneur, C. Neveu, *Bull. Soc. Chim. Fr.*, **1956**, 1345.
12) F. K. Velichko, N. A. Kuz'mina, L. D. Ermolaeva, *Zh. Prikl. Khim.*, **38**, 153 (1965) [*Chem. Abstr.*, **62**, 13036*a* (1965)].
13) J. M. Chapman, Jr., G. H. Cocolas, I. H. Hall, *J. Pharm. Sci.*, **72**, 1344 (1983).
14) F. S-Legagneur, C. Neveu, A. Belot, *Bull. Soc. Chim. Fr.*, **1957**, 1463.
15) A. G. Anderson, Jr., J. Tazuma, *J. Am. Chem. Soc.*, **74**, 3455 (1952).
16) R. L. Markus, J. G. O'Brien, *J. Org. Chem.*, **30**, 2063 (1965).
17) P. B-Bobillo, A. Bienvenue, C. Broquet, L. Maurin, *Chem. Phys. Lipids*, **37**, 215 (1985).
18) W. J. Brehm, *J. Am. Chem. Soc.*, **71**, 3541 (1949).