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Photocyclization of ω-Anilinoalkylphthalimides: A Photochemical Macrocyclic Synthesis[1]

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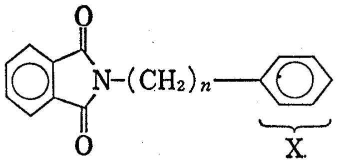
Upon irradiation, a homologous series of *N*-[ω-(methylanilino)alkyl]phthalimides **5**, having a nonconjugated bichromopholic system, undergoes regioselective remote photocyclization to give medium- to large-sized (up to twenty-two-membered) diazacyclols **6**.

Keywords——*N*-[ω-(methylanilino)alkyl]phthalimide; bichromopholic system; diazacyclol; charge transfer; electron transfer; electron donor–acceptor pair system; remote photocyclization

The photochemistry of imide carbonyl compounds has been extensively investigated and has generated considerable interest.[2] We have previously found that, in the photolysis of *N*-aralkylphthalimides **1** (X=electron-donating substituents), the cyclization occurred most smoothly when *n* was 4, where a usually unfavorable 8-membered transition state could be formed.[3] Furthermore, certain phthalimides **2** possessing a terminal sulfide function in their *N*-alkyl side chain undergo unusually facile regioselective remote photocyclization to give macrocyclic azathiacyclols **3**.[2,4] We have already reported in our preliminary communication an additional new example of the photocyclization of such bichromophoric systems, in which an anilino group acts as the second chromophore.[5] The present report is concerned with the detailed results of further research on this system.



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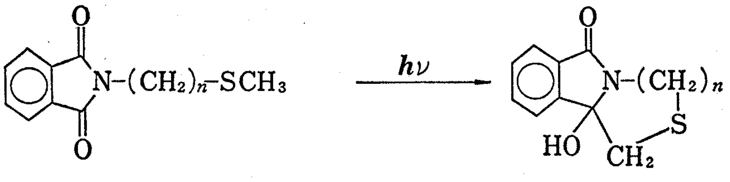


2 **3**

Chart 1

N-(ω-Bromoalkyl)phthalimides **4**, prepared from potassium phthalimide and an excess of dibromoalkanes, were treated with *N*-methylaniline in *N*,*N*-dimethylformamide (DMF) to give *N*-[ω-(*N*′-methylanilino)alkyl]phthalimides **5** (n=2,3,4....16) (Chart 2 and see "Experimental"). Compound **5a** was prepared from phthalimide by means of the Mannich reaction.[6] Melting points and analytical data of these phthalimides are listed in Table I.

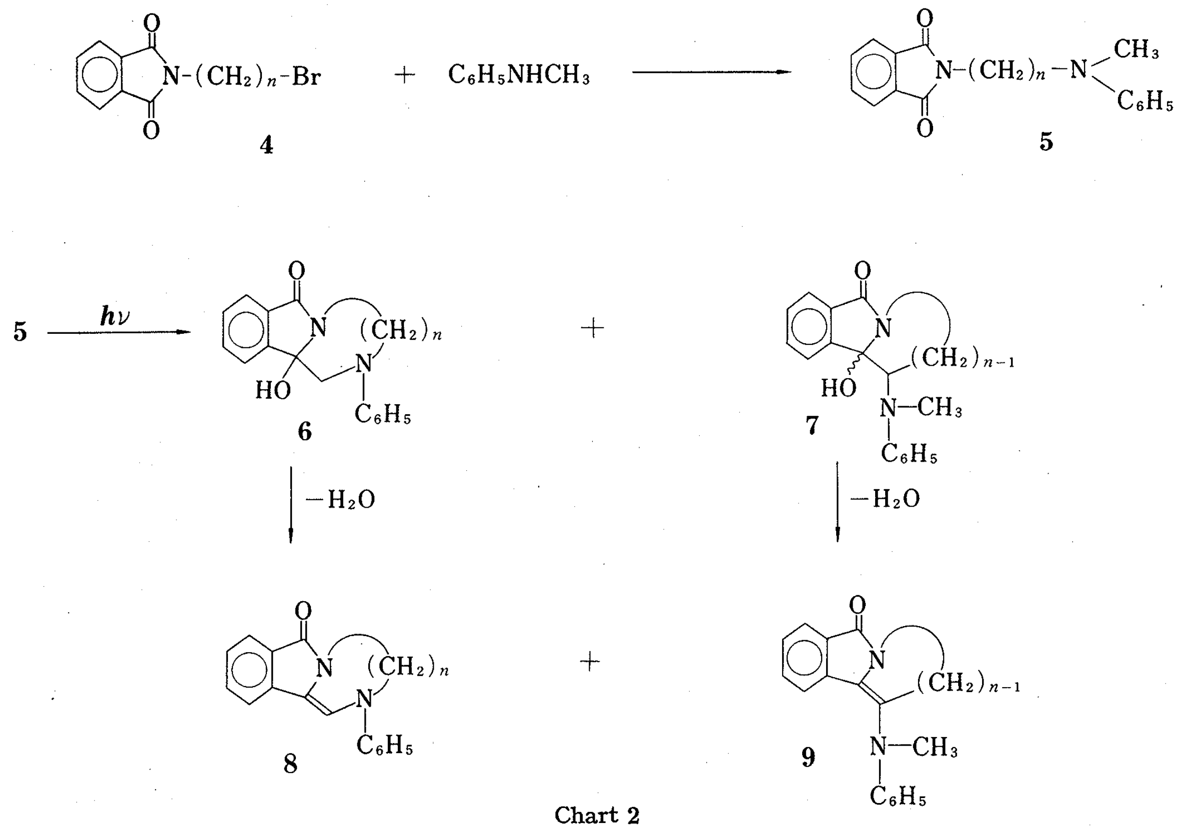
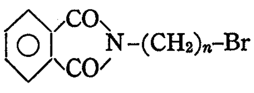


Chart 2

TABLE I. Preparation of Phthalimide Derivatives



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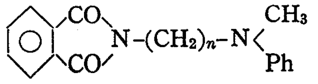

5

	n	4 mp °C (lit. mp °C)	5 mp °C (lit. mp °C)	Formula	Analysis (%) Calcd C	Calcd H	Calcd N	Found C	Found H	Found N
a	1		92—95 (93)[d]	$C_{16}H_{14}N_2O_2$	72.16	5.30	10.52	72.42	5.44	10.44
b	2	78—79 (81—82)[a]	108—109 (107—109)[e]	$C_{17}H_{16}N_2O_2$	72.84	5.75	9.99	72.77	5.93	10.05
c	3	72—74 (71—73)[a]	76.5—78 (75)[f]	$C_{18}H_{18}N_2O_2$	73.45	6.16	9.52	73.50	6.12	9.61
d	4	78—79 (80)[a]	69—71	$C_{19}H_{20}N_2O_2$	74.00	6.54	9.09	73.99	6.51	9.16
e	5	57—59 (61)[b]	30—32	$C_{20}H_{22}N_2O_2$	74.51	6.88	8.69	74.43	7.04	8.58
f	6	52—54 (58)[b]	46—47	$C_{21}H_{24}N_2O_2$	74.97	7.19	8.33	75.25	7.07	8.28
g	10	59.5—61 (56)[b]	56—58	$C_{25}H_{32}N_2O_2$	76.49	8.22	7.14	76.54	8.18	7.11
h	12	63.5—64.5 (56—58)[c]	30—30.5	$C_{27}H_{36}N_2O_2$	77.10	8.63	6.66	77.00	8.63	6.49
i	18	65—67	39.5—41	$C_{33}H_{48}N_2O_2$	78.52	9.59	5.55	78.82	9.40	5.67

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b) W. Dirscherl and F.W. Weingarten, *Ann. Chem.*, **574**, 131 (1951).
c) R.B. Barlow, H. Blaschko, J.M. Himms, and U. Trendelenburg, *Brit. J. Pharmacol.*, **10**, 116 (1955).
d) H.W. Heine *et al.*, see ref. 7).
e) S.I. Lur'e, *Zhur. Obshchec Khim.* (*J. Gen. Chem.*), **22**, 265 (1952) [*C.A.*, **47**, 1626 (1953)].
f) K. Nakazima, *Nippon Kagaku Zasshi*, **81**, 1746 (1960).

In order to investigate the solvent effect on the photoreaction, **5c** (n=3) as a typical substrate and various solvents were used (Table II). The irradiation of **5c** in methanol or acetonitrile proceeded extremely slowly, while in acetone the reaction was a little faster but the recovery of **5c** was very poor. In the photolysis in a petroleum ether solution the yield of **6c** was still low but with much better recovery of **5c**. Therefore, in view of the reaction efficiency and the solubility, a mixture of acetone and petroleum ether was selected.

TABLE II. Photolysis of **5c** in Various Solvents

Solvent	Reaction time (h)	Yield (%) of product (**6c**)	Recovery of **5c** (%)
Acetone	0.5	21	11
Petroleum ether: Acetone (2.7: 1 v/v)	2	20	63
Petroleum ether	2	16	71
Petroleum ether: EtOH (2.7: 1 v/v)	2	15	80
MeOH	8	Trace	92
CH_3CN	8	Trace	95

Typical photolysis of **5** was run on 20—36 mM solutions in a mixture of acetone and petroleum ether using a 500 W high-pressure mercury lamp at room temperature for 0.5—2.5 h. In all cases studied the photolyses afforded the expected cyclized products **6** in yields of 6—20% (see Table III) as a result of C–C bond formation between the imide carbonyl and the *N*-methyl group, and included compounds with a ring size of up to twenty-two members (**6i**). Their structural assignments were supported by the following spectral data.

In the IR spectra of **6a**—**i**, the bands in the regions of 3150—3360 cm^{-1} and 1660—1680 cm^{-1} indicated the presence of the cyclol and lactam moieties, respectively. In the ^{1}H-NMR

TABLE III. Photoproducts from **5**

Substrate	n	Ring size	Irradiation time (h)	mp[a] (°C)	Yield (%)	Recovery of **5** (%)	Products **6** Formula	Analysis (%) Calcd (Found) C	H	N
5a	1	5	1.5	177—178.5	13	83	$C_{16}H_{14}N_2O_2$	72.16 (72.10	5.30 5.35	10.52 10.46)
5b	2	6	2	169—170.5	12	61	$C_{17}H_{16}N_2O_2$	72.84 (72.96	5.75 5.73	9.99 10.05)
5c	3	7	2	206—207.5	20	63	$C_{18}H_{18}N_2O_2$	73.45 (73.62	6.16 6.24	9.52 9.44)
5d	4	8	2.5	207.5—209	6	73	$C_{19}H_{20}N_2O_2$	74.00 (74.16	6.54 6.48	9.09 9.09)
	4	6 (**7d**)		199—201	5		$C_{19}H_{20}N_2O_2$	74.00 (74.00	6.54 6.46	9.09 9.00)
5e	5	9	1.5	192—194	15	66	$C_{20}H_{22}N_2O_2$	74.51 (74.46	6.88 6.91	8.69 8.70)
5f	6	10	2	159—161	10	51	$C_{21}H_{24}N_2O_2$	74.97 (74.90	7.19 7.16	8.33 8.47)
5g	10	14	2	176—177	8	16	$C_{25}H_{32}N_2O_2$	76.49 (76.53	8.22 8.32	7.14 7.07)
5h	12	16	2	191—192	9	22	$C_{27}H_{36}N_2O_2$	77.10 (76.90	8.63 8.64	6.66 6.70)
5i	18	22	0.5	123—125[b]	9	14	$C_{33}H_{48}N_2O_2$	78.52 (78.51	9.59 9.63	5.55 5.61)

[a] All products were recrystallized from ethanol to give colorless prisms or needles.
[b] Recrystallized from CH_2Cl_2–hexane.

spectra, a singlet (1H) at δ 4.27—5.88 (**6a**—**f**), exchangeable with D_2O, was assigned to a hydroxyl group. Since the integrated values of the band area at δ 2.8—4.1, 2.8—3.8, and 3.0—3.8 for **6g**, **6h**, and **6i**, respectively, decreased on treatment with D_2O, it seems that the peak of the exchangeable hydrogen in **6g**—**i** is buried in a complex multiplet at the above regions.

TABLE IV. Spectral Data for Photoproducts **6**

Products	IR $\nu_{\max}^{\text{Nujol}}$ (cm^{-1}) (OH, NC=O)	UV $\lambda_{\max}^{\text{EtOH}}$ nm (ε)	MS (M^+, M^+-18)	^{1}H-NMR (in $CDCl_3$, δ)
6a	3360 1680	248(25400) 285(3000)	266 248	3.38 and 3.86 (2H, dd, $J=10$ Hz, N-C$\underline{\text{H}}_2$-C-OH), 4.65 and 5.10 (2H, dd, $J=7$ Hz, CO-N-C$\underline{\text{H}}_2$-N), 5.88 (1H, s, OH), 6.5—8.0 (9H, m, aromatic H)
6b	3300 1680	230(12400) 251(17000)	280 262	2.63 and 4.07 (2H, dd, $J=12$ Hz, N-C$\underline{\text{H}}_2$-C-OH), 4.48 (1H, s, OH), 6.8—7.8 (9H, m, aromatic H)
6c	3250 1675	230(10100) 251(17000) 300(2800)	294 276	1.6—2.1 (2H, m, CO-N-CH$_2$C$\underline{\text{H}}_2$CH$_2$-N), 2.95—3.80 (4H, m, CO-N-C$\underline{\text{H}}_2$CH$_2$C$\underline{\text{H}}_2$-N), 3.93 (2H, s, N-C$\underline{\text{H}}_2$-C-OH), 4.39 (1H, s, OH), 6.45—6.70 (3H, m, aromatic H), 6.90—7.15 (2H, m, aromatic H), 7.3—7.7 (4H, m, aromatic H)
6d	3270 1660	231(11700) 253(21700) 284(3900, sh)	308 290	1.3—2.2 (4H, m, CO-N-CH$_2$-(C$\underline{\text{H}}_2$)$_2$-CH$_2$-N), 4.20 (1H, d, $J=16$ Hz, N-C$\underline{\text{H}}_2$-C-OH), 4.27 (1H, s, OH), 6.5—7.8 (9H, m, aromatic H)
7d	3300 1685	231(10000) 254(19900) 300(2600)	308 290	1.5—2.4 (4H, m, CO-N-CH$_2$-(C$\underline{\text{H}}_2$)$_2$-CH), 2.13 (3H, s, N-Me), 4.13 (1H, s, OH) 6.5—6.9 (3H, m, aromatic H), 7.0—7.5 (6H, m, aromatic H)
6e	3150 1680	231(10500) 253(17300) 284(3500, sh)	322 304	1.3—2.0 (5H, m), 2.0—2.6 (1H, m), 4.25 (1H, d, $J=14$ Hz, N-C$\underline{\text{H}}_2$-C-OH), 4.30 (1H, s, OH), 6.6—8.0 (9H, m, aromatic H)
6f	3250 1670	231(9800) 252(12600) 284(2800, sh)	336 318	1.3—2.3 (8H, m, CO-N-CH$_2$-(C$\underline{\text{H}}_2$)$_4$-CH$_2$-N), 3.97 (1H, d, $J=15$ Hz, N-C$\underline{\text{H}}_2$-C-OH), 4.27 (1H, s, OH), 6.7—7.5 (9H, m, aromatic H)
6g	3250 1680	231(9900) 254(18200) 304(2900, sh)	392 274	0.8—2.3 (16H, m, CO-N-CH$_2$-(C$\underline{\text{H}}_2$)$_8$-CH$_2$-N), 2.8—4.1 (7H, m, containing one hydrogen exchangeable with D_2O), 6.3—7.7 (9H, m, aromatic H)
6h	3250 1680	231(9800) 253(18400) 304(2800)	420 402	0.8—2.0 (20H, m, CO-N-CH$_2$-(C$\underline{\text{H}}_2$)$_{10}$-CH$_2$-N), 2.8—3.8 (6H, m, containing one hydrogen exchangeable with D_2O), 3.95 (1H, d, $J=15$ Hz, N-C$\underline{\text{H}}_2$-C-OH), 6.3—7.7 (9H, m, aromatic H)
6i	3260 1675	231(9800) 253(17900) 284(2900, sh) 301(2700)	504 486	1.0—1.8 (32H, m, CO-N-CH$_2$-(C$\underline{\text{H}}_2$)$_{16}$-N), 3.0—3.8 (6H, m, containing one hydrogen exchangeable with D_2O), 3.98 (1H, d, $J=15$ Hz, N-C$\underline{\text{H}}_2$-C-OH), 6.4—6.8 (3H, m, aromatic H), 6.9—7.7 (6H, m, aromatic H)

Disappearance of the *N*-methyl singlets at δ 2.90—3.10 of **5** in the products **6** confirmed that the *N*-methyl group takes part in the C–C bond formation. Further, the newly formed methylene groups appeared as doublets of doublets at δ 3.38, 3.86 ($J=10$ Hz) and 2.63, 4.07 $J=12$ Hz) in **6a** and **6b**, respectively, and as a singlet at 3.93 in **6c**. In the spectra of **6d**, **6e**, **6f**, **6h**, and **6i**, a half of this methylene group appeared as doublets at δ 4.20, 4.25, 3.97, 3.95, and 3.98, respectively, integrating for only one proton, which indicates that the other proton is buried in other bands. In **6g** the peak due to the newly formed methylene group was not clearly identified.

In order to confirm the cyclol structure **6** chemically, some of the products were treated with alcoholic hydrogen chloride to yield the dehydrated products **8b**—**f** which exhibited only one vinyl proton at δ 6.27—6.86 as a singlet in their ^{1}H-NMR spectra, thus excluding the pos-

TABLE V. Spectral Data for Dehydrated Compounds **8** and **9**

Compd.	mp (°C)	IR $\nu_{\max}^{\text{Nujol}}$ (cm^{-1}) (NC=O)	UV $\lambda_{\max}^{\text{EtOH}}$ nm (ε)	MS (M$^+$)	^{1}H-NMR (in $CDCl_3$, δ)
8b	143—145	1660	265 (9300) 389 (30300)	262	3.63—4.33 (4H, m, $\mathrm{CO{-}N{-}C\underline{H}_2C\underline{H}_2{-}N}$), 6.86 (1H, s, C=CH), 6.9—8.0 (9H, m, aromatic H)
8c	130—132	1665	266 (8600) 381 (31400)	276	2.1—2.4 (2H, m, $\mathrm{CO{-}N{-}CH_2C\underline{H}_2CH_2{-}N}$), 3.85—4.20 (4H, m, $\mathrm{CO{-}N{-}C\underline{H}_2CH_2C\underline{H}_2{-}N}$), 6.83 (1H, s, C=CH), 7.0—7.9 (9H, m, aromatic H)
8d	129—131	1670	256 (16100) 384 (25300)	290	1.5—2.2 (4H, m, $\mathrm{CO{-}N{-}CH_2{-}(C\underline{H}_2)_2{-}CH_2}$), 3.5—3.9 and 3.9—4.2 (4H, m and m, $\mathrm{CO{-}N{-}C\underline{H}_2{-}(CH_2)_2{-}C\underline{H}_2}$), 6.47 (1H, s, C=CH), 6.7—8.0 (9H, m, aromatic H)
9d	160—161	1690	251 (20600) 300 (8200) 321 (7000, sh) 374 (7100)	290	1.9—2.3 (2H, m, $\mathrm{CO{-}N{-}CH_2C\underline{H}_2CH_2}$), 2.42 (2H, t, $J=6$ Hz, $\mathrm{CH_2C\underline{H}_2{-}C{=}C}$), 3.18 (3H, s, N–Me), 3.83 (2H, t, $J=6$ Hz, $\mathrm{CO{-}N{-}C\underline{H}_2{-}CH_2}$), 6.6—6.9 (3H, m, aromatic H), 7.1—7.5 (4H, m, aromatic H), 7.6—7.9 (2H, m, aromatic H)
8e	164—166	1700 1655 (C=C)	254 (23400) 303 (7700) 378 (10000)	304	1.5—2.0 (6H, m, $\mathrm{CO{-}N{-}CH_2{-}(C\underline{H}_2)_3{-}CH_2}$), 3.5—3.7 and 3.8—4.1 (4H, m and m, $\mathrm{CO{-}N{-}C\underline{H}_2{-}(CH_2)_3{-}C\underline{H}_2}$), 6.38 (1H, s, C=CH), 6.7—7.0 (3H, m, aromatic H), 7.1—8.0 (6H, m, aromatic H)
8f	143—144.5	1700 1660 (C=C)	252 (19600) 304 (6500) 380 (11300)	318	1.4—2.1 (8H, m, $\mathrm{CO{-}N{-}CH_2{-}(C\underline{H}_2)_4{-}CH_2}$), 3.62 and 3.99 (4H, t, $J=6$ Hz and t, $J=6$ Hz, $\mathrm{CO{-}N{-}C\underline{H}_2{-}(CH_2)_4{-}C\underline{H}_2{-}N}$), 6.27 (1H, s, C=CH), 6.7—7.0 (3H, m, aromatic H), 7.1—8.0 (6H, m, aromatic H)

sibility of the structure **7**. If the imide carbonyl carbon is joined to the methylene carbon, the dehydrated product **9** should not have the vinyl proton. Physical and spectral data of these dehydrated compounds are listed in Table V.

In the photolysis of **5d** ($n=4$), two products **6d** and **7d** were obtained in yields of 6 and 5%, respectively. In the ^{1}H-NMR spectrum, **7d** had a singlet peak due to three protons at δ 2.13, indicating the presence of the *N*-methyl group. On further treatment of **7d** with HCl-chloroform, a new product was formed which showed the presence of peaks due to *N*-methyl protons but showed no vinyl proton in the ^{1}H- NMR spectrum; it was thus assigned the structure **9d**. From these results, we concluded that the cyclization of **5d** takes dual courses and that the new bond formation of the imide carbonyl occurred at both the *N*-methyl and the methylene carbon atoms of the side chain adjacent to the nitrogen atom of the anilino residue. Interestingly, products such as **7d** were not obtained except from the photolysis of **5d** ($n=4$).

In spectroscopic studies, it is known that there are intramolecular interactions in compounds in which a phthalimide and another chromophore are separated by non-conjugated groups.[7] Davidson and Lewis[8] reported that compounds **5a**—**d** showed charge transfer properties in their absorption spectra. As shown in Fig. 1, we have observed that their higher homologs (**5e**—**i**) also show similar absorption spectra with charge transfer character, but the intensity at around 360 nm decreases with increase in the number of the interposing methylene groups. These measurements were carried out in very dilute solutions by using a 10 cm path length cell so as to minimize possible intermolecular interactions.

In order to study the effect of irradiation wavelength, compound **5c** was selected and irradiation at various wavelengths was carried out by using a monochromator (Fig. 2), since

5c showed a moderate intensity of absorption (Fig. 1), and gave the photo-product in a moderate yield (Table III). The ratios of the product **6c** and recovery of the starting material (**5c**) were plotted against irradiation wavelength. The curve thus obtained (Fig. 2) was very close to the absorption spectrum of **5c**. On a preparative scale, the photolysis of **5c** was carried out for 2 h using a 500 W high-pressure mercury lamp. The combination of a Pyrex glass filter sleeve and a 0.4% aqueous solution of 2,3-dihydro-5,7-dimethyl-1,4-diazepine perchlorate⁹⁾ was used as a filter to isolate wavelengths longer than 340 nm. This photolysis in the longer wavelength region gave the product **6c** in only 1.6% yield, in contrast to the 20% yield of the same product (**6c**) in the absence of the filter. From these results it appears that the photocyclization is not solely a result of irradiation of the charge transfer absorption band.

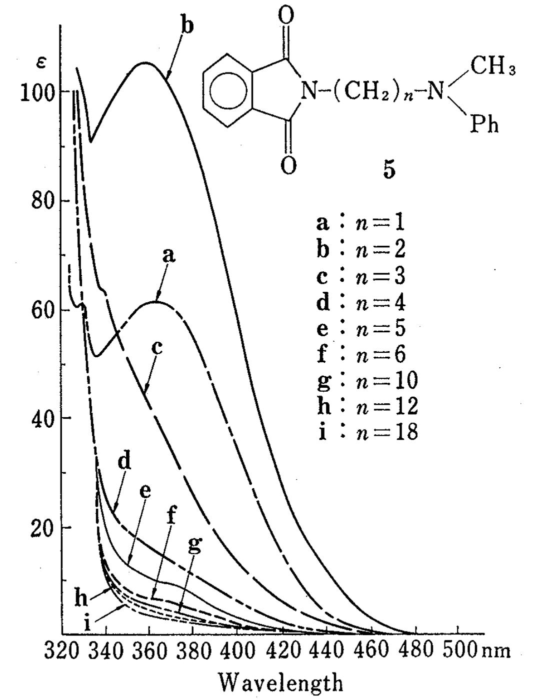


Fig. 1. Absorption Spectra of *N*-[ω-(*N*′-Methylanilino)alkyl]phthalimides (**5**)

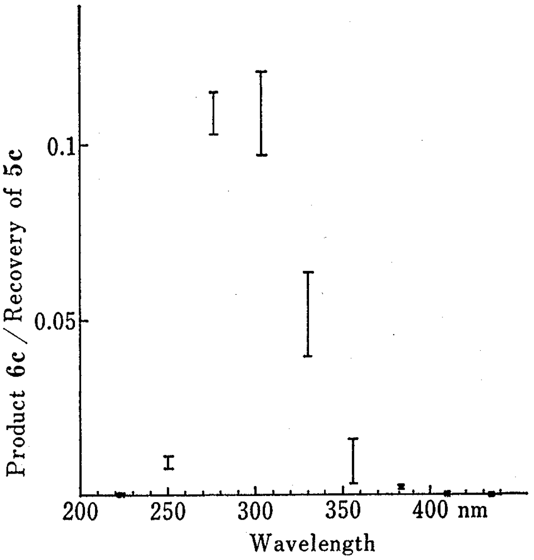
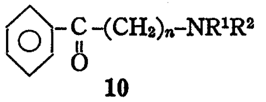


Fig. 2. Wavelength Dependence of the Photocyclization of **5c**

In our study on imide photochemistry, we have applied methodology in which the photochemical behavior of imides is systematically compared with that of simple carbonyls. The parent keto system of **5** in this work is that of aminoketones such as **10**. Wagner *et al.* found that charge transfer quenching of the ketone triplet of **10** by the remote amino group competes with Norrish type II processes.¹⁰ᵃ⁾ Among the type II processes, the major process for **10** was photoelimination, whereas the important photoreaction for **5** was cyclization. It is generally accepted that γ-hydrogen abstraction is a major path for simple carbonyl systems.¹⁰⁾ However, the results in Table III reveal that the reaction takes place, at least formally, by transfer of a hydrogen adjacent to the nitrogen not only to the γ- or the δ- position of the imide carbonyl but also to very remote positions. This behavior of **5** is consistent with our earlier observations of the "cyclophilic" nature²⁾ of phthalimide systems with side chains containing hetero atoms⁴,¹¹,¹²⁾ or aromatic substituents.³,⁵⁾ Cohen first proposed that amines reduce ketone triplets and the resulting radical ions often collapse to radicals by proton transfer (Chart 3).¹³⁾ Such interactions can well occur also with the phthalimide system, both in the intermolecular²,¹⁴⁾ and intramolecular²,⁵⁾ modes. We consider that the present photocyclization reaction resembles the anodic oxidation reactions of the following analogous system:



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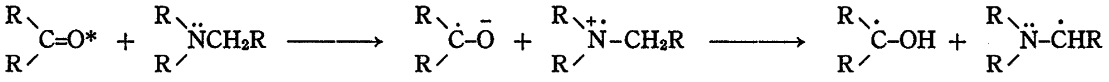


Chart 3

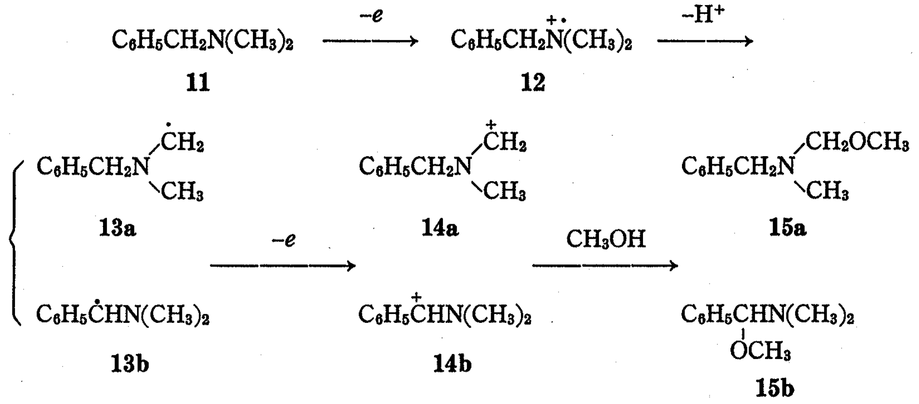


Chart 4

An anodic oxidation of *N*,*N*-dimethylbenzylamine **11** in methanol[15] is initiated by electron transfer from the amine, and the resulting cation radical **12** loses a proton then an electron to give cations **14**, which react with methanol to yield **15**; the *N*-methoxymethyl derivative **15a** is always produced predominantly over the *N*-methyl derivative **15b** (Chart 4). In contrast to *a priori* expectations, the methyl hydrogens in the cation radical **12** are much more reactive than the methylene hydrogens. The preference for attack on the carbon of the *N*-methyl group in the photolysis of **5** in the present work is in good agreement with the results of the above anodic oxidation, so that a similar mechanism may be operating. Although further work is required for an exact understanding of the photoreaction of **5**, the electron transfer mechanism[2,4a,5,14,16] involving a radical ion intermediate such as **12**, shown in Chart 4 seems to account well for the observed reactions.

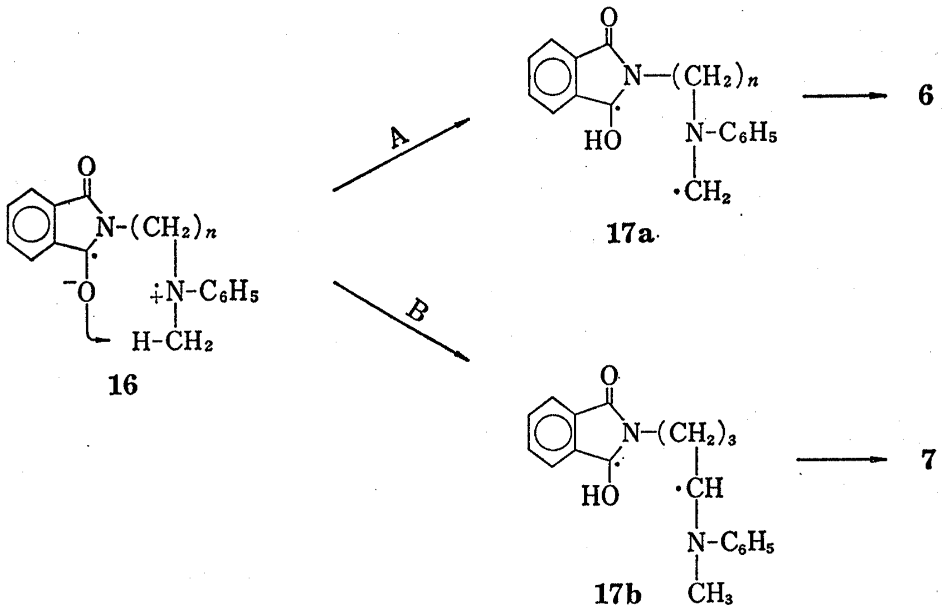
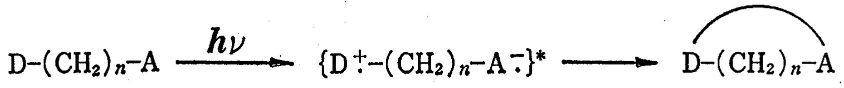


Chart 5



$$D\text{–}(CH_2)_n\text{–}A \xrightarrow{h\nu} \{D^{\dot{+}}\text{–}(CH_2)_n\text{–}A^{\dot{-}}\}^* \longrightarrow D\text{–}(CH_2)_n\text{–}A$$

Chart 6

Much attention has been recently paid to "remote" photoreactions with regard to general theoretical studies of cyclization,[17] as well as to the reactions of non-conjugated bichromophoric systems.[18] It is worth noting that in the photocyclization of the *N*-(ω-anilinoalkyl)-phthalimide system **5** with a flexible long chain, the products **6** with medium and large rings up to twenty-two members are easily formed with regioselectivity. In an electron donor–acceptor (D–A) pair system in which an electron donor (D) and an acceptor (A) are separated by a carbon chain, the exciplex state may be considered as a resonance hybrid of the electron transfer configuration (A^-D^+) mixed with the locally excited configuration (A^*D) or (AD^*)[19] (Chart 6). Our remote photocyclization can also be rationalized in terms of a rapid proton transfer from an amino cation radical **16**, initially formed by an intramolecular electron transfer in **5**, to the phthalimide moieties *via* a charge transfer complex in the excited state.[20] In a subsequent proton transfer step, the formation of **17a** should be faster than that of **17b**, thus giving the products **6** predominantly over **7**. The above assumption, coupled with the results for **1**[3] and **2**,[4a] suggests that further applications of the common working hypothesis "photolysis of donor–acceptor systems" may be fruitful for general synthetic purposes.

Experimental

All melting points were determined on a Yanagimoto micromelting point apparatus, model MP-J3 (a hot-stage type), and are uncorrected. Infrared (IR) spectra were recorded on a Shimadzu IR-400 or a JASCO A-102 spectrometer. Ultraviolet absorption (UV) spectra were measured with a Hitachi 556 double-wavelength double-beam spectrophotometer. Nuclear magnetic resonance (NMR) spectra were obtained with a Hitachi R-40 spectrometer or a JEOL JNM-PMX 60 spectrometer. 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; q, quartet; m, multiplet. Mass spectra (MS) were determined with a Shimadzu-LKB 9000 gas chromatograph–mass spectrometer with a direct inlet system.

Irradiations of phthalimide derivatives were conducted using a 500 W high-pressure mercury lamp and a water-cooled quartz immersion well (Eikosha PIH-500). Stirring of the reaction mixture was effected by the introduction of a stream of nitrogen at the bottom of the outer jacket. All column and thin layer chromatography procedures were conducted using silica gel (Merck, Kieselgel 60, 70—230 mesh) and plates coated with silica gel GF_{254}, respectively. The products were isolated by column and thin layer chromatographies utilizing the following solvent systems: **6a**; CH_2Cl_2, **6b**—**e** and **7d**; CH_2Cl_2: acetone=10: 1 (v/v), **6f**—**h**; benzene: AcOEt=5: 1, **6i**; *n*-hexane: AcOEt=4: 1.

N-(18-Bromooctadecyl)phthalimide (**4i**)——1,18-Dibromooctadecane was prepared from the Grignard reagent (1,6-hexanedimagnesium chloride) and an excess of 1,6-dibromohexane in the presence of a catalytic amount of dilithium tetrachlorocuprate by a modification of the method of Friedman and Shani.[21] The resulting product (77%) had $bp_{0.6}$ 170—180°C, mp 58—60.5°C (from petroleum ether) (lit. mp 60.5—62.5°C).[22] A mixture of potassium phthalimide (2.77 g, 15 mmol) and 1,18-dibromooctadecane (18.3 g, 44 mmol) in 80 ml of *N*,*N*-dimethylformamide was warmed at 80—90°C on the oil bath for 5.5 h, then left to stand overnight at room temperature. A precipitate was filtered off and the filtrate was distilled *in vacuo* until the excess 1,18-dibromooctadecane was no longer removed. The resulting residue was chromatographed over a silica gel column. Elution with CH_2Cl_2 and *n*-hexane (1: 1 v/v) gave 4 g (56%) of **4i** as colorless fine needles of mp 65—67°C.

Syntheses of *N*-[ω-(*N'*-Methylanilino)alkyl]phthalimides (**5**): **General Procedure**——The phthalimide derivative **5a** was prepared from phthalimide, formaldehyde and *N*-methylaniline according to the procedure of Heine *et al.*[6] The other phthalimide derivatives **5b**—**i** were obtained as follows. A mixture of *N*-methylaniline (84 mmol) and ω-bromoalkylphthalimide (**4**) (28 mmol) in *N*,*N*-dimethylformamide (10 ml) was warmed at 80—90°C for 2 h. The solvent and excess *N*-methylaniline were removed *in vacuo*, and the residue was treated with benzene and water. The benzene layer was further washed with water, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The phthalimides **5** were recrystallized from *n*-hexane. The melting points of these phthalimide derivatives are listed in Table I.

Irradiation of 5: General Procedure——A solution of **5** (20—36 mM) in acetone and petroleum ether (2.7: 1, v/v) was irradiated with a 500 W high-pressure mercury lamp for 0.5—2.5 h under a nitrogen atmosphere. After removal of the solvent by evaporation, the residue was chromatographed over silica gel and the products were purified by recrystallization.

Dehydration of 6b: Typical Run——One drop of c. HCl was added to a solution of **6b** (110 mg) in 3 ml of EtOH, and the mixture was refluxed for 0.5 h. The reaction mixture was concentrated to dryness *in vacuo*, and the residue was purified by filtration through a short silica gel column, giving 99 mg (97%) of **8b**. Recrystallization from EtOH afforded yellow prisms, mp 143—145°C.

Irradiation of 5c at Various Wavelengths——Solutions of **5c** (23 mM) in undegassed acetone and petroleum ether (2.7: 1, v/v) in quartz test tubes were irradiated with a spectro irradiator (JASCO CRM-FA) for 2 h at wavelengths of 223, 250, 276, 303, 330, 356, 383, 410 and 436 nm. The ratio of the product **6c** to the recovered starting material **5c** was determined on a Thinchrograph (Iatron Laboratories Inc., Type TFG-10).

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