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The Norrish Type II Reaction of Thiophthalimides Having a Benzylic Hydrogen in an *N*-Alkyl Side Chain[1]

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Upon irradiation, thiophthalimides (4 and 5) possessing an *N*-ω-phenylalkyl substituent undergo the Norrish type II cyclization to give tricyclic isoindole derivatives (6—8). In the case of thiophthalimides (11) possessing an indene in the *N*-side chain, two competitive pathways, the Norrish type II and a Paterno–Büchi like type, were observed.

Keywords thiophthalimide; isoindole; photocyclization; Norrish type II reaction; Paterno–Büchi reaction; thietane; hydrogen abstraction

Intramolecular hydrogen abstraction in excited carbonyl compounds, Norrish type II reaction, is among the more extensively studied of photoreactions.[2] In the photochemistry of thiones, the sulfur analogues, the related reaction has also been well established.[3] In our general study of the photochemistry of thioimide systems, we have found some instances of behavior strikingly different from that of the imides,[4] the oxygen counterparts; *i.e.*, the thioimides[5] efficiently undergo photocycloaddition (Paterno–Büchi type reaction), but seem substantially inert to the Norrish type I and II processes. Recently, however, we have found that certain cyclic thioimides having an *N*-ω-phenylalkyl substituent undergo the Norrish type II cyclization when a benzylic hydrogen is available at the δ- or ε-position relative to the thiocarbonyl group.[6]

We now present a full account of these results including the photoreaction of thiophthalimides which have an indenyl group in place of a phenyl group at the *N*-alkyl side chain.

It seemed worthwhile to see whether the intermolecular reaction between the thioimides and compounds with a benzylic hydrogen proceeds or not. Thus, in preliminary experiments, photolysis of *N*-methylthiophthalimides (**1**) in benzene (500 ml) was examined in the presence of alkylbenzenes (**2a**—**c**, 30 mol eq), for 1—5 h with a 1 kW high-pressure mercury lamp through a Pyrex filter under a nitrogen atmosphere at room temperature (Chart 1). Under these conditions, in the presence of toluene (**2a**), thiophthalimide **1** was recovered unchanged even upon prolonged irradiation for 10 h. With ethylbenzene (**2b**), diastereoisomers (**3b**-i and **3b**-ii) were obtained in 18 and 7% yields, respectively, along with **1** in a 54% yield. Further, in the case of isopropylbenzene (**2c**) having a tertiary carbon at the benzylic position, a single addition product (**3c**) was obtained in 64% yield (Table I).

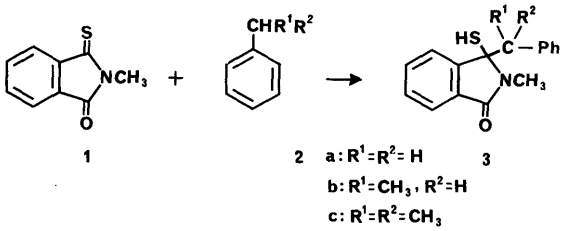

Chart 1

The structures of addition products were assigned on the basis of elemental analyses and spectral data. The mass spectra (MS) of **3b**-i and **3b**-ii showed the molecular ion peak ($M^+ = 283$) consistent with the adduct of **1** to **2b**, and a significant fragment peak ($M^+ - 34$) corresponding to the loss of hydrogen sulfide from the molecular ion.[5a] In the proton nuclear magnetic resonance (^{1}H-NMR) spectrum of **3b**-i (or **3b**-ii), a doublet and a quartet, with coupling constants of $J = 6$ Hz, appeared at 1.30 (1.50) and 3.50 (3.40) ppm, indicating the presence of a methyl group and a methine group, respectively. In addition, a singlet peak due to the *N*-methyl group of **3b**-i showed upfield shift from 3.20 to 2.70 ppm compared with that of **3b**-ii, due to the anisotropic effect of the phenyl ring adjacent to a methyl group ($R^1 = CH_3$). On the basis of the ^{1}H-NMR data and Dreiding models, the configurations at the methyl-substituted tertiary carbon at the benzylic position were tentatively assigned to be S^* for **3b**-i and R^* for **3b**-ii. Similarly, the structure of **3c** was also determined on the

TABLE I. Photoreaction of **1** in the Presence of Alkylbenzenes (**2**)[a]

Alkylbenzene	Product	Yield (%)	Appearance	mp (°C)	Formula	Analysis (%) Calcd (Found) C	H	N	S
2b	**3b**-i	18	Colorless oil		$C_{17}H_{17}NOS$	72.05	6.05	4.97	11.32
						(71.95	6.13	4.93	11.38)
	3b-ii	7	Colorless needles	94—96	$C_{17}H_{17}NOS$	72.05	6.05	4.97	11.32
						(72.09	6.13	4.79	11.45)
2c	**3c**	64	Colorless oil		$C_{18}H_{19}NOS$	72.60	6.44	4.71	10.78
						(72.55	6.38	4.89	10.96)

a) Irradiation time: 5 h (**2b**), 1 h (**2c**).

basis of spectral data (Table II).

Next, in order to investigate systematically the intramolecular photocyclization involving the Norrish type II reaction, irradiation of a series of *N*-ω-phenylalkylmonothio- (**4a**—**d**) and dithiophthalimides (**5b, c**) was performed under similar conditions (Chart 2). The results are listed in Table III. In the case of **4a** (when $n=2$), no photoproducts were isolated even upon prolonged irradiation for 10 h, and **4a** was quantitatively recovered. But, when $n=3$, δ-hydrogen abstraction reaction proceeded most effectively, giving Norrish type II products (**6b** and **7b** from **4b**, and **8b** from **5b**). Similarly, when $n=4$, the dithioimide **5c** underwent ε-hydrogen abstraction to give the unsaturated compound (**8c**) in 61% yield, whereas the monothioimide **4c** gave two stereoisomers (**6c** and **7c** in 16 and 9% yields, respectively) due to ε-hydrogen abstraction. Further, in order to investigate whether ζ-hydrogen abstraction occurs of not, photolysis of monothioimide **4d** was carried out for 10 h, but **4d** was recovered unchanged (82%). No attempt at photolysis of the dithioimide

TABLE II. Spectral Data for Photoproducts (3)

Compound	IR (cm^{-1})	MS (*m/z*)	^{1}H-NMR (CDCl$_3$) δ	^{13}C-NMR (CDCl$_3$) δ
3b-i	2500 1670	283 (M$^+$) 249 (M$^+$−34)	1.30 (3H, d, J=6 Hz, CH$_3$), 2.70 (3H, s, N–CH$_3$), 3.50 (1H, q, J=6 Hz, C$\underline{H}$–CH$_3$), 5.30 (1H, s, –SH), 7.0—7.9 (9H, m, aromatic H)	
3b-ii	2500 1670	283 (M$^+$) 249 (M$^+$−34)	1.50 (3H, d, J=6 Hz, CH$_3$), 3.20 (3H, s, N–CH$_3$), 3.40 (1H, q, J=6 Hz, C$\underline{H}$–CH$_3$), 5.40 (1H, s, –SH), 6.8—7.8 (9H, m, aromatic H)	
3c	2500 1670	297 (M$^+$) 263 (M$^+$−34)	1.60 (3H, s, CH$_3$), 1.70 (3H, s, CH$_3$), 3.20 (3H, s, N–CH$_3$), 5.10 (1H, s, –SH), 7.0—8.3 (9H, m, aromatic H)	20.9 (q), 24.8 (q), 31.7 (q), 42.0 (s), 71.8 (d), 123.1 (d), 123.9 (d), 126.1 (d × 2), 128.0 (d), 129.0 (d × 3), 130.3 (d), 135.2 (s), 144.2 (s), 144.3 (s), 169.8 (s)

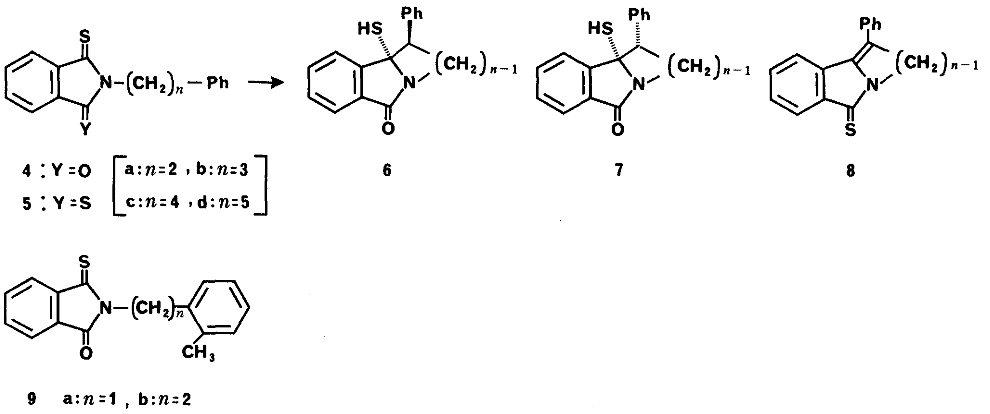

Chart 2

TABLE III. Photoproducts from **4**, **5** and **11**

Substrate	Time (h)	Product	mp (°C)	Yield (%)	Appearance	Formula	Analysis (%) Calcd (Found) C	H	N	S
4b	0.5	**6b**	160—162.5	54	Colorless plates	$C_{17}H_{15}NOS$	72.57 (72.80	5.37 5.19	4.98 4.98	11.40 11.45)
		7b	125.5—127	18	Colorless plates	$C_{17}H_{15}NOS$	72.57 (72.60	5.37 5.48	4.98 4.79	11.40 11.36)
4c	5	**6c**	134—136	16	Colorless plates	$C_{18}H_{17}NOS$	73.19 (73.16	5.80 5.59	4.74 4.73	10.86 10.85)
		7c	165 (dec.)	9	Colorless plates	$C_{18}H_{17}NOS$	73.19 (73.20	5.80 5.99	4.74 4.78	10.86 10.63)
5b	0.2	**8b**	189—191.5	82	Pale yellow plates	$C_{17}H_{13}NS$	77.53 (77.62	4.98 4.98	5.32 5.48	12.18 12.42)
5c	0.5	**8c**	140—142	61	Pale yellow plates	$C_{18}H_{15}NS$	77.94 (77.98	5.45 5.60	5.05 5.19	11.56 11.64)
11a	1	**12a**		72	A mixture of two isomers	$C_{20}H_{17}NOS$	75.20 (75.12	5.36 5.40	4.39 4.55	10.04 10.16)
11b	4	**13b**	154—156	34	Colorless prisms	$C_{22}H_{21}NOS$	76.05 (76.17	6.09 6.14	4.03 3.88	9.39 9.26)
11c	10	**13c**	112—114	18	Colorless plates	$C_{27}H_{31}NOS$	77.66 (77.52	7.48 7.56	3.35 3.39	7.68 7.68)

corresponding to **4d** was made as it was inaccessible. Likewise, in order to see whether the photocyclization at the ε- or ζ-position across a benzene ring occurs or not, *o*-xylylmonothiophthalimides (**9a, b**) were irradiated for 10 h. No photoproducts were isolated and the starting materials **9a, b** were recovered quantitatively. Interestingly, this observation is different from a precedent[7] in the photochemistry of phthalimides (the oxygen analogues of **9a, b**), in which the photocyclization does occur at the ε- or ζ-position (a methyl group) across a benzene ring.

The structures of products **6**, **7**, and **8** were assigned on the basis of elemental analyses and spectral data (Table IV). The MS of **6b, c** and **7b, c** showed the molecular ion peak consistent with the molecular weights of **4b, c**, and the characteristic fragment peak corresponding to the loss of hydrogen sulfide from the molecular ion. The ^{1}H-NMR spectra of **6** and **7** showed some multiplet peaks except for the peak due to the thiol group. Signals of the thiol groups of **7b, c** (1.80—1.90 ppm) appeared in the upfield region compared with those of **6b, c** (2.60—2.70 ppm). This can be explained on the basis of anisotropic effects of the phenyl ring on the pyrrolidine or piperidine moiety, suggesting that the thiol group and the phenyl group are in a *cis* relationship for **7** and *trans* for **6**. In the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectra of **6b, c** and **7b, c**, the chemical shifts of the carbonyl carbon in the lactam and the tertiary carbon substituted by a thiol group showed similarity to those proposed to discriminate between pyrroloisoindoles and pyridoisoindoles.[8] Similarly, the structures of **8b** and **8c** also were determined on the basis of spectral data. In the ^{1}H-NMR spectra of **8b, c** no signal due to a thiol group was seen, in contrast to the cases of **6** and **7**. The ^{13}C-NMR spectra showed the presence of the newly formed carbon–carbon double bond, although the signals were buried in the aromatic carbon region.

In order to investigate the competition between Norrish type II and Paterno–Büchi type reactions, photolysis of a series of *N*-[ω-(inden-3-yl)alkyl]monothiophthalimides (**11a, b, c**: $n=3$, 5, 10) having both olefin and allylic hydrogens (benzylic-like) was examined (Chart 3). The thiophthalimides (**11a, b, c**) were prepared from the corresponding phthalimides (**10a, b, c**)[9] by using Lawesson's reagent.[10] Upon irradiation under similar conditions, **11a** ($n=3$) effectively underwent δ-hydrogen abstraction to give the Norrish type II product (**12a**) in 72% yield, analogously to the photoreaction of **4b** ($n=3$) as mentioned above (Table III). The photoproducts were an inseparable mixture (1 : 1) of stereoisomers (**12a**), whose configurations are *cis* and *trans* with respect to the thiol group and the indene substituted on the pyrrolidine ring on the basis of ^{13}C-NMR spectroscopy. The ^{13}C-NMR spectrum showed five pairs of signals (a singlet, a doublet, and three triplets) in the aliphatic region and nine pairs of doublets in the olefinic and aromatic regions. The ^{1}H-NMR spectrum of the mixture **12a** showed a singlet at 2.0 ppm due to the thiol group, which disappeared on adding deuterium oxide. A

Table IV. Spectral Data for Photoproducts **6**, **7**, **8**, **12** and **13**

Compound	IR (cm^{-1})	MS (*m/z*)	^{1}H-NMR (CDCl$_3$) δ	^{13}C-NMR (CDCl$_3$) δ
6b	2500 1675	281 (M$^+$) 247 (M$^+$ − 34)	2.2—3.3 (2H, m), 2.60 (1H, s, –SH), 3.5—4.5 (3H, m), 6.7—7.6 (9H, m, aromatic H)	35.8 (t), 40.6 (t), 54.6 (d), 80.2 (s), 123.2 (d), 123.9 (d), 127.0 (d × 2), 127.3 (d), 127.7 (s), 128.3 (d × 2), 128.5 (d), 131.8 (d), 139.8 (s), 148.3 (s), 168.2 (s)
7b	2500 1675	281 (M$^+$) 247 (M$^+$ − 34)	1.90 (1H, s, –SH), 2.4—3.3 (3H, m), 3.5—4.0 (2H, m), 7.1—7.9 (9H, m, aromatic H)	32.9 (t), 40.2 (t), 54.1 (d), 78.9 (s), 123.5 (d), 124.1 (d), 128.3 (d), 128.4 (d × 2), 129.1 (d), 129.3 (d × 2), 130.8 (s), 132.2 (d), 135.8 (s), 150.5 (s), 169.2 (s)
6c	2500 1670	295 (M$^+$) 261 (M$^+$ − 34)	1.5—2.1 (2H, m), 2.70 (1H, s, –SH), 3.5—6.2 (5H, m), 7.0—8.0 (9H, m, aromatic H)	26.0 (t), 28.2 (t), 35.7 (t), 54.2 (d), 73.0 (s), 123.5 (d), 124.4 (d), 127.8 (d × 2), 128.6 (d), 128.9 (d), 130.2 (d × 2), 130.9 (d), 131.5 (s), 139.3 (s), 149.5 (s), 164.2 (s)
7c	2500 1670	295 (M$^+$) 261 (M$^+$ − 34)	1.80 (1H, s, –SH), 1.5—4.6 (7H, m), 6.6—8.0 (9H, m, aromatic H)	25.9 (t), 26.0 (t), 37.2 (t), 54.2 (d), 72.8 (s), 123.7 (d), 124.2 (d), 125.0 (d × 2), 128.3 (d × 2), 130.8 (d × 2), 131.3 (d), 132.0 (s), 138.4 (s), 149.1 (s), 164.2 (s)
8b		263 (M$^+$)	3.5 (2H, t, $J=6$ Hz), 4.2 (2H, t, $J=6$ Hz), 7.3—8.1 (9H, m, aromatic H)	37.5 (t), 42.7 (t), 121.5 (d), 124.5 (d), 127.8 (d × 2), 128.3 (s), 128.5 (s), 129.0 (d × 2), 129.2 (d), 129.5 (d), 129.9 (s), 130.5 (d), 133.8 (s), 143.2 (s), 179.9 (s)
8c		277 (M$^+$)	2.2 (2H, quint, $J=4$ Hz), 2.7 (2H, t, $J=4$ Hz), 4.2 (2H, t, $J=4$ Hz), 6.7—7.8 (9H, m, aromatic H)	22.1 (t), 31.7 (t), 41.2 (t), 122.0 (d), 124.3 (d), 126.5 (s), 128.6 (d × 3), 129.0 (d × 2), 129.2 (s), 130.7 (d), 132.5 (s), 137.5 (s), 139.0 (s), 178.5 (s)
12a		319 (M$^+$) 285 (M$^+$ − 34)	0.8—1.8 (3H, m), 2.0 (1H, s, –SH), 2.3—3.3 (2H, m), 3.4—3.9 (2H, m), 5.7 (1H, br s, vinylic H), 6.6—7.6 (8H, m, aromatic H)	34.4 (t), 35.3 (t), 37.6 (t), 38.1 (t), 39.8 (t), 40.2 (t), 46.0 (d), 46.6 (d), 78.9 (s), 79.5 (s), 118.8 (d), 119.6 (s), 120.1 (d), 121.4 (s), 122.6 (d), 123.5 (d), 123.8 (d × 2), 124.6 (d), 124.8 (d), 124.9 (s), 125.1 (d), 125.6 (d), 126.8 (s), 128.1 (d × 2), 128.9 (d), 129.1 (d), 129.3 (s), 131.1 (d), 131.7 (d × 2), 132.0 (s), 132.8 (d), 139.9 (s), 143.2 (s), 144.1 (s), 150.1 (s), 168.9 (d × 2)
13b	1690	347 (M$^+$) 315 (M$^+$ − 32)	1.5—2.7 (8H, m), 3.3—3.5 (2H, m, $\mathrm{PhC\underline{H}_2}$), 3.9—4.2 (2H, m), 4.2—4.4 (1H, m, SCH), 6.1—7.8 (8H, m, aromatic H)	22.9 (t), 25.8 (t), 26.4 (t), 39.0 (t), 40.2 (t), 40.7 (d), 41.2 (t), 73.4 (s), 78.7 (s), 122.0 (d), 125.5 (d), 126.2 (d), 126.7 (d), 127.2 (d), 128.2 (d), 128.6 (d), 130.2 (d), 130.6 (s), 140.2 (s), 146.6 (s), 147.4 (s), 169.3 (s)
13c	1685	417 (M$^+$)	1.4—3.8 (18H, m), 3.4—3.5 (2H, m, $\mathrm{PhC\underline{H}_2}$), 3.9—4.2 (2H, m), 4.2—4.4 (1H, m, SCH), 6.1—6.4 (2H, m, aromatic H), 6.5—7.5 (5H, m, aromatic H), 7.5—7.8 (1H, m, aromatic H)	23.4 (t), 25.4 (t), 25.8 (t), 26.5 (t), 27.8 (t), 30.1 (t), 32.4 (t), 33.5 (t), 35.1 (t), 40.9 (d), 42.3 (t), 43.5 (t), 72.0 (s), 79.0 (s), 122.3 (d), 124.3 (d), 125.9 (d), 126.8 (d), 128.0 (d), 129.2 (d), 129.5 (d), 130.1 (d), 132.7 (s), 140.6 (s), 145.9 (s), 148.3 (s), 170.1 (s)

signal due to one olefinic proton on the indene moiety appeared at 5.7 ppm, suggesting that original olefin group in indene remains intact through the photoreactions. The ^{13}C-NMR spectrum also supported the presence of the original olefin group in the indene moiety. The MS of **12a** showed the molecular ion peak at m/z 319 and a characteristic fragment peak at m/z 285 (M^+-34), consistent with the loss of hydrogen sulfide from the molecular ion. In the case of **11b** ($n=5$), upon irradiation for 4 h, a product (**13b**) was obtained in 34% yield as the sole product. The MS of **13b** showed the molecular ion peak at m/z 347 and a fragment peak at m/z 315 (M^+-S), suggesting the formation of a thietane ring. The formation of the thietane was supported by the ^{1}H-NMR spectrum of **13b**, in which diagnostic signals due to the thiol group and the olefinic proton in the indene moiety had disappeared. Also signals due to a methine adjacent to sulfur, and two benzylic protons appeared at 4.2—4.4 and 3.3—3.5 ppm, respectively, as multiplets. This result indicated that the newly formed methine is linked to the benzylic carbon. The ^{13}C-NMR spectrum showed the presence of one tertiary and two quaternary carbons at 40.7, 73.4, and 78.7 ppm, while the signals of a thiocarbonyl group and olefinic carbons in the indene moiety had disappeared. These changes suggested the occurrence of photocycloaddition (Paterno–Büchi type reaction) between the thiocarbonyl group and the olefinic group. To confirm the structure of **13b**, some reference compounds were required. To obtain them, irradiation of a mixture of *N*-methylmonothiophthalimide (**1**) and indene (**15**) was performed under similar conditions for 10 h. As expected, two products (**16** and **17**) were obtained in 29 and 24% yields, respectively (Table V). In the ^{1}H-NMR spectrum of **16**, two multiplets and a doublet with the coupling constant of 9 Hz appeared at 3.4—3.6, 4.1—4.4, and 5.05 ppm, indicating the presence of a methylene group at a benzylic position, a sulfur-methine, and a methine moiety at a benzylic position, respectively. Also in a decoupling experiment, selective irradiation of the multiplet at 4.1—4.4 ppm affected two signals, the multiplet at 3.4—3.6 ppm and the doublet at 5.05 ppm. Analysis of the coupling partners indicated that the newly formed methine adjacent to sulfur is linked to the methylene at the benzylic position. Similarly, the structure of **17** was assigned on the basis of ^{1}H-NMR data. Although two regioisomers were possible for each of **16** and **17**, the regioisomers (**16**-i for **16** and **17**-i for **17**) were excluded by ^{1}H-NMR spectroscopy (decoupling technique). In addition, these stereoisomers were distinguished easily on the basis of the ^{1}H-NMR signal of the *N*-methyl group by considering the anisotropic effects of the phenyl ring in indene (Table VI). It was concluded that the **16** and **17** are *anti* and *syn*, respectively, with respect to the plane of the thietane ring. By comparison of the ^{1}H-NMR spectra of reference compounds (**16** and **17**) with that of **13b**, the stereochemistry of **13b** was confirmed to be the same *syn* form as that of **17**.

To explore the possibility of forming a large-sized ring

Table V. Photoreaction of **1** in the Presence of Indene (**15**)[a]

Compound	Yield (%)	Appearance	mp (°C)	Formula	Analysis (%) Calcd (Found) C	H	N	S
16	29	Colorless plates	171—172	$C_{18}H_{15}NOS$	73.69 (73.55	5.15 5.05	4.77 4.56	10.93 10.73)
17	24	Colorless plates	183—185	$C_{18}H_{15}NOS$	73.69 (73.95	5.15 5.11	4.77 4.81	10.93 10.67)

a) Irradiation time: 10 h.

Table VI. Spectral Data for Photoproducts (**16** and **17**)

Compound	IR (cm^{-1})	MS (m/z)	^{1}H-NMR ($CDCl_3$) δ
16	1685	293	2.45 (3H, s, N–CH_3), 3.4—3.6 (2H, m, $PhCH_2$), 4.1—4.4 (1H, m, SCH), 5.05 (1H, d, $J=9$ Hz, PhCH), 6.9—8.2 (8H, m, aromatic H)
17	1685	293	3.3—3.4 (2H, m, $PhCH_2$), 3.55 (3H, s, N–CH_3), 4.2—4.5 (1H, m, SCH), 4.77 (1H, d, $J=7$ Hz, PhCH), 6.2—7.8 (8H, m, aromatic H)

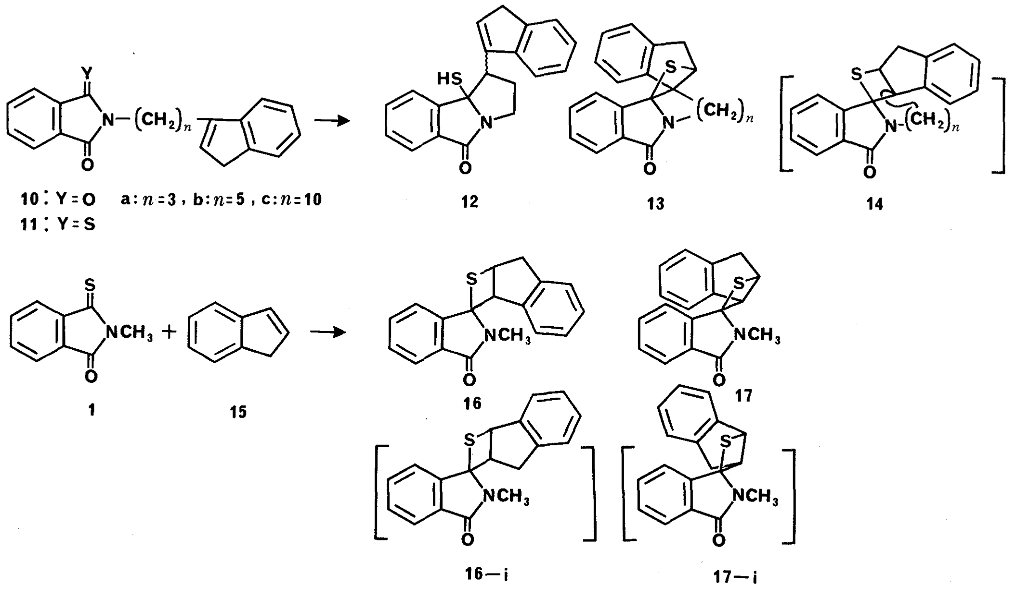

Chart 3

through remote photoreaction,[9,11] **11c** ($n=10$), a substrate with a long side chain, was irradiated under similar conditions for 10 h. A remote photocycloaddition product **13c** was obtained in 18% yield together with unchanged **11c** (24%). The structure of **13c** was confirmed on the basis of the spectral data [MS: 417 (M^+); IR: 1685 cm^{-1} (lactam); ^{1}H-NMR δ: 1.4—3.8 (18H, m, -$(CH_2)_9$-), 3.4—3.5 (2H, m, PhC$\underline{H}_2$), 3.9—4.2 (2H, m, N-CH_2), 4.2—4.4 (1H, m, S-CH), 6.1—6.4 (2H, m, ArH), 6.5—7.6 (5H, m, ArH), 7.5—7.8 (1H, m, ArH)]. In the ^{1}H-NMR spectrum of **13c**, the signals in the aromatic region showed upfield shifts compared with those of **16**. Therefore, the stereochemistry of **13c** was assigned as *syn* on the basis of the anisotropic effects between two phenyl rings. Further, the ^{1}H-NMR spectrum of **13c** showed similarity to that of **17**. These results exclude the possibility of the structure **14** (a stereoisomer of **13**).

In thioimide photochemistry, it has become apparent that intermolecular hydrogen abstraction from the benzylic position followed by coupling does take place to give the addition products, according to the precedent with phthalimides.[12] The reaction susceptibility depends highly upon the substrate structure [3° (64%) > 2° (25%) > 1° (0%)], suggestive of the involvement of radical intermediates. Similarly, irradiation of a series of *N*-ω-phenylalkylmono- (**4**) or dithiophthalimides (**5**) results in the formation of products **6**—**8** which are expected from the Norrish type II cyclization initiated by δ- or ε-hydrogen abstraction (Table III). It is noteworthy that the γ-hydrogen (when $n=2$), which is definitely reactive in the ketones,[2] is inert in the thioimide system. However, in a series of *N*-[ω-(inden-3-yl)alkyl]monothiophthalimides (**11a**—**c**), the Norrish type II and the Paterno–Büchi type pathways are competitive, depending on the number of methylenes in the alkyl side chain. Compound **11c** ($n=10$) undergoes remote photocycloaddition giving a large (thirteen-membered) ring *via* the Paterno–Büchi pathway in competition with the Norrish type II one. In the case of **11a** having δ-hydrogens to be abstracted, the Norrish type II reaction only occurs to give **12**, which is analogous to **4b** and **5b**, whereas with **11b, c** the Paterno–Büchi type reaction only occurs, according to the precedent[11] with phthalimides having an indole group at the *N*-alkyl side chain. By contrast, the phthalimides (**10a**—**c**, oxygen counterparts) with an indene at the *N*-alkyl side chain undergo only photocyclization with an alkene to give spiro-pyrroloisoindoles,[9] not the Paterno–Büchi product, probably involving an electron transfer process. Thus, in this study the indene is shown to be an excellent Paterno–Büchi acceptor (thietane partners) in forming a large-sized ring, due to remote photocyclization.[11] This photoreaction may provide a novel synthetic route to tricyclic isoindole derivatives.

TABLE VII. Thioimides **4**, **5**, **9**, and **11**

Thio-imide	Yield (%)	bp (°C)/mmHg mp (°C)	Formula	Analysis (%) Calcd (Found) C	H	N	S
4a	54	156—159/2	$C_{16}H_{13}NOS$	71.88	4.90	5.24	11.99
				(72.00	4.76	5.11	11.86)
4b	59	161—166/2	$C_{17}H_{15}NOS$	72.57	5.37	4.98	11.40
				(72.33	5.36	5.08	11.40)
4c	46	159—164/1	$C_{18}H_{17}NOS$	73.19	5.80	4.74	10.86
				(73.08	5.96	4.73	10.89)
4d	57	166—170/2	$C_{19}H_{19}NOS$	73.75	6.19	4.53	10.36
				(73.71	6.03	4.44	10.56)
5a	42	48—50	$C_{16}H_{13}NS_2$	67.81	4.62	4.94	22.63
				(67.79	4.48	4.68	22.56)
5b	48	55—56	$C_{17}H_{15}NS_2$	68.65	5.08	4.71	21.56
				(68.49	5.23	4.49	21.39)
5c	51	51—53	$C_{18}H_{17}NS_2$	69.41	5.50	4.50	20.59
				(69.19	5.55	4.58	20.56)
5d	44	46—47	$C_{19}H_{19}NS_2$	70.11	5.88	4.30	19.70
				(70.23	5.86	4.33	19.85)
9a	43	148—150	$C_{16}H_{13}NOS$	71.88	4.90	5.24	11.99
				(71.76	4.79	5.23	11.86)
9b	50	101—103	$C_{17}H_{15}NOS$	72.57	5.37	4.98	11.40
				(72.66	5.32	4.95	11.33)
11a	43	124—125	$C_{20}H_{17}NOS$	75.20	5.36	4.39	10.04
				(75.23	5.45	4.25	10.15)
11b	55	96—98	$C_{22}H_{21}NOS$	76.05	6.09	4.03	9.23
				(75.96	6.09	4.15	9.14)
11c	43	47—48	$C_{27}H_{31}NOS$	77.66	7.48	3.35	7.68
				(77.82	7.52	3.59	7.55)

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. NMR spectra were taken on Hitachi R-40, JEOL FX-60, and JEOL JNM-FX-90Q spectrometers. Chemical shifts are reported in ppm (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. MS were obtained on a JEOL JMS-QH-100 gas chromatograph–mass spectrometer. Preparative irradiations were conducted by using a 1 kW high-pressure mercury lamp (Eikosha EHB-W-1000) through a Pyrex filter 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. Column chromatography was conducted using silica gel (Merck, Kieselgel 60, 70—230 mesh).

Preparation of Thiophthalimide Derivatives (1, 4, 5, 9 and 11): General Procedure Phthalimide derivatives[9a,13] were prepared by the reported procedures. Next, thiophthalimides (**1**, **4**, **5**, **9** and **11**) were prepared from the corresponding phthalimides and Lawesson's reagent by the procedure described in ref. 10, and purified by column chromatography (Table VII).

Irradiation of 1 with 2: General Procedure A solution of the thiophthalimide (**1**, 5 mmol) and an alkylbenzene (**2**, 150 mmol) in benzene (500 ml) was irradiated for 1—5 h. After removal of the solvent *in vacuo*, the residue was chromatographed on a silica gel column (using benzene as solvent) and the photoproduct was purified by recrystallization.

Irradiation of 4, 5, 9 and 11: General Procedure A solution of the thiophthalimide (5 mmol) in benzene (500 ml) was irradiated under similar conditions. Work-up was carried out in a usual manner.

Irradiation of 1 with 15 A solution of **1** (5 mmol) and indene (**15**, 25 mmol) in benzene (500 ml) was irradiated for 10 h. Work-up of the reaction mixture as described above gave two products, **16** and **17**.

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