Intermolecular Photoreaction of Thiohomophthalimides with Olefins: Thietane Formation Through [2 + 2] Cycloaddition[1]

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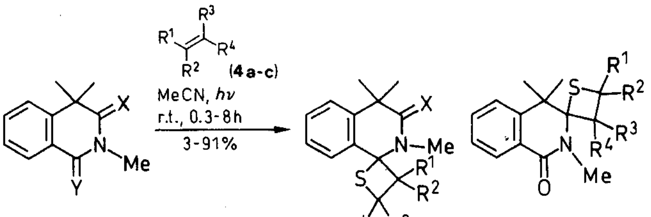
Received 6 September 1991

Upon irradiation of thiohomophthalimides (1,2,3,4-tetrahydro-2,4,4-trimethyl-1,3-dithioxo[3-oxo-1-thioxo or 1-oxo-3-thioxo]isoquinolines, **1–3**) in the presence of olefins **4**, **9**, regioselective [2 + 2] cycloaddition occurred to give oxo- or thioxospiro[isoquinoline-1,2′(or 3,2′)-thietane] derivatives **5**, **6**, **8**, **10–12** and related compounds 1-alkylidene-1,2,3,4-tetrahydro-2,4,4-trimethyl-3-thioxoisoquinolines **7a**, **c**.

Photoreactions of cyclic thioimide systems have been studied extensively.[3,4] It was found that aliphatic and aromatic thioimides (e.g., thiophthalimides and thiosuccinimides) in each case, undergo mainly [2 + 2] photocycloaddition (Paterno–Büchi type reaction) with olefins to give various thietanes and related compounds. However, studies on the photocycloadditions are limited to five-membered thioimide systems except for certain six-membered aliphatic thioimide systems.[5] As a logical extension of cyclic thioimide photochemistry, intermolecular photoreactions of thiohomophthalimide systems (e.g. 1,2,3,4-tetrahydro-1,3-dithioxoisoquinolines) having both an aromatic thiocarbonyl and an aliphatic thiocarbonyl in their framework were examined.

Photolyses of thiohomophthalimides **1–3** in the presence of olefins **4** or **9** were performed in acetonitrile (or methanol) using a 1 kW high-pressure mercury lamp through a Pyrex filter at room temperature. The results are listed in Table 1. The progress of reactions was monitored by thin layer chromatography.

In the photoreaction of dithioimide **1** with 2,3-dimethyl-2-butene (**4a**), thietane **5a** was obtained in 88 % yield, accompanied with a small amount of isopropylidene compound **7a**. Probably, compound **7a** arises from the initially formed **5a** through photochemical fission of the thietane ring.[3,4] Similarly, in the case of 2-methyl-2-butene (**4b**), thietane isomers **5bi** and **5bii** were obtained in 51 and 38 % yield, respectively, again accompanied with an unsaturated product **7a**. Since the compound **7a** was easily obtained from each photolysate of **5bi** and **5bii**, it was confirmed that **7a** is a secondary product from **5b**, and that **5bi** and **5bii** are stereoisomeric with each other relating to the methine carbon on the thietane ring. Further, photolyses of **1** with aromatic conjugated olefins [1,1-diphenylethene (**4c**) or indene (**9**)] were carried out. In the case of **4c**, only the alkylidene compound **7c** was obtained in 60 % yield, whereas in the reaction of **9**, thietane isomers **10i** and **10ii** were obtained in 30 and 29 % yield, respectively, without giving the corresponding alkylidene compound.

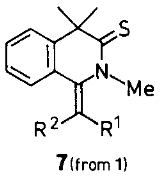


1 X = Y = S
2 X = O, Y = S
3 X = S, Y = O

5 X = S (from **1**)
6 X = O (from **2**)

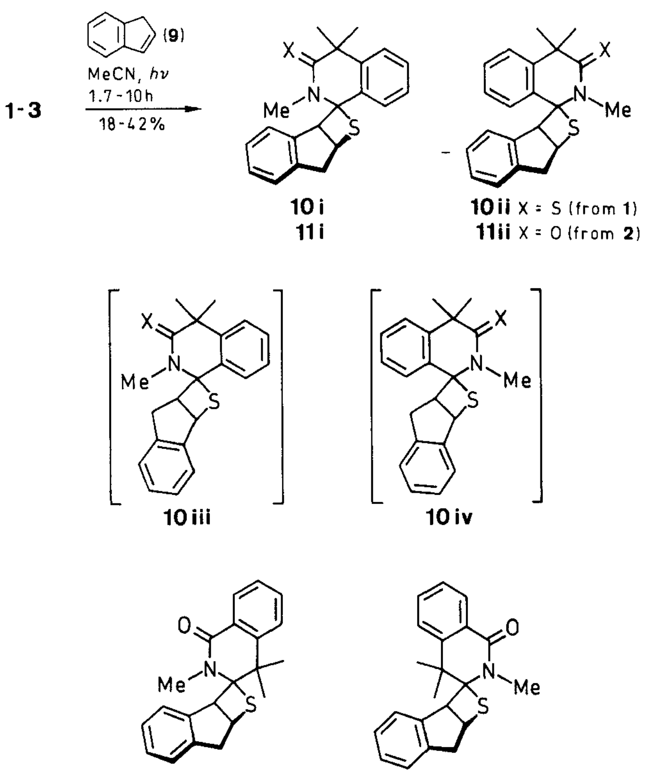
8 (from **3**)

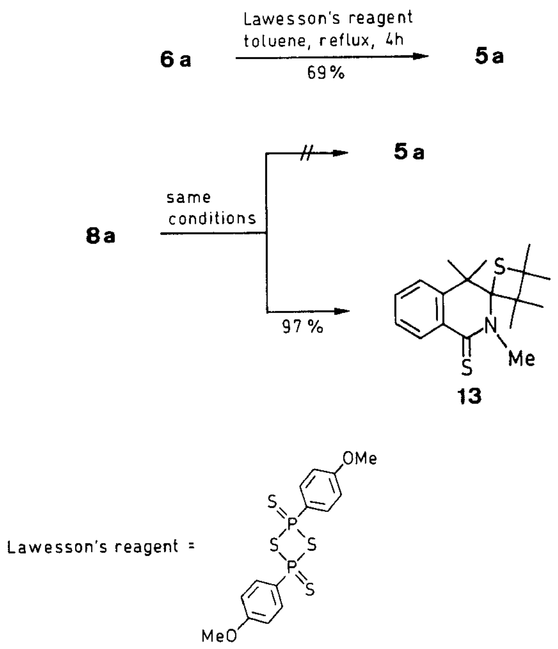
4,5,6,7,8	R1	R2	R3	R4
a	CH_3	CH_3	CH_3	CH_3
b	CH_3	CH_3	CH_3	H
c	Ph	Ph	H	H



7 (from **1**)

$$\mathbf{5} \xrightarrow[60\text{-}68\%]{\text{MeCN}, h\nu, \text{r.t.}, 4\text{h}} \mathbf{7}$$





The structures of all products were determined on the basis of analytical and spectral data. The mass spectra of thietanes **5a, b, 10** showed molecular ion peaks (M^+) consistent with the adduct of **1** to olefins **4**, **9**, and isopropylidene compounds **7a, c** showed molecular ion peaks (M^+) corresponding to the loss of thioacetone, thioacetaldehyde or thioformaldehyde from the corresponding parent thietanes **5a–c**, respectively. The addition site of the olefin could easily be distinguished on the basis of ^{13}C NMR spectra; dithioimide **1** showed two characteristic singlet peaks due to an aromatic thiocarbonyl and an aliphatic thiocarbonyl at δ = 194.5 and 213.5, respectively. While, in the thietanes **5a, b, 10** and alkylidene compounds **7a, c**, signals due to a thiocarbonyl in the newly formed thioamide appeared at δ = 207.6–210.7, suggesting that regioselective photoaddition of olefin **4**, **9** occurred at the aromatic thiocarbonyl group (1-position). Further, in the case of the thietanes **5a, b, 10**, the singlet peaks due to the quaternary carbon adjacent to a sulfur and a nitrogen atom appeared at δ = 76.6–82.2, respectively. When indene (**9**) was used as an olefin component, dithioimide **1** afforded two stereoisomers of the thietanes **10i**, **10ii**. Although the formation of four regio- and stereoisomeric thietanes (**i–iv** forms) is possible, a regioisomer **iii**-form for the **i**-form and **iv**-form for the **ii**-form were excluded on the basis of ^1H NMR spectra, which are analogous to that of phthalimidyl indenothietanes as described previously.[6] Namely, the signals due to methine adjacent to sulfur and two benzylic

Table 1. Photoproducts 5–8 and 10–12 Prepared

Imide	Olefin (equiv)	Time (h)	Product	Yield (%)	mp (°C)	Appearance (solvent)	IR (Nujol) ν (cm^{-1})	MS (70 eV) m/z (M^+)	Molecular Formula[a]
1	**4a** (10)	0.7	**5a**	88	104–106	pale yellow needles (EtOH)		319	$C_{18}H_{25}NS_2$ (319.1)
			7a	3	103–103.5	colorless prisms (EtOAc/hexane)		245	$C_{25}H_{19}NS$ (245.1)
1	**4b** (10)	0.3	**5bi**[b]	51	127–128.5	colorless prisms (EtOAc/hexane)		305	$C_{17}H_{23}NS_2$ (305.1)
			5bii	38	semisolid			305	$C_{17}H_{23}NS_2$[c] (305.1)
1	**4c** (10)	8	**7c**	60	180–181.5	pale yellow prisms (EtOAc/hexane)		369	$C_{25}H_{23}NS$ (369.2)
1	**9** (5)	1.7	**10i**	30	164–165.5	colorless prisms (EtOAc/hexane)		351	$C_{21}H_{21}NS_2$ (351.1)
			10ii	29	173.5–175	colorless column (EtOAc/hexane)		351	$C_{21}H_{21}NS_2$ (351.1)
2	**4a** (10)	0.4	**6a**	91	129–131	colorless prisms (EtOAc/hexane)	1650	303	$C_{18}H_{25}NOS$ (303.2)
2	**9** (5)	1.7	**11i**	30	154–156	colorless prisms (EtOAc/hexane)	1640	335	$C_{21}H_{21}NOS$ (335.1)
			11ii	42	140–142	colorless prisms (EtOAc/hexane)	1650	335	$C_{21}H_{21}NOS$ (335.1)
3	**4a** (20)	1.5[d]	**8a**	45	134–136	colorless prisms (hexane)	1640	303	$C_{18}H_{25}NOS$ (303.2)
3	**9** (5)	10	**12i**	27	168–169	colorless prisms (EtOAc/hexane)	1640	335	$C_{21}H_{21}NOS$ (335.1)
			12ii	18	143–144	colorless prisms (EtOAc/hexane)	1640	335	$C_{21}H_{21}NOS$ (335.1)

[a] Satisfactory microanalyses obtained: C ±0.22, H ±0.19, N ±0.10, S ±0.29.
[b] Compound **7a** was formed in 5% yield as a byproduct.
[c] HRMS: calc: 305.1272; found: 305.1293.
[d] Reaction in MeOH.

Table 2. NMR Data of Photoproducts **5**–**8** and **10**–**12**

Product	^{1}H NMR ($CDCl_3$/TMS) δ, *J* (Hz)	^{13}C NMR ($CDCl_3$/TMS) δ, *J* (Hz)
5a	0.60 (s, 3H, CH_3), 1.15 (s, 3H, CH_3), 1.52 (s, 3H, CH_3), 1.63 (s, 3H, CH_3), 1.69 (s, 3H, CH_3), 1.95 (s, 3H, CH_3), 4.34 (s, 3H, $N-CH_3$), 7.20–7.50 (m, 3H_{arom}), 8.30–8.50 (m, 1H_{arom})	22.7 (q), 25.3 (q), 28.2 (q), 28.7 (q), 35.2 (q), 35.6 (q), 45.5 (s), 47.1 (q), 47.6 (s), 61.2 (s), 79.0 (s), 125.7 (d) × 2, 128.5 (d), 130.4 (d), 133.1 (s), 141.1 (s), 210.7 (s)
7a	1.33 (s, 3H, CH_3), 1.90 (s, 3H, CH_3), 1.94 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 3.60 (s, 3H, $N-CH_3$), 7.2–7.5 (m, 4H_{arom})	21.5 (q), 21.9 (q), 26.6 (q), 27.4 (q), 46.1 (q), 49.5 (s), 123.7 (s), 123.9 (d), 125.8 (d), 126.5 (d), 127.7 (d), 133.6 (s), 136.5 (s), 142.1 (s), 207.6 (s)
5bi	0.52 (s, 3H, CH_3), 1.23 (s, 3H, CH_3), 1.38 (d, 3H, *J* = 7, CH_3), 1.66 (s, 3H, CH_3), 1.94 (s, 3H, CH_3), 3.36 (q, 1H, *J* = 7, $CH_3C\underline{H}S$), 4.23 (s, 3H, $N-CH_3$), 7.20–7.50 (m, 3H_{arom}), 8.30–8.50 (m, 1H_{arom})	16.5 (q), 20.5 (q), 28.4 (q), 35.2 (q), 35.6 (q), 41.2 (d), 47.3 (q), 47.7 (s), 60.8 (s), 79.6 (s), 126.1 (d), 126.5 (d), 128.7 (d), 129.1 (d), 133.0 (s), 141.0 (s), 210.7 (s)
5bii	0.72 (s, 3H, CH_3), 1.04 (s, 3H, CH_3), 1.31 (d, 3H, *J* = 7, CH_3), 1.64 (s, 3H, CH_3), 1.95 (s, 3H, CH_3), 3.67 (q, 1H, *J* = 7, $CH_3C\underline{H}S$), 4.38 (s, 3H, $N-CH_3$), 7.20–7.50 (m, 3H_{arom}), 8.20–8.40 (m, 1H_{arom})	16.0 (q), 23.0 (q), 26.2 (q), 34.7 (q), 35.9 (q), 42.7 (d), 45.5 (q), 47.6 (s), 59.5 (s), 82.2 (s), 125.5 (d), 125.8 (d), 128.7 (d), 131.4 (d) × 2, 131.4 (s), 141.3 (s), 210.6 (s)
7c	1.88 (s, 6H, CH_3 × 2), 3.19 (s, 3H, $N-CH_3$), 6.86 (d, *J* = 4, 2H_{arom}), 7.00–7.50 (m, 12H_{arom})	27.9 (q), 46.2 (q), 49.4 (s), 123.5, 125.6, 127.3, 127.4, 127.8, 128.0, 128.3, 128.6, 128.9, 129.5, 138.4 (s), 139.6 (s), 140.1 (s), 141.7 (s), 207.6 (s)
10i	1.71 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 3.36 (s, 3H, $N-CH_3$), 3.30–3.50 (m, 2H, $SCHC\underline{H}_2$), 4.10–4.40 (m, 1H, $SC\underline{H}CH_2$), 4.75 (d, 1H, *J* = 7, PhCH), 7.00–7.60 (m, 7H_{arom}), 8.50–8.70 (m, 1H_{arom})	31.5 (q), 35.5 (q), 35.6 (d), 40.7 (t), 46.3 (q), 47.8 (s), 70.3 (d), 76.6 (s), 125.4 (d), 125.9 (d), 127.4 (d), 127.9 (d), 128.8 (d), 129.1 (d), 136.8 (s), 139.1 (s), 139.8 (s), 143.0 (s), 208.6 (s)
10ii	1.67 (s, 3H, CH_3), 2.01 (s, 3H, CH_3), 3.43 (d, 2H, *J* = 4, $SCHC\underline{H}_2$), 4.20–4.50 (m, 1H, $SC\underline{H}CH_2$), 4.47 (s, 3H, $N-CH_3$), 4.79 (d, 1H, *J* = 7, PhCH), 6.07 (d, *J* = 8, 1H_{arom}), 6.60–6.90 (m, 2H_{arom}), 7.00–7.40 (m, 5H_{arom})	31.4 (q), 36.5 (d), 36.8 (q), 40.6 (t), 43.5 (q), 47.5 (s), 67.3 (d), 80.2 (s), 124.7 (d), 125.3 (d), 125.8 (d), 126.7 (d), 128.1 (d), 128.7 (d), 130.7 (s), 131.3 (d), 138.8 (s), 140.0 (s), 142.8 (s), 208.6 (s)
6a	0.61 (s, 3H, CH_3), 1.17 (s, 3H, CH_3), 1.50 (s, 3H, CH_3), 1.53 (s, 3H, CH_3), 1.60 (s, 3H, CH_3), 1.63 (s, 3H, CH_3), 3.71 (s, 3H, $N-CH_3$), 7.20–7.40 (m, 3H_{arom}), 8.40–8.60 (m, 1H_{arom})	22.8 (q), 28.5 (q), 28.9 (q), 29.0 (q), 31.5 (q), 36.9 (q), 41.9 (s), 45.3 (s), 59.9 (s), 76.0 (s), 125.4 (d), 125.7 (d), 128.5 (d), 130.8 (d), 134.7 (s), 141.9 (s), 176.1 (s)
11i	1.59 (s, 3H, CH_3), 1.70 (s, 3H, CH_3), 2.71 (s, 3H, $N-CH_3$), 3.30–3.40 (m, 2H, $SCHC\underline{H}_2$), 4.10–4.30 (m, 1H, $SC\underline{H}CH_2$), 4.70 (d, 1H, *J* = 7, PhCH), 7.00–7.60 (m, 7H_{arom}), 8.50–8.70 (m, 1H_{arom})	25.9 (q), 32.0 (q), 34.8 (q), 35.4 (d), 41.1 (t), 41.7 (s), 70.2 (d), 74.8 (s), 125.0 (d), 125.7 (d), 127.2 (d), 127.7 (d), 127.8 (d), 128.5 (d), 128.7 (d), 137.8 (s), 139.5 (s), 140.1 (s), 143.1 (s), 174.5 (s)
11ii	1.54 (s, 3H, CH_3), 1.67 (s, 3H, CH_3), 3.30–3.50 (m, 2H, $SCHC\underline{H}_2$), 3.90 (s, 3H, $N-CH_3$), 3.2–3.4 (m, 1H, $SC\underline{H}CH_2$), 4.73 (d, 1H, *J* = 7, PhCH), 6.03 (d, *J* = 7, 1H_{arom}), 6.6–6.9 (m, 2H_{arom}), 7.0–7.6 (m, 5H_{arom})	26.3 (q), 32.1 (q), 32.2 (q), 35.7 (d), 40.7 (t), 41.4 (s), 67.9 (d), 78.1 (s), 124.4 (d), 125.0 (d), 125.2 (d), 125.8 (d), 126.5 (d), 127.8 (d), 128.5 (d), 131.2 (s), 131.5 (d), 139.3 (s), 140.7 (s), 142.7 (s), 174.4 (s)
8	0.65 (s, 3H, CH_3), 0.97 (s, 3H, CH_3), 1.05 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 3.54 (s, 3H, $N-CH_3$), 7.20–7.50 (m, 3H_{arom}), 7.90–8.10 (m, 1H_{arom})	24.4 (q), 25.0 (q), 26.6 (q), 28.3 (q) 28.5 (q), 29.4 (q), 35.2 (q), 44.5 (s), 45.2 (s), 58.0 (s), 81.2 (s), 123.4 (d), 126.8 (d), 128.1 (d), 128.8 (s), 132.3 (d), 146.1 (s), 165.4 (s)
12i	1.20 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 2.70 (s, 3H, $N-CH_3$), 3.10–3.30 (m, 2H, $SCHC\underline{H}_2$), 3.70–3.90 (m, 1H, $SC\underline{H}CH_2$), 4.33 (d, 1H, *J* = 7, PhCH), 6.40–6.60 (m, 1H_{arom}), 7.00–7.60 (m, 6H_{arom}), 8.00–8.20 (m, 1H_{arom})	21.9 (q), 25.9 (q), 33.9 (q), 35.9 (d), 41.5 (t), 44.1 (s), 59.6 (d), 80.6 (s), 125.0 (d), 125.3 (d), 125.8 (d), 127.3 (d), 127.9 (d), 128.3 (d), 128.7 (s), 132.4 (d), 139.5 (s), 142.5 (s), 143.4 (s), 163.9 (s)
12ii	0.98 (s, 3H, CH_3), 1.11 (s, 3H, CH_3), 3.37 (d, 2H, *J* = 6, $SCHC\underline{H}_2$), 3.78 (s, 3H, $N-CH_3$), 3.7–4.1 (m, 1H, $SC\underline{H}CH_2$), 4.54 (d, 1H, *J* = 9, PhCH), 5.46 (d, *J* = 8, 1H_{arom}), 6.6–7.5 (m, 6H_{arom}), 8.0–8.29 (m, 1H_{arom})	22.8 (q), 28.0 (q), 32.1 (q), 32.8 (d), 42.0 (t), 43.1 (s), 64.7 (d), 84.1 (s), 124.7 (d), 125.0 (d), 126.0 (d), 126.4 (d), 127.0 (d), 128.1 (d), 128.5 (d), 132.4 (d), 140.2 (s), 143.8 (s), 144.2 (s), 164.6 (s)

protons in the spectra of **10** [δ = 4.10–4.40 (m, 1 H) and δ = 3.30–3.50 (m, 2 H) for **10i**, and δ = 4.20–4.50 (m, 1 H) and δ = 3.43 (d, 2 H) for **10ii**] showed the chemical shift pattern similar to those of thietane which was obtained from intramolecular photoreaction of *N*-[3-(inden-3-yl)propyl]monothiophthalimide [δ = 4.20–4.40 (m, 1 H) and δ = 3.30–3.50 (m, 2 H), respectively]. Further, stereochemistry of **10i** and **10ii** was easily confirmed by the ^{1}H NMR spectra. For **10i**, the peak due to *N*-methyl showed an upfield shift at δ = 3.36 compared with that at δ = 4.47 for **10ii**, as a result of an anisotropic effect of the benzene ring. In addition, for the **10ii** isomer, aromatic protons of the isoquinolone moiety showed an upfield shift at δ = 6.07–6.90, indicating that the two benzene rings are close to each other. Thus, **10i** is the anti, while **10ii** is the syn isomer.

In order to gain more information about the role of the sulfur atom in the thiohomophthalimide system, the photochemical behavior of monothioimide **2**, **3** was studied. In the case of monothioimide **2** having an aromatic thiocarbonyl and an aliphatic carbonyl group, photoaddition of olefins **4a**, **9** occurred only at the aromatic thiocarbonyl group (1-position), giving the corresponding thietanes **6a** and **11**, respectively. In contrast, for counterpart **3**, which has an aliphatic thiocarbonyl and an aromatic carbonyl group, irradiations in the presence of olefins **4a, 9** gave aliphatic imide thietanes **8** and **12**, respectively, which were the products from the reaction with the thiocarbonyl moiety (3-position). But none of the corresponding oxetane was isolated in any case.

The structures of addition products **6, 8, 11, 12** were determined on the basis of elemental analyses and spectral data. The mass spectra of photoproducts **6, 8, 11, 12** gave molecular ion peaks (M^+), corresponding to the molecular weight of the addition products of **2** or **3** to olefins **4, 9**, respectively. In the ^{13}C NMR spectra, thietanes **6** and **11** (photoproducts from **2**) showed peaks due to an amide carbonyl and an quaternary carbon adjacent to a sulfur and a nitrogen atom at δ = 174.4–176.1 and δ = 74.8–78.1, respectively. Similarly, photoproducts **8, 12** from **3** showed an amide carbonyl and a quaternary carbon at δ = 163.9–165.4 and δ = 80.6–84.1, respectively. Although the IR spectra of thioamides **5a, b, 7a, c, 10** from **1** showed no characteristic absorptions in the region of ν = 1600–1700 cm^{-1}, the photoproducts **6a, 8a, 11, 12** from **2** and **3** showed an absorption band due to an amide group at ν = 1640–1650 cm^{-1}. This suggests that the photoaddition of **2** or **3** took place at the thiocarbonyl group, i.e., monothioimide **2** reacted at the 1-position (aromatic thiocarbonyl) and monothioimide **3** reacted at the 3-position (aliphatic thiocarbonyl). To further confirm the position of thietane formation of **1–3**, the photoproducts **6a** and **8a** were treated with Lawesson's reagent. The thionation product from **6a** was identified as **5a** (which derived from **1** and **4a**), while **8a** afforded **13**. These results indicated that in both dithioimide **1** and monothioimide **2**, the aromatic thiocarbonyl group reacted in preference to the aliphatic thiocarbonyl and carbonyl group, though monothioimide **3** reacted at the aliphatic thiocarbonyl group. Stereochemistries of **11 (i, ii)** and **12 (i, ii)** were confirmed on the basis of ^1H NMR spectra. Since the ^1H NMR spectra of **11i** and **11ii** were analogous to that of **10i** and **10ii**, respectively, it was concluded that **11i** is the anti, and **11ii** is the syn isomer. Further, with **12**, *N*-methyl protons in **12i** and methyl protons at benzylic position in **12ii** appeared upfield cf. those of the corresponding isomers (**12ii** and **12i**, respectively). By considering the anisotropic effect of benzene ring, it was concluded that **12i** has the anti, and **12ii**, has the syn conformation.

In conclusion, the aromatic thiocarbonyl group in the six-membered thioimide system underwent efficiently [2 + 2] cycloaddition with olefins to give thietanes in preference to the aliphatic thiocarbonyl or other carbonyl groups in the same framework, demonstrating that the photochemical behavior mainly parallels that of the five-membered thiophthalimide system.[6] Further, in the Paterno–Büchi reaction as seen in **3**, the aliphatic thiocarbonyl group showed enhanced reactivity in comparison with that of the aromatic carbonyl group. This reaction would provide a useful method for the construction of heterocycles through the regioselective C–C bond formation. Application of this method, including synthesis of isoquinoline derivatives by intramolecular reactions is underway.

All melting points were determined on a Yamato melting point apparatus (Model MP-21) and are uncorrected. IR spectra were recorded on a JASCO A-102 spectrophotometer. NMR spectra were taken on a JEOL-JNM-FX 90Q spectrometer. Mass spectra were determined with a JEOL JMS-QH 100 mass spectrometer and HRMS spectra were recorded using a JEOL-JMS-DX 303 mass spectrometer. Irradiation was conducted by using a 1 kW high-pressure mercury lamp (Eikosha EHB-W-1000).

1,2,3,4-Tetrahydro-2,4,4-trimethyl-1,3-dithioxoisoquinoline (1) and 1,2,3,4-Tetrahydro-2,4,4-trimethyl-3-oxo-1-thioxoisoquinoline (2):
A solution of 2-methyl-1,3-dioxoisoquinoline[7] (8.75 g, 0.05 mol) in 1,2-dimethoxyethane (DME) (200 mL) was added dropwise to a stirred suspension of NaH (2.88 g, 0.12 mol) in dry DME (75 mL) at 0 °C. The mixture was stirred at the same temperature for 30 min, then MeI (15 mL) was added, and the whole was stirred for 30 min. Then the mixture was taken up with H_2O (200 mL) and extracted with EtOAc (3 × 100 mL). The organic layer was dried ($MgSO_4$) and evaporated in vacuo to yield the crude dialkylated product, which was recrystallized from EtOAc and hexane to give 1,2,3,4-tetrahydro-2,4,4-trimethyl-1,3-dioxoisoquinoline (9.08 g, 89 %); mp 100–101 °C.

IR (Nujol): ν = 1710, 1665 cm^{-1} (C=O).

^1H NMR ($CDCl_3$/TMS): δ = 1.63 (s, 6H, $CH_3 \times 2$), 3.38 (s, 3H, N-CH_3), 7.3–7.8 (m, 3 H_{arom}), 8.2 (m, 1 H_{arom}).

Next, dithiohomophthalimide **1** and monothiohomophthalimide **2** are prepared from 2,4,4-trimethyl-1,3-dioxoisoquinoline and Lawesson's reagent by the procedure of Ref. 8 and purified by column chromatography (eluent: EtOAc/hexane, 1:50).

1; mp 46–47 °C

$C_{12}H_{13}NS_2$	calc.	C 61.26	H 5.57	N 5.96	S 27.20
(235.0)	found	61.40	5.57	5.84	27.29

^1H NMR ($CDCl_3$/TMS): δ = 1.75 (s, 6H, $CH_3 \times 2$), 4.34 (s, 3H, N-CH_3), 7.1–7.6 (m, 3 H_{arom}), 8.3–8.5 (m, 1 H_{arom}).

^{13}C NMR ($CDCl_3$/TMS): δ = 32.8 (q), 44.5 (q), 51.2 (s), 123.7 (d), 127.3 (d), 132.1 (s), 132.8 (d), 133.6 (d), 140.7 (s), 194.5 (s), 213.5 (s).

2; mp 62–64 °C

$C_{12}H_{13}NOS$	calc.	C 65.73	H 5.98	N 6.39	S 14.59
(219.1)	found	65.67	5.88	6.31	14.75

IR (Nujol): ν = 1700 cm^{-1} (C=O).

^1H NMR ($CDCl_3$/TMS): δ = 1.64 (s, 6H, $CH_3 \times 2$), 3.82 (s, 3H, N-CH_3), 7.2–7.7 (m, 3 H_{arom}), 8.6–8.8 (m, 1 H_{arom}).

^{13}C NMR ($CDCl_3$/TMS): δ = 28.8 (q), 35.4 (q), 43.8 (s), 124.5 (d), 127.2 (d), 130.0 (s), 133.2 (d), 133.6 (d), 141.0 (s), 175.0 (s), 197.3 (s).

1,2,3,4-Tetrahydro-2,4,4-trimethyl-1-oxo-3-thioxoisoquinoline (3):
A solution of dithiohomophthalimide **1** (1.8 g, 7.5 mmol) in MeCN (500 mL) was irradiated with 1 kW high-pressure mercury lamp through a Pyrex filter for 7.5 h under an air atmosphere. After removal of the solvent in vacuo, the residue was purified by silica gel column chromatography (eluent: EtOAc/hexane, 1:50) to give recovered **1** (0.32 g, 18 %), monothioimide **2** (0.13 g, 8 %), monothioimide **3** (0.86 g, 52 %), and 2,4,4-trimethylhomophthalimide (0.32 g, 18 %).

3; mp 101–103 °C.

$C_{12}H_{13}NOS$	calc.	C 65.73	H 5.98	N 6.39	S 14.59
(219.1)	found	65.65	5.91	6.27	14.75

IR (Nujol): ν = 1675 cm^{-1} (C=O).

^1H NMR ($CDCl_3$/TMS): δ = 1.82 (s, 6H, $CH_3 \times 2$), 3.84 (s, 3H, N-CH_3), 7.3–7.8 (m, 3 H_{arom}), 8.2–8.3 (m, 1 H_{arom}).

^{13}C NMR ($CDCl_3$/TMS): δ = 35.0 (q), 35.7 (q), 49.9 (s), 125.5 (d), 127.4 (d), 129.3 (d), 133.9 (d), 147.1 (s), 161.2 (s), 216.2 (s).

Irradiation of Thioxoisoquinoline Derivatives 1–3 in the Presence of Olefins 4, 9:
A solution of **1–3** (10 mM) and olefins **4, 9** (**1–2/4** = 1:10 molar ratio, **3/4a** = 1:20 molar ratio, and **1–3/9** = 1:5 molar ratio) in MeCN was irradiated using a 1 kW high-pressure mercury lamp

through a Pyrex filter under a N_2 atmosphere for 0.3–10 h. After removal of the solvent, the photolysate was subjected to column chromatography on silica gel. Following solvent systems were used as the eluents: **5a**; EtOAc/hexane (1:40, v/v); **5b**; EtOAc/hexane (1:100, v/v); **7c** and **10**; EtOAc/hexane (1:20, v/v); **6a, 11** and **12**; EtOAc/hexane (1:10, v/v); and **8a**; EtOAc/hexane (1:5, v/v). Spectral and elemental analysis data are summarized in Table 1 and 2.

Irradiation of 1,2,3,4-Tetrahydro-2,4,4-trimethyl-3-thioxospiro[isoquinoline-1,2′-thietane] Derivatives 5bi and 5bii:

A solution of **5bi** (42 mg, 0.14 mmol) in MeCN (14 mL) was irradiated for 4 h under similar conditions as described above. Separation by silica gel column chromatography (eluent: EtOAc/hexane, 1:40) gave 1,2,3,4-tetrahydro-1-isopropylidene-2,4,4-trimethyl-3-thioxoisoquinoline (**7a**) (23 mg, 68 %). Similarly, irradiation of thietane **5bii** gave **7a** in 62 % yield.

Thionation of 1,2,3,4-Tetrahydro-2,4,4,3′,3′,4′,4′-heptamethyl-3 (or 1)-oxospiro[isoquinoline-1,2′(or 3,2′)-thietane] (6a) (or 8a):

A solution of thietane **8a** (65 mg, 0.2 mmol) and Lawesson's reagent (81 mg, 0.2 mmol) in toluene (6 mL) was refluxed for 4 h, and separation by silica gel column chromatography (eluent: EtOAc/hexane 1:20) gave the corresponding thioamide **13** (65 mg, 97 %); mp 157–158 °C.

HRMS: m/z, $C_{18}H_{25}NS_2$ calc.: 319.1428; found: 319.1432 (M^+).

^1H NMR ($CDCl_3$/TMS): δ = 0.55 (s, 3 H, CH_3), 0.98 (s, 6 H, $CH_3 \times 2$), 1.44 (s, 6 H, $CH_3 \times 2$), 2.04 (s, 3 H, CH_3), 4.09 (s, 3 H, N—CH_3), 7.20–7.50 (m, 3 H_{arom}), 8.30–8.50 (m, 1 H_{arom}).

^{13}C NMR ($CDCl_3$/TMS): δ = 24.2 (q), 25.4 (q), 26.7 (q), 27.5 (q), 28.1 (q), 28.6 (q), 43.9 (s), 44.7 (q), 45.4 (s), 58.2 (s), 84.5 (s), 123.0 (d), 126.9 (d), 132.0 (d) × 2, 134.2 (s), 141.4 (s), 192.7 (s).

Under these conditions, the thietane **6a** was converted to **5a** in 69 % yield.

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