Photochemical reactions of thiobenzamides bearing an allylic substituent on the nitrogen atom: double-bond migration *via* tandem 1,4- and 1,6-hydrogen transfer

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***N*-(2-Phenylprop-2-enyl)thiobenzamides 1a–d underwent double-bond migration on irradiation to give *N*-(2-phenylprop-1-enyl)thiobenzamides 2a–d *via* consecutive 1,4- and 1,6-hydrogen transfer. Photoreaction of an *N*-(prop-2-enyl)thiobenzamide 1e and an *N*-(3-phenylprop-2-enyl)thiobenzamide 1f did not give migration products, but afforded pyrroles 3e and 3f and dealkylation products 4a in low yields.**

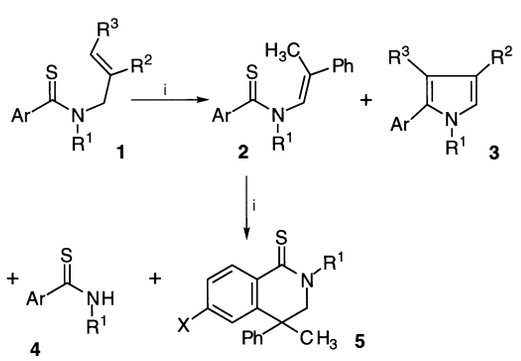
Introduction

Thiocarbonyl compounds such as thioketones[1] and thioimides[2] undergo photochemical reactions similar to those of carbonyl compounds. Thioamides are, however, photochemically much less reactive than these compounds and few reports have been published on their photochemical reactions. Recently, Nishio and Okuda reported [2 + 2] cycloaddition of cyclic thioanilides.[3] Similar reactions of thiobenzamides have also been reported by Oda *et al.*[4] In relation to our previous study on the photochemistry of nitrogen-containing thiocarbonyl compounds,[5] I report here photochemical reactions of thiobenzamides having an allylic substituent on the nitrogen atom. These reactions involve a novel double-bond migration *via* consecutive 1,4- and 1,6-hydrogen transfer and provide the first example of hydrogen abstraction by excited thioamides.

Results and discussion

Photoreactions in solution

When *N*-isopropyl-*N*-(2-phenylprop-2-enyl)thiobenzamide **1a** in benzene was irradiated with a high-pressure mercury lamp, a thioenamide **2a** and a pyrrole **3a** were obtained as main products together with a dealkylation product **4a** and a cyclization product **5a** (Scheme 1). Among these products, compound **5a** was found to be a secondary product from thioenamide **2a** since irradiation of this substrate **2a** gave compound **5a**. The photoreaction of compound **1a** was clean at low conversion (Table 1), but became sluggish at higher conversion and a considerable amount of the cyclization product **5a** was produced along with unidentified by-products. This is apparently due to the secondary reactions of intermediate **2a**; the extinction coefficient of compound **2a** is larger than that of substrate **1a** in the range 300–440 nm. Reactions similar to the photocyclization of compound **2a** to the isoquinolinethione **5a** have been reported.[6]



a; Ar = R^2 = Ph, R^1 = Pr^i, R^3 = X = H
b; Ar = 4–ClC_6H_4, R^1 = Pr^i, R^2 = Ph, R^3 = H, X = Cl
c; Ar = 4–$MeOC_6H_4$, R^1 = Pr^i, R^2 = Ph, R^3 = H, X = MeO
d; Ar = R^2 = Ph, R^1 = Me, R^3 = X = H
e: Ar = Ph, R^1 = Pr^i, R^2 = R^3 = H
f; Ar = R^3 = Ph, R^1 = Pr^i, R^2 = H

Scheme 1 *Condition:* i, *hν*

Table 1 Photoreactions of compounds **1** in benzene

Compound	Conversion (%)	Yield (%) **2**	**3**	**4**	**5**
1a	28	77	5	*a*	*a*
1b	26	69	9	*a*	*a*
1c	20	60	*b*	*a*	*a*
1d	31	22	12	3	*a*
1e	32	*b*	14	10	*b*
1f	36	*b*	12	6	*b*

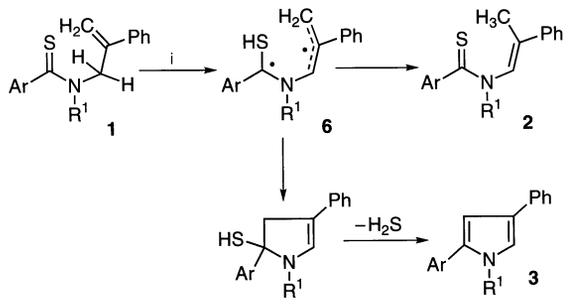
[a] Trace. [b] Not detected.

Photoreaction of 4-chloro- and 4-methoxy-thiobenzamide **1b** and **1c** gave similar results (Table 1). The structures of the thioenamides **2a–c** were confirmed by independent syntheses *via* thionation of the corresponding enamides,[6] and the *E* geometry of the enamides was determined on the basis of nuclear Overhauser effect (NOE) difference spectra. The structures of the pyrroles **3a** and **3b** were also established by unequivocal syntheses (see Experimental section).[7]

Irradiation of an N-methyl derivative **1d** also gave the corresponding thioenamide **2d** and pyrrole **3d** as with the reactions of analogues **1a–c**, although the yield of compound **2d** was low. In this case product **2d** was a mixture of *E* and *Z* isomers. Meanwhile, photochemical reaction of *N*-allyl-*N*-isopropylthiobenzamide **1e** and *N*-cinnamyl-*N*-isopropylthiobenzamide **1f** did not yield thioenamides but instead afforded pyrroles **3e** and **3f** and *N*-isopropylthiobenzamide **4a** as main products, although these reactions were not clean. The structure of compound **3d** was determined by direct comparison with an authentic sample,[7] and that of compound **3e** was confirmed by its independent synthesis *via* photocyclization of an enamino ketone,[8] whereas that of compound **3f** was elucidated on the basis of spectral data and elemental analysis.

Mechanism

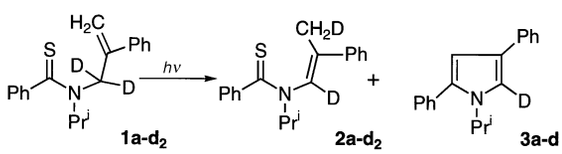
The formation of the thioenamides **2** and the pyrroles **3** can be



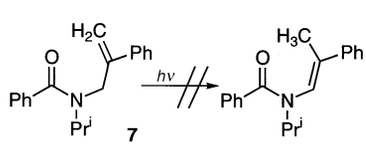
Scheme 2 *Condition:* i, *hν*

rationalized by the mechanism shown in Scheme 2. β-Hydrogen abstraction (1,4-hydrogen transfer) by the excited thiocarbonyl group gives a diradical **6**. Hydrogen transfer in diradicals **6** *via* a seven-membered cyclic transition state (1,6-hydrogen transfer) yields the thioenamide **2**, whereas cyclization of diradical **6** followed by elimination of hydrogen sulfide produces the pyrrole **3**.

In confirmation of this mechanism, photoreaction of a deuteriated thiobenzamide **1a**-d_2 was carried out. The resulting thioenamide **2a**-d_2 possessed one of the deuterium atoms in the allylic methyl group and the other one on the olefinic carbon adjacent to the nitrogen atom, whereas the pyrrole **3a**-d carried a deuterium atom at the 5-position: the positions of the deuterium atoms were determined on the basis of NMR spectroscopy. This observation is consistent with the above mechanism. Further, the comparison of the quantum yield for the formation of **2a**-d_2 ($\Phi = 0.0050$) with that for the parent **2a** ($\Phi = 0.026$) supports the mechanism since the large isotope effect ($\Phi_H/\Phi_D = 5.2$) indicates that the cleavage of the allylic C–H bond is involved in the transition state of the photoreaction of compounds **1**.



It may be conceivable that compounds **2** are formed by direct 1,3-hydrogen transfer of the styrene moiety of compounds **1** since concerted suprafacial 1,3-sigmatropic reactions of alkenes are photochemically allowed. This mechanism is, however, improbable as detailed below. Photochemical 1,3-hydrogen shifts of styrenes have not been reported in spite of extensive studies on their photochemistry.[9] The thioenamide **2a** was formed on selective excitation of the thioamide group of compound **1a** with visible radiation (436 nm). The concomitant formation of the pyrroles is consistent with the mechanism involving the corresponding diradical intermediate **6**. Further, the amide **7**, an oxygen analogue of compound **1a**, did not



undergo double-bond migration on direct excitation of the styryl group or on xanthone-sensitized irradiation. These findings clearly show that the present photoreactions are reactions of the excited thioamides rather than those of the excited styrenes.

The fact that the *N*-cinnamyl thioamide **1f** does not undergo the double-bond shift is not unreasonable since the reaction requires destruction of the conjugation in the cinnamyl group.

The formation of the *N*-alkylthiobenzamides **4** (cleavage products) can be rationalized in terms of homolysis of the C–N bond; some amides and esters are known to undergo similar photoreactions.[10] The cyclization of compounds **2** to isoquinolinethiones **5** is explicable by 6π electrocyclization and subsequent 1,5-hydrogen shift as in the case of photocyclization of enamides.[6]

The present reaction provides the first example of photochemical hydrogen abstraction of thioamides and the double-bond shift *via* consecutive 1,4- and 1,6-hydrogen transfer is without precedent to our best knowledge. The efficient intramolecular hydrogen abstraction by these excited thioamides is presumed to be due to the high reactivity of the allylic hydrogens toward abstraction; the hydrogens are further activated by the adjacent nitrogen atom. Moreover, it is known that excited thioketones undergo 1,4- or 1,6-hydrogen transfer efficiently[11] in contrast to the selective 1,5-hydrogen transfer (γ-hydrogen abstraction) of excited carbonyl compounds.

Experimental

Mps were measured on a Yanagimoto micromelting point apparatus and are not corrected. Distillation was effected with a cold-finger-type apparatus for molecular distillation (only oven temperature is given). IR Spectra were measured in $CHCl_3$ and NMR spectra were obtained in $CDCl_3$. *J*-Values are in Hz.

General procedure for preparation of thiobenzamides 1

N-Isopropyl-*N*-(2-phenylprop-2-enyl)amine, *N*-isopropyl-*N*-(prop-2-enyl)amine, *N*-isopropyl-*N*-(3-phenylprop-2-enyl)-amine and *N*-methyl-*N*-(2-phenylprop-2-enyl)amine were synthesized from the corresponding alkenyl bromide and an alkylamine. After benzoylation of the amines with benzoyl chloride or other aroyl chlorides, the resulting amides were treated with the Lawesson's reagent in refluxing toluene for 1 h. After evaporation off of the solvent, the residue was chromatographed on silica gel to give the thioamides **1**. The thioamides obtained were mixtures of two rotational isomers in solution.

***N*-Isopropyl-*N*-(2-phenylprop-2-enyl)thiobenzamide 1a.** Mp 121–122 °C; ν_{max}/cm^{-1} 1460; λ_{max}(hexane)/nm 245 (ε 17 300), 280sh (10 100), 379 (220) and 400 (210); λ_{max}(MeOH)/nm 250 (15 700), 282 (10 900) and 369 (135); δ_H 1.20 and 1.36 (6 H in total, ~3:1, both d, *J* 7), 4.34 and 5.01 (2 H in total, ~1:3, both s), 4.42 and 6.03 (1 H in total, ~3:1, both sept, *J* 7), 5.19, 5.23, 5.42 and 5.47 (2 H in total, ~3:1:1:3, each s) and 6.9–7.55 (10 H, m); δ_C 19.8 and 20.8 (CH_3), 49.2 and 50.7 (CH_2), 52.8 and 55.6 (CH), 111.9 and 114.6 (=CH_2), 124.9–129.1, 139.0 (C), 139.7 (C), 140.8 (C), 144.1 (C), 144.8 (C), 202.4 and 203.3 (C=S) (Found: C, 76.85; H, 7.12; N, 4.76. $C_{19}H_{21}NS$ requires C, 77.24; H, 7.16; N, 4.74%).

4-Chloro-*N*-isopropyl-*N*-(2′-phenylprop-2′-enyl)thiobenzamide 1b. Mp 133–136 °C; ν_{max}/cm^{-1} 1465; δ_H 1.19 and 1.35 (6 H in total, ~3:1, both d, *J* 7), 4.35 and 4.99 (2 H in total, ~1:3, both s), 4.38 and 5.99 (1 H in total, ~3:1, both sept, *J* 7), 5.14, 5.20 and 5.46 (2 H in total, ~3:1:4, each s) and 6.9–7.6 (9 H, m); δ_C 19.77 and 20.77 (CH_3), 49.2 and 50.7 (CH_2), 53.0 and 55.8 (CH), 111.9, 114.6 (=CH_2), 125.8–128.8, 134.1 (C), 138.6 (C), 139.5 (C), 140.8 (C), 142.4 (C), 144.6 (C), 200.9 and 201.7 (C=S) (Found: C, 68.72; H, 6.12; N, 4.10. $C_{19}H_{20}ClNS$ requires C, 69.18; H, 6.11; N, 4.24%).

***N*-Isopropyl-4-methoxy-*N*-(2′-phenylprop-2′-enyl)thiobenzamide 1c.** Mp 155–156 °C; ν_{max}/cm^{-1} 1455; δ_H 19.9 and 20.8 (CH_3), 49.3 and 50.8 (CH_2), 53.2 and 55.4 (CH), 1.19 and 1.35 (6 H in total, ~5:1, both d, *J* 7), 3.77 and 3.82 (3 H in total, ~1:5, both s), 4.39 and 5.01 (2 H in total, ~1:5, both s), 4.51 and 6.00 (1 H in total, both sept, *J* 7), 5.16, 5.22 and 5.45 (2 H in total, each s) and 6.85–7.6 (9 H, m); δ_C 55.7 (CH_3), 111.8 and 114.5 (=CH_2), 113.2, 113.9, 125.9–128.5, 136.7 (C), 136.9 (C), 139.7 (C), 144.0 (C), 144.7 (C), 159.6 (C), 202.7 (C=S) (Found: C, 73.68; H, 7.19; N, 4.20. $C_{20}H_{23}NOS$ requires C, 73.81; H, 7.12; N, 4.30%).

***N*-Methyl-*N*-(2-phenylprop-2-enyl)thiobenzamide 1d.** Bp

150 °C/2 mmHg; ν_{max}/cm^{-1} 1495; δ_H 2.91 and 3.55 (3 H in total, both s, ~1:0.9), 4.46 and 5.30 (2 H in total, both s), 5.19, 5.30, 5.52 and 5.60 (2 H in total, each s) and 7.0–7.6 (10 H, m); δ_C 40.7 and 41.4 (CH_3), 57.4 and 59.6 (CH_2), 114.8 and 115.4 (=CH_2), 125.4–128.7, 137.6 (C), 138.1 (C), 142.6 (C), 143.05 (C), 143.11 (C), 143.4 (C), 202.4 and 202.6 (C=S) (Found: C, 76.08; H, 6.39; N, 5.24. $C_{17}H_{17}NS$ requires C, 76.36; H, 6.41; N, 5.24%).

***N*-Isopropyl-*N*-(prop-2-enyl)thiobenzamide 1e.** Mp 55–57 °C; ν_{max}/cm^{-1} 1455; δ_H 1.18 and 1.35 (6 H in total, ~3:1, both d, *J* 7), 4.03 and 4.66 (2 H in total, ~1:3, both m), 4.29 and 5.93 (1 H in total, ~3:1, both sept, *J* 7), 4.90–5.07, 5.23–5.35, 5.56–5.70 and 6.05–6.19 (3 H in total, each m) and 7.1–7.4 (5 H, m); δ_C 19.9 and 21.0 (CH_3), 48.6 and 50.2 (CH_2), 52.7 and 55.5 (CH), 117.3 and 117.8 (=CH_2), 114.7–134.2, 114.0 (C), 114.1 (C), 201.0 and 202.2 (C=S) (Found: C, 71.26; H, 7.70; N, 6.30. Calc. for $C_{13}H_{17}NS$: C, 71.18; H, 7.81; N, 6.39%).

***N*-Isopropyl-*N*-(3-phenylprop-2-enyl)thiobenzamide 1f.** Mp 108–109 °C; ν_{max}/cm^{-1} 1460; δ_H 1.21 and 1.38 (6 H in total, ~3:1, both d, *J* 7), 4.17 and 4.81 (2 H in total, ~1:3, both d, *J* 5), 4.31 and 5.97 (1 H in total, both sept, *J* 7), 5.83–6.09 and 6.51–6.68 (2 H in total, both m) and 7.2–7.5 (10 H, m); δ_C 19.9 and 21.1 (CH_3), 48.4 and 49.7 (CH_2), 52.5 and 55.5 (CH), 124.5–133.1, 136.0 (C), 136.7 (C), 144.0 (C), 144.1 (C), 200.9 and 202.2 (C=S) (Found: C, 77.16; H, 7.16; N, 4.57. $C_{19}H_{21}NS$ requires C, 77.24; H, 7.16; N, 4.74%).

Synthesis of the deuterium-labelled compound 1a-d_2

N-Isopropyl-*N*-phenacylamine was prepared by the reaction of phenacyl bromide (α-bromoacetophenone) with an excess of isopropylamine and was converted to the corresponding benzamide by treatment with benzoyl chloride in the presence of triethylamine. To a mixture of D_2O (3 g) and dry tetrahydrofuran (THF) (30 cm^3) was added sodium (100 mg). *N*-Isopropyl-*N*-phenacylbenzamide (500 mg) was added to the mixture and the resulting solution was refluxed for 12 h. After removal of most of the THF, benzene (30 cm^3) was added and the organic layer was separated and dried over anhydrous $MgSO_4$. The benzene solution was dried by azeotropic distillation and concentrated to 15 cm^3. The dry benzene solution was added to a cold THF solution (30 cm^3; 0 °C) of the phosphorus ylide prepared from methyltriphenylphosphonium bromide (3 g) and butyllithium. After the solution had been stirred for 1 h at room temperature, methanol (5 cm^3) and water (100 cm^3) were added. The aqueous layer was extracted with benzene and the combined organic layer was washed with saturated aq. NaCl, dried over anhydrous $MgSO_4$ and evaporated. The deuteriated *N*-isopropyl-*N*-(2-phenylprop-2-enyl)benzamide was isolated by flash chromatography on silica gel and thionated as in the case of compound **1a**.

General procedure for preparative photolyses

A benzene solution (100 cm^3) of a thioamide (500 mg) in a Pyrex tube was de-aerated by argon bubbling and irradiated with a high-pressure mercury lamp (1000 W) for 4–10 h. After removal of the solvent, products were isolated by flash chromatography on silica gel or HPLC. The thioenamide **2** and the cyclization product **5** were separated by fractional recrystallization. *N*-Isopropylthiobenzamide **4a**, *N*-isopropyl-4-chlorothiobenzamide **4b**, *N*-isopropyl-4-methoxythiobenzamide **4c** and *N*-methylthiobenzamide **4d** were identified by direct comparison with authentic samples.[13]

***(E)*-*N*-Isopropyl-(2-phenylprop-1-enyl)thiobenzamide 2a.** Mp 161–164 °C; ν_{max}/cm^{-1} 1425; λ_{max}(hexane)/nm 265 (ε 10 700) and 420sh (290); δ_H 1.34 (6 H, d, *J* 7), 1.67 (3 H, d, *J* 1.6), 5.82 (1 H, sept, *J* 7), 6.25 (1 H, br s) and 7.0–7.5 (5 H, m); δ_C 17.0 (CH_3), 19.1 (CH_3), 54.3 (CH), 125.1–128.8, 139.1 (C), 139.8 (C), 144.8 (C) and 202.0 (C=S) (Found: C, 77.19; H, 7.20; N, 4.70. $C_{19}H_{21}NS$ requires C, 77.24; H, 7.16; N, 4.74%).

1-Isopropyl-2,4-diphenylpyrrole 3a. Bp 200 °C/1 mmHg; ν_{max}/cm^{-1} 1605; δ_H 1.41 (6 H, d, *J* 7), 4.48 (1 H, sept, *J* 7), 6.44 (1 H, d, *J* 1.7) and 7.1–7.7 (11 H, m); δ_C 24.1 (CH_3), 47.4 (CH), 106.3 (3-C), 114.0 (5-C), 124.5–129.2, 133.5 (C), 135.0 (C) and 135.8 (C) (Found: C, 87.28; H, 7.36; N, 5.36. $C_{19}H_{19}N$ requires C, 87.30; H, 7.33; N, 5.36%).

2-Isopropyl-4-methyl-4-phenyl-3,4-dihydroisoquinoline-1(2*H*)-thione 5a. Mp 144–145 °C; ν_{max}/cm^{-1} 1485; δ_H 0.78 (3 H, d, *J* 7), 1.22 (3 H, d, *J* 7), 1.74 (3 H, s), 3.42 and 3.70 (2 H, ABq, *J* 13), 6.02 (1 H, sept, *J* 7), 7.0–7.5 (8 H, m) and 8.7 (1 H, m); δ_C 18.2 (CH_3), 18.5 (CH_3), 24.5 (CH_3), 41.7 (C), 51.9 (CH), 54.5 (CH_2), 125.0–133.1, 134.6 (C), 140.4 (C), 143.7 (C) and 190.5 (C=S) (Found: C, 77.01; H, 7.20; N, 4.73. $C_{19}H_{21}NS$ requires C, 77.24; H, 7.16; N, 4.74%).

***(E)*-4-Chloro-*N*-isopropyl-*N*-(2′-phenylprop-1′-enyl)thiobenzamide 2b.** Mp 62–64 °C; ν_{max}/cm^{-1} 1420; δ_H 1.34 (6 H, d, *J* 7), 1.68 (3 H, d, *J* 1), 5.78 (1 H, sept, *J* 7), 6.28 (1 H, q, *J* 1) and 7.0–7.5 (9 H, m); δ_C 16.9 (CH_3), 19.1 (CH_3), 54.5 (CH), 124.8–128.6, 134.7 (C), 139.3 (C), 139.5 (C), 143.1 (C) and 200.3 (C=S) (Found: C, 69.20; H, 6.12; N, 4.32. $C_{19}H_{20}ClNS$ requires C, 69.18; H, 6.11; N, 4.25%).

2-(4′-Chlorophenyl)-1-isopropyl-4-phenylpyrrole 3b. Mp 131–132 °C; δ_H 1.43 (6 H, d, *J* 7), 4.42 (sept, *J* 7), 6.43 (1 H, s) and 7.1–7.6 (10 H, m); δ_C 24.1 (CH_3), 47.5 (CH), 106.6 (3-C), 114.4 (5-C), 124.7–130.4, 131.9 (C), 133.2 (C), 133.7 (C) and 135.6 (C) (Found: C, 77.14; H, 6.12; N, 4.71. $C_{19}H_{18}ClN$ requires C, 77.15; H, 6.13; N, 4.74%).

6-Chloro-2-isopropyl-4-methyl-4-phenyl-3,4-dihydroisoquinoline-1(2*H*)-thione 5b. Mp 146–149 °C; ν_{max}/cm^{-1} 1475; δ_H 0.78 (3 H, d, *J* 7), 1.21 (3 H, d, *J* 7), 1.73 (3 H, s), 3.41 and 3.69 (2 H, ABq, *J* 13), 5.99 (1 H, sept, *J* 7), 6.95–7.5 (7 H, m) and 8.67 (1 H, d, *J* 9); δ_C 18.2 (CH_3), 18.5 (CH_3), 41.8 (quat), 52.0 (CH), 54.4 (CH_2), 125.1–128.9, 135.1, 133.0 (C), 138.3 (C), 142.1 (C), 142.9 (C) and 189.3 (C=S) (Found: C, 69.13; H, 6.10; N, 4.14. $C_{19}H_{20}ClNS$ requires C, 69.18; H, 6.11; N, 4.24%).

***(E)*-*N*-Isopropyl-4-methoxy-*N*-(2′-phenylprop-1′-enyl)thiobenzamide 2c.** Bp 200 °C/1 mmHg; ν_{max}/cm^{-1} 1420; δ_H 1.34 (6 H, d, *J* 7), 1.64 (3 H, d, *J* 1), 3.75 (3 H, s), 5.79 (1 H, sept, *J* 7), 6.32 (1 H, q, *J* 1), 6.74 (2 H, d, *J* 9) and 7.1–7.5 (7 H, m); δ_C 16.7 (CH_3), 19.1 (CH_3), 54.6 (CH), 55.3 (OCH_3), 112.5 (CH), 125.2–129.5, 137.3 (C), 138.5 (C), 139.9 (C), 160.1 (C) and 201.7 (C=S) (Found: C, 73.77; H, 7.04; N, 4.27. $C_{20}H_{23}NOS$ requires C, 73.81; H, 7.12; N, 4.30%).

2-Isopropyl-6-methoxy-4-methyl-4-phenyl-3,5-dihydroisoquinoline-1(2*H*)-thione 5c. Mp 130–131 °C; ν_{max}/cm^{-1} 1480; δ_H 0.77 (3 H, d, *J* 7), 1.20 (3 H, d, *J* 7), 1.72 (3 H, s), 3.39 and 3.67 (2 H, ABq, *J* 13), 3.78 (3 H, s), 6.03 (1 H, sept, *J* 7), 6.49 (1 H, d, *J* 3), 6.87 (1 H, dd, *J* 3 and 9), 7.1–7.35 (5 H, m) and 8.71 (1 H, d, *J* 9); δ_C 18.3 (CH_3), 18.6 (CH_3), 24.5 (CH_3), 41.8 (C), 51.6 (CH), 54.4 (CH_2), 55.4 (OCH_3), 110.4, 112.1, 127.1, 127.2, 128.4 and 136.0 (CH), 128.0, 142.6, 143.6 and 162.6 (C) and 189.8 (C=S) (Found: C, 73.74; H, 7.20; N, 4.32. $C_{20}H_{23}NOS$ requires C, 73.80; H, 7.12; N, 4.30%).

***N*-Methyl-*N*-(2-phenylprop-1-enyl)thiobenzamides 2d.** This was a mixture of *E* and *Z* isomers and only the Z *isomer* was isolated by fractional recrystallization: mp 86–88 °C; ν_{max}/cm^{-1} 1460; δ_H 1.89 and 2.18 (3 H in total, ~2:1, both d, *J* 2), 2.78 and 3.38 (3 H in total, ~1:2, both s), 6.23 and 6.88 (1 H in total, ~2:1, both q, *J* 2) and 7.1–7.5 (10 H, m); δ_C 21.58 and 21.64 (CH_3), 43.4 and 44.0 (NCH_3), 125.6–133.2, 138.2 (C), 139.1 (C), 143.1 (C), 143.5 (C) and 201.5 and 201.9 (C=S) (Found: C, 76.48; H, 6.36; N, 5.26. $C_{17}H_{17}NS$ requires C, 76.36; H, 6.41; N, 5.24%). The *E* isomer was not completely purified: characteristic signals δ_H 1.90 (d, *J* 1), 3.70 (s) and 6.37 (q, *J* 1).

1-Methyl-2,4-diphenylpyrrole 3d. This was identified by direct comparison (IR, ^{1}H NMR, ^{13}C NMR and HPLC) with an authentic sample.[7]

2,4-Dimethyl-4-phenyl-3,4-dihydroisoquinoline-1(2*H*)-thione 5d. Mp 126–128 °C; ν_{max}/cm^{-1} 1500; δ_H 1.71 (3 H, s), 3.56 (3 H, s), 3.70 and 4.00 (2 H, ABq, *J* 13), 7.1–7.5 (8 H, m) and 8.66 (1 H, dd, *J* 1 and 8); δ_C 24.9 (CH_3), 42.4 (C), 44.9 (CH_2), 63.3

(NCH_3), 125.0–132.7, 133.8 (C), 140.5 (C), 143.7 (C) and 191.4 (C=S) (Found: C, 75.93; H, 6.38; N, 5.00. $C_{17}H_{17}NS$ requires C, 76.36; H, 6.41; N, 5.24%).

1-Isopropyl-2-phenylpyrrole 3e. Bp 100 °C/2 mmHg; ν_{max}/cm^{-1} 1600; δ_H 1.39 (6 H, d, *J* 7), 4.48 (1 H, sept, *J* 7), 6.13 (1 H, dd, *J* 2 and 3), 6.25 (1 H, t, *J* 3), 6.88 (1 H, dd, *J* 2 and 3) and 7.3–7.5 (5 H, m); δ_C 24.1 (CH_3), 47.1 (CH), 108.0 and 108.2 (3- and 4-C), 126.9, 128.3 and 129.3 (CH), 133.86 (C) and 133.94 (C) (Found: C, 84.38; H, 8.09; N, 7.38. $C_{13}H_{15}N$ requires C, 84.28; H, 8.16; N, 7.56%).

1-Isopropyl-2,3-diphenylpyrrole 3f. Mp 131–132 °C; ν_{max}/cm^{-1} 1600; δ_H 4.36 (6 H, d, *J* 7), 4.23 (1 H, sept, *J* 7), 6.47 (1 H, d, *J* 3), 6.88 (1 H, d, *J* 3) and 7.0–7.5 (10 H, m); δ_C 23.9 (CH_3), 47.1 (CH), 108.1 (4-C), 116.2 (5-C), 124.8–131.3, 122.0, 133.3 (C) and 136.6 (C) (Found: C, 86.99; H, 7.42; N, 5.31. $C_{19}H_{19}N$ requires C, 87.30; H, 7.33; N, 5.36%).

1-Isopropyl-2,4-diphenylpyrrole 3a

To an ethereal solution (30 cm^3) of (*E*)-β-bromomethylchalcone[13] (500 mg) was added isopropylamine (400 mg) and the resulting mixture was stirred overnight at room temperature. After filtration of isopropylamine hydrochloride, the solution was evaporated and the residue was chromatographed on silica gel. The pyrrole obtained in this reaction (72%) was identical with the photoproduct **3a** above (IR, NMR and HPLC).

1-Isopropyl-2-phenylpyrrole 3e

A benzene solution (250 cm^3) of β-[methyl(isopropyl)amino]-vinyl phenyl ketone (600 mg), which was prepared by the reaction[8] of β-chlorovinyl phenyl ketone with methylisopropylamine, was irradiated with a 1000 W high-pressure lamp through a Pyrex filter for 5 h. After removal of the solvent, the residue was chromatographed on silica gel. The pyrrole **3e** (7%) obtained in this reaction was identical with the product in the photoreaction of compound **1e** (IR, NMR and HPLC) (see above).

Determination of quantum yield

Benzophenone–benzhydrol actinometry[14] was used. Irradiation was performed with a 500 W high-pressure mercury lamp in a merry-go-round apparatus. The 313-nm line was isolated with a filter solution containing 0.002 M K_2CrO_4 and 1.0 M $NiSO_4$ in 5% aq. K_2CO_3.[14] The sample, in a Pyrex tube, was de-aerated by argon bubbling. After irradiation, the degree of reaction (formation of **2a** or **2a**-d_2) was determined by HPLC (ODS, aq. MeOH) using xanthone as internal standard.

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