PERKIN 2

Photochemical transformation of *S*-aryl 2-benzoylbenzothioates to 3-phenyl-3-arylthiobenzofuranones involving aryl migration

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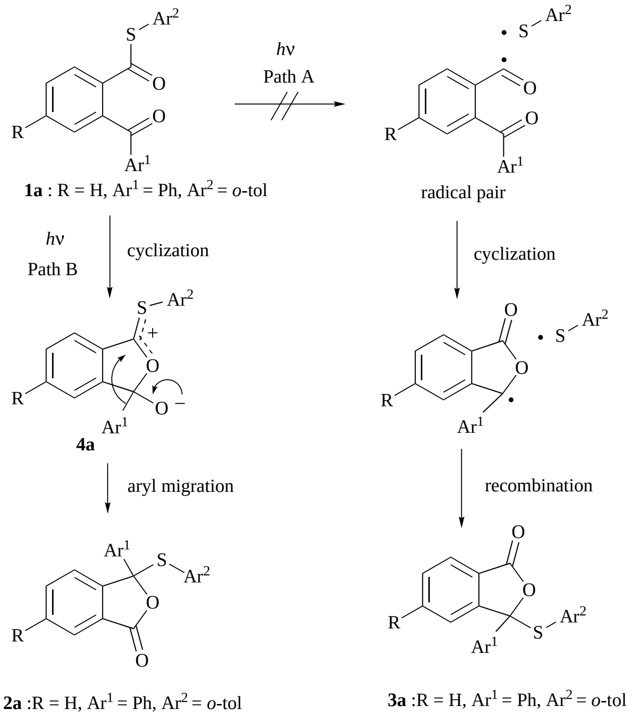
Photochemical reactions of *S*-aryl 2-benzoylbenzothioates 1 in solution media have been investigated. These thioesters undergo photoinduced cyclization to 3-aryl-3-arylthioisobenzofuranones 2 in yields of 14–46% upon direct irradiation. The photocyclization reaction is accompanied by a subsequent homolytic cleavage reaction of the isobenzofuranone leading to the dihydroisobenzofuranone dimer, (±)- and *meso*-3,3′-dioxo-1,1′-diphenyl-1,1′,3,3′-tetrahydro-1,1′-bi(isobenzofuranyl) 5. The formation of the dihydroisobenzofuranone 2 can be explained by a stepwise mechanism involving (*i*) intramolecular cyclization to a zwitterionic intermediate and (*ii*) subsequent aryl migration. Furthermore, sensitization and quenching studies reveal that the photochemical process occurs from the singlet excited states of the thioesters 1.

Introduction

It is well accepted that, upon irradiation, thioesters undergo homolytic cleavage to form an acyl and a thiyl radical pair, with subsequent reaction.[1–5] Recently, we reported the absolute asymmetric photochemical cyclization of *S*-(*o*-tolyl) 2-benzoylbenzothioate **1a** to a dihydroisobenzofuranone derivative **2a** in the crystalline state (Scheme 1).[6] This reaction could be understood in terms of a mechanism involving a novel phenyl migration[7–12] (Path B) which differs from a mechanism involving the commonly accepted homolytic C(=O)–S cleavage giving **3a** (Path A). In such a case, stereo- and regio-chemical correlation studies would provide an important stimulus for mechanistic studies since each reaction mechanism would be expected to develop different stereo- and regio-selectivities. Prior study of this photochemistry attempted to establish whether the solution photoreaction proceeds *via* a C–S cleavage (Path A) or phenyl migration mechanism (Path B). To resolve this question, we examined the photoreaction of variously substituted thioesters in solution. We found that thioesters **1** followed the same pathway observed in the solid-state photoreaction (Path B) to give the photoproducts **2** and the secondary photoreaction of dihydroisobenzofuranones **2** also proceeded, giving dihydroisobenzofuranone dimers.



Scheme 1

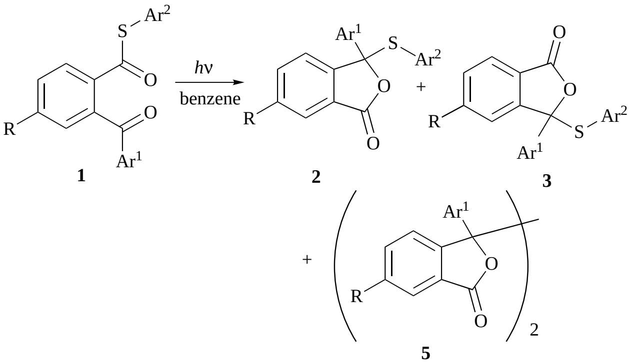
Results and discussion

The thioesters **1** were prepared by condensation of the corresponding 2-aroylbenzoyl chlorides with thiols in the presence of triethylamine (Table 1). Typically, photochemical experiments were carried out by irradiation of an argon-degassed benzene solution containing 100 mg of **1** (0.02 M) at room temperature for 6 h with Pyrex-filtered light from a 500 W high-pressure mercury lamp. For example, irradiation of a benzene solution of *S*-(*o*-tolyl) thioester **1a** led to the production of 3-(*o*-tolylthio)dihydroisobenzofuran-1-one **2a** in 29% isolated yield, though the photolysis in the solid state gave **2a** in 65% yield.[6] The lower chemical yield of **2a** can be attributed in part to another process leading to a dihydroisobenzofuranone dimer **5a** (65% yield), accompanied by loss of the thioaryl group resulting in the formation of di(*o*-tolyl) disulfide. The dimer **5a** was isolated by column chromatography and characterized by ^{1}H, ^{13}C NMR and IR spectroscopy. The structure of **5a** is further supported by the mass spectrum showing intense peaks at *m*/*z* 209 $[(M/2)]^+$ and 419 (MH^+), which are characteristic of 3-phenyldihydroisobenzofuran-1-one and **5a**, respectively. Similar results were observed in other thioesters **1b–g**. In fact, not only thioesters **1b–d** and **1g** bearing a benzoyl group at the C2 position, but also 2-(*p*-methylbenzoyl) **1e** and 2-(*p*-chlorobenzoyl) derivatives **1f** underwent the reaction to give the corresponding **2b–g**, respectively (Table 1).

These thioesters **1** do not show the distinct band that can be attributed to an n,π* transition, since this band is obscured by intense π,π* absorption (Fig. 1). In some cases of irradiation with light at 365 nm filtered through a uranyl glass filter, these thioesters gave **2** in higher chemical yields than those obtained with the Pyrex filtered light, because the secondary reaction would be suppressed by long wavelength light (Table 1). The quantum yields for the consumption of **1** upon excitation using light at 365 nm range from 0.028 to 0.085.

The spin multiplicities of the excited state responsible for these reactions were studied by quenching and sensitization

Table 1 Product distribution and quantum yields in the photolysis of thioesters **1**



				>290 nm[a]		365 nm[a]		
Thioester	R	Ar¹	Ar²	**2** (%)	**5** (%)[b]	**2** (%)	**5** (%)[b]	$\Phi(\times 10^{-2})$[c]
1a	H	Ph	*o*-Tol	29	59	58	24	4.4
1b	H	Ph	Ph	28	61	37	50	8.5
1c	H	Ph	*m*-Tol	29	57	34	58	6.4
1d	H	Ph	*p*-Tol	46	40	59	35	5.6
1e	H	*p*-Tol	Ph	14	82	75	11	6.4
1f	H	*p*-ClC_6H_4	Ph	20	73	28	55	2.8
1g	Me	Ph	Ph	19	66	32[d]	59[d]	6.3

[a] Photolyzed in a benzene solution at 100% conversion, and chemical yields are isolated yields. Benzofuranone **3** is different from **2** only in the case of thioester **1g**. [b] Compounds **5a–d** are the same material. [c] 365 nm line was isolated by the use of a uranyl glass filter. Quantum yields were measured for the consumption of thioesters **1** at a conversion of <40% using light at 365 nm filtered through a uranyl glass filter and a benzophenone–benzhydrol actinometer. [d] Benzofuranone **3g** was not detected.

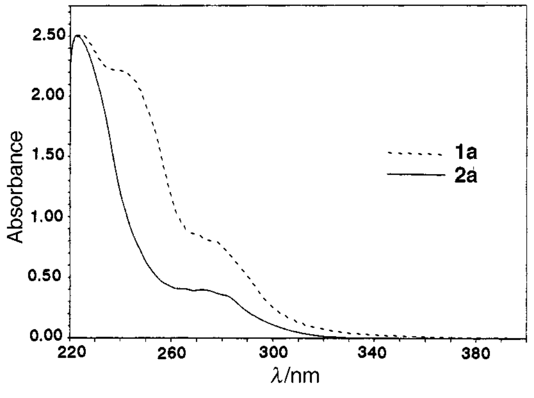


Fig. 1 UV spectra of **1a** (1.0×10^{-4} mol dm^{-3}) and **2a** (9.6×10^{-5} mol dm^{-3}) in cyclohexane

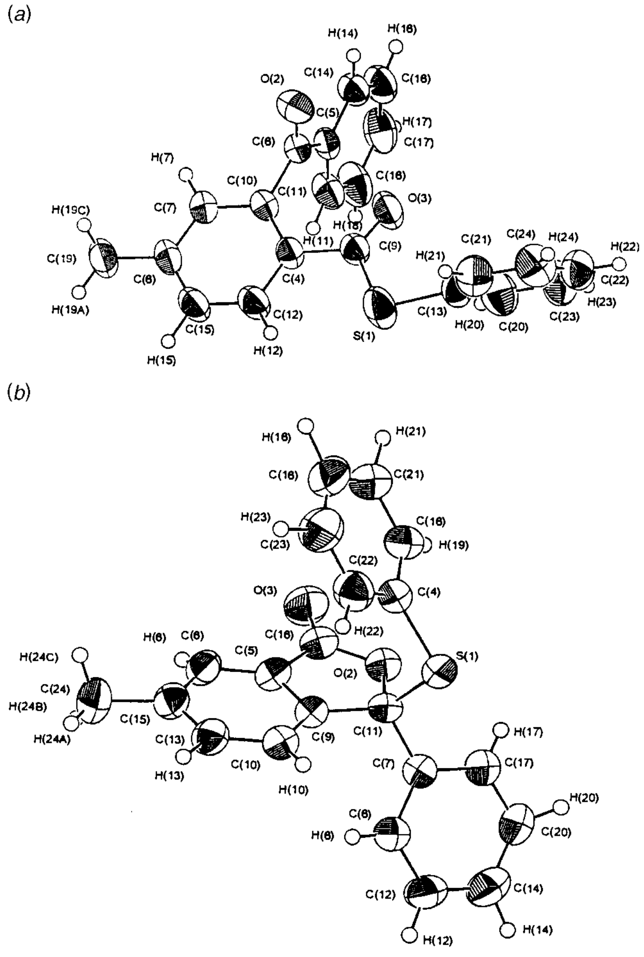


Fig. 2 ORTEP drawing of (*a*) **1g** and (*b*) **2g**

experiments. Attempted triplet sensitization of **1a** in argon-saturated benzene solution at 365 nm with acetophenone ($E_T = 73.7$ kcal mol^{-1}), 3-methoxyacetophenone ($E_T = 72.4$ kcal mol^{-1}) or acetone ($E_T = 78.0$ kcal mol^{-1})[13] gave no reaction, and the starting thioester **1a** was recovered. Furthermore, addition of triplet quenchers such as (*E*)-stilbene ($E_T = 50.0$ kcal mol^{-1}) and penta-1,3-diene ($E_T = 59.2$ kcal mol^{-1})[13] to the solution of **1a** in benzene[13] undergoing photolysis using light at 365 nm did not affect the efficiency of the photoreaction. Since all attempts to detect either a triplet sensitizing or a quenching reaction of **1a** proved fruitless, it is concluded that photoreaction of thioesters **1** takes place from the singlet excited state.

From Scheme 1 it is apparent that, when R ≠ H, Path A and Path B lead to isomeric dihydroisobenzofuranones **3** and **2**, respectively. After irradiation of the benzene solution of **1g** (0.02 M), the ^{1}H NMR spectrum of the crude photolysate exhibited three different methyl singlets (δ 2.40, 2.50 and 2.56) assignable to three different materials containing methyl protons with no signal due to **1g**. The signal detected at δ 2.50 is in accord with the chemical shift for **2g** (yield 19%); the other signals (δ 2.40 and 2.56) were tentatively identified as a mixture of two diastereomeric dihydroisobenzofuranone dimers (±)-**5g** and *meso*-**5g** in a yield of 66% [(±) : *meso* = 1.0, as determined by ^{1}H NMR spectroscopy of the crude reaction mixture], whereas the mass spectrum (FABMS) showed characteristic intense peaks at m/z 223 [$(M/2)^+$] and 447 (MH^+). The structures of **1g** and **2g** were confirmed by X-ray crystallographic analysis (Fig. 2). Considering the lack of 5-methyl-3,3-diphenyl-1,3-dihydroisobenzofuran-1-one **3g**,[14] it may be concluded that the radical mechanism involving the thioaryl migration (Path A) may be ruled out, and that the solution photochemistry of **1** may share a common feature of the solid-state photochemical process involving 1,4-aryl migration (Path B).

When the thioester **1a** was irradiated in benzene containing methanol (0.5 M), there was no change in the product selectivity. However, a remarkable change in the product profile occurred when thiols were used for this reaction.[15] Photolysis of the *S*-(*o*-tolyl) substituted thioester **1a** in the presence of thiophenol (0.5 M) yielded *S*-phenyl substituted dihydroisobenzofuranone **2b** quantitatively with complete suppression of the formation of dimer **5a**. Moreover, it is interesting to note that a thioester exchange reaction was observed in this photoreaction, where the recovered thioester **1** was composed of a mixture of both *o*-tolyl and phenyl thioesters, **1a** and **1b**. A mechanism involving thermal thioester exchange can be ruled out since neither **1a** nor **2a** reacts with thiophenol to form the alternatively substituted thioester **1b** or dihydroisobenzofuranone **2b** in the dark at room temperature. Such a 'crossed' reaction was also observed in the corresponding photoreaction of **1b** in the presence of *o*-toluenethiol which produced **2a**, and the dimerization was not observed.

The exchange of the arylthio group in **1** is understood just as well on the basis of the radical pair of the Path A as on the basis of the zwitterion **4** of Path B (Scheme 1). To ascertain the mechanism for the process, irradiation of **1g** in the presence of thiol was investigated. Irradiation of a benzene solution of **1g** in the presence of thiophenol (0.5 M), where both reagents share a common phenylthio group, led to exclusive generation of *S*-phenyl dihydroisobenzofuranone **2g**, which is formed *via* Path B; **3g** was not detected at all. These results indicated that the arylthio group exchange does not occur from the radical pair intermediate (Path A) but involves addition to zwitterion **4** (Path B). It can be concluded that the photochemical transformation of **1** into **2** (Path B) involves a stepwise mechanism rather than a concerted one (Scheme 1).

In conclusion, the solution photochemistry of *S*-aryl 2-benzoylbenzothioates **1** may share a common feature of the solid-state photochemical process, in which the key step involves intramolecular cyclization *via* zwitterion intermediates **4** and subsequent aryl migration to dihydroisobenzofuranones **2**. This phenyl migration involves the singlet-excited state. It is known that isobenzofuranones are particularly useful materials as synthetic intermediates.[16,17] The present reaction provides a useful synthesis of isobenzofuranones as well as insight into the photochemistry of thioesters.

Experimental

General

NMR spectra were recorded in $CDCl_3$ solutions on a JEOL GSX-400 and 500 operating at 400 and 500 MHz, respectively, for ^1H and ^{13}C NMR spectroscopy unless otherwise noted. Chemical shifts are reported in parts per million (ppm) relative to TMS as internal standards. Elemental analyses were made using a Perkin-Elmer-240 instrument. Ultraviolet (UV) spectra were determined with a JASCO model V-570 UV–VIS–NIR spectrophotometer. IR spectra were recorded on a JASCO FTIR-230 spectrometer as KBr disks, unless otherwise noted.

General procedure for the preparation of *S*-aryl 2-aroylbenzothioates (1a–g)

All *S*-aryl 2-aroylbenzothioates **1a**–**g** were prepared by the condensation of 2-aroylbenzoyl chloride and the corresponding arylthiol in the presence of triethylamine. For methyl substituted thioester **1g**, the requisite 4-methyl-2-benzoylbenzoic acid was prepared by the Friedel–Crafts condensation of 3-methylphthalic anhydride with benzene. A synthesis of **1a** is exemplified as follows. To a solution containing 0.90 g (8.17 mmol) of the thiophenol and 1.1 g (10.6 mmol) of triethylamine in 50 ml of dried benzene was added dropwise to a solution containing 2.0 g (8.17 mmol) of 2-benzoylbenzoyl chloride in 20 ml of dried benzene at 0 °C. The resulting mixture was stirred overnight, and extracted with an additional 100 ml of diethyl ether, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residual mixture was subjected to chromatography on silica gel and the crystalline thioester **1a** was recrystallized from $CHCl_3$–hexane; affording colorless prisms. The structures of **1a**–**g** were determined on the basis of spectral data and elemental analyses.

S-(*o*-Tolyl) 2-benzoylbenzothioate **1a** was obtained as colorless prismatic crystals from hexane–chloroform: yield 92%; mp 118–119 °C; $\lambda_{max}(C_6H_{12})$/nm 240 (ε/dm^3 mol^{-1} cm^{-1} 2.1×10^4), 278 (7.0×10^3); ν_{max}(KBr)/cm^{-1} 1677; δ_H 2.14 (s, 3H), 7.1–7.8 (m, 12H), 8.1–8.2 (m, 1H); δ_C 20.4, 126.2, 126.5, 128.3, 128.4, 128.6, 129.6, 129.9, 130.3, 130.7, 132.3, 133.0, 135.9, 136.9, 137.0, 139.6, 142.6, 189.8, 196.5. (Calc. for $C_{21}H_{16}O_2S$: C, 75.88; H, 4.85; N, 0.00. Found: C, 75.75; H, 4.79; N, 0.10%.)

S-Phenyl 2-benzoylbenzothioate **1b** was obtained as colorless prismatic crystals from hexane–chloroform: yield 88%; mp 96–97 °C; ν_{max}(KBr)/cm^{-1} 1672; $\lambda_{max}(C_6H_{12})$/nm 241 (ε/dm^3 mol^{-1} cm^{-1} 2.2×10^4), 280 (7.7×10^3); δ_H 7.2–7.8 (m, 13H), 8.0–8.1 (m, 1H); δ_C 126.9, 128.2, 128.4, 128.7, 129.1, 129.5, 129.6, 130.0, 132.3, 133.0, 134.6, 136.9, 137.0, 139.4, 190.4, 196.5. (Calc. for $C_{20}H_{14}O_2S$: C, 75.45; H, 4.43; N, 0.00. Found: C, 75.35; H, 4.31; N, 0.05%.)

S-(*m*-Tolyl) 2-benzoylbenzothioate **1c** was obtained as colorless prismatic crystals from hexane–chloroform: yield 85%; mp 98–99 °C; ν_{max}(KBr)/cm^{-1} 1670; $\lambda_{max}(C_6H_{12})$/nm 242 (ε/dm^3 mol^{-1} cm^{-1} 2.3×10^4), 277 (7.1×10^3); δ_H 2.29 (s, 3H), 7.0–7.8 (m, 12H), 8.0–8.1 (m, 1H); δ_C 21.2, 126.4, 128.1, 128.4, 128.7, 129.0, 129.6, 130.1, 130.4, 131.6, 132.3, 133.0, 135.2, 137.0, 137.2, 139.0, 139.4, 190.6, 196.6. (Calc. for $C_{21}H_{16}O_2S$: C, 75.88; H, 4.85; N, 0.00. Found: C, 75.70; H, 4.87; N, −0.01%.)

S-(*p*-Tolyl) 2-benzoylbenzothioate **1d** was obtained as colorless prismatic crystals from hexane–chloroform: yield 83%; mp 96–97 °C; ν_{max}(KBr)/cm^{-1} 1665, 1677; $\lambda_{max}(C_6H_{12})$/nm 242 (ε/dm^3 mol^{-1} cm^{-1} 2.5×10^4), 279 (8.5×10^3); δ_H 2.31 (s, 3H), 7.1–7.6 (m, 12H), 8.0–8.1 (m, 1H); δ_C 21.6, 123.6, 128.5, 128.7, 129.0, 129.9, 130.3, 132.6, 133.3, 134.9, 137.3, 137.4, 139.7, 140.2, 191.1, 196.9. (Calc. for $C_{21}H_{16}O_2S$: C, 75.88; H, 4.85; N, 0.00. Found: C, 76.02; H, 4.81; N, 0.01%.)

S-Phenyl 2-(*p*-tolylcarbonyl)benzothioate **1e** was obtained as colorless prismatic crystals from hexane–chloroform: yield 83%; mp 85–86 °C; ν_{max}(KBr)/cm^{-1} 1665, 1675; $\lambda_{max}(C_6H_{12})$/nm 244 (ε/dm^3 mol^{-1} cm^{-1} 2.1×10^4), 285 (7.7×10^3); δ_H 2.40 (s, 3H), 7.2–7.7 (m, 12H), 8.0–8.1 (m, 1H); δ_C 21.7, 127.0, 128.2, 128.6, 129.1, 129.5, 129.8, 129.9, 132.2, 134.5, 134.6, 137.0, 139.7, 143.9, 190.3, 196.2. (Calc. for $C_{21}H_{16}O_2S$: C, 75.88; H, 4.85; N, 0.00. Found: C, 75.85; H, 4.76; N, 0.06%.)

S-Phenyl 2-(*p*-chlorophenylcarbonyl)benzothioate **1f** was obtained as colorless prismatic crystals from hexane–chloroform: yield 85%; mp 106–107 °C; ν_{max}(KBr)/cm^{-1} 1666; $\lambda_{max}(C_6H_{12})$/nm 249 (ε/dm^3 mol^{-1} cm^{-1} 2.2×10^4), 256 (2.2×10^4); δ_H 7.2–8.1 (m); δ_C 126.7, 128.4, 128.5, 128.7, 129.3, 129.7, 130.2, 130.9, 132.6, 134.7, 135.4, 136.8, 139.0, 139.5, 190.3, 195.4. (Calc. for $C_{20}H_{13}O_2SCl$: C, 68.08; H, 3.71; N, 0.00. Found: C, 67.93; H, 3.61; N, −0.17%.)

S-Phenyl 4-methyl-2-benzoylbenzothioate **1g** was obtained as colorless prismatic crystals from hexane–chloroform: yield 87%; mp 118–119 °C; ν_{max}(KBr)/cm^{-1} 1667, 1678; $\lambda_{max}(C_6H_{12})$/nm 245 (ε/dm^3 mol^{-1} cm^{-1} 2.2×10^4), 282 (7.0×10^3); δ_H 2.45 (s, 3H), 7.2–7.8 (m, 12H), 7.9–8.0 (m, 1H); δ_C 21.5, 127.0, 128.2, 128.3, 128.4, 129.0, 129.1, 129.1, 129.4, 129.6, 130.4, 134.6, 134.7, 137.0, 139.7, 143.6, 189.7, 196.8. (Calc. for $C_{21}H_{16}O_2S$:

C, 75.88; H, 4.85; N, 0.00. Found: C, 75.75; H, 4.75; N, −0.04%.)

X-Ray crystallographic analysis of 1g. Colorless prismatic crystals from hexane–chloroform, molecular formula $C_{21}H_{16}O_2S$, molecular weight 332.40, monoclinic space group $P\bar{1}$, $a = 8.774(4)$, $b = 9.919(3)$, $c = 10.469(4)$ Å, $\alpha = 81.87(2)$, $\beta = 79.16(3)$, $\gamma = 75.48(3)°$, $V = 862.1(5)$ Å^3, $Z = 2$, $\rho = 1.28$ g cm^{-3}, μ(Cu-Kα) = 1.54 cm^{-1}, $F(000) = 347$; $R = 0.0591$, $R_W = 0.0656$ for 2467 reflections. The structure was solved by the direct method and refined by the method of full-matrix least squares.†

General procedure for the photochemical reaction in benzene

A benzene solution of thioesters **1a**–**g** (0.02 mol l^{-1}) was purged with deoxygenated and dried argon for 30 min prior to photolysis and was irradiated with a 500 W Eikosha high-pressure mercury lamp through a Pyrex filter. After irradiation, the photolysate was chromatographed using Merck Kieselgel 60 with benzene as the eluent. The ratios of the benzofuranone dimers (±)-**3** and *meso*-**3** were quantified by the comparison of the relative intense peak of each isomer in the ^{1}H and ^{13}C NMR spectra of the product mixture. Unfortunately, the relative stereochemistry of the dimers **3** could not be determined since analyses of their NMR studies did not allow an easy correlation to be established.

3-Phenyl-3-(*o*-tolylthio)-1,3-dihydroisobenzofuran-1-one **2a** was obtained as colorless prismatic crystals from hexane–chloroform: mp 141–142 °C; ν_{max}(KBr)/cm^{-1} 1772; λ_{max}(C_6H_{12})/nm 283 (ε/dm^3 mol^{-1} cm^{-1} 3.2 × 10^3); δ_H 2.45 (s, 3H), 6.8–7.8 (m, 13H); δ_C 21.2, 97.3, 123.7, 125.0, 125.3, 125.8, 128.3, 128.6, 129.1, 129.5, 130.0, 130.4, 134.0, 137.7, 137.8, 143.8, 149.9, 168.0. (Calc. for $C_{21}H_{16}O_2S$: C, 75.88; H, 4.85; N, 0.00. Found: C, 75.75; H, 4.79; N, 0.06%.)

(±)- and *meso*-3,3′-dioxo-1,1′-diphenyl-1,1′,3,3′-tetrahydro-1,1′-bi(isobenzofuranyl) **5a** were analyzed by IR, ^{1}H and ^{13}C NMR spectroscopy as a mixture [(±) : *meso* = 1.0]: ν_{max}(KBr)/cm^{-1} 1776; δ_H 7.0–8.0 (m, 18H); δ_C 20.8, 21.4, 90.0, 90.8, 124.5, 125.1, 125.5, 125.6, 125.7, 126.2, 126.3, 126.8, 127.8, 128.1, 128.3, 128.4, 129.6, 129.7, 134.2, 134.6, 134.9, 136.6, 149.0, 149.1, 168.7, 169.2; *m*/*z* (LRMS, FAB) 209, 419.

3-Phenyl-3-phenylthio-1,3-dihydroisobenzofuran-1-one **2b** was obtained as colorless prismatic crystals from hexane–chloroform: mp 107–108 °C; ν_{max}(KBr)/cm^{-1} 1774; λ_{max}(C_6H_{12})/nm 269 (ε/dm^3 mol^{-1} cm^{-1} 2.8 × 10^3); δ_H 7.1–7.8 (m, 14H); δ_C 96.9, 123.7, 125.0, 125.4, 125.9, 128.6, 128.7, 129.0, 129.1, 129.4, 129.6, 134.1, 136.6, 137.5, 149.9, 168.2. (Calc. for $C_{20}H_{14}O_2S$: C, 75.45; H, 4.43; N, 0.00. Found: C, 75.32; H, 4.37; N, −0.05%.)

3-Phenyl-3-(*m*-tolylthio)-1,3-dihydroisobenzofuran-1-one **2c** was obtained as colorless prismatic crystals from hexane–chloroform: mp 90–91 °C; ν_{max}(KBr)/cm^{-1} 1770; λ_{max}(C_6H_{12})/nm 271 (ε/dm^3 mol^{-1} cm^{-1} 3.0 × 10^3); δ_H 2.16 (s, 3H), 7.0–7.8 (m, 13H); δ_C 21.1, 97.0, 123.9, 125.1, 125.6, 126.0, 128.4, 128.8, 129.2, 129.5, 130.4, 133.6, 134.1, 137.3, 137.7, 138.5, 150.0, 168.4. (Calc. for $C_{21}H_{16}O_2S$: C, 75.88; H, 4.85; N, 0.00. Found: C, 75.69; H, 4.84; N, −0.07%.)

3-Phenyl-3-(*p*-tolylthio)-1,3-dihydroisobenzofuran-1-one **2d** was obtained as colorless prismatic crystals from hexane–chloroform: mp 95–96 °C; ν_{max}(KBr)/cm^{-1} 1777; λ_{max}(C_6H_{12})/nm 283 (ε/dm^3 mol^{-1} cm^{-1} 2.1 × 10^3); δ_H 2.20 (s, 3H), 6.8–7.8 (m, 13H); δ_C 21.2, 96.9, 123.7, 125.0, 125.3, 125.4, 125.9, 128.7, 129.1, 129.3, 129.4, 134.1, 136.5, 137.6, 139.9, 150.0, 168.3. (Calc. for $C_{21}H_{16}O_2S$: C, 75.88; H, 4.85; N, 0.00. Found: C, 75.74; H, 4.88; N, −0.01%.)

3-(*p*-Tolyl)-3-phenylthio-1,3-dihydroisobenzofuran-1-one **2e** was obtained as colorless prismatic crystals from hexane–chloroform: mp 123–124 °C; ν_{max}(KBr)/cm^{-1} 1765; λ_{max}(C_6H_{12})/nm 268 (ε/dm^3 mol^{-1} cm^{-1} 3.6 × 10^3); δ_H 2.34 (s, 3H), 7.1–7.8 (m, 13H); δ_C 21.1, 97.0, 123.7, 124.9, 125.4, 125.8, 128.5, 129.1, 129.4, 129.5, 134.1, 134.5, 136.6, 139.2, 150.0, 168.3. (Calc. for $C_{21}H_{16}O_2S$: C, 75.88; H, 4.85; N, 0.00. Found: C, 75.69; H, 4.90; N, −0.01%.)

(±)- and *meso*-3,3′-dioxo-1,1′-diphenyl-1,1′,3,3′-tetrahydro-1,1′-bi(isofuranyl) **5e** were analyzed by IR, ^{1}H and ^{13}C NMR spectroscopy as a mixture [(±) : *meso* = 1.0]: ν_{max}(KBr)/cm^{-1} 1778; δ_H 2.14 and 2.22 (each s, total 6H), 6.8–8.4 (m, 16H); δ_C 20.8, 21.4, 90.2, 90.9, 124.4, 125.0, 125.4, 125.5, 126.1, 126.2, 126.6, 128.4, 128.8, 129.5, 129.6, 132.0, 133.7, 134.0, 134.4, 138.0, 138.2, 149.3, 149.4, 168.8, 169.3; *m*/*z* (LRMS, FAB) 223, 447.

3-(*p*-Chlorophenyl)-3-phenylthio-1,3-dihydroisobenzofuran-1-one **2f** was obtained as colorless prismatic crystals from hexane–chloroform: mp 135–136 °C; ν_{max}(KBr)/cm^{-1} 1765; λ_{max}(C_6H_{12})/nm 267 (ε/dm^3 mol^{-1} cm^{-1} 3.4 × 10^3); δ_H 7.1–7.8 (m, 13H); δ_C 96.2, 123.5, 125.2, 125.3, 127.4, 128.6, 128.7, 128.8, 129.7, 129.8, 134.3, 135.2, 136.2, 136.5, 149.5, 167.9. (Calc. for $C_{20}H_{13}O_2SCl$: C, 68.18; H, 3.72; N, 0.00. Found: C, 68.34; H, 3.71; N, 0.00%.)

(±)- and *meso*-3,3′-dioxo-1,1′-diphenyl-1,1′,3,3′-tetrahydro-1,1′-bi(isobenzofuranyl) **5f** were analyzed by IR, ^{1}H and ^{13}C NMR spectroscopy as a mixture [(±) : *meso* = 1.0]: ν_{max}(KBr)/cm^{-1} 1777; δ_H 7.0–7.8 (m, 16H); δ_C 89.4, 90.2, 124.2, 124.7, 125.2, 125.4, 125.8, 125.9, 127.6, 128.0, 128.6, 128.8, 129.0, 130.0, 130.1, 133.4, 134.5, 134.7, 134.8, 135.1, 136.5, 148.3, 148.4, 168.1, 168.7; *m*/*z* (LRMS, FAB) 243, 487.

6-Methyl-3,3-diphenylthio-1,3-dihydroisobenzofuran-1-one **2g** was obtained as colorless prismatic crystals from hexane–chloroform: mp 59–60 °C; ν_{max}(KBr)/cm^{-1} 1778; λ_{max}(C_6H_{12})/nm 285 (ε/dm^3 mol^{-1} cm^{-1} 1.4 × 10^3); δ_H 2.50 (s, 3H), 7.1–7.8 (m, 13H); δ_C 22.2, 96.5, 123.9, 124.8, 125.9, 128.5, 128.6, 129.0, 129.2, 129.5, 130.7, 136.5, 137.8, 145.5, 150.5, 168.3; *m*/*z* (LRMS, FAB) 223, 333. (Calc. for $C_{21}H_{16}O_2S$: C, 75.88; H, 4.85; N, 0.00. Found: C, 75.72; H, 4.84; N, −0.03%.)

(±)- and *meso*-3,3′-dioxo-1,1′-diphenyl-1,1′,3,3′-tetrahydro-1,1′-bi(isobenzofuranyl) **5g** were analyzed by IR, ^{1}H and ^{13}C NMR spectroscopy as a mixture [(±) : *meso* = 1.0]: ν_{max}(KBr)/cm^{-1} 1778; δ_H 2.40 (s, 6H), 2.56 (s, 6H), 7.0–7.8 (m, 16H); δ_C 22.2, 22.3, 89.8, 90.6, 123.0, 125.0, 125.2, 125.3, 126.2, 126.7, 127.7, 128.1, 128.2, 128.3, 130.8, 135.2, 137.1, 145.6, 145.9, 149.6, 149.7, 168.9, 169.4; *m*/*z* (LRMS, FAB) 223, 447.

X-Ray crystallographic analysis of 2g. Colorless prismatic crystals from hexane–chloroform, molecular formula $C_{21}H_{16}O_2S$, molecular weight 332.40, monoclinic space group $P2_1/n$, $a = 10.796(4)$, $b = 16.288(7)$, $c = 10.311(4)$ Å, $\beta = 108.66(3)°$, $V = 1718(1)$ Å^3, $Z = 4$, $\rho = 1.28$ g cm^{-3}, μ(Cu-Kα) = 1.54 cm^{-1}, $F(000) = 695$; $R = 0.0729$, $R_W = 0.0771$ for 2315 reflections. The structure was solved by the direct method and refined by the method of full-matrix least-squares.

Quantum yield measurements

All quantum yields were determined at < 40% conversion of the thioesters using light, filtered through a uranyl glass filter with a 500 W high-pressure mercury lamp, at 365 nm. The light flux was calibrated using a benzophenone–benzhydrol actinometer.[13] The amount of products formed in each irradiation was determined by use of HPLC analyses. The concentration of thioester used for the quantum yield determinations was 0.05 mol l^{-1}.

Sensitization experiments of thioesters 1a

Sensitization was carried out by irradiating a benzene solution of thioesters **1a** with light at 313 nm using K_2CrO_4/Na_2CO_3

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† Full crystallographic details for both **1g** and **2g**, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see ‘Instructions for Authors’, *J. Chem. Soc.*, *Perkin Trans. 2*, available *via* the RSC Web page (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 188/119.

solution filter.[13] A benzene solution of **1a** (100 mg, 0.02 mol l^{-1}) and triplet sensitizers was irradiated under conditions where the sensitizers should absorb >95% of the incident light. After the solvent was removed *in vacuo*, the crude reaction mixture was analyzed by ^{1}H NMR spectroscopy, with response factors for product distribution.

Quenching experiments of thioesters 1a

The irradiation was performed at room temperature using a uranyl glass filtered light with a high-pressure mercury lamp. A benzene solution of **1a** (100 mg, 0.02 mol l^{-1}) containing triplet quenchers (0.2 mol l^{-1}) was irradiated. The quenchers do not absorb light in the excitation region of **1a**. The reactions were monitored by ^{1}H NMR spectroscopy.

Preparation of 5-methyl-3,3-diphenylthio-1,3-dihydroisobenzofuran-1-one 3g

This substance was prepared by the condensation of 2-benzoyl-4-methylbenzoyl chloride and thiophenol in the presence of triethylamine as the following synthetic procedure. To a solution containing 2.0 g (8.32 mmol) of 2-benzoyl-4-methylbenzoyl chloride and 0.92 g (8.32 mmol) of the thiophenol in 50 ml of dried benzene was added dropwise a solution containing 1.1 g (10.8 mmol) of triethylamine in 20 ml of dried benzene at room temperature. The resulting mixture was stirred overnight, and extracted with an additional 100 ml of diethyl ether, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residual mixture was subjected to chromatography on silica gel and the crystalline benzofuranone **3g** was recrystallized from $CHCl_3$–hexane; affording colorless prisms: yield 75%; mp 144–145 °C; ν_{max}(KBr)/cm^{-1} 1776; λ_{max}(C_6H_{12})/nm 249 (ε/dm^3 mol^{-1} cm^{-1} 6.4 × 10^3), 255 (4.9 × 10^3), 261 (3.9 × 10^3); δ_H 2.36 (s, 3H), 7.1–7.8 (m, 13H); δ_C 21.1, 96.7, 123.4, 125.0, 125.6, 125.9, 128.5, 128.6, 129.0, 129.2, 129.5, 135.3, 136.5, 137.8, 139.9, 147.3, 168.4; *m*/*z* (LRMS, FAB) 223, 333. (Calc. for $C_{21}H_{16}O_2S$: C, 75.88; H, 4.85; N, 0.00. Found: C, 75.82; H, 4.92; N, 0.05%.)

Photoreaction of thioesters 1 with thiols

A benzene solution of thioesters **1** (100 mg, 0.02 mol l^{-1}) with thiols (0.5 mol l^{-1}) was irradiated under the standard conditions (Pyrex, room temperature). After separation by column chromatography on silica gel (toluene–hexane, 1 : 1 as eluent), benzofurans **2** were obtained in a yield of >95%.

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