PHOTOCYCLIZATION REACTIONS OF *N*-SUBSTITUTED THIOPHTHALIMIDES

JOHN D. COYLE and PATRICIA A. RAPLEY
Chemistry Department, The Open University, Milton Keynes MK7 6AA (Gt. Britain)
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Summary

N-(Dialkylaminomethyl)thiophthalimides have been prepared; irradiation leads to cleavage products, namely *N*-(thioformyl)dialkylamines and β-isoindigo, as well as small amounts of oxidation products. The cleavage products may arise by way of initial hydrogen abstraction or by way of heterolytic C—N bond fission. Photo-oxidation occurs readily for *N*-methylthiophthalimide or *N*-methyldithiophthalimide in the presence of oxygen. No products of intramolecular hydrogen abstraction processes could be isolated after irradiation of a variety of other *N*-substituted thiophthalimides.

1. Introduction

The photochemistry of imides has received considerable attention [1, 2], in part because of the range of fused heterocyclic systems that can be produced, either by intermolecular or intramolecular cycloaddition to alkenes [3], or by intramolecular hydrogen transfer accompanied by cyclization. The latter includes reactions leading to macrocyclic compounds involving sulphur [4] or nitrogen [5] atoms in the large ring. Previous studies in our laboratories have included the synthesis of polycyclic systems with a new imidazolidine ring derived from aromatic imides [6], aliphatic imides [7] or hydantoins [8]. The products from methoxy-substituted aromatic imides can be converted to oxygenated alkaloids of the protoberberine family [9], but reduction of the photoproducts (*e.g.* 1) from aromatic imides has proved difficult to effect, probably because of the presence of an *N*-α-hydroxyalkyllactam unit.

For this reason we turned our attention to sulphur analogues, in the expectation that the corresponding sulphur-containing photoproducts would, if formed, be amenable to desulphurization. Although our studies have included the isolation of thietanes or thietes from the photocycloaddition reactions between thioimides and alkenes [10] (thietanes have also been postulated as intermediates in the photoreactions of thiobenzamide

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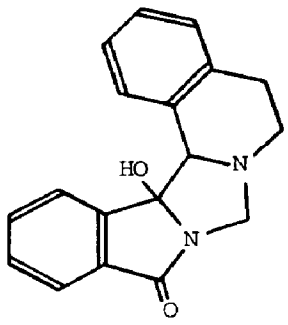

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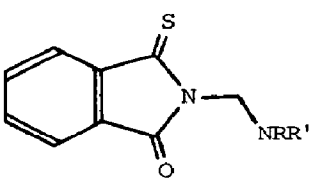
with alkenes [11] and of thioindolinones with alkenes [12]) or alkynes [13], there have been few other literature reports of photochemistry involving the C=S group of thioimides. Only recently has the first account appeared [14] of a reaction involving intramolecular hydrogen abstraction in a related system (a thioaroylurea). The same research group has shown [15] that acyclic *N*-alkylthioimides rearrange to α-acylaminothioketones on irradiation, and this is best accounted for by an initial hydrogen abstraction. Because we wanted to make a direct comparison with the phthalimide system, we chose to start with nitrogen Mannich bases derived from thiophthalimide; however, although Mannich bases have been made from many amide, imide or related NH compounds, none has been reported for thioimides.

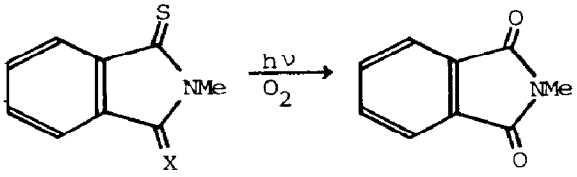
2. Results and discussion

Mannich bases have not previously been prepared from thioimides, although thiohydantoins have been successfully employed as substrates in the Mannich reaction [16], and there is an isolated account [17] relating to a thioamide, 2,6-dichloro-*N*-(dimethylaminomethyl)thiobenzamide. We find that certain Mannich bases (2) can be successfully prepared by heating together thiophthalimide, formaldehyde and a secondary amine in aqueous ethanol; products could not be isolated when dimethylamine, *N*-methylbenzylamine, *N*-methylcyclohexylamine or 1,2,5,6-tetrahydropyridine was used, nor in the single instance when the reaction was attempted with dithiophthalimide.



2a R,R′ ≡ $CH_2CH_2OCH_2CH_2$
2b R,R′ ≡ $(CH_2)_5$
2c R,R′ ≡ *o*-$CH_2C_6H_4CH_2CH_2$
2d R ≡ R′ ≡ CH_2Ph
2e R ≡ R′ ≡ *c*-C_6H_{11}

The electronic absorption spectrum of *N*-methylthiophthalimide (3; X ≡ O) in acetonitrile shows four major bands, at 234, 296, 328 and 484 nm (ϵ (l mol^{-1} cm^{-1}) = 20 000, 14 500, 10 500 and 34 respectively), and the spectra of the derivatives (2) are similar. All of the Mannich bases are light sensitive, and solid samples or solutions in benzene or acetonitrile left in sunlight behind window glass changed colour from orange–red to yellow over a period of several weeks. The solutions deposited a brownish precipitate. Complex mixtures of products were formed, and thin-layer chromatography (TLC) analysis showed that the same range of products was formed in the solid state as in solution. In each case one of the products was tentatively identified (from its R_f value) as the corresponding phthalimide Mannich base. This photo-oxidation would parallel the reaction in which thioketones are converted to ketones by irradiation in the presence of oxygen [18], and as a model we irradiated *N*-methylthiophthalimide (3; X ≡ O) in acetonitrile with oxygen present. *N*-Methylphthalimide was isolated in 66% yield, elemental sulphur was deposited and sulphur dioxide was detected in the exit gases. Proton nuclear magnetic resonance (NMR) analysis of the crude product mixture suggests that little else other than *N*-methylphthalimide was formed. A similar result was obtained when *N*-methyldithiophthalimide (3; X ≡ S) was irradiated under the same conditions.



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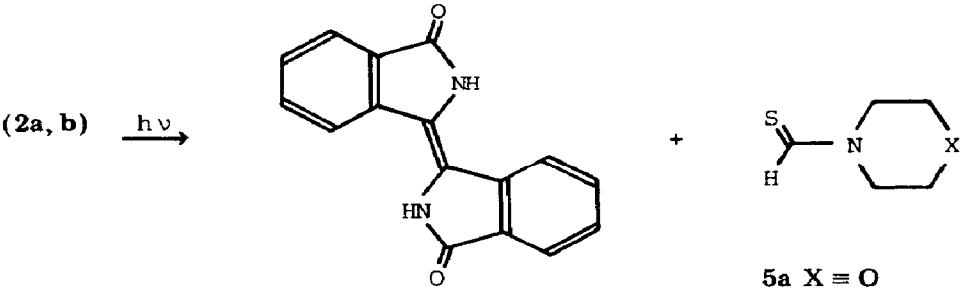
Larger-scale irradiations of the Mannich bases in acetonitrile were carried out using a medium pressure mercury arc (Pyrex filter) as light source, effectively exciting at 313, 366, 405, 408 and 436 nm. The insoluble yellow–brown material was deposited most heavily from solutions of **2a** and **2b**, and it was isolated by filtration, dissolving it in concentrated sodium hydroxide solution and re-precipitation using glacial acetic acid to give a bright yellow solid. This was identified as β-isoindigo (3,3′-dioxo-1,1′-biisoindolinylidene) (4) by comparison with an authentic sample prepared from thiophthalimide and metallic silver [19].



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5a X ≡ O
5b X ≡ CH_2

The yields obtained from a number of experiments ranged up to 58% from **2a** and 17% from **2b**; the quantity deposited during the irradiation of **2c** was too small to isolate. After removal of solvent from the filtered reaction mixtures, silica-gel column chromatography yielded *N*-thioformylamines (**5a** and **5b**) as major components. The crude yields were 57% - 67% and 18% respectively, and the yields after purification were 23% and 11%. The structures of these products were elucidated from their spectral properties: in particular, from a signal in the proton NMR spectra at 9.2 - 9.3 ppm and a doublet in the carbon-13 NMR spectra at about 186 ppm, and by comparison with published data [20].

The formation of β-isoindigo and the thioformylamine in approximately equal amounts implies that a cleavage mechanism operates in the excited state reactions of the thioimide Mannich bases. Thiophthalimide and *N*-methylthiophthalimide are stable under the irradiation conditions, which suggests that the aminomethyl substituent plays a part in the cleavage process. The two most plausible pathways involve either direct heterolytic β cleavage to give ions that recombine by attack of nucleophilic sulphur on the carbon of an iminium species (Fig. 1), or β-hydrogen abstraction (probably by sulphur initially, with subsequent transfer to carbon) and cyclization followed by cleavage of the 1,3-thiazetidine (Fig. 2); it has been proposed [21] that cleavage of 1,3-thiazetidines accounts for the products observed when thioketones react photochemically with imines. In both mechanisms the β-isoindigo is formed by the known dimerization of isoindolone [22].

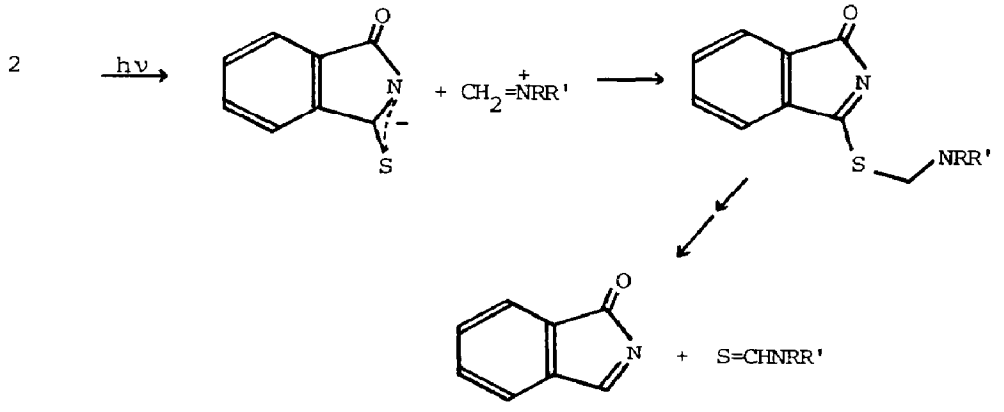


Fig. 1.

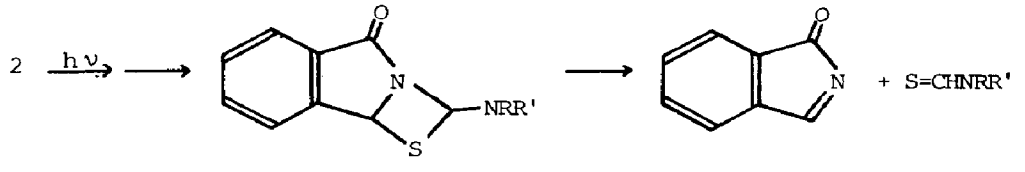
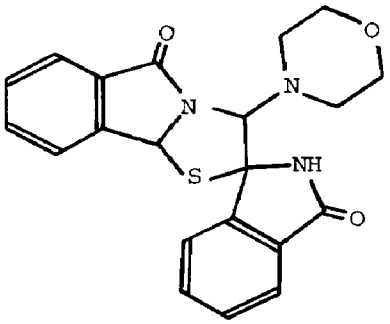


Fig. 2.

Certain thioketones, such as thiofenchone, undergo a β-hydrogen abstraction reaction to yield cyclopropanethiols [23], and thiobenzoylformamides can undergo photochemical hydrogen abstraction and cyclization to give thiazolidinone products in which the sulphur is incorporated in the new ring system [24]. Hence we have a preference, in the absence of further evidence, for the second of the two postulated mechanisms.

Most of the Mannich bases gave product mixtures on irradiation from which it was difficult to isolate any component in a pure state, except for the cleavage products described just above. From the reaction of **2b** a large amount (30%) of thiophthalimide was obtained, which might be formed by protonation of the anion that results from heterolytic β fission. However, there is no obvious reason why it is produced in such large quantities only from this particular substrate; we cannot rule out the possibility that some of it was formed from unchanged starting material during the chromatographic work-up procedure. From the reaction of **2a** small amounts of thiophthalimide and *N*-(morpholinomethyl)phthalimide were isolated, together with a compound (19% crude, 5% after recrystallization) with a high melting point, whose structure is assigned as either **6** or **7**.



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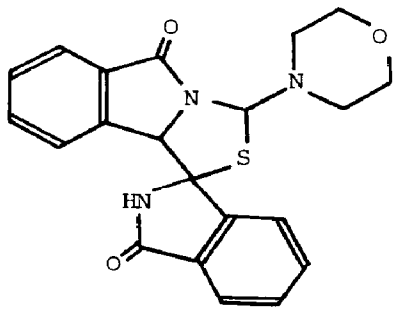

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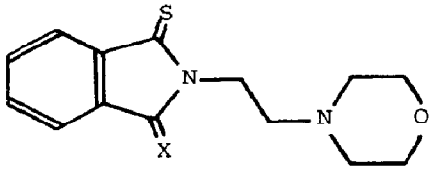
A satisfactory microanalysis could not be obtained, but fast-atom bombardment mass spectrometry showed the parent ion to be $C_{21}H_{19}N_3O_3S$. The carbon-13 NMR spectrum indicated the presence of two amide carbonyls, an intact morpholino substituent, two low-field aliphatic CH units and 12 aromatic carbon atoms. Supporting evidence came from the NMR and IR spectra, which also indicated the presence of one amide NH proton. It is not possible to distinguish between **6** and **7** on the basis of the spectral evidence, since there are no suitable model compounds with appropriately substituted methine carbons; either compound might arise by reaction of a thiazetidine (Fig. 2) with isoindolone.

From the complex mixture obtained after irradiation of **2c** a small fraction (less than 2%) was isolated that gave a proton NMR spectrum with a signal at 9.45 ppm. This suggests that *N*-(thioformyl)-1,2,3,4-tetrahydroisoquinoline had been formed, but fuller characterization was not possible; the small quantity isolated is in keeping with the small amount of β-isoindigo formed from this substrate. A larger fraction (4% - 5% after some

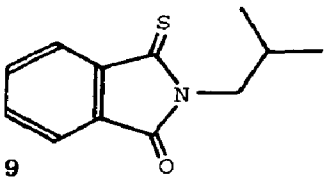
purification) gave IR, proton NMR and carbon-13 NMR spectra consistent with some kind of cyclized structure. However, microanalysis and mass spectral results indicated that sulphur was not present, although the other spectral data do not correspond to those for either of the diastereoisomers of **1** [25], which is the expected product of photocyclization of the *N*-substituted phthalimide that might be derived by oxidation of **2c**. We were therefore unable to assign a structure to this product.

The absence of high yields of photocyclized products in the mixtures obtained by irradiating the Mannich bases **2** led us to prepare and irradiate the analogue **8a**, in which there is a 2-morpholinoethyl substituent on the thioimide, and also the dithio derivative **8b**. Both **8a** and **8b** were made successfully by the thionation of the corresponding phthalimide, but irradiation led to complex mixtures of products from which we were unable to isolate any pure material.



8a X ≡ O
8b X ≡ S

To test for the occurrence of intramolecular hydrogen abstraction reactions in substrates that do not contain a nitrogen atom in the *N*-substituent, we prepared and irradiated *N*-isobutylthiophthalimide (**9**), *N*-(*o*-tolyl)thiophthalimide (**10a**) and *N*-(*o*-tolyl)dithiophthalimide (**10b**) (the phthalimide analogues of **9** and **10** give photoproducts quite efficiently: see refs. 26 and 7 respectively). For each of these compounds extended irradiation (up to 10 times that required for substantial reaction of **2a**, **2b** and **2c**) with a medium pressure or high pressure mercury arc led only to mixtures of starting material and oxidized product (*N*-substituted phthalimide), together with small amounts of one or more additional components detected by TLC analysis. Irradiation of *N*-methylthiophthalimide with toluene as the solvent did give a complex mixture of products on extended irradiation, but one was identified as *N*-methylphthalimide (*i.e.* the product of oxidation), and other fractions gave spectra that suggested reaction had taken place between this imide, rather than the thioimide, and toluene.



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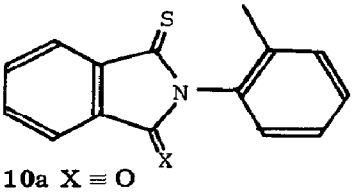

10a X ≡ O
10b X ≡ S

It appears that hydrogen abstraction in the excited state(s) of these thioimide systems is less efficient than the reaction for analogous imides. This may be because the triplet excited state is much lower in energy and the process is consequently not so favourable thermodynamically, although other energy terms also need to be considered. The non-oxidized products that are formed in the Mannich base systems arise by an overall cleavage process which may involve hydrogen abstraction as an initial step.

3. Experimental details

Thiophthalimide was prepared from phthalonitrile by reaction with Na_2S and H_2S in aqueous ethanol and then hydrolysis of the iminoisoindolinethione [27] with aqueous HCl. The red needles had a melting point (m.p.) of 175 - 177 °C, ν_{max} at 3200, 1750 and 1730 cm^{-1}, and $\delta_H(CDCl_3)$ of 2.6 (1H, broad, reduced in D_2O) and 7.8 (4H, m).

The Mannich bases (2) were obtained by dissolving thiophthalimide in warm ethanol (15 cm^3 g^{-1}), adding excess aqueous formaldehyde solution (1 cm^3 per gram of thiophthalimide) and a slight excess of liquid secondary amine, and boiling. The precipitate obtained by filtering the cooled solution was recrystallized from ethanol.

3.1. N-(Morpholinomethyl)thiophthalimide

N-(Morpholinomethyl)thiophthalimide (2a) was obtained as red crystals (65%): m.p., 92 - 94 °C; found composition: C, 59.73%; H, 5.35%; N, 10.59%; S, 12.33%; $C_{13}H_{14}N_2O_2S$ requires: C, 59.54%; H, 5.38%, N, 10.69%; S, 12.21%; ν_{max} = 1715 cm^{-1}; $\delta_H(CDCl_3)$: 2.7 (4H, m), 3.65 (4H, m), 4.90 (2H, s) and 7.6 - 8.1 (4H, m); $\delta_C(CDCl_3)$: 51.6, 61.7, 66.9, 122.9, 124.1, 127.1, 133.4, 134.3, 137.2, 170.7 and 199.1.

3.2. N-(Piperidinomethyl)thiophthalimide

N-(Piperidinomethyl)thiophthalimide (2b) was obtained as red crystals (80%): m.p., 74 - 76 °C; found composition: C, 64.42%; H, 6.21%; N, 10.50%; $C_{14}H_{16}N_2OS$ requires: C, 64.62%; H, 6.15%; N, 10.77%; ν_{max}: 1740 and 1705 cm^{-1}; $\delta_H(CDCl_3)$: 1.2 - 1.75 (6H, m), 2.5 - 2.85 (4H, m), 4.95 (2H, s) and 7.6 - 8.1 (4H, m); $\delta_C(CDCl_3)$: 23.8, 26.0, 52.7, 62.5, 122.0, 123.3, 124.0, 133.2, 134.0, 137.2, 170.8 and 199.2.

3.3 N-(1,2,3,4-Tetrahydroisoquinolin-2-ylmethyl)thiophthalimide

N-(1,2,3,4-Tetrahydroisoquinolin-2-ylmethyl)thiophthalimide (2c) was obtained as red crystals (74%): m.p., 102 - 104 °C; found composition: C, 70.25%; H, 5.15%; N, 9.12%; S, 10.03%; $C_{18}H_{16}N_2OS$ requires: C, 70.13%; H, 5.19%; N, 9.09%; S, 10.39%; ν_{max} = 1735 cm^{-1}; $\delta_H(CDCl_3)$: 3.0 (4H, m), 3.95 (2H, s), 5.15 (2H, s), 7.0 - 7.25 (4H, m) and 7.6 - 8.1 (4H, m);

$\delta_C(CDCl_3)$: 29.2, 49.3, 53.4, 61.5, 122.8, 124.0, 125.5, 126.0, 126.5, 127.1, 128.6, 133.2, 133.7, 134.1, 134.4, 137.1, 170.7 and 198.9.

3.4. N-(Dibenzylaminomethyl)thiophthalimide

N-(Dibenzylaminomethyl)thiophthalimide (2d) was obtained as red crystals (29%): m.p., 107 - 108 °C; found composition: C, 74.58%; H, 5.35%; N, 7.55%; S, 8.51%; $C_{23}H_{20}N_2OS$ requires: C, 74.19%; H, 5.38%; N, 7.53%; S, 8.60%; ν_{max}: 1740 and 1710 cm^{-1}; $\delta_H(CDCl_3)$: 3.85 (4H, s), 5.05 (2H, s), 7.35 (10H, m) and 7.65 (4H, m); δ_C: 56.2, 59.6, 122.6, 123.2, 123.9, 126.8, 128.0, 128.5, 133.0, 133.9, 137.1, 139.0, 170.5 and 198.5.

3.5. N-(Dicyclohexylaminomethyl)thiophthalimide

N-(Dicyclohexylaminomethyl)thiophthalimide (2e) was obtained as red crystals (70%): m.p., 96 - 97 °C; found composition: C, 70.74%; H, 8.09%; N, 7.82%; S, 8.86%; $C_{21}H_{28}N_2OS$ requires: C, 70.79%; H, 7.87%; N, 7.87%; S, 8.99%; ν_{max}: 1750 and 1715 cm^{-1}; $\delta_H(CDCl_3)$: 0.8 - 2.1 (20H, m), 2.5 - 3.0 (2H, m), 5.10 (2H, s) and 7.55 - 8.1 (4H, m); $\delta_C(CDCl_3)$: 26.0, 26.7, 32.7, 56.5, 58.3, 122.5, 123.9, 127.7, 132.9, 133.7, 137.4, 170.4 and 198.0; *m/z*: 356 (M^+), 273, 194(base), 192, 180, 176 and 163. (*m/z* = 356.1930; $C_{21}H_{28}N_2OS$ requires *m/z* = 356.1922).

3.6. N-Methylthiophthalimide

N-Methylthiophthalimide (3; X ≡ O) was made from thiophthalimide [28], or, more successfully, from *N*-methylphthalimide using Lawesson's reagent (details are given in ref. 29 for thiophthalimide; we adapted the method for the *N*-methyl derivative). With the latter method, yields ranged from 29% - 49%, accompanied by 6% - 22% *N*-methyldithiophthalimide (3; X ≡ S), when a 2:1 ratio of *N*-methylphthalimide to Lawesson's reagent was employed. (3; X ≡ O) had m.p. 97 - 98 °C (literature value [28], 97 °C); ν_{max} = 1735 cm^{-1}; $\delta_H(CDCl_3)$: 3.42 (3H, s) and 7.5 - 8.0 (4H, m); $\delta_C(CDCl_3)$: 27.5, 122.6, 123.6, 127.4, 132.2, 133.0, 134.0, 137.1, 169.7 and 197.3. (3; X ≡ S) had m.p. 103 - 104 °C; ν_{max}: 1465 and 1330 cm^{-1}; $\delta_H(CDCl_3)$: 3.75 (3H, s) and 7.45 - 7.9 (4H, m); $\delta_C(CDCl_3)$: 31.1, 123.1, 133.0, 134.9 and 197.5; λ_{max}(MeCN): 218 (9000), 244 (14 000), 356 (20 000) and 484 nm (81) (ϵ ($l\ mol^{-1}\ cm^{-1}$) in parentheses).

3.7. N-(2-Morpholinoethyl)thiophthalimide and N-(2-morpholinoethyl)dithiophthalimide

N-(2-Morpholinoethyl)thiophthalimide (8a) and *N*-(2-morpholinoethyl)dithiophthalimide (8b) were prepared by the action of Lawesson's reagent on *N*-(2-morpholinoethyl)phthalimide, which itself had been made from phthalimide and *N*-(2-chloroethyl)morpholine [7]. The substituted phthalimide (1.95 g, 0.006 mol) and Lawesson's reagent (1.50 g) were refluxed in toluene (50 cm^3) for 3 h. After removing the solvent *in vacuo*, the residue was subjected to column chromatography (silica gel, 50vol.%toluene–50vol.%chloroform) to yield 8a (47%) and 8b (16%). For

8a: m.p., 75 - 79 °C; ν_{max}: 1740 and 1705 cm^{-1}; $\delta_H(CDCl_3)$: 2.5 (4H, m), 2.70 (2H, t, J = 7 Hz), 3.65 (4H, m), 4.15 (2H, t, J = 7 Hz) and 7.35 - 8.25 (4H, m); $\delta_C(CDCl_3)$: 37.8, 53.5, 55.6, 66.8, 122.5, 133.6, 127.1, 133.0, 133.9, 137.0, 169.4 and 196.6.

For **8b**: m.p., 64 - 68 °C; found composition: C, 57.60%; H, 5.49%; N, 8.84%; S, 21.38%; $C_{14}H_{16}N_2OS_2$ requires: C, 57.53%; H, 5.48%; N, 9.59%; S, 21.92%; $\delta_H(CDCl_3)$: 2.55 (4H, m), 2.67 (2H, t, J = 7 Hz), 3.65 (4H, m), 4.55 (2H, t, J = 7 Hz) and 7.2 - 8.2 (4H, m).

3.8. N-Isobutylthiophthalimide

N-Isobutylthiophthalimide (**9**) was made from thiophthalimide [28] and purified by column chromatography (silica gel, chloroform–methanol). Found composition: C, 65.12%; H, 5.94%; N, 6.24%; S, 14.17%; $C_{12}H_{13}NOS$ requires: C, 65.75%; H, 5.94%; N, 6.39%; S, 14.61%; ν_{max}(liquid film) = 1740 cm^{-1}; $\delta_H(CDCl_3)$: 0.90 (6H, d, J = 7 Hz), 2.2 (1H, m), 3.80 (2H, d, J = 7 Hz) and 7.3 - 8.0 (4H, m); $\delta_C(CDCl_3)$: 20.2, 27.5, 48.0, 122.4, 123.6, 126.9, 132.8, 133.7, 136.8, 169.6 and 196.9.

3.9. N-(o-Tolyl)thiophthalimide and N-(o-tolyl)dithiophthalimide

N-(*o*-Tolyl)thiophthalimide (**10a**) and *N*-(*o*-tolyl)dithiophthalimide (**10b**) were made from *N*-(*o*-tolyl)phthalimide and Lawesson's reagent [29] using a 1:2 ratio of sulphurating reagent to imide. The crude mixture was separated by column chromatography (silica gel, 50vol.%toluene–50vol.%chloroform). **10a** was obtained in 26% yield: m.p., 112 °C; found composition: C, 71.07%; H, 4.25%; N, 5.49%; S, 12.89%; $C_{15}H_{11}NOS$ requires: C, 71.15%; H, 4.35%; N, 5.53%; S, 12.65%; ν_{max}(KBr) = 1755 cm^{-1}; $\delta_H(CDCl_3)$: 2.15 (3H, s), 7.1 - 7.65 (4H, m) and 7.65 - 8.2 (4H, m); $\delta_C(CDCl_3)$; 17.8, 123.2, 124.1, 126.9, 127.1, 129.0, 129.7, 131.0, 132.9, 133.5, 134.3, 136.7, 137.1, 169.2 and 196.8.

10b was obtained in 6% yield: m.p., 152 - 154 °C; found composition: C, 66.74%; H, 3.92%; N, 5.14%; S, 23.77%; $C_{15}H_{11}NS_2$ requires: C, 66.91%; H, 4.09%; N, 5.20%; S, 23.79%; $\delta_H(CDCl_3)$: 2.05 (3H, s) and 7.0 - 8.05 (8H, m); $\delta_C(CDCl_3)$: 17.9, 123.5, 126.9, 129.2, 129.9, 131.0, 133.4, 134.4, 135.0, 135.5, 136.9 and 197.4.

3.10. Irradiations

Irradiations were performed on 0.01 - 0.02 mol thioimide in acetonitrile solvent, using light from a medium pressure mercury arc filtered through a Pyrex water-cooling jacket. The progress of the reaction was monitored by TLC, and the crude reaction mixture (after removal of solvent) was separated by column chromatography on silica gel with a chloroform–methanol eluent.

3.10.1. Irradiation of 2a

Irradiation of **2a** gave a precipitate of β-isoindigo (up to 58%), which was filtered from the solution before evaporation, then **5a** (up to 67%), **6**

(19%) and small amounts (less than 5%) of thiophthalimide and *N*-(morpholinomethyl)phthalimide. *N*-(Thioformyl)morpholine (5a) was obtained as an off-white solid: m.p., 65 - 67 °C; ν_{max}(Nujol): 1510, 1440 and 1230 cm^{-1}; $\delta_H(CDCl_3)$: 3.65 - 3.75 (2H, m), 3.75 - 3.85 (4H, m), 4.15 (2H, t, J = 7 Hz) and 9.34 (1H, s); $\delta_C(CDCl_3)$: 45.5, 55.0, 66.0, 66.9 and 186.9; *m/z*: 131 (base, M^+), 100, 86, 74, 73, 56 and 45; (*m/z* = 131.0405; C_5H_9NOS requires 131.0375). Compound 6 was obtained as a high melting point (above 320 °C) solid: found composition: C, 64.11%; N, 10.63%; S, 8.07%; $C_{21}H_{19}N_3O_3S$ requires: C, 64.10%; N, 10.68%; S, 8.15%; ν_{max}(Nujol): 3200 and 1700 cm^{-1}; $\delta_H(CDCl_3)$: 2.5 - 2.9 and 3.1 - 3.4 (4H, m), 3.82 (4H, t, J = 7 Hz), 5.67 (1H, s), 6.3 (1H, m), 6.68 (1H, s), 7.1 - 8.0 (7H, m) and 8.56 (1H, s); $\delta_C(CDCl_3)$: 48.7 (t), 67.0 (t), 75.5 (d), 82.9 (d), 122.0, 123.2, 124.8, 125.3, 130.3, 130.7, 132.7, 132.9, 133.3, 133.9, 139.8, 142.2, 168.3 and 169.7; *m/z*: 393 (M^+), 307, 263, 262, 230 (base), 131, 117 and 103.

3.10.2. Irradiation of 2b

Irradiation of 2b gave a precipitate of β-isoindigo (17%), then 5b (18%) and thiophthalimide (30%). *N*-(Thioformyl)piperidine (5b) was obtained as a yellow oil: $\delta_H(CDCl_3)$: 1.5 - 1.95 (6H, m), 3.6 (2H, m), 4.0 (2H, m) and 9.25 (1H, s); $\delta_C(CDCl_3)$: 24.2, 24.8, 26.7, 45.8, 56.5 and 185.7.

3.10.3. Irradiation of 2c

Irradiation of 2c gave an oil (1% - 2%) whose proton NMR spectrum showed δ = 9.45, and a solid (4% - 5%) with ν_{max}(Nujol) at 1710 and 3210 cm^{-1}; $\delta_H(CDCl_3)$: 2.9 - 3.5 (4H, m), 4.51 (1H, d, J = 9 Hz), 4.51 (1H, s), 4.80 (1H, d, J = 9 Hz), 5.74 (1H, d, J = 8 Hz), 6.1 (1H, broad, reduced in D_2O), 6.6 - 6.9 (1H, m), 7.1 (2H, m) and 7.4 - 8.0 (≈5H, m); $\delta_C(CDCl_3)$: 29.1, 46.2, 61.8, 75.2, 96.0, 122.9, 123.6, 123.8, 124.9, 126.1, 127.9, 129.0, 133.2, 133.4, 134.3, 143.0 and 168.5.

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