

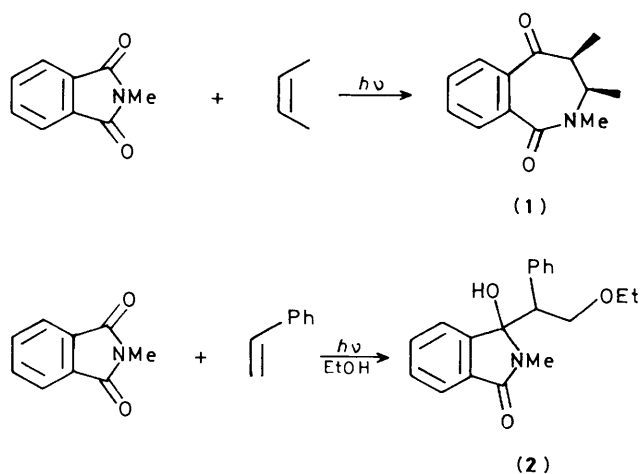
Photochemical Cycloaddition Reactions of *N*-Methyl(thiophthalimide) and *N*-Methyl(dithiophthalimide) with Alkenes

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Irradiation of *N*-methyl(thiophthalimide) with alkenes leads to reaction at the thiocarbonyl, rather than at the carbonyl, group of the thioimide. Products isolated include (2 + 2) cycloadducts (isoindeole-1-spiro-2'-thietanes), a cleavage product (a 3-alkylideneisoindeol-1-one) derived from such cycloadducts, or (2 + 2 + 2) cycloadducts incorporating two molecules of thioimide (1,4-dithiane-2,3-bis-spiroisoindeoles). The products are consistent with a mechanism that involves an intermediate 1,4-biradical, and they contrast markedly with those obtained from *N*-methylphthalimide with alkenes. *N*-Methyl(dithiophthalimide) is less effective in photoreactions with alkenes, and in only one instance was a cycloadduct formed at a reasonable rate and isolated; possible reasons for this difference are discussed.

The photochemical reactions of thioketones parallel those of their oxygen counterparts in many respects,¹ although differences arise because sulphur-containing radical intermediates undergo a wider range of reactions than analogous oxygen-containing radicals, and because thioketones can react by way of an upper excited state (S_2 , π,π^*) as well as through the lowest triplet state. The photochemistry of imides² is different in many respects from that of ketones. Although saturated cyclic imides, such as succinimides, do take part in photocyclisation initiated by abstraction of a γ - or δ -hydrogen atom, and do react with alkenes to form spiro-oxetanes, aromatic 1,2-dicarboximides exhibit a more varied array of light-induced reactions. Hydrogen abstraction followed by cyclisation can be a high-yielding reaction for *N*-substituted phthalimides, and this extends to systems in which a very remote position, activated by an adjacent sulphur or nitrogen group, is attacked, leading to products with new, very large rings (up to 38 atoms).³ With alkenes, aromatic imides rarely form spiro-oxetanes;⁴ instead a singlet-state process provides a pathway to benzazepinediones (1), or to products (2) arising from capture of a charged intermediate by hydroxylic solvents.⁵



Our investigations of the photochemistry of thiophthalimides have shown that products derived by hydrogen abstraction and cyclisation are not normally formed⁶ (a conclusion arrived at

also by other workers⁷), although an exceptional case is an *N*-(but-3-enyl) compound.⁸ Initial abstraction from a β -position may be responsible for a reaction of *N*-dialkylaminomethyl-(thiophthalimides) that leads eventually to cleavage products.⁶ We then set out to determine the nature of the photochemical reactions between aromatic thioimides and alkenes – do they parallel those of related imides (in which case a question of orientation arises as to which carbon–nitrogen bond is broken in forming a thioxobenzazepinone), or those of related thioketones (which raises the question of selectivity towards the carbonyl or thiocarbonyl group), or do new reactions arise? At the time of our preliminary report⁹ there was no literature precedent, although since then an independent report has appeared,⁷ and our own work has extended to reactions of thioimides with alkynes¹⁰ or with ketene derivatives.¹¹ These reports indicate that thioimides behave more like thioketones, in that spirothietanes or related compounds, such as spirothietes from alkynes, predominate. We now present a full report of our studies with alkenes which shows that 1,4-dithiane-bis-spiro cycloadducts are formed as well as spirothietanes, thus reinforcing the parallel between thioimides and thioketones.

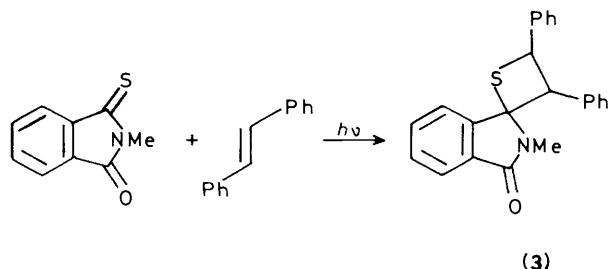
Results and Discussion

Thiophthalimide itself did not react cleanly on irradiation with *trans*-stilbene, and attempted isolation of products led only to small quantities of brown solids. This parallels the situation with phthalimides, where reported intermolecular photocycloadditions are restricted to *N*-methyl compounds. It seems that the labile N–H provides a route for ready breakdown of any initial cycloadducts.

However, irradiation of *N*-methyl(thiophthalimide) with *trans*-stilbene gave two products that were characterised as stereoisomers of a spirothietane adduct (3). The major photo-product gave microanalytical data consistent with a 1:1 adduct between the substrates; a cyclic amide carbonyl was indicated in the i.r. (1708 cm^{-1}) and ^{13}C n.m.r. ($\delta_{\text{C}} 167.5$) spectra, and the latter spectrum showed no signal for a thiocarbonyl group; the mass spectrum gave an intense peak corresponding to loss of $\text{PhCH}=\text{S}$ from the parent ion, which accords with a thietane structure; and in the ^1H n.m.r. spectrum doublets at $\delta_{\text{H}} 5.42$ and 5.53 , together with signals at $\delta_{\text{C}} 42.7$, 62.0 , and 73.0 (quaternary) in the ^{13}C n.m.r. spectrum, were in keeping with those expected for the hydrogen and carbon atoms of the thietane ring.

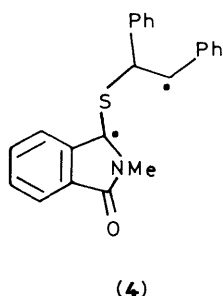
The second cycloadduct was similarly characterised, although the mass spectrum showed loss of sulphur from the

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molecular ion, rather than loss of thiobenzaldehyde, to be a major process. The cycloadducts possess three chiral centres, and in principle four pairs of enantiomers might be produced. The major product exhibits a coupling constant of 10 Hz between the two protons of the thietane ring; this is more in keeping with a *trans* orientation of the protons, and hence of the phenyl groups. Kanaoka⁷ came to the same conclusion about the major cycloadduct that he isolated, whose properties match those of our compound very well. However, Kanaoka's second isomer, also judged by him to be a *trans* isomer, is different from our second cycloadduct,¹² most noticeably in its m.p. and its mass spectrum, though the ¹H and ¹³C n.m.r. spectra are broadly similar, allowing for the different solvents used. These two minor products may be different diastereoisomers; if so, this may well arise from the different irradiation conditions employed by the two groups (high-pressure mercury lamp for 1 h, compared with medium-pressure lamp for 6 h) especially since we found that repeating the irradiation for a longer period resulted in a higher proportion of the major isomer. Such an influence of irradiation conditions suggests that the thietane isomers may be interconvertible photochemically. The major thietane cycloadduct is, by contrast, thermally stable (no change on heating to 80 °C for 2 h, nor on melting at nearly 200 °C) and stable also to acid (2 h at 80 °C in the presence of benzenesulphonic acid).

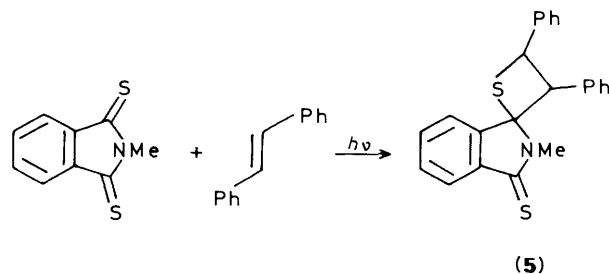
Irradiation of *N*-methyl(thiophthalimide) with *cis*-stilbene produced the same two isomers of the spirothietane as did the reaction with *trans*-stilbene, though in lower isolated yield. Other products were formed, but none was isolated in a pure condition. The fact that the same major products arise from either *trans*- or *cis*-stilbene implies either that a biradical intermediate (4) is formed first, which retains only partial



stereochemical 'memory' from the initial alkene, or that rapid photoisomerisation of *cis*-stilbene to its *trans* isomer precedes photocycloaddition. The recovered stilbene from the irradiation of *N*-methyl(thiophthalimide) with *cis*-stilbene contained around 40% of *trans*-stilbene, but, unless the rate of reaction with *trans*-stilbene is very much faster than that with *cis*-stilbene, it seems unlikely that alkene isomerisation alone can account for the not dissimilar product ratios in the two reactions.

Reaction between *N*-methyl(dithiophthalimide) and *trans*-stilbene gave one major product in 65% (crude) yield, which

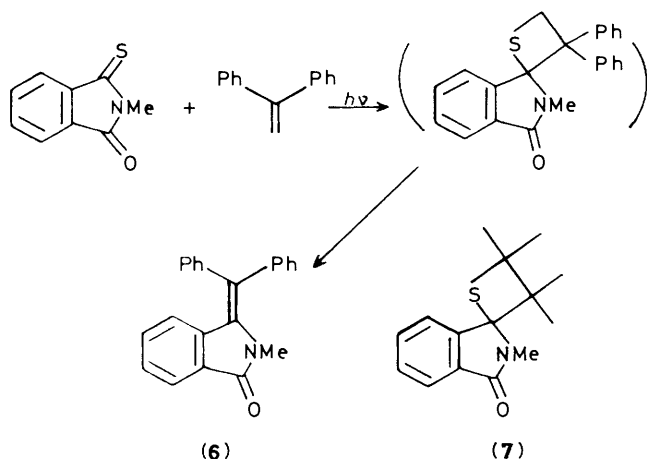
is assigned a spirothietane structure (5). Its spectral properties are closely similar to those of the major product from *N*-methyl(thiophthalimide) and stilbene, except for the differences expected for a thiolactam rather than a lactam; there is also a small shift in the position of the ¹H n.m.r. signal for the *N*-methyl protons, which is consistent with their proximity to the thiocarbonyl sulphur. The coupling constant of 11 Hz between the two protons on the thietane ring indicates a *trans* arrangement of phenyl groups.



Although this reaction worked well, in no other case could we isolate a cycloadduct when *N*-methyl(dithiophthalimide) was irradiated with an alkene. In most cases there was very little loss of substrate on prolonged irradiation, but some evidence for slow oxidation to the thioimide and to *N*-methylphthalimide. A small amount of dark, very polar material was also evident, and both this and the oxidation products were obtained in control experiments in which *N*-methyl(dithiophthalimide) was irradiated without added alkene. A spirothietane has been reported⁷ from the reaction of the dithioimide with 2,5-dimethylhexa-2,4-diene. The reason for the general lack of success using the dithioimide is not clear. The reaction of *N*-methyl(thiophthalimide) most likely involves the lowest (*n,π**) triplet state of the thioimide, on the grounds that the reaction works with u.v. or visible light, and that excitation in the *S*₂ absorption band produces the same emission as does excitation in the *S*₁ band.¹³ Both of these observations indicate that a higher excited state is not involved, unlike the situation with thioketones,¹ and there is likely to be very rapid *S*₁ → *T*₁ intersystem crossing because the singlet-triplet splitting is very small. In this respect the thioimide reactions to form thietanes resemble the few aromatic imide reactions that do form oxetanes, which are also triplet-state processes.⁴ If the dithioimide reaction is derived from a triplet state, the generally lower efficiency of thietane formation can be accounted for in terms of the much shorter lifetime of its triplet state (2 × 10⁻⁷ s, as opposed to 1 × 10⁻⁶ s for the thioimide¹³); other factors may be the lower energy of the triplet (< 185 kJ mol⁻¹, as opposed to ~210 kJ mol⁻¹ for the thioimide), or the less effective stabilisation of a thiocarbonyl-containing (bi)radical intermediate (with the sequence S=C-C=C-C-N) than of the corresponding carbonyl species.

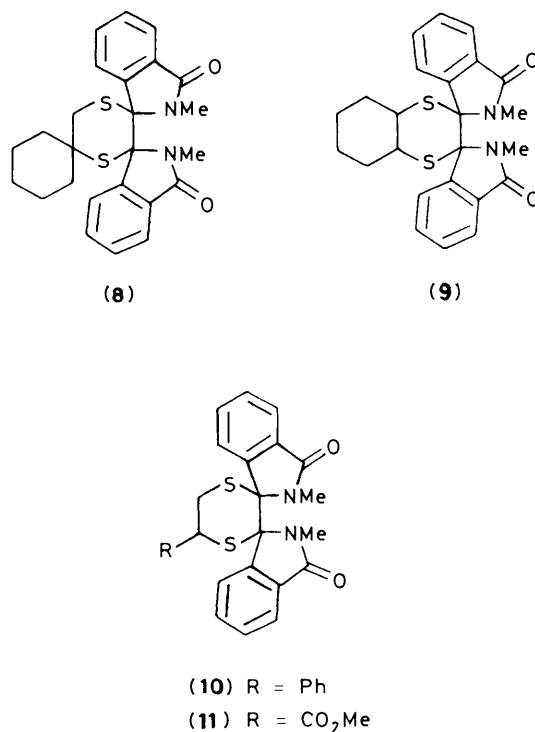
1,1-Diphenylethene was employed with *N*-methyl(thiophthalimide) in order to investigate the regioselectivity of the cycloaddition. However, no thietane was isolated, but instead a reasonable yield (62%) of a diphenylmethyleneisoindolone (6). The structure of this product is fully supported by the results of elemental microanalysis and by spectral data, as well as by comparison with the same compound obtained in the photochemical reaction of *N*-methyl(thiophthalimide) and diphenylketene.¹¹ It most probably arises by ring-cleavage of the first formed spirothietane, for which there is ample precedent in the diphenylketene reaction¹¹ and in related systems derived from thioketones.¹⁴ The ease of cleavage in this case may be enhanced by the formation of a diphenyl-

conjugated product. The orientation of the intermediate thietane, deduced from the product structure, is in keeping with expectations based on its formation *via* the more stable of two possible biradical precursors. Although we cannot estimate an upper limit for the amount of any regioisomer that might be present in the crude reaction mixture, there were no significant signs of such a compound in the t.l.c. data or in the ^1H n.m.r. spectra.



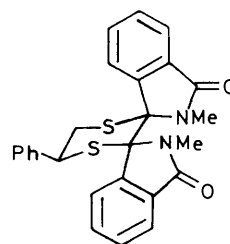
One of our earliest attempts to prepare cycloadducts from *N*-methyl(thiophthalimide) involved 2,3-dimethylbut-2-ene as the alkene. Irradiation of the two compounds without a solvent led to a mixture, the work-up of which proved to be difficult, though eventually a spirothietane (7) was isolated as a yellowish oil. Its structure was established on the basis of evidence from the ^1H n.m.r. (five Me singlets) and ^{13}C n.m.r. (carbonyl signal, no thiocarbonyl signal, aliphatic quaternary carbon signal at δ_{C} 93.9, and five Me carbon signals) spectra, and from the mass spectrum, in which loss of $\text{Me}_2\text{C}=\text{S}$ from the parent ion is a major process. When the reaction was repeated in acetonitrile as solvent, isolation of the product was no easier since additional minor products were formed, though a higher yield was reported subsequently⁷ from the reaction in benzene.

To test the scope of the reaction, irradiations were carried out with a range of alkenes - methylenecyclohexane, cyclohexene, styrene, methyl acrylate, acrylonitrile, and ethyl vinyl ether. In each case several products were detected by t.l.c., but separation and isolation of pure components proved difficult. Even when a relatively pure sample was achieved, several recrystallisations or further column chromatography were required before the purity was satisfactory for full characterisation. This made it impossible to achieve satisfactory mass balance for the reactions in terms of the finally isolated product materials. Some product fractions gave n.m.r. evidence for the formation of spirothietane, particularly on the basis of a signal at δ_{H} 5.0–5.2 arising from hydrogen(s) on the alkene-derived carbon adjacent to the sulphur atom. However, a different type of cycloadduct was characterised in the reactions of methylenecyclohexane, cyclohexene, styrene, and methyl acrylate, namely a 1,4-dithiane that represents a product of (2 + 2 + 2) cycloaddition. The four assigned structures are (8)–(11), and in each system except that from methylenecyclohexane two different stereoisomers were obtained. Evidence for the structures comes from the results of elemental microanalysis, integration ratios in the ^1H n.m.r. spectra, chemical-shift values in both ^1H and ^{13}C n.m.r. spectra (which rule out the alternative 1,3-dithiane isomers), and fragmentation patterns in the mass spectra



[particularly the loss of an alkene unit in the cyclohexene case, or the loss of $\text{SCH}_2\text{CH}(\text{R})\text{S}$ for the styrene and methyl acrylate adducts].

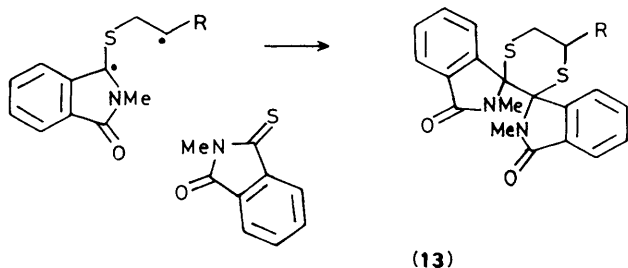
The stereochemistry could not be assigned with confidence in most cases, although the spectra for one isomer of the cyclohexene adduct point to an almost symmetrical molecule (single signal, or two very close signals, for two *N*-methyl groups and for two carbonyls). If the ring junction between the cyclohexane and dithiane rings has *trans* stereochemistry, this would imply that at the two adjacent spiro positions there is a *trans* arrangement of like groups. The major product from the styrene reaction gave a clear ABX pattern for the aliphatic styrene-derived protons, and the AX coupling constant (11 Hz) points to an axial H_{x} , and hence an equatorial phenyl group, in this compound. In this n.m.r. spectrum the signals for the *N*-methyl groups are at very low chemical shift (δ_{H} 2.05 and 2.17), which suggests that the two nitrogen atoms have a *trans* diequatorial configurational relationship (12). In this structure the *N*-methyl groups lie close to, and above the plane of, the aromatic ring of the adjacent spiro unit. An extension of this argument suggests that if the *N*-methyl signals are in the δ_{H} 3.5–4.0 region (as for the other isolated stereoisomer), a *trans* diaxial arrangement of nitrogen atoms may be indicated.



(12)

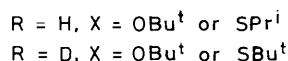
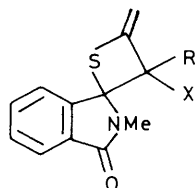
[an isomer of (10)]

The isolation of 1,4-dithianes is in keeping with a biradical mechanism, since it is not surprising that a thioimide is able to trap such an intermediate through its thiocarbonyl group to give a product such as (13). Precedents for the reaction include the formation of related compounds from thiobenzophenone with cyclohexene, styrene,¹⁵ ethyl vinyl ether,¹⁶ acrylonitrile,¹⁷ or methyl acrylate.¹⁶ The process is in stark contrast to the reactions of *N*-methylphthalimide, which lead to a benzazepinedione from styrene; ethyl acrylate and acrylonitrile do not react photochemically with the imide,¹⁸ whilst with cyclohexene a hydrogen-abstraction process occurs. The differences arise because phthalimides can react by way of electron transfer, depending on the electron-donor properties of the alkene, but this initial step is not a major route for thioimides.



In the reactions of thiobenzophenone with electron-deficient alkenes, additional, often major, products arise by way of internal attack on one of the phenyl rings by one of the radical centres in the biradical intermediate.¹⁶ We found no evidence for analogous products in the thiophthalimide reactions, although this conclusion must be qualified by the comment that small amounts may not have been detected. The difference probably arises because the five-membered fused lactam ring imposes additional constraints on the flexibility of the biradical.

Allenes are known to react with thioketones both thermally¹⁹ and photochemically;^{20,21} the photochemical reaction produces isomeric (2 + 2) cycloadducts, methylene-substituted spirothietanes. With *N*-methylphthalimide, 3-methylbuta-1,2-diene gives a benzazepinedione on irradiation,¹⁸ and we therefore studied the photochemistry of *N*-methyl(thiophthalimide) with a number of allenes. N.m.r. analysis of the crude reaction mixtures indicated that mixtures of cycloadducts were formed fairly cleanly, though in no case was sufficiently pure product isolated for full characterisation; it seems that some decomposition may occur in the work-up procedure. The products isolated (14) all show the same orientation of



reaction, as judged from spectral data and a comparison with related thioketone-allene adducts. This orientation is the same as that observed in the photochemical cycloaddition with

diphenylketene or a related ketenimine.¹¹ Once again the regioselectivity is in accord with reaction *via* the more stable of two types of biradical intermediate.

In conclusion, *N*-methyl(thiophthalimide) and the corresponding dithioimide are found to undergo photocycloaddition with alkenes to give (2 + 2) or (2 + 2 + 2) adducts arising from reaction at the thiocarbonyl group; the mechanism is likely to involve a 1,4-biradical intermediate. In these reactions the thioimides resemble thioketones in their behaviour, rather than analogous phthalimides.

Experimental

Thiophthalimide was prepared from benzene-1,2-dicarbonylnitrile.²² *N*-Methyl(thiophthalimide) and *N*-methyl(dithiophthalimide) were prepared from *N*-methylphthalimide using Lawesson's reagent.^{6,23} Liquid alkenes were purified by distillation, and allenes were kindly provided by Professor H. J. T. Bos. Unless otherwise stated, irradiations were carried out using a 125-W or 400-W medium-pressure mercury arc and a Pyrex filter; solutions were outgassed by bubbling with oxygen-free nitrogen. Separation of product mixtures after photolysis was by silica gel flash chromatography with chloroform-toluene (50:50) to methanol-chloroform (10:90) as eluant.

Control irradiations were carried out using thiophthalimide, *N*-methyl(thiophthalimide), or *N*-methyl(dithiophthalimide) in the absence of added alkene. The first two compounds showed no sign of significant reaction on prolonged irradiation, as judged by t.l.c., and i.r. and ¹H n.m.r. spectra. The dithioimide gave rise to small amounts of oxidised material (strong i.r. absorption at 1 740 or 1 725 cm⁻¹), and to dark green material with a very low retention factor on silica gel t.l.c. Similar material was present in the mixtures obtained from all irradiations of *N*-methyl(dithiophthalimide) with alkenes.

Reactions with Stilbene.—Thiophthalimide (0.0050 mol) and *trans*-stilbene (0.0075 mol) were irradiated for 16 h in benzene. Attempted purification of separated product fractions by recrystallisation from ethanol or toluene led only to small quantities of brown solids.

N-Methyl(thiophthalimide) (0.0050 mol) and *trans*-stilbene (0.0075 mol) were irradiated for 6 h in benzene. Separation of the reaction mixture gave stilbene (0.78 g), *N*-methyl(thiophthalimide) (0.14 g), *N*-methylphthalimide (10 mg, 15%), and two stereoisomers (25 and 45%) of 2-methyl-3',4'-diphenyl-1*H*-isoidole-1-spiro-2'-thietan-3(2*H*)-one (3). The major isomer was obtained as a white solid after recrystallisation from ethanol, m.p. 193–196 °C (Found: C, 77.5; H, 5.4; N, 3.9; S, 8.9. C₂₃H₁₉NOS requires C, 77.3; H, 5.3; N, 3.9; S, 9.0%); ν_{max} (KBr) 1 708 cm⁻¹; δ_{H} (CDCl₃) 3.04 (3 H, s), 5.42 (1 H, d, *J* 10 Hz), 5.53 (1 H, d, *J* 10 Hz), and 6.5–8.2 (14 H, m); δ_{C} (CDCl₃) 26.1, 42.7, 62.0, 73.0, 123.3, 124.4, 125.1, 125.8, 125.9, 127.5, 127.7, 128.3, 128.7, 128.9, 129.4, 130.9, 131.7, 132.5, 136.8, 140.6, 147.8, and 167.5; *m/z* 235, 180 (base), 165, and 121.

The minor isomer was similarly obtained as a white solid, m.p. 236–238 °C (Found: C, 77.2; H, 5.3; N, 4.1. C₂₃H₁₉NOS requires C, 77.3; H, 5.3; N, 3.9%); ν_{max} (KBr) 1 715 cm⁻¹; δ_{H} (CD₃CN) 3.34 (3 H, s), 4.96 (1 H, d, *J* 14 Hz), 5.69 (1 H, d, *J* 14 Hz), and 6.9–7.9 (14 H, m); δ_{C} ([²H₆]acetone) 24.4, 45.0, 71.8, 108.2, 122.2, 124.1, 127.4, 127.7, 128.0, 128.5, 129.5, 130.1, 130.2, 131.8, 131.9, 141.8, and 166.2; *m/z* 325, 248, 234, 180, 178, 146, 117, 91, and 77.

The reaction was repeated but with 30 h irradiation; the major product was obtained in 90% crude yield.

N-Methyl(thiophthalimide) (0.0056 mol) and *cis*-stilbene (0.0085 mol) were irradiated for 31 h in benzene using light from a high-pressure mercury arc (125-W Philips HPL-N) filtered through a solution of acidified copper(II) chloride and calcium

chloride. Separation of the reaction mixture gave stilbene (1.05 g, ca. 60% *cis*), *N*-methyl(thiophthalimide) (0.34 g), *N*-methylphthalimide (10 mg, 2%), the same major product (34% from ethanol) as was obtained from the reaction of *trans*-stilbene, the same minor product (18 mg, 1%), and a mixture of other products.

N-Methyl(dithiophthalimide) (0.0052 mol) and *trans*-stilbene (0.0104 mol) were irradiated for 8 h in benzene. Separation of the reaction mixture gave a mixture of *trans*-stilbene and *N*-methyl(dithiophthalimide) (2.05 g, in the ratio 1.27:0.78 as determined by ^1H n.m.r. spectroscopy), and 2-methyl-3',4'-diphenyl-1*H*-isoindole-1-spiro-2'-thietane-3(2*H*)-thione (**5**) (46% from ethanol), m.p. 145–147 °C (Found: C, 73.5; H, 5.1; N, 3.6; S, 17.4. $\text{C}_{23}\text{H}_{19}\text{NS}_2$ requires C, 73.95; H, 5.1; N, 3.75; S, 17.15%); $\delta_{\text{H}}(\text{CDCl}_3)$ 3.41 (3 H, s), 5.48 (1 H, d, J 11 Hz), 5.60 (1 H, d, J 11 Hz), 6.6–6.75 (2 H, m), 7.0–7.9 (10 H, m), and 8.0–8.15 (2 H, m); $\delta_{\text{C}}(\text{CDCl}_3)$ 31.9, 42.9, 61.9, 78.4 (in $[\text{C}_6\text{H}_6]$ benzene), 122.8, 124.8, 125.2, 125.6, 127.8, 128.6, 128.9, 129.1, 129.9, 132.4, 136.6, 137.0, 140.3, 145.7, and 193.2; m/z 341, 250, 180 (base), 165, 146, 121, and 76.

Reactions with 1,1-Diphenylethene.—*N*-Methyl(thiophthalimide) (0.0056 mol) and 1,1-diphenylethene (0.0083 mol) were irradiated for 8.5 h in acetonitrile. Separation of the product mixture gave 1,1-diphenylethene (0.87 g), *N*-methyl(thiophthalimide) (0.51 g), *N*-methylphthalimide (3 mg, <1%), and 3-(diphenylmethylene)-2-methyl-2,3-dihydro-1*H*-isoindol-1-one (**6**)¹¹ (62% crude, 35% after three recrystallisations from ethanol), m.p. 173–178 °C (Found: C, 84.9; H, 5.4; N, 4.3. Calc. for $\text{C}_{22}\text{H}_{17}\text{NO}$: C, 84.9; H, 5.5; N, 4.5%); ν_{max} 1 700 cm^{-1} ; $\delta_{\text{H}}(\text{CDCl}_3)$ 2.89 (3 H, s), 6.40 (1 H, m), 7.0–7.7 (12 H, m), and 7.85 (1 H, m); $\delta_{\text{C}}(\text{CDCl}_3)$ 31.5, 122.8, 123.3, 126.0, 127.8, 128.1, 128.3, 128.9, 129.5, 130.7, 130.9, 131.3, 135.2, 137.5, 140.9, 141.3, and 169.1; m/z 311 (M^+ , base), 252, 234, 156, and 91 (Found: M^+ , 311.1305; Calc. for $\text{C}_{22}\text{H}_{17}\text{NO}$: M , 311.1310).

N-Methyl(dithiophthalimide) (0.0052 mol) and 1,1-diphenylethene (0.0083 mol) were irradiated for 36 h in acetonitrile. In another experiment irradiation was conducted for 100 h in benzene using light from a high-pressure mercury arc with a filter solution. Separation of the product mixtures gave mainly unchanged starting materials, together with small amounts of carbonyl-containing material and very polar, dark green material.

Reaction with 2,3-Dimethylbut-2-ene.—*N*-Methyl(thiophthalimide) (0.0056 mol) and 2,3-dimethylbut-2-ene (12 g) were irradiated in Pyrex test-tubes for 4.5 h. Separation of the product mixture gave *N*-methyl(thiophthalimide) (0.47 g), *N*-methylphthalimide (74 mg, 15%), and 2,3',3',4',4'-pentamethyl-1*H*-isoindole-1-spiro-2'-thietan-3(2*H*)-one (**7**) as a yellowish oil (185 mg, 22%) (Found: S, 12.3. $\text{C}_{15}\text{H}_{19}\text{NOS}$ requires S, 12.3%); ν_{max} 1 705 cm^{-1} ; $\delta_{\text{H}}(\text{CDCl}_3)$ 1.01 (3 H, s), 1.22 (3 H, s), 1.69 (3 H, s), 1.70 (3 H, s), 3.50 (3 H, s), 7.50 (1 H, t, J 9 Hz), 7.65 (1 H, t, J 9 Hz), 7.82 (1 H, d, J 9 Hz), and 8.00 (1 H, d, J 9 Hz); $\delta_{\text{C}}(\text{CDCl}_3)$ 23.5, 26.4, 29.1, 29.4, 30.0, 46.9, 56.7, 93.9, 122.7, 125.8, 128.4, 128.6, 130.7, 147.5, and 168.8; m/z 214, 187, 178, 172, 117, 84 (base), and 69.

Reaction with Methylene-cyclohexane.—*N*-Methyl(thiophthalimide) (0.0056 mol) and methylenecyclohexane (0.0084 mol) were irradiated for 14 h in acetonitrile. Separation of the product mixture gave *N*-methyl(thiophthalimide) (0.78 g), *N*-methylphthalimide (27 mg, 14%), and 2,2'-dimethyl-1*H*-isoindole-1-spiro-2'-[1',4']dithiane-3'-spiro-1''-1''*H*-isoindole-5'-spiro-1'''-cyclohexane-3,3''(2*H*,2''*H*)-dione (**8**) (150 mg, 27%, crude; 5% from ethanol), m.p. 137 °C (Found: C, 66.6; H, 5.8; N, 6.2; S, 14.8. $\text{C}_{25}\text{H}_{26}\text{N}_2\text{O}_2\text{S}_2$ requires C, 66.7; H, 5.8; N, 6.2; S, 14.2%); ν_{max} 1 715 cm^{-1} ; $\delta_{\text{H}}(\text{CDCl}_3)$ 1.2–2.0 (7 H, m), 3.15 (2 H,

m), 3.40 (1 H, s), 3.93 (3 H, s), 4.07 (3 H, s), and 7.0–7.5 (8 H, m); $\delta_{\text{C}}(\text{CDCl}_3)$ 21.3, 21.5, 25.2, 30.0, 30.6, 30.7, 32.5, 32.9, 36.0, 42.1, 80.3, 122.8, 123.1, 123.5, 124.2, 127.4, 129.1, 129.5, 130.1, 130.6, 131.4, 142.0, 170.0, and 172.0; m/z 240, 177 (base), 117, and 76.

Reaction with Cyclohexene.—*N*-Methyl(thiophthalimide) (0.0056 mol) and cyclohexene (0.0060 mol) were irradiated for 39 h in acetonitrile. Separation of the product mixture gave *N*-methylphthalimide (185 mg, 21%), and two stereoisomers of 2,2''-dimethyl-1*H*-isoindole-1-spiro-2'-octahydro[1',4']benzodithiane-3'-spiro-1''-1''*H*-isoindole-3,3''(2*H*,2''*H*)-dione (**9**). The first isomer (28 mg, 2%) had ν_{max} 1 700 cm^{-1} ; $\delta_{\text{H}}(\text{CDCl}_3)$ 1.15–1.75 (4 H, m), 1.75–2.15 (6 H, m), 2.8–3.3 (2 H, m), 3.99 (6 H, s), and 7.05–8.0 (8 H, m); $\delta_{\text{C}}(\text{CDCl}_3)$ 26.5, 29.7, 31.1, 32.1, 45.7, 73.5, 122.9, 123.9, 128.9, 129.7, 131.1, 131.6, 133.8, 142.1, and 168.2.

The second isomer (191 mg, 16%, crude; 4% from ethanol) had m.p. 237–239 °C (Found: C, 66.3; H, 5.3; N, 6.1; S, 13.7. $\text{C}_{24}\text{H}_{24}\text{N}_2\text{O}_2\text{S}_2$ requires C, 66.1; H, 5.5; N, 6.4; S, 14.7%); ν_{max} 1 699 cm^{-1} ; $\delta_{\text{H}}(\text{CDCl}_3)$ 1.4–2.2 (8 H, m), 3.04 (3 H, s), 3.94 (3 H, s), 4.0 (2 H, m), 6.15 (1 H, d, J 8 Hz), 6.90 (1 H, t, J 8 Hz), 7.25 (1 H, m), 7.5–7.9 (4 H, m), and 8.90 (1 H, m); $\delta_{\text{C}}(\text{CDCl}_3)$ 26.0, 26.3, 28.1, 31.7, 31.9, 46.8, 47.9, 85.0, 123.5, 124.0, 124.5, 125.3, 129.4, 129.8, 131.0, 142.0, 148.0, 168.0, and 169.0; m/z 354 (M^+ – C_6H_{10}), 290, 177 (base), 117, and 107.

Reaction with Styrene.—*N*-Methyl(thiophthalimide) (0.0056 mol) and styrene (0.0069 mol) were irradiated for 44 h in benzene. Separation of the product mixture gave *N*-methyl(thiophthalimide) (0.027 g), *N*-methylphthalimide (33 mg, 3%), and two stereoisomers of 2,2''-dimethyl-5'-phenyl-1*H*-isoindole-1-spiro-2'-[1',4']dithiane-3'-spiro-1''-1''*H*-isoindole-3,3''-(2*H*,2''*H*)-dione (**10**). The first isomer (4% from ethanol) had m.p. 264–268 °C; ν_{max} (KBr) 1 696 cm^{-1} ; $\delta_{\text{H}}(\text{CDCl}_3)$ 3.55 (1 H, d, J 11 Hz), 3.61 (3 H, s), 3.65 (3 H, s), 4.03 (1 H, d, J 11 Hz), 4.50 (1 H, m), 6.85 (2 H, m), 7.0–7.2 (3 H, m), and 7.2–7.6 (8 H, m); $\delta_{\text{C}}(\text{CDCl}_3)$ 29.2, 29.7, 35.6, 50.0, 84.6, 88.0, 122.7, 122.9, 123.3, 124.3, 127.1, 127.7, 128.7, 129.2, 129.6, 131.7, 131.8, 134.9, 141.1, 141.7, 168.5 and 169.0; m/z 290 (M^+ – SCH_2CHPhS), 249 (base), 158, 117, and 91.

The second isomer (14% from ethanol) had m.p. 259–267 °C (decomp.); ν_{max} 1 696 cm^{-1} ; $\delta_{\text{H}}(\text{CDCl}_3)$ 2.05 (3 H, s), 2.17 (3 H, s), 3.89 (1 H, dd, J 12 and 9 Hz), 4.00 (1 H, dd, J 12 and 11 Hz), 4.73 (1 H, dd, J 11 and 9 Hz), 6.7–7.15 (6 H, m), 7.4–7.9 (6 H, m), 8.07 (1 H, m), and 8.46 (1 H, m); $\delta_{\text{C}}(\text{CDCl}_3)$ 27.7, 29.0, 31.9, 46.2, 80.7, 81.7, 123.2, 123.9, 124.2, 125.2, 127.4, 127.8, 128.1, 128.4, 129.1, 129.4, 129.8, 130.1, 130.9, 131.8, 132.2, 134.4, 142.1, 150.2, 167.9, and 168.7; m/z 290, 249 (base), 158, 117, and 91.

Reaction with Methyl Acrylate.—*N*-Methyl(thiophthalimide) (0.0056 mol) and methyl acrylate (2.6 g, 0.030 mol) were irradiated for 50 h in acetonitrile; further quantities of methyl acrylate were added at intervals, to replace any lost in the nitrogen stream. Separation of the reaction mixture gave *N*-methyl(thiophthalimide) (0.19 g), *N*-methylphthalimide (24 mg, 3%), and two stereoisomers of methyl 2,2''-dimethyl-3,3''-dioxo-2,2',3,3'-tetrahydro-1*H*-isoindole-1-spiro-2'-[1',4']dithiane-3'-spiro-1''-1''*H*-isoindole-5'-carboxylate (**11**). The first isomer had m.p. 207–209 °C (Found: C, 60.0; H, 4.6; N, 6.3; S, 14.5. $\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}_4\text{S}_2$ requires C, 60.0; H, 4.55; N, 6.4; S, 14.55%); ν_{max} 1 725 and 1 710 cm^{-1} ; $\delta_{\text{H}}(\text{CDCl}_3)$ 2.95 (1 H, d, J 3 Hz), 3.18 (3 H, s), 3.40 (1 H, m), 4.03 (3 H, s), 4.11 (3 H, s), 4.20 (1 H, d, J 3 Hz), and 7.0–7.5 (8 H, m); $\delta_{\text{C}}(\text{CDCl}_3)$ 28.2, 30.9, 32.7, 34.0, 48.9, 52.6, 68.0, 120.3, 121.0, 121.3, 122.0, 122.9, 123.6, 124.9, 125.3, 130.2, 131.3, 131.9, 132.2, 132.6, 166.0, and 169.0; m/z 290 (M^+ – $\text{SCH}_2\text{CH}(\text{CO}_2\text{Me})\text{S}$), 263, 230, 177 (base), 158, 117, 102, and 76.

The second isomer had m.p. 198–199 °C (Found: C, 59.6; H,

4.6; N, 6.2; S, 14.2%); ν_{\max} , 1 725 and 1 710 cm^{-1} ; $\delta_{\text{H}}(\text{CDCl}_3)$ 3.00 (3 H, s), 3.20 (2 H, m), 3.34 (3 H, s), 3.99 (3 H, s), 4.40 (1 H, m), 5.80 (1 H, d, J 8 Hz), 6.85 (1 H, dt, J 8 and 1 Hz), 7.25 (1 H, d, J 8 Hz), 7.5—7.8 (4 H, m), and 8.75 (1 H, d, J 7 Hz); $\delta_{\text{C}}(\text{CDCl}_3)$ 28.4, 31.3, 32.7, 46.3, 52.6, 123.7, 124.0, 127.9, 129.8, 130.3, 130.4, 131.0, 131.4, and 168.8 (some quaternary signals not detected); m/z 290, 263, 230, 177 (base), 172, 158, 117, and 76.

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