

Photochemical Cycloaddition of Thiocarbonyl Compounds to Diphenylketene and a Related Ketenimine

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Diphenylketene undergoes photocycloaddition with *N*-methylthiophthalimide, *N*-methylthiophthalimide or xanthene-9-thione, to give a spiro-adduct containing a thietan-2-one ring. The photo-products from the thioimide substrates are themselves photolabile, eliminating COS to form an alkene. Diphenyl-*N*-(*p*-tolyl)ketenimine gives analogous 2-iminothietanes on irradiation with the thioimides.

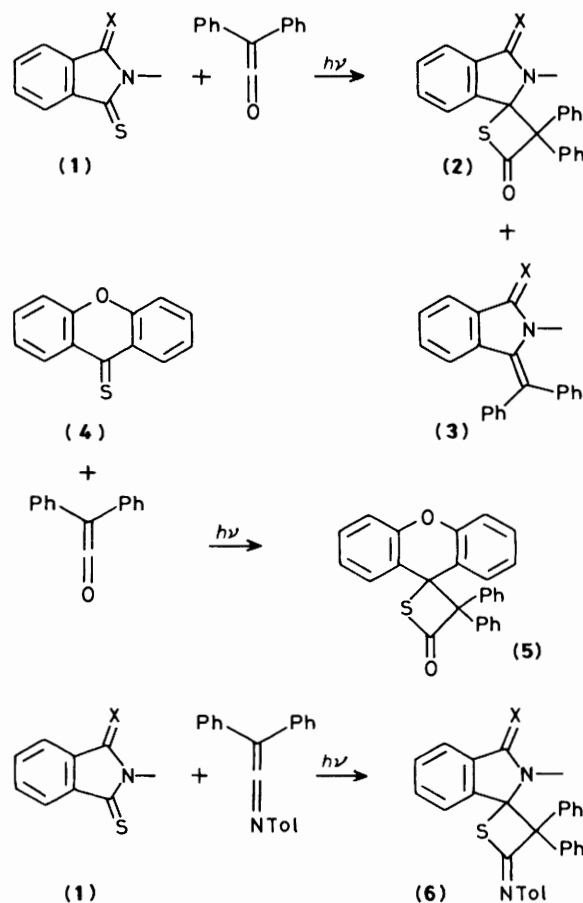
In recent years there has been a growing interest in the photochemistry of organic thiocarbonyl compounds. The majority of the reported reactions involve thioketones, which undergo intermolecular¹ or intramolecular² hydrogen abstraction, cycloaddition with alkenes,³ allenes,⁴ or alkynes,⁵ and a variety of other processes.⁶ Our interest in the photochemistry of phthalimides⁷ led us to look at the related thiophthalimide systems, which we have shown to give spirothietanes⁸ or spirothietes⁹ on irradiation with alkenes or alkynes, respectively. There are relatively few reports of photochemical reactions involving the C=S group of thioimides, although the related *N*-aryl(thiocarbonyl)ureas undergo a reaction involving intramolecular hydrogen abstraction in the excited state.¹⁰

We now report that thiophthalimides react with diphenylketene on irradiation to give thietan-2-ones (β -thiolactones), and with diphenyl-*N*-(*p*-tolyl)ketenimine to give 2-iminothietanes. It is known that thioketones react with ketenimines, both thermally¹¹ and photochemically,¹² but there has been no previous report of photocycloaddition involving a thiocarbonyl compound and a ketene. We also report that the ketene reaction occurs with a thioketone substrate, and that the spirothietan-2-ones from the imide substrates lose COS on further irradiation to give a 3-diphenylmethyleisindolin-1-one or the corresponding 1-thione.

Results and Discussion

Irradiation of a cooled solution of *N*-methylthiophthalimide (1; X = O) and diphenylketene in dichloromethane, using light from a high-pressure mercury arc filtered through an aqueous solution of copper(II) chloride and calcium chloride acidified with HCl, gave two products. The major one was characterised as the spiro-thietan-2-one (2; X = O) on the basis of microanalysis results and i.r. (C=O stretch at 1755 and 1700 cm⁻¹), proton n.m.r. (*N*-methyl at 2.6 p.p.m., plus fourteen aromatic protons), carbon-13 n.m.r. (CO signals at 181.5 and 168.2, quaternary aliphatic signals at 91.0 and 75.4 p.p.m.), and mass spectral data. The mass spectrum did not show a parent ion, but the dominant peak at *m/z* = 311 (C₂₂H₁₇NO) corresponds to loss of COS from the parent by cleavage of the thietanone ring; this cleavage pattern points to the orientation of addition as shown, rather than the alternative mode to give a thietan-3-one. The minor product was identified as 3-diphenylmethylene-2-methyl-2,3-dihydro-1*H*-isoindol-1-one (3; X = O); this compound has been isolated previously⁸ as the major product obtained when *N*-methylthiophthalimide reacts photochemically with 1,1-diphenylethylene.

It seems likely that (3) is formed from (2) by loss of COS; irradiation of (2; X = O) with light from a medium-pressure mercury arc (filtered through Pyrex) converts it cleanly and efficiently into (3; X = O). However, under the original reaction



conditions the photocleavage of (2) may be sensitised by (1). There is precedent for the photochemical cleavage of a spirothietane, since that obtained from xanthene-9-thione and methyl acrylate breaks down on sensitised irradiation to give an unsaturated ester and, presumably, thioformaldehyde.¹³ Control experiments demonstrated that (2; X = O) can be converted into (3; X = O) by prolonged heating under reflux in ethanol; this thermal reaction is not as clean as the photochemical reaction, and some (1; X = O) is also formed [the ratio of (3) to (1) is *ca.* 4:1, or 8:1 with added benzenesulphonic acid].

N-Methyldithiophthalimide (1; X = S) reacted with diphenylketene in a similar way to give mainly a spiro-thietanone (2; X = S) with an isoindoline-1-thione (3; X = S). The orientation of the photocycloaddition was indicated most

clearly in the mass spectrum, in which the base peak was at $m/z = 327$ ($C_{22}H_{17}NS$), which is the parent ion minus COS. Control experiments again demonstrated that (**3**; X = S) can be generated cleanly from (**2**; X = S) photochemically; prolonged heating of (**2**; X = S) under reflux in ethanol produces mainly (**1**; X = S), together with a smaller amount of (**3**; X = S).

This is the first reported example of photocycloaddition of a thiocarbonyl compound with a ketene, although the thermal reaction of diphenylketene with 1,2-dithiole-3-thiones and other thiocarbonyl compounds is known,¹⁴ and so we tried the reaction also with a thioketone, xanthene-9-thione (**4**). This led to a near quantitative yield of the cycloadduct (**5**), but in this case there was no accompanying product that might arise by cleavage of the thietanone ring. The reduced tendency to cleave in the alternative manner is reflected in the mass spectrum, where a small peak is observed at $m/z = 346$ (parent minus COS), but the base peak is at $m/z = 212$ (xanthenethione), corresponding to a reverse of the original cycloaddition.

Ketenimines form cycloadducts with thioketones both thermally¹¹ and photochemically.¹² We find that thioimides (**1**) are inert to diphenyl-*N*-(*p*-tolyl)ketenimine at room temperature in the absence of light, but on exposure to filtered radiation from a high-pressure mercury arc a single major photoproduct was obtained in each case. This was characterised as the 2-iminothietane (**6**) arising by [2 + 2] photocycloaddition; the presence of (S)C=N was indicated by a strong i.r. absorption near $1\ 670\text{ cm}^{-1}$ and by a signal in the carbon-13 n.m.r. spectrum near 160 p.p.m., and the orientation was confirmed by the mass spectral fragmentation pattern which showed cleavage by loss of the S=C=NTol unit. The cycloadduct (**6**; X = O) was stable to heat in ethanol under reflux, but heating under these conditions with added benzenesulphonic acid led to the formation of substantial amounts of (**1**; X = O).

Thus the reaction of thioimides with the ketenimine is regio-specific, like that of thioketones,¹² giving 2-iminothietanes, and like the photocycloaddition of analogous ketones with ketenimines which gives 2-imino-oxetanes.¹⁵

Experimental

N-Methylthiophthalimide and *N*-methylthiophthalimide were prepared from *N*-methylphthalimide using Lawesson's reagent.¹⁶ Diphenylketene¹⁷ and diphenyl-*N*-(*p*-tolyl)-ketenimine¹⁸ were made by literature methods.

Irradiations were carried out in dichloromethane at ca. $-60\text{ }^\circ\text{C}$, using light from a high-pressure mercury arc (Phillips HPLN-125 Watt, with outer envelope removed) filtered through an aqueous acidic solution of CuCl_2 and CaCl_2 (for the thioimides) or CuSO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ (for the thioketone).¹⁹ Equimolar amounts (0.003 to 0.005 mol) of thiocarbonyl compound and ketene or ketenimine were used, except for (**1**; X = O) or (**4**) with the ketene, when a two-fold to four-fold excess of ketene was employed, the excess being removed by evaporation during work-up. The progress of the reaction was monitored by t.l.c., and after evaporation of the solvent the product mixture was, in most instances, separated by silica-gel chromatography using toluene-chloroform or dichloromethane-methanol as eluants.

2-Methyl-3',3'-diphenyl-2,3-dihydro-1H-isoindole-3-spiro-2'-thietane-1,4'-dione (**2**; X = O).—This was obtained in 59% yield (26% after repeated purification); m.p. $149\text{--}151\text{ }^\circ\text{C}$ (ethanol) (Found: C, 74.8; H, 4.5; N, 3.8. $C_{23}H_{17}NO_2S$ requires C, 74.4; H, 4.6; N, 3.8%; ν_{max} (KBr) $1\ 755$ and $1\ 700\text{ cm}^{-1}$; δ_{H} (CDCl_3) 2.60 (3 H, s), 6.50 (1 H, d, J 8 Hz), 7.0—7.55 (12 H, m), and 7.90 (1 H, d, J 8 Hz); δ_{C} (CDCl_3) 27.4, 75.4, 91.0, 123.4, 125.8, 127.6, 127.8, 127.9, 128.5, 128.9, 129.7, 130.7, 131.4, 138.9, 144.0, 168.2, and 181.5; m/z 311 (100%), 194, and 165. Also isolated was 3-

diphenylmethylene-2-methyl-2,3-dihydro-1*H*-isoindol-1-one (**3**; X = O) in 22% yield (16% after repeated purification); m.p. $178\text{--}180\text{ }^\circ\text{C}$ (ethanol); ν_{max} (KBr) $1\ 695\text{ cm}^{-1}$; δ_{H} (CDCl_3) 2.90 (3 H, s), 6.3—6.6 (1 H, m), 6.9—7.55 (12 H, m), and 7.7—8.0 (1 H, m); δ_{C} (CDCl_3) 31.5, 122.9, 123.4, 126.0, 127.8, 128.2, 128.4, 128.9, 129.5, 130.7, 131.0, 131.3, 135.2, 137.5, 140.8, 141.3, and 169.1.

2-Methyl-3',3'-diphenyl-1-thioxo-2,3-dihydro-1H-isoindole-3-spiro-2'-thietan-4'-one.—(**2**; X = S).—This was isolated in 42% yield from the mixture obtained from (**1**; X = S) and diphenylketene; m.p. $152\text{--}153\text{ }^\circ\text{C}$ (Found: C, 71.5; H, 4.4; N, 3.7. $C_{23}H_{17}NOS_2$ requires C, 71.3; H, 4.4; N, 3.6%; ν_{max} (KBr) $1\ 750\text{ cm}^{-1}$; δ_{H} (CDCl_3) 3.00 (3 H, s), 6.35 (1 H, d, J 8 Hz), 7.0—7.55 (12 H, m), and 8.10 (1 H, d, J 8 Hz); δ_{C} (CDCl_3) 33.0, 56.6, 80.3, 123.2, 124.8, 125.2, 125.4, 127.5, 127.8, 128.2, 128.6, 129.0, 130.1, 131.0, 131.1, 133.0, 138.3, 138.6, 191.0, and 194.3; m/z 327 (100%), 326, 250, 194, 165, 91, and 60. Also isolated in 55% yield was 3-(diphenylmethylene)-2-methyl-2,3-dihydro-1*H*-isoindole-1-thione (**3**; X = S) [obtaining a sample completely free from (**2**; X = S) was best achieved by irradiation of (**2**; X = S) in benzene with a medium-pressure mercury arc through Pyrex, followed by several fractional crystallisations from ethanol]; m.p. $164\text{--}165\text{ }^\circ\text{C}$ (Found: C, 80.65; H, 5.0; N, 4.2. $C_{22}H_{17}NS$ requires C, 80.7; H, 5.2; N, 4.3%; ν_{max} (KBr) $1\ 340\text{ cm}^{-1}$; δ_{H} (CDCl_3) 3.30 (3 H, s), 6.4 (1 H, m) 7.1—7.6 (12 H, m), and 8.05 (1 H, m); δ_{C} (CDCl_3) 37.1, 122.5, 124.5, 125.4, 127.8, 127.9, 128.3, 128.6, 129.0, 129.1, 129.4, 130.9, 131.0, 131.2, 140.9, and 192.2; m/z 327 (M^+ , 100%), 326, 250, 165, and 91.

3',3'-Diphenylxanthene-9-spiro-2'-thietan-4'-one (**5**). This was obtained in quantitative yield after evaporation of the solvent and removal of excess ketene under reduced pressure at low temperature; m.p. $115\text{--}117\text{ }^\circ\text{C}$; ν_{max} (KBr) $1\ 745\text{ cm}^{-1}$; δ_{C} (CDCl_3) 54.1, 97.0, 116.1, 122.1, 122.9, 126.6, 127.9, 128.6, 129.3, 130.6, 138.9, 152.2, and 194.8; m/z 378, 346, and 212 (100%).

2-Methyl-3',3'-diphenyl-4'-p-tolylimino-2,3-dihydro-1H-isoindole-3-spiro-2'-thietan-1-one (**6**; X = O). This was obtained as colourless crystals, m.p. $183\text{--}184.5\text{ }^\circ\text{C}$ (ethanol) (Found: C, 78.15; H, 5.3; N, 6.0. $C_{30}H_{24}N_2OS$ requires C, 78.25; H, 5.2; N, 6.1%; ν_{max} (KBr) $1\ 715$ and $1\ 665\text{ cm}^{-1}$; δ_{H} (CDCl_3) 2.35 (3 H, s), 2.65 (3 H, s), 6.50 (1 H, d, J 7.5 Hz), 6.8—7.5 (16 H, m), and 7.5—7.95 (2 H, m); δ_{C} (CDCl_3) 20.9, 26.9, 78.1, 81.3, 120.5, 123.0, 125.6, 126.7, 127.2, 127.3, 127.9, 128.2, 128.6, 128.8, 129.2, 130.0, 130.6, 131.1, 135.7, 140.6, 140.8, 144.5, 144.9, 160.2, and 168.0; m/z 461 ($M + 1^+$), 311, 301, 283, 177, and 165 (100%).

2-Methyl-3',3'-diphenyl-4'-p-tolylimino-2,3-dihydro-1H-isoindole-2'-thietane-1-thione (**6**; X = S). This was obtained as yellowish crystals, m.p. $145\text{--}148\text{ }^\circ\text{C}$ (ethanol) (Found: 75.5; H, 5.3; N, 5.7. $C_{30}H_{24}N_2S_2$ requires C, 75.6; H, 5.0; N, 5.9%; ν_{max} (KBr) $1\ 670\text{ cm}^{-1}$; δ_{H} (CDCl_3) 2.40 (3 H, s), 3.05 (3 H, s), 6.35 (1 H, d, J 7.5 Hz), 7.0—7.8 (16 H, m), and 8.10 (1 H, d, J 7.5 Hz); δ_{C} (CDCl_3) 20.9, 32.5, 82.0, 83.4, 120.5, 124.8, 126.4, 127.3, 127.7, 128.1, 128.3, 128.8, 129.7, 130.1, 130.7, 136.0, 137.1, 140.3, 140.6, 141.2, 144.6, 159.6, and 193.5; m/z 476 (M^+) 327, 283, 193, 165 (100%), 146, and 117.

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