

PHOTOCYCLOADDITION OF N-METHYLTHIOPHTHALIMIDE WITH ALKYNES

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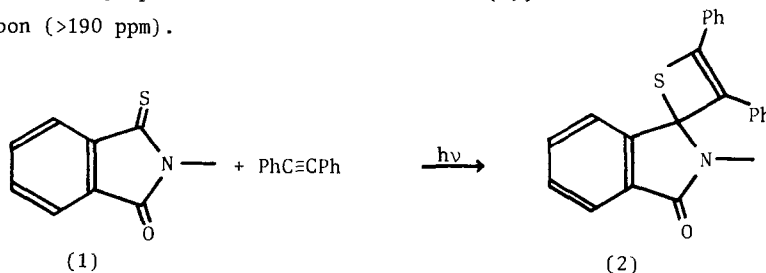
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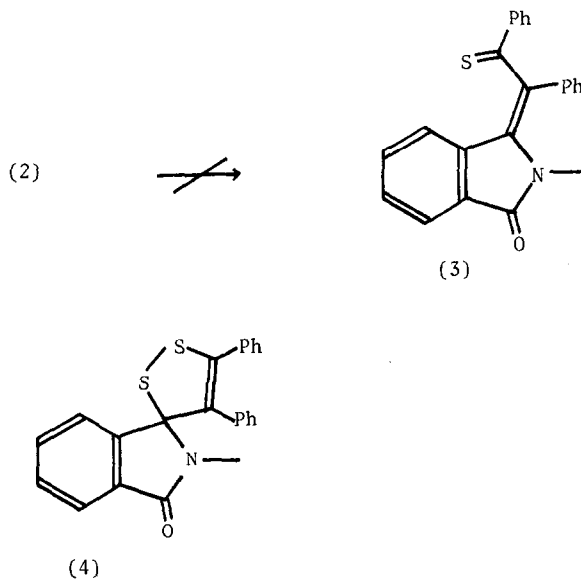
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N-Methylthiophthalimide undergoes photochemical cycloaddition reactions with diphenylacetylene, hex-3-yne and bis(methylthio)acetylene to form spiro-thietes; in solution the spiro-thiete from the bis(methylthio)alkyne is in equilibrium with its ring-opened isomer.

It has recently been reported^{1,2} that thioimides undergo photochemical cycloaddition with alkenes to give thietanes, in a reaction which is similar to that for the more widely studied thioketones,³ as well as for thiophosgene,⁴ O-alkyl thiocarboxylates,⁵ thioparabanates,⁶ and thiouracils.⁷ The analogous photocycloaddition with alkynes to give thietes is known for thioketones,⁸ but only for thioparabanates⁹ amongst other thiocarbonyl compounds, and with these latter substrates a variety of products is formed. We now report that a thiophthalimide gives good yields of spiro-thietes with three substituted acetylenes, and that in one system the product in solution is an equilibrium mixture of the spiro-thiete and an α,β -unsaturated thiocarbonyl compound derived from it by ring-opening.

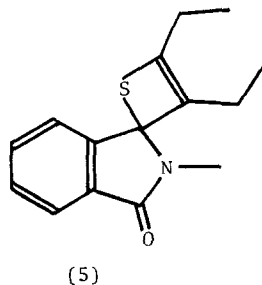
Irradiation (125-Watt medium-pressure mercury arc, Pyrex filter) of N-methylthiophthalimide (1) with diphenylacetylene in benzene with nitrogen bubbling gives largely one product that can be isolated in 52% yield. The structure is assigned as (2) on the basis of microanalytical results and spectral data. The carbon-13 n.m.r. spectrum shows that in solution the compound is not isomerised to the ring-opened unsaturated thioketone (3), since there is no signal for a thiocarbonyl carbon (>190 ppm).



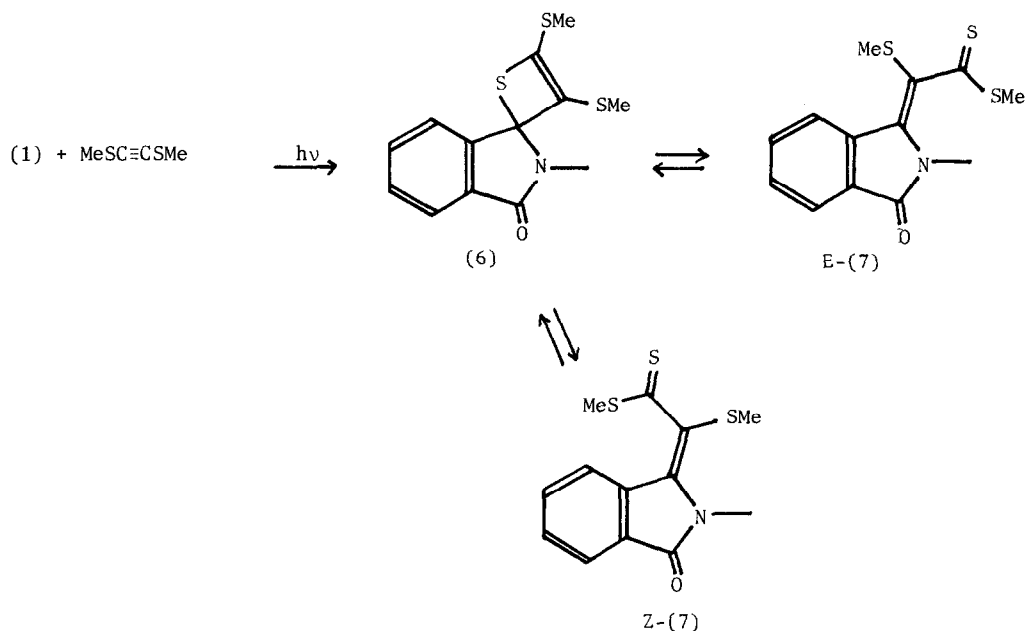


Treatment of (2) with benzenesulphonic acid in ethanol under reflux provides no evidence for clean isomerisation to (3), but leads instead to a mixture of several other products. The absence of unsaturated thioketone would be in keeping with the pattern seen for thietes obtained from thioketones, where only those derived from bis-heteroatom-substituted alkynes undergo ring-opening of this kind; the related oxetes obtained from ketones and alkynes by photocycloaddition at $-70\text{ }^{\circ}\text{C}$ rapidly isomerise to α,β -unsaturated ketones on warming.¹⁰ A second product is isolated in small quantities from the reaction mixture obtained from (1) with diphenylacetylene; it is assigned the structure (4) on the basis of microanalytical results and mass spectral data (parent ion $\text{C}_{23}\text{H}_{17}\text{NOS}_2$, and a fragmentation pattern showing loss of two sulphur atoms as the major pathway), and by analogy with similar products formed from diphenylacetylene and either a thioparabanate or a thiobarbituric acid.⁹ The formation of (4) may involve reaction of a (biradical) intermediate with a second molecule of ground state thioimide, but the detailed mechanism is not clear.

We obtain an analogous spiro-thiete (5) as the major isolated product when (1) is irradiated under similar conditions with hex-3-yne.

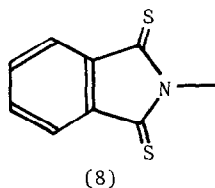


Irradiation (125-Watt high-pressure mercury arc, aq. $\text{CuCl}_2/\text{CaCl}_2$ filter) of (1) with bis(methylthio)acetylene in dichloromethane with nitrogen bubbling gives a two-component mixture from which a red crystalline compound can be isolated (the total solid mixture appears yellow and red). Microanalytical results suggest that the product is formed from one molecule of each addend, and we propose structure (7), E- or Z-isomer, for the red solid, namely the α,β -unsaturated dithioester obtained by ring-opening of the spiro-thiete (6). The proposal is based on the colour, which is similar to that of related thioketones obtained in the photoaddition of bis(alkylthio)acetylenes and thioketones.¹¹ On dissolving the red crystals in deuteriochloroform (or other solvents), the original two-component mixture is regenerated, as evidenced by the identity of the proton n.m.r. spectra. This spectrum can be analysed in terms of a 2:1 mixture (major component has δ_{Me} 2.38, 2.77 and 3.29; minor component has δ_{Me} 2.36, 2.80 and 3.76), and the carbon-13 n.m.r. spectrum shows a similar duplication of methyl signals (major component at 17.5, 20.4 and 29.8; minor component at 17.7, 21.0 and 31.2). It is likely that the two components in solution are E-(7) and Z-(7), interconverted readily through (6) as intermediate; the yellow crystals are likely to be the spiro-thiete (6).



The proton n.m.r. spectrum of the mixture of E and Z-(7) varies very little over a range of temperatures up to 55 °C, which is not unexpected for a 2:1 equilibrium mixture. Using hexamethyldisiloxane as internal standard in the spectrum of the original crude reaction mixture it is estimated that the analytical yield of E and Z-(7) from (1) is close to 100%.

When (1) is irradiated for long periods with phenylacetylene, we can detect no photoadduct between the two compounds. Preliminary results with (1) and bis(t-butylthio)acetylene, and with N-methylthiophthalimide (8) and bis(methylthio)acetylene, suggest that there is one major product in each case. T.l.c. analysis of the reaction mixtures from (1) or (8) with 1-(methylthio)propyne indicates that two photoadducts are present in each, and further work is in progress with these systems.



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