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PHOTOCYCLOADDITION REACTIONS OF N-METHYLTHIOPHTHALIMIDE

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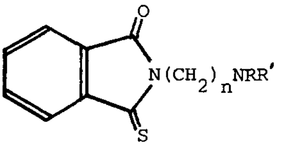
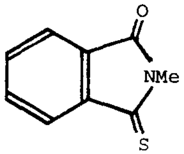
Summary: N-Methylthiophthalimide undergoes a photochemical cycloaddition reaction with 2,3-dimethylbut-2-ene or with stilbene to give products containing a spiro-thietane system; with 1,1-diphenylethene the product isolated is a diphenylmethyleneisoindoline.

Thioketones exhibit a varied photochemistry[1] that is in some respects analogous to that of their oxygen analogues, but which also shows significant differences. There is little reported photochemistry involving the C=S group of thio-compounds corresponding to amides or imides, and because of the considerable interest in the photochemistry of imides[2] we extended our studies to the photoreactions of thiophthalimides.

We first looked for intramolecular hydrogen abstraction reactions of N-substituted thioimides of type (1), but this proved to be generally unsuccessful, although some interesting photocleavage products were formed that we are following up. Only recently has the first example of intramolecular hydrogen abstraction by any thioamide-like compound (an acyclic thioaroylurea) been reported.[3] We then discovered that N-methylthiophthalimide(2) is photochemically active towards alkenes.

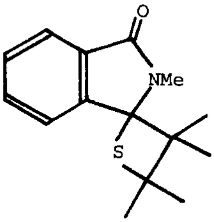


(1;n=1,2)

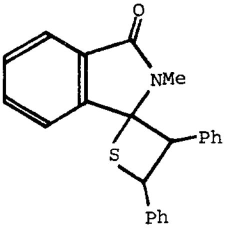


(2)

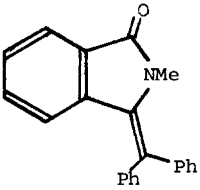
N-Methylphthalimide reacts with alkenes to give, normally, ring-expanded benzazepinediones or products that incorporate a hydroxylic solvent.[2,4] Only in a few cases have oxetanes been formed.[5] We find, however, that irradiation (400-watt medium-pressure mercury arc, Pyrex filter, nitrogen bubbling) of (2) with 2,3-dimethylbut-2-ene or with stilbene gives thietane products (3,4) in moderate yields (22% for 3, 45 + 21% for 4). The product structures were elucidated from the results of microanalysis and from ms, ^{1}H-nmr, ^{13}C-nmr and ir spectral properties. A small amount (1-3%) of oxidised starting material, i.e. N-methylphthalimide, was also isolated; this is the major product if (2) is irradiated without alkene in the presence of oxygen.



(3)



(4)



(5)

With 1,1-diphenylethene the major product (62%) is (5), which is probably formed by elimination of thioformaldehyde from an intermediate thietane.

The observed reactions highlight the photochemical reactivity of the thiocarbonyl group and the differences between C=S photochemistry and that of related C=O compounds. Our studies are continuing, to determine the scope and mechanism of the cycloaddition reactions.

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