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THE PHOTOCHEMISTRY OF THIOCARBONYL COMPOUNDS

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INTRODUCTION

Organic carbonyl compounds, especially ketones, featured prominently in the earliest studies by organic photochemists. They also served as substrates for many of the pioneering mechanistic studies in photochemistry, and they continue to provide a very fertile field for photochemical research. In comparison their sulfur analogues have received scant attention until quite recently, and yet organic thiocarbonyl compounds are proving to have a photochemistry that is quite distinct from the oxygen compounds. There have been a number of fairly short general reviews of thiocarbonyl photochemistry,[1-3] a review of wavelength-dependent photochemistry including that of thiones,[4] and fuller accounts of photocycloadditions,[5,6] photo-oxidation,[7] and photophysical investigations.[8] The purpose of this report is to provide an extensive and up-to-date account from the viewpoint of an organic photochemist, emphasizing synthetic applications and the mechanistic appreciation that is relevant to the development of such applications.

In comparing thiocarbonyl and carbonyl photochemistry the most striking difference seen by the researcher is that the sulfur substrates are very often coloured, which means that visible light can be employed rather than ultraviolet radiation. The observed photoreactions of thiocarbonyl compounds often follow a different course from those of analogous carbonyl compounds because the chemical reactivity and the thermodynamic properties are significantly different: for example, the lowest excited state energies for C=S compounds are considerably lower than those for their C=O counterparts, $R_2\dot{C}$—SR type radicals have a different chemistry from that of $R_2\dot{C}$—OR radicals, and thiocarbonyl compounds (unlike carbonyl compounds) can act as efficient radical traps or as dienophiles. If ultraviolet radiation is used with thiocarbonyl compounds, it is not unusual for a different photoreaction to be observed than with visible light; this is because the second excited singlet state is generated and undergoes chemical reaction, which provides an exception to the broad generalization made by Kasha, that only the lowest excited singlet and triplet states of a compound are directly involved in photochemical reactions.

There are different ways of providing broad classifications for the photoreactions of compounds containing the C=S chromophores. A functional classification (thioketones, thioaldehydes,

thioamides, and so on) is not particularly helpful here, because reactivity patterns in electronically excited states do not parallel those in ground-state processes. The approach used in this report is a combination of overall reaction classification and mechanistic classification. Reactions that involve (or appear to involve) similar initial steps in the mechanism are described together, but similarities in overall reaction consequences are also recognized in sectional or sub-sectional groupings. This combination avoids the obscuring of mechanistic parallels (e.g. in photoreduction and photocyclization via initial hydrogen transfer), whilst allowing room for reactions whose mechanism is uncertain.

PHOTOPHYSICAL PROPERTIES

The fascinating area of photophysical studies involving thiocarbonyl compounds has been well reviewed,[8] and in this short section only those properties most relevant to an organic photochemist are summarized briefly.

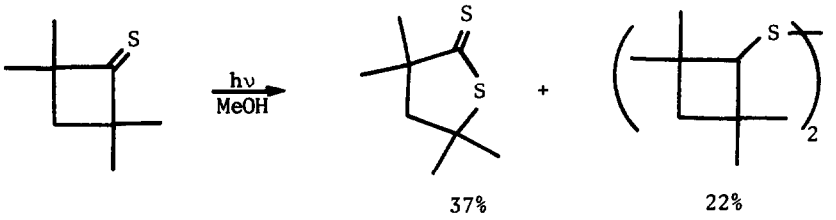
Most organic C=S compounds have an absorption spectrum that exhibits a relatively weak long-wavelength band: λ_{max}/nm (ε_{max}/l mol^{-1} cm^{-1}) are 503 (10) for heptane-4-thione and 599 (180) for thiobenzophenone. This band is responsible for the colour of thioketones, aromatic thioimides, and so on, and it can be attributed[9] to a dipole-forbidden n → π^* transition. The spectra show more intense absorption bands at shorter wavelengths, 316 (16,000) and 235 (9000) for thiobenzophenone, that arise from $\pi \rightarrow \pi^*$ transitions. The large energy gap between $S_2(\pi, \pi^*)$ and $S_1(n, \pi^*)$, up to 200 kJ (50 kcal) mol^{-1}, is responsible for one of the outstanding features of thiocarbonyl photophysics, namely that fluorescence is quite commonly observed from S_2. One of the best studied examples is xanthene-9-thione, whose fluorescence is enhanced in non-reactive perfluoroalkane solvents.[10] Fluorescence from S_1 occurs for a few small thiocarbonyl compounds, such as $Cl_2C{=}S$, but for many compounds $S_1 \rightsquigarrow T_1$ intersystem crossing is very fast. These factors underlie the observation that most photochemical reactions of thiones and related compounds derive from the S_2 or T_1 states.

For (n, π^*) states in C=S compounds the singlet–triplet splitting is very small, often less than 2000 cm^{-1} (e.g. approx. 800 cm^{-1} for xanthenethione), and this leads to the very high rate constants for intersystem crossing ($> 10^{11}$ s^{-1} for xanthenethione). Phosphorescence can be observed from the T_1 (n, π) state,[11] but a significant feature of triplet state photophysics is the very high rate of self-quenching. Ground-state thiocarbonyl compound acts as an efficient quencher of the T_1 state, with the result for the synthetic photochemist that quantum yields for a triplet reaction can decrease substantially as the substrate concentration is increased. The mechanism of self-quenching may involve a triplet excimer, but evidence for such an intermediate is not readily achieved.[12]

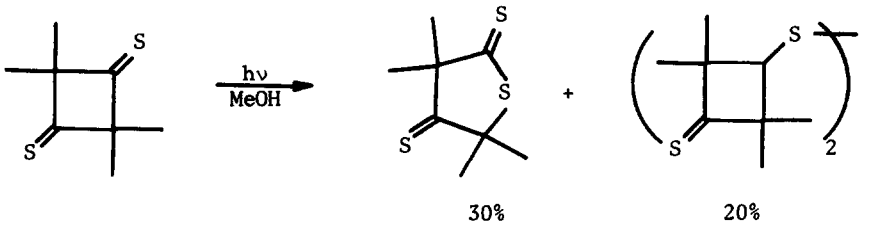
REACTIONS INVOLVING INITIAL BOND CLEAVAGE

Ketones and related compounds undergo a number of interesting and useful photochemical reactions that begin with cleavage of the alpha (O=)C—C bond, but the same range of reactions is not observed with thioketones because the lower energy of the C=S reactive excited state alters the thermodynamic balance and makes cleavage of an adjacent bond less favourable energetically. Exceptions arise when this bond is particularly weak as a result of high strain factors. Thus, although di-t-butyl thioketone does not undergo cleavage on irradiation with either visible or near-ultraviolet radiation, 2,2,4,4-tetramethylcyclobutanethione does give a product (eqn (1)) that arises by cleavage of one of the ring bonds adjacent to the thione group;[13] a photoreduction product is also formed. The mechanism by which the thiolane-2-thione is formed is not clear, but trapping of a ring-opened biradical by a ground-state thione molecule is a likely possibility.

Analogous products are formed from cyclobutane-1,3-dithiones (eqn (2)); with these substrates there are additional products, 5-methoxythiolane-3-thiones and 3-methoxy-5-methylene-1,2-dithiolanes, that are produced by reaction of methanol with an α-thiacarbene, itself formed by ring-closure in the initial ring-opened 1,4-biradical.[14] A further type of product from some cyclobutane-1,3-dithiones is a 4-methylenethietane-2-thione (a methylenedithio-β-lactone, eqn (3)), which can also be rationalized on the basis of α-cleavage followed by the alternative re-closure of the biradical.[15] The reverse reaction (4-methylenethietane-2-thione to cyclobutane-1,3-dithione) has also been reported.[16] With 3-thioxocyclobutanones (eqn (4)) the analogous reaction leads efficiently to 4-methylenethietan-



(1)



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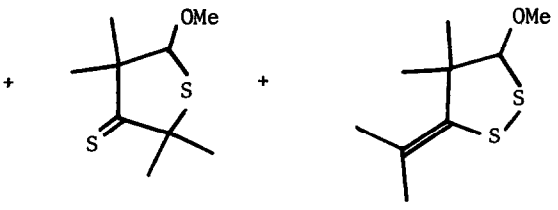
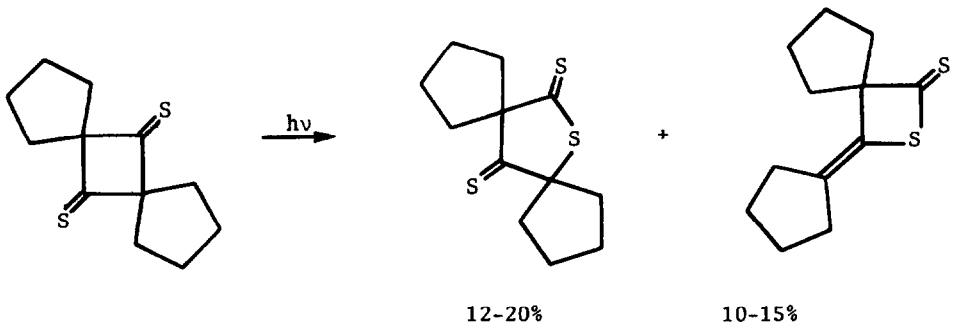


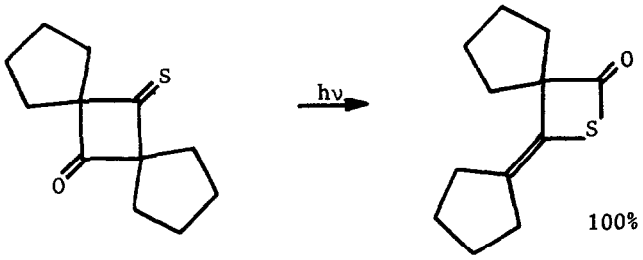
2-ones,[17] by a process that must involve cleavage of the bond adjacent to carbonyl rather than to thiocarbonyl.



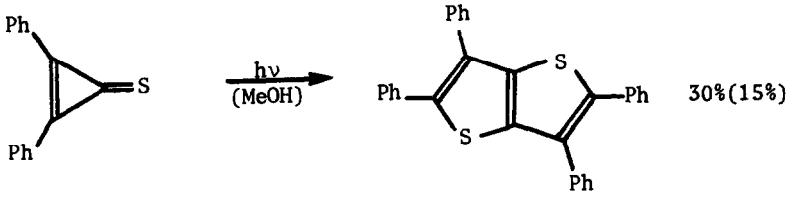
(3)

Diphenylcyclopropenethione gives photoproducts (eqn (5)) that can be accounted for on the basis of initial strain-assisted α-cleavage.[18] In the absence of methanol the thieno[3,2-*c*]thiophene is the only product,[19] but with methanol the 4-methoxythiete is formed through a cyclic carbene, and the 3-methoxythioacrylate through a ring-opened carbene; the latter product requires an oxidation process at some stage in its formation.

Cleavage is a common feature in the photochemistry of dithioesters and related compounds, in which the carbon–sulfur alpha bond is sufficiently weak for its homolytic cleavage to be energetically feasible from the lowest excited state of the substrate. Thus diaryl trithiocarbonates eliminate CS to produce diaryl disulfides in high yield (eqn (6)).[20] However, an alternative β-cleavage route appears to be preferred in some systems. Bis(trifluoromethyl) trithiocarbonate gives rise to hexakis(trifluoromethylthio)ethane (eqn (7)),[21] and the formation of alkenes (or their further phototransformation products) from 1,3-dithiolane-2-thiones (eqn (8)), which are cyclic trithiocarbonates, can be interpreted in terms of a β-cleavage process, although initial α-cleavage cannot be ruled out.[22]



(4)



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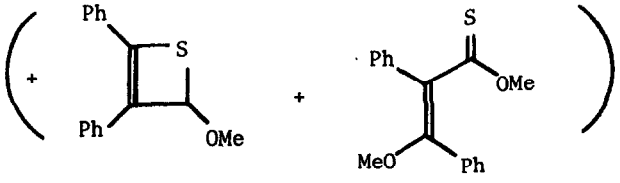
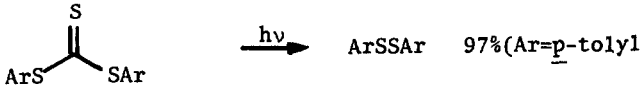
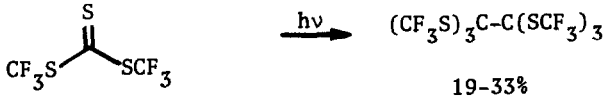
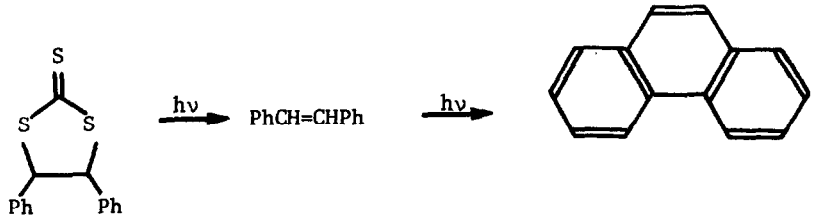




(6)



(7)

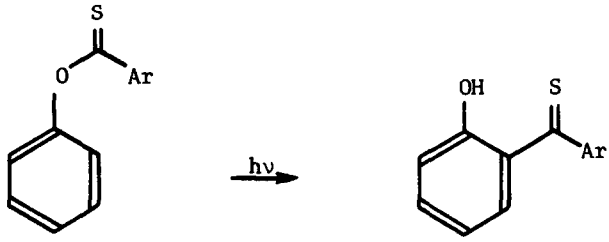


(8)

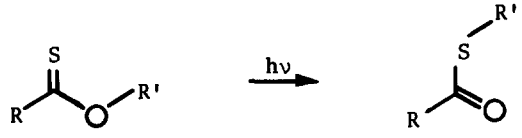
In solution 1,3-dithiole-2-thiones form dimeric, desulfurated products (see the section on cycloaddition), but matrix studies[23] show that under these conditions CS_2 and a thiirene are formed, in contrast to the COS and ketene observed on matrix irradiation of 1,3-dioxole-2-thiones.[24]

Irradiation of an O-aryl thioester yields the isomeric *o*-hydroxyaryl thioketone (eqn (9)) in a reaction that involves α-cleavage and parallels the photo-Fries reaction of aryl carboxylates.[25] However, with O-alkyl thioesters the preferred reaction is a 1,3-shift to give the S-alkyl thioester

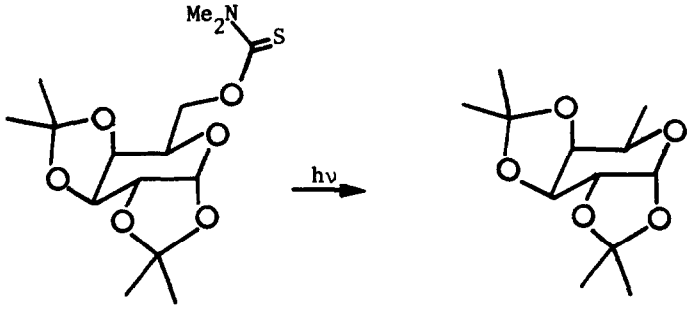
(eqn (10)), which is formally a β-cleavage process. The S-alkyl thioesters can undergo facile C—S bond cleavage, which opens up the possibility of a mild method for deoxygenation, for example with the N,N-dimethylthiocarbamates of protected pyranoses to provide a route to 6-deoxy derivatives (eqn (11)).[26]



15%(Ar=p-tolyl) (9)

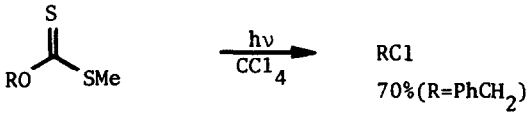


(10)

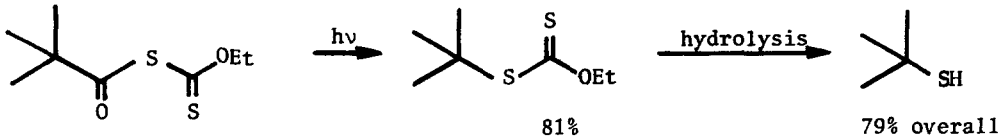


35-45% (11)

In a related process O-alkyl S-methyl dithiocarbonates (xanthates) give alkyl chlorides when irradiated in carbon tetrachloride (eqn (12)),[27] and a mild method for overall decarbonylation of certain thiocarboxylic acids is based on a similar sequence of reactions with an additional decarbonylation in one of the intermediate radicals (eqn (13)).[28] Bond cleavage is also reported on irradiation of mixed anhydrides such as MeNHC(=S)SC(=O)Ph,[29] and it is implicated in the photoisomerization of 1,2,4-oxadiazole-5-thiones to 1,2,4-thiadiazol-5-ones.[30]



70%(R=$PhCH_2$) (12)



81% 79% overall (13)

REACTIONS INVOLVING HYDROGEN ABSTRACTION

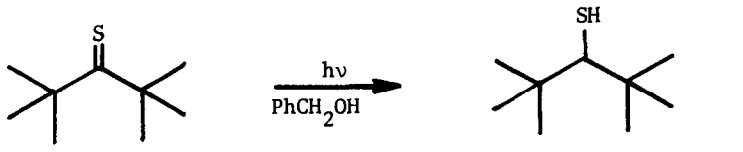
Photoreduction by way of initial hydrogen atom abstraction is a commonly encountered process for ketones; it has been studied thoroughly for benzophenone, for which the major product under many conditions is benzpinacol (eqn (14)). The sulfur analogue, thiobenzophenone, also reacts photochemically with hydrogen donors such as primary alcohols,[31] but a greater range of products is observed (eqn (15)). The reactive excited state in this system is the (n, π^*) triplet of the thione, and the initially formed radical is $Ph_2\dot{C}$—SH, analogous to the ketyl radical obtained from benzophenone; ESR evidence for this relatively stable radical has been reported[32] in tetrahydrofuran as solvent. The differences in the secondary reactions of the radical arise because ground state thiobenzophenone is a good radical trap, and because there is little difference in energy between $R_2\dot{C}$—SR and R_3C—$\dot{S}$ species.

$$Ph_2C{=}O \xrightarrow[Pr^iOH]{h\nu} (Ph_2\overset{OH}{\overset{|}{C}})_2 \qquad (14)$$

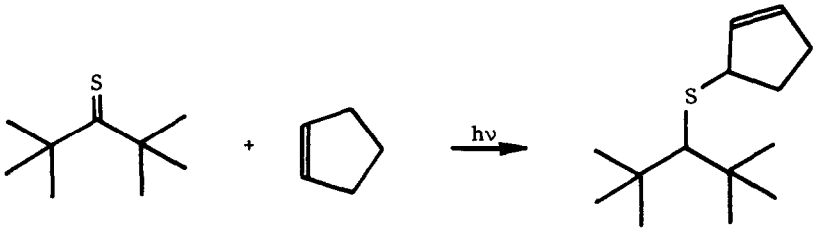
$$Ph_2C{=}S \xrightarrow[EtOH]{h\nu} (Ph_2CHS)_2 \ (32\%) + Ph_2CHSH \ (29\%) + (Ph_2CHSS)_2CPh_2 \ (28\%) + (Ph_2CH)_2S \ (6\%) \qquad (15)$$

Thiobenzophenone is unreactive in cyclohexane when long wavelength excitation is used, but with shorter wavelength radiation di(benzhydryl) sulfide and di(benzhydryl) disulfide are formed as major products. In this reaction it is presumably the S_2 (π, π^*) state that is responsible for hydrogen abstraction. With certain more reactive hydrocarbons, such as cyclohexa-1,4-diene where an important driving force is the formation of benzene as the oxidation product of the hydrocarbon, either long or short wavelengths are effective.[33] An electron-transfer mechanism has been postulated for reactions involving these hydrocarbons, but the evidence is not conclusive.

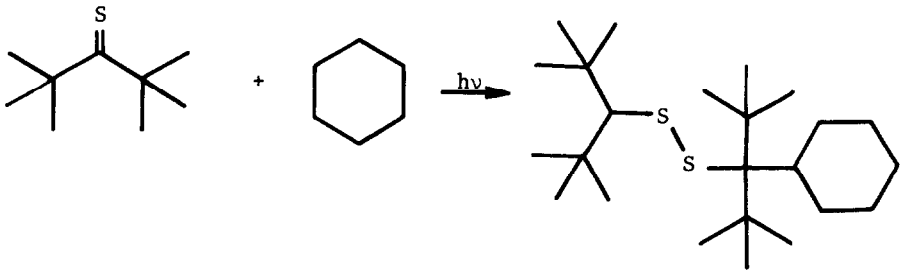
Two aliphatic thioketones have been studied in some detail, di-t-butyl thioketone and adamantanethione. With the first of these, excitation to S_1 or triplet sensitization is effective only with donors such as amines, toluene or benzyl alcohol (eqn (16)).[34] Isopropanol or diethyl ether is not suitable for this reaction, which lends support to the proposed electron-transfer mechanism. Excitation to S_2, however, promotes reaction with a wide variety of hydrogen donors,[35] and photoadducts as well as reduction products are formed (eqn (17)). With cyclohexane as solvent, an increase in thioketone concentration leads to the formation of a mixed disulfide (eqn (18)), reflecting the increased importance of radical trapping by ground-state thioketone.



(>0.2M) 82% (16)

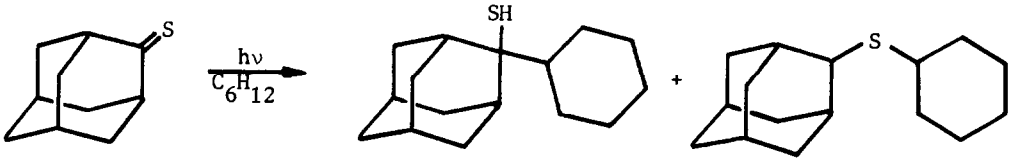


70% (17)



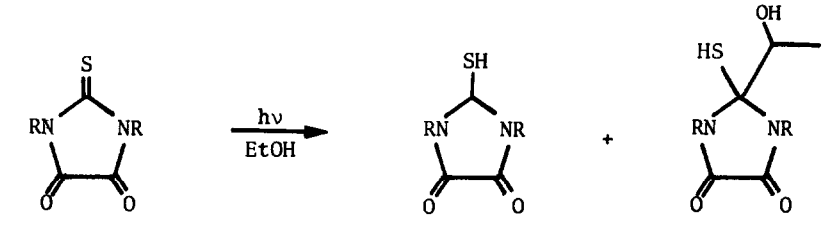
(18)

The lowest triplet state of adamantanethione similarly reacts only with a very good hydrogen donor, such as adamantane-2-thiol to give (ϕ = 1–4) di(2-adamantyl) disulfide.[36] With shorter wavelengths the second excited singlet state is formed, and this is a fairly indiscriminate abstractor of hydrogen atoms;[37] in cyclohexane as solvent, both thiol and sulfide adducts are produced (eqn (19)). The product distribution varies with the solvent viscosity, and this is interpreted[38] in terms of a solvent cage effect: only if radicals escape from the solvent cage is di(2-adamantyl) disulfide formed. Similar conclusions were reached from results of a study using a mixture of cyclohexane and cyclohexane-d_{12}.

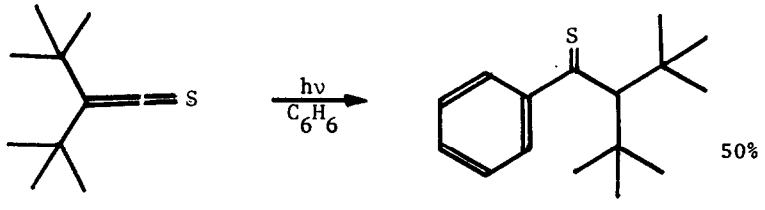


(19)

Xanthene-9-thione is another thioketone that undergoes photochemical hydrogen abstraction,[39] and thioparabanates similarly give rise to photoreduction and photoaddition products (eqn (20)) when irradiated in alcohols.[40] A recently reported example involves di-t-butyl thioketene,[41] and this is unusual in giving a photoadduct with benzene (eqn (21)); such a process is unknown for thioketones or ketones. The thioketene in alcohols gives an O-alkyl thioester and an alkoxythiirane; it is proposed that the thiirane arises by way of a cyclic carbene, and this carbene may be the intermediate that initiates attack on the benzene ring.



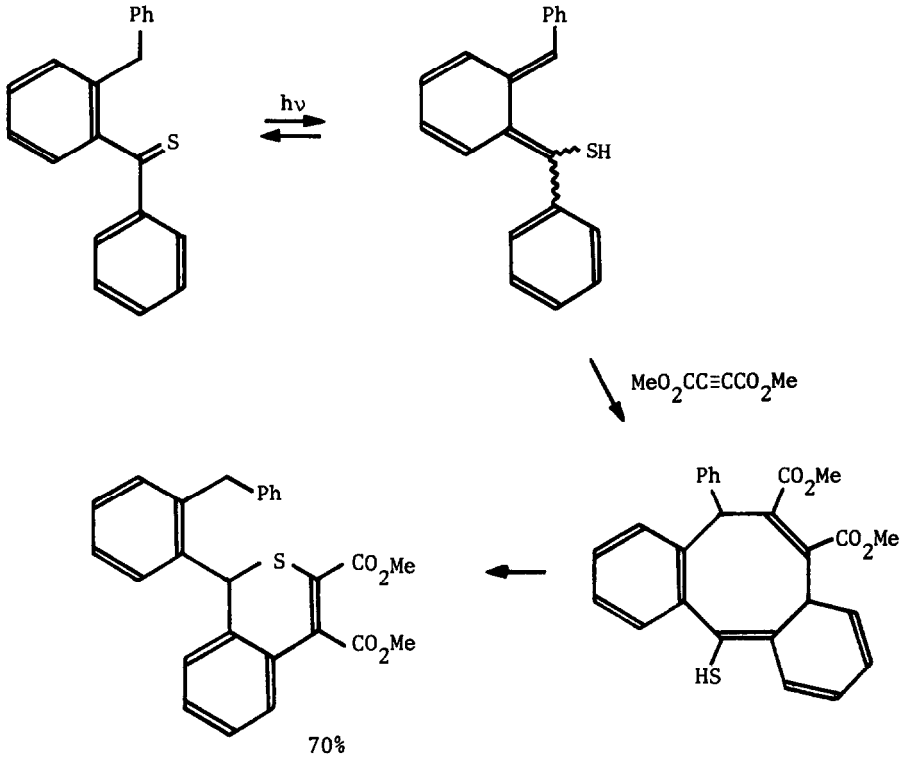
(20)



(21)

Intramolecular hydrogen abstraction processes in thiocarbonyl compounds have been widely reported. An early account[42] of the photochemistry of *o*-benzylthiobenzophenone indicated that reversible photoisomerization occurs to give a conjugated enethiol (eqn (22)). In methanol-O-d deuterium exchange leads to recovery of the starting material deuterated at the benzylic position.

Diazomethane traps the enethiol as a methylthioalkene, and with dimethyl acetylenedicarboxylate an initial (6+2) cycloadduct leads on to a benzothiapyran.



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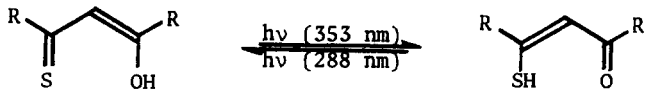
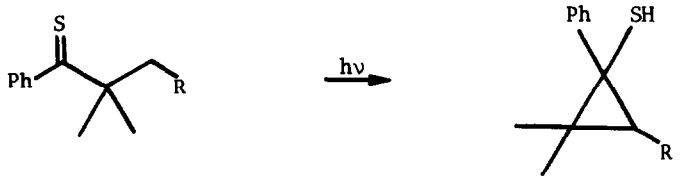


(R=Me,Ph)

(23)

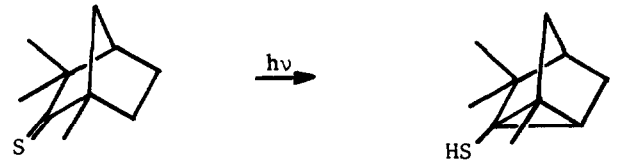
Similar to this photo-enethiol formation is the interconversion of the enol–thione and enethiol–ketone tautomers of β-thioxoketones (eqn (23)) that takes place at low temperature in either direction according to the wavelength of light used.[43] However, many of the intramolecular hydrogen abstraction reactions of thiones lead to cyclic products, and reported ring-sizes in these products range from three to six. In compounds with structural constraints abstraction from a β position can occur to give cyclopropanethiols, as with 1,3-diarylpropane-1-thiones (eqn (24); R = Ar)[44] or with thiofenchone (eqn (25)).[45] The thiofenchone reaction has been shown[46] to occur by way of the S_2 (π, π^*) state, and heating this and related cyclopropanethiol photoproducts causes reversion to the original thione or to a rearranged thione. β-Abstraction occurs with some thiones that, in principle, could also undergo δ-abstraction, for example 2-methylthio derivatives (eqn (24); R = SMe).[44] In this the thiones resemble certain β-dialkylaminoketones that produce cyclopropanols, but the preference for β- over δ-abstraction is not universal, since appropriately substituted thioaroylureas or thioaroylthioureas can be converted in good yield to imidazolidin-2-ones or imidazolidine-2-thiones (eqn (26)).[47]

In some reactions β-hydrogen abstraction has been proposed as the initial process that leads eventually to products other than a cyclopropanethiol. Acyclic N-alkylthioimides rearrange to α-acylaminothioketones on irradiation (eqn (27)), and this is best accounted for in terms of an intermediate cyclopropanethiol.[48] N-(Dialkylaminomethyl)thiophthalimides undergo overall cleavage to N-thioformylamines and a dimer of isoindolone (eqn (28)), and a likely mechanism for this process begins with abstraction of hydrogen from the β-position.[49]

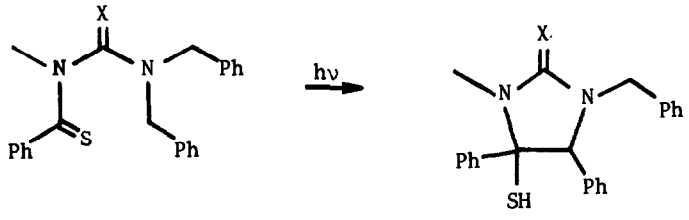


82% (R=p-tolyl)
87% (R=SMe)

(24)

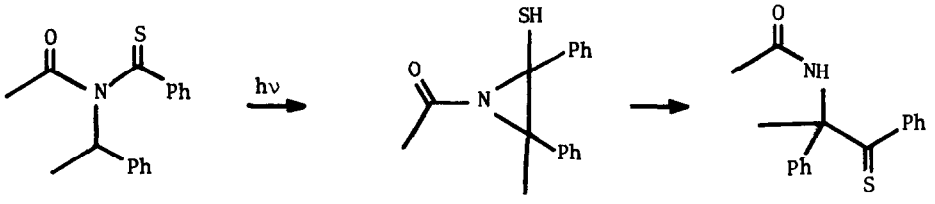


(25)



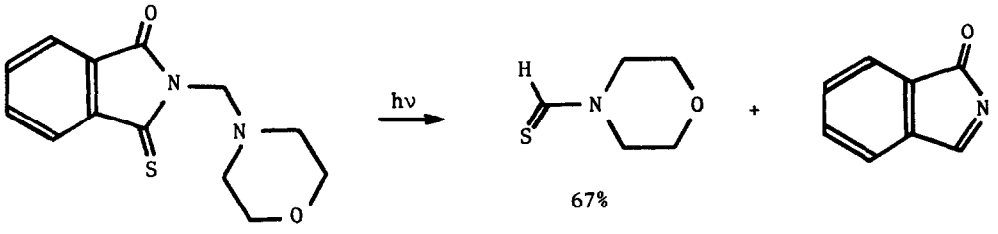
68% (X=O)
56% (X=S)

(26)

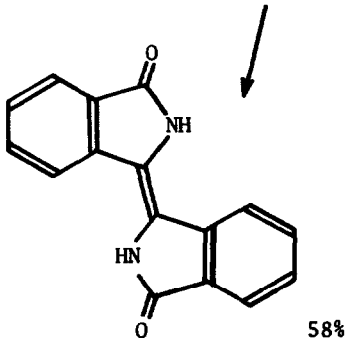


95%

(27)



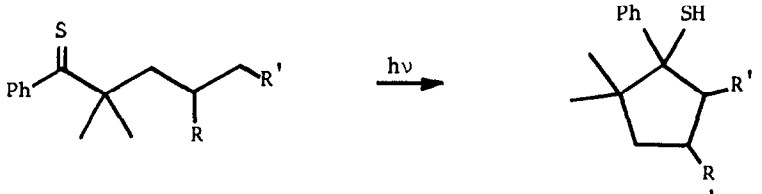
67%



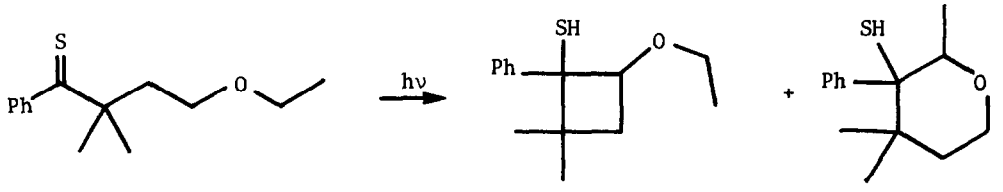
58%

(28)

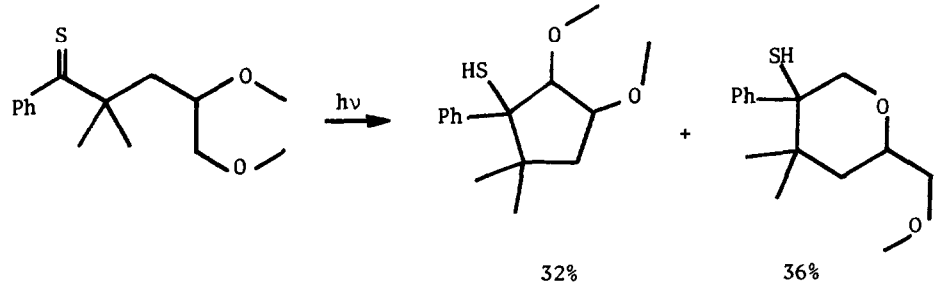
In unconstrained aryl alkyl thioketones that offer a choice of position for internal hydrogen abstraction, the general preference on excitation to the $S_2(\pi, \pi^*)$ state is for δ-abstraction and cyclization to a cyclopentanethiol (eqn (29)).[50] Detailed mechanistic studies suggest that the reactive state is S_2, and that an intermediate biradical is formed which disproportionates efficiently rather than cyclizing, thus accounting for the low quantum yields of reaction ($\phi = 0.032$ for R = Me, R′ = H); rate constants and activation energies have been determined.[51] A range of alkoxy-substituted compounds have been investigated[52] with available hydrogen atoms in γ, δ or ε positions, and products arising from all three modes of attack can be isolated (eqns (30) and (31)). An interesting feature of these reactions is that only products involving γ-abstraction are formed when long wavelength radiation is employed, and under such conditions an optically active thione with a chiral γ-carbon is racemized. These results point to the involvement of the $T_1(n, \pi^*)$ state in γ-hydrogen abstractions, which parallels the preference for γ-abstraction in aryl alkyl ketones that react through their $T_1(n, \pi^*)$ state. A theoretical study[53] of possible directions of approach of the hydrogen atom to the thione excited states has attempted to provide a rationale for the observed differences.



70% (R=R′=H) (29)

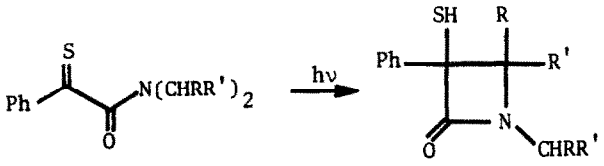


(30)

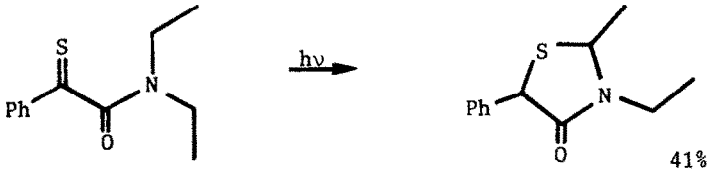


32% 36% (31)

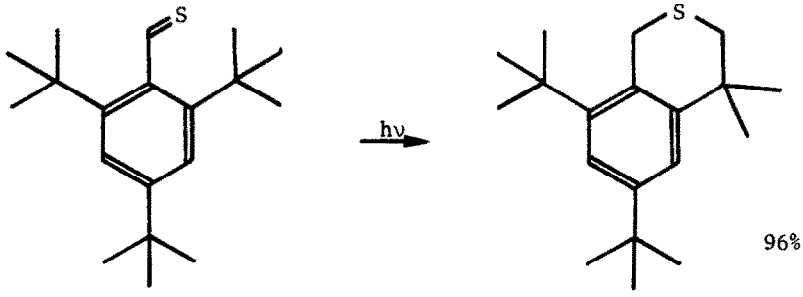
β-Lactams are formed in moderate yields when appropriately substituted thiobenzoylformamides are irradiated (eqn (32)),[54] although some compounds preferentially give thiazolidin-4-ones (eqn (33)) as a result of overall transfer of hydrogen to the carbon, rather than to the sulfur, of the thiocarbonyl group. Such transfer to carbon is also evident in the photocyclization of 2,4,6-tri-t-butylthiobenzaldehyde, one of the few thermally stable thioaldehydes, where a thiapyran ring is present in the product (eqn (34)).[55] An alternative fate for the intermediate biradical in γ (or δ) abstraction intervenes in 5-substituted 4-thiouracils (eqn (35)), and the products arise by ring closure to position 6 of the uracil system.[56]



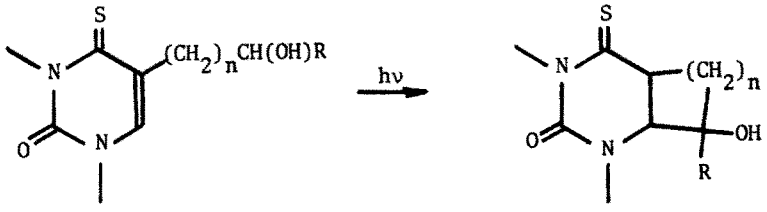
25-38% (32)



41% (33)



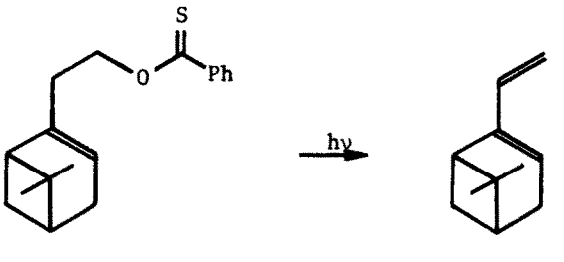
96% (34)



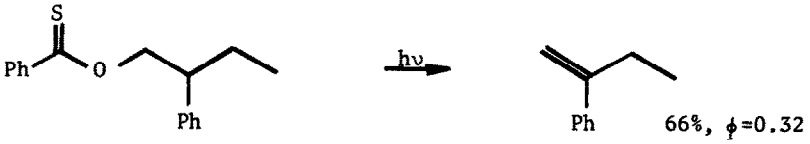
50% (n=1, R=Me)
30% (n=2, R=H) (35)

Reactions analogous to the Norrish type 2 photoelimination of alkyl benzoates are observed with O-alkyl thiobenzoates.[57] This can provide a useful route for the dehydration of homoallylic alcohols to give dienes under mild conditions (eqn (36)), including steroidal compounds such as cholesterol.[58] Simpler O-alkyl thiobenzoates give reasonable yields of alkenes in many cases, and the quantum yields can be high (eqn (37)).[59] With some substituent patterns a competing process becomes important, that leads by way of a ring-closed oxetane-2-thiol to a β-hydroxythioketone (eqn (38)).[60,61]

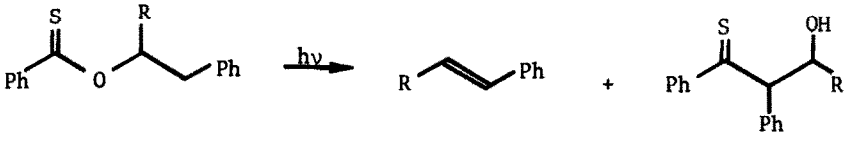
Although O-alkyl thiobenzoates react readily, N-substituted thiobenzamides and alkyl dithiobenzoates do not, either because the lowest triplet state is (π, π^*) rather than (n, π^*) in nature, or because the triplet state energy is too low. However, N-acylthiazolidine-2-thiones do give ethyl esters on irradiation in ethanol (eqn (39)) that are formed by way of a ketene;[62] this is proposed as the basis for a protecting group for carboxylic acids that can be removed under mild, neutral conditions.



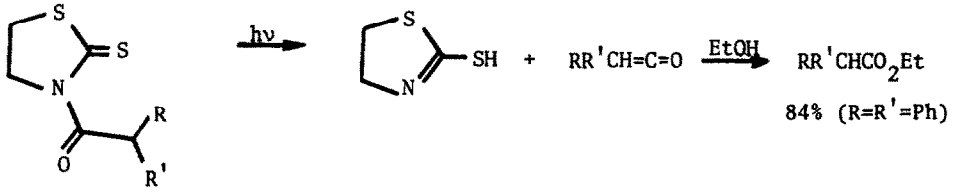
85% (36)



(37)



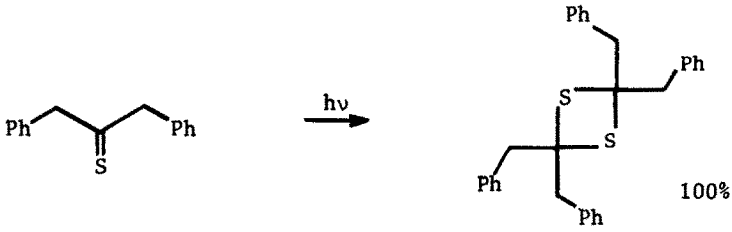
(38)



(39)

CYCLOADDITION REACTIONS

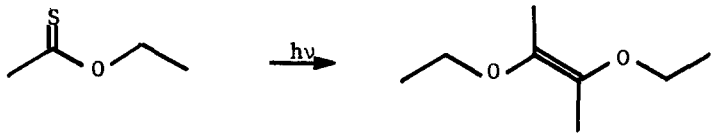
There is a rich variety of photochemical cycloaddition involving a thiocarbonyl compound and an addend with a multiple bond, and because a greater range of sulfur than of oxygen four-membered heterocycles are stable, the scope of the reaction is wider for thiocarbonyl than for carbonyl substrates. Some thioketones undergo photodimerization when irradiated alone, to give 1,3-dithietanes that can be isolated readily. Such a thione is dibenzyl thioketone, 1,3-diphenylpropane-2-thione (eqn (40));[63] adamantanethione behaves in a similar way,[64] and a very early report of such a reaction involved thiophosgene.[65]



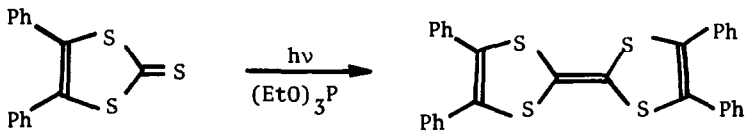
(40)

Compounds in which the C=S bond is relatively electron rich seem to produce 1,2-dithietanes (not 1,3-dithietanes), although these are not isolated, but rather the alkene obtained from them by loss of sulfur. This was first reported[66] as a way of making symmetrical dialkoxyalkenes from O-alkylthioesters (eqn (41)), although such thioesters can also give high yields of linear oligomers on

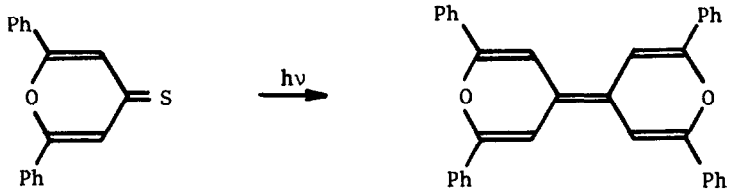
irradiation.[67] The reaction has been used[68] to convert 1,3-dithiole-2-thiones into tetrathiafulvalenes (eqn (42)), and for a pyran-4-thione (eqn (43)),[69] although in the latter system a more detailed mechanistic study[70] suggests that the reaction may occur by a route involving hydrogen abstraction from solvent rather than through a 1,2-dithietane. Although not strictly a cyclization, the equilibrium between α-di(thioketones) and 1,2-dithietes (eqn (44)) is related to dithietane formation, and the position of this equilibrium can be influenced by irradiation.[71]



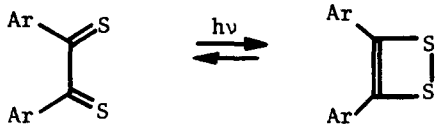
63% (41)



93% (42)



80% (43)

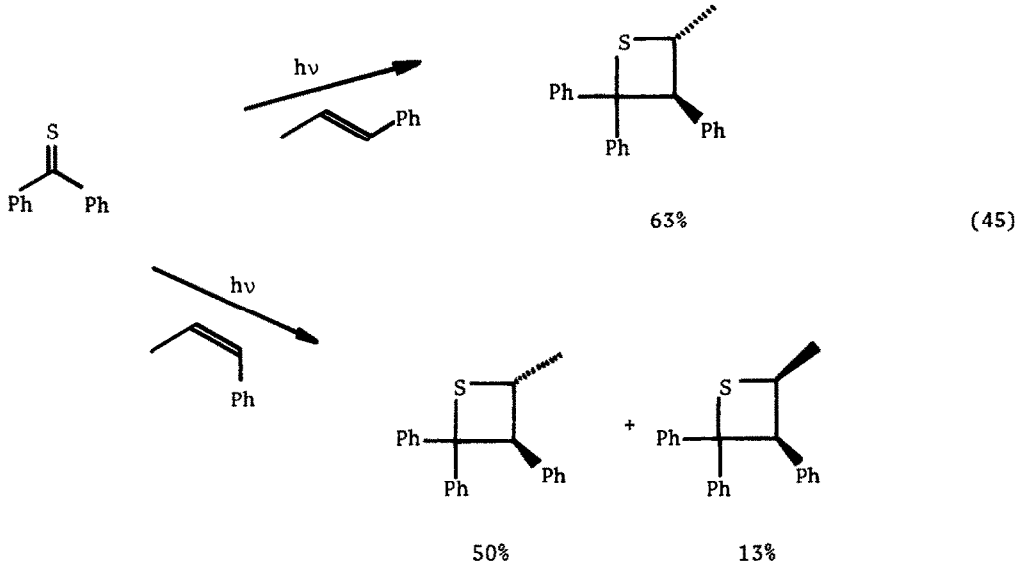


(44)

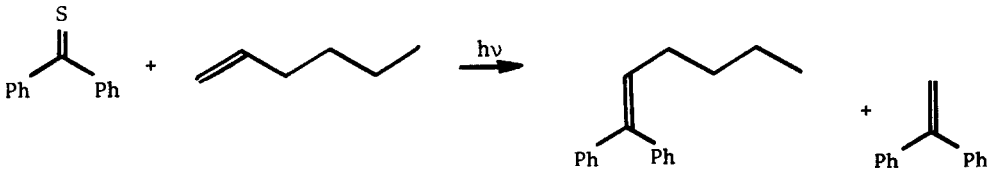
A very considerable amount of work has been done on the photocycloaddition reactions of thiocarbonyl compounds with alkenes. Earlier these were classified according to three types of alkene addend,[3,5] but this distinction seems too rigid, and an alternative description highlights more the differences between reactions initiated by the T_1 state of thioketones and those initiated by the S_2 state. The $T_1(n, \pi^*)$ excited state generally reacts in a regioselective, but non-stereoselective, manner with alkenes to give thietanes. The orientation of addition corresponds with that expected on the basis of the more stable biradical intermediate, and alternative products may arise that can also be understood on the basis of interception or diversion of such a biradical. The T_1 state is especially reactive towards electron-rich alkenes. The $S_2(\pi, \pi^*)$ excited state generally reacts in a highly stereoselective, but often non-regioselective, manner with alkenes to give thietanes. It is possible that an excimer is involved, and the smaller range of alternative products seems to be more adequately explained on the basis of an

intermediate with dipolar character. The S_2 state is much less selective with regard to electron density on the alkene. These generalizations are illustrated in the description that follows, which is based largely on a substrate classification.

Thiobenzophenone (and other aromatic thiones) reacts readily with eletron-rich alkenes (those carrying alkyl, aryl, alkoxy or alkylthio substituents) on long-wavelength irradiation to give thietanes and/or 1,4-dithianes. The reaction with 1-phenylpropene (eqn (45)) shows the regioselective but non-stereoselective nature of the process,[72] and that with ethyl vinyl ether (eqn (46)) shows the formation of dithiane product as well as the orientational preference.[73] The divergence of pathways between thietane and 1,4-dithiane arises because the intermediate biradical can be trapped by a molecule of ground-state thioketone. In keeping with this, the proportion of 1,4-dithiane increases with increasing concentration of thioketone. Steric effects also play a part, and greater steric bulk in the alkene (e.g. with styrene or butyl vinyl ether)[74] promotes dithiane formation.

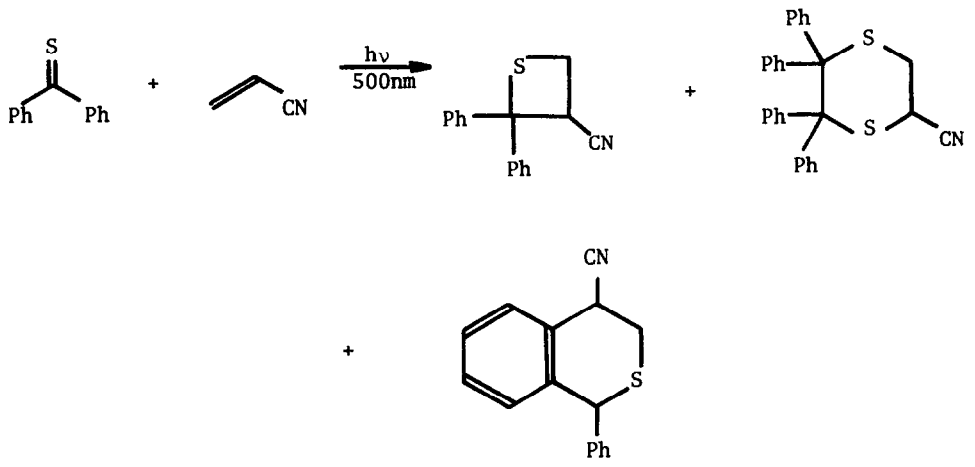


The observed *cis–trans* isomerization of recovered alkene[75] supports the proposed biradical intermediate, and a study[76] of relative rates of attack on a series of alkenes points to a mechanism that involves intermediates with radical character. Examples of systems that give reasonable yields of cycloadducts are thiobenzophenone with cyclohexene, butyl vinyl sulfide,[74] and acenaphthylene,[77] and xanthene-9-thione with 1,2-dimethoxyethylene,[78] and acenaphthylene.[79] A mechanistic study of xanthenethione with a wide range of alkenes provides relative rate constants for attack by triplet thioketone on the alkenes.[80] In one of the earliest reports[81] of photocycloadditions between thiobenzophenone and alkenes, the products isolated were alkenes derived from the thietane by ring cleavage (eqn (47)). A similar process is observed[82] thermally when thiobenzophenone is heated with the distorted alkenes bis(9-xanthylidene) or bis(9-thioxanthylidene).

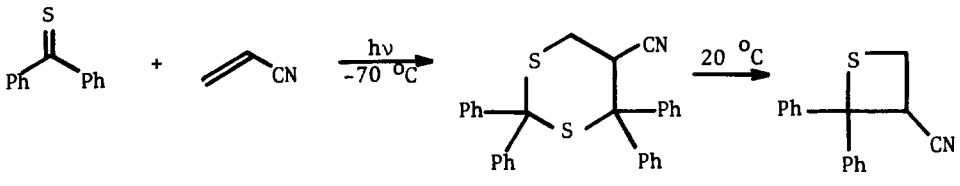


3:2 (47)

It was originally thought[5] that thiobenzophenone and electron-poor alkenes do not react on irradiation with long-wavelength light, but in fact a low efficiency reaction does take place, and with acrylonitrile the products (eqn (48)) are a thietane, a 1,4-dithiane, and a benzothiapyran that arises by attack on one phenyl ring in an intermediate (biradical?).[83] At shorter wavelengths (366 nm) the reaction is more efficient, and the major product (93%) is the thietane. It has been proposed[84] that a 1,3-dithiane, which can be isolated from low-temperature irradiations (eqn (49)), is a precursor to the thietane in this system, and a detailed kinetic analysis lends support to this, as well as to the involvement of the upper excited singlet state.[85] A similar dichotomy arises in the photoreactions of thiobenzophenone with methyl acrylate, in which 369 nm irradiation leads to a thietane, but 539 nm irradiation gives mainly a benzothiapyran product.[86]

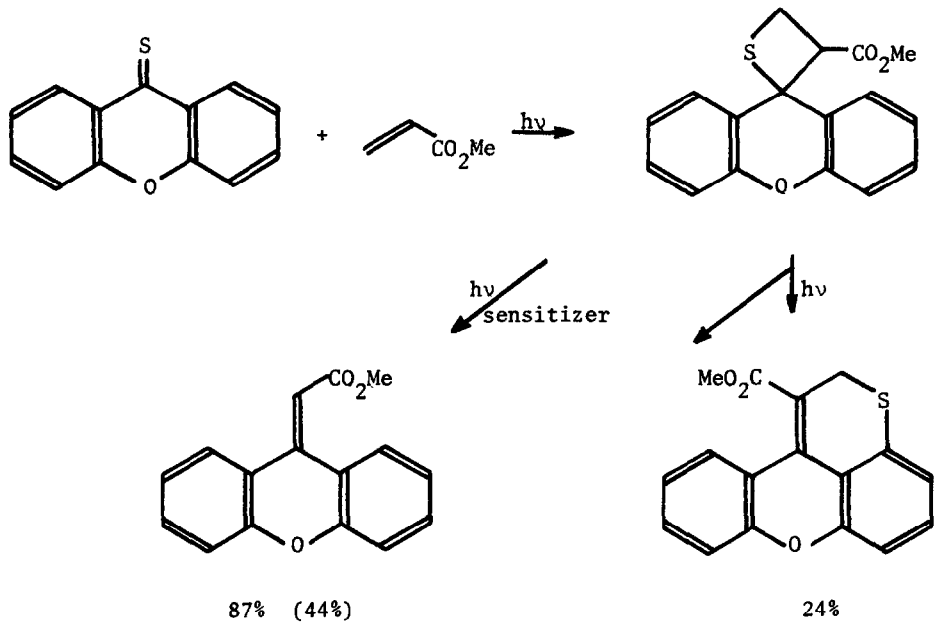


(48)



(49)

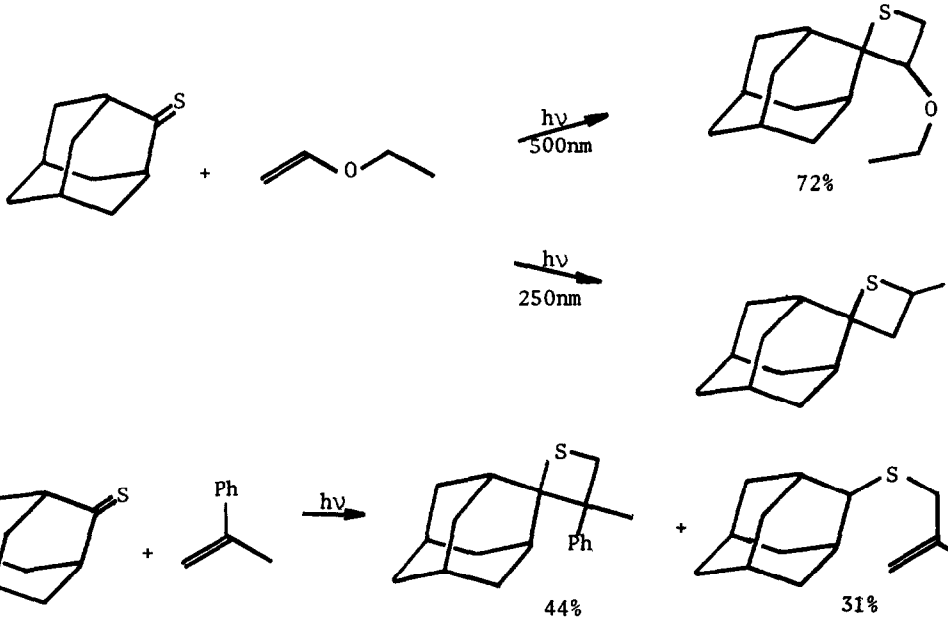
The reaction of thiobenzophenone with *cis* or *trans* 1,2-dichloroethylene,[76] or of xanthene-9-thione with diethyl fumarate or maleate,[87] demonstrates that the reaction (via S_2) is highly stereoselective, but complications arise in the corresponding process with methyl acrylate. The initially formed thietane undergoes a photosensitized cleavage with elimination of $H_2C{=}S$ (eqn (50)), or if it absorbs light directly it produces both this α,β-unsaturated ester and a tetracyclic product in which attack has occurred by sulfur on one of the aromatic rings.[86] A study[88] of xanthene-9-thione with a methacrylate ester of an optically active alcohol reveals that the optical purity of the product is greater in the reaction from T_1 than in that from S_2.



(50)

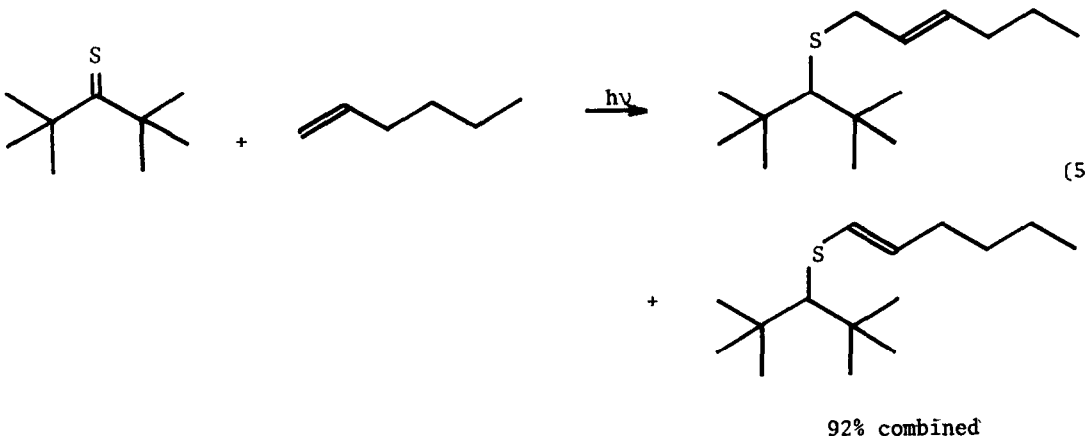
Aliphatic thioketones react photochemically with alkenes in a manner that parallels to a large extent the behaviour of their aromatic counterparts. Adamantanethione and ethyl vinyl ether produce a thietane (eqn (51)) in low quantum yield ($\phi = 0.0009$) on irradiation at 500 nm, but with light of wavelength 250 nm, the reaction occurs more efficiently ($\phi = 0.019$), and the opposite regioisomer is also formed.[89] The use of acrylonitrile and of fumaronitrile or maleonitrile demonstrates that the T_1 reaction is regioselective but not stereoselective, whereas the opposite is true for the S_2 reaction. With 2-phenylpropene an acyclic product is formed (eqn (52)) in the T_1 reaction, that arises by way of hydrogen transfer in the intermediate biradical. Di-t-butyl thioketone forms thietanes only on S_2 excitation, again in a stereoselective but non-regioselective process,[90] and with alkenes such as hex-1-ene a high yield of acyclic products (eqn (53)) is obtained;[91] presumably with this very hindered system ring closure is less favourable.

Conjugated dienes can react with thioketones to form (2+2) or (2+4) cycloadducts. Thietanes are formed from thiobenzophenone with cycloocta-1,3-diene,[92] or with α-phellandrene (eqn (54)).[93] (2+4) Products can be formed in a thermal reaction,[94] but photocycloaddition is more rapid and leads to dihydrothiapyrans from thiobenzophenone with cyclopentadiene,[92] with cyclooctatetraene,[77] or with



(51)

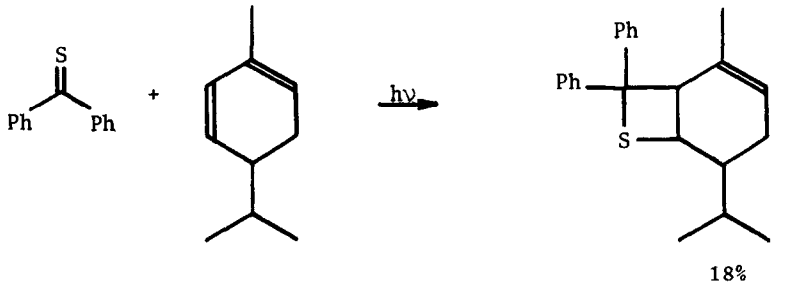
(52)



(53)

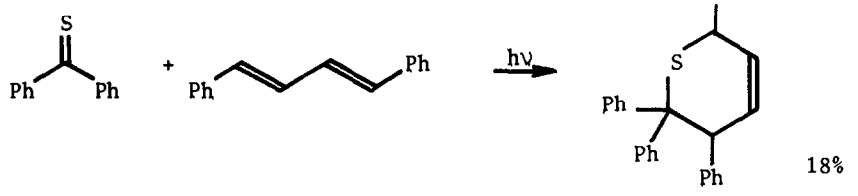
92% combined

acyclic dienes such as isoprene or 1,4-diphenylbuta-1,3-diene (eqn (55)). Allenes (1,2-dienes) give rise to 2-methylenethietanes from aromatic thioketones,[95,96] and from 2,4,6-tri-t-butylthiobenzaldehyde (eqn (56)).[97] As with the alkene reactions, diversion of the biradical intermediate can lead to co-products, as shown in the reaction of xanthene-9-thione with methoxyallene (eqn (57)).[98]



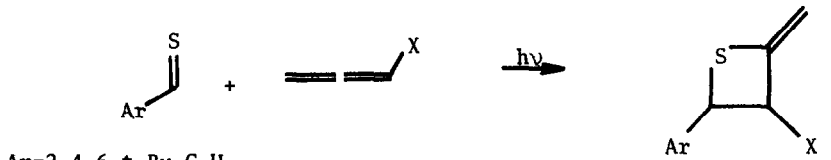
(54)

18%



(55)

18%

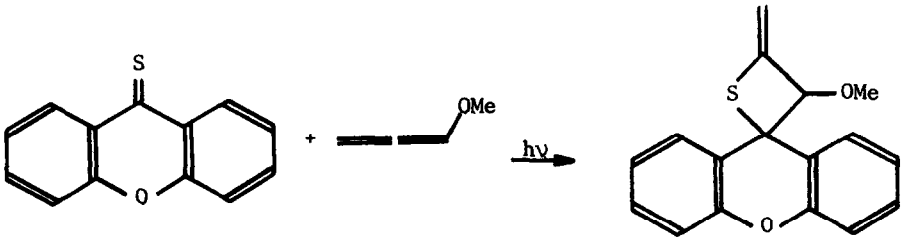


(56)

Ar=2,4,6-t-$Bu_3C_6H_2$

X=Ph,OR,SR

high yield



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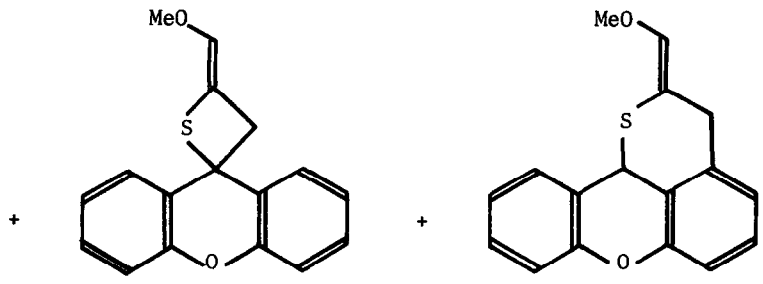
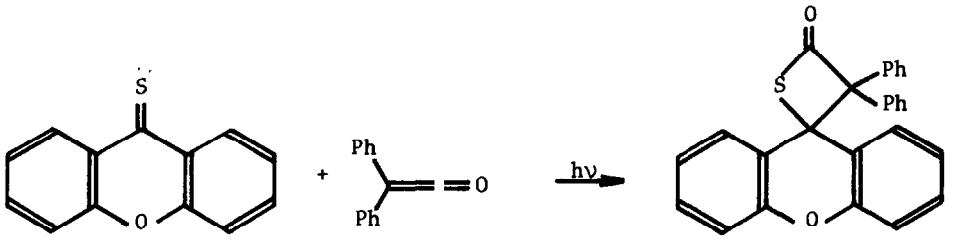


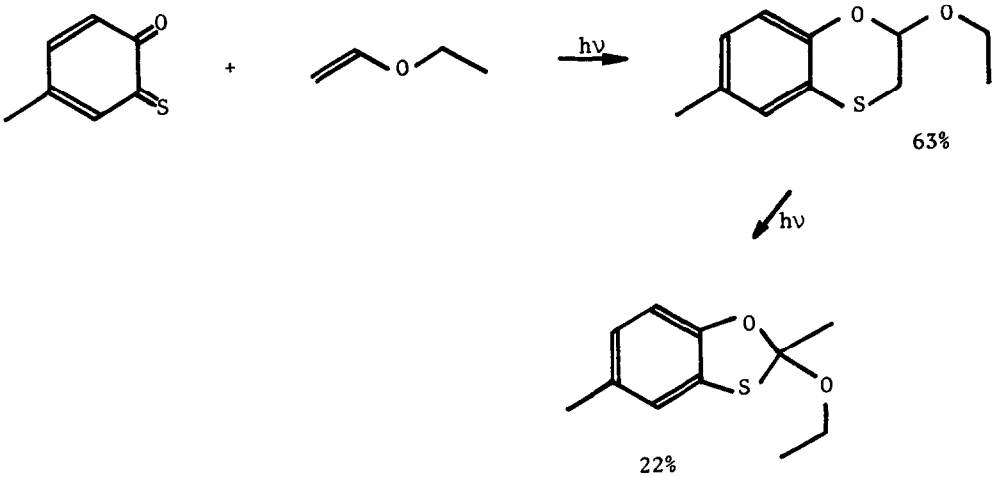
5% 15% (57)

Similar photocycloadditions have been reported for other cumulenes (butatrienes[99] and pentatetraenes),[100] for diphenylketene (eqn (58)),[101] and for a ketenimine.[102]

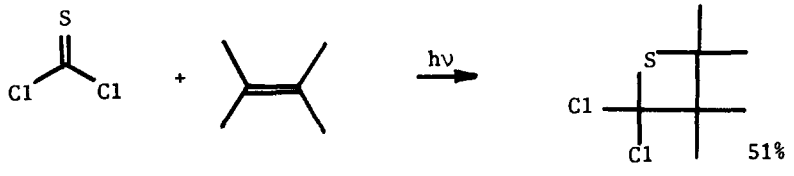


100% (58)

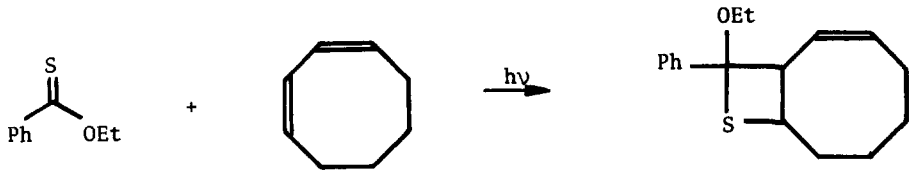
A monothio-*o*-quinone reacts photochemically with ethyl vinyl ether to give a 1,4-benzoxathiane and, in a subsequent photorearrangement, a 1,3-benzoxathiole (eqn (59)).[103] Amongst the derivatives of thiocarboxylic acids, thiophosgene (eqn (60))[104] and di-O-phenyl thiocarbonate[95] give thietanes in reasonable yields. O-Alkylthioesters can give 2-alkoxythietanes (eqn (61)) or 2,4-dialkoxy-1,3-dithianes (eqn (62)),[83] but often the alkoxythietane undergoes (sensitized) cleavage under the reaction conditions to give an enol ether that provides a ketone on work-up (eqn (63)).[105]



(59)



(60)



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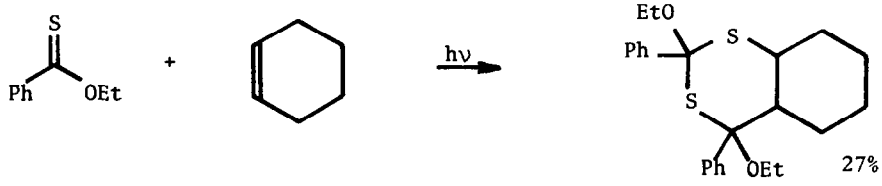
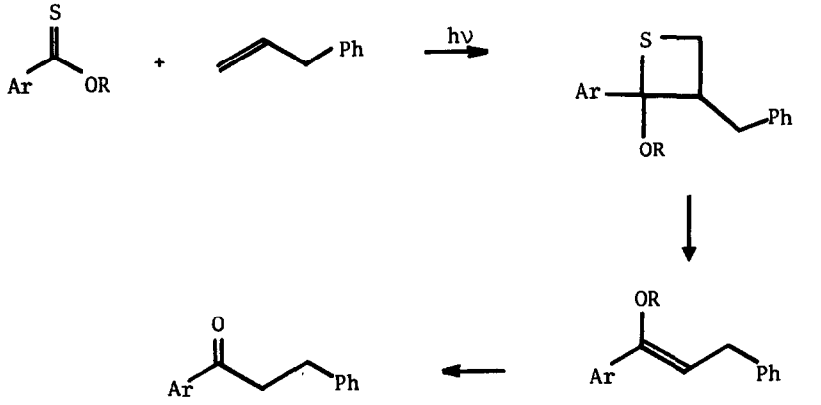
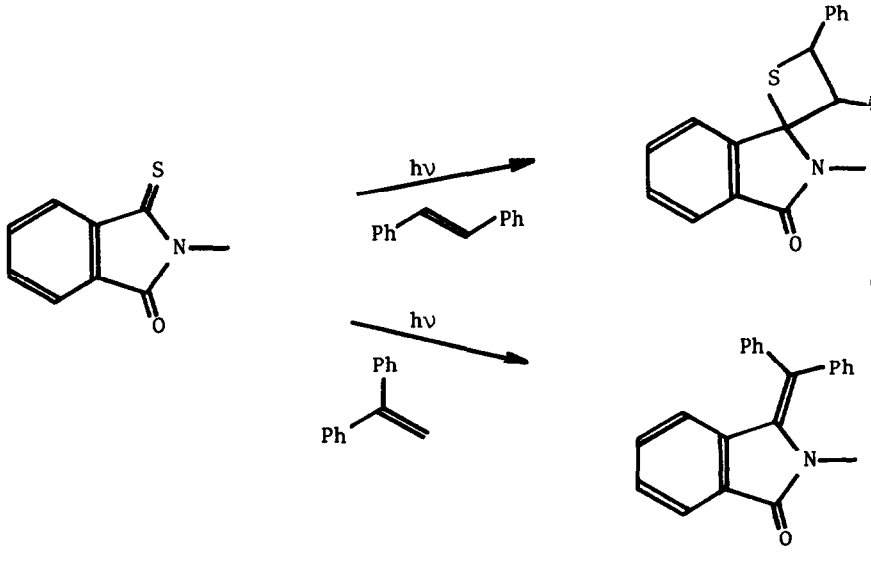


(62)



(63)

Thiophthalimides with alkenes give either spirothietanes or alkenes derived from them by elimination of thioformaldehyde (eqn (64)).[106] An intramolecular example of such thioimide photocycloaddition has been used[107] in a route to fused β-lactams (eqn (65)). Thioparabanates behave in a similar way (eqn (66)),[108] although in neither system is it clear which factors control the relative proportions of the two products. In the case of N-methylthiophthalimide or N-methyldithiophthalimide with diphenylketene two products can be isolated (eqn (67)), and it has been shown[101] that the thietan-2-one eliminates COS to form the second product.



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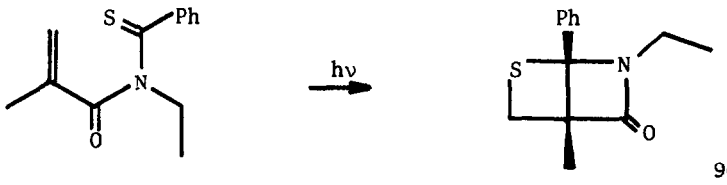
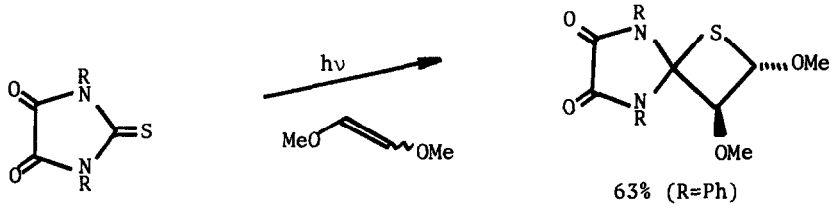
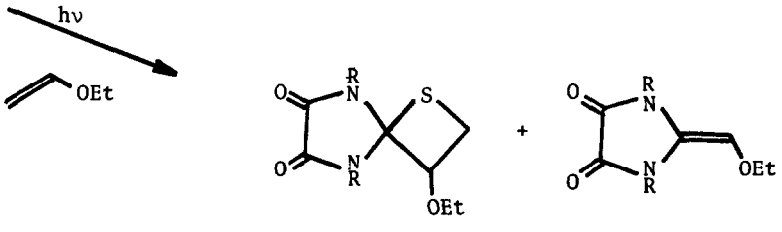
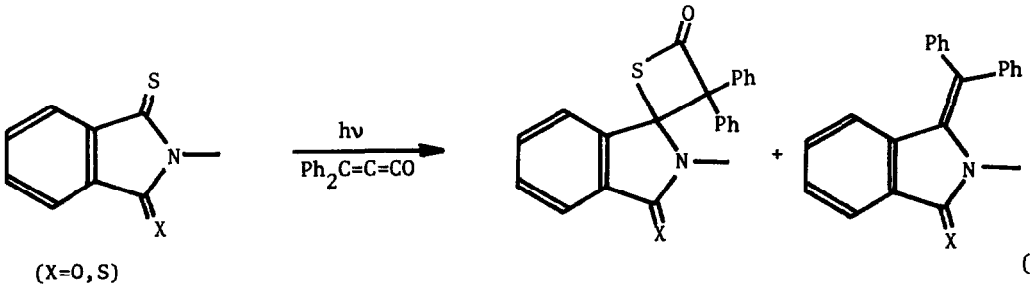


(65)



(66)

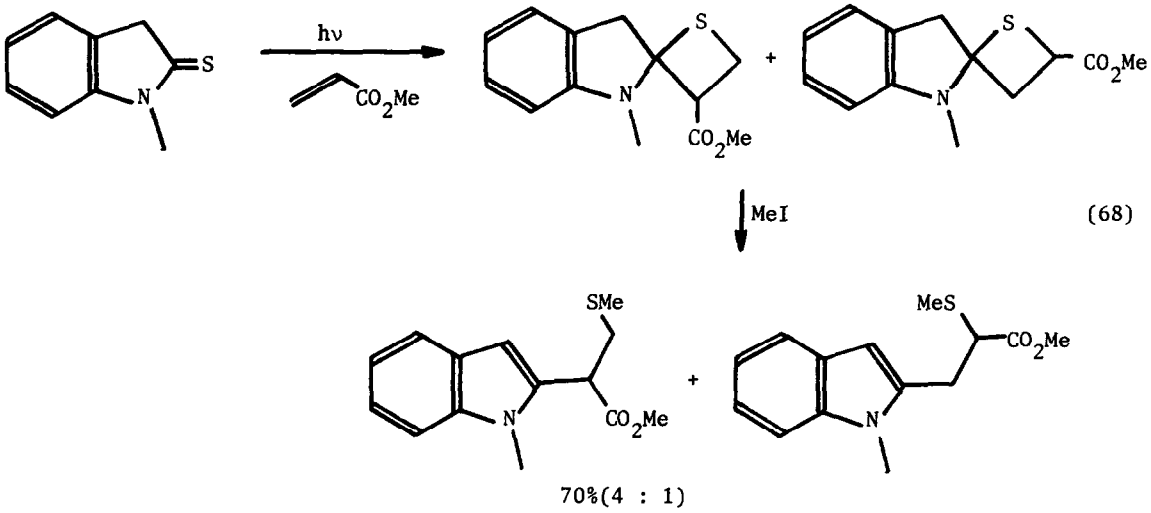




(67)

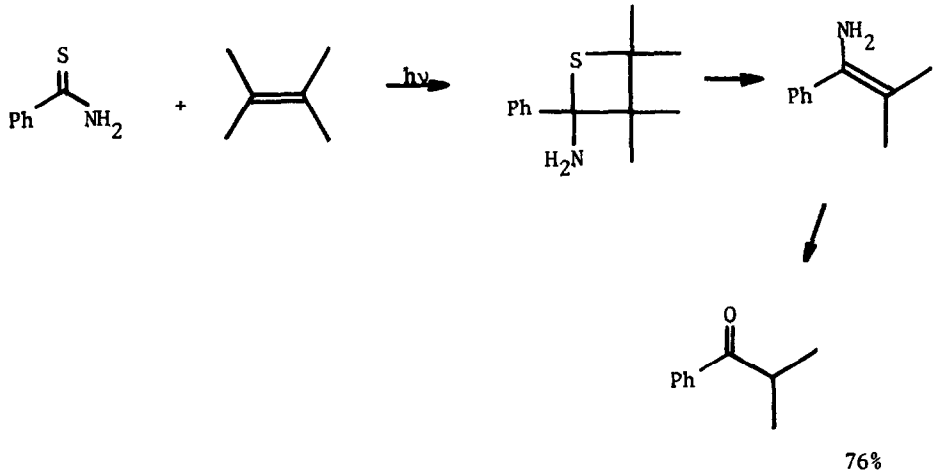
No amino-thietane has been isolated from the photoreactions of thioamides with alkenes, but there are several reactions where such compounds have been invoked as intermediates. Indoline-2-thiones react with methyl acrylate to give, after methylation, a mixture of isomeric substituted indoles (eqn (68)).[109] One of these isomers has been employed[110] as a key intermediate in a synthesis of desethylcatharanthine. Thiobenzamides with 2,3-dimethylbut-2-ene give isobutyrophenones (eqn (69)), and these probably arise by cleavage of a 2-aminothietane followed by hydrolysis.[111] N-Vinylthiobenzamides give rise to thiazolines on irradiation (eqn (70)); although this reaction might proceed by way of initial intramolecular cycloaddition, a mechanism involving the mercapto-imine tautomer ($ArC(SH)=NCH=CR_2$) is also possible.[112] The internal photocycloaddition of N-(*o*-vinylphenyl)thioamides offers a useful route to quinolines (eqn (71))[113] after loss of H_2S.

Examples have been reported in which the products isolated from photochemical reaction of a nitrogen-containing thiocarbonyl compound with an alkene represent a diversion from the pathway leading to a thietane. The thiobenzoyl-enamine in (eqn (72)) reacts with acrylonitrile to give a moderate yield of a 2H-thiapyran,[114] presumably through an intermediate 4-dimethylamino-3,4-dihydro derivative. A 2,3-dihydropyridazine-3-thione gives rise to a thieno fused product (eqn (73)) when irradiated with 2-methylbut-2-ene.[115] Thiouracils often give thietanes in a normal photocycloaddition reaction with alkenes,[116] but with methacrylonitrile an unusual fused 1,3-dithiane and a (1-cyanoethylidene) product are isolated (eqn (74)).[117]



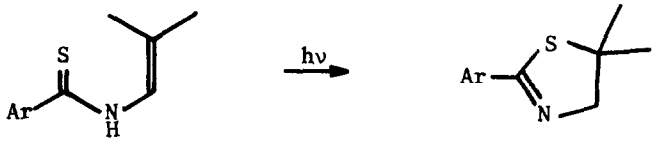
(68)

70%(4 : 1)



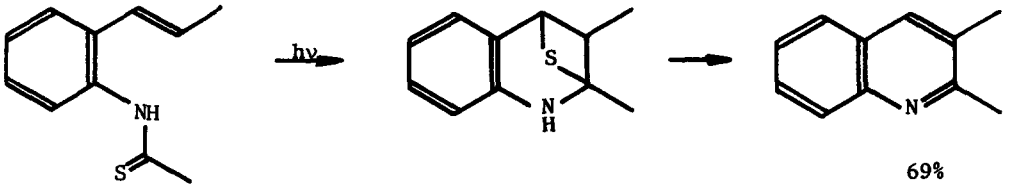
(69)

76%



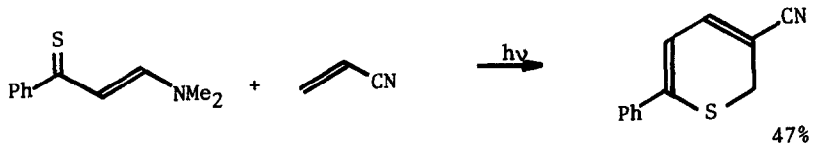
(70)

75%(Ar=Ph)

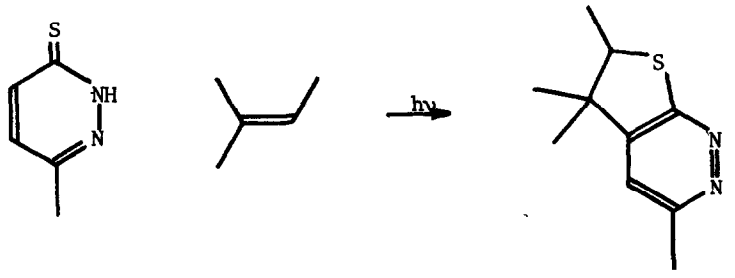


(71)

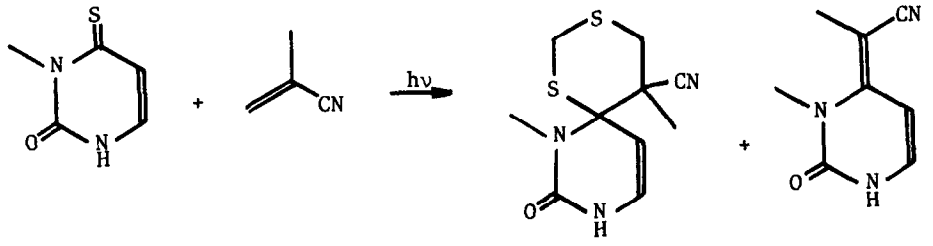
69%



(72)

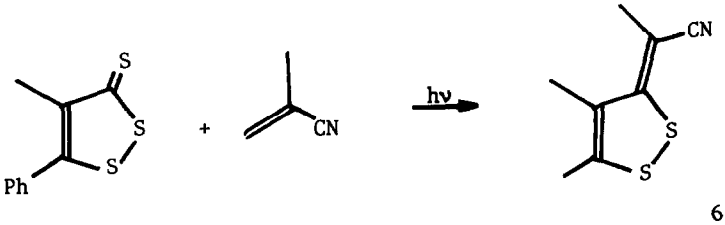


(73)



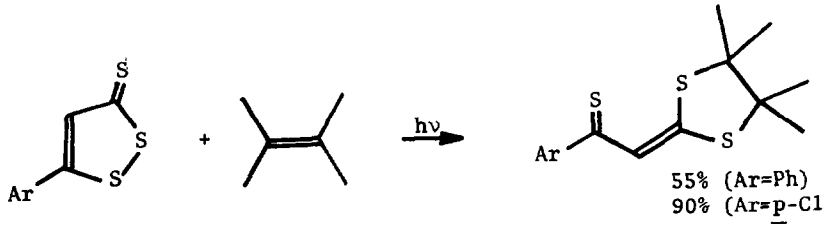
(74)

The 1,2-dithiole-3-thione system reacts photochemically with alkenes to give cycloadducts, but in only one case[118] is the isolated product derived from an initial thietane (eqn (75)). More commonly the biradical is diverted to give a 2-(thiobenzoylmethylene)-1,3-dithiolane (eqn (76)),[119] or a 3-vinylthio-1,2-dithiole if hydrogen transfer occurs (eqn (77)).[120] 1,2,4-Dithiazole-3-thiones behave in a similar way (eqn (78)).[121] The product that arises from an alkene and a benzo-fused dithiolethione (eqn (79)) can be trapped by added dienophile,[122] or it can form (4+4) cyclodimers.[123]



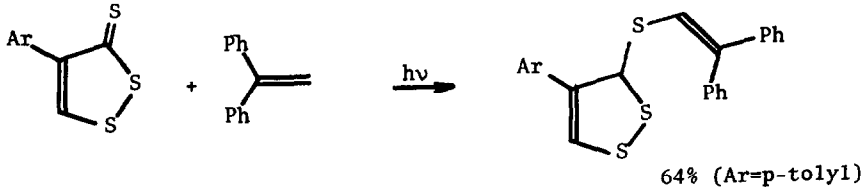
68%

(75)



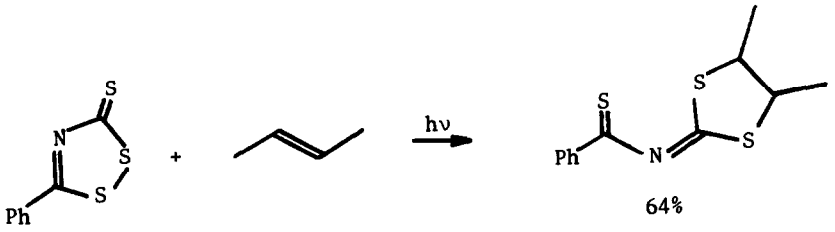
55% (Ar=Ph)
90% (Ar=p-ClC$_6$H$_4$)

(76)

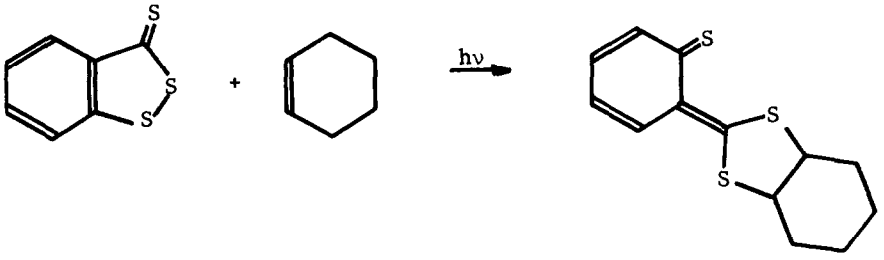


64% (Ar=p-tolyl)

(77)

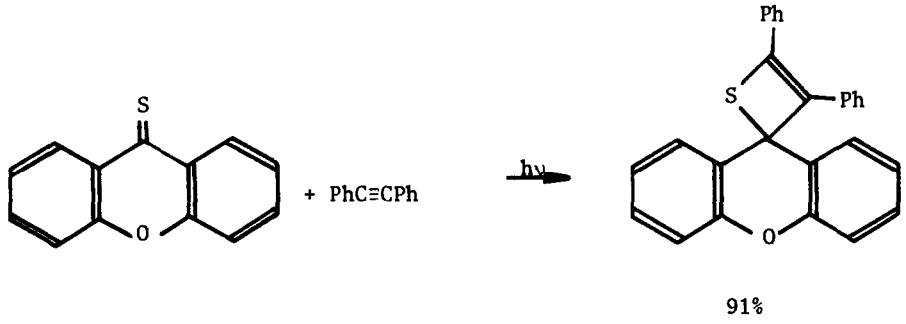


(78)



(79)

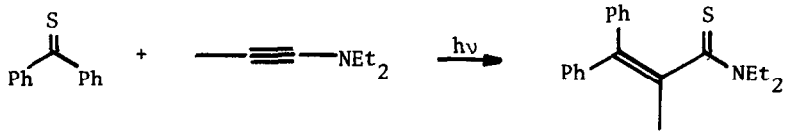
Photocycloaddition of diphenylacetylene to xanthene-9-thione gives a spirothiete in high yield (eqn (80)),[124] and when an amino-alkyne is employed with thiobenzophenone the product is an unsaturated thioamide (eqn (81)) that comes from ring opening of the initial thiete.[125] Bis(alkylthio)alkynes can lead to an equilibrium mixture of thiete and unsaturated dithioester (eqn (82)),[126,127] although some additional products may arise by internal attack on an aromatic ring. The earliest reports of the photochemical cycloaddition of aromatic thioketones to alkynes involved thiobenzophenone, and from this thione the major products (eqn (83)) are isothiochromenes.[128] The mechanism has been elucidated from the results of deuterium-labelling studies, which confirm the proposed intramolecular hydrogen transfer.



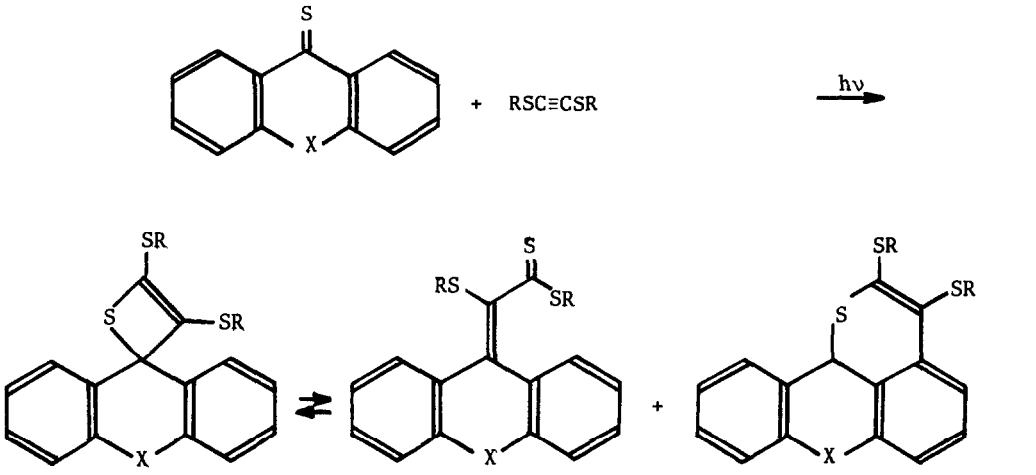
(80)

Thiocamphor reacts with bis(methylthio)acetylene in much the same way as xanthenethione does, but instead of the product that involves attack on the aromatic ring there is a divinyl sulfide (eqn (84)) that comes from an internal hydrogen transfer;[129] with some alkenes, aliphatic ketones give vinyl ethers in an analogous process.

Thiophthalimides react photochemically with alkynes to give spirothietes (eqn (85)),[130] and thioparabanates do the same,[124,131] although they also lead to a variety of additional products (eqns (86) and (87)), often by subsequent reaction of the thiete. 1,2-Dithiole-3-thiones react to produce 2-(thiobenzoylmethylene)-1,3-dithioles (eqn (88)),[118] in a reaction that parallels the corresponding process with alkenes (eqn (76)). With the isomeric 1,3-dithiolane-2-thiones a reaction occurs to produce 1,3-dithiole-2-thiones (eqn (89)), and this has proved useful[132] for particular substituent patterns that cannot be obtained readily by a thermal reaction, namely those not involving an electron-deficient alkene.

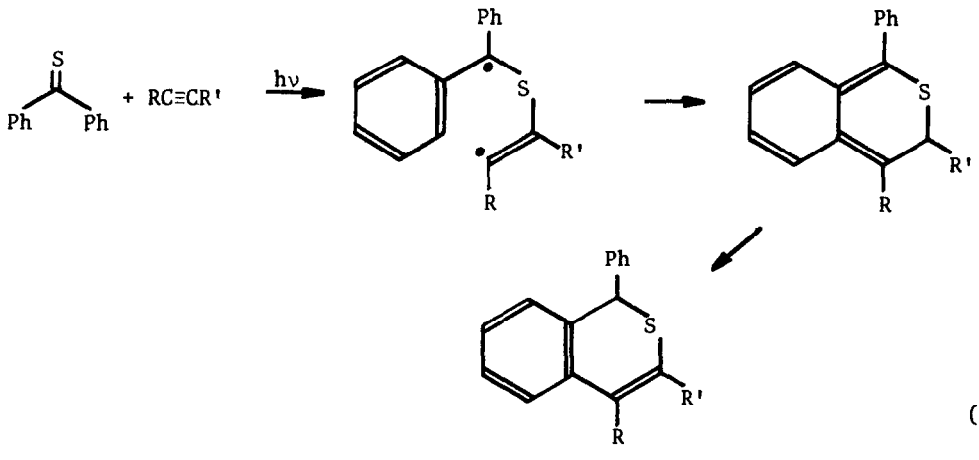


(81)



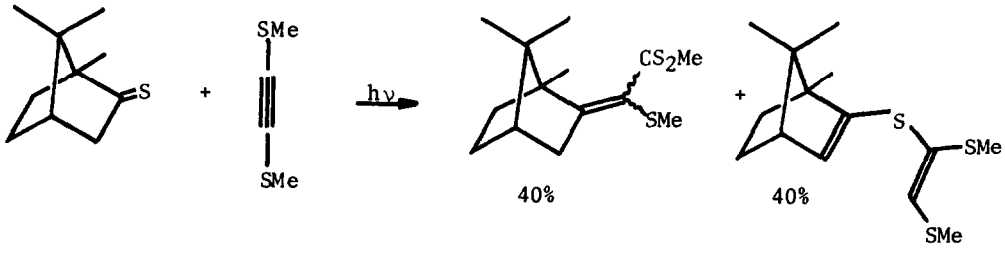
60% 40% 0% (X=O;R=t-Bu)
0% 70% 5% (X=S;R=Me)

(82)



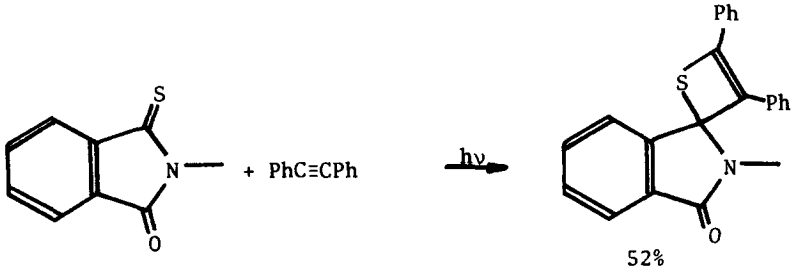
56% (R=Ph; R'=H)

(83)

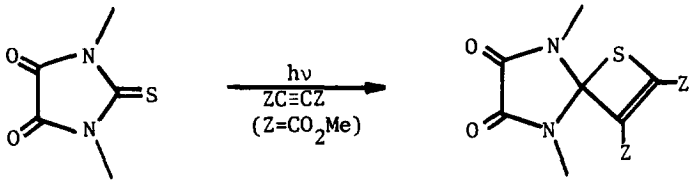


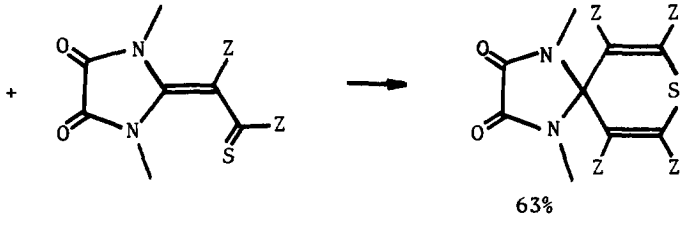
40% 40%

(84)

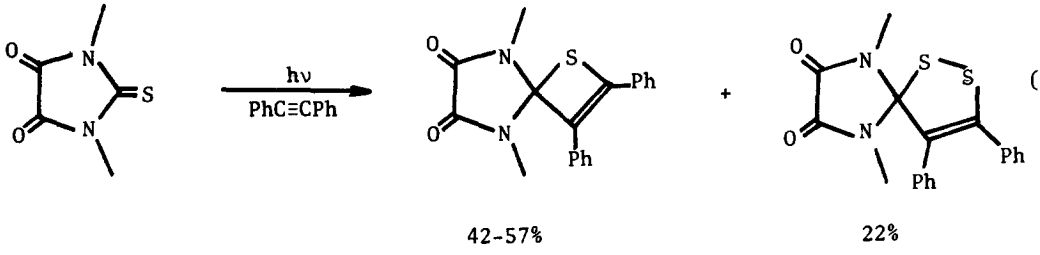

+ PhC≡CPh
hν
52%

(85)

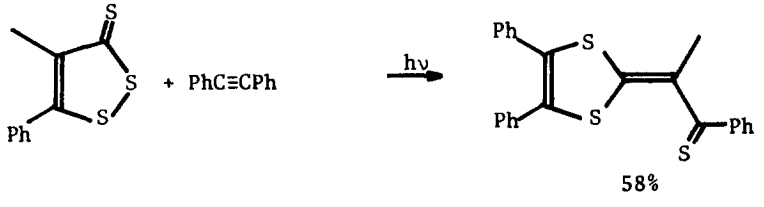

hν
ZC≡CZ
(Z=CO2Me)


63%

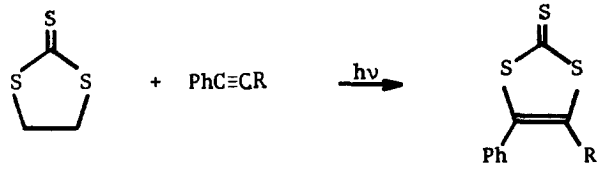
(86)


hν
PhC≡CPh
42-57%
22%

(87)

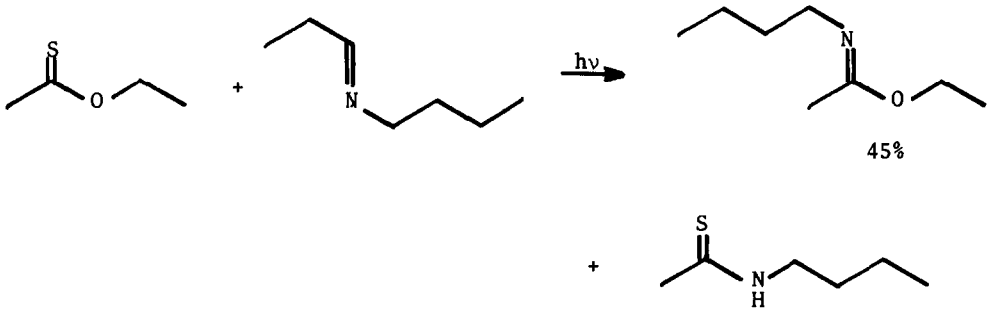

+ PhC≡CPh
hν
58%

(88)

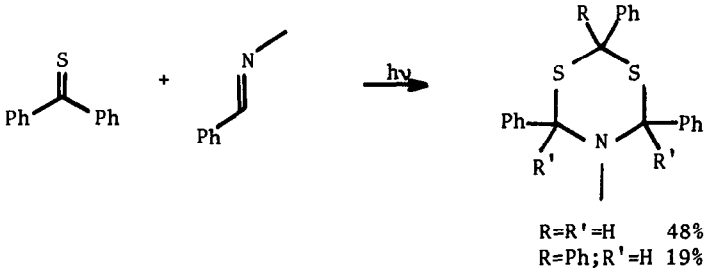

+ PhC≡CR
hν
39% (R=Me)
22% (R=H)

(89)

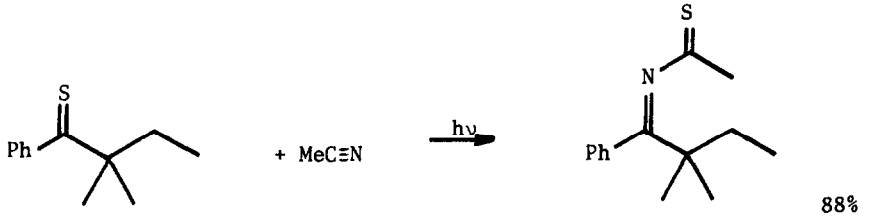
There are two early reports of photochemical cycloaddition between a thiocarbonyl compound and an aldimine. An O-alkyl thioester reacts to give an imidate (eqn (90)) in a process that probably occurs by way of an intermediate 1,3-thiazetidine.[66] Irradiation of thiobenzophenone and an aldimine leads to a mixture of 1,3,5-dithiazinanes (eqn (91)), which again is best explained in terms of the breakdown of an intermediate 1,3-thiazetidine and reaction of the thioaldehyde so obtained with imines.[133] Thioketones react photochemically with nitriles,[134] and this leads to an N-thioacylketimine (eqn (92)) via ring opening of a 1,3-thiazete.



(90)



(91)



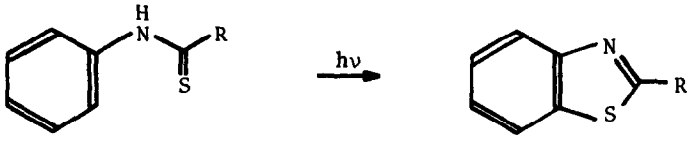
(92)

CYCLIZATION REACTIONS

Photocyclizations that involve a hydrogen atom transfer and generally result in the formation of a new carbon–carbon bond have been described in an earlier section. Some photoreactions of thiocarbonyl compounds result in cyclization with formation of a new carbon–sulfur bond, and these are often initiated by interaction of the excited C=S group with a carbon–carbon multiple bond elsewhere in the molecule.

N-Phenylthiobenzamide does not undergo a rearrangement on irradiation analogous to the photo-anilide reaction of N-acylanilines, but rather cyclizes to 2-phenylbenzothiazole (eqn (93); R = Ph), though the nature of the oxidative steps in the mechanism is not clear.[135] With N-phenylthiourethane (eqn (93); R = OEt) oxygen needs to be present for the reaction to proceed,[136] although the yield is very low. Good yields of substituted benzothiazoles are obtained from N-thioacetyl-2-haloanilines (eqn (94)),[137] where elimination of hydrogen halide is required, without oxidation, to give the observed products. The general reaction has been extended to halo-substituted

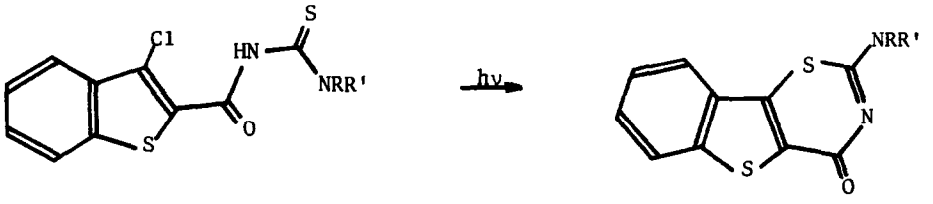
N-thiocarbonyl aromatic amides such as those derived from benzothiophene (eqn (95))[138] as well as benzamide derivatives (eqn (96)),[139] and in these systems the photocyclized product is a benzo-1,3-thiazin-4-one.



(93)

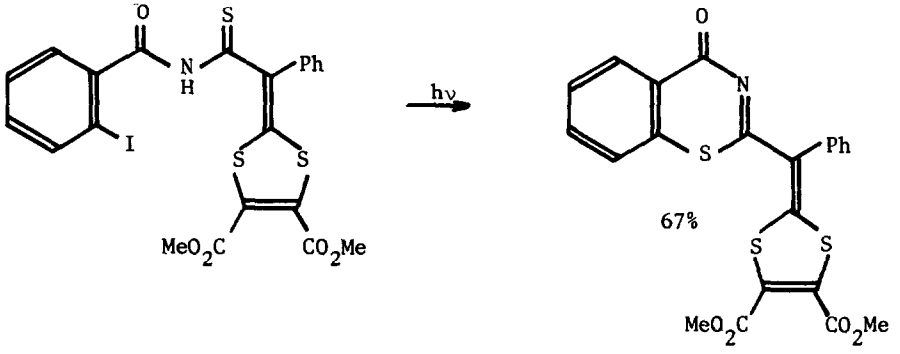
64%

(94)



55-80%

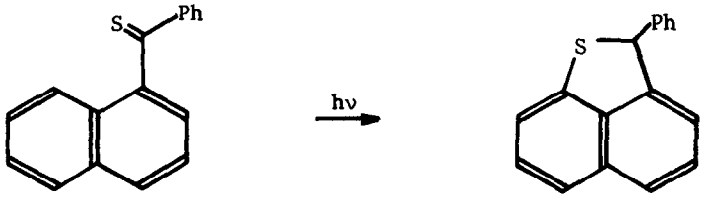
(95)



67%

(96)

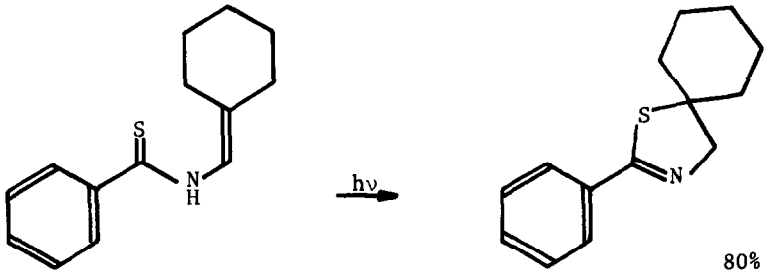
A number of phenyl aryl thioketones, where the aryl group is 1-naphthyl (eqn (97)) or another polycyclic hydrocarbon radical, take part in a non-oxidative photocyclization that produces a new five-membered sulfur-containing ring.[140] A mechanistic investigation suggests that (unusually) the lowest singlet excited state (S_1) may be responsible for this process, and the incorporation of deuterium from D_2O indicates that a dipolar intermediate may be involved.[141]



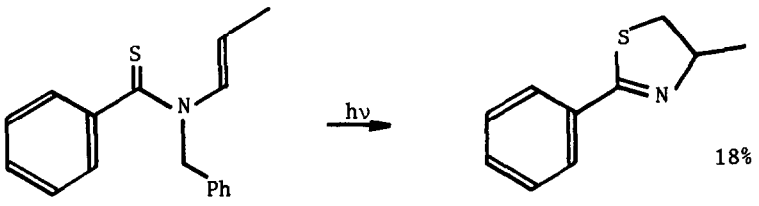
60%, $\phi \sim 10^{-3}$

(97)

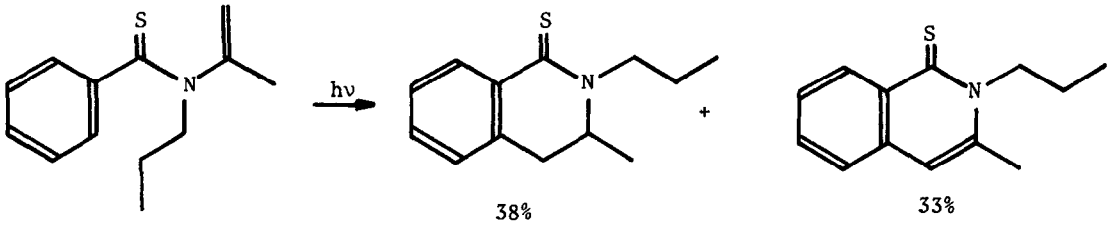
The interaction of excited thioamide with an alkene double bond also leads to a non-oxidative cyclization with N-vinylthiobenzamide systems (eqn (98)).[142] N-Benzylated derivatives give similar thiazoline products (eqn (99)), and the overall process in these examples includes debenzylation.[143] Although initial N-benzyl bond cleavage was presumed to be responsible for the reaction, carbon–sulfur bond formation might be the first step. With other substituents on nitrogen a different pathway is followed, and the products are an isoquinoline-1-thione and its dihydro-derivative (eqn (100)). This reaction is very similar to that of the N-vinylbenzamide systems widely used in the formation of isoquinoline alkaloid skeletons; it probably involves six-electron electrocyclic ring closure followed by a thermal 1,5-hydrogen shift. The mechanism of the oxidation to the isoquinolinethione is not known.[143]



(98)



(99)



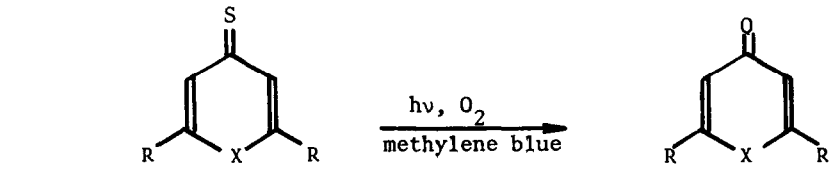
(100)

PHOTO-OXIDATION

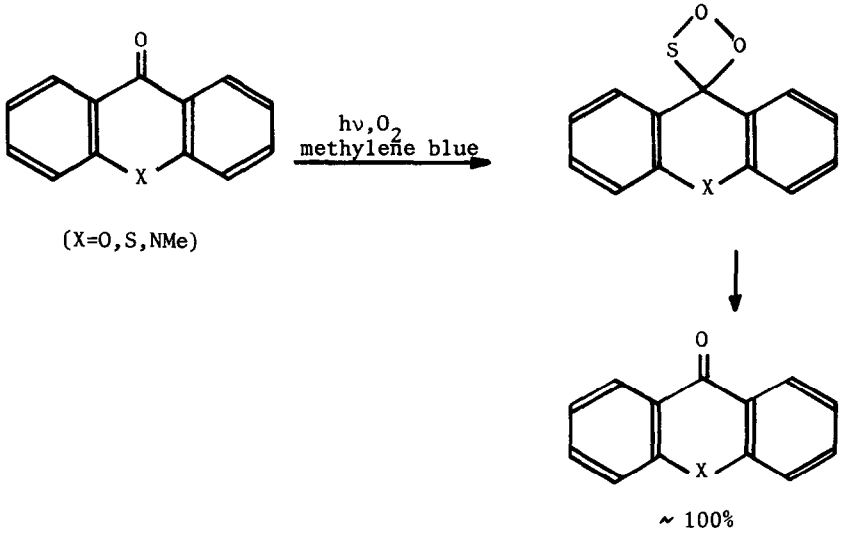
The photo-oxidation of thiocarbonyl compounds to give the corresponding carbonyl compounds has been known for a long time. Of the thioketones, some (such as thiobenzophenone)[144] are sensitive to thermal oxidation in air and the process is accelerated by light; others (such as xanthene-9-thione) react only in the presence of light, and some (such as 4-thioflavone) are not oxidized even on irradiation.[145] A similar pattern holds for other thiocarbonyl compounds, and thiophthalimides, for example, produce phthalimides on irradiation with oxygen,[49] whereas some thioamides are resistant to photo-oxidation or react to give products other than amides.

Many photo-oxidations are sensitized by dyes known to generate singlet oxygen (eqn (101)),[146,147] and the effect of singlet oxygen quenchers supports the idea that this is the reactive oxidizing agent.[148] In the absence of an added sensitizer, the thiocarbonyl compound may itself act as a triplet sensitizer towards ground-state (triplet) oxygen.[63] Studies with xanthene-9-thione and related compounds show

that a weak chemiluminescence accompanies the oxidation,[149] which can be enhanced by an added fluorescer, and this is taken as evidence for a 1,2,3-dioxathietane intermediate (eqn (102)).



(X=O,S; R=H,Me,Ph) 60% (101)



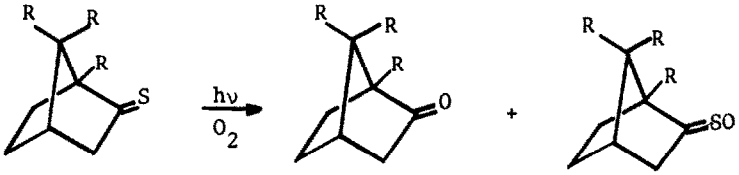
(X=O,S,NMe) ~ 100% (102)

The co-products of most oxidations are sulfur and sulfur dioxide, which may arise by disproportionation of the sulfur monoxide that is eliminated from a dioxathietane. However, the results are more complex with some aliphatic thioketones. Di-t-butyl thioketone, for example, gives a sulfine in addition to the ketone (eqn (103)).[150,151] The ratio of the two products is affected by the solvent polarity (the ketone predominates in non-polar solvents, and the sulfine in polar solvents), and by the presence or absence of added sensitizer, although the latter effect is not necessarily to be taken as indicating an additional oxidation route that does not involve singlet oxygen.

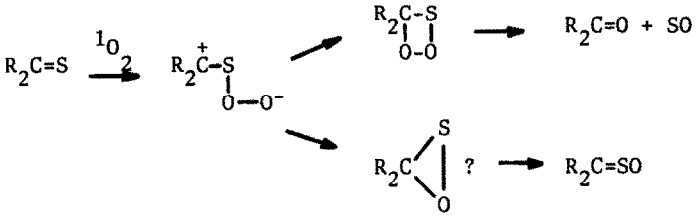
(103)

Steric effects also play a part in determining the ratio of ketone to sulfine formed. Under conditions where di-t-butyl thioketone gives mainly sulfine, 2,2,4,4-tetramethylcyclobutanethione produces largely ketone.[152] Similarly, norbornane-2-thione (eqn (104); R = H) leads to ketone, whereas thiocamphor (eqn (104); R = Me) gives both ketone and sulfine.[153] These observations are interpreted in terms of a mechanism (eqn (105)) in which a dipolar acyclic intermediate can cyclize to a dioxathietane, which in turn breaks down to give ketone, or it can eliminate an oxygen atom to give the sulfine directly or via an oxathiirane. The possibility of two different acyclic intermediates is raised by consideration of different singlet oxygen interactions with a non-bonding orbital on sulfur or with a π-orbital.[154] π-Orbital interaction, which predominates with diaryl thioketones, leads to ketone only, but n-orbital interaction, which is the major process for dialkyl or alkyl aryl thioketones, leads mainly to sulfine with some ketone formation. In a study that includes a wider range of alkyl thioketones,[153]

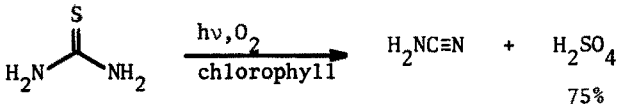
the quenching of singlet oxygen was found to parallel the ionization energies of the n, rather than the π, electrons.



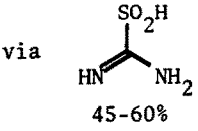
(104)

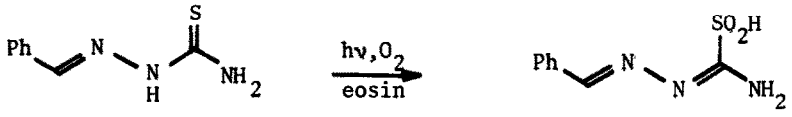


(105)

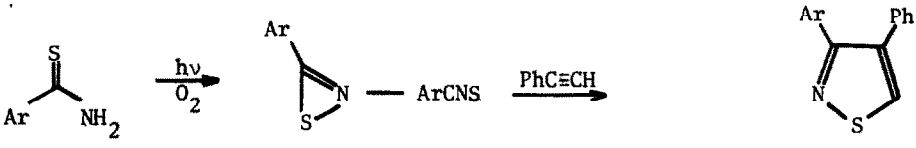


(106)





(107)



(108)

Other thiocarbonyl compounds that can be photo-oxidized to the corresponding carbonyl compounds or sulfines include a cyclopropenethione,[18] O-alkyl thioesters,[155] 1,2-benzodithiole-3-thione,[156] and di-t-butyl thioketene.[157] Some nitrogen-containing derivatives behave differently. Thiourea has long been known to undergo chlorophyll-sensitized oxidation to cyanamide and sulfuric acid (eqn (106)) in a process that has been used in actinometry.[158] An intermediate can be isolated[159] in which the sulfur has been raised to a higher oxidation state but remains bonded to carbon, and a similar product is formed from benzaldehyde thiosemicarbazide (eqn (107)). Thiobenzamides are photo-oxidized to aryl nitrile sulfides (eqn (108)), and it is proposed that this occurs by way of a thiazirine.[111]

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