The Photoreactivity of Thiocarbonyl Compounds

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Based on 115 recent literature references this review draws up the present status of the photochemistry of thiocarbonyl compounds.

CONTENTS

1. INTRODUCTION

Over the past two decades, the photochemistry of thiocarbonyl compounds has received increasing attention.[1] In large part this attention has resulted from the propensity of the electronically excited states of thiocarbonyl compounds to yield unique photoproducts, not observed from those of structurally analogous carbonyl compounds. This review deals with the organic aspects of the photochemistry of thiocarbonyl compounds; special importance is given to the nature of the excited states involved and the pathways that lead to the various photoproducts. It also provides the mechanistic basis on which such reactions can be assessed for further applications.

In presenting the photoreactivity of thiocarbonyl compounds, a functional-group classification approach has been used in this review. This approach is particularly advantageous considering the fact that the spectroscopic, photophysical and photo-chemical properties of the thiocarbonyl chromophore depend on the molecular frame-work in which the chromophore is present. In addition to that, this approach presents the up-to-date status of the photochemistry of each class of thiocarbonyl compounds for readers to plan further research in this area.
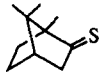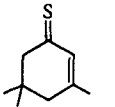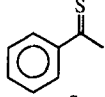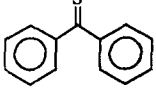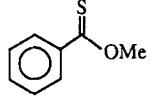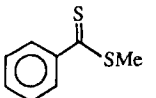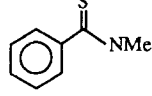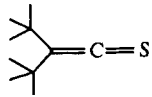
2. GENERAL PROPERTIES OF GROUND AND EXCITED STATES OF THIOCARBONYL COMPOUNDS

This short section begins with the general ground-state properties of thiocarbonyl compounds, followed by a brief summary of their electronic absorption and photophysical properties. For details of spectroscopy and photophysics, readers can refer to the excellent reviews by Steer and Ramamurthy.[2] The purpose of this section is to provide the reader with some exposure to the physical aspects of the excited-state thiocarbonyl chromophore.

2.1. Ground-State Properties

Structurally, thiocarbonyl compounds are characterized by the C=S linkage in which bivalent sulfur is bonded to the carbon by overlap of a carbon $2p$ orbital and a sulfur $3p$ orbital. This overlap, however, is less efficient than the $2p$-$2p$ overlap of a C=O bond due to the differences in spatial symmetry and electron density distribution between the orbitals involved. Consequently, the thiocarbonyl bonds ($E_{C=S} = 103$ Kcal/mol) are weaker and more reactive than the corresponding carbonyl bonds ($E_{C=O} = 152$ Kcal/mol). The average length of the carbon–sulfur bond is 1.60 Å compared to 1.20 Å for the carbon–oxygen bond in carbonyl compounds. These compounds exhibit either C_S or C_{2v} local symmetry and are planar in the ground state. Both the theoretical perturbation molecular orbital (PMO) studies[3] and experimental photoelectron spectroscopic investigations[4] carried out on simple thiocarbonyl compounds reveal that the sulfur p-type lone

Table 1. Spectroscopic data for a few selected thiocarbonyl compounds in cyclohexane.

Thiocarbonyls	$S_0 \rightarrow T_1$ λ_{max}	ε	$S_0 \rightarrow S_1(n\pi^*)$ λ_{max}	ε	$S_0 \rightarrow S_2(\pi\pi^*)$ λ_{max}	ε
	545	2	483	11	240	10000
			572	25	297	19000
			567	111	298	3900
	685	89	609	178	314.5	15500
			418	121	287	11647
			504	128	329	6309
			402	301	288	6456
			570	8	239	4200

pair ($n_{C=S}$, HOMO) as well as the $\pi_{C=S}$ orbitals are higher in energy when compared to those of the corresponding carbonyl compounds, whereas the $\pi^*_{C=S}$ orbital is lower in energy than that of the corresponding carbonyl group. Consequently, thiocarbonyl compounds are more electrophilic (lower LUMO) and more nucleophilic (higher HOMO) than carbonyl compounds. The chemistry of thiocarbonyl compounds has been reviewed[5] frequently and the reader is referred to these reviews for a better knowledge of their ground-state behavior.

2.2. Electronic Transitions

All thiocarbonyl compounds show a relatively weak, long-wavelength absorption band in the visible region (400–700 nm) (Table 1). This band is responsible for the color in thiocarbonyl compounds and can be attributed to the dipole forbidden $n \rightarrow \pi^*$ tran-

sitions.[6] Because of the low ionization of the sulfur $3p$ orbital, this band is substantially red-shifted in thiocarbonyl compounds when compared to the $n \rightarrow \pi^*$ transitions in carbonyl compounds. Because of the strong overlap between the $^1n \rightarrow \pi^*$ and $^3n \rightarrow \pi^*$ transitions, it is often difficult to differentiate these transitions in thiocarbonyl compounds. However, in some thioketones, it has been possible to discern the weak $S_0 \rightarrow T_1$ absorption band from the $S_0 \rightarrow S_1$ absorption band by its appearance as a shoulder or a single band on the long-wavelength side of the latter, and the difference in oscillator strengths of these transitions. At short wavelengths (ultraviolet region), these compounds show high-intensity absorption bands and the lower-energy band is attributed to the allowed $\pi \rightarrow \pi^*$ transition $(S_0 \rightarrow S_2)$.[6] Because of the difference in energies of the $n\pi^*$ and $\pi\pi^*$ bands, some thiocarbonyl compounds display unique photophysical and photochemical (e.g., reactivity from the upper excited states)[7] properties not exhibited by the corresponding carbonyl counterparts.

2.3. Photophysical Properties of Thiocarbonyl Compounds

In regard to the photophysical properties of thiocarbonyl compounds, the observation of fluorescence from the second excited singlet state $(S_2, \pi\pi^*)$ is one of the most unusual features of the excited thiocarbonyl chromophore. Several diaryl, aryl alkyl and conjugated thioketones, and some thiocarbonyl halides display this anomalous emission,[8] against Kasha's well known Golden rule.[9] The occurrence of $S_2 \rightarrow S_0$ fluorescence may be ascribed to the large energy gap (ΔE) between the first and the second excited states, i.e., $\Delta E\,(S_2-S_1)$. With the advent of picosecond lasers, it has now been possible to study the S_2-related properties of thioketones in solution.[2b] In order to understand the decay dynamics of these excited states, intermolecular processes such as diffusion controlled self-quenching by ground-state thioketones[10] and non-chemical quenching by the solvents[11] have to be minimized. While the former process introduces the need to extrapolate the lifetimes and quantum yields of these states to infinite dilution, the latter limits the choice of the solvent to one which has a minimum interaction with the excited state. In thioketone systems perfluoroalkane solvents are sufficiently chemically and physically inert so that the excited thioketone decays primarily by intramolecular processes, with the solvent acting only as a classical heat bath.[12] In the absence of strong intermolecular interactions, the possible decay pathways of the excited states have been identified as (a) internal conversion pathways: $S_2 \rightarrow S_1/S_0$, (b) intersystem crossing to the triplet manifold: $S_2 \rightarrow T_2/T_1$ and (c) intramolecular photochemistry. While the mechanistic studies ruled out the involvement of the direct intersystem crossing process in the decay of these excited states,[13] the intramolecular photochemistry mode of decay operates only in certain systems such as dialkyl and aryl alkyl thioketones. In rigid aromatic and conjugated thioketones,[8,11,14] evidence suggests that the major mode of deactivation is internal conversion from S_2 to S_1. In contrast, the S_2 states of rigid alicyclic thioketones such as adamantanethione are almost non-fluorescent and decay to the ground state primarily by a mechanism which does not involve direct $S_2 \rightarrow S_1$ internal conversion.[15] Their intramolecular decay pathways have not been unequivocally identified, but there is some evidence supporting a reversible photoisomerization mechanism involving the transfer of hydrogen atoms β to the thiocarbonyl group.[16] Even

in aromatic thioketones, a small fraction of their second excited singlet states appears to undergo direct decay to S_0 by a similar mechanism.[14] The S_2 photophysics of other classes of thiocarbonyl compounds is yet to be examined.

The lowest excited singlet states (S_1, $n\pi^*$) of larger thioketones do not emit to any measurable extent in solution. However, a few thiocarbonyl halides and small thiocarbonyl compounds decay radiatively with large quantum yields in the gas phase.[17] The lack of fluorescence from larger thioketones in solution has been attributed to the rapid rates of $S_1 \rightarrow T_1$ ($\sim 5 \times 10^{10} s^{-1}$) intersystem crossing.[18] The observation of phosphorescence from the lowest triplet state is quite common for many thiocarbonyl compounds in solution.[19] The decay dynamics of thioketone triplets have been studied by measurement of their phosphorescence lifetimes and quantum yields,[19] and by monitoring of their triplet–triplet absorption intensities in laser flash photolysis.[20] Most triplet thiones decay predominantly by non-radiative means in the absence of reactive intermolecular interactions. The lifetime data obtained with several thioketones reveal that these triplets are intrinsically short-lived ($\sim 10^{-9} \sim 10^{-6} s$). The short-lived nature of the triplets can often be attributed to the fast radiationless decay ($S_0 \leftarrow T_1$) associated with high spin-orbit coupling. Self-quenching rate constants measured for thioketones are considerably large ($\sim 10^9$–10^{10}; for the corresponding carbonyl compounds: $\sim 10^8$) and are dependent on the molecular framework in which the thiocarbonyl chromophore is present. It has been suggested that n-n orbital interaction between the ground-state and the triplet thioketone is involved in the self-quenching phenomenon. The implications of these high rates of self-quenching are important for organic photochemists as the quantum yields of triplet mediated reactions drastically decrease with increasing ground-state concentration. Another noticeable feature is the unit intersystem crossing efficiencies of thiocarbonyl compounds which are independent of the nature of the substituents, and should solely be understood on the basis of the inherent nature of the chromophore. However, the ISC efficiencies for carbonyl compounds are highly sensitive to the molecular structure such as the presence or absence of heavy atoms, etc. Some of the more recent observations in the photophysics of the lowest excited states of thioketones are thermally activated fluorescence[21] from S_1 and solvent dependent mixing of their $n\pi^*$ and $\pi\pi^*$ triplets.[22]

3. PHOTOCHEMISTRY OF THIOCARBONYL COMPOUNDS

During the past several years, considerable research has been directed toward understanding the excited-state behavior of thiocarbonyl compounds. Electronically excited thiocarbonyl compounds have been reported to undergo a wide variety of reactions from both lower (T_1, $n\pi^*$) and higher (S_2, $\pi\pi^*$) excited states. Perusal of the literature reveals that thiocarbonyl compounds are capable of undergoing five general types of photoreactions: cycloaddition, reduction, oxidation, dimerization and cleavage. A comparison of the excited-state behavior of thiocarbonyl compounds with that of structurally similar carbonyl compounds reveals that the excited thiocarbonyl chromophore has distinctive characteristics of its own which cannot simply be extrapolated from those of the corresponding carbonyl compounds. This section presents the photoreactivity of several

classes of thiocarbonyl compounds (saturated thioketones, aromatic thioketones, thio-amides and thioimides, thioesters and dithioesters, conjugated thiocarbonyl compounds and miscellaneous thiocarbonyl compounds) and discusses their structure-reactivity correlation.

3.1. Saturated Thiones

The excited-state reactivity of saturated thioketones which include both acyclic and cyclic thioketones, is presented in this sub-section. The major excited-state processes discovered to date in this class of thioketones are Norrish type I α-cleavage, inter-molecular hydrogen abstraction from solvents and intramolecular hydrogen abstraction such as Norrish type II reactions, cycloaddition to multiple bonds and reaction between a triplet thioketone and ground-state oxygen. These are discussed below.

3.1.1. α-Cleavage   Norrish type I α-cleavage is an efficient and well known process in both cyclic and acyclic carbonyl compounds.[27] However, such a cleavage in the structur-ally similar thioketones is a less efficient process and has been observed only in thioketones which suffer from internal strain. For example, di-*t*-butyl ketone upon excitation leads to products derived from α-bond cleavage, whereas di-*t*-butyl thioketone does not undergo α-cleavage on irradiation with either visible light or near-ultraviolet irradiation; instead, it yields photoreduction products. However, α-cleavage has been observed in cyclobutanethiones where the α-bond is weak due to high strain factors. Ramamurthy and coworkers have studied the photochemical behavior of several substituted cyclobutanethiones in two solvents (benzene and meth-anol) and a brief summary of their work is presented below.[23-26]
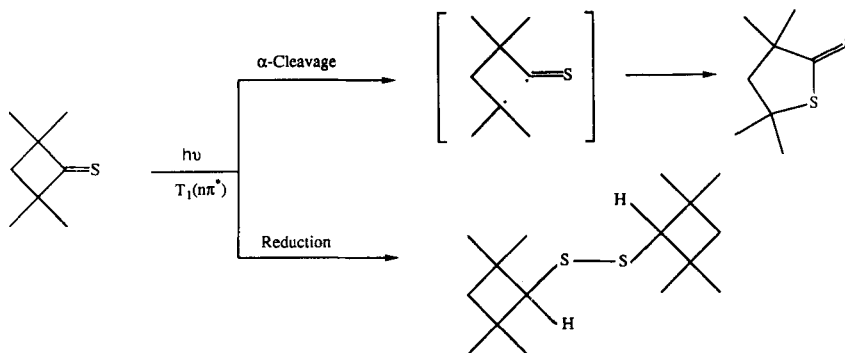
Scheme 1

2,2,4,4-Tetramethylcyclobutanethione upon excitation into the S_2 or S_1 bands forms a dithiolactone and a reduction product, a disulfide, as shown in Scheme 1.[23] The formation of photoproducts is solvent independent as the same set of products is observed in benzene and methanol. Sensitization and quenching studies have established that this thioketone reacts from the lowest T_1 $(n\pi^*)$. The proposed mechanistic pathway for the formation of the dithiolactone involves an α-cleavage as the primary process and the reaction is believed to proceed by way of an initially ring-opened 1,4-diradical which
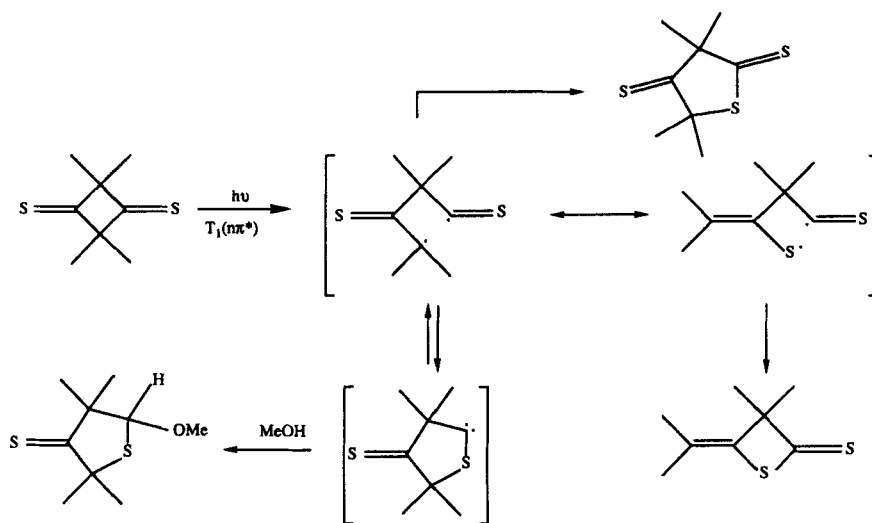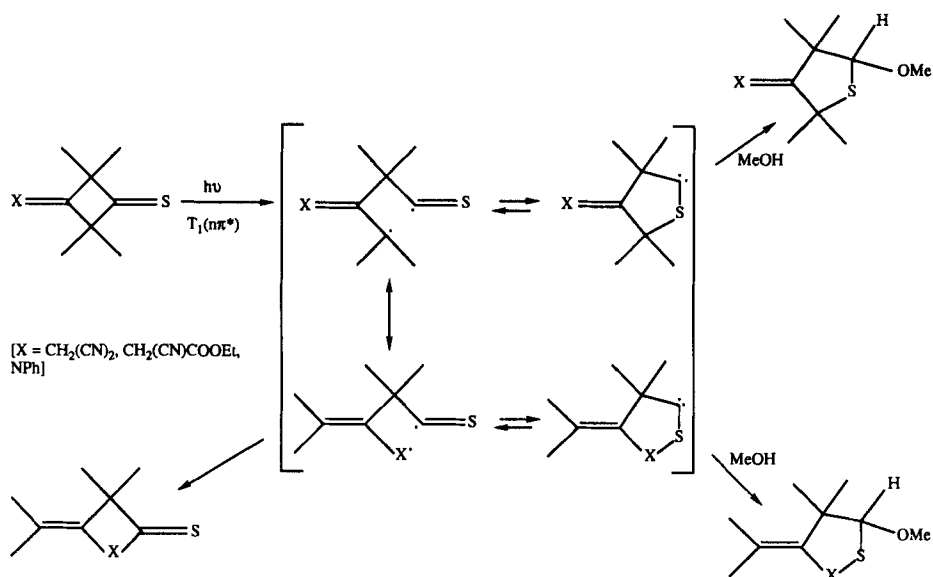
Scheme 2

is effectively trapped by the ground-state thioketone. It is interesting to note that the α-cleavage, resulted from the S_1 ($n\pi^*$) state, observed in the photochemistry of the corresponding ketone, leads to decarbonylation and ring expansion products via a cyclic oxacarbene intermediate. Neither ring expansion (thiacarbene formation) nor dethiocarbonylation is seen in the photochemistry of 2,2,4,4-tetramethylcyclobutanethione.

Analogous products are formed on irradiation of 2,2,4,4-tetramethylcyclobutane-1,3-dithione (Scheme 2).[24] However, the formation of products in dithione photochemistry is solvent dependent: alcoholic solvents such as methanol lead to cyclic acetal type products. The formation of these cyclic acetals has been attributed to the chemical quenching of cyclic thiacarbene intermediates. Thus, the presence of an additional thiocarbonyl group (at the 3-position of the ring) opens up another pathway for the α-cleavage derived 1,4-diradical. This diradical could also decompose to thioketenes through a β-cleavage reaction and/or undergo dethiocarbonylation. Products derived from these processes are not observed. Comparison of the α-cleavage behavior of these mono- and dithiones reveals that further reactions (such as cyclization, ring expansion leading to thiacarbene intermediates, trapping by ground-state thioketone) of the 1,4-diradical are highly influenced by the additional substituents present at the 3-position of the cyclobutane ring. Recent MINDO/3 calculations[25] carried out on these thioketones support the experimental observations and predict that the α-cleavage process to give a diradical is kinetically feasible in small-ring thiones only when stabilizing alkyl or conjugating groups are present. Experimentally, unsubstituted cyclobutanethione and -dithione have not been investigated.

In order to generalize the photochemical behavior of this class of strained thioketones, several bischromophoric cyclobutanethiones (3-substituted derivatives: dicyanomethylene, cyanocarbethoxymethylene, phenylimino groups) have been investigated (Scheme 3).[25a] In these systems, α-cleavage occurs from the lowest triplet state leading

Scheme 3

to a rearranged product via 1,3-migration of the initially generated 1,4-diradical.
Evidence for 1,3-migration is further obtained by the observation of two cyclic
thioacetals in alcoholic solvents. An interesting wavelength effect is observed in 2,2,4,4-
tetramethyl-3-thioxocyclobutan-1-one.[25a,26] Product studies reveal that α-cleavage
occurs from the carbonyl and thiocarbonyl chromophores from the respective $n\pi^*$ states
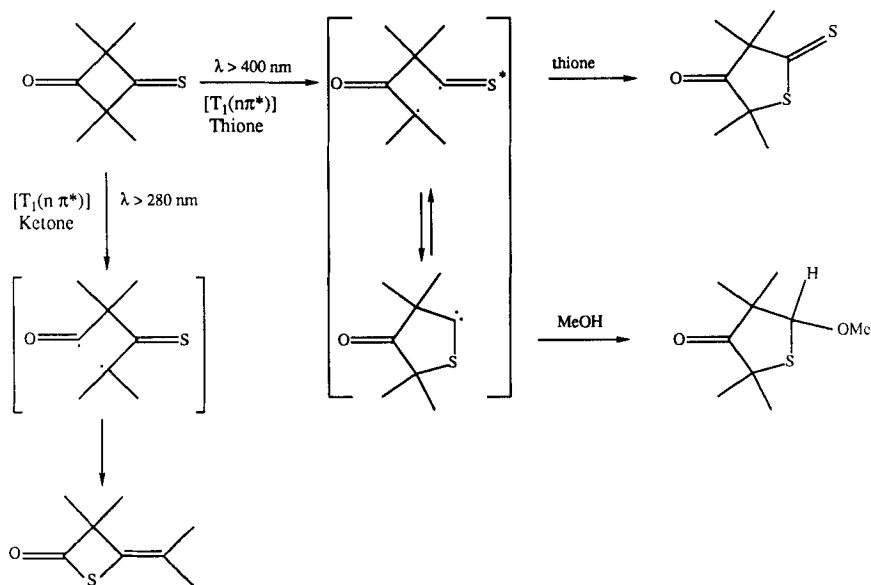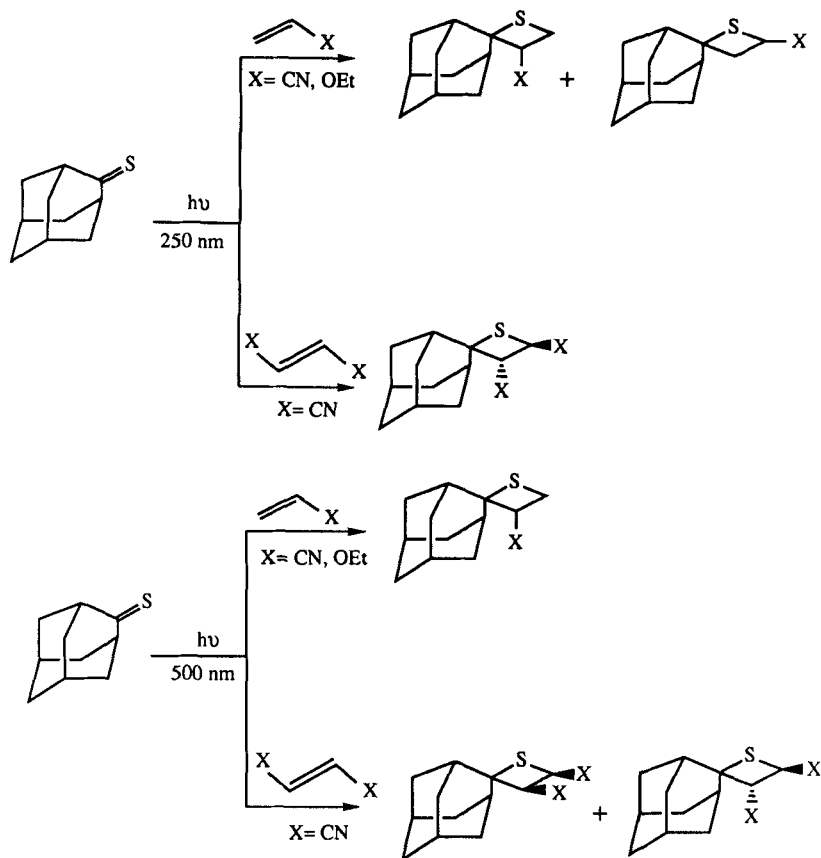

Scheme 4

depending on the wavelength of excitation (Scheme 4). However, no product due to decarbonylation or dethiocarbonylation was encountered. In conclusion, α-cleavage seems to be a general process but restricted to only strained cyclobutanethione systems. The feasibility of α-cleavage with unstrained systems remains to be established.

3.1.2. Dimerization Some saturated thioketones undergo photodimerization when irradiated alone, to give 1,3-dithietanes which can be isolated directly (Scheme 5). 1,3-Dibenzyl thioketone, for example, produces a stable 1,3-dithietane upon S_1 or S_2 irradiation.[28,32] It is interesting to note that the structurally similar dibenzyl ketone has been observed to undergo α-cleavage to produce a benzyl radical and a substituted acyl radical; the latter fragment also leads to a benzyl radical upon decarbonylation.[29] The lack of α-cleavage in dibenzyl thioketone is believed to be due to the lower energy of the C=S reactive excited state that alters the thermodynamic process and makes cleavage of an adjacent bond less favorable energetically. Adamantanethione is also found to give a 1,3-dithietane upon S_1 and S_2 irradiation.[30,31] Quenching and sensitizing experiments established that T_1 is the reactive state upon S_1 excitation and S_2 is the reactive state upon S_2 excitation. It is to be noted here that photodimerization resulting from the T_1 state has a very low quantum yield in spite of the fact that the observed triplet self-quenching rates are diffusion controlled.[31] This suggests that the process of self-quenching which leads to dimerization is a minor pathway. Non-chemical quenching of thione triplets by ground-state thione has been proposed to proceed via a triplet excimer intermediate which rapidly decays non-radiatively to the ground state molecules. Photodimerization to give 1,2-dithietanes instead of 1,3-dithietanes has been observed only in cases where the thiocarbonyl chromophore is substituted by electron-rich substituents and will be discussed in Section 3.5.

Scheme 5
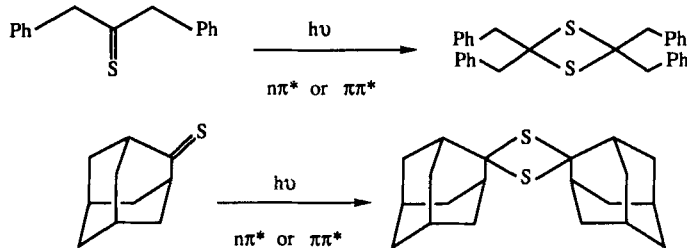
3.1.3. Cycloaddition Light-induced photocycloadditions involving thiocarbonyl compounds and multiple bonds constitute a major part of thiocarbonyl photochemistry. This is partly because a greater number of sulfur-containing four-membered heterocycles (thietanes) are stable and can be isolated. Investigations carried out on the photocycloaddition reactions of acyclic and cyclic saturated thiones are summarized below.[31,33–36]

Saturated thioketones undergo cycloaddition to both electron-rich and electron-deficient olefins upon S_1 ($n\pi^*$) or S_2 ($\pi\pi^*$) band irradiation. In this regard, di-t-butyl thioketone[33] and adamantanethione[31,34] have been studied, the latter in detail. Excitation

Scheme 6

of adamantanethione into its $n\pi^*$ state in the presence of olefins (α-methylstyrene, ethyl vinyl ether, 1,1-diphenylethylene, trans-stilbene and fumaronitrile) leads to thietane (1 : 1 adduct) formation (Scheme 6). The formation of a thietane under these conditions of irradiation is non-stereospecific (stereoisomeric thietanes are observed in the addition of trans-stilbene and fumaronitrile), but regiospecific (only one regioisomer is observed in the addition of ethyl vinyl ether and acrylonitrile).[31] Quenching and sensitization experiments established the participation of the T_1 ($n\pi^*$) excited state. A 1,4-diradical intermediacy has been suggested on the basis of regiospecific and non-stereospecific addition, and the isolation of an open-chain product in the case of α-methylstyrene. Similar irradiation into the S_1 band of di-t-butyl thioketone failed to give thietanes; open-chain ene type products are the major products of addition.[33] This resistance to cyclization has been attributed to the steric repulsion of the t-butyl groups during the cyclization of the intermediate 1,4-diradical.

Excitation of adamantanethione into S_2 in the presence of ethyl vinyl ether/acrylonitrile leads to thietane formation. In contrast to S_1 irradiation, this addition is stereo-

specific and non-regiospecific. This clearly indicates that the cycloaddition of olefins to adamantanethione is a wavelength dependent reaction. Furthermore, the large difference in the quantum yields of product formation obtained upon S_1 and S_2 irradiations reveal that the reactive states are not the same during these two irradiations. Quenching studies suggest that the reactive state is S_2 upon excitation at 250 nm. The lifetime of the state (S_2) being quenched has been calculated to be $\sim 10^{-10}$ s based on the quenching data. More recently, a report by Steer and coworkers indicates that the S_2 state of adamantanethione is almost nonfluorescent and the estimated lifetime of its second excited singlet state is $< 10^{-12}$ s. The disparity between chemical quenching studies and photophysical investigations leaves an element of doubt about the participation of the S_2 reactive state in these cycloadditions.

On irradiation, thiocamphor reacts with bis(methylthio)acetylene to give a dithioester and divinyl sulfide (Scheme 7).[35] The formation of the dithioester can be attributed to the cleavage of a cyclic thiete intermediate; the product divinyl sulfide is believed to come from internal hydrogen transfer. Another example of cycloaddition of saturated thioketones from a higher excited state is the addition of a nitrile function (Scheme 7).[36] The observed product corresponds to the ring-opened electrocyclic isomer of the initially formed four-membered cycloadduct. This reaction does not seem to proceed upon excitation to the S_1 state.
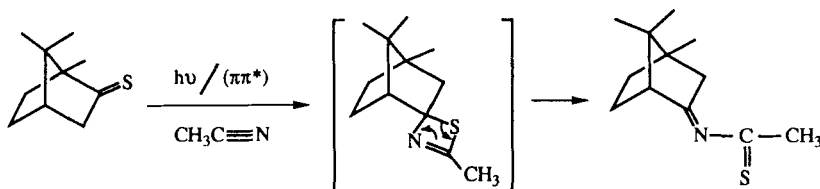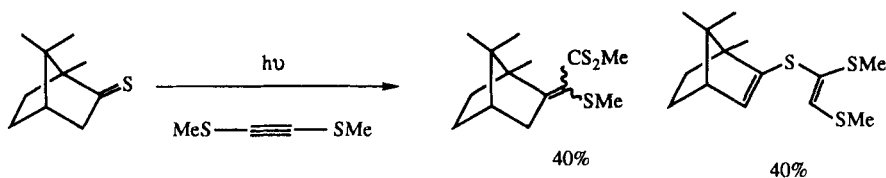
Scheme 7

3.1.4. Oxidation   The practical application of thioketones and their photochemistry is limited for reasons inherent in the thiocarbonyl chromophore. Perhaps the greatest stumbling block, besides ground-state reactivity in the form of thioenolization and polymerization, is the instability of thiones toward air, especially in the presence of light. The photooxidation of thiocarbonyl compounds to give the corresponding carbonyl compounds has been known for quite a long time.[37] Kinetic studies revealed that the reaction proceeds via $n\pi^*$ thioketone and triplet oxygen, and suggested that the excited state of the thioketone photosensitizes the formation of singlet oxygen. The important
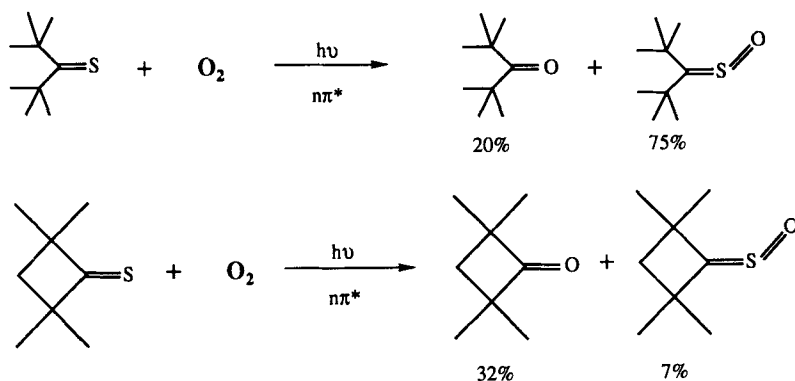
Scheme 8

features recognized in the photooxidation of saturated thioketones are summarized below.[38-40]

Among the saturated thioketones, di-*t*-butyl thioketone was the first one to be oxidized photochemically.[38] Direct excitation of di-*t*-butyl thioketone into the $n\pi^*$ band
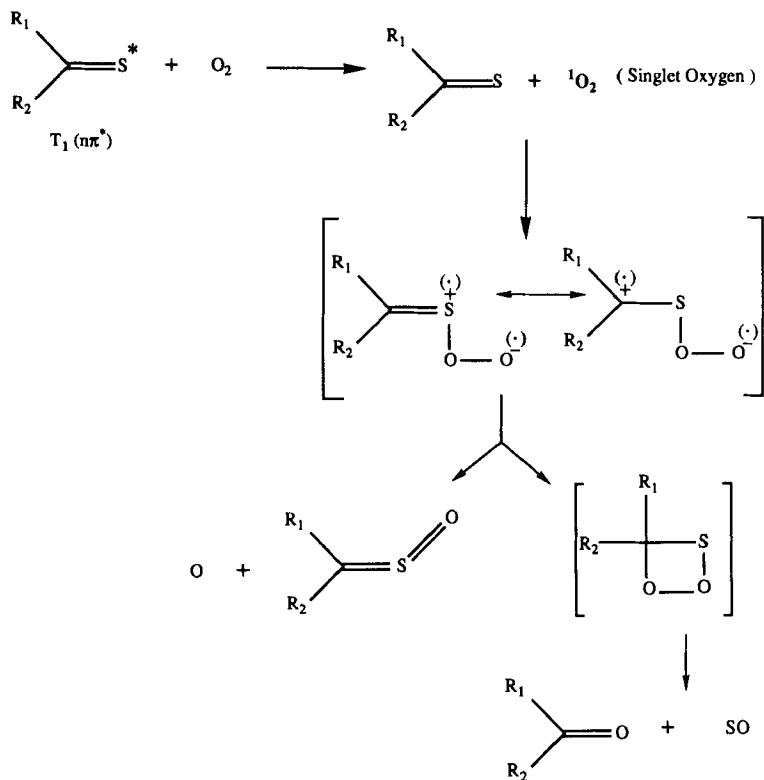
Scheme 9

in the presence of oxygen leads to the formation of the corresponding sulfine in addition to the ketone (Scheme 8). This is very interesting considering the fact that earlier photooxidation studies on thiocarbonyl compounds resulted only in ketone formation.[37] The ratio of sulfine to ketone in this photooxidation is affected by the solvent polarity (the ketone predominates in nonpolar 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. The proposed general mechanism involving the attack of singlet oxygen on the *n*-lobe of the thiocarbonyl chromophore is shown in Scheme 9. Based on the isolation of co-products such as sulfur monoxide and sulfur dioxide, it is considered that a thiadioxetane is the precursor of the ketone formation. A zwitterionic/diradical intermediate is regarded to be the precursor of the thiadioxetane and the sulfine.

Steric factors seem to play an important 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 (Scheme 8).[39] Similarly, norbornane-2-thione leads to ketone whereas thiocamphor gives both ketone and sulfine (Scheme 10).[40] These observations are interpreted in terms of the constraints imposed on the zwitterionic or diradical intermediate. The presence of a 7-methyl group in the bicyclic thioketones probably hinders the ring closure of the dipolar intermediate to the corresponding thiadioxetane. As a result, sulfine formation is enhanced in the oxidation of thiocamphor. The oxidation studies so far carried out on saturated thioketones reveal that steric factors play a significant role in the product distribution.
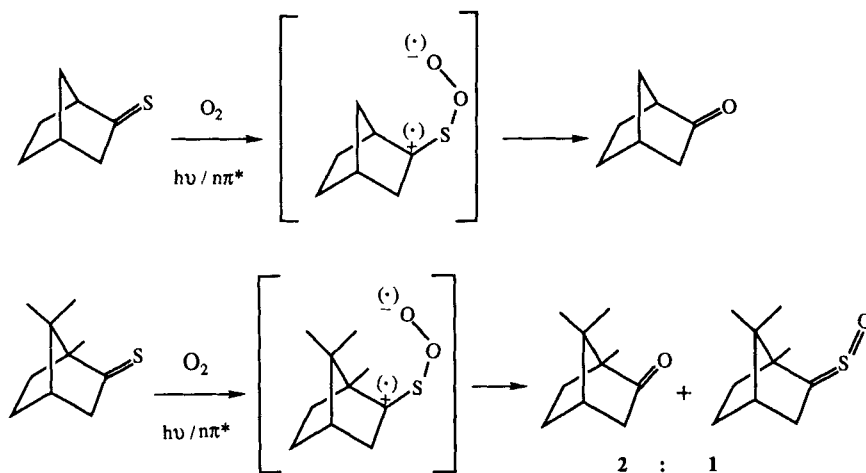
Scheme 10

3.1.5. Reduction Hydrogen abstraction (both inter- and intramolecular) is a commonly encountered process for carbonyl compounds. Among many photoreduction processes, Norrish Type II γ-hydrogen abstraction is a well studied reaction in ketones. Similar intramolecular hydrogen abstraction processes (β-, γ-, δ-, ε-hydrogens) have been

reported with thiocarbonyl compounds. The most important feature which is to be noted here is that the photoreduction of thiocarbonyl compounds is a wavelength-dependent reaction. Most of the studies in this regard have been carried out with diaryl and aryl alkyl thioketones, and will be discussed at length in Section 3.2. Only studies related to the acyclic and cyclic thioketones are summarized below.[41-43]
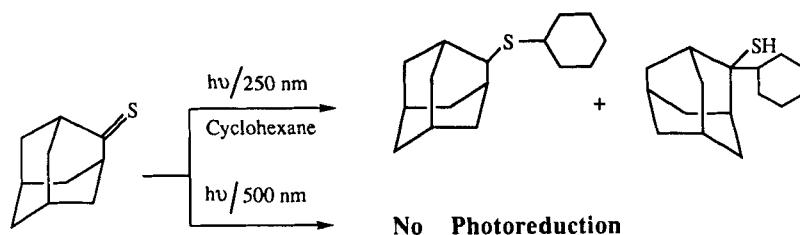
Scheme 11

Adamantanethione has been studied in greater detail than any other thioketone with respect to photoreduction.[41] Adamantanethione on irradiation (> 500 nm) in cyclohexane gives only a 1,3-dithietane; no reduction products were observed. However, excitation into its S_2 band leads to an efficient photoreaction with the solvent cyclohexane: the products derived from the solvent are a thiol and a sulfide (Scheme 11). The product distribution varies with the solvent viscosity and this is interpreted in terms of a solvent cage effect. On the basis of formation of cross products in the cyclohexane-cyclohexane-d_{12} mixture, the cage effect is estimated to be ca. 90%. There are relatively few reactions with such a high cage effect reported in the literature. In order to obtain information about the reactive excited state which precedes the radical pair a kinetic investigation was carried out on this reaction and the reactive state was assigned to be S_2 with a lifetime of $\sim 10^{-10}$ s. This conclusion has to be taken with reservation in the light of a recent study by Steer and Falk which reveals that S_2 states are not immediate precursors responsible for these intermolecular hydrogen abstractions. The lowest triplet of adamantanethione has been shown to participate in the photoreduction process provided the solvent is a good hydrogen donor. For example, irradiation of adamantanethione in the presence of adamantane-2-thiol gives di(2-adamantyl) disulfide. Similar to adamantanethione, di-t-butyl thioketone has also been investigated. Excitation of an dialkyl thioketone into either the S_2 or the S_1 band in the presence of strong hydrogen donors such as an amine leads to the corresponding thiol and disulfide.[42] The reduction by amines is proposed to occur via an initial electron transfer from the amine to the electron deficient sulfur atom of the np^* excited thiocarbonyl group. This is followed by proton transfer and electron redistribution to yield the products.

De Mayo and Blackwell have observed an intramolecular β-hydrogen abstraction in bridged bicyclic thioketones (Scheme 12).[43] This reaction, which is restricted to only bicyclic thioketones having endo hydrogens, has no analogy in carbonyl photochemistry. Thiofenchone/thiocamphor upon irradiation into the second excitation band (~ 254 nm) undergo β-hydrogen abstraction to give tricyclic thiols. The hydrogen abstraction in these bicyclic systems is demonstrated, by deuterium labeling studies, to involve β-endo hydrogen. Compounds which lack the apparently well situated endo
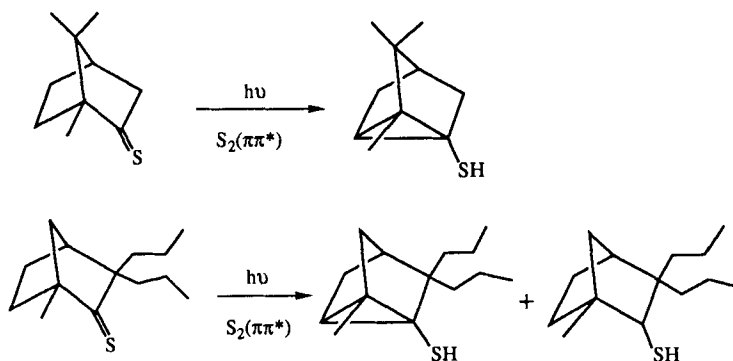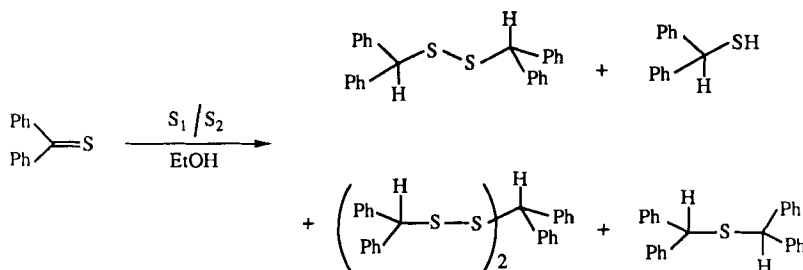
Scheme 12

hydrogen have also been examined. Reactions in these cases were very slow. Cyclopropanethiols together with other products are obtained from tetraalkyl substituted cyclopentanethiones and cyclohexanethiones on S_2 irradiation. These reactions are believed to originate from S_2.

3.2. Aromatic Thioketones

This section presents the excited-state reactivity of aromatic thioketones which include both diaryl and aryl alkyl thioketones. Among the many thiocarbonyl compounds which have been studied in the context of photochemistry, aromatic thioketones have received the greatest attention. In fact, the synthetic and mechanistic studies carried out with aromatic thioketones provide largely the fundamental understanding of the chemistry of the excited thiocarbonyl chromophore, and contribute to the present development of this field. A great part of this work is briefly summarized below.

3.2.1. Hydrogen abstraction Photoreduction via initial hydrogen abstraction is a well known process of diaryl and aryl alkyl ketones. For example, benzophenone undergoing photoreduction to give benzopinacol has been thoroughly studied. The sulfur analog of benzophenone, i.e. thiobenzophenone, upon excitation reacts with hydrogen donors such as primary alcohols;[44] however, the products of this hydrogen abstraction are quite different from those of benzophenone (Scheme 13). This reaction has been suggested to
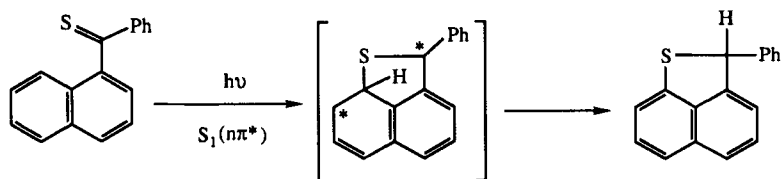

Scheme 13

proceed via the $n\pi^*$ triplet state of thiobenzophenone. On the basis of the ESR evidence[45] it is concluded that the initial hydrogen abstraction by thiobenzophenone leads to the thioketyl radical similar to the ketyl radical in the photoreduction of benzophenone. The differences in the secondary reactions of the radical arise because ground-state thiobenzophenone is a good radical trap.

Photoreduction of thiobenzophenone in the presence of other hydrogen donors such as 1,4-cyclohexadiene and 1,4-dihydronaphthalene leads to the formation of diphenylmethanethiol and the corresponding aromatic compounds.[46] An electron-transfer mechanism has been postulated for reactions involving these hydrocarbons, but the evidence is not conclusive. In another investigation, thiobenzophenone is reported to be inert toward hydrocarbon solvents such as cyclohexane upon excitation to its $n\pi^*$ band. However, excitation with > 300 nm light (into the S_2 band) is effective in causing a reaction between thiobenzophenone and hydrocarbons.[45,47] The major reduction products are di(benzhydryl) sulfide and di(benzhydryl) disulfide. Under these conditions diphenylmethanethiol is not the primary product. Photoreduction of thiobenzophenone in solvents such as ether and tetrahydrofuran has also been reported and in those cases solvent incorporated compounds are the major products. These are parallel to the products formed in the photoreduction of adamantanethione shown in Scheme 11.

Ohno's work[48] on the photochemistry of o-benzyl-thiobenzophenone represents the first example of intramolecular hydrogen abstraction reaction in aromatic thiones (Scheme 14). Upon excitation, o-benzyl-thiobenzophenone undergoes photoenethiolization via an intramolecular hydrogen abstraction process. The photoenethiol is observed to be stable at very low temperatures and reverts to the thione at room temperature. Dimethyl acetylenedicarboxylate traps it as an initial [6 + 2] cycloadduct, leading to a benzothiopyran.
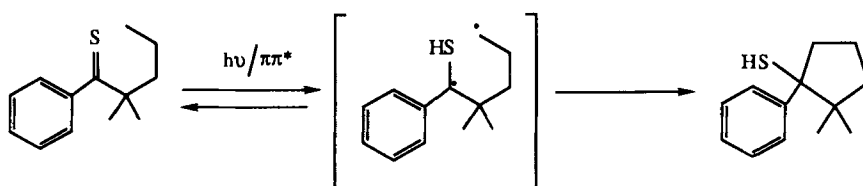

Scheme 14
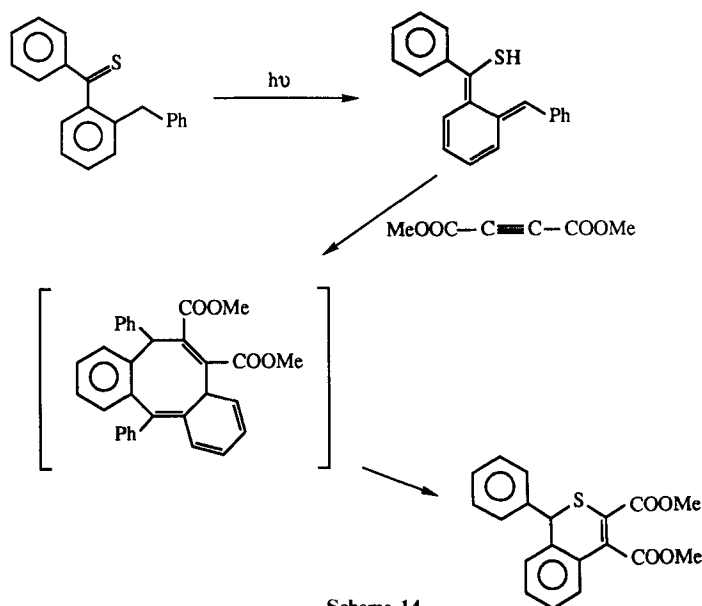
De Mayo's studies[49] related to intramolecular hydrogen abstraction reactions reveal that a number of phenyl aryl thioketones where the aryl group is 1-naphthyl or a polycyclic hydrocarbon group having a vacant peri position adjacent to the substituent, take part in a non-oxidative photocyclization that produces a new five-membered sulfur-containing ring (Scheme 15). This cyclization occurs with alternant hydrocarbons but apparently fails with non-alternant hydrocarbons. A mechanistic investigation suggests that the lowest singlet excited state (S_1) may be responsible for this process, and the incorporation of deuterium from D_2O indicates that dipolar intermediates may be involved. More recently, Das et al. have reported[50] a laser flash photolysis study of 1-thiobenzoylnaphthalene. They estimated the lifetime of the singlet state in benzene as < 50 ps and observed a transient species at 520 nm which was not definitely assigned except that it is neither a triplet nor a triplet-derived product and that it arises via the photochemistry from S_1.

Scheme 15

The photochemical intramolecular hydrogen abstraction reactions of aryl alkyl thioketones have been thoroughly studied and several interesting conclusions have been drawn. Aryl alkyl thioketones containing a hydrocarbon side chain upon irradiation into the S_2 band result in a cyclization product, a cyclopentanethiol, via δ-hydrogen abstraction from the alkyl chain (Scheme 16).[51] These reactions do not occur upon excitation to the lowest absorption band, i.e. S_1 of aryl alkyl thiones. Furthermore, aryl alkyl thiones which lack δ-hydrogen do not undergo cyclization. On the basis of quenching and sensitizing experiments it has been suggested that the second excited singlet state is the reactive state and that the reaction proceeds via a 1,5-diradical.[52] The synthetic importance of δ-hydrogen abstraction has been demonstrated by the use of this reaction as the primary step in the synthesis of a sesquiterpene, ($\pm$)-cuparene.[53]

Scheme 16

The selectivity in the hydrogen abstraction is lost in the case of aryl alkyl thioketones possessing heteroatoms in the side chain.[54] Particularly, blocking the δ-position by oxygen leads to γ- and ε-insertion resulting in the formation of four- and six-membered cyclic thiols (Scheme 17). The altered reactivity resulting from heteroatom substitution

Scheme 17
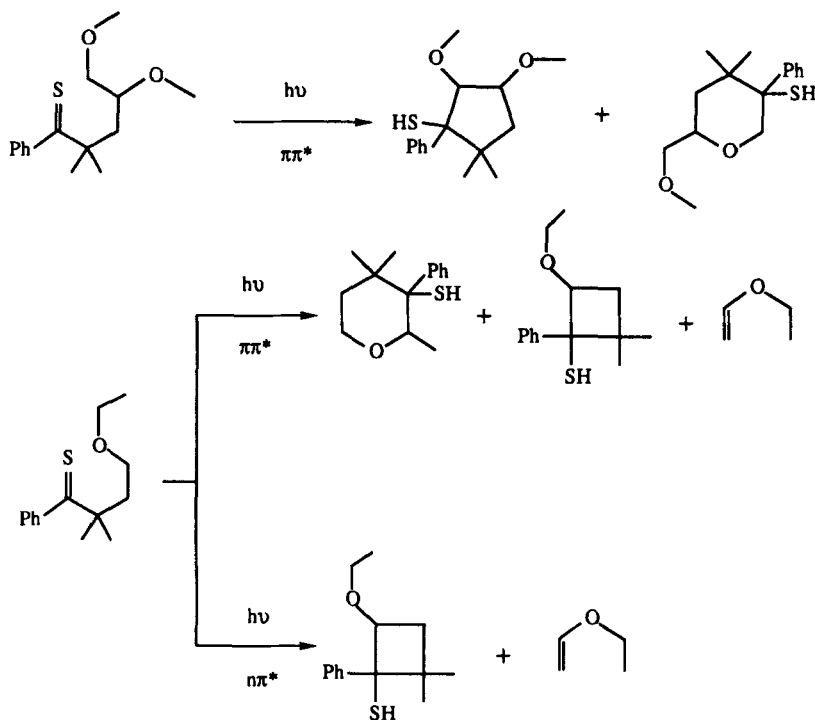
can be either due to activation of the adjacent hydrogens or the consequence of intramolecular charge transfer from oxygen to the excited thioketone. Although ε-insertion occurs only from the $\pi\pi^*$ state, abstraction, followed by cyclization or cleavage, can occur from both S_2 and T_1 states. Another series of aryl alkyl thioketones such as γ-arylalkyl thioketones having only β-hydrogens have been reported to undergo β-hydrogen abstraction giving rise to cyclopropanethiols (Scheme 18).[55] A similar reaction is observed in the case of monocyclic and bicylic thioketones,[43] and suggests that the activation toward β-hydrogen is not due to the aromatic nucleus present in the aryl alkyl thioketone. This reaction takes place upon excitation to either the S_2 or the S_1 band. Kinetic and quenching studies suggest that the reaction proceeds from both excited states.

Scheme 18
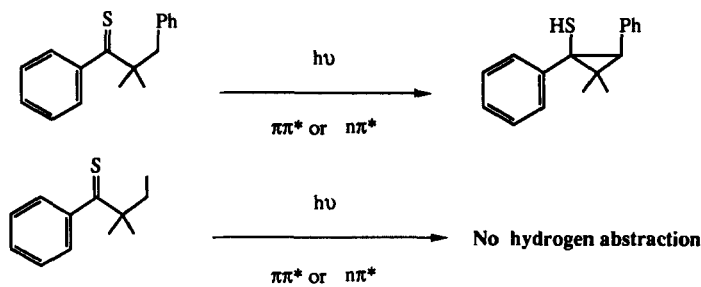
3.2.2. Cycloaddition A considerable amount of work has been done with photocyclo-addition reactions of aromatic thioketones with alkenes. These studies have mainly been carried out with two thioketones, namely thiobenzophenone and xanthione. The products of these cycloadditions and the nature of the excited state involved are dependent on the substituents present on the olefins. The first addition reaction of an aromatic thioketone (thiobenzophenone) and an olefin (1-hexene or *cis*-2-butene) was reported by Kaiser and Wulfurs.[56] They recognized the wavelength dependent nature of the addition but failed to identify both the primary products and the reactive state. Since then, a number of reports on the addition reactions of aromatic thioketones have appeared.[57-62] However, only those which ushered in the initial development and understanding of the excited state behavior are included.

Thiobenzophenone reacts readily with electron-rich olefins (alkyl, alkoxy and alkylthio substituted olefins) on either long-wavelength (> 500 nm) or short-wavelength (> 300 nm) irradiation to give thietanes and/or 1,4-dithianes (Scheme 19).[57] The reaction with 1-phenylpropene shows the regioselective, but non-stereoselective nature of the process. On the other hand, the reaction with ethyl vinyl ether shows the formation of a dithiane product as well as the orientational preference. The proposed mechanism
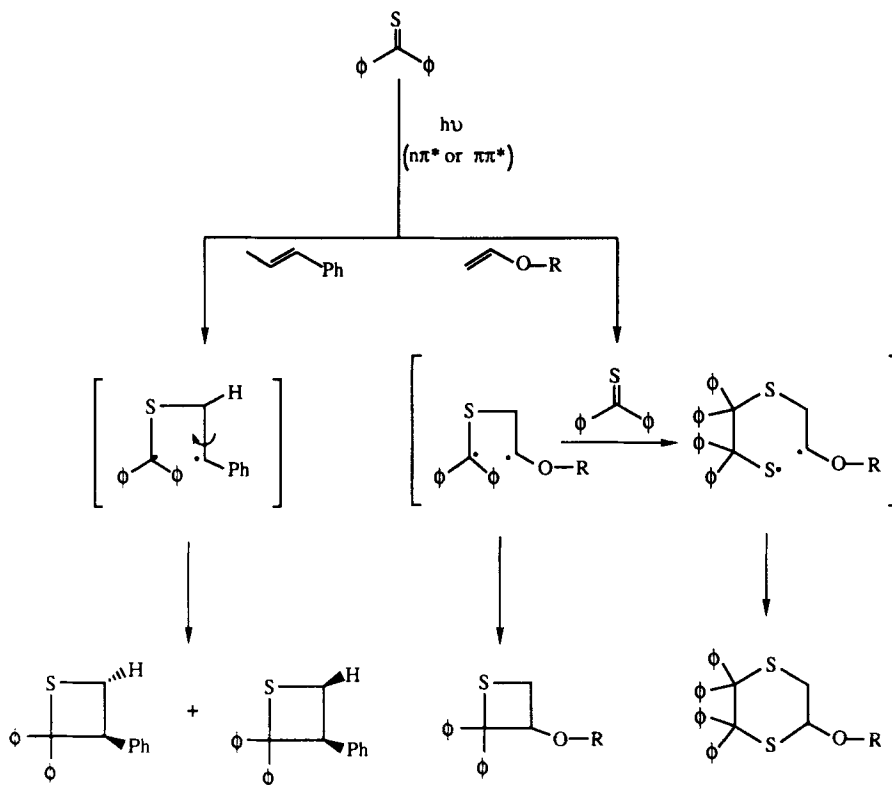
Scheme 19

suggests the reactive state as an $n\pi^*$ triplet (T_1) and that the addition proceeds via a pre-thietane diradical intermediate. Another factor which is attributed to the diradical intermediacy is the observed dependency of the thietane-to-dithiane ratio on the concentration of the ground-state thioketone. It is believed that the pre-thietane diradical may be trapped by the ground state thioketone to give a 1,6-diradical which upon ring closure gives the 1,4-dithiane. Steric effects also play a part, and greater steric bulk in the alkene (e.g., in the case of styrene) promotes dithiane formation. Another observation which supports the proposed diradical intermediate is the cis-trans isomerization of the recovered olefin. A mechanistic study of the reactions of xanthione with a wide range of alkenes provides relative rate constants for attack by a triplet aromatic thioketone on the alkenes.[58]
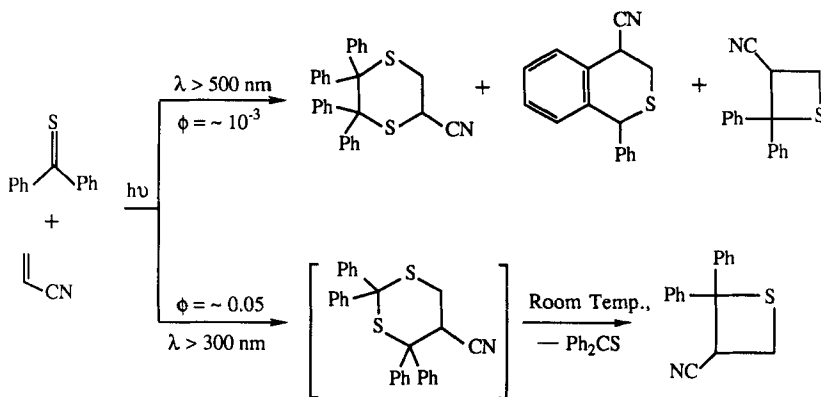
Scheme 20

Wavelength-dependent product formation has been observed in the addition of electron-deficient olefins to aromatic thioketones (Scheme 20).[59] Upon excitation to the S_2 band, thiobenzophenone adds to electron-poor olefins (acrylonitrile, crotononitrile, fumaronitrile and acrolein) to give only thietanes and no dithianes. The addition is shown to be stereospecific (fumaronitrile yields only one stereoisomeric thietane). Mechanistic studies[60] carried out with this system reveal some interesting facts about the nature of this addition: (1) The product of low-temperature irradiation (S_2) of thiobenzophenone in the presence of acrylonitrile is not the same as the one observed at room temperature, the former conditions yield a 1,3-dithiane which decomposes at room temperature to a thietane; (2) the quantum yield of the thietane formation decreases with an increase in thiobenzophenone concentration, suggesting that the intermediate complex can be intercepted by ground-state thioketone to yield the starting compounds; (3) quenching studies suggest the involvement of the S_2 reactive excited state. Based on the above evidence, an exciplex intermediate is suggested to be involved in the formation of the 1,3-dithiane product. Although it was originally thought that S_1 does not react with electron-deficient olefins, de Mayo studied[61] the thiobenzophenone-acrylonitrile system more carefully and identified three addition products (all in low quantum yields, $\sim 10^{-3}$) following S_1 (> 500 nm) excitation. Based on quenching and sensitization studies, the addition following S_1 excitation is suggested to proceed via the T_1 reactive state and a
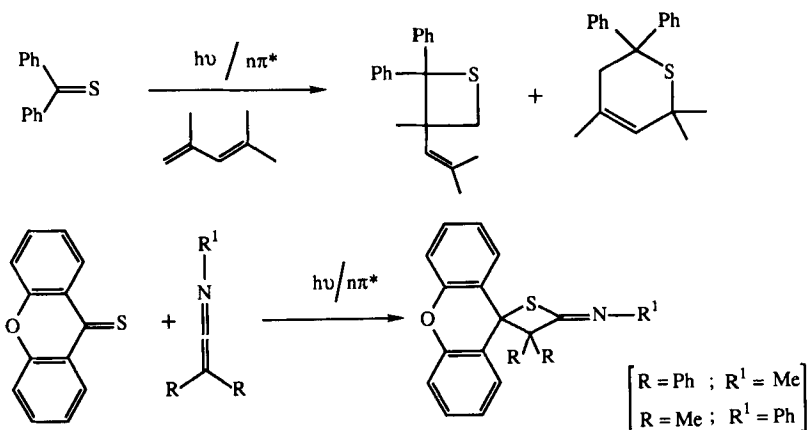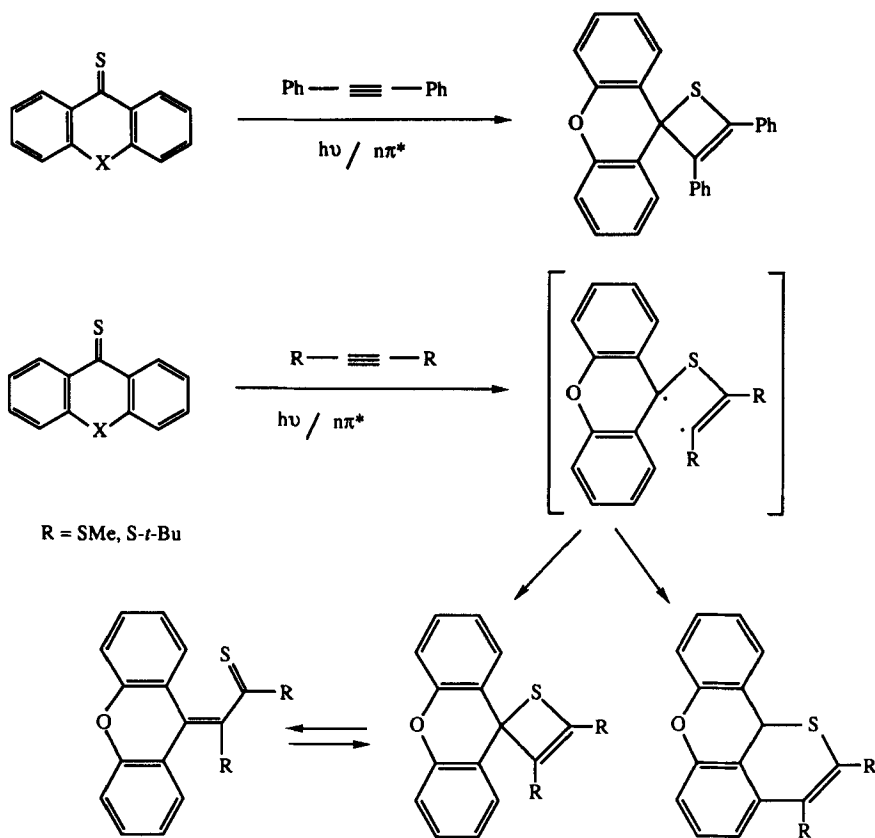
Scheme 21

1,4-diradical intermediate. Addition of olefins to xanthione and substituted thio-benzophenones has also been reported.[62]

Similar to olefins, other multiple-bond systems such as imines,[63] 1,3-dienes,[64] 1,2-dienes (allenes),[65] cumulenes,[66] ketenes,[67] and ketenimines[68] have also been reported to undergo addition reactions with excited (T$_1$, $n\pi*$) xanthione, thiobenzophenone, and their derivatives (Scheme 21). In all these cases, the addition generally results in thietane formation, with very few exceptions. In view of the observed products, additions to acetylenic[69] and nitrile[36] bonds are interesting. Photocycloaddition of diphenylacetylene to xanthione gives a spirothiete in high yield. However, addition of bis(alkylthio)alkynes leads to an equilibrium mixture of a thiete and its decomposed product, the unsaturated ester, and a benzothiopyran type product arises by internal attack on the aromatic ring (Scheme 22). The ratio of these products varies with the nature of the aromatic thioketone. Addition of an aromatic thioketone to a nitrile function is believed to be an upper excited-state reaction and the products of addition are similar to those observed with bicyclic thioketones.[36]

3.2.3. Oxidation One of the earliest photoreactions of aromatic thioketones to be recognized is the reaction of an excited thioketone with oxygen. Several earlier reports discussed the oxidation of thiobenzophenone both in the presence and absence of light. All these studies reveal that the major product of oxidation is the corresponding benzophenone and the oxidation is a result of the reaction between the excited $n\pi*$ thioketone and ground-state oxygen. Light-catalyzed oxidation giving the correspond-ing ketone as the sole product for a number of aromatic thioketones has been reported by several groups of workers.[37]

The variation in the product distribution in the oxidation of several aryl alkyl and diaryl thioketones in solution has been reported by Ramamurthy and coworkers.[40b] Such studies reveal some interesting mechanistic details. In solution, both sulfine and ketone are observed as the oxidation products both upon $n\pi*$ excitation and in the reaction of singlet oxygen. Only electron-withdrawing substituents in diaryl thioketones and aryl

Scheme 22

alkyl thioketones favor sulfine formation (Scheme 23). These observations have been rationalized in terms of electronic factors operating on the zwitterionic or diradical intermediate shown in Scheme 9.

In another study, the oxidizabilities of diaryl thioketones in solution and in the solid state have been compared.[70] The results obtained in the solid-state photooxidation of diaryl thioketones reveal that there is no direct relationship in their oxidation behavior

R = OMe	80%	2%
R = Cl	52%	25%
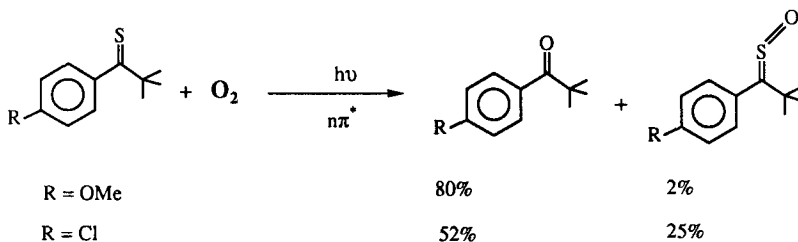
Scheme 23

in solution and in the solid state. While in solution the oxidizability of diaryl thioketones is dependent on the substituents present on the phenyl rings, such a relationship does not seem to exist in the solid-state photooxidation. For example, 4,4′-dimethoxythiobenzophenone which is most reactive in solution, is inert in the crystalline state (Scheme 24). The oxidation behavior of diaryl thioketones in the solid state has been rationalized on the basis of the presence or absence of a channel in the crystal structure of the thioketones. It appears that the channel is essential for oxygen to diffuse into the crystal and to effect oxidation.
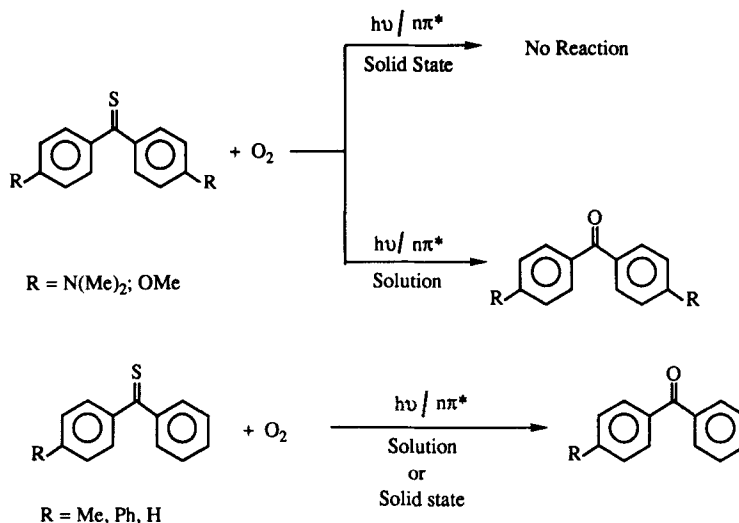
Scheme 24

3.3. Thioamides and Thioimides

The photochemistry of thioamides and thioimides has received increasing attention during the last decade. Currently, a major part of the research in thiocarbonyl compounds seems to be directed toward understanding the photochemical behavior of thioamides and thioimides; part of this special attention may be attributed to the synthetic applications of many of these reactions. The major photoreactions recognized in this class of compounds are intramolecular hydrogen abstraction, α-cleavage, intramolecular and intermolecular cycloaddition, oxidative cyclization and rearrangement.

The first photoreaction of thioimides was reported by Grellmann and Tauer in 1967.[71] Thioacetanilide on excitation undergoes oxidative cyclization to give a methyl substituted benzothiazole (Scheme 25). A similar cyclization is noticed even in o-halo-
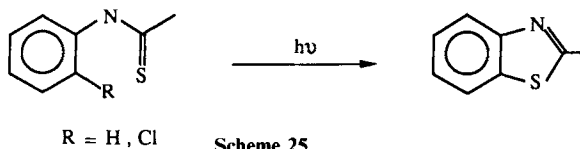
R = H , Cl   **Scheme 25**

thioacetanilides.[72] It is interesting to note that these thioanilides do not undergo photo-Fries rearrangement, which might have been expected based on the photochemical behavior of the corresponding carbonyl counterparts.

α-Cleavage reactions of thioimides have not been explored to the same extent as those of strained thioketones. A recent report by M. Sakamoto *et al.* suggests that strained β-thiolactams such as 3,3-diphenyl-4-thioxoazetidin-2-ones can in fact undergo such an α-cleavage process (Scheme 26).[73] In alcoholic solvents such as methanol a ring expanded thioacetal is observed. It is assumed that the reaction proceeds via cleavage of the α-bond adjacent to the thiocarbonyl group to give a 1,4-diradical, followed by ring expansion to give a thiacarbene type intermediate which then is trapped by alcoholic solvents to give thioacetals. No products resulting from the cleavage of the α-bond adjacent to the carbonyl group are observed.
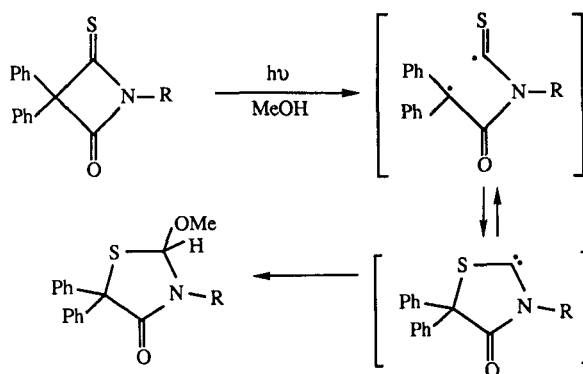
Scheme 26

Photodesulfurization of thioamides, a reaction which is rarely observed in the photochemistry of thiocarbonyl compounds, has been reported to T. Nishio *et al.*[74] Indoline-2-thiones undergo desulfurization to the corresponding indole derivatives on irradiation in benzene, possibly via intermediate thiiranes. Irradiation of the same indoline-2-thiones in the presence of triethylamine, however, affords indolines;[75] a pathway involving an electron transfer and the formation of zwitterions has been proposed and is outlined in Scheme 27.

R^1 = Ph, PhCH$_2$, *n*-Bu, Me or H

R^2 = R^3 = Me, Ph or (CH$_2$)$_5$
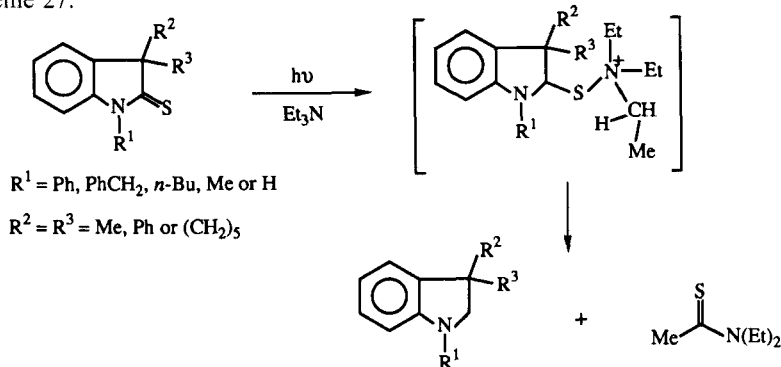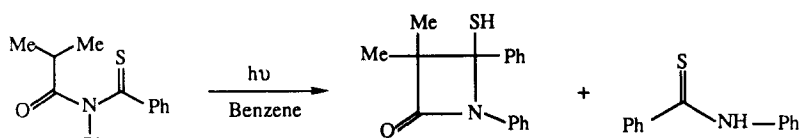
Scheme 27

Scheme 28

Norrish type II photocyclization via intramolecular hydrogen abstraction in thio-amides is a relatively novel reaction. The monoimide is converted, on irradiation in benzene, into the β-lactam and thiobenzamide by competing type II photocyclization and cleavage pathways (Scheme 28).[76] This transformation is the first example of a γ-hydrogen abstraction in a thioimide and provides an attractive route to sulfur-containing β-lactams. This reaction has been generalized to many structurally related thio-imides.[77] In N-alkylphthalimides where the alkyl chain has several abstractable hydro-gens, type II hydrogen abstraction is observed to take place only from the hydrogen that is activated by other substituents such as phenyl groups (Scheme 29).[78]
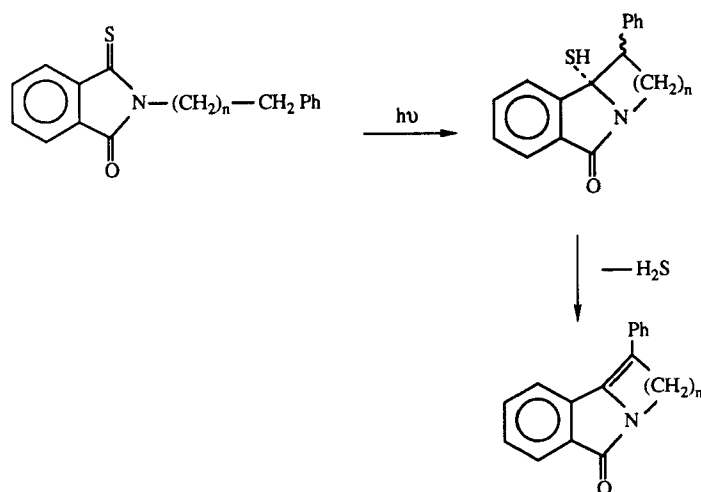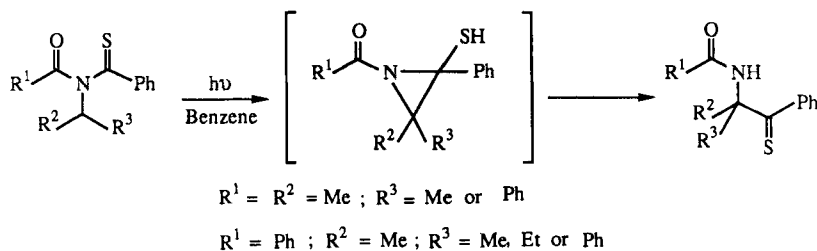

Scheme 29

An interesting photoarrangement which is believed to proceed via β-hydrogen abstraction has been reported in acyclic N-alkylthioimides.[79] As illustrated in Scheme 30, the rearrangement of acyclic N-alkylthioimides to α-acylamino thioketones on irradiation proceeds via an aziridine intermediate which has been detected at low temperatures.

The photoaddition of olefins to thioimides and thioamides has been the subject of several investigations.[80] The primary products of addition are always thietanes; the thietanes resulting from the photoaddition of some thioimides to olefins are stable. However, thietanes remain as intermediate products in the photoaddition of thioamides to olefins; the observed products have always been of a cleavage type derived from the primary thietane intermediates. Some of the recent studies are shown in Scheme 31. They include (a) photorearrangement of the 3-allylindoline-2-thiones to the corresponding

S.R.   K

R^1 = R^2 = Me ; R^3 = Me or Ph

R^1 = Ph ; R^2 = Me ; R^3 = Me, Et or Ph

Scheme 30

2-allylthioindoles in benzene, (b) photoaddition of arenecarbothioamides to furan derivatives to give 3-aroylfurans; (c) photochemically induced conversion of N-(o-styryl)-thioamides into quinolines and (d) photorearrangement of thioenamides to the corresponding 5,5-dimethylthiazolines. As illustrated in Scheme 31, thietanes are the primary products of the addition. Photoadditions to acetylenes are also known[81] and the observed photobehavior is similar to that of thioketones discussed in earlier sections of this review.

a)

R^1 = R^2 = Me or Ph; R^3 = H or Me

b)

c)

R^1 = R^2 = Me or Ph
R^1 = Me; R^2 = CN

d)

Ar = Ph, α-naphthyl or o-biphenyl
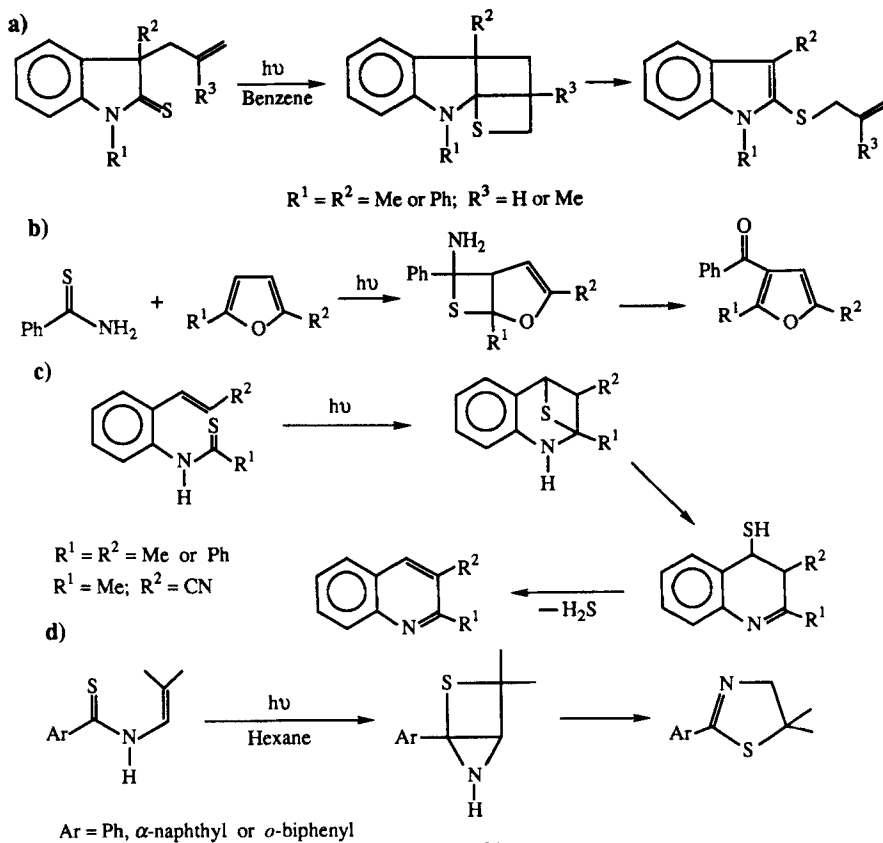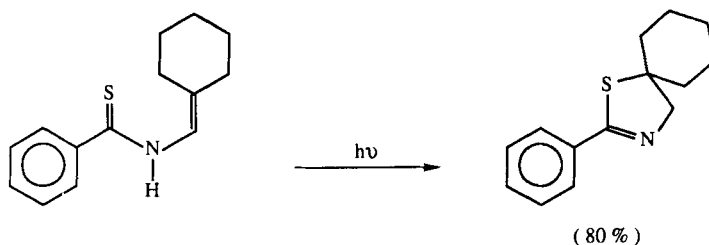
Scheme 31

Scheme 32

The interaction of an excited thioamide with an alkene double bond leading to a non-oxidative cyclization of a different type has been reported in N-vinylthiobenzamide systems (Scheme 32).[82] In the case of N-alkylvinylthiobenzamides, the products of the irradiation are an isoquinoline-1-thione and its dihydro derivative (Scheme 33).
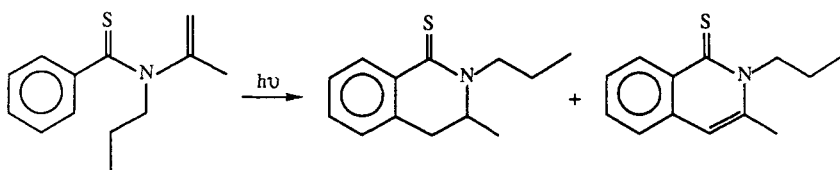
Scheme 33

This process can be visualized as a photochemical 6π electrocyclic ring closure, followed by a thermal 1,5-hydrogen migration.[83] An alternative pathway (via initial carbon-sulfur bond formation, followed by 1,4-hydrogen transfer) is preferred in the photo-cyclization of N-(β,γ-unsaturated carbonyl)thioamides which results in bicyclic lactams (Scheme 34).[84,85]

R = H or Me

n = 1-3
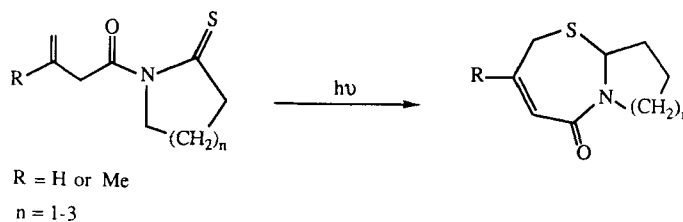
Scheme 34

3.4. Thioesters and Dithioesters

Thioesters undergo distinct photoreactions which correspond to dimerization, Norrish type I and II reactions, and cycloaddition to olefins. Some of these reactions have achieved synthetic importance.

Photodimerization of thioketones which leads to 1,3-dithietanes is a well documented reaction and was discussed briefly in preceding sections. Dithionolactones of the type shown in Scheme 35 have been reported to undergo a similar photodimerization (it could

R = CH$_2$ CH$_2$ Si (CH$_3$)$_3$
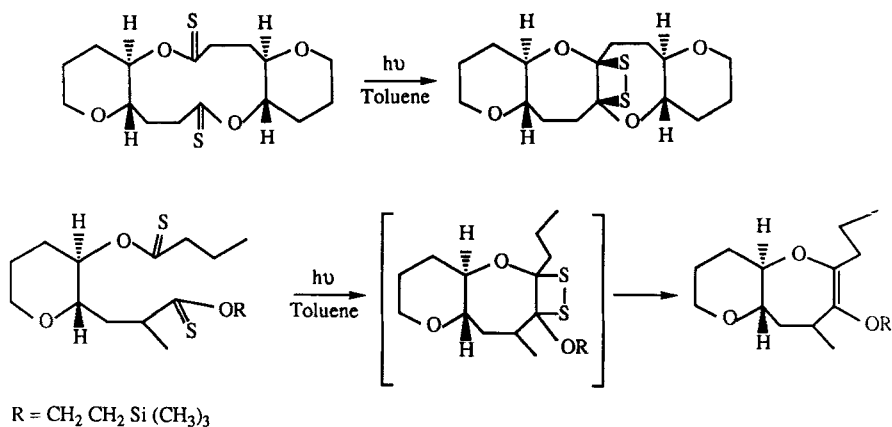
Scheme 35

also be classified as an intramolecular cycloaddition) to yield dithiatopazine, a stable 1,2-dithietane.[86] This represents the first example of a stable and well characterized 1,2-dithietane obtained in the photochemistry of thiocarbonyl compounds. On thermolysis, this dithietane loses molecular sulfur (presumably singlet sulfur) to yield a tetrasubstituted olefin. Irradiation of a structurally similar dithionoester (Scheme 35) in toluene, however, results in a tetrahydrooxepine in a reaction which is believed to proceed by an analogous cycloaddition pathway via a 1,2-dithietane and subsequent loss of sulfur.[86,87]

A reaction which involves α-cleavage and parallels the photo-Fries reaction of aryl carboxylates has been reported in O-aryl thioesters. Irradiation of an O-aryl thioester yields an isomeric o-hydroxyaryl thioketone (Scheme 36).[88] However, with O-alkyl thioesters the preferred reaction is a 1,3-shift to give an S-alkyl thioester, formally a β-cleavage process.[89] The S-alkyl thioesters can undergo facile C—S bond cleavage, which opens up the possibility of a mild method for deoxygenation. Strained dithiolactones of the type shown in Scheme 37, on irradiation in benzene and in methanol,
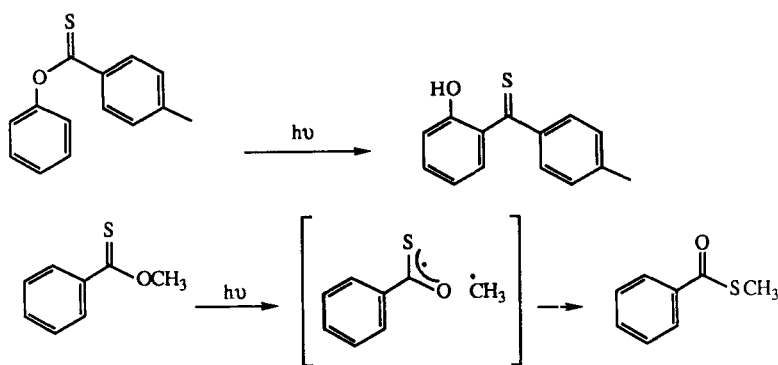
Scheme 36
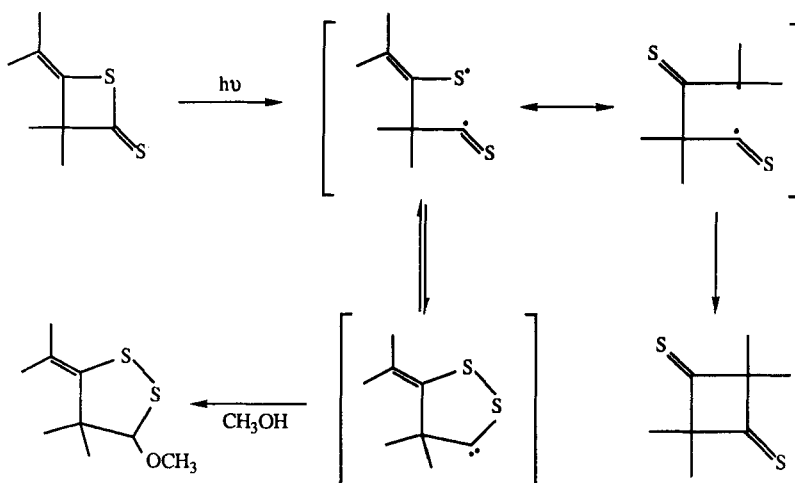
Scheme 37

undergo Norrish type I α-cleavage.[90] The products of irradiation in benzene are a rearranged dithione and a sulfur incorporated dithiolactone. This reaction has been suggested to proceed from the lowest singlet state ($^1n\pi^*$). This conclusion should be taken with reservation since thiocarbonyl compounds possess fast intersystem crossing rates and rarely react from S_1. Based on the isolation of thioacetals and a rearranged dithione, a diradical type and a ring expanded thiacarbene type intermediate have been invoked.
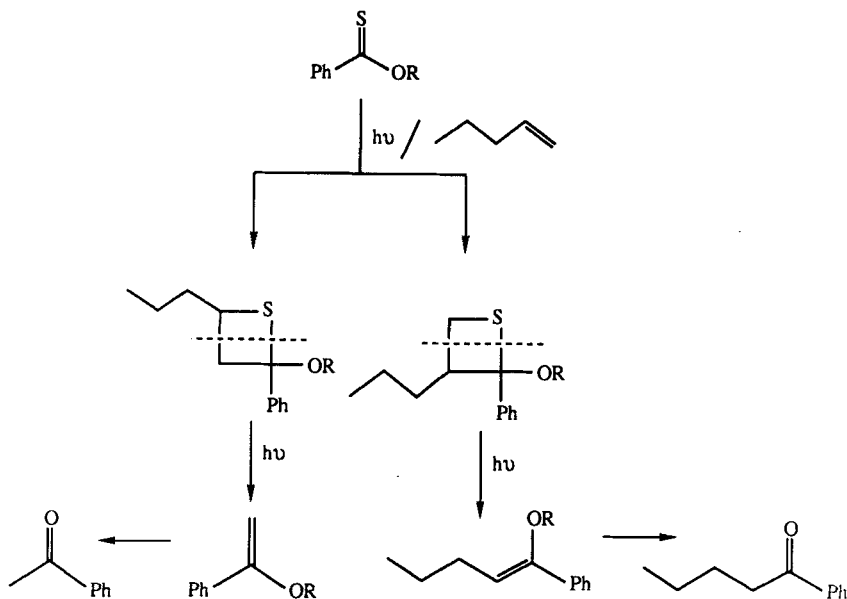
Scheme 38

Photocycloadditions of olefins to thioesters have been studied by Ohno and coworkers.[91] The cycloaddition which is suggested to originate from the triplet $n\pi^*$ state, results in both stable thietanes and products derived therefrom. The products of the decomposition of the thietane are generally ketones and, in some cases, the precursor enol ethers are also isolated (Scheme 38).

Reactions analogous to the Norrish type II photoelimination of alkyl benzoates are observed with O-alkyl thiobenzoates (Scheme 39).[92] This reaction has been established to be a general process which occurs when an activated hydrogen is present in the γ-position. Thioesters which do not possess γ-hydrogen are photostable unlike thioketones where hydrogen abstraction is observed from β-, γ-, δ-, and ε-positions. This reaction is seen in thioesters whose lowest excited state is only of $n\pi^*$ character, but not of $\pi\pi^*$ character. The initial 1,4-diradical formed by hydrogen abstraction prefers to undergo elimination rather than cyclization. Some of these reactions provide useful routes for the dehydration of homoallylic alcohols to give dienes under mild conditions, including steroidal compounds such as cholesterol.[92]
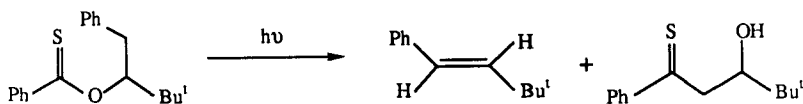
Scheme 39

3.5. Conjugated Thiocarbonyl Compounds

Conjugated carbonyl compounds, in particular enones, have been thoroughly studied in the context of photochemistry.[93] They undergo deep-seated rearrangements and a wide variety of cycloaddition reactions which have found extensive use in organic synthesis. In contrast to these intense investigations of conjugated carbonyl compounds, there are relatively few photoreactions known with the corresponding thiocarbonyl compounds. This may be primarily due to the instability of conjugated thioketones as many of the alicyclic conjugated thiocarbonyl compounds exist as [4 + 2] dimers.[94] For the same reason, most of the studies so far carried out with conjugated thiocarbonyl compounds involve only cyclic systems. This section presents the photoreactivity of conjugated thiocarbonyl compounds (viz. conjugated thioketones, cross-conjugated thioketones, conjugated thiolactones and thiolactams).

3.5.1. Conjugated thioketones

In a fashion analogous to saturated thioketones, conjugated thioketones such as thioisophorone and thioverbenone also undergo oxidation upon direct excitation.[95] Singlet oxygen has been shown to be the oxidizing species in the photooxidation of conjugated thioketones and the products of oxidation are the corresponding conjugated ketones. No sulfine formation is observed. The absence of sulfine can be attributed to the general electronic factors operating on the zwitterionic or diradical intermediate shown in Scheme 9. It may be interesting to note that the reactivity of α,β-unsaturated ketones toward singlet oxygen is strongly dependent on the conformation of the unsaturated system. Those α,β-unsaturated carbonyl systems which
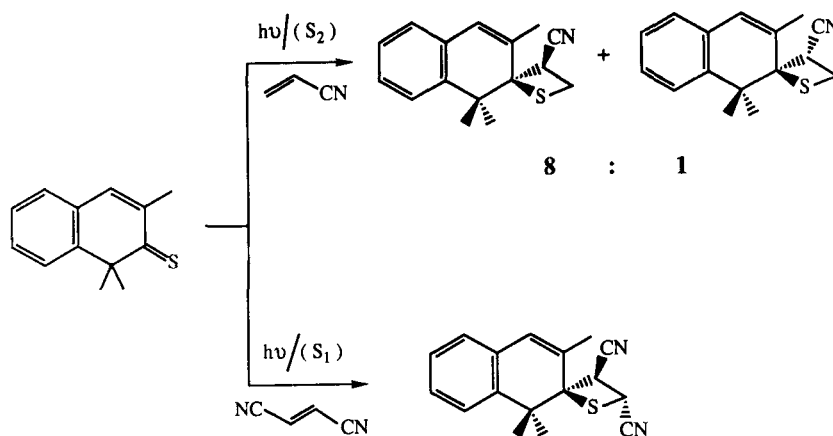
Scheme 40

prefer the cisoid conformation are rapidly oxidized by singlet oxygen, whereas those systems which prefer the transoid conformation react slowly or not at all.[96]

Detailed studies on the photocycloaddition of olefins to cyclic enethiones have been reported by Rao and Ramamurthy.[97] Electron-deficient olefins such as acrylonitrile, add to 1,1,3-trimethyl-1,2-dihydronaphthalene-2-thione upon $\pi\pi^*$ excitation. Cycloaddition occurs to the thiocarbonyl chromophore preferentially from the less hindered side to yield thietanes and not to the carbon–carbon double bond (Scheme 40). The thietane formation is stereospecific and regioselective. This addition has been inferred to originate from the second excited singlet state, S_2 ($\pi\pi^*$), and an exciplex has been proposed as an intermediate in this addition based on the dependence of the fluorescence quenching rate constant on the electron-acceptor properties of the olefin. A molecular orbital analysis of such additions has been undertaken and the results have proved useful in the rationalization of the observed regiochemistries.[98]

The cycloaddition of the same thioketone to electron-rich olefins such as dihydrofuran, ethyl vinyl ether, etc., upon excitation to either S_2 ($\pi\pi^*$) or S_2 ($n\pi^*$) states has also been studied.[99] Excitation to the S_1 level resulted in the same mixture of products, namely thietane and 1,4-dithiane, as excitation to S_2 (Scheme 41). This addition is site specific
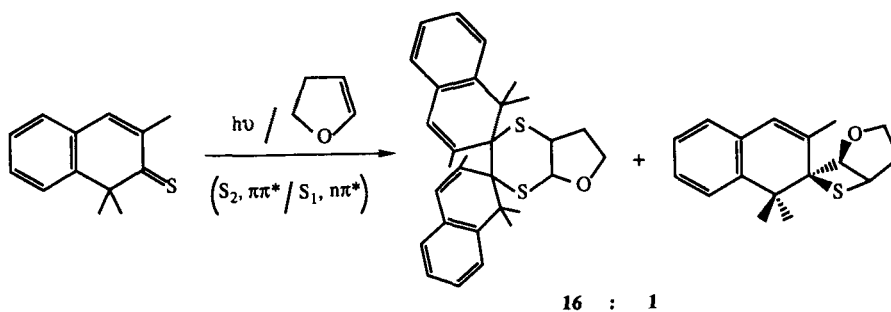
Scheme 41

and the formation of thietane is regiospecific. The ratio of thietane to dithiane in the product mixture is dependent on the concentration of the enethione. This addition is suggested to originate from the lowest triplet state (T_1) and involves diradical intermediates. In conclusion, Rao and Ramamurthy demonstrated that the behavior of enethiones toward olefins is quite different from that of the corresponding enones, in the latter system addition of olefins occurs to the carbon–carbon double bond. Comparison of the photochemical behavior of thioenones toward olefins with that of saturated thioketones reveals that the conjugation present in enethiones has a special influence on the photoproduct formation.
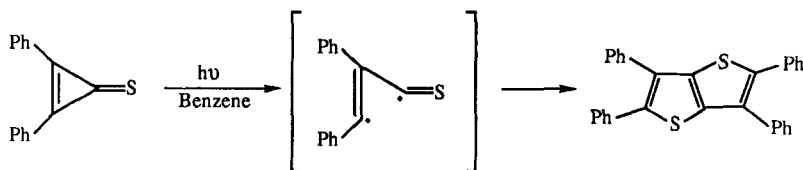
Scheme 42

Strained conjugated thioketones such as cyclopropenethiones have been reported to undergo a special type of dimerization (not of a conventional [2 + 2] type) via Norrish type I α-cleavage from the lowest triplet state.[100] Diphenylcyclopropenethione upon excitation into either S_1 ($n\pi^*$) or S_2 ($\pi\pi^*$) bands in benzene results in a dimer, thieno[3,2-b]thiophene (Scheme 42). Quenching and sensitization studies established T_1 as the
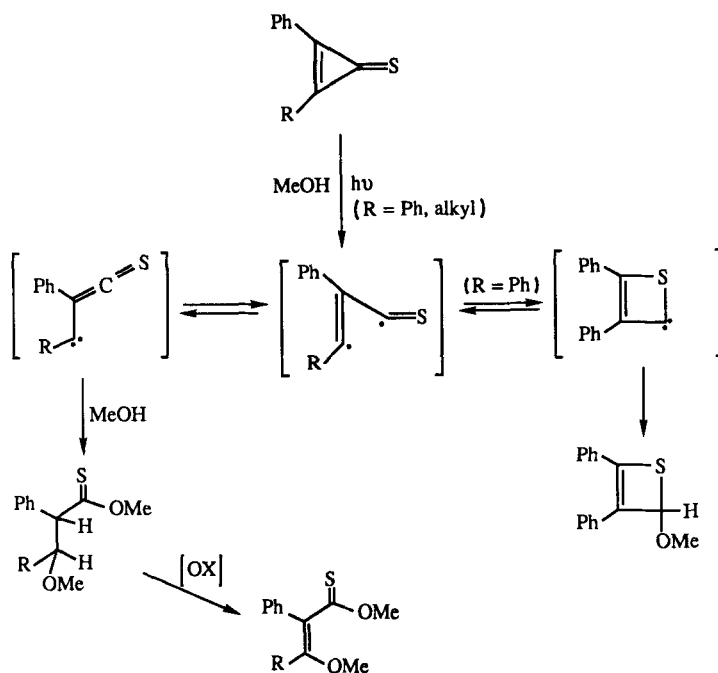
Scheme 43

reactive state. The same thioketone in alcoholic solvents produces α-cleavage derived products: 4-methoxythiete and 3-methoxythiocinnamate (Scheme 43). The former product could result from a cyclic carbene, whereas the latter one from a ring opened thioketene carbene. A remarkable regioselectivity is observed during the α-cleavage process of arylalkylcyclopropenethiones.[101] A reasonable rationale to account for this behavior has been offered with the use of MINDO semi-empirical calculations.[102] Comparison of the behavior of cyclopropenethiones with that of the structurally analogous cyclopropenones reveals that while the α-cleavage process leads to the elimination of carbon monoxide in the former systems, such an elimination is not feasible in the latter systems. Thus, there is a similarity in the photobehavior of strained conjugated thioketones and cyclobutanethiones.

3.5.2. Cross-conjugated thiones   Excited state behavior of only two thioketones has been studied in this category. Pyran-4-thione[103] on irradiation undergoes dimerization through its thiocarbonyl function and yields a dimeric olefin shown in Scheme 44. This dimerization has been suggested to proceed from the lowest excited triplet state. Pyridine-4-thione has been reported to undergo cycloadditions to olefins to give thietanes as the only intermediates: the isolated products have always been pyridine derivatives (Scheme 44).[104]


R=H,Ph

R = CN; COOMe
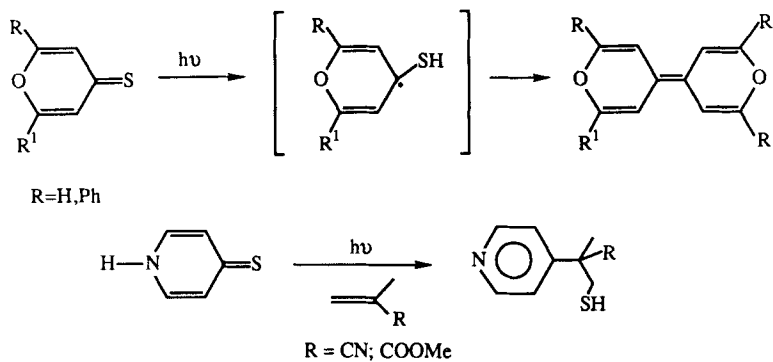
Scheme 44

3.5.3. Conjugated thiolactones and thiolactams   In this class of compounds, addition of thiocoumarin to olefins has been studied systematically.[105] Similar to conjugated thioketones, addition occurs only to the thiocarbonyl function and not to the carbon–carbon double bond (Scheme 45). The only products are thietanes; no dithiane formation is observed even with electron-rich olefins. With respect to the reactive excited state causing the addition, there is no distinction between electron-deficient and electron-rich olefins. All the olefins react only from the lowest excited triplet. The addition is neither regio- nor stereoselective. The suggested mechanism involves intermediates of both diradical and exciplex type. Photochemical addition of 1,2-dithiole-3-thione (another type of conjugated dithiolactone) to olefins results in a cyclic adduct which is different
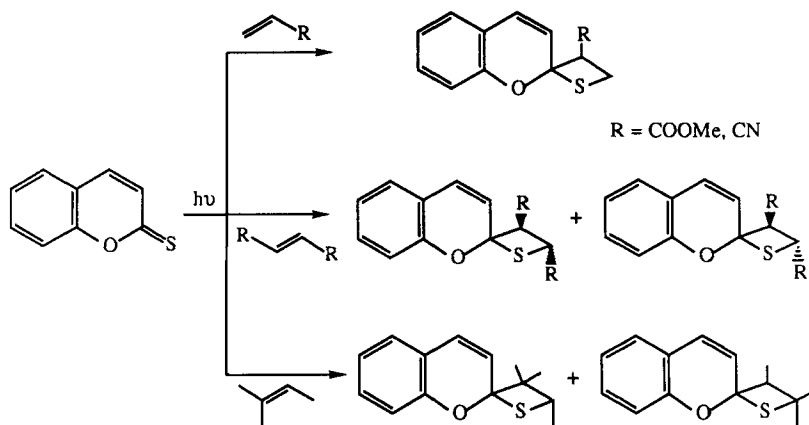
Scheme 45

from the commonly observed thietane adduct (Scheme 46).[106] The addition has been inferred to originate from the T_1 excited state. The observed addition product reveals the involvement of the adjacent conjugated double bond. It is proposed that the initial attack of the olefin takes place on the thiocarbonyl function and the resultant diradical follows a different pathway to yield the observed adduct instead of undergoing a simple cyclization to give a thietane. In some cases, this diradical leads to products via intramolecular hydrogen transfer.[107]
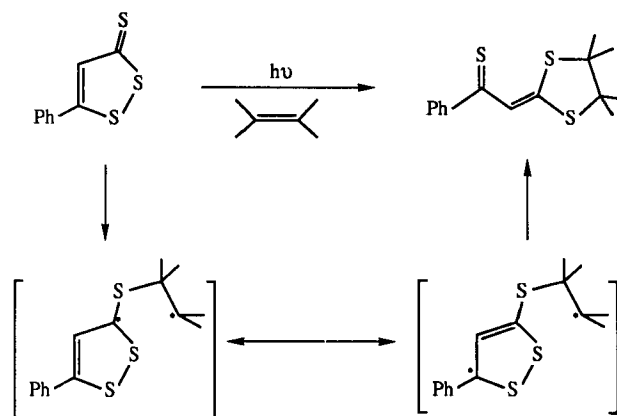
Scheme 46

Conjugated thiocarbonyl compounds such as thiouracil derivatives undergo photoreduction in the presence of amine donors.[108] These reactions originate from the lowest triplet state and are believed to proceed via electron transfer processes. Thiouracil substituted at the 2-position by hydroxyalkyl groups, upon excitation into the S_1 band, suffers intramolecular hydrogen abstraction to yield a 1,2- or 1,3-diradical. This does not undergo the usual cyclization or elimination. Instead, it takes an alternative path-

50% n = 1; R = Me

30% n = 2; R = H
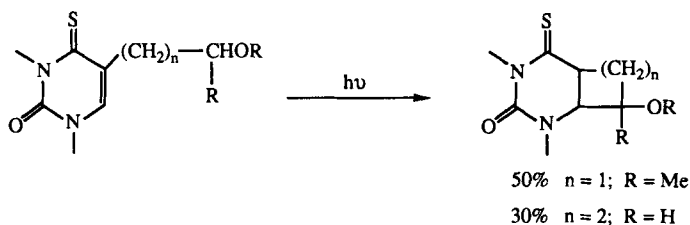
Scheme 47

way which involves the delocalization of the adjacent carbon–carbon double bond (Scheme 47).[109] The validity of this novel cyclization is yet to be tested in more general systems. Thiouracil, thiouridine derivatives, pyridine-2-thiones and pyrimidinethiones have been reported to undergo cycloaddition to olefins to give thietanes or olefins derived therefrom.[110]

3.6. Miscellaneous Thiocarbonyl Compounds

A very brief discussion of the photochemical behavior of the less conventional thiocarbonyl compounds (viz. thioketenes,[111] thiocarbonates,[112] thiocarbamates,[113] thioparabanates[114] and thioaldehydes[115]) is included in this section. Attention has been paid only to those reactions which represent the general photochemical behavior of these classes and no effort is made to include the mechanistic details of these less explored classes.

3.6.1. Thioketenes[111] Two photoreactions of stable thioketenes in solution have been investigated for the first time by Ramamurthy *et al.* The observed photochemical behavior is unique and cannot be extrapolated from that of the structurally analogous ketenes and ketenimines. In benzene, di-*t*-butyl thioketene on excitation with 254 nm light reacts to give a photoadduct with benzene (Scheme 48). The same thioketene in
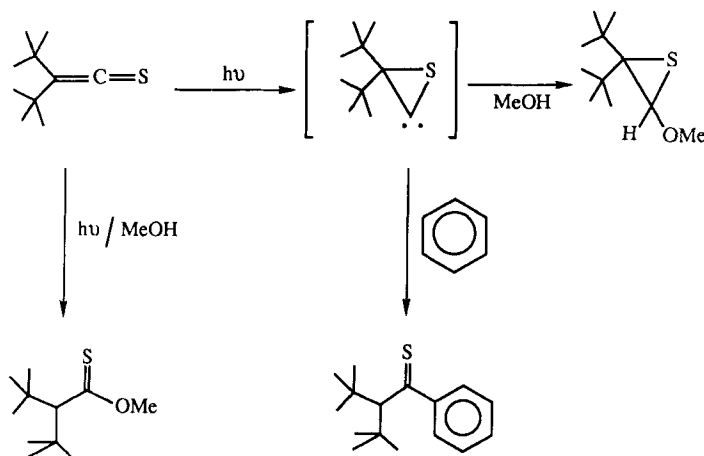
Scheme 48

alcoholic solvents gives an *O*-alkyl thioester and an alkoxythiirane as photoproducts: it is proposed that the thiirane arises by way of a cyclic thiirenylcarbene which may be the intermediate that initiates the attack on the benzene ring. Based on quenching studies it is proposed that the second excited singlet state is responsible for bringing out this transformation. Excitation of the thioketene into its first excited singlet state does not lead to any detectable photoreaction. In contrast to the photooxidation behavior of thioketones, direct excitation of thioketenes leading to oxidation products is very slow. However, oxidation of thioketenes by singlet oxygen yields a number of products.[11c,d] Most of the observed oxidation products are quite unexpected by analogy to the photobehavior of ketenes and ketenimines.

3.6.2. Thiocarbonates[112] The photoreactions identified in this class of compounds include α- and β-cleavages, dimerization and rearrangement. Like in dithioesters, cleavage is a common feature in thiocarbonates. As shown in Scheme 49, diaryl trithiocarbonates on excitation lose carbon monosulfide via α-cleavage to produce diaryl sulfides. A β-cleavage has been proposed to be an initial process in the photoconversion of bis(trifluoromethyl) trithiocarbonate to hexakis[(trifluoromethyl)-thio]ethane and in the production of olefins from the photolysis of cyclic trithiocarbonates. 1,3-Dithiole-2-thiones on excitation in solution form dimeric, desulfurated products such as tetra-thiafulvalenes which have extensive applications as their charge-transfer salts. More recently, a photoinduced rearrangement of 4,5-(ethylenedithio)-1,3-dithiole-2-thione to the isomeric 4,5-(ethylenedithio)-1,2-dithiole-3-thione has been reported.
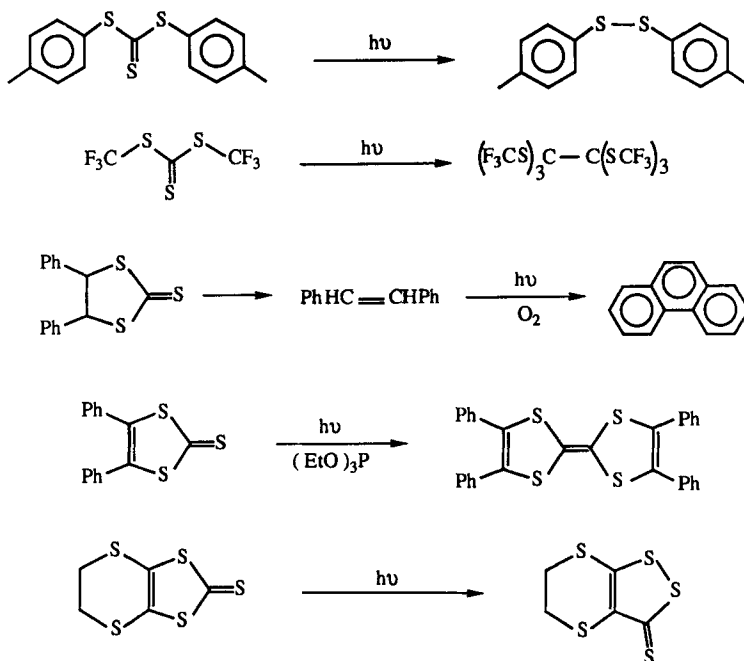
Scheme 49

3.6.3. Thioparabanates[114]   Similar to thioketones, thioparabanates undergo photo-reduction and photocycloaddition reactions. The products isolated as well as the mechanism of the reaction are similar to those presented for other thiocarbonyl com-pounds. A representative example of photoreduction and photoaddition reactions observed in the irradiation of a thioparabanate in alcoholic solvents is shown in Scheme 50.
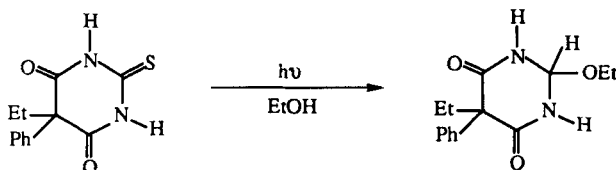
Scheme 50

3.6.4. Thioaldehydes[115]   Most thioaldehydes are unstable at room temperature and are characterized as their [4 + 2] adducts with dienes. Thiopivaldehyde is the first aliphatic thioaldehyde to be characterized under normal laboratory conditions. An interesting photocyclization via hydrogen abstraction has been reported with 2,4,6-tri-*t*-butyl-thiobenzaldehyde (Scheme 51). This constitutes one of the very few examples where the cyclization leads to a new carbon–sulfur bond instead of a carbon–carbon bond. Photocycloaddition of the same thioaldehyde to cumulenes has also been studied.
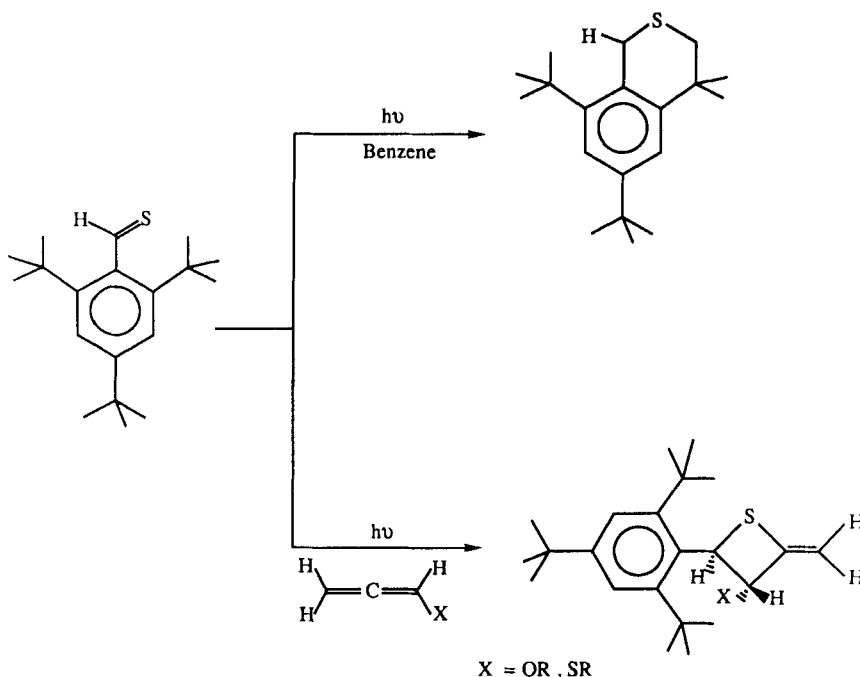
X = OR , SR

Scheme 51

ACKNOWLEDGMENTS

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