

PHOTOCHEMISTRY OF NITROGEN-CONTAINING THIOCARBONYL
COMPOUNDS

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Abstract- Photochemical reactions of nitrogen-containing thiocarbonyl compounds, such as thioamides and thioimides, are reviewed. The thiocarbonyl compounds exhibit high photochemical reactivity for [2+2] photocycloaddition with alkenes leading to thietanes; this is often followed by ring opening-reaction or rearrangement. Photochemical hydrogen abstraction of thioimides gives lactams and cyclic amines. Some thioamides show activity for cyclization *via* electron transfer, α -cleavage reaction, desulfurization and other miscellaneous reactions. The photochemical reaction of thioamides and thioimides provides not only a new photochemical aspect in the area of organic photochemistry but also a useful synthesis of nitrogen-containing heterocycles.

1. INTRODUCTION

The photochemistry of thiocarbonyl compounds has been extensively studied over the past three decades, and many new photochemical reactions are developed.¹⁻⁷ Thiocarbonyl compounds, such as thioketones and thioesters, show considerably high photochemical reactivity toward [2+2] cycloaddition and hydrogen abstraction by thiocarbonyl sulfur. However, they are not easy to handle, because of unpleasant odors, high reactivity leading to the formation of dimers, trimers or polymers, and a strong tendency to thienolyze with an α -hydrogen atom. On the other hand, thioamides and thioimides possessing C(=S)-N function are easily available and generally obtained as stable solids. Most

of the thietane ring leading to zwitterions (**B**) or diradicals (**C**), followed by subsequent reactions. The unstability of aminothietanes (**A**) may be ascribed to the participation of lone-pair electrons on the nitrogen atom. Therefore, suppressing the participation will stabilize the aminothietanes. In fact, thietanes derived from thioimides, which nitrogen atom is cross-conjugated with a carbonyl or thiocarbonyl group, show considerable stability, and many such thietanes are isolated. The photochemical cycloaddition of thioamides and thioimides with multiple bonds provides a facile route for the formation of new C-C bonds of nitrogen-containing heterocycles.

2.1.1 PHOTOCHEMICAL [2+2] CYCLOADDITION REACTION OF THIOAMIDES

Photoreaction of six-membered thioamides, such as pyridinethiones, acridinethiones, pyrimidinethiones, pyridazinethiones, thiouracils and thiouridines as shown in **Figure 1** gives a variety of types of adducts in the presence of alkenes, where thietanes are believed to be intermediates. Most of the reactions are already documented in previous reviews.⁸⁻¹¹

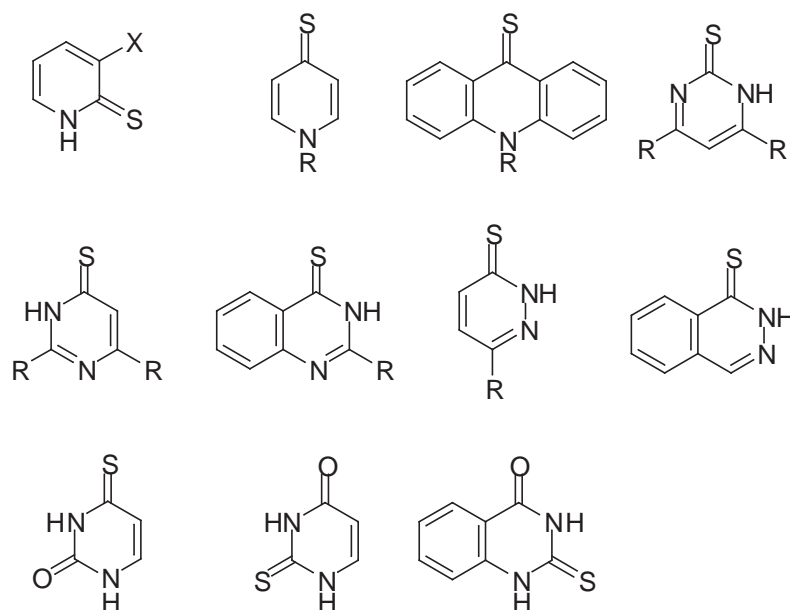
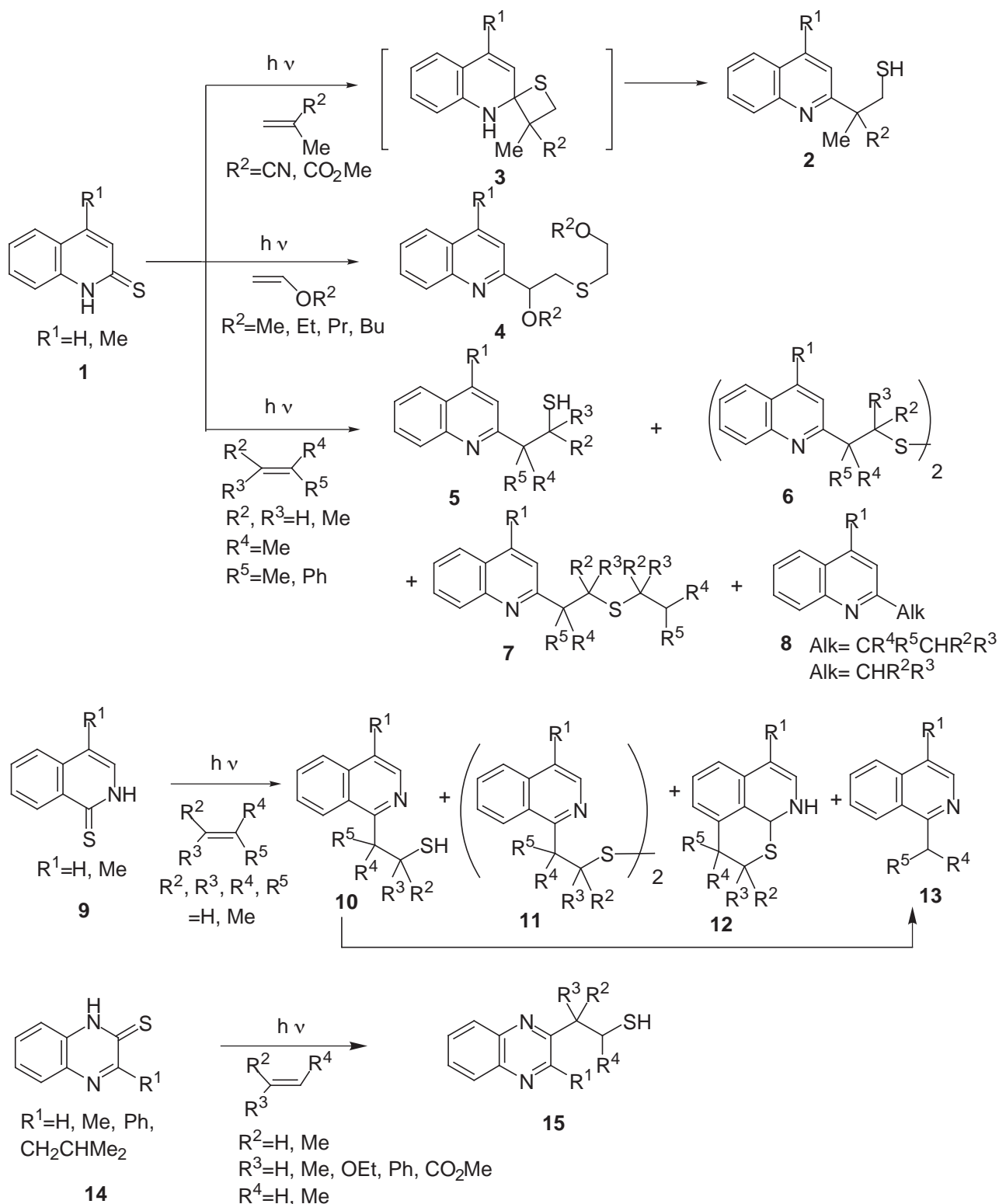


Figure 1

Photochemical reaction of benzo-analogues, quinoline-2-thiones (**1**), in the presence of electron-deficient alkenes gives 1:1 photoadducts (**2**) *via* a thietane intermediate (**3**). Irradiation of **1** in the presence of alkyl vinyl ether gives 1:2 adducts (**4**). On the other hand, irradiation with other electron-rich alkenes, such as isobutene or 2,3-dimethylbut-2-ene, gives various products (**5-8**). The transpositional isomer, isoquinoline-2-thiones (**9**), also gives many types of adducts (**10-13**) upon irradiation in the presence of electron-rich alkenes.¹²⁻¹⁵

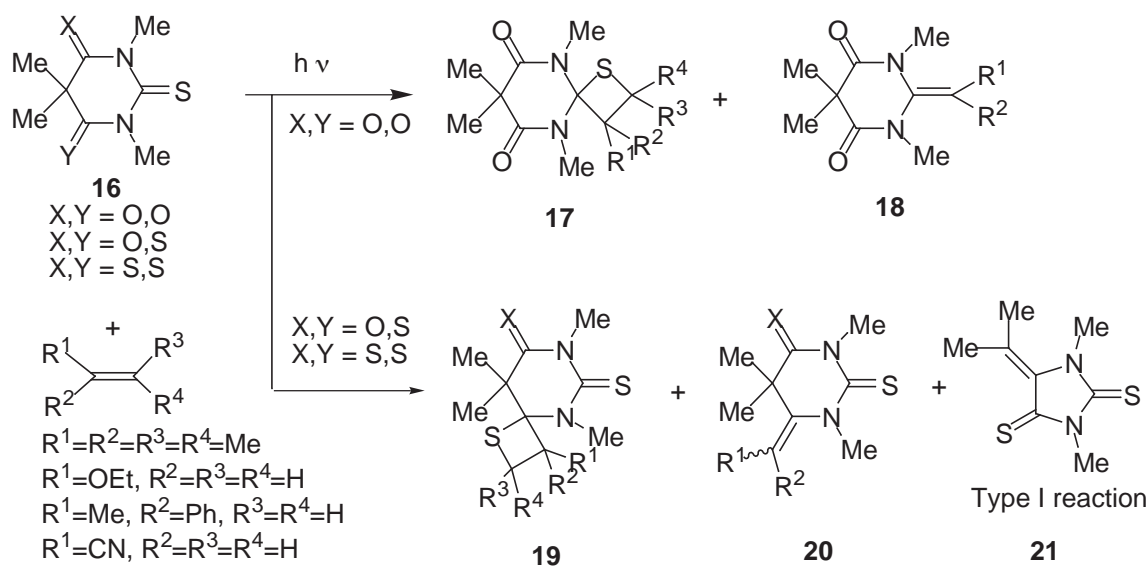
Thietanes are also intermediates in the photoreaction of quinoxaline-2-thiones (**14**) with alkenes leading

to 2-substituted quinoxalines (**15**).¹⁶ This behavior is strikingly different from the photoreaction of oxo-analogues, quinoxalin-2-ones, which undergo photoaddition to carbon-nitrogen double bonds. Thiobarbiturates (**16**) undergo [2+2] cycloaddition with alkenes (2,3-dimethylbut-2-ene, ethyl vinyl ether,



Scheme 2

α -methylstyrene, acrylonitrile) to give the thietanes (**17**) and the methylene derivatives (**18**) by secondary photolysis involving elimination of either thioacetone or thioformaldehyde (**Scheme 3**).^{17,18} Dithiobarbiturate and trithiobarbiturate undergo analogous reactions. For trithiobarbiturate a competing conversion to dithiohydantoin (**21**) occurs in all cases accompanied by the formation of **19** and **20**, possibly involving α -cleavage reaction adjacent to the gem-dimethyl group, reclosure to form a sulfur heterocycle and subsequent carbon-carbon bond formation with exclusion of sulfur.

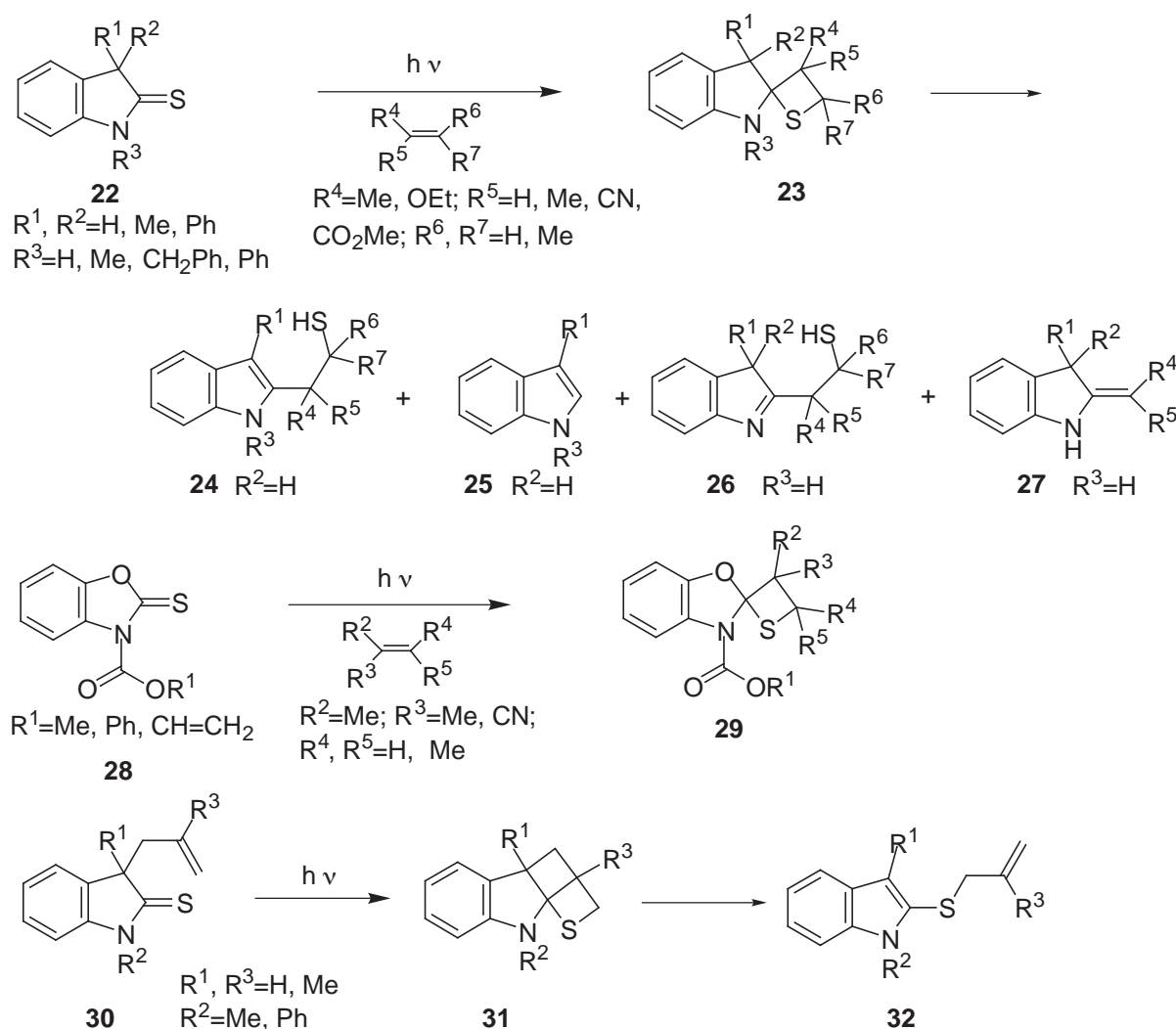


Scheme 3

Irradiation of indoline-2-thiones (**22**) in the presence of alkenes gives 2-alkyl-3*H*-indoles and 2-alkylindoles (**24-27**) through the ring cleavage of the intermediates, spirocyclic aminothietanes (**23**), initially derived by [2+2] cycloaddition of the C=S bond and alkenes (**Scheme 4**).¹⁹ Stable aminothietanes (**29**) have been isolated and characterized from the regiospecific photoaddition of *N*-alkyloxycarbonyl-2-thiones (**28**) to alkenes. The *N*-vinyloxycarbonyl derivative (**28**: R = -CH=CH₂) undergoes intramolecular [2+2] cycloaddition to give the analogous multi-fused aminothietane.²⁰ Intramolecular photoaddition has been also reported in the photoreaction of **30**, in which allyl indole sulfide (**32**) is obtained.²¹ The highly strained aminothietane intermediate (**31**) is also proposed for the reaction.

Photolysis of indoline-1-thiones (**33**), which are the structural isomer of indoline-2-thiones, undergoes cycloaddition with various electron-rich and deficient alkenes, yielding tricyclic isoindoline derivatives (**34**).²² The plausible mechanism for this transformation is explained in **Scheme 5**, and involves aminothietane intermediate (**35**), which undergoes ring opening to form zwitterions, followed by further reaction. In contrast to isoindoline-1-thiones (**33**), stable thietanes (**38, 39**) are formed by the

photoreaction of isobenzofuran-1-thione (**36**) and isobenzothiophene-1-thione (**37**) in the presence of alkenes.²³



Scheme 4

Irradiation of a benzene solution of 4-ethoxy-2,3-dihydro-1*H*-pyrrole-2-thione (**40**) and electron-rich alkenes gives 2-mercaptoalkylpyrroles (**41**), which are alkylated with methyl iodide to give **42**.²⁴

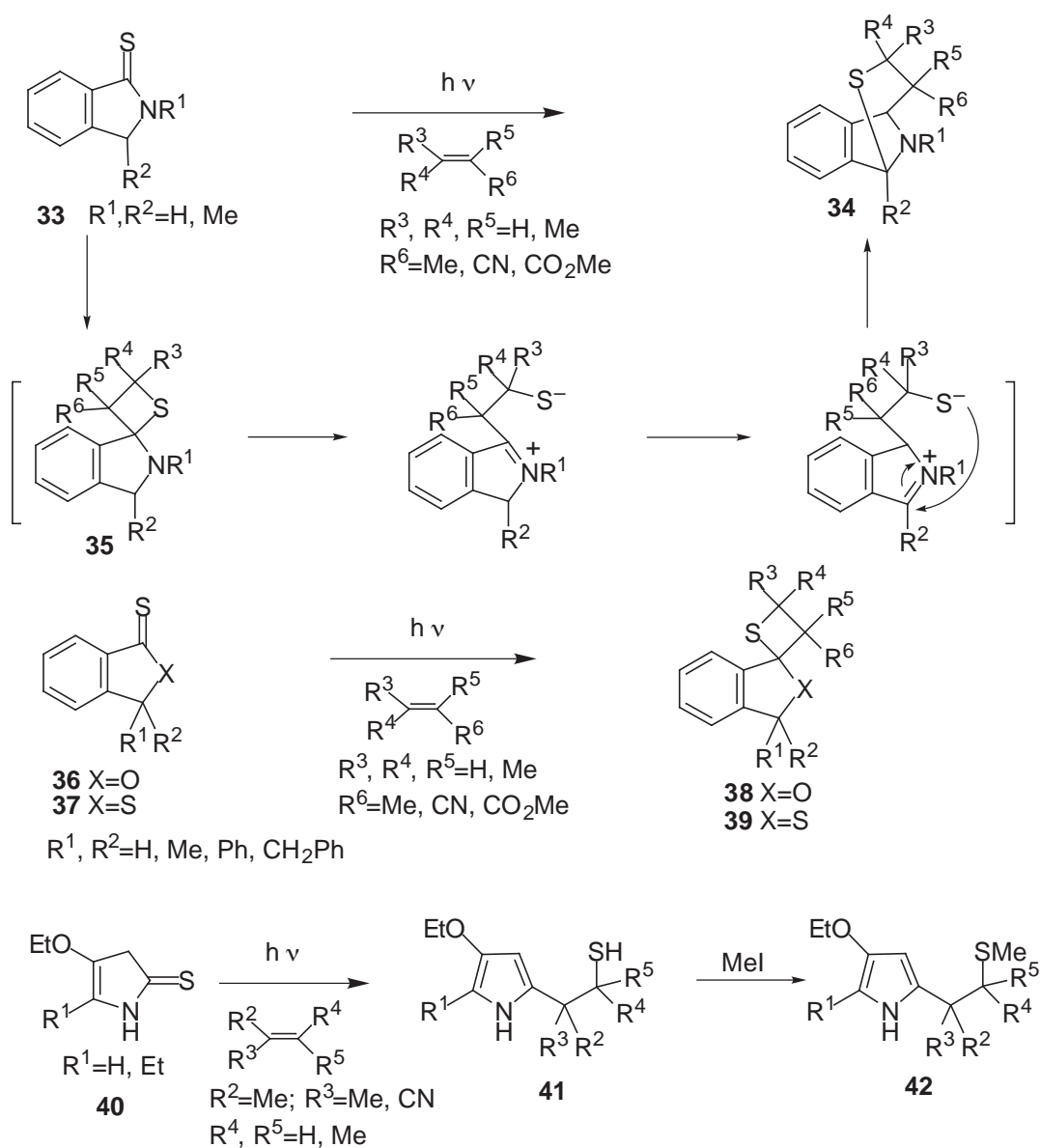
Photochemical addition of benzoxazoline-2-thiones (**43**) to alkenes affords the 2-substituted benzoxazolines (**44-46**) or ring-opened products (**47**) depending on the substituent R^1 and alkenes used. The formation of these products may be rationalized in terms of zwitterionic intermediate (**48**), from ring-opening of an aminothietane, formed by regioselective [2+2] photoaddition of C=S bond of **43** to C=C bond of alkene as shown in **Scheme 6**.^{25,26}

N-Acybenzoxazole-2-thiones (**49**) also photocycloadd to alkenes regioselectively to give the 2-substituted benzoxazoles (**51, 52**) and/or the imino-thietanes (**53**) by intramolecular trapping of zwitterionic intermediates (**54**) and (**55**), respectively.^{26,27}

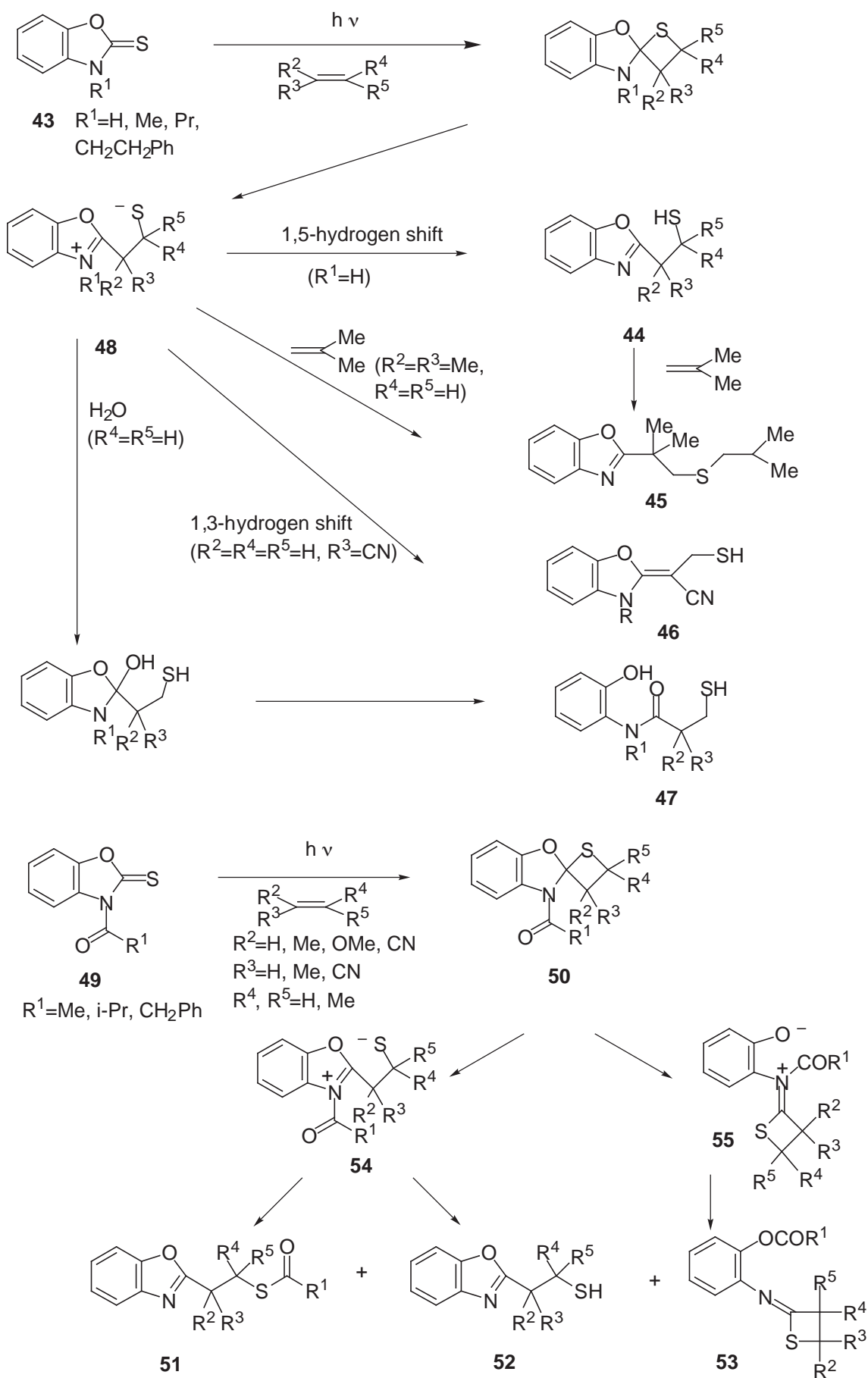
Irradiation of benzothiazoline-2-thiones (**56**) and acrylonitrile affords 2-alkylidenethiazoles (**57**). On

the other hand, two products (**58**, **59**) are formed by the photoaddition of **56** with 1,1-disubstituted alkenes such as methacrylonitrile and methyl methacrylate.²⁸ Aminothietanes are proposed as intermediates in these photoreactions. Thioformaldehyde formed by the decomposition of the intermediate has been detected by trapping by diene. Photocycloaddition reaction of *N*-unsubstituted benzothiazole-2-thione (**60**) with electron-rich alkenes gives 2-substituted benzothiazole (**61**), whereas that of *N*-methyl derivatives (**62**) to 2,3-dimethylbut-2-ene gives three types of products (**63-65**) via aminothietanes.²⁹

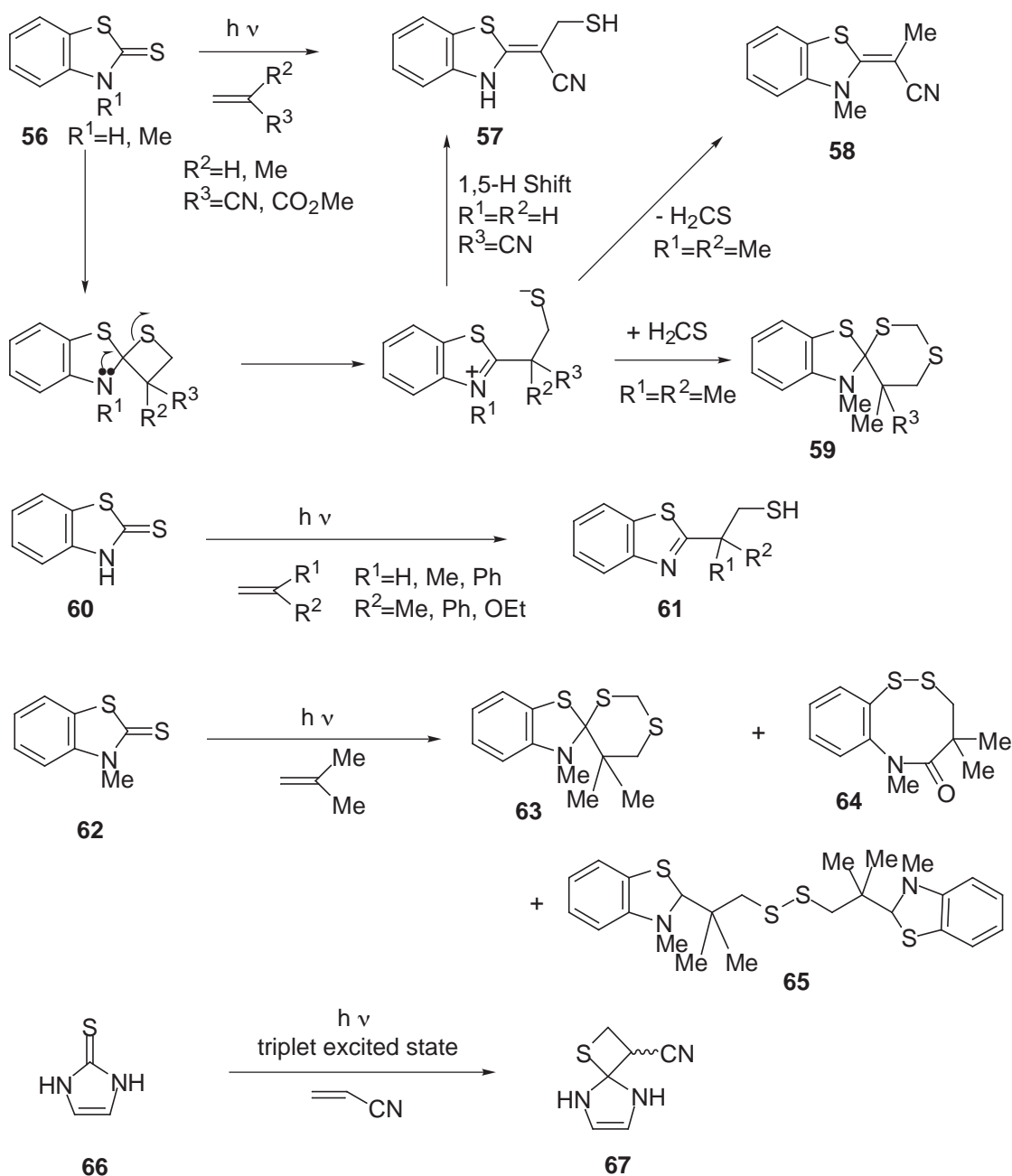
Laser flash photolysis has been used to identify that the triplet excited state of **66** is involved in the addition reaction which occurs to electron-deficient alkenes such as acrylonitrile giving thietane (**67**), for example.³⁰



Scheme 5



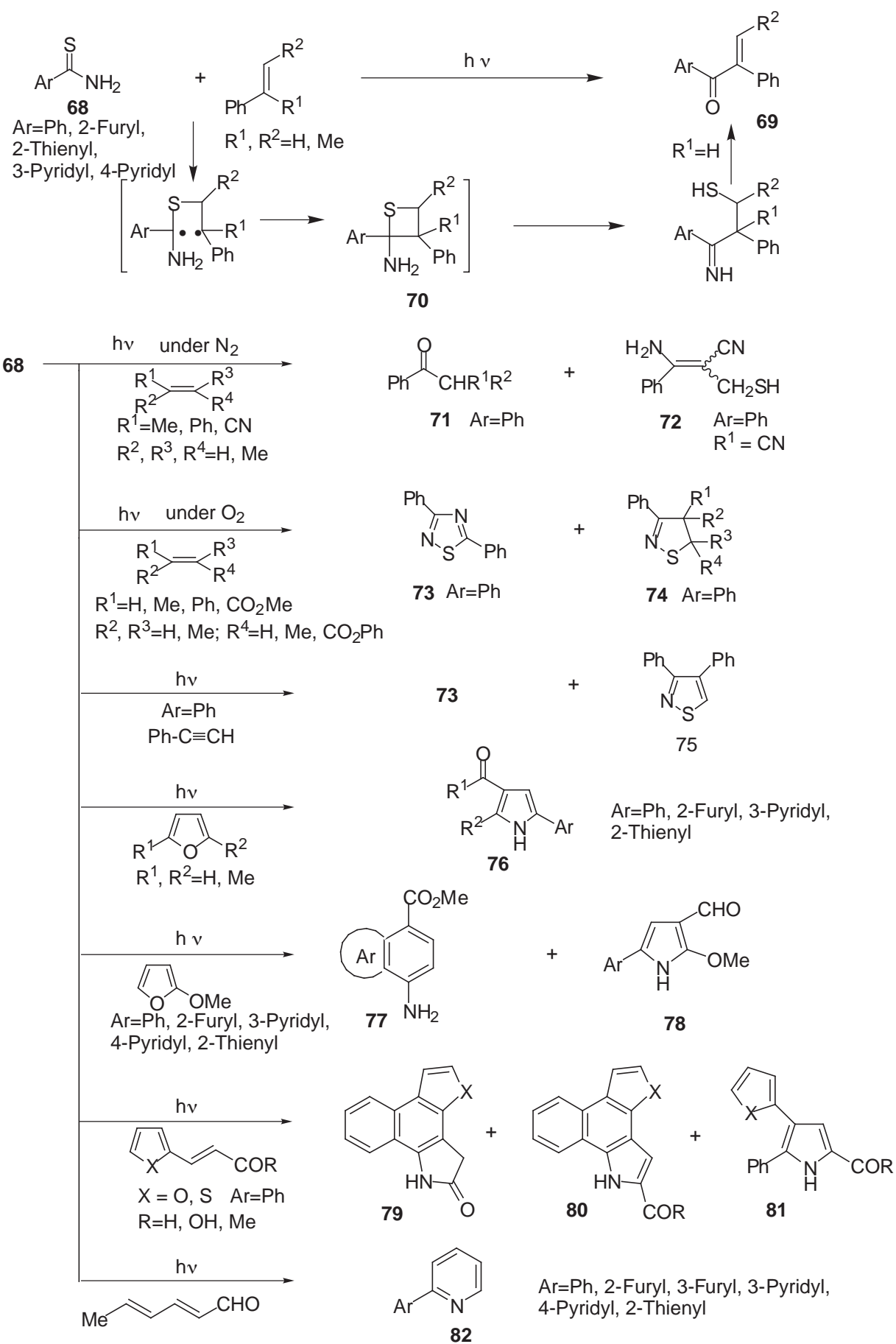
Scheme 6



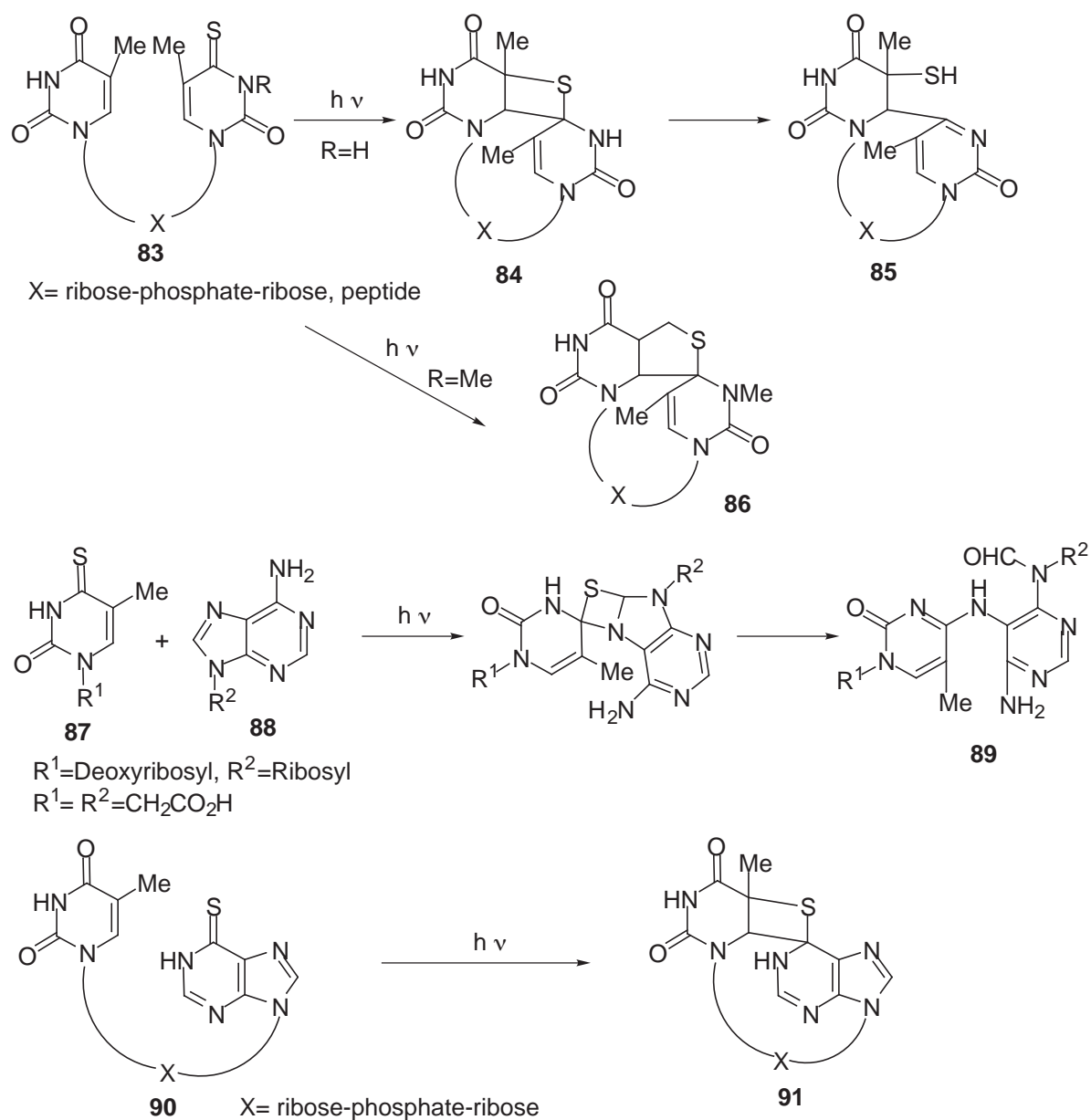
Scheme 7

The formation of enones (**69**) by irradiation of the arylcarbothioamides (**68**) in the presence of styrene derivatives proceeds by initial formation of the thietane (**70**): this conversion provides a potentially valuable route for the arylation of simple alkenes as shown in **Scheme 8**.³¹ Several types of photoproducts are obtained by the irradiation of **68** in the presence of alkenes, which depend on the alkenes used and the reaction conditions.

Irradiation of arylcarbothioamide (**68**) with alkenes under nitrogen atmosphere gives arylketone (**71**) and thiol (**72**).³² The reaction takes a different course in the presence of oxygen and yields 1,2,4-thiadiazoles (**73**) and isothiazol (**74**).



Scheme 8



Scheme 9

Photoaddition of **68** toward acetylene gives **73** and isotiazole (**75**). Irradiation of **68** in the presence of five-membered heteroaromatics such as furan, thiophene, and pyrrole in benzene regioselectively gives the corresponding 3-arylpyrrol derivatives (**76**).^{33,34} For the formation of **76**, cycloaddition of the C-N bond with furan was proposed.³⁵⁻³⁷ Photolysis with 2-methoxyfuran yields unstable thietanes which rearrange to give moderate yields of benzo-fused arene derivatives (**77**) and pyrrole derivatives (**78**).^{38,39} The intermediary of the thietane is suggested in the formation of the fused furan and thiophene derivatives (**79-81**) which are produced from irradiation of thiobenzamide with 2-vinylfurans and thiophenes.^{40,41} Irradiation of **68** in the presence of aldehyde gives tetracyclic imidazole,⁴² and pyridine derivatives (**82**) are obtained by the photolysis of thioamide in the presence of diene (**Scheme 8**).⁴³

Intramolecular photocycloaddition is also reported to occur in the thiothymidine thymidinyI phosphates (**83**) and this gives the thietane (**84**) and the ring-opened thiol (**85**).^{44,45} The importance of this process is related to lesion in DNA. Thietane formation has been observed in the thymidylthiothymidine (**83**; R=Me); on irradiation, it gives a new types of photoproduct (**86**) in the nucleic acid series which involves attack of the thiocarbonyl across the propene moiety of the thymidine ring.⁴⁶

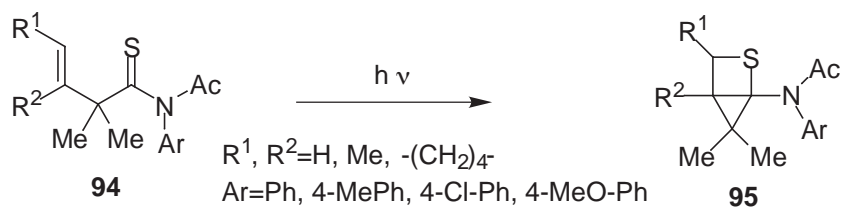
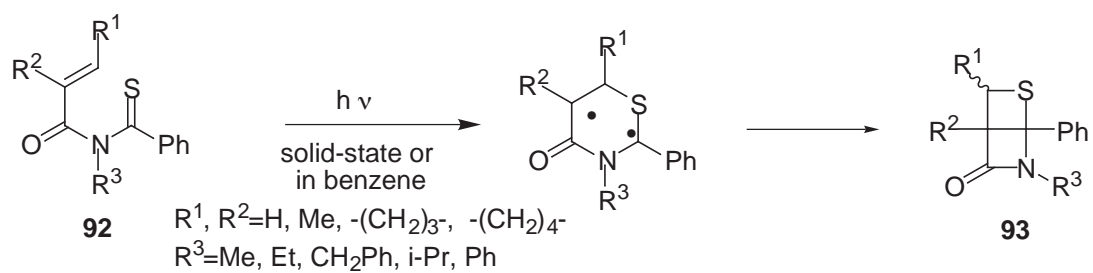
Irradiation at 366 nm in aqueous solution of the thiothymine (**87**) in the presence of adenine derivative (**88**) results in the formation of the adduct (**89**): this is formed presumably by way of the [2+2] cycloaddition reaction between the C=S and the C=N bonds as shown in **Scheme 9**.⁴⁷ Intermolecular [2+2] cycloaddition is also reported in the photoreaction of **87** with pyrimidinone derivative.⁴⁸ Intramolecular photocycloaddition also occurs between two heterocycles tethered with ribose-phosphate-ribose in **90**, and thietane (**91**) is obtained.⁴⁹⁻⁵¹

2.1.2 PHOTOCHEMICAL [2+2] CYCLOADDITION REACTION OF THIOIMIDES

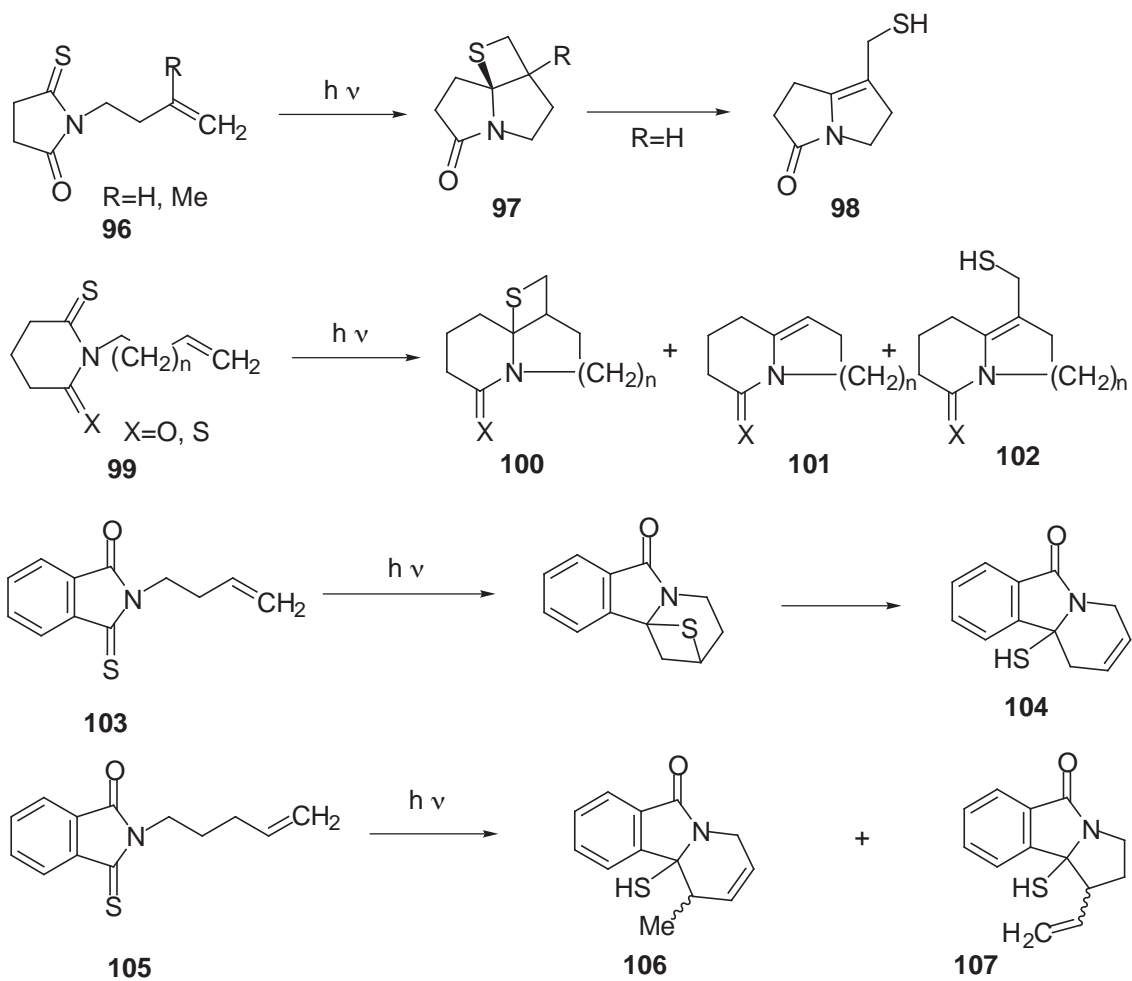
Many mono- and di-thioimides show high reactivity for intra- and intermolecular [2+2] cycloaddition with alkenes. Introduction of an acyl group to the amide function shares the lone pair electrons of nitrogen atoms into carbonyl and thiocarbonyl groups; also, the acyl group of aminothietane decreases the activity for ring-opening reaction. Therefore, stable thietanes are isolated in many cases. This reaction provides a powerful method to synthesize nitrogen-containing heterocycles by efficient modeling of the starting materials.

Photoreaction of the acyclic imides (**92**) promotes [2+2] cycloaddition to thietane-fused β -lactams (**93**) (**Scheme 10**).⁵² Since the mechanism involves the 1,4-diradical intermediate, more efficient reaction occurs when R² is not hydrogen. Furthermore, the imide (**92**: R¹=H, R²=Me, R³=Ph) crystallizes in a chiral fashion, and the solid-state photoreaction gives an optically active product.⁵³ Irradiation of a benzene solution of *N*-[(*R*)-phenyl]-*N*-tigloylthiobenzamide, for example, gives four stereoisomeric β -lactams. On the contrary, high diastereoselectivity has been observed in the corresponding solid-state photoreaction.⁵⁴

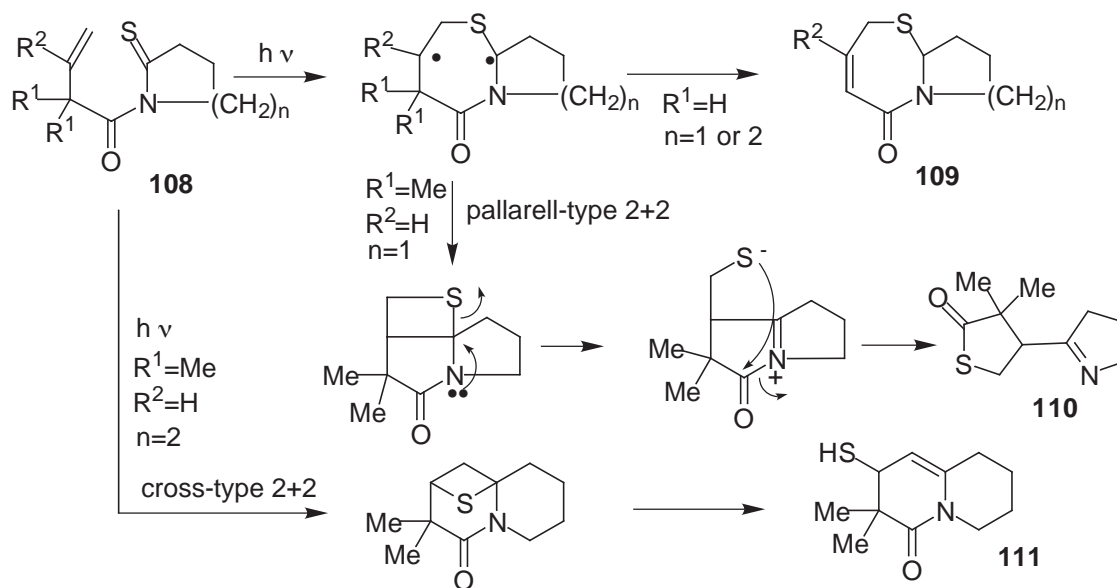
The intramolecular [2+2] cycloaddition is observed in β,γ -unsaturated thioimides (**94**) which have been converted photochemically into the 2-thiabicyclo[2.1.0]pentanes (**95**) in high yields.⁵⁵ Cyclic thioimides (**96**) undergo intramolecular photocycloaddition in a regiospecific manner to afford spirocyclic amidothietanes (**97**) (**Scheme 11**).^{56,57} These highly strained multicycles undergo a subsequent ring-opening reaction to furnish novel fused pyrrolidinones (**98**). Intramolecular photoreaction of *N*-(3-alkenyl)- or *N*-(4-alkenyl)glutarimides (**99**), gives thietanes (**100**) and their fission products (**101**, **102**).⁵⁸ Similarly, intramolecular thietane formation is observed in the photolysis of cyclic monothioimides (**103**),



Scheme 10



Scheme 11



Scheme 12

and thiol (**104**) is isolated.⁵⁹ Photolysis of **105** also gives the fission products (**106**) accompanied by **107**, which is formed by hydrogen abstraction by thiocarbonyl sulfur atom.⁸ Photoreaction of thioimides (**108**) gives lactams (**109**) and thiolactone (**110**), in which the products are dependent on the substituents on the alkenes and the ring size of thiolactam chromophore (**Scheme 12**).⁶⁰ Photoproducts (**109**, **110**) are formed *via* parallel-type C-S bond formation, and another type [2+2] cycloaddition leads to bicyclic lactam (**111**).

Photoreaction of cyclic thiocarbamates (**112**) also proceeds thietane formation, which is followed by ring opening reaction leading to oxylanes (**113**) (**Scheme 13**).⁶¹ Semicyclic thiocarbamates or dithiocarbamates (**114**) give tricyclic β -lactams (**115**) and β -thiolactones (**116**).⁶² The formation of **116** is reasonably explained *via* a zwitterionic intermediate (**117**). Irradiation of *N*-(β,γ -unsaturated carbonyl)thiocarbamates and -dithiocarbamates (**118**) promotes [2+2] thietane formation, and subsequently yields bicyclic lactams (**119**) and γ -thiolactone derivatives (**120**).⁶³ Similar reaction also proceeds in the solid-state, and absolute asymmetric synthesis is performed from the photoreaction of acyclic β,γ -unsaturated carbonylthionocarbamate (**121**) leading to optically active thiolactones (**122**).⁶⁴ Many other cyclic, semicyclic, and acyclic thioimides give the corresponding thietanes by intermolecular reaction when they are irradiated in the presence of variety of alkenes, alkynes, allenes, or ketenes.⁸⁻¹¹

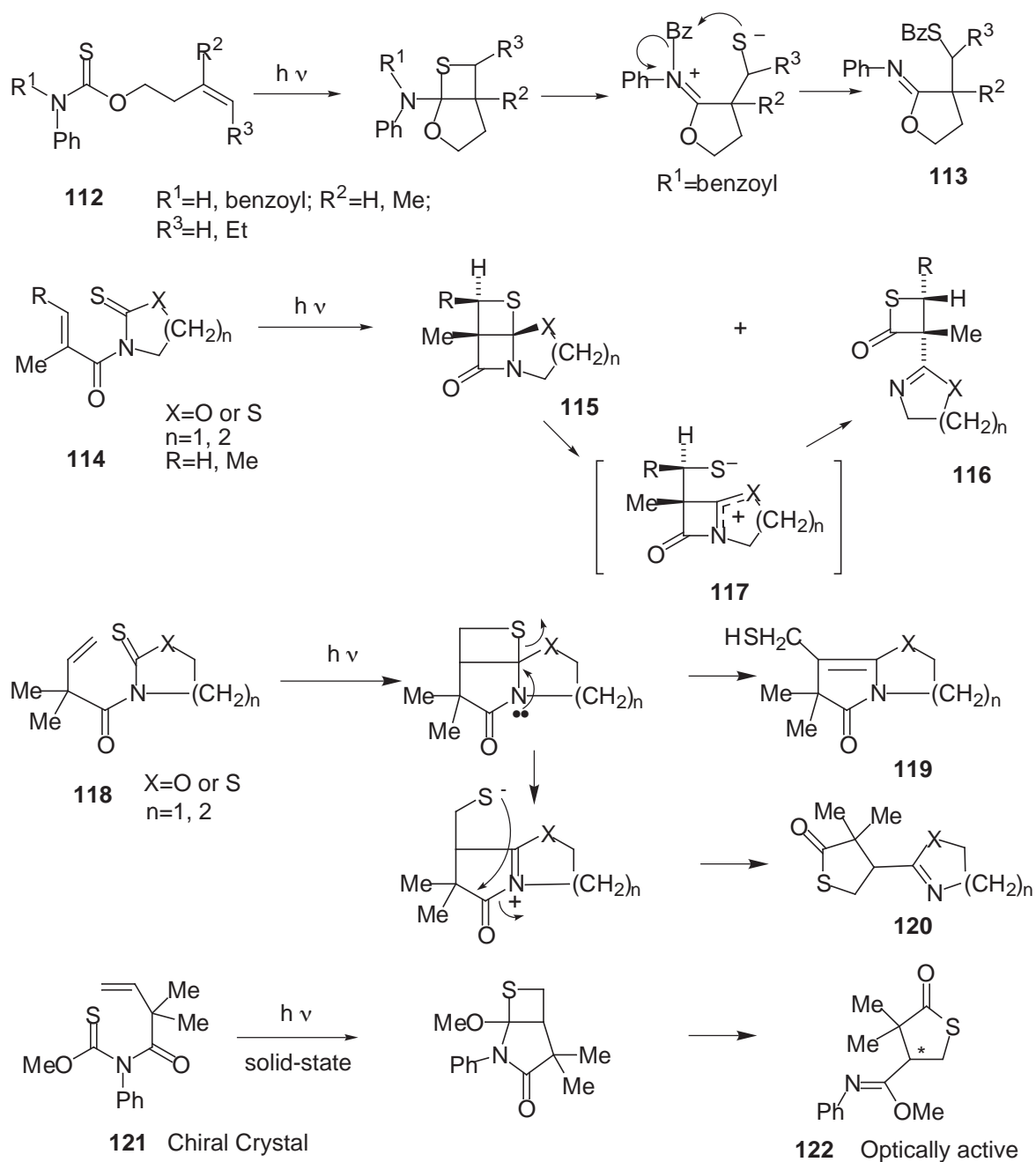
2.2 PHOTOCHEMICAL HYDROGEN ABSTRACTION OF THIOAMIDES AND THIOIMIDES

Photochemical hydrogen abstraction of a thiocarbonyl function is a common reaction, the same as [2+2] cycloaddition. This process is generally inert in the photochemistry of thioamides; however, thioimides undergo hydrogen abstraction by thiocarbonyl sulfur of (C=S)-N chromophore from the β , γ , δ -position

to yield various heterocycles.

A rare example has been reported for the hydrogen abstraction reaction of thioamides. Irradiation of amide (**123**) proceeds β -hydrogen abstraction to generate a 1,3-diradical intermediate, where 1,3-hydrogen shift occurs and results in two pathways. One is the formation of thioenamides (**124**), the other is cyclization of a 1,5-diradical intermediate to yield pyrrole derivatives (**125**) (**Scheme 14**).⁶⁵

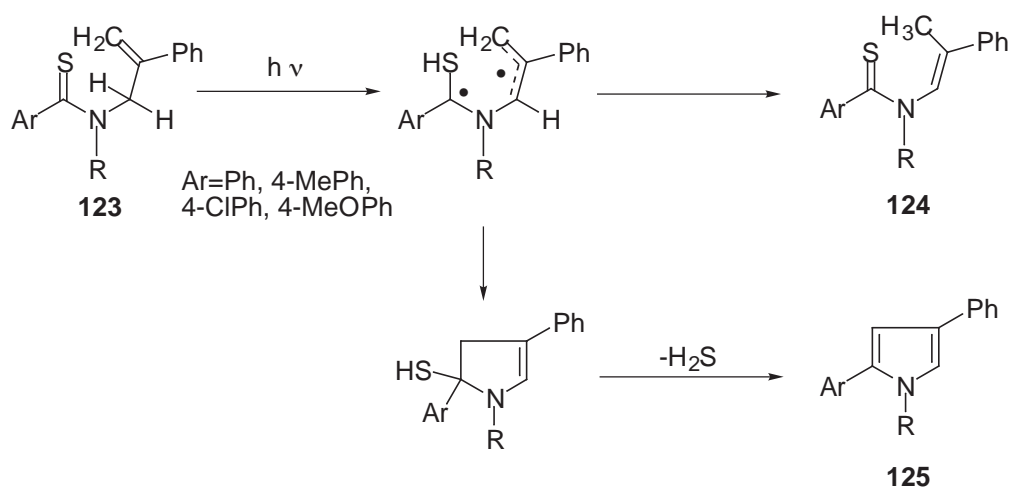
In another case, β -hydrogen abstraction of acyclic monothioimides followed by cyclization leads to aziridine derivatives. When acyclic monothioimides (**126**) are irradiated at room temperature, thioketones (**127**) is formed *via* ring-opening reaction of unstable mercaptoaziridines (**128**). Irradiation



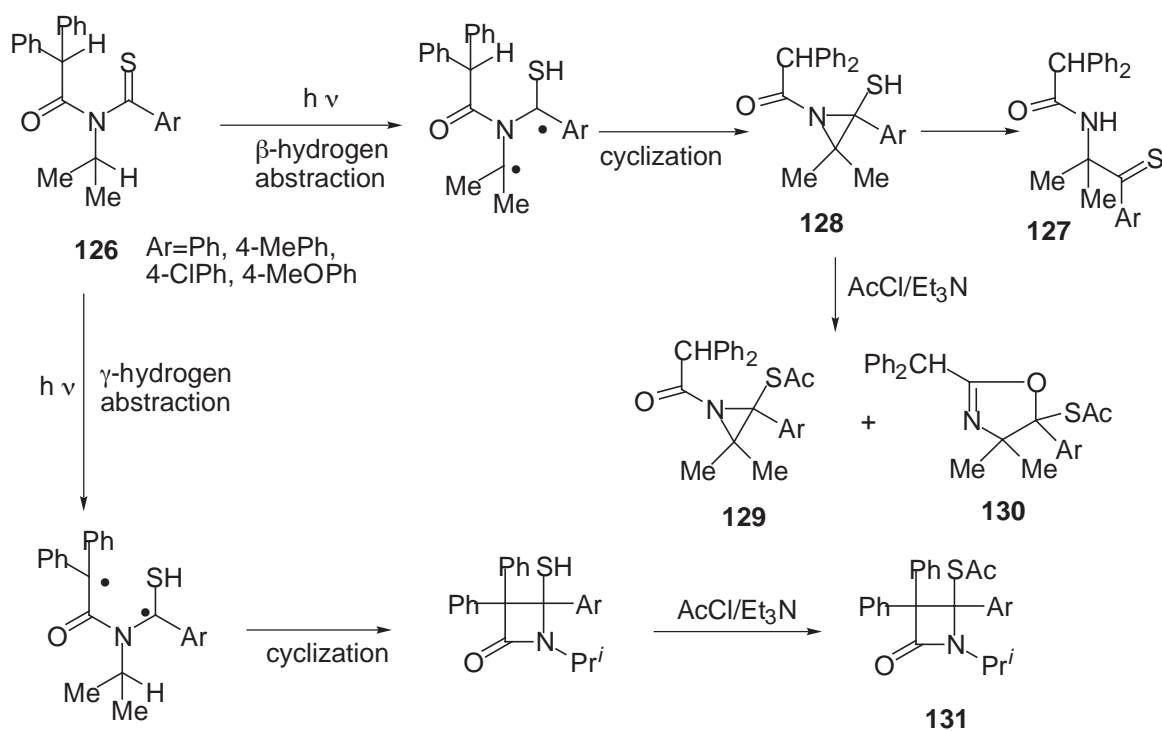
Scheme 13

of monothioimides (**126**) at low temperature, followed by acetylation, gives stable aziridine (**129**) and rearranged oxazolidine (**130**). The β -lactams (**131**) are also obtained *via* γ -hydrogen abstraction followed by cyclization.⁶⁶

Furthermore, three achiral monothioimides, Ar=Ph, 4-ClPh and 4-MeOPh derivatives (**126**), crystallize in a chiral fashion, and the solid-state photolysis followed by acylation gives optically active aziridines (**129**), oxazolidines (**130**), and β -lactams (**131**).



Scheme 14

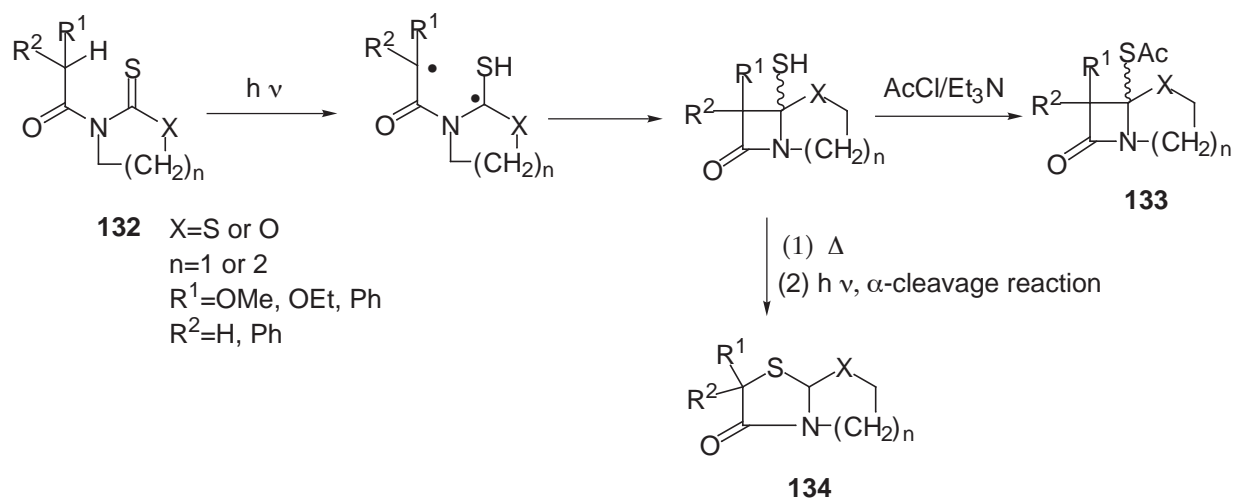


Scheme 15

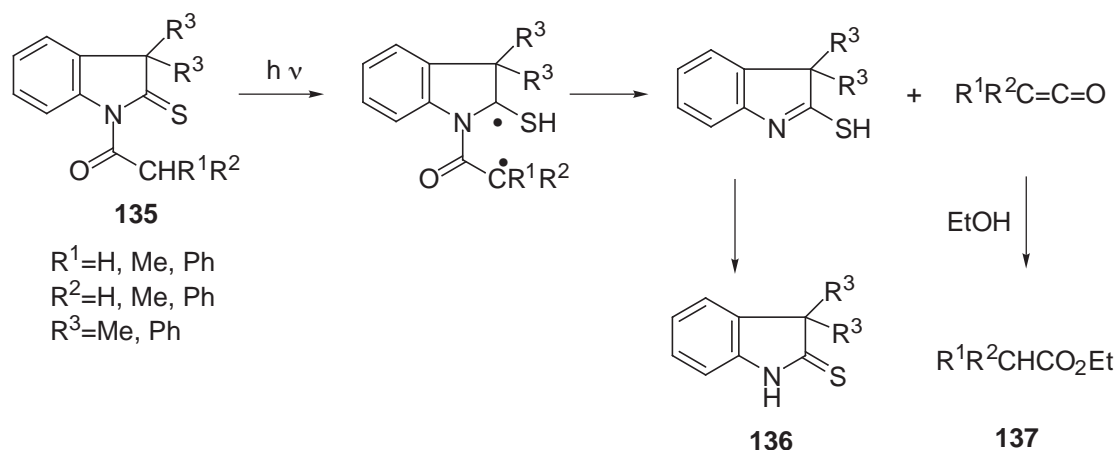
Hydrogen abstraction has been reported in *N*-acylthionocarbamates and dithiocarbamates (**132**) leading to cyclization products (**133**, **134**).⁶⁷ The formation of **134** is reasonably explained in terms of ring-opening reaction followed by α -cleavage reaction of the C=S group. And the resulting carbene is trapped intramolecularly to yield **134** as shown in **Scheme 16**.

Irradiation of 1-acylindoline-2-thiones (**135**) gives deacylation products (**136**) via a γ -hydrogen abstraction. Simultaneously formed ketene is trapped by ethanol to yield the corresponding esters (**137**).¹⁹ Similar deacylation involving γ -hydrogen abstraction has been observed in the photolysis of *N*-acyl-2-thionothiazolidines (**Scheme 17**).⁶⁸

Photolysis of the monothioimides (**138**) gives γ -lactams (**139**) and disproportionation products (**140**, **141**), via a 1,5-diradical intermediate generated by δ -hydrogen abstraction; and also thioamides (**142**) are obtained via γ -hydrogen abstraction (**Scheme 18**).⁶⁹ Irradiation of *N*-(3-phenylpropionyl)-2-pyrrolidinethione, in which R³ and R⁴ substituents are tethered, gives isomers of the pyrrolopyrrolidone.



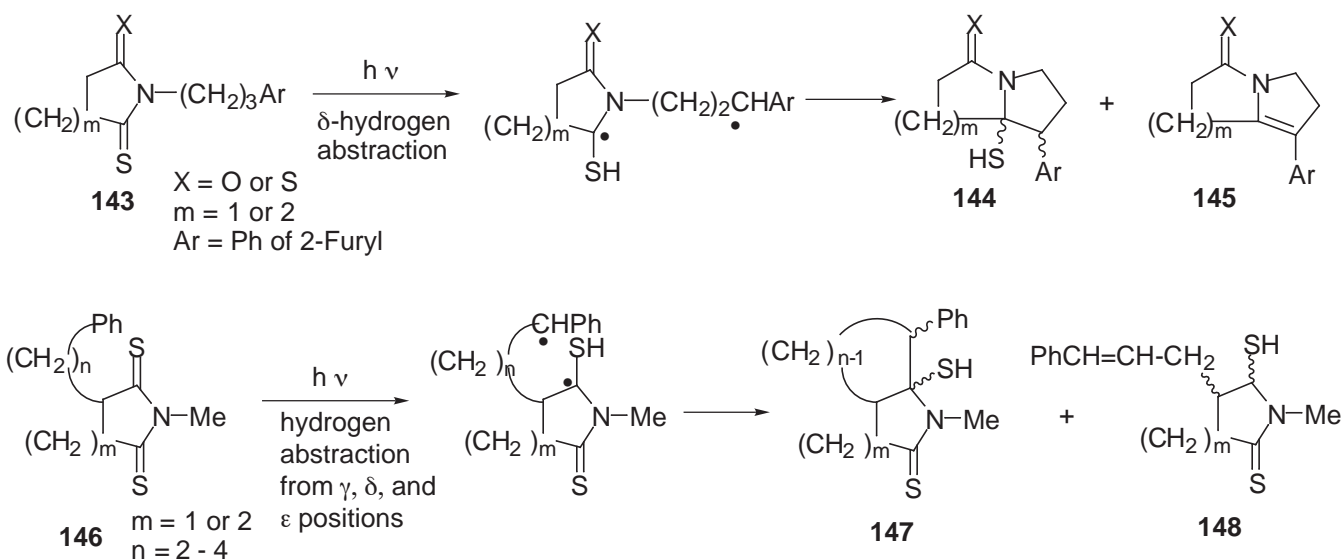
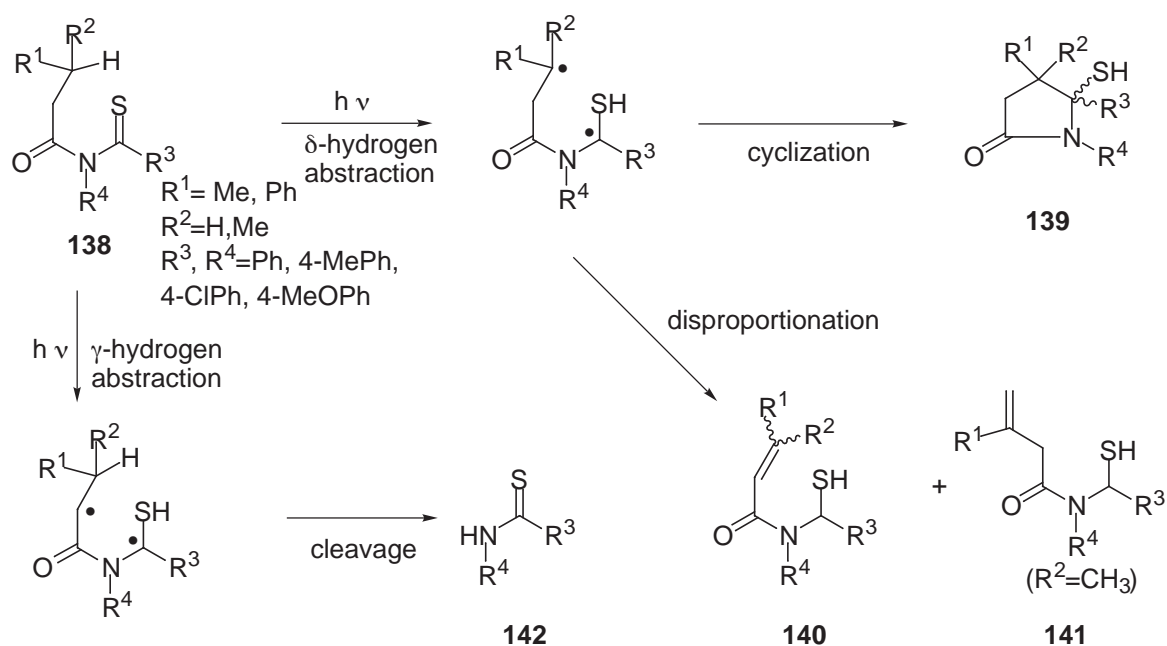
Scheme 16



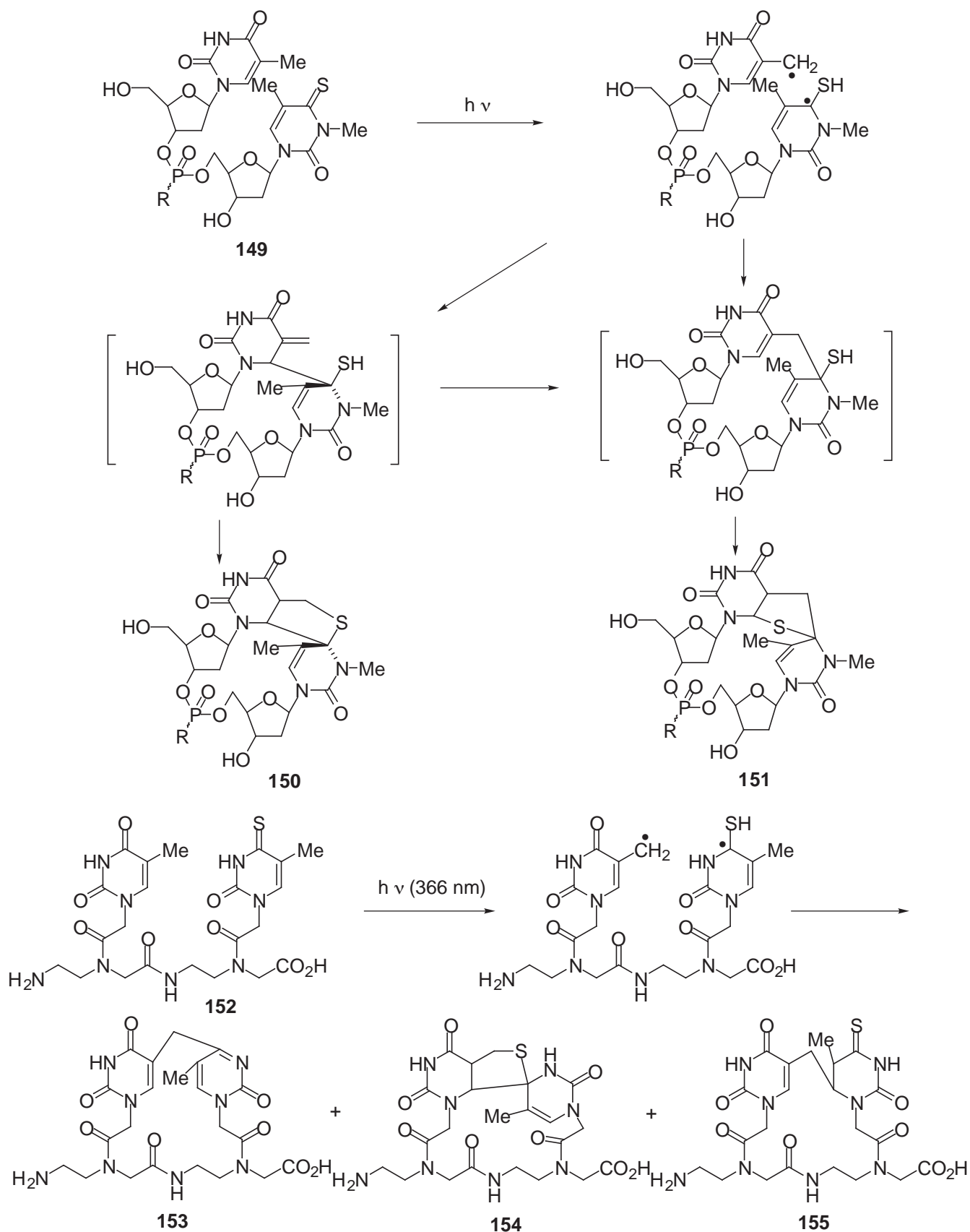
Scheme 17

Photolysis of 1-(ω -aralkyl)cyclic thioimides (**143**: X=O, S; m=1, 2; R=Ph, 2-furyl) gives a pair of stereoisomers of 1-azabicycloalkanes (**144**, **145**) in moderate yields (**Scheme 19**).⁷⁰ Similarly, phenylalkylcyclic dithioimides (**146**: m=1, 2; n=2-4) give 2-azabicycloalkanes (**147**) and disproportionation products (**148**) on irradiation.

Irradiation of thiouracil tethered by peptide or ribose-phosphate (**149**) at 366 nm in water results in the formation of the products (**150**, **151**), and similar treatment of a peptide nucleic acid dimer such as **152**



leads to intramolecular hydrogen abstraction reactions yielding three new products (**153-155**) as shown in **Scheme 20**.^{46,50,71}

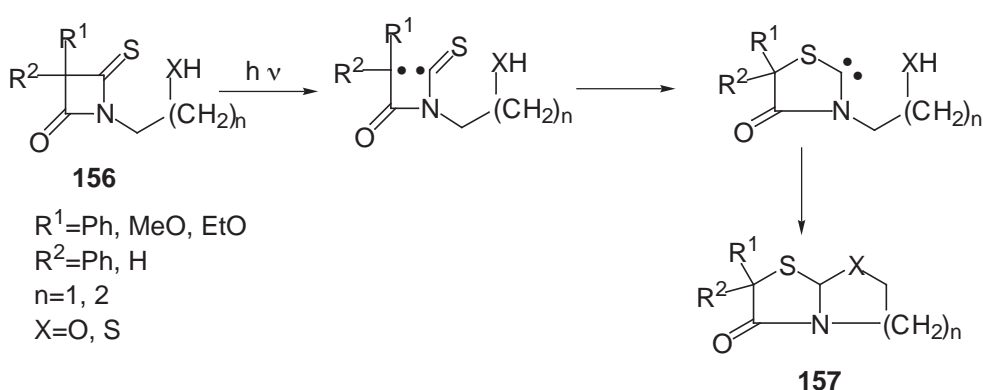


Scheme 20

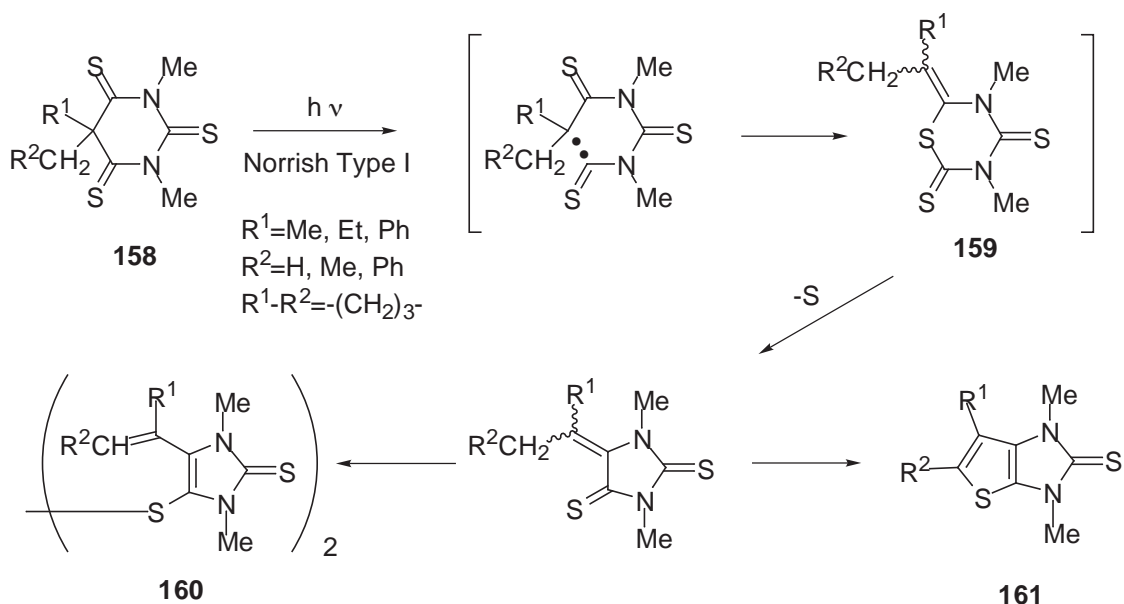
2.3 MISCELLANEOUS PHOTOREACTION OF THIOAMIDES AND THIOIMIDES

Norrish type I reaction (α -cleavage reaction) is a popular reaction in carbonyl photochemistry; however, it is very rare in thiocarbonyl photochemistry. One of the reasons derives from the lower triplet energy than that of the C=O analogues. Some strained thiocarbonyl compounds are known to undergo C-(C=S) bond cleavage in four-membered thioketone and thioesters (**Scheme 21**).⁷⁻⁹ Photolysis of four-membered thioimides (**156**) promotes an α -cleavage reaction leading to thiocarbene, and is trapped intramolecularly by thiol or alcohol to bicyclic lactams (**157**).⁶⁷

Another example is reported in six-membered trithiobarbiturate (**158**) leading to thiohydantoin (**160**) and a small amount of imidazolinothiophene derivatives (**161**); the reaction mechanism is explainable in terms of the initial formation of a 1,6-biradical intermediate which is generated by α -cleavage (Norrish type I reaction) of the thiocarbonyl group, and is followed by recyclization to **159**, and then ring contraction leading to **160** and **161** with the loss of a sulfur atom as shown in **Scheme 22**.¹⁸



Scheme 21

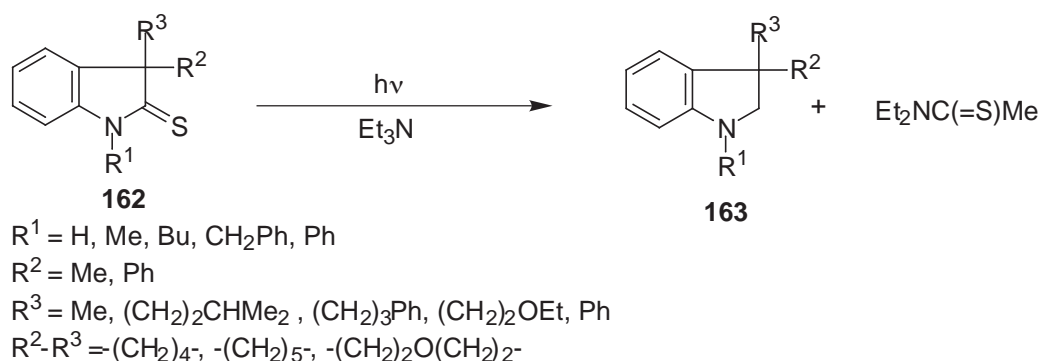


Scheme 22

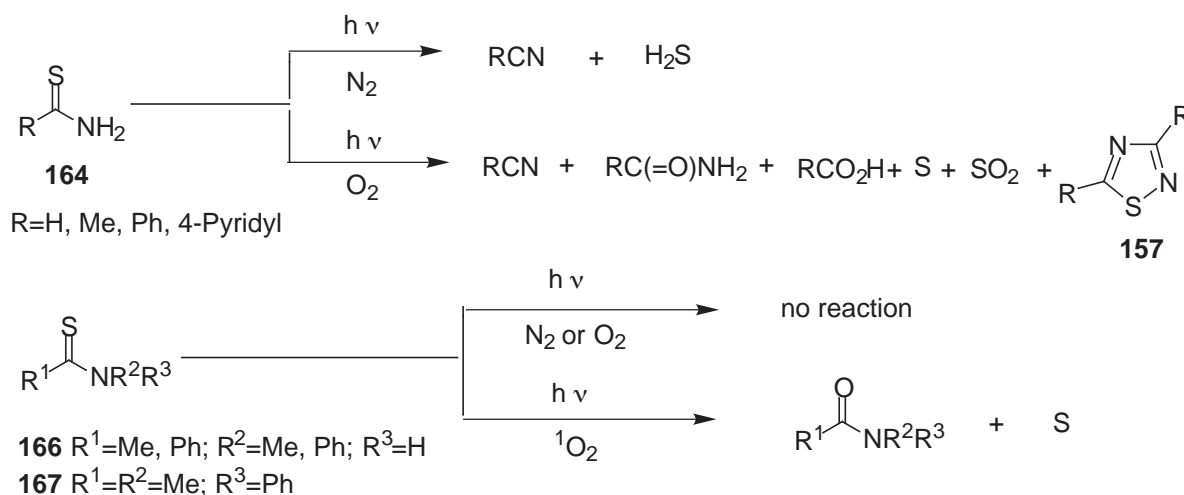
Irradiation of indoline-2-thiones (**162**) in the presence of Et₃N yields the desulfurization products, indolines (**163**), along with Et₂NCSMe (**Scheme 23**). The photodesulfurization reactions can be explained by a sequential electron/proton-transfer mechanism from amine to the excited indoline-2-thione (**162**).⁷²

Primary thioamides (**164**) are photolyzed by UV light in nitrogen to the corresponding nitriles with evolution of H₂S (**Scheme 24**). Irradiation in the presence of oxygen gives nitriles, amides, carboxylic acids, and 3,5-disubstituted 1,2,4-thiadiazoles (**165**) together with S, SO₂ and SO₄²⁻ but no H₂S. Secondary thioamides (**166**) and tertiary thioamides (**167**) are stable under both conditions. Singlet oxygen also reacts with secondary and tertiary thioamides forming the corresponding amides with expulsion of S.⁷³

Examples of photocyclization involving the thiocarbonyl group have been reported. The 2-substituted benzothiazoles (**169**) are prepared in this way from *o*-halogenothiobenzanilides (**168**) via a dehydrohalogenation initiated by electron transfer (**Scheme 25**).⁷⁴ Similarly, the 2-thiaquinazolinones (**170**),

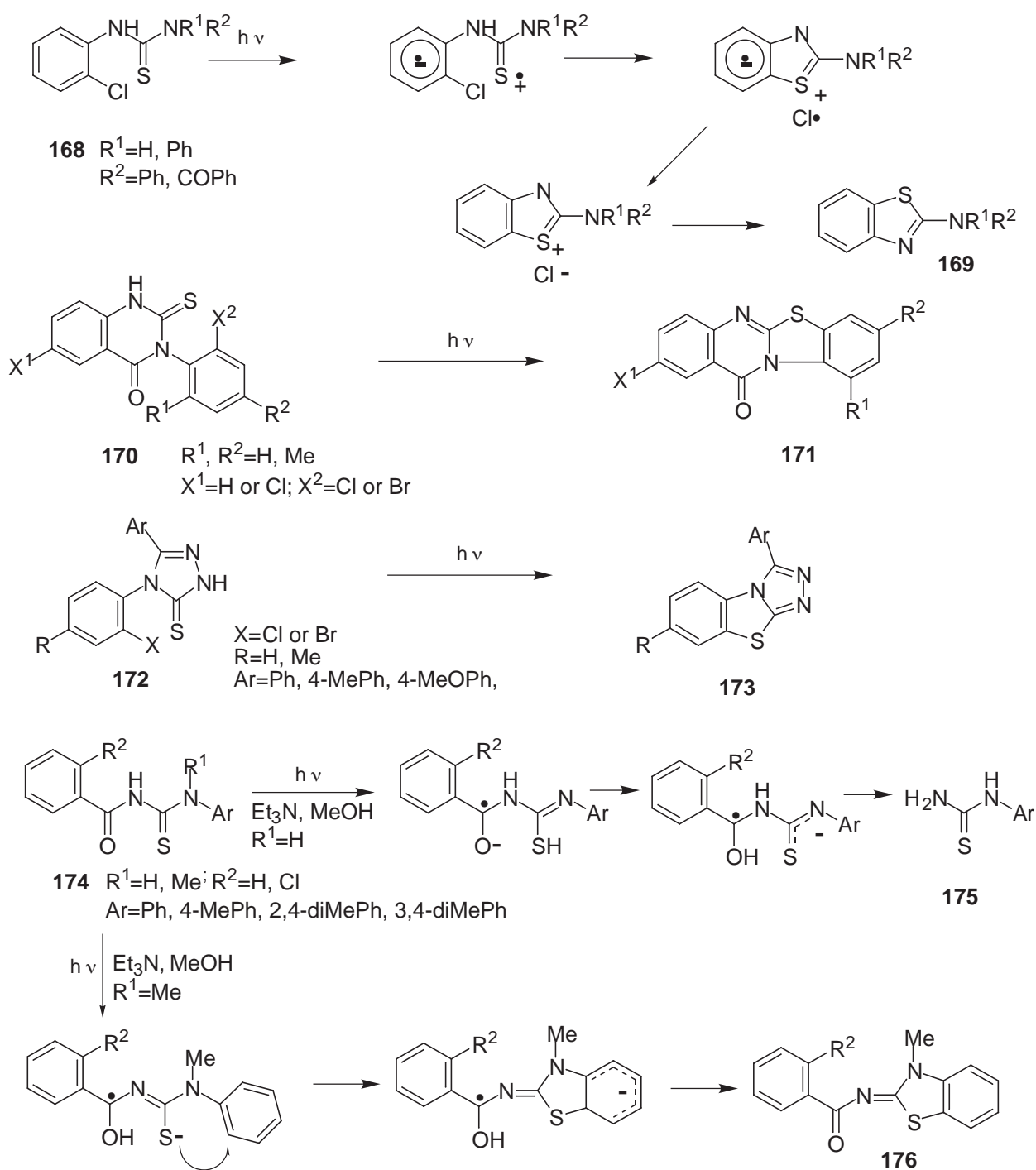


Scheme 23



Scheme 24

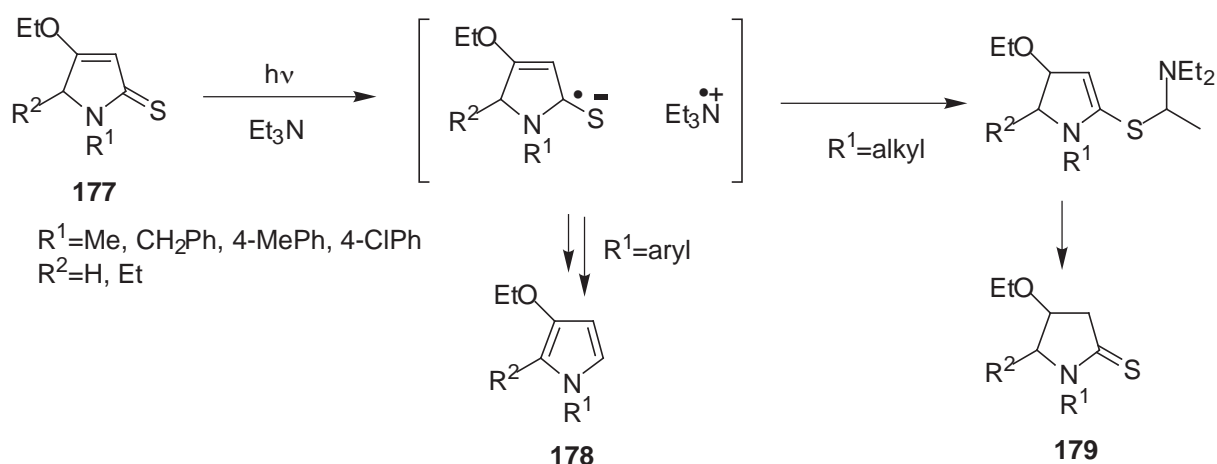
for example, have been prepared photochemically and converted into the 12*H*-benzothiazolo[2,3-*b*]quinazolin-12-ones (**171**).⁷⁵ The 4-(2-haloaryl)-5-aryl-1,2,4-triazole-3-thiones (**172**) are also converted into the benzothiazole derivatives (**173**).⁷⁶ Irradiation of *N*-acylthiourea (**174**) gives thiourea (**175**) and benzothiazoles (**176**).⁷⁷



Scheme 25

Irradiation of 2,5-dihydro-1*H*-pyrrole-2-thiones (**177**) in the presence of triethylamine gives desulfurization products, pyrroles (**178**), or reduction products, pyrrolidine-2-thiones (**179**), depending on the substituent on the nitrogen atom. This reaction can be explained by a sequential electron/proton-transfer mechanism from the amine to the excited pyrrole-2-thione as shown in **Scheme 26**.²⁴

Photolysis of a benzene solution of acyclic monothioimides (**180**) promotes δ -hydrogen abstraction leading to δ -lactams as shown in **Scheme 17**.⁶⁹ However, irradiation of **180** in the solid-state affords only thioamides (**182**) and the corresponding acid (**183**), where the mechanism *via* the 1,3-oxazetidinium ion (**181**) is proposed (**Scheme 27**).^{78,79} Irradiation of 2-methyl-4-phenyl-substituted benzaldehyde thiosemicarbazones **184** leads to the corresponding Δ^2 -1,2,4-triazoline-5-thione derivatives (**186**) through the formation of stable 1,2,4-triazolidine-5-thione derivatives (**185**).⁸⁰ A photochemically induced Dimorth rearrangement has been reported in the 1,2-thiazolino[5,4-*d*]-1,2-thiazoline-3,6-dithione (**187**) and yields the 3*H*,6*H*-1,2-dithiolo[4,3-*c*]-1,2-dithiole (**188**).⁸¹



Scheme 26

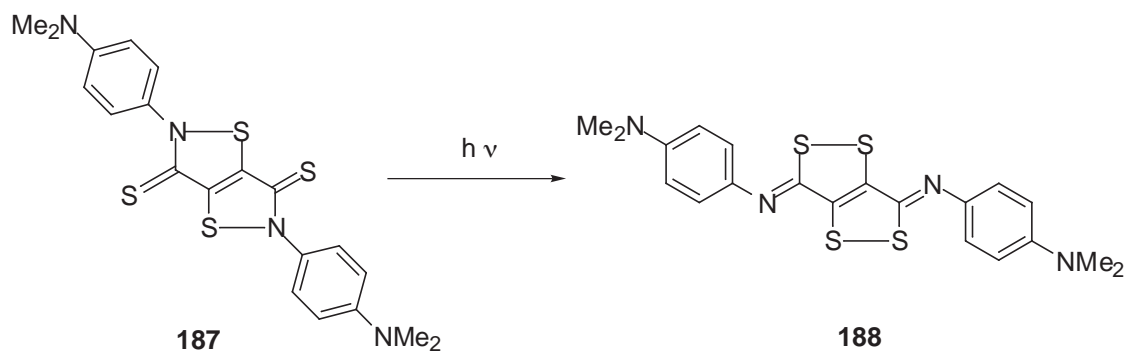
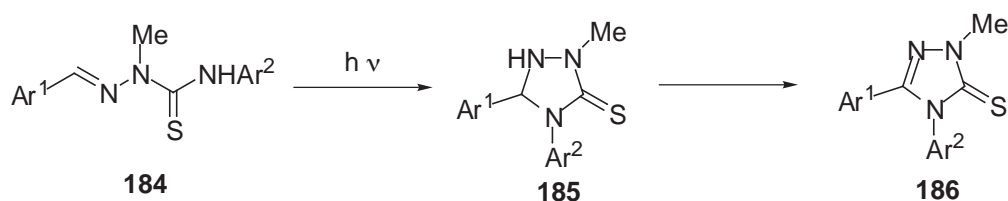
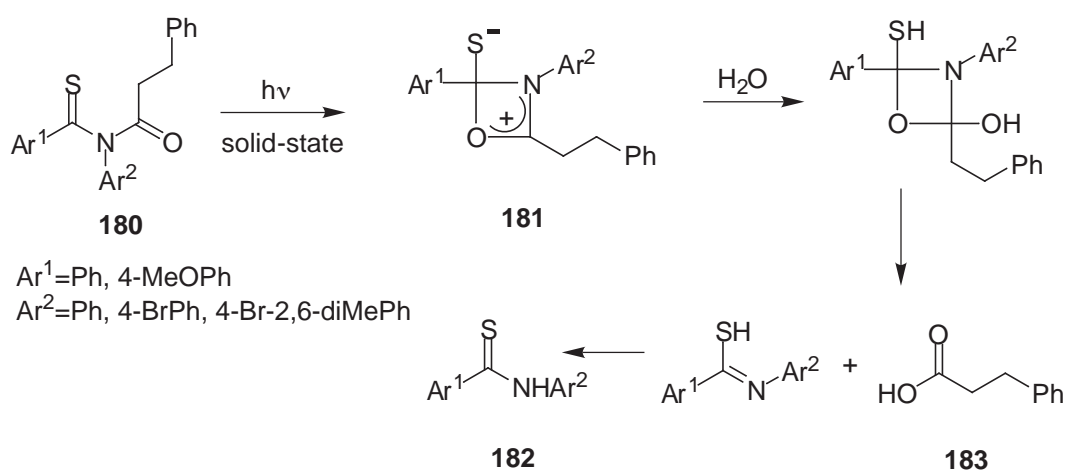
2.4 PHOTOREACTION OF α,β -UNSATURATED THIOAMIDES

Photochemical isomerization of monosubstituted α,β -unsaturated thioamides (**189**) gives iminothietanes, *N*-(2-thietanylidene)amines (**190**), in good yields. The iminothietanes revert quantitatively to the starting materials on heating.⁸²

The singlet $\pi-\pi^*$ excited state of the *N,N*-disubstituted thioamides (**191**) is responsible for conversion to the thioazetidiones (**192**) accompanied by the fragmentation product (**193**). This product is presumed to be formed by a hydrogen abstraction path to afford the zwitterionic intermediate.⁸³ Furthermore, *N,N*-dibenzyl-1-cyclohexenecarbothioamide (**191**: $\text{R}^1\text{-R}^2 = -(\text{CH}_2)_4-$) crystallizes in a chiral space group $P2_1$ and the photolysis in the solid-state leads to exclusive production of optically active thioazetidione (**192**) in

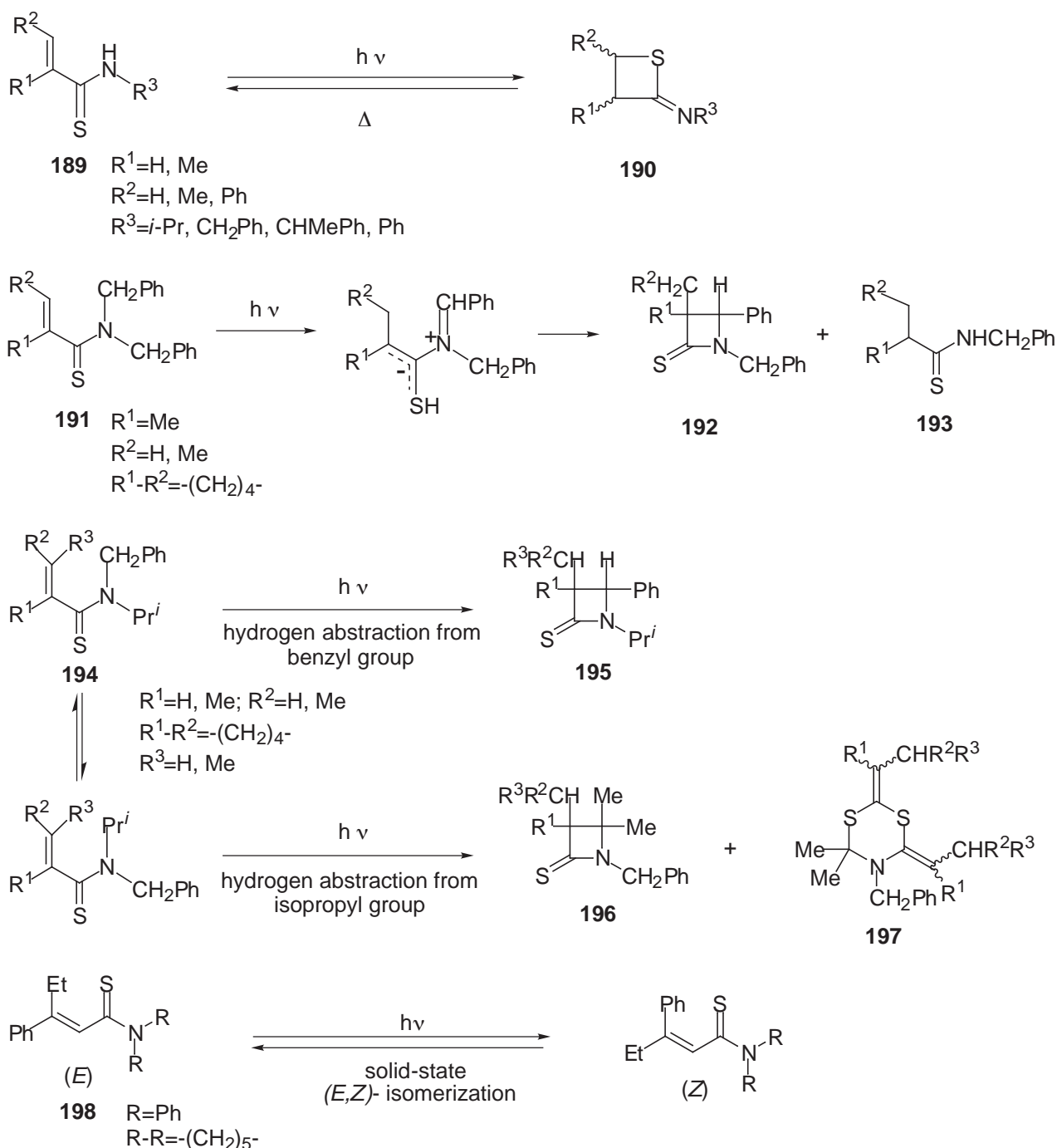
97% enantiomeric yield without phase separation. The crystal-to-crystal reaction is followed by X-Ray diffraction analysis.⁸⁴⁻⁸⁶

Unsymmetrically substituted *N*-benzyl-*N*-isopropyl- α,β -unsaturated thioamides (**194**) exist in an equilibrium between two rotamers owing to the rotation of the C(=S)-N bond. The free energy of activation lies in a range 18.4-19.5 kcal mol⁻¹. Irradiation in benzene solution induces hydrogen abstraction by the alkenyl carbon from the benzyl and isopropyl groups to give a β -thiolactam (**195**) and 1,3,5-dithiazinane products (**197**) as products, respectively. In the solid-state, however, photolysis causes hydrogen abstraction from only the isopropyl group to give isomeric β -thiolactam (**196**).⁸⁷



Scheme 27

Photochemical (*E,Z*)-isomerization of *N,N*-disubstituted tigloylthioamide (**191**) occurs in solution and in the solid-state.^{83,84} Furthermore, photochemical (*E,Z*)-isomerizability of cinnamthioamide derivatives (**198**) in the solid-state has been reported. Crystallographic analysis reveals that the isomerizability of α,β -unsaturated amides and thioamides in the solid-state partially depends on their molecular conformation in crystal.⁸⁸ In addition, it is found that the packing coefficient has correlation with the isomerizability; a smaller value of the packing coefficient causes an increased formation of (*Z*)-isomers.



Scheme 28

3. CONCLUSIONS

Photochemical reactions of thioamides and thioimides have received a great deal of attention and have exhibited reactivity for many types of photoreaction. Thioamides showed considerably high photochemical reactivity in cycloaddition with alkenes leading to aminothietanes as primary products, which are generally unstable due to the participation of lone-pair electrons on the nitrogen atom and undergo ring-opening reaction to transform fragmentation products. The [2+2] cycloaddition is a facile method of C-C bond formation of nitrogen-containing heterocycles. Furthermore, thioimides show higher activity for photochemical hydrogen abstraction inter- and intramolecularly. These reactions provide useful synthesis of nitrogen-containing heterocycles such as lactams and cyclic amines.

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