Chapter 2

Studies on Crystal Structure and Conformation Assisted Photochemical Reactions of Bis(cinnamoyl) Ketene Dithioacetals

2.1 Introduction

Among functionalized ketene dithioacetals, cinnamoyl ketene dithioacetals have a pivotal role as key precursors for a host of interesting synthetic transformations. Acyl ketene dithioacetals on α'-deprotonation with mild bases add to aromatic aldehydes to provide easy access to these valuable intermediates. Selective conversion of the cinnamoyl double bond to cyclopropane or oxirane functionalities provide highly functionalized ketene dithioacetals which have been successfully employed in the synthesis of cyclopentanoids and substituted heterocycles. Recent studies from our laboratory have shown that the α'-deprotonation of diacetyl ketene dithioacetals followed by addition to aromatic aldehydes afford bis(cinnamoyl) ketene dithioacetals. We have successfully extended many reactions of alkenoyl ketene dithioacetals to these intermediates. In continuation of our ongoing synthetic explorations, we have studied a conformation assisted intramolecular photochemical [2+2] cycloaddition reaction of the bis(cinnamoyl) ketene dithioacetals, induced by the push-pull nature of the ketene dithioacetal moiety.
2.1.1 Cinnamoyl Ketene Dithioacetals: Synthesis and Reactivity

Cinnamoyl ketene dithioacetals 3 can be conveniently prepared from acyl ketene dithioacetals 2 by the base catalysed Claisen-Schmidt condensation with aromatic aldehydes (Scheme 1).

![Scheme 1](image)

\[ R_1 \text{CHO} + \begin{array}{c}
\text{O} \\
\text{SCH}_3
\end{array} \xrightarrow{\text{NaOEt}} \begin{array}{c}
\text{O} \\
\text{SCH}_3
\end{array} \]

\[ R_1 = \text{Ar, } R = \text{CH}_3, \text{-CH}_2\text{CH}_2, \quad R_2, R_3 = \text{H, alkyl} \]

The ketene dithioacetal functionality may be considered as a latent ester group since it can be converted to an ester under Lewis acid catalyzed solvolytic conditions. The \( \gamma,\delta \)-unsaturated \( \beta \)-ketoesters obtained by the solvolysis of cinnamoyl ketene dithioacetals belong to the class of intermediates known as Nazarov reagents, which are extensively used in six-membered ring annulation reactions.\(^5\) Studies from this laboratory have shown that substituted cinnamoyl ketene dithioacetals 4 afforded the corresponding \( \gamma,\delta \)-unsaturated \( \beta \)-ketoesters 5 on treatment with boron trifluoride etherate in refluxing dioxane (Scheme 2).\(^5\)

![Scheme 2](image)

The addition of allyl and crotyl magnesium bromides to the carbonyl group of the cinnamoyl ketene dithioacetals 6 followed by treatment with boron trifluoride etherate resulted in cycloaromatization to afford functionalized stilbenes 8 (Scheme 3).\(^6\)
Cinnamoyl ketene dithioacetals have been employed in the synthesis of styryl substituted heterocycles. For example, cinnamoyl ketene dithioacetal 9 on reaction with 5-lithiomethyl-3-methylisoxazole followed by BF₃ etherate assisted cycloaromatization afforded styryl benzisoxazoles 10 (Scheme 4).⁷

Junjappa et al. have demonstrated the utility of cinnamoyl ketene dithioacetals in the synthesis of conjugated polyenes, which are key precursors in the synthesis of many natural products. They have shown that the carbonyl group of the cinnamoyl ketene dithioacetals 11 undergo selective reduction with sodium borohydride in ethanol to afford allylic alcohols 12, which on boron trifluoride assisted solvolysis afford conjugated polyene esters 13 (Scheme 5).⁸
The allylic carbinols obtained from cinnamoyl ketene dithioacetals were found to undergo interesting electrocyclic ring closures. The geometry of the cyclopentadienyl cations formed in the presence of a Lewis acid has a significant role in the cyclization process. The starting compounds that contain alkyl substituents at the 2- and 4-positions lead to cyclizations. This is due to the preferred ‘U’ conformation of the intermediate pentadienyl cations generated, induced by the presence of the methyl substituents. Thus the pentadienyl cations derived from bis-allylic carbinols 15 by treatment with boron trifluoride afforded substituted cyclopentanones 16 (Scheme 6).\(^9\)

\[\begin{align*}
\text{H}_2\text{C} & \quad \quad \text{NaBH}_4/\text{EtOH} \\
\text{14} & \quad \quad \quad \quad \text{H}_3\text{C} \\
& \quad \quad \quad \quad \text{Ar} \\
\text{S} & \quad \quad \quad \quad \text{SCH}_3 \\
& \quad \quad \quad \quad \text{CH}_3
\end{align*}\]

\[\begin{align*}
\text{H}_2\text{C} & \quad \quad \text{OH} \\
\text{15} & \quad \quad \quad \quad \text{H}_3\text{C} \\
& \quad \quad \quad \quad \text{Ar} \\
\text{S} & \quad \quad \quad \quad \text{SCH}_3 \\
& \quad \quad \quad \quad \text{CH}_3
\end{align*}\]

\[\begin{align*}
\text{H}_2\text{C} & \quad \quad \text{NaBH}_4/\text{EtOH} \\
\text{14} & \quad \quad \quad \quad \text{H}_3\text{C} \\
& \quad \quad \quad \quad \text{Ar} \\
\text{S} & \quad \quad \quad \quad \text{SCH}_3 \\
& \quad \quad \quad \quad \text{CH}_3
\end{align*}\]

\[\begin{align*}
\text{H}_2\text{C} & \quad \quad \text{OH} \\
\text{15} & \quad \quad \quad \quad \text{H}_3\text{C} \\
& \quad \quad \quad \quad \text{Ar} \\
\text{S} & \quad \quad \quad \quad \text{SCH}_3 \\
& \quad \quad \quad \quad \text{CH}_3
\end{align*}\]

**Scheme 6**

The cinnamoyl ketene dithioacetals 17 when treated with dimethyl sulphoxonium methyldide under phase transfer conditions could undergo regioselective cyclopropanation to afford cyclopropyl ketones 18 (Scheme 7).\(^{3b}\)

\[\begin{align*}
\text{R}_2 & \quad \quad \quad \quad \text{O} \\
\text{17} & \quad \quad \quad \quad \text{Me} \\
& \quad \quad \quad \quad \text{SMe} \\
& \quad \quad \quad \quad \text{Me} \\
\text{SMe} & \quad \quad \quad \quad \text{Me}
\end{align*}\]

\[\begin{align*}
\text{R}_2 & \quad \quad \quad \quad \text{O} \\
\text{18} & \quad \quad \quad \quad \text{Me} \\
& \quad \quad \quad \quad \text{SMe} \\
& \quad \quad \quad \quad \text{Me} \\
\text{SMe} & \quad \quad \quad \quad \text{Me}
\end{align*}\]

**Scheme 7**

Conjugate adducts obtained by the base induced 1,4-addition-elimination of aryl acetonitriles with 2-arylcyclopropyl ketones underwent acid induced
domino carbocationic rearrangement to afford either peri-fused or angularly fused polycyclic aromatic frameworks (Scheme 8).\(^3\)

The chemoselective epoxidation of the styryl double bond of the ketene dithioacetals 21 afforded epoxy ketones 22 which underwent boron trifluoride etherate assisted rearrangement to the β-ketoaldehyde 23 which was later cyclized in the presence of ethanolic acetic acid to the corresponding 2-methylthio-5-aryl pyran-4-ones 24 (Scheme 9).\(^{3a}\)
While the sodium borohydride reduction occurs selectively at the carbonyl group of the cinnamoyl ketene dithioacetals, Grignard reagents were found to undergo conjugate addition at the less hindered double bond (Scheme 10).

2.1.2 Bis(cinnamoyl) Ketene Dithioacetals: Synthesis and Reactions

The bis(cinnamoyl) ketene dithioacetals derived from aromatic aldehydes and diacetyl ketene dithioacetals are excellent precursors for the synthesis of curcumin and its analogs, which are potential inhibitors of chemical carcinogenesis. Studies from this laboratory have led to the development of a facile synthesis of 1,7-diphenyl 1,6-heptadiene-3,5-diones 29 by the Claisen-Schmidt condensation of diacetyl ketene dithioacetals 28 with substituted benzaldehydes 27 (Scheme 11).
However, our attempts to extend this methodology to other analogues of curcumin resulted in debenzoylated products, which could have been formed via the pyrone intermediate 31 (Scheme 12).\(^\text{12}\)

![Scheme 12](image-url)

The Lewis acid mediated condensation of diacetyl ketene dithioacetal 28 with benzaldehyde 33 also afforded the expected product 29a in 27% yield (Scheme 13).

![Scheme 13](image-url)

When the reaction was extended to substituted aldehydes like \(p\)-chloro benzaldehyde 34, a partially hydrolysed product 35 was obtained.
Thus the aldol type condensation reactions of diacetyl ketene dithioacetals containing a bis(methylthio) methylene functionality almost always proceeded with the removal of the ketene dithioacetals moiety, dearylation or partial hydrolysis of the ketene dithioacetal moiety to the thiol ester group. So efforts were made to extend this protocol to cyclic diacetyl ketene dithioacetals, whereby curcumin analogues containing a 1,3 dithiolan-2-ylidene moiety could be prepared. It was envisaged that the cyclic ketene dithioacetal moiety present in these compounds will be more resistant to hydrolysis. Thus, the base catalyzed condensation reactions of acyl ketene dithioacetals 37 derived from 1,3 diketones 36 with aromatic aldehydes afforded bis(cinnamoyl) ketene dithioacetals 38. (Scheme 15).

Conformational studies of bis(cinnamoyl) ketene dithioacetals revealed that the 1,3-dithiolan-2-ylidene moiety present in these systems could play a crucial role in their chemical reactivity. Thus we have investigated an intramolecular [2+2] cycloaddition reaction of bis(cinnamoyl) ketene dithioacetals under photochemical conditions.
2.1.3 Photochemical [2+2] Cycloaddition Reactions

The photochemical [2+2] cycloaddition reaction of alkenes leading to cyclobutane derivatives is one of the most commonly used strategy level reactions for complex molecule synthesis. Its utility has been established for cycloadditions of ground state alkenes with excited state alkenes, dienes and chromophores incorporating these groups. Though intermolecular [2+2] cycloadditions have also been studied, only very few are found to have practical value as most of the reactions are reported to give complex reaction mixtures.

Excitation of the ground state alkene which involves either a \( \pi,\pi^* \) or an \( n,\pi^* \) transition normally produces its singlet excited state. Several pathways are available for the singlet excited state of the alkene. It can combine with the ground state of the alkene to form a singlet exciplex. A concerted cycloaddition of the excited singlet state with the ground state alkene would lead to the formation of cyclobutane. The excited state can also undergo either an intersystem crossing to give the excited triplet state or decay back to the ground state. The singlet excited state is very short lived, particularly for the \( \alpha,\beta \)-unsaturated carbonyl compounds. They can easily collapse to the ground state if cis-trans isomerism can occur. The singlet exciplex can also decay to the ground state or degenerate to the cyclobutane. It can also produce a 1,4-biradical, which can collapse to the ground state or proceed to form a cyclobutane.

The first report of intramolecular [2+2] cycloaddition was carried out by the prolonged exposure of carvone 39 to sunlight, whereby carvone camphor 40 was obtained in moderate yields (Scheme 16).\(^{13}\)

\[
\begin{array}{c}
\text{39} \\
\text{\textbf{Scheme 16}} \\
\text{40}
\end{array}
\]
Intramolecular [2+2] cycloadditions have the potential of circumventing the selectivity problems of its intermolecular version and has been exploited in the synthesis of many substitutionally complex eight membered rings through rearrangement of divinylcyclobutane photoproducts. Wender et al. have used this strategy effectively in the construction of cyclooctane skeleton 42 (Scheme 17).14

![Scheme 17](image)

The versatility of this reaction in the construction of complex molecular architecture is exemplified by the intramolecular [2+2] cycloaddition of the Diels-Alder adduct 46 of cyclopentadiene 45 and benzoquinone 44 (Scheme 18).15

![Scheme 18](image)

The synthesis of cubane framework from the Diels-Alder adduct of \(\alpha\)-bromocyclopentadieneone is another classic example of [2+2] cycloaddition (Scheme 19).16

![Scheme 19](image)
The efficiency of the photocycloaddition was found to increase when the two *endo*-dicyclopentadiene derivatives in the substrate 51 were linked by a tether containing either an alkyl chain or an adamantane spacer (Scheme 20).\(^\text{17}\)

\[
\text{hv} \quad \text{C} \quad \text{O} \quad \text{THF} \quad 70-80\%
\]

**Scheme 20**

### 2.1.4 Photoreactions of Cinnamic Acid Derivatives

During the past two decades, the photosensitive nature of cinnamates has been exploited in the synthesis of polymer materials, UV filters, molecular assemblies etc.\(^\text{18}\) Cinnamic acid 54 gives photodimers on irradiation in the solid state. The reaction is stereospecific, depending on the crystal form of the starting material. The metastable β-form gives truxinic acid 55, while the stable α-form gives α-truxinic acid 56 (Scheme 21).\(^\text{19}\)

\[
\text{hv} \quad \beta\text{-form} \quad \text{Ph} \quad \text{COOH}
\]

\[
\text{hv} \quad \alpha\text{-form} \quad \text{Ph} \quad \text{HOOC}
\]

**Scheme 21**

However, irradiation of cinnamic acid in solution only gave *cis*-trans isomerisation products.\(^\text{20}\) Liquid ethyl cinnamate 57 afforded a mixture of two ethyl truxinates 58 and 59 (Scheme 22).\(^\text{21}\)
When ethyl cinnamate 57 was irradiated in an emulsion of water, cyclohexane, butanol and sodium dodecyl sulphate, dimers 58 and 60 were formed in the ratio 8:2 (Scheme 23).22

The solution phase irradiation of cinnamates in methanol results in E,Z isomerization and usually do not lead to any products.19a Our survey of literature revealed that many research groups have attempted to transfer the topochemical control of crystalline state [2+2] cycloaddition of cinnamates to the solution phase. Efficient photodimerisation of cinnamates in solution was observed only when high local concentrations were achieved by omission of solvents. When the irradiation was carried out in the presence of Lewis acids like boron trifluoride etherate, a mixture of several isomeric truxinates was obtained. Akabori and coworkers have reported an efficient route to photoresponsive cyclobutane-1,2-capped 2.\(n\) diazacrown ethers 62 employing the intramolecular [2+2] photocycloaddition of \(p,p'\)-trimethylene dicinnamoyl capped 2.\(n\) diazacrown ethers 61 (Scheme 24).23
In solution, the [2+2] cycloaddition to become significant, the minimum length of the spacer required to separate the two cinnamoyl groups was found to be eight bonds.\textsuperscript{24} Ors and Srinivasan have reported the internal photocycloaddition of α,ω-cinnamate 63 wherein the chromophores are separated by 17 bonds.\textsuperscript{25} The tricyclic adduct 64 was formed in 32% yield on direct irradiation, catalyzed by cuprous chloride (Scheme 25).

The same research group has subsequently reported similar intramolecular photocycloadditions of α,ω-dicinnamates separated by 21, 27, 31 and 35 bonds, employing benzophenone as sensitizer at 350 nm. As expected, the quantum yield of the cyclization was found to decrease as the separation between the chromophores increased.\textsuperscript{26} When the two cinnamoyl moieties are appended at both the ends of a polyethylene glycol chain as in compound 65, Kimura \textit{et al.} observed that the topology of the product 66 can be controlled through the circumferential organization provided by alkali metal cations (Scheme 26).\textsuperscript{27}

When a sonicated suspension of 65 and LiClO\textsubscript{4} in benzene was irradiated, a tetralin derivative 68 was also formed in addition to the expected β-truxinate 67 (Scheme 27).
Rennert et al. have observed that irradiation of the \( \alpha,\alpha \)-cinnamate 69a in solution gave a mixture of internal diester of \( \beta \)-truxinic acid and \( \delta \)-truxinic acid in the ratio 9:1, whereas the irradiation of 69b afforded the corresponding internal diester of \( \delta \)-truxinic acid as the sole product.\(^{24b,c}\)

In another approach, Jones and co-workers have prepared appropriately substituted [2,2] paracyclophane derivatives, which are known for their rigidly defined intra-annular distances.\(^{28}\) The pseudo gem isomer of [2,2] cinnamophane 70 was found to mimic the stacking arrangement of the \( \beta \)-type structure of trans-cinnamic acid. The irradiation of 70 in methanol using a high pressure mercury lamp gave the corresponding cyclobutane derivative 71 in quantitative yield (Scheme 28).
2.2 Results and Discussion

Studies on the crystal structure of diacetyl ketene dithioacetals 37 containing a 1,3 dithiolan moiety revealed an Z,Z-conformation in which both the ketene dithioacetal group and the oxygen atoms are on the same plane, with sulfur atoms close to the respective oxygen atoms (Fig. 1). These conformational preferences can be attributed to the push-pull nature of the rigid 1,3-dithiolan-2-yliden moiety, due to which a partial positive charge is developed on sulfur and partial negative charge on oxygen. The interaction between polarized oxygen and sulfur leads to a rigidity in the conformation of the molecule.

Fig 1

It has been reported earlier that diacetyl ketene dithioacetals 28 with bis(methylthio)methylene functionality has a slight twist about the carbon-carbon double bond with the two acyl groups having a highly twisted E,E-conformation (Fig. 2) and lacks the rigidity in conformation observed in 37. The steric effect of the methyl group as well as the absence of a ring strain as in 1,3-dithiolane moiety could be responsible for this.
It is possible that the presence of a cross conjugating group like a styryl group near the carbonyl group could delocalize the electrons more efficiently thereby effecting conformational changes in the molecule. Thus, the crystal structure of the cinnamoyl ketene dithioacetals 72 derived from the acyl ketene dithioacetal and p-chlorobenzaldehyde showed Z-geometry for the α-oxoketene dithioacetal moiety though the O-S bond distance is longer compared to that of 37. It was also observed that the phenyl ring present in the molecule is planar with the chlorine atom lying in the phenyl plane. The crystal structure also reveals that one of the methylthio groups is cis with the double bond whereas the other is in trans conformation, which could be due to the steric crowding by the two methyl groups (Fig 3).
In continuation of these investigations, ketene dithioacetals containing substituted styryl groups were subjected to conformation studies. Thus the bis(cinnamoyl) ketene dithioacetals 38, obtained by the Claisen-Schimdt condensation reaction of bis(acetyl) ketene dithioacetals with aromatic aldehydes, were selected for the study. The crystal studies of these bis(alkenoyl) ketene dithioacetals revealed that the two cinnamoyl groups present in the molecule are aligned parallel and close to each other. The carbon atoms α to the carbonyl groups are separated by just 2.9 Å. The crystal studies on 1,6-heptadiene-3,5-diones, having an unsubstituted methylene group show that they have a linear structure due to the keto-enol tautomerisation. For example, natural curcumin, which is 1,7 bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione exists in the completely enolized form. The extended conjugation resulting from the enolization contributes to the stability of the linear structure (Fig 4).

Fig. 4
In the case of bis(cinnamoyl) ketene dithioacetals, the delocalization of electrons would result in developing partial negative charges on oxygen and partial positive charges on sulfur atoms (Fig. 5).

![Fig. 5](image)

This assumption is supported by the observed bond lengths in the crystal structure of 38a and also by the fact that both the carbonyl groups as well as the carbon and sulfur atoms of the ketene dithioacetal moiety lie on the same plane (Fig. 6).

![Fig. 6](image)

**Fig. 6.** ORTEP drawing of 4-(1,3-dithiolan-2-yliden)1,7-diphenyl-1,6-heptadiene-3,5-dione 38a
This parallel alignment of the cinnamoyl moieties apparently results from the *push-pull* nature of the ketene dithioacetal moiety. We envisaged that this conformational rigidity promoted by the ketene dithioacetal moiety could assist an internal [2+2] cycloaddition under photochemical conditions. Thus we have prepared several bis(cinnamoyl) ketene dithioacetals and subjected them to photoreaction. As expected, the substrates 38a-f on irradiation afforded the corresponding cycloadducts as the sole product in impressive yields (Scheme 29).  

![Scheme 29](image)

<table>
<thead>
<tr>
<th>38, 73</th>
<th>Ar</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>C₆H₅</td>
<td>50</td>
</tr>
<tr>
<td>b</td>
<td>4-MeOC₆H₄</td>
<td>50</td>
</tr>
<tr>
<td>c</td>
<td>Thieryl</td>
<td>30</td>
</tr>
<tr>
<td>d</td>
<td>2-MeOC₆H₄</td>
<td>60</td>
</tr>
<tr>
<td>e</td>
<td>4-ClC₆H₄</td>
<td>65</td>
</tr>
<tr>
<td>f</td>
<td>3-MeOC₆H₄</td>
<td>40</td>
</tr>
</tbody>
</table>

The $^1$H NMR spectrum (CDCl₃) of compound 73a shows a singlet due to methylene protons at $\delta$ 3.57 ppm. The protons of the cyclobutane ring were present as two double doublets, one at $\delta$ 3.6 ppm and the other at $\delta$ 3.9 ppm. Aromatic protons were present as multiplets between $\delta$ 6.96 and 7.30 ppm. The $^{13}$C NMR spectrum shows the peaks due to the methylene groups at $\delta$ 29.1 and 37.7 ppm. The four carbons of the cyclobutane ring appeared at $\delta$ 46.8, 47.2, 47.8
and 48.6 ppm respectively. The peak at \( \delta \) 109 ppm is due to the carbon atom in between the carbonyl groups. The signal at \( \delta \) 138.9 ppm is due to the carbon of the ketene dithioacetal moiety where both the sulfur atoms are attached. The signals between \( \delta \) 120.0 and 130.0 ppm are due to the aromatic carbons. The carbonyl groups gave a signal at \( \delta \) 200.9 ppm. The IR spectrum showed bands at 1625, 1440, 1285 and 1225 cm\(^{-1}\). The mass spectrum (FABMS) of the product gave a peak at 379 (M\(^{+}\)+1). The stereochemical aspects of the photoproducts were later confirmed by X-ray structural analysis (Fig. 7).\(^{31}\) The compound 73a crystallizes in the orthorhombic space group P2\(_1\)/cn (which is transformed to the conventional space group Pna2\(_1\)) with four molecules in the unit cell. The unit cell dimensions are \( a = 31.600(7) \text{Å} \), \( b = 5.6302(12) \text{Å} \), \( c = 10.199(6) \text{Å} \) and \( v = 1814.5(11) \text{Å}^3 \). The X-ray data were collected using Cu-K\(\alpha\) radiation (\( \lambda = 1.5418 \text{Å} \)). The structure was refined to a conventional factor of 0.047 using 1687 unique reflections. The crystal structure is held together by van der Waals forces only. The closest interaction between two neighboring molecules is found to be between the oxygen atom of one of the carbonyl groups and one of the dithiolan protons.

Fig.7. ORTEP drawing of 3-(1,3-dithiolan-2-yliden)-6,7-diphenyl bicyclo[3.2.0]heptane-2,4-dione 73a
When the starting material 38a was irradiated as a more dilute solution (2.75 \times 10^{-5} \, \text{M}), the complete conversion to the photoproduct 73a occurred in less than five minutes (Fig 8).

Fig. 8. Electronic absorption spectra of 38a in methanol (a) before and (b) after irradiation for 5 minutes at >300 nm.

We next attempted to extend this reaction protocol to more complex systems wherein the sterically hindered conformation of the photoproducts could trigger ring openings, leading to more interesting macrocycles. Thus the chloro substituted 3,4-dihydronaphthalene carbaldehyde 75 derived from \( \alpha \)-tetralone 74 by the Vilsmeier-Haack reaction was condensed with the diacetyl cyclic ketene dithioacetal.

\[
\begin{align*}
74 & \xrightarrow{\text{POCl}_{3}/\text{DMF}} 75
\end{align*}
\]

Scheme 30

However, unlike in the case of other bis(cinnamoyl) ketene dithioacetals, the photoreaction of 76 afforded a complex mixture.
Thus, our studies on the intramolecular photochemical reactions of bis (cinnamoyl) ketene dithioacetals establish the fact that the push-pull nature of the 1,3 dithiolan moiety has resulted in conformational changes in these substrates, making them ideal precursors for further synthetic transformations.

2.3 Experimental

Melting points are uncorrected and were obtained on a Buchi-530 melting point apparatus. Infra red spectra were recorded on Shimadzu IR-470 spectrometer and the frequencies are reported in cm\(^{-1}\). Proton NMR spectra were recorded on a Bruker DRX-300 (300 MHz), Bruker WM 250 (250 MHz) or on a Bruker WM 200 (200 MHz) spectrometer in CDCl\(_3\). Chemical shifts are expressed in parts per million downfield from internal tetramethyl silane. Coupling constants \(J\) are given in Hz. Electron impact Mass spectra were obtained on a Finnigen-Mat 312 instrument and FAB mass spectra on a Jeol SX-102 instrument.
2.3.1 Claisen-Schmidt Reaction of 3-(1,3-Dithiolan-2-yliden)-2,4-heptanedione, 38a-f

Sodium metal (0.45 g, 20 mmol) was dissolved in ethanol (20 mL) to which the cyclic ketene dithioacetal 37 (1.01 g, 5 mmol) was added followed by aromatic aldehyde (10 mmol). The reaction mixture was stirred at 0-5°C for four hours. The solid product obtained was filtered, washed with ethanol and recrystallized from a mixture of hexane and ethyl acetate.

The starting materials 38a-e were prepared by the above procedure and have been characterized and reported earlier by our group.\textsuperscript{12}

\begin{center}
\textbf{(1E,6E)-4-(1,3-Dithiolan-2-yliden)-1,7-bis(2-methoxyphenyl)-1,6-heptadiene-3,5-dione 38f}
\end{center}

This compound was obtained by the Claisen-Schmidt reaction of cyclic ketene dithioacetal 37 (2 g, 10 mmol) with 2-methoxy benzaldehyde (2.8 g, 20 mmol) as yellow crystalline solid. Yield 3.2 g (73%), mp 118-120 °C. \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 3.37 (s, 4H, SCH\textsubscript{2}), 3.74 (s, 6H, OMe), 6.86 (m, 4H, aromatic & vinylic), 7.27 (m, 6H, aromatic), 8.02 (d, \(J = 16\) Hz, 2H, vinylic).

\begin{center}
\textbf{(1E,6E)-1,7 Bis(1-chloro 3,4-dihydro-2-napthalenyl)-4-(1,3-dithiolan-2-yliden)-1,6-heptadiene-3,5-dione 76}
\end{center}

This compound was obtained by the Claisen-Schmidt reaction of cyclic ketene dithioacetal 37 (2 g, 10 mmol) with 1-chloro-3,4-dihydro-2-napthalene carbaldehyde 75 (3.8 g, 20 mmol) as yellow crystalline solid. Yield 3.85 g (70%), mp 170-172 °C. \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 2.5 (m, 4H, -CH\textsubscript{2}-), 2.8 (m, 4H, -CH\textsubscript{2}-), 3.4 (s, 4H, SCH\textsubscript{2}), 6.7 (d, 2H, \(J = 15\) Hz, olefinic), 7.3 (m, 6H, aromatic), 7.7 (m, 2H, aromatic), 8.2 (d, 2H, \(J = 15\) Hz, olefinic).
2.3.2 Photochemical [2+2] Cycloaddition Reaction of Bis(cinnamoyl) Ketene Dithioacetals

A solution of the bis(cinnamoyl) ketene dithioacetal 38a-f in benzene (2.5 x 10^{-3} M) was irradiated with Pyrex filtered light for one hour. The solution, on concentration and purification over silica gel using hexane: ethyl acetate (9:1) as eluent, gave bicyclo[3,2,0]heptane-2,4-dione 73a-f as brilliant yellow crystals (mp 170-173 °C) in 50 % yields, while the rest of the starting material was recovered unchanged.

\[
3-(1,3-Dithiolan-2-yliden)-6,7-diphenylbicyclo[3.2.0]heptane-2,4-dione 73a
\]

was obtained by the photochemical reaction of (1E,6E)-4-(1,3-dithiolan-2-yliden)-1,7-diphenyl-1,6-heptadiene-3,5-dione 38a (0.5 g, 1.3 mmol) as yellow crystalline solid. Yield 0. 52 g (50%), mp 170-173 °C. IR ν_max/cm^{-1} 1625, 1440, 1285, 1225. \(^1\)H NMR (300 MHz, CDCl\textsubscript{3}) δ 3.52 (s, 4H, SCH\textsubscript{2}), 3.63 (d, 2H, J = 11 Hz, cyclobutane), 4.13 (d, 2H, J = 11 Hz, cyclobutane), 7.1 (m, 10H, aromatic) ppm. \(^13\)C NMR (300 MHz, CDCl\textsubscript{3}) δ 29.1, 37.7, 46.8, 47.2, 47.8, 48.6, 109.2, 127.8, 138.9, 200.9 ppm. FABMS m/z (%) 379 (M^+1, 95), 199 (90), 165 (24), 155 (50), 149 (30), 138 (58), 57 (100)
was obtained by the photochemical reaction of \((1E,6E)-4-(1,3\text{-dithiolan-2-yldien})-1,7\text{-bis(4-methoxyphenyl)}-1,6\text{-heptadiene-3,5-dione} \) \(38b\) (0.5 g, 1.1 mmol) as yellow crystalline solid. Yield 0.25 g (50%), mp 128-131 °C. IR \(\nu_{\text{max}}/\text{cm}^{-1}\) 1630, 1510, 1450, 1250, 1180. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 3.51 (s, 4H, SCH\(_2\)), 3.72 (s, 6H, OMe), 3.84 (d, 2H, \(J = 11\) Hz, cyclobutane), 3.95 (d, 2H, \(J = 11\) Hz, cyclobutane), 6.9 (m, 8H, aromatic) ppm.

\(3-(1,3\text{-Dithiolan-2-yldien})-6,7\text{-bis(4-methoxyphenyl)bicyclo[3.2.0]heptane-2,4-dione} \) \(73b\)

\(3-(1,3\text{-Dithiolan-2-yldien})-6,7\text{-di(2-thienyl)bicyclo[3.2.0]heptane-2,4-dione} \) \(73c\)

was obtained by the photochemical reaction of \((1E,6E)-4-(1,3\text{-dithiolan-2-yldien})-1,7\text{-di(3-thienyl)}-1,6\text{-heptadiene-3,5-dione} \) \(38c\) (0.5 g, 1.2 mmol) as yellow crystalline solid. Yield 0.15 g (33%), mp 157-159 °C. IR \(\nu_{\text{max}}/\text{cm}^{-1}\) 1620, 1570, 1440, 1280, 1220. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 3.51 (s, 4H, SCH\(_2\)), 3.62 (d, 2H, \(J = 11\) Hz, cyclobutane), 4.14 (d, 2H, \(J = 11\) Hz, cyclobutane), 6.8 (m, 6H, aromatic) ppm.
3-(1,3-Dithiolan-2-yliden)-6,7-bis(2-methoxyphenyl)bicyclo[3.2.0]heptane-2,4-dione 73d was obtained by the photochemical reaction of 38d (0.5 g, 1.1 mmol) as yellow crystalline solid. Yield 0.3 g (60%) mp 168-170 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 3.50 (s, 6H, OMe), 3.56 (s, 4H, SCH$_2$), 3.74 (d, 2H, J = 11 Hz, cyclobutane), 4.26 (d, 2H, J = 11 Hz, cyclobutane), 6.47 (d, 2H, J = 8 Hz, aromatic), 6.76 (f 2H, J = 8 Hz, aromatic), 6.96 (d, 2H, J = 8 Hz, aromatic) ppm. $^{13}$C NMR (300 MHz, CDCl$_3$) δ 38.6, 44.25, 47.9, 55.8, 110.4, 120.5, 123.1, 128.4, 128.9, 129.7, 157.9, 184.0, 202.9 ppm

3-(1,3-Dithiolan-2-yliden)-6,7-bis(4-chlorophenyl)-3-(1,3-dithiolan-2-yliden) bicyclo[3.2.0]heptane-2,4-dione 73e was obtained by the photochemical reaction of 38e (0.5 g, 1.1 mmol) as yellow crystalline solid. Yield 0.32 g (65%) mp 120-122 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 3.55 (s, 4H, SCH$_2$), 3.59 (d, 2H, J = 11 Hz, cyclobutane), 4.00 (d, 2H, J = 11 Hz, cyclobutane), 6.88 (d, 4 H, J = 8 Hz, aromatic), 7.05(d, 4 H, J = 8 Hz, aromatic) ppm.
73f was obtained by the photochemical reaction of (1E,6E)-4-(1,3-dithiolan-2-yliden)-1,7-bis(3,4-methoxyphenyl)-1,6-heptadiene-3,5-dione 38f (0.5 g, 1.1 mmol) as yellow crystalline solid. Yield 0.20 g (40%) mp 146-148 °C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 3.55 (m, 6H, SCH$_2$, cyclobutane), 3.77 (s, 6H, OMe), 4.31 (d, $J = 11$ Hz, 2H, cyclobutane), 6.75 (m, 6H, aromatic), 6.87 (d, $J = 8$ Hz, 2H, aromatic) ppm
References

1. For reviews see: a) Dieter, R. K. *Tetrahedron* 1986, 42, 3029
   b) Junjappa, H.; Ila, H.; Asokan, C. V. *Tetrahedron* 1990, 46, 5423
   c) Kolbe, M. *Synthesis* 1990, 171
   d) Junjappa, H.; Ila, H.; Mohanta, P. K. *Progress in Heterocyclic Chemistry* 2001, 13, 1


   b) Asokan, C.V.; Ila, H.; Junjappa, H. *Synthesis* 1985, 163


         CA 124


c) Schmidt, G. M. J. Pure Appl. Chem. 1971, 27, 647


b) Rennert, J.; Phototgr. Sci. Eng. 1971, 15, 60
c) Rennert, J.; Soloway, S.; Waltcher, I.; Leons, B. J. Am. Chem. Soc. 1972, 94, 7242


