Chapter 5

REATIONS OF SUBSTITUTED 2-YLIDENE-1,3-DITHIOLANES
WITH DIMSYL ANION

5.1 Introduction

Sodium methylsulfenylmethylide, popularly known as dimsy1 anion, is a very useful reagent for carrying out a variety of base promoted transformations. It is a powerful Bronsted base and a nucleophile.\(^1\) It is usually prepared by the deprotonation of dimethyl sulfoxide with sodium hydride. DMSO is often used as the solvent. Recent studies from this laboratory have shown that dimsy1 anion induced demethylation of dimethyl ketenedithioacetals lead to the formation of methyl dithiocarboxylates. Similar reactions of 2-ylidine-1,3-dithiolanes have resulted in ring opening to afford vinyl dithiocarboxylates.\(^2\) In continuation to these studies we have examined the reactivity of several substituted ketenedithioacetals with dimsy1 anion. This chapter describes the results of our investigations on the reactions of 2-ylidine-1,3-dithiolanes with sodium methylsulfenyl methylide.

5.2 Reactions of Dimsyl anion

Dmsyl sodium in DMSO is a strong base, and is useful for the preparation of phosphorus and sulfur ylides from their respective salts. This is often considered as the reagent of choice for carrying out Wittig reactions.\(^3\) A few examples of base promoted
fragmentation reactions are available in literature. For example when 1 was treated with dimethyl sodium at 25 °C for 5 min the fragmentation product 2 was obtained (Scheme 1).

\[
\begin{array}{c}
\text{MeO} \\
\text{MeO} \\
\text{Me} \\
\text{Me}
\end{array} \quad \frac{\text{NaDMSO}}{25^\circ\text{C}, 5 \text{ min}} \quad \begin{array}{c}
\text{MeO} \\
\text{MeO} \\
\text{Me} \\
\text{Me}
\end{array}
\]

Scheme 1

Treatment of 1 with dimethyl sodium for a longer time resulted in an addition reaction leading to the formation of product 3 while the reaction at higher temperature gave 4 which must have resulted from a subsequent demethylation at one of the methoxy group. (Scheme 2).

\[
\begin{array}{c}
\text{MeO} \\
\text{MeO} \\
\text{Me} \\
\text{Me}
\end{array} \quad \begin{array}{c}
\text{Me} \\
\text{Me} \\
\text{Me}
\end{array} \quad \text{SOCH}_3
\]

\[
\begin{array}{c}
\text{MeO} \\
\text{MeO} \\
\text{Me} \\
\text{Me}
\end{array} \quad \begin{array}{c}
\text{Me} \\
\text{Me} \\
\text{Me}
\end{array} \quad \text{SOCH}_3
\]

Scheme 2

Sodium dimethylate is extensively used for the double bond isomerization leading to aromatization. Anionotropic rearrangements and carbanion assisted Claisen rearrangements
have been effectively carried out in the presence of dimethyl sodium. Scheme 3 shows an example of Grob type fragmentation reaction mediated by dimethyl anion (Scheme 3).

\[
\begin{align*}
\text{TsO} & \quad \text{NaDMSO} \\
\text{HO} & \quad \text{OMe} \\
\text{H} & \quad \text{H} \\
\text{CO}_2\text{Me} & \quad \text{OMe} \\
\end{align*}
\]

Scheme 3

Dimethyl anion can be used to produce carbanions which can then be functionalized via normal alkylation or acylation. Ketone-enolate generation followed by intramolecular alkylation using dimethyl anion has been reported. Sodium methylsulfonyl methylide has been effectively used in Williamsons ether synthesis as well. \( \beta \)-Ketosulfoxides, a versatile synthon, can be generated by the condensation of dimethyl anion with esters. For example, ester 7 on condensation with dimethyl anion generate \( \beta \)-ketosulfoxides 8 which can be converted to ketones on treatment with amalgamated aluminium (Scheme 4).

\[
\begin{align*}
\text{R} & \quad \text{OMe} \quad \text{NaDMSO} \quad \text{R} \quad \text{SOCH}_3 \quad \text{Al/Hg} \quad \text{R} \quad \text{CH}_3 \\
\end{align*}
\]

Scheme 4

When non-enolizable ketones and aldehydes are treated with dimethyl sodium, \( \beta \)-hydroxy sulfoxides are obtained which on subsequent dehydration is converted to \( \alpha,\beta \)-unsaturated sulfoxides. Enolizable ketones, however, undergo competing deprotonation and addition reactions limiting the synthetic utility of this process. The reaction of
2-aminobenzophenone 10 with excess of dimsyl anion, leading to the formation of 3-phenylindole 11 apparently involves an intermediate β-hydroxysulfoxide (Scheme 5).\textsuperscript{13}

![Scheme 5](image)

Hamda and coworkers have reported interesting transformations involving dimsyl anion and heterocyclic compounds possessing imine functional groups.\textsuperscript{14} For example, dibenzo (a,f) quinolizine 13 has been synthesised by the addition of dimsyl anion to imine 12 followed by trapping of the resulting amine with a pendant benzyne (Scheme 6).\textsuperscript{15}

![Scheme 6](image)

Addition reactions of dimsyl anion to alkenes or alkynes conjugated to an aryl ring, are also known.\textsuperscript{11a} In the methylation of stilbene initially the addition of dimsyl anion on the
unsaturated system takes place followed by the elimination of methane sulfenic acid and isomerization (Scheme 7).\textsuperscript{16}

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \quad \text{Ph} \quad \text{NaDMSO} \quad 67\% \quad \text{Ph} \quad \text{Ph} \quad \text{CH}_3 \\
14 & \quad 15
\end{align*}
\]

\textbf{Scheme 7}

Sodium dimethylsulfate reacts with chlorobenzene through benzene intermediates to afford a mixture of sulfoxides (Scheme 8)\textsuperscript{17} whereas octafluoronaphthalene reacts with dimethylsulfoxide anion to produce the substitution product 20 through addition-elimination mechanism (Scheme 9).\textsuperscript{18}

\[
\begin{align*}
\text{Cl} & \quad \text{Ph} \quad \text{S} & \quad \text{Me} \quad + \quad \text{Ph} \quad \text{S} & \quad \text{Me} \\
16 & \quad 17 \quad 18
\end{align*}
\]

\textbf{Scheme 8}

\[
\begin{align*}
\text{F} & \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{NaDMSO} \quad 34\% \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{S} & \quad \text{Me} \\
19 & \quad 20
\end{align*}
\]

\textbf{Scheme 9}

Sodium dimethylsulfate on alkylation, using primary halides or tosylates, leads to the formation of the expected sulfoxides.\textsuperscript{19} However, more hindered systems favour elimination
reactions. The reaction of 1,2,5,6-tetrabromocyclooctane with dimsyl anion resulted in debromination to afford 1,5-cyclooctadiene (Scheme 10).

![Scheme 10](image)

Epoxides on reaction with dimsyl anion afford corresponding secondary alcohols. The trimethyl silyl substituted epoxide 23 on reaction with dimsyl anion gave the allyl alcohol 24 through ring opening at the TMS substituted carbon, followed by desilylation and elimination of sulfenate group (Scheme 11).

![Scheme 11](image)

A few examples cited above highlights the versatile nature of dimsyl anion as a base, as a nucleophile and as a reagent for bringing about a variety of interesting transformations.

### 5.3 Results and Discussion

The reactions of α-oxoketenedithioacetals with carbon nucleophiles have been studied extensively. While organolithium reagents preferably add to the carbonyl group, organocuprates and bulky Grignard reagents undergo conjugate addition resulting in the displacement of the methylthio group. We have examined the reactivity of dimsyl anion with α-oxoketenedithioacetals to see whether dimsyl anion acts as a base or nucleophile. If the dimsyl anion acts as a nucleophile it will undergo a direct addition to the carbonyl group or prefer a conjugate addition. The reactions of aroyl ketene dithioacetals with dimsyl anion
have been studied in this laboratory. It has been found that dimsyl anion induces a demethylation at one of the methylthio group resulting in the formation of methyl β-oxodithiocarboxylates rather than adding to the ketenedithioacetal (Scheme 12). Several α-oxoketenedithioacetals derived from aliphatic, cyclic and aryl alkyl ketones have been shown to undergo effective demethylation reaction under these conditions. The reaction apparently proceeds via a nucleophilic attack of the dimsyl anion at the methylthio group.

\[
\begin{align*}
\text{R}^1 = \text{aryl, alkyl; } \text{R}^2 = \text{H, alkyl; } \text{R}^1 - \text{R}^2 = \text{cyclic}
\end{align*}
\]

Scheme 12

α-Oxoketenedithioacetals, in which the ketenedithioacetal part is present as a 2-ylidene-1,3-dithiolane moiety, with dimsyl anion was also studied. When 2-substituted phenacylidene-1,3-dithiolanes were treated with dimsyl anion vinyl β-oxodithiocarboxylates were obtained in excellent yields. The reaction was further extended to several substituted 1,3-dithiolanes prepared from carbonyl compounds (Scheme 13).

\[
\begin{align*}
\text{R}^1 = \text{aryl, alkyl; } \text{R}^2 = \text{H, alkyl; } \text{R}^1 - \text{R}^2 = \text{cyclic}
\end{align*}
\]

Scheme 13
A probable mechanism would involve base induced fragmentation of the 1,3-dithiolane moiety (Scheme 14).

\[
\text{Scheme 14}
\]

In continuation to these studies, aiming at the development of a method for the synthesis of γ, δ-unsaturated β-oxidithiocarboxylates, we have examined the dimethyl anion promoted fragmentation reaction of cinnamoyl ketenedithioacetals, wherein the ketenedithioacetal part is present as a 2-ylidene-1,3-dithiolane moiety. Dihydrothiopyran-4-one derivatives are obtained instead of the expected γ,δ-unsaturated dithiocarboxylates. The reaction has been extended to other substituted cinnamoyl ketenedithioacetals and 5-aryl-2,4-pentadienoyl ketenedithioacetals. This provides an efficient method for the synthesis of dihydrothiopyrone derivatives.

5.3.1 Synthesis of Substituted Cinnamoyl Ketenedithioacetals

The cinnamoyl ketenedithioacetals 32 were prepared by the Claisen-Schmidt condensation reactions of acyl ketenedithioacetal 30 with substituted benzaldehydes. When 2-acetylethylene-1,3-dithiolane 30 was allowed to react with benzaldehyde in the presence of sodium ethoxide in ethanol at 0-5 °C for 4 h and the product mixture was poured into cold water, an yellow solid was separated which was filtered dried and recrystallized from methanol. With the help of spectral data the product was characterized as 1-(1,3-dithiolan-2-ylidene)-4-phenyl-3-butene-2-one 32 (Scheme 15).
The proton NMR spectrum (90 MHz, CDCl₃) of 32a showed a singlet at δ 3.50 ppm due to methylene groups of 1,3-dithiolan moiety. One of the vinylic protons of the cinnamoyl group which is α to the carbonyl group appeared as a doublet at δ 6.85 ppm (J=15 Hz). The vinylic proton on the ketenedithioacetal moiety appeared as a singlet at δ 7.00 ppm. The multiplet between δ 7.30-7.90 ppm was due to the five aromatic and a vinylic proton. The IR spectrum of the compound showed carbonyl stretching frequency at 1640 cm⁻¹. The bands at 1570 and 1490 cm⁻¹ are due to the carbon-carbon double bonds.

Other substituted cinnamoyl ketenedithioacetals 32b-d were also prepared similarly in good yields (Scheme 15). The structure of all cinnamoyl ketenedithioacetals prepared were confirmed with the help of spectral data (see experimental).
Similar condensation reactions of the 2-acetylmethylene-1,3-dithiolane 33 derived from 2-butanone with substituted benzaldehydes gave the cinnamoyl ketenedithioacetals 34a-c in good yields (Scheme 16). The cinnamoylketenedithioacetals 34 also have been characterized with the help of spectral data (experimental).

![Chemical structures](image)

<table>
<thead>
<tr>
<th>31, 34</th>
<th>X</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>H</td>
<td>80</td>
</tr>
<tr>
<td>b</td>
<td>Me</td>
<td>85</td>
</tr>
<tr>
<td>c</td>
<td>OMe</td>
<td>85</td>
</tr>
</tbody>
</table>

Scheme 16

The 5-phenyl-2,4-pentadienoyl ketenedithioacetals 36 were also prepared in good yields by the Claisen-Schmidt condensation reaction of 2-acetylmethylene-1,3-dithiolane 30 and 33 with cinnamaldehyde (Scheme 17). Thus the condensation of cinnamaldehyde 35 with the acyl ketenedithioacetal 30 in the presence of sodium ethoxide in ethanol gave the 5-phenyl-2,4-pentadienoyl ketenedithioacetal 36a in 82% yield as an yellow crystalline solid. The structure of 36a was confirmed with the help of spectral data.
The proton NMR spectrum (90 MHz, CDCl₃) shows a multiplet between δ 3.25 and 3.55 ppm due to the methylene protons of the 1,3-dithiolane moiety. The doublet at δ 6.45 ppm (J = 15 Hz) is due to a vinylic proton which is α to the carbonyl group. The multiplet between 6.85 and 7.15 ppm is due to three vinylic protons. The five aromatic protons along with a vinylic proton appeared as a multiplet between 7.35 and 7.70 ppm. The IR (KBr) spectrum of the compound shows a band due to carbonyl group at 1625 cm⁻¹ while the bands due to the double bonds were present at 1565 and 1480 cm⁻¹.

In a similar fashion the acyl ketenedithioacetal 33 also underwent smooth Claisen-Schmidt condensation to afford the expected 5-phenyl-2,4-pentadienoyl ketenedithioacetal 36b in 80% yield. The structure of 36b was also confirmed with the help of spectral data (experimental).
5.3.2 Reactions of Substituted 2-Ylidene-1,3-dithiolanes with Dimsyl Anion: Formation of Substituted 5,6-Dihydrothiopyran-4-one Derivatives

It has been reported that cinnamoyl ketenedithioacetals undergo partial hydrolysis\textsuperscript{23} in the presence of Lewis acids to afford $\gamma,\delta$-unsaturated $\beta$-ketoesters. We envisaged that since the 2-ylidene dithiolane moiety would undergo dimsyl anion induced ring opening the cinnamoyl ketenedithioacetals on a similar fragmentation would afford $\gamma,\delta$-unsaturated $\beta$-ketodithiocarboxylates. However it has been found that the intermediate sodium salt of $\gamma,\delta$-unsaturated $\beta$-ketodithiocarboxylates formed undergo in situ cyclization leading to the formation of substituted 5,6-dihydrothiopyran-4-one derivatives.

Sodium methyl sulfenyl methylide was prepared by heating DMSO in the presence of sodium hydride at 70 $^\circ$C for 1h, with stirring. To the dimsyl anion in DMSO thus prepared, an equivalent of cinnamoyl ketenedithioacetal 32a was added. The reaction mixture was allowed to stir at 70 $^\circ$C for another hour. After cooling to room temperature the mixture was poured into cold water, acidified with dil. HCl, extracted with dichloromethane and dried over anhydrous sodium sulfate. The crude product obtained was purified by column chromatography over silica gel using hexane:ethyl acetate (20:1) as the eluent. A reddish brown liquid was isolated in 75% yield. Based on spectral data the product was identified to be 6-phenyl-2-vinylthio-5,6-dihydrothiopyran-4-one 37a (Scheme 18).

The proton NMR spectrum (CDCl$_3$, 300 MHz, Fig 1) shows a double doublet at $\delta$ 2.92 ppm ($J = 16.5$ and 3.0 Hz) and another double doublet at $\delta$ 3.10 ppm ($J = 16.5$ and 13.5 Hz) due to $H_a$ and $H_b$ respectively. $H_a$ and $H_b$ shows a geminal coupling of 16.5 Hz while $H_b$ and $H_c$ shows a diaxial coupling of 13.5 Hz. The axial equatorial coupling of $H_c$ and $H_a$ has been found to be 3 Hz.
Scheme 18

<table>
<thead>
<tr>
<th>32, 37</th>
<th>X</th>
<th>Yield(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>H</td>
<td>75</td>
</tr>
<tr>
<td>b</td>
<td>MeO</td>
<td>85</td>
</tr>
<tr>
<td>c</td>
<td>Me₂N</td>
<td>78</td>
</tr>
<tr>
<td>d</td>
<td>Me</td>
<td>80</td>
</tr>
</tbody>
</table>

The proton attached to C-6 (H₆) also shows a double doublet at δ 4.67 (J = 13.5 Hz and 3 Hz). The vinylic protons of the vinylthio group appeared as an ABX system. The doublet at δ 5.67 ppm is due to vinylic proton H₃ with trans coupling value of 16.8 Hz. The other proton H₅ appeared as a doublet at 5.63 ppm with a cis coupling constant of 9.6 Hz. The doublet of doublet at δ 6.58 ppm is due to vinylic proton Hₓ. The coupling constant being 16.8 and 9.6 Hz. The geminal coupling of H₃ and H₅ is almost zero. The vinylic proton in the thiopyrone ring appeared at δ 6.31 ppm. The aromatic protons gave a singlet at 7.31 ppm. The structure was further confirmed by ¹³C NMR spectrum (50.32 MHz, CDCl₃, Fig 2). It showed a peak at δ 191.55 ppm due to the presence of carbonyl group. The peaks at δ 119.11, 123.05, 125.96, 127.3, 128.49, 136.74 and 160.73 ppm are due to aromatic and vinylic carbons. The other peaks which are due to the methylene group.
Fig. 1 $^1$H NMR Spectrum (300 MHz) of compound 37a
Fig. 2 $^{13}$C NMR Spectrum (50.32 MHz) of compound 37a
Fig. 3 IR Spectrum (KBr) of compound 37a
Fig. 4 Mass Spectrum (ElMS) of compound 37a
and the methyne group of the dihydrothiopyran ring has been found at δ 44.33 and 47.33 ppm respectively.

The IR (KBr, Fig 3) spectrum showed a strong band for the carbonyl group at 1640 cm⁻¹. The other bands at 1580, 1510 and 1450 cm⁻¹ have been assigned to double bonds. The mass spectrum (EIMS, Fig+) showed the molecular ion peak at 248 (M⁺, 40 %) and other peaks due to fragments appeared at 231 (16.3%), 215 (18.4%), 128 (15.2%), 115 (7.5%), 104 (10.6%), and 85 (60.6%).

This reaction has been shown to be general to other substituted substrates as well. Thus the cinnamoyl ketenedithioacetals 32b-d derived by the similar condensation reactions of substituted benzaldehydes with the acyl ketenedithioacetal 30 also gave the corresponding thiopyran-4-ones 37b-d on reaction with dimsyl anion under similar conditions (Scheme 18).

This reaction has been extended to cinnamoyl ketenedithioacetals 34a-b having an α-methyl substituent which has been prepared by the condensation reactions of the acyl ketenedithioacetal 33 with benzaldehydes. Thus the cinnamoyl ketenedithioacetals 34a on treatment with dimsyl sodium prepared from NaH and DMSO at 70 °C for 1h gave 3-methyl-6-phenyl-2-vinylthio-5,6-dihydrothiopyran-4-one 38a in 82% yield (Scheme 19). The structure of 38a was confirmed with the help of spectral data (experimental). Similarly the p-methoxy substituted derivative also gave the expected substituted dihydrothiopyran-4-one 38b in 87% yield. The spectral data of the compound 38b are given in the experimental section.
A probable mechanism for the formation of 6-aryl-5,6-dihydrothiopyran-4-ones 37 has been depicted in Scheme 20. The dimethyl anion induced fragmentation of the 1,3-dithiolane ring has been observed earlier in the formation of vinyl dithiocarboxylates from 2-ylidene-1,3-dithiolane derivatives. In the case of reactions involving cinnamoyl ketenedithioacetals it is probable that the intermediate thiolate anion can undergo a conjugate addition to the enone moiety due to the high nucleophilicity of the sulfur resulting in the formation of the dihydrothiopyran-4-one 37.
The 5-phenyl-2,4-pentadienoyl ketenedithioacetal 36a derived by the condensation of cinnamaldehyde with 2-acetyl)methylene-1,3-dithiolane 30 also was treated with dimsy anion under similar reaction conditions. When 36a was treated with the reagent prepared from sodium hydride and DMSO for 1h, the product mixture after usual workup and column chromatographic purification gave 6-styryl-2-vinylthio-5,6-dihydrothiopyran-4-one 40a in 82% yield (Scheme 21). The $^1$H NMR spectrum of 40a was similar to that of the phenyl substituted dihydrothiopyran-4-one 37a-d but for the presence of the signals due to the trans styryl double bond. However the signals due the methylene and methyne protons of the dihydrothiopyran ring of 40a appeared as complex multiplets (experimental).

In a similar fashion the 5-phenyl-2,4-pentadienoyl ketenedithioacetal 40b having a methyl substituent also gave the corresponding styryl substituted dihydrothiopyran-4-one on treatment with dimsy anion in DMSO for 1h at 70 °C (Scheme 21).
The mechanism involved in the formation of styryl substituted dihydrothiopyran-4-ones is similar to the one that has been described for the reaction of cinnamoyl ketene dithioacetals.

A few examples involving intramolecular Michael type additions of sulfur leading to the formation of dihydrothiopyrans have been described in the literature. For example, the intermediate dithiocarboxylic acid 42 formed by the reaction of α,β-unsaturated ketone 41 with carbon disulfide in the presence of base, undergo cyclization to give the 2-methylthio substituted dihydrothiopyran-4-ones 43 (Scheme 22).  

<table>
<thead>
<tr>
<th>36, 40</th>
<th>R</th>
<th>Yield(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>H</td>
<td>83</td>
</tr>
<tr>
<td>b</td>
<td>Me</td>
<td>75</td>
</tr>
</tbody>
</table>

Scheme 21
Similar reactions involving phenyl isothiocyanate gives the respective amino substituted dihydrothiopyran-4-ones. Our method described above provides a convenient alternative for the synthesis of dihydrothiopyranones. Since the vinylthio group can be replaced effectively by other heteronucleophiles several substituted dihydrothiopyranone derivatives can be derived from the dihydrothiopyranone 37 and 40.

5.3.3 Reactions of Substituted 2-ylidene 1,3-dithiolanes with Dimsyl anion Followed by Alkylation with Methyl iodide

The in situ alkylation of the intermediate formed by the dimsyl anion induced fragmentation of cinnamoyl ketenedithioacetal 32a was examined next. It was expected that the intermediate carbanion formed after the cyclization involving the thiolate anion may undergo stereoselective alkylation leading to the formation of substituted thiopyran-4-ones. The reaction was carried out as usual in the presence of sodium hydride in DMSO at 70 °C for 1h. The product mixture after purification by column chromatography gave a viscous liquid which showed a single spot on TLC. However, the proton NMR spectrum of this liquid indicated that it could be a mixture of isomers. Apparently the alkylation with methyliodide occurs before the cyclization to afford 1-methylthio-5-phenyl-1-vinylthio-1,4-pentadiene-3-one 44A and 44B as a mixture of geometrical isomers (Scheme 23).
The major isomer (70%) has been identified as \(Z,E-1\)-methylthio-1-vinylthio-5-phenyl-1,4-pentadiene-3-one \(44A\). In the \(^1\)H NMR spectrum (300 MHz, Fig 5) it shows a singlet at \(\delta 6.27\) ppm which is due to the proton attached to the ketenedithioacetal moiety at the \(\alpha\) position. The double doublet \(H_X\) of the vinylthio group was present at \(6.91\) ppm (\(J = 16.5\) Hz, 9.3Hz). The proton \(H_A\) which is \(trans\) to \(H_X\) was present at \(\delta 5.74\) (\(J = 16.5\) Hz) and \(H_B\) which is \(cis\) to \(H_X\) is present as a doublet at \(\delta 5.74\) ppm (\(J = 9.3\) Hz). The methylthio group shows a singlet at \(\delta 2.49\) ppm. The proton adjacent to the carbonyl group which belongs to the cinnamoyl moiety appears as a doublet at \(\delta 6.83\) ppm (\(J = 16\) Hz). The aromatic protons appeared as two multiplets between 7.26 and 7.56 ppm. The other vinylic proton of the cinnamoyl group appeared at \(\delta 7.61\) ppm as a doublet (\(J = 16\) Hz).

The minor isomer (30%) which is characterized as \(E,E-1\)-methylthio-5-phenyl-1-vinylthio-1,4-pentadiene-3-one \(44B\) shows a singlet in the NMR spectrum (Fig 5) at \(\delta 6.47\) ppm which is attributed to the vinylic proton at the \(\alpha\)-position of the ketenedithioacetal moiety. The double doublet \(H_X\) of the vinylic group appeared at \(\delta 6.53\) ppm (\(J = 16.5\) Hz and 9.3Hz) and \(H_A\) which is \(trans\) to \(H_X\) gave its signal at \(\delta 5.74\) ppm (\(J = 16.5\) Hz). The proton \(H_B\) which is \(cis\) to \(H_X\) also gave a doublet at \(\delta 5.74\) ppm (\(J = 9.3\) Hz).
Fig. 5b $^1$H NMR Spectrum (300 MHz) of compound 44
Fig. 5a $^1$H NMR Spectrum (300 MHz) of compound 44
Fig. 6 IR Spectrum (KBr) of compound 44
Fig. 7 Mass Spectrum (EIMS) of compound 44
The assignment of configuration of 44A and 44B was based on the δ value of the vinylic proton H₆ of the ketenedithioacetal moiety which is α to the carbonyl group. The normal chemical shift value of this proton is δ 6.20 ppm when the β position is substituted with methylthio groups. Replacement of a methylthio group by a vinylthio group results in a downfield shift of this signal. This shift is more pronounced when the vinylthio group is cis to the vinylic proton. Therefore the minor isomer which has a higher δ value (δ = 6.27 ppm), compared to cinnamoyl ketenedithioactals having methylthio substituents, for the vinylic proton α-to the carbonyl group (H₆) has been assigned a trans configuration at the ketenedithioacetal moiety. Similarly the major isomer which has a still higher δ value for H₆ has been assigned as the cis isomer.26

![Diagram](image.png)

The IR (KBr, Fig 6) spectrum showed peaks due to carbonyl group at 1660 cm⁻¹ and due to double bonds at 1590 and 1480 cm⁻¹. The mass spectrum (EIMS, Fig 7) of the compound showed molecular ion peak at m/z 262 (24.4%). The other prominent peaks were at 248 (11.2%), 218 (20.3%), 194 (28.5%), 166 (56.3%), 136 (100%), 121 (96.6%), 106 (86.2%).

The mechanism involved in the formation of vinylthio substituted cinnamoyl ketenedithioacetals is similar to the one that has been described for the formation of 5,6-dihydrothiopyran-4-one. The dimethyl anion induced fragmentation of the 2-ylidene-1,3-dithiolane 32a leads to the formation of the thiolate anion 45A and 45B which on alkylation can lead to the mixture of stereoisomers (Scheme 24). Apparently, alkylation of the thiolate anion which leads to the formation of the cis ketenedithioacetal is favoured.27
5.3.4. Reaction of 2-(4-Methylbenzoylmethylene)-1,3-dithiolane 46 with dimethyl anion
Followed by Alkylation with Phenacyl bromide

We have next examined the dimethyl anion assisted fragmentation of 2-ylidene-1,3-
dithiolanes followed by alkylation with functionalized electrophiles. We have already shown
that alkylation of aroyl dithioacetate with phenacyl bromide in the presence of sodium
hydride leads to the formation of 2-phenacylidene-1,3-oxathiole derivatives. The mechanism
of this transformation involve an in situ displacement of methylthio group by an
intramolecular attack of the thiolate anion. Fragmentation of 2-ylidene-1,3-dithiolanes also
lead to the formation of an intermediate thiolate anion of a vinyl β-oxodithiocarboxylate.
Alkylation of this intermediate also may lead to the formation of the respective 2-
phenacylidene-1,3-oxathiole derivative via the intramolecular attack of the thiolate anion
displacing the vinylthio group. Alternative modes of cyclizations leading to the formation of
thiophene derivatives are also possible. The 2-(4-methylbenzoylmethylene)-1,3-dithiolane
46 was treated with dimethyl anion in DMSO for 1h at 70 °C. The mixture was then cooled to
room temperature and phenacyl bromide was added and stirred at room temperature for
48h. After usual work up and purification by column chromatography a crystalline solid of mp 114-115 °C was obtained as the sole isolated product in 51% yield. The structure of the compound was confirmed as 5-phenyl-2-(4-methylbenzoylmethylene)-2,3-dihydro-1,3-oxathiole 48 (Scheme 25) by comparing their spectral and physical data with that of the compound isolated earlier.

\[ \text{Scheme 25} \]

Since the alkylation of methyl \( p \)-methylbenzoyl dithioacetate by phenacyl bromide also gave the same product in comparable yield (55%) this reaction did not seem to offer any advantage in terms of yield or product selectivity. Therefore no further explorations were carried out in this direction.

5.4 Conclusions

A variety of cinnamoyl ketenedithioacetals, wherein the ketenedithioacetal group is present as a 1,3-dithiolane moiety, are prepared by the base catalysed condensation of acyl ketenedithioacetal with substituted benzaldehydes. Cinnamoyl ketenedithioacetals with an \( \alpha \)-methyl substituent are prepared by the condensation of acyl ketenedithioacetals derived
from methyl ethyl ketone with substituted benzaldehydes. Similarly 5-phenyl-2,4-pentadienoyl ketenedithioacetals are obtained by the Claisen-Schmidt condensation of acyl ketenedithioacetals 30 and 33 with cinnamaldehyde.

The dimethyl anion induced fragmentation reaction of cinnamoyl and 5-aryl-2,4-pentadienoyl ketenedithioacetals have been examined in detail. It has been found that the intermediate thiolate anion formed by the fragmentation undergo subsequent cyclization leading to the formation of vinylthio substituted 5,6-dihydrothiopyran-4-one derivatives in good yields. The method has been found to be very general and can be considered as a useful protocol for the synthesis of vinylthio substituted thiopyran-4-ones. The vinylthio functionality can be easily displaced by other nucleophiles such as alkoxydes and alkane thiolates. Therefore they are valuable substrates for subsequent transformations as well. A probable mechanism leading to the formation of these products has been proposed.

Some preliminary examinations on the alkylation of the intermediate thiolate anions obtained by the dimethyl anion induced fragmentation reactions of cinnamoyl ketenedithioacetals were also carried out. Alkylation prior to cyclization was preferred for the thiolate anion of vinyl γ,δ-unsaturated-β-oxodithiocarboxylate when treated with methyl iodide. The reaction gave a mixture of E and Z isomers of the respective cinnamoylketene dithioacetal. It has also been shown that the thiolate anion of vinyl β-oxodithiocarboxylate obtained by the fragmentation of 2-(benzoylmethylene)-1,3-dithiolanes on alkylation with phenacyl bromide gave respective 1,3-oxathiole derivatives.

5.5 Experimental

The general experimental details are given in Chapter 3. Anhydrous DMSO was purchased from M/s Spectrochem Ltd, Mumbai and was kept over molecular sieves type 4A before use.

5.5.1 Preparation of 2-Acetylmethylene-1,3-dithiolanes 30 and 33.

2-Acetylmethylene-1,3-dithiolanes 30 and 33 were prepared by the known method. To a suspension of sodium t-butoxide (19.2g, 0.2mol), prepared by refluxing molecular sodium (4.6g, 0.2mol) in t-butanol (100mL) and benzene (100mL), a solution of ketone
(0.1mol) and carbon disulfide (0.1mol) was added. The reaction mixture was stirred at room temperature for 3-4 h. 1,2-Dibromoethane (18.60g, 0.1mol) was added slowly over 15 min to a well cooled (0-5 °C) and stirred reaction mixture and was then allowed to stand at room temperature for 12 h. The mixture was poured into cold water, the benzene layer was separated and the aqueous layer was extracted with benzene (3 x 50 mL). The combined extracts were washed with water, dried with sodium sulfate and concentrated to give crude ketenedithioacetal. This was further purified by crystallization. The ketenedithioacetals 30 and 33 were prepared and characterized by comparing their spectral and physical data with reported values.

1-(1,3-dithiolane-2-ylidene)-2-propanone 30 isolated as pale yellow crystalline solid mp 73-74°C (lit mp 74-75 °C)

3-(1,3-dithiolane-2-ylidene)-2-butanone 33 Isolated as reddish brown crystalline solid mp 60°C

5.5.2 Reaction of 2-Acetylmethylene-1,3-dithiolane 30 with substituted Benzenaldehydes.

Sodium metal (0.46g, 20 mmol) was dissolved in ethanol (20 mL) to which 2-acetylmethylene-1,3-dithiolane 30 (1.6g, 10 mmol) was added followed by the substituted benzaldehyde 31 (10 mmol). The reaction mixture was stirred at 0-5 °C for 4 h. The solid separated was filtered and recrystallized from methanol.

1-(1,3-Dithiolan-2-ylidene)-4-phenyl-3-butene-2-one 32a was obtained by the reaction of benzaldehyde (1.06g, 10mmol) and 2-acetylmethylene-1,3-dithiolane 30 (1.6g, 10 mmol) as an yellow crystalline solid. Yield: 1.86g (75%) mp 150-151 °C

$^1$H NMR (90 MHz, CDCl$_3$) $\delta$ 3.50 ppm (s, 4H, SCH$_2$); 6.85 (d, $J = 15$ Hz, 1H, vinylic); 7.0 ppm (s, 1H, vinylic); 7.30-7.90 (m, 6H, 5 arom and vinylic).

IR (KBr, $v_{max}$) 1640, 1570, 1490, 1340, 1320, 1280,
1-(1,3-Dithiolan-2-ylidene)-4-(4-methylphenyl)-3-butene-2-one 32b was obtained by the reaction of \( p \)-methylenzaldehyde (1.2g, 10mmol) with 2-acetylethylenylene-1,3-dithiane 30 (1.6g, 10mmol) as yellow crystalline solid. Yield: 1.83g (70%) mp 153-154 °C

\(^1\)H NMR (90 MHz, CDCl\(_3\)) \( \delta \) 2.45 (s, 3H, CH\(_3\)); 3.30-3.65 (m, 4H, SCH\(_2\)); 6.85 (d, \( J = 15 \) Hz 1H, vinylic ); 7.00 (s, 1H, vinylic); 7.20-7.90 (m, 5H, arom and vinylic). IR (KBr, \( \nu_{\text{max}} \)) 1640, 1580, 1500, 1330, 1270, 1240, 1200, 1180, 1140, 1120 and 980 cm\(^{-1}\).

1-(1,3-Dithiolan-2-ylidene)-4-(4-methoxyphenyl)-3-butene-2-one 32c was obtained by the reaction of \( p \)-methoxybenzaldehyde (1.36g, 10mmol) and 2-acetylethylenylene-1,3-dithiane 30 (1.6g, 10mmol) obtained as yellow crystalline solid. Yield: 2.22g (80%) mp 104-105 °C

\(^1\)H NMR (90 MHz, CDCl\(_3\)) \( \delta \) 3.35-3.65 (m, 4H, SCH\(_2\)); 3.95 (s, 3H, OMe); 6.75 (s, 1H, vinylic); 6.85-7.20 (m, 3H, arom and vinylic); 7.60-8.00 (m, 3H, arom and vinylic). IR (KBr, \( \nu_{\text{max}} \)) 1640, 1580, 1480, 1420, 1300, 1280, 1240, 1160, 1115, 1020 and 970 cm\(^{-1}\).
4-(1,3-Dithiolan-2-ylidene)-1-phenyl-1-pentene-3-one 34a was obtained by the reaction of benzaldehyde (1.06 g, 10 mmol) and 3-(1,3-dithiolane-2-ylidene)-2-butanone 33 (1.74 g, 10 mmol) as yellow crystalline solid. mp 105-106 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.35 (s, 3H, CH\(_3\)); 3.35-3.45 (m, 4H, SCH\(_2\)); 7.24 (d, \(J = 16\) Hz, 1H, vinylic); 7.32-7.62 (m, 5H, arom); 7.74 (d, \(J = 16\) Hz, 1H, vinylic). IR (KBr \(v_{\text{max}}\)) 1630, 1580, 1480, 1440, 1330, 1280, 1230, 1080, 1020 and 980 cm\(^{-1}\).

4-(1,3-Dithiolan-2-ylidene)-1-(4-Methylphenyl)-1-pentene-3-one 34b was obtained by the reaction of 1.2 g (10 mmol) \(p\)-methylbenzaldehyde with 2-acetylmethylene-1,3-dithiolane 33 (1.74 g, 10 mmol) as yellow crystalline solid. Yield: 2.35 g (85%) mp 148-150 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 2.33 (s, 3H, CH\(_3\)); 2.38 (s, 3H, CH\(_3\)); 3.30-3.45 (m, 4H, SCH\(_2\)); 7.18 (d, \(J = 8\) Hz, 2H, arom); 7.25 (d, \(J = 16\) Hz, 1H, vinylic); 7.48 (d, \(J = 8\) Hz, 2H, arom); 7.72 (d, \(J = 16\) Hz, 1H, vinylic). \(^13\)C NMR (400 MHz, CDCl\(_3\)) \(\delta\) 19.48 (Me), 21.5 (Me), 35.7 (SCH\(_2\)), 39.44 (SCH\(_2\)), 119.98, 121.17, 128.21, 129.5, 132.66, 140.37, 143.12, 161.04 (arom and vinylic), 185.6 (C=O).
4-(1,3-Dithiolan-2-ylidene)-1-(4-Methoxyphenyl)-1-pentene-3-one 34c was obtained by the reaction of p-methoxybenzaldehyde with 2-acetylmethylene-1,3-dithiolane 33 (1.74g, 10mmol) as an yellow crystalline solid. Yield: 2.48g (85%) mp 120-121 °C. 

\[ \text{\(^1\)H NMR (300 MHz, CDCl\(_3\)) \delta} \]

- 2.29 (s, 3H, CH\(_3\));
- 3.33-3.34 (m, 4H, CH\(_2\));
- 3.79 (s, 3H, OCH\(_3\));
- 6.85 (d, J = 9 Hz, 2H, arom);
- 7.05 (d, J = 15 Hz, 1H, vinylic);
- 7.56 (d, J = 9 Hz, 2H, arom);
- 7.64 (d, J = 15 Hz, 1H, vinylic).

IR (KBr, \(v_{max}\)) 1640, 1600, 1575, 1500, 1475, 1440, 1370, 1330, 1300, 1280, 1250, 1230, 1160, 1090, 1020 and 970 cm\(^{-1}\).

1-(1,3-Dithiolan-2-ylidene)-6-phenyl-3,5-hexadiene-2-one 36a was obtained by the reaction of cinnamaldehyde (1.32g, 10mmol) with 2-acetylmethylene-1,3-dithiolane 30 (1.6g, 10mmol) as yellow crystalline solid. Yield: 2.2g (82%) mp 159-160 °C

\[ \text{\(^1\)H NMR (90 MHz, CDCl\(_3\)) \delta} \]

- 3.25-3.55 (m, 4H, SCH\(_2\));
- 6.45 (d, J = 15 Hz, 1H, vinylic);
- 6.85 - 7.15 (m, 3H, vinylic);
- 7.35-7.70 (m, 6H, arom and vinylic).

IR (KBr, \(v_{max}\)) 1625, 1565, 1480, 1270, 1240, 1270, 1220, 1150, 1100, 1000 and 900 cm\(^{-1}\).
2-(1,3-Dithiolan-2-ylii)de)-7-phenyl-4,6-heptadiene-3-one 36b was obtained by the reaction of cinnamaldehyde (1.32g, 10mmol) and 2-acetylmethylene-1,3-dithiolane 33 (1.72g, 10mmol) as an yellow crystalline solid. Yield: 2.3g (80%)

$^1$H NMR (300 MHz, CDCl$_3$) δ 2.10 (s, 3H, CH$_3$); 3.18-3.37 (m, 4H, SCH$_2$); 6.72 (d, J=15 Hz, 1H, vinylic); 6.80-6.95 (m, 1H, vinylic); 7.20-7.50 (m, 7H, arom and vinylic). IR (KBr, $v\text{max}$) 1620, 1560, 1470, 1350, 1280, 1080, 1020 and 995 cm$^{-1}$.

5.5.3 Reactions of Cinnamoyl Ketenedithioacetals 32a-d and 34a-b with Dimsyl anion:

Formation 5,6-dihydrothiopyran-4-ones 37a-d and 38a-b. General procedure.

Sodium hydride (50%) (0.24g, 5mmol) was taken in 15 mL dimethyl sulfoxide and the mixture was stirred at 70 °C for 1 h. To the dimsyl anion thus formed cinnamoyl ketenedithioacetal (5 mmol) was added. The reaction mixture was stirred at 70 °C for another 1 h, the mixture was then poured into cold water and made neutral with dil. HCl. Extracted with methylene chloride (3 x 25 mL). The combined organic layer was washed with water (3 x 25 mL). Removal of solvent under vacuum gave the crude product. This was further purified through column chromatography using hexane as the eluent.

6-Phenyl-2-vinylthio-5,6-dihydrothiopyran-4-one

37a was obtained by the reaction of 1-(1,3-Dithiolan-2-ylii)de)-4-phenyl-3-butene-2-one 32a (1.24g, 5 mmol) with dimsyl anion in DMSO at 70 °C for 1 h as reddish brown liquid. Yield: 0.93g (75%) $^1$H NMR (300 MHz, CDCl$_3$) δ 2.92 (dd, J = 16.5 Hz and 3.0 Hz, 1H, $H_b$); 3.10 (dd, J = 16.5 Hz and 13.5 Hz,
$^{1}H$, $H_b$); 4.67 (dd, $J = 13.5$ Hz and 3 Hz, 1H, $H_c$); 5.67 (d, $J = 16.8$ Hz, 1H, $H_A$); 5.63 (d, $J = 9.6$ Hz, 1H, $H_b$); 6.31 (s, 1H, vinylic); 6.58 (dd, $J = 16.8$ Hz and 9.6 Hz, 1H, $H_x$); 7.31 (s, 5H, arom) ppm. \(^{13}\)C NMR (50.32 MHz, CDCl\(_3\)) \(\delta\) 44.33(CH\(_2\)), 47.43 (CH), 119.00, 115.00, 123.04, 125.96, 127.30, 128.49, 136.74, 160.72, 191.55 ppm. IR (KBr, $\nu_{\text{max}}$) 1640, 1580, 1510, 1450, 1400, 1310, 1255, 1140, 1020 and 950 cm\(^{-1}\) EIMS (m/z) 248 (M\(^+\), 40%), 231 (16.3%), 215 (18.4%), 192 (11.8%), 144 (100%), 128 (15.2%), 115 (7.5%), 104 (10.6%) and 85 (60.6%).

6-(4-Methoxyphenyl)-2-vinylthio-5,6-dihydrothiopyran-4-one 37b was obtained by the reaction of 1-(1,3-Dithiolan-2-ylidene)-4-(4-methoxy-phenyl)-3-butene-2-one\(^{32}\)b (1.45 g, 5 mmol) with dimsyl anion with DMSO at 70°C for 1 h as reddish brown liquid. Yield: 1.2 g (85%) \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.95 (dd, $J = 16.5$ Hz and 3.0 Hz, 1H, $H_a$); 3.15 (dd, $J = 16.5$ Hz and 13.5 Hz, 1H, $H_b$); 3.85 (s, 3H, OMe); 4.70 (dd, $J = 13.5$ Hz and 3 Hz, 1H, $H_c$); 5.80 (d, $J = 16.8$ Hz, 1H, $H_a$); 5.70 (d, $J = 9.6$ Hz, 1H, $H_b$); 6.35 (s, 1H, vinylic); 6.70 (dd, $J = 16.8$Hz and 9.6 Hz, 1H, $H_x$); 7.0 (d, $J = 9$Hz, 2H, arom); 7.4 (d, $J = 9$Hz, 2H, arom) EIMS (m/z) 278 (M\(^+\), 55.5%), 218(13.9%), 144 (100%), 134 (77.6%), 119 (20.2%), 91 (26%), 85 (84%)
6-(N,N-dimethylaminophenyl)-2-vinylthio-5,6-dihydrothiopyran-4-one 37c was obtained by the reaction of 1-(1,3-dithiolan-2-ylidene)-4-(4-N,N-dimethylaminophenyl)-3-butene-2-one 32c (1.45g, 5 mmol) with dimethyl anion at 70 °C for 1 h as yellow crystals. Yield: 1.13g (78%) mp 90-92 °C ¹H NMR (300 MHz, CDCl₃) δ 2.89 (dd, J = 16.5 Hz and 3.0 Hz, 1H, H₄); 2.96 (s, 6H, NMe₂); 3.09 (dd, J = 16.5Hz and 14.1Hz, 1H, H₃); 4.62(dd, J = 14.1 Hz and 3 Hz, 1H, H₂); 5.63 (d, 1H, H₆, J = .3 Hz); 6.77 (d, 1H, H₆, J = 16.8 Hz); 6.29 (s, 1H, vinyl); 5.60 (dd, J = 16.8Hz and 9.3Hz, 1H, H₅); 6.68 (d, J = 9Hz, 2H, arom); 7.24(d, J = 9Hz, 2H, arom) ppm. ¹³C NMR (75.46 MHz, CDCl₃) δ 40.40 (CH₂), 45.00 (NMe₂), 47.74 (CH), 112.44, 119.21, 123.08, 123.88, 126.42, 128.43, 150.62, 161.84 (arom and vinyl), 192.81(C=O) ppm. IR (KBr, νmax) 1635 (C=O), 1600, 1500, 1440 (C=C), 1400, 1355, 1310, 1280, 1250, 1230, 1295, 1140, 1060, 1020, and 980 cm⁻¹. EIMS (m/z) 291(M⁺, 76.3%), 246 (8.2%), 232 (24.3%), 190 (10.2%), 160 (17.7%), 147 (100%), 134 (44.7%), 130 (34%), 85 (75.4%)

6-(4-Methylphenyl)-2-vinylthio-5,6-dihydrothiopyran-4-one 37d was obtained by the reaction of 1-(1,3-dithiolan-2-ylidene)-4-(4-methylphenyl)-3-butene-2-one 32d (1.31g, 5mmol) with dimethyl anion in DMSO at 70 °C for 1 h as an yellow liquid. Yield: 1.05g. (80%) ¹H NMR (300
MHz, CDCl₃) δ 2.35 (s, 3H, CH₃); 2.91 (dd, J = 15 Hz and 3 Hz, 1H, Hₔ); 3.09 (dd, 15Hz and 12Hz, 1H, Hₜ); 4.65 (dd, J = 12Hz and 3 Hz, 1H, Hₖ); 5.64 (d, J = 9.3 Hz, 1H, Hₑ); 5.68 (d, J = 16.5 Hz, 1H, Hₕ); 6.31 (s, 1H, vinylic); 6.59 (dd, J = 16.5 Hz and 9.3Hz, 1H, Hₓ), 7.18 (d, J = 9Hz, 2H, arom) 7.26 (d, 2H, arom, 9Hz) ¹³C NMR (75.46 MHz, CDCl₃) δ 21.33 (CH₃), 44.9 (CH₂), 47.72 (CH), 119.47, 123.47, 126.43, 127.6, 129.9, 134.1, 138.89, 161.56 (arom and vinylic) and 192.37 (C=O) ppm. IR (KBr, v_max) 1640, 1580, 1520, 1410, 1310, 1280, 1250, 1180, 1140, 1020 and 955 cm⁻¹. EIMS (m/z) 263 (M⁺, 37.7%), 203 (4.6%), 144 (100%), 118 (34.8%), 91 (16.7%) and 85(92.4%).

3-Methyl-6-phenyl-2-vinylthio-5,6-dihydrothiopyran-4-one 38a was obtained by the reaction of 4-(1,3-dithiolan-2-ylidene)-1-phenyl-1-pentene-3-one 34a 1.25g (5mmol) with dimethyl anion in DMSO at 70°C for 1 h. Yield: 1.07g (82%) ¹H NMR (400 MHz, CDCl₃) δ 2.0 (s, 3H, CH₃); 2.95 (dd, J = 16.5 Hz and 3 Hz, 1H, Hₔ); 3.15 (dd, J = 16.5 Hz and 13.5 Hz, 1H, Hₕ); 4.55 (dd, J = 13.5Hz and 3Hz, 1H, Hₜ); 5.65 (d, J = 16.8 Hz,1H, Hₐ); 5.55 (d, J = 9.6 Hz, 1H, Hₕ); 6.65 (dd, J = 16.8 Hz and 9.6 Hz, 1H, Hₓ); 7.35 (s, 5H, arom). ¹³C NMR (75.46 MHz, CDCl₃) δ 13.6 (CH₃), 44.7 (CH₂), 46.7 (CH), 121.7, 126.8, 127.3, 127.5, 128.7, 129.1, 137.4, 152.20 (arom and vinylic) and 190.95 ppm. IR (KBr,v_max) 1640, 1500,
1300 and 1260 cm⁻¹ EIMS (m/z) 262 (M⁺, 33.4%), 204 (13.3%), 158 (54.2%) 104 (37%), 99 (100%)

6-(4-Methoxyphenyl)-3-methyl-2-vinylthio-5,6-
dihydro thiopyran-4-one 38b was obtained by the reaction of 4-(1,3-dithiolan-2-ylidene)-1-(4-
methoxyphenyl)-1-pentene-3-one 34b (1.45g, 5mmol) with dimethyl anion in DMSO at 70 °C for 1 h.
Yield: 1.21g. (87%). ¹H NMR (300 MHz, CDCl₃)
δ 1.95 (s, 3H, CH₃), 2.86-3.10 (m, 2H, H₆ and H₇), 3.80 (s, 3H, OCH₂), 4.49 (dd, J = 13 Hz and 3 Hz, 1H, H₈); 5.50 (d, J = 9.6 Hz, 1H, H₉); 5.56 (d, 16.5 Hz, 1H, HA); 6.61 (d, J = 16.5 Hz and 9.6 Hz, 1H, HX); 6.80 (d, J = 9 Hz, 2H, arom); 7.20 (d, J = 9 Hz, 2H, arom). ¹³C NMR (400 MHz, CDCl₃) δ 13.70, 17.37, 44.90, 45.66, 46.27, 55.41, 114.4, 122, 126.7, 127.00, 128.90, 129.44, 153, 159.86 and 191.55 ppm.
IR (KBr, νmax) 1640, 1605, 1580, 1505, 1460, 1440, 1420 1300, 1240, 1180, 1110, 1080, 1020, 950 and 920 cm⁻¹. EIMS (m/z) 292 (M⁺, 75.5%), 266 (77.9%), 262 (100%), 234 (38.5%), 233 (44.1%), 158 (23.9%) 134 (64%).

5.5.4 Reactions of 36a and 36b with Dimsyl anion: Formation of 5,6-
Dihydrothiopyran-4-ones 40a and 40b. General procedure
Sodium hydride (50%) (0.24g, 5 mmol) was taken in 15 mL dimethyl sulfoxide and the mixture was stirred at 70 °C for 1 h. To the dimethyl anion thus formed 5-phenyl-2,4-
pentadienoyketenedithioacetal 36a or 36b (5 mmol) was added. The reaction mixture was stirred at 70 °C for another 1 h, cooled and poured into cold water and made neutral with
dil. HCl. Extracted with methylene chloride (3 x 25 mL) and the combined organic layer was washed with water (3 x 25 mL). Removal of solvent under vacuum gave the crude product. This was further purified by column chromatography using hexane as the eluent.

6-Styryl-2-vinylthio-5,6-dihydrothiopyran-4-one 40a was obtained by the reaction of 1-(1,3-dithiolan-2-ylidene)-6-phenyl-3,5-hexadiene-2-one 36a (1.37g 5mmol) with dimsyl anion in DMSO at 70 °C for 1 h. Yield: 1.09g. (80%) mp 55-56 °C 1H NMR (300 MHz, CDCl₃), δ 2.78-2.92 (m, 2H, Hₘ and Hₙ); 4.28 (m, 1H, H₂); 5.67 (d, J = 16.8 Hz, 1H, H₄); 5.63 (d, J = 9.6 Hz, 1H, H₆); 6.17 (dd, J = 16 Hz and 9 Hz, 1H, H₆); 6.24 (s, 1H, vinylic); 6.52-6.64 (m, 2H, vinylic); 7.24-7.34 (m, 5H, arom), IR (KBr vmax) 1635 (C=O), 1580, 1520 (C=C), 1275, 1250, 1230, 1150, 1020, 910 and 810 cm⁻¹. EIMS (m/z), 274 (M⁺ 31.9%), 218 (18.1%), 177 (24.2%), 144 (70.2%), 129 49.2%), 115 (33.8%), 85 (100%)

6-Styryl-3-methyl-2-vinylthio-5,6-dihydrothiopyran-4-one 40b was obtained by the reaction of 2-(1,3-dithiolane-2-ylidene)-7-phenyl-4,6-heptadiene-3-one 36b (1.44g, 5mmol) with dimsyl anion in DMSO at 70 °C for 1 h as yellow liquid. Yield: 1.08g (75%). 1H NMR (400 MHz, CDCl₃), δ 2.00 (s, 1H, CH₃); 2.87 (dd, J = 16.2 Hz and 11 Hz, 1H, Hₙ); 2.99 (dd, J = 16.2 Hz and 4.3Hz, 1H, Hb); 4.19-4.28 (m, 1H, H₃); 5.60 (d, J = 9.6 Hz, 1H, Hₙ); 5.65 (d, J = 16.8 Hz, 1H, H₄); 6.20 (dd, J = 16.8 Hz and 9.6 Hz, 1H,
Hx); 6.55-6.75 (m, 2H, vinylic); 7.25-7.40 (m, 5H, arom), $^{13}$C NMR (400 MHz, CDCl$_3$), 13.59 (CH$_3$), 43.83 (CH$_2$), 44.82 (CH), 121.76, 124.90, 126.59, 127.44, 128.38, 128.65, 129.00, 134.02, 135.62, 151.78 (arom and vinylic) and 190.82 (C=O) ppm. IR (KBr, $\nu$)$_{max}$ 1640, 1580, 1510, 1440, 1400, 1365, 1300, 1260, 1150, 1075, 1020, 960 and 920 cm$^{-1}$ EIMS (m/z) 288 (M$^+$, 100%), 262 (41.3%), 232 (22.2%), 169 (35.3%), 158 (22.3%) ppm.

5.5.5 Reactions of 1-(1,3-Dithiolan-2-ylidene)-4-phenyl-3-butene-2-one 32a with Dimsyl anion followed by Alkylation with Methyl iodide

A suspension of sodium hydride (50%) (0.24g, 5mmol) in dimethyl sulfoxide (15 mL) was stirred at 70 °C for 1h. To the dimsyl anion thus formed cinnamoylketenedithioacetal 32a (1.24 g, 5 mmol) was added. The reaction mixture was stirred at this temperature for 1h, cooled and methyl iodide (0.31 mL, 5 mmol) was added and stirred at room temperature for 48 h. The mixture was then poured into cold water and made neutral with dil. HCl. Extracted with methylene chloride (3x25 mL). The combined organic layer was washed with water (3x25 mL) and dried (Na$_2$SO$_4$). Removal of solvent under vacuum gave brown viscous residue which was passed through a column of silica gel using hexane as the eluent.

$I$-Methylthio-5-phenyl-1-vinylthio-1,4-pentadiene-3-one 44A and 44B was isolated as reddish brown liquid as a mixture of geometrical isomers. ($Z : E$ 70 : 30) Yield: 0.95g (72%)

$^1$H NMR (300 MHz, CDCl$_3$) $Z, E$ $I$-methylthio-5-
**phenyl-1-vinylthio-1,4-pentadiene-3-one** δ 2.49 (s, 3H, SMe); 5.74 (d, J = 16.5 Hz, 1H, H₆); 5.74 (d, J = 9.3 Hz, H₈);
6.27 (s, 1H, vinyl); 6.83 (d, J = 16 Hz, 1H, vinyl); 6.91 (dd, J = 16.5 Hz, 9.3 Hz, 1H, Hₓ);
7.26 - 7.56 (m, 5H, arom); 7.61 (d, J = 16 Hz, 1H, vinyl). IR (KBr, v_max) 1650 (C=O), 1590, 1480 (C=C), 1320, 1250, 1200, 1110 and 950 cm⁻¹.
EI-MS (m/z) 262 (M⁺, 24.4%), 248 (11.2%), 218 (20.3%), 194 (28.5%), 176 (33.2%), 166 (56.3%),
136 (100%), 121 (96.6%), 121 (96.6%), 106 (86.2%), 77 (74%).

**E,E-1-methylthio-5-phenyl-1-vinylthio-1,4-pentadiene-3-one** ¹H NMR (300 MHz, CDCl₃) δ 2.49 (s, 3H, SMe); 5.74 (d, J = 16.5 Hz, 1H, H₆);
5.74 (d, J = 9.3 Hz, H₈); 6.47 (s, 1H, vinyl); 6.83 (d, J = 16 Hz, 1H, vinyl); 6.53, (dd, J =
16.5 Hz, 9.3 Hz, 1H, Hₓ); 7.26-7.56 (m, 5H, arom); 7.61 (d, J = 16 Hz, 1H, vinyl)

### 5.5.6 Reaction of 2-(4-Methylbenzoylmethylene)-1,3-dithiolane 46 with dimethyl anion followed by alkylation with phenacyl bromide

Sodium hydride (50%, 5mmol) was taken in 15mL dimethyl sulfoxide and the mixture was stirred at 70 °C for 1h. To the dimethyl anion thus formed 2-(4-
methylbenzoylmethylene)-1,3-dithiolane 46 (1.18g, 5mmol) was added. The reaction mixture was stirred at this temperature for 1h and cooled to 0-5 °C. Phenacyl bromide (1g, 5mmol) was then added slowly with stirring and continued stirring at room temperature for 48h. The mixture was poured in to cold water, made neutral with dil. HCl and extracted
with methylene chloride (3x25 mL). The combined organic layer was washed with water (3x25 mL) and dried (Na₂SO₄). Removal of solvent under vacuum gave the crude product. This was further purified by column chromatography using hexane:ethyl acetate (20:1) as the eluent.

5-Phenyl-2-(4-methylbenzoylmethylene)-2,3-dihydro-1,3-oxathiole 48 was obtained as yellow crystalline solid. Yield: 0.75 g (51%) mp 115 °C. The spectral data of this compound has been described in Chapter 3.
5.6 References


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