Chapter 3

The Vilsmeier-Haack reactions of ketene dithioacetals: Synthesis of 2-aryl-3,3-bis(alkylsulfanyl)acrylaldehydes

3.1 Introduction

The Vilsmeier-Haack reaction, which involves electrophilic substitution of a suitable carbon nucleophile with a chloromethyleneiminium salt, provides one of the widely used methods for formylation. A large number of aromatic and aliphatic substrates undergo iminoalkylation by the Vilsmeier-Haack reagent. Earlier reports from our laboratory have proved the synthetic utility of functionalized halomethyleniminium salts in the synthesis of carbocyclic and heterocyclic compounds. We have also reported some interesting transformations of acylketene dithioacetals and \( \beta \)-oxodithiocarboxylates under Vilsmeier-Haack reaction conditions. As a continuation to this ketene dithioacetals were treated with chloromethyleneiminium salt to afford 2-aryl-3,3-bis(alkylsulfanyl)acrylaldehydes and the results are discussed here.

3.1.1 The Vilsmeier-Haack reactions of \( \alpha \)-oxoketene dithioacetals and \( \beta \)-oxodithiocarboxylates

\( \alpha \)-Oxoketene dithioacetals and \( \beta \)-oxodithiocarboxylates are valuable 1,3-bielectrophilic compounds, extensively used in heterocyclic synthesis. Due to the presence of electron releasing alkylsulfanyl substituent in these molecules they were expected to be amenable to Vilsmeier-Haack reaction. Our unpublished results show that the Vilsmeier-Haack reactions of acyl ketene dithioacetals afford 1,1-bis(methylsulfanyl)-3-chloro-1,3-butadienes instead of the expected pentadienaldehydes (Scheme 1).
Recently, Liu et al. have reported that the use of excess Vilsmeier-Haack reagent in the above reaction leads to the formation of pentadienaldehydes 3 and on keeping at room temperature 3 is cyclized to form 2H-pyrans 4 (Scheme 2).\(^{5b}\)

They have synthesized 2-[2-chloro-1-(1-chlorovinyl)allylidene]-1,3-dithiane 6 also by the Vilsmeier-Haack reaction of 3-(1,3)-dithianylidenepentane-2,4-dione 5, which found application as nonthiolic 1,3-propanedithiol equivalent in thioacetylation (Scheme 3).\(^{6}\)

In our laboratory, we treated the ketene dithioacetal 7 derived from acetylacetone with the chloromethyleneiminium salt to afford 3-[bis(alkylsulfanyl)methylene]-2,4-dichloro-1,4-pentadiene 8 (Scheme 4).\(^{7}\)
α-Hydroxyketene dithioacetals, which are easily obtained by the chemoselective reduction of α-oxoketene dithioacetals, are known to undergo dehydration and subsequent iminoolkylation in the presence of Vilsmeier-Haack reagent. For example, the carbinol 9 derived from 1,2 reduction of acyl ketene dithioacetals 1 undergo facile Vilsmeier-Haack reaction to give 5,5-bis(methylsulfanyl) substituted pentadienaldehydes 10 (Scheme 5). Ketene dithioacetals derived from cyclic ketones can also be similarly transformed to the respective pentadienaldehydes.

\[
\begin{align*}
1 & \xrightarrow{\text{NaBH}_4, \text{MeOH}} 9 \xrightarrow{\text{DMF, POCl}_3} 10 \\
\text{Scheme 5}
\end{align*}
\]

The pentadienaldehydes 10 prepared by the above method have been shown to be valuable intermediates in carbonyl group transposition reactions (Scheme 6).

\[
\begin{align*}
11 + 10 & \xrightarrow{\text{NaOMe, MeOH}} 12 \xrightarrow{\text{DMF, POCl}_3} 14 \\
\text{Scheme 6}
\end{align*}
\]

When the above protocol was extended to the ketene dithioacetals 15 prepared from acetyl acetone 4-[bis(methylsulfanyl)methylene]-2,5-heptadiene-1,7-dials 17 were formed in moderate yields (Scheme 7).

\[
\begin{align*}
15 & \xrightarrow{\text{NaBH}_4, \text{MeOH}} 16 \xrightarrow{\text{DMF, POCl}_3} 17 \\
\text{Scheme 7}
\end{align*}
\]
We expected the Vilsmeier-Haack reaction of the carbinols 18 derived from \( \alpha \)-oxoketene dithioacetals might lead iminoalkylated intermediates 19, which on aqueous work up would afford conjugated pentadienaldehydes. Contrary to our expectations, the iminoalkylated intermediates 19 underwent a 1,5-shift of one of the methylsulfanyl groups to afford the corresponding pentadienethioates 20 in good yields (Scheme 8).\(^9\)

![Scheme 8](image)

Similar 1,5-shifts have been reported in the reaction of the ketene dithioacetals 21 prepared from substituted phenyl acetones with the Vilsmeier-Haack reagent generated from POCl\(_3\) and DMF, at room temperature to afford corresponding pentadienethioates 22 (Scheme 9).\(^{2a}\)

![Scheme 9](image)

Recent studies from this laboratory found that the Vilsmeier-Haack reaction of \( \alpha \)-hydroxyketene dithioacetals 18, followed by quenching with ammonium acetate, lead to pyridine carbaldehydes 23 (Scheme 10).\(^{2b}\)

![Scheme 10](image)
The Vilsmeier-Haack reaction of dithioketals 25 to afford β-alkylsulfanyl ethylenic aldehydes 26 also have been reported from our laboratory (Scheme 11).  

![Scheme 11](image)

The doubly activated ketene dithioacetals undergo an addition elimination sequence with primary and secondary amines to yield the corresponding N,S-acetals and N,N-acetals in high yields. Junjappa et al. have studied the reactivities of various α-oxoketene-N,S-acetals 27 with the Vilsmeier-Haack reagent to afford functionalized quinolines 28 in good yields (Scheme 12).  

![Scheme 12](image)

When β-oxodithiocarboxylates 29 are treated with the Vilsmeier-Haack reagent, they afford chlorinated aryl propanones 30 in good yields (Scheme 13).  

![Scheme 13](image)

When the reaction was extended to β-oxodithiocarboxylates 31 prepared from cyclohexanone, it underwent further iminoalkylation to afford dichloropent-2,4-dienal 32 (Scheme 14).  

![Scheme 14](image)
An interesting transformation of the dithiocarboxylate 33 prepared from ethyl acetoacetate to thiopyrone derivative 34 also have been reported from our laboratory (Scheme 15).

![Scheme 15]

3.1.2 Formylketene dithioacetals

Usually α-formyl derivatives of ketene dithioacetals are obtained indirectly from the corresponding bis(methylsulfonyl)ethylene esters via a reduction-oxidation process. This is exemplified by the oxidation of β-hydroxyketene dithioacetal 36, synthesized by the lithium aluminium hydride reduction of bis(methylsulfonyl)ethylene ester 35 to afford formyl ketene dithioacetal 37 (Scheme 16).

![Scheme 16]

Rudorf et al. have reported the synthesis of formyl ketene dithioacetals 40 from aroyl acetaldehydes 38 using usual procedure for the synthesis of α-oxoketene dithioacetals (Scheme 17). In their reactions the formyl ketene dithioacetals 40 were obtained in 40-50% yields.

![Scheme 17]

Using various alkylating agents like methyl iodide, ethyl iodide, dibromoethane, phenacyl bromide, bromoacetone etc they synthesized a variety of
formyl ketene dithioacetals. When the alkylation of the dithiolate anion 39 was carried out with two equivalents of α-haloketones or α-halonitriles, the resulted formyl ketene dithioacetals were *in situ* cyclized to form corresponding substituted thiophenes 41 and thienothiophenes 42 (Scheme 18).\(^{13}\)

\[ \text{Scheme 18} \]

In another approach 2-(4-methoxybenzoyl)-3,3-bis(methylsulfanyl)-2-propanal 43 was converted into pyridinethione 44 which is in equilibrium with 45 (Scheme 19).\(^{14}\)

\[ \text{Scheme 19} \]

In our knowledge there is no other method reported for their synthesis of 2-arylc-3,3-bis(alkylsulfanyl)acrylaldehydes. Due to the stabilizing effect of sulfur atom on the neighbouring positive as well as negative charges, we expected the double bonds in arylo ketene dithioacetals are amenable to electrophilic attack by Vilsmeier-Haack reagent to afford 2-arylc-3,3-bis(alkylsulfanyl)acrylaldehydes.

### 3.2 Results and discussion

#### 3.2.1. The Vilsmeier-Haack reaction of α-oxoketene dithioacetals: Synthesis of 2-arylc-3,3-bis(alkylsulfanyl)acrylaldehydes

The benzoylketene dithioacetal 46a was dissolved in dry DMF and the solution was added to 1.5 equivalent Vilsmeier-Haack reagent, prepared by mixing phosphorous oxychloride and N, N-dimethyl formamide at 0 °C. The reaction mixture was well stirred at room temperature for 12 hrs and worked up using aqueous potassium carbonate. The reaction led to the formation of 2-benzoyl-3,3-
bis(methylsulfanyl)acrylaldehyde \(47a\) as the single product in 98% yield. Literature review showed that most of the Vilsmeier-Haack reactions are conducted at room temperature or at a temperature within the limits of 40-80 °C. In order to decrease the reaction time, the temperature of the reaction was slightly increased (50 °C) and the reaction became complex with the formation of several additional products. So the reaction condition was optimized at room temperature and was extended to various aroylketene dithioacetals \(46a-f\), naphthoylketene dithioacetal \(46g\) and thienoylketene dithioacetal \(46h\) to afford corresponding 2-aryloyl-3,3-bis(alkylsulfanyl)acrylaldehydes \(47\) (Scheme 20).

![Scheme 20](image)

<table>
<thead>
<tr>
<th>(46, 47)</th>
<th>(\text{Ar})</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>C(_6)H(_5)</td>
<td>98</td>
</tr>
<tr>
<td>b</td>
<td>4-CH(_3)C(_6)H(_4)</td>
<td>83</td>
</tr>
<tr>
<td>c</td>
<td>4-CH(_3)OC(_6)H(_4)</td>
<td>96</td>
</tr>
<tr>
<td>d</td>
<td>4-BrC(_6)H(_4)</td>
<td>98</td>
</tr>
<tr>
<td>e</td>
<td>4-ClC(_6)H(_4)</td>
<td>90</td>
</tr>
<tr>
<td>f</td>
<td>4-NO(_2)C(_6)H(_4)</td>
<td>92</td>
</tr>
<tr>
<td>g</td>
<td>2-Naphthyl</td>
<td>98</td>
</tr>
<tr>
<td>h</td>
<td>2-Thienyl</td>
<td>62</td>
</tr>
</tbody>
</table>

The reaction of S-benzylketene dithioacetal \(48\) with the Vilsmeier-Haack reagent afforded the 2-benzoyl-3,3-bis(benzylsulfanyl)acrylaldehyde \(49\) in 76% yield along with some unidentified products (Scheme 21).
The formation of 2-aroyl-3,3-bis(alkylsulfanyl)acrylaldehydes 47 involve nucleophilic addition of the \(\alpha\)-carbon atom of the ketene dithioacetals 46 to the chloromethyleneiminium salt and subsequent loss of hydrogen chloride from 50 to afford vinamidinium salt intermediate 51, followed by hydrolysis of the intermediate 51 (Scheme 23).

![Scheme 21](image)

It has been noticed that these 2-aroyl-3,3-bis(alkylsulfanyl)acrylaldehydes are stable at room temperature but easily undergo facile deformylation reaction in the presence of bases like sodium hydride, sodium hydroxide, potassium tertiary-butoxide etc. Synthesis of 2-aroyl-3,3-bis(alkylsulfanyl)acrylaldehydes by the usual procedure in the presence of base should be ineffective due to this facile deformylation. However the reported 2-aroyl-3,3-bis(alkylsulfanyl)acrylaldehydes except 47g were characterized by comparing their physico-chemical properties and spectral properties with the reported ones. The product 47g was characterised by IR, \(^1\)H NMR and EIMS spectra (Fig 1-3).
Figure 1  Infrared Spectrum of 3,3-bis(methylsulfanyl)-2-(2-naphthoyl) acrylaldehyde 47g

Figure 2  $^1$H NMR Spectrum of 3,3-bis(methylsulfanyl)-2-(2-naphthoyl) acrylaldehyde 47g
3.2.2 The Vilsmeier-Haack reaction of α-oxoketene dithioacetals: Synthesis of 1-aryl-2-(1,3-dithiolan-2-yliden)-3-butene-1-one

The benzoylketene dithioacetal 52a was dissolved in dry DMF and the solution was added to 1.5 equivalent Vilsmeier-Haack reagent, prepared by mixing phosphorous oxychloride and N,N-dimethyl formamide at 0 °C. The reaction mixture was well stirred at room temperature for 16 h and worked up using aqueous potassium carbonate. The reaction led to the formation of 2-(1,3-dithiolan-2-yliden)-1-phenyl-3-butene-1-one 53a as the single product in 95% yield. It was noticed that the cyclic ketene dithioacetals are less reactive than the corresponding methylsulfanyl substituted ketene dithioacetals and so it required 16-18 h at room temperature to complete the reaction (Scheme 22).
The reaction is attractive as it lead to the functionalization of simple aroylketene dithioacetals by the electrophilic substitution reaction on the \( \alpha \)-carbon atom. Though the \( \alpha \)-position of \( \alpha \)-oxoketene-N,S-acetals, \( \alpha \)-oxoketene-N,O-acetals are well known to react with electrophiles there are only a few reports on such electrophilic substitution reactions on \( \alpha \)-oxoketene dithioacetals. As the Vilsmeier-Haack reactions of acylketene dithioacetals affords 3-chloro-1,1-bis(alkylsulfanyl)butadienes, the formylation reaction is limited to aroylketene dithioacetals. However, when this strategy was extended to cinnamoylketene dithioacetals, the starting materials were quantitatively converted into a polymeric mixture of products. As our interest was on the synthesis of various formyl ketene dithioacetals and their applications in heterocyclic synthesis, we have not attempted the characterization of these product mixtures.

3.3 Conclusion

In this chapter we have reported a facile high yielding protocol for the synthesis of 2-aryl-3,3-bis(alkylsulfanyl)acrylaldehydes from aroylketene dithioacetals via chloromethyleneimininium salt intermediate. The Vilsmeier-Haack reaction of cinnamoyl ketene dithioacetals did not afford the expected aldehyde while aliphatic \( \alpha \)-oxoketene dithioacetals led to the formation of chlorosubstituted butadienes.

<table>
<thead>
<tr>
<th>52, 53</th>
<th>X</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>H</td>
<td>95</td>
</tr>
<tr>
<td>b</td>
<td>CH₃</td>
<td>89</td>
</tr>
<tr>
<td>c</td>
<td>Cl</td>
<td>95</td>
</tr>
<tr>
<td>d</td>
<td>Br</td>
<td>92</td>
</tr>
<tr>
<td>e</td>
<td>CH₃O</td>
<td>92</td>
</tr>
</tbody>
</table>
3.4 Experimental

Melting points were determined on a Buchi 530 melting point apparatus and were uncorrected. The IR spectra were recorded KBr pellets on a Schimadzu IR-470 spectrometer and the frequencies are reported in cm⁻¹. The ¹H NMR spectra were recorded on a Brucker WM 300 (300 MHz) spectrometer using TMS as internal standard and CDCl₃ as solvent. The ¹³C NMR spectra were recorded on a Brucker WM 300 (75.47 MHz) spectrometer using CDCl₃ as solvent. Both ¹H NMR and ¹³C NMR values are expressed as δ (ppm). The Electron Impact Mass spectra were obtained on a Yinnigen-Mat 312 instrument or GCMS-Schimadzu 5050 model instrument. The CHN analyses were done on an Elementar Vario EL III Carlo Erba 1108 instrument.

All reagents were commercially available and were purified before use. The previously reported arylketene dithioacetals were prepared by the known procedure. Anhydrous sodium sulphate was used as drying agent. All purified compounds gave a single spot upon TLC analyses on silicagel 7GF using an ethyl acetate/hexane mixture as eluent. Iodine vapors or KMnO₄ solution in water was used as developing agent for TLC.

3.4.1 The Vilsmeier-Haack reaction of α-oxoketene dithioacetals: Synthesis of 2-aryl-3,3-bis(alkylsulfanyl)acrylaldehydes

General procedure

In order to prepare the Vilsmeier-Haack reagent, phosphorous oxychloride (0.67 mL, 7 mmol) was added to dimethyl formamide (6 mL, 70 mmol) at 0 °C and the mixture was left to stand for 20 min. at room temperature. The α-oxoketene dithioacetal 46 (4.7 mmol) was added to this and the solution was stirred well for 10-12 hrs at room temperature. When the TLC analyses showed complete conversion of the ketene dithioacetals 46 the reaction mixture was poured into ice-cold water and treated with saturated K₂CO₃ (36 mmol) solution. The semisolid separated in the aqueous solution was extracted with ether (3 X 25 mL). The combined organic phases were washed with water, dried and the solvent was
evaporated off. The crude product obtained was filtered through a column using ethyl acetate-hexane (1:50) as the eluent and silica gel as the adsorbent. The structures of the compounds were confirmed by comparing the analytical results with the reported values.\(^{14}\)

\[
\text{2-Benzoyl-3,3-bis(methylsulfanyl)acrylaldehyde 47a}
\]

was obtained from the Vilsmeier-Haack reaction of 3,3-bis(methylsulfanyl)-1-phenyl-2-propen-1-one 46a (1.06 g, 4.7 mmol) as yellow colored oil; yield 1.16 g (98%).

\[
\text{3,3-Bis(methylsulfanyl)-2-(4-methylbenzoyl)acrylaldehyde 47b}
\]

was obtained from the Vilsmeier-Haack reaction of 3,3-bis(methylsulfanyl)-1-(4-methylphenyl)-2-propen-1-one 46b (1.13 g, 4.7 mmol) as yellow colored oil; yield 1.04 g (83%).

\[
\text{3,3-Bis(methylsulfanyl)-2-(4-methoxybenzoyl)acrylaldehyde 47c}
\]

was obtained from the Vilsmeier-Haack reaction of 3,3-bis(methylsulfanyl)-1-(4-methoxyphenyl)-2-propen-1-one 46c (1.20 g, 4.7 mmol) as yellow colored crystalline solid; yield 1.09 g (96%); mp 90-92 °C (reported mp, 91.5-93 °C).

\[
\text{3,3-Bis(methylsulfanyl)-2-(4-bromobenzoyl)acrylaldehyde 47d}
\]

was obtained from the Vilsmeier-Haack reaction of 3,3-bis(methylsulfanyl)-1-(4-bromophenyl)-2-propen-1-one 46d (1.43 g, 4.7 mmol) as yellow colored oil; yield 1.4g (90%).

\[
\text{3,3-Bis(methylsulfanyl)-2-(4-chlorobenzoyl)acrylaldehyde 47e}
\]

was obtained from the Vilsmeier-Haack reaction of 3,3-bis(methylsulfanyl)-1-(4-chlorophenyl)-2-propen-1-one 46e (1.22 g, 4.7 mmol) as yellow colored oil; yield 1.32g (98%).
3,3-Bis(methylsulfanyl)-2-(4-nitrobenzoyl)acrylaldehyde

47f was obtained from the Vilsmeier-Haack reaction of 3,3-bis(methylsulfanyl)-1-(4-nitrophenyl)-2-propen-1-one 46f (1.28 g, 4.7 mmol) as yellow colored oil; yield 1.29 g (92%).

3,3-Bis(methylsulfanyl)-2-(2-naphthoyl)acrylaldehyde 47g was obtained from the Vilsmeier-Haack reaction of 3,3-bis(methylsulfanyl)-1-(2-naphthyl)-2-propen-1-one 46g (1.29 g, 4.7 mmol) as yellow colored crystalline solid; yield 1.39 g (98%); mp 78-80 °C; IR (KBr) νmax/cm⁻¹ = 3055, 2925, 1670, 1624, 1513, 1287, 1169, 1119, 923, 750, 480; ¹H NMR (300 MHz, CDCl₃) δ = 2.37 (s, 6H, SCH₃), 7.49 (m, 2H, ArH), 7.84 (m, 4H, ArH), 8.21 (s, 1H, ArH), 10.15 (s, 1H, CHO) ppm; EIMS m/z (%) = 302 (M⁺, 12), 255 (24), 227 (32), 207 (18), 155 (100), 127 (98), 99 (82), 85 (14), 77 (43).

3,3-Bis(methylsulfanyl)-2-(2-thienylcarbonyl)acrylaldehyde 47h was obtained from the Vilsmeier-Haack reaction of 3,3-bis(methylsulfanyl)-1-(2-thienyl)-2-propen-1-one 46h (1.08 g, 4.7 mmol) as deep yellow coloured crystalline solid; yield 0.75 g (62%); mp 60-62 °C (reported mp, 61.5-63.5°C).

3,3-Bis(benzylsulfanyl)-2-phenlacrylaldehyde 49 was obtained from the Vilsmeier-Haack reaction of 3,3-bis(benzylsulfanyl)-1-phenyl-2-propen-1-one 48 (1.08 g, 4.7 mmol) as deep yellow coloured crystalline solid; yield 0.75 g (62%); mp 108-110 °C (reported mp, 106-108°C).

3.4.2 The Vilsmeier-Haack reaction of α-oxoketene dithioacetals: Synthesis of 1-aryl-2-(1,3-dithiolan-2-yliden)-3-butene-1-one

General procedure

In order to prepare the Vilsmeier-Haack reagent, phosphorous oxychloride (0.67 mL, 7 mmol) was added to dimethyl formamide (6 mL, 70 mmol) at 0 °C and
the mixture was left to stand for 20 min. at room temperature. The \( \alpha \)-oxoketene dithioacetal \( 52 \) (4.7 mmol) was added to this and the solution was stirred well for 16-18 hrs at room temperature. When the TLC analyses showed complete conversion of the ketene dithioacetals \( 52 \) the reaction mixture was poured into ice-cold water and treated with saturated \( \text{K}_2\text{CO}_3 \) (36 mmol) solution. The solid separated in the aqueous solution was filtered and recrystallized from hexane: ethyl acetate (5: 1) solvent mixture. The structures of the compounds were confirmed by comparing the analytical results with the reported values.\(^1\)

\[
\begin{align*}
\text{2-(1,3-Dithiolan-2-yliden)-1-phenyl-3-butene-1-one} & \quad \text{53a} \\
\text{2-(1,3-Dithiolan-2-yliden)-1-(4-methylphenyl)-3-butene-1-one} & \quad \text{53b} \\
\text{1-(4-Chlorophenyl)-2-(1,3-dithiolan-2-yliden)-3-butene-1-one} & \quad \text{53c} \\
\text{1-(4-Bromophenyl)-2-(1,3-dithiolan-2-yliden)-3-butene-1-one} & \quad \text{53d}
\end{align*}
\]

2-(1,3-Dithiolan-2-yliden)-1-phenyl-3-butene-1-one \( \text{53a} \) was obtained from the Vilsmeier-Haack reaction of 2-(1,3-dithiolan-2-yliden)-1-phenyl-1-ethanone \( \text{52a} \) (1.05 g, 4.7 mmol) as cream coloured crystalline solid; yield 1.16 g (95%); mp 102-104 °C (reported mp, 100-102 °C).

2-(1,3-Dithiolan-2-yliden)-1-(4-methylphenyl)-3-butene-1-one \( \text{53b} \) was obtained from the Vilsmeier-Haack reaction of 2-(1,3-dithiolan-2-yliden)-1-(4-methylphenyl)-1-ethanone \( \text{52b} \) (1.11 g, 4.7 mmol) as cream coloured crystalline solid; yield 1.16 g (89%); mp 152-154 °C (reported mp, 152-153 °C).

1-(4-Chlorophenyl)-2-(1,3-dithiolan-2-yliden)-3-butene-1-one \( \text{53c} \) was obtained from the Vilsmeier-Haack reaction of 1-(4-chlorophenyl)-2-(1,3-dithiolan-2-yliden)-1-ethanone \( \text{52c} \) (1.2 g, 4.7 mmol) as cream coloured crystalline solid; yield 1.27 g (95%); mp 146-148 °C (reported mp, 144-146 °C).

1-(4-Bromophenyl)-2-(1,3-dithiolan-2-yliden)-3-butene-1-one \( \text{53d} \) was obtained from the Vilsmeier-Haack reaction of 1-(4-bromophenyl)-2-(1,3-dithiolan-2-yliden)-1-ethanone \( \text{52d} \) (1.4 g, 4.7 mmol) as cream coloured crystalline solid; yield 1.42 g (89%); mp 144-146 °C (reported mp, 144 °C).
2-(1,3-Dithiolan-2-yliden)-1-(4-methoxyphenyl)-3-butene-1-one 53e was obtained from the Vilsmeier-Haack reaction of 2-(1,3-dithiolan-2-yliden)-1-(4-methoxyphenyl)-1-ethanone 52e (1.2 g, 4.7 mmol) as cream coloured crystalline solid; yield 1.2 g (91%); mp 130-132 °C (reported mp, 132-133 °C).

3.5 References


