CHAPTER IV

REACTION OF ORGANO GRIGNARD REAGENTS WITH 

α - OXOKETENE DITHIOACETALS IN THE PRESENCE OF ZnCl₂.

TMEDA COMPLEX. A NEW GENERAL METHOD FOR THE SYNTHESIS 

OF HIGHLY STEREOSELECTIVE [β-ALKYL-β-ALKYLTHIO-α,β]- 
ENONES WITH E-CONFIGURATION

The α-oxoketene dithioacetals¹ of general formula 1 (Scheme-1) possess ambident 1,3-dielectrophilic centers with two methylthio leaving groups at the β-carbon atom. The differential reactivity of various nucleophiles with α-oxoketene dithioacetals is an area of recent interest and a number of reagents have been developed for directed 1,2-attack or 1,4-attack so that these addition products from 1,2-attack and addition-elimination products from 1,4-attack could be used as important synthetic intermediates. The presence of β,β-methylthio groups in α-oxoketene dithioacetals has
immensely altered the electrophilicity of β-carbon atom from that of the carbonyl carbon. Generally, the soft sulfur atoms have contributed to the softness of β-carbon atom while carbonyl carbon remains either unaltered or even more electrophilic towards nucleophiles. If it were oxygen the greater resonance interaction of non-bonded electrons would have rendered the carbon atom less electrophilic. On the other hand, the poor donor property of sulfur atoms has left carbonyl carbon more electrophilic towards nucleophiles. Thus α-oxoketene dithioacetals are unique 1,3-dielectrophilic structural units displaying differential electrophilicity towards various nucleophiles. The reaction of various hydride reagents and carbon nucleophiles with α-oxoketene dithioacetals has been examined in this laboratory to ascertain their regioselectivity towards 1. The metal borohydrides examined have been known to add exclusively in a 1,2-manner to afford the corresponding carbinol acetals in near quantitative yields. These carbinol acetals underwent facile methanolysis to yield α,β-unsaturated esters in good yields\(^2\).

Subsequently it was shown in our laboratory that Grignard reagents particularly methyl magnesium iodide reacts with 1 in an exclusive 1,2-fashion to yield the carbinol acetals 2 which on methanolysis in the presence of BF\(_3\)-Et\(_2\)O yielded crotonates 3 in excellent yields\(^3\) (Scheme-1).
The higher alkyl Grignard reagents, i.e. ethyl, n-propyl, n-butyl etc. however followed sequential 1,4- and 1,2-addition modes to give the corresponding carbinols 4 which on hydrolysis in the presence of BF$_3$.Et$_2$O and methanol yielded the $\alpha,\beta$-unsaturated ketones 5 in good yields (Scheme 2).
The higher alkyl Grignard reagents unlike the lower ones have followed 1,4-addition-elimination mode followed by 1,2-addition. These controlled addition modes were subsequently extended to allyl anions which followed exclusively 1,2-addition mode to give the corresponding carbinol acetals 6 (Scheme-3). These carbinol acetals 6 when treated with BF₃·Et₂O in refluxing benzene underwent ring closure instead of simple dehydration to give substituted benzenes 8. Thus a new aromatic annelation methodology was discovered which has been extensively studied in our laboratory. These reactions were extended to benzyl Grignard reagent 9 to afford the carbinols 10 which underwent acid assisted cyclization to yield the benzyl substituted naphthalenes 11 in good yields (Scheme-4). Obviously the benzyl Grignard reagent 9 followed sequential 1,4- and 1,2-addition modes with 1 to yield 10.
followed by BF₃·Et₂O cyclization to yield benzyl substituted naphthalenes 11 in good yields. By changing the stoichiometry of 9 with 1 it was not possible
to isolate exclusively the 1,4-addition-elimination product 12 and indeed 12 was found to compete with 1 in its reactivity towards 9. Thus even with one equivalent of 9 only 10 was obtained and not 12. The 1,4-addition-elimination products 12 were considered of interest due to the fact that these intermediates can be cyclized to get angularly substituted and annelated naphthalenes 13 and also 1-aryl naphthalenes (13, R = Ar), the skeleton of which is present in many naturally occurring lignans.

However, it was possible to achieve the 1,4-addition-elimination product 12 by reacting 1 with organo copper reagent derived from 9 instead of 9 itself. Thus when 1 was reacted with 9 in the presence of CuCl, in THF/Et₂O as reaction medium, the 1,4-addition-elimination product 12a was obtained in good yield (Scheme-5). Also the stereochemistry of the product was found to be exclusively Z configuration and no traces of E-isomer was detected in the reaction mixture. The Z configuration of 12a was confirmed on the basis of NOE studies and also by its conversion to thiophene by the method developed in our laboratory as shown in scheme-5. Thus 12a with thiomethyl group lying cis-to carbonyl function undergoes intramolecular aldol addition-elimination sequence when treated with Simon-Smith reagent to yield the corresponding thiophene 14 in good yields. The E-isomer 12b however did not undergo thiophene formation because thiomethyl group is trans- to carbonyl functionality. Thus the Z configuration of the addition-elimination product 12a was fully established.
Subsequently a number of alkyl and benzyl copper reagents derived from Grignard reagents were reacted with various α-oxoketene dithioacetals, and in all the cases 1,4-addition-elimination products were obtained with exclusive Z configuration. Methoxy substituted benzyl copper reagents also reacted with α-oxoketene dithioacetals and the 1,4-addition-elimination product 16 was obtained exclusively, though the corresponding Grignard reagents are known to add exclusively in a 1,2-fashion to give 15 in good yields (Scheme-6).
Scheme 6

The displacement of alkylthio group of α-oxoketene dithioacetals 1, on the other hand by alkyl groups were indeed known in the literature and one of the earlier studies for the displacement of methylthio group by methyl group was investigated by Corey and Chen as early as 1973. They reacted dimethyl lithiocuprates with two equivalents of 1 to afford the corresponding 2-isopropylidene cyclohexanone 17 in 96% overall yields (Scheme-7).

Scheme 7

Subsequently Dieter and co-workers made some detailed investigation of organo cuprates with 1. When they reacted one equivalent of
organo cuprates with 1, the product isolated (18) was found to be a mixture of 
$E$ and $Z$-isomers. Similarly, when $\alpha$-oxoketene dithioacetals were reacted with 
two equivalents of organo cuprates, both thiomethyl groups were displaced to 
give the $\beta,\beta$-dialkyl-$\alpha,\beta$-unsaturated carbonyl compound 19. They also 
reacted three equivalents of organo cuprates with 1 to afford $\beta$-tertiary alkyl 
ketones 20 in high yields involving the third addition in the Michael fashion 
(Scheme-8).

\[
\begin{align*}
\text{R}_2\text{CuLi} (1 \text{ eq}) & \quad \text{O} \quad \text{R}^2 \\
\text{R}_2\text{CuLi} (2 \text{ eq}) & \quad \text{O} \quad \text{R}^2 \\
\text{R}_2\text{CuLi} (3 \text{ eq}) & \quad \text{O} \quad \text{R}^2
\end{align*}
\]

Scheme-8

Apparently in the preceding examples, the organo Grignard reagents 
have shown 1,4-addition mode exclusively, when reacted in the presence of 
Cu (I) salts. A literature survey revealed that there are no specific reagents 
or methods available for the preparation of 1,4-addition-elimination products
derived from $\alpha$-oxoketene dithioacetals in their exclusive $E$ configuration. In search of these reagents as well as in continuation of a programmed study of the C-C bond forming reactions of organometallic reagents with $\alpha$-oxoketene dithioacetals, we examined the reactivity of organo Grignard reagents with $\alpha$-oxoketene dithioacetals in the presence of (N,N,N',N'-Tetramethyleneethylenediamine)Zinc(II) chloride. Surprisingly when $\alpha$-oxoketene dithioacetals were reacted with Grignard reagents in the presence of ZnCl$_2$.TMEDA complex, 1,4-addition-elimination products were obtained exclusively in $E$ configuration which proved to be a general method for the synthesis of $E$-$\beta$-alkyl-$\beta$-methylthio-$\alpha,\beta$-enones. It may be noted here that $Z$-isomers were not formed at all in these reactions. The results of this study are described in the following section.

RESULTS AND DISCUSSION

In the preceding section of this chapter the nucleophilic addition studies on $\alpha$-oxoketene dithioacetals have been described. $\alpha$-oxoketene dithioacetals have been found to react with organo Grignard reagents, showing variation of preference depending on the nature of the reagent. Bulkier organo Grignard reagents generally followed sequential 1,4- followed by 1,2-addition mode while the smaller groups generally followed 1,2-addition mode with $\alpha$-oxoketene dithioacetals. The presence of Cu (I) salts however directed the organo Grignard reagents to react in a 1,4-fashion yielding exclusively 1,4-addition-elimination products of $Z$ configuration.

We have in the present investigation thus found that when $\alpha$-oxoketene dithioacetals reacted with organo Grignard reagents in the presence
of ZnCl₂:TMEDA complex 1,4-addition-elimination products were obtained but exclusively in the $E$ configuration. Thus in a typical experiment magnesium triorganozincate, was prepared by reacting three equivalents of Grignard reagents with with one equivalent of ZnCl₂:TMEDA complex using diethyl ether/THF (solvent combination) 50: 50 at -20°C.

$$3 \text{RMgX} + 1 \text{ZnCl}_2 \cdot \text{TMEDA} \rightarrow \text{R}_2\text{ZnMgX} \quad \text{(equation 1)}$$

Since there is no indication of the formation of magnesium triorganozincate, trial experiments were carried out and it was found that generally the magnesium triorganozincates formed within twenty minutes of the reaction. The magnesium triorganozincate prepared in this way were reacted with $\alpha$-oxoketene dithioacetals at -20°C in ether/THF solvent combination and stirred for 45 minutes to yield 1,4-addition-elimination products 22 (Scheme 9).

![Scheme 9](image)

Scheme 9

Acetophenone mercaptal was first reacted with nBu₂ZnMgCl. To a cooled solution i.e. -20°C of nBu₂ZnMgCl in Et₂O/THF solvent combination a
solution of acetophenone mercaptal was slowly added maintaining a temperature of -20°C, until the addition was complete. The temperature of the reaction mixture was gradually raised to 0°C and stirring continued for another 45 minutes. The reaction mixture after work up yielded 1-phenyl-3-methylthio-2-hepten-1-one 22d in 71% yield. The structure of 22d was confirmed from its analytical and spectral data.

**DATA**

IR (CCl$_4$) $\nu_{\text{max}}$ = 2950, 1670, 1560, 1240 cm$^{-1}$. $^1$H NMR (90 MHz, CDCl$_3$): $\delta$ = 0.9 (t, $J = 6$ Hz, 3H, CH$_3$); 1.40-1.62 (m, 4H, CH$_2$CH$_2$); 2.29 (s, 3H, SCCH$_3$); 2.8 (q, $J = 6$ Hz, 2H, CH$_2$); 6.42 (s, 1H, =CH); 7.31-7.49 (m, 3H, ArH); 7.8-7.91 (m, 2H, ArH). MS m/z (235.74) (M+, 37.6) 187 (18.3), 117 (100); Anal. Calcd. for C$_{14}$H$_{18}$OS (234): C, 71.32; H, 8.29%. Found C, 71.48; H, 8.50%.

**Assignment of E configuration**

1-phenyl-3-methylthio-2-hepten-1-one 22d was found to be a single geometrical isomer since all the signals in $^1$H NMR spectrum were found to be sharp and near overlapping signals were not detected. Therefore it was presumed that the compound must be a single geometrical isomer. The vinylic proton of 22d was observed at $\delta$ 6.42 which is far below from those systems for which we had assigned Z configuration, which was in turn obtained by reacting Grignard reagents in the presence of Cu (I) chloride with $\alpha$-oxoketene dithioacetals as described earlier. The Z-isomers generally displayed the vinylic protons at $\delta$ 6.94, indicating approximate idea of the possible trans
geometry for 22d. This was further confirmed by subjecting 22d for NOE studies.

From NOE studies carried out, the absorption signals of appropriate proton centres indicated the compounds 22 in its $E$ configuration. The detailed studies are graphically represented in the structure 22d where the enhancement of the vinylic protons was 3.35% when thiomethyl protons were irradiated. The vinylic proton showed an enhancement of 8.19% when $H_a$ was irradiated. On the other hand enhancement of the proton of n-butyl group was a minimal
0.5% when the vinylic proton was irradiated, confirming the thiomethyl group and H-atom on the same side of the double bond. Thus E configuration was confirmed unequivocally for 22d. It is also important to note that the chemical shifts of the vinylic protons at δ 6.4 or values below this were taken as markers to assign E configuration to the other open chain systems examined in this work.

Similarly magnesium trimethyl, triethyl, n-tripropyl zincates were prepared and reacted with acetophenone mercaptal as described earlier to afford the corresponding 1,4-addition-elimination products 22a-22c in 66-80% overall yields. The vinylic protons in 22a appeared at δ 6.40, of 22b appeared at δ 6.50 and 22c at δ 6.48 confirming E conformation of the products 22a-22c (Table 1). Acetone mercaptal was next examined as a typical example of aliphatic ketone derivative. Thus when acetone mercaptal was reacted with magnesium trimethylzincate under similar reaction conditions as described above the unreacted reagent, acetone mercaptal was observed (TLC). The reaction did not proceed even after prolonging the reaction time and raising the temperature of the reaction. In a particular attempt the reaction mixture containing magnesium trimethylzincate and acetone mercaptal was cooled to -78°C, but the reaction failed in our hands. It was then decided to examine some of the higher alkyl magnesium zincate reagents and react it with acetone mercaptal.
<table>
<thead>
<tr>
<th>E isomers of β-alkyl thio α,β-enoens</th>
<th>% yield</th>
<th>δ H vinylic</th>
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<tbody>
<tr>
<td>a</td>
<td>67</td>
<td>6.40</td>
</tr>
<tr>
<td>b</td>
<td>66</td>
<td>6.50</td>
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<td>g</td>
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Thus magnesium $n$-tripropylzincate reagent was prepared as described earlier followed by addition of acetone mercaptal maintaining reaction temperature at -20°C. The reaction temperature was raised to 0°C and stirring continued for an additional 45 minutes and subsequent work up yielded the compound 22e which was characterised as 4-methylthio-3-hepten-2-one in 66% overall yields. The structure and configuration of 22e was confirmed from its spectral and analytical data (see experimental). The vinyl protons appeared at $\delta$ 5.7 on the basis of which $E$ configuration was assigned to 22e (Table 1). Similarly 22f was prepared by reacting magnesium $n$-tributylzincate with acetone mercaptal to yield the corresponding 4-methylthio-3-octen-2-one 22f in 67% overall yields. The position of the vinylic proton in this compound also appeared at $\delta$ 5.7 confirming the assignment of $E$ configuration (Table 1). Also acetone mercaptal was reacted with magnesium $n$-trihexyl zincate to yield the corresponding 4-methylthio-3-decen-2-one 22g in 65% overall yields (Table 1). The position of the vinylic proton in this compound also appeared at $\delta$ 5.7 confirming the assignment of $E$ confirmation. It is thus evident that the higher alkyl magnesium zinicates reacted in a facile manner with $\alpha$-oxoketene dithioacetals to yield the desired products.

Magnesium $n$-tributylzincate was next reacted with mercaptal derived from 2-acetyl furan which, under the described reaction conditions to yield the desired product 22h in 82% overall yields. The position of vinylic
proton at δ 6.46 was again used as a marker to assign E configuration to the product enone (Table II).

(Table II) E isomers of β-alkylthio α,β-enones

<table>
<thead>
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<th></th>
<th>% yield</th>
<th>δ H vinylic</th>
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<tbody>
<tr>
<td>h</td>
<td>82</td>
<td>6.46</td>
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<tr>
<td>i</td>
<td>63</td>
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<tr>
<td>j</td>
<td>82</td>
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</tr>
<tr>
<td>k</td>
<td>50</td>
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<tr>
<td>l</td>
<td>89</td>
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</table>

The reactivity of these magnesium zincate reagents with cyclic α-oxoketene dithioacetals was next examined. Thus when cyclohexanone mercaptal was reacted with magnesium n-tributyl, n-trihexyl and triphenyl
zinc reagents under similar reaction conditions as described earlier it afforded the corresponding β-alkyl-β-methylthio-α,β- enones 22i, 22j and 22k in 63, 82 and 50% yields respectively (Table II). The structures of 22i, 22j and 22k were in conformity with their analytical and spectral data (see experimental). The E configuration is tentatively assigned on the basis of the geometry observed in the open chain systems.

Tetralone mercaptal 22l was also reacted with magnesium n- tributyl zincate and it yielded the corresponding β-n-butyl-β- methylthiotetralone 22l in 89% overall yields (Table II). The structure of 22l was confirmed from its analytical and spectral data (see experimental). The NMR and IR data of all these compounds 22a-22l however, could not be used to distinguish between E and Z-isomers. The exact geometry needs to be confirmed possibly by X-ray studies of one of the crystalline compounds. All these compounds derived from alkyl, aryl, cyclic ketones etc. were liquids and efforts are being made to prepare one of the solid derivatives to get good crystals suitable for X-ray analysis.

In Scheme-10 we have described that simple n-butyl magnesium chloride is shown to react with 1 due to its bulk in a sequential 1,4- and 1,2- addition mode to yield 23. However when n-butyl magnesium halide is reacted with 1 in the presence of Cu (I) iodide the reaction assumes full regio- and stereo control to afford the corresponding Z-β-methylthio-β-n-butyl α,β- enones 24 exclusively. Under these conditions no 1,2-adducts were detected.
Under no circumstances it was possible to alter the course of the reaction using these conditions of Cu (I) assisted organo Grignard reagents to obtain 1,2-addition products. It was found that these reactions yielded 1,4-addition-elimination products exclusively in its Z configuration. It therefore became necessary to develop another reagent to get only E-isomers of these 1,4-addition-elimination products so that we have ready methods in hand to prepare either Z- or E-isomers as the case may be. In this context the work described in this chapter using magnesium triorganozincate as reagent of choice is a good method to obtain only the corresponding E-isomers without any trace of Z-isomers. Thus we have methods to prepare either cis- or trans-\(\beta\)-alkyl-\(\beta\)-methylthio-\(\alpha,\beta\)-enones in good yields.
In conclusion we have been able to make some important generalisations on the stereoelectronic control process of reagents and their reactivity towards ambident 1,3-electrophilic centers in α-oxoketene dithioacetals.

EXPERIMENTAL SECTION

General

Proton NMR spectra were recorded as CCl₄ or CDCl₃ solutions either on a Varian EM-390 or Bruker 300 MHz spectrometer instrument. Chemical shifts are reported relative to tetramethyl silane as internal standard. IR spectra were recorded on a Perkin-Elmer 297 and 983 spectrometer in CCl₄ solutions. Mass spectra were recorded on a Jeol JMS-D-300 spectrometer. Elemental analysis were carried out on a Heraeus CHN-O-RAPID analyser.

CHEMICALS AND REAGENTS

Grignard grade magnesium turnings (SISCO) were used for preparing various Grignard reagents which were carried out under an atmosphere of oxygen free dry nitrogen. Methyl iodide, ethyl bromide, n-propyl bromide, n-butylchloride, hexyl chloride, phenyl bromide, were purchased and used as supplied. Tetramethylethylendiamine (TMEDA) was purchased (E. Merck) and purified before use by distillation under reduced pressure. THF was initially deperoxidised and then dried by keeping over sodium wire followed
by distillation. ZnCl₂ (E Merck) was used as such. Tl.C (silica gel Acme’s) was used for monitoring the reactions.

**STARTING MATERIALS**

The commercially available acetophenone, acetone, cyclohexanone were purified by distillation under pressure before use. 1-Tetralone, bp.140-150°C (10mm)¹⁴ were prepared according to reported procedures. Furfuraldehyde was distilled before use. The α-oxoketene dithioacetals required for the present investigation were prepared according to the earlier reported procedures¹⁵-¹⁷. The following α-oxoketene dithioacetals were prepared according to the general procedure described in the following section, 3,3-[Bis (methylthio)]-1-phenyl-2-propen-1-one, mp 93°C¹⁸, 4,4-[bis (methylthio)]-3-buten-2-one mp 57°C¹⁹, 2-[bis (methylthio) methylene] cyclohexanone bp 118°C (1mm)²⁰, 3,3-[bis (methylthio)]-1-(2'-furyl)-2-propen-1-one¹⁸, 2-[ bis (methylthio)] methylene-1-tetralone mp 58°C¹⁵.

**General method for the preparation of α-oxoketene dithioacetals using sodium-t-butoxide**

A mixture of corresponding ketone (0.5 mol) and carbon disulphide (0.5 mol) in dry benzene (100 ml) was added drop wise to an ice cooled and well stirred suspension of sodium-t-butoxide (1.0 mol) in dry benzene and the reaction mixture was stirred for 4-5 hrs. Methyl iodide (1.1 mol) was then gradually added with cooling and the reaction mixture was further stirred for 6 hrs, cooled and poured into ice cold water. The benzene layer was separated
and the aqueous phase was extracted with benzene (200 ml), dried (anhydrous Na₂SO₄) and evaporated to give the crude dithioacetals which were purified either by crystallization or by distillation under reduced pressure.

**General procedure for the preparation of N,N,N',N'-TMEDA Zn(II) chloride.**

Five ml TMEDA was added to 10 ml saturated ZnCl₂ THF solution and allowed to stand for several hours at room temperature. The crystalline product was filtered and recrystallised from THF mp 177 °C ²¹.

**General procedure for the reaction of α-oxoketene dithioacetals with organozinc reagents:**

The reaction of α-oxoketene dithioacetals with organozinc reagents is representative. To a stirred suspension of N,N,N',N'-TMEDA Zinc(II) chloride (0.01 mol) in 25 ml of dry THF, under nitrogen atmosphere at -20°C, n-butyl magnesium chloride (0.03 mol), prepared from magnesium (0.5 g, 0.02 mol) and n-butyl chloride (0.92 ml, 0.01 mol) in 150 ml of Et₂O THF (1:1) was added drop wise and the reaction mixture was further stirred for 20 min followed by addition of acetophenone mercaptal (0.005 mol) in THF (15 ml) at -20°C. The reaction mixture was continuously stirred for 45 min (monitored by TLC) at 0°C and poured into saturated NH₄Cl solution (100 ml), extracted with chloroform (3 × 50ml) and the organic extracts were
washed with water (2 × 50 ml), dried (anhydrous Na₂SO₄) and evaporated under reduced pressure to give the crude product which was purified by column chromatography over silica gel using hexane as eluent. Similar reaction conditions were maintained when other α-oxoketene dithioacetals were reacted with organozinc reagents to afford crude thiomethyl displaced products which after purification gave analytically pure β-alkyl-β-methylthio-α,β-enones. The analytical and spectral data of β-alkyl-β-methylthio-α,β-enones 22 are given below.

1-phenyl-3-methylthio-2-buten-1-one (22a): yield 67%; brown dense oil; IR (CCl₄) ν max = 2950, 1760, 1720, 1620, 1420, 1290, 820 cm⁻¹. ¹H NMR (90 MHz, CCl₄) δ = 0.9 (t, 3H, CH₃); 1.4-1.6 (m, 4H, (CH₂)₂); 2.25 (s, 3H, CH₃); 2.35 (s, 3H, SCH₃); 6.40 (s, 1H, =CH); 7.2-7.4 (m, 3H, ArH); 7.66-7.90 (m, 2H, ArH). Anal. Calcd. for C₁₁H₁₂OS (193.19): C, 68.38; H, 6.75%. Found C, 68.55; H, 6.90%.

1-phenyl-3-methylthio-2-pente-1-one (22b): yield 66%; yellow liquid; IR (CCl₄) ν max = 2913, 2367, 1566, 1323, 1177, 780, 760 cm⁻¹. ¹H NMR (90 MHz, CCl₄) δ = 1.26 (t, 3H, CH₃); 2.36 (s, 3H, SCH₃); 2.9 (q, 2H, CH₂); 6.50 (s, 1H, =CH); 7.48-7.64 (m, 3H, ArH); 7.2-8.1 (m, 2H, ArH). MS m/z (207.37); (M⁺, 18.5%) 157 (71.1), 105 (84.8), 77 (100); Anal. Calcd. for C₁₂H₁₄OS (207.37): C, 69.50; H, 7.33%. Found C, 70.0; H, 7.68%.

1-phenyl-3-methylthio-2-hexen-1-one (22c): yield 80%; brown viscous liquid; IR (CCl₄) ν max = 2930, 1645, 1552, 1226, 700 cm⁻¹. ¹H NMR (90 MHz,
CCI₄) δ = 1.0 (t, 2H, CH₂); 1.65 (q, 3H, CH₃); 2.35 (s, 3H, SCH₃); 2.85 (t, 2H, CH₂); 6.48 (s, 1H, =CH); 7.35-7.52 (m, 3H, ArH); 7.84-8.0 (m, 2H, ArH).

Anal. Calcd. for C₁₃H₁₆OS (221.56): C, 70.47; H, 7.84%. Found C, 70.23; H, 7.52%.

1-phenyl-3-methylthio-2-hepten-1-one (22d): yield 71%; yellow oil; IR (CCI₄) ν_max = 2950, 1670, 1240 cm⁻¹. ¹H NMR (90 MHz, CDCl₃) δ = 0.9 (t, J = 6Hz, 3H, CH₃); 1.40-1.62 (m, 4H, CH₂CH₂); 2.29 (s, 3H, SCH₂); 2.8 (q, J = 6 Hz, 2H, CH₂); 6.45 (s, 1H, =CH); 7.31-7.49 (m, 3H, ArH); 7.8-7.91 (m, 2H, ArH). MS m/z (235.74) (M⁺, 37.6) 187 (18.3), 17 (100); Anal. Calcd. for C₁₄H₁₈OS (235.74): C, 71.32; H, 8.29%. Found C, 71.48; H, 8.50%.

4-methylthio-3-hepten-2-one (22e): yield 66%; yellow oil; IR (CCI₄) ν_max = 2926, 1673, 1427, 1353, 1188, 867 cm⁻¹. ¹H NMR (90 MHz, CCl₄) δ = 0.9 (t, J = 6Hz, 3H, CH₃); 1.46 (m, 2H, CH₂); 2.0 (s, 3H, CH₃); 2.18 (s, 3H, SCH₂); 2.6 (t, 2H, CH₂) 5.70 (s, 1H, =CH). Anal. Calcd. for C₉H₁₄OS (159.33): C, 60.30; H, 9.54%. Found C, 60.72; H, 9.73%.

4-methylthio-3-octen-2-one (22f): yield 67%; yellow oil; IR (CCI₄) ν_max = 2940, 1690, 1590, 1365, 925 cm⁻¹. ¹H NMR (90 MHz, CCl₄) δ = 0.9 (t, J = 6Hz, 3H, CH₂); 1.31-1.5 (t, 2H, CH₃); 2.1 (s, 3H, CH₃); 2.2 (s, 3H, SCH₂); 2.69 (t, 2H, CH₂); 5.70 (s, 1H, =CH). Anal. Calcd. for C₁₀H₁₆OS (173.52): C, 62.29; H, 10.01%. Found C, 62.08; H, 9.89%.

4-methylthio-3-decen-2-one (22g): yield 65%; yellow oil; IR (CCI₄) ν_max = 2925, 1673, 1556, 1454, 1256, 1010, 971 cm⁻¹. ¹H NMR (90 MHz, CCl₄) δ =
0.74-0.94 (m, 2H, CH₂); 1.3-1.46 (m, 8H, (CH₂)₄); 2.1 (s, 3H, CH₃); 2.2 (s, 3H, SCH₃); 2.66 (q, 3H, CH₃); 5.70 (s, 1H, =CH). Anal. Calcd. for C₁₁H₂₀OS (201.88): C, 65.44; H, 10.76%. Found C, 65.12; H, 10.45%.

1-(2-furyl)-3-methylthio-2-hepten-1-one (22h): yield 82%; yellow oil; IR (CCl₄) ν_max = 2923, 1623, 1542, 1431, 1248, 883 cm⁻¹. ¹H NMR (90 MHz, CDCl₃) δ = 0.95 (t, 3H, CH₃); 1.43 (m, 2H, CH₂); 1.61 (m, 2H, CH₂); 2.40 (s, 3H, SCH₃); 2.86 (t, 3H, CH₃); 6.46 (s, 1H, =CH). Anal. Calcd. for C₁₂H₁₄O₂S (225.54): C, 63.90; H, 7.70%. Found C, 64.0; H, 7.88%.

2-[1'-(methylthio)pentylidene]cyclohexanone (22i): yield 63%; yellow oil; IR (CCl₄) ν_max = 2933, 2926, 1716, 1566, 1448, 1420, 1323, 1245, 1119, 1067, 970, 888 cm⁻¹. ¹H NMR (90 MHz, CCl₄) δ = 0.9-1.2 (t, 3H, CH₃); 1.32-1.56 (m, 4H, (CH₂)₂); 1.78 (t, 2H, CH₂); 2.28 (s, 3H, SCH₃); 2.2-2.4 (m, 4H, (CH₂)₂); 2.41-2.78 (m, 4H, (CH₂)₂). MS m/z (212) (M⁺, 40.6); 197 (100) 165 (19.8); 135 (39.0). Anal. Calcd. for C₁₂H₁₄O₂S (213.89): C, 67.38; H, 10.15%. Found C, 67.59; H, 10.48%.

2-[1'-(methylthio)heptylidene]cyclohexanone (22j): yield 82%; yellow oil; IR (CCl₄) ν_max = 2853, 1651, 1456, 1265, 1135, 968, 889, 682 cm⁻¹. ¹H NMR (90 MHz, CDCl₃) δ = 0.89 (t, 3H, CH₃); 1.26 (brs, 18H, (CH₂)₉); 2.35 (s, 3H, SCH₃). Anal. Calcd. for C₁₄H₂₄O₂S (242.25): C, 69.41; H, 10.76%. Found C, 70.02; H, 10.93%.
2-[[1'- (methylthio)benzylidene]cyclohexanone (22k): yield 50%; yellow oil; IR (CCl₄) νmax = 2925, 1658, 1564, 1002, 978, 698 cm⁻¹. ¹H NMR (90 MHz, CDCl₃) δ = 1.2-1.32 (m, 2H, CH₂); 1.77-2.09 (m, 6H, (CH₂)₃); 2.32 (s, 3H, SCH₃) 7.15-7.2 (m, 5H, ArH). Anal. Calcd. for C₁₅H₁₄O (233.27): C, 74.99; H, 7.44%. Found C, 72.0; H, 7.63%.

3,4-Dihydro-2-[[1'- (methylthio)pentylidene]naphthalene-1-one (22l): yield 89%; yellow oil; IR (CCl₄) νmax = 2945, 1660, 1640, 1470, 1300, 1260, 915 cm⁻¹. ¹H NMR (90 MHz, CDCl₃) δ = 0.90 (t, 3H, CH₃); 1.48 (q, 3H, CH₃); 2.3 (s, 3H, SCH₃); 2.6 (d, 2H, CH₂); 2.82 (m, 6H, (CH₂)₃); 7.5-7.35 (m, 3H, ArH); 7.9 (m, 1H, ArH). Anal. Calcd. for C₁₆H₂₇O₃ (261.93): C, 73.36; H, 8.29%. Found C, 73.82; H, 8.32%.
References