CHAPTER V

REDUCTIVE DETHIOMETHYLATION OF $\alpha$-OXOKETENE DITHIOACETALS WITH SODIUM CYANOBOROHYDRIDE: A NEW GENERAL METHOD FOR 2-METHYLTHIO-1-ALKENYL KETONES.

V.I INTRODUCTION

The vinylogous thioesters 1 belong to an interesting class of three carbon fragments with 1,3-electrophilic centres (as shown by the broken arrows) of which the terminal thioalkyl carbon can be considered as masked aldehyde functionality.

![Chemical Diagram]

It could be cleaved under mild hydrolytic conditions when desired and the $\alpha$-carbon in these compounds is activated by the electron withdrawing substituants at the $\beta$-position and can thus undergo facile displacement.
of the thiomethyl group with a wide variety of nucleophiles to further diversify the product range. The vinylogous thiol esters are useful synthetic intermediates in organic synthesis and they provide unique opportunities for devising new reactions leading to the synthesis of many natural products. There have been many reports in recent years concerning their synthetic utility rather than the methods of their preparation.

A brief survey of some important synthetic applications of vinylogous thiol esters is described as follows. Thus in a synthesis of \( \beta \)-vetivone 4 the 2-(n-butylthiomethylene) ketone 2 was subjected to a 1,2-reduction with sodium borohydride followed by the mercuric chloride catalyzed hydrolysis to afford the key intermediate enaldehyde 3 (Scheme 1)\(^{10}\).

The alkylthiomethylene group has also been used to introduce regio-specific methyl substituent involving reductive desulfurization with \( W-2 \) Raney Nickel or sodium in liquid ammonia in the synthesis of \((\pm)\) loganin 7 (Scheme 1)\(^{11}\).

The vinylogous thiol esters have been useful intermediates in the construction of stereoselective polyene side chains starting from appropriate aldehydes. Thus a synthesis of isorenieraten 13 has been reported involving an efficient use of this intermediates. Thus 2,3,6-trimethyl benzaldehyde 8 was condensed with 4-(t-butylthio)-buten-2-one 9 to yield the corresponding dienone 10 in high yields. On subsequent alkylative carbonyl transposition the dienal 11 was obtained, which could be further used to lengthen the side chain by repeating the aldol condensation and carbonyl transposition sequence to obtain the next higher tetraene aldehyde 12. The aldehyde 12 treatment with TiCl\(_3\)/LiAlH\(_4\) yielded the
Scheme 1

1. NaBH₄, MeOH
2. HgCl₂, H₃O⁺, Acetone

Several steps

CHO

Several steps

β-Vetivone

Several steps

CO₂CH₃

OMe

Several steps

CO₂CH₃

CHO
\[
\begin{align*}
8 & \quad + \quad 9 \\
\xrightarrow{\text{NaOEt, EtOH, -15°-0°C}} & \quad 10
\end{align*}
\]

(i) MeLi, Et₂O
(ii) 1 M H₂SO₄

\[
\begin{align*}
11 & \quad \xrightarrow{9, \text{NaOH/EtOH-H₂O}} \quad 12
\end{align*}
\]

\[
\xrightarrow{\text{TiCl₃, LiAlH₄, 96%}} \quad 13 \quad \text{isorenieratene}
\]

Scheme 2
In the course of our studies on $\alpha$-oxoketene dithioacetals, we aimed at developing a method for its conversion to vinylogous thiolesters $1$ by devising a route involving displacement of one of the thiomethyl groups by hydrogen. Such a method would provide a convenient synthetic entry to the alkylthio enones $1$ from a wide variety of easily available active methylene compounds. The reported methods for the preparation of these compounds are briefly discussed here. Ireland and co-workers have prepared$^{1,10,12}$ the vinylogous thiolesters $15$ by reacting the active methylene ketones with ethyl formate to yield the corresponding formyl derivatives $14$ which were subsequently converted into the corresponding alkylthio enones $15$ either directly by reaction with n-butyl mercaptan or through their tosylates $16$ (Scheme 3). This method has been used by these authors for the subsequent conversion of butyl thioenones $15$ to the corresponding $\alpha,\beta$-unsaturated aldehydes. The $\beta$-arylox/acyl acetylenes $17$ undergo Michael addition with aryl/alkyl mercaptans in the presence of a mild base like Triton B (Scheme 4) to give the corresponding $\beta$-alkyl/arylthioenones $18$ in excellent yields$^{13-17}$. The method requires polarized triple bonded structural moiety and thus cannot be applied to the cyclic systems. The $\beta$-chlorovinyl ketones $19$ are perhaps more versatile intermediates, which can undergo displacement with aryl mercaptans to give the $\beta$-arylthio enones $18$ in fairly good yields. However, when alkyl mercaptans were used the reaction further proceeded to yield the $\beta$-dithioacetals $20$ (Scheme 5)$^{18}$. Recently Akiyama and co-workers have reported$^{13}$ the preparation of $\beta$-t-butylthioenone $18n$ ($R'=Me; R''=t-Bu$) by displacement reaction of $19$ with t-butyl mercaptan (Scheme 5).
Scheme 3

\[ \begin{align*}
\text{n-BuSH} & \rightarrow \text{H}_2\text{O} \\
\text{R} & \text{O} \text{Bu}^n \\
\text{R} & \text{O} \\
\text{H} & \text{OH} \\
\text{R} & \text{O} \\
\end{align*} \]
Scheme 4

\[
\begin{align*}
R_2 &= \text{Alkyl or Aryl} \\
R' &= \text{Alkyl or Aryl}
\end{align*}
\]
Scheme 5
Rudorf and co-workers have reported\textsuperscript{19} the partial cleavage of the thiomethyl group under electrolytic reduction of \( \alpha \)-oxoketene dithioacetal 21a when the corresponding methylthioenone 1a was formed in 64\% yield (Scheme 6) through protonation of the intermediate carbanion 22. However, the authors have not studied the generality of the reaction. The vinylogous thiolesters underwent further reduction to give the corresponding saturated ketone as well as the saturated dithioacetal through Michael addition of the methyl mercaptan on 1a (Scheme 6).

Junjappa, Ilia and Myrboh\textsuperscript{20} have developed an efficient method for the partial dethiomethylation of \( \alpha \)-oxoketene dithioacetals\textsuperscript{21} in the presence of sodium borohydride and Nickel chloride (Nickel boride), to afford the vinylogous thiolesters 1 in moderate to good yields (Scheme 7). However, the method suffers from limitations (Scheme 7), due to increased adsorption on Nickel boride. The synthesis of \( \beta \)-alkyl substituted vinylogous thiolesters from an unsymmetrical \( \beta \)-diketones entails problems of regioselectivity and the best approach to these compounds involves the chemo- and stereoselective reaction of organocuprates with \( \alpha \)-oxoketene dithioacetals\textsuperscript{21} (Scheme 8).\textsuperscript{21,22} The substitution reaction generally affords the \( E \)-stereoisomer in a highly stereoselective fashion.

In the present investigation it was considered of interest to develop more efficient methodology that can be applied to wide structural variants of \( \alpha \)-oxoketene dithioacetals under simple reaction conditions with improved yields.

From the literature retrieval it is found that the sodium cyanoborohydride is an extremely non-aggressive reducing agent\textsuperscript{23}. Normally, even sensitive groups such as aldehydes and ketones are reduced only when the electrophilic
Scheme 8

(i) = $R''$/CuX
(ii) = Enolate anions

$R'$ = Ar, Alkyl

$R''$ = Aryl, Alkyl
of the carbonyl group is increased by protonation 24. However, even under acidic conditions, other carbonyl derivatives, including esters, acids and amides remain unaffected 25. The following examples prove the argument for the potential use of sodium cyanoborohydride as a chemoselective 1,4-reducing agent on \( \alpha \)-oxoketene dithioacetals. Thus when the alkenes 26 with electron withdrawing substituents such as ester, nitrile etc. were reacted with sodium cyanoborohydride, reducing the double bond without affecting the other functional groups. The general procedure utilized was mild and convenient (Scheme 9) 25. Interestingly the sodium cyanoborohydride in methanolic hydrochloric acid cleaved the C-O bond of acetals 28, 30, 32 and ketals 34 to yield the corresponding methylethers 29, 31, 33 and 35 respectively. The reaction conditions are simple and efficient (Scheme 10) 26. Similarly enaminones 36 are rapidly reduced to saturated amines 37 by sodium cyanoborohydride at an initial pH of 4 in 15:1 tetrahydrofuran/methanol solvent mixture (Scheme 11) 24. The reduction of aldoximes 38 with sodium cyanoborohydride provides the corresponding amine ethers 39 (Scheme 11) 27. It is therefore apparent that the sodium cyanoborohydride is much more efficient, selective and safe as compared to other reducing agents and should be a suitable choice as a reagent in the study of selective dethiomethylation of \( \alpha \)-oxoketene dithioacetals where such selectivity can be used to the advantage.

V.2 RESULTS AND DISCUSSION

In principle, a large variety of \( \alpha \)-oxoketene dithioacetals can be used to demonstrate the efficacy of the sodium cyanoborohydride. A selected number of \( \alpha \)-oxoketene dithioacetals were studied only to establish the
\[
\text{R} \quad \text{R'} \quad \text{R''} \quad \text{R'''}
\]

\[
\begin{array}{cccc}
\text{C}_6\text{H}_5 & \text{H} & \text{CO}_2\text{C}_2\text{H}_5 & \text{CO}_2\text{C}_2\text{H}_5 \\
o-\text{NO}_2\text{C}_6\text{H}_5 & \text{H} & \text{CO}_2\text{C}_2\text{H}_5 & \text{CO}_2\text{C}_2\text{H}_5 \\
\text{C}_6\text{H}_5 & \text{H} & \text{CO}_2\text{C}_2\text{H}_5 & \text{CN} \\
\text{CH}_3 & \text{CH}_3 & \text{CO}_2\text{C}_2\text{H}_5 & \text{CO}_2\text{C}_2\text{H}_5 \\
\text{C}_6\text{H}_5 & \text{H} & \text{H} & \text{CO}_2\text{C}_2\text{H}_5 \\
\end{array}
\]

Scheme 9
Scheme 10

\[
\begin{align*}
\text{Me} & \xrightarrow{\text{NaBH}_3\text{CN, HCl, CH}_3\text{OH, 0°C, 83%}} \text{CH}_3\text{O} & \text{Me} \\
\text{Ph} & \xrightarrow{\text{NaBH}_3\text{CN, HCl, CH}_3\text{OH, 0°C}} \text{CH}_3\text{O} & \text{Me} \\
\end{align*}
\]
Scheme 11
scope and generality of the methodology. All the α-oxoketene dithioacetals employed in this study were prepared as per the reported methods. They were fully characterized by analytical and spectroscopic data for their structural authenticity. After carrying out the reaction with different acids to maintain the pH, it was found out that the acetic acid (pH 0.9) was found to be the most satisfactory medium.

Thus in one of the typical experiments when the α-oxoketene dithioacetal 21a (R=C₆H₅, R'=H) was treated with sodium cyanoborohydride in presence of refluxing acetic acid for 12 hours, the reaction mixture after work-up and purification gave a liquid in 76% yield, which was characterized as 3-methylthio-1-phenyl-2-propen-1-one 1a. The spectral and analytical data were compared with that of the reported compound and were found identical (superimposable i.r. and n.m.r.). The geometry of 1a was assigned as E on the basis of the coupling constant (15 Hz) of vinylic protons. Thus the compound 1a is exactly identical and obtained in much higher yield 76% against the 62% of Nickel boride reaction. Similarly, under identical reaction conditions the S,S-acetals 21b-α (Scheme 12) derived from the corresponding active methylene ketones gave the respective methylthioenones 1b-α in 60-73% overall yields. The analytical and spectral data of these compounds were in conformity with their structures. The geometry of the thioenones 1b-α and α was found to be E and only in case of 1f a mixture of cis (46%) and trans (54%) isomers was obtained. Also, the acetal 21h gave the corresponding thiomethylene ketone 1h (Scheme 12) exclusively as E-isomer (i.r., n.m.r.) in 40% yield. The analogous compound 18a (Scheme 5) which is used in polyene synthesis was previously prepared by the Michael addition of t-butyl mercaptan with acetylacetylene as a mixture of cis and trans-isomers. The
Scheme 13

21, 1. n = 1, \\
21, 1. n = 2.

[Diagram of chemical structures]
vinyl chloride method, although gave exclusively the trans isomer, the preparation of the acetyl vinyl chloride itself is not easy as for the preparation of 21h. The compound 1h being an important intermediate in olefinic synthesis, the present approach of its preparation should be the method of choice.

When the method was extended to the cyclic ketene dithioacetals 2li–j derived from the respective cyclopentanone and cyclohexanone, the corresponding vinylogous thiolesters 1i and 1j were obtained in 69% and 68% yields respectively (Scheme 13). The analytical and spectral data are in conformity with the assigned trans structure. Similarly the tetralone, 6-methoxytetralone and benzuberone acetals 2lk–m gave the corresponding methylthioenones 1k–m (Scheme 14) exclusively as E-isomers in 82%, 69% and 78% yields respectively. Their analytical and spectral data are described in the experimental section.

The geometry of all the compounds were assigned on the basis of the n.m.r. coupling constants of the vinyl protons as described in the experimental section.

V.3 CONCLUSION

In conclusion, it may be summarised: A new route for the preparation of vinylogous thiolesters 1 has been formulated from the easily available ketones via the α-oxoketene dithioacetals 21. The method is shown to be applicable with liberal structural variations. The method is also suitable for the synthesis of both thiomethyl and its higher homologs, whereas the existing methods use only high boiling mercaptans, since the methyl mercaptan is a gas.
Scheme 14

21. 1, k  
R = H, n = 1  
R = OMe, n = 1  
R = H, n = 2

1
EXPERIMENTAL

General Methods

Melting points were determined on Thomas Hoover Capillary apparatus and are uncorrected. The i.r. spectra were recorded on 'Perkin-Elmer 297' Spectrometer. The n.m.r. spectra were recorded on a Varian EM-390, 90 MHz spectrometer using TMS as internal standard and the chemical shifts are recorded as δ (ppm). Mass spectra were recorded on Jeol-D 300 Mass Spectrometer.

Starting Materials

The commercial samples of acetophenone, p-methylacetophenone, p-chloroacetophenone, p-methoxyacetophenone, propiophenione, acetone, tetralone, cyclopentanone and cyclohexanone were purified before use. Commercially available sodium cyanoborohydride was purified according to reported procedure before use.

Benzsuberone b.p. 138-39°C (12mm) was prepared according to the reported procedures.

The previously reported OC-oxoketene dithioacetals were prepared by the general method described below.

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

A mixture of ketone (0.02 mol) and carbodisulphide (0.2 mol) was added to a well stirred suspension of sodium t-butoxide (0.4 mol) in dry benzene (170 ml) and the reaction mixture was allowed to stand at room temperature for 5-6 hr. Dimethylsulfate (neutral) (0.2 mol) was gradually added with stirring and external cooling (exothermic reaction)
and the reaction mixture was allowed to stand (5 hr) at room temperature with occasional shaking and then refluxed on a water bath for 0.5-1 hr. The mixture was poured on crushed ice and the benzene layer was separated. The aqueous portion was extracted with benzene and the combined extract was washed with water, dried over sodium sulfide and concentrated. The products thus obtained were purified by crystallization or by column chromatography.

**General method for the preparation of 2-methylthio-1-alkenyl ketones (1a-m).**

To a well stirred solution of α-oxoketene dithioacetals 21 (0.01 mol) in acetic acid (30 ml), excess of sodium cyanoborohydride (1.95, 0.03 mol) was added in small portions during 5 min. and the reaction mixture was stirred at room temperature for two hrs. Then the reaction mixture was refluxed for 6-10 hrs. (monitored by TLC). The mixture was then cooled to room temperature, poured into crushed ice (150 g), and extracted with chloroform (3x50 ml). The organic layer washed with bicarbonate solution, then with water (3x100 ml), dried over sodium-sulfate and evaporated to give crude methylthioenones (1a-m), which are column chromatographed on silica gel using ethylacetate/hexane (1:9) as eluent to give pure 1a-m.

The data of these compounds are given below.

**E-3-Methylthio-1-phenyl-2-propen-1-one (1a)** was obtained as yellow viscous oil; yield 76%; i.r. (CCl₄): \(\nu_{\text{max}} = 1643 \text{ cm}^{-1}\); \(^1\text{H} \text{n.m.r. (CCl₄):} \delta 2.32(\text{s,3H,CH}_3); 6.70(\text{d,1H,J=15Hz olefin}); 7.19-7.47(\text{m,3H arom}); 7.89-7.98(\text{m,3H arom+olefin}). (\text{Found: C,67.70; H,5.92. Calc. for C}_{10}H_{10}OS (178.2): C,67.41; H,5.62%).
E-3-Methylthio-1-(4-chlorophenyl)-2-propen-1-one (lb) was obtained as pale yellow solid; yield 69%; m.p. 69-70°C; i.r. (KBr): \( \nu_{\text{max}} = 1640 \text{ cm}^{-1} \);

1H n.m.r. (CDCl\(_3\)): \( \delta \) 2.42 (s, 3H, SCH\(_3\)); 6.65 (d, 1H, J=15Hz \text{ olefin}); 7.32 (d, J=9Hz, 2H \text{ arom}); 7.70-8.05 (m, 3H \text{ arom+olefin}). (Found: C, 56.75; H, 4.54.

Calc. for C\(_{10}\)H\(_9\)ClOS (212.7): C, 56.47; H, 4.23%.

E-3-Methylthio-1-(4-methoxyphenyl)-2-propen-1-one (lc) was obtained as yellow viscous oil; yield 68%; i.r. (CCl\(_4\)): \( \nu_{\text{max}} = 1650 \text{ cm}^{-1} \); 1H n.m.r. (CDCl\(_3\)): \( \delta \) 2.29 (s, 3H, SCH\(_3\)); 3.70 (s, 3H, OCH\(_3\)); 6.70-7.05 (m, J=9Hz, 2H \text{ arom+olefin}); 7.78-8.03 (m, 3H \text{ arom+olefin}). (Found: C, 63.31; H, 5.70. Calc. for C\(_{11}\)H\(_{12}\)O\(_2\)S (208.3): C, 68.42; H, 5.81%.

E-3-Methylthio-1-(4-methylphenyl)-2-propen-1-one (ld) was obtained as pale yellow solid; yield 72%; m.p. 120-121°C; i.r. (CCl\(_4\)): \( \nu_{\text{max}} = 1645 \text{ cm}^{-1} \); 1H n.m.r. (CDCl\(_3\)): \( \delta \) 2.32 (s, 3H, CH\(_3\)); 2.35 (s, 3H, SCH\(_3\)); 6.75 (d, 1H, J=15Hz \text{ olefin}); 7.19 (d, J=9Hz, 2H \text{ arom}); 8.91 (d, J=15Hz, 2H \text{ olefin}). (Found: C, 68.97; H, 6.50. Calc. for C\(_{11}\)H\(_{12}\)O\(_2\)S (192.2): C, 68.75; H, 6.25%.

E-3-Methylthio-2-methyl-1-phenyl-2-propen-1-one (le) was obtained as yellow viscous oil; yield 60%; i.r. (CCl\(_4\)): \( \nu_{\text{max}} = 1639 \text{ cm}^{-1} \); 1H n.m.r. (CDCl\(_3\)): \( \delta \) 1.89 (s, 3H, SCH\(_3\)); 2.28 (s, 3H, CH\(_3\)); 6.98 (s, 1H \text{ olefin}); 7.21-7.62 (m, 5H \text{ arom}). (Found: C, 68.81; H, 6.17. Calc. for C\(_{11}\)H\(_{12}\)O\(_2\)S (192.3): C, 68.64, H, 6.24%).

E and Z-3-methylthio-1-thienyl-2-propene-1-one (lf) was obtained as yellow crystalline solid; yield 73%; m.p. 128-129°C; i.r. (KBr): \( \nu_{\text{max}} = 1612 \text{ cm}^{-1} \); 1H n.m.r. (CCl\(_4\)): \( \delta \) 2.40 (s, 3H, SCH\(_3\)); 2.45 (s, 3H, SCH\(_3\)); 6.60 (d, 1H, J=15Hz \text{ olefin}); 6.80 (d, 1H, J=9Hz \text{ olefin}); 6.98-7.13 (m, 1H, \text{olefin}).
7.19(d,1H,J=0Hz olefin); 7.42-7.71(m,2H,H-3',5'); 7.33(d,1H,J=15Hz olefin).
(Found: C,51.98; H,4.47. Calc. for C$_8$H$_8$O$_2$(184.2): C,52.12; H,4.34%).

E-3-Methylthio-1-naphthyl-2-propen-1-one (1g) was obtained as viscous oil; yield 71%;
I.r.(CCl$_4$): $\nu_{max}=1643$ cm$^{-1}$; $^1$H n.m.r.(CCl$_4$): $\delta$ 2.32 (s,3H,SCH$_3$); 6.81(d,1H,J=15Hz olefin); 7.08-8.31(m,8H arom+olefin).
(Found: C,73.52; H,5.41. Calc. for C$_{14}$H$_{12}$O$_2$(228.3): C,73.65; H,5.30%).

E-4-Methylthio-3-buten-2-one (1h) was obtained as yellow viscous oil; yield 40%;
i.r.(CCl$_4$): $\nu_{max}=1670$ cm$^{-1}$; $^1$H n.m.r.(CDCl$_3$): $\delta$ 2.21(s,3H,CH$_3$); 2.35(s,3H,SCH$_3$); 6.05(d,1H,J=15Hz olefin); 7.70(d,1H,J=15Hz olefin).
(Found: C,51.43; H,6.45. Calc. for C$_5$H$_8$O$_2$(116.2): C,51.63; H,6.88%).

The viscous oil solidifies on cooling m.p. 22°C.

E-2-(Methylthiomethylene)cyclopentanone (1i) was isolated as pale yellow solid; yield 69%; m.p. 47-48°C; i.r.(CCl$_4$): $\nu_{max}=1701$ cm$^{-1}$;
$^1$H n.m.r.(CCl$_4$): $\delta$ 1.79-2.38[m,6H,(CH$_2$)$_3$]; 2.45(s,3H,SCH$_3$); 7.10 (t,1H, J=1.5Hz olefin). (Found: C,58.96; H,7.54. Calc. for C$_7$H$_{10}$O$_2$(142.2): C,59.07; H,7.30%).

E-2-(Methylthiomethylene)cyclohexanone (1j) was obtained as pale yellow oil; yield 68%; i.r.(CCl$_4$): $\nu_{max}=1712$ cm$^{-1}$; $^1$H n.m.r.(CCl$_4$):
$\delta$ 1.50-2.00[m,4H-(CH$_2$)$_2$]; 2.00-2.60[m,4H,-(CH$_2$)$_2$]; 2.45(s,3H,SCH$_3$); 7.25(t,1H,J=1.5Hz olefin). (Found: C,61.71; H,7.92. Calc. for C$_8$H$_{12}$O$_2$(156.2): C,61.60; H,7.68%).

E-2-(Methylthiomethylene)tetralone (1k) was isolated as pale yellow solid; yield 82%; m.p. 68-69°C; i.r.(KBr): $\nu_{max}=1660$ cm$^{-1}$; $^1$H n.m.r. (CCl$_4$): $\delta$ 2.43(s,3H,SCH$_3$); 2.79[A$_2$B$_2$,q,4H,-(CH$_2$)$_2$]; 7.00-7.40(m,3H arom); 7.51(s,1H olefin); 7.90-8.05(m,1H arom). (Found: C,70.72; H,5.91. Calc. for C$_{12}$H$_{12}$O$_2$(204.3): C,70.48; H,5.87%).
E-2-(Methylthiomethylene)6-Methoxytetralone (11) was isolated as pale yellow solid; yield 69%; m.p. 92-96°C; i.r. (KBr): $\nu_{\text{max}} = 1640, 1595 \text{ cm}^{-1}$; $^1$$H$ n.m.r. (CDCl$_3$): $\delta$ 2.50 (s, 3H, SCH$_3$); 2.63-3.05 [m, 4H, -(CH$_2$)$_2$-]; 3.78 (s, 3H, OCH$_3$); 6.51-6.88 (m, 2H arom); 7.61 (s, 1H olefin); 7.98 (d, J = 9 Hz, 1H arom). (Found: C, 66.51; H, 5.97; Calc. for C$_{14}$H$_{12}$O$_2$ (228.3): C, 68.64; H, 6.02%).

E-2-(Methylthiomethylene)benzosuberone (1m) was isolated as yellow liquid; yield 78%; i.r. (KBr): $\nu_{\text{max}} = 1650 \text{ cm}^{-1}$; $^1$$H$ n.m.r. (CCl$_4$): $\delta$ 1.88 [A$_2$B$_2$ q, -(CH$_2$)$_2$-]; 2.25 [t, 2H, -(CH$_2$)$_2$-]; 2.40 (s, 3H, SCH$_3$); 2.71 [t, 2H, -(CH$_2$)$_2$-]; 6.90-7.60 (m, 5H arom+olefin). (Found: C, 71.33; H, 6.53. Calc. for C$_{13}$H$_{14}$O$_2$ (218.2): C, 71.49; H, 6.45%).
References

23. For a review see: C.F. Lane, Synthesis, 135 (1975).