CHAPTER V

STUDIES ON 1,5-, 1,7-, 1,9- AND 1,11-CARBONYL GROUP TRANSPOSITIONS VIA OXOKETENE DITHIOACETALS

V.1 INTRODUCTION

The term 'carbonyl group transposition' is defined as migration of carbonyl functionality within the same molecular framework\(^1,2\). The most intensively investigated carbonyl transpositions are the 1,2-carbonyl transpositions\(^3\) and the examples of 1,3-carbonyl transpositions are relatively less in number. The methods for 1,4-carbonyl transpositions described in the literature are very few, whereas the studies involving 1,5-carbonyl transpositions are largely confined to isomerization of hydroxy ketones involving hydride migrations. Few 1,6-carbonyl transpositions involving hydride migrations
known, and there appears to be no examples in the literature involving carbonyl transpositions beyond 1,6. However, while the present investigation was in progress, Duhamel and co-workers have reported the reactions of functionalized silyloxy or alkoxypolyenelithium reagents with aldehydes or ketones followed by hydrolysis in mild conditions which leads to polyenals. These reactions may be considered as special cases of alkylative 1,5 and 1,7 carbonyl group transpositions, where the carbonyl group migration is associated with homologation.

The carbonyl group is the most important functional group in organic chemistry. Although there is an abundance of carbonyl functionality in organic chemistry, serious studies involving carbonyl transpositions, which can be used as general methods for organic synthesis have not been attempted. Even the extensively studied 1,2-carbonyl transpositions have been developed as a part of specific design to introduce carbonyl group in an appropriate position in a given molecule. Since there exists no general methods in the literature, particularly for higher carbonyl transpositions, which may be used to design synthetic strategies for various biologically important molecules, it is desirable to investigate and evolve efficient methodologies for 1,5- and higher carbonyl transpositions. It was contemplated in the present investigation to undertake systematic investigation to develop new methodologies for higher carbonyl transpositions.

The oxoketene dithioacetals are a versatile group of synthons which have been extensively investigated to explore their synthetic potential and shown to be highly useful building blocks in organic
Their applications in 1,3 carbonyl transpositions involving borohydride reduction or reaction with Grignard or organolithium reagents to give the corresponding carbinol acetals followed by methanolysis to the corresponding ene-esters are well documented\textsuperscript{8,9,10,11}. This 1,3 carbonyl transposition methodology has been further extended to the cinnamoyl and 5-aryl 2,4-pentadienyl ketene dithioacetals to afford pentadienoates\textsuperscript{12} and heptatrienoates\textsuperscript{13} respectively. In the present work the acyl ketene dithioacetals have been successfully used to achieve 1,5-, 1,7-, 1,9- and 1,11- carbonyl group transpositions. Such methods will be of immense synthetic value particularly in the total absence of any carbonyl transpositions beyond 1,7.

V.2. Current Status of Literature involving 1,5-, 1,6- and 1,7-Carbonyl Group Transpositions

V.2.1 1,5-Carbonyl Transposition

The first report on a 1,5 hydroxy-ketone transposition appears to have been that of Acklin and Prelog in 1959\textsuperscript{14}. They have demonstrated that the hydroxy ketone \textsubscript{1} (Scheme 1) undergoes a 1,5-carbonyl transposition to give \textsubscript{2} in the presence of activated alumina. Similarly, Wicha and Caspi\textsuperscript{15} have reported a migration of carbonyl group of cyclohexanone \textsubscript{3} to the exocyclic carbon to give \textsubscript{4} (Scheme 1) whereas the carbonyl group of \textsubscript{5} has been shown to be transposed to an adjacent fused ring by Parker and Stevenson\textsuperscript{16}. The other example (\textsubscript{7} \rightarrow \textsubscript{8}, Scheme 1) also involves a hydride transfer along with the 1,5 carbonyl transposition\textsuperscript{17}. The variation and diversity in these examples of 1,5- carbonyl transposition is limited merely to intramolecular hydride transfer.
Scheme 2

\[
\text{Ether, } \rightarrow \text{H} \quad -70^\circ C \quad \rightarrow \text{H}
\]

9, 11a $R^2=\text{CH}_3$

b $R^2=\text{Ph}$
c $R^2=\text{Ph}$
d $R^2=$
e $R^2=$
f $R^2=$

10a $R^1=\text{Et}$

b $R^1=\text{Si(Me)}_3$
Recently Duhamel and co-workers\textsuperscript{5} have developed a new reagent i.e. lithiosilyloxy or ethoxybutadiene\textsuperscript{10} by reacting 1-butyllithium with the corresponding bromo-, silyloxy- or ethoxybutadienes. The butadienyllithium reagents react with carbonyl compounds followed by hydrolysis to give polyenealdehydes\textsuperscript{11} (Scheme 2). This reaction may be considered as an alkylative 1,5 carbonyl transposition where the migration of the carbonyl group is through the side chain introduced, involving simultaneous 4-carbon homologation as well.

V.2.2 1,6-Carbonyl Transposition

Examples involving 1,6-carbonyl transpositions are limited to intramolecular hydride transfer. An interesting example is the preparation of \( \text{p-hydroxyphenyl lactic acid} \)\textsuperscript{15} (Scheme 3) from involving a 1,6-hydride migration\textsuperscript{18}. Similarly, an example of 1,6-carbonyl transposition through hydride transfer in the conversion of acyclic hydroxy ketone\textsuperscript{16} to \textsuperscript{17} has also been reported (Scheme 3).

V.2.3 1,7-Carbonyl Transposition

The only report on a 1,7 carbonyl transposition is of Duhamel and co-workers\textsuperscript{6}, which appeared recently. They have prepared the vinylogous lithium reagents\textsuperscript{19} by lithiation of the corresponding bromo compounds (Scheme 4). The reaction of these reagents with aldehydes or ketones leads to polyenaldehydes\textsuperscript{20}. The reaction involves an alkylative 1,7 carbonyl transposition, where the migration of the carbonyl group takes place through the side chain introduced. They have reported the synthesis of dehydrocitral, \( \gamma \)-retinal and retinal through a one step reaction from acetone, \( \omega \)-ionone and \( \beta \)-ionone respectively. The examples illustrated for 1,5-, 1,6-, and 1,7-carbonyl transpositions are very few in number and mostly confined to intramolecular hydride transfer.
Scheme 4.

$$\text{Ether} \quad -70^\circ \text{C}$$

18 $\text{R}^2 \quad \text{R}^3 \text{CO}_3$ $\text{Li}$

19 $\text{R}^1 = \text{Et, SiMe}_3$

18 $\text{R}^1$

18a $\text{R}^2 = \text{Ph}$; $\text{R}^3 = \text{H}$

18b $\text{R}^2 = \text{CH}_3$; $\text{R}^3 = \text{CH}_3$

18c $\text{R}^2 = \text{CH}_3$; $\text{R}^3 = \text{CH}_3$

18d $\text{R}^2 = $
**RESULTS AND DISCUSSION**

**V.3.1 Synthesis of 5,5-Bis(methylthio)-pentadienals**

During the course of this investigation it was considered that the pentadienals \( \text{23} \) (Scheme 5) would be suitable candidates for the 1,5 and 1,7 carbinol transpositions. These hitherto unreported dienaldehydes \( \text{25} \) were conveniently prepared by the Vilsmeier-Haack acylation of the carbinol acetals \( \text{22} \) obtained by a 1,2-reduction of the respective \( \alpha \)-oxoketene dithioacetals \( \text{21} \). Thus the 5,5-bis(methylthio)-2,4-pentadienaldehyde \( \text{23a} \) was obtained in 59% yield from the corresponding \( \alpha \)-oxoketene dithioacetal \( \text{21a} \) through the carbinol acetal \( \text{22a} \). It was analyzed for \( \text{C}_{7}\text{H}_{10}\text{O}_{2}\text{S}_{2} \) and its i.r. spectrum displayed characteristic bands at 1670 and 1592 cm\(^{-1}\). Further structural proof was obtained from its \( ^1\text{H} \) n.m.r. spectrum (CCl\(_4\)), which showed two singlets at \( \delta \) 2.40(3H) and 2.41(3H) due to the two methylthio groups. The double doublet at \( \delta \) 5.98(1H, J=16Hz,8Hz) which was assigned to H-2 proton thus showing trans along C\(_2\)C\(_3\) double bond. The H-4 proton absorbed at \( \delta \) 6.30(1H, J=12Hz), while the H-3 proton appeared as a double doublet at \( \delta \) 7.47(1H, J=16Hz,12Hz). The doublet at \( \delta \) 9.52(1H, J=8Hz) was assigned to the aldehydic proton. The coupling constants of H-2 and H-3 confirm the 2-\( \text{E} \) geometry of the aldehyde formed and shows that the reaction is stereospecific unlike other formylations of polyenes under Vilsmeier-Haack reaction conditions. Similarly \( \text{23b} \) and \( \text{23c} \) were also prepared from the corresponding \( \text{21a} \) and \( \text{21b} \) respectively in 70 and 74% yields. They also show characteristic trans coupling at H-2 and H-3 confirming the 2-\( \text{E} \) geometry of the aldehydes.
The dienaldehydes 23 with a protected ester functionality at one terminal and a reactive aldehyde functionality at the other end, which can be used for new C-C bond forming reactions, such as aldol condensations, reactions with organolithium and magnesium reagents, Reformatsky and Wittig reactions, are of high synthetic importance, particularly when the other polyenaldehydes 28, which may be prepared by Vilsmeier reaction from the acetals are of limited use because of the dimethylamino substitution 20, 21.

[Scheme 6]

V.3.2 Studies on 1,5-Carbonyl Transposition

The dienaldehydes 23a–c were considered as appropriate precursors for the study of 1,5 carbonyl transposition, as well as for the preparation of 7,7-bis(methylthio) heptatrienones and 7,7-bis(methylthio) heptatrienals which would be the precursors for 1,7 carbonyl transpositions. The 1,5 carbonyl transpositions were achieved from the bis(methylthio) dienaldehydes as described in the following section. When the dienaldehyde 23a was reacted with phenylmagnesium bromide, the resultant pentadienol 24a was obtained in nearly quantitative yield (Scheme 5). The alcohol 24a was not characterized and used as such for the next step without further purification. After boron trifluoride etherate assisted methanolysis, work-up and column chromatography of the reaction mixture afforded the corresponding
Scheme 5

1. $\text{POCl}_3$ in DMF

2. $\text{NaBH}_4$ in EtOH

3. $\text{BF}_3\cdot\text{Et}_2\text{O}$ in MeOH

4. $\text{C}_6\text{H}_5\text{MgBr}$
methyl 2,4-pentadienoate 25a in 90% yield. The structure of 25a was confirmed by comparison with authentic sample prepared by methods reported earlier (m.m.p.; superimposable i.r. and n.m.r. spectra). The other diene esters 25b and 25c were also obtained in 85 and 87% yields from 23b and 23c respectively. The analytical and spectral data of all 25a-c were in conformity with the assigned structures and are described in the experimental. The diene esters were assigned $E$,$E$ geometry based on the spectral data. The method is of particular synthetic importance, since it provides a facile route to dieneesters from the active methylene ketones via oxoketene dithioacetals through the sequence of reactions described (Scheme 5).

V.3.3 Synthesis of 7,7-Bis(methylthio)-1-aryl/alkyl (or cycloalkyl)-2,4,6-heptatriene-1-ones

According to the present scheme of investigation, the precursors for the study of 1,7 carbonyl transpositions can be of two kinds: (a) the heptatrienaldehyde 39 (Scheme 12); (b) the heptatrienone 30 (Scheme 7) or 31 (Scheme 8). The hitherto unreported 7,7-Bis (methylthio)heptatrienones 30a-i and 31a-i were prepared by condensation of the dienaldehyde 23a or 23b with various ketones. When the aldehyde 23a was reacted with acetophenone in the presence of sodium methoxide in methanol, the corresponding 7,7-bis(methylthio)-1-phenyl-2,4,6-heptatriene-1-one 30a was obtained in 95% yield. The structure and stereochemistry of the trienone 30a was established with the help of its spectral and analytical data. Thus the compound 30a exhibited the molecular ion peak in its mass spectrum at m/z 276 ($M^+$,10%) and was analyzed for $C_{15}H_{16}OS_2$. The i.r.(KBr) spectrum displayed
\[
\text{NaOMe/MeOH}
\]

\[
\begin{align*}
23a + 29a-i & \rightarrow 30a-i \\
29-30 & \begin{align*}
a & \quad R = C_6H_5; \quad R^1 = H \\
b & \quad R = 4-MeC_6H_4; \quad R^1 = H \\
c & \quad R = 4-MeOC_6H_4; \quad R^1 = H \\
d & \quad R = 4-ClC_6H_4; \quad R^1 = H \\
e & \quad R = R^1 = \text{aromatic ring} \\
f & \quad R = R^1 = \text{aromatic ring} \\
g & \quad R = \text{furanyl}; \quad R^1 = H \\
h & \quad R = \text{furanyl}; \quad R^1 = H \\
i & \quad R = \text{CH}_3; \quad R^1 = H
\end{align*}
\]

\text{Scheme-7}
bands at 1643, 1590 and 1586 cm\(^{-1}\) due to the carbonyl and olefin groups respectively. The \(^1\)H n.m.r. spectrum (CDCl\(_3\), 300 MHz) showed two singlets at \(\delta 2.39\) and \(\delta 2.40\) due to the two methylthio groups. The doublet at \(\delta 6.36(1H, J=11.4\text{Hz})\) was assigned to the H-6 proton while the H-5 proton appeared as a double doublet at \(\delta 6.45(1H, J=15\text{Hz}\) and \(11.4\text{Hz}\)). The H-2 proton was present as a doublet at \(\delta 6.96(1H, J=15\text{Hz})\) while H-5 proton absorbed at \(\delta 7.26\text{(dd,}1H, J=15\text{Hz,}11.1\text{Hz})\). The multiplet at \(\delta 7.40\text{-}7.60(4H)\) was due to three aromatic protons along with H-3 and the other two aromatic protons absorbed between \(\delta 7.92\text{-}7.94\). The clear trans couplings of the H-3, H-4 and H-5 confirm the 2-E, 4-E geometry of the molecule. Similarly the heptatrienones 30b-i and 31a-i were prepared by the condensation of 23a or 23b with the active methylene compounds 29a-i in 80-95% overall yields (Scheme 7 and 8). The n.m.r. spectral data showed that the 2-E, 4-E geometry remained consistent in all these compounds. The structures and stereochemistry of all the heptatrienones were confirmed with the help of spectral and analytical data and are described in the experimental section.

V.3.4 Studies on 1,7-carbonyl transpositions of 7,7-bis(methylthio)-1-aryl 2,4,6-heptatrienones.

After the synthesis and structural assignment, the heptatrienones 30 and 31, were subjected to 1,7 carbonyl transposition studies and the results of the present investigation are depicted in the Scheme 9 and Scheme 10. Thus the heptatrienone 30a underwent smooth 1,2-reduction with sodium borohydride to give the corresponding heptatrienol 32a in nearly quantitative yield, which without further purification was subjected to boron trifluoride etherate assisted
methanolysis and the corresponding transposed triene-ester 33a was obtained in 72% yield. The structure of the methyl 2,4,6-heptatrienoate 33a was confirmed by comparison with authentic sample prepared by reported methods as described in Chapter III of the thesis (m.m.p., superimposable i.r. and n.m.r. spectra). Other bis(methylthio) heptatrienones 30b-g and 31a-g also underwent 1,2-reduction with sodium borohydride, followed by boron trifluoride assisted methanolysis to give the heptatrienoates 33b-g (Scheme 9) and 35a-g (Scheme 10) respectively. However, the 7,7-bis(methylthio)-1-furyl-2,4,6-heptatrienones 30h and 31h though underwent the 1,2-reduction smoothly, failed to give the corresponding triene esters. It appears that the furan ring undergoes ring cleavage or polymerization in the presence of methanolic boron trifluoride etherate.

As a model reaction to examine the feasibility of alkylative 1,7 carbonyl transposition, the heptatrienone 31e was subjected to 1,2-addition with methyl magnesium iodide to give the carbinol acetal 36 in nearly quantitative yields. The triene alcohol 36, without further purification was subjected to boron trifluoride etherate catalyzed methanolysis to afford the methyl 2-methyl-5-(3,4-dihydro-1-methylnapthyl)-2,4-pentadienoate 37 in 75% yield (Scheme 11). The structure of 37 was fully characterized with the help of spectral and analytical data. Thus its mass spectrum exhibited molecular ion peak at m/z 268(100%) and it was analyzed for \( \text{C}_{16}\text{H}_{22}\text{O}_{2} \). Its i.r.(KBr) spectrum showed bands at 1700 and 1610 cm\(^{-1}\) due to ester carbonyl and olefinic groups respectively. The \(^1\text{H}\) n.m.r. spectrum exhibited two singlets at \( \delta 1.95(3\text{H}) \) and \( \delta 2.22(3\text{H}) \) due to the methyl groups while the methylene protons appeared as a multiplet.
between 6 2.36-2.88(4H). The absorption due to methoxy protons was present at 6 3.70(s,3H), while a double doublet at 6 6.57(1H,J=15Hz, 11Hz) was assigned to the H-4 proton. Other olefinic and aromatic protons were present as a multiplet between 6 6.98-7.41(6H). Thus it has been shown that the hexatrienones 30 and 31 can also be used as precursors for alkylative carbonyl transpositions, though a detailed investigation was not undertaken in the present study.

V.3.5 Synthesis of 7,7-Bis(methylthio)-2,4,6-heptatrienals

The reductive and alkylative 1,7 carbonyl transpositions have been achieved from the heptatrienones 30 or 31 as described in Scheme 9, 10 and 11. An alkylative carbonyl transposition can also be achieved from the heptatrienals 39 (Scheme 12) by reacting them with organo-lithium or grignard reagents followed by solvolysis. To study these transformations as well as the higher carbonyl transpositions, the heptatrienal 39 was prepared employing the sequence of reactions shown in Scheme 12. Thus the pentadienal 23a was reacted with methylmagnesium iodide to give the hexadienol 38 in nearly quantitative yield, which was subjected to formylation under Vilsmeier-Haack reaction conditions to give 7,7-bis(methylthio) 2,4,6-heptatrienal 39a in 56% yield. The structure of 39a was confirmed with the help of spectral and analytical data. Thus it was analyzed for C9H12OS2. Its i.r.(neat) spectrum showed bands at 1670 and 1600 cm⁻¹ due to the carbonyl and olefin functionalities. The structure was further confirmed from its ¹H n.m.r. spectrum (CCl₄). The two singlets at 6 2.31 and 6 2.32 integrating for 3H each were assigned to the two methylthio groups. The H-2 proton appeared at 6 6.01 (dd, J=16Hz, 8Hz) thus showing trans configuration around 2,3 double
Scheme 9

30, 32h, R = O

30, 3233, a R = C₆H₅; R¹ = H
b R = P-MeC₆H₄; R¹ = H
c R = P-MeOCC₆H₄; R¹ = H
d R = P-ClC₆H₄; R¹ = H

BF₃·Et₂O/MeOH

NaBH₄/EtOH
bond. The signal at $\delta$ 6.29(d,1H,J=12Hz) was assigned to H-6 proton while H-4 proton was present at $\delta$ 6.36(dd,1H,J=16Hz,12Hz). The signal due to H-5 proton appeared at $\delta$ 7.08(dd,1H,J=16Hz,12Hz) while another double doublet (J=15Hz,8Hz) at $\delta$ 7.29 was assigned to H-3 proton respectively. The low field signal at $\delta$ 9.52(d,1H, J=8Hz) was assigned to the aldehydic proton. The elegant spectral data in which all the protons of the molecule have appeared in highly distinguishable chemical shifts was helpful in the assignment of stereochemistry of the aldehyde. The coupling constants have been consistantly in favour of $2E$, $4E$, geometry of 39a. It is important to note that the polyenaldehydes obtained through Vilsmeier-Haack reactions have generally resulted in a mixture of geometrical isomers (Scheme 7), whereas in the present investigation, the geometries of 39a and other similar compounds described in this chapter have been obtained exclusively as a single isomer with all trans configuration. It appears that the POCl$_3$/DMF complex in association with sulphur lone pair leads to exclusive trans geometry. The validity of this reasoning requires further investigation and the present explanation is only a tentative one. The other heptatrienal 39b was obtained 80% yield from 23b, through the described sequence and its structure and stereochemistry were fully confirmed with the help of spectral and analytical data (experimental).

V.3.6 Reaction of Phenylmagnesium bromide with 7,7-bis(methylthio)-2,4,6-heptatrienals ; An alternative approach to 1,7-carbonyl transposition. The objective of the synthesis of the heptatrienals 39a and 39b was to study their alkylative 1,7 carbonyl transpositions employing Grignard reagents as well as to use them as precursors in the
synthesis of polyenaldehydes and ketones required in the present studies. The \(1,7\) carbonyl transposition using Grignard reagents has been achieved as shown in Scheme 12.

The aldehyde \(39a\) was reacted smoothly with phenylmagnesium bromide in a \(1,2\) fashion to yield the corresponding trienol \(32a\) in nearly quantitative yields. The boron trifluoride etherate assisted methanolysis of the trienol \(32a\) gave the corresponding heptatrienoate \(33a\) in 80\% yield (Scheme 12). The triene ester thus obtained was found to be exactly identical with the one prepared before as described in Scheme 9 (m.m.p., superimposable i.r., n.m.r. spectra). Similarly, \(35a\) was prepared under identical conditions (Scheme 12) from \(39b\) in 75\% yield and found to be identical with the same triene ester which was prepared earlier (Scheme 10).

V.3.7 Synthesis of \(1\)-Aryl(or cycloalkyl)-9,9-Bis(methylthio)-2,4,6,8-nonatetraenones

In the preceding paragraph, synthesis of the heptatrienal \(39\) has been described which have been shown to undergo alkylative \(1,7\) carbonyl transposition. They have been now used for further condensation with active methylene ketones to give the corresponding tetraenones \(40\), which are suitable candidates for \(1,9\) carbonyl transposition studies (Scheme 13). Thus \(39a\) was reacted with acetophenone in the presence of sodium methoxide in methanol to afford \(9,9\)-Bis(methylthio)-1-aryl-2,4,6,8-nonatetraen-1-one \(40a\) in 92\% yield. The structure of \(40a\) was elucidated from its analytical and spectral data. Thus it was analyzed for \(C_{17}H_{18}OS_{2}\) (302.4) and in its i.r. (neat) spectrum, it exhibited bands at
Scheme 12

Reactions:

1. Reaction of \( \text{POCl}_3 \) with \( \text{DMF} \)

2. Reaction of \( \text{C}_6\text{H}_5\text{MgBr} \)

3. Reaction of \( \text{BF}_3\cdot\text{Et}_2\text{O} \) with \( \text{MeOH} \)

Reagents and Products:

- \( 23, 38, 39 \) a: \( R = \text{H} \)
- \( 32\text{a or 34\text{a}} \)
- \( 33\text{a or 35\text{a}} \)
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1652 and 1598 cm\(^{-1}\) which were attributed to the carbonyl group and the olefinic double bonds respectively. The structure was further confirmed by its \(^1\)H n.m.r. (CCl\(_4\)) spectrum. The two singlets at \(\delta 2.33(3\text{H})\) and \(\delta 2.34(3\text{H})\) were assigned to the two methylthio groups, while the doublet (J=11Hz) at \(\delta 6.29\) was due to the H-8 proton. The H-2, H-4, H-5, H-6 and H-7 protons were present as a complex multiplet between \(\delta 6.50-7.18\). Aromatic protons along with H-3 also appeared as a multiplet from \(\delta 7.23-8.01\). The stereochemistry was assumed to be 2-E, 4-E, 6-E on the basis of the assignments made earlier for analogous systems. Similarly, the nonatetraenones 40b-d were prepared from 39b and acetophenone, 4-chloroacetophenone and 6-methoxy tetralone respectively in 70-78% overall yields. The analytical and spectral data of 43b-d were in agreement with the assigned structures and are described in the experimental section.

V.3.8 1,9-Carbonyl Transposition Studies

After the synthesis and characterization of the bis(methylthio) nonatetraenyl ketones 40, their 1,9 carbonyl transposition studies were undertaken (Scheme 14). The tetraenone 40a was reduced with sodium borohydride in ethanol to give the corresponding tetraenol 41a in nearly quantitative yield, which on subsequent boron trifluoride etherate assisted methanolysis yielded the corresponding methyl 9-phenyl-2,4,6,8-nonatetraenoate 42a in 70% yield. The structure of 42a was confirmed from its analytical and spectral data. Thus it was analyzed for C\(_{16}\)H\(_{16}\)O\(_2\) and its i.r. (KBr) spectrum exhibited bands at 1708 and 1618 cm\(^{-1}\) due to the ester carbonyl group and the olefinic double bonds respectively. The structure was further confirmed by its \(^1\)H n.m.r. spectrum. The singlet at
Scheme 14

40, 41, 42

40. $R=\text{C}_6\text{H}_5$; $R^1=\text{R}^2=\text{H}$

41. $R=\text{C}_6\text{H}_5$; $R^1=\text{H}$; $R^2=\text{Me}$

42. $R=4\text{-ClC}_6\text{H}_4$; $R^1=\text{H}$; $R^2=\text{Me}$

d. $R=R^1=\text{Me}$; $R^2=\text{Me}$
§3.81(3H) was assigned to the methoxy protons. The H-2 proton appeared at §5.89(d,1H,J=15Hz) which was in confirmity with the trans geometry. The multiplet between §6.22-6.89(7H) were due to the various olefinic protons, whereas the other multiplet between §7.02-7.25(5H) was assigned to the aromatic protons. The ester 42a was assumed to have all trans stereochemistry on the basis of earlier observations. The other tetraenoates 42b-d were similarly obtained in 70-80% overall yields. The spectral and analytical data of these compounds have been in agreement with the assigned structures and are described in the experimental section.

V.3.9 Synthesis of 9,9-Bis(methylthio)-8-methyl 2,4,6,8-nonatetraenal (44) and its 1,9 carbonyl transposition

The nonatetraenaldehyde 44 was prepared by employing the sequence of reactions described in Scheme 15. The intermediate alcohol 43 was obtained either by the reduction of the octatrieneone 31i, the preparation of which has been already described, or by reacting the heptatrienaldehyde 39b with methylmagnesium iodide. The alcohol 43 was subjected to formylation under Vilsmeier-Haack reaction conditions, and after work-up, 9,9-bis(methylthio)-8-methyl-2,4,6,8-nonatetraenal (44) was obtained in 70% yield. The structure of 44 was confirmed from its analytical and spectral data. Thus it was analyzed for C_{12}H_{16}OS_{2}(240.6) and it exhibited molecular ion peak in its mass spectrum at m/z 240(100%). The i.r. (neat) spectrum of 44 showed a strong band at 1675 cm\(^{-1}\) due to aldehyde functionality, whereas the bands at 1612 and 1585 cm\(^{-1}\) were due to the olefinic double bonds. The structure was further
confirmed by its $^1$H n.m.r. (CDCl$_3$) spectrum. The singlet (3H) at $\delta$ 2.11 was assigned to the methyl group, while the protons of the methylthio groups absorbed at $\delta$ 2.25(3H) and $\delta$ 2.34(3H). The H-2 proton appeared as a double doublet (J=15Hz, 8Hz) at $\delta$ 5.98 while the multiplet between $\delta$ 6.23-7.21 was assigned to four olefinic protons. The doublet (J=15Hz) at $\delta$ 7.42 was assigned to H-7 proton whereas the absorption due to aldehydic proton appeared at $\delta$ 9.49 (J=8Hz). The compound was assigned 2R,4-F,6-E geometry, on the basis of n.m.r. data as well as in analogy with the dienaldehyde 23 and trienaldehyde 39 described earlier.

As an alternative approach towards 1,9 carbonyl transposition, the tetraenaldehyde 44 was reacted with phenylmagnesium bromide, when the corresponding alcohol 41b was obtained in quantitative yield, which was subsequently subjected to boron trifluoride etherate catalyzed methanolysis to afford the corresponding nonatetraenoate 42b in 70% yield. The nonatetraenoate 42b obtained by this reaction was found to identical with that obtained by reductive 1,9 carbonyl transposition of 40b (Scheme 14) (m.m.p., superimposable i.r. and n.m.r. spectra). Thus the synthesis of 42b from the tetraenal 44 further confirmed its structure. It is therefore possible to evolve at least two alternative methods for 1,9 carbonyl transposition, one through the tetraenyl ketone 40 and the other through the aldehyde 44.

V.3.10 Synthesis of 11,11-Bis(methylthio)-1-aryl(or cycloalkyl)-10-methyl 2,4,6,8,10-undecapentaene-1-ones

The pentaenones 45a and 45b were required as precursors for the study of 1,11 carbonyl transposition studies. They were conveniently
Scheme 16

NaOMe / MeOH

26a or 26f

26a, 45a: R = C₆H₅; R¹ = H
b: R = R¹ = MeO
prepared by the condensation of the tetraenaldehyde 44 with acetophenone 26a and 6-methoxystetralone 26f respectively (Scheme 16). Thus when the tetraenaldehyde 44 was condensed with acetophenone in the presence of sodium methoxide and methanol the 11,11-bis (methylthio)-1-phenyl-9-methyl 2,4,6,8,10-decapentaene-1-one 45a was obtained in 90% yield. The structure of 45a was confirmed with the help of spectral and analytical data. Thus 45a was analyzed for C_{20}H_{22}O_{2}S_{2}(342.6) and its i.r.(neat) spectrum showed bands at 1655 and 1595 cm\(^{-1}\) which were assigned to the carbonyl group and the olefinic double bond respectively. The structure was further confirmed from its \(^1\)H n.m.r.(CCl\(_4\)) spectrum. The singlet at \(\delta\) 2.00 was due to the CH\(_3\) protons while the two methylthio groups were present at \(\delta\) 2.13(s,3H) and \(\delta\) 2.23(s,3H) respectively. The olefinic protons along with the aromatic protons appeared as a complex multiplet between \(\delta\) 6.15-8.20(13H). The product was assigned 2-E, 4-E,6-E,8-E geometry in analogy with assignments made earlier for similar polyenones prepared by similar sequence of reactions. Similarly the condensation of the nonatetraenal 44 with 6-methoxystetralone gave the pentaenones 45b in 95% yield. The structure and stereochemistry was confirmed with the help of spectral and analytical data and are described in the experimental section.

V.3.11 1,11-Carbonyl Transposition Studies

After synthesis and characterization for the bis(methylthio) undecapentaenones 45, their 1,11 carbonyl transposition studies were undertaken. The pentaenone 45a underwent smooth 1,2-reduction with sodium borohydride in methanol to afford the bis(methylthio)pentaenols 46a in nearly quantitative yield. The polyene
alcohol, when subjected to boron trifluoride etherate assisted methanolysis yielded the corresponding methyl 11-phenyl-2-methyl 2,4,6,8,10 undeca-pentaenoate 47a in 85% yield (Scheme 17). The structure of the polyene ester 47a was confirmed with the help of its spectral and analytical data. Thus it was analyzed for C_{19}H_{20}O_2 (280.4) and in its i.r.(KBr) spectrum exhibited bands at 1705 and 1617 cm⁻¹ due to the ester carbonyl and olefinic double bonds respectively. Further proof for the structure was obtained from ¹H n.m.r. (CDCl₃) spectrum, in which the methyl group appeared as a singlet at 6 2.00 (3H) and the methoxy protons were present at 6 3.36 (s, 3H). The multiplet at 6.30-7.10 (8H) was assigned to eight olefinic protons, while the aromatic protons along with an olefinic proton absorbed as a multiplet between 6 7.10-7.85 (8H). The polyene ester 47a was assigned all trans geometry in analogy with the other polyene esters prepared earlier. Similarly the bis(methylthio) pentaenone 45b also underwent 1,11 carbonyl transposition under the described reaction conditions to give the polyene ester 47b in 80% yield (Scheme 17). The structure and stereochemistry of 47b was confirmed with the help of its spectral and analytical data, and are described in the experimental section. Further proof for stereochemical assignment of polyenes 42, 44, 45 and 47 would be obtained from their high resolution ¹H n.m.r. and ¹³C n.m.r. spectra, which is awaited.

V.4 EXPERIMENTAL

The general experimental conditions were same as in Chapter II. The ¹H n.m.r. spectra were recorded on a Varian EM 390 (90 MHz) or on a Varian XL 300 (300 MHz) spectrometer.

Starting Materials
The commercial samples of acetone, ethylmethyl ketone, methylpropyl ketone, acetophenone, p-methylacetophenone, p-methoxyacetophenones, p-chloroaceto phenone, tetralone, 6-methoxytetralone, 2-acetylthiophene and 2-acetylfuran were purified before use.
The previously reported ketene S,S-acetals 4,4-bis(methylthio)-3-
butene-2-one (21a) m.p. 66-67°C, 4,4-bis(methylthio)-3-methyl-3-butene-
2-one 21b, b.p. 68°C (0.1 mm) and 4,4-bis(methylthio)-3-ethyl-3-butene-2-
one 21c were prepared by the general method described in Chapter II.

5,5-Bis(methylthio)-2,4-pentadienals (23a-c); General Procedure:
To a solution of α-oxoketene dithioacetal 21 (0.01 mol) in absolute
ethanol, excess sodium borohydride (0.76 g, 0.02 mol) was added slowly
and the reaction mixture was then refluxed for 1.5 hrs. The mixture
was cooled and poured over saturated ammonium chloride solution (200 ml),
extracted with ether (4x50 ml) washed with water (2x50 ml) dried
(Na₂SO₄) and evaporated to give the 4,4-bis(methylthio)-3-butene-2-
ols 22 in nearly quantitative yields which were used as such for
the next step without further purification. The hydroxy dithioacetal
22 (0.01 mol) in 5 ml DMF was added slowly to a well cooled (0°C) and
stirred Vilsmeier reagent [prepared by adding phosphorous oxychloride
(3.83 g, 0.025 mol) to N,N-dimethyl formamide (20 ml, 0.25 mol) with
stirring and cooling and further stirring for 30 min at room temperature].
The reaction mixture was stirred for 10-15 hrs for completion of
reaction after which it was poured over crushed ice (300 g) followed
by slow addition of cold saturated potassium carbonate solution (100 ml)
to liberate the aldehyde. The reaction mixture was then extracted
with ether (4x100 ml) and the combined ether extracts were washed with
water, dried (Na₂SO₄) and evaporated to give the crude pentadienals
(23) which were further purified by column chromatography over silica
gel using EtOAc:hexane (1:20) as eluent.

5,5-Bis(methylthio)-2,4-pentadienal (23a) was obtained as orange viscous
liquid; yield 59%; spectral data described in text. (Found: C, 48.39;
5,5-Bis(methylthio)-4-methyl-2,4-pentadienal (23b) was obtained as an orange viscous liquid; yield 70%; i.r. (neat): \( \nu_{\text{max}} \) 1660, 1590 cm\(^{-1}\); 

\[ ^1H \text{n.m.r. (CCl}_4\): \delta 2.11(s,3H,CH\(_3\)); 2.33(s,3H,SCH\(_3\)); 2.42(s,3H,SCH\(_3\)); 6.11(dd,1H,J=16Hz,8Hz,H\(_2\)); 8.06(d,1H,J=16Hz,H-3); 9.58(d,1H,J=8Hz,CHO). \]

(Found: C, 51.30; H, 6.34. Calc. for C\(_g\)H\(_{12}\)OS\(_2\)(188.3): C, 51.02; H, 6.43%). m/z 188(M\(^+\), 5%); 141(M\(^+\)-47, 100%).

5,5-Bis(methylthio)-4-ethyl-2,4-pentadienal (23c) was obtained as an orange liquid; yield 74%; i.r. (neat): \( \nu_{\text{max}} \) 1710, 1660, 1590 cm\(^{-1}\); 

\[ ^1H \text{n.m.r. (CCl}_4\): \delta 1.18(t,3H,J=7Hz,CH\(_2\)CH\(_3\)); 2.47(s,3H,SCH\(_3\)); 2.58(s,3H,SCH\(_3\)); 2.78(q,2H,J=7Hz,CH\(_2\)CH\(_3\)); 6.23(dd,1H,J=16Hz,7Hz,H-2); 8.12(d,1H,J=16Hz,H-3); 9.71(d,1H,7Hz,CHO). \]

(Found: C, 53.56; H, 6.86. Calc. for C\(_g\)H\(_{14}\)OS\(_2\)(202.3): C, 53.42; H, 6.97%). m/z 202(M\(^+\), 31%); 155(M\(^+\)-47, 100%).

1,5-Carbonyl transpositions of 1,1-bis(methylthio)-2,4-pentadienals 23: Synthesis of Methyl 5-phenyl-2,4-pentadienoates (25a-c); General Procedure:

To a well stirred and cooled solution of phenyl magnesium bromide (0.015 mol) in ether (30 ml), the pentadienal 23 (0.01 mol) in ether (20 ml) was added slowly, the reaction mixture was stirred at room temperature for 1 hr, poured into a saturated ammonium chloride solution (100 ml), extracted with ether (2x50 ml), washed with water, dried (Na\(_2\)SO\(_4\)) and evaporated to give the crude dienol 24, which were used as such for further transformations, without purification.

The crude diene alcohol 24 (0.01 mol) was dissolved in absolute methanol (50 ml) and boron trifluoride etherate (2 ml) was added
with stirring; the mixture was then refluxed for 15-20 hrs. The cooled mixture was added to a saturated solution of sodium bicarbonate (100 ml), extracted with chloroform (2x50 ml), washed with water, dried (Na$_2$SO$_4$) and evaporated to give the crude pentadienoates 25 which were further purified by column chromatography over silica gel using ethyl acetate:hexane (1:20) as eluent.

Methyl 1-phenyl 2,4-pentadienoate (25a) was isolated as colourless crystalline solid; yield 90%; m.p. 70-71°C (reported m.p. 71°C)

Spectral data reported earlier (superimposable i.r. and n.m.r. data). (Found: C, 76.67; H, 6.59. Calc. for C$_{12}$H$_{12}$O$_2$: C, 76.56; H, 6.43%).

Methyl 1-phenyl-2-methyl-2,4-pentadienoate (25b) was isolated as colourless crystalline solid; yield 85%; m.p. 86°C (reported m.p. 86-87°C)

Spectral data reported earlier (superimposable i.r. and n.m.r. spectra). (Found: C, 77.25; H, 6.81. Calc. for C$_{13}$H$_{14}$O$_2$: C, 77.21; H, 6.98%).

Methyl 1-phenyl-2-ethyl-2,4-pentadienoate (25c) was obtained as a pale yellow liquid; yield 87%; i.r.(neat): $\nu_{\text{max}}$ 1720, 1620 cm$^{-1}$; $^1$H n.m.r.(CCl$_4$): $\delta$ 1.09(t, J=7Hz,CH$_2$CH$_3$); 2.45(q, J=7Hz,CH$_2$CH$_3$); 3.68(s, 3H,0CH$_3$); 6.79-7.54(m, 8H arom+olefin). (Found: C, 77.66; H, 7.53. Calc. for C$_{14}$H$_{16}$O$_2$: C, 77.77; 7.46%). m/z 216(93%).

7,7-Bis(methylthio-l-aryl/alkyl(or cycloalkyl)-2,4,6-heptatriene-1-ones 30a-i and 31a-i; General Procedure:

To a well stirred and cooled solution of sodium methoxide (0.54g, 0.01 mol) in methanol (20 ml), a mixture of dienaldehyde 23a or 23b (0.005 mol) and appropriate active methylene ketone 29 (0.005 mol)
in methanol (5 ml) was added dropwise and the mixture was stirred at
room temperature for 6-8 hrs. The solid separated (30a, b, e, f, 31a, e, 
g, h) was filtered, washed with water and recrystallized from methanol
to give pure 30 or 31. In cases where the products were viscous
semisolid (30c, d, g-i, 31b-d, f), the reaction mixture was diluted
with water (50 ml), extracted with chloroform (3x30 ml), washed
with water (2x50 ml), dried (Na$_2$SO$_4$), evaporated and the crude products
thus obtained were column chromatographed over silica gel using ethyl
acetate:hexane (1:20) as eluent to give the pure 30 or 31.

7,7-Bis(methylthio)-1-phenyl-2,4,6-heptatriene-1-one (30a) was obtained
as deep red crystals; yield 95%; m.p. 62°C; spectral data described
in the text. (Found: C, 65.30; H, 5.97. Calc. for C$_{19}$H$_{16}$O$_2$ (276.4):
C, 65.17; H, 5.83%). m/z 276(M$^+$, 10%); 261(M$^+-15$, 16%).

7,7-Bis(methylthio)-1-(4-methylphenyl)-2,4,6-heptatriene-1-one (30b)
was obtained as reddish brown crystalline solid; yield 92%; m.p.
68-70°C; i.r. (KBr): $\nu_{max}$ 1640, 1600, 1575 cm$^{-1}$; $^1$H n.m.r. (CCl$_4$):
2.31(s, 3H, CH$_3$); 2.32(s, 3H, SCH$_2$); 2.33(s, 3H, SCH$_2$); 6.31(d, 1H, J=11Hz,
H$_6$); 6.33(dd, 1H, J=15Hz, 11Hz, H-4); 6.82(d, 1H, J=15Hz, H-2); 7.00-7.91(m,
6H$_{arom+olefin}$). (Found: C, 66.30; H, 6.40. Calc. for C$_{19}$H$_{18}$O$_2$ (290.4):
C, 66.16; H, 6.25%).

7,7-Bis(methylthio)-1-(4-methoxyphenyl)-2,4,6-heptatriene-1-one (30c)
was obtained as reddish brown semisolid; yield 90%; i.r. (neat):
$\nu_{max}$ 1638, 1598 cm$^{-1}$; $^1$H n.m.r. (CCl$_4$): 2.33(s, 3H, SCH$_2$); 2.34(s, 3H,
SCH$_3$); 3.82(s, 3H, OCH$_3$); 6.32(d, 1H, J=11Hz, H$_6$); 6.34(dd, 1H, J=15Hz, 11Hz,
H-4); 6.83(d, 1H, J=15Hz, H-2); 7.00-8.01(m, 6H$_{arom+olefin}$). (Found:
C, 62.80; H, 5.81. Calc. for C$_{19}$H$_{18}$O$_2$S$_2$ (306.4): C, 62.71; H, 5.92%).
7,7-Bis(methylthio)-1-(4-chlorophenyl)-2,4,6-heptatriene-1-one (3pd) was obtained as reddish brown semisolid; yield 94%; i.r.(neat):

\[ \nu_{\text{max}} \text{ cm}^{-1}; {^1}H \text{ n.m.r. (CCl}_4): \delta 2.32(s,6H,SCH}_3); 6.23(d,1H, J=11Hz,H_6); 6.24(dd,1H,J=16Hz,11Hz,H_4); 6.81(d,1H,J=16Hz,1H,H_2);
7.22(dd,1H,J=16Hz,11Hz,H_5); 7.25-7.95(m,5H arom+olefin). (Found: C,57.91; H,5.30. Calc. for C_{15}H_{15}ClO_2S_2(310.8): C,57.77; H,5.17%).

2-[1,1-Bis(methylthio)-1,3-pentadienylidene]-1-tetralone (30e) was obtained as orange crystalline solid; yield 92%; m.p. 102°C; i.r. (KBr): \[ \nu_{\text{max}} \text{ cm}^{-1}; {^1}H \text{ n.m.r. (CCl}_4): \delta 2.32(s,6H,SCH}_3); 2.86(s,4H,CH_2); 6.36(d,1H,J=11Hz,H_2); 6.48(dd,1H,J=15Hz,11Hz,H_4);
7.00-8.21(m,6H arom+olefin). (Found: C,67.61; H,6.09. Calc. for C_{17}H_{18}O_2S_2(302.5): C,67.50; H,6.00%).

2-[1,1-Bis(methylthio)-1,3-pentadienylidene]-6-methoxy-1-tetralone (30d) was isolated as orange crystalline solid; yield 93%; m.p. 136°C; i.r. (KBr): \[ \nu_{\text{max}} \text{ cm}^{-1}; {^1}H \text{ n.m.r. (CCl}_4)(300 MHz): \delta 2.38(s,3H,SCH}_3); 2.39(s,3H,SCH}_3); 2.85-2.95(m,4H,CH_2); 3.82(s,3H,OCH}_3); 6.42(d,1H,J=11Hz,H_2); 6.56(dd,1H,J=15Hz,12Hz,H_4); 6.70-6.87(m, 2H arom); 7.27(dd,1H,J=15Hz,11Hz,H_3); 7.46(d,1H,J=12Hz,1H,H_5); 8.07(d,J=8Hz,1H arom). (Found: C,65.15; H,6.21. Calc. for C_{18}H_{20}O_2S_2(332.5): C,65.02; H,6.06%). m/z 332(H^+,13%); 317(M^+-15,24%).

7,7-Bis(methylthio)-1-(2-thienyl)-2,4,6-heptatriene-1-one (30g) was isolated as reddish brown semisolid; yield 90%; i.r.(neat): \[ \nu_{\text{max}} \text{ cm}^{-1}; {^1}H \text{ n.m.r. (CCl}_4): \delta 2.33(s,6H,SCH}_3); 6.32(d,1H,J=15Hz,H_2);
6.33(dd,1H,J=15Hz,11Hz,H_4); 6.79(d,1H,J=11Hz,H_6); 7.05-7.85(m, 5H thienyl+olefinic). (Found: C,55.35; H,5.21. Calc. for C_{13}H_{14}OS_3(282.4): C,55.28; H,5.00%). m/z 282(M^+,9%); 267(M^+-15,15%).
7,7-Bis(methylthio)-l-(2-furyl)-2,4,6-heptatriene-l-one\((30h)\) was isolated as reddish brown semisolid; yield 94%; i.r.(neat): \(\nu_{\text{max}}\) 1645, 1580 cm\(^{-1}\); \(^1\)H n.m.r.(CCl\(_4\)): \(\delta\) 2.33(s,6H,SCH\(_3\)); 6.31(d,1H,\(J=11\text{Hz},\text{H-2}\)); \(6.32(\text{dd},1\text{H,}J=15\text{Hz,11Hz,}\text{H-4}); 6.79(\text{d,1H,}J=15\text{Hz,}\text{H-6}); 7.03-7.71(\text{m,5Hfuryl+olefinic})\). (Found: C,58.71; H,5.45. Calc. for \(\text{C}_{30}\text{H}_{28}\text{O}_{2}\text{S}_{2}\) (466.4): C,58.71; H,5.45. \(m/z 266(M^+,13%); 251(M^+-15,19%).\)

8,8-Bis(methylthio)-3,5,7-octatriene-2-one \((30i)\) was obtained as reddish brown semisolid; yield 80%; i.r.(neat): \(\nu_{\text{max}}\) 1670, 1595 cm\(^{-1}\); \(^1\)H n.m.r.(CCl\(_4\)): \(\delta\) 2.25(s,3H,CH\(_3\)); 2.32(s,6H,SCH\(_3\)); 5.98-6.49(m,3H,H-3, H-5 and H-7); 6.75-7.40(m,2H,H-4 and H-6). (Found: C,56.23; H,6.66. Calc. for \(\text{C}_{16}\text{H}_{18}\text{O}_{2}\) (214.3): C,56.03; H,6.58%).

7,7-Bis(methylthio)-6-methyl-l-phenyl-2,4,6-heptatriene-l-one \((31a)\) was isolated as reddish brown crystalline solid; yield 90%; m.p. 71°C; i.r.(KBr): \(\nu_{\text{max}}\) 1640, 1590 cm\(^{-1}\); \(^1\)H n.m.r.(CCl\(_4\)): \(\delta\) 2.16(s,3H, CH\(_3\)); 2.27(s,3H,SCH\(_3\)); 2.34(s,3H,SCH\(_3\)); 6.47(dd,1H,\(J=15\text{Hz,11Hz,}\text{H-4}); \(6.96(\text{d,1H,}J=15\text{Hz,}\text{H-2}); 7.33-8.00(\text{m,7H}\text{arom+olefin})\). (Found: C,66.26; H,6.35. Calc. for \(\text{C}_{16}\text{H}_{18}\text{O}_{2}\) (290.4): C,66.16; H,6.24%. \(m/z 290(M^+,5%); 275(M^+-15,17%).\)

7,7-Bis(methylthio)-6-methyl-l-(4-methylphenyl)-2,4,6-heptatriene-l-one \((31b)\) was isolated as reddish brown semisolid; yield 88%; i.r. (neat): \(\nu_{\text{max}}\) 1680, 1650, 1605 cm\(^{-1}\); \(^1\)H n.m.r.(CCl\(_4\)): \(\delta\) 2.15(s,3H, CH\(_3\)); 2.31(s,3H,Ar-CH\(_3\)); 2.41(s,3H,SCH\(_3\)); 2.43(s,3H,SCH\(_3\)); 6.50(dd,1H,\(J=15\text{Hz,}\text{H-4}); \(6.89-7.95(\text{m,7H}\text{arom+olefin})\). (Found: C,67.27; H,6.51. Calc. for \(\text{C}_{17}\text{H}_{20}\text{O}_{2}\) (304.4): C,67.07; H,6.62%).

7,7-Bis(methylthio)-6-methyl-l-(4-methoxyphenyl)-2,4,6-heptatriene-l-one \((31c)\) was isolated as reddish brown semisolid; yield 92%; i.r. (KBr): \(\nu_{\text{max}}\) 1675, 1600 cm\(^{-1}\); \(^1\)H n.m.r.(CCl\(_4\)): \(\delta\) 2.20(s,3H,CH\(_3\)); 2.31
(s,3H,SCH$_3$); 2.38(s,3H,SCH$_3$); 3.85(s,3H,OCH$_3$); 6.56(d,1H,J=15Hz,11Hz,
H-4 ); 6.75-8.01(m,7H$_{arom+olefin}$). (Found: C,63.80; H,6.31. Calc. for
C$_{17}$H$_{20}$O$_2$S$_2$(320.4): C,63.71; H,6.29%). m/z 320(M$^+$,2%); 305(M$^+$-15,4%).

7,7-Bis(methylthio)-6-methyl-1-(4-chlorophenyl)-2,4,6-heptatriene-
1-one (31d) was isolated as reddish brown semisolid; yield 90%; i.r.
(neat): $\nu_{max}$ 1658, 1591 cm$^{-1}$; $^1$H n.m.r.(CCl$_4$): $\delta$ 2.20(s,3H,CH$_3$); 2.31
(s,3H,SCH$_3$); 2.33(s,3H,SCH$_3$); 6.51(dd,1H,J=15Hz,11Hz,H-4); 6.90(d,1H,
for C$_{16}$H$_{17}$ClOS$_2$(324.8): C,59.15; H,5.09%).

2-[1,1-Bis(methylthio)-2-methyl-1,3-pentadienylidene]-1-tetralone(31e)
was isolated as reddish brown crystalline solid; yield 94%; m.p.89-90°C;
i.r.(KBr): $\nu_{max}$ 1647, 1599 cm$^{-1}$; $^1$H n.m.r.(CCl$_4$,300MHz); $\delta$ 2.22(s,3H,
CH$_3$); 2.30(s,3H,SCH$_3$); 2.40(s,3H,SCH$_3$); 2.92-2.93(m,4H,CH$_2$); 6.65(dd,
1H,J=15Hz,12Hz,H-4); 7.25(d,J=7.5Hz,1H$_{arom}$); 7.34(t,J=7.5Hz,1H$_{arom}$);
7.46(t,J=7.5Hz,1H$_{arom}$); 7.56(d,1H,J=12Hz,H$_5$); 7.77(d,1H,J=15Hz,H$_3$);
8.10(d,J=7.5Hz,1H$_{arom}$). (Found: C,68.40; H,6.21. Calc. for C$_{18}$H$_{20}$OS$_2$
(316.5): C,68.31; H,6.37%). m/z 316(M$^+$,5%); 301(M$^+$-15,43%).

2-[1,1-Bis(methylthio)-2-methyl-1,3-pentadienylidene]-6-methoxy-
1-tetralone (31f) was isolated reddish brown semisolid; yield 94%;
i.r.(KBr): $\nu_{max}$ 1640, 1595 cm$^{-1}$; $^1$H n.m.r.(CCl$_4$): $\delta$ 2.18(s,3H,CH$_3$);
2.22(s,3H,SCH$_3$); 2.31(s,3H,SCH$_3$); 2.72-2.89(m,4H,CH$_2$); 6.30-6.81(m,
3H$_{arom+olefin}$); 7.38(d,1H,J=12Hz,H$_5$); 7.65(d,1H,J=15Hz,H$_3$); 7.92
(d,1H,J=7.5Hz,1H$_{arom}$). (Found: C,65.91; H,6.50. Calc. for C$_{19}$H$_{22}$O$_2$S$_2$
(346.5): C,65.86; H,6.40%).

7,7-Bis(Methylthio)-6-methyl-1-(2-thienyl)-2,4,6-heptatriene-1-one(31g)
was isolated as reddish brown crystalline solid; yield 95%; m.p.105-106°C;
i.r. (KBr): $\nu_{\text{max}}$ 1659, 1629, 1569 cm$^{-1}$; $^1$H n.m.r. (CCl$_4$): $\delta$ 2.18 (s, 3H, CH$_3$); 2.29 (s, 3H, SCH$_3$); 2.41 (s, 3H, SCH$_3$); 6.51 (dd, 1H, J=15Hz, H-4); 6.89 (d, 1H, J=15Hz, H-2); 6.91-7.87 (m, 5H, thiényl+olefin). (Found: C, 56.71; H, 5.52. Calc. for C$_{14}$H$_{16}$O$_2$ (296.7): C, 56.67; H, 5.43%). m/z 296 (M$^+$, 4%); 281 (M$^+$-15, 48%).

7,7-Bis(methylthio)-6-methyl-1-(2-furyl)-2,4,6-heptatriene-1-one (31h) was isolated as reddish brown crystalline solid; yield 92%; m.p. 148-149°C; i.r. (KBr): $\nu_{\text{max}}$ 1640, 1590 cm$^{-1}$; $^1$H n.m.r. (CCl$_4$, 300MHz): $\delta$ 2.13 (s, 3H, CH$_3$); 2.30 (s, 3H, SCH$_3$); 2.40 (s, 3H, SCH$_3$); 6.54 (dd, J=15Hz, 11Hz, H-4); 6.94 (d, 1H, J=15Hz, H-2); 7.15 (dd, J=4Hz, 5Hz, 1H$_{\text{furyl}}$); 7.59-7.77 (m, 4H$_{\text{furyl+olefin}}$). (Found: C, 59.81; H, 5.61. Calc. for C$_{14}$H$_{16}$O$_2$ (280.4): C, 59.97; H, 5.75%). m/z 280 (M$^+$, 32%); 265 (M$^+$-15, 98%).

8,8-Bis(methylthio)-7-methyl-3,5,7-octatriene-2-one (31i) was isolated as reddish brown semisolid; yield 85%; i.r. (KBr): $\nu_{\text{max}}$ 1658, 1600, 1580 cm$^{-1}$; $^1$H n.m.r. (CCl$_4$): $\delta$ 2.09 (s, 3H, CH$_3$); 2.11 (s, 3H, CH$_3$); 2.25 (s, 3H, SCH$_3$); 2.35 (s, 3H, SCH$_3$); 6.09 (d, 1H, J=15Hz, H-3); 6.31 (dd, 1H, J=11Hz, 15Hz, H-5); 7.19 (dd, 1H, J=11Hz, 15Hz, H-4); 7.57 (d, 1H, J=15Hz, H-6). (Found: C, 57.90; H, 7.21. Calc. for C$_{14}$H$_{16}$O$_2$ (228.4): C, 57.83; H, 7.06%). m/z 228 (M$^+$, 9%); 213 (M$^+$-15, 29%).

1,7-Carbonyl transposition of 7,7-Bis(methylthio)-1-aryl/cycloalkyl-2,4,6-heptatriene-1-ones 30a-g and 31a-g: General Procedure:

To a well stirred solution of heptatrienone 30 or 31 (0.01 mol) in absolute ethanol (50 ml), excess sodium borohydride (1.2g, 0.035 mol) was added and the reaction mixture was refluxed for 1 hr. The cooled reaction mixture was then poured onto crushed ice (100g) and extracted with chloroform (2x50 ml). The extract was washed with saturated
salt solution (2x50 ml) dried (Na$_2$SO$_4$) and evaporated under vacuum to give the crude heptatrienol 32 or 34 in nearly quantitative yields, which were used as such for the next step without further purification. The crude heptatrienol 32 or 34 (0.01 mol) was dissolved in absolute methanol (50 ml) and boron trifluoride etherate (2 ml) was added with stirring. The reaction mixture was then refluxed for 10-15 hrs. The cooled reaction mixture with chloroform (2x50 ml), washed with water, dried (Na$_2$SO$_4$) and evaporated to give the methyl heptatrienotes 33 or 35 which were further purified by column chromatography using hexane as eluent.

Methyl 1-phenyl-2,4,6-heptatrienoate (33a) was isolated as pale yellow crystalline solid; yield 80%; m.p. 111-112°C (reported m.p. 112°C$^{27}$; (superimposable i.r. and n.m.r. spectra$^{28}$).

Methyl 1-(4-methylphenyl)-2,4,6-heptatrienoate (33b) was isolated as isolated as pale yellow crystalline solid; yield 78%; m.p. 131°C (reported m.p. 131-132°C$^{28}$; superimposable i.r. and n.m.r. spectra$^{28}$).

Methyl 1-(4-methoxyphenyl)-2,4,6-heptatrienoate (33c) was isolated as pale yellow crystalline solid; yield 76%; m.p. 166°C (reported m.p. 167-168°C$^{29}$; superimposable i.r. and n.m.r. spectra$^{28}$).

Methyl 1-(4-chlorophenyl)-2,4,6-heptatrienoate (33d) was isolated as pale yellow crystalline solid; yield 75%; m.p. 152°C; i.r.(KBr):

\[ \gamma_{\text{max}} 1715, 1610 \text{ cm}^{-1}; \text{ } ^1\text{H n.m.r. (CCl}_4\text{): } \delta 3.68(\text{s,3H,OCCH}_3\text{); } 5.80(\text{d, } 1\text{H,J=15Hz,H}^-2\text{); } 6.30-7.40(\text{m,9H arom+olefin}). \text{ (Found: C,67.81; H,5.31. Calc. for C}_{14}\text{H}_{13}\text{ClO}_2 (248.7): C,67.60; H,5.26%}). \]

Methyl 5-(3,4-dihydronaphth-2-yl)-2,4-pentadienoate (33e) was isolated as pale yellow crystalline solid; yield 78%; m.p. 86-87°C; i.r.(KBr):
Methyl 5-(3,4-dihydro-6-methoxynaphth-2-yl)-2,4-pentadienoate (33f) was isolated as pale yellow crystalline solid; yield 76%; m.p. 108-109°C; i.r.(KBr): $\gamma_{\text{max}}$ 1710, 1608 cm$^{-1}$; $^1\text{H n.m.r.}(\text{CCl}_4)$: $\delta$ 2.31-3.12(m,4H,CH$_2$); 3.81(s,3H,0CH$_3$); 5.86(d,1H,J=16Hz,H-2); 6.20-7.60(m,8H$_{\text{arom+olefin}}$). (Found: C,75.75; H,6.61. Calc. for C$_{12}$H$_{12}$O$_3$(220.3): C,75.53; H,6.71%).

Methyl 7-(2-thienyl)-2,4,6-heptatrienoate (33g) was isolated as pale yellow semisolid; yield 70%; i.r.(neat): $\gamma_{\text{max}}$ 1718, 1590 cm$^{-1}$; $^1\text{H n.m.r.}(\text{CCl}_4)$: $\delta$ 3.66(s,3H,0CH$_3$); 5.79(d,1H,J=16Hz,H-2); 6.31-7.50(m,8H$_{\text{thienyl+olefin}}$). (Found: C,65.50; H,5.58. Calc. for C$_{12}$H$_{12}$O$_2$S (220.3): C,65.42; H,5.49%).

Methyl 2-Methyl-7-phenyl-2,4,6-heptatrienoate (35a) was isolated as pale yellow crystalline solid; yield 87%; m.p. 173°C (reported m.p. 174°C$^{30}$; superimposable i.r. and n.m.r. spectra$^{28}$).

Methyl 2-methyl 7-(4-methylphenyl)-2,4,6-heptatrienoate (35b) was isolated as yellow crystalline solid; yield 85%; m.p. 101-102°C (reported m.p. 101-102°C$^{28}$; superimposable i.r. and n.m.r. spectra$^{28}$).

Methyl 2-methyl 7-(4-methoxyphenyl)-2,4,6-heptatrienoate (35c) was isolated as yellow crystalline solid; yield 84%; m.p. 95-96°C (reported m.p. 95-96°C$^{28}$; superimposable i.r. and n.m.r. spectra$^{28}$).

Methyl 2-methyl 7-(4-chlorophenyl)-2,4,6-heptatrienoate (35d) was isolated as pale yellow crystalline solid; yield 82%; m.p. 115-117°C;
Methyl 5-(3,4-dihydronaphth-2-yl)-2-methyl-2,4-pentadienoate (35e)
was isolated as yellow crystalline solid; yield 78%; m.p. 82-84°C;
i.r.(KBr): υ max 1705, 1608 cm⁻¹; ¹H n.m.r.(CCl₄): δ 2.00(s, 3H,CH₃);
2.55(t,2H,J=8Hz,CH₂); 2.89(t,2H,J=8Hz,CH₂); 3.77(s,3H,OC₂H₃);
6.57-7.35(m,8H, arom+olefin). (Found: C,68.61; H,5.91. Calc. for C₁₅H₁₅ClO₂
(262.7): C,68.58; H,5.76%).

Methyl 5-(3,4-dihydro-6-methoxynaphth-2-yl)-2-methyl-2,4-pentadienoate
(35f) was isolated as yellow crystalline solid; yield 76%; m.p. 99-101°C;
i.r.(KBr): υ max 1700, 1605 cm⁻¹; ¹H n.m.r.(CCl₄): δ 2.23-2.84(m,4H,CH₂);
3.60(s,3H,OC₂H₃); 3.64(s,3H,Ar-OC₂H₃); 6.31-7.31(m,7H, arom+olefin).
(Found: C,76.15; H,7.18. Calc. for C₁₈H₂₀O₃(284.3): C,76.04; H,7.09%).

Methyl 2-methyl-7-(2-thienyl)-2,4,6-heptatrienoate (35g) was isolated
as pale yellow semisolid; yield 79%; i.r.(KBr): υ max 1705, 1595 cm⁻¹;
¹H n.m.r.(CCl₄): δ 1.98(s,3H,CH₃); 3.68(s,3H,OC₂H₃); 6.45-7.28(m,
8H, thienyl+olefin). (Found: C,66.78; H,6.21. Calc. for C₁₃H₁₄O₂S
(234.3): C,66.64; H,67.03%).

Alkylative 1,7 carbonyl transposition of 2-[1,1-bis(methylthio)-2-
methyl-1,3-pentadienylidene]-1-tetralone (3Je):
To a well cooled and stirred solution of methyl magnesium iodide
(0.015 mol) in dry ether (30 ml), the bis(methylthio) trienone 3Je
(3.1g, 0.01 mol) in dry ether (20 ml) was added dropwise (5 min) under
nitrogen atmosphere, followed by stirring for 1.5 hrs. The reaction
mixture was poured into a cold saturated solution of ammonium chloride (50 ml), was extracted with ether (3x50 ml), washed with water, dried (Na$_2$SO$_4$) and evaporated to give the crude heptatrienol 36 in nearly quantitative yield. The carbinol 36 (0.01 mol) was dissolved in absolute methanol (50 ml) and boron trifluoride etherate (2 ml) was added with stirring. The reaction mixture was then refluxed for 16 hrs, the cooled reaction mixture was poured into a saturated solution of sodium bicarbonate (100 ml) and extracted with chloroform (2x50 ml). The chloroform extract was washed with water, dried (Na$_2$SO$_4$) and evaporated to give the crude triene ester 37 which was further purified by passing through a silica gel column using hexane as eluent.

Methyl 5-(3,4-dihydro-2-methylnaphth-2-yl)-2-methyl-2,4-pentadienoate (37) was isolated as pale yellow crystalline solid; yield 75%; m.p. 102°C; spectral data described in text. (Found: C,80.61; H,7.71. Calc. for C$_{18}$H$_{20}$O$_2$ (268.3): C,80.56; H,7.51%). m/z 268(M$^+$,100%).

Synthesis of 7,7-Bis(methylthio)-2,4,6-heptatrienal (39a and 39b);

General Procedure:

To a well cooled solution of methyl magnesium iodide (0.015 mol) in dry ether (30 ml), the pentadienal 23 (0.01 mol) in ether (20 ml) was added dropwise under nitrogen atmosphere. After stirring for 1.5 hrs the reaction mixture was poured into cold saturated solution of ammonium chloride (100 ml) and was extracted with ether (2x50 ml). The ether extract was washed with water (2x50 ml) dried (Na$_2$SO$_4$) and evaporated to give crude hexadienol 38 which was used as such for the subsequent Vilsmeier formylation.

The hexadienol 38 (0.01 mol) in 5 ml of DMF was added slowly to a well cooled (0°C) and stirred Vilsmeier reagent (0.025 mol prepared as
described earlier). The reaction mixture was stirred for 10-15 hrs for completion of reaction, after which it was poured into crushed ice (300g) and a cold saturated potassium carbonate solution (100 ml) was added slowly to liberate the trienal. The reaction mixture was then extracted with ether (5x50 ml), the combined ether layer was washed with water dried (Na\textsubscript{2}SO\textsubscript{4}) and evaporated to give the crude heptatrienals \textit{39} which were further purified by column chromatography over silica gel using ethyl acetate:hexane (1:20) as eluent.

\textit{7,7-Bis(methylthio)-2,4,6-heptatrienal} (39a) was obtained as orange viscous liquid; yield 56%; spectral data described in text. (Found: C, 54.01; H, 6.15. Calc. for C\textsubscript{9}H\textsubscript{12}O\textsubscript{2}(200.3): C, 53.96; H, 6.04%).

\textit{7,7-Bis(methylthio)-6-methyl-2,4,6-heptatrienal} (39b) was isolated as orange viscous liquid; yield 80%; i.r. (neat): \(\nu\)\textsubscript{\text{max}} 1670, 1600 cm\textsuperscript{-1}; ^{1}H n.m.r. (CCl\textsubscript{4}): \(\delta\) 2.14(s, 3H, CH\textsubscript{3}); 2.23(s, 3H, SCH\textsubscript{2}); 2.37(s, 3H, SCH\textsubscript{3}); 6.10(dd, 1H, J=16Hz, 8Hz, H-2); 6.41(dd, 1H, J=16Hz, 12Hz, H-4); 7.06(dd, 1H, J=16Hz, 12Hz, H-3); 7.62(d, 1H, J=16Hz, H-5); 9.52(d, 1H, J=8Hz, CHO). (Found: C, 56.21; H, 6.61. Calc. for C\textsubscript{10}H\textsubscript{14}O\textsubscript{2}(214,3): C, 56.04; H, 6.58%). m/z 214(M\textsuperscript{+}, 12%); 192(M\textsuperscript{+}-15, 39%).

Alkylative 1,7-carbonyl transposition of \textit{7,7-bis(methylthio)-2,4,6-heptatrienals} (39a and 39b); General Procedure:

To a well cooled solution of phenyl magnesium bromide (0.01 mol) in dry ether (30 ml), the heptatrienal 39 in ether (20 ml) was added dropwise (5 min) under a nitrogen atmosphere. After stirring for 2 hrs, the reaction mixture was poured into a cold saturated solution of ammonium chloride (50 ml), and extracted with ether (3x50 ml). The ether extract was washed with water (3x50 ml) dried and evaporated to give the crude heptatrienol 32a or 34a in nearly quantitative
yields. The heptatrienol 32a or 34a (0.01 mol) was dissolved in absolute methanol (100 ml) and boron trifluoride etherate (2 ml) was added with stirring and the reaction mixture was refluxed for 15-17 hrs. The cooled reaction mixture was poured into a saturated solution of sodium bicarbonate (50 ml) and extracted with chloroform, the extract was washed with water, and dried (Na₂SO₄) and evaporated to give crude heptatrienoates 33a or 35a which were further purified by column chromatography over silica gel using ethyl acetate:hexane (1:20) as eluent.

Methyl 7-phenyl-2,4,6-heptatrienoate (33a) was isolated as a pale yellow crystalline solid; yield 80%; m.p. 111-113°C (reported m.p. 112°C; m.m.p. superimposable i.r. and n.m.r. spectra).

Methyl 2-methyl-7-phenyl-2,4,6-heptatrienoate (35a) was isolated as a pale yellow crystalline solid; yield 75%; m.p. 107-108°C (reported m.p. 107-108°C; m.m.p. superimposable i.r. and n.m.r. spectra).

Synthesis of 9,9-Bis(methylthio)-1-aryl/cycloalkyl-2,4,6,8-nonatetraene-1-ones (40a-d); General Procedure:
To a well stirred and cooled solution of sodium methoxide (0.54g, 0.01 mol) in methanol (20 ml), a mixture trienaldehyde 39 (0.005 mol) and active methylene ketone 29 (0.005 mol) in methanol (5 ml) was added dropwise and the reaction mixture was stirred at room temperature for 6-8 hrs. The solid separated (40c,d) was filtered washed with water and recrystallized from methanol to give pure 40. In the cases were the products were liquid (40a,b), the reaction mixture was diluted with water (50 ml), extracted with chloroform (3x30 ml) washed with water, dried (Na₂SO₄), evaporated and the crude products thus obtained were column chromatographed over silica gel using ethyl acetate:hexane (1:20) as eluent to give pure 40.
9,9-Bis(Methylthio)-1-phenyl-2,4,6,8-nonatetraene-1-one (40a) was obtained as reddish brown semisolid; yield 92%; spectral data described in text. (Found: C, 67.60; H, 6.21. Calc. for C_{17}H_{18}O_{S_{2}} (302.4): C, 67.51; H, 6.00%).

9,9-Bis(methylthio)-8-methyl-1-phenyl-2,4,6,8-nonatetraene-1-one (40b) was isolated as reddish brown semisolid; yield 70%; i.r. (neat): ν_{max} 1658, 1590 cm^{-1}; \^1H n.m.r. (CCl₄): δ 2.10 (s, 3H, CH₃); 2.21 (s, 3H, SCH₂); 2.35 (s, 3H, SCH₂); 6.22-8.18 (m, 11H arom+olefin). (Found: C, 68.51; H, 6.44. Calc. for C_{18}H_{20}O_{S_{2}} (316.4): C, 68.32; H, 6.37%).

9,9-Bis(methylthio)-8-methyl-1-(4-chlorophenyl)-2,4,6,8-nonatetraene-1-one (40c) was isolated as reddish brown crystalline solid; yield 75%; m.p. 120-123°C; i.r. (KBr): ν_{max} 1642, 1602 cm^{-1}; \^1H n.m.r. (CCl₄, 300 MHz): δ 2.17 (s, 3H, CH₂); 2.29 (s, 3H, SCH₂); 2.38 (s, 3H, SCH₂); 6.45 (dd, 1H, J=15Hz, 11Hz, H-6); 6.52 (dd, 1H, J=15Hz, 11Hz, H-4); 6.84 (dd, 1H, J=15Hz, 11Hz, H-5); 6.93 (d, 1H, J=15Hz, H-2); 7.42-7.56 (m, 4H arom+olefin); 7.87-7.90 (m, 2H arom). (Found: C, 61.82; H, 5.66. Calc. for C_{19}H_{19}ClO_{S_{2}} (350.8): C, 61.62; H, 5.46%). m/z 350 (M^+, 24%); 351 (5%).

2-[1,1-Bis(methylthio)-1,3,5-heptatrienylidene]-6-methoxy-1-tetralone (40d) was isolated as reddish brown crystalline solid; yield 78%; m.p. 114-115°C; i.r. (KBr): ν_{max} 1647, 1602 cm^{-1}; \^1H n.m.r. (CDCl₃, 300 MHz): δ 2.17 (s, 3H, CH₂); 2.29 (s, 3H, SCH₂); 2.38 (s, 3H, SCH₂); 2.93 (s, 4H, CH₂); 3.86 (s, 3H, OCH₂); 6.49 (dd, 1H, J=15Hz, 11Hz, H-4); 6.61-6.87 (m, 4H arom+olefin); 7.43 (d, 1H, J=15Hz, H-7); 7.47 (d, 1H, J=12Hz, H-3); 8.07 (d, 1H, J=8Hz, aromatic). (Found: C, 67.75; H, 6.51. Calc. for C_{21}H_{24}O_{S_{2}} (372.5): C, 67.70; H, 6.49%). m/z 372 (M^+, 49%).
1,9 Carbonyl transposition of 9,9-bis(methylthio)-1-aryl/cycloalkyl-2,4,6,8-nonatetraene-1-ones (40a-d); General Procedure:

To a well stirred solution of the tetraenone 40 (0.01 mol) in absolute ethanol (50 ml), excess sodium borohydride [1.2g (0.035 mol)] was added slowly and the reaction mixture was refluxed for 1.5 hrs. It was then cooled, poured into crushed ice (100g) and extracted with chloroform (3x50 ml). The chloroform extract was washed with saturated sodium chloride solution (2x50 ml) dried (Na$_2$SO$_4$) and evaporated to give the crude tetraene carbinol 41 in nearly quantitative yields, which were used as such without further purification for the next step. The tetraenol 41 (0.01 mol) was dissolved in absolute methanol (50 ml) and boron trifluoride etherate (2 ml) was added with stirring, the reaction mixture was refluxed for 18-20 hrs and cooled reaction mixture was poured into saturated sodium bicarbonate solution (100 ml), washed with water dried and evaporated to give the crude tetraene esters 42 which were further purified by column chromatography over silica gel using ethyl acetate:hexane (1:20) as eluent.

Methyl 9-phenyl-2,4,6,8-nonatetraenoate (42a) was isolated as yellow crystalline solid; yield 70%; m.p. 151-153°C; spectral data described in text. (Found: C,80.11; H,6.91. Calc. for C$_{16}$H$_{16}$O$_2$(240.3): C,79.97; H,6.71%).

Methyl 2-methyl-9-phenyl-2,4,6,8-nonatetraenoate (42b) was isolated as isolated as yellow crystalline solid; yield 75%; m.p. 103-104°C; i.r.(KBr): $\nu_{max}$ 1695, 1598 cm$^{-1}$; $^1$H n.m.r.(CCl$_4$): $\delta$ 1.95(s,3H,CH$_3$); 3.69(s,3H,0CH$_3$); 6.25-7.48(m,12H); 6.25-7.48(m,12H$_{arom\,olefin}$). (Found: C,80.40; H,7.25. Calc. for C$_{17}$H$_{16}$O$_2$(254.3): C,80.28; H,7.13%).
Methyl 2-nitro-9-(4-chlorophenyl)-2,4,6,8-nonatetraenoate (42c) was isolated as yellow crystalline solid; yield 70%; m.p. 150°C; i.r.(KBr): 
\[ \gamma_{\text{max}} 1705, 1608 \text{ cm}^{-1} \]; \(^1\text{H n.m.r.(CDCl}_3,300 \text{ MHz)}: 1.98(\text{s,3H},\text{CH}_3); 3.76(\text{s,3H,OC}_3); 6.41-6.86(\text{m,6H},\text{olefin}); 7.24-7.34(\text{m,5H},\text{arom+olefin}).
\)
(Found: C,70.75; H,6.01. Calc. for C\(_{17}\)H\(_{17}\)ClO\(_2\): C,70.69; H,5.93%). m/z 288(M\(^+\),100%).

Methyl 2-methyl-7-[3,4-dihydro-6-methoxynaphth-2-yl]-2,4,6-heptatrienoate (42d) was isolated as yellow crystalline solid; yield 80%; m.p.139-140°C; i.r. (KBr): 
\[ \gamma_{\text{max}} 1700, 1608 \text{ cm}^{-1} \]; \(^1\text{H n.m.r.(CDCl}_2,300 \text{ MHz): 1.97(}\text{s,3H,CH}_3); 2.48(\text{t,2H,J=8.5Hz},\text{CH}_2): 2.85(\text{t,2H,8.5Hz},\text{CH}_2); 3.76(\text{s,3H,OC}_3); 3.79(\text{s,3H,OC}_3); 6.41-6.70(\text{m,7H},\text{arom+olefin}); 7.01(\text{d,J=9Hz},\text{1H},\text{arom}); 7.27(\text{d,10Hz},\text{1H},\text{arom}).
\)
(Found: C,77.591; H,7.29. Calc. for C\(_{20}\)H\(_{22}\)O\(_3\): C,77.38; H,7.14%). m/z 310(M\(^+\),100%).

9,9-Bis(methylthio)-8-methyl-2,4,6,8-nonatetraenal (44) (a) from Bis(methylthio)-7-methyl-3,5,7-octatriene-2-one (31i):
To a well stirred solution of trienone 31i (2.28g, 0.01 mol), excess sodium borohydride (1.25g, 0.035 mol) was added and the reaction mixture was refluxed for 1 hr. The cooled mixture was then poured into crushed ice (100g) and extracted with chloroform (2x150 ml). The chloroform extract is washed with saturated salt solution (2x100 ml) dried with sodium sulphate and evaporated under vacuum to give the crude octatrienol 43 in nearly quantitative yield.

To a well cooled (0°C) and stirred Vismeyer reagent (0.025 mol, prepared as described earlier), the triene alcohol 43 was added slowly (10 min) and the reaction mixture was stirred at 0-10°C for 16 hrs, after which it was poured into crushed ice (300g) and the tetraenaldehyde
was liberated by a slow addition cold saturated potassium carbonate solution (100 ml). It was then extracted with ether (4x100 ml) and the combined ether layer was washed with water (4x50 ml), dried (Na₂SO₄), evaporated and column chromatographed over silica gel using ethylacetate:hexane (1:20) as eluent to give pure tetraenealdehyde 44.

9,9-Bis(methylthio)-8-methyl-2,4,6,8-nonatetraenal 44 was obtained as reddish brown liquid; yield 70%; spectral data described in text. (Found: C, 60.01; H, 6.80. Calc. for C₁₂₂₆₂₈O₅₅ (240.4): C, 59.96; H, 6.71%), m/z 240(M⁺, 100%).

(b) Synthesis of 44 from 7,7-bis(methylthio)-6-methyl-2,4,6-heptatrenal (39b): To a well stirred and cooled solution of methyl magnesium iodide (0.015 mol) in dry ether, a solution of the heptatrienal 39b in 20 ml dry ether was added dropwise and the reaction mixture was stirred for 1.5 hrs. It was then poured over saturated ammonium chloride solution (100 ml) and extracted with ether (3x50 ml). The combined organic layer was washed with water, dried (Na₂SO₄) and evaporated to give the octatrienol 43 in nearly quantitative yield. The crude triene alcohol 43 was subjected to Vilsmeier formylation as described above to give after work-up and column chromatography, the 9,9-bis(methylthio)-8-methyl-2,4,6,8-nonatetraenal 44 in 80% yield (superimposable i.r. and n.m.r. spectra).

Alkylative 1,9 carbonyl transposition of 9,9-bis(methylthio)-8-methyl-2,4,6,8-nonatetraenal 44:
To a well stirred and cooled solution of phenylmagnesium bromide in dry ether (40 ml), the tetraenaldehyde 44 (2.4g, 0.01 mol) in dry ether (20 ml) was added slowly and the reaction mixture was stirred
for 2 hrs. It was then poured over saturated ammonium chloride solution (100 ml) and extracted with ether (5x50 ml). The combined organic layer was washed with water and evaporated to give the crude tetraenol 41b in nearly quantitative yield. The tetraenol 41b was dissolved in methanol and boron trifluoride etherate (2 ml) was added with cooling and stirring. The reaction mixture was then refluxed for 16 hrs, cooled and poured into saturated sodium bicarbonate solution. It was then extracted with chloroform (3x50 ml) and the combined organic layer was washed with water, dried (Na$_2$SO$_4$), evaporated and purified by column chromatography over silica gel using ethyl acetate:hexane (1:20) as eluents to give methy 2-methyl-9-phenyl-2,4,6,8-nonatetraenoate 42b in 70% yield; (m.m.p. superimposable i.r. and n.m.r. spectra).

Synthesis of 11,11-Bis(methylthio)-1-aryl/cycloalkyl-1-methyl-2,4,6,8,10-undecapentaene-1-ones (45a-b); General Procedure:

To a well cooled and stirred solution of sodium methoxide (0.54g, 0.01 mol) in methanol (30 ml) a mixture of the tetraenaldehyde 44 (0.005 mol) and the active methylene ketone 26 (0.005 mol) as added dropwise. The reaction mixture was further stirred for 8 hrs, diluted with water (50 ml), extracted with chloroform (2x50 ml) and the combined organic layer was washed with water, dried (Na$_2$SO$_4$) and evaporated to give the crude nonapentaenone 45 which were further purified by column chromatography over silica gel using ethylacetate:hexane (1:20) as eluent to give the pure 45.

11,11-Bis(methylthio)-1-methyl-1-phenyl-2,4,6,8,10-undecapentaene-1-one (45a) was isolated as deep red semisolid; yield 90%; spectral
data described in the text. (Found: C, 70.25; H, 5.91. Calc. for C_{20}H_{22}OS_2 (342.5): C, 70.13; H, 5.89%).

2-[1,1-Bis(methylthio)-2-methyl-1,3,5,7-nonatetraenyldene]-6-methoxy 1-tetralone (45b) was isolated as deep red semisolid; yield 95%;
i.r. (neat): \( \nu_{\text{max}} \) 1650, 1610 cm\(^{-1}\); \(^1\)H n.m.r. (CCl\(_4\)): 6 1.96 (s, 3H, CH\(_3\)); 2.10 (s, 3H, \text{SCH}_3\)); 2.23 (s, 3H, \text{SCH}_2\)); 2.73 (s, 4H, \text{CH}_2\)); 3.66 (s, 3H, O\text{CH}_3\)); 6.10-7.50 (m, 9H, \text{arom+olefin}); 7.93 (d, \text{J}=8Hz, 1H, \text{arom}). (Found: C, 72.31; H, 6.90. Calc. for C\(_{25}\)H\(_{26}\)OS\(_2\) (382.6): C, 72.20; H, 6.85%).

1,11 Carbonyl transposition of 11,11-Bis(methylthio)-1-aryl/cycloalkyl-10-undecapentaene-1-ones (45a-b); General Procedure:
To a well stirred solution of the pentaenone 45 (0.01 mol) in absolute ethanol (50 ml) excess sodium borohydride (1.25 g, 0.035 mol) was added and the reaction mixture was refluxed for 2 hrs. It was then cooled and poured into crushed ice (100 g) and extracted with chloroform (3x50 ml). The combined organic layer was washed with water, dried (Na\(_2\)SO\(_4\)) and evaporated to give the crude pentaene alcohols 46 in nearly quantitative yields which were used as such, without further purification for the next step.

The crude pentaene alcohol 46 was dissolved in absolute methanol and boron trifluoride etherate (2 ml) was added with cooling and stirring. The reaction mixture was then refluxed for 16 hrs, cooled, and poured into saturated sodium bicarbonate solution (100 ml), extracted with chloroform (3x50 ml), washed with water (2x50 ml), dried (Na\(_2\)SO\(_4\)) and evaporated to give the pentaene ester 47 which were further purified by column chromatography over silica gel using ethylacetate: hexane (1:20) as eluent.
Methyl 2-methyl-11-phenyl-2,4,6,8,10-undecapentaenoate (47a) was isolated as yellow crystalline solid; yield 85%; m.p. 142-143°C; spectral data described in text. (Found: C, 81.41; H, 7.20. Calc. for C_{19}H_{20}O_2 (280.4): C, 81.39; H, 7.19%).

Methyl-2-methyl-[3,4-dihydro-6-methoxynaphth-2-y1]-2,4,6,8-nonatetraenoate (47b) was isolated as yellow crystalline solid; yield 80%; m.p. 149-151°C; i.r. (KBr): \( \nu_{max} \) 1705, 1600 cm\(^{-1}\); \(^1\)H n.m.r. (CCl\(_4\)): \( \delta \) 1.83 (s, 3H, CH\(_3\)); 2.20-2.80 (m, 4H, CH\(_2\)); 3.61 (s, 3H, OCH\(_3\)); 6.34 (s, 3H, OCH\(_3\)); 6.15-7.35 (m, 11H, arom+olefin). (Found: C, 78.66; H, 7.33. Calc. for C\(_{22}\)H\(_{24}\)O\(_3\) (336.4): C, 78.54; H, 7.19%).
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3. For a review see V.V. Kane, V. Singh, A. Martin and D.L. Doyle, Tetrahedron 39, 345 (1983).

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