A new 1,5- to 1,11-carbonyl transposition protocol involving ketene dithioacetal chemistry: an efficient polyene synthesis

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An efficient strategy for alternative 1,5-, 1,7-, 1,9- and 1,11- carbonyl transposition has been developed via 1,2-reductive or alkylative addition to 5,5-bis(methylthio)-2,4-pentadienals 3a-b, 7,7-bis(methylthio)-2,4,6-heptatrienones 5, 9,9-bis(methylthio)-2,4,6,8-nonatetraenones 8 and 11,11-bis(methylthio)-2,4,6,8,10-undecapentaenones 11 followed by BF3.Et2O induced methanolysis of the resulting carbinols to the corresponding polyene esters. The synthesis of the novel polyene aldehydes 3a-b, 7a-b, 10b and polyenones 5, 8, 11 precursors has also been described following iterative Vielsmeier-Haack reaction and aldol condensation.

The term carbonyl transposition1,2 is generally defined to mean the effective movement of the carbonyl functionality from one position to another within the same carbon framework. Theoretically it is possible to move a carbonyl functionality from one carbon to another carbon either in an acyclic or cyclic product via appropriate reagents or by the appropriate design of the substrate or the combination of both. The 1,2-carbonyl transposition protocol has been by far the largest group of reactions described in the literature2. The 1,3-carbonyl transposition in α,β-unsaturated ketones, β-alkylthioenones and α-oxoketene dithioacetals3 have also been examined extensively in recent years. However, only limited number of 1,4-carbonyl transposition reactions were found in the literature while 1,5- and 1,6-carbonyl transpositions are confined only to the intramolecular hydride shift1. Recently 1,7-carbonyl transposition has been reported in the literature which involves the conversion of 3,4-dehydro-β-ionone to megastigma-4,6,8-triene-1-one through a series of 2,3-sigmatropic rearrangements of the intermediate allylic sulfoxide4. Duhumel and coworkers5 have also reported the reaction of functionalized silyloxy and alkoxypolyenyl lithium and other organometallic reagents with aldehydes and ketones followed by hydrolysis to yield the corresponding polyenals. These examples clearly demonstrate the synthetic usefulness of 1,5- and 1,7-carbonyl transpositions. Apparently, there has been no example beyond 1,7-carbonyl transposition in the literature. Thuillier and coworkers6 and also Dieter and coworkers7 have studied the transformation of carbinol dithioacetals in the presence of sulphuric acid6 and HgO/AcOH in HBF4 to afford the corresponding thiol esters which can be considered as examples of 1,3-carbonyl transpositions. We have reported in our earlier publications8,9a-d that the carbinol thioacetals obtained by the 1,2-addition of sodium borohydride or alkyl Grignard reagents to α-oxoketene dithioacetals undergo BF3.Et2O assisted methanolysis to yield the corresponding ene- esters 2c-d in high yields (Scheme I). The overall transformation can be recognized as the homologation of the active methylene ketones at the α-position involving 1,3-carbonyl transposition. The formation of α,β-unsaturated methyl esters from active methylene ketones via α-oxoketene dithioacetals has emerged as a new general method for the synthesis of cinnamonates, α-substituted cinnamates and the corresponding crotonates9e. Subsequently in our preliminary communication11 we have reported 1,5- to 1,11-carbonyl transposition via bis(methylthio)polyenals and their enones and we now describe these results in detail in the present paper.

Synthesis of 2,4-pentadienals 3a-b

Our strategy to 1,5-, 1,7-, 1,9- and 1,11-carbonyl group transposition involves the synthesis of the appropriate bis(methylthio)enals 3a-b (Scheme I), 7a-b (Scheme III), 10b (Scheme V) and the
**Scheme I**

1-3a, $R = H$

b, $R = CH_3$

2c, $R = H$

d, $R = Me$

**Scheme II**

<table>
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<tr>
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<th>$R_1$</th>
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<tr>
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<td>$C_2H_5$</td>
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</tr>
<tr>
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<td>H</td>
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<td>c</td>
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<td>d</td>
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</tr>
<tr>
<td>e</td>
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<td>i</td>
<td>Me</td>
<td>H</td>
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**Scheme III**

3, 6, 7a, $R = H$

b, $R = Me$

7a (56%)

b (80%)

**Scheme IV**

8a, $R = H$, $R_1 = C_6H_5$, $R_2 = H$

ab, $R = Me$, $R_1 = C_6H_5$, $R_2 = H$

db, $R = Me$, $R_1 = ClC_6H_4$, $R_2 = H$

hb, $R = Me$, $R_1 = ClC_6H_4$, $R_2 = H$
corresponding enones 5 (Scheme II), 8 (Scheme IV) and 11 (Scheme V). We first describe the synthesis of these enals and enones from the basic three carbon active methylene ketones as described in the Schemes 1-5. Thus the 5,5-bis(methylthio)-2,4-pentadienal 3a and 5,5-bis(methylthio)-4-methyl-2,4-pentadienal 3b (Scheme I) were prepared starting from ketene dithioacetals 1a-b 11,12 (Scheme VII) derived from acetone and ethyl methyl ketone respectively. These ketene dithioacetals 1a-b were subjected to sodium borohydride reduction in ethanol to afford the corresponding carbinol thioacetals 2a-b in nearly quantitative yields. The transformation of 2a to methyl crotonate 2c under BF₃·Et₂O assisted methanolsy has been reported in our earlier papers 8a-d. The carbinol acetals 2a and 2b were subjected to Vilsmeier-Haack reaction (POCl₃/DMF) 13a-b to afford the corresponding dienealdehydes 3a and 3b in 70% and 74% yields respectively. On the basis of their ¹H NMR data, the dienealdehydes were assigned 2E geometry. These intermediates 3a-b are not only the candidates for 1,5-carbonyl transposition but also
used as a precursors for the synthesis of the corresponding 7,7-bis(methylthio)-2,4,6-heptatrienones \(5\) and heptatrienals \(7a-b\) (Schemes II-III). Thus \(3a\) was condensed with acetophenone in the presence of sodium methoxide in methanol to afford the corresponding 7,7-bis(methylthio)-1-phenyl-2,4,6-triene-1-one \(5aa\) in 95% yield. The dienealdehyde \(3b\) was similarly condensed with acetophenone under the identical conditions to afford the corresponding 7,7-bis(methylthio)-1-phenyl-6-methyl-2,4,6-trien-1-one \(5ab\) in 90% yield (Scheme 2). On the basis of their \(^1\)H NMR spectral data, the \(2E,4E\) configuration was assigned for both the compounds. The other 7,7-bis(methylthio)-2,4,6-trien-1-ones \(5\) and the corresponding 6-methyl analogs (Scheme II) were similarly obtained by condensing \(3a\) and \(3b\) with various active methylene ketones under identical reaction conditions (Scheme II).

**Synthesis of 2,4,6-heptatrienals 7a-b (precursors for 1,7- and 1,9-carbonyl transposition)**

The dienealdehyde \(3a\) was reacted with methylmagnesium iodide to afford the carbinal thioacetal \(6a\) in nearly quantitative yield, which was then subjected to Vilsmeier-Haack (POCl\(_3\)/DMF) reaction to give the corresponding 7,7-bis(methylthio)-2,4,6-heptatrienal \(7a\) in 56% yield (Scheme III). Similarly the corresponding 6-methyl-2,4,6-heptatrienal \(7b\) was obtained from \(3b\) under identical conditions in 80% yield. From their \(^1\)H NMR data, both \(7a-b\) were assigned the \(2E,4E\) configuration. These aldehydes apart from being precursors for the 1,7-carbonyl transposition, they are also starting materials for the synthesis of nonatetraenones \(8\) (Scheme IV). Thus \(7a\) was condensed with acetophenone in the presence of sodium methoxide in methanol to afford the corresponding 9,9-bis(methylthio)-2,4,6,8-nonatetraenal \(8aa\) in 92% yield. Similarly the other nonatetraenones \(8ab-8hb\) were obtained under the described reaction conditions in 70-78% overall yields (Scheme IV). The stereochemical assignment for these tetaenones were in conformity with the \(2E,4E,6E\) configuration on the basis of their \(^1\)H NMR data. These tetaenones were few selected candidates for the 1,9-carbonyl transposition in our subsequent studies (Scheme IX).

**Synthesis of 2,4,6,8-nonatetraenals 10b (precursors for 1,11-carbonyl transposition) (Scheme V)**

The 9,9-bis(methylthio)-8-methyl-2,4,6,8-nonatetraenal \(10b\) was the sole polynenealdehyde prepared for our 1,11-carbonyl transposition study. It was possible to prepare \(10b\) from both trienone \(5ib\) (Scheme II) or tetraenaldehyde \(7b\) (Scheme V). Thus the enone \(5ib\) was reduced with NaBH\(_4\) to give the carbinal thioacetal \(9b\) in nearly quantitative yield which was also prepared in identical yield by adding methylmagnesium iodide to \(7b\). The carbinal thioacetal \(9b\) was subjected to Vilsmeier-Haack reaction to afford the corresponding 9,9-bis(methylthio)-8-methyl-2,4,6,8-nonatetraenal \(10b\) in 70% yield which was assigned \(2E,4E,6E\) configuration on the basis of \(^1\)H NMR data (Scheme V). The aldehyde \(10b\) is our precursor for 1,9-carbonyl transposition as well as for synthesizing higher homologues \(2,4,6,8,10\)-undecapenten-1-ones \(11\) for 1,11-carbonyl transposition. Thus \(10b\) was condensed with acetophenone in the presence of methanolic NaOH to afford the corresponding 11,11-bis(methylthio)-1-phenyl-2,4,6,8,10-undecapenten-1-one (11ab) in 90% yield. Similarly the pentaeneone 11hb was prepared in 95% yield by condensing \(10b\) with 6-methoxytetralone under identical conditions. These pentaenones \(11\) are our precursors for 1,11-carbonyl transposition and we have tentatively assigned \(2E,4E,6E,8E\) geometry for the double bonds in these compounds on the basis of preceding examples. We have thus synthesized appropriate polynene precursors bearing a carbonyl and bis(methylthio) functionality at the two terminal end of a conjugated polynene which are suitable precursors for our 1,5-, 1,7-, 1,9- and 1,11-carbonyl transposition studies.

**1,5-Carbonyl transposition from 5,5-bis(methylthio)-2,4-pentadienals (3a-b) (Scheme VI)**

Although in principle, one can choose a large number of organometallic reagents which can be reacted with dieneldehydes \(3a\) and \(3b\) (Scheme 6), we have treated them only with phenylmagnesium bromide to highlight the 1,5-carbonyl transposition protocol. Thus both \(3a\) and \(3b\) underwent a facile 1,2-addition with \(\text{C}_6\text{H}_5\text{MgBr}\) to afford the corresponding carbinal thioacetals 12a and 12b (Scheme 6) in nearly quantitative yields. These carbinals without further purification were directly treated with BF\(_3\)Et\(_2\)O in refluxing methanol to afford the corresponding dieneesters 13a and 13b in 90% and 85% yields respectively. Both 13a and 13b were earlier reported in the literature\(^{10}\) and their mp, mmp, IR and \(^1\)H NMR spectra were found to be identical with the reported data. On the basis of \(^1\)H NMR data \(2E,4E\)
configuration was assigned to both dieneesters 13a and 13b.

1,7-Carbonyl transposition from 7,7-bis(methylthio)-2,4,6-heptatriene-1-ones (Scheme VII)

The newly prepared trienones 5 were reduced with sodium borohydride to afford the carbinol thioacetals 14 in nearly quantitative yields (Scheme VII). These carbinol thioacetals without further purification were subjected to BF₃·Et₂O assisted methanolysis to afford the corresponding tetraeneesters 15 in 80-90% overall yields. However, the carbinol acetal 14fa and 14tb from furyl ketone failed to yield the corresponding ene esters and only intractable product mixtures were obtained.

1,7-Carbonyl Transposition from 7,7-bis(methylthio)-2,4,6-heptatrienals 7a-b (Scheme VIII)

The heptatrienal 7a was similarly reacted with CsH₅MgBr to afford the corresponding carbinol thioacetal 14aa in quantitative yield (Scheme VIII), which was subjected to BF₃·Et₂O assisted methanolysis as described earlier to afford the corresponding trienoate 15aa in 80% yield. The compound 15aa was fully characterized and found to be identical with that reported in the literature with 2E,4E,6E double bond configuration. The trieneester 15ab was similarly prepared in 87% yield starting from 7b which was found to be identical with that reported in the literature.

1,9-Carbonyl transposition from 9,9-bis(methylthio)-2,4,6,8-nonatetraenones 8 (Scheme IX)

The bis(methylthio)tetraenones 8 were examined for 1,9-carbonyl transposition protocol. Thus 8aa was reduced with sodium borohydride to afford the corresponding carbinol thioacetal 16aa in quantitative yield which was subjected to BF₃·Et₂O assisted methanolysis as described earlier to afford the corresponding tetraenoate 17aa in 70% yield (Scheme IX). On the basis of the earlier trends and ¹H NMR data 2E,4E,6E,8E configuration was assigned for the double bonds in 17aa. The other tetraenoates 17 (Scheme IX) were similarly prepared in 70-80% overall yields and were assigned E configuration around all four double bonds. The carbinol 16ab could also be obtained by addition of phenyl Grignard reagent to tetraenal 10b (Scheme IX).

1,11-Carbonyl transposition from 11,11-bis(methylthio)-2,4,6,8,10-undecapenten-1-ones 11 (Scheme X)

We have selected only two examples of undecapentaenones (11ab, 11hb) to demonstrate the 1,11-carbonyl transposition protocol. Thus enone 11ab was reduced with NaBH₄ as described before to afford the carbinol thioacetal 18ab in quantitative yield which was in situ subjected to BF₃·Et₂O assisted methanolysis as described earlier to afford the
1,11- Carbonyl Transposition

![Scheme X](image)

corresponding methyl undecapentaenoate 19ab in 85% yield. The analytical and spectral data of 19ab are in full agreement with the structure and we have assigned tentatively 2E,4E,6E,8E,10E configuration for all double bonds in line with 1H NMR spectral data for lower homologues. The pentaenoate 20hb was similarly prepared as described in Scheme X in 80% yield which was tentatively assigned all trans configuration. In conclusion we have clearly demonstrated the versatile chemistry of α-oxoketene dithioacetals as basic precursors for 1,5- to 1,11-carbonyl transpositions which we hope, will provide a convenient synthetic route for polyene esters starting from simple carbonyl compounds.

Experimental Section

Melting points were determined on Thomas Hoover apparatus (capillary method) and are uncorrected. IR Spectra were obtained on Perkin-Elmer 137 and 983 spectrometers. 1H NMR spectra were recorded on Varian A-60D (60 MHz) and EM-390 (90MHz) spectrometers using TMS as internal standard. Mass spectra were obtained on Hitachi RMU-6E and Jeol D-300 spectrometers. Elemental analyses were carried out on a Heraeus CHN-O rapid analyzer. All the known ketene dithioacetals11,12 were prepared according to the reported procedures.

General procedure for the synthesis of carbinols 2a-b, 9b, 14, 16 and 18 by sodium borohydride reduction of the enals and enones. To a solution of α-oxoketene dithioacetal (0.01 mole) in absolute ethanol (25mL), excess sodium borohydride (0.02mole) was added slowly and the reaction mixture was then refluxed for 1.5 hr. The mixture was cooled and poured over saturated ammonium chloride solution (200 mL). This was extracted with ether (2x50mL), washed with water, dried (Na2SO4) and evaporated to give the carbinols in near quantitative yields which were used as such for the next step without further purification.

General procedure for the synthesis of carbinols 6a-b, 9b, 12a-b, and 14 by addition of alkyl/aryl Grignard reagent to enals and enones. To a well-cooled and stirred solution of alkyl/aryl magnesium iodide (0.015mole) in dry ether (30mL), appropriate enone/enal from 3a-b, 7a-b and 10b (0.01mole) in dry ether (20mL) was added dropwise (5min) under nitrogen atmosphere, followed by stirring for 1.5 hr. The reaction mixture was poured into a cold saturated solution of ammonium chloride (50mL), extracted with ether (3x50mL), washed with water, dried (Na2SO4) and evaporated to give the crude carbinols in quantitative yields which were used as such for further transformation.

General procedure for the synthesis of enals 3a-b, 7a-b, 10b by Vilsmeier-Haack reaction. The carbinol dithioacetals (0.01mole) in DMF (5mL) was added slowly to a well-cooled (0°C) stirred Vilsmeier reagent (prepared by adding phosphorus oxychloride (0.025mole) to N, N-dimethyl formamide (0.25mole) with stirring and cooling and further stirring for 30 min at room temperature). The reaction mixture was stirred for 10 to 15 hr for completion of reaction after which it was poured over crushed ice followed by slow addition of cold saturated potassium carbonate solution (100mL) to liberate aldehyde. The reaction mixture was then extracted with ether (4x100 mL) and combined ether extracts were washed with water, dried (Na2SO4) and evaporated to give crude enals which were further purified by column chromatography over silica gel using EtOAc : Hexane (1:20) as eluent.

General procedure for the 1,3-, 1,5-, 1,7-, 1,9- and 1,11-carbonyl transposition from carbinols 2a-b, 12a-b, 14 and 16 and 18. The carbinol (0.01mole) was dissolved in absolute methanol
The reaction mixture was then refluxed for 16 hr. It was then cooled to room temperature, poured into saturated solution of sodium bicarbonate (100mL) and extracted with CHCl₃ (2×50mL). The chloroform extracts were washed with water (2×50mL), dried (Na₂SO₄) and evaporated to give the crude ester.

5,5-Bis(methylthio)-2,4-pentadienal 3a: Orange viscous liquid, Yield 99%; IR (neat): 1670, 1592 cm⁻¹; "H NMR (CDCl₃): δ 2.40 (s, 3H, CH₃), 2.33 (s, 3H, S), 5.98 (dd, J=16Hz, 8Hz, 1H, H-2), C₂-C₃ E configuration, 6.30 (d, 1H, J=12Hz, H-4), 7.47 (1H, dd, J=16Hz, 12Hz, H-3), 9.52 (d, 1H, J = 8Hz, H-1), The coupling constant for H₂ and H₃ confirm dd, J=16 Hz, 8Hz, H-2), 9.58 (d, 1H, J=8Hz, CHO); Anal. Calcd for C₁₁H₁₂O₂S₂ (276.4): C, 51.02; H, 6.43%. M/z 276(M+, 5%); 261 (M+-15.16 %).

5,5-Bis(methylthio)-4-methyl-2,4-pentadienal 3b: Orange viscous liquid; yield: 70%; IR (neat): 1660, 1590 cm⁻¹; "H NMR (CDCl₃): δ 2.11 (s, 3H, CH₃), 0.24 (s, 3H, S), 2.42 (s, 3H, S), 6.11 (dd, 1H, J=16Hz, 8Hz, H-2), 8.06 (d, 1H, J=16Hz, H-3) ( C₂-C₃ E configuration), 9.58 (d, 1H, J=8Hz, CHO); Anal. Calcd for C₁₁H₁₄O₂S₂ (290.4): C, 65.17; H, 5.83. Found: C, 65.30; H, 5.97%. m/z 290 (M⁺, 10%); 275 (M⁺-15, 17%).

5,5-Bis(methylthio)-2,4,6-heptatriene-1-one 5aa: Reddish brown crystalline solid; yield 95%; m.p. 62°C; IR (KBr): 1640, 1600, 1590 cm⁻¹; "H NMR (CDCl₃): δ 2.31 (s, 3H, CH₃), 2.33 (s, 3H, S), 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, ArH + olefinic H). Anal. Calcd for C₁₇H₁₈O₂S₂ (320.4): C, 67.07; H, 6.62. Found: C, 67.27; H, 6.51%.

5,5-Bis(methylthio)-2,4,6-heptatriene-1-one 5ab: Reddish brown semi-solid; Yield: 90% ; IR (neat): 1638,1598 cm⁻¹; "H NMR (CDCl₃): δ 2.33 (s, 3H, CH₃), 2.34 (s, 3H, S), 3.82 (s, 3H, OCH₃), 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, ArH + olefinic H). Anal. Calcd for C₁₇H₁₉O₂S₂ (320.4): C, 76.21; H, 5.92. Found: C, 62.80; H, 5.81%.

7,7-Bis(methylthio)-6-methyl-1-(4-methoxyphenyl)-2,4,6-heptatriene-1-one 5b: Reddish brown semi-solid; yield 92% ; IR (KBr): 1675, 1600 cm⁻¹; "H NMR (CDCl₃): δ 2.33 (s, 3H, CH₃), 3.85 (s, 3H, OCH₃), 6.56 (dd, 1H, J=15Hz, 11Hz, H-4), 6.75-8.01 (m, 7H, ArH + olefinic H); MS m/z (%): 320(M⁺, 2%); 305(M+-15, 4%); 303(M⁻-15%, 4%); Anal. Calcd for C₁₇H₁₈O₂S₂ (320.4): C, 67.11; H, 6.29. Found: C, 63.80; H, 6.31%.

7,7-Bis(methylthio)-6-methyl-1-(4-chlorophenyl)-2,4,6-heptatriene-1-one 5c: Reddish brown semi-solid; yield: 99%; IR (neat): 1675, 1600 cm⁻¹; "H NMR (CDCl₃): δ 2.33 (s, 3H, CH₃), 7.00-8.01 (m, 6H, ArH + olefinic H); MS m/z (%): 320(M⁺, 2%); 305(M⁻-15%, 4%); Anal. Calcd for C₁₇H₁₈O₂S₂ (320.4): C, 57.77; H, 5.17. Found: C, 57.91; H, 5.30%.

7,7-Bis(methylthio)-6-methyl-1-(4-thienyl)-2,4,6-heptatriene-1-one 5d: Reddish brown semi-solid; yield 90%; m.p. 62°C; IR (KBr): 1640, 1600 cm⁻¹; "H NMR (CDCl₃): δ 2.15 (s, 3H, CH₃), 2.31 (s, 3H, S), 2.38 (s, 3H, S), 3.85 (s, 3H, OCH₃), 6.56 (dd, 1H, J=15Hz, 11Hz, H-4), 6.75-8.01 (m, 7H, ArH + olefinic H); MS m/z (%): 320(M⁺, 2%); 305(M⁻-15%, 4%); Anal. Calcd for C₁₇H₁₈O₂S₂ (320.4): C, 67.11; H, 6.29. Found: C, 63.80; H, 6.31%.
6H, SCH₃), 6.32 (d, 1H, J = 15Hz, H-2), 6.33 (dd, 1H, 
\( J = 15 \) Hz, 11 Hz, H-4), 6.79 (d, 1H, J=11Hz, H-6), 
7.05-7.8 (m, 5H, thiényl + olefinic H); MS m/z (%) 
282 (M⁺, 9%); 267 (M⁺-15, 15%). Anal. Calcd for 
C₁₃H₂₀O₂S₂ (346.5): C, 65.02; H, 6.06. Found: C, 
67.61; H, 6.09%.

2-(1,1-Bis(methylthio)-2-methyl-1,3-pentadienyli-
)diene)-6-methoxy-1-tetralone 5ha: Reddish brown 
crystalline solid; yield 94%; m.p. 89-90°C; IR (KBr): 
1647, 1599 cm⁻¹; \( \delta \) 2.28 (s, 3H, CH₃), 2.30 (s, 3H, 
SCH₃), 2.40 (s, 3H, CH₃), 2.92-2.93 (m, 4H, CH₂), 
6.65 (dd, 1H, J =15Hz, 12Hz, H₄), 7.25 (d, 1H, J = 7.5Hz, 
ArH), 7.34 (t, 1H, J = 7.5Hz, ArH), 7.46 (t, 1H, J = 7.5Hz, 
ArH), 7.56 (d, 1H, J = 12Hz, H-5), 7.77 (d, 1H, J = 15Hz, H-3), 8.10 (d, 
J = 7.5Hz, 1H, ArH); MS (m/z, %): 316 (M⁺ 5%), 
301 (M⁺-15, 43%); Anal. Calcd for C₁₈H₂₀O₂S₂ 
(316.5): C, 68.31; H, 6.37. Found: C, 68.40; H, 
6.21%.

7,7-Bis(methylthio)-6-methyl-1-(2-thienyl)-2,4,6-
heptatrien-1-one 5fb: Reddish brown semi-solid; yield 
95%; m.p. 105-106°C; IR (KBr): 1659, 1629, 
1569 cm⁻¹; \( \delta \) NMR (CCl₄): \( \delta \) 2.18 (s, 3H, CH₃), 
2.29 (s, 3H, SCH₃), 2.41 (s, 3H, SCH₃), 6.51 (dd, 1H, 
\( J = 15 \) Hz, H-4), 6.89 (d, 1H, J = 15Hz, H-2), 6.91- 
7.8 (m, 5H, thiényl + olefinic H); MS m/z (%) 296 
(M⁺, 4%); 281 (M⁺-15, 48%). Anal. Calcd for 
C₁₃H₁₆O₂S₂ (296.7): C, 58.71; H, 5.52%. Found: C, 
58.71; H, 5.45%.

2-(1,1-Bis(methylthio)-1,3-pentadienylidene)-6-
methoxy-1-tetralone 5hb: Orange crystalline solid, 
yield 93%; m.p. 136°C; IR (KBr): 1647, 1603, 1571 
cm⁻¹; \( \delta \) NMR (CCl₄, 300 MHz): \( \delta \) 2.38 (s, 3H, 
CH₃), 2.85-2.95 (m, 4H, CH₂), 6.65 (dd, 1H, J = 11Hz, 
H-2), 6.56 (dd, 1H, J = 16Hz, 12Hz, H-4), 6.50-6.70 (m, 2H, 
CH₂), 7.27 (d, 1H, J = 15Hz, 1H, ArH); MS (m/z, %): 332 
(M⁺, 13%); 317 (M⁺-15, 24%). Anal. Calcd for 
C₁₈H₂₀O₂S₂ (332.5): C, 65.02; H, 6.06. Found: C, 
65.15; H, 6.21%.

8,8-Bis(methylthio)-7-methyl-3,5,7-octatetra-
en-1-one 5cb: Reddish brown semisolid; yield 85%; IR 
(KBr): 1658, 1600, 1580 cm⁻¹; \( \delta \) NMR (CCl₄): \( \delta \) 2.09 
(s, 3H, CH₃), 2.11 (s, 3H, CH₃), 2.25 (s, 3H, 
SCH₃), 2.35 (s, 3H, CH₃), 2.61 (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, 
1H, ArH); MS (m/z, %): 228 (M⁺, 9%), 213 (M⁺-15, 29%). Anal. Calcd for 
C₁₃H₁₆O₂S₂ (228.4): C, 59.97; H, 5.75%. Found: C, 
59.81; H, 5.61%.

2-(1,1-Bis(methylthio)-1,3-pentadienylidene)-
1-tetralone 5ga: Reddish brown semi-solid; yield 
94%; IR (KBr): 1640, 1595 cm⁻¹; \( \delta \) NMR (CCl₄): \( \delta \) 2.18 
(s, 3H, CH₃), 2.22 (s, 3H, CH₃), 2.31 (s, 3H, 
SCH₃), 2.72-2.89 (m, 4H, -CH₂), 6.60-6.81 (m, 3H, 
ArH + olefinic H), 7.38 (d, 1H, \( J = 12 \) Hz, H-5), 7.65 
(d, 1H, \( J = 15 \) Hz, H-3), 7.92 (d, 1H, \( J = 7.5 \) Hz, 
1H, ArH). Anal. Calcd for C₁₃H₁₆O₂S₂ (346.5): C, 65.86; 
H, 6.40. Found: C, 65.91; H, 6.50%.

2-(1,1-Bis(methylthio)-2-methyl-1,3-pentadienyl-
diene)-1-tetralone 5gb: Orange crystalline solid; 
yield 92%; m.p. 102°C; IR(KBr): 1648, 1599 cm⁻¹; \( \delta \) NMR 
(CCl₄): \( \delta \) 2.32 (s, 6H, SCH₃), 2.86 (s, 4H, CH₂), 
6.36 (d, 1H, \( J = 11 \) Hz, H-2), 6.48 (dd, 1H, J = 11Hz, 
15Hz, H-4), 7.00-8.21 (m, 6H, ArH + olefin). Anal. 
Calcd for C₁₇H₂₂O₂ (302.5): C, 67.50; H, 6.00. Found: C, 
67.61; H, 6.09%.

7,7-Bis(methylthio)-6-methyl-1-(2-thienyl)-2,4,6-
heptatrien-1-one 5eb: Reddish brown 
crystalline solid; yield 95%; m.p. 102°C; IR (KBr): 
1647, 1599 cm⁻¹; \( \delta \) 2.28 (s, 3H, CH₃), 2.30 (s, 3H, 
SCH₃), 2.40 (s, 3H, CH₃), 2.92-2.93 (m, 4H, CH₂), 
6.65 (dd, 1H, \( J = 15 \) Hz, 12Hz, H₄), 7.25 (d, 1H, J = 7.5Hz, 
ArH), 7.34 (t, 1H, \( J = 7.5 \) Hz, ArH), 7.46 (t, 1H, J = 7.5Hz, 
ArH), 7.56 (d, 1H, J = 12Hz, H-5), 7.77 (d, 1H, J = 15Hz, H-3), 8.10 (d, 
J = 7.5Hz, 1H, ArH); MS (m/z, %): 316 (M⁺ 5%), 
301 (M⁺-15, 43%); Anal. Calcd for C₁₈H₂₀O₂S₂ 
(316.5): C, 68.31; H, 6.37. Found: C, 68.40; H, 
6.21%.
4H, olefinic H), 7.42 (d, 1H, J = 15Hz, H-7); 9.49 (d, 1H, J = 8Hz, -CHO); MS (m/z, %): 240 (M+, 100%). Anal. Calcd for C12H16O2S2 (240.4): C, 59.96; H, 6.71. Found: C, 60.01; H, 6.80%.

9,9-Bis(methylthio)-1-phenyl-2,4,6,8-nonatetraene-1-one 8aa: Reddish brown semi-solid; yield 92%; IR (KBr): 1652, 1598cm⁻¹; ¹H NMR (CDCl₃): δ 2.33 (s, 3H, SCH₃), 2.34 (s, 3H, SCH₃), 6.29 (d, J = 11Hz, H-8), 6.50-7.18 (m, 1H, olefinic H). Anal. Calcd for C12H16O2S2 (302.4): C, 70.13; H, 5.89. Found: C, 70.25; H, 5.91%.

9,9-Bis(methylthio)-8-methyl-1-phenyl-2,4,6,8-nonatetraene-1-one 8ab: Reddish brown semi-solid; yield 70%; IR (KBr): 1678, 1590cm⁻¹; ¹H NMR (CDCl₃): δ 2.10 (s, 3H, CH₃), 2.21 (s, 3H, CH₃), 2.35 (s, 3H, SCH₃), 6.22-8.18 (m, 11H, ArH + olefinic H). Anal. Calcd for C18H18O2S2 (316.4): C, 68.32; H, 6.37. Found: C, 68.5; H, 6.44%.

9,9-Bis(methylthio)-8-methyl-1-(4-chlorophenyl)-2,4,6,8-nonatetraene-1-one 8bb: Colourless crystalline solid; yield 90%; m.p. 70-71°C (IR and NMR data)⁹.

Methyl 5-phenyl-2,4-pentadienoate 13b: Colourless crystalline solid; yield 85%; m.p. 86°C (IR and NMR data)⁹.

Methyl 1-phenyl-2,4,6-heptatrienoate 15aa.

Methyl 1-(4-methyl phenyl)-2,4,6-heptatrienoate 15ab:

Methyl 2-methyl-7-(4-methylphenyl)-2,4,6-heptatrienoate 15bb:

Methyl 1-(4-methyl phenyl)-2,4,6-heptatrienoate 15ba:

Methyl 1-(4-methoxyphenyl)-2,4,6-heptatrienoate 15ca:

Methyl 2-methyl-7-(4-methoxyphenyl)-2,4,6-heptatrienoate 15cb:

Methyl 1-(4-chlorophenyl)-2,4,6-heptatrienoate 15da:

11,11-Bis(methylthio)-1-methyl-1-phenyl-2, 4, 6, 8, 10-undecapentene-1-one 11ab: Deep red semi-solid; yield 90%; IR (KBr): 1655, 1595cm⁻¹; ¹H NMR (CCl₄): δ 2.00 (s, 3H, CH₃), 2.13 (s, 3H, SCH₃), 2.23 (s, 3H, SCl₂), 6.15-8.20 (m, 13H, ArH+olefinic H). Anal. Calcd for C20H22O2S2 (342.5): C, 70.13; H, 5.89. Found: C, 70.25; H, 5.91%.

2-[1,1-Bis(methylthio)-2-methyl-1, 3, 5, 7-nonatraenylidene]-6-methoxy-1-tetralone 11bb: Deep red semi-solid; yield 95%; IR (KBr): 1650, 1610cm⁻¹; ¹H NMR (CCl₄): δ 1.96 (s, 3H, CH₃), 2.10 (s, 3H, SCH₃), 2.23 (s, 3H, SCl₂), 2.73 (s, 4H, CH₂), 3.66 (s, 3H, OCH₃), 6.10-7.50 (m, 9H, ArH + olefin), 7.93 (d, J = 8Hz, 1H, ArH). Anal. Calcd for C23H26O2S2 (382.6): C, 72.20; H, 6.85. Found: C, 72.31; H, 6.90%.

Yellow crystalline solid; yield 87%; m.p. 173°C (IR and NMR data)⁹.

Methyl 1-(4-phenyl 1,3,5-heptatrienylidene)-6-methoxy-1-tetralone 8bb: Reddish brown crystalline solid; yield 85%; m.p. 131°C (IR and NMR data)⁹.

Methyl 2-methyl-7-(4-methoxyphenyl)-2,4,6-heptatrienoate 15cb:

Yellow crystalline solid; yield 76%; m.p. 166°C (IR and NMR data)⁹.

Methyl 2-methyl-7-(4-chlorophenyl)-2,4,6-heptatrienoate 15cc:

Yellow crystalline solid; yield 84%; m.p. 95-96°C (IR and NMR data)⁹.

Methyl 1-(4-chlorophenyl)-2,4,6-heptatrienoate 15da: Pale yellow crystalline solid; yield 78%; m.p. 131°C (IR and NMR data)⁹.

2-[(1,1-Bis(methylthio)-1,3,5-heptatrienylidene)-2,4,6,8-nonatetraene-1-one 8dd: Reddish brown semi-solid; yield 70%; IR (KBr): 1642, 1597cm⁻¹; ¹H NMR (CDCl₃, 300MHz): δ 2.17 (s, 3H, CH₃), 2.29 (s, 3H, SCH₃), 2.38 (s, 3H, SCl₂), 2.93 (s, 4H, CH₂), 3.86 (s, 3H, OCH₃), 6.49 (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, ArH + olefinic H). Anal. Calcd for C₂₁H₂₄O₂S₂ (350.8): C, 61.62; H, 5.46. Found: C, 61.82; H, 5.66%; MS (m/z) 350 (M+, 24%); 351 (5%).

2-[(1,1-Bis(methylthio)-1,3,5-heptatrienylidene)-6-methoxy-1-tetralone 8bb: Reddish brown crystalline solid; yield 78%; m.p. 114-115°C; IR (KBr): 1647,1602cm⁻¹; ¹H NMR (CDCl₃, 300MHz): δ 2.17 (s, 3H, CH₃), 2.29 (s, 3H, SCH₃), 2.38 (s, 3H, SCl₂), 2.93 (s, 4H, CH₂), 3.86 (s, 3H, OCH₃), 6.49 (dd, 1H, J = 15Hz, 11Hz, H-4), 661-6.87 (m, 4H, ArH + olefinic H), 7.43 (d, 1H, J = 15Hz, H-7), 7.47 (d, 1H, J = 12Hz, H-3), 8.07 (d, 1H, J = 8Hz, ArH). Anal. Calcd for C₂₀H₂₂O₂S₂ (350.8): C, 67.70; H, 6.49. Found: C, 67.75; H, 6.51%; MS (m/z) 372 (M+, 49%).

9,9-Bis(methylthio)-8-methyl-2, 4, 6, 8-nonatetraenal 10b: Reddish brown liquid; yield, 70%; IR (KBr): 1675, 1612, 1585cm⁻¹; ¹H NMR (CCl₄): δ 2.11 (s, 3H, CH₃), 2.25 (s, 3H, SCH₃), 2.34 (s, 3H, SCl₂), 5.98 (dd, 1H, J = 15Hz, 8Hz), 6.83-7.21 (m, 4H, olefinic H). Anal. Calcd for C₁₁H₁₆O₂S₂ (240.4): C, 59.96; H, 6.71. Found: C, 60.01; H, 6.80%.

**Methyl 7-(2-thienyl)-2,4,6-heptatrienoate 15ea:**
Yellow semi-solid; yield 70%; IR (neat): 1718, 1590 cm⁻¹; ¹H NMR (CCL₃): δ 3.66 (s, 3H, OCH₃), 5.79 (d, 1H, J = 16Hz, H-2), 6.31-7.50 (m, 8H, thienyl + olefinic H). Anal. Calcd for C₁₅H₁₁ClO₂ (262.7): C, 68.58; H, 5.76. Found: C, 68.61; H, 5.91 %.

**Methyl 2-methyl-7-(2-thienyl)-2,4,6-heptatrienoate 15eb:**
Pale yellow semisolid; yield 79%; IR (KBr): 1705, 1595 cm⁻¹; ¹H NMR (CCL₃): δ 1.98 (s, 3H, CH₃), 3.68 (s, 3H, OCH₃), 6.45-7.28 (m, 8H, thienyl + olefinic H). Anal. Calcd for C₁₃H₁₄O₂ S (234.3): C, 66.64; H, 6.03%. Found: C, 66.78; H, 6.21%.

**Methyl 5-(3,4-dihydroanthracen-2-yl)-2,4-pentadienoate 15ga:**
Pale yellow crystalline solid; yield 78%; m.p. 86-87°C; IR (KBr): 1716, 1605 cm⁻¹; ¹H NMR (CCL₃): δ 2.33-3.13 (m, 4H, CH₂), 3.80 (s, 3H, OCH₃), 5.86 (d, J = 16Hz, H-2) 6.31-7.76 (m, 8H, ArH + olefinic H). Anal. Calcd for C₁₅H₁₂O₂ S (240.3): C, 79.97; H, 6.71. Found: C, 80.01; H, 6.81 %.

**Methyl 5-(3,4-dihydroanthracen-2-yl)-2-methyl-2,4-pentadienoate 15gb:**
Pale yellow crystalline solid; yield 78%; m.p. 82-84°C; IR (KBr): 1700, 1608 cm⁻¹; ¹H NMR (CCL₃, 300MHz): δ 3.18 (s, 3H, OCH₃), 5.89 (d, 1H, J = 15Hz, H-2), 6.22-6.89 (m, 7H, ArH + olefinic H). Anal. Calcd for C₁₆H₁₃ClO₂ (288.3): C 77.38; H, 7.14. Found: C, 77.59; H, 7.29%. MS (%) m/z: 288 (M⁺, 100%).

**Methyl 9-phenyl-2,4,6,8-nonatetraenoate 17aa:**
Yellow crystalline solid; yield 70%; m.p. 151-153°C; IR (KBr): 1708, 1618 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 3.18 (s, 3H, OCH₃), 5.89 (d, 1H, J = 15Hz, H-2), 6.22-6.89 (m, 7H, ArH+olefin H), 7.02-7.25 (m, 5H, ArH + olefinic H). Anal. Calcd for C₁₇H₁₈O₂ (284.3): C 76.54; H, 7.19. Found: C, 78.66; H, 7.33%.

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References