Tetrahedron Vol. 50, No. 1, pp. 255-264, 1994
Printed in Great Britain

0040-4020/94 $6.00+.00

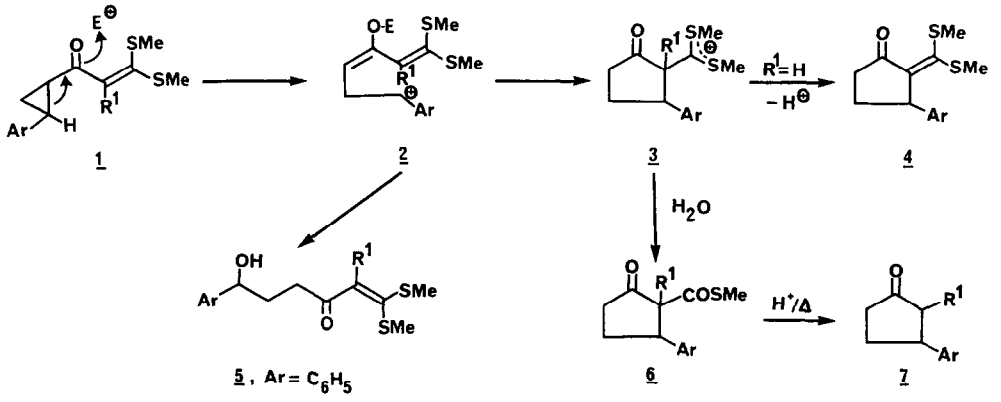
Rearrangement Studies on 3,3-Bis(methylthio)-1-(arylcyclopropyl) -2-propen-1-ols : Synthesis of Functionalized Cyclopentenes and Polyene Esters

Balaram Patro, Bishwajit Deb, Hiriyakkanavar Ila* and Hiriyakkanavar Junjappa*

Department of Chemistry, North-Eastern Hill University
Shillong - 793 003, Meghalaya, India

Abstract *: The cyclopropyl carbinols* ***8*** *and* ***9*** *obtained by either borohydride reduction (or Grignard addition) of the cyclopropyl ketones* ***1*** *are shown to undergo acid induced ring opening and intramolecular cyclization (5-exo or 6-endo) or deprotonation to afford either cyclopentene, biphenyl or conjugated polyene derivatives depending on the nature of Lewis acid, reaction conditions and the structural features present in the cyclopropyl carbinol. A probable mechanism for the formation of various products has been suggested.*

During the course of our ongoing synthetic programme on α-oxoketene dithioacetals, we had recently shown that cyclopropyl ketones of the general structure **1** undergo facile ring opening and intramolecular carbocationic cyclization through participation of the bis(methylthio)methylene double bond to afford either the ketene dithioacetal **4**, the corresponding 2-carbothioates **6** or 3-arylcyclopentanones **7** depending on the reaction conditions (Scheme 1).[1,2] This methodology has also been extended to styryl cyclopropyl ketones, their higher enyl analogs and successfully employed for the synthesis of 11-oxosteroid precursors.[3] The ketene dithioacetal moiety which is a masked ester functionality serves as an efficient cationic cyclization terminator in these reactions.[4] It was further considered that the carbinols **8** and **9** obtained by 1,2-addition of either metal hydride or organometallic respectively to the ketone **1** (Scheme 1) could prove to be useful precursors of interest, since they are likely to undergo acid induced rearrangement via a series of cationic intermediates (**19A-F**) to afford

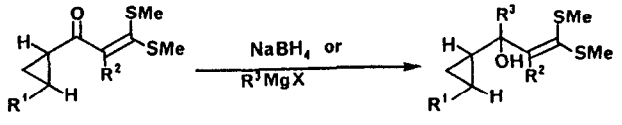


Scheme 1

various products (Scheme 7). Cyclopropyl carbinols like their carbonyl counterparts are well recognized as a class of important precursors in organic synthesis and the chemistry of their rearrangements have been extensively studied both from mechanistic and synthetic point of view.[5,6] In the present case, the homohexadienylic cation **19** generated through acid induced ionization and ring openings of the carbinols **8** or **9**, could undergo either intramolecular 5-*exo* or 6-*endo* cyclization through participation of ketene dithioacetal double bond to afford either cyclopentene or cyclohexene (or aromatic) derivatives. Alternatively, deprotonation of **19** may yield conjugated bis(methylthio)methylene polyenes which are useful precursors for ß,γ - unsaturated polyene esters (Scheme 4). The choice of these pathways will be governed by the geometry of the carbocation **19**, nature of Lewis acid, its acid strength and reaction conditions. Sorensen and co-workers[7-9] have studied the rearrangements of cyclopropyl allylic and homohexadienylic carbocations, however no attempts have been made to develop synthetically useful transformations based on these rearrangements. We have closely examined these systems with a view to develop useful product selective methodology and the results are reported in this paper.

RESULTS AND DISCUSSION

A few of the selected 2-aryl (**1a-d**), 2-styryl (**1e-f**) and 2-(4-aryl-1,3-butadienyl) (**1g-h**) cyclopropyl ketones were prepared according to our earlier reported procedure.[1-3] The ketones **1a-h** underwent facile 1,2-reduction with sodium borohydride to afford the corresponding carbinol **8a -h** in nearly quantitative yield (Scheme 2). Similarly the addition of methyl or propyl Grignard reagents to either **1a** or **1b** afforded the corresponding carbinols **9a-c** (Scheme 2) in good yields. The cyclopropyl carbinols **8a-h** and **9a-c** were used as such for subsequent transformations without any further purification.



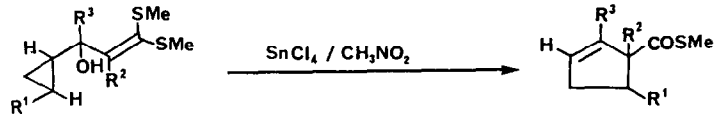
1

8, R^3 = H
9, R^3 = alkyl

Entry	Starting Material	Nucleophile	Product 8/9	R^1	R^2	R^3
1	1a	$NaBH_4$	8a	4-$MeOC_6H_4$	H	H
2	1b	$NaBH_4$	8b	C_6H_5	H	H
3	1c	$NaBH_4$	8c	3,4-$CH_2O_2C_6H_3$	H	H
4	1d	$NaBH_4$	8d	4-$MeOC_6H_4$	Me	H
5	1e	$NaBH_4$	8e	4-$MeOC_6H_4CH$=CH	H	H
6	1f	$NaBH_4$	8f	3,4-$CH_2O_2C_6H_3CH$=CH	H	H
7	1g	$NaBH_4$	8g	C_6H_5-(CH=CH)$_2$	H	H
8	1h	$NaBH_4$	8h	4-$MeOC_6H_4$(CH=CH)$_2$	H	H
9	1a	MeMgI	9a	4-$MeOC_6H_4$	H	Me
10	1b	MeMgI	9b	C_6H_5	H	Me
11	1a	n-PrMgI	9c	4-$MeOC_6H_4$	H	n-Pr

Scheme 2

Rearrangement of **8a** in the presence of various Lewis acids was attempted. In most of the cases ($SnCl_4$/ CH_2Cl_2,$SnCl_4$/ CH_3NO_2,$BF_3.Et_2O$/ CH_2Cl_2,$TiCl_4$/ CH_2Cl_2,CF_3CO_2H) ß,γ - unsaturated cyclopentene carbothioate **10a** was isolated in varying yields along with inseparable mixture of products. Best results were obtained in $SnCl_4/CH_3NO_2$, which afforded **10a** in 68% yield (Scheme 3). Interestingly the phenyl substituted cyclopropyl carbinol **8b** from **1b** also underwent cyclization under these conditions (entry 2) to afford the corresponding cyclopentene carbothioate **10b** in 55% yield. These results are significant since the corresponding phenyl substituted cyclopropyl ketone **1b** ($R^1=C_6H_5$) failed to cyclize to cyclopentanone under various conditions and gave only the open chain carbinol **5** (Scheme 1).[1,2,10]The other substituted carbinols **8c-8d** also yielded the corresponding cyclopentenyl carbothioate **10c-10d** under identical conditions (entry 3,4).The cyclopropyl carbinols **9a** obtained by addition of methyl-magnesium iodide to **1a** respectively also followed identical pathway under these conditions to give methyl substituted ß,γ - unsaturated cyclopentene carbothioates **11a** in 58% yield (entries 5,Scheme 3). The ^1H NMR spectra of all the cyclopentene carbothioates (**10a-d**,**11a**) showed the formation of only one stereoisomer (probably *trans*) which was evident from their ^1H and ^{13}C NMR spectra.[11]



10 , R^3 = H
11 , R^3 = alkyl

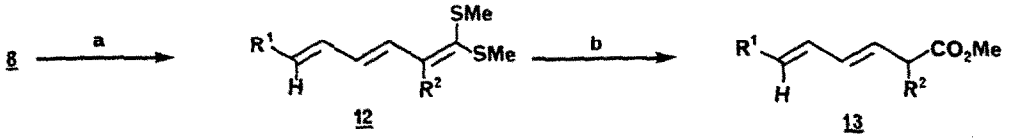
Entry	Carbinol	Product	R^1	R^2	R^3	% Yield 10,11
1	8a	10a	4-$MeOC_6H_4$	H	H	68
2	8b	10b	C_6H_5	H	H	55
3	8c	10c	3,4-CH_2(O)(O)C_6H_3	H	H	71
4	8d	10d	4-$MeOC_6H_4$	Me	H	73
5	9a	11a	4-$MeOC_6H_4$	H	Me	58

Scheme 3

Our initial attempts to obtain acyclic triene **12a** from **8a** under the influence of various acids were not successful. However when **8a** was treated with pyridinium tosylate in refluxing CCl_4, the triene **12a** was obtained exclusively in 89% yield (Scheme 4). These reaction conditions were successfully extended for other substituted trienes (**12b-d**), tetraenes (**12e-f**) and pentaenes (**12g-h**) from the respective carbinols **8a-h** in 79-85% overall yields (Scheme 4). Some of these polyenes (**12a-c**, **12f-g**) were subjected to $BF_3.Et_2O/HgCl_2$ catalyzed methanolysis[12] to afford the corresponding ß,γ -unsaturated diene (**13a-13c**), triene (**13f**) and tetraene (**13g**) esters in high yields (Scheme 4). The structural assignments for both polyene and polyene esters described above were confirmed by their analytical and spectral data. The tetraenes (**12e-f**) and pentaenes (**12g-h**) were obtained as sharp melting solids and their ^1H and ^{13}C NMR spectra showed the presence of single geometrical isomer.

The carbinols **9a-c** obtained by addition of Grignard reagents to **1a-b** failed to give alkyl substituted trienes **12** under these conditions (Py^+Tos^-) and yielded only cyclopentenes **14a-c** with intact dithioacetal functionality (Scheme 4). A similar trend was also observed under the influence of Vilsmeier reagent . Thus whereas treatment of **8a** with $DMF/POCl_3$ afforded only acyclic triene aldehyde **15** (72%), the corresponding cyclopentene aldehyde **16** was obtained from the carbinol **9a** under these conditions (Scheme 5).

The various carbinols (**8a-d**, **9a-b**) examined under the influence of different Lewis acids did not yield any of the six membered cyclic compound formed through 6-*endo trig*cyclization of the carbocation



8 , 12 , 13a , R^1= 4-$MeOC_6H_4$; R^2= H

8 , 12 , 13b , R^1= C_6H_5; R^2= H

8 , 12 , 13c , R^1= 3,4-$CH_2O_2C_6H_3$; R^2= H

8 , 12d , R^1= 4-$MeOC_6H_4$; R^2= Me

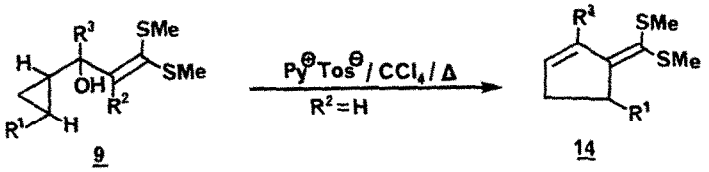
8 , 12e , R^1= 4-$MeOC_6H_4$-CH=CH; R^2= H

8 , 12 , 13f , R^1= 3,4-$CH_2O_2C_6H_3$-CH=CH; R^2= H

8 , 12 , 13g , R^1= $C_6H_5(CH=CH)_2$-; R^2= H

8 , 12h , R^1= 4-$MeOC_6H_4(CH=CH)_2$-; R^2= H

a, $Py^+ Tos^-$ / CCl_4/Δ; b, BF_3.Et_2O/$HgCl_2$/MeOH.

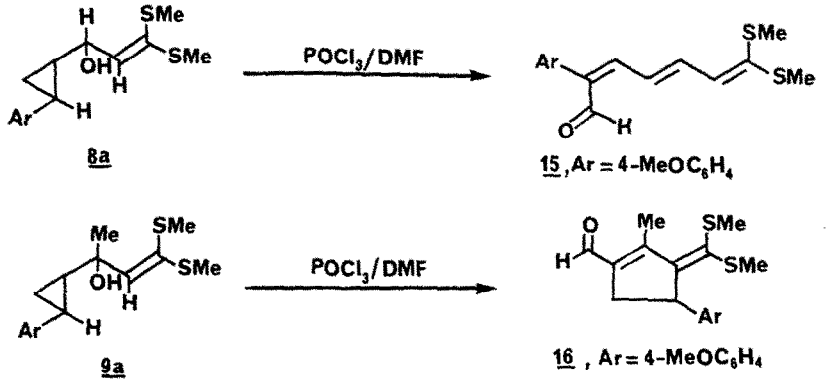


9 , 14a , R^1= 4-$MeOC_6H_4$; R^3= Me

b , R^1= C_6H_5; R^3= Me

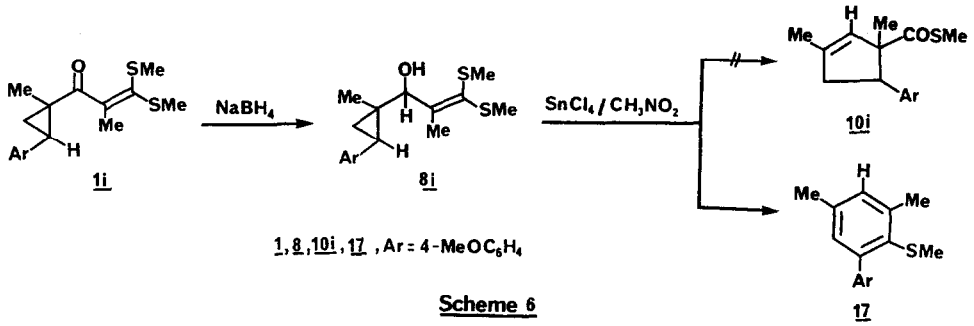
c , R^1= 4-$MeOC_6H_4$; R^3= n-Pr

Scheme 4



Scheme 5

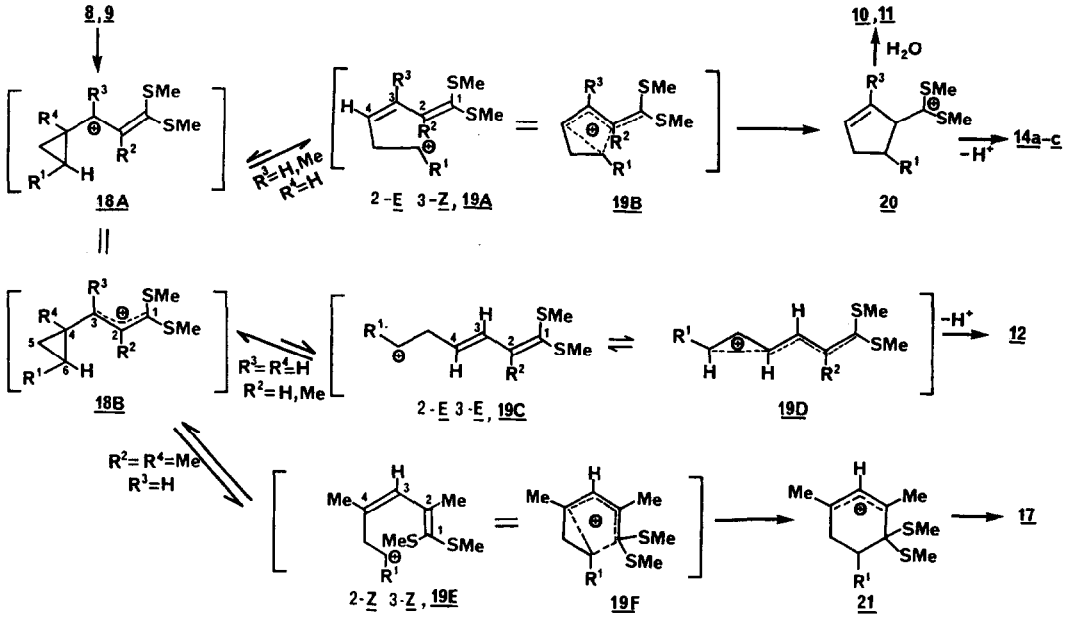
19 (*Scheme* 7). *Evidently*, the ketene dithioacetal moiety acts as a powerful cationic cyclization terminator to facilitate the 5-*exo trig* process leading to cyclopentene derivatives. We therefore investigated the acid induced cyclization of the carbinol **8i** (obtained by $NaBH_4$ reduction of **1i**) since the presence of two methyl groups at the 2-and 4-positions of the resulting hexadienylic cations **19** would not only force it to acquire **2*Z*, 3*Z*** *conformation* (**19E**, **19F**)(due to steric interaction in **2*E*,3*E*** conformation) necessary for 6- *endo* cyclization, but also stabilize the resulting cyclohexenyl cation **21** at both the terminals.[12,13] Thus when **8i** was cyclized in the presence of $SnCl_4/CH_3NO_2$, work-up of the reaction mixture afforded exclusively one product (62%) characterized as 3,5-bis(methyl)-2-methylthiobiphenyl **17** formed through 6-*endo* cyclization of homohexadienylic cation (**19E**) (Scheme 6).



Scheme 6

MECHANISM

A probable mechanistic pathway for the formation of various products is shown in the Scheme 7. The initially formed cyclopropylallyl carbocation (**18A,18B**) rearranges to homohexadienylic cation (**19A-F**) through regioselective cleavage (C_4-C_6 bond) of cyclopropyl ring. In highly ionic medium ($SnCl_4/CH_3NO_2$), the thermodynamically more stable **2*E*, 3*E*** (**19C, 19D**) conformation may predominate, which would slowly isomerize to **2*E*, 3*Z*** form (**19A, 19B**) having favourable geometry for intramolecular π-participation of bis(methylthio)methylene double bond through 5-*exo* cyclization to give carbocation **20**. Subsequent hydrolysis of **20** affords the carbothioates **10** or **11**. Under less polar reaction conditions (Py^+Tos^-/CCl_4), the **2*E*, 3*E*** carbocation (**19C,19D**, R^3=H) undergoes fast deprotonation to give trienes and their higher homologs.[12] However, when R^3= Me, n-Pr, the **2*E*, 3*Z*** carbocations **19A, 19B** might exist predominantly, leading to bis(methylthio)methylene cyclopentenes **14a-c**[14] through intramolecular cyclization and deprotonation of carbocation **20** (R^3=alkyl). Finally, the introduction of methyl groups at 2- and 4-positions of the dienylic cation facilitates its 6-*endo* cyclization through **2*Z*,3*Z*** (**19E, 19F**) conformation to give cyclohexenyl carbocation **21** stabilized by methyl groups at both the terminals.



Scheme 7

Subsequent deprotonation and elimination of methyl mercaptan in **21** affords biphenyl derivative **17** as the exclusive product. However, the facile cyclization of phenyl substituted cyclopropyl carbinols (**8b** and **9b**) to the corresponding cyclopentene derivatives **10b** and **14b** does not rule out an alternative concerted mechanism involving ionization, ring opening and intramolecular cyclization of the carbinols in one step.

In conclusion, we have demonstrated that the acid induced ionization of cyclopropyl carbinols **8** and **9** can follow different pathways leading to either cyclopentenes, polyenes or six membered (aromatic) derivatives depending on the reaction conditions (nature of Lewis acid, reaction medium) and the structural features present in the carbinols. The transformation of **1** to **13** through polyenes **12** provides a useful synthetic route to ß,γ - unsaturated polyene ester. It is noteworthy that in all these reactions, ß,γ -unsaturated esters were formed exclusively and no isomerization of double bond to α,ß-unsaturated eneesters was observed.

EXPERIMENTAL

Melting points were determined on a 'Thomas Hoover' capillary melting point apparatus and are uncorrected. IR spectra were obtained on a Perkin-Elmer 297 spectrophotometer. The ^{1}H NMR spectra were recorded on a Varian EM-390 (90 MHz) spectrometer in $CDCl_3$ or CCl_4 using TMS as internal stardard, while ^{13}C NMR spectra were recorded on a Brucker WM-400 spectrometer and chemical shifts are expressed in δ (PPM) units downfield from TMS. Mass Spectra were obtained on a Jeol JMS-D-300 spectrometer Elemental analysis were performed on a Heraeous CHN-O-Rapid Elemental analyzer.

All the starting cyclopropyl ketones **1a** -**i** and their ketene dithioacetal precursors were prepared according to the earlier reported procedures.[3,15a,b]

General Procedure for $NaBH_4$ Reduction of Ketones 1a-i

To a well stirred solution of cyclopropyl ketone **1** (10 mmol) in absolute EtOH (50 ml) excess of $NaBH_4$ (1.25g, 35 mmol) was added and the mixture was refluxed for 2 hr. The cooled reaction mixture was then poured into crushed ice and extracted with chloroform (2x100 ml). The combined chloroform extract was washed with saturated aq. NaCl (2x100 ml), dried over Na_2SO_4 and evaporated under reduced pressure to give the crude carbinols **8** in nearly quantitative yields as undistillable thick liquids which were used as such without further purification.

General Procedure for Addition of Grignard Reagents to 1a-b

To an ice-cooled solution (0-5°C) of Grignard reagent [0.03 mol, prepared from magnesium turnings (1.0g) and alkyl halide (0.03 mol) in dry ether (50 ml)], cyclopropyl ketone **1** (0.015 mol) in dry benzene (25 ml) was added dropwise, under N_2 atmosphere with stirring. The reaction mixture was further stirred for 2 hr and the temperature was raised to room temperature (monitored by TLC). It was then decomposed by pouring over saturated aq. NH_4Cl solution (40 ml), extracted with ether (2x50ml), and the combined ether extracts were washed with water (100 ml), dried (Na_2SO_4) and evaporated to give the crude carbinols **9**, which were used as such for further rearrangement studies.

General Procedure for Rearrangement of Carbinols (8 or 9) with $SnCl_4/CH_3NO_2$

To a cooled (0°C) solution of carbinol **8** or **9** (10 mmol) in CH_3NO_2 (15 ml), $SnCl_4$ (4.14g, 15 mmol) was added and the reaction mixture was stirred at 0°C for 1 hr. It was then brought to room temperature (monitored by TLC), poured into cold aq. 5% NaOH and extracted with $CHCl_3$ (3x60 ml). The organic layer was washed with water, dried over Na_2SO_4 and evaporated to afford the respective cyclopentenes or biphenyl as viscous residues, which were purified by column chromatography over silica gel using hexane as eluent.

S-Methyl-5-(4-methoxyphenyl)-2-cyclopentene-1-carbothioate (10a). Colorless oil; (68%); IR(neat) 2931, 1690, 1512 cm^{-1}; δ_H (CCl_4) 2.23 (3H, s, SCH_3), 2.52-2.67 (1H, m, CH_2), 2.74-3.00 (1H, m, CH_2), 3.76

(3H, s, OCH_3), 3.64-3.79(2H,m,C*H*-1 and C*H*-5), 5.68-5.90(1H, m, =C*H*), 5.97-6.16(1H, m, =C*H*), 6.85 (2H, d, J = 9Hz,Ar*H*), 7.23 (2H, d, J = 9Hz, Ar*H*); m/z 248 (M^+, 13%), 173 (M^+-75). (Anal. Calcd. for $C_{14}H_{16}O_2S$: C, 67.71; H, 6.50. Found: C, 67.92; H, 6.68%).

S-Methyl-5-phenyl-2-cyclopentene-1-carbothioate (10b). Colorless oil; 55%; IR (neat) 2965, 1695 cm^{-1}; δ_H (CCl_4) 2.19 (3H, s, SCH_3), 2.46-2.68 (1H,m,CH_2), 2.73-3.20(1H,m,CH_2), 3.63-3.78(2H, m, C*H*-1 and C*H*-5), 5.62-5.76(1H, m, =C*H*), 5.82-6.03 (1H, m, =C*H*), 7.07-7.26 (5H, m, Ar*H*). (Anal. Calcd. for $C_{13}H_{14}OS$: C, 71.52; H, 6.46. Found : C, 71.82; H, 6.64%).

S-Methyl-5-(3,4-methylenedioxyphenyl)-2-cyclopentene-1-carbothioate (10c). Colorless oil; 71% ;IR (neat) 2910,1683,1588cm^{-1}; δ_H ($CDCl_3$,300MHz) 2.29(3H,s,SCH_3), 2.42-2.52(1H,m,CH_2), 2.91-3.0(1H,m,CH_2), 3.63-3.70(1H,m,C*H*-5), 3.77-3.81(1H,m,C*H*-1), 5.72-5.76(1H,m,=C*H*), 5.92 (2H,s,O-CH_2-O), 5.98-6.02 (1H,m,=C*H*), 6.67-6.74(3H,m,Ar*H*); δ_C($CDCl_3$,75MHz) 12.63 (S*C*H_3), 42.82 (*C*H_2), 48.13 (*C*-5), 69.42 (*C*-1), 101.96 (O-*C*H_2-O), 128.97,135.07(=*C*H), 108.31,109.23,121.19 (Ar*C*H), 140.13,147.17,148.86 (Ar*C*), 202.24 (*C*OSMe). (Anal.Calcd. for $C_{14}H_{14}O_3S$: C,64.10;H,5.38. Found : C, 64.39; H, 5.57%).

S-Methyl-1-methyl-5-(4-methoxyphenyl)-2-cyclopentene-1-carbothioate (10d). Colorless oil; 73%; IR (neat) 3010, 2950, 2860, 1700, 1630, 1600, 1500 cm^{-1}; δ_H($CDCl_3$,300MHz) 0.88(3H, s, CH_3), 2.29(3H, s, SCH_3), 2.66-2.88(2H, m, CH_2), 3.79 (3H, s, OCH_3), 3.85 (1H, t, J = 7.8Hz, C*H*-5), 5.71-5.74(1H, m, =C*H*), 6.04- 6.07(1H, m, =C*H*), 6.82 (2H, d, J = 9Hz, Ar*H*), 7.10 (2H, d, J = 9Hz, Ar*H*); δ_C($CDCl_3$, 75MHz) 12.91 (S*C*H_3), 20.62 (*C*H_3), 38.87 (*C*H_2), 52.03 (O*C*H_3), 56.28 (*C*-5), 67.20 (*C*-1), 134.36,135.83(=*C*H), 114.46,130.76(Ar*C*H), 133.34,159.41(Ar*C*), 206.65 (*C*OSMe). (Anal. Calcd. for $C_{15}H_{18}O_2S$. C, 68.67; H, 6.92. Found : C, 68.93; H, 7.12%).

S-Methyl-2-methyl-5-(4-methoxyphenyl)-2-cyclopentene-1-carbothioate (11a). Colorless oil; 58%; IR (neat) 2950, 1700, 1520 cm^{-1}; δ_H (CCl_4) 1.72 (3H, brs, CH_3), 2.27 (3H, s, SCH_3), 2.30-2.45 (1H, m, CH_2), 2.66-3.09 (1H, m, CH_2), 3.75 (3H, s, OCH_3), 3.36-3.78(2H, m, C*H*-1, C*H*-5), 3.75 (3H, s, OCH_3), 5.59 (1H, brs, =C*H*), 6.77 (2H, d, J = 9Hz, Ar*H*), 7.08 (2H, d, J = 9Hz, Ar*H*). (Anal. Calcd. for $C_{15}H_{18}O_2S$: C, 68.67; H, 6.92. Found : C, 68.92; H, 7.15%).

3,5-Bis(methyl) -2-methylthiobiphenyl (17). Colorless oil; 62%; IR (neat) 2900, 1580, 1260 cm^{-1}; δ_H (CCl_4) 1.82 (3H, s, CH_3), 2.29 (3H, s, SCH_3), 2.53 (3H, s, CH_3), 3.80 (3H, s, OCH_3), 6.83-7.06(4H, m, Ar*H*), 7.29-7.49 (2H, d, J = 9Hz, Ar*H*); m/z 258 (M^+, 100%), 243(29), 228(45), 211(3). (Anal. Calcd. for $C_{16}H_{18}OS$: C, 74.38; H, 7.03. Found : C, 74.64; H, 7.21%).

General Procedure for Dehydrative Rearrangement of Carbinols 8 and 9 in Pyridinium tosylate : Synthesis of Polyenes 12 and cyclopentenes 14

A suspension of carbinol **8** or **9** (10 mmol), pyridinium tosylate (5g, 20 mmol) in CCl_4 (25ml) was refluxed with stirring for 15-30min (monitored by TLC). The reaction mixture was concentrated on water bath and unreacted pyridinium tosylate was filtered. The filtrate was evaporated to give the crude products which were purified by passing through a silica gel column using hexane as eluent.

1,1-Bis (methylthio)-6-(4-methoxyphenyl)-1,3,5-hexatriene (12a). Yellow viscous oil; 89%; IR(neat) 1662, 1600 cm^{-1}; δ_H (CCl_4) 2.16 (3H, s, SCH_3), 2.21 (3H, s, SCH_3), 3.61 (3H, s, OCH_3), 5.94-6.83 (5H, m, =C*H*), 6.67 (2H, d, J = 9Hz, Ar*H*), 7.19 (2H, d, J = 9Hz, Ar*H*); δ_C ($CDCl_3$,75MHz) 16.55, 17.30 (S*C*H_3), 55.02 (OCH_3), 127.56, 129.94, 131.07, 132.14, 132.97 (=CH), 113.87, 127.03, 127.35, 128.39 (Ar*C*H), 130.33, 158.97 (Ar*C*), 134.83 (*C*-1). (Anal. Calcd. for $C_{15}H_{18}OS_2$: C, 64.71; H, 6.52. Found : C, 64.93; H, 6.68%).

1,1-Bis(methylthio)-6-phenyl-1,3,5-hexatriene (12b). yellow viscous oil; 81%; IR (neat) 1675, 1600 cm^{-1}; δ_H (CCl_4) 2.25 (3H, s, SCH_3), 2.31 (3H, s, SCH_3), 5.91-7.04 (5H, m, = C*H*), 7.10-7.52 (5H, m, Ar*H*). (Anal. Calcd. for $C_{14}H_{16}S_2$: C,67.69; H,6.49. Found :C, 67.82; H,6.58%).

1,1-Bis(methylthio)-6-(3,4-methylenedioxyphenyl)-1,3,5-hexatriene (12c). Yellow viscous oil; 86%; IR(neat) 2672, 1686, 1595 cm^{-1}; δ_H (CCl_4) 2.34 (6H, s, SCH_3), 5.94 (2H, s, CH_2), 6.15-7.04 (8H, m, =C*H* and Ar*H*). (Anal. Calcd. for $C_{15}H_{16}O_2S_2$: C, 61.69; H, 5.52. Found : C, 61.86; H, 5.69%).

1,1-Bis(methylthio)-2-methyl-6-(4-methoxyphenyl)-1,3,5-hexatriene (12d). yellow viscous oil; 74%; IR (neat) 1675, 1595 Cm^{-1}; δ_H (CCl_4) 2.16 (3H,s,CH_3), 2.27 (3H,s,SCH_3), 2.31 (3H,s,SCH_3), 3.76 (3H,s, OCH_3), 6.30-6.62 (3H,m, =C*H*), 6.78 (2H, d, J=9Hz, Ar*H*), 7.33 (2H, d, J=9Hz, Ar*H*). (Anal. Calcd. for $C_{16}H_{20}OS_2$: C,65.71; H,6.89. Found : C,65.93; H,7.04%).

1,1-Bis(methylthio)-8-(4-methoxyphenyl)-1,3,5,7-octatetraene (12e). yellow solid; 78%; m.p. 73-74°C; IR(KBr)1600, 1590, 1500 cm^{-1}; δ_H($CDCl_3$,400MHz) 2.35 (3H, s, SCH_3), 2.36 (3H, s, SCH_3), 3.81 (3H, s, OCH_3), 6.30-6.45 (4H, m, = C*H*), 6.51 (1H, d, J = 14Hz, =C*H*), 6.70-6.85 (4H, m, =C*H* and Ar*H*), 7.34 (2H, d, J = 9Hz, Ar*H*); δ_C ($CDCl_3$,100MHz) 16.76, 17.49 (SCH_3), 55.21 (OCH_3), 128.90, 129.13, 131.21, 132.23, 132.54, 132.95, 133.91 (= *C*H), 114.09, 127.16, 127.56, 127.88 (Ar*C*H), 130.19, 159.20 (Ar*C*), 135.43 (*C*-1); m/z 304 (M^+, 100%), 257 (12), 242 (16). (Anal. Calcd. for $C_{17}H_{20}OS_2$: C, 67.05; H, 6.62. Found : C, 67.27, H, 6.78%).

1,1-Bis(methylthio)-8-(3,4-methylenedioxyphenyl)-1,3,5,7-octatetraene (12f). Viscous oil; 87%; IR(neat) 1678, 1602 cm^{-1}; δ_H (CCl_4) 2.34 (6H, s, SCH_3), 5.94 (2H, s, CH_2), 6.03-7.44 (10H, m, =C*H* and Ar*H*); m/z 318 (M^+, 32%), 271 (14), 224(15). (Anal. Calcd. for $C_{18}H_{20}O_2S_2$: C, 64.12; H, 5.70. Found : C, 64.36; H, 5.84%).

1,1-Bis(methylthio)-10-phenyl-1,3,5,7,9-decapentane (12g). Yellow solid; 91% m.p. 105-106°C; IR(KBr) 1670, 1597 cm^{-1}; δ_H ($CDCl_3$) 2.31 (3H, s, SCH_3), 2.34 (3H, s, SCH_3), 6.05-7.04 (9H, m, =C*H*), 7.13-7.51 (5H, m, Ar*H*); m/z 300 (M^+, 100%), 206 (10). (Anal. Calcd. for $C_{18}H_{20}S_2$: C, 71.96; H,6.71. Found : C, 72.19; H,6.84%).

1,1-Bis(methylthio)-10-(4-methoxyphenyl)-1,3,5,7,9-decapentaene (12h). Yellow solid; 87%; m.p. 109-110°C; IR(KBr) 1667, 1600, 1509 cm^{-1}; δ_H ($CDCl_3$) 2.34 (6H, s, SCH_3), 3.87 (3H, s, OCH_3), 6.20-6.81 (8H, m, =C*H*), 6.62 (1H, d, J= 8Hz,C*H*-2), 6.92 (2H, d, J = 9Hz, Ar*H*), 7.40 (2H, d, J = 9Hz, Ar*H*); δ_C ($CDCl_3$) 16.86, 17.55 (SCH_3), 55.17 (OCH_3), 127.15, 128.89, 131.14, 132.22, 132.53, 132.96, 133.91, (=*C*H), 114.19, 127.63 (Ar*C*H), 130.19, 159.27 (Ar*C*), 135.47 (*C*-1); m/z 330 (M^+, 100%). (Anal. Calcd. for $C_{19}H_{22}OS_2$: C, 69.05; H, 6.71. Found : C, 69.24; H, 6.87%).

3-Bis(methylthio)methylene-2-methyl-4-(4-methoxyphenyl)-1-cyclopentene (14a). Colorless oil; 87%; IR (neat) 1610, 1507 cm^{-1}; δ_H(CCl_4) 2.00 (3H, s, SCH_3), 2.23 (3H, s, SCH_3), 2.29 (3H, d, J = 2Hz, CH_3), 2.66-3.08 (2H, m, CH_2), 3.73 (3H, s, OCH_3), 4.30 (1H, d, J = 7.5Hz, C*H*-4), 6.00 (1H, brs, =C*H*), 6.82 (2H, d, J = 9Hz, Ar*H*), 7.17 (2H, d, J = 9Hz, Ar*H*); m/z 292 (M^+, 10%). (Anal. Calcd. for $C_{16}H_{20}OS_2$: C, 65.71; H, 6.89. Found: C, 65.93; H, 7.04%).

3-Bis(methylthio)methylene-2-methyl-4-phenyl-4-cyclopentene (14b). Colorless oil; 78%; IR (neat) 1610, 1600 cm^{-1}; δ_H (CCl_4) 1.91 (3H, s, SCH_3), 2.17 (3H, s, SCH_3), 2.26 (3H, d, J = 2Hz, CH_3), 2.61-3.04 (2H, m, CH_2), 4.34 (1H, d, J = 7.5Hz, C*H*-4), 5.90 (1H, brs, =C*H*), 6.95-7.32 (5H, m, Ar*H*); m/z 262 (M^+, 13%), 215 (41). (Anal. Calcd. for $C_{15}H_{18}S_2$: C, 68.65; H, 6.91. Found : C, 68.87; H, 7.08%).

3-Bis(methylthio)methylene-4-(4-methoxyphenyl)-2-propyl-1-cyclopentene (14c). colorless oil; 84%; IR(neat) 1611, 1512 cm^{-1}; δ_H (CCl_4) 0.89 (3H, t, J = 6Hz, CH_3), 1.24-1.68 (2H, m, CH_2), 1.88 (3H, s, SCH_3), 2.14 (3H, s, SCH_3), 1.88-3.0 (4H, m, ring CH_2 and -CH_2CH_3), 3.61 (3H, s, OCH_3), 4.20 (1H, d, J = 7.5Hz, C*H*-4), 5.88 (1H, brs, =C*H*), 6.61 (2H, d, J = 9Hz, Ar*H*), 6.93 (2H, d, J = 9Hz, Ar*H*); m/z 319 (M^+, 11%). (Anal. Calcd. for $C_{18}H_{24}OS_2$: C, 67.45; H, 7.55. Found : C, 67.69; H, 7.69%).

General Procedure for $BF_3.Et_2O/HgCl_2$ Assisted Methanolysis of Polyenes (12a-c,12f-g): Synthesis of Polyene Esters (13a-13c,13f-g)

A suspension of polyene **12** (10 mmol), $HgCl_2$ (2.70g, 10 mmol) and $BF_3.Et_2O$ (5 ml) in anhydrous methanol was stirred at room temperature for 8-10 hr (monitored by TLC). The reaction mixture was filtered through a sintered funnel to remove traces of $HgCl_2$, the filtrate diluted with $CHCl_3$ (100 ml), washed with saturated $NaHCO_3$ solution (3x100 ml), water (2x50 ml), dried over Na_2SO_4 and evaporated to give crude esters, which were purified by column chromatography over a silica gel with hexane : ethylacetate (50 : 1) as eluent.

Methyl 6-(4-methoxyphenyl)-3,5-hexadienyl carboxylate (13a). Colorless solid; 84%; m.p. 48°C; IR (KBr) 1735, 1610 cm^{-1}; δ_H (CCl_4) 2.99 (2H, d, J = 7Hz, CH_2), 3.53 (3H, s, OCH_3), 3.65 (3H, s, OCH_3), 5.37-6.53 (4H, m, = CH), 6.68 (2H, d, J = 9Hz, ArH), 7.14 (2H, d, J = 9Hz, ArH); m/z 232 (M^+, 100%), 200 (3). (Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.39; H, 6.95. Found : C, 72.62; H, 7.11%).

Methyl 6-phenyl-3,5-hexadienylcarboxylate (13b). Colorless oil; 78%; IR (neat) 1720, 1645 cm^{-1}; δ_H (CCl_4) 3.11 (2H, d, CH_2), 3.71 (3H, s, OCH_3), 5.56-6.96 (4H, m, =CH), 7.06-7.58 (5H, m, ArH); m/z 202 (M^+, 100%), 200 (3). (Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found : C, 77.46; H, 7.18%).

Methyl 6-(3,4-methylenedioxyphenyl)-3,5-hexadienyl carboxylate (13c). Colorless oil; 83%; IR (neat) 1735, 1600 cm^{-1}; δ_H (CCl_4) 3.03 (2H, d, J = 7Hz, CH_2), 3.60 (3H, s, OCH_3), 5.35-6.48 (4H, m, =CH), 5.83 (2H, s, CH_2), 6.54-6.88 (3H, m, ArH); m/z 246 (M^+, 10%). (Anal. Calcd. for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found : C, 68.48; H, 5.59%).

Methyl 8-(3,4-methylenedioxyphenyl)-3,5,7-octatriene carboxylate (13f). Colorless solid; 84%; m.p. 61-62°C; IR (KBr) 1740, 1600, 1500 cm^{-1}; δ_H (CCl_4) 3.05 (2H, d, J = 9Hz, CH_2), 3.63 (3H, s, OCH_3), 5.27-6.54 (6H, m, =CH), 5.90 (2H, s, CH_2), 6.62-6.93 (3H, m, ArH); m/z 272 (M^+, 94%), 213 (20). (Anal. Calcd. for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92. Found : C, 70.81; H, 6.09%).

Methyl 10-phenyl-3,5,7,9-decatetraene carboxylate (13g). Colorless solid; 87%; m.p. 84-85°C; IR (KBr) 1733, 1510 cm^{-1}; δ_H (CCl_4) 3.11 (2H, d, J = 7Hz, CH_2), 3.68 (3H, s, OCH_3), 5.46-6.97 (8H, m, =CH), 7.12-7.58 (5H, m, ArH); m/z 254 (M^+, 90%), 195 (19). (Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found : C, 80.49; H, 7.27%).

General Procedure for Rearrangement of Carbinols 8a and 9a with $POCl_3$ /DMF (Vilsmeier-Haack Reagent)

To a cooled (0°C) and stirred solution of the carbinol **8a** or **9a** (10 mmol) in DMF (5 ml) was added dropwise, the Vilsmeier reagent [prepared from $POCl_3$ (2.0g, 13 mmol) and DMF (2 ml)]. The bath temperature was slowly raised to 80°C during 1 hr and maintained at the same temperature for 3 hr. After cooling the reaction mixture, a solution of NaOAc (25ml, 40%) was slowly added with stirring and it was further heated at 80°C for 10 min, cooled, extracted with ether (2x50 ml). The organic layer was washed with water, dried (Na_2SO_4) and evaporated to give crude residue, which was purified by column chromatography using EtOAc/hexane (1:50) as eluent.

1,1-Bis(methylthio)-6-(4-methoxyphenyl)-1,3,5-heptatrienal (15). yellow solid; 72%; m.p. 86-88°C; IR (KBr) 1665, 1610, 1590, 1515 cm^{-1}; δ_H(CCl_4) 2.42 (3H, s, SCH_3), 2.47 (3H, s, SCH_3), 3.72 (3H, s, OCH_3), 6.56-6.90 (5H, m, =CH and ArH), 7.17-7.40 (3H, m, =CH and ArH), 10.13 (1H, d, J = 3H, CHO); m/z 306 (M^+, 94%), 259 (61), 231 (56). (Anal. Calcd. for $C_{16}H_{18}S_2O_2$: C, 62.71; H, 5.93. Found : C, 62.96; H, 6.05%).

3-Bis(methylthio)methylene-2-methyl-4-(4-methoxyphenyl)-1-cyclopentene carboxaldehyde (16). viscous oil; 76%; IR(neat) 2926, 1657, 1547 cm^{-1}; δ_H (CCl_4) 2.16 (3H, s, SCH_3), 2.28 (3H, s, SCH_3), 2.46 (1H, brd, J= 11Hz, CH_2), 2.76 (3H, brs, CH_3), 2.79-3.32 (1H, m, CH_2), 3.62 (3H, s, OCH_3), 4.35 (1H, d, J= 7.5Hz,

C*H*-4), 6.78 (2H, d, J = 9Hz, Ar*H*), 7.04 (2H, d, J = 9Hz, Ar*H*), 10.27 (1H, s, C*H*O); m/z 320 (M^+, 100%), 273 (42), 257 (25). (Anal. Calcd. for $C_{17}H_{20}O_2S_2$: C, 63.71; H, 6.29. Found : C, 63.92; H, 6.46%).

ACKNOWLEDGEMENT : B. Patro thanks CSIR, New Delhi for Senior Research Fellowship. Financial assistance under CSIR research scheme is also acknowledged.

REFERENCES

1. Deb, B.; Asokan, C.V.; Ila, H., Junjappa, H. *Tetrahedron Lett*. **1988**, *29*, 2111-2114.
2. Deb, B.; Ila, H.; Junjappa H. *J. Chem. Res.(s)* **1990**, 356-357; *J. Chem. Res.(m)* **1990**, 2728-2758.
3. Patro, B.; Deb, B.; Ila, H.; Junjappa, H. *J. Org. Chem*. **1992**, *57*, 2257-2263.
4. (a) Kolb, M. *Synthesis* **1990**, 177-179. (b) Chamberlin, A.R.; Nguyen, H.D.; Chung, J.Y.L. *J. Org. Chem*. **1984**, *49*, 1682-1688. (c) Chamberlin, A.R.; Chung, J.Y.L. *Tetrahedron Lett*. **1982**, *23*, 2619-2622. (d) Chamberlin, A.R.; Chung, J.Y.L. *J. Am. Chem. Soc.* **1983**, *105*, 3653-3656.
5. Seko, S.; Tanabe, Y.; Suzukamo, G. *Tetrahedron Lett*. **1990**, *31*, 6883-6886 and references therein.
6. Wong, H.N.C.; Hon, M-Y.; Tse, C-W.; Yip, Y-C; Tanko, J.; Hudlicky, T. *Chem. Rev*. **1989**, *89*, 165-198 and references therein.
7. Rajeshwari, K.; Sorensen, T.S. *J. Am. Chem. Soc*. **1971**, *93*, 4222-4232.
8. Rajeshwari, K.; Sorensen, T.S. *J. Am. Chem. Soc*. **1973**, *95*, 1239-1246.
9. Sorensen, T.S.; Rauk, K. in "*Pericyclic Reactions*" Ed. Marchand, A.P.; Lehr, R.E. Academic Press, New York **1977**, Vol. II, pp.29-40.
10. (a) Murphy, W.S. and Wattanasin, S. *J. Chem. Soc. Perkin Trans I* **1982**, 271-276. (b) Murphy, W.S., Wattanasin, S. *J. Chem. Soc. Perkin Tran I* **1982**, 1029-1035. (c) Murphy, W.S.; Wattanasin, S. *J. Chem. Soc. Perkin Trans I* **1981**, 2920-2926. (d) Hantawong, K.; Murphy, W.S.; Russell, N.; Boyd, D.R. *Tetrahedron Lett*. **1984**, *25*, 999-1000.
11. All the cyclopentene carbothioates **10a-d** and **11a** exhibited sharp peaks due to SCH_3, CH_3 and OCH_3 in their ^1H and ^{13}C NMR spectra.
12. Asokan, C.V., Ila, H.; Junjappa H. *Synthesis* **1987**, 284-285.
13. Asokan, C.V., Ila, H.; Junjappa H. *Tetrahedron Lett*. **1985**, *26*, 1087-1090.
14. Cyclopentene dithioacetals **14** (R^2=H) could not be isolated from the carbinols **8** obtained by borohydride reduction.
15. (a) Chauhan, S.M.S.; Junjappa, H. *Tetrahedron* **1976**, *36*, 1779-1787. (b) Thuillier, A.; Vialle, J. *Bull. Soc. Chim. Fr*. **1962**, 2182-2186.

(*Received in UK* 11 *August* 1993; *revised* 1 *October* 1993; *accepted* 8 *October* 1993)