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Facile One Pot Thermal Dehydration and Dethioacetalization of β-Hydroxydithioacetals with Dimethyl sulphoxide : Synthesis of α,β-Unsaturated Aldehydes

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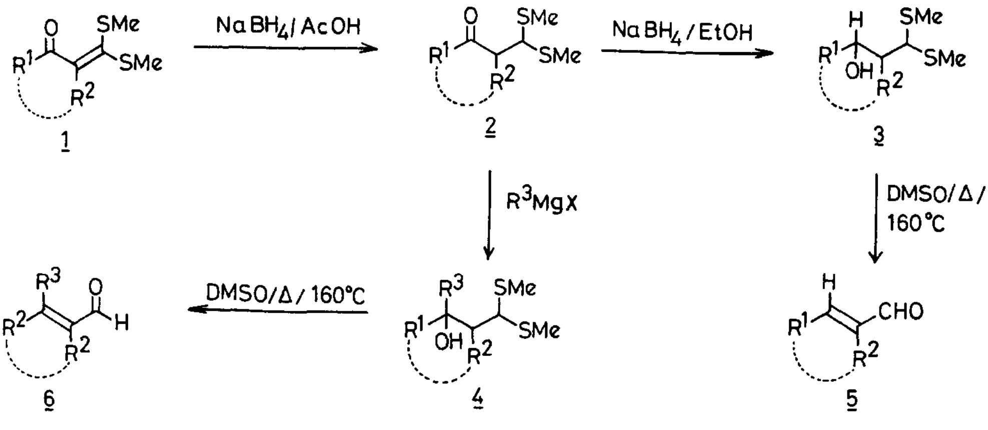
Abstract: *The acyclic and cyclic ß-hydroxydithioacetals 3a-m and 4a-b obtained by sodium borohydride reduction (or Grignard addition) of the corresponding ß-oxodithioacetals 2a-m are shown to undergo facile one pot thermal dehydration and dethioacetalization in the presence of dimethyl sulphoxide to afford the corresponding ene- and polyene aldehydes 5a-m and 6a-b in good yields. The probable mechanism of dethioacetalization with dimethyl sulphoxide has also been discussed.*

We have recently reported that α-oxoketene dithioacetals 1 undergo highly regio- and chemoselective 1,4-reduction on treatment with sodium borohydride in the presence of acetic acid to afford the corresponding ß-oxodithoacetals 2 in good yields[1] (Scheme 1). These ß-oxodithioacetals are masked ß-ketoaldehydes where the more reactive aldehyde function is protected by dithioacetal moeity and consequently various organometallic and hydride reagents add to ketone carbonyl of 1 to afford ß-hydroxydithioacetals 3 or 4 (Scheme 1). In our recent work, we have utilized these intermediates for the synthesis of sulfur free condensed aromatics [2a] and polyenes [3] by nucleophilic addition of allyl, benzyl and 1- or 2-(napththylmethyl)magnesium halides to 2 followed by cycloaromatization of the resulting carbinols in the presence of boron trifluoride etherate. This aromatic annelation via ß-oxodithioacetals 2 became important since the corresponding α-oxoketene dithioacetals underwent sequential 1,4 followed by 1,2-addition with benzyl[2b] and 2-(naphthylmethyl) [2a] Grignard reagents to afford the corresponding aromatic compounds with benzyl/(2-naphthylmethyl) substituents in place of easily removable thiomethyl group. These studies prompted us further to explore the synthetic potentials of ß-oxodithioacetals for other important transformations. In the present work we have converted 2 to ß-hydroxydithioacetals 3 by sodium borohydride (or addition of RMgI) reduction and examined their synthetic applications to afford the corresponding enedithioacetals 7, ene- and polyene aldehydes 5 - 6 and the enones 10 (Scheme 1-3). Thus a facile one pot procedure for thermal dehydrative dethioacetalization of



Scheme 1

ß-hydroxydithioacetals **3** with dimethyl sulphoxide to the corresponding enealdehydes has been developed and the results of these studies along with the mechanistic details are reported herein.

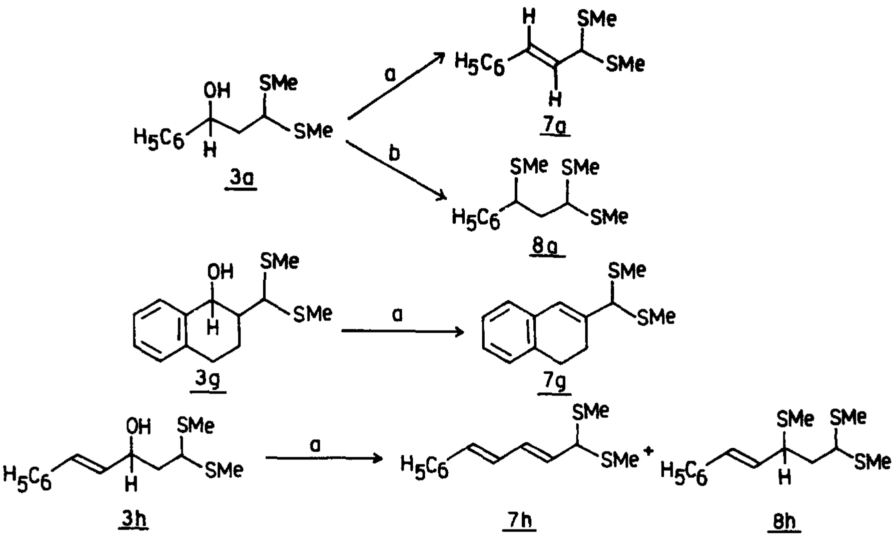
RESULTS AND DISCUSSION

Preparation of β-Hydroxydithioacetals

The desired ß-hydroxydithioacetals **3a-m** required for the present study were obtained in nearly quantitative yield by reduction of the corresponding ß-oxodithioacetals **2a-m** with sodium borohydride in ethanol (Scheme 1 and Table). The products **3a-m** were found to be stable and a few selected compounds were characterized by analytical and spectral data. However the isolation of **3** was not necessary and they were used for subsequent transformation without further purification. Also, the carbinols **4a** and **4b** were prepared by addition of methyl and phenyl Grignard reagents respectively to ß-oxodithioacetal **2a** (Table). This procedure provides an easy access for ß-hydroxydithioacetals which are masked aldol equivalents. A few of the related 1,3-dithiane analogs of **3** are reported in the literature which are prepared by ring opening of epoxides by lithio 1,3-dithiane[4].

Dehydration and Dethioacetalization of β-Hydroxydithioacetals 3

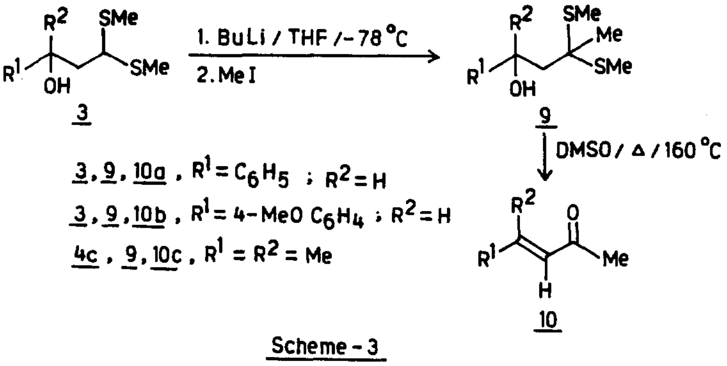
ß-Hydroxydithioacetals **3** were considered excellent precursors for the synthesis of the corresponding enedithioacetals **7** which are useful substrates for regioselective metallation studies[5]. However, attempted dehydration of **3a** under thermal conditions (boiling ethylene glycol, xylene) or in the presence of various dehydrating agents (I_2/C_6H_6, PTSA/C_6H_6, $KHSO_4$, DMF/$POCl_3$, Py^+Tos^-/CCl_4, Ac_2O) did not meet with desired success, either starting material was recovered unchanged or the complex mixtures were formed. The presence of two methylthio groups in **3a** appears to complicate the reaction and the formation of tris(methylthio)propane **8a** was observed in varying amounts in most of the experiments. However **3a** and **3g** could be dehydrated to the respective enedithioacetals **7a** and **7g** with $BF_3.Et_2O/C_6H_6$ at room temperature under controlled conditions (Scheme 2). The ß-styryl hydroxydithioacetal **3h** however afforded the mixture of enedithioacetal **7h** and the corresponding trismethylthio compound **8h** under identical conditions.



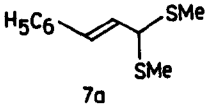
a, BF_3·Et_2O / C_6H_6 / RT ; b, BF_3·Et_2O / C_6H_6 / Δ

Scheme - 2

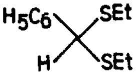
Having little success with selective dehydration of **3** to **4**, we next examined the hydrolysis and dehydration (stepwise or concurrent) of ß-hydroxydithioacetals **3**, so that these intermediates form an excellent group of precursors for the synthesis of the corresponding ene- and polyene aldehydes. However, direct hydrolysis of **3a** with reported reagents (HgO, HgO/CdCO$_3$, NBS, HgO/BF$_3$.Et$_2$O, Hg(OAc)$_2$/BF$_3$.Et$_2$O)[6] posed difficulties and the initial experiments failed to produce either the hydroxyaldehyde or the cinnamaldehyde **5a**. In few cases, cinnamaldehyde was obtained in low yields (20-30%) with poor material balance. We therefore decided to look for more efficient reagents that could simultaneously affect both dehydration and hydrolysis so that one pot conversion of ß-hydroxydithioacetals **3** or **4** to the corresponding enealdehydes **5** or **6** is available. Among others, dimethyl sulphoxide was first examined since this reagent is known to be a versatile dehydrating agent[7]. Also the combination of dimethyl sulphoxide with iodine[8a], t-butyl bromide[8b] or HCl[8c] are reported to hydrolyze dithioacetals and 1,3-dithianes to the corresponding carbonyl compounds in facile manner. We had recently described[9] in a preliminary communication that just the dimethyl sulphoxide itself in the absence of any other reagent is capable of hydrolysing both acyclic and cyclic dithioacetals to the corresponding carbonyl compounds in high yields under thermal and neutral conditions. We have now discovered that dimethyl sulphoxide is remarkably effective for both concurrent dehydration and dethioacetalization of **3** to the corresponding ene and polyene aldehydes (Scheme 1, Table). In a typical experiment, when **3a** was heated in dimethyl sulphoxide (4 eqv.) at 160 °C for 3-4 hr, work-up of the reaction mixture afforded cinnamaldehyde **5a** in 91% yield (Scheme 1, Table). Similarly the other substituted **5b-e** and the cyclic **5f-g** enealdehydes were obtained in 63-94% overall yields (Table). The transformation was equally facile when the ß-hydroxydithioacetals **3h-j** were heated with DMSO under identical conditions to afford the corresponding 5-substituted 2,4-dienealdehydes **5h-j** in good yields.



Scheme - 3



7a



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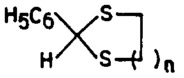
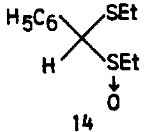


12, n = 1
13, n = 2



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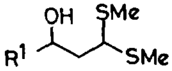
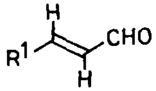
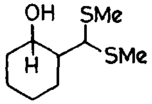
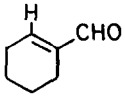
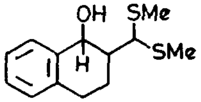
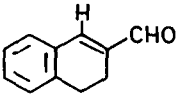
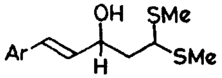
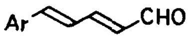
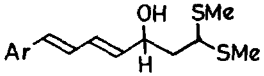
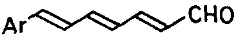
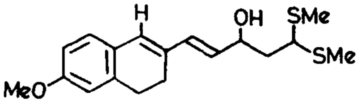
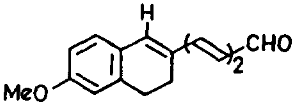
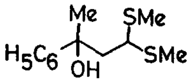
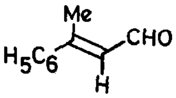
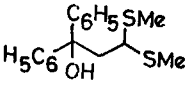
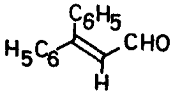
Also the acyclic **3k-l** and the cyclic **3m** dienyl hydroxydithioacetals underwent facile dehydration and dethioacetalization to yield the corresponding triene aldehydes **5k-m** under similar conditions (Table). The carbinols **4a-b** obtained by addition of Grignard reagents to **2a** afforded the corresponding ß-substituted cinnamaldehydes **6a-b** in good yields (Table).

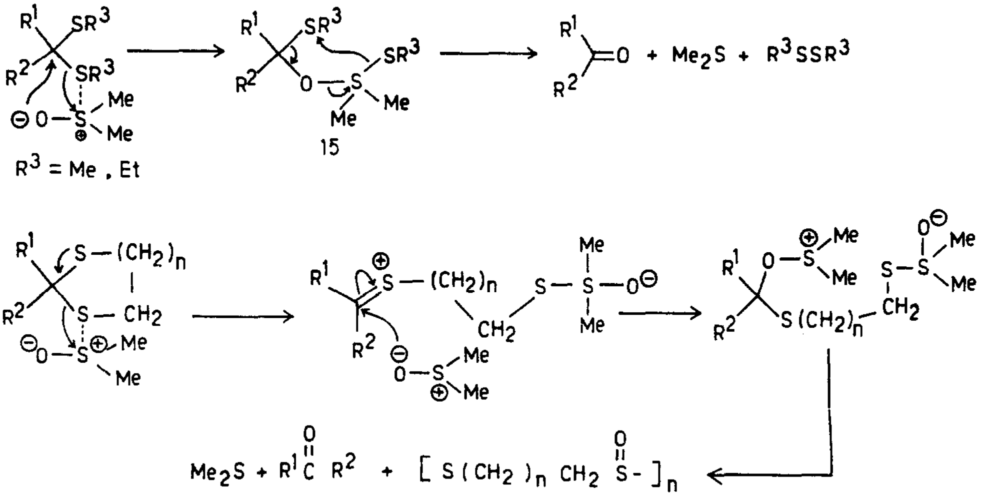
We have also examined the deprotonation and alkylation of **3** in presence of n-butyllithium with a view to convert the resulting ß-hydroxydithioketals **9** to the corresponding enones **10** through the reaction sequence shown in the Scheme 3. The carbinol **3a** on treatment with n-butyllithium (2.5 eqv.) followed by alkylation with methyl iodide afforded the ß-hydroxydithioketal **9a** in quantitative yield. The ketal **9a** on heating in DMSO as described earlier yielded the corresponding enone **10a** in 65% yield. Similarly **9b** and **9c** were prepared as above from **3b** and **4c** respectively and converted to the corresponding enones **10b-c** in good yields. However, the alkylation of **3** with higher alkyl halides to give the corresponding thioketals was not satisfactory.

Mechanistic Studies on DMSO Assisted Dethioacetalization of Dithioacetals and β-Hydroxydithioacetals

Hydrolysis of thioacetals and 1,3-dithianes with DMSO in the presence of iodine[8a], t-butyl chloride[8b] and dil HCl[8c] has been reported in the literature. The halosulfonium ion generated *insitu* has been suggested as the intermediate responsible for the facile cleavage of C-S bond in these reactions. However dethioacetalization of thioacetals in DMSO alone at higher temperature appeared to be interesting and different from other mechanisms[9]. We have therefore examined in some detail, the possible mechanistic pathways involved in these transformations. A few of the dithioacetals **7a**, **11**, dithiolan **12** and 1,3-dithiane **13** were selected for the present study. Dimethyl sulphoxide was freed from acidic impurities and other contaminants (by keeping over CaH_2 and vacuum distillation) and the pH of the reaction mixture was found to be neutral (pH = 7) only. However, dimethyl sulphoxide (DMSO) is known to undergo decomposition [10] upon prolonged heating and this complicates the

Table 1 : Synthesis of Enealdehyde from ß-hydroxydithioacetals

Entry	**3, 4**	**5, 6**	% Yield
			
1.	**3a**, $R^1 = C_6H_5$	**5a**, $R^1 = C_6H_5$	90
2.	**3b**, $R^1 = 4\text{-MeOC}_6H_4$	**5b**, $R^1 = 4\text{-MeOC}_6H_4$	95
3.	**3c**, R^1 = 2-Furyl	**5c**, R^1 = 2-Furyl	82
4.	**3d**, R^1 = 2-Thienyl	**5d**, R^1 = 2-Thienyl	63
5.	**3e**, R^1 = Me	**5e**, R^1 = Me	63
6.	 **3f**	 **5f**	65
7.	 **3g**	 **5g**	63
			
8.	**3h**, Ar = C_6H_5	**5h**, Ar = C_6H_5	86
9.	**3i**, Ar = 4-MeOC_6H_4	**5i**, Ar = 4-MeOC_6H_4	89
10.	**3j**, Ar = 2-Furyl	**5j**, Ar = 2-Furyl	89
			
11.	**3k**, Ar = C_6H_5	**5k**, Ar = C_6H_5	72
12.	**3l**, Ar = 4-MeOC_6H_4	**5l**, Ar = 4-MeOC_6H_4	81
14.	 **3m**	 **5m**	74
15.	 **4a**	 **6a**	89
16.	 **4b**	 **6b**	92



Scheme - 4

attempts to exclude impurities at higher temperature although the pH of the reaction mixture remained unaltered after completion of the reaction. Our preliminary studies revealed that the reaction does not proceed to completion unless the DMSO is present in excess (1:5 ratio) in the reaction mixture and the temperature is maintained below 140°C. There was no difference in the yields and rate of formation of carbonyl compounds when either the pure dried DMSO or its commercial sample (98%) was employed[11], though the dethioacetalization with water free sample demonstrates that the origin of carbonyl oxygen is from DMSO itself[12].

Dimethyl sulphoxide is known to oxidize the sulphides to the corresponding sulphoxides[13], therefore the possibility of intermediacy of mercaptal sulfoxide formation was examined, since these compounds are reported to undergo pyrolytic decomposition to the carbonyl compounds[14]. Attempts to trap the sulphoxide **14** during dethioacetalization of **11** were not successful, though the seperate experiments proved that the sulphoxide **14** on heating in DMSO afforded the benzaldehyde in quantitative yield. The reported yields of sulphoxides by DMSO oxidations are not very high and only the limited number of sulfides could be oxidized by this reagent[13]. Therefore it is very unlikely that the present reaction proceeds by prior oxidation of thioacetals to sulfoxides.

A careful analysis of the reaction mixture revealed the formation of dimethyl sulphide and dimethyl disulphide (from **7a**) or diethyl disulphide (from **11**) as bye-products in the hydrolysis of dimethyl and diethylmercaptals **7a** and **11** respectively. On the otherhand, the residues from dithiolan **12** and 1,3-dithiane **13** obtained after isolation of carbonyl compounds were found to be only intractable polymeric mixtures. It is therefore possible to propose a tentative mechanism to account for the formation of dimethyl sulphide and dialkyl disulfide and other observations (Scheme 4). The reaction is probably initiated by association of dithioacetal sulfur with dimethyl sulphoxide thus assisting the cleavage of one of the C-S bonds of dialkyl mercaptal and subsequent nucleophilic attack of sulphoxide oxygen on electrophilic carbon of thioacetal to give the corresponding sulphoxonium intermediate **15** which spontaneously cleaves to give carbonyl compound, Me_2S and Me_2S_2 (or Et_2S_2) (Scheme 4). However the mechanism of the cleavage of cyclic dithioacetal and 1,3-dithiane under the described reaction conditions appears to be different from the acyclic one and probably involves two molecules of DMSO for complete hydrolysis yielding the departing sulfur residue as polymeric mixtures (Scheme 4)[12].

In conclusion, we have developed a facile one pot high yield procedure for thermal dehydration and dethioacetalization of ß-hydroxydithioacetals to the corresponding ene- and polyene aldehydes in the presence of dimethyl sulphoxide. The usual methods for ene and polyene aldehydes involve condensation of aldehyde with polyene esters (Reformatsky, Wittig or its variants) followed by two step conversion of ester to an aldehyde (reduction and their partial reoxidation). Dimethyl sulphoxide has been shown to be useful reagent for hydrolysis of 1,3-dithianes and dithioacetals.

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 ^1H NMR spectra were recorded on a Varian EM-390 (90 MHz) spectrometer in $CDCl_3$ or CCl_4 using TMS as internal standard and chemical shifts are expressed in δ(ppm) units downfield from TMS. Elemental analysis were performed on a Heraeous CHN-O-Rapid Elemental analyzer.

Commercially available AR grade DMSO was dried by refluxing over calcium hydride followed by distillation under reduced pressure.[7b] The pH of DMSO was determined by Systronics Digital pH meter 335 prior to the reaction. All the starting ß-oxodithioacetals **3a-m** were prepared according to the earlier reported procedures.[1]

General Procedure for Preparation of β-Hydroxydithioacetals 3a-m

To a well stirred solution of **2** (10mmol) in absolute ethanol (30ml), $NaBH_4$ (25mmol) was added and the contents were refluxed for 2hr (monitored by TLC). The ethanol was evaporated and the residue was poured over saturated solution of NH_4Cl. It was extracted with $CHCl_3$ (2x25ml), washed with water (3x50ml), dried (Na_2SO_4) and evaporated to give **3** in quantitative yield. The carbinol **3a** was further purified for spectral and analytical data by passing through a silica gel column using hexane as eluent. The spectral data is in agreement with the data reported earlier[15].

The other ß-hydroxydithioacetals **3b-m** were obtained from the corresponding **2b-m** and they were used as such for further transformation.

General Procedure for Preparation of β-Methyl/phenyl β-hydroxy dithioacetals 4a-c

To an ice cooled solution of methyl/phenyl magnesium halide (30mmol) [prepared from Mg turnings (1.0g) and MeI/PhBr (30mmol)] in dry ether (50ml), a solution of **2a** in dry benzene (25ml) was added dropwise under nitrogen atmosphere. The reaction mixture further stirred for 45 min and then brought to room temperature, treated with saturated NH_4Cl solution (75ml) and extracted with water (2x75ml), dried (Na_2SO_4) and evaporated under reduced pressure to afford nearly quantitative yields of **4a-c** which were used as such for subsequent transformation without further purification.

General Procedure for Alkylation of β-Hydroxydithioacetals 4a-c : Synthesis of β-Hydroxydithioketals 9a-c

To a stirred solution of ß-hydroxydithioacetals (**4a-c**) (10mmol) in THF (15ml) at -78°C under N_2 atmosphere was added n-BuLi (25mmol) in THF (10ml) over a period of 5min. The reaction mixture was further stirred for 30min followed by addition of MeI (30mmol) in THF (5ml) at -78°C. After further stirring for 15min at -78°C, it was brought to room temperature, poured over saturated NH_4Cl solution and extracted with ether (2x50ml). The combined ether extract were washed with water (3x50ml), dried (Na_2SO_4) and concentrated to afford **9a-c** in quantitative yields, which were used for further reaction.

General Procedure for $BF_3.Et_2O$ Catalyzed Dehydration of β-Hydroxydithioacetals 3a, 3g and 3h

To a well stirred solution of ß-hydroxydithioacetals (10mmol) in dry C_6H_6 (20ml) under N_2 atmosphere, $BF_3.Et_2O$ (2ml) was added and the reaction mixture was further stirred at room temperature for 3hr (monitored by TLC). It was then poured into ice-cold water (50ml), the benzene layer was separated and the aqueous layer was extracted with benzene (2x25ml). The combined extracts were washed with 5% $NaHCO_3$ solution (2x25ml), water (2x100ml), dried (Na_2SO_4) and evaporated under reduced pressure to give viscous residues which were chromatographed over silica gel (hexane as eluent) to give the pure products. Column chromatography of the reaction mixture from **3h** afforded first **7h** and further elution with hexane gave **8h**.

When the above reaction with **3a** was carried out at high temperature (70°C) under identical conditions and work-up, the product **8a** was isolated.

3,3-Bis(methylthio)-1-phenyl-1-propene (7a). Yellow viscous liquid; 89%; IR(neat) 2940, 1442cm^{-1}; $\delta_H(CCl_4)$ 2.21 (s, 6H, SCH_3), 4.32 [d, J = 7Hz, 1H, $CH(SCH_3)_2$], 6.20 (dd, J = 7 and 15Hz, 1H, =CH), 6.62 (d, J = 15Hz, 1H, =CH), 7.26-7.64 (m, 5H, ArH). (Anal. Calcd. for $C_{11}H_{14}S_2$: C, 62.80; H, 6.70. Found : C, 63.01; H, 6.93%).

2,2-Bis(methylthio)methyl-3,4-dihydronaphthalene (7g). Yellow viscous liquid; 83%; IR(neat) 2910, 1505, 1446, 1260 cm^{-1}; $\delta_H(CCl_4)$ 2.02 (s, 6H, SCH_3), 2.31 (t, J = 6Hz, 2H, CH_2), 2.76 (t, J = 6Hz, 2H, CH_2), 4.18 [brs, 1H, $CH(SCH_3)_2$], 6.34 (brs, 1H, =CH), 6.89-7.26 (m, 4H, ArH). (Anal. Calcd. for $C_{13}H_{16}S_2$: C, 66.05; H, 6.82. Found : C, 66.17; H, 6.94%).

1,3,3-Tris(methylthio)-1-phenylpropane (8a). Colourless viscous liquid; 63%; IR(neat) 2941, 1560, 1445 cm^{-1}; $\delta_H(CCl_4)$ 1.99 (s, 3H, SCH_3), 2.03 (s, 6H, SCH_3), 2.05-2.15 (m, 2H, CH_2), 3.52 (t, J = 7Hz, 1H, CH), 4.01 [t, J = 7Hz, 1H, $CH(SCH_3)_2$], 7.20 - 7.48 (m, 5H, ArH). (Anal. Calcd. for $C_{12}H_{18}S_3$: C, 55.76; H, 7.02. Found : C, 55.98; H, 7.23%).

1,1-Bis(methylthio)-5-phenyl-1,3-pentadiene (7h). Yellow viscous liquid; 53%; IR(neat) 2920, 1580, 1470 cm^{-1}; $\delta_H(CCl_4)$ 2.08 (s, 6H, SCH_3), 4.28 [d, J= 7Hz, 1H, $CH(SCH_3)_2$], 5.98 (dd, J= 7 and 15Hz, 2H, =CH), 6.29 (dd, J=9 and 15Hz, 1H, =CH), 6.49 (d, J= 15Hz, 1H, =CH), 7.11-7.43(m, 5H, ArH). (Anal.

Calcd. for $C_{13}H_{16}S_2$: C, 66.05; H, 6.82. Found : C, 66.26; H, 6.97%).

3,5,5-Tris(methylthio)-1-phenyl-1-pentene (8h). Yellow viscous liquid; 34%; IR(neat) 2954, 1548, 1449 cm^{-1}; $\delta_H(CCl_4)$ 1.98 (s, 3H, SCH_3), 2.00 (s, 6H, SCH_3), 1.81 - 2.13 (m, 2H, CH_2), 3.58 (t, J = 9Hz, 1H, CH), 3.81 [t, J = 9Hz, 1H, CH(SCH_3)$_2$], 6.02 (dd, J = 9 and 15Hz, 1H, =CH), 6.51 (d, J = 15Hz, 1H, =CH), 7.21-7.60 (m, 5H, ArH). (Anal. Calcd. for $C_{14}H_{20}S_3$: C, 59.10; H, 7.09. Found : C, 59.34; H, 7.29%).

General Procedure for Dehydration and Dethioacetalization of β-Hydroxydithioacetals with Dimethylsulphoxide : Synthesis of Ene- and Polyene Aldehydes 5a-m, 6a-b and Enones 10a-c

A solution of β-hydroxydithioacetals (10mmol) and DMSO (3.9ml, 50mmol) was heated at 160°C for 3-5hr (monitored by TLC). It was cooled to room temperature and then poured over saturated NH_4Cl solution and extarcted with ether (2x50ml). The combined extracts were washed with water (2x50ml), dried (Na_2SO_4) and evaporated under reduced pressure to afford the crude products 5 which were purified by passing through neutral alumina using EtOAc/hexane (2:98) as eluent (Table). All the known aldehydes were characterised by comparison of their physical and spectral data with the reported values. The spectral and analytical data of unknown compounds is given below.

trans-Cinnamaldehyde (5a). Colourless liquid; superimposable IR and NMR spectra[16a].

4-Methoxycinnamaldehyde (5b). White crystals; m.p. 58-59°C(lit.[17] m.p. 61°C); Spectral and analytical data as reported [17].

3-(2-Furylacrolein) (5c). Brown solid; m.p. 57°C (lit.[16b,18] m.p. 54°C); spectral and analytical data as described earlier [18].

3-(2-Thienylacrolein) (5d). Viscous liquid; spectral and analytical data as reported [16c,19].

trans-2-Butenal (5e). Colourless liquid; b.p. 102-103°C (lit.[16d] 104-105°C); spectral and analytical data as described earlier [16d].

1-Cyclohexen-1-carboxaldehyde (5f). Colourless liquid; b.p. 80-81°C at 20mm (72°C[16e] at 15mm); spectral and analytical data reported [16e,20].

3,4-Dihydronaphthalene 2-carboxaldehyde (5g). Viscous liquid[21]; IR(neat) 2926, 1691, 1533 cm^{-1}; $\delta_H(CCl_4)$ 2.50 (m, 2H, CH_2), 2.88 (m, 2H, CH_2), 7.28 (brs, 5H, =CH, ArH), 9.78 (s, 1H, -CHO). (Anal. Calcd. for $C_{11}H_{10}O$: C, 83.51; H, 6.37. Found : C, 83.79; H, 6.51%).

5-Phenyl-2,4-pentadienal (5h). Yellow solid; m.p. 40-41°C (lit.[16f] m.p. 42°C); spectral and analytical data as described earlier [16f].

5-(4-Methoxyphenyl)-2,4-pentadienal (5i). Yellow solid; m.p. 78-79°C (lit.[17] m.p. 80°C); spectral and analytical data as reported [17].

5-(2-Furyl)-2,4-pentadienal (5j). Colourless solid; m.p.63-64°C(lit.[22] m.p. 65-66°C);spectral and analytical data as reported [22].

7-Phenyl-2,4,6-heptatrienal (5k) Yellow solid; m.p.112-113°C(lit.[23] m.p. 115°C); spectral and analytical data as reported [23].

7-(4-Methoxyphenyl)-2,4,6-heptatrienal (5l). Brown solid; m.p. 135-136°C(lit.[24] m.p. 138°C); spectral and analytical data as reported [24].

5-(6-Methoxy-3,4-dihydronaphthyl)-2,4-pentadienal (5m). Yellow solid; m.p. 108°C; IR(KBr) 3090, 1700, 1610, 1120 cm^{-1}; δ_H(CDCl$_3$) 2.28-2.56(m, 2H, -CH_2), 2.71-2.98(m, 2H, CH_2), 3.80 (s, 3H, OCH_3), 6.16 (dd, J = 15 and 4.5Hz, 1H, =C*H*), 6.61-6.90(m, 5H, =C*H*, Ar*H*), 7.09-7.48(m, 2H, Ar*H*), 9.62 (d, J = 4.5Hz, 1H, -C*H*O). (Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found : C, 80.19; H, 6.58%).

trans-3-Phenyl-2-butenal (6a). Pale yellow solid; m.p. 90-91°C(lit.[25] m.p. 95°C); IR(KBr) 3095, 1680, 1235 cm^{-1}; δ_H(CCl$_4$) 2.55 (s, 3H, CH_3), 6.38 (d, J = 6Hz, 1H, =C*H*), 7.25-7.68(m, 5H, Ar*H*), 10.28 (d, J = 6Hz, 1H, -C*H*O). (Anal. Calcd. for $C_{10}H_{10}O$: C, 82.15; H, 6.89. Found : C, 82.28; H, 7.06%).

3,3-Diphenyl-2-propenal (6b). Pale yellow solid; m.p. 40-41°C (lit.[16g] m.p. 44°C); spectral and analytical data as described earlier [16g].

4-Phenyl-3-buten-2-one (10a). Colourless solid; 81%; m.p. 39-40°C (lit.[16h] m.p. 42°C); spectral and analytical data as described earlier [16h].

4-(4-Methoxyphenyl)-3-buten-3-one (10b). Colourless solid; 86%; m.p. 69-70°C(lit.[16i] m.p. 73°C); spectral and analytical data as described earlier [16i].

4-Methyl-3-penten-2-one (10c). Colourless viscous liquid; 79%; spectral and analytical data as reported [16j].

Typical Experiment to trap Dimethylsulphide and Dialkyldisulphide in DMSO induced Dethioacetalization

A solution of **7a** or **11** (50mmol) in DMSO (20ml, 225mmol) was heated for 5hr in a round bottom flask (100ml) and the vapours were condensed in a receiving flask containing a solution of MeI (7.05g, 50mmol) in ether. The ether solution was stirred for 4hr at room temperature followed by addition of hexane and left overnight. The precipitate was filtered, washed with ether (2x10ml) followed by hexane (2x15ml). Recrystallization from ether/hexane gave a colourless crystalline solid (11.5g), which was characterised as trimethyl sulphonium iodide with m.p. 191-192°C(lit.[26] m.p. 193-194°C). The residue in the reaction flask was column chromatographed (hexane) to give enealdehyde and dimethyl disulphide (4.7g, b.p. 105°C) (lit.[16k] 109.7°C) or diethyl disulphide 147-148°C (lit.[16l] 150°C).

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