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REGIO- AND CHEMOSELECTIVE CONJUGATE 1,4-REDUCTION OF α-OXOKETENE DITHIOACETALS WITH SODIUM BOROHYDRIDE AND SODIUM CYANOBOROHYDRIDE

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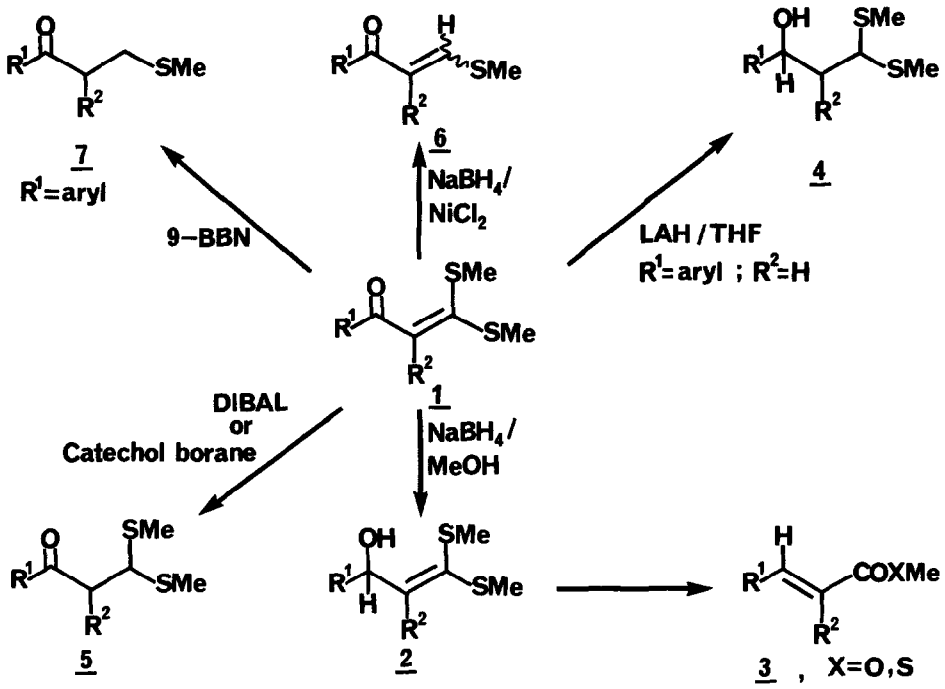
Summary: The α-oxoketene dithioacetals 1 are shown to undergo conjugate 1,4-reduction in highly regio- and chemoselective manner with sodium borohydride in acetic acid to afford the corresponding β-oxodithioacetals 5 in good yields. These results have been rationalized according to HSAB principle in terms of 'hard soft affinity inversion' concept. The reduction of 1 with sodium cyanoborohydride also proceeds in 1,4-conjugate addition-elimination manner to afford the corresponding vinylogous thiolesters 6 in good yields.

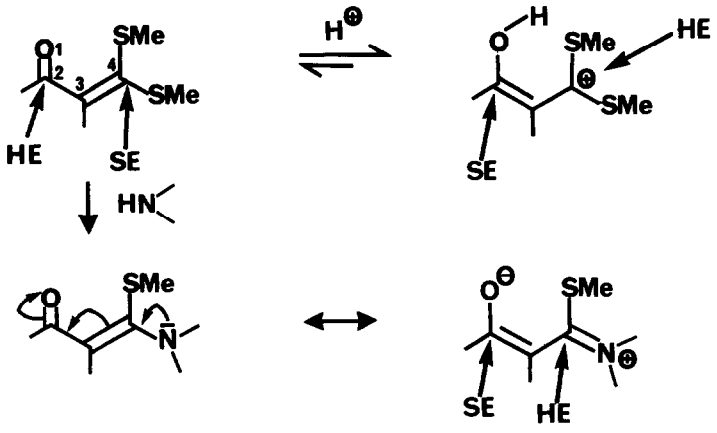
The reduction of α-oxoketene dithioacetals can follow different pathways depending on the nature of reducing agents and reaction conditions. Simple carbonyl group reduction affords the corresponding allyl alcohols in high yields[1,2]. Alternatively, the reduction can also be effected at C=C and C-S bonds or at both the carbonyl and olefinic functionalities[1]. Therefore, development of the specific procedures with effective regiocontrol of the reduction pathways assumes considerable synthetic importance and enhances the synthetic utility of these intermediates. Thus 1,2-reduction of carbonyl group by sodium borohydride in methanol has been shown to yield the corresponding carbinolacetals 2, which on BF_3-etherate assisted methanolysis or hydrolysis yield the corresponding α, β-unsaturated O-methyl or S-methyl esters 3 respectively[3,4]. These transformations have been shown to involve reductive 1,3-carbonyl transpositions (Scheme 1). Gammill[5] has reported that the α-oxoketene dithioacetals undergo regio- and stereospecific reduction at C_1 and C_2 to afford the corresponding β-hydroxydithioacetals 4 in the presence of lithium aluminium hydride. The mechanism of the reduction was shown to proceed by initial regiospecific reduction of carbonyl group followed by intramolecular hydroalumination of the double bond. We had earlier reported that the α-oxoketene dithioacetals undergo chemoselective reduction with Nickel Boride ($NaBH_4$-$NiCl_2$) to afford the corresponding vinylogous thiolesters 6 in moderate to good yields (Scheme 1)[6]. Gammill[7] and coworkers have also reported the reduction of 1 with electrophilic reducing agents such as DIBAL, 9-BBN and catecholborane. In these studies, while DIBAL and catecholborane gave predominantly the 1,4-reduction products 5, the 9-BBN affected the further reduction to afford the ketosulphide 7. In the case of DIBAL reductions, triethylamine was added to suppress the 1,2-reduction process. The mechanism of these conjugate reductions by electrophilic reagents appears



Scheme 1

to follow the initial complex formation with the carbonyl oxygen followed by double bond reduction probably through intramolecular hydride delivery.

Our continued interest in the chemistry of α-oxoketene dithioacetals has been centred around exploitation of differential electrophilicity of 1,3-electrophilic centres in these systems for regioselective C-C, C-H and C-heteroatom bond forming reactions to construct various carbo- and heterocyclic ring systems[8]. The two electrophilic carbon atoms in these systems can be considered as hard (carbonyl carbon) and soft (bismethylthio β-carbon) according to HSAB principle and should accordingly react with hard and soft nucleophiles leading to new regioselective bond forming reactions[9,10]. Thus the hard nucleophiles such as organolithium, organomagnesium reagents, lithium aluminium hydride and sodium borohydride (in methanol) have been shown to react with α-oxoketene dithioacetals in 1,2-manner, while the softer organocuprates and the other delocalized anions undergo 1,4-conjugate addition-elimination or 1,4-addition followed by 1,2-addition[10] (in the case of delocalized Grignard reagents). Recently a more sophisticated interpretation of ambident reactivity of α,β-enones has been proposed in which the inversion of relative atomic coefficients occurs due to complexation with hard cations[11]. Thus the coefficient C_2^2 is smaller than that of C_4^2 in the uncomplexed species while in the case of complexed or protonated species, C_2^2 becomes larger than C_4^2 resulting in the change of reactivity of the enones towards a given nucleophile. This hard-soft affinity inversion, if achieved under a suitable reaction conditions, the softer β-carbon of the oxoketene dithioacetals can be converted into hard electrophile thus permitting the charge controlled attack by the hard



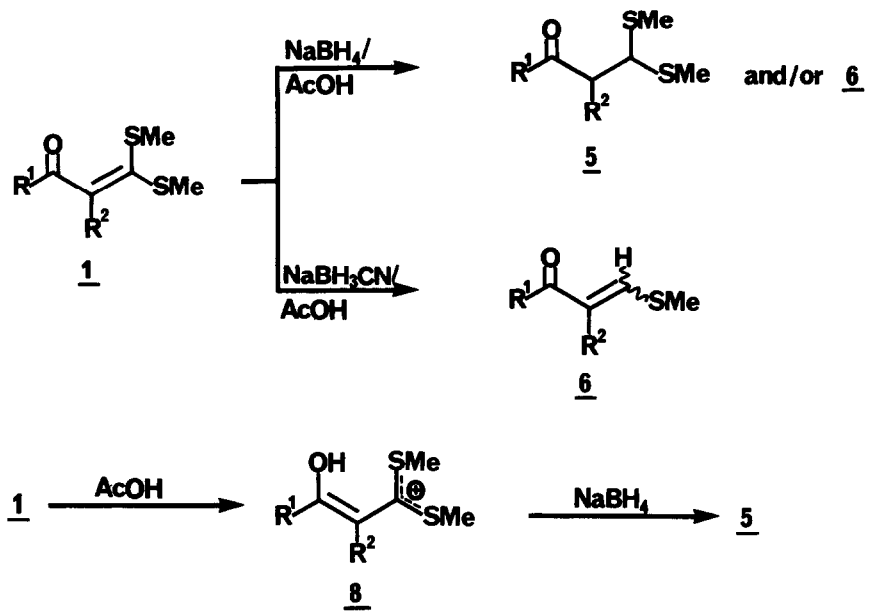
Scheme 2. Hard soft affinity inversion in oxoketene dithioacetals;

SE = Soft electrophile; HE = Hard electrophile

nucleophiles in the 1,4-fashion. Further, such a charge inversion will be greatly facilitated by the cation stabilizing ability of the adjacent sulfur atoms in these systems. Thus the α-oxoketene dithioacetals are an attractive group of intermediates for the hard-soft affinity inversion[12] studies which can be achieved either by changing the reaction conditions or by replacing one of the methylthio groups by an amino group (Scheme 2) to afford the corresponding S,N-acetals which exhibit clear 1,4-addition mode towards hard nucleophiles. We have successfully utilized this concept in our recent report for the regioselective synthesis of 5- and 3-alkylthioisoxazoles by subjecting the α-oxoketene dithioacetals to react with hydroxylamine under different pH conditions. Thus the hydroxylamine at a pH range between 5-9 follows the oxime pathway to afford the corresponding 5-alkylthioisoxazoles, while at pH 2.2, hydroxylamine nitrogen attacks the β-carbon to afford the corresponding 3-alkylthioisoxazoles in high yields[13]. These results manifestly agree with the hard-soft affinity inversion concept. We have further extended these studies to conjugate reduction of α-oxoketene dithioacetals with sodium borohydride in the presence of a strong proton donor solvent as a medium and our results are presented in this paper.

RESULTS AND DISCUSSION

When the α-oxoketene dithioacetal 1a was treated with four-fold excess of sodium borohydride in acetic acid as a solvent, the corresponding dihydrodithioacetal 5a was obtained in 80% yield (Table 1). No other side product of 1,2-reduction process was observed in the reaction mixture. When less than four equivalents of $NaBH_4$ was used, only an unreacted starting material was recovered along with 5a. The other representative examples undergoing this regioselective reduction are described in the Table 1. However, some substrates (entries 8 , 14

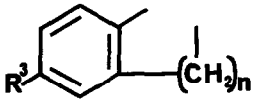


Scheme 3

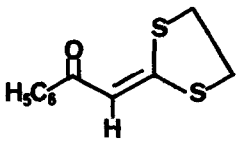
and 15) suffered elimination of thiomethyl group to afford the corresponding vinylogous thiol esters 6 in substantial yields, while 1i and 1p (entries 9 and 16) yielded only the corresponding 6i and 6p exclusively. Steric crowding appears to enhance the elimination of MeSH group in these systems. But in no case, the corresponding allylic alcohols or the products due to reduction of both double bond and the carbonyl group were observed. Interestingly the α-cinnamoylketene dithioacetals 1q and 1r and the corresponding α-(5-phenyl-2,4-pentadienoyl)ketene dithioacetals (1s) underwent chemoselective reduction of bis(methylthio) double bond to yield 5q-s respectively in good yields. However, the corresponding cyclic 1-phenyl-2-(1,3-thiolan-2-ylidene)ethanone 1t remained unchanged under similar reaction conditions while the corresponding six membered 2-(1,3-dithian-2-ylidene)-1-phenyl ethanone 1u gave the 1,4-reduced product 5u in 50% yield with excess of sodium borohydride (6 eqv).

The reduction of activated double bond with sodium borohydride has been observed in conjugated esters, nitroalkenes and enolacetates[14]. A few of the α, β-unsaturated ketones have also been shown to undergo 1,4-reduction with sodium borohydride in the presence of pyridine[15]. Marshall and co-workers[16] have reported the reduction of enamine double bond with sodium borohydride in the presence of acetic acid and proposed protonation-hydride transfer mechanism for the reduction. On the otherhand, in the reduction of isolated double bond with sodium borohydride, which is generally carried out in the presence of one or at best five equivalents of acetic acid, the hydroboration pathway was considered plausible[17,18]. In the present studies, the reduction of 1 to 5 with sodium borohydride in the presence of large excess of acetic acid (solvent medium) should proceed by initial protonation of 1 followed by a charge controlled

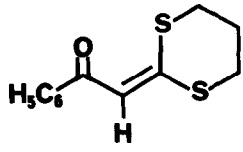
Table 1. Conjugate Reduction of α-Oxoketene Dithioacetals with Sodium Borohydride and Sodium Cyanoborohydride

Entry	R^1	R^2	Substrate	Products[a]	% Yield[a] 5, 6	Product[b]	% Yield[b] 6
1	C_6H_5	H	1a	5a	80	6a	76
2	4-$MeOC_6H_4$	H	1b	5b	76	6b	68
3	4-ClC_6H_4	H	1c	5c	71	6c	69
4	2-Naphthyl	H	1d	5d	69	6d	71
5	2-Thienyl	H	1e	5e	60	6e	73
6	2-Furyl	H	1f	5f	58	-	-
7	Me	H	1g	5g	55	6g	40
8	Me	Me	1h	5h+6h	30, 59	6h	64
9	C_6H_5	Me	1i	6i	- 70	6i	60
10	$-(CH_2)_3-$		1j	5j	65	6j	69
11	$-(CH_2)_4-$		1k	5k	68	6k	68
12	$-(CH_2)_5-$		1l	5l	90	-	-
13	 R^3=H; n=1		1m	5m	80	-	-
14	R^3=H; n=2		1n	5n+6n	65, 35	6n	89
15	R^3=MeO; n=2		1o	5o+6o	65, 35	6o	69
16	R^3=H; n=3		1p	6p	- 95	6p	78
17	$C_6H_5CH=CH-$	H	1q	5q	70	-	-
18	4-$MeOC_6H_4CH=CH-$	H	1r	5r	75	-	-
19	$C_6H_5(CH=CH)_2-$	H	1s	5s	76	-	-

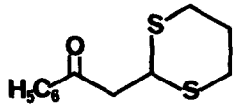
[a] From $NaBH_4$/AcOH reduction; [b] From $NaBH_3CN$/AcOH reduction



1t



1u



5u

1,4-hydride delivery as observed in the enamine reduction under similar reaction conditions. This was supported by carrying out reduction of 1a with $NaBH_4$/AcOH under varying conditions (Table 2). Thus when 1a was treated with sodium borohydride/AcOH in THF in the same stoichiometric ratio as reported by Hack[18] (diborane path) (run 1 and 2), no reduction was observed

Table 2: Reduction of Oxoketene Dithioacetal 1a with Sodium Borohydride in Acetic Acid

Run	Substrate 1a (mmol)	$NaBH_4$ (mmol)	AcOH (mmol)	Solvent (mL)	% Yield 1a	% Yield 5a
1	10	3.70	3.70	THF (5)	88	-
2	10	5.50	5.50	THF (5)	90	-
3	10	20.00	20.00	THF (13)	75	10
4	10	59.00	760.00	THF (130)	-	70

and unreacted 1 was recovered, whereas under Marshall's hydroboration conditions[17] (run 3), 5a was obtained only in 10% yield along with unreacted 1a. On the otherhand when 1a was treated with sodium borohydride with large excess of acetic acid[16], the yield of 5a was raised to 70% (run 4). It is therefore concluded that sodium borohydride/acetic acid reduction of 1 does not proceed through hydroboration and a mechanism involving protonation of oxoketene dithioacetal to give intermediate 8 followed by charge controlled hydride transfer to the β-carbon is suggested (Scheme 3). The mechanism is similar to the reduction of simple ketene dithioacetals with organosilicon hydride in the presence of trifluoroacetic acid[19].

Incidently it was considered of interest to examine the reduction of 1 with sodium cyanoborohydride which is softer reducing agent, with unique acid stability (among metal hydrides) and exhibits high regioselectivity in 1,4-addition mode to α, β-unsaturated ketones[20]. Thus when 1a was treated with sodium cyanoborohydride in refluxing acetic acid (12 h, pH 0.9), the corresponding vinylogous thiolester 6a was obtained in 76% yield, which is higher than that (56%) obtained by nickel boride reduction[6]. The method was found to be general with other ketene dithioacetals (1b-e, 1g-k and 1n-p) and yielded the corresponding vinylogous thiolesters (6b-e, 6g-k and 6n-p) in overall good yields (Table 1) except for 6g (entry 7). However in the case of cinnamoyl (1r) and the corresponding dienoyl (1t) ketene dithioacetals, reaction with sodium cyanoborohydride under similar conditions yielded complex mixture of products due to reduction of both styryl and bis(methylthio)methylene double bonds.

In summary, it has been demonstrated that the α-oxoketene dithioacetals are attractive substrates for many regioselective C-C, C-H and C-heteroatom bond forming reactions involving either 1,2- or 1,4-conjugate addition. The sodium borohydride reduction of 1 in methanol yields exclusively the corresponding carbinolacetals through 1,2-addition, while in the presence of excess of acetic acid only 1,4-reduction products are formed. These observations have been rationalized according to hard-soft-acid-base (HSAB) principle in terms of 'hard soft affinity inversion.

EXPERIMENTAL SECTION

Melting points were determined on a Thomas Hoover apparatus and are uncorrected. The IR spectra were obtained on a Perkin Elmer 297 Spectrophotometer. ^{1}H NMR spectra were recorded on Varian EM-390, 90MHz spectrometer and are reported in δ units downfield from Me_4Si. The coupling constants are given in Hertz(Hz). Mass spectra were obtained on a Jeol D-300 spectrometer. T.l.c. (silica gel, BDH) was used for monitoring the reactions.

All the oxoketene dithioacetals 1a-u required for the present investigation were prepared according to the earlier reported procedures[21-23].

General Procedure for Reduction of α-Oxoketene Dithioacetals with Sodium Borohydride in Acetic Acid:

To a well stirred solution of α-oxoketene dithioacetals (10 mmol) in glacial acetic acid (60 mL), sodium borohydride (40 mmol) was added slowly (portion wise) (30 min.) at 5-10°C. The reaction mixture was further stirred at room temperature for 3 hr (monitored by t.l.c.), poured into ice-cold water (100 mL), extracted with chloroform (3x50 mL). The combined organic layer was washed with water (3x100 mL), dried over sodium sulfate and concentrated to give the viscous residue, which on column chromatography over silica gel (hexane eluent) gave pure β-oxodithioacetals 5 and/or β-methylthioalkenyl ketones 6(from 1i and 1p). In the case of ketene dithioacetals 1h, 1n and 1o, column chromatography of reaction mixture (elution with hexane) gave first the corresponding β-oxodithioacetals 5h, 5n and 5o followed by the respective 6h, 6n and 6o.

In the case of ketene dithioacetal 1u, reduction was carried out with excess of $NaBH_4$(60 mmol) for prolonged time (12 hr.).

General Procedure for Reduction of α-Oxoketene Dithioacetals with Sodium Cyanoborohydride in Acetic Acid:

To a well stirred solution of α-oxoketene dithioacetals 1 (10 mmol) in acetic acid (30 mL), excess of sodium cyanoborohydride (1.95g, 30 mmol) was added in small portions (10 min.) and the reaction mixture was further stirred at room temperature (2 hr.), followed by refluxing for 6-10 hr. (monitored by t.l.c.). It was then cooled to room temperature, poured into crushed ice (150g) and extracted with $CHCl_3$ (3x50 mL). The organic layer was washed with saturated sodium bicarbonate solution, water (3x100 mL), dried over sodium sulfate and evaporated to give crude 6, which were purified by column chromatography over silica gel using EtOAc/hexane (1:9) as eluent.

All the known β-oxodithioacetals 5 and β-methylthioalkenyl ketones 6 were characterized by comparison of their melting points, NMR, IR spectra with those of reported data and of authentic samples. The spectral and analytical data for the unknown 5 and 6 are given below:

3,3-Bis(methylthio)-1-phenyl-1-propanone (5a); viscous liquid (lit.[7] superimposable IR and NMR).

3,3-Bis(methylthio)-1-(4-methoxyphenyl)-1-propanone (5b); m.p. 58-59°C (lit.[7] m.p. 56-57°C; superimposable IR and NMR).

3,3-Bis(methylthio)-1-(4-chlorophenyl)-1-propanone (5c); colourless crystalline solid (hexane); m.p. 78–79°C; IR ν_{max}(KBr) 1680, 1582, 1562 cm^{-1}; ^1H NMR($CDCl_3$): 2.20(s,6H,SCH_3); 3.41(d,2H, J=7.5,CH_2CH); 4.31(t,1H,J=7.5,CH_2CH); 7.49(d,2H,J=8,arom); 7.93(d,2H,J=8,arom); m/z 262,260 (M^+,1%,3%), 215,213(3,38). (Anal. Calcd. for $C_{11}H_{13}ClOS_2$: C,50.66; H,5.02. Found: C,50.89; H,4.83%).

3,3-Bis(methylthio)-1-(2-naphthyl)-1-propanone (5d); colourless crystalline solid (hexane); m.p. 72–73°C; IR ν_{max}(KBr) 1668, 1620, 1590 cm^{-1}; ^1H NMR($CDCl_3$): 2.24(s,6H,SCH_3); 3.61(d,2H, J=7.5,CH_2CH); 4.50(t,1H,J=7.5,CH_2CH); 7.61-7.72(m,2H,arom); 7.90–8.20(m,4H,arom); 8.51(s,1H, arom); m/z 276(M^+,12%),156(100).(Anal. Calcd. for $C_{15}H_{16}OS_2$: C,65.18; H,5.84. Found:C,64.98; H,6.05%).

3,3-Bis(methylthio)-1-(2-thienyl)-1-propanone (5e); viscous oil; IR ν_{max}(neat) 1668, 1415 cm^{-1}; ^1H NMR(CCl_4): 2.10(s,6H,SCH_3); 3.20(d,2H,J=7,CH_2CH); 4.24(t,1H,J=7,CH_2CH); 7.09–7.14(m,1H, thienyl); 7.62–7.76(m,2H,thienyl); m/z 232(M^+,10%), 185(24), 111(100). (Anal. Calcd. for $C_9H_{12}OS_3$: C,46.51; H,5.21. Found: C,46.79; H,5.48%).

3,3-Bis(methylthio)-1-(2-furyl)-1-propanone (5f); colourless crystalline solid (hexane); m.p. 42–23°C; IR ν_{max}(KBr) 1695, 1575, 1470 cm^{-1}; ^1H NMR(CCl_4): 2.12(s,6H,SCH_3); 3.14(d,2H,J=7.5, CH_2CH); 4.27(t,1H,J=7.5,CH_2CH); 6.51(dd,1H,J=4,1.5,H-4'furyl); 7.19(brd,1H,J=4,H-3' furyl); 7.59(brs,1H,H-5' furyl). (Anal. Calcd. for $C_9H_{12}O_2S_2$: C,49.97; H,5.59. Found: C,49.23; H,5.81%).

4,4-Bis(methylthio)-2-butanone (5g); viscous oil; IR ν_{max}(neat) 1715, 1510, 1420 cm^{-1}; ^1H NMR ($CDCl_3$): 2.13(s,6H,SCH_3); 2.19(s,3H,CH_3); 2.89(d,2H,J=7.5,CH_2CH); 4.19(t,1H,J=7.5,CH_2CH); m/z 164(M^+,36%), 117(100). (Anal. Calcd. for $C_6H_{12}OS_2$: C,43.86; H,7.37. Found: C,43.61; H,7.12%).

4,4-Bis(methylthio)-3-methyl-2-butanone (5h); viscous oil; IR ν_{max}(neat) 1725, 1543 cm^{-1}; ^1H NMR($CDCl_3$): 1.49(d,3H,J=7.5,$-CHCH_3$): 2.18(s,6H,SCH_3); 2.48–2.67(m,merged with CH_3,1H,CH_3CH–); 2.67(s,3H,CH_3CO); 4.38[d,1H,J=7.5,$(CH_3S)_2CH$]. (Anal. Calcd. for $C_7H_{14}OS_2$: C,47.15; H,7.91. Found: C,46.87; H,8.19%).

2-[Bis(methylthio)methyl]cyclopent-1-one (5j); viscous oil; IR ν_{max}(neat) 1740, 1630, 1532 cm^{-1}; ^1H NMR(CCl_4): 1.67–2.10[m,4H(CH_2)$_2$]; 2.11(s,6H,SCH_3); 2.29–2.59(m,3H,CH_2 and COCH); 4.10[(d,1H, J=5,$CH(SCH_3)_2$]; m/z 190(M^+,26%), 143(95). (Anal. Calcd. for $C_8H_{14}OS_2$: C,50.49; H,7.41. Found: C,50.22; H,7.66%).

2-[Bis(methylthio)methyl]cyclohex-1-one (5k); viscous oil; IR ν_{max}(neat) 1710, 1543 cm^{-1}; ^1H NMR(CCl_4): 1.59–1.90[m,6H,$(CH_2)_3$]; 2.12(s,6H,SCH_3); 2.16–2.31(m,2H,CH_2); 2.43–2.70(m,1H,COCH); 4.09[d,1H,J=7.5,$CH(SCH_3)_2$]; m/z 204(M^+,38%), 157(100). (Anal. Calcd. for $C_9H_{16}OS_2$: C,52.90; H,47.89. Found: C,53.16; H,8.17%).

2-[Bis(methylthio)methyl]cyclohept-1-one (5l); viscous oil; IR ν_{max}(neat) 1708, 1452 cm^{-1}; ^1H NMR(CCl_4): 1.12–1.92[m,8H,$(CH_2)_4$]; 2.31(s,6H,SCH_3); 2.31–2.81(m,3H,CH_2 and COCH); 3.98[d,1H, J=7.5,$CH(SCH_3)_2$]; m/z 218(M^+,25%), 171(100). (Anal. Calcd. for $C_{10}H_{18}OS_2$: C,55.00; H,8.31. Found: C,54.73; H,8.59%).

2-[Bis(methylthio)methyl]-indan-1-one (5m); m.p. 44–45°C (lit.[7] m.p. 45–47°C; superimposable IR and NMR).

2-[Bis(methylthio)methyl]-1-tetralone (5n); viscous oil; IR ν_{max}(neat) 1685, 1598, 1480 cm^{-1}; ^1H NMR(CCl_4): 2.10(s,6H,SCH_3); 2.10–2.32(m,2H,CH_2); 2.55–3.00(m,3H,CH_2 and COCH); 4.43[d,1H, J=4,$CH(SCH_3)_2$]; 7.03–7.40(m,3H,arom); 7.84–7.98(m,1H,arom); m/z 252(M^+,35%), 205(100). (Anal. Calcd. for $C_{13}H_{16}OS_2$: C,61.86; H,6.39. Found: C,62.15; H,6.11%).

2-[Bis(methylthio)methyl]-6-methoxy-1-tetralone (5o); viscous oil; IR ν_{max}(neat) 1680, 1600, 1595 cm^{-1}; ^1H NMR($CDCl_3$): 2.20(s,6H,SCH_3); 2.20–2.41(m,2H,CH_2); 2.80–3.01(m,3H,CH_2 and COCH); 3.80(s,3H,OCH_3); 4.60[d,1H,J=5,$-CH(SCH_3)_2$]; 6.88–6.95(m,2H,arom); 8.09(d,1H,J=9,arom). (Anal. Calcd. for $C_{14}H_{18}O_2S_2$: C,59.54; H,6.42. Found: C,59.40; H,6.34%).

1,1-Bis(methylthio)-5-phenyl-4-penten-3-one (5q); viscous oil; IR ν_{max}(neat) 1685, 1660, 1605, cm^{-1}; ^1H NMR(CCl_4): 2.14(s,6H,SCH_3); 3.01(d,2H,J=7.5,CH_2CH); 4.22(t,1H,J=7.5,CH_2CH); 6.71(d,1H, J=15,olefinic); 7.28–7.61(m,6H,arom and olefinic). (Anal. Calcd. for $C_{13}H_{16}OS_2$: C,61.90; H,6.35. Found: C,62.12; H,6.14%).

1,1-Bis(methylthio)-5-(4-methoxyphenyl)-4-penten-3-one (5r); white crystalline solid (hexane); m.p. 44–45°C; IR ν_{max}(KBr) 1685, 1658, 1595 cm^{-1}; ^1H NMR(CCl_4): 2.14(s,6H,SCH_3); 2.99(d,2H,

J=7.5,CH_2CH); 3.79(s,3H,OCH_3); 4.20(t,1H,J=7.5,CH_2CH); 6.53(d,1H,J=15,olefinic); 6.85(d,2H, J=9,arom); 7.38-7.68(m,3H,arom and olefinic). (Anal. Calcd. for $C_{14}H_{18}O_2S_2$: C,59.57; H,6.38. Found: C,59.76; H,6.49%).

1,1-Bis(methylthio)-7-phenyl-4,6-heptadien-3-one (5s); white crystalline solid (hexane); m.p. 85-86°C; IR ν_{max} (KBr) 1679, 1615,1599 cm^{-1}; ^1H NMR($CDCl_3$):2.26(s,6H,SCH_3); 3.09(d,2H,J=7.5, CH_2CH); 4.31(t,1H,J=7.5,CH_2CH); 6.02(d,1H,J=15,olefinic); 6.98-7.49(m,8H,arom and olefinic). (Anal. Calcd. for $C_{15}H_{18}OS_2$: C,64.75; H,6.47. Found: C,64.87; H,6.36%).

1-Phenyl-2-(1,3-dithian-2-yl)ethanone (5u); m.p. 58-59°C (lit.[7] m.p. 59-61°C; superimposable IR and NMR).

E-3-Methylthio-1-phenyl-2-propen-1-one (6a); viscous oil (lit.[6] superimposable IR and NMR).

E-3-Methylthio-1-(4-methoxyphenyl)-2-propen-1-one (6b); viscous oil; IR ν_{max}(neat) 1600 cm^{-1}; ^1H NMR($CDCl_3$): 2.29(s,3H,SCH_3); 3.70(s,3H,OCH_3); 6.70-7.05(m,3H,arom and olefinic); 7.78-8.03 (m,3H,arom and olefinic). (Anal. Calcd. for $C_{11}H_{12}O_2S$: C,63.42; H,5.81. Found: C,63.37;H,5.66%).

E-3-Methylthio-1-(4-chlorophenyl)-2-propen-1-one (6c); m.p. 69-70°C (lit.[6] 69-70°C; superimposable IR and NMR).

E-3-Methylthio-1-(2-naphthyl)-2-propen-1-one (6d); viscous oil; IR ν_{max}(neat) 1643 cm^{-1}; ^1H NMR(CCl_4): 2.32(s,3H,SCH_3); 6.81(d,1H,J=15,olefinic); 7.08-8.31(m,8H,arom and olefinic). (Anal. Calcd. for $C_{14}H_{12}OS$: C,73.65; H,5.30. Found: C,73.41; H,5.49%).

E and Z(1:1)-3-Methylthio-1-thienyl-2-propen-1-one (6e); yellow crystalline solid; m.p. 128-131°C; IR ν_{max}(KBr) 1612 cm^{-1}; ^1H NMR(CCl_4): 2.40(s,3H,SCH_3); 6.60(d,1H,J=15,olefinic); 6.80(d, 1H,J=9,olefinic). (Anal. Calcd. for $C_8H_8OS_2$: C,52.12; H,4.34. Found: C,51.88; H,4.47%).

E-4-Methylthio-3-buten-2-one (6g); viscous oil; (lit.[6] superimposable IR and NMR).

E-4-Methylthio-3-methyl-3-buten-1-one (6h); viscous oil; IR ν_{max}(neat) 1660, 1570, 1430 cm^{-1}; ^1H NMR($CDCl_3$): 1.82(s,3H,CH_3); 2.29(s,3H,SCH_3); 2.48(s,3H,CH_3); 7.38(brs,1H,olefinic). (Anal. Calcd. for $C_6H_{10}OS$: C,55.38; H,7.69. Found: C,55.17; H,7.82%).

Z-3-Methylthio-2-methyl-1-phenyl-2-propen-1-one (6i); viscous oil; IR ν_{max}(neat) 1638, 1572, 1441 cm^{-1}; ^1H NMR($CDCl_3$): 1.89(s,3H,SCH_3); 2.28(s,3H,CH_3); 6.98(s,1H,olefinic); 7.21-7.98(m,5H, arom). (Anal. Calcd. for $C_{11}H_{12}OS$: C,68.64; H,6.24. Found:C,68.39; H,6.41%).

E-2-(Methylthiomethylene)cyclopentanone (6j); m.p. 46-47°C; (lit.[6] m.p. 47-48°C; superimposable IR and NMR).

E-2-(Methylthiomethylene)cyclohexanone (6k); viscous oil; (lit.[6] superimposable IR and NMR).

E-2-(Methylthiomethylene)-1-tetralone (6n); m.p. 68-69°C;(lit.[6] m.p.68°C;superimposable IR and NMR)

E-2-(Methylthiomethylene)-6-methoxytetralone (6o); m.p. 92-93°C; IR ν_{max}(KBr) 1642, 1600,1555 cm^{-1}; ^1H NMR($CDCl_3$): 2.50(s,3H,SCH_3); 2.63-3.05[m,4H,(CH_2)]; 3.82(s,3H,OCH_3); 6.70-6.95(m,2H, arom); 7.70(s,1H,olefinic); 8.10(d,1H,J=9,arom). (Anal. Calcd. for $C_{13}H_{14}O_2S$: C,66.64; H,6.02. Found: C,66.73; H,5.88%).

Reduction of 1a with Sodium Borohydride/Acetic Acid in Tetrahydrofuran:

All reductions of 1a shown in Table 2 were carried out under identical conditions as described by Hack[18] (run 1 and 2) and Marshall[17] (run 3) for hydroboration of olefin and for reduction of 3-N-pyrrolidylcholestadiene-3,5 to 3-β-N-pyrrolidylcholesten-5[16] (run 4).

The reaction mixtures were worked up by pouring into ice cold water (100 mL) and extracting with $CHCl_3$(2x50 mL). The organic layer was dried (Na_2SO_4) and evaporated to give residues which were column chromatographed over silica gel using hexane as eluent to give either 1a or 5a (Table 2).

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