Tetrahedron Vol. 47, No 2, pp 305-312, 1991
Printed in Great Britain

0040-4020/91 $3 00+00
Pergamon Press plc

STUDIES ON LEAD TETRAACETATE OXIDATION OF α-OXOKETENE DITHIOACETALS

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(*Received in UK 4 October* 1990)

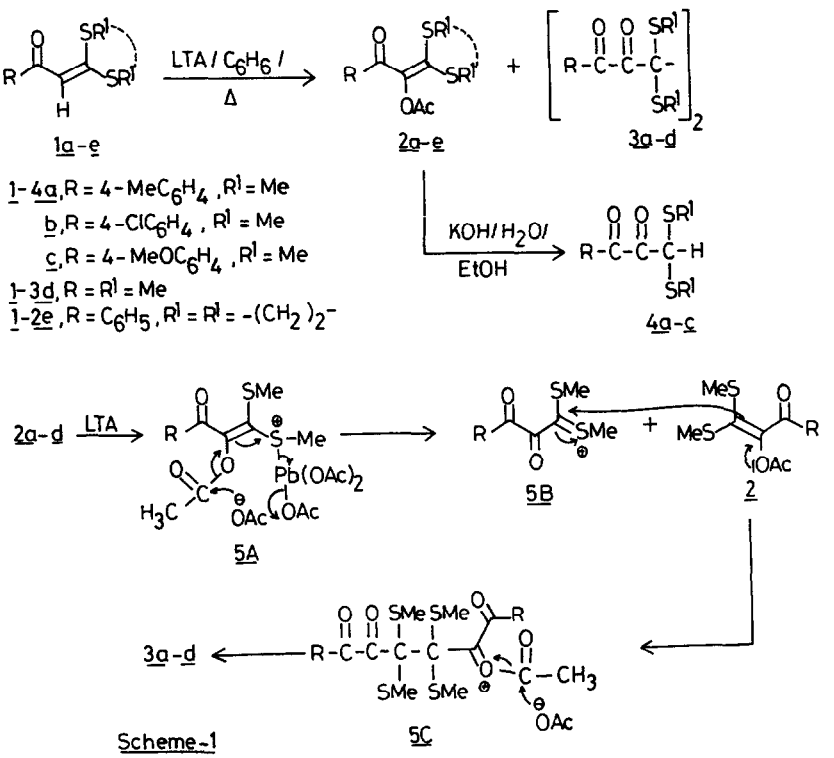
Abstract *- Lead Tetraacetate oxidation of acyclic α-acylketene dithioacetals 1 in refluxing benzene affords α-acetoxyketene dithioacetals 2 as major products which could be hydrolyzed to α-diketone dithioacetals 4 under mild alkaline conditions. Under similar oxidative conditions, α-cinnamoyl ketene dithioacetals 8 yield 2-acetoxycyclopentenone derivatives 9 through an interesting oxidative Nazarov cyclization involving intermediate α-acetoxy dithioacetals accompanied with 1,2-acyl group migration.*

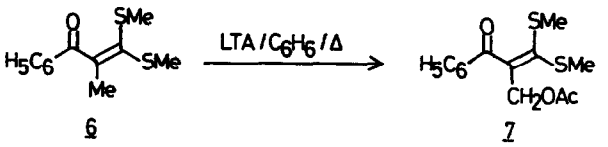
Lead Tetraacetate oxidation of organonitrogen compounds have been extensively reported in the literature[1]. However, there have been only limited studies on the oxidation of organosulfur compounds with this reagent[1]. The oxidative dimerization of thiols, oxidation of thioethers and disulfides to the corresponding sulfoxides and sulfinate esters involving oxidation of the sulfur atom are among the few examples reported earlier[1]. However, the reactions of greater synthetic utility are sulfur directed oxidative cleavage and acetoxylation of organosulfur compounds with LTA, in which sulfur atom remains unaffected. Thus Trost and co-workers have reported regioselective oxidative cleavage of α-sulfenylated carbinols to the corresponding acetoxyhemithioacetals which could be converted to ketoaldehydes under mild hydrolytic conditions[2]. The same workers[3] and others[4] have also described the oxidative seco-rearrangement of α-hydroxy-dithioacetals to either α-thiothioesters or to ketenedithioacetals with unprotected carbonyl functionality. Other examples include regioselective allylic acetoxylation of enol thioethers[5] to α-(phenylthio)allylic acetates, which are found to be useful intermediates in many synthetic transformations. Also, the 2-alkylidene-1,3-dithianes have been similarly reacted[6] with LTA to afford 3-alkyl-1,4-dithiepan-2-one involving oxidative ring cleavage. However, the 2-benzylidene-1,3-dithiane yielded only the corresponding α-acetoxy derivative under identical reaction conditions These studies along with our earlier reports on LTA oxidation of α-oxo[7] and α-cyano[8] ketene S,N- and N,N-acetals prompted us to investigate α-oxoketene dithioacetals under similar oxidative conditions, which afford otherwise inaccessible diketonedithioacetals 4 on hydrolytic cleavage of the initially formed α-acetoxy oxoketene dithioacetals 2 (Scheme 1). We now report these and other results in this paper

Results and Discussion

In one of the experiments, when equimolar quantities of a mixture of 1a and LTA was stirred at room temperature in benzene or acetic acid, the unreacted 1a was recovered. However under optimized conditions,when 1a was refluxed with excess of LTA (2 eqv.) in benzene for prolonged time (28 hr), the products isolated after work-up were characterized as the α-acetoxydithioacetal 2a and the diketone dimer 3a formed in 56% and 25% yields respectively (Scheme 1)[9]. Similarly the dithioacetals 1b-d afforded the acetates 2b-d (53-59%) and dimers 3b-d (28-30%) which were characterized on the basis of analytical and spectral data. The dimeric ketone 3b displayed in its ^{13}C NMR spectrum, the peaks corresponding to the monomer, thus confirming its symmetrical structure. Under similar reaction conditions, the cyclic α-oxoketene dithioacetal 1e gave only the α-acetoxydithioacetal 3e in 62% yield and the corresponding dimeric product was not formed. The utility of acetoxylation reaction was illustrated by hydrolysis of 2a-c to the corresponding diketonedithioacetals 4a-c possessing the protected aldehyde functionality[10] which remained unaffected during alkaline hydrolytic conditions.

The possible pathway for the the formation of diketone dimers 3 appears to involve the unstable thionium ion intermediate 5B formed by the cleavage of lead tetraacetate methylthio complex 5A (Scheme 1). The intermediate 5B is subsequently attacked by another molecule of 2 followed by acetoxy group



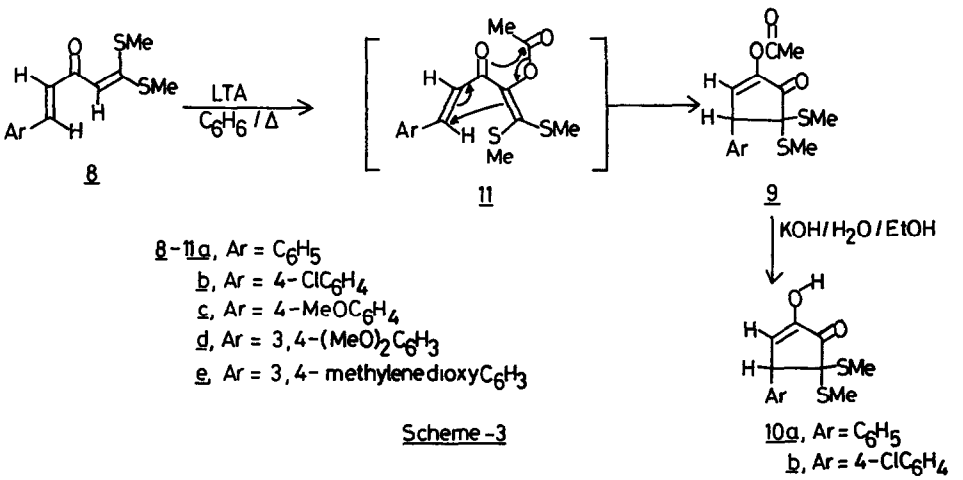


6 7

Scheme-2

cleavage to give 3. Interestingly, the α-methyl oxoketene dithioacetal 6 derived from propiophenone underwent allylic acetoxylation with LTA under similar reaction conditions to afford 7 in 68% yield (Scheme 2).

The α-cinnamoyl ketenedithioacetals 8 were next examined under similar reaction conditions to study the chemoselectivity of the reagent that might react with only the sulfur substituted double bond to yield the corresponding acetoxy product. However when 8a was oxidized with LTA under the described reaction conditions, the product isolated (74%) was found to be 2-acetoxy-5,5-bis(methylthio)-4-phenylcyclopenten-2-one (9a). The structure of 9a was supported by its elemental composition, spectral properties and its further conversion to 10a (Scheme 3). The acetoxycyclopentenone 9a displayed characteristic enolacetate carbonyl frequency at 1770 cm^{-1} in addition to a strong band at 1710 cm^{-1} due to ring carbonyl group. The ^1H NMR spectrum (250 MHz) of 9a showed three singlets (3H each) at δ 1.80, 2.15 and 2.30 for two methylthio and one acetoxy group protons. The absorption due to benzylic methine proton appeared as a doublet (J=3.5 Hz) at δ4.35, while the signal due to olefinic proton was present at δ7.20 (d, J=3.5Hz) partially merged with aromatic protons at δ7.30 (brs, 5H) The structure of 9a was further supported by its ^{13}C NMR spectrum (experimental) and its hydrolysis to α-diketone 10a under mild alkaline conditions The other cinnamoyl ketene dithioacetals 8b-e similarly afforded the corresponding α-acetoxycyclopetenones 9b-e in 61-78% overall yields and 9b on hydrolysis gave the corresponding α-diketone 10b in 71% yield as described above.



8 11 9

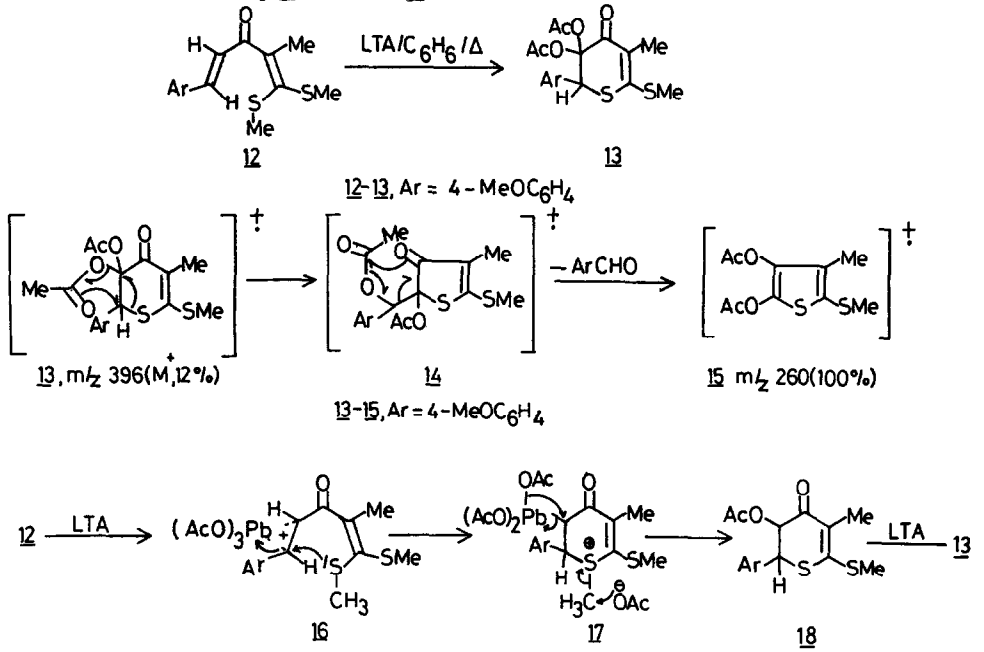
8-11a, Ar = C_6H_5
b, Ar = 4-ClC_6H_4
c, Ar = 4-$MeOC_6H_4$
d, Ar = 3,4-$(MeO)_2C_6H_3$
e, Ar = 3,4- methylenedioxyC_6H_3

Scheme-3

10a, Ar = C_6H_5
b, Ar = 4-ClC_6H_4

The probable mechanism for the formation of 9 from 8 apparently involves α-acetoxy dithioacetal[11] intermediate 11 through chemoselective acetoxylation of mercapto double bond in preference to cinnamoyl double bond as envisaged. Such a selectivity also proves the possible sulphur assisted carbon plumbylated bond leading to the observed formation of 11 which undergoes intramolecular cyclization followed by 1,2-O-acyl group migration to yield 9. The overall transformation represents a novel oxidative Nazarov type cyclization[12] and opens a facile entry to substituted cyclopentane 1,2-diones.

Interestingly, when α-methyl cinnamoyl ketenedithioacetal 12 was oxidized with LTA under the reported conditions, the reaction took entirely different course and the product isolated (68%) was characterized as 3,3-bis (acetoxy)dihydrothiopyran-4-one 13 (Scheme 4) on the basis of its analytical and spectral data. The mass spectrum of 13 exhibited interesting fragmentation pattern as depicted in Scheme. The base peak at m/z 260 (100%) was assigned to the fragment ion 15, formed through rearrangement of 13 to 14 under electron impact, followed by loss of 4-methoxybenzaldehyde. Hydrolysis of 13, under mild alkaline conditions, gave only a complex product mixture, from which only 4-methoxybenzaldehyde (42%) could be isolated. The probable mechanism for the formation of 13 from 12 is shown in Scheme 4. Apparently, the styryl double bond undergoes chemoselective attack by LTA in preference to the α-blocked mercapto double bond to give π-bridged plumbonium ion intermediate 16 which rearranges to plumbylated adduct 17 through intramolecular attack by sulphur subsequent decomposition and demethylation of 17 leads to 18[9] which undergoes further acetoxylation with LTA to give the product 13.



Scheme-4

Experimental

Melting points were determined on a 'Thomas Hoover' capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 297 spectrophotometer. The ^{1}H NMR spectra were obtained on a Varian EM 390 (90 MHz) spectrometer, while ^{13}C NMR spectra were recorded on a Brucker WM-400 spectrometer. 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 Heraeus CHN-O-Rapid Elemental Analyzer.

All the starting α-oxoketene dithioacetals 1a-e, 6, 8a-e and 12 were prepared according to the earlier reported procedures[13,14].

LTA Oxidation of Oxoketene Dithioacetals 1a-e, 8a-e and 12: General Procedure:

To a solution of oxoketene dithioacetal (10 mmol) in dry benzene (50 ml), LTA (8.80g,20 mmol) was added and the suspension was heated (60-70°C) with stirring for 18-28 hr (monitored by TLC). The reaction mixture was cooled and the precipitated Lead(II) acetate was removed by filtration. The filtrate was treated with a few drops of ethylene glycol to decompose traces of lead(IV) acetate, washed with water (3x100 ml), dried (Na_2SO_4) and evaporated on water bath. The viscous brown residues thus obtained were purified by column chromatography over silica-gel using EtOAc/hexane (1:20) as eluent to give first dimeric diketones 3 followed by α-acetoxy dithioacetals 2.

2-Acetoxy-3,3-bis(methylthio)-1-(4-methylphenyl)-2-propen-1-one (2a); viscous liquid; 56%; IR (neat) 1761, 1650 cm^{-1}; δ_H ($CDCl_3$) 2.19 (3H, s, SCH_3); 2.24 (3H, s, SCH_3); 2.43 (6H, brs, CH_3 and CH_3CO_2); 7.27 (2H, d, J=9Hz, ArH); 7.90 (2H, d, J=9Hz, ArH); m/z 296 (M^+, 5%); 253 (7); 119(100). (Anal.Calcd.for $C_{14}H_{16}O_3S_2$:C,56.73;H,5.44.Found:C,56.96;H, 5.62%).

2-Acetoxy-3,3-bis(methylthio)-1-(4-chlorophenyl)-2-propen-1-one (2b); viscous liquid; 55%; IR(neat) 1761, 1659 cm^{-1}; δ_H (CCl_4)2.10(3H,s, SCH_3) 2.19 (3H,s,SCH_3); 2.31 (3H, s, CH_3CO_2); 7.49 (2H, d, J=9Hz, ArH); 7.83 (2H, d, J=9Hz, ArH); m/z 316 (M^+, 2%); 274 (24); 276 (10), 107 (100). (Anal.Calcd. for $C_{13}H_{13}ClO_3S_2$: C, 49.28; H,4.14.Found: C,49.42;H, 4.40%)

2-Acetoxy-3,3-bis(methylthio)-1-(4-methoxyphenyl)-2-propen-1-one (2c); pale yellow crystals ($CHCl_3$/hexane); 59%, m p.68-69°C; IR(KBr) 1770, 1645, 1600 cm^{-1}; δ_H($CDCl_3$) 2.08 (3H, s, SCH_3); 2.10 (3H, s, SCH_3); 2.31 (3H, s, CH_3CO_2); 3.76 (3H, s, OCH_3); 6 84 (2H, d, J=9Hz, ArH); 7 85 (2H, d, J=9Hz, ArH); m/z 312 (M^+,2%); 270 (20); 135 (100). (Anal. Calcd. for $C_{14}H_{16}O_4S_2$· C, 53.82; H, 5.16. Found: C, 54.03; H, 5 01%).

2-Acetoxy-1,1-bis(methylthio)-1-buten-3-one (2d); viscous liquid; 53%; IR (neat) 1769, 1689 cm^{-1}; δ_H (CCl_4) 2.17 (3H, s, SCH_3); 2.28 (3H, s, SCH_3); 2.35 (3H, s, $COCH_3$); 2.40 (3H, s, CH_3CO_2); m/z 178 (M^+-42, 12%). (Anal. Calcd. for $C_8H_{12}O_3S_2$: C, 43.61; H, 5.49. Found: C, 43.88; H, 5.72%).

2-Acetoxy-1-phenyl-2-(1,3-thiolan-2-ylidine)ethanone (2e); pale yellow crystals ($CHCl_3$/hexane); 62%; m.p. 88-89°C;IR (KBr) 1768, 1630, 1500 cm^{-1}; δ_H ($CDCl_3$) 2.02 (3H, s, CH_3CO_2); 3.39 (4H, brs, CH_2); 7.41-7 62 (3H, m, ArH); 7.72-7.93 (2H, m, ArH); m/z 280 (M^+, 3%); 238 (78); 105 (100). (Anal

Calcd. for $C_{13}H_{12}O_3S_2$: C, 55.69; H, 4.32. Found: C, 55.77; H, 4.53%).

1,6-Di(4-methylphenyl)-3,3,4,4-tetra(methylthio)hexane-1,2,5,6-tetraone (3a): yellow viscous semisolid; 25%; IR (neat) 1691, 1665, 1600 cm^{-1}; δ_H (CCl_4) 2.10 (12H, s, SCH_3); 2.39 (6H, s, CH_3); 7.23 (4H, d, J=8.5Hz, ArH); 7.76 (4H, d, J=8.5 Hz, ArH); m/z No M^+;153 (65%); 107 (19); 119(100). Anal. Calcd. for $C_{24}H_{26}O_4S_4$; C, 56.88; H, 5.17. Found: C, 57.11; H, 5.36%).

1,6-Di(4-chlorophenyl)-3,3,4,4-tetra(methylthio)hexane-1,2,5,6-tetraone (3b); yellow crystals ($CHCl_3$/hexane);30%;m.p.94-95°C;IR(KBr)1690,1680 cm^{-1}; δ_H ($CDCl_3$) 2.16 (12H, s, SCH_3); 7.41 (4H, d, J=8.5Hz, ArH); 7.82 (4H, d, J=8.5Hz, ArH); δ_C ($CDCl_3$) 13.66 (SCH_3); 73.95 [$C(SCH_3)_2$]; 129.00, 130.08 (CH, Ar); 132.01, 141.19 (C-1',C-4',Ar); 190.53(CO); 192.17 (CO); m/z 273 (M^+/2,2%); 153 (100); 155(13). (Anal. Calcd. for $C_{22}H_{20}Cl_2O_4S_4$: C, 48.25; H, 3.68. Found: C, 48.52; H, 3.85%).

1,6-Di(4-methoxyphenyl)-3,3,4,4-tetra(methylthio)hexane-1,2,5,6-tetraone (3c); yellow crystals ($CHCl_3$/hexane); 28%; m.p. 89-90°C; IR (KBr) 1690, 1660 cm^{-1}; δ_H ($CDCl_3$) 2.23 (12H, s, SCH_3); 3.96 (6H, s, OCH_3); 7.08 (4H, d, J=9Hz,ArH); 7.98 (4H, d, J=9Hz, ArH); m/z No M^+; 153 (90%); 135 (100).(Anal.Calcd.for $C_{24}H_{26}O_6S_4$:C,53.51;H,4.87.Found:C,53.78;H, 5.13%).

4,4,5,5-Tetra(methylthio)-octane-2,3,6,7-tetraone (3d); yellow viscous liquid; 28%; IR(neat) 1711, 1690, 1563 cm^{-1};δ_H (CCl_4) 2.08 (12H, s, SCH_3); 2.46 (6H, s, CH_3); m/z 177 (M^+/2, 4%); 153 (100). (Anal. Calcd. for $C_{12}H_{18}O_4S_4$: C, 40.65; H, 5.12. Found: C, 40.44; H, 4.98%).

2-Acetoxymethylene-3,3-bis(methylthio)-1-phenyl-2-propen-1-one (7); was obtained by LTA oxidation of 6 under similar conditions; yellow crystals; ($CHCl_3$/hexane); 68%; m.p. 83-84°C; IR(KBr) 1742,1698,1596 cm^{-1};δ_H (CCl_4)2.12(6H,s, SCH_3); 2.20 (3H,s,CH_3CO_2);5.50 (2H,s,CH_2); 7.48-7.71 (3H,m,ArH);7.89-8.10 (2H, m,ArH). (Anal.Calcd.for $C_{14}H_{16}O_3S_2$: C,56.73; H,5.44. Found: C, 56.98; H, 5.41%).

General Procedure for Alkaline Hydrolysis of 2a-c and 9a-b.
A solution of α-acetoxydithioacetal (2a-c) or 2-acetoxycyclopentenone (9a-b) (2.5 mmol) in 10ml of aqueous ethanolic (1:1) KOH (10%) was stirred at 45-50°C for 10-12 hr (monitored by TLC). The reaction mixture was cooled, poured over crushed ice, neutralized with AcOH and extracted with chloroform (2x30 ml). The organic layer was washed with water (2x50 ml), dried (Na_2SO_4) and evaporated to give crude products which were further purified by passing through a short length silica gel column using EtOAc/hexane (1:15) as eluent.

3,3-Bis(methylthio)-1-(4-methylphenyl)propan-1,2-dione (4a); yellow crystals ($CHCl_3$/hexane); 90%;m.p.116-117°C;IR(KBr)1700,1660,1600 cm^{-1}; δ_H ($CDCl_3$)2.19(6H,s,SCH_3);2.48(3H,s,CH_3);5.47 [1H, s, $HC(SCH_3)_2$]; 7.43 (2H, d, J=9Hz, ArH); 8.09 (2H, d, J=9Hz, ArH); δ_C ($CDCl_3$) 12.10 (SCH_3); 21.90 (CH_3); 55.72 [$HC(SCH_3)_2$]; 129.57 (CH, Ar); 130.11 (CH,Ar); 130.34, 146.08 (C-1', C-4',Ar);187.08 (CO); 190.82 (CO); m/z No M^+; 119(64%); 109 (132). (Anal. Calcd.for $C_{12}H_{14}O_2S_2$:C,56.66;H,5.55. Found: C, 56.51; H, 5.54%).

3,3-Bis(methylthio)-1-(4-chlorophenyl)-propan-1,2-dione (4b); yellow crystals($CHCl_3$/hexane); 93%; m.p.78-79°C; IR(KBr) 1700, 1670, 1600 cm^{-1}; δ_H

($CDCl_3$) 2.14 (6H, s, SCH_3); 5.40 [1H, s, $CH(SCH_3)_2$]; 7.51 (2H, d, J=9Hz, ArH); 8.08 (2H, d, J=9Hz, ArH). (Anal. Calcd. for $C_{11}H_{11}ClO_2S_2$: C, 48.08; H, 4.04. Found: 47.97; H, 4.09%).

3,3-Bis(methylthio)-1-(4-methoxyphenyl)propan-1,2-dione (4c); yellow crystals ($CHCl_3$/hexane); 90%; m.p. 58-59°C; IR(KBr) 1708,1661,1605 cm^{-1};δ_H ($CDCl_3$) 2.10 (6H, s, SCH_3); 3.84 (3H, s, OCH_3); 5.33 [1H, s, $CH(SCH_3)_2$]; 6.90 (2H, d, J=9Hz, ArH); 8.00 (2H, d, J=9Hz, ArH); δ_C ($CDCl_3$) 11.88 (SCH_3); 55.29 [$CH(SCH_3)_2$]; 55.47 (OCH_3); 113.91, 132.22 (CH, Ar); 125.60, 164.63 (C-1', C-4', Ar); 187.3(CO); 190.1 (CO). (Anal. Calcd. for $C_{12}H_{14}O_3S_2$: C, 53.31; H, 5.22. Found: C, 53.50, H, 5.09%).

2-Acetoxy-5,5-bis(methylthio)-4-phenyl-2-cyclopenten-1-one(9a); colourless crystals ($CHCl_3$/hexane);74%;m.p.94-95°C;IR (KBr) 1770,1710,1630 cm^{-1}; ^1H NMR described in text. δ_C($CDCl_3$) 12.22 (SCH_3); 13.20 (SCH_3); 20.83 (CH_3CO_2);54.72 (C-4);62.21 (C-5); 128.14, 128.32, 129.92 (CH, Ar); 135.71 (C-1', Ar); 141.61 (=CH); 146.35 (C-2); 167.44 (CH_3CO_2); 192.85 (CO); m/z 308 (M^+, 44%); 266 (29); 218 (55). (Anal. Calcd. for $C_{15}H_{16}O_3S_2$: C, 58.41; H, 5.23. Found: C, 58.48; H, 5.29%).

2-Acetoxy-5,5-bis(methylthio)-4-(4-chlorophenyl)-2-cyclopenten-1-one (9b); colourless crystals ($CHCl_3$/hexane); 78%; m.p. 113-114°C; IR (KBr) 1756, 1710 cm^{-1}; δ_H ($CDCl_3$) 1.91 (3H, s, SCH_3); 2.18 (3H, s, SCH_3); 2.33 (3H, s, CH_3CO_2), 4.31(1H, d, J=3.5Hz, H-4); 7.17-7.44 (5H, m, ArH, =CH); δ_C ($CDCl_3$) 12.80 (SCH_3); 13.88 (SCH_3); 20.48 (CH_3); 53.83 (C-4); 61.71 (C-5); 128.87, 130.93 (CH, Ar); 134.84 (C-1', Ar); 140.65 (=CH); 146.33 (C-2); 167.89 (CH_3CO_2); 192.20 (CO); m/z 342 (M^+, 46%); 300 (42). (Anal. Calcd. for $C_{15}H_{15}ClO_3S_2$: C, 52.55; H, 4.41. Found: C, 52.78; H, 4.56%).

2-Acetoxy-5,5-bis(methylthio)-4-(4-methoxyphenyl)-2-cyclopenten-1-one (9c); yellow viscous liquid; 69%; IR (neat) 1776, 1720 cm^{-1}; δ_H ($CDCl_3$) 1.94 (3H, s, SCH_3); 2.20 (3H, s, SCH_3); 2.33 (3H, s, CH_3CO_2);3.83 (3H, s, OCH_3); 4.35 (1H, d, J=3.5Hz, H-4); 6.92 (2H, d, J=9Hz, ArH); 7.24 (2H, d, J=9Hz, ArH); 7.29 (1H, d, J=3.5Hz, =CH); m/z 338 (M^+, 44%); 296 (35); 200 (20).(Anal.Calcd.for $C_{16}H_{18}O_4S_2$:C,56.78;H,5.36. Found: C, 56.61; H, 5.22%).

2-Acetoxy-5,5-bis(methylthio)-4-(3,4-dimethoxyphenyl)-2-cyclopenten-1-one (9d); viscous liquid; 65%; IR (neat) 1775, 1725 cm^{-1}; δ_H($CDCl_3$) 1.90 (3H, s, SCH_3); 2.14 (3H, s, SCH_3); 2.30 (3H,s,CH_3CO_2); 3.87 (6H,brs,OCH_3); 4.30 (1H, d, J=3.5Hz, H-4); 6.83 (3H, s,ArH), 7.28 (1H,d,J=3.5Hz,=CH); m/z 368 (M^+,25%); 326(25); 278(20); 191(100). (Anal. Calcd. for $C_{17}H_{20}O_5S_2$:C,55.41; H, 5.47. Found: C, 55.69; H, 5.23%).

2-Acetoxy-5,5-bis(methylthio)-4-(3,4-methylenedioxyphenyl)-2-cyclopentene-1-one (9e); viscous liquid; 61%; IR(neat) 1778, 1722 cm^{-1}; δ_H ($CDCl_3$) 1.98 (3H, s, SCH_3); 2.17 (3H, s, SCH_3); 2.32 (3H, s, CH_3CO_2); 4.32 (1H, d, J=3.5Hz, H-4); 5.98 (2H, s, CH_2); 6.83 (3H, brs, ArH); 7.30 (1H, d, J=3.5Hz, =CH); m/z 352 (M^+, 32%); 310(12); 264(13); 215(16). (Anal. Calcd. for $C_{16}H_{16}O_5S_2$: C, 54.53; H, 4.58. Found: C, 54.61; H, 4.66%).

3,3-Bis(acetoxy)-2-(4-methoxyphenyl)-5-methyl-6-(methylthio)-2,3-dihydrothiopyran-4-one (13); colourless crystals ($CHCl_3$/hexane); 68%; m.p. 148-149°C; IR (KBr) 1747, 1666 cm^{-1}; δ_H ($CDCl_3$) 1.71 (3H, s, SCH_3); 1.91 (3H, s, CH_3); 2.01 (3H, s, CH_3CO_2); 2.58 (3H, s, CH_3CO_2); 3.85 (3H, s, OCH_3);

6.26 (1H,s, ArCH); 6.95 (2H, d, J=9Hz, ArH); 7.55 (2H, d, J=9Hz, ArH); δ_C ($CDCl_3$) 10.12 (SCH_3); 14.41 (CH_3); 20.45(CH_3CO_2);55.85 (OCH_3);75.47 (C-2 ArCH);91.79 (C-3); 113.19, 129.12 (CH, Ar); 122.88 (C-1',Ar); 126.91(C-5); 159.94(C-4',Ar); 166.97, 168.33,(CH_3CO_2);169.44(C-6);193.50(CO);m/z 396 (M^+, 12%); 336 (M^+-CH_3CO_2H); 294 (15); 260 (100); 218 (95); 176 (92). (Anal.Calcd.for $C_{18}H_{20}O_6S_2$:C,54.53;H,5.09. Found:C, 54.20; H, 5.29%).

5,5-Bis-(methylthio)-2-hydroxy-4-phenyl-2-cyclopentene-1-one (10a) colourless crystals ($CHCl_3$/hexane);70%;m.p. 65-66°C;IR (KBr) 3480,1690,1630 cm^{-1}; δ_H ($CDCl_3$) 1.90 (3H,s,SCH_3); 2.20 (3H,s, SCH_3); 4.36 (1H, d, J=3.5Hz, H-4); 6.71 (1H, d, J=3.5Hz, =CH); 6.82 (1H, brs, OH); 7.03-7.48 (5H, m, ArH). (Anal. Calcd.for $C_{13}H_{14}O_2S_2$:C,58.62;H,5.30. Found: C, 58.89; H, 5.18%).

5,5-Bis(methylthio)-2-hydroxy-4-(4-chlorophenyl-2-cyclopentene-1-one (10b); colourless crystals ($CHCl_3$/hexane);71%;m.p.72-73°C;IR(KBr) 3330, 1691,1650, 1613 cm^{-1};δ_H ($CDCl_3$) 1.91 (3H,s,SCH_3);2.17(3H,s,SCH_3); 4.30 (1H, d, J=3.5Hz, H-4);6.37(1H,brs, OH); 6.47 (1H, d, J=3.5Hz, =CH);7.20-7.48(4H,m, ArH). (Anal. Calcd.for $C_{13}H_{13}ClO_2S_2$: C,51.90; H,4.36 Found: C, 52.15; H, 4.59%).

Alkaline hydrolysis of 13 and subsequent work-up as described above gave a viscous residue which on column chromatography (hexane as eluent) afforded 4-methoxybenzaldehyde, 42%; b.p. 90-91°C /5mm (lit.[15] 83°C/2mm, superimposable IR and NMR spectra).

Acknowledgement: LNB and AT thank organon research centre, Calcutta and CSIR, New Delhi for Junior and Senior Research Fellowships. Financial assistance from UGC, New Delhi under COSIST programme is also acknowledged.

References and Notes

1. Butler, R.N. in "Synthetic Reagents", Pizey, J.S. Ed , Vol. 3, Chapt.4, p. 277 -419.
2. Trost, B.M.; Hiroi, K. *J. Am. Chem. Soc.* **1975**, 97, 6911-6914.
3. Trost, B.M.; Hiroi, K. *J. Am. Chem. Soc.* **1976**, 98, 4313-4315.
4. Lottenbach, W.; Graf, W. *Helv. Chim. Acta* **1978**, 61, 3087-3095.
5. Trost, B.M.; Tanigawa, Y. *J. Am. Chem. Soc.* **1979**, 101, 4413-4416.
6. Hiroi, K.; Sato, S. *Chem. Lett.* **1979**, 923-926
7. Thomas, A.; Vishwakarma, J.N.; Apparao, S.; Ila, H.; Junjappa, H. *Tetrahedron* **1988**, 44, 1667-1672.
8. Vishwakarma, J.N.; Thomas, A.; Apparao, S.; Ila, H.; Junjappa, H. *J. Chem. Soc. Perkin Tans. I*, **1988**, 169-173.
9. With lesser amount of LTA (1-1.5 eqv.) complete conversion of starting material was not observed.
10. Kawamoto, I., Muramatsu,S.; Yura, Y. *Tetrahedron Lett.* **1974**, 4223-4226.
11. Attempts to isolate α-acetoxy dithioacetals 11 under varying conditions were not successful.
12. Santelli-Rouvier, C.; Santelli, M *Synthesis* **1983**, 429-442.
13. Chauhan, S.M.S.; Junjappa, H. *Tetrahetron* **1976**, 32, 1779-1787.
14. Thuillier, A.; Vialle, J. *Bull. Soc. Chem. Fr.* **1962**, 2182-2186.
15. "CRC Handbook of Data on Organic Compounds", Weast, R.C.; Astle, M.J., Ed., CRC Press Inc., **1985**, Vol.1, p. 145.