SYNTHESIS OF 2-ALKYLIDENE-3,3-DIALKYL-1,4-DITHIANES AND THEIR OXATHIANE ANALOGUES BY 1,2-SULPHUR MIGRATION

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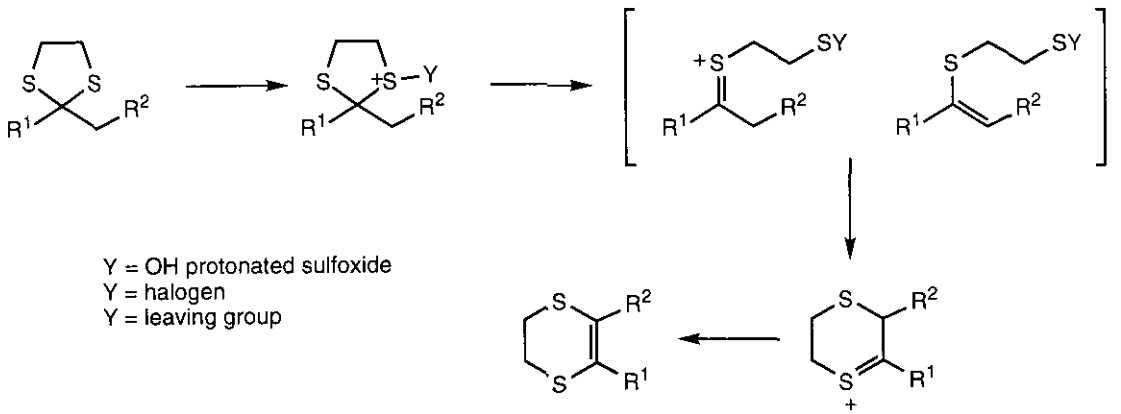
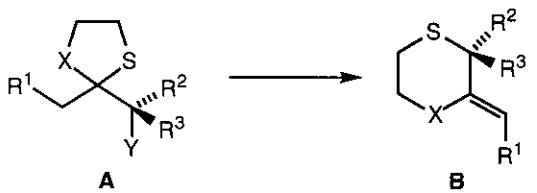
Abstract - 2-Alkylidene-3,3-dialkyl-1,4-dithianes and their oxathiane analogues were prepared from 1,2-diketones by a process involving formation of the monodithioacetal, transformation to a tertiary alcohol with organometallic reagents and ultimately 1,2-sulphur migration using methanesulphonyl chloride in pyridine as the activating agent.

1,2-Heteroatom migration in 1,3-hetero substituted cyclopentanes[1-4] causing ring expansion to form unsaturated 1,4-hetero substituted cyclohexanes is well documented. The synthesis of 5,6-dihydro-1,4-dithiins by 1,2-sulphur migration in 1,3-dithiolanes has been studied by several research groups[2-5] and usually involves two types of reaction. The first type, described in Scheme 1, involves activation[2] of one of the sulphur atoms of the dithiolane ring to form a sulphonium ion which undergoes ring opening, assisted by the adjacent sulphur atom. Proton loss produces a vinyl sulphide which is nucleophilic at the β-carbon. Formation of the expanded ring occurs *via* attack at the electrophilic sulphur atom. Within the same mechanistic type we have the thermal or acid catalysed rearrangement of sulphoxides (Scheme 1, Y=OH) *via* a similar ring opened intermediate.[3] With this procedure regiochemical and stereochemical control is difficult and R^1 is normally a non-enolisable group in order to prevent complex product mixtures.

Scheme 1

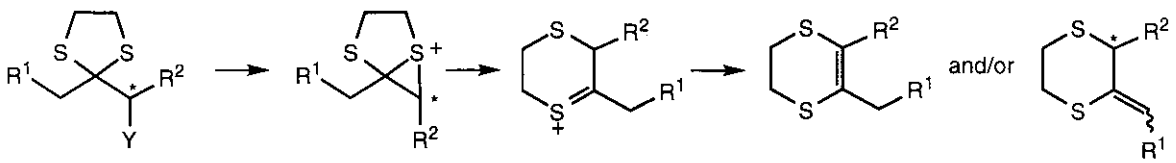


We[4] and others[5] have reported the second type, which we call the α-activation process. This process passes through a thiiranium ion intermediate (Scheme 2). This route provides greater control over the product and also permits the retention of asymmetry. We have studied the ring expansion of 2-(1-hydroxyalkyl-1,3-dithiolanes) and found that under suitable conditions a mixture of dithiin and alkylidenedithianes can be obtained depending upon the substrate. We have never obtained exclusively the alkylidenedithianes in situations where the isomeric dithiin is possible, even under kinetically controlled conditions. In systems where a seven membered ring is formed, by the ring expansion of a dithiane, the main product is an alkylidenedithiepane.[4] From this study it appeared that the only way to avoid dithiin (or oxathiin) formation during these ring expansion reactions was to eliminate the deprotonation pathway which produced them and for this we required the activated compounds of type (**A**) where Y is a good leaving group.



Initially we needed to know if the 1,2-heteroatom shift was applicable to tertiary alcohols, since the stability of possible intermediate carbocations could cause simple elimination or even carbon skeleton rearrangement reactions.We also envisioned that the alkylidene-1,4-dithianes (**B**) (X=S) and alkylidene-1,4-oxathianes (**B**) (X=O) could serve as a source of compounds with diverse reactivity. They have an electron rich double bond for addition reactions,[6] the stereo- and chemoselectivity of reactions, such as sulphoxidations, at the different sulphur atoms of compounds of type (**B**) is of interest as well as the effect of one sulphinyl group upon the reactivity of the remaining sulphide sulphur atom to reactions such as oxidation.[7] Pummerer rearrangement of these sulfoxides should produce highly substituted dithianes. Some fungicidal activity could also be expected from these molecules since structural analogues show considerable activity.[8] The oxathiane analogues are of interest for mechanistic reasons and also for a study of their stability compared to the corresponding dithianes.

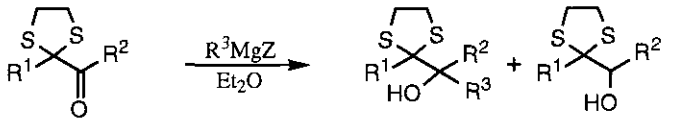
Scheme 2



Our starting materials were again the readily available 1,2-diketones. Monodithioacetalisation of several 1,2-dicarbonyl compounds was carried out uneventfully. The corresponding oxathiolanes were prepared similarly *albeit* in lower yields. Reaction of these substrates with various organomagnesium reagents at the hindered carbonyl gave the corresponding tertiary alcohols (Table 1) along with secondary alcohols in certain cases. These latter resulted from reduction by hydride from the decomposition of the

organomagnesium by β-hydride elimination. The efficiency of these reactions was dependent upon the nature of the reagent and the substrate (see Table 1). Larger groups R^1 or R^2 produced slightly more secondary alcohol than smaller ones, as would be expected. Benzoyldithiolanes were reduced significantly to the corresponding secondary benzylic alcohol and little tertiary alcohol was produced. Similar reaction of the acyloxathiolanes afforded good yields of tertiary alcohol and the degree of reduction of these analogues was much diminished. Some diastereoselectivity was also observed in these reactions (Table 2).

Table 1. Conversion of ketone (**1**) to tertiary alcohol (**3**).

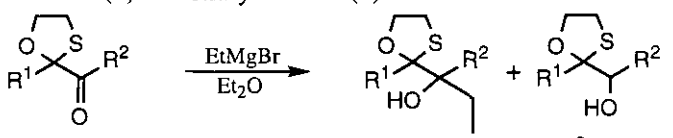


1 **3** **4**

Entry	1			Z	Time	3	4
	R^1	R^2	R^3		h	yield (%)	yield (%)
a	Me	Me	Et	Br	4	85	7.3
b	Et	Et	Et	Br	3	83	10
c	Me	Pr	Et	Br	18	75	*
d	Pr	Me	Et	Br	14	79	13
e	Me	Et	Et	Br	14	80	4.6
f	Et	Me	Et	Br	4	81	*
g	Me	Ph	Et	Br	19	29	66
h	Ph	Me	Et	Br	18	35	*
i	Ph	Ph	Et	Br	24	**	65
j	Me	Me	Me	I	14	99	-
k	Me	Et	Ph	Br	18	87	-
l	*Me*	*Me*	*Ph*	*Br*	15	82	-

* Although detected the amount was not determined ** Not detected, 22% of starting material recovered.

Table 2. Conversion of ketone (**7**) to tertiary alcohol (**8**).



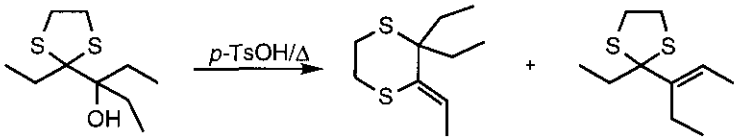
7 **8** **9**

Entry	7		Time	8	Diastereomer	9
	R^1	R^2	h	yield (%)	ratio[a]	yield (%)
a	Me	Me	5	79	1.8:1	4
b	Et	Et	26	86	-	2.5
c	Pr	Me	18	85	1.8:1	*b*
d	Me	Ph	20	81	2.1:1	17.5
e	Me	Et	19	81	-	3.4
f	Et	Me	18	73	-	8
g	Me	Pr	17	81	1:0	4.4

a) Diastereomer ratio determined by nmr for compound (**8**) only. *b*) Detected but not determined quantitatively.

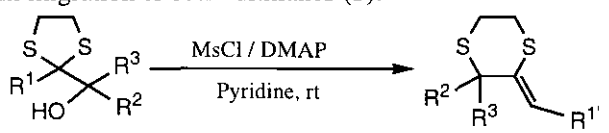
Attempts to promote the 1,2-sulfur migration by activating the hydroxyl group by protonation were not successful. When substrate (**3b**) was treated with *p*-toluenesulphonic acid (*p*TsA) in refluxing benzene, the ring expanded product (**5b**) was produced but considerable amounts of the unsaturated compound (**6**) were also generated (Scheme 3).

Scheme 3



Since heating the alkylidenedithiane (**5b**) under similar acid conditions did not afford (**6**), we assume that (**6**) is formed by deprotonation of the intermediate carbocation before sulphur migration occurs. This activation process thus appeared to be inefficient and inappropriate for the synthesis of the required product. Previous experience had shown that the formation of a sulphonate was a much milder activation method. Activation of the tertiary hydroxyl with *p*-toluenesulphonyl chloride (*p*TsCl) in the presence of pyridine and 4-dimethylaminopyridine (4-DMAP) was not possible because of the low reactivity of the tertiary hydroxyl group. The less bulky, more reactive reagent, methanesulphonyl chloride (MsCl) under similar conditions produced the alkylidenedithianes in good yields. Since the tertiary hydroxyl group is highly hindered it reacts only very slowly even with methanesulphonyl chloride and decomposition of this reagent effectively destroys it. One equivalent of the sulphonyl chloride resulted in low yields of the required rearrangement product. Large excesses of methanesulphonyl chloride are therefore necessary for complete reaction.

Table 3. 1,2-Sulphur atom migration to form dithianes (**5**).



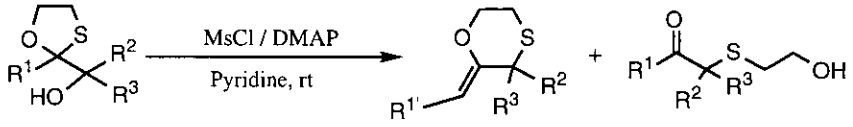
3 **5**

Entry	3			Equivalents of MsCl	Time d	5 yield(%)
	R^1	R^2	R^3			
a	Me	Me	Et	6	3	79
b	Et	Et	Et	6	3	87
c	Me	Pr	Et	6	5	73
d	Pr	Me	Et	8	5	75
e	Me	Et	Et	6	3	73
f	Et	Me	Et	6	3	71
g	Me	Me	Ph	6	3	59
h	Me	Et	Ph	10	5	14
i	Me	Me	Me	6	2	60

Similar treatment of the corresponding oxathiolanes gave, after purification, moderate yields of the alkylideneoxathiane (**10**) along with quantities of hydrolysis product (**11**). We were unable to find conditions where the formation of compound (**11**) could be completely avoided. The alkylideneoxathianes

hydrolyse readily to the corresponding ketone and cannot be stored. The expected microanalyses of these compounds were obtained only if the determination was carried out immediately after purification. The alkylidenedithianes, on the other hand, are perfectly stable under mildly acidic or basic conditions and can be stored for long periods.

Table 4. Formation of oxathianes (**10**) by 1,2-sulphur atom migration.



8 **10** **11**

Entry	8			Equivalents of MsCl	Time d	10 yield (%)	11 yield (%)
	R^1	R^2	R^3				
a	Me	Me	Et	3	4	40	a
b	Et	Et	Et	4	4	49	26
c	Pr	Me	Et	5	4	59	11
d	Et	Me	Ph	6	5	31	a,*
e	Me	Et	Et	5	4	44	16
f	Et	Me	Et	4	4	55	17
g	Me	Pr	Et	5	5	42	25

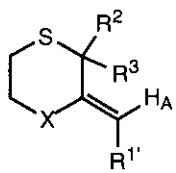
[a] The corresponding compound (**11**) was detected but not determined. * 25% of starting material recovered.

Initially we expected both geometric isomers about the double bond but in all possible cases only one isomer was detected by NMR and chromatography. The alkyl groups at the 3-position of the dithiane ring would certainly interact unfavourably with the alkyl group linked to the planar π-system in the *E*-isomer and thus the *Z*-isomer would be expected to be thermodynamically more stable. Analysing the NMR chemical shifts of the products we observe for the methylidene compounds, two vinylic signals with a separation of from 0.1 to 0.4 ppm. We can thus assume that the protons *cis*- or *trans*- to the ring sulphur atom in all of these compounds would have similar relative chemical shifts to these. Table 5 indicates the chemical shifts observed for the vinylic protons in the examples formed. Our assignments are made upon the basis of the work by Warren[9] where reference is also made to theoretical studies for the assignment of *E*- and *Z*-isomers in vinyl sulphides by analysis of NMR spectra. The vinylic proton *trans* to the sulphur atom of a trisubstituted thioenol ether resonates at lower field than the *cis* proton of its geometric isomer. From the NMR spectra of the vinylic sulphides (**5a-i**) it can be seen that the chemical shift of the vinylic proton H_A, which we assign as *trans*- to the ring sulphur atom, is slightly dependent on the ring substituents R^1 and R^2 as well as upon the nature of R^3. When $R^3 = H_B$ and R^1 and R^2 are both alkyl groups the H_A resonances appear within a range $\Delta\delta$ of about 0.2 ppm (centred about 5.45 ppm). When R^1 is a phenyl group the signal moves downfield to about 5.7 ppm. The signal for H_B appears within a narrower range ($\Delta\delta$ .05 ppm) about 5.2 ppm for R^1 and R^2 = alkyl which rises to about 5.45 ppm when R^1 = Ph. The effect of substituting R^3 = H for R^3 = alkyl is a downfield shift of about 0.3ppm for the H_A signal. If we invert the

geometry at the double bond, in (**5b**) for example, we would expect the proton, now in the position of R^3=H_B, to resonate about 0.3 ppm downfield from the value for R^3=H_B of its analogue (**5e**).

Table 5. Chemical shift data for the vinylic protons of the dithianes (**5**) and oxathianes (**10**).

Compound	R^2	R^3	$R^{1'}$	δH_A	$\delta R^{1'}$=H_B
5a	Et	Me	H	5.46	5.21
5b	Et	Et	Me	5.80	–
5c	Et	Pr	H	5.53	5.19
5d	Et	Me	Et	5.73	–
5e	Et	Et	H	5.54	5.19
5f	Et	Me	Me	5.81	–
5g	Ph	Me	H	5.66	5.44
5h	Ph	Et	H	5.71	5.45
5i	Me	Me	H	5.36	5.24
10a	Me	Et	H	4.38	4.57
10b	Et	Et	Me	4.83	–
10c	Et	Me	Et	4.79	–
10d	Me	Ph	Me	5.10	–
10e	Et	Et	H	4.37	4.65
10f	Et	Me	Me	4.88	–
10g	Et	Pr	H	4.36	4.63



5 X = S
10 X = O

Chemical shift calculations for enol ethers, using factors based upon experimental observation,[10] indicate that the proton *trans* to the oxygen atom resonates in the NMR at higher field with respect to the *cis* proton. For the methylidene compounds the NMR signals for the vinylic protons are well separated, more so than indicated by the additive rules.

Adding a factor of +0.45 ppm (for the alkyl group) to the H_A values of the methylidene compounds, we obtain numbers very close to those experimentally observed for the compounds (**10b,d,e,g**) having R^3 = alkyl. We are thus confident that the double bonds of these oxathianes also have the *Z*-geometry.

The alkylideneoxathianes (enol ethers) are unstable and cannot be stored for any length of time even in the cold. Formation of the ketones (**11**) occurs on silica gel, such that silica gel chromatographic analysis of these compounds is not very useful. Comparison of the NMR spectra of freshly purified and stored alkylideneoxathianes does show significant differences. Their instability makes further studies difficult as does their particularly unpleasant odour.

EXPERIMENTAL SECTION

Reagent quality solvents were distilled prior to use. Benzene was dried by standing over sodium wire and pyridine was dried by standing over CaH_2 followed by fractional distillation and stored under dry Ar. Anhydrous ether was prepared by distillation from sodium/benzophenone ketyl under argon. Anhydrous *p*-TsOH was prepared from commercial monohydrate by azeotropic distillation with benzene. Column chromatography was performed using silica gel Merck 60 H and for analytical TLC aluminium-backed silica gel Merck 60 F_{254} plates. MS and HRMS were obtained using a Kratos MS 25 RF and AEI/VG MS 9 mass spectrometers. IR spectra were recorded on a Buck Scientific Mod. 500 infrared spectrophotometer.

^1H and ^{13}C NMR were recorded on a Bruker CXP300 spectrometer. Chemical shifts are reported as δ values relative to tetramethylsilane (δ_H = 0 ppm) and $CDCl_3$ (δ_C = 77.0 ppm).

General procedure for the preparation of 2-hydroxyalkyl-1,3-dithiolanes (3) and 2-hydroxyalkyl-1,3-oxathiolanes (8).

To a suspension of magnesium (0.6 g; 24 mmol) in dry ether (15 mL) under an argon atmosphere, was slowly added a solution of alkyl or aryl halide (24 mmol) in dry ether (20 mL). The normal exothermic reaction was observed resulting in the disappearance of the metal. To the freshly prepared solution of Grignard reagent a solution of 2-acyl-2-alkyl-1,3-dithiolane or analogous 1,3-oxathiolane (12 mmol) in dry ether (7 mL) was slowly added and the mixture stirred for several hours at rt. Ice (5 g) was then added followed by concentrated sulphuric acid (2 mL), and the product then extracted with ether (3 x 30 mL). The combined organic phase was then washed with a saturated solution of $NaHCO_3$ and distilled water. After drying ($MgSO_4$) and solvent evaporation, the crude mixture was chromatographed on a silica gel column to separate the rquired (**3**) from the reduction product (**4**). The characterisation data for all the compounds (**4**) are available elsewhere.[4] Similarly the hydroxyalkyl-1,3-oxathiolanes (**8**) were separated from the reduction products (**9**).

This procedure was used for the synthesis of the following racemic 2-hydroxyalkyl-1,3-dithiolanes:

2-(1-Hydroxy-1-methylpropyl)-2-methyl-1,3-dithiolane (3a).

Oil. **^1H NMR** (300 MHz, $CDCl_3$) δ: 1.01 (3H, t, J=7.2; $C\underline{H}_3CH_2$); 1.33 (3H, s, $COHC\underline{H}_3$); 1.72 (2H, m, CH_3 $C\underline{H}_2$); 1.84 (3H, s, $C\underline{H}_3CSS$); 2.39 (1H, s, $CO\underline{H}CH_3$); 3.30 (4H, s, $S(C\underline{H}_2)_2S$). **IR** (film) 3462 (OH); 2974; 2917; 2872; 1453; 1384; 1282; 1179; 1134; 1100; 1066; 998; 861; cm^{-1}. **MS** (m/z) 192.064 (M^+); 177.038 (M^+ - CH_3); 163.024 (M^+ - C_2H_5); 120.006 (M^+ - C_4H_8O); 104.984 (M^+ - $C_5H_{11}O$). **Anal. Calcd** for $C_8H_{16}OS_2$: C, 49:96; H, 8.38; S, 33.34. **Found**: C, 50.16; H, 8.41; S, 33.64.

2-(1-Hydroxy-1-ethylpropyl)-2-ethyl-1,3-dithiolane (3b).

Oil. **^1H NMR** (300 MHz, $CDCl_3$) δ: 0.98 (6H, t, J=7.1, $(C\underline{H}_3CH_2)_2COH$); 1.21 (3H, t, J=7.1, $C\underline{H}_3CH_2$); 1.72-1.85 (4H, m, $(CH_3C\underline{H}_2)_2COH$); 1.91 (2H, q, J=7.1, $CH_3C\underline{H}_2$); 2.47 (1H, s, $CO\underline{H}(C_2H_5)_2$); 3.21 (4H, s, $S(C\underline{H}_2)_2S$). **IR** (film) 3462 (OH); 2951; 2925; 2868; 1452; 1372; 1270; 1236; 1123; 1100; 1054, 998; 952; 850; 725 cm^{-1}. **MS** (m/z) 221.097 (M^+ + H); 220.099 (M^+); 191.055 (M^+ - C_2H_5); 173.049 (M^+ - C_2H_5, H_2O); 134.018 (M^+ - $C_5H_{10}O$); 104.984 $(C_3H_5S_2)^+$. **Anal. Calcd** for $C_{10}H_{20}OS_2$: C, 54:50; H, 9.15; S, 29.09. **Found**: C, 54.64; H, 9.18; S, 29.32.

2-(1-Hydroxy-1-ethylbutyl)-2-methyl-1,3-dithiolane (3c).

Oil. **^1H NMR** (300 MHz, $CDCl_3$) δ: 0.93 (3H, t, J=6.9, $C\underline{H}_3CH_2CH_2$); 0.99 (3H, t, J=7.4, $C\underline{H}_3CH_2$); 1.46 (2H, m, $CH_3C\underline{H}_2CH_2$); 1.60-1.88 (4H, m, $CH_3CH_2C\underline{H}_2$ + $CH_3C\underline{H}_2$); 1.85 (3H, s, $C\underline{H}_3CSS$); 2.44 (1H, br, OH); 3.28 (4H, s, S $(C\underline{H}_2)_2S$). **IR** (film) 3462 (OH); 2951; 2917; 2860; 1452; 1372; 1270; 1236; 1123; 1100; 998; 952; 850; 725; 680; cm^{-1}. **MS** (m/z) 220.094 (M^+);

191.056 (M^+ - C_2H_5); 177.040 (M^+ - C_3H_7); 120.008 (M^+ - $C_6H_{12}O$). **Anal. Calcd** for $C_{10}H_{20}OS_2$: C, 54.50; H, 9.15; S, 29.09. **Found**: C, 54.63; H, 9.29; S, 28.79.

2-(1-Hydroxy-1-methylpropyl)-2-propyl-1,3-dithiolane (3d).
Oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 0.99 (3H, t, J=7.2, $C\underline{H}_3CH_2CH_2$); 1.00 (3H, t, J=7.4, $C\underline{H}_3CH_2$); 1.32 (3H, s, CH_3); 1.75 (6H, m, $CH_3C\underline{H}_2C\underline{H}_2$ + $CH_3C\underline{H}_2$); 3.22 (4H, s, $S(C\underline{H}_2)_2S$). **IR** (film) 3462 (OH); 2963; 2917; 2883; 1452; 1372; 1282; 1157; 998; 929; 839 cm^{-1}. **MS** (m/z) 220.095 (M^+); 191.078 (M^+ - C_2H_5); 148.080 (M^+ - C_4H_8O).

2-(1-Hydroxy-1-ethylpropyl)-2-methyl-1,3-dithiolane (3e).
Oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 0.99 (6H, t, J=7.3, $2(C\underline{H}_3CH_2)$); 1.76-1.85 (4H, m, $2(CH_3C\underline{H}_2)$); 1.85 (3H, s, $C\underline{H}_3CSS$); 2.41 (1H, s, OH); 3.28 (4H, s, $S(C\underline{H}_2)_2S$). **IR** (film) 3470 (OH); 2970; 2930; 2880; 1460; 1420; 1376; 1324; 1276; 1124; 1100; 964; 920 cm^{-1}. **MS** (m/z) 206.079 (M^+); 189.078 (M^+ - OH); 177.042 (M^+ - C_2H_5); 104.986 $(C_3H_5S_2)^+$. **Anal. Calcd** for $C_9H_{18}OS_2$: C, 52.38; H, 8.79; S, 31.07. **Found**: C, 52.74; H, 8.52; S, 30.75 .

2-(1-Hydroxy-1-methylpropyl)-2-ethyl-1,3-dithiolane (3f).
Oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 1.00 (3H, t, J=7.5, $C\underline{H}_3CH_2CSS$); 1.21 (3H, t, J=7.2, $C\underline{H}_3CH_2COH$); 1.32 (3H, s, CH_3); 1.64-1.75 (2H, m, $2(CH_3C\underline{H}_2CSS)$); 1.89 (2H, m, $2(CH_3C\underline{H}_2COH)$); 2.40 (1H, br, OH); 3.23 (4H, s, $S(C\underline{H}_2)_2S$). **IR** (film) 3462 (OH); 2963; 2917; 2872; 1463; 1418; 1372; 1282; 1157; 1043; 998; 918; 827 cm^{-1}. **MS** (m/z) 206.073 (M^+); 191.051 (M^+ - CH_3); 177.035 (M^+ - C_2H_5); 134.019 (M^+ - C_4H_8O); 104.982 (M^+ - $C_6H_{13}O$). **Anal. Calcd** for $C_9H_{18}OS_2$: C, 52:38; H, 8.79; S, 31.07. **Found**: C, 52.67; H, 8.82; S, 30.74.

2-(1-Hydroxy-1-phenylpropyl)-2-methyl-1,3-dithiolane (3g).
Oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 0.75 (3H, t, J=7.3, $C\underline{H}_3CH_2$); 1.76 (3H, s, CH_3); 2.03 (1H, dq, J=14.0, 7.3, if irradiated at 0.75 ppm, $CH_3C\underline{H}_2$); 2.53 (1H, dq, J=14.0, 7.3, $CH_3C\underline{H}_2$); 2.67 (1H, br, OH); 3.20-3.30 (4H, m, $SC\underline{H}_2C\underline{H}_2S$); 7.22-7.34 (3H, m, Ar-H *meta* + *para*); 7.56 (2H, d, J=7.3, Ar-H, *ortho*). **IR** (film) 3451 (OH); 3042; 3008; 2963; 2917; 2849; 1486; 1441; 1361; 1338; 1282; 1179; 1145; 1066; 1020; 907; 839; 759; 691 cm^{-1}. **MS** (m/z) 254.080 (M^+); 225.080 (M^+); 225.042 (M^+ - C_2H_5); 156.026 (M^+ - $C_8H_{10}O$). **Anal. Calcd** for $C_{13}H_{18}OS_2$: C, 61:38; H, 7.13; S, 25.20. **Found**: C, 61.05; H, 7.23; S, 25.29.

2-(1-Hydroxy-1-methylpropyl)-2-phenyl-1,3-dithiolane (3h).
Oil. **^{1}H NMR** (60 MHz, $CDCl_3$) δ: 0.81-1.12 (3H, t, J=7.3, $C\underline{H}_3CH_2$); 1.35 (3H, s, CH_3); 1.35-1.83 (2H, m, $CH_3C\underline{H}_2$); 2.62 (1H, br s, OH); 3.15-3.53 (4H, m, $S(C\underline{H}_2)_2S$); 7.20-8.15 (5H, m, Ar-H). **Anal. Calcd** for $C_{13}H_{18}OS_2$: C, 61.38; H, 7.13; S, 25.20. **Found**: C, 61.04; H, 7.32; S, 25.09.

2-(1-Hydroxy-1-methylethyl)-2-methyl-1,3-dithiolane (3j).

Oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 1.42 (6H, s, 2($C\underline{H}_3$)); 1.86 (3H, s, CH_3); 2.58 (1H, s, OH); 3.32 (4H, s, $S(C\underline{H}_2)_2S$). **IR** (film) 3440 (OH); 2970; 2920; 2860; 1448; 1420; 1365; 1336; 1276; 1180; 1134; 1100; 1068; 956; 872 cm^{-1}. **MS** (m/z) *178.045* (M^+); *163.030* (M^+ - CH_3); *120.001* ($C_4H_8S_2)^+$; 104.984 ($C_3H_5S_2$). **Anal. Calcd** for $C_7H_{14}OS_2$: C, 47:15; H, 7.91; S, 35.96. **Found:** C, 47.22; H, 8.02; S, 35.88.

2-(1-Hydroxy-1-phenylethyl)-2-methyl-1,3-dithiolane (3l).
Oil. **^{1}H NMR** (60 MHz, $CDCl_3$) δ: 1.75 (3H, s, $C\underline{H}_3CSS$); 1.84 (3H, s, CH_3); 2.91 (1H, br, OH); 3.26 (4H, m, $SC\underline{H}_2C\underline{H}_2S$); 7.28 (3H, m, Ar-H *meta + para*); 7.62 (2H, d, J=7, 1, Ar-H *orto*). **IR** (film) *3451 (OH); 3042; 3008; 2963; 2917; 2849; 1486; 1441; 1361; 1338; 1282; 1179; 1145; 1066; 1020;* 907; 839; 759; 691 cm^{-1}. **MS** (m/z) 204.063 (M^+); 223.062 (M^+ - OH); 118.997 $(C_4H_7S_2)^+$. **Anal. Calcd** for $C_{12}H_{16}OS_2$: C, 59:96; H, 6.71; S, 26.67 **Found**: C, 60.03; H, 6.90; S, 26.80.

2-(1-Hydroxy-1-methylpropyl)-2-methyl-1,3-oxathiolane (8a).
Oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 0.98 (3H, m, $C\underline{H}_3CH_2$); 1.23 (1.5H, s, $C\underline{H}_3CSO$, one diastereomer); 1.25 (1.5H, s, $C\underline{H}_3CSO$, one diastereomer); 1.52-1.64 (1H, m, $C\underline{H}_2CH_3$); 1.64 (3H, s, $C\underline{H}_3COH$); 1.77 (1H, m, $C\underline{H}_2CH_3$); 2.08 (1H, s, OH); 2.96-3.03 (2H, m, $SC\underline{H}_2CH_2O$); 4.07 (1H, m, $SCH_2C\underline{H}_2O$); 4.39 (1H, m, $SCH_2C\underline{H}_2O$). **IR** (film) 3462 (OH); 2974; 2929; 2872; 1453; 1361; 1259; 1123; 1077; 1054; 941; 895; 827 cm^{-1}. **MS** (m/z) 176.086 (M^+); 158.075 (M^+ - H_2O); 147.048 (M^+ - C_2H_5); 103.021 $(C_4H_5SO)^+$. **Anal. Calcd** for $C_8H_{16}O_2S$: C, 54.51; H, 9.15; S, 18.19. **Found**: C, 54.70; H, 9.02; S, 17.91.

2-(1-Hydroxyethyl)-2-methyl-1,3-oxathiolane (9a).
Oil. **^{1}H NMR** (60 MHz, CCl_4) δ: 1.15 (3H, d, J= 6.7, $CH(OH)C\underline{H}_3$); 1.45 (3H, s, CH_3); 2.64 (IH, br, OH); 3.01 (2H, t, J=5.3, $SC\underline{H}_2CH_2O$); 3.72 (IH, m, $C\underline{H}OH$); 4.15 (2H, t, J=5.3, $SCH_2C\underline{H}_2O$). **IR** (film): 3440 (OH); 2985; 2924; 2860; 1429; 1316; 1270; 1213; 1134; 1077; 918; 861, 839; cm^{-1} **MS** (m/z) 149(M^++H); 147(M^+-H); 71(M^+-C_2H_5OS)

2-(1-Hydroxy-1-ethylpropyl)-2-ethyl-1,3-oxathiolane (8b).
Oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 0.88-1.06 (9H, m, 3($C\underline{H}_3CH_2$)); 1.44 (1H, m, one $CH_3C\underline{H}_2$); 1.63-1.78 (4H, m, ($CH_3C\underline{H}_2)_2$); 1.98 (1H, m, $CH_3C\underline{H}_2$); 2.26 (1H, s, $O\underline{H}$); 2.94 (2H, t, J=5.8, $SC\underline{H}_2CH_2O$); 4.24 (2H, m, $SCH_2C\underline{H}_2O$). **IR** (film) 3462; 2963; 2929; 2872; 1656; 1463; 1372; 1338; 1259; 1168; 1157; 1066; 1054; 1020 952; 884; 850 cm^{-1}. **MS** (m/z) 186.109 (M^+ - H_2O); 175.078 (M^+ - C_2H_5); 157.069 (M^+- H_2O, C_2H_5); 117.038 (M^+ - $C_5H_{11}O$). **Anal. Calcd** for $C_{10}H_{20}O_2S$: C, 58.78; H, 9.87; S, 15.69. **Found**: C, 58.99; H, 9.63; S, 15.91.

2-(1-Hydroxypropyl)-2-ethyl-1,3-oxathiolane (9b).
Oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 1.02 (6H, m, 2($C\underline{H}_3CH_2$)); 1.63-2.04 (4H, m, 2($CH_3C\underline{H}_2$)); 2.15 (0.5H, d J=6.1, one diastereomer, $CHO\underline{H}$); *2.46 (0.5H, br, CHOH)*; 2.99 (2H, *t J=5.8*, $SC\underline{H}_2CH_2O$);

3.59 (IH, m, C<u>H</u>OH); 4.18 (2H, m, $SCH_2C\underline{H}_2O$). **IR** (film): 3462 (OH); 2963; 2929; 2872; 1463; 1372; 1270; 1157; 1088; 1054; 975; 861; 759; cm^{-1}. **MS** (m/z) 177(M^++H); 175(M^+-H); 99(M^+-C_2H_5OS.

2-(1-Hydroxy-1-methylpropyl)-2-propyl-1,3-oxathiolane (8c).
Oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 0.90-1.01 (6H, m, $C\underline{H}_3(CH_2)_2$ + $CH_3C\underline{H}_2$); 1.17 (1.5H, s, $C\underline{H}_3COH$, one diastereomer); 1.24 (1.5H, s, $C\underline{H}_3COH$, one diastereomer); 1.42-1.93 (6H, m, $CH_3(C\underline{H}_2)_2$ + $CH_3C\underline{H}_2$); 2.28 (1H, s, O<u>H</u>); 2.97 (2H, m, $SC\underline{H}_2CH_2O$); 4.18-4.32 (2H, m, $SCH_2C\underline{H}_2O$). **IR** (film) 3462 (OH); 2951; 2872; 1453; 1361; 1270; 1123; 1054; 998; 907; 829 cm^{-1}. **MS** (m/z) 204.122 (M^+); 175.077(M^+ - C_2H_5); 131.051(M^+ -C_4H_9O); 103.022 $(C_4H_7SO)^+$. **Anal. Calcd** for $C_{10}H_{20}O_2S$: C, 58.78; H, 9.87 S, 15.69. **Found**: C, 58.50; H, 9.95; S, 16.79.

2-(1-Hydroxyethyl)-2-propyl-1,3-oxathiolane (9c).
Oil (one diastereomer). **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 0.94 (3H, t, J=7.3, $C\underline{H}_3(CH_2)_2$); 1.22 (3H, d, J=6.4, $C\underline{H}_3CHOH$); 1.38-1.94 (4H, m, $CH_3(C\underline{H}_2)_2$); 2.47 (IH, s, OH); 2.99 (2H, t, J=5.7, $SC\underline{H}_2CH_2O$); 3.85-3.91 (IH, q, J=6.4, $CH_3C\underline{H}OH$); 4.06-4.17 (2H, t, J=5.7, $SCH_2C\underline{H}_2O$). **IR** (film): 3451 (OH); 2951;2929; 2860; 1453; 1361; 1259; 1213; 1066; 963; 941; 907; 873; 816 cm^{-1}. **MS** (m/z) 177(M^++H); 175(M^+-H); 99(M^+-C_2H_5OS).

2-(1-Hydroxy-1-phenylpropyl)-2-methyl-1,3-oxathiolane (8d).
Oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 0.74 (3H, t, J=7.4, $C\underline{H}_3CH_2$); 1.47 (3H, s, $C\underline{H}_3CSO$); 1.86 (0.5H, dq, J=14.3, 7.4, $CH_3C\underline{H}_2$, one diastereomer); 2.07 (0.5H, dq, J=14.3, 7.4, $CH_3C\underline{H}_2$, one diastereomer); 2.26 (0.5H, dq, J=14.3, 7.4, $CH_3C\underline{H}_2$, one diastereomer); 2.43 (1.5H, m, $CH_3C\underline{H}_2$, one diastereomer + O<u>H</u>); 2.86 (1H, m, one $SC\underline{H}_2CH_2O$); 3.98 (1H, m, one $SC\underline{H}_2CH_2O$); 4.02 (1H, m, one $SCH_2C\underline{H}_2O$); 4.36 (1H, m, one $SCH_2C\underline{H}_2O$); 7.21-7.34 (3H, m, Ar); 7.55 (2H, m, Ar). **IR** (film): 3462 (OH); 3042; 3008; 2951; 2929; 2860; 1497; 1452; 1372; 1270; 1157; 1123; 1066; 1043; 975; 907; 839; 736; 691 cm^{-1}. **MS (m/z):** 238.097 (M^+); 221.096(M^+ - OH); 135.087 $(C_9H_{11}O)^+$; 103.018 $(C_4H_7SO)^+$. **Anal. Calcd** for $C_{13}H_{18}O_2S$: C, 65.51; H, 7.61; S, 13.45. **Found**: C, 65.26; H, 7.68; S, 13.70.

2-(1-Hydroxy-1-phenylmethyl)-2-methyl-1,3-oxathiolane (9d)
Oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 1.42 (1.5H, s, $C\underline{H}_3CSO$, one diastereomer); 1.48 (1.5H, s, $C\underline{H}_3CSO$, one diastereomer); 2.88-3.08 (3H, m, $SC\underline{H}_2CH_2O$ + OH); 4.06-4.40 (2H, m, $SCH_2C\underline{H}_2O$); 4.75 (0.5H, s, C<u>H</u>OH, one diastereomer); 4.76 (0.5H, s, C<u>H</u>OH, one diastereomer); 7.24-7.32 (3H, m, Ar C<u>H</u> *para* + 2C<u>H</u> *meta*); 7.42 (IH, d, J=6.9, Ar C<u>H</u> *ortho*, one diastereomer); 7.48 (IH, d, J=7.2, Ar C<u>H</u> *ortho,* one diastereomer). **IR** (film): 3428 (OH); 3042; 3019; 2963; 2929; 2872; 1486; 1453; 1372; 1077; 1043; 827; 759, 702 cm^{-1} **MS** (m/z) 211(M^++1); 209(M^+-1); 133(M^+-C_2H_5)S. **Anal. Calcd** for $C_{11}H_{14}O_2S$: C, 62.83; H, 6.71; S, 15.25. **Found**: C, 62.92; H, 6.81; S, 15.10.

2-(1-Hydroxy-1-ethylpropyl)-2-methyl-1,3-oxathiolane (8e).

Oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 0.91-0.98 (6H, m, $(C\underline{H}_3CH_2)_2$); 1.52-1.78(4H, m, $(CH_3C\underline{H}_2)_2$); 1.61 (3H, s, CH_3); 2.26 (1H, s, OH); 2.93-3.01 (2H, m, $SC\underline{H}_2CH_2O$); 3.98-4.06 (1H, m, one of $SCH_2C\underline{H}_2O$); 4.34-4.40 (1H, m, one of $SCH_2C\underline{H}_2O$). **IR** (film) 3485 (OH); 2974; 2940; 2883; 1463; 1372; 1123; 1088; 975; 861 cm^{-1}. **Anal. Calcd** for $C_9H_{18}O_2S$: C, 56.80; H, 9.53; S, 16.85. **Found**: C, 56.99; H, 9.60; S, 16.60.

2-(1-Hydroxypropyl)-2-methyl-1,3-oxathiolane (9e).
Oil. **^{1}H NMR** (300 MHz,$CDCl_3$) δ: 1.04 (1.5H, t, J=7.4, $C\underline{H}_3CH_2$, one diastereoisomer); 1.05 (1.5H, t, J=7.4, $C\underline{H}_3CH_2$, one diastereoisomer); 1.54 (3H, m, $C\underline{H}_3CHOH$); 1.30-1.69 (2H, m, $CH_3C\underline{H}_2$); 1.54 (3H, m, $C\underline{H}_3CHOH$); 2.21 (1H, s, OH); 2.98-3.12 (2H, m, $SC\underline{H}_2CH_2O$); 3.54 (IH, m, $CH_3C\underline{H}OH$); 4.03-4.35 (2H, m, $SCH_2C\underline{H}_2O$). **IR** (film): 3451 (OH); 2974; 2940; 2883; 1452; 1372; 1259; 1088; 884 cm^{-1}. **MS** (m/z) 163(M^++1); 161(M^+-1); 85(M^+-C_2H_5OS).

2-(1-Hydroxy-1-methylpropyl)-2-ethyl-1,3-oxathiolane (8f).
Oil. **^{1}H NMR** *(300 MHz, CDCl3) δ: 0.90–0.98 (6H, m, 2x*$C\underline{H}_3CH_2$*); 1.15 (3H, s,* $C\underline{H}_3COH$ major diastereoisomer); 1.22 (3H, s, $C\underline{H}_3COH$ minor diastereoisomer); 1.41-1.62 (2H, m, $CH_3C\underline{H}_2COH$); 1.80-2.42 (2H, m, $CH_3C\underline{H}_2$); 2.20 (1H, br s, OH minor diastereoisomer); 2.24 (1H, br s, OH major diastereoisomer); 2.90-3.05 (2H, m, $SC\underline{H}_2CH_2O$); 4.20-4.30 (2H, m, $SCH_2C\underline{H}_2O$). **Anal. Calcd** for *$C_9H_{18}O_2S$: C, 56.80; H, 9.53; S, 16.85. **Found**: C, 56.99; H, 9.61; S, 16.67.*

2-(1-Hydroxyethyl)-2-ethyl-1,3-oxathiolane (9f).
Oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 1.00 (3H, t, J=7.4, $C\underline{H}_3CH_2$); 1.22 (3H, m, $C\underline{H}_3CHOH$); 1.70-2.04 (2H, m, $CH_3C\underline{H}_2$); 2.31 (IH, s, *OH*); 3.00 (2H, t, *J=5.7, $SC\underline{H}_2CH_2O$*); 3.91 (IH, q, J=6.3, $CH_3C\underline{H}OH$); 4.10-4.34 (2H, m, $SCH_2C\underline{H}_2O$). **IR** (film): 3440 (OH); 2963; 2929; 2872; 1452; 1372; 1327; 1259; 1225; 1168; 1066; 963; 895; 861; 770 cm^{-1}. **MS** (m/z) 163(M^++1); 161(M^+-1); 85(M^+-C_2H_5OS).

2-(1-Hydroxy-1-ethylbutyl)-2-methyl-1,3-oxathiolane (8g).
Oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 0.91 (3H, t, J=6.3, $C\underline{H}_3(CH_2)_2$); 0.96 (3H, t, J=7.4, $C\underline{H}_3CH_2$); 1.37-1.57 (3H, m, 2H of $CH_3(C\underline{H}_2)_2$ and 1H of $CH_3C\underline{H}_2$); 1.61 (3H, s, $C\underline{H}_3CSO$); 1.64-1.80 (3H, m, 2H of $CH_3(C\underline{H}_2)_2$ and 1H of $CH_3C\underline{H}_2$); 2.25 (1H, br s, OH); 2.90-3.04 (2H, m, $SC\underline{H}_2CH_2O$); 4.01 (1H, m, one $SCH_2C\underline{H}_2O$); 4.36 (1H, m, one $SCH_2C\underline{H}_2O$). **IR (film)** 3462 (br, OH); 2963; 2917; 2872; 1452; 1372; 1282; 1123; 1100; 998; 964; 850 cm^{-1}. **Anal. Calcd** for $C_{10}H_{20}O_2S$: C, 58.78; H, 9.87; S, 15.69. **Found**: C, 59.01; H, 9.96; S, 15.77.

2-(1-Hydroxybutyl)-2-methyl-1,3-oxathiolane (9g).
Oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 0.94 (3H, t, J=7.4, $C\underline{H}_3(CH_2)_2$); 1.36-1.46 (2H, m, $CH_3C\underline{H}_2CH_2$); 1.49-1.88 (2H, m, $CH_3CH_2C\underline{H}_2$); 1.54 (3H, s, $C\underline{H}_3SO$); 2.21 (0.5H, d, J=4.8, OH, one diastereomer); 2.46 (0.5H, br s, OH, one diastereomer); 2.99-3.08 (2H, m, $SC\underline{H}_2CH_2O$); 3.63 (IH,

m, CHOH); 4.13-4.31 (2H, m, SCH_2CH_2O). **IR** (film): 3460 (OH); 2970; 2930; 2860; 1464; 1442; 1372; 1268; 1216; 1068; 972; 836; cm^{-1}. **MS** (m/z) 177(M^++1); 175(M^+-1); 99(M^+-C_2H_5OS).

Migration reaction.

Preparation of 3,3-diethyl-2-ethylidene-1,4-dithiane (5b) and 3-ethyl-4,4-(1,2-ethanedithio)-2-hexene (6) using *p*-toluenesulphonic acid as activator.

To a stirred refluxing solution of racemic 2-(1-hydroxy-1-ethyl propyl)-2-ethyl-1,3-dithiolane (**3b**) (2 g; 9 mmol) in dry benzene (16.5 mL) under Ar atmosphere was added anhydrous *p*-TsOH (0.16 g; 0.9 mmol) and reflux was continued for 3 h. Sat. $NaHCO_3$ solution (5 mL) and water (2 mL) were then added and this mixture was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic phase was dried ($MgSO_4$) and the crude product was chromatographed on a silica gel column (eluent: CH_2Cl_2) to afford a mixture of (**5b**) and (**6**) . This mixture was further chromatographed on silica gel (eluent: *n*-hexane), thus affording the separated isomers (**5b**) and (**6**), the latter being identified as the more polar component. The respective yields were (**5b**) (1.05 g, 58%) and (**6**) (0.40 g, 22%).

Data for (**5b**) is reported later.

(**6**) Oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 0.94 (3H, t, J=6.6, CH_3CH_2); 1.09 (3H, t, J=6.6, CH_3CH_2); 1.67 (3H, d, J=7.3, CH_3CH); 2.20 (4H, m, CH_2CH_3); 3.22 (4H, m, S (CH_2)$_2$S); 5.82 (1H, q, J=7.3, CH_3CH). **IR** (film) 3019 (C=C-H); 2963; 2929; 2906; 2872; 1453; 1418; 1372; 1304; 1282; 1157; 1111; 1054; 929; 861; 804; 793 cm^{-1}. **Anal. Calcd** for $C_{10}H_{18}S_2$: C, 59.35; H, 8.96; S, 31.68. **Found**: C, 59.49; H, 8.75; S, 31.59.

General procedure for the preparation of 2-alkylidene-3,3-disusbstituted 1,4-dithianes (5) and the corresponding 1,4-oxathianes (10):

To a solution of 2-hydroxyalkyl-1,3-dithiolane (1.6 mmol) in dry pyridine (1 mL, 12.4 mmol), under an argon atmosphere and in an ice bath, were added 4,4-dimethylaminopyridine (0.006 g, 0.05 mmol) and methanesulphonyl chloride) (MsCl) (0.36 g; 3.2 mmol). After 15 min the temperature of the mixture was allowed to rise and the solution was stirred at rt (2 to 5 d.) adding MsCl (0.36 g, 3.2 mmol) at 24 h intervals. Sat. $NaHCO_3$ solution (5 mL) and water (2 mL) were added and the mixture vigorously stirred for 24 h more. Ether (10 mL) was added followed by a 10% aqueous solution of HCl (2 mL, pH < 5), when synthesizing 1,4-dithianes (a saturated solution of $CuSO_4$ was used for this wash, instead of HCl when synthesizing 1,4-oxathianes).The mixture was then extracted with ether (3 x 10 mL). The combined organic phase was then washed with a sat. $NaHCO_3$ solution and these washings extracted with ether (2 x 20 mL). After drying ($MgSO_4$) and solvent evaporation, the crude mixture was chromatographed on a silica gel plate or column. For the oxathianes the chromatography was carried out using solvents containing trace quantities of triethylamine to reduce the acidity of the silica and hence to prevent excessive decomposition. The required compound (**10**) was separated from the ketone (**11**) during this process.

3-Ethyl-3-methyl-2-methylidene-1,4-dithiane (5a).

Oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 0.83 (3 H, t, J=7.3, $C\underline{H}_3CH_2$); 1.39 (3H, s, CH_3); 1.85 (1H, dq, J=13.7, 7.3, $CH_3C\underline{H}_2$); 2.33 (1H, dq, J=13.7, 7.3, $CH_3C\underline{H}_2$); 2.79 (2H, m, $SC\underline{H}_2C\underline{H}_2S$); 3.13 (1H, m, $SC\underline{H}_2C\underline{H}_2S$); 3.33 (1H, m, $C\underline{H}$, $SC\underline{H}_2C\underline{H}_2S$); 5.21 (1H, s, one $C\underline{H}_2$); 5.46 (1H, s, one $C\underline{H}_2$). **IR** (film) 2963; 2929; 2906; 2872; 1588; 1453; 1406; 1372; 1282; 1088; 895 cm^{-1}. **MS** (m/z) 174.059 (M^+); 146.027 ($M^+ - C_2H_4$); 145.019 ($M^+ - C_2H_5$). **Anal. Calcd** for $C_8H_{14}S_2$: C, 55.12; H, 8.09; S, 36.78. **Found**: C, 55.24; H, 8.01; S, 36.70.

3,3-Diethyl-2-ethylidene-1,4-dithiane (5b).
Oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 0.83 (6 H, t, J=7.4, $2(C\underline{H}_3CH_2)$); 1.70-1.87 (1H, dq, J=14.5, 7.3, $CH_3C\underline{H}_2$); 1.88-1.90 (3H, d, J=6.3, $C\underline{H}_3CH$); 2.16-2.28 (1H, dq, J=14.5, 7.3, $CH_3C\underline{H}_2$); 2.91-3.13 (4H, m, $S(C\underline{H}_2)_2S$); 5.80 (1H, q, J=6.3, $C\underline{H}_3CH$). **IR** (film) 2963; 2929; 2906; 2872; 1463; 1418; 1384; 1293; 1123; 873; 816; cm^{-1}. **MS** (m/z) 201 (M^+ - H). **Anal. Calcd** for $C_{10}H_{18}S_2$: C, 59.35; H, 8.96; S, 31.68. **Found**: C, 559.50; H, 9.03; S, 31.53.

3-Ethyl-2-methylidene-3-propyl-1,4-dithiane (5c).
Oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 0.86 (3H, t, J=7.3, $C\underline{H}_3CH_2CH_2$); 0.93 (3H, t, J=7.1, $C\underline{H}_3CH_2$); 1.19 (1H, m, $CH_3C\underline{H}_2CH_2$); 1.37 (1H, m, $CH_3C\underline{H}_2CH_2$); 1.63-1.72 (1H, m, $CH_3CH_2C\underline{H}_2$); 1.73-1.81 (1H, dq, J=13.6, 7.1, $CH_3C\underline{H}_2$); 2.07-2.17 (1H, m, $CH_3CH_2C\underline{H}_2$); 2.17-2.27 (1H, dq, J=13.6, 7.1, $CH_3C\underline{H}_2$); 2.94-3.06 (4H, m, $S(C\underline{H}_2)_2S$); 5.19 (1H, s, $C\underline{H}_2$=C); 5.53 (1H, s, $C\underline{H}_2$=C). **IR** (film) 2951; 2929; 2906; 2872; 1588; 1453; 1406; 1372; 1282; 1111; 895; 850 cm^{-1}. **MS** (m/z) 203 (M^+ + H). **Anal. Calcd** for $C_{10}H_{18}S_2$: C, 59.35; H, 8.96; S, 31.68. **Found**: C, 59.65; H, 8.85; S, 31.53.

3-Ethyl-3-methyl-2-propylidene-1,4-dithiane (5d).
Oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 0.78 (3 H, t, J=7.3, $C\underline{H}_3CH_2$); 0.98 (3H, t, J=7.4, $C\underline{H}_3CH_2CH$); 1.37 (3H, s, CH_3); 1.81 (1H, dq, J=13.8, 7.4, $CH_3C\underline{H}_2$); 2.27-2.47 (3H, m, $CH_3C\underline{H}_2CH$ + $CH_3C\underline{H}_2$); 2.65-2.82 (2H, m, $S(C\underline{H}_2)_2S$); 3.02 (1H, m, $S(C\underline{H}_2)_2S$); 3.30-3.40 (1H, m, $S(C\underline{H}_2)_2S$); 5.73 (1H, t, J=7.1, $CH_3CH_2C\underline{H}$). **IR** (film) 2951; 2929; 2906; 2872; 1453; 1418; 1384; 1293; 1134; 1100; 861; 793; 691 cm^{-1}. **MS** (m/z) 202.083 (M^+); 173.041 ($M^+ - C_2H_5$); 128.059 ($M^+ - C_2H_5 - C_3H_8$). **Anal. Calcd** for $C_{10}H_{18}S_2$: C, 59.35; H, 8.96; S, 31.68. **Found**: C, 59.54; H, 9.05; S, 31.97.

3,3-Diethyl-2-methylidene-1,4-dithiane (5e).
Oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 0.85 (6 H, t, J=7.5, $2(C\underline{H}_3CH_2)$); 1.78 (2H, dq, J=14.3, 7.5, $2(CH_3C\underline{H}_2)$); 2.22 (2H, dq, J=14.3, 7.5, $2(CH_3C\underline{H}_2)$); 3.01 (4H, m, $S(C\underline{H}_2)_2S$); 5.19 (1H, s, $C\underline{H}_2CH$); 5.54 (1H, s, $C\underline{H}_2CH$). **IR** (film) 2963; 2929; 2906; 2872; 1600; 1463; 1418; 1384; 1293; 1202; 1111; 1054; 907; 861; 793 cm^{-1}. **Anal. Calcd** for $C_9H_{16}S_2$: C, 57.39; H, 8.56; S, 34.04. **Found**: C, 57.54; H, 8.64; S, 33.90.

3-Ethyl-2-ethylidene-3-methyl-1,4-dithiane (5f).
Oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 0.78 (3 H, t, J=7.4, $C\underline{H}_3CH_2$); 1.30 (3H, s, CH_3); 1.78-1.91 (1H, dq, J=13.7, 7.4, $CH_3C\underline{H}_2$); 1.86-1.88 (3H, d, J=6.4, $C\underline{H}_3CH$); 2.36-2.45 (1H, dq, J=13.7, 7.4, $CH_3C\underline{H}_2$); 2.66-2.84 (2H, m, $S(C\underline{H}_2)_2S$); 2.98-3.07 (1H, m, $S(C\underline{H}_2)_2S$); 3.30-3.40 (1H, m, $S(C\underline{H}_2)_2S$); 5.78-5.85 (1H, q, J=6.4, $CH_3C\underline{H}$). **IR** (film) 2963; 2917; 2906; 2872; 1453; 1418; 1372; 1282; 1123; 1088; 998; 918; 839; 804 cm^{-1}. **MS** (m/z) 188.069 (M^+); 159.039 ($M^+ - C_2H_5$). **Anal. Calcd** for $C_9H_{16}S_2$: C, 57.39; H, 8.56; S, 34.04. **Found**: C, 57.21; H, 8.63; S, 34.16.

3-Methyl-3-phenyl-2-methylidene-1,4-dithiane (5g).
Oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 1.68 (3H, s, CH_3); 2.66 (2H, m, $S(C\underline{H}_2)_2S$); 2.99 (1H, m, $S(C\underline{H}_2)_2S$); 3.20 (1H, m, $S(C\underline{H}_2)_2S$); 5.44 (1H, s, $C\underline{H}_2$); 5.66 (1H, s, $C\underline{H}_2$); 7.24 (1H, t, J=7.2, Ar C*H para*); 7.35 (1H, t, J=7.4, Ar C*H meta*); 7.60 (2H, d, J=8.1, Ar C*H ortho*). **IR** (film) 3042 (C=C-H); 3008 (C=C-H); 2963; 2906; 2860; 1588; 1486; 1441; 1406; 1361; 1282; 1191; 1054; 1038; 895; 850; 759; 691 cm^{-1}. **MS** (m/z) 222.052 (M^+); 162.051 ($M^+ - C_2H_4S$); 130.079 ($M^+ - C_2H_4S_2$). **Anal. Calcd** for $C_{12}H_{14}S_2$: C, 64.82; H, 6.35; S, 28.84. **Found**: C, 65.05; H, 6.47; S, 28.99.

3-Ethyl-3-phenyl-2-methylidene-1,4-dithiane (5h).
Oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 0.79 (3H, t, J=7.3, $C\underline{H}_3CH_2$); 1.99-2.15 (2H, m, $CH_3C\underline{H}_2$); 2.67-2.83 (2H, m, $S(C\underline{H}_2)_2S$); 2.99-3.24 (2H, m, $S(C\underline{H}_2)_2S$); 5.45 (1H, s, $C\underline{H}_2$=C); 5 .71 (1H, s, $C\underline{H}_2$=C); 7.25 (1H, t, J=7.1, Ar-H *para*); 7.36 (2H, t, J=7.6, Ar-H *meta*); 7.54 (2H, d, J=8.1, Ar-H *ortho*). **IR** (film) 3042; 3008; 2963; 2929; 2906; 2872; 1600; 1486; 1441; 1406; 1384; 1293; 1157; 1077; 1032; 907; 861; 748; 691 cm^{-1}. **Anal. Calcd** for $C_{13}H_{16}S_2$: C, 66.05; H, 6.82; S, 27.12. **Found**: C, 66.20; H, 6.90; S, 27.35.

3,3-Dimethyl-2-methylidene-1,4-dithiane (5i).
Oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 1.63 (6H, s, $2CH_3$); 2.98-3.09(4H, m, $S(C\underline{H}_2)_2S$); 5.24 (1H, s, $C\underline{H}_2$=C); 5.36 (1H, s, $C\underline{H}_2$=C). **^{13}C NMR** ($CDCl_3$) δ: 28.18 (C-5); 29.01 ($\underline{C}H_3CS$); 34.41 (C-6); 43.09 (C-3); 113.24 ($H_2\underline{C}$=C); 147.03 (H_2C=$\underline{C}$). **IR** (film) 3100 (C=C-H); 2970 (C-H); 2929 (C-H); 1590; 1460; 1416; 1364; 1304; 1292; 1268; 1128; 908; 860 cm^{-1}.**MS** Calculated for $C_7H_{12}S_2$: 160.0380. Found: 160.0380. **Anal. Calcd** for $C_7H_{12}S_2$: C, 52.45; H, 7.55; S, 40.00. **Found**: C, 52.75; H, 7.65; S, 40.23.

3-Ethyl-3-methyl-2-methylidene-1,4-oxathiane (10a).
Oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 0.89 (3H, t, J=7.5, $C\underline{H}_3CH_2$); 1.31(3H, s, CH_3); 1.79 (1H, dq, J=14.1, 7.5, $CH_3C\underline{H}_2$); 2.44 (1H, dq, J=14.1, 7.5, $CH_3C\underline{H}_2$); 2.42-2.49 (1H, m, $SC\underline{H}_2CH_2O$); 3.11-3.20 (1H, m, $SC\underline{H}_2CH_2O$); 3.95-4.03 (1H, m, $OC\underline{H}_2CH_2S$); 4.29-4.35 (1H, m, $OC\underline{H}_2CH_2S$); 4.38 (1H, s, CH_2); 4.57 (1H, s, CH_2). **IR** (film) 2963; 2929; 2872; 1452;1372; 1350; 1304; 1213; 1123; 1034; 1100; 1009; 952; 895 cm^{-1}. **MS** (m/z) 159 (M^++H); 158 (M^+)115 (M^+-C_2H_7). **Anal. Calcd** for $C_8H_{14}OS$: C, 60.72; H, 8.92; S, 20.26. **Found**: C, 60.90; H, 9.00; S, 20.11.

3-Ethyl-6-hydroxy-3-methyl-4-thia-2-hexanone (11a).
Oil. **MS** (m/z) 176.273 (M^+).

3,3-Diethyl-2-ethylidene-1,4-oxathiane (10b).
Oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 0.84 (3H, t, J=7.4, 2($C\underline{H}_3CH_2$)); 1.60-1.62 (3H, d, J=6.6, $CHC\underline{H}_3$); 1.56-1.71 (2H, dq, J=14.1, 7.4, 2($CH_3C\underline{H}_2$)); 1.96-2.03 (2H, dq, J=14.1, 7.4, 2($CH_3C\underline{H}_2$)); 2.82 (2H, t, J=5.1, $SC\underline{H}_2CH_2O$); 4.09 (2H, t, J=5.1, $OC\underline{H}_2CH_2S$); 4.83 (1H, q, J=6.6, $C\underline{H}CH_3$). **IR** (film) 2963; 2929; 2860; 1668; 1452; 1372; 1304; 1123; 1077; 793 cm^{-1}. **MS** (m/z) 186 (M^+); 157 ($M^+ - C_2H_5$). **Anal. Calcd** for $C_{10}H_{18}OS$: C, 64.47; H, 9.74; S, 17.21. **Found**: C, 64.70; H, 9.82; S, 17.51

4,4-Diethyl-7-hydroxy-5-thia-3-heptanone (11b).
Oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 0.87 (6H, t, J=7.4, 2($C\underline{H}_3CH_2$)); 1.08 (3H, t, J=7.3, $C\underline{H}_3CH_2CO$); 1.71-1.86 (4H, m, 2($CH_3C\underline{H}_2$)); 2.25 (1H, br, OH); 2.45 (2H, t, J=6.2, $SC\underline{H}_2CH_2OH$); 2.69-2.76 (2H, q, J=7.3, $CH_3C\underline{H}_2CO$); 3.63 (2H, t, J=6.2, $SCH_2C\underline{H}_2OH$). **IR** (film) 3417 (OH); 2963; 2929; 2872; 1690 (C=O); 1463; 1384; 1282; 1191; 1100; 1054; 861; 725 cm^{-1}. **MS** (m/z) 203 (M^+ - H); 147 ($M^+ - C_2H_5O$). **Anal. Calcd** for $C_{10}H_{20}O_2S$: C, 58.78; H, 9.87; S, 15.69. **Found**: C, 59.05; H, 9.91; S, 15.78.

3-Ethyl-3-methyl-2-propylidene-1,4-oxathiane (10c).
Oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 0.85 (3H, t, J=7.4, $C\underline{H}_3CH_2$); 0.96 (3H, t, J=7.7, $C\underline{H}_3CH_2CH$); 1.27 (3H, s, CH_3); 1.68-1.77 (2H, m, $CH_3C\underline{H}_2$); 2.02-2.13 (2H, m, $CH_3C\underline{H}_2CH$); 2.41-2.48 (1H, m, $SC\underline{H}_2CH_2O$); 3.15-3.23 (1H, m, $SC\underline{H}_2CH_2O$); 3.85-3.92 (1H, m, $OC\underline{H}_2CH_2S$); 4.28-4.33 (1H, m, $OC\underline{H}_2CH_2S$); 4.79 (1H, t, J=7.1, $CH_3CH_2C\underline{H}$). **IR** (film) 2951; 2917; 2872; 1690; 1668; 1453; 1372; 1304; 1077; 1020; 793; 736 cm^{-1}. **MS** (m/z) 187 (M^+ + H); 186 (M^+). **Anal. Calcd** for $C_{10}H_{18}OS$: C, 64.47; H, 9.74; S, 17.21. **Found**: C, 64.70; H, 9.83; S, 17.31.

5-Ethyl-8-hydroxy-5-methyl-6-thia-4-octanone (11c).
Oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 0.87-0.98 (6H, m, $C\underline{H}_3CH_2CH_2CO$ + $C\underline{H}_3CH_2$); 1.38 (3H, s, CH_3); 1.57-1.95 (4H, m, $CH_3C\underline{H}_2$ + $CH_3C\underline{H}_2CH_2$); 2.26 (1H, br, $O\underline{H}$); 2.51-2.74 (4H, m, $CH_3CH_2C\underline{H}_2$ + $SC\underline{H}_2CH_2OH$); 3.65 (2H, t, J=6.2, $SCH_2C\underline{H}_2OH$). **IR** (film) 3418 (OH); 2963; 2929; 2872; 1690 (C=O); 1463; 1384; 1202; 1123; 1043; 1020; 725 cm^{-1}. **MS** (m/z) 203 (M^+ - H); 133 (M^+ - Me - Et); 127 ($M^+ - SCH_2CH_2OH$). **Anal. Calcd** for $C_{10}H_{20}O_2S$: C, 58.78; H, 9.87; S, 15.69. **Found**: C, 59.08; H, 9.98; S, 15.87.

2-Ethylidene-3-methyl-3-phenyl-1,4-oxathiane (10d).
Oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 1.54 (3H, s, CH_3); 1.72 (3H, t, J=6.6, $C\underline{H}_3CH$); 2.35 (1H, m, $SC\underline{H}_2CH_2O$); 2.85 (1H, m, $SC\underline{H}_2CH_2O$); 3.94 (1H, m, $SCH_2C\underline{H}_2O$); 4.25 (1H, m, $SCH_2C\underline{H}_2O$); 5.10 (1H, q, J=6.6, $C\underline{H}CH_3$); 7.21 (1H, t, J=7.4, Ar-H); 7.32 (2H, t, J=7.6, Ar-H); 7.32 (2H, t, J=7.7,

Ar-H). **Anal. Calcd** for $C_{13}H_{16}OS$: C, 70.87; H, 7.32; S, 14.55. **Found**: C, 71.02; H, 7.38; S, 14.31.

7-Hydroxy-4-methyl-4-phenyl-5-thia-3-heptanone (11d).
Oil. **MS** (m/z) 238.105 (M^+).

3,3-Diethyl-2-methylidene-1,4-oxathiane (10e).
Oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 0.87 (6H, t, J=7.5, 2($C\underline{H}_3CH_2$)); 1.57-1.76 (2H, m, 1 each of 2($CH_3C\underline{H}_2$)); 1.95-2.07 (2H, m, 1 each of 2($CH_3C\underline{H}_2$)); 2.80-2.83 (2H, t, J=5.1, $SC\underline{H}_2CH_2O$); 4.14-4.17 (2H, t, J=5.1, $SCH_2C\underline{H}_2O$); 4.37 (1H, s, CH_2); 4.65 (1H, s, CH_2). **IR** (film) 2963; 2929; 2860; 1634; 1463; 1418; 1316; 1293; 1066; 850 cm^{-1}. **Anal. Calcd** for $C_9H_{16}OS$: C, 62.74; H, 9.36; S, 18.61. **Found**: C, 62.88; H, 9.47; S, 18.68.

3,3-Diethyl-6-hydroxy-4-thia-2-hexanone (11e).
Oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 0.88 (6H, t, J=7.4, 2($C\underline{H}_3CH_2$)); 1.67-1.85 (4H, m, 2($CH_3C\underline{H}_2$)); 2.32 (3H, s, CH_3); 2.47 (2H, t, J=6.3, $SC\underline{H}_2CH_2OH$); 3.64 (2H, t, J=6.3, $SCH_2C\underline{H}_2OH$). **IR** (film) 3406 (OH); 2951; 2929; 2872;1690 (C=O); 1453; 1372; 1282; 1202; 1123; 1100; 1043 cm^{-1}. **MS** (m/z) 191 (M^++H); 189 (M^+-H); 113 (M^+-C_2H_5OS). **Anal. Calcd** for $C_9H_{18}O_2S$: C, 56.80; H, 9.53; S, 16.85. **Found**: C, 56.88; H, 9.60; S, 17.05.

3-Ethyl-2-ethylidene-3-methyl-1,4-oxathiane (10f).
Oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 0.85 (3H, t, J=7.6, $C\underline{H}_3CH_2$); 1.28 (3H, s, CH_3); 1.60 (3H, d, J=6.7, $CHC\underline{H}_3$); 1.76 (1H, m, one $CH_3C\underline{H}_2$); 2.04 (1H, m, $CH_3C\underline{H}_2$); 2.42-2.49 (1H, m, $SC\underline{H}_2CH_2O$); 3.14-3.24 (1H, m, $SC\underline{H}_2CH_2O$); 3.86-3.94 (1H, m, $OC\underline{H}_2CH_2S$); 4.27-4.33 (1H, m, $OC\underline{H}_2CH_2S$); 4.81-4.88 (1H, q, J=6.7, $C\underline{H}CH_3$). **MS** (m/z) 173 (M^+ + H); 143 (M^+ - C_2H_5). **Anal. Calcd** for $C_9H_{16}OS$: C, 62.74; H, 9.36; S, 18.61. **Found**: C, 62.95; H, 9.40; S, 18.86.

4-Ethyl-7-hydroxy-4-methyl-5-thia-3-heptanone (11f).
Oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ:0.91(3H, t, J=7.4, $C\underline{H}_3CH_2$); 1.07 (3H, t, J=7.3, $C\underline{H}_3CH_2CO$); 1.39 (3H, s, CH_3); 1.73 (1H, m, one $CH_3C\underline{H}_2$); 1.91 (1H, m, one $CH_3C\underline{H}_2$); 2.46 (1H, br, OH); 2.54 (2H, t, J=6.2, $SC\underline{H}_2CH_2OH$); 2.61-2.78 (2H, m, $CH_3C\underline{H}_2CO$); 3.64 (2H, t, J=6.2, $SCH_2C\underline{H}_2OH$). **IR** (film) 3428 (OH); 2985; 2940; 2883; 1690 (C=O); 1463; 1418; 1384; 1350; 1191; 1043; 975 cm^{-1}. **MS** (m/z) 189 (M^+ - H). **Anal. Calcd** for $C_9H_{18}O_2S$: C, 56.80; H, 9.53; S, 16.85. **Found**: C, 56.92; H, 9.60; S, 17.00.

3-Ethyl-2-methylidene-3-propyl-1,4-oxathiane (10g).
Oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 0.85 (3H, t, J=7.5, $C\underline{H}_3(CH_2)_2$); 0.93 (3H, t, J=7.3, $C\underline{H}_3CH_2$); 1.22-1.38 (2H, m, $CH_3C\underline{H}_2CH_2$); 1.55-1.75 (2H, m, $CH_3CH_2C\underline{H}_2$+$CH_3C\underline{H}_2$); 1.87-2.06 (2H, m, $CH_3CH_2C\underline{H}_2$+$CH_3C\underline{H}_2$); 2.79-2.83 (2H, m, $SC\underline{H}_2CH_2O$); 4.15 (2H, t, J=5.1, $OC\underline{H}_2CH_2S$); 4.36

(1H, s, vinylic H); 4.63 (1H, s, vinylic H). **IR** (film) 2951; 2872; 1645; 1463; 1307; 1157; 1077; 1043; 861 cm^{-1}. **MS** (m/z) 187 (M^++H); 143 (M^+-Pr). **Anal. Calcd** for $C_{10}H_{18}OS$: C, 64.47; H, 9.74; S, 17.21. **Found**: C, 64.58; H, 9.80; S, 17.32.

3-Ethyl-6-hydroxy-3-propyl-4-thia-2-hexanone (11g).
Oil. ^{1}**H NMR** (300 MHz, $CDCl_3$) δ: 0.89 (3H, t, J=7.4, $C\underline{H}_3CH_2CH_2$); 0.95 (3H, t, J=7.2, $C\underline{H}_3CH_2$); 1.15 (1H, m, $CH_3C\underline{H}_2CH_2$); 1.40 (1H, m, $CH_3C\underline{H}_2CH_2$); 1.60-1.82 (4H, m, $CH_3C\underline{H}_2$ + $CH_3CH_2C\underline{H}_2$); 2.31 (3H, s, CH_3); 2.43-2.52 (3H, m, $SC\underline{H}_2CH_2OH$ + OH); 3.64 (2H, t, J=6.3Hz, $SCH_2C\underline{H}_2OH$). **IR** (film) 3406 (OH); 2951; 2929; 2872; 1702; 1463; 1350; 1202; 1077; 1054; 929; 736 cm^{-1}. **MS** (m/z) 203 (M^+-H); 161 (M^+-C_2H_3O); 127 (M^+-SCH_2CH_2OH). **Anal. Calcd** for $C_{10}H_{20}O_2S$: C, 58.78; H, 9.87; S, 15.69. **Found**: C, 58.66; H, 10.08; S, 15.98.

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