Synthesis of Thionolactones from Homoallylic Xanthates

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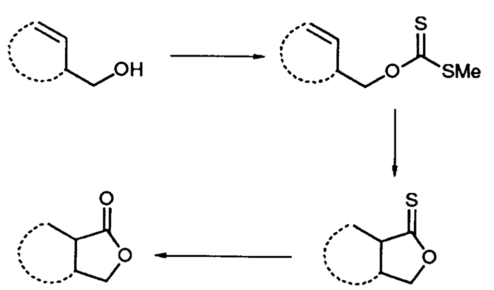
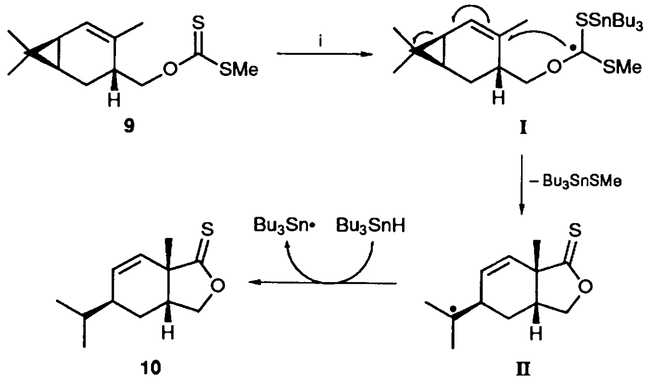
The intramolecular radical cyclisation of cyclic homoallylic xanthates were explored. In five- or six-membered ring systems, the homoallylic xanthates were easily cyclised to give fused thionolactone derivatives. The thionolactones were converted into their corresponding lactones in high yield, which constitutes a transformation of homoallylic alcohols into lactones.

Much attention has been focused on radical-initiated cyclisation reactions from both synthetic and mechanistic viewpoints in the last decade.[1] On the other hand, the synthetic utility of xanthates has been quite limited except for the reduction of the corresponding alcohol *via* a radical process.[2] Intramolecular radical cyclisations of linear homoallylic xanthates were pioneered by Bachi and Bosch;[3] however, their study was focused on the mechanism rather than on synthetic utility. We recently reported the tributyltin hydride-assisted, highly stereo- and regio-selective lactonisation of homoallylic xanthates in which initially formed thionolactones were conveniently converted with peracid into the corresponding lactones in high yields.[4] To establish a general route to synthetically useful, fused lactones using this radical methodology, cyclisation of various cyclic homoallylic xanthates has been investigated (Scheme 1). We report herein the scope and limitations of our lactonisation procedure.



Scheme 1

Cyclic homoallylic xanthates can be easily synthesized from homoallylic alcohols,[5] carbon disulphide, and methyl iodide under basic conditions.[2b] The xanthates were treated with tributyltin hydride (1.2 mol equiv.) in thiophene-free, degassed, dry toluene and heated at 80 °C for 1–2 h with portionwise addition of 10% azoisobutyronitrile (AIBN) under argon to afford fused thionolactones in 33–71% yield. The results are summarised in Table 1. Low yields in entries 3–5 might be the result of the simple reduction of xanthates to afford volatile hydrocarbons; no by-product was detected. The intramolecular radical cyclisations were highly regioselective to give the 5-*exo-trig* cyclised thionolactones, all with *cis* ring-fusions.[6] The stereochemistry of the ring junctions was determined from nuclear Overhauser effect (NOE) enhancements. In the NOESY spectrum of compound **4**, a cross-signal between protons 8-H and 9-H was observed, attesting to a *cis* ring-junction. There is a clear trend in yields of the cyclisation products. In the case of five- or six-membered-ring systems, cyclisation proceeded in high yield (entries 1 and 2) while lower yields were observed in the case of seven-, eight- and sterically hindered, six-membered systems (entries 3–5). The results can be rationalised in terms of geometric requirements for frontier molecular orbital interactions due to the larger entropy factor for larger ring formation. Therefore, medium and strained ring systems are inferior to five- and six-membered ones in these cyclisations.



Scheme 2 *Reagents:* i, Bu_3SnH, AIBN

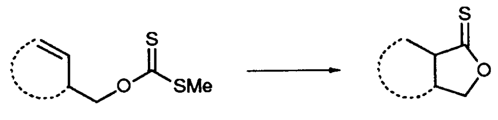
In entry 5, the tandem radical reaction (ring closure–ring opening) proceeded regio- and stereo-selectively. The resulting carbon-centred radical from thionolactone annulation *via* intermediates I and II readily underwent scission of the adjacent cyclopropane ring[7] (Scheme 2). However, xanthate **7** did not give the tandem reaction product since the reaction would require unfavourable internal 3-*exo* or 4-*endo* cyclisation.

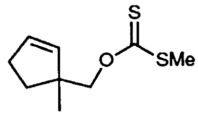
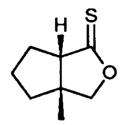
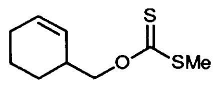
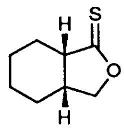
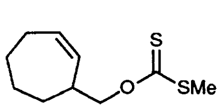
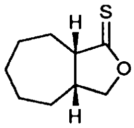
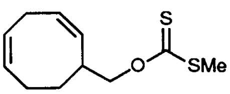
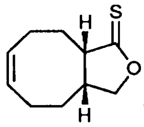
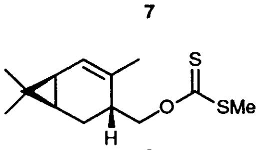
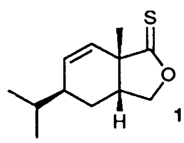
The thionolactones obtained were easily oxidised to the corresponding lactones in high yields with *m*-chloroperbenzoic acid (MCPBA) (1.3 mol equiv.) in CH_2Cl_2 at room temperature.[8] The results are shown in Table 2. The established transformation of homoallylic alcohols to γ-lactones should have wide applicability in organic synthesis.

Experimental

^1H NMR spectra were observed with Hitachi R-24B, R-600, JOEL JNM-GX270, JNM-FX270, GSX-400 and GSX-500 spectrometers. *J*-values are given in Hz. ^{13}C NMR spectra were observed on JEOL JNM-GX270 and JNM-FX270 spectrometers. Chemical shifts are reported in parts per million (δ; ppm) relative to Me_4Si as internal standard in $CDCl_3$ or CCl_4. IR spectra were obtained on a Hitachi 215 or a JASCO A-202 IR spectrophotometer. Mass spectra were taken with an RNU-7M mass spectrometer at 70 eV. Column chromatography was performed on Merck Art 7734, Wako gel C-200, Fujigel BW-200, or BW-820MH. Centrifugal liquid chromatography was performed on Fujigel KT-2061. All solvents were freshly distilled and stored under nitrogen. Tetrahydrofuran (THF) was distilled from lithium aluminium hydride and stored over molecular sieves 5 Å. Toluene, benzene and hexane were

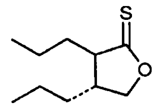
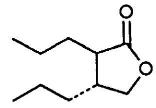
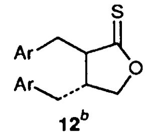
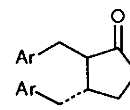
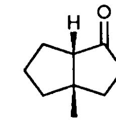
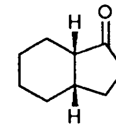
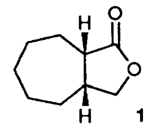
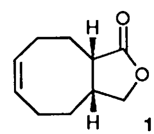
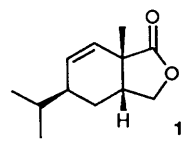
Table 1 Intramolecular radical cyclisation of cyclic homoallylic xanthates



Entry	Xanthate	Product	Yield (%)[a]
1	 **1**	 **2**	70
2	 **3**	 **4**	71
3	 **5**	 **6**	47
4	 **7**	 **8**	42
5	 **9**	 **10**	33

[a] Isolated yield.

Table 2 Oxidation of thionolactones

Entry	Thionolactone	Product	Yield (%)[a]
1	 **11**[b]	 **13**	67[b]
2	 **12**[b] Ar = m-MeOC$_6$H$_4$	 **14**	65[b]
3	**2**	 **15**	80
4	**4**	 **16**	75
5	**6**	 **17**	74
6	**8**	 **18**	65
7	**10**	 **19**	70

[a] Isolated yield. [b] Ref. 4.

dried over sodium wire. Unless otherwise noted, other solvents were used after simple distillation. High-performance liquid chromatography (HPLC) was performed on a Merck Lichrosorb Si 60 column. The purity of all new compounds was demonstrated to be >95% by HPLC, ^{1}H NMR and ^{13}C NMR.

General Procedure for the Preparation of the Xanthate **3**.—To a stirred suspension of NaH (0.62 g, 15.5 mmol; 60% in oil) in dry THF (10 cm^3) was added a solution of the corresponding cyclic homoallylic alcohol (1.447 g, 13.2 mmol) in THF (3 cm^3). The resulting suspension was stirred for 1 h, and then treated with dry CS$_2$ (4 cm^3). The mixture was stirred for 1 h, when MeI (2 cm^3) was added to the reddish suspension. A white precipitate was immediately generated, saturated aq. NH$_4$Cl was added, and the organic layer was separated, washed (brine), and dried (MgSO$_4$). The reaction products were purified by flash column chromatography on silica gel (hexane) to give the *xanthate* **3** (2.129 g) as a pale yellow oil in 82% yield, ν_{max}(neat)/cm^{-1} 2925, 2850, 1640, 1210 and 1060; δ_H(CDCl$_3$) 1.45 (1 H, m, 5-H′), 1.60 (1 H, m, 5-H″), 1.77 (1 H, m, 6-H′), 1.86 (1 H, m, 6-H″), 2.00 (2 H, br s, 4-H$_2$), 2.56 (3 H, s, SMe), 2.68 (1 H, br s, 1-H), 4.48 (2 H, d, $J_{1,1'}$ 6.1, OCH$_2$), 5.60 (1 H, dd, $J_{2'3'}$ 9.9, $J_{2'1'}$ 2.2, 2-H′) and 5.83 (1 H, m, 3-H′); INEPT δ_C(CDCl$_3$) 18.86 (Me), 20.56 (CH$_2$), 25.15 (CH$_2$), 25.69 (CH$_2$), 34.70 (CH), 77.28 (CH$_2$), 126.43 (CH), 129.93 (CH) and 215.89 (C) (Found: C, 53.7; H, 7.0. C$_9$H$_{14}$OS$_2$ requires C, 53.46; H, 6.98%).

Radical Cyclisation of Cyclic Homoallylic Xanthates; General Procedure for Compound **4**.—A stirred mixture of the xanthate **3** (50 mg, 0.25 mmol), tributyltin hydride (88.9 mg, 0.31 mmol) and a catalytic amount of AIBN in thiophene-free, degassed dry toluene (25 cm^3) were heated at 80 °C for 2 h under argon. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (benzene) to give of *compound* **4** (27.4 mg) as an oil in 71% yield, ν_{max}(neat)/cm^{-1} 2950, 2875, 1450, 1370, 1260, 1230, 1180, 1130 and 900; δ_H(CDCl$_3$) 1.10–1.40 (3 H, m, 5-H$_2$ and 6-H), 1.40–1.80 (4 H, m, 4-H$_2$, 6-H, and 7-H), 2.34 (1 H, br d, $J_{7,7'}$ 10.8, 7-H′), 2.58 (1 H, m, 8-H), 2.83 (1 H, ddd, $J_{9,7'}$ 10.8 $J_{9,8}$ 6.6, $J_{9,7'}$ 3.6, 9-H), 4.28 (1 H, dd, $J_{3,3'}$ 9.2, $J_{3,8}$ 1.5, 3-H) and 4.50 (1 H, dd, $J_{3,3'}$ 9.2, $J_{3',8}$ 5.2, 3-H′); δ_C(CDCl$_3$) 21.59 (t), 23.55 (t), 25.87 (t), 26.68 (t), 36.89 (d), 52.89 (d), 79.28 (t) and 225.58 (s) (Found: M$^+$, 156.0602. C$_8$H$_{12}$OS requires *M*, 156.0607).

Oxidation of the Thionolactones; General Procedure for Lactone **16**.—To a stirred solution of compound **4** (50.0 mg, 0.32 mmol) in dry CH$_2$Cl$_2$ (5 cm^3) was added MCPBA (80.0 mg).

The resulting mixture was stirred for 1 h. Saturated aq. $NaHCO_3$ was added, and the organic layer was separated, washed (brine), and dried ($MgSO_4$). The reaction products were purified by flash column chromatography on silica gel (4:1 v/v hexane–EtOAc) to give *lactone* **16** (33.6 mg) as an oil in 75% yield, ν_{max}(neat)/cm^{-1} 2925, 2850, 1770, 1440, 1370, 1160, 1005 and 940; δ_H($CDCl_3$) 1.15–1.30 (3 H, m, 5-H_2 and 6-H), 1.55–1.70 (3 H, m, 4-H_2 and 6-H), 1.80–1.85 (1 H, m, 7-H), 2.15 (1 H, m, 7-H′), 2.45 (1 H, m, 8-H), 2.63 (1 H, m, 9-H), 3.96 (1 H, dd, $J_{3,3'}$ 8.8, $J_{3,8}$ 1.10, 3-H) and 4.20 (1 H, dd, $J_{3,3'}$ 8.8, $J_{3',8}$ 4.8, 3-H′); δ_C($CDCl_3$) 22.48 (C-5), 22.90 (C-6), 23.42 (C-4), 27.17 (C-7), 35.38 (C-8), 39.93 (C-9), 71.74 (C-3) and 178.52 (C=O) (Found: M$^+$, 140.0836. $C_8H_{12}O_2$ requires M, 140.0835).

The following compounds were similarly prepared following the respective General Procedure.

Xanthate **1**: Pale yellow oil (70% yield); ν_{max}(neat)/cm^{-1} 2950, 2850, 1630, 1450, 1210, 1060 and 960; δ_H($CDCl_3$) 1.15 (3 H, s, Me), 1.64 (1 H, dt, $J_{5',5''}$ 13.3, $J_{5',4'}$ 7.4, 5-H′), 1.92 (1 H, dt, $J_{5',5''}$ 13.3, $J_{5'',4''}$ 6.7, 5-H″), 2.38–2.44 (2 H, m, 4-H_2), 2.55 (3 H, s, SMe), 4.38 (1 H, d, $J_{1,1}$ 10.5, OCH), 4.43 (1 H, d, $J_{1,1}$ 10.5, OCH), 5.54 (1 H, dt, $J_{2',3'}$ 5.6, $J_{2',4'}$ 2.1, 2-H′) and 5.76 (1 H, dt, $J_{2',3'}$ 5.6, $J_{3',4'}$ 2.4, 3-H′); δ_C($CDCl_3$) 18.67 (SMe), 23.81 (Me), 31.70 (C-5), 34.25 (C-4), 49.27 (C-1), 80.63 (OCH_2), 131.58 (C-2), 135.99 (C-3) and 215.91 (C=S) (Found: M$^+$, 202.0691. $C_9H_{14}OS_2$ requires *M*, 202.0691).

Thionolactone **2**: Oil (70% yield); ν_{max}(neat)/cm^{-1} 2930, 2850, 1450, 1230, 1155, 1060 and 960; δ_H($CDCl_3$) 1.25 (3 H, s, Me), 1.60–1.70 (2 H, m, 5-H_2), 1.70–1.80 (2 H, m, 4-H_2), 2.20 (2 H, m, 6-H_2), 2.97 (1 H, dd, $J_{6,8}$ 8.5, $J_{6',8}$ 4.3, 8-H), 4.25 (1 H, d, $J_{3,3'}$ 9.6, 3-H′); δ_C($CDCl_3$) 24.53 (Me), 25.31 (C-5), 33.95 (C-4), 39.93 (C-6), 48.35 (C-7), 67.18 (C-8), 87.25 (C-8) and 229.16 (C=S) (Found: M$^+$, 156.0610. $C_8H_{12}OS$ requires *M*, 156.0612).

Lactone **15**: Oil (80% yield); ν_{max}(neat)/cm^{-1} 2950, 2875, 1770, 1450, 1280, 1160 and 1010; δ_H($CDCl_3$) 1.25 (3 H, s, Me), 1.60–1.70 (2 H, m, 5-H_2), 1.75–1.83 (2 H, m, 4-H_2), 2.00–2.10 (2 H, m, 6-H_2), 2.55 (1 H, dd, $J_{6,8}$ 9.0, $J_{6'8}$ 3.3, 8-H), 4.06 (1 H, d, $J_{3,3'}$ 9.0, 3-H) and 4.10 (1 H, d, $J_{3,3'}$ 9.0, 3-H′); δ_C($CDCl_3$) 4.76 (Me), 25.58 (C-5), 29.84 (C-4), 40.22 (C-6), 46.76 (C-7), 51.58 (C-8), 78.90 (C-3) and 180.95 (C=O) (Found: M$^+$, 140.0844. $C_8H_{12}O_2$ requires *M*, 140.0842).

Xanthate **5**: Pale yellow oil (68% yield); ν_{max}(neat)/cm^{-1} 2925, 2850, 1650, 1440, 1220, 1060 and 960; δ_H($CDCl_3$) 1.30–1.40 (2 H, m, 6-H_2), 1.55–1.65 (1 H, m, 5-H′), 1.70–1.75 (2 H, m, 7-H′ and 5-H″), 1.95–2.05 (1 H, m, 7-H″), 2.05–2.55 (2 H, m, 4-H_2), 2.55 (3 H, s, SMe), 2.80 (1 H, br s, 1-H′), 4.52 (2 H, d, $J_{11'}$ 6.9, OCH_2), 5.60 (1 H, m, 2-H′) and 5.90 (1 H, m, 3-H′); INEPT δ_C($CDCl_3$) 18.87 (Me), 26.69 (CH_2), 28.73 (CH_2), 28.73 (CH_2), 30.06 (CH_2), 30.09 (CH_2), 39.14 (CH), 77.76 (CH_2), 132.37 (CH), 133.22 (CH) and 215.99 (C) [Found: *m/z*, 124.1248. C_9H_{13} ($M^+ - CH_4OS_2$) requires *m/z* 124.1248; Found: C, 55.8; H, 7.4. $C_{10}H_{16}OS_2$ requires C, 55.54; H, 7.46%].

Thionolactone **6**: Oil (47% yield); ν_{max}(neat)/cm^{-1} 2900, 2850, 1450, 1370, 1280, 1250, 1210, 1170 and 950; δ_H($CDCl_3$) 1.20–1.45 (3 H, m, 6-H_2 and 5-H), 1.45–1.55 (1 H, m, 5-H′), 1.65–1.80 (2 H, m, 7-H_2), 1.80–1.90 (2 H, m, 4-H_2), 1.90–2.00 (1 H, m, 8-H), 2.30 (1 H, m, 8-H′), 2.80 (1 H, m, 9-H), 3.12 (1 H, ddd, $J_{8,10}$ 14.2, $J_{8',10}$ 9.3, $J_{9,10}$ 5.0, 10-H), 4.24 (1 H, dd, $J_{3,3'}$ 9.1, $J_{3,9}$ 5.5, 3-H) and 4.71 (1 H, dd, $J_{3,3'}$ 9.1, $J_{3',9}$ 7.9, 3-H′); δ_C($CDCl_3$) 27.80 (C-6), 28.33 (C-7), 30.20 (C-5), 30.26 (C-4), 31.22 (C-8), 41.51 (C-9), 58.60 (C-9), 81.34 (C-3) and 228.07 (C=S) (Found: M$^+$, 170.0765. $C_9H_{14}OS$ requires *M*, 170.0765).

Lactone **17**: Oil (74% yield); ν_{max}(neat)/cm^{-1} 2925, 2850, 1770, 1330, 1170 and 1010; δ_H($CDCl_3$) 1.20–1.40 (3 H, m, 6-H_2 and 5-H), 1.45–1.70 (3 H, m, 5-H′ and 7-H_2), 1.70–1.95 (3 H, m, 4-H_2 and 8-H_2), 2.07 (1 H, m, 8-H′), 2.80 (2 H, m, 9- and 10-H), 3.91 (1 H, dd, $J_{3,3'}$ 9.1, $J_{3,9}$ 5.3, 3-H) and 4.40 (1 H, dd, $J_{3,3'}$ 9.1, $J_{3',9}$ 8.0, 3-H′); δ_C($CDCl_3$) 27.49 (C-6), 28.06 (C-5), 28.10 (C-7), 31.02 (C-4), 31.46 (C-8), 40.38 (C-9), 44.21 (C-10), 72.53 (C-3) and 181.00 (C=O) (Found: M$^+$, 154.0984. $C_9H_{14}O_2$ requires *M*, 154.0993).

Xanthate **7**: Pale yellow oil (74% yield); ν_{max}(neat)/cm^{-1} 2925, 2850, 1640, 1440, 1420, 1220, 1060 and 960; δ_H($CDCl_3$) 1.20–1.32 (1 H, m, 8-H′), 1.50–1.64 (1 H, m, 8-H″). 2.00–2.10 (1 H, m, 7-H′), 2.50–2.70 (2 H, m, 7-H″ and 4-H′), 2.55 (3 H, s, SMe), 2.85 (1 H, br s, 1-H′), 3.35–3.40 (1 H, m, 4-H′), 4.54 (1 H, dd, $J_{1,1'}$ 10.3, $J_{1,1'}$ 6.5, 1-H), 4.58 (1 H, dd, $J_{1,1'}$ 10.3, $J_{1',1'}$ 5.2, 1-H′), 5.20 (1 H, dd, $J_{1',2}$ $J_{2',3'}$ 9, 2-H′), 5.45 (1 H, dt, $J_{2',3'}$ and $J_{3',4'}$ 9, 3-H′), 5.70 (1 H, dt, $J_{5',6'}$ 11.0, $J_{6',7'}$ 5.2, 6-H′) and 5.80 (1 H, dt, $J_{5',6'}$ 11.0, $J_{5',4'}$ 5.2, 5-H′); INEPT δ_C($CDCl_3$) 18.83 (Me), 24.07 (CH_2), 26.23 (CH_2), 29.76 (CH_2), 35.30 (CH), 77.85 (CH_2), 128.49 (CH), 128.89 (CH), 129.97 (CH), 130.48 (CH) and 215.99 (C) (Found: M$^+$, 228.0657. $C_{11}H_{16}OS_2$ requires *M*, 228.0642).

Thionolactone **8**: Oil (42% yield); ν_{max}(neat)/cm^{-1} 2925, 2850, 1430, 1210 and 1005; δ_H($CDCl_3$) 1.20–1.35 (1 H, m, 4-H), 1.50–1.60 (1 H, m, 4-H′), 1.80–1.92 (1 H, m, 9-H), 2.15–2.30 (3 H, m, 5-H_2 and 9-H′), 2.35–2.45 (1 H, m, 8-H), 2.45–2.60 (2 H, m, 8-H′ and 10-H), 2.83 (1 H, ddd, $J_{9,11}$ 11.6, $J_{10,11}$ 8.7, $J_{9',11}$ 4.7, 11-H), 4.05 (1 H, t, $J_{3,3'} = J_{3,10}$ = 9.5, 3-H), 4.75 (1 H, t, $J_{3,3'} = J_{3',10}$ = 9.5, 3-H′) and 5.70 (2 H, m, 6- and 7-H); δ_C 23.97 (C-4), 24.73 (C-9), 31.02 (C-5), 34.59 (C-8), 41.65 (C-10), 57.25 (C-11), 80.02 (C-3), 129.92 (C-7), 129.97 (C-6) and 228.74 (C=S) (Found: M$^+$, 182.0719. $C_{10}H_{14}OS$ requires *M*, 182.0764).

Lactone **18**: Oil (65% yield); ν_{max}(neat)/cm^{-1} 2950, 2850, 1770, 1640, 1170 and 1040; δ_H($CDCl_3$) 1.35 (1 H, m, 4-H), 1.40–1.60 (1 H, m, 4-H′), 1.80–1.90 (1 H, m, 9-H), 2.15–2.30 (4 H, m, 5-H_2, 8-H, and 9-H′), 2.30–2.40 (1 H, m, 8-H′), 2.40–2.55 (2 H, m, 10- and 11-H), 3.70 (1 H, t, $J_{3,3'} = J_{3,10}$ = 9.2, 3-H), 4.39 (1 H, t, $J_{3,3'} = J_{3'10}$ 9.2, 3-H′) and 5.65–5.79 (2 H, m, 6- and 7-H); δ_C($CDCl_3$) 23.75 (C-4), 24.69 (C-9), 30.22 (C-5), 31.66 (C-8), 40.74 (C-10), 43.35 (C-11), 71.64 (C-3), 129.72 (C-7), 130.26 (C-6) and 180.76 (C=O) (Found: M$^+$, 166.1014. $C_{10}H_{14}O_2$ requires *M*, 166.0993).

Xanthate **9**: Pale yellow oil (85% yield); ν_{max}(neat)/cm^{-1} 2950, 2875, 1440, 1210, 1060 and 960; δ_H($CDCl_3$) 0.85 (1 H, m, 6-H′), 0.90 (3 H, s, 7-Me′), 0.95 (1 H, H, br d, 1-H′), 1.05 (3 H, s, 7-Me″), 1.55 (1 H, m, 5-H′), 1.75 (3 H, s, 3-Me), 2.05 (1 H, m, 5-H′), 2.25 (1 H, m, 4-H′), 2.55 (3 H, s, SMe), 4.55 (2 H, d, $J_{1,1'}$ 6.5, 1-H_2) and 5.50 (1 H, br s, 2-H′); INEPT δ_C($CDCl_3$) 15.04 (Me), 16.92 (CH), 18.81 (Me), 20.01 (C), 21.98 (CH_2), 22.63 (CH), 23.30 (Me), 27.64 (Me), 37.35 (CH), 75.21 (CH_2), 122.86 (CH), 135.45 (C) and 215.85 (C) [Found: *m/z* 209.0992. $C_{12}H_{17}OS$ ($M - CH_3S$) requires *m/z* 209.0999. Found: C, 61.2; H, 7.5. $C_{13}H_{20}OS_2$ requires C, 60.92; H, 7.87%].

Thionolactone **10**: Oil (33% yield); ν_{max}(neat)/cm^{-1} 2925, 2910, 2850, 1650, 1450, 1270, 1190 and 950; δ_H($CDCl_3$) 0.91 (3 H, d, $J_{11,12}$ 7.8, Me), 0.94 (3 H, d, $J_{11,13}$ 7.8, Me), 1.37 (3 H, s, 10-H_3), 1.50–1.60 (1 H, m, 4-H), 1.70 (1 H, m, 4-H′), 1.80 (1 H, m, 11-H), 2.00 (1 H, m, 5-H), 2.60 (1 H, m, 8-H), 4.30 (1 H, dd, $J_{3,3'}$ 8.8, $J_{3,8}$ 6.3, 3-H), 4.60 (1 H, dd, $J_{3,3'}$ 8.8, $J_{3',8}$ 6.8, 3-H′), 5.55 (1 H, ddd, $J_{6,7}$ 10.2, $J_{5,6}$ 2.47, $J_{6,11}$ 1.10, 6-H) and 5.75 (1 H, dd, $J_{6,7}$ 10.2, $J_{5,7}$ 1.9, 7-H); δ_C($CDCl_3$) 19.19 (C-12), 19.43 (C-13), 21.60 (C-10), 26.44 (C-4), 31.48 (C-11), 36.72 (C-5), 41.01 (C-8), 55.80 (C-9), 75.80 (C-3), 129.47 (C-6), 130.83 (C-7) and 228.84 (C=S) (Found: M$^+$, 210.1071. $C_{12}H_{18}OS$ requires *M*, 210.1076).

Lactone **19**: Oil (70% yield); ν_{max}(neat)/cm^{-1} 2950, 2850, 1760, 1635, 1450, 1080 and 1005; δ_H($CDCl_3$) 0.91 (3 H, d, $J_{11,12}$ 6.3, Me), 0.93 (3 H, d, $J_{11,13}$ 6.3, Me), 1.28 (3 H, s, 10-H_3), 1.55 (1 H, m, 4-H), 1.62–1.73 (2 H, m, 4-H′ and 11-H), 2.00 (1 H, m, 5-H), 2.53–2.62 (1 H, m, 8-H), 4.03 (1 H, dd, $J_{3,3'}$ 9.5, $J_{3,8}$ 8.6, 3-H), 4.28 (1 H, t, $J_{3,3'} = J_{3',8}$ = 8.6, 3-H′), 5.53 (1 H, ddd, $J_{6,7}$ 10.2 $J_{5,6}$ 2.5, $J_{6,11}$ 1.4, 6-H) and 5.80 (1 H, dd, $J_{6,7}$ 10.2, $J_{5,7}$ 1.9, 7-H); δ_C($CDCl_3$) 19.17 (C-12), 19.46 (C-13), 21.34 (C-10), 22.91 (C-4), 31.55 (C-11), 36.64 (C-5), 40.00 (C-8), 43.40 (C-9), 68.23 (C-3), 126.70 (C-6), 132.10 (C-7) and 180.01 (C=O) (Found: M$^+$, 194.1305. $C_{12}H_{18}O_2$ requires *M*, 194.1305).

Supplementary material is available; copies of ^{1}H NMR and ^{13}C NMR spectra for compounds **1–10** and **15–19** are available from the British Library Document Centre (BLDC).*

* See Instructions for Authors (1991), *J. Chem. Soc., Perkin Trans. 1*, 1991, Issue 1.

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