The First Preparation of β -Lactones by Radical Cyclization

Kerstin Castle, Chee-San Hau, J.B. Sweeney* and Craig Tindall

Department of Chemistry, University of Reading, Reading RG6 6AD, UK

e-mail: j.b.sweeney@rdg.ac.uk

Supplementary Material

Notes

1. ^{13}C nmr data are assigned by inference from correlated spectra.
2. Radical cyclization reactions were carried out using solvents which had been purged of O_2 .

General Experimental Procedures

Dry organic solvents were obtained from Fluka Sure-Seal[®] Anhydrous High Purity solvents or freshly distilled under an atmosphere of N_2 prior to use. Where appropriate, commercial reagents were purified by standard procedures. Light petroleum refers to the fraction with the boiling range 40°C to 60°C. THF was distilled from sodium benzophenone ketyl; toluene and benzene from phosphorous pentoxide, and dichloromethane, chloroform, and triethylamine from calcium hydride.

Melting points were recorded on a Reichert hot-stage apparatus and are uncorrected. IR spectra were recorded on a Perkin Elmer 881 or a Perkin Elmer 1720-X spectrophotometers. Mass spectra were recorded on a Fisons VG Autospec machine. ^1H and ^{13}C nmr spectra were recorded on a Bruker WM250, or a Jeol EX-400 spectrometers. Unless otherwise stated, deuteriochloroform was used as solvent and tetramethylsilane was used as the internal standard. Chemical shifts in ^1H nmr spectra are expressed as ppm downfield from tetramethylsilane, and in ^{13}C nmr, relative to the internal solvent standard. Coupling constants (J) are quoted in Hz.

Reactions involving chemicals or intermediates sensitive to air and/or moisture were performed under an argon atmosphere in flame- or oven-dried apparatus. Reactions involving radical intermediates were performed in solvents deoxygenated by vigorously bubbling Ar or by freeze-thaw techniques. Flash column chromatography was performed using Merck Kieselgel 60 or Fluka Kieselgel 60 silica. Preparative plate thin layer chromatography was performed on Kieselgel 60 F₂₅₄₊₃₆₆. Analytical thin layer chromatography (tlc) was performed on precoated Merck Kieselgel 60 F₂₅₄ aluminium or glass backed plates and were visualised under U.V. conditions at 254 nm, and by staining with iodine or acidic ammonium molybdate.

Preparation of 3-Benzyl-4-ethyl oxetan-2-one (5)

1. From *E*-(1-bromoethyl)cinnamate (4) (table 1, entry 4)

A solution of AIBN (0.02g, 0.12mmol) in deoxygenated toluene (300 mL) was heated at between 80...C and 85...C under an argon atmosphere. A deoxygenated toluene (50 mL) solution of tributyltin hydride (0.12 mL, 0.45mmol) and 1-bromopropyl (3-phenyl)-*E*-prop-2-enoate (0.12g, 0.45mmol) was added, dropwise using a syringe pump, over 2 hours (final concentration of tributyltin hydride, 0.0012 mol dm⁻¹). Once the addition was complete the temperature of the solution was maintained at between 80...C and 85...C: after heating for 3 hours the reaction mixture was allowed to cool to room temperature. The solvent was removed under reduced pressure to give a pale yellow oil, which was partitioned between acetonitrile and petroleum. The acetonitrile layer was evaporated to give the crude products as a colourless oil. Purification by column chromatography using diethyl ether-petroleum (1:5) as eluent gave 3-benzyl-4-ethyl oxetan-2-one (**5**) (0.0205g, 23%) as a 1:1 mixture of *cis* and *trans* isomers, and propyl (3-phenyl)-*E*-prop-2-enoate (**6**) (0.02g, 23%), both as clear, colourless oils. 3-Benzyl-4-ethyl oxetan-2-one *R*_f 0.25 [diethyl ether-petroleum ether (1:5)]; ν_{max} (neat)/cm⁻¹ 3066, 3030, 2969, 2938, 2878 (CH), 1828 (vs, C=O), 1605, 1577, 1497 (ArH); δ H (400MHz, CDCl₃) (*trans*) 0.78 (3H, t, *J* 7.4, CH₃CH₂R), 1.54-1.61 (1H, m, CH₃CH₂R), 1.77-1.86 (1H, m, CH₃CH₂R), 3.00 (1H, dd, *J* 14.9, 9.4, PhCH₂R), 3.18 (1H, dd, *J* 14.9, 5.7, PhCH₂R), 3.47 (1H, ddd, *J* 9.4, 5.7, 4.0, PhCH₂CHCHR), 4.24 (1H, dt, *J* 6.6, 4.0, CH₃CH₂CHCHR), 7.19-7.34 (5H, m, ArH); (*cis*) 0.92 (3H, t, *J* 7.3, CH₃CH₂R), 1.62-1.71 (1H, m, CH₃CH₂R), 1.77-1.86 (1H, m, CH₃CH₂R), 2.99 (1H, dd, *J* 14.4, 9.2, PhCH₂R), 3.18 (1H, dd, *J* 14.4, 6.6, PhCH₂R), 4.02 (1H, dt, *J* 9.2, 6.6, PhCH₂CHCHR), 4.53 (1H, ddd, *J* 10.0, 6.3, 3.7, CH₃CH₂CHCHR), 7.19-7.34 (5H, m, ArH); δ C (*cis*- and *trans*-isomer) (67.5 MHz, CDCl₃) 8.71 (RCH₂CH₃), 9.94 (RCH₂CH₃), 23.72 (RCH₂CH₃), 27.26 (RCH₂CH₃), 29.61 (PhCH₂R), 33.79 (PhCH₂R), 53.17 (CH), 56.90 (CH), 77.32 (CH), 78.56 (CH), 126.82, 127.06, 128.31, 128.64, 128.76, 128.87 (*ortho* and *meta* ArCH), 137.17 (*ipso* ArC), 137.61 (*ipso* ArC), 170.73 (C=O), 171.41 (C=O); *m/z* (CI) 191 (MH⁺, 7%), 145 (M-CO₂, 100), 91 (58). Found MH⁺ 191.10774. C₁₂H₁₅O₂ requires 191.1072.

2. From 1-((1*H*)-pyridine-2-thione-*N*-oxycarbonyl)propyl (*E*)-3-phenylprop-2-enoate (8**) (Table 1, entry 10)**

To toluene (300 mL), under an argon atmosphere, at 80°C, irradiated with a 300 W tungsten lamp, a solution of 1-((1*H*)-pyridine-2-thione-*N*-oxycarbonyl)propyl (*E*)-3-phenylprop-2-enoate (**8**) (172 mg, 0.5 mmol) and tri-*n*-butyltin hydride (0.13 mL, 0.5 mmol) in toluene (50 mL) was added dropwise, *via* mechanical syringe pump, over 2 hours, after which time the solution was heated to 80°C and irradiated with a 300 W tungsten lamp for 4 hours. The reaction mixture was returned to ambient temperature and concentrated *in vacuo*, yielding a clear brown oil which was partitioned between acetonitrile (50 mL) and light petroleum (10 mL), the acetonitrile layer extracted with light petroleum (2 x 10 mL), dried (MgSO₄), filtered, and concentrated *in vacuo*, yielding a clear pale yellow oil which was pre-absorbed onto silica gel and purified by flash column chromatography on silica gel with diethyl ether:light petroleum (1:5) as eluent to afford, in order of elution, (*E*)-propyl ester (**6**) as a clear colourless liquid (36 mg, 38%). *R*_f 0.37 [diethyl ether-light petroleum (1:9)]; *v*_{max} (liquid film)/cm⁻¹ 1716 (C=O) and 1635 (C=C); δ_{H} (400 MHz, CDCl₃) 1.00 (3H, t, *J* 7.5, CH₃CH₂), 1.74 (2H, tq, *J* 14.5, 7.0, OCH₂CH₂), 4.17 (2H, t, *J* 7.0, OCH₂CH₂), 6.45 (1H, d, *J* 16.0, PhCHCH), 7.37-7.39 (3H, m, ArH), 7.52-7.54 (2H, m, ArH), 7.69 (1H, d, *J* 16.0, PhCHCH); *m/z* (CI) 191 (MH⁺, 100%), 148 (MH⁺-Pr, 68), 131 (M-OPr, 76), 103 (M-CO₂Pr, 18), 77 (Ph, 12), 69 (15), 49 (7). Found MH⁺ 191.1069. C₁₂H₁₅O₂ requires 191.1072; 1:1 mixture of *cis*-oxetanone (*cis*-**5**) and *trans*-oxetanone (*trans*-**5**) as an inseparable clear colourless oil (21 mg, 22%). *R*_f 0.24 [diethyl ether:light petroleum (3:17)] (data as above); and (*E*)-2-pyridylsulfide (**9**) as a clear colourless oil (6 mg, 4%). *R*_f 0.26 [diethyl ether-light petroleum (1:3)]; *v*_{max} (CHCl₃)/cm⁻¹ 1716 (C=O), 1634 (C=C), 1578 and 1559; δ_{H} (400 MHz, CDCl₃) 1.12 (3H, t, *J* 7.5, CH₃CH₂), 2.10 (2H, dq, *J* 14.0, 7.5, OCHCH₂), 6.42 (1H, d, *J* 16.0, PhCHCH), 6.95 (2H, t, *J* 6.5, OCHCH₂), 7.01 (1H, dd, *J* 6.5, 5.0, NCHCH), 7.25 (1H, d, *J* 8.0, NC(S)CH), 7.34-7.37 (3H, m, ArH), 7.47-7.49 (2H, m, ArH), 7.50 (1H, dd, *J* 7.5, 2.0, NC(S)CHCH), 7.69 (1H, d, *J* 16.0, PhCHCH), 8.45 (1H, d, *J* 5.0, NCH); δ_{C} (100 MHz, CDCl₃) 10.1 (CH₃CH₂), 28.4 (OCHCH₂), 79.8 (OCHCH₂), 117.6 (PhCHCH), 120.4 (NCHCH), 123.1 (NC(S)CH), 128.0 (ArC),

128.8 (ArC), 130.3 (*para* ArC), 134.2 (*ipso* ArC), 136.3 (NC(S)CHCH), 145.3 (PhCHCH), 149.7 (NCH), 156.6 (NC_S), 165.8 (CO₂); *m/z* (CI) 300 (MH⁺, 9%), 241 (13), 213 (12), 152 (94), 131 (M-OCH(SPy)CH₂CH₃, 100), 112 (41), 77 (Ph, 9), 58 (12). Found MH⁺ 300.1057. C₁₇H₁₈NO₂S requires 300.1058.

Preparation of 3-(1,1-diphenylmethyl)-4-ethyl oxetan-2-one (11a) (Table 2, entry 1)

To toluene (300 mL), under an argon atmosphere, at 80°C, irradiated with a 300 W tungsten lamp, a solution of 1-((1*H*)-pyridine-2-thione-*N*-oxycarbonyl)propyl 3,3-diphenylprop-2-enoate (**10a**) (210 mg, 0.5 mmol) and tri-*n*-butyltin hydride (0.13 mL, 0.5 mmol) in toluene (50 mL) was added dropwise, *via* mechanical syringe pump, over 2 hours, after which time the solution was heated to 80°C and irradiated with a 300 W tungsten lamp for 4 hours. The reaction mixture was returned to ambient temperature and concentrated *in vacuo*, yielding a clear yellow oil which was partitioned between acetonitrile (50 mL) and light petroleum (10 mL), the acetonitrile layer extracted with light petroleum (2 x 10 mL), dried (MgSO₄), filtered, and concentrated *in vacuo*, yielding a clear pale yellow oil which was pre-absorbed onto silica gel and purified by flash column chromatography on silica gel with diethyl ether:light petroleum (1:5) as eluent to afford, in order of elution, propyl ester (**12a**) as a clear colourless oil (7 mg, 5%). *R_f* 0.28 [diethyl ether-light petroleum (1:9)]; *v*_{max} (liquid film)/cm⁻¹ 1722 (C=O) and 1615 (C=C); *δ*_H (400 MHz, CDCl₃) 0.81 (3H, t, *J* 7.5, CH₃CH₂), 1.50 (2H, tq, *J* 14.5, 7.5, OCH₂CH₂), 3.95 (2H, t, *J* 7.0, OCH₂CH₂), 6.37 (1H, s, Ph₂CCH), 7.20-7.22 (2H, m, ArH), 7.29-7.39 (8H, m, ArH); *δ*_C (100 MHz, CDCl₃) 10.3 (CH₃CH₂), 21.8 (OCH₂CH₂), 65.8 (OCH₂CH₂), 117.5 (Ph₂CCH), 127.8 (ArC), 128.1 (*para* ArC), 128.3 (ArC), 128.3 (ArC), 129.1 (ArC), 129.3 (*para* ArC), 139.0 (*ipso* ArC), 140.8 (*ipso* ArC), 156.3 (Ph₂CCH), 166.3 (CO₂); *m/z* (CI) 267 (MH⁺, 100%), 224 (MH⁺-Pr, 29), 207 (M-OPr, 43), 178 (26). Found MH⁺ 267.1373. C₁₈H₁₉O₂ requires 267.1385; *trans*-oxetan-2-one (*trans*-**11a**) as a clear colourless oil (36 mg, 27%). *R_f* 0.35 [diethyl ether-light petroleum (1:3)]; *v*_{max} (CHCl₃)/cm⁻¹ 1820 (C=O); *δ*_H (250 MHz, CDCl₃) 0.74 (3H, t, *J* 7.5, CH₃CH₂),

1.65 (2H, m, CH₃CH₂), 3.91 (1H, dd, *J* 9.5, 4.0, Ph₂CHCH), 4.15 (1H, ddd, *J* 7.0, 5.5, 4.0, OCHCH₂), 4.32 (1H, d, *J* 9.5, Ph₂CHCH), 7.15-7.27 (10H, m, ArH); δ_C (63 MHz, CDCl₃) 9.3 (CH₃CH₂), 27.6 (CH₃CH₂), 50.5 (Ph₂CHCH), 60.1 (Ph₂CHCH), 78.1 (OCHCH₂), 127.6 (*para* ArC), 127.7 (*para* ArC), 128.5 (ArC), 128.6 (ArC), 129.1 (ArC), 129.4 (ArC), 140.9 (*ipso* ArC), 141.8 (*ipso* ArC), 170.2 (CO₂); *m/z* (CI) 266 (M, 20%), 222 (M-CO₂, 19), 193 (39), 167 (100), 115 (20), 91 (13), 77 (Ph, 5). Found 266.1298. C₁₈H₁₈O₂ requires 266.1307; *cis*-oxetan-2-one (*cis*-**11a**) as clear colourless crystals (43 mg, 32%). *R*_f 0.25 [diethyl ether-light petroleum (1:3)]; m.p. 103-104°C (ethyl acetate-light petroleum); ν_{max} (CHCl₃)/cm⁻¹ 1819 (C=O); δ_H (250 MHz, CDCl₃) 0.74 (3H, t, *J* 7.5, CH₃CH₂), 1.16 (1H, m, CH₃CH₂), 1.52 (1H, m, CH₃CH₂), 4.26-4.43 (3H, m, Ph₂CHCH, Ph₂CHCH and OCHCH₂), 7.02-7.17 (10H, m, ArH); δ_C (63 MHz, CDCl₃) 10.4 (CH₃CH₂), 24.2 (CH₃CH₂), 47.1 (Ph₂CHCH), 56.8 (Ph₂CHCH), 78.1 (OCHCH₂), 127.5 (ArC), 127.6 (ArC), 127.7 (ArC), 128.5 (ArC), 129.1 (ArC), 129.5 (ArC), 141.6 (*ipso* ArC), 141.8 (*ipso* ArC), 170.5 (CO₂); *m/z* (CI) 284 ([M+NH₄]⁺, 50), 267 (MH⁺, 20%), 222 (M-CO₂, 34), 167 (100), 115 (37), 91 (25), 77 (Ph, 11). Found [M+NH₄]⁺ 284.1643. C₁₈H₂₂NO₂ requires 284.1651; and 2-pyridylsulfide (**13a**) as clear colourless crystals (4 mg, 2%). *R*_f 0.21 [diethyl ether-light petroleum (1:3)]; m.p. 80°C (diethyl ether); ν_{max} (CHCl₃)/cm⁻¹ 1725 (C=O), 1617 (C=C) and 1578; δ_H (400 MHz, CDCl₃) 0.97 (3H, t, *J* 7.5, CH₃CH₂), 1.91 (2H, dq, *J* 14.5, 7.5, OCHCH₂), 6.34 (1H, s, Ph₂CCH), 6.73 (2H, t, *J* 6.0, OCHCH₂), 7.02 (1H, ddd, *J* 7.5, 5.0, 1.0, NCHCH), 7.17-7.21 (3H, m, NC(S)CH and ArH), 7.25-7.36 (8H, m, ArH), 7.50 (1H, ddd, *J* 7.5, 7.5, 2.0, NC(S)CHCH), 8.45 (1H, d, *J* 4.0, NCH); δ_C (100 MHz, CDCl₃) 10.0 (CH₃CH₂), 28.2 (OCH₂CH₂), 79.4 (OCHCH₂), 116.9 (Ph₂CCH), 120.3 (NCHCH), 123.1 (NC(S)CH), 127.8 (ArC), 128.2 (*para* ArC), 128.3 (ArC), 129.2 (ArC), 129.4 (*para* ArC), 136.3 (NC(S)CHCH), 138.6 (*ipso* ArC), 140.7 (*ipso* ArC), 149.6 (NCH), 157.0 (Ph₂CCH), 157.2 (NCS), 164.8 (CO₂); *m/z* (CI) 376 (MH⁺, 3%), 318 (14), 225 (23), 207 (M-OCH(SP_y)CH₂CH₃, 100), 178 (17), 152 (75), 112 (12). Found MH⁺ 376.1378. C₂₃H₂₂NO₂S requires 376.1371.

To toluene (300 mL), under an argon atmosphere, at 80°C, irradiated with a 300 W tungsten lamp, a solution of 1-methyl-1-((1*H*)-pyridine-2-thione-*N*-oxycarbonyl)ethyl 3,3-diphenylprop-2-enoate (**10a**) (210 mg, 0.5 mmol) and tri-*n*-butyltin hydride (0.13 mL, 0.5 mmol) in toluene (50 mL) was added dropwise, *via* mechanical syringe pump, over 2 hours, after which time the solution was heated to 80°C and irradiated with a 300 W tungsten lamp for 5 hours. The reaction mixture was returned to ambient temperature and worked-up in the usual manner as (above), yielding a clear brown oil which was pre-absorbed onto silica gel and purified by flash column chromatography on silica gel with diethyl ether:light petroleum (1:4) as eluent to afford, in order of elution, *iso*-propyl ester (**12a**) as clear colourless crystals (9 mg, 7%); *R*_f 0.31 [diethyl ether-light petroleum (1:9)]; m.p. 35°C (light petroleum); ν_{max} (CHCl₃)/cm⁻¹ 1704 (C=O), 1619 (C=C); δ_{H} (400 MHz, CDCl₃) 1.09 (6H, d, *J* 6.0, CH(CH₃)₂), 4.92 (1H, m, OCH), 6.34 (1H, s, Ph₂CCH), 7.19-7.22 (2H, m, ArH), 7.28-7.31 (4H, m, ArH), 7.33 (1H, m, ArH), 7.36-7.38 (3H, m, ArH); δ_{C} (100 MHz, CDCl₃) 21.6 (CH(CH₃)₂), 67.4 (OCH), 118.2 (Ph₂CCH), 127.8 (ArC), 128.0 (ArC), 128.2 (ArC), 128.3 (ArC), 129.1 (ArC), 129.3 (ArC), 139.1 (*ipso* ArC), 140.8 (*ipso* ArC), 155.7 (Ph₂CCH), 165.7 (C=O); *m/z* (CI) 267 (MH⁺, 100%), 225 (43), 207 (M-OPr, 38), 180 (40). Found MH⁺ 267.1381. C₁₈H₁₉O₂ requires 267.1385; 2-oxetanone (**11a**) as clear colourless crystals (81 mg, 61%); *R*_f 0.26 [diethyl ether-light petroleum (1:3)]; m.p. 90-91°C (ethyl acetate-light petroleum); ν_{max} (CHCl₃)/cm⁻¹ 1814 (C=O); δ_{H} (250 MHz, CDCl₃) 1.20 (3H, s, OC(CH₃)₂), 1.49 (3H, s, OC(CH₃)₂), 4.09 (1H, d, *J* 13.0, Ph₂CHCH), 4.34 (1H, d, *J* 13.0, Ph₂CHCH), 7.06-7.26 (10H, m, ArH); δ_{C} (63 MHz, CDCl₃) 22.8 (OC(CH₃)₂), 28.5 (OC(CH₃)₂), 48.3 (Ph₂CHCH), 62.1 (Ph₂CHCH), 81.1 (OC(CH₃)₂), 127.6 (*para* ArC), 127.7 (*para* ArC), 127.8 (ArC), 128.4 (ArC), 129.1 (ArC), 129.5 (ArC), 141.4 (*ipso* ArC), 141.4 (*ipso* ArC), 169.8 (C=O); *m/z* (CI) 284 ([M+NH₄]⁺, 7%), 222 (M-CO₂, 87), 207 (M⁺-OC(CH₃)₂, 100), 167 (52), 105 (24), 91 (26). Found [M+NH₄]⁺ 284.1653. C₁₈H₂₂NO₂ requires 284.1651; and 2-pyridylsulfide (**13b**) as clear colourless crystals (15 mg, 8%); *R*_f 0.22 [diethyl ether-light petroleum (1:3)]; m.p. 106-107°C (diethyl ether); ν_{max} (CHCl₃)/cm⁻¹ 1717 (C=O), 1626 (C=C), 1580 and 1561; δ_{H} (250 MHz, CDCl₃) 1.10 (3H, s, C(CH₃)₂), 1.63 (3H, s, CH(CH₃)₂), 5.62 (1H, s, Ph₂CCH), 6.76 (1H, ddd, *J* 8.0, 1.0, 1.0, NCHCH), 6.91 (1H, ddd, *J* 7.5, 2.5, 1.0, NC(S)CHCH), 6.97-7.09 (3H, m, ArH), 7.11-7.23 (4H, m, NC(S)CH and ArH), 7.33-7.36 (2H, m, ArH), 7.44-7.48 (2H, m, ArH), 8.29 (1H, ddd, *J* 5.0, 2.0, 1.0, NCH); δ_{C} (63 MHz, CDCl₃) 24.0 (CH₃), 29.9 (CH₃), 83.3 (OC(CH₃)₂), 122.6, 127.4, 127.8, 128.0 (ArC), 128.5 (ArC), 129.0 (ArC), 129.2 (ArC), 130.1, 136.7 (NC(S)CHCH), 143.7, 143.9, 149.7 (NCH), 155.4, 170.3

(CO_2); m/z (CI) 376 (MH^+ , 13%), 317 (5), 265 (M-SPy, 14), 221 (100), 178 (13), 143 (15), 112 (79), 67 (12). Found MH^+ 376.1367. $\text{C}_{23}\text{H}_{22}\text{NO}_2\text{S}$ requires 376.1371.

Preparation of 3-(1,1-di{4-methylphenyl}sulfanyl)methyl)-4-ethyloxetan-2-one (11e) (Table 2, entry 12)

Tri-*n*-butyltin hydride (0.5 mmol, 1 equivalent) was added to hexane (50 mL) and acetonitrile (50 mL) and the resulting solution heated to 59°C whilst irradiated with a 300W sun-lamp. In a separate vessel, 1-((1H)-pyridine-2-thione-N-oxycarbonyl)propyl 3-(1,1-di{4-methylphenyl}sulfanyl)prop-2-enoate (**15**) (320 mg, 0.6 mmol) was added to 50 mL of acetonitrile and this solution was transferred to a gas-tight syringe. The syringe was covered in aluminium foil and the contents added to the heated, irradiated tin hydride solution *via* syringe pump, over a 2 hour period. After the addition was complete, the solution was stirred at 59°C and irradiated for a further 4 hours. Stirring was stopped, the 2-phase mixture was allowed to cool to room temperature, the hexane layer was separated and the acetonitrile layer washed with petrol (2x 30 mL). The acetonitrile layer was concentrated *in vacuo* to give a clear brown oil which was purified by column chromatography dichloromethane/hexane (1:1) to give, in order of elution, *cis*-3-(di(phenylthio)methyl)-4-ethyloxetan-2-one (*cis*-**11e**) (43 mg, 20%); R_f 0.24 [CHCl_3 / hexane (1:1)]; ν_{max} (CHCl_3)/ cm^{-1} 1819 (C=O), 1492 and 1381; δ_{H} (250 MHz, CDCl_3) 1.06 (3H, t, J 7.0, CH_3CH_2), 1.79 (1H, m, CH_3CH_2), 2.24 (1H, m, CH_3CH_2), 2.29 (3H, s, ArCH_3), 2.30 (3H, s, ArCH_3), 3.72 (1H, dd, J 11.1, 6.4, $\text{CHC}(\text{O})$), 4.41 (1H, ddd, 9.1, 6.4, 2.6 OCHCH_2), 4.48 (1H, d, J 11.1, $(\text{ArS})_2\text{CH}$), 7.04-7.13 (4H, m, ArH), 7.32-7.40 (4H, m, ArH); δ_{C} (62.5 MHz, CDCl_3) 10.5 (CH_3CH_2), 21.7 (ArCH_3), 24.2 (OCHCH_2), 55.2 (OCHCH_2), 56.5 ($\text{CHC}(\text{O})$), 78.5 ($\text{CH}(\text{SAr})_2$), 128.1 (ArC), 128.9 (ArC), 130.2 (ArC), 130.4 (ArC), 134.6 (ArC), 135.8 (ArC), 139.6 (ArC), 139.7 (ArC), 168.7 (CO_2); m/z (CI) 376.1409 ($\text{M}+\text{NH}_4^+$, $\text{C}_{20}\text{H}_{26}\text{NO}_2\text{S}_2^+$ requires 376.1405), 235 (35%), 191 (100), 124 (34), 91 (21); *trans*-3-(1,1-di{4-methylphenyl}sulfanyl)methyl)-4-ethyloxetan-2-one (*trans*-**11e**) (70 mg, 32%) R_f 0.26 [CHCl_3 / hexane (1:1)]; ν_{max} (CHCl_3)/ cm^{-1} 1819 (C=O), 1466 and 1382, δ_{H} (250 MHz, CDCl_3) 1.05 (3H, t, J 7.0, CH_3CH_2), 1.83 (2H, m, CH_3CH_2), 2.37 (6H, s,

ArCH₃), 3.62 (1H, dd, *J* 5.9, 4.3, CH C(O)), 4.56 (1H, d, *J* 5.9, (ArS)₂CH), 4.60 (1H, ddd, 7.3, 5.2, 4.3 OCHCH₂), 7.13-7.17 (4H, m, ArH), 7.32-7.41 (4H, m, ArH); δ_C (62.5 MHz, CDCl₃) 9.6 (CH₃CH₂), 21.6 (ArCH₃), 27.8 (OCHCH₂), 57.1 (OCHCH₂), 60.1 (CHC(O)), 128.1 (ArC), 128.9 (ArC), 130.4 (ArC), 134.2 (ArC), 134.6 (ArC), 139.6 (ArC), 168.3 (CO); *m/z* (CI) 359.1133 (MH⁺, C₂₀H₂₃O₂S₂ requires 359.1139), 191 (100%), 124 (30), 91 (16); and propyl 3-(1,1-di{4-methylphenyl}sulfanyl)prop-2-enoate (**12e**) (39 mg, 18%). M.p. 75-77°C; R_f 0.30 [CHCl₃/ hexane (1:1)]; ν_{max} (CHCl₃)/cm⁻¹ 1685 (C=O), 1534 (C=C); δ_H (250 MHz, CDCl₃) 0.92 (3H, t, *J* 7.0, CH₃CH₂), 1.63 (2H, m, CH₃CH₂), 2.38 (3H, s, ArCH₃), 2.42 (3H, s, ArCH₃), 4.05 (1H, t, *J* 7.0 OCHCH₂), 5.24 (1H, s, (C=CH), 7.18-7.30 (6H, m, ArH), 7.57-7.62 (2H, m, ArH); δ_C (62.5 MHz, CDCl₃) 10.9 (CH₃CH₂), 21.8 (ArCH₃), 21.9 (ArCH₃), 22.5 (OCHCH₂), 66.0 (OCHCH₂), 107.5 (C=CH), 125.9 (ArC), 127.0 (ArC), 130.0 (ArC), 131.1 (ArC), 135.8 (ArC), 137.4 (ArC), 140.8 (ArC), 140.9 (ArC), 163.3 (CO₂CH), 166.0 (C=CH); *m/z* (CI) 359.1132 (MH⁺, C₂₀H₂₃O₂S₂ requires 359.1139), 299 (100%), 234 (30), 193 (16), 149 (20), 124 (30), 19 (18).