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SYNTHESES WITH SULFONES XLIX : STEREO- AND ENANTIOSELECTIVE SYNTHESIS OF (S)-(-)-3,9-DIMETHYL 6-(1-METHYLETHYL) (E)-5,8-DECADIEN 1-OL ACETATE, SEXUAL PHEROMONE OF YELLOW SCALE.

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ABSTRACT : *The stereo- and enantioselective synthesis of the yellow scale pheromone, (S)-(-)-3,9-dimethyl 6-(1-methylethyl)(E)-5,8-decadien 1-ol acetate, from 3-(R)-(+)-valerolactone 5 and [(4-methyl 3-pentenyl)sulfonyl] benzene 8 is described. The key step is the introduction of the isopropyl group by the stereoselective cross-coupling reaction of the dienesulfone 12 with isopropylmagnesium chloride in the presence of* $FeCl_3$.

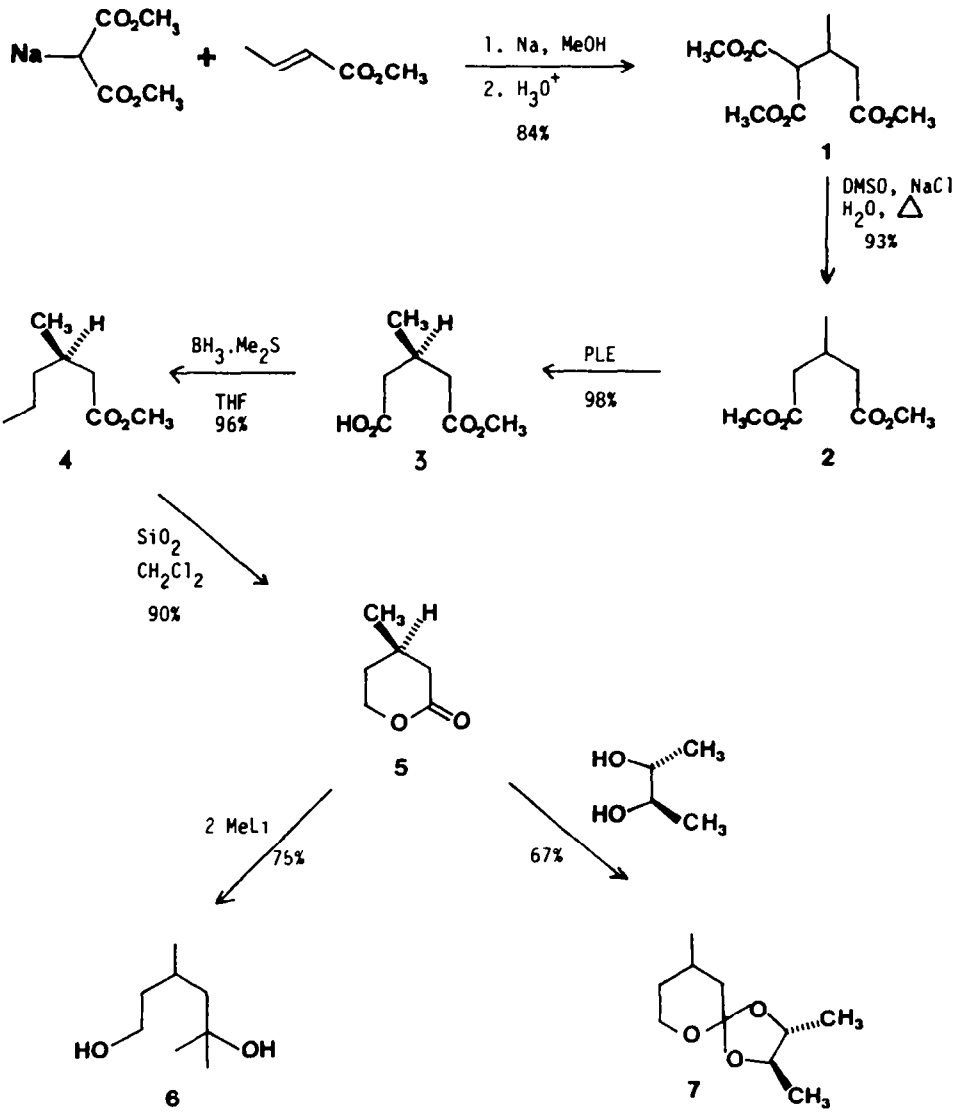
The yellow scale, Aonidiella citrina, is a severe pest of ornamental plants and citrus fruit in California and Japan. In 1979 Gieselmann and Coll. [1] isolated the sexual pheromone of yellow scale, (E)-3,9-dimethyl 6-isopropyl 5,8-decadien 1-yl acetate 13b. The structure assignment was confirmed by two independent syntheses of both (E)- and (Z)-isomers as racemates [2,3]. Recently, Mori and Kuwahara [4] have prepared both R-(+) and S-(-) enantiomers of 13b from optically active (R)-(+)-methylcitronellate in 10% and 7% overall yields. Only the latter S enantiomer is biologically active.

The major difficulty in the preparation of pheromone 13b is the (E)-5 double bond bearing the isopropyl group. Pure E or Z vinylsulfones are readily available from α-sulfonyl carbanions and aldehydes [5]. These techniques have been extended to the syntheses of 2-benzenesulfonyl 1,3 [6] and 1,4-dienes [6,7]. The stereospecific replacement of the sulfonyl moiety of 2-benzenesulfonyl 1,4-dienes by the isopropyl group was reported in the preceding paper [8]. This strategy appeared well-suited to the problem at hand and required the homoallylic sulfone 8 and (R)-3-methylvalerolactone 5 as starting materials.

Preparation of chiral lactone 5, outlined in scheme 1, is well- documented. 1,4-Addition of sodium methylmalonate to methylcrotonate [9a] furnished 84% of triester 1. Decarboxylation of 1 upon refluxing in DMSO [10] yielded diester 2 [9,10,11]. Dimethyl 3-methylglutarate was enantioselectively hydrolysed with pig liver esterase [11] at pH 7 to afford 98% of optically active monoester 3. Reduction of this latter compound with $BH_3 \cdot SMe_2$ [11] gave 96% of the hydroxyester 4 which was cyclised with silica gel in 90% yield to chiral lactone 5. For comparative purposes, the racemate of 13b was also prepared [9b].

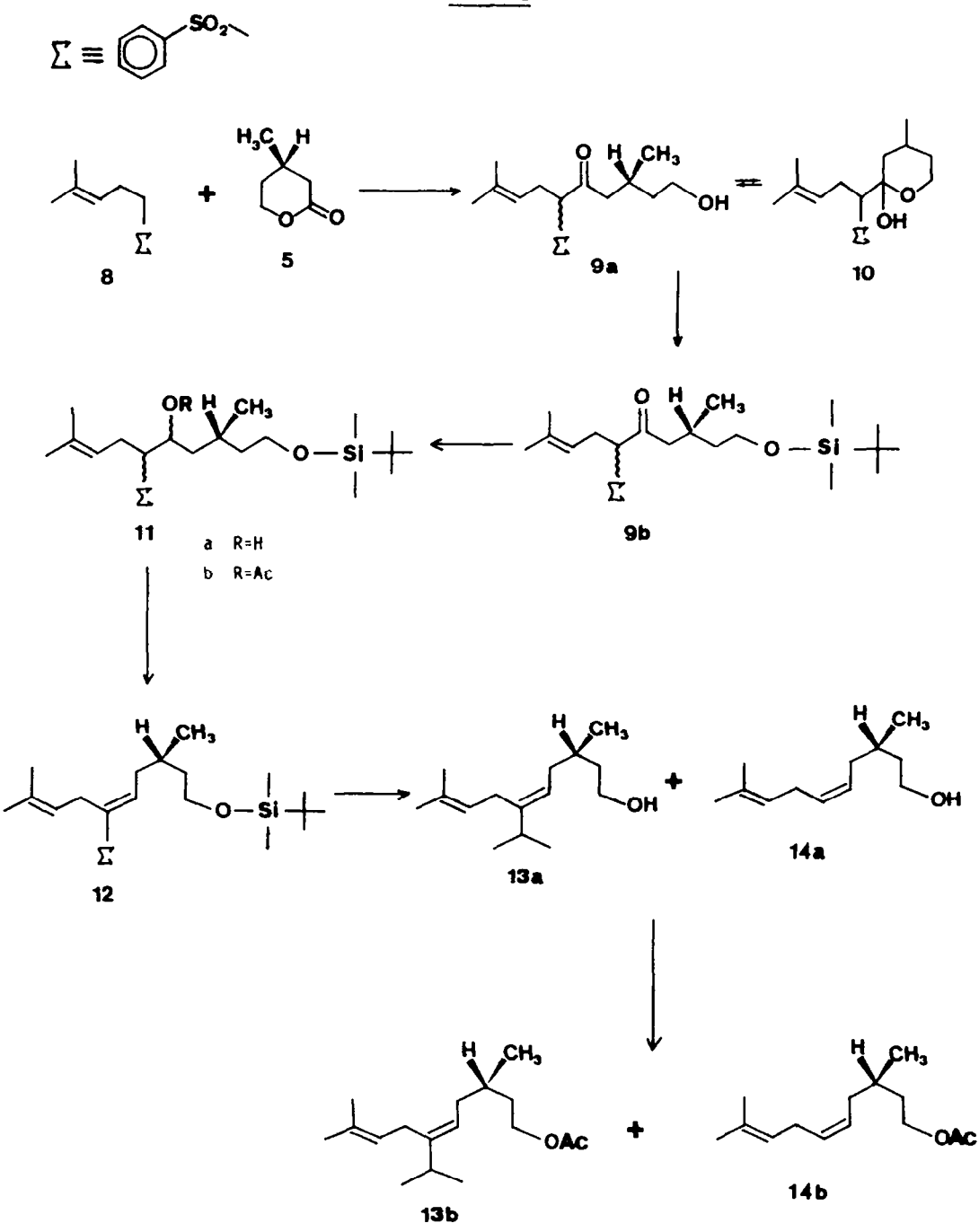
In order to establish the optical purity of this lactone, it was transformed into diol 6 with methyllithium [12]. Comparison of the ^1H NMR spectra of chiral and racemic diols 6 in the presence of $Eu(tfc)_3$ [12] indicated that the enantiomeric excess of (R)-(-)-6 was at least 90% (±5%). Lactone 5 was also converted into orthoester 7 with (R)-2, (R)-3-butanediol [13]. Capillary-GLC of this derivative confirmed that the enantiomeric excess of precursor 5 must have been at least 90% (±2%).

SCHEME 1



The condensation [14] of lithiated sulfone 8[8] with lactone (R)-5 afforded a 54/46 mixture of sulfoneketols 9a (threo/erythro 53/47) and sulfonehemiketals 10 (2 isomers in a 64/36 ratio) in 62% yield. Treatment of this mixture with TBDMS-Cl[15] furnished 97% of silylated compounds 9b. The carbonyl group of 9b was reduced with $NaBH_4$ to give 92% of hydroxysulfones 11a which were acetylated with DMAP [17] to yield acetoxysulfones 11b. Elimination of acetic acid in the usual way [6-8] afforded dienesulfone 12 which contained > 98% of the E-isomer according to HPLC and ^1H NMR analyses. The cross-coupling reaction of 12 with isopropylmagnesium chloride in the presence of $FeCl_3$ followed by removal of the silyl group with $Bu_4NF.\ 3H_2O$[18] furnished a mixture of alcohols 13a (36%) and 14a (32%). These dienic alcohols were acetylated [17] (96%) and then separated on silver nitrate-charged silica gel [19] to give pure 13b and 14b. Both 13a and 13b contained 3 isomers in a 98/1.5/0.5 ratio according to capillary-GLC-mass. In the case of compounds 14a and 14b 2 isomers were detected, 98% and 2% respectively. The optical rotation of pheromone 13b was $[\alpha]_D^{25}$ - 9.48° (*n*-hexane)(lit. $[\alpha]_D^{31}$ - 9.89 (*n*-hexane)[4a] and $[\alpha]_D^{21.5}$ - 11.9° (*n*-hexane)[4b].

SCHEME 2



EXPERIMENTAL

Elemental analysis (see Table III) were conducted at Paris VI, Centre de Spectrochimie. Spectra were recorded on the following : Cameca 250 or Bruker AM400 for ^{1}H NMR, Bruker WH-90 or Bruker AM 400 for ^{13}C NMR, Perkin-Elmer 599 for IR, and Varian-Mat CH7 or Riber Nermag R10-10/B for m/z. Analytical GLC were conducted on a Girdel 30 equipped either with a pyrex column (2.5m x 3.2mm ; OV 101 on chromosorb WHP 100-120 mesh) or with a capillary Chrompack column (CP SiL 8 CB). Flash chromatography was performed according to ref. 20 using Merck silica gel (0.063-0.2mm of 5-40 μm, Art. 7734 or 7736) with a pentane/ether gradient unless stated otherwise. Basic silica gel was prepared by treating 200g of Merck silica gel with 500ml of a saturated aqueous solution of $NaHCO_3$, filtering, washing (successively with water, methanol, ethyl acetate, ether and pentane) and drying.

TABLE I : IR, m/z and ^{1}H NMR data.

Compound	IR (KBr)	m/z [a]	250MHz ^{1}H NMR [b] (J in Hz ; δ_{TMS} = 0 p.p.m.)
1	2970, 1745, 1445, 1275, 1210, 1165	C.I. (NH_3) 250(100), 233(97), 201(20)	1.07(d,7,3H), 2.34(dd, J_1=16, J_2=8.5, 1H), 2.56(dd, J_1=16, J_2=5, 1H), 2.67 to 2.87(m,1H), 3.48(d,7,1H), 3.70(s,3H), 3.75 (s,3H), 3.76(s,3H).
2	2970, 1745, 1445, 1275, 1210, 1165	175(100), 143(25), 114(17)	1.01(d,6.5,3H), 2.16 to 2.52(m,5H), 3.62(s,6H).
3	3100, 2970, 1745, 1220	C.I. (NH_3) 178(100), 160(89)	1.04(d,6,3H), 2.21 to 2.56(m,5H), 3.71(s,3H), 11.52(s,1H).
4	3500, 2980, 1745	146( ), 128(0.8), 114(21), 74(57)	0.97(d,6,3H), 1.22 to 1.61(m,6H), 3.69(s,3H), 3.78(d,6,2H).
5	2960, 1735, 1260, 1230, 1080	114(17), 70(22), 56(100)	1.08(d,6.5,3H), 1.43 to 1.66(m,1H), 1.86 to 2.03(m,1H), 2.24 (m,2H), 2.60 to 2.79(m,1H), 4.23 to 4.53(m,2H).
6	3370, 2980	138(4), 113(21), 95(16), 83(33), 58(100)	1.00(d,7,3H), 1.20 to 1.70(m,10H including a s : δ 1.24,6H), 1.78 to 1.97(m,1H), 2.13 to 2.68(m,2H), 3.61 to 3.84(m,2H).
7 RRR		186(22), 171(31), 141(14), 114(100), 69(59)	0.96(d,6.5,3H), 1.10 to 1.61(m,8H including 2 d : δ 1.29, J=6, 3H and δ 1.31, J=6, 3H), 1.74 to 2.06(m,2H), 3.66 to 3.90(m,3H),4.05 to 4.18(m,1H).
7 RR(R+S)			0.94(d,6.5, 3x0.5H), 0.96(d,6.5, 3x0.5H), 1.10 to 1.66(m,8H including 3 d : δ 1.29, J=6, 3H), δ 1.31, J=6, 3x0.5H and δ 1.33, J=6, 3x0.5H), 1.74 to 2.06(m,2H), 3.66 to 4.03(m,3.5xH), 4.05 to 4.18(m,0.5H).
9a + 10	3460, 2985, 2880, 1720, 1310, 1150	C.I.(NH_3) 356(100), 338(42), 321(55), 258(28)	0.58 to 1.72(m,11.8H including 4d, J=6.5 : δ 0.64, 3x0.29H ; δ 0.71, 3x0.16H ; γ 0.79, 3x0.25H ; δ 0.84, 3x0.29H ; and 6a : δ-1.31, δ 1.33, δ 1.41, δ 1.42, δ 1.52 and δ 1.55), 1.82 to 2.82(m, 3.79H), 3.02 to 4.20(m,3.29H including 2br t, J=5.8 : δ 3.24, 0.29H ; δ 3.32, 0.16H ; and 2 m : δ 3.79, 0.29H ; δ 3.94, 0.16H ; and 2 dd, J_1 = 11, J_2=3.6 : δ 4.10, 0.29H ; δ 4.15, 0.29H), 4.73 to 4.85(m,0.54H), 4.96 to 5.05(m,0.16H), 5.13(d,2, 0.29H), 5.28 to 5.37 (m,0.29H), 5.83(d,2,0.16H), 6.88 to 7.13(m,3H), 7.74 to 7.80(m,2H).
9b	2920, 2840, 1710, 1445, 1305, 1250, 1070, 835, 765	C.I. (NH_3) 470(100), 453(80), 313(46)	0.01(s,6H), 0.81 to 0.81(m,12H), 1.26 to 1.45(m,2H), 1.47(s,3H), 1.57(s,3H), 2.03 to 2.17(m,1H), 2.40(q, J_1=18), J_2=7.5, 1H), 2.47 1145, to 2.61(m,2H), 2.72(q, J_1=18, J_2=5, 1H), 3.54 to 3.65(m,2H), 4.04(m, 1H), 4.77 to 4.89(m,1H), 7.46 to 7.64(m,5H).
11a	3500, 2920, 2910, 2850, 1300, 1250, 1140, 840	C.I. (NH_3) 472(13), 456(95), 315(100), 295(28), 258(25), 221(23), 160(45)	-0.08 to 0.02(3s,6H), 0.65 to 0.91(m,12H), 1.07 to 1.81(m,11H including 2 br s : δ 1.37 and δ 1.53), 2.31 to 2.65(m,2H), 2.95 to 3.25(m,2H), 3.51 to 3.73(m,2H). 4.15 to 4.35(m,1H). 4.81 to 4.97(m,1H), 7.50 to 7.72(m,3H), 7.84 to 7.95(m,2H).
11b	2960, 2940, 2865, 1740, 1315, 1250	C.I. (NH_3) 514(58), 497(100)	-0.08 to -0.02(4s,6H), 0.83 to 0.89(m,12H), 1.05 to 1.91(m,14H including 6br s : δ 1.42, δ 1.44, δ 1.51, δ 1.53, δ 1.56, δ 1.58 ; and 3s : δ 1.74, δ 1.75 and δ 1.85), 2.19 to 2.77(m,2H), 3.07 to 3.45(2m,1H), 3.45 to 3.67(m,2H), 4.85 to 5.15 (2m,1H), 5.19 to 5.47(2m,1H), 7.46 to 7.67(m,3H), 7.80 to 7.92 (m,2H).
12	2950, 2920, 2850, 1300, 1145	C.I. (NH_3) 454	0.03(s,6H). 0.89(s,9H). 0.91(d,6.5,3H). 1.25 to 1.73(m,8H including 2 s : δ 1.48,3H ; δ 1.52,3H), 1.73 to 1.85(m,1H), 2.05(m,1H : J_1=14.5, J_2=7.6, J_3=7.5), 2.24(m,1H) : J_1=14.5, J_2=6.5, J_3=6.5), 2.97(br d,7.5, 2H), 3.62(m,1H : J_1=10.5, J_2=6.5, J_3=6.5), 3.66(m,1H : J_1=10.5, J_2=6.5, J_3=6.5), 4.62(m,1H), 6.98(t,7.5,1H), 7.44 to 7.87(m,5H).
13a	2980, 2885	224(5), 127(8), 123(54), 109(17), 95(40), 81(44), 69(100)	0.88(d,6.5,3H), 0.98(d,6.5,6H), 1.18 to 1.51(m,3H), 1.65(s,3H), 1.67(s,3H), 1.77 to 2.11(m,3H), 2.11 to 2.31(7 peaks 6.5,1H), 2.71(brd, 6.5,2H), 3.58 to 3.78(m,2H), 4.95(tq, J_1=7, J_2=1.5, 1H). 5.15(t,7.1H).
13b [c]	2950, 2920, 2870, 1720, 1250	266(13), 183(14), 135(15), 123(60), 107(85), 95(51), 83(38), 81(49), 79(30), 77(15), 69(100) H.R. 266.2240	0.84(d,7,3H), 1.05(d,7,6H), 1.20 to 1.79(m,12H including 3 s : δ 1.60, 3H ; δ 1.64, 3H ; δ 1.68,3H), 1.88(m,1H : J_1=14, J_2=7, J_3=7), 2.02(m,1H : J_1=14, J_2=7. J_3=7, 2.29(7 peaks,7,1H), 2.78(br t,7,2H), 4.08(br t,7,2H), 5.15(br t,7,1H), 5.22(br t,7,1H).
14a	3610, 3470, 2975, 2910, 2880	182(2), 165(2), 149(3), 137(8), 123(13), 109(16), 95(44), 81(60), 69(65), 67(89), 55(100)	0.87(d,6.5,3H), 1.18 to 1.85(m,9H including 2s, 3H : δ 1.61 and δ 1.67), 1.85 to 2.13(m,3H), 2.71(br t,6.5,2H). 3.57 to 3.79(m, 2H), 5.08(tq, J_1=7. J_2=1.5, 1H), 5.27 to 5.51(m,2H-AB, J_{AB}=10).
14b	2960, 2930, 2870, 1725, 1250	224(1), 164(9), 149(11), 121(15), 108(27), 93(100), 82(67), 79(61), 77(20), 69(38) H.R 224,1765	0.88(d,6.5,3H). 1.33 to 1.85(m,9H including 2 s : δ 1.62,3H ; δ 1.67,3H), 1.85 to 2.25(m,5H including a s : δ 2.03,3H). 2.70(dd, J_1=6.5, J_2=6.0,2H), 4.01 to 4.19(m,2H), 5.01 to 5.17(m,1H), 5.26 to 5.49(m,2H-AB : J_{AB}=10).

[a] Electronic Impact unless Chemical Ionisation (C.I.) or High Resolution (HR) indicated.

Silver nitrate-charged silica gel was prepared according to a known procedure [19]. Analytical HPLC was conducted on a Du Pont 850 Liquid Chromatograph equipped with a Du Pont B 1500 Zorbax Sil (4.6mm x 25cm) column. All optical rotations were measured on either a Perkin Elmer 141 or 241 at 589nm (sodium band D) with a 1dm cell.

After workup all organic layers were dried over anhydrous magnesium sulfate. All solvents were distilled over appropriate reagents : benzophenone-sodium (THF, dioxane, ether), P_2O_5 (pentane), calcium hydride (dichloromethane, chloroform), sodium (benzene, toluene, xylene), magnesium (methanol, ethanol). Grignard reagents and n-BuLi were titrated with a 0.5M solution of 2-butanol in xylene using 2,2'-biquinoline [21] as the indicator. All reactions were run under a positive pressure of dry nitrogen.

IR, m/z, and ^1H NMR data for all compounds are collected in Table 1. ^{13}C NMR are given in Table II.

Trimethyl 2-methyl 1,1,3-propanetricarboxylate 1 [9a]. A mixture of 63.4g (0.48mol) of methyl malonate and 40g (0.48mol) of methyl crotonate was added dropwise to 200ml of stirred 2.05M solution of sodium methoxide in methanol so as to maintain solvent reflux. At the end of the addition methanol was removed by rapid distillation. The mixture was cooled to 0°C and 300ml of ether were added precipitating the sodium salt of 1. 82ml of a 5M aqueous solution of HCl cooled to 0°C were added and the acidic reaction mixture was extracted with ether. After washing with brine until neutral and the usual workup, distillation (B.p.112°C/0.1mm) yielded 78.2g (84%) of 1 as a colourless liquid, pure according to G.L.C.

TABLE II : ^{13}C NMR spectra

Compound	100 MHz ^{13}C NMR referenced to $CDCl_3$ (77.00 ppm)(multiplicity [a] or parity [b])
5	20.49(q), 25.47(d), 29.58(t), 37.16(t), 67.39(d), 169.60(s)
9b	-5.21(q), 17.74(q), 18.29(s), 19.49(q), 19.65(q), 25.34, 25.60, 25.95, 26.22, 26.35, 39.07(t), 39.29(t), 52.60(t), 60.75(t), 74.05(d), 74.38(d), 117.16(d), 128.62(d), 128.98(d),133.77(s), 136.03(s), 136.45(s), 136.58(s), 200.63(s), 200.86(s).
11a	-5.36(+), 17.66(+), 18.23(-), 19.09(+), 19.70(+), 20.71( ), 21.80(-), 22.16(-), 24.82(-), 24.95(-), 25.50(+), 25.92(+), 26.42(+), 26.71(+), 26.89(+), 38.71(-), 39.53(-), 39.89(-), 40.39(-), 41.42(-), 41.86(-), 60.99(-), 61.16(-), 61.46(-), 66.93(+), 67.02(+), 68.04(+), 68.21(+), 68.79(+), 69.37(+), 69.70(+), 69.91(+), 119.68(+), 120.66(+), 120.79(+), 128.49(+), 128.57(+), 129.00(+), 129.13(+), 133.52(+), 133.70(+), 134.17(-), 134.81(-), 138.63(-).
11b	-5.43(+), 17.40(+), 17.69(+), 18.12(-), 18.66(+), 18.84(+), 18.89(+), 19.93(+), 20.55(+), 20.64(+), 22.77(-), 22.94(-), 23.07(-), 23.34(-), 25.47(+), 25.83(+), 25.94(+), 26.39(+), 26.57(+), 36.95(-), 37.43(-), 38.78(-), 39.21(-), 39.51(-), 39.61(-), 40.31(-), 60.49(-), 60.54(-), 60.65(-), 60.80(-), 66.27(+), 66.43(+), 67.20(+), 68.40(+), 68.67(+), 69.36(+), 69.79(+), 119.90(+), 120.00(+), 120.18(+), 120.34(+), 128.56(+), 128.90(+), 133.69(-), 139.77(-), 169.48(-), 169.79(-), 169.89(-).
12	-5.18(q), 17.77(q), 18.29(s), 19.68(q), 25.38(t), 25.57(q), 25.95(q), 29.75(d), 35.51(t), 39.52(t), 119.72(d), 127.62(d), 128.49(d), 132.51(s), 132.80(d), 140.08(s), 140.60(s), 140.95(d).
13b	17.77(+), 19.52(+), 20.93(+), 22.04(+), 25.61(+), 28.55(-), 30.93(+), 34.63(+), 34.88(-), 35.40(-), 63.13(-), 120.48(+), 123.72(+), 130.87(-), 146.05(-), 171.03(-).

[a] Gated decoupling. [b] J-Modulated Spectrum 24 with d and q=(+) whereas s and t=(-).

Dimethyl 3-methylpentanedioate 2. 69.6g (0.30mol) of 1, 300ml of DMSO, 5.4g (0.30mol) of water, and 35g (0.60mol) of NaCl were refluxed for 4.5h (complete reaction according to GLC) as described in a literature procedure [10]. The reaction mixture was cooled and poured onto a liter of ice water. After extraction with ether and the usual workup, distillation (B.p. 65°C/0.1mm ; lit. [22] B.p. 91-92°C/7mm) afforded 48.5g (93%) of 2 pure according to GLC and NMR analyses.

Monomethyl (R)-3-methylpentanedioate 3 [11]. 1000 units of pig liver esterase (Boehringer) were added at 23°C to a vigorously stirred suspension of 15.0g (86mmol) of 2 in 100ml of a 0.1M phosphate buffer at pH 7 according to a known procedure [11]. A pH of 7 was maintained by pH-Stat controlled addition of a 1M solution of aqueous NaOH. After addition of an equivalent of base with respect to 2, the mixture was homogeneous and base was added until the pH was 9. The aqueous layer was washed twice with ether and the ethereal layers were washed twice with water. The combined aqueous layers were acidified to pH 2 and then extracted with ether. The usual workup yielded 13.47g of monoester 3 (98%), pure according to NMR and elemental analyses.

Methyl 5-hydroxy (R)-3-methylpentanoate 4 [11]. 42ml (82mmol) of a 2M solution of $BH_3(CH_3)_2S$ in THF were added dropwise to a solution of 12.8g (0.080mol) of 3 in 20ml of THF slowly enough so that the temperature did not exceed 30°C. After stirring for 1h at 20°C, 5.6ml of water were added at 0°C, the solvent was removed in vacuo and the residue dissolved in ethyl acetate. This solution was dried, filtered and evaporated to furnish 11.2g (96%) of an oil containing 92% of 4 and 8% of 5 according to ^1H NMR [11].

(R)-4-Methyltetrahydro 2H-pyran 2-one 5. 10g of silica gel (Merck 7736) were added to a vigorously stirred solution of 10g (0.068ml) of 4 in 500ml of anhydrous dichloromethane. After stirring for 18h at 20°C the mixture was filtered and the solvent evaporated. Distillation (B.p. 64-66°C/0.1mm ; lit. [23] B.p. 110-115°C/15mm) afforded 6.5g (84%) of lactone 5 pure by RMN and GLC analyses, $[\alpha]_D^{25}$ + 23.7° (c=5.7 $CHCl_3$)(lit. [11a] $[\alpha]_D^{23}$ +23.4° (c=5.7 $CHCl_3$) for a lactone with 90% e.e.).

(R)-3-5-Dimethyl 1,5-hexanediol 6 [12]. 5.6ml (9mmol) of a 1.6M solution of MeLi in ether were added rapidly to a stirred solution of 342mg (3mmol) of 5 in 5ml of THF at -78°C according to a known procedure. The solution was warmed to room temperature and stirred for 1h. The reaction mixture was hydrolysed with 2ml of saturated aqueous solution of ammonium chloride at 0°C and extracted with ether. After washing with a saturated aqueous solution of $NaHCO_3$ and then brine the ethereal layers were dried over potassium carbonate. Evaporation followed by distillation (Kugelrohr : 80-85°C under 0.3mm of Hg) afforded 330mg (75%) of diol 6, pure according to NMR and elemental analyses, $[\alpha]_D^{25}$ -15.4° (c=5.7 $CHCl_3$).

(R)-2,(R)-3,(R)-9-Trimethyl 1,4,6-trioxa 4,5-spirodecane 7 [13]. 135mg (1.5mmol) of (-)-(R)-2,(R)-3-butanediol (Janssen), 159mg (1.5mmol) of trimethyl orthoformate (Janssen) and 3 drops of concentrated H_2SO_4 were added successively to a solution of 115mg (1 mmol) of 5 in 2ml of THF. The mixture was stirred at 20°C for 24h, 0.25ml of triethylamine were added and the reaction mixture was poured onto a saturated solution of $NaHCO_3$. After extraction with benzene and the usual workup, flash chromatography (pentane/acetone : 9/1) furnished 123mg (67%) of 7 >95% pure according to NMR analysis. Two diastereoisomers in a 95/5 ratio were detected by capillary GLC (oven 60°C ; P_{He} 1 bar : retention times - 31.7 and 33.3 Min. respectively).

(R)-3,9-Dimethyl 5-oxo (R,S)-6-phenylsulfonyl 8-decen 1-ol 9a. 31.6ml(0.038mol) of a 1.2M solution of n-BuLi in hexane were added to a stirred solution of 4.0g (0.018mol) of sulfone 8 and 5.7ml (0.038mol) of TMEDA in 20ml of THF at -78°C according a known method [19]. The solution was warmed to room temperature for 0.5h, cooled to -78°C, and syphoned into a second reaction vessel containing a solution of 2.3g (0.020mol) of lactone 5 (α^{25} + 23.7° (c=5.7$CHCl_3$)) in a 5/1 mixture of THF/HMPT at -78°C. The reaction mixture was warmed to 20°C and stirred for 5h. 16ml of a 5M aqueous solution of HCl were added at 0°C and the solution was extracted with ether. After the usual workup, flash chromatography on basic silica gel afforded 857mg (21%) of starting sulfone 8 and 3.8g (62%) of a 54/46 mixture of sulfoneketols 9a (threo/erythro : 53/47) and sulfonehemiketals 10 (a 64/36 mixture of two isomers).

1-t-Butyldimethylsilyloxy (R)-3,9-dimethyl (R,S)-6-phenylsulfonyl 8-decen 5-one 9b
As previously described [15], 3g (8.88mmol) of the above 54/46 mixture of compounds 9a and 10, 1.48g (8.76mmol) of TBDMS-Cl, 2.7ml (19.5mmol) of triethylamine, and 43mg (0.36mmol) of DMAP in 60ml of dichloromethane were mixed at 0°C and then stirred at 20°C for 5h. 20ml of a saturated aqueous solution of ammonium chloride were added and the mixture was extracted with ether. After washing with a saturated solution of $NaHCO_3$ and the usual workup, flash chromatography on basic silica gel furnished 3.9g (97%) of 9b (2 diastereoisomers according to ^1H NMR), $[\alpha]_D^{25}$ + 0.09° (c=2.0 $CHCl_3$).

1-t-Butyldimethylsilyloxy (R)-3,9-dimethyl (R,S)-6-phenylsulfonyl 8-decen (R,S)-5-ol 11a
According to a literature procedure [16], a solution of 1.6g (0.042mol) of $NaBH_4$ in 15ml of water was added to a solution of 3.8g (8.41mmol) of 9b in 75ml of methanol at 20°C. The mixture was stirred for 5h and then the methanol was removed in vacuo. The residue was acidified to pH 3-4 with a 0.5M solution of HCl at 0°C and extracted with ether at this temperature. The ethereal layers were washed with a saturated solution of $NaHCO_3$ and after the usual workup, flash chromatography on basic silica gel yielded 3.5g (92%) of sulfonealcohols 11a (4 diastereoisomers according to ^1H NMR), $[\alpha]_D^{25}$ - 0.025° (c=1.4 $CHCl_3$).

1-t-Butyldimethylsilyloxy (R)-3,9-dimethyl (R,S)-6-phenylsulfonyl 8-decen (R,S)-5-yl acetate 11b
0.92g (9mmol) of acetic anhydride were added to a solution of 3.4g (7.49mmol) of sulfonealcohols 11a, 1.13g (11.2mmol) of triethylamine and 44mg (0.36mmol) of DMAP in 25ml of

dichloromethane at 0°C according to ref. 17. The solution was stirred for 5h at 20°C and 3ml of 1M aqueous solution of NaOH were added at 0°C. The mixture was extracted with ether and the ethereal layers were washed successively with a saturated solution of ammonium chloride, water, and brine. After the usual workup, flash chromatography on basic silica gel afforded 3.53g (95%) of acetoxysulfones 11b as a colourless oil (4 diastereoisomers according to ^{1}H NMR analysis), $[\alpha]_D^{25}$ + 0.004° (c=8.1 $CHCl_3$).

1-t-Butyldimethylsilyloxy (S)-3,9-dimethyl 6-phenylsulfonyl (E)-5,8-decadiene 12
0.5g (1.01mmol) of acetoxysulfone 11b, 101mg (2.52mmol) of powdered NaOH, and 12ml of ether were stirred at 20°C for 5h as previously described [5,6]. The usual workup and flash chromatography on basic silica gel yielded 0.41g (94%) of dienesulfone 12, $[\alpha]_D^{25}$ - 8.71° (c=1.7 n-hexane). A single isomer was detected by HPLC under conditions previously described [7,8] for analysis of 2-benzenesulfonyl 1,4-dienes (eluent : isooctane/ethylacetate - 97/3). The E-configuration of the newly-created double bond was confirmed by ^{1}H NMR.

(S)-3,9-Dimethyl 6-(1-methylethyl) (E)-5,8-decadien 1-ol 13a
(S)-3,9-Dimethyl (Z)-5,8 decadien 1-ol 14a
1.6ml (0.78mmol) of 0.5M iPrMgCl in ether were added to a solution of 170mg (0.39mmol) of dienesulfone 12 in 1.2ml of 0.01M $FeCl_3$ in ether at -78°C as previously described [8]. The black solution was stirred for 3h at 20°C and 2ml of a saturated solution of ammonium chloride were added at 0°C. After the usual workup and flash chromatography on basic silica gel, the mixture of silylated alcohols and sulfur-containing impurities was dissolved in 6ml of THF and stirred with 369mg (1.17mmol) of $Bu_4NF \cdot 3H_2O$ at 0°C for 2h as previously described [18]. After workup, flash chromatography furnished 55mg of a 58/42 mixture of 13a (36%) and 14a (32%) according to GLC and capillary GLC-mass analysis.

(S)-3,9-Dimethyl 6-(1-methylethyl)(E)-5,8-decadien 1-yl acetate 13b
(S)-3,9-Dimethyl (Z)-5,8-decadien 1-yl acetate 14b
55mg of the above mixture of 13a and 14a, 28 µl (0.29mmol) of acetic anhydride, 47 µl (0.36mmol) of triethylamine, 1.6mg (0.013mmol) of DNAP, and 3ml of dichloromethane were stirred for 5h at 20°C as described for 11a [17]. Workup afforded 59mg of a residue which was purified by flash chromatography on silver nitrate-charged silica gel to yield 31mg of 13b, $[\alpha]_D^{25}$ - 9.48° (c=1.16 n-hexane) (lit.[4a] $[\alpha]_D^{31}$ - 9.83° (c=1.16 n-hexane)), and 22mg of 14b, $[\alpha]_D^{25}$ - 1.98° (c=1.2 n-hexane). The yield of acetylation products was 96%.

TABLE III : Elemental analysis.

Compound	Formulae	Calculated C %	Calculated H %	Found C %	Found H %
1	$C_{10}H_{16}O_6$	51.72	6.94	51.55	6.96
2	$C_8H_{14}O_4$	55.16	8.10	55.18	7.99
3	$C_7H_{12}O_4$	52.49	7.55	52.46	7.56
5	$C_6H_{10}O_2$	63.14	8.83	63.29	8.85
6	$C_8H_{18}O_2$	65.71	12.41	65.38	12.32
9a + 10	$C_{18}H_{26}O_4S$	63.87	7.74	64.01	7.77
9b	$C_{24}H_{40}O_4SSi$	63.75	9.01	63.67	8.91
11a	$C_{24}H_{42}O_4SSi$	63.39	9.31	63.31	9.41
11b	$C_{26}H_{44}O_5SSi$	62.86	8.93	62.80	8.99
12	$C_{24}H_{40}O_3SSi$	66.00	9.23	66.18	9.31
13b	$C_{17}H_{30}O_2$	76.64	11.35	76.25	11.28
14b	$C_{14}H_{24}O_2$	74.95	10.78	74.68	10.99

Capillary GLC analysis indicated that 13b contained 3 isomers in a 98/1.5/0.5 ratio whereas 14b contained 2 isomers in a 98/2 ratio. The major isomers were identified as (E)-13b and (Z)-14b by ^{1}H NMR.

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