CHIRAL SYNTHESIS OF (R)-(+)-CITRONELLAL VIA STEREOSELECTIVE PROTONATION

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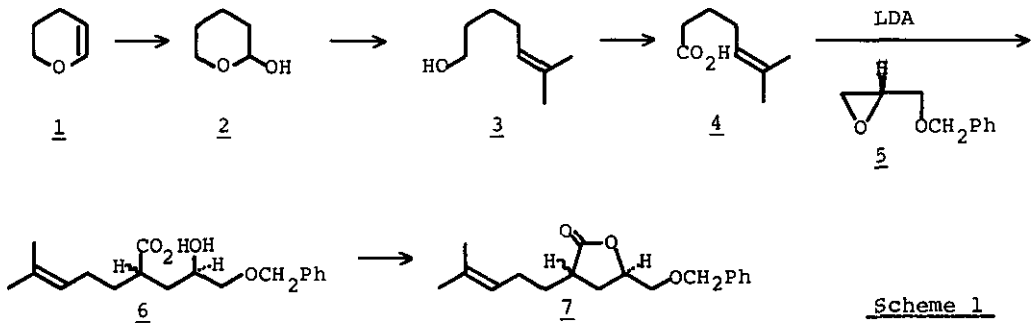
Abstract——Protonation of the enolates (8) and (12) generated from an epimeric mixture of the α,γ-disubstituted γ-lactone (7) is shown to yield the syn-α/γ-disubstituted γ-lactone (10) predominant over the anti-α/γ-disubstituted γ-lactone (11). When the silyl enol ether (12) generated in situ is protonated with trifluoroacetic acid, the best selectivity is obtained. The syn-epimer (10) thus obtained is converted into (R)-(+)-citronellal (17) in four steps of reactions.

Controlling the stereochemistry of enolizable chiral center via an enolate intermediate by stereoselective protonation under thermodynamically controlled or kinetically controlled conditions has been often employed in organic synthesis.[1-3] We have been successfully employing these methods for the construction of a new chiral center at the position of five, six and seven membered lactone substrates reflecting the stereochemistry of the remaining center.[4-11] In the present report we describe that an improved method for the stereoselective protonation of the α,γ-disubstituted γ-lactone (7) which did not allow highly stereoselective protonation under conventional conditions and its application to a new synthesis of (R)-(+)-citronellal (17).[12] The chiral α,γ-disubstituted γ-lactone (7) used as the substrate was prepared from the known δ-lactol (2)[13] obtained from dihydropyran (1) via a sequence of five steps of reactions. Thus, 2 was converted into the unsaturated alcohol (3)[14] which was then oxidized to the known acid (4)[15] with

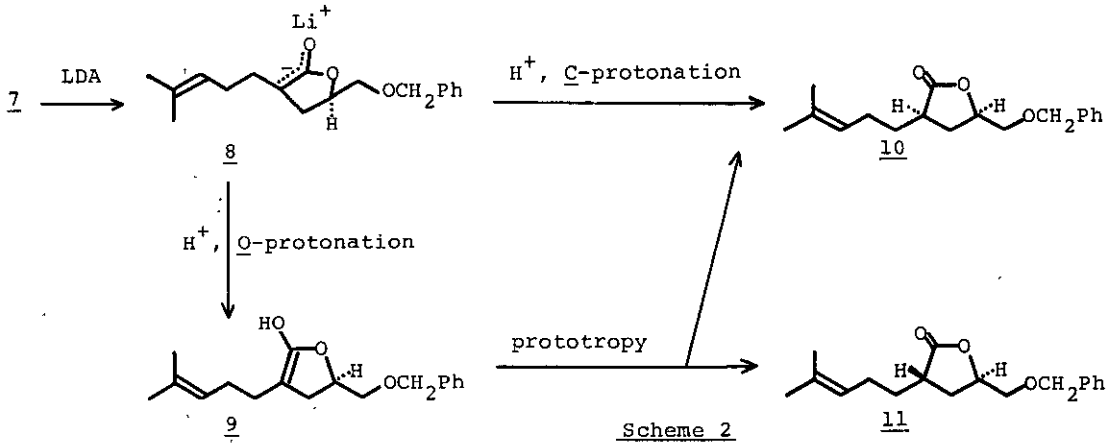


1 2 3 4 5 6 7

Scheme 1

pyridinium dichromate. The acid (4) was treated with lithium diisopropylamide (LDA) in tetrahydrofuran (THF) to generate the dianion which was immediately condensed with (S)-O-benzylglycidol (5)[16] to give rise to the hydroxy-acid (6) after acid work-up. On reflux in toluene 6 gave the α,γ-disubstituted γ-lactone (7),[16] as a 1:1 mixture of epimers, which could be separated by a silica gel column chromatography. Although we could not determine each stereochemistry at this point, we later knew the major isomer possessing low polarity to be the syn epimer (10) as expected from the related cases.[5,8-11]

As conventional methods, we applied 5% hydrochloric acid[11] and both (D)- and (L)-camphorsulfonic acid in THF[17] to the lithium enolate (8) generated from the lactone mixture (7) with LDA in THF, respectively. As shown in Table, although stereoselection was observed in all cases, the best ratio was only 2.9:1 (Entry 1-3). Since it was reasoned that this could be brought about by preferential O-



Scheme 2

Table

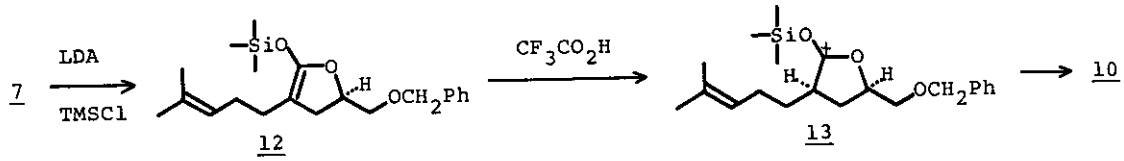
Entry	Substrate	Conditions	Ratio (syn (10):anti (11))[a]	Total yield(%)
1	7[b]	A	2.9 : 1	81.6
2	7[b]	B	2.7 : 1	86.4
3	7[b]	C	2.6 : 1	86.7
4	7[b]	D	5.4 : 1	85.4

A: LDA (1.2 equiv) at -70°C then 5% hydrochloric acid at -70°C
B: " then 10% D-camphorsulfonic acid monohydrate in THF at -70°C
C: " then 10% L-camphorsulfonic acid monohydrate in THF at -70°C
D: " then TMSCl (1.2 equiv) in THF at -70°C, then trifluoroacetic acid at -70°C

(a) Ratio was determined by HPLC. (b) A syn/anti mixture (1:1) was used as substrate.

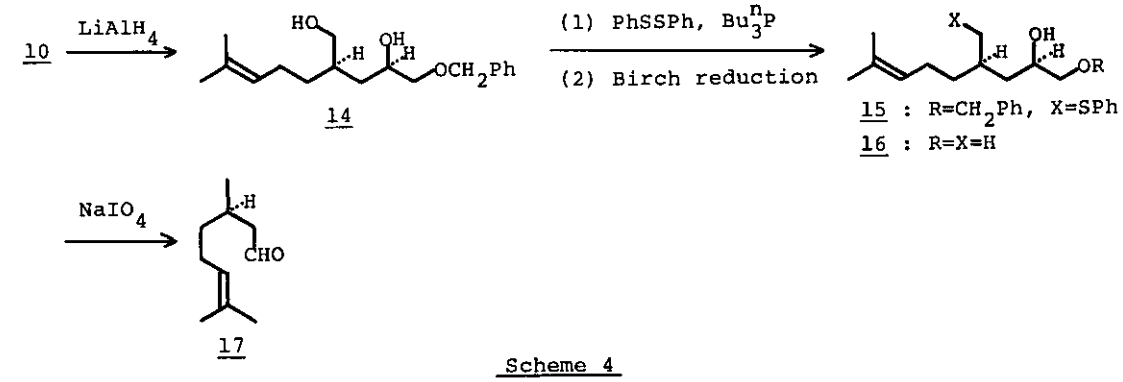
protonation to C-protonation to form the enol (9) followed by non-stereoselective

prototropy to give the syn/anti mixture (7), the mixture (7) was first converted into the silyl enol ether (12) in precedent to the protonation. It was hoped that the silyl enolate (12) could be more selectively converted into the syn-epimer (10) by selective C-protonation from the least hindered face generating the β-silyl cation (13) due to the stabilizing effect of silicon atom.[18] As expected, when the trimethylsilyl enol ether (12), generated in situ by treating the lactone mixture (7) with LDA followed by trimethylsilyl chloride, was protonated with trifluoroacetic acid at -70°C a 5.4:1 ratio of syn:anti epimers was obtained in 85.4% total yield (Entry 4). Although the ratios obtained under the present conditions were not extremely high probably owing to insufficient directing effect of trimethylsilyl group suggested by Tidwell and co-workers,[19] the undesirable anti-epimer (11) could be separated and recycled.



Scheme 3

In order to find synthetic utility as well as to ascertain the stereochemistry, we attempted the synthesis of optically active citronellal (17) using the major protonation product. It should yield the target molecule (17) with R-configuration provided that it has the syn configuration as presumed. Reduction of the lactone (10) could be carried out with lithium aluminum hydride to give the diol (14) in quantitative yield. Treatment of 14 with diphenyl disulfide and tri-n-butylphosphine in pyridine[20,21] at room temperature allowed a selective reaction at the primary hydroxy group to give the monosulfide (15) in 71% yield. Concurrent removal of both the sulfide and the ether groups could be achieved efficiently under the Birch conditions to give the 1,2-glycol (16) in 86% yield. Finally, 16 was oxidatively cleaved with sodium periodate to give (R)-(+)-citronellal (17) in 71% yield. This constituted the confirmation of syn-α,γ-relationship of the major protonation product (10) as well as a new chiral synthesis of (R)-(+)-citronellal (17).



Scheme 4

EXPERIMENTAL

All the reactions were carried out under argon. Ir spectra were recorded on a JASCO A-102 instrument, and ^{1}H-nmr spectra were measured for solutions in deuteriochloroform on JEOL-PMX 60 and JEOL-FX 100 spectrometers. Optical rotations were measured with a JASCO-DIP-4 automatic polarimeter. HPLC was carried out on EYELA PLC-10 instrument using a column of Microsorb (80-115, 4.6 x 150 mm) with 2% isopropanol in n-hexane.

6-Methylhept-5-en-1-ol (3)———To a stirred solution containing isopropylidene triphenylphosphorane, prepared in situ from isopropyltriphenylphosphonium iodide (197.86 g, 0.46 mol) and 15% (w/v) n-butyl-lithium in n-hexane (257 ml, 400 mmol) in THF (560 ml) at 0°C, was added the lactol (2)[13] (19.47 g, 191 mmol) dropwise at 0°C. After stirring for 45 min at the same temperature, the mixture was treated with saturated aqueous ammonium chloride (100 ml) and filtered to remove the separated inorganic precipitate which was washed with ether (3 x 100 ml). The combined organic layers were washed with brine (150 ml), dried ($MgSO_4$), evaporated in vacuo, and distilled to give the unsaturated alcohol (3) (17.86 g, 73.1%) as a colorless oil; bp 97-102°C (19 mm Hg) (lit.[14] bp 94-95°C (16 mm Hg)).

6-Methylhept-5-enoic Acid (4)———To a stirred solution of pyridinium dichromate (87.43 g, 232 mmol) in DMF (175 ml) was added 3 (8.50 g, 66.4 mmol) in DMF (30 ml) dropwise at 0°C. After stirring at room temperature for 4 h, ether (300 ml) was added to the mixture and the organic layer was decanted. The residue was stirred with Florisil (87 g) in methylene dichloride (250 ml) and ether (200 ml) for 12 h and the mixture was filtered through Celite. The combined organic layers were evaporated in vacuo and the residue was filtered through silica gel (50 g) with n-hexane-ethyl acetate (2:1) as eluent. After evaporating the solvent the residue was mixed with water (200 ml) and the mixture was extracted with ether (4 x 100 ml). The extract was evaporated to 100 ml amount and was extracted with saturated aqueous sodium hydrogen carbonate (4 x 50 ml). The combined aqueous layers were acidified with 6 N hydrochloric acid and extracted with methylene dichloride (4 x 100 ml). The extract was washed with brine (100 ml), dried (Na_2SO_4), and evaporated in vacuo to give the crude acid (4) (6.5 g). On the other hand, the ether layer was evaporated to give the oily residue (5.07 g) containing a substantial amount of the ester generated from 4 and 3, which was refluxed in methanolic potassium hydroxide (6.63 g, 100 mmol in 70 ml) for 5 h to give the acid (4). After evaporating the solvent in vacuo, the residue was dissolved in water (60 ml), washed with ether (3 x 50 ml), acidified with 6 N hydrochloric acid, and was extracted with methylene dichloride (3 x 100 ml). The extract was washed with brine (50 ml), dried (Na_2SO_4), and evaporated to give the crude acid (4) (2.39 g). The combined crude acid was distilled under vacuum to give the acid (4) (7.88 g, 83.6%) as a colorless oil; bp 120-125°C (0.35 mm Hg) (Kugelrohr) (lit.[15] bp 110-111°C (4 mm Hg)).

(3-R/S,5R)-5-(Benzyloxymethyl)-3-(4-methylpent-3-enyl)-tetrahydrofuran-2-one (7)———To a stirred solution containing lithium diisopropylamide, prepared in situ from diisopropylamine (7.33 ml, 52.4 mmol) and 15% (w/v) n-butyl-lithium

(33.64 ml, 52.4 mmol) at -58°C in THF (45 ml), was added hexamethylphosphoric triamide (HMPA) (0.41 ml, 2.4 mmol) followed by the acid (4) (3.38 g, 23.8 mmol) in THF (15 ml) dropwise at the same temperature. The mixture was gradually warmed to room temperature and after 5 min was cooled again to -58°C. To the cooled mixture was then added the epoxide (5) (3.90 g, 23.8 mmol) in THF (15 ml) dropwise and the mixture was gradually warmed to -20°C. After stirring for 4 h at -20°C, the mixture was further stirred at room temperature for 8 h. The mixture was treated with saturated aqueous sodium hydrogen carbonate (120 ml), washed with ether (2 x 50 ml), made acidic with 6 N hydrochloric acid, and extracted with methylene dichloride (3 x 100 ml). The extract was dried (Na_2SO_4), evaporated *in vacuo* to give the crude acid (6) (7.29 g) which was azeotropically refluxed in toluene (200 ml) for 4 h using a Dean-Stark apparatus. After cooling the mixture was washed with saturated aqueous sodium hydrogen carbonate (2 x 50 ml), dried (Na_2SO_4), and evaporated *in vacuo* to give the lactone (7) (5.48 g, 80%) as an epimeric mixture (ca. 1:1) which was used for the next reaction. The ratio was determined by HPLC.

Protonation of the Lactone (7) with Hydrochloric Acid via the Lithium Enolate (8)———To a solution containing lithium diisopropylamide, prepared in situ from diisopropylamine (3.11 ml, 22.2 mmol) and 15% (w/v) n-butyl-lithium in hexane (14.25 ml, 22.2 mmol) in THF (16 ml) at -60°C, was added the lactone (7) (5.32 g, 18.5 mmol) in THF (16 ml) dropwise at -60°C. The mixture was kept stirring for 30 min at the same temperature and was then gradually warmed to room temperature. After stirring for 10 min, the mixture was again cooled to -60°C and was treated with 5% hydrochloric acid (50 ml) all at once. After warming to room temperature, the mixture was extracted with ether (3 x 100 ml), washed with brine (50 ml), dried (Na_2SO_4), and evaporated. The residue was chromatographed on a silica gel column (250 g) with n-hexane-ethyl acetate (6:1) as eluent to give the *anti*-epimer (11) (0.54 g, 10.1%) as the less polar material, the mixture (7) (0.56 g, 10.5%), and the *syn*-epimer (10) (3.25 g, 61%) as the more polar material.

The Syn-Epimer, (-)-(3R,5R)-5-(Benzyloxymethyl)-3-(4-methylpent-3-enyl)-tetrahydrofuran-2-one (10): a colorless oil; bp 160-170°C (0.08 mm Hg) (Kugelrohr); $[\alpha]_D^{18}$ -34.44° (c 2.1 in $CHCl_3$); ν_{max} (neat) 1770 cm^{-1}; δ 1.20-2.76 (7H, m), 1.59 (3H, s, $C=CCH_3$), 1.67 (3H, s, $C=CCH_3$), 3.57 (1H, dd, J 10.7, 5 Hz, $OC\underline{H}_2CH$), 3.67 (1H, dd, J 10.7, 3.6 Hz, $OC\underline{H}_2CH$), 4.37-4.66 (1H, m, CHO), 4.57 (2H, s, $PhCH_2O$), 5.04 (1H, br t, J 6.4 Hz, C=CH), 7.30 (5H, s, PhH); m/z 288 (M^+), 91 (100%) (Found: C, 75.13; H, 8.38. $C_{18}H_{24}O_3$ requires C, 74.97; H, 8.39%).

The Anti-Epimer, (-)-(3S,5R)-5-(Benzyloxymethyl)-3-(4-methylpent-3-enyl)-tetrahydrofuran-2-one (11): a colorless oil; bp 150-160°C (0.08 mm Hg) (Kugelrohr); $[\alpha]_D^{18}$ -14.61° (c 1.9, in $CHCl_3$); ν_{max} (neat) 1770 cm^{-1}; δ 1.14-2.44 (6H, m), 1.58 (3H, s, $C=CCH_3$), 1.66 (3H, s, $C=CCH_3$), 2.51-2.90 (1H, m), 3.51 (1H, dd, J 10, 4.3 Hz, $OC\underline{H}_2CH$), 3.67 (1H, dd, J 10, 3.6 Hz, $OC\underline{H}_2CH$), 4.46-4.71 (1H, m, CHO), 4.53 (2H, s, $PhCH_2O$), 5.06 (1H, br t, J 6.4 Hz, C=CH), 7.29 (5H, s, PhH); m/z 288 (M^+), 100 (100%), 91 (Found: C, 74.59; H, 8.40. $C_{18}H_{24}O_3$ requires C, 74.97; H, 8.39).

Protonation of the Lactone (7) with Camphorsulfonic Acid via the Lithium Enolate (8)———To a solution containing lithium diisopropylamide, prepared in situ from diisopropylamine (0.06 ml, 0.42 mmol) and 15% w/v n-butyl-lithium in hexane (0.27

ml, 0.42 mmol) in THF (2 ml) at -70°C, was added the lactone (7) (100.6 mg, 0.35 mmol) in THF (2 ml) at -70°C. The mixture was kept stirring for 30 min at the same temperature for 30 min and was then gradually warmed to room temperature. After 10 min, the mixture was again cooled to -70°C and was treated with D-camphorsulfonic acid hydrate (264 mg, 1.05 mmol) in THF (2.6 ml) all at once. After stirring for 1.5 h, the mixture was diluted with ether (20 ml) and was washed with saturated aqueous sodium hydrogen carbonate (2 x 20 ml), brine (20 ml), dried ($MgSO_4$), and evaporated to give the lactone mixture (86.9 mg, 86.4%). The syn/anti ratio was determined to be 2.7:1 by HPLC.

Protonation of the lactone (7) with Trifluoroacetic Acid via the Trimethylsilyl Enolate (12)———To a solution containing lithium diisopropylamide, prepared in situ from diisopropylamine (0.17 ml, 1.2 mmol) and 15% (w/v) n-butyl-lithium in hexane (0.77 ml, 1.2 mmol) in THF (2 ml) at -70°C, was added the lactone (7) (288 mg, 1.0 mmol) in THF (2 ml) at -70°C. The mixture was kept stirring for 30 min at the same temperature and was then gradually warmed to room temperature. After 10 min, the mixture was again cooled to -70°C and was treated with trimethylsilyl chloride (0.15 ml, 1.2 mmol) and the stirring was continued for 30 min at the same temperature and 5 min at room temperature. The mixture was again cooled to -70°C and was then treated with trifluoroacetic acid (0.15 ml, 2 mmol) all at once. After 30 min, the mixture was diluted with ether (20 ml) and was washed with saturated aqueous sodium hydrogen carbonate (2 x 20 ml), brine (20 ml) dried (Na_2SO_4), and evaporated. The residue was chromatographed on a silica gel column (6.0 g) with n-hexane-ether (10:1) as eluent to give the pure mixture (187 mg, 85.4%) whose syn/anti ratio was determined to be 5.4:1 by HPLC.

(+)-(2R,4R)-1-Benzyloxy-4-hydroxymethyl-8-methylnon-7-en-2-ol (14)———To a stirred suspension of lithium aluminum hydride (66 mg, 1.74 mmol) in THF (20 ml) was added the syn-lactone (10) (0.50 g, 1.74 mmol) in THF (15 ml) dropwise at 0°C. After 10 min, 30% ammonium hydroxide (5 ml) was added to the mixture at the same temperature. The mixture was filtered through Celite and the filtrate after addition of water (10 ml) was extracted with methylene dichloride (3 x 30 ml). The extract was washed with brine (15 ml), dried (Na_2SO_4), and evaporated in vacuo to give the diol (14) (0.51 g, 100%) as practically pure state: bp 200-210°C (0.35 mm Hg) (Kugelrohr); $[\alpha]_D^{15}$ +1.61° (c 3.1 in $CHCl_3$); ν_{max} (neat) 3350 cm^{-1}; δ 1.00-2.40 (7H, m), 1.60 (3H, s, $C=CCH_3$), 1.68 (3H, s, $C=CCH_3$), 3.31 (2H, br s, exchangeable, OH x 2) , 3.13-3.68 (4H, m, CH_2O, CH_2OH), 3.73-4.07 (1H, m, CHOH), 4.54 (2H, s, $PhCH_2O$), 5.08 (1H, br t, J 7 Hz, C=CH), 7.30 (5H, s, PhH); m/z 292 (M^+), 91 (100%) (Found: C, 73.45; H, 9.51. $C_{18}H_{28}O_3$ requires C, 73.93; H, 9.65).

(+)-(2R,4R)-1-Benzyloxy-8-methyl-4-phenylthiomethylnon-7-en-2-ol (15)———A mixture of the diol (14) (0.75 g, 2.57 mmol), diphenyl disulfide (0.84 g, 3.85 mmol), and tri-n-butyl-phosphine (0.96 ml, 3.85 mmol) in pyridine (7 ml) was stirred at room temperature for 13.5 h. The solvent was removed under reduced pressure and the residue was chromatographed on a silica gel column (30 g) with n-hexane-ethyl acetate (8:1) as eluent to give the sulfide (15) (0.70 g, 71%) as a colorless oil: bp 230-235°C (0.4 mm Hg) (Kugelrohr); $[\alpha]_D^{15}$ +3.76° (c 3.2 in $CHCl_3$); ν_{max} (neat) 3450 cm^{-1}; δ 1.21-2.38 (7H, m), 1.59 (3H, s, $C=CCH_3$), 1.68 (3H, s, $C=CCH_3$), 2.19 (1H, br s, exchangeable, OH), 2.99 (2H, d, J 5 Hz, $PhSCH_2$),

3.42 (2H, m, CH_2O), 3.92 (1H, m, CHOH), 4.53 (2H, s, $PhCH_2O$), 5.08 (1H, br t, J 7 Hz, C=CH), 7.27 (5H, m, PhH), 7.31 (5H, s, PhH); m/z 384 (M^+), 91 (100%) (Found: C, 75.22; H, 8.18; S, 8.34. $C_{24}H_{32}O_2S$ requires C, 74.96; H, 8.39; S, 8.76). The unreacted starting material (14) (90 mg, 12.1%) was recovered using more polar eluent (n-hexane-ethyl acetate: 2:1).

(+)-(2R,4R)-4,8-Dimethylnon-7-ene-1,2-diol (16)———The sulfide (15) (0.58 g, 1.51 mmol) in ethanol (1 ml) was added to liquid ammonia (ca. 60 ml) in a flask equipped with a dry ice-acetone condenser. To this stirred mixture was added sodium metal (0.26 g, 11.3 mm atom) portionwise and the stirring was continued for 1 h. The mixture was treated with ammonium chloride and the ammonia was evaporated by removing the dry ice condenser. The residue was dissolved in saturated aqueous ammonium chloride (15 ml) and was extracted with ethyl acetate (3 x 30 ml). The extract was washed with brine (30 ml), dried (Na_2SO_4), and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (15 g) with n-hexane-ether (1:1) as eluent to give the diol (16) (0.24 g, 85.7%) as a colorless oil: bp 105-110°C (0.4 mm Hg) (Kugelrohr); $[\alpha]_D^{15}$ +8.42° (c 3.3 in $CHCl_3$); ν_{max} (neat) 3360 cm^{-1}; δ 0.95 (3H, d, J 5 Hz, $CHCH_3$), 1.08-2.30 (7H, m), 1.61 (3H, s, $C=CCH_3$), 1.69 (3H, s, $C=CCH_3$), 2.90 (2H, br s, exchangeable, OH), 3.15-4.11 (3H, m, CH_2OH, CHOH), 5.07 (1H, br t, J 7 Hz, C=CH); m/z 186 (M^+), 70 (100%) (Found: C, 70.62; H, 11.93. $C_{11}H_{22}O_2$ requires C, 70.92; H, 11.90).

(+)-(R)-Citronellal (17)———To a stirred solution of the diol (16) (0.29 g, 1.56 mmol) in methylene dichloride (5 ml) was added sodium periodate (0.33 g, 1.56 mmol) in water (2 ml) dropwise at 0°C. After stirring for 45 min at the same temperature, brine (10 ml) and methylene dichloride (20 ml) was added to the suspension and the organic layer was separated. The aqueous layer was extracted with methylene dichloride (20 ml). The combined organic layers were washed with 5% aqueous sodium thiosulfate (20 ml) and brine (20 ml), dried (Na_2SO_4), and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (10 g) with n-hexane-ether (9:1) as eluent to give (R)-(+)-citronellal (17) (0.17 g, 70.8%) as a colorless oil: bp 85°C (14 mm Hg) (Kugelrohr) (lit.[12] bp 94-96°C (8 mm Hg)); $[\alpha]_D^{18}$ +16.50° (c 2.5 in $CHCl_3$) (lit.[22] $[\alpha]_D$ +16.50° (neat)). Optical purity of 17 was deduced to be > 95% e.e. by ^{1}H-nmr (500 MHz) spectrum of MTPA ester of (R)-(+)-citronellol derived from 17.

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