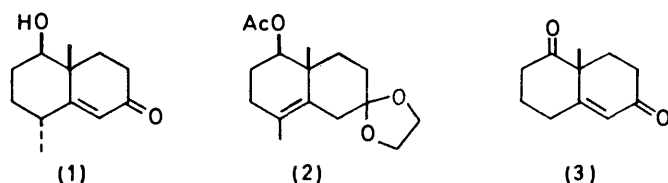


## Total Synthesis of Racemic Geijerone and $\gamma$ -Elemene

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Representative elemanoids, geijerone (4) and  $\gamma$ -elemene (5), were synthesised in racemic form *via* reductive fragmentation of 4 $\beta$ -methylsulphonyloxy-4,4a,5,6,8,8a $\alpha$ -hexahydro-1 $\alpha$ ,4a $\beta$ -dimethylnaphthalene-2,7(1*H*,3*H*)-dione 7-ethylene acetal (10) or 2 $\beta$ -hydroxy-4 $\beta$ -methylsulphonyloxy-2,3,4,4a,5,6,8,8a $\alpha$ -octahydro-1 $\alpha$ ,4a $\beta$ -dimethylnaphthalen-7(1*H*)-one ethylene acetal (11), both readily available from the Wieland–Miescher ketone (3).

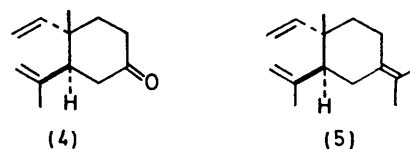
RECENTLY we reported a convenient synthesis of the hydroxy-octalone (1) and its precursor (2) from the Wieland–Miescher ketone (3); these products were discussed as versatile synthetic key intermediates leading



to some representative sesquiterpenes such as eudesmanes, guaianes, elemanes, and germacranes.<sup>1</sup>

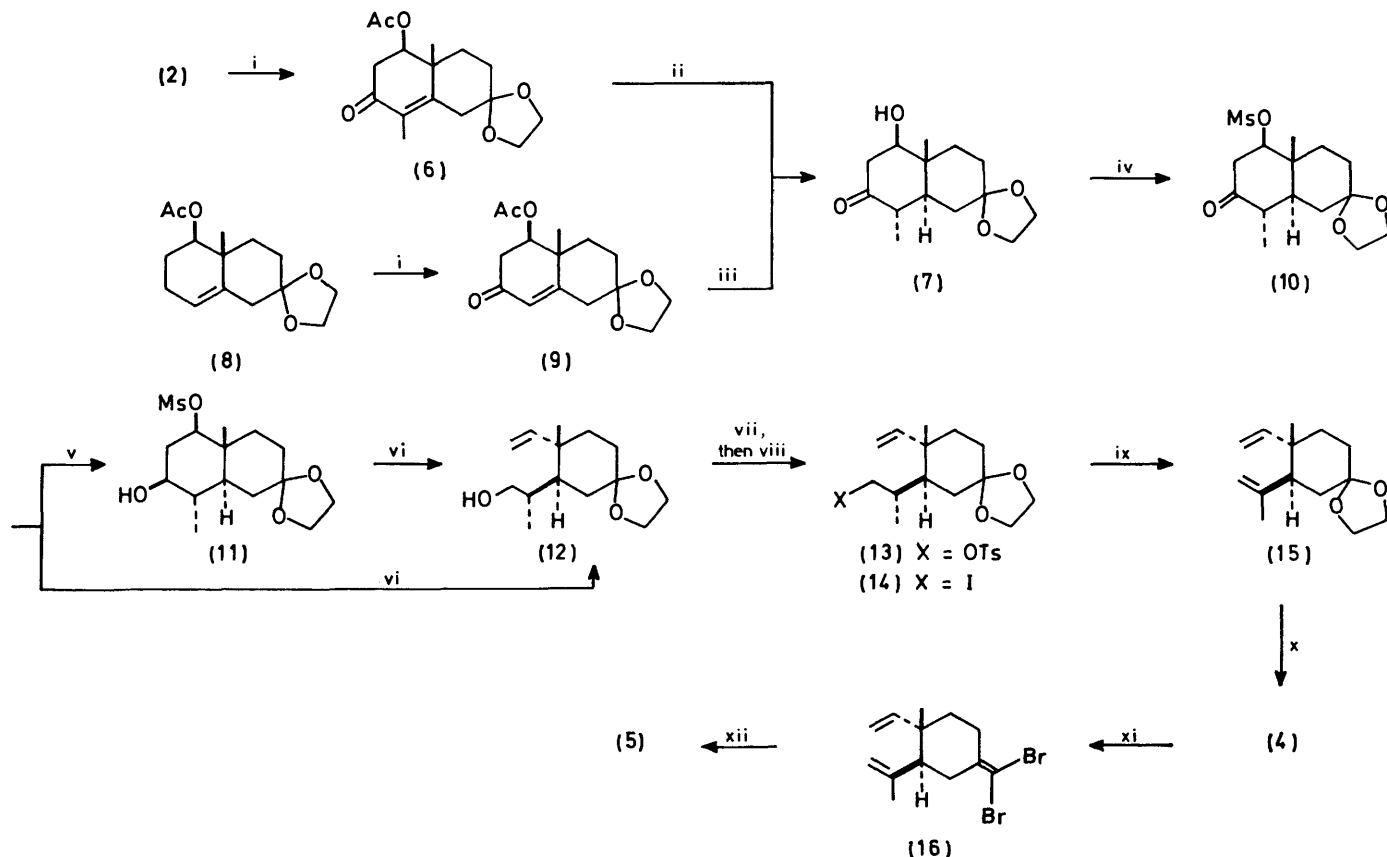
In this paper we describe the peripheral bond fragmentation<sup>2</sup> of the mesyloxy-alcohol (11), obtainable from (2), and the total synthesis of some elemanoids, *i.e.* geijerone<sup>3</sup> (4) and  $\gamma$ -elemene<sup>4</sup> (5), in racemic form.

The hydroxy-decalone (7) was prepared by allylic oxidation of the acetoxy-acetal (2) with Collins' reagent, followed by the reduction by lithium–ammonia of the resultant acetoxy-enone (6), in 82% overall yield (Scheme). More conveniently, compound (7) was also obtained from the acetoxy-acetal<sup>5</sup> (8) by allylic oxidation followed by reductive methylation of the resultant



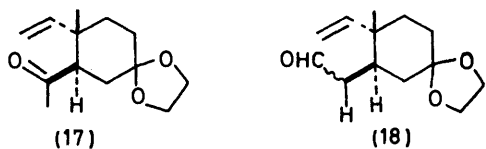
acetoxy-enone (9). The latter route is shorter and gives nearly the same overall yield [ten *vs.* five steps and 42 *vs.* 40% yield from (3)].

The oxo-mesyloxy (10) was prepared by the reaction of



SCHEME 1, CrO<sub>3</sub>·(C<sub>6</sub>H<sub>5</sub>N)<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub>; ii Li–NH<sub>3</sub>; iii, Li–NH<sub>3</sub>–MeI; iv, MeSO<sub>2</sub>Cl–C<sub>6</sub>H<sub>5</sub>N; v, LiAlH<sub>4</sub>–THF (0 °C); vi, LiAlH<sub>4</sub>–(MeOCH<sub>2</sub>)<sub>2</sub>Me (reflux); vii, *p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Cl–C<sub>6</sub>H<sub>5</sub>N; viii, NaI–Me<sub>2</sub>CO; ix, Bu<sup>+</sup>OK–Me<sub>2</sub>SO; x, H<sub>3</sub>O<sup>+</sup>; xi, CBr<sub>4</sub>–Ph<sub>3</sub>P–C<sub>6</sub>H<sub>6</sub>; xii, Me<sub>2</sub>CuLi–Et<sub>2</sub>O

(7) with mesyl chloride and triethylamine in dichloromethane in high yield. On treatment with lithium aluminium hydride in tetrahydrofuran at 0 °C, compound (10) produced the crystalline mesyloxy-alcohol (11) in nearly quantitative yield. The configuration of the newly formed hydroxy group was assigned as equatorial on the basis of the presumed less-hindered-face approach of the reagent, as verified by n.m.r. evidence; overlapped *CHOH* and *CHOMs* signals were cleanly separated on the addition of  $\text{Eu}(\text{dpm})_3$  [molar ratio of (11) to shift reagent, 2 : 1]. Irradiation at  $\delta$  3.50 † (3 H, d, *J* 6 Hz) caused collapse of a one-proton multiplet at  $\delta$  5.08 into a sharp triplet (*J* 11 Hz), indicating the presence of axial



methine systems on both sides of the secondary methyl group. This was further confirmed by irradiation at  $\delta$  5.08, causing collapse of a doublet at  $\delta$  3.50 and a broad multiplet at  $\delta$  8.68 (1 H,  $W_{1/2}$  23 Hz) into a sharp singlet and a simplified multiplet, respectively.

Base-induced fragmentation of (11) with  $\text{Bu}^t\text{OK}$  in *t*-butyl alcohol did not give the desired results. The reaction afforded a mixture of the methyl ketone (17) and the epimeric aldehydes (18) (presumably the initial product). The proportions of the ketone and aldehydes varied according to the work-up procedure; the ketone seemed to be an auto-oxidation product of the aldehydes.<sup>6</sup> Attempted transformation of (17) into the diene acetal (15) with methylenetriphenylphosphorane in dimethyl sulphoxide resulted in recovery of the ketone.

On the other hand, the mesyloxy-alcohol (11) underwent ready fragmentation on refluxing with lithium aluminium hydride in 1,2-dimethoxyethane, giving the olefinic alcohol (12) in nearly quantitative yield. Reductive fragmentation of the oxo-mesyloxy (10) to (12) was also achieved by treatment with lithium aluminium hydride in boiling dimethoxyethane. The olefinic alcohol (12) was then converted into the diene acetal (15) in 66% overall yield through the following conventional sequence: (i) tosylation of (12) in pyridine, (ii) substitution of the tosyloxy group of the product (13) with sodium iodide in acetone, (iii) double bond formation by dehydroiodination of the resultant iodide (14) with  $\text{Bu}^t\text{OK}$  in dimethyl sulphoxide. Deacetalisation of the product (15) with toluene-*p*-sulphonic acid in acetone afforded racemic geijerone (4) in 57% overall yield from (12). Introduction of the isopropylidene group instead of the oxo-function of (4) was performed by reaction with carbon tetrabromide and triphenylphosphine, followed by treatment of the resultant dibromide (16) with lithium dimethylcuprate,<sup>7</sup> giving racemic  $\gamma$ -elemene (5) in 58% overall yield from (15). The spectra (i.r., n.m.r., and

mass) of both synthetic elemenoids were identical with those of the natural products.

#### EXPERIMENTAL

I.r. spectra were taken with a JASCO A-3 spectrophotometer, and n.m.r. spectra with a JEOL C-60-HL spectrometer (60 MHz) for  $\text{CDCl}_3$  solutions, using tetramethylsilane as internal standard. Coupling constants are given in Hz. G.l.c.-mass spectra were recorded on a Shimadzu-LKB gas chromatograph-mass spectrometer fitted with a column (1 m) packed with OV-1 (1%).

**4 $\beta$ -Acetoxy-4,4a,5,6-tetrahydro-1,4a $\beta$ -dimethylnaphthalene-2,7(3H,8H)-dione 7-Ethylene Acetal (6).**—A mixture of the acetoxy-acetal (2), (2.01 g, 139 mmol), Collins' reagent (36.1 g, 139 mmol), and dry dichloromethane (200 ml) was stirred at room temperature for 12 h under nitrogen, and then poured into aqueous sodium chloride. The product was extracted with dichloromethane and the extract was washed with water, aqueous copper sulphate, and brine, and dried. The residual oil obtained on evaporation was passed through a short silica gel column with ether, affording an oil which crystallised. Recrystallisation from dichloromethane-light petroleum (5 : 1) gave the *acetoxy-enone* (6) (1.83 g, 87%), m.p. 122.5–123 °C,  $\nu_{\text{max}}$  (KBr) 1 735, 1 680, 1 630, and 1 150  $\text{cm}^{-1}$ ,  $\delta$  1.28 (3 H, s), 1.3–3.0 (6 H, m), 1.78 (3 H, s), 1.80 (2 H, s, =C-CH<sub>2</sub>), 2.08 (3 H, s, Ac), 4.00 (4 H, s, OCH<sub>2</sub>CH<sub>2</sub>O), and 5.15 (1 H, dd, *J* 8 and 1.5, CO<sub>2</sub>CH) (Found: C, 65.7; H, 7.7. C<sub>16</sub>H<sub>22</sub>O<sub>5</sub> requires C, 65.3; H, 7.5%).

**4 $\beta$ -Hydroxy-4,4a,5,6,8 $\alpha\alpha$ -hexahydro-1 $\alpha$ ,4a $\beta$ -dimethylnaphthalene-2,7(1H,3H)-dione 7-Ethylene Acetal (7) from (6).**—Small pieces of lithium metal (140 mg, 0.02 g atom) were added to liquid ammonia (50 ml), freshly distilled from sodium metal, and the mixture was stirred for a few min under nitrogen. A solution of the acetoxy-enone (6) (492 mg, 1.67 mmol) in dry THF (10 ml) was added and stirring was continued at –60 °C for 30 min. An excess of ammonium chloride was added cautiously and the ammonia was evaporated off with stirring. The residue was diluted with water and extracted with ether. The extract was washed with brine and dried. Evaporation left a viscous oil, which was passed through a short silica gel column with ether-light petroleum (1 : 1) to give the crystalline *hydroxy-decalone* (7) (395 mg, 93%). Recrystallisation from dichloromethane-light petroleum (1 : 3) gave a sample, m.p. 130.5–131.5 °C,  $\nu_{\text{max}}$  (KBr) 3 400 and 1 700  $\text{cm}^{-1}$ ,  $\delta$  0.96 (3 H, d, *J* 8), 1.08 (3 H, s), 1.1–2.5 (10 H, m), 2.7 (1 H, br, s, OH), 3.53 (1 H, m, CH-O), and 3.95 (4 H, s, OCH<sub>2</sub>CH<sub>2</sub>O) (Found: C, 66.1; H, 9.1. C<sub>14</sub>H<sub>22</sub>O<sub>4</sub> requires C, 66.1; H, 8.7%).

**The Hydroxy-decalone (7) from (9).**—Small pieces of lithium metal (84 mg) were added to liquid ammonia (20 ml) and the mixture was stirred at –78 °C for 20 min under nitrogen. A solution of the acetoxy-enone (9) (167 mg, 0.6 mmol) and *t*-butyl alcohol (0.03 ml) in dry THF (2 ml) was added dropwise. After stirring for 30 min, freshly distilled methyl iodide (0.8 ml, 10 equiv.) was added dropwise and stirring was continued at the same temperature for 1 h. Work-up gave a pale yellow oil, which was purified by preparative t.l.c. on silica gel in ether to give the crystalline hydroxy-decalone (7) (90 mg, 51%).

**4 $\beta$ -Acetoxy-4,4a,5,6-tetrahydro-4a $\beta$ -methylnaphthalene-2,7(3H,8H)-dione 7-Ethylene Acetal (9).**—A mixture of the acetoxy-acetal (8) (1.03 g, 3.9 mmol), Collins' reagent (21 g), and dry dichloromethane (200 ml) was stirred at room tem-

† Chemical shift values at 100 MHz.

perature overnight under nitrogen. The product was worked up as described for (6). Filtration of the crude solid through a short silica gel column with ether, followed by recrystallisation from dichloromethane–light petroleum (10 : 1), afforded the *acetoxy-enone* (9) (983 mg, 87%) as crystals, m.p. 113–114 °C,  $\nu_{\max}$  (KBr) 1 723, 1 672, 1 615, and 1 240  $\text{cm}^{-1}$ ,  $\delta$  1.39 (3 H, s), 1.4–2.5 (6 H, m), 1.78 (2 H, br, s, =C–CH<sub>2</sub>), 2.08 (3 H, s, Ac), 3.95 (4 H, s, OCH<sub>2</sub>CH<sub>2</sub>O), 5.1 (1 H, dd, *J* 13.5 and 7, CO<sub>2</sub>CH), and 5.74 (1 H, br, s, =CH) (Found: C, 64.0; H, 7.4. C<sub>15</sub>H<sub>20</sub>O<sub>5</sub> requires C, 64.3; H, 7.2%).

4 $\beta$ -Methylsulphonyloxy-4,4a,5,6,8,8a $\alpha$ -hexahydro-1 $\alpha$ ,4a $\beta$ -dimethylnaphthalene-2,7(1H,3H)-dione 7-Ethylene Acetal (10).—Mesityl chloride (286 mg, 2.84 mmol) was added to a solution of the hydroxy-decalone (7) (480 mg, 1.89 mmol) and triethylamine (286 mg, 2.85 mmol) in dichloromethane (10 ml) at –10 °C under nitrogen. The mixture was stirred at the same temperature for 30 min and poured into ice–water. The product was extracted with dichloromethane and the extract was washed with water and brine, and dried. The oily residue obtained on evaporation *in vacuo* crystallised. Recrystallisation from ether–light petroleum (8 : 1) gave the *oxo-mesyate* (10) (573 mg, 91%), m.p. 75–77 °C,  $\nu_{\max}$  (KBr) 1 710  $\text{cm}^{-1}$ ,  $\delta$  0.95 (3 H, d, *J* 6), 1.15 (3 H, s), 1.2–3.0 (8 H, m), 3.02 (3 H, s, Ms), 3.95 (4 H, s, OCH<sub>2</sub>CH<sub>2</sub>O), and 4.45 (1 H, dd, *J* 10 and 6, SO<sub>3</sub>CH) (Found: C, 54.2; H, 7.5. C<sub>15</sub>H<sub>24</sub>O<sub>6</sub>S requires C, 54.2; H, 7.3%).

2 $\beta$ -Hydroxy-4 $\beta$ -methylsulphonyloxy-2,3,4,4a,5,6,8,8a $\alpha$ -octahydro-1 $\alpha$ ,4a $\beta$ -dimethylnaphthalen-7(1H)-one Ethylene Acetal (11).—A suspension of the *oxo-mesyate* (10) (207 mg, 0.62 mmol), lithium aluminium hydride (7 mg, 0.19 mmol), and dry tetrahydrofuran (5 ml) was stirred at 0 °C for 2 h under nitrogen. The excess of reagent was decomposed with wet ether. Work-up gave an oil (201 mg, 96%), which crystallised. Recrystallisation from ether–light petroleum (4 : 1) gave a *sample*, m.p. 144–145 °C,  $\nu_{\max}$  (KBr) 3 550, 1 150, 1 020, and 910  $\text{cm}^{-1}$ ,  $\delta$  0.95 (6 H, overlapped two methyls), 1.1–2.9 (11 H, m), 3.0 (3 H, s, Ms), 3.75 (1 H, m, CH–O), 3.95 (4 H, s, OCH<sub>2</sub>CH<sub>2</sub>O), and 4.35 (1 H, dd, *J* 12 and 5, SO<sub>3</sub>CH) (Found: C, 54.1; H, 8.0; S, 9.5. C<sub>15</sub>H<sub>26</sub>O<sub>4</sub>S requires C, 53.9; H, 7.8; S, 9.6%).

3 $\beta$ -(2-Hydroxy-1-methylethyl)-4 $\beta$ -methyl-4 $\alpha$ -vinylcyclohexanone Ethylene Acetal (12).—A suspension of the mesyloxy-alcohol (11) (156 mg, 0.47 mmol), lithium aluminium hydride (36 mg, 0.93 mmol), and dry dimethoxyethane (8 ml) was gently refluxed for 8 h under nitrogen. The excess of reagent was decomposed with wet ether. The usual work-up gave the olefinic alcohol (12) (112 mg, 99%) as an almost homogeneous oil (t.l.c. and g.l.c.). Further purification was performed by preparative t.l.c. on silica gel with ether–light petroleum (2 : 1),  $\nu_{\max}$  (neat) 3 400, 3 070w, 1 638, 1 100, 1 020, 950, and 910  $\text{cm}^{-1}$ ,  $\delta$  0.78 (3 H, d, *J* 6.5), 1.04 (3 H, s), 1.0–2.1 (8 H, m), 2.9 (1 H, br, s, OH), 3.30 (2 H, d, *J* 6.5, CH<sub>2</sub>OH), 3.95 (4 H, s, OCH<sub>2</sub>CH<sub>2</sub>O), 4.92 (1 H, dd, *J* 17 and 2, *cis*-CH=CHH), 5.05 (1 H, dd, *J* 9 and 2, *trans*-CH=CHH), and 5.75 (1 H, dd, *J* 17 and 9, CH=CH<sub>2</sub>). The 3,5-dinitrobenzoate was obtained as an oil (Found: C, 57.9; H, 6.2; N, 6.2. C<sub>21</sub>H<sub>26</sub>N<sub>2</sub>O<sub>8</sub> requires C, 58.1; H, 6.0; N, 6.5%).

The Olefinic Alcohol (12) by Reductive Fragmentation of (10).—A suspension of the *oxo-mesyate* (10) (156 mg, 0.47 mmol), lithium aluminium hydride (36 mg, 0.93 mmol, 4 equiv.), and dry dimethoxyethane (8 ml) was gently refluxed under nitrogen. Work-up gave an oil, which was purified by preparative t.l.c. on silica gel with ether–light

petroleum (2 : 1). The olefinic alcohol (12) (112 mg, 99%) obtained was identified by spectral comparison.

3 $\beta$ -(2-Iodo-1-methylethyl)-4 $\beta$ -methyl-4 $\alpha$ -vinylcyclohexanone Ethylene Acetal (14).—Toluene-*p*-sulphonyl chloride (134 mg, 0.70 mmol, 1.5 equiv.) was added to a solution of (12) (112 mg, 0.47 mmol) in dry pyridine (2 ml) and the mixture was stirred for 6 h at room temperature under nitrogen. The usual work-up gave the tosylate (13) (179 mg, 97%) as an oil, which crystallised (m.p. 58–60 °C), but the crystals did not give satisfactory analytical data;  $\nu_{\max}$  (KBr) 3 060w, 1 640w, 1 600, 1 190, 1 180, 1 100, 970, and 920  $\text{cm}^{-1}$ ,  $\delta$  0.75 (3 H, d, *J* 6.5), 0.98 (3 H, s), 1.0–2.4 (8 H, m), 2.43 (3 H, s), 3.75 (2 H, d, *J* 6, CH<sub>2</sub>–OTs), 3.93 (4 H, s, OCH<sub>2</sub>CH<sub>2</sub>O), 4.83 (1 H, dd, *J* 18 and 2, *cis*-CH=CHH), 4.90 (1 H, dd, *J* 8.5 and 2, *trans*-CH=CHH), and 5.57 (1 H, dd, *J* 18 and 8.5, CH=CH<sub>2</sub>). A suspension of the tosylate (13) (179 mg) and sodium iodide (203 mg) in dry acetone (10 ml) was gently refluxed overnight under nitrogen. Work-up gave the iodide (14) (136 mg, 86%) as an oil,  $\nu_{\max}$  (neat) 3 070w, 1 640w, 1 595w, 1 100, 950, and 905  $\text{cm}^{-1}$ ,  $\delta$  0.85 (3 H, d, *J* 7), 1.0 (3 H, s), 1.1–2.5 (8 H, m), 3.05 (2 H, d, *J* 6, CH<sub>2</sub>I), 3.90 (4 H, s, OCH<sub>2</sub>CH<sub>2</sub>O), 4.8–5.1 (2 H, m, CH=CH<sub>2</sub>), and 5.75 (1 H, dd, *J* 18.5 and 9, CH=CH<sub>2</sub>). The iodide (14) was unstable and gradually became coloured in air at room temperature. It was used without purification for the next reaction.

3 $\beta$ -Isopropenyl-4 $\beta$ -methyl-4 $\alpha$ -vinylcyclohexanone Ethylene Acetal (15).—A mixture of the iodide (14) (136 mg, 0.39 mmol), potassium *t*-butoxide (86 mg, 0.77 mmol), dimethyl sulphoxide (0.8 ml), and benzene (0.8 ml) was stirred at room temperature for 3 h under nitrogen, poured into water, and then extracted with ether. The extract was washed with water and brine, and dried. Removal of the solvent left a pale yellow oil, which was purified by preparative t.l.c. on silica gel with ether–light petroleum (2 : 1) giving the diene acetal (15) (67 mg, 77%) as an oil,  $\nu_{\max}$  (neat) 3 060w, 1 640w, 1 100, 1 040, 1 010, 960, 950, 910, and 890  $\text{cm}^{-1}$ ,  $\delta$  1.1 (3 H, s), 1.0–2.5 (7 H, m), 1.7 (3 H, br, s), 3.90 (4 H, s, OCH<sub>2</sub>CH<sub>2</sub>O), 4.53–5.15 (4 H, m, 2  $\times$  =CH<sub>2</sub>), and 5.80 (1 H, dd, *J* 17 and 10, CH=CH<sub>2</sub>). The oil did not give satisfactory analytical data.

( $\pm$ )-Geijerone (4).—A solution of (15) (67 mg) and a catalytic amount of toluene-*p*-sulphonic acid in acetone (2 ml) was stirred at room temperature for 20 min, poured into water, and extracted with ether. The extract was washed with water and brine, and dried. An oil (64 mg) obtained on evaporation was purified by preparative t.l.c. on silica gel with light petroleum to give racemic geijerone (4) (58 mg, 88%) as an oil, whose spectral data (mass, i.r., and n.m.r.) were identical with those of natural geijerone.

( $\pm$ )- $\gamma$ -Elemene (5).—A mixture of racemic geijerone (4) (58 mg, 0.3 mmol), triphenylphosphine (401 mg, 1.53 mmol), carbon tetrabromide (199 mg, 0.60 mmol), and dry benzene (35 ml) was stirred overnight at reflux under nitrogen. After cooling, the mixture was filtered, and the filtrate was evaporated to dryness. The residue was triturated with light petroleum and filtered, and the filtrate was evaporated *in vacuo* to give an oil, which was purified by preparative t.l.c. on silica gel with light petroleum affording the dibromide (16) (70 mg, 64%) as an oil,  $\delta$  1.03 (3 H, s), 1.70 (3 H, s), 4.6–5.8 (5 H, m, CH=CH<sub>2</sub> and =CH<sub>2</sub>). The dibromide (70 mg, 0.2 mmol) in dry ether (7 ml) was added to a solution of lithium dimethylcuprate, prepared from copper(I) iodide (762 mg, 4.0 mmol) and ethereal 1.7-methyl-lithium (4.3 ml). After stirring at room tempera-

ture for 12 h, under nitrogen, methyl iodide (2 ml) was added. The mixture was stirred for an additional 1 h, poured into saturated aqueous ammonium chloride, and then extracted with ether. Evaporation gave an oil, which was purified by preparative t.l.c. on silica gel with light petroleum, giving racemic  $\gamma$ -elemene (5) (39 mg, 90%) as an oil. Spectral data (i.r., n.m.r.) were identical with data reported.<sup>5c</sup>

**3 $\beta$ -Acetyl-4 $\beta$ -methyl-4 $\alpha$ -vinylcyclohexanone Ethylene Acetal (17).**—A mixture of the mesyloxy-alcohol (11) (34 mg, 0.1 mmol), potassium t-butoxide (40 mg, 0.5 mmol), and t-butyl alcohol (1 ml) was stirred at room temperature for 1 h, under nitrogen. N.m.r. and g.l.c.–mass spectral analyses revealed that the product was a diastereoisomeric mixture of the aldehydes (18) [ $\delta$  9.45 (d, *J* 8.5, CHO) and 9.50 (d, *J* 8.5, CHO),  $M^+$  238] and the methyl ketone (17) in the ratio *ca.* 1.5 : 1.0. The mixture was diluted with water and extracted with ether. The extract was washed, dried, and evaporated to leave an oil (19 mg); n.m.r. and t.l.c. showed that a trace of the aldehydes (18) remained. The methyl ketone (17) was obtained as an oil by filtering the above oil through a short silica gel column with ether–light petroleum (1 : 2);  $\nu_{\max}$  3 060w, 1 700, 1 100, 940, and 910

cm<sup>-1</sup>,  $\delta$  1.0–2.0 (8 H, m), 1.15 (3 H, s), 2.15 (3 H, s), 3.90 (4 H, s, OCH<sub>2</sub>CH<sub>2</sub>O), 5.0 and 5.7 (2 H and 1 H, m, each, CH=CH<sub>2</sub>) (Found: C, 69.8; H, 8.6. C<sub>13</sub>H<sub>20</sub>O<sub>3</sub> requires C, 69.6; H, 8.9%).

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