(100) C_5H_8OI, 201,1633 (12), 111.0478 (19) $C_6H_7O_2$, 107.0828 (16), 93.0700 (17), 81.0693 (21), 79.0538 (20).

Isopropyl (2*E*,4*E*)-13-[^{125}I]Iodo-11-hydroxy-3,7,11-trimethyl-2,4,12-tridecatrienoate (10a). In a 5-mL test tube was added 0.5 mL of a 5% sodium acetate/acetic acid buffer solution (pH 4.54) containing sodium [^{125}I]iodide (5.0 mCi). To this was added 3 mg (0.005 mmol) of stannane **9** in 0.5 mL of THF, followed by 0.5 mL of a 2:1 hydrogen peroxide/acetic acid solution. The reaction was stirred for 24 h at room temperature and extracted with four 1.5-mL portions of EtOAc. The organics were washed (5 mL of 5% aqueous $NaHSO_3$) and chromatographed on activity III neutral alumina in a disposable pipet column to give 2.2 mCi of the [^{125}I]IVMA (**10a**; 44% radiochemical yield). Use of silica gel for this purification resulted in decomposition of IVMA to a less polar byproduct. Autoradiography of TLC plates indicated that the radioactivity comigrated with radioinert IVMA (**10**).

Isopropyl (2*E*,4*E*)-13-[^{125}I]Iodo-11-methoxy-3,7,11-trimethyl-2,4,12-tridecatrienoate (11a). To 0.5 g of 10% ferric chloride on silica gel (prepared in methanol) was added 0.6 mCi of **10a** in 1.5 mL of 1:9 EtOAc/hexane. The slurry was stirred vigorously for 5 min, filtered through glass wool, and purified with activity III alumina to give 0.4 mCi of the [^{125}I]IVM (**11a**; 66% radiochemical yield). Autoradiography of TLC plates indicated that the radioactivity comigrated with radioinert IVM (**11**).

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Dilithiated Vicinal Diester Route to Sesquiterpenes. Total Synthesis of (±)-Vetiselinene and the Formal Synthesis of Other Eudesmane Sesquiterpenes

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Since our original disclosures that the dianions of vicinal diesters can be readily prepared[1] and that these dianions undergo classical alkylation and acylation reactions[2] and can be annelated,[2-4] we[2-7] and others[8-12] explored the application of these reactions in the synthesis of natural and nonnatural products.[13] We have investigated the annelation of the dilithiated dimethyl cyclohex-4-ene-1,2-dioate to produce intermediates for the preparation of the eudesmane sesquiterpenes[5] and now report the total synthesis of (±)-vetiselinene (**19**)[14] and the formal syntheses of a number of other sesquiterpenes by this route. Treatment of dimethyl cyclohex-4-enedioate (**1a**) with LDA in THF gave a solution of the dianion **2a**, which on addition of ethyl 4-bromobutanoate (**3**) gave, over 5 days at −78 °C, the desired bicyclo[4.4.0]decanone diester derivative **4a** in 40% yield.[5] The corresponding diethyl **1b** and di-*tert*-butyl **1c** diesters gave higher yields of annelated product, but purification and saponification of the diethyl derivative proved more difficult. Treatment of **4a** with NaCl in Me_2SO at 160 °C[15] gave the keto ester **5** as a mixture of cis and trans isomers. Ketalization of **5** with 1,2-ethanediol gave **6** in poorer yield than expected but exclusively as the trans isomer. Reduction of **6** with $LiAlH_4$ gave the desired alcohol **7** in 81% yield, the spectral properties again only indicating the presence of the trans isomer. Selenation of **7** with *N*-(phenylseleno)phthalimide[16] gave the seleno ether **8**, the spectral properties again indicating only the presence of the trans isomer. Reduction of **8** with Raney nickel gave the desired alkene **9** in 76% yield, contaminated by 8% of a compound tentatively identified as the corresponding alkane **10**. The spectral properties of **9** were in accord with those of Torii and co-workers,[17] and the chemical shift of the angular methyl group substantiates the trans ring junction.[18] Treatment of **9** with *m*-chloroperoxybenzoic acid gave the desired epoxide **11** of the stereochemistry shown. Reduction of **11** with lithium in a mixture of liquid NH_3 and dimethoxyethane at low temperature gave the alcohol **12**, which was not purified but was oxidized directly to the ketone **13** with pyridinium chlorochromate in 61% overall yield from **11**. The spectral properties of compounds **11**–**13** were in accord with those reported by Torii and co-workers.[17] The ketone **13** was then treated with isopropylmagnesium chloride in THF at −50 °C, and the resulting alcohol **14** was not purified but was dehydrated with H_2SO_4 to give a mixture of ketones in 42% yield. This mixture was separated by HPLC to give **15**, **16**, **17**, and **18** in the approximate proportions 6:2:1:1. The ^{1}H NMR spectrum of **15** shows signals at δ 5.39 (br s, 1 H), 2.4–1.6 (m, 12 H), 0.94 (d, 6 H, J = 6.8 Hz), and 0.71 (s, 3 H), and the decoupled ^{13}C NMR spectrum had 14 signals. Ketone **16** has signals in the ^{1}H NMR spectrum at δ 5.34 (br s, 1 H), 2.60–1.38 (m, 12 H), 1.05 (s, 3 H), and 0.95 (d, 6 H, J = 6.8 Hz). The chemical shifts of the angular methyl groups are consistent with the assigned stereochemistries. Treatment of **15** with $Ph_3P{=}CH_2$ in Me_2SO gave (±)-vetiselinene (**19**) in 75% yield. The ^{1}H NMR spectrum shows signals at δ 5.39 (br s, 1 H), 4.75 (br s, 1 H), 4.52 (br s, 1 H), 1.20–2.40 (m, 12 H), 0.96 (d, 6 H, J = 6.6 Hz), and 0.65 (s, 3 H), and the decoupled ^{13}C NMR spectrum showed 15 signals. The carbonyl absorption present in the

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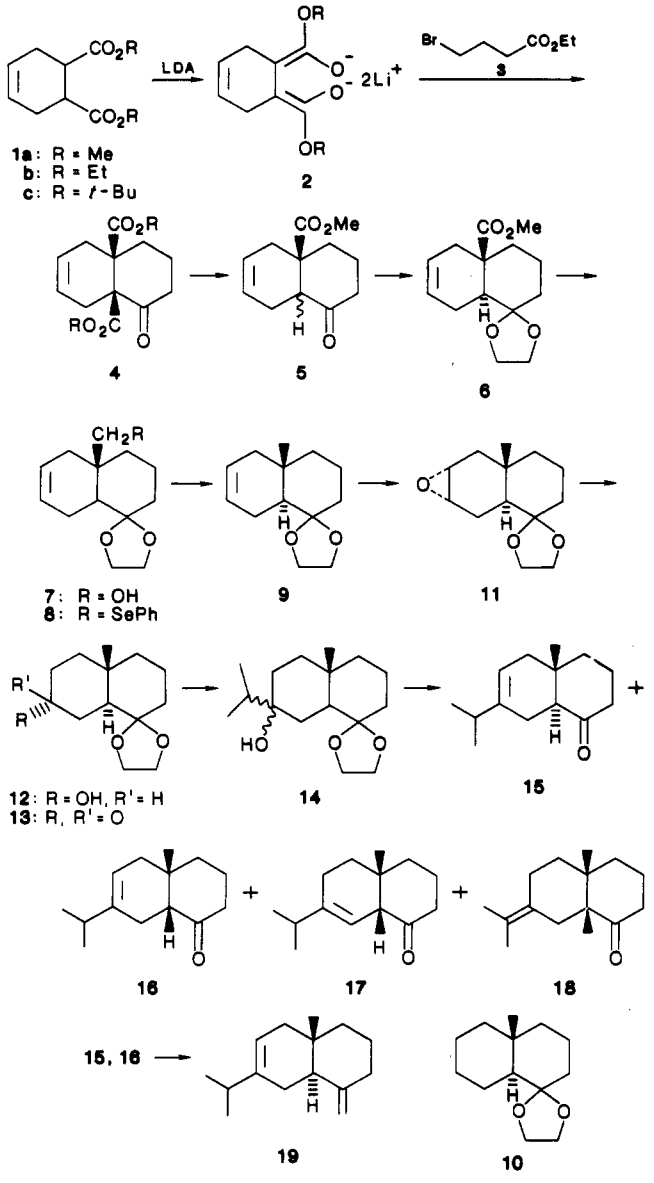
Scheme I



precursor was absent, and a new absorption band had appeared at 1641 cm^{-1}. These data are all consistent with those published for **19**.[14] Treatment of ketone **16** with the same reagent also gave **19**, in this case in 62% yield. The isomerization to the trans stereochemistry has precedent with this type of reagent[19] (Scheme I).

Torii and co-workers[17] have converted **9** into (±)-β-costol, arctiol, and eudesma-4(14),7(11)-dien-8-one, and this route provides a formal synthesis of these compounds. The ketone **15** would also seem a suitable alternative to Marshall's ketone,[20] a key intermediate in the synthesis of a wide range of eudesmane sesquiterpenes.

Experimental Section

^1H NMR spectra were recorded on a Jeol PMX60si or Varian XL-200 spectrometer in $CDCl_3$ as solvent with Me_4Si as internal standard. ^{13}C NMR spectra were recorded on a Varian XL-200 spectrometer in $CDCl_3$ as solvent with Me_4Si as internal standard. Mass spectra were obtained on a VG-7000G spectrometer. IR spectra were recorded on a Perkin-Elmer 983 spectrometer, and only significant bands are reported. Melting points were taken on a Kofler Hot-stage melting point apparatus and are uncorrected. Unless stated otherwise, reactions were worked up by addition of water and extraction with ether, the ethereal extract being washed with aqueous $NaHCO_3$ solution and water and dried. Solvents were dried by standard methods, and those used for generating anions were flushed with N_2 or Ar.

Lithiation of Diesters. A solution of the diester (0.1 mol) in THF (100 mL) was added dropwise to a stirred solution of lithium diisopropylamide (0.2 mol) [prepared by addition of *n*-butyllithium (10.5 M, 0.2 mol) to diisopropylamine (0.21 mol)] in THF (110 mL) containing HMPA (50 mL) at −75 °C under N_2 or Ar. The deep red solution was stirred at this temperature for a further 30 min after completion of addition.

Annelation of the Dilithiated Diesters. A solution of ethyl 4-bromobutanoate (0.1 mol) in THF (100 mL) was added over 18 h by means of a syringe pump to the solution of dilithiated diester described above at −75 °C under N_2 or Ar. Stirring was continued for a further 5 days, and the reaction mixture was treated with aqueous acetic acid (33%, 150 mL) and subjected to aqueous workup. The annelated diesters were isolated as oils that, in the case of **4a**, crystallized on addition of pentane–ether (1:1) as white crystals, recrystallized from CCl_4; ca. 0.04 mol; mp 103–105 °C.[6]

Decarbomethoxylation of 4a. The keto diester **4a** (16.0 g, 60 mmol) in $(CH_3)_2SO$ (20 mL) was added to a N_2-preflushed flask containing a mixture of NaCl (3.84 g, 65.6 mmol), H_2O (3.5 mL), and $(CH_3)_2SO$ (40 mL). The mixture was stirred and heated to 150 °C under a N_2 flow, monitoring CO_2 evolution by a $Ba(OH)_2$ trap. After aqueous workup, an oil was obtained that, if excessively colored, was decolorized with activated charcoal. The oil was used without further purification, but a sample was purified by spinning-plate chromatography (Si gel, EtOAc–hexane) to give *cis*-**5** (mp 71–73 °C) and *trans*-**5** (mp 76–78 °C) with spectral properties in accord with those reported.[21]

Preparation of Ketal 6. The keto ester **5** (8.43 g, 40.5 mmol), 1,2-ethanediol (21.34 g, 0.34 mol), *p*-toluenesulfonic acid (0.61 g, 3.2 mmol), and benzene (100 mL) were heated to reflux for 48 h, water being removed by a Dean–Stark collector. The cooled mixture was extracted with aqueous $NaHCO_3$ and the aqueous layer extracted with EtOAc and CH_2Cl_2 and dried. Distillation [130 °C (0.1 mm) gave a colorless oil [5.8 g (57%)], identified as **6**: Ms, *m/e* 252 (M^+), 193, 99 (100%); ^1H NMR δ 5.39 (br s, 2 H), 3.68 (br d, 4 H, *J* = 3.8 Hz), 3.44 (s, 3 H), 2.4–1.1 (m, 11 H); ^{13}C NMR δ 124.5, 123.8, 110.9, 64.6, 63.9, 51.6, 45.1, 39.4, 33.4, 31.2, 29.2, 23.6, 19.8; IR 3029, 1722, 1428 cm^{-1}.

Reduction of 6. The ketal **6** (5.45 g, 22.0 mmol) in THF (10 mL) was added to a stirred slurry of $LiAlH_4$ (1.67 g, 44 mmole in THF (50 mL) at 0 °C under N_2. Stirring was continued for 10 min, and the mixture was then heated to reflux for 24 h. After it was quenched with saturated aqueous NH_4Cl, the mixture was worked up to give an oil. Flash chromatography (SiO_2, Et_2O–pentane, 1:1) gave **7** as a white solid: 4.01 g (81%); mp 41–44 °C; MS, *m/e* 224.1422 ($C_{13}H_{20}O_3$ requires 224.1411), 224 (M^+), 193, 99 (100%); ^1H NMR δ 5.39 (AB m, 2 H), 3.78 (br s, 4 H), 3.54, 3.42 (AB d, 2 H, *J* = 12 Hz), 2.50–1.28 (m, 11 H); ^{13}C NMR δ 125.0, 124.5, 111.6, 69.4, 65.0, 64.3, 39.8, 37.9, 33.2, 30.9, 30.6, 22.75, 18.9; IR 3670, 3088, 3009, 1659, 1035 cm^{-1}. Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.98. Found: C, 69.58; H, 8.70.

Preparation of the Phenylseleno Ether 8.[16] A solution of the alcohol **7** (0.10 g, 0.45 mmol) in THF (5 mL) was added to a solution of *N*-(phenylseleno)phthalimide (0.27 g, 0.9 mmol) and tri-*n*-butylphosphine (0.18 g, 0.9 mmol) in THF (5 mL), which had previously been stirred for 20 min under N_2 at 20 °C. The resulting yellow solution was stirred for a further 20 min at 20 °C and then heated to reflux for 3 h. The solution was cooled to 20 °C and syringed into rapidly stirred petroleum ether 40–60 (50 mL). Stirring was continued for a further 10 min, and the resulting white precipitate was removed by filtration. The residue was washed with petroleum ether 40–60 (2 × 10 mL). The combined petroleum ether layers were washed with 2 M NaOH solution (2 × 20 mL) and water (20 mL) and dried ($MgSO_4$). Removal of the solvent gave a yellow oil that was flash chromato-

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graphed (SiO_2, petroleum ether 40–60, and then 20% EtOAc–petroleum ether) to give **8**: 0.12 g (80%); colorless oil; MS *m/e* 364.0939 ($C_{19}H_{24}O_5{}^{80}Se$ requires 364.0941), 364 (M^+); ^1H NMR δ 7.52 (m, 2 H), 7.24 (m, 3 H), 5.56 (AB m, 2 H), 3.91 (s, 4 H), 3.17 (AB m, 2 H), 2.54–1.25 (m, 11 H); ^{13}C NMR δ 132.6, 131.8, 128.9, 126.5, 124.9, 124.8, 111.2, 65.3, 64.2, 43.3, 42.4, 37.5, 34.8, 34.2, 32.1, 22.3, 19.0; IR 3020 cm^{-1}.

Reduction of the Phenylseleno Ether 8. Activated Raney nickel (15.90 g, 5 wet weight equiv) was added to a solution of **8** (3.18 g, 8.76 mmol) in absolute ethanol (50 mL), and the vigorously stirred mixture was then heated to reflux for 45 min. The hot solution was filtered, the residue was washed with hot absolute ethanol (5 × 50 mL), the filtrates were combined, and the solvent was removed to give an oil. Flash chromatography (SiO_2, 15% CH_2Cl_2–petroleum ether 40–60) gave **9**: colorless oil; 1.53 g (76%); ^1H NMR δ 5.57 (AB m, 2 H), 3.90 (s, 4 H), 2.46–1.00 (m, 11 H), 1.00 (s, 3 H); ^{13}C NMR δ 125.5, 124.4, 65.4, 64.0, 45.6, 38.3, 34.8, 33.65, 33.0, 29.6, 19.3. A second fraction was isolated and identified as **10**: colorless oil; 0.15 g (8%); ^1H NMR δ 3.72 (s, 4 H), 1.9–0.6 (m, 15 H), 0.92 (s, 3 H).

Epoxidation of 9. Alkene **9** (0.15 g, 0.72 mmol) was treated with *m*-chloroperoxybenzoic acid (0.22 g, 1.08 mmol) as described by Torii[17] to give **11**, 0.10 g (62%).

Reduction of 11. Epoxide **11** (0.35 g, 1.56 mmol) was reduced with lithium (0.28 g, 39.3 mmol) in liquid NH_3 as described by Torii[17] to give crude **12** [0.33 g (94%)], which was used without further purification.

Oxidation of 12. The crude alcohol **12** (0.33 g, 1.46 mmol) was oxidized with pyridinium chlorochromate as described by Torii[17] to give the ketone **13**, 0.22 g (66%).

Preparation of Ketones 15 and 16. Isopropylmagnesium chloride (2.0 M in Et_2O, 1.25 mL, 2.5 mmol) was added to a stirred solution of ketone **13** (0.22 g, 1 mmol) in THF (5 mL) at −50 °C. Stirring was continued for a 3 h, and aqueous acetic acid (30%, 1 mL) was then added to the yellow solution. The mixture was then worked up to give a oil, which was subjected to the same procedure twice more. The resulting crude product was dissolved in hexane (10 mL), sulfuric acid (50%, 10 mL) was added, and the mixture was stirred overnight at room temperature. Workup gave a colorless oil, purified by flash chromatography to give an oil, 0.9 g. HPLC (SiO_2, 5% EtOAc–pentane) of this oil gave the following:

15: 38.8 mg (18%); MS, *m/e* 206.1681 ($C_{14}H_{22}O$ requires 206.1670), 206 (M^+), 191, 163 (100%); ^1H NMR, see discussion; ^{13}C NMR δ 150.5, 141.5, 116.9, 106.1, 44.9, 42.4, 41.9, 37.2, 35.0, 34.6, 25.4, 23.7, 21.5, 21.1, 16.9; IR 1705 cm^{-1}.

16: 12.5 mg (6%); MS, *m/e* 206.1675 ($C_{14}H_{22}O$ requires 206.1670), 206 (M^+), 191, 163 (100%); ^1H NMR δ 5.34 (br s, 1 H), 2.60–1.38 (m, 13 H), 1.05 (s, 3 H), 0.95 (d, 6 H, J = 6.8 Hz); IR 1718 cm^{-1}.

17: 8.4 mg (4%); MS, *m/e* 206 (M^+), 191, 163, 131 (100%); ^1H NMR δ 5.05 (br s, 1 H), 2.42–1.46 (m, 13 H), 1.05 (s, 3 H), 0.94 (d, 6 H, J = 6.8 Hz); IR 1705 cm^{-1}.

18: 6.6 mg (3%); MS, *m/e* 206 (M^+), 191, 163, 124, 108 (100%); ^1H NMR δ 2.90–1.20 (m, 11 H), 1.70 (s, 3 H), 1.66 (s, 3 H), 0.66 (s, 3 H); IR 1708 cm^{-1}.

Preparation of (±)-Vetiselinene. Dry triphenylphosphonium bromide (0.375 g, 0.01 mmol) was added to a stirred solution prepared by heating a mixture of NaH (0.036 g, 1.5 mmol) and $(CH_3)_2SO$ (2 mL) at 75 °C until H_2 evolution ceased. The resulting bright yellow solution was stirred at room temperature for 10 min and then added to a solution of ketone **15** (40 mg, 0.19 mmol) in $(CH_3)_2SO$ (1.5 mL) and the mixture stirred for 16 h under N_2 at 55 °C. Workup gave a yellow solid that was purified by flash chromatography (SiO_2, pentane) to give **19**: 29.1 mg (75%); MS, *m/e* 204.1879 ($C_{15}H_{24}$ requires 204.3585), 204 (M^+), 189, 176, 161, 93 (100%); ^1H NMR 5.39 (br s, 1 H), 4.75 (br s, 1 H), 4.52 (br s, 1 H), 2.40–1.20 (m, 12 H), 0.96 (d, 6 H, J = 6.6 Hz), 0.65 (s, 3 H); ^{13}C NMR δ 150.5, 141.5, 116.9, 106.1, 44.9, 42.4, 41.9, 37.2, 35.0, 34.6, 25.4, 23.7, 21.5, 21.1, 16.9; IR 3079, 1641, 1374, 884 cm^{-1}.

Treatment of ketone **16** (12.5 mg, 0.06 mmol) under the same conditions gave **19** (7.6 mg, 62%), in all observed respects identical with that above.

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A Selective Method for Deuterium Exchange in Hydroaromatic Compounds

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We recently noticed that the deuterium atoms that were introduced into the 5-, 6-, 7-, and 8-positions of 1-naphthalenecarboxylic acid during the initial rapid, palladium-catalyzed reduction reaction in acetic acid under a dideuterium atmosphere were selectively exchanged from the 5- and 8-positions in a slower second reaction. In as much as the more conventional procedure for benzylic hydrogen atom exchange employing the dimsyl-d_5 anion in dimethyl-d_6 sulfoxide[1] often requires long reaction times and produces noxious mixtures, we examined the scope and selectivity of the catalytic reaction for the exchange of the benzylic hydrogen atoms. The results of reactions carried out with several hydroaromatic compounds using dideuterium and palladium on carbon in acetic acid-*d* at 50–85 °C are summarized in Table I.

The deuteriation of the substrates listed in Table I with the palladium catalyst gave products that were selectively deuteriated in the benzylic positions. The exchange rates for bulky molecules such as triphenylmethane were noticeably slower than the exchange rates of simple arylmethyl groups. In general, more than 90% deuterium was incorporated in one reaction, and the yields ranged from 70 to 95% with the principal losses realized during distillations and recrystallizations.

The location of deuterium in the products was determined by both ^1H and ^2H NMR spectroscopies. The observations for 1,3-diphenylpropane are typical of the results obtained in this study (eq 1). Comparison of the relative

$$C_6H_5CH_2CH_2CH_2C_6H_5 \xrightarrow[\text{Pd, 55 °C, 24 h}]{D_2,\ DOAc} C_6H_5CD_2CH_2CD_2C_6H_5 \quad (1)$$

signal strengths shown in the ^1H NMR spectra (Figure 1, spectra A and B) indicates that about 90% of the hydrogen atoms in the 1- and 3-positions have been exchanged. Even more significant, the ^2H NMR spectrum (Figure 1, spectrum C) indicates that the exchange reaction proceeded with very high selectivity with virtually no incorporation of deuterium atoms at the other aromatic or aliphatic positions in the molecule. The same high selectivity was observed in reactions with toluene. Thus, high levels of enrichment and rather high isotopic purities can be realized.

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