methanol (1:4) and placed in an 8 × 0.375 in. Pyrex tube. The sample was handled as outlined above; after 100 hr of irradiation, the ^{1}H NMR spectrum showed no change.

Nortricyclyl chloride (200 mg, 1.6 mmol) in 5.0 ml of chlorobenzene treated similarly showed no change in the ^{1}H NMR spectrum, even after 75 hr of irradiation.

Irradiation of *exo*-Dehydronorbornyl Chloride (5) in Chlorobenzene–Methanol. *exo*-Dehydronorbornyl chloride (250 mg, 1.94 mmol) was dissolved in 5.0 ml of chlorobenzene–methanol (1:4) solution and the sample was treated as outlined for nortricyclyl chloride. After 75 hr of irradiation, ^{1}H NMR analysis indicated that the product was composed of 20% of **5** and 80% of saturated compounds, of which at least 80% was dimeric or polymeric material. No absorption corresponding to –OMe could be detected.

Irradiation of *exo*-Dehydronorbornyl Chloride (5) in Chlorobenzene. To two Pyrex tubes were added, respectively, 47 mg (0.37 mmol) and 85 mg (0.66 mmol) of **5** in 1.0 ml of chlorobenzene. The samples were then treated as outlined above. After 100 hr of irradiation, ^{1}H NMR analysis indicated that the first tube contained 56% of **5** and 44% of dimeric or polymeric material, while the second contained 43% of **5** and 57% of dimeric or polymeric material. No isomerization was detected.

Quantum Yield Determination for *exo*-Norbornyl Chloride (7) and *endo*-Norbornyl Chloride (8). *exo*-Dehydronorbornyl chloride (**5**, 29.5 mg, 0.230 mmol) was diluted to 3.0 ml with acetone and placed in a preconstricted Pyrex test tube. The sample was degassed on a vacuum line and sealed at pressures less than 10^{-5} Torr. After irradiation for 48 hr, analysis by gas chromatography (25% Carbowax 20M on Chromosorb P 60/80, 6 ft × 0.25 in. Al column) indicated that the tube contained 20% of **7** ($\phi = 0.007$).

endo-Dehydronorbornyl chloride (**6**) treated similarly gave 12% of **8** after 48 hr ($\phi = 0.002$).

Acknowledgments. G.A.L. was a NDEA Fellow during the course of this work. A portion of the work was supported by Public Health Service Grant CA-13199 from the National Cancer Institute.

Registry No.—4-Cl, 3509-46-4; **5,** 3721-19-5; **6,** 3721-18-4; **7,** 765-91-3; **8,** 2999-06-6; **11,** 4634-77-9; *endo*-dehydronorborneol, 694-97-3; *exo*-dehydronorborneol, 2890-98-4; *exo*-dehydronorbornyl acetate, 5257-37-4; *endo*-dehydronorbornyl acetate, 2890-95-1.

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Oxidations of Valencene

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Epoxidation of valencene (**1**) gives predominantly the β-epoxide **3**, and similarly, dihydrovalencene (**15**) gives predominantly **20**. Photosensitized oxidation of **1** gives 4α,10α-dimethyl-6β-isopropenyl-Δ^1-9β-octalol (**5**) and 4α,10α-dimethyl-6β-isopropenyl-Δ^8-1α-octalol (**6**). Epoxidation of nootkatone (**2**) gives β-epoxide **10**, which undergoes the Wharton–Bohlen rearrangement to β-octalol **5**. Hydroboration of dihydrovalencene (**15**) gives predominantly 4α,10α-dimethyl-6β-isopropyl-*trans*-1β-decalol (**16**). Stereochemical correlations are made and the results are discussed in reference to similar oxidations of other octalin derivatives.

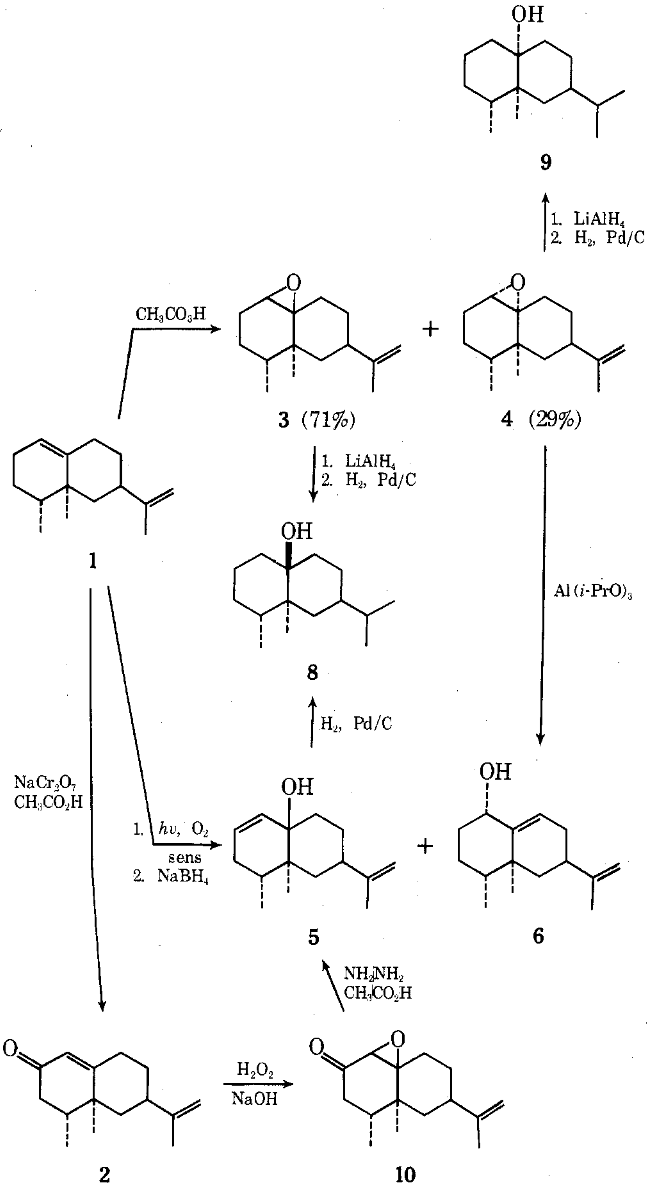
The sesquiterpene valencene (**1**),[1] which is present in valencia orange oil, has been of considerable interest both for the synthesis of nootkatone (**2**) and for the synthetic challenge posed by the 4α,10α-dimethyl substituents. Because of the desirable fragrance–flavor properties of nootkatone (**2**), we embarked on a study of some of the other oxidative chemistry of the parent hydrocarbon, valencene (**1**).

Epoxidation of valencene (**1**) by means of 40% peracetic acid afforded a mixture of mono- and diepoxides in a ratio of 3.5:1. The stereochemistry of the monoepoxides, isolated by distillation, was initially assigned by inspection of the NMR spectra. The epoxy hydrogens of *trans*-5,6-epoxy steroids and *trans*-1,9-epoxy-2,2,5,5,10-pentamethyldecalin resonate at higher field than the corresponding hydrogens of the cis isomers.[2] Since the NMR spectrum of the major valencene epoxide (71%) showed the epoxy hydrogen as a triplet at δ 2.90, whereas the minor epoxide (29%) had this corresponding triplet at δ 3.00, the major and minor epoxides were assigned structures **3** and **4** (Scheme I), respectively. Preferential epoxidation of **1** trans to the C-10 axial methyl group is consistent with the observation[3] that epoxidation of 10-methyl-1(9)-octalin gives 60% trans epoxide.

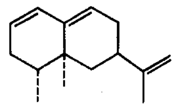
Support for this stereochemical assignment was obtained by correlation of the major epoxide with the major product derived from photosensitized oxidation of **1**, which was first reported by Ohloff.[7]

Photosensitized oxygenation of **1** followed by reduction

Scheme I



of the hydroperoxides with sodium borohydride gave two major alcohols, **5** and **6** (Scheme I), in 44 and 14% respective yield, and a considerable amount of nootkatene (**7**).[4,5]



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Alcohol **5** was isolated from the photooxidation mixture by preparative GLC on a Carbowax–KOH column and alcohol **6** was isolated by chromatography on a silica gel column. Except for the stereochemistry of the hydroxy groups, the structures of **5** and **6** were evident from their spectral data (see Experimental Section).

The stereochemistry of the major alcohols from type II photosensitized oxidation of cyclic olefins can normally be predicted. Attack of singlet oxygen occurs at either end of the double bond, preferentially from the face that allows concurrent abstraction of the quasi-axial allylic hydrogen.[6] Based on this mechanism, inspection of a molecular model of **1** shows that the hydroxyl group of tertiary alcohol **5** should have the β configuration and that of secondary alcohol **6** the α configuration.

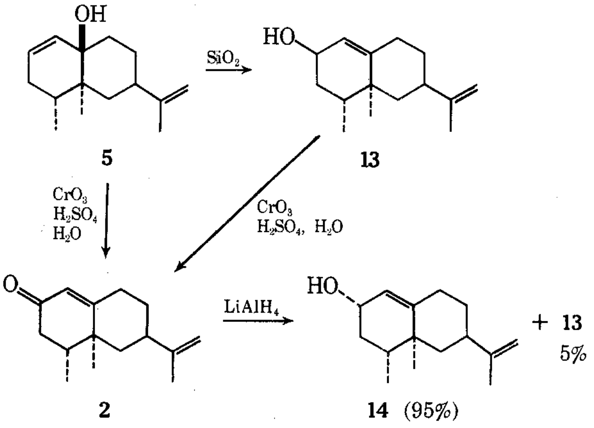
Ohloff and coworkers have also concluded[7] that **5** and **6** are the major products in 50 and 15% respective yields from photosensitized oxygenation of **1**. During their work, they were able to isolate and characterize the hydroxy epimers of **5** and **6**, both formed in 2% yield.

Reduction of a mixture of epoxides **3** and **4** (78% **3** by GLC) with lithium aluminum hydride, followed by hydrogenation over palladium catalyst, gave a 70:30 mixture of **8** and **9** which was separated by chromatography on silica gel. The major alcohol, **8**, was identical (ir and NMR spectra, GLC retention time) with the alcohol obtained by hydrogenation of **5**. This correlation of **3** with **5** substantiates the initial β stereochemistry assigned to the major valencene epoxide **3**.

Previously, a tertiary allylic alcohol of unknown stereochemistry had been derived[4] from the Wharton–Bohlen rearrangement[8] of nootkatone oxide (**10**). In order to correlate the stereochemistry of this alcohol with the other oxidation products of **1**, this reaction was repeated (Scheme I) and the alcohol obtained was identical (ir and NMR spectra, GLC retention time) with **5** isolated from the photosensitized oxidation of **1**. Alcohol **5**, as obtained crude from **10**, was essentially free of the epimeric alcohol, thus implying that epoxidation of nootkatone (**2**) with alkaline hydrogen peroxide occurs almost exclusively from the β face. The NMR spectrum of crude nootkatone oxide (**10**) shows a sharp singlet at δ 3.02 for the epoxide proton. There is no evidence in the spectrum of a second singlet near δ 3 as would be expected for the epimeric epoxide. The almost exclusive formation of **10** is in sharp contrast to the results[9] from 10-methyl-1(9)-octal-2-one and Δ^4-3-keto steroids, where epoxidation occurs predominantly cis to the axial bridgehead methyl group.

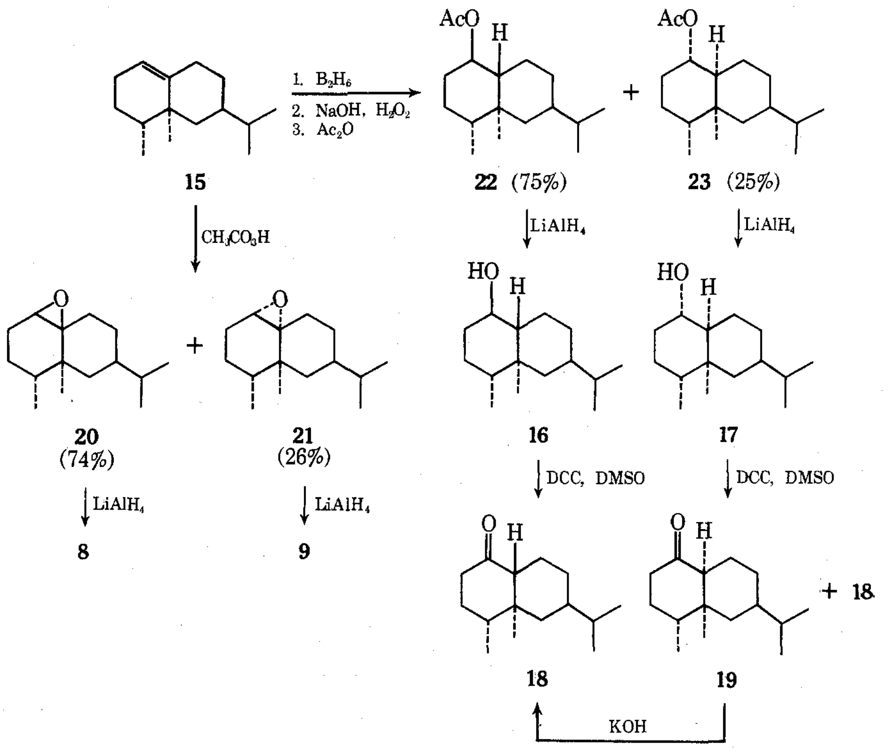
Alcohol **5**, when chromatographed on Merck silica gel, rearranged to epinootkatol (**13**) in 87% yield (Scheme II). A small amount (5%) of **13** was also present in the crude photooxidation mixture of **1**. The observation that **13** was a secondary allylic alcohol and oxidized quantitatively to nootkatone (**2**) established the general structure. Reduction of **2** with lithium aluminum hydride gave 95% of an alcohol epimeric with **13** and assigned structure **14**. The vinylic hydrogen NMR absorption of **14** appears as a broad singlet, consistent with a molecular model dihedral angle of nearly 90° between the vinylic and vicinal hydrogens, whereas the corresponding absorption of **13** appears as a doublet (J = 5 Hz), also consistent with the observed dihedral angle of 30–40°. Alcohol **5** can also be readily oxidized to **2**.

Scheme II



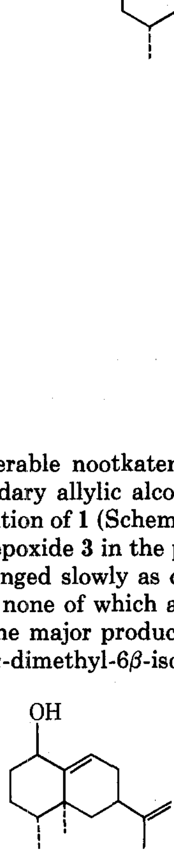
Rearrangement of the minor valencene epoxide **4** with aluminum isopropoxide gave one major alcohol, in addition

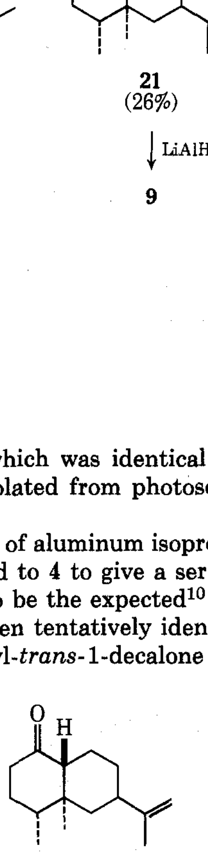
Scheme III



to considerable nootkatene (7), which was identical with the secondary allylic alcohol 6 isolated from photosensitized oxidation of 1 (Scheme I).

Major epoxide 3 in the presence of aluminum isopropoxide rearranged slowly as compared to 4 to give a series of products, none of which appear to be the expected[10] alcohol 11. The major product has been tentatively identified as 4α,10α-dimethyl-6β-isopropenyl-*trans*-1-decalone (12),


11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which could arise from epimerization of the corresponding *cis*-1-decalone. This implies that aluminum isopropoxide is functioning as a Lewis acid in the opening of epoxide 3. Assuming the rearrangement of an epoxide to an allylic alcohol with aluminum isopropoxide to be a concerted reaction,[10] it is not obvious from molecular models why this rearrangement is not observed for epoxide 3. This question, as well as the rearrangement of 3 and 4 under Lewis acid conditions, is presently under study.

Dihydrovalencene (15) was treated with diborane followed by alkaline hydrogen peroxide to give a mixture of alcohols which were separated as their acetates (22 and 23) by Nester–Faust spinning band distillation. The pure alcohols 16 and 17 were regenerated by reduction of the acetates with lithium aluminum hydride. Moffatt oxidation[11] of the major alcohol (75%) gave 4α,10α-dimethyl-6β-isopropyl-*trans*-1-decalone (18) (Scheme III). Similar oxidation of the minor alcohol (25%), after purification by chromatography on silica gel, gave a 1:1 mixture of 18 and *cis*-1-decalone 19. When this mixture was allowed to react with 5% methanolic potassium hydroxide solution, the ratio of 18 to 19, as determined by GLC analysis, changed from 56:44 to 89:11 thus establishing that 18 has a trans ring fusion. Consequently, the major alcohol obtained from hydroboration of dihydrovalencene is the β isomer 16.

The stereochemical results for hydroboration of 15 almost exactly parallel the stereochemical results for epoxidation of 1, although they differ from those of 10-methyl-1(9)-octalin, where hydroboration occurs 2:1 in favor of the cis isomer.[12]

The stereochemical results for epoxidation of dihydrovalencene (15) are identical with those for epoxidation of valencene (1). Reduction of 1,9-epoxydihydrovalencene (74% 20 and 26% 21 by GLC) with lithium aluminum hydride, followed by separation of the alcohols by chromatography on silica gel, gave 72% 8 and 28% 9 by GLC (Scheme III).

Although the 10-methyl group of the valencene skeleton is the only axial substituent, the stereochemical differences for epoxidation of 2 as compared to 10-methyl-1(9)-octal-2-one and for hydroboration of 15 as compared to 10-methyl-1(9)-octalin indicates that distal equatorial substituents, such as the 4-methyl group, must play a role in the steric determination of these reactions. Similar effects have been observed for oxidations of substituted cyclohexenes.[13]

Experimental Section

Infrared spectra were taken as neat samples on a Perkin-Elmer 457 and absorptions are reported as reciprocal centimeters, NMR spectra were taken on a Varian A-60A as chloroform-d_1 solutions and are reported as δ units relative to Me_4Si, and molecular weights were determined from mass spectra obtained with a Perkin-Elmer 270. Gas–liquid chromatography (GLC) was done, except where noted, on a 10% Carbowax 20M column (12 ft × 0.125 in.).

Valencene (1). Valencene (4α,10α-dimethyl-6β-isopropenyl-$\Delta^{1,9}$-octalin) was obtained by distillation of Valencia orange essence oil (Libbey, McNeil, and Libby, Inc.) where it is present in ca. 2% concentration: bp 98° (2 mm); n^{20}D 1.5050; ir, 1637, 885 cm^{-1}; NMR δ 5.31 (1 H, vinylic H), 4.69 (2 H, broad s, terminal methylene H), 1.70 (3 H, vinylic methyl H), 0.95 (3 H, s, methyl H), 0.9 (3 H, d, J = ca. 5 Hz, methyl H).

The valencene (1) was contaminated with 2–3% of an antioxidant, 2,6-di-*tert*-butyl-4-methylphenol (BHT).

1α,9α- and 1β,9β-Epoxy-4α,10α-dimethyl-6β-isopropenyldecalin (4 and 3). To a stirred mixture of 175 g (0.858 mol) of valencene (1), 200 ml of benzene, and 22 g of sodium carbonate, was added, dropwise over 1 hr while controlling the temperature at 30–40°, a solution of 22 g of sodium carbonate in 220 g (1.16 mol) of 40% peracetic acid. After addition was completed, the mixture was stirred at 35° for 30 min and poured into 500 ml of cold water, the layers were separated, and the aqueous phase was extracted with benzene. The combined organic extract was washed with water, neutralized with 10% sodium hydroxide solution, washed with water, dried, filtered, and concentrated under reduced pressure. The residual oil (185 g) showed the following composition by GLC, in order of elution: 6% valencene (1), 21% 1α,9α-epoxy-4α,10α-dimethyl-6β-isopropenyldecalin (4), 52% 1β,9β-epoxy-4α,10α-dimethyl-6β-isopropenyldecalin (3), and 21% of the two diepoxides. The ratio of 4:3 was 29%:71%.

Distillation gave 118 g (63% yield) of a mixture of 3 and 4, bp 90–97° (1 mm), $n^{20}\mathrm{D}$ 1.4995–1.5000.

Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.83; H, 11.06.

Redistillation on a Nester-Faust Teflon spinning band column gave 75–80% pure 4, bp 78° (0.5 mm), and 99% pure 3, bp 84° (0.5 mm).

1α,9α-Epoxy-4α,10α-dimethyl-6β-isopropenyldecalin (4): ir 1640, 1236, 984, 968, 941, 914, 885 cm^{-1}; NMR δ 4.70 (2 H, broad s, terminal methylene H), 3.00 (1 H, t, J = 2 Hz, epoxy H), 1.71 (3 H, vinylic methyl H), 1.00 (3 H, s, methyl H), 0.93 (3 H, d, J = 7 Hz, methyl H); mass spectrum M^+ m/e 220.

1β,9β-Epoxy-4α,10α-dimethyl-6β-isopropenyldecalin (3): ir 1639, 954, 900, 884 cm^{-1}; NMR δ 4.72 (2 H, broad s, terminal methylene H), 2.90 (1 H, t, J = 2 Hz, epoxy H), 1.72 (3 H, vinylic methyl H), 0.99 (3 H, s, methyl H), 0.70 (3 H, d, J = 7 Hz, methyl H); mass spectrum M^+ m/e 220.

1α,9α- and 1β,9β-Epoxy-4α,10α-dimethyl-6β-isopropyldecalin (21 and 20). Dihydrovalencene (15, containing a few percent of BHT and tetrahydrovalencene) was epoxidized with peracetic acid as described above. The mixture of epoxides was 26% 1α,9α-epoxy-4α,10α-dimethyl-6β-isopropyldecalin (21) (eluted first from GLC) and 74% 1β,9β-epoxy-4α,10α-dimethyl-6β-isopropyldecalin (20): bp 108–110° (1 mm); ir 1455, 1375, 1358, 892, 725 cm^{-1}; NMR δ 2.85–3.07 (1 H, m, epoxy H), 0.93 (s, isopropyl methyl), 0.84 (s, methyl), 0.71 (d, J = 6.5 Hz, methyl); mass spectrum M^+ m/e 222 for both isomers.

Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 81.08; H, 11.95.

Photosensitized Oxidation of Valencene (1). A solution at 0° of 40.0 g (0.196 mol) of valencene (1) (containing about 8% of 2,6-di-*tert*-butyl-4-methylphenol, BHT), 0.5 g of Rose Bengal, 700 ml of methanol, and 500 ml of benzene was continuously aerated with oxygen and irradiated with a 400-W Lucalox lamp for 8 hr. After 4 hr of irradiation, an additional 0.5 g of Rose Bengal was added.

After irradiation, the solution was transferred to a three-necked flask and 10.0 g of sodium borohydride was added portionwise while keeping the temperature at 5–10°. After addition, the solution was allowed to warm to room temperature and was stirred overnight. The solution was concentrated under reduced pressure, diluted with water, and extracted with ether. The ethereal solution was washed with saturated sodium chloride solution, dried, filtered, and concentrated.

The residual oil (38.7 g) on GLC showed 57% unreacted valencene (1) and the following products in order of GLC elution: 31% nootkatene (7) and BHT, 44% 4α,10α-dimethyl-6β-isopropenyl-Δ^1-9β-octalol (5), 14% 4α,10α-dimethyl-6β-isopropenyl-Δ^8-1α-octalol (6), 5% 4α,10α-dimethyl-6β-isopropenyl-$\Delta^{1,9}$-2β-octalol (13), 2% 4α,10α-dimethyl-6β-isopropenyl-$\Delta^{1,9}$-2α-octalol (14, tentatively identified on the basis of identical GLC retention time with authentic 14), and 4% of several unidentified products.

Nootkatene (7) from the photooxidation mixture had an identical GLC retention time with that of synthetic nootkatene[4] but was not isolated from the mixture.

Octalol 5 was isolated by preparative GLC on a Carbowax–KOH column and was identical (ir and NMR spectra, GLC retention time) with the alcohol obtained from the Wharton–Bohlen rearrangement of nootkatone oxide (10).

Octalol 6 was isolated (80% pure) by chromatography of the crude photooxidation mixture on silica gel (50:1 benzene–ether). This alcohol was identical (ir and NMR spectra, GLC retention time) with the alcohol obtained from opening of 4α,10α-dimethyl-6β-isopropenyl-1α,9α-epoxydecalin (4) with aluminum isopropoxide.

Octalol 13 was isolated as crystalline material by continued elution of the silica gel chromatogram with 50:1 benzene–ether: mp 71–73.5°; ir 3370, 1635, 1044, 1004, 926, 882 cm^{-1}; NMR δ 5.46 (1 H, d, J = 5 Hz, vinylic H), 4.67 (2 H, broad s, terminal vinylic H), 4.05 (1 H, broad, α H), 1.70 (3 H, broad s, vinylic methyl), 0.90 (3 H, s, methyl), 0.90 (3 H, d, J = 5 Hz, methyl); NMR (DMSO) δ 4.30 (1 H, d, J = 5 Hz, hydroxy H); mass spectrum M^+ m/e 220.

Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.48; H, 11.06.

On GLC, 13 had an identical retention time with that of the minor epimer obtained by reduction of nootkatone (2) with lithium aluminum hydride. Jones oxidation[14] of 13 gave nootkatone (2).

Pure 5, when chromatographed on silica gel (Merck, 50:1 benzene–ether), rearranged to 13 in 87% yield.

When the crude photooxidation mixture was subjected to Jones oxidation,[14] alcohols 5, 13, and 14 were converted to nootkatone (2) in 45% isolated yield based on unrecovered valencene (1).

4α,10α-Dimethyl-6β-isopropyl-9α- and -9β-decalol (9 and 8). Reduction of 1,9-epoxyvalencene (22% 4, 78% 3 by GLC) with lithium aluminum hydride in diethyl ether under reflux gave 4α,10α-dimethyl-6β-isopropenyl-9α- and -9β-decalol: one peak on GLC; ir 3470, 1640, 885 cm^{-1}; NMR δ 4.60 (2 H, broad s, terminal vinylic H), 1.69 (3 H, broad s, vinylic methyl), 0.87 (3 H, s, methyl), 0.71 (3 H, d, J = 6.5 Hz, methyl); NMR (DMSO) δ 3.55 (25% α-ol, s, hydroxyl H), 3.40 (75% β-ol, s, hydroxyl H).

An ethanol solution of the crude alcohols was hydrogenated on a Parr apparatus with 5% palladium on carbon as catalyst to give 4α,10α-dimethyl-6β-isopropyl-9α- and -9β-decalol: two peaks on GLC, 70% 8, 30% 9; NMR (DMSO) δ 3.50 (24% α-ol, s, hydroxyl H), 3.32 (76% β-ol, s, hydroxyl H); mass spectrum m/e 206 ($M - H_2O$) for both epimers.

A sample (2.5 g) of the alcohols was chromatographed on 90 g of silica gel and 1% ether in hexane first eluted pure 8 (1.3 g) and then pure 9 (0.5 g).

4α,10α-Dimethyl-6β-isopropyl-9β-decalol (8): major alcohol; ir 3455, 1462, 1382, 1365, 1174, 1008, 964, 932, 918, 867 cm^{-1}; NMR δ 0.70, 0.80, 0.84, 0.86, 0.92 (methyl multiplet).

Anal. Calcd for $C_{15}H_{28}O$: C, 80.29; H, 12.58. Found: C, 80.21; H, 12.32.

4α,10α-Dimethyl-6β-isopropyl-9α-decalol (9): minor alcohol; ir 3475, 1465, 1381, 1364, 1138, 1045, 1019, 967, 923 cm^{-1}; NMR δ 0.81, 0.90, 1.00, 1.20 (methyl multiplet).

Anal. Calcd for $C_{15}H_{28}O$: C, 80.29; H, 12.58. Found: C, 80.14; H, 12.55.

The epoxides 20 and 21 obtained from epoxidation of dihydrovalencene (15) were reduced with lithium aluminum hydride and the alcohols were separated by chromatography on silica gel. The major alcohol (72% by GLC) was identical with 8 and the minor alcohol (28% by GLC) was identical with 9.

4α,10α-Dimethyl-6β-isopropenyl-Δ^1-9β-octalol (5) from Wharton–Bohlen Rearrangement of Nootkatone Oxide (10) and Reduction to 4α,10α-Dimethyl-6β-isopropyl-9β-decalol (8). By GLC and NMR analysis, nootkatone oxide (10)[4] is >95% of one isomer: ir, 1712, 886 cm^{-1}; NMR δ 4.72 (2 H, terminal vinylic H), 3.02 (1 H, s, epoxy H), 1.73 (3 H, vinylic methyl), 0.96 (3 H, s, methyl), 0.80 (3 H, d, J = 6 Hz, methyl). There was no evidence in the NMR spectrum of a second singlet near δ 3 for the isomeric epoxide.

4α,10α-Dimethyl-6β-isopropenyl-Δ^1-9β-octalol (5) was obtained[4,8] by the Wharton–Bohlen rearrangement of nootkatone oxide (10): ir 3450, 1644, 887 cm^{-1}; NMR δ 5.59 (2 H, vinylic H), 4.67 (2 H, terminal vinylic H), 1.73 (3 H, broad s, vinylic methyl), 0.80 (3 H, s, methyl), 0.80 (3 H, d, J = 6 Hz, methyl); NMR (DMSO) δ 3.77 (1 H, s, hydroxyl H). Alcohol 5 partially decomposes during GLC analysis to a hydrocarbon with an identical GLC retention time with that of synthetic nootkatene (7).[4] Jones oxidation[14] of 5 gave an essentially quantitative yield of nootkatone (2).

An ethanol solution of 5 was hydrogenated on a Parr apparatus using 5% palladium on carbon as catalyst until hydrogen uptake ceased (2.0 mol hydrogen consumed per mole of 5) to give predominantly one product (>95% pure by GLC, 1–2% of the epimeric alcohol could be present by GLC), which was identical (ir and NMR spectra, GLC retention time) with 4α,10α-dimethyl-6β-isopropyl-9β-decalol (8) obtained from reduction of the major isomer 3 of 1,9-epoxyvalencene.

Reaction of 1α,9α- and 1β,9β-Epoxy-4α,10α-dimethyl-6β-isopropenyldecalin (4 and 3) with Aluminum Isopropoxide. A solution of 1.0 g (0.005 mol) of 1α,9α-epoxy-4α,10α-dimethyl-6β-isopropenyldecalin (4, 80–85% pure, containing 10% of 3), 20 mg of aluminum isopropoxide, and 10 ml of toluene was heated under reflux for 3 hr. The solution was allowed to cool to room temperature, washed with 30% sodium hydroxide solution, and then dried, filtered, and concentrated under reduced pressure. The residual oil (0.84 g) showed the following composition by GLC on a Carbowax-KOH column: 20% nootkatene (**7**), 40% unreacted **4**, 9% **3**, 20% 4α,10α-dimethyl-6β-isopropenyl-Δ^8-1α-octalol (**6**), and 11% of several other minor components.

Nootkatene, collected from GLC, was identical (NMR spectrum, GLC retention time) with a synthetic sample.[4]

4α,10α-Dimethyl-6β-isopropenyl-Δ^8-1α-octalol (**6**) was isolated by preparative GLC: ir 3350, 1637, 1039, 987, 882 cm^{-1}; NMR δ 5.55 (1 H, d of d, J = 4.5, 2.5 Hz, vinylic H), 4.69 (2 H, broad s, terminal vinylic H), 4.18 (1 H, t, J = 2 Hz, α H), 1.70 (3 H, broad s, vinylic methyl), 1.13 (3 H, s, methyl), 0.87 (3 H, misshapen d, J = 5–6 Hz, methyl); mass spectrum m/e 205 (M − CH_3), 202 (M − H_2O).

Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.52; H, 10.94.

When pure **6** was subjected to the above reaction conditions, a considerable amount of nootkatene was formed.

The rearrangement of **4** to **6** proceeded rapidly for 0.5–1 hr and then essentially stopped. The rearrangement resumed at a good rate when an additional 20 mg of aluminum isopropoxide was added.

1β,9β-Epoxy-4α,10α-dimethyl-6β-isopropenyldecalin (**3**), 95% pure, in the presence of aluminum isopropoxide under the above reaction conditions rearranged slower than **4** (half of the rate of **4** by GLC internal standard) to give a mixture of four products, including nootkatene (**7**). The major product was isolated from GLC and tentatively identified as 4α,10α-dimethyl-6β-isopropenyl-*trans*-1-decalone (**12**): ir, 1708, 1638, 885 cm^{-1}: NMR δ 4.68 (2 H, broad s, terminal vinylic H), 1.71 (3 H, broad s, vinylic methyl), 0.89 (3 H, d, J = 5.5 Hz, methyl), 0.68 (3 H, s, methyl). The other products, as yet unidentified, are two alcohols, neither of which appears to be 4α,10α-dimethyl-6β-isopropenyl-Δ^8-1β-octalol (**11**).

4α,10α-Dimethyl-6β-isopropenyl-$\Delta^{1,9}$-2α-octalol (14). Reduction of nootkatone (**2**) with lithium aluminum hydride gave a mixture of two alcohols: 95% **14** and 5% **13**; ir 3310, 1640, 1020, 884 cm^{-1}; NMR δ 5.31 (1 H, broad s, vinylic H), 4.67 (2 H, broad s, terminal vinylic H), 4.20 (1 H, broad t, J = 7 Hz, α H), 1.70 (3 H, broad s, vinylic methyl H), 0.99 (3 H, s, methyl), 0.89 (3 H, d, J = 5.5 Hz, methyl); NMR (DMSO) δ 4.44 (1 H, d, J = 5.5 Hz, hydroxyl H of **14**), 4.30 (very small, d, J = 5 Hz, hydroxy H of **13**).

4α,10α-Dimethyl-6β-isopropyl-*cis*-decal-1α-ol (17) and 4α,10α-Dimethyl-6β-isopropyl-*trans*-decal-1β-ol (16). A solution of valencene (**1**) in ethanol was hydrogenated on a Parr apparatus at a hydrogen pressure of 50 psi using 5% palladium on carbon as catalyst until 1.1 mol of hydrogen per mole of valencene was consumed. The mixture, after filtration and concentration, showed the following composition by GLC in order of elution: 14% tetrahydrovalencene, 80% dihydrovalencene (**15**), and 2% valencene (**1**).

Pure dihydrovaleneene (**15**) was isolated by preparative GLC: NMR δ 5.3 (1 H, broad, vinylic H), no terminal methylene H; mass spectrum M$^+$ m/e 206.

Anal. Calcd for $C_{15}H_{26}$: C, 87.30; H, 12.70. Found: C, 87.24; H, 12.89.

A solution of borane in tetrahydrofuran (6 ml of 1 M solution, 0.006 mol) was added dropwise under nitrogen to an ice-cold solution of 2.0 g (0.008 mol of **15**) of the above hydrocarbon mixture in 40 ml of tetrahydrofuran. After addition was complete, the solution was stirred for 30 min in the cold, allowed to warm to room temperature, and stirred overnight.

Water was cautiously added until the exothermic reaction ceased, a solution of 5 ml of 10% sodium hydroxide solution and 5 ml of 30% hydrogen peroxide was added dropwise, and the mixture was stirred at 50–60° for 1 hr. The mixture was diluted with 50 ml of water and extracted with ether. The ethereal extract was washed with water, washed with saturated ferrous sulfate solution, washed again with water, dried, filtered, and concentrated.

The residual oil (2.1 g) was chromatographed on 100 g of alumina (neutral III, 1.5 × 64 cm). Hexane and benzene eluted the unreacted hydrocarbons and impurities, and ether eluted a mixture of 4,10-dimethyl-6-isopropyl-2-decalols: 1.34 g (77% based on dihydrovalencene); 98% pure; one peak on GLC; NMR (DMSO) δ 4.09 and 4.15 (1 H, 2 d in ca. 70:30 ratio, J = 5.5 Hz, hydroxyl H).

A mixture of the corresponding acetates, prepared by allowing the above alcohols to react with refluxing acetic anhydride, was resolved by GLC into two peaks (ca. 25%:75%). The acetates were separated by distillation on a Nester-Faust Teflon spinning band (bp 105–114°, 0.5 mm).

1α-Acetoxy-4α,10α-dimethyl-6β-isopropyl-*cis*-decalin (**23**): minor isomer, distilled first, 85% pure; ir, 1735, 1248 cm^{-1}; NMR δ 4.7–5.3 (1 H, broad, α H), 2.02 (3 H, s, acetoxy methyl H), 0.84, 0.90, 0.97, 1.06 (12 H, methyl H); mass spectrum m/e 206 (M − HOAc).

1β-Acetoxy-4α,10α-dimethyl-6β-isopropyl-*trans*-decalin (**22**): major isomer, distilled last, 95% pure; ir 1740, 1248 cm^{-1}; NMR δ 4.5–5.0 (1 H, broad, α H), 2.00 (3 H, s, acetoxy methyl H), 0.75, 0.80, 0.90 (12 H, methyl H); mass spectrum m/e 206 (M − HOAc).

Reduction of the minor acetate with lithium aluminum hydride gave 4α,10α-dimethyl-6β-isopropyl-*cis*-decal-1α-ol (**17**): ir 3320 cm^{-1}; NMR δ 3.5–4.0 (1 H, broad, α H), 0.81, 0.90, 0.95, 1.04 (12 H, methyl H); NMR (DMSO) δ 4.16 (1 H, d, J = 5.5 Hz, hydroxyl H); mass spectrum M$^+$ m/e 224.

Anal. Calcd for $C_{15}H_{28}O$: C, 80.29; H, 12.58. Found: C, 80.21; H, 12.76.

Reduction of the major acetate with lithium aluminum hydride gave 4α,10α-dimethyl-6β-isopropyl-*trans*-decal-1β-ol (**16**): ir 3280 cm^{-1}; NMR δ 3.1–3.6 (1 H, broad, α H), 0.70, 0.81, 0.90 (12 H, methyl H); NMR (DMSO) δ 4.09 (1 H, d, J = 5.5 Hz, hydroxyl H); mass spectrum M$^+$ m/e 224.

Anal. Calcd for $C_{15}H_{28}O$: C, 80.29; H, 12.58. Found: C, 80.10; H, 12.56.

4α,10α-Dimethyl-6β-isopropyl-*cis*- and -*trans*-1-decalone (19 and 18). Moffatt oxidation[11] of 4α,10α-dimethyl-6β-isopropyl-*trans*-decal-1β-ol (**16**) (major alcohol from hydroboration of dihydrovalencene) gave 4α,10α-dimethyl-6β-isopropyl-*trans*-1-decalone (**18**): 91% pure; ir 1705 cm^{-1}; NMR δ 0.82, 0.91, 0.93 (9 H, isopropyl and methyl H), 0.63 (3 H, s, methyl H); mass spectrum M$^+$ m/e 222.

Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 81.29; H, 11.86.

Moffatt oxidation[11] of 4α,10α-dimethyl-6β-isopropyl-*cis*-decal-1α-ol (**17**) (minor alcohol from hydroboration of dihydrovalencene), after purification by chromatography on silica gel (50:1 benzene–ether), gave a 1:1 mixture of **18** and 4α,10α-dimethyl-6β-isopropyl-*cis*-1-decalone (**19**): ir 1705 cm^{-1}; NMR, same four methyl absorptions as above plus additional peaks at δ 0.87, 1.08, and 1.21; two peaks on GLC; mass spectrum M$^+$ m/e 222 for both isomers. When this mixture was allowed to react for a few minutes with 5% methanolic potassium hydroxide at room temperature, the GLC ratio of **19** to **18** (**19** eluted first) changed from 44:56 to 11:89. After work-up, the NMR spectrum of the ketone obtained was identical with that obtained above for **18**.

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