mixture was stirred a further 15 min in the cold and finally 15 min at room temperature. It was then filtered and the solvent evaporated at 35°. The residue, a viscous light-brown oil, was triturated with petroleum ether, the solid which formed was allowed to settle, the petroleum ether was removed, and the trituration was repeated to give the product as a fine white powder, pure by tlc (15% MeOH–$CHCl_3$): mp 123–124°; nmr ($CDCl_3$) 7.55 (1 H, s, H-2), 6.82 (1 H, s, H-4(5)), 3.09 (2 H, d, H_α, J = 6.0 Hz), 4.74 (1 H, t, H_β, J = 6.0 Hz), 7.82 (1 H, d, H_N, J = 8.0 Hz), 2.00 (3 H, s, NAc), 3.72 (3 H, s, OCH_3).

Anal. Calcd for $C_9H_{13}O_2N_3$: C, 51.2; H, 6.2; N, 19.9. Found: C, 51.3; H, 6.0; N, 20.0.

Alkylation of *N*-α-Acetylhistidine Methyl Ester with Methyl Iodoacetate. *N*-α-Acetylhistidine methyl ester (1 g) was dissolved in 50 ml of dry acetone, and powdered potassium carbonate (anhydrous, 0.981 g, 1.5 equiv) was added followed by a solution of methyl iodoacetate (0.948 g, 1 equiv) in 20 ml of dry acetone. The resulting mixture was heated at reflux and samples were taken for tlc at 2, 12, and 24 hr. After 24 hr, the product distribution had stabilized; the mixture was cooled and filtered and the filtrate evaporated. The residue was digested with 15% methanol in chloroform, the solid material was removed, and the filtrate was evaporated. The residue was dissolved in a small amount of 15% methanol–chloroform, applied to a column of Kieselgel packed in the same solvent (120 g, 60 cm × 2.4 cm) and eluted with the same solvent. Two products were eluted; the first (592 mg) was the expected 1,4-imidazole (C) and the second (152 mg) was the expected 1,5-imidazole (D).

Anal. of C: Calcd for $C_{12}H_{17}N_3O_5$: C, 50.9; H, 6.1; N, 14.8. Found: C, 50.7; H, 6.0; N, 14.9.

Hydrolyses of *N*-α-Acetyl-1-methoxycarbonyl-4-histidine Methyl Ester (C). A solution of 200 mg of C in 6 *N* HCl (80 ml) was refluxed for 6 hr, cooled, and evaporated *in vacuo* at 40°. The residue was dissolved in CO_2-free distilled water and applied to an ion-exchange column (Dowex 2-X10, 15 × 1.5 cm).[18] The column was washed with 50 ml of CO_2-free distilled water and then 1 *N* acetic acid. The effluent was collected in 5-ml fractions and the amino acid located by ninhydrin on filter paper. After evaporation of the acetic acid, the N^{Im}-carboxymethylhistidine was recrystallized from ethanol–water. Its ir was identical with that reported.[4e]

Anal. Calcd for $C_8H_{11}N_3O_4$: C, 41.6; H, 5.7; N, 18.2. Found: C, 42.1; H, 5.6; N, 18.1.

Alkylation of *N*-α-Acetylhistidine Methyl Ester with Iodoacetonitrile. The alkylation was carried out in the same way as the alkylation with methyl iodoacetate described above. The crude product was chromatographed on Kieselgel in methanol–glacial acetic acid–chloroform, 2:1:7, and the elution of products was followed by tlc. The first product to elute is the 1,5 isomer, the second the 1,4 isomer, followed closely by starting material. Samples containing one product only were pooled, the solvent was removed by rotary evaporation at 30° (20 mm), and the remaining acetic acid was removed by lyophilization. The powdery residue was extracted with ethyl acetate and the solid residue was removed by centrifugation. This material is silica, leeched from the column in the presence of acetic acid. Evaporation of the ethyl acetate solution gave the particular cyanomethylhistidine as its acetic acid salt. These salts are quite stable and do not dissociate even at 1 μ (room temperature). Their stability at higher temperatures, however, was not tested. The cyanomethylhistidine salts were each dissolved in enough saturated Na_2CO_3 solution to maintain pH ~10. The water was removed by lyophilization and the residue extracted with ethyl acetate. The 1-cyanomethyl-4-histidine derivative was recovered from this solution and recrystallized from ethyl acetate–hexane. A small amount of the 1-cyanomethyl-5-histidine derivative was likewise recovered, but could not be crystallized. Its structure was determined by mass spectral, hydrolytic, and nmr analysis. The room temperature reaction gave a 1,4/1,5 ratio of about 10:1.

***N*-α-Acetyl-1-cyanomethyl-5-histidine methyl ester:** mass spectrum *m/e* 250 (M+), 207, 191, 160, 152, 149, 121, 120, 88, 82, 81, 43; nmr ($CDCl_3$) 1.98 (3 H, N-Ac, s), 2.99 (2 H, 5-CH_2–, d), 3.64 (3 H, -OCH_3, s), 4.76 (1 H, -C*H*NAc, m), 5.71 (2 H, CH_2CN, s), 6.83 (1 H, H-4, s), 7.1 (1 H, NHAc, m), 7.54 (1 H, H-2, d, J = 0.99 Hz).

***N*-α-Acetyl-1-cyanomethyl-4-histidine methyl ester:** mass spectrum *m/e* 250 (M+), 207, 191, 160, 149, 121, 120, 88, 81, 45, 43; nmr ($CDCl_3$) 1.95 (3 H, N-Ac, s), 3.00 (2 H, 4-CH_2, d), 3.63 (3 H, OCH_3, s), 4.70 (1 H, C*H*NAc, m), 4.92 (2 H, CH_2CN, s), 6.85 (1 H, H-2, s), 7.26 (1 H, NH, d, J = 8 Hz), 7.49 (1 H, H-5, d, J = 1.10 Hz).

Anal. Calcd for $C_{11}H_{14}N_4O_3$: C, 52.8; H, 5.6; N, 22.4. Found: C, 52.8; H, 6.1; N, 22.2.

(18) A. M. Crestfield, W. H. Stein, and S. Moore, *J. Biol. Chem.*, **238**, 2413 (1963).

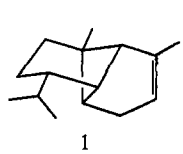
A Total Synthesis of (±)-α- and (±)-β-Copaenes and Ylangenes

E. J. Corey* and David S. Watt

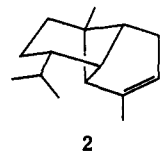
Contribution from the Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138. *Received September 21, 1972*

Abstract: Syntheses of racemic α-copaene (**1**), α-ylangene (**2**), β-copaene (**33**), and β-ylangene (**34**) are described. The *cis*-decalin "envelope" ring component of these substances was constructed by the orientationally selective reaction of 3-carbomethoxy-2-pyrone (**3**) with 4-methyl-3-cyclohexenone (**4**) which afforded the keto ester **5**. Epoxidation of the ethylene ketal of **5** using peracid afforded the α-oxide **14** which was further transformed into the dienone ketal **18**, a key intermediate for the synthesis of the four title compounds. Reduction of **18** using lithium in liquid ammonia (to **19**), tosylation, deketalization, and internal S_N2 cyclization then afforded the tricyclic ketone **23** which was further converted to (±)-**1** and (±)-**2** by a sequence which transformed the carbonyl group into >CH-*i*-C_3H_7. Reduction of the dienone ketal **18** using zinc–acetic acid led to the *exo*-methylene keto ketal **28** from which (±)-β-copaene (**33**) and (±)-β-ylangene (**34**) were obtained by a sequence paralleling that used for the synthesis of **1** and **2** from **19**.

The tricyclic sesquiterpenes, α-copaene (**1**) and α-ylangene (**2**), pose an interesting synthetic problem which centers about the unusual ring system.[1] For some time, we have been studying an approach which involves direct formation of a *cis*-decalin structure using the Diels–Alder reaction and subsequent generation of the tricyclic system by four-membered ring closure.



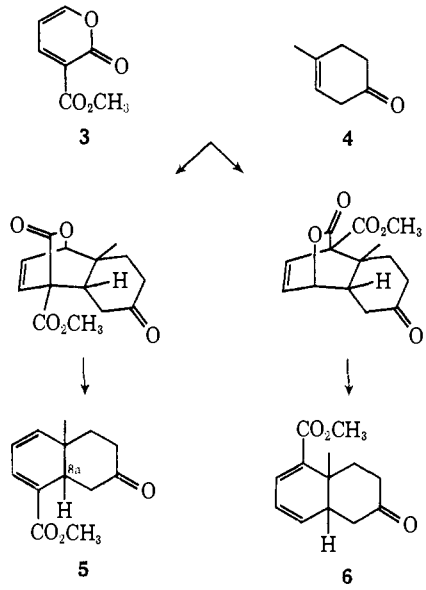
1



2

(1) One solution has already been devised by Heathcock; see (a) C. H. Heathcock, *J. Amer. Chem. Soc.*, **88**, 4110 (1966); (b) C. H. Heathcock, R. A. Badger, and J. W. Patterson, Jr., *ibid.*, **89**, 4113 (1967).

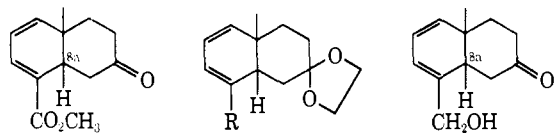
This approach seemed to offer the possibility of a relatively simple and direct synthesis if a suitable Diels–Alder addition could be achieved. The most attractive possibility appeared to be the use of 3-carbomethoxy-2-pyrone (**3**)[2] and 4-methyl-3-cyclohexenone



3 **4** **5** **6**

(**4**). This reaction could, in principle, afford two monoadducts, since both the diene **3** and the dienophile **4** are unsymmetrical. Decarboxylation of the initial adducts would then provide the keto esters **5** and **6**. In practice, the Diels–Alder reaction at 150° furnished only the desired keto ester **5** in yields of up to 40%.

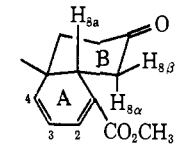
The purified keto ester was assigned structure **5** principally on the basis of its nmr spectrum. The low-field chemical shift of the C-8a methine proton (δ 2.93) was consistent with the close proximity of the deshielding carbomethoxy group. The ketone function in keto ester **5** was protected as the ethylene ketal. The ketal



5 **7**, R = CO_2CH_3 **8**, R = CH_2OH **9**

ester **7** was reduced to the ketal dienol **8**. Acidic hydrolysis of **8** removed the protecting group and provided the keto dienol **9**. The conversion of the carbomethoxy group in keto ester **5** to a hydroxymethyl group in keto dienol **9** caused a shift in the C-8a methine signal 1.27 ppm to higher field but changed the angular methyl signal by only 0.03 ppm.

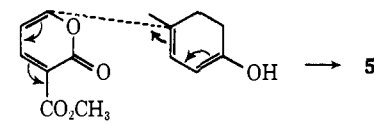
The spin–spin coupling of the H-8a proton in the nmr spectrum of the keto ester **5** also allowed a decision as to the preferred conformation of the cis-fused bicyclic system. The coupling constants ($J_{8a,8\alpha}$ = 12.3 Hz, $J_{8a,8\beta}$ = 5.3 Hz, and $J_{4,8a}$ = 1.2 Hz) were consistent only with the "nonsteroidal" conformation[3] **5a** for the keto ester.



5a

The remarkable selectivity of the Diels–Alder reaction in the assembly of **3** and **4** to yield **5** appears to be due to the intervention of the enol form of **4** as the true dienophilic partner. Preferential bonding in the transition state as shown in Scheme I would take advantage

Scheme I



of the favorable interaction of strong electron donor (OH) and acceptor (C=O) groups to provide a major driving force and would lead selectively to **5** instead of **6**. If the ketone **4** were the active dienophile, the keto ester **6** would be the anticipated product.

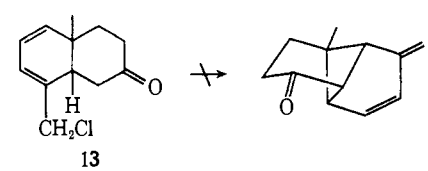
Consistent with the above argument was the failure of the alcohol **10**, acetate **11**, and dithioketal **12** to

10, R = H **11**, R = Ac **12**

undergo a Diels–Alder reaction with 3-carboethoxy-2-pyrone[4] under similar conditions. Such olefins do not possess the electron-donating power of the dienol and hence are expected to be less reactive toward the highly electrophilic pyrone.

Of the cyclization modes envisaged for the construction of the tricyclo[4.4.0.$0^{2,7}$]decane skeleton, the intramolecular Michael reaction[5] seemed worthy of trial. A suitable intermediate to test this approach was readily available in the keto ester **5** which possessed the requisite nonsteroidal conformation for cyclization. An examination of several reactions failed to reveal anything of promise.[6]

Another approach which appeared to be attractive involved the intramolecular S_N2'' alkylation of the easily available bicyclic derivative **13**. Unfortunately,



13

this process also could not be realized despite a number of attempts using a variety of basic reagents,[6] and so this possibility was set aside in favor of other alternatives.

(2) The presence of an electron-withdrawing substituent in the 3 position of 2-pyrones was incorrectly reported to deactivate the pyrone ring toward Diels–Alder addition: N. P. Shusherina, N. D. Dmitrieva, E. A. Lukyanets, and R. Ya. Levina, *Russ. Chem. Rev.*, **36**, 187 (1967).

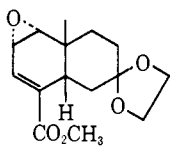
(3) The steroidal and nonsteroidal terminology indicates whether the angular methyl group is equatorial or axial, respectively, relative to ring A with the designation of rings as A and B as indicated in **5a**.

(4) 3-Carboethoxy-2-pyrone was used in the initial stages of this work until the starting material, 1,1,3,3-tetraethoxypropane, ceased to be commercially available.

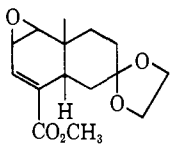
(5) (a) E. J. Corey, M. Ohno, R. B. Mitra, and P. A. Vatakencharry, *J. Amer. Chem. Soc.*, **86**, 478 (1964); (b) R. B. Woodward, F. I. Brutschy, and H. Baer, *ibid.*, **70**, 4216 (1948).

(6) For details, see D. S. Watt, Ph.D. Thesis, Harvard University, 1972.

The intramolecular SN2 cyclization of a bicyclic intermediate in a nonsteroidal conformation to the desired tricyclic skeleton would require a leaving group at the C-4β position. Epoxidation of the γ,δ double bond appeared a feasible way to introduce the requisite functionality provided that the β-epoxide **15** could be obtained. The epoxidation of the ketal ester **7** with *m*-chloroperbenzoic acid was selective for the γ,δ double bond as expected, but both of the isomeric 3,4-epoxides **14** and **15** were obtained. A detailed analysis[6]



14

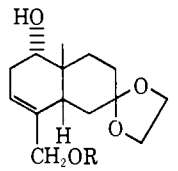


15

of the nmr spectra of the epoxides allowed the assignment of configuration to the α-epoxide **14** and β-epoxide **15**.

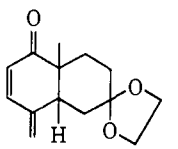
The α-epoxide **14** was found to predominate over the β-epoxide **15** using a range of different solvents, and no conditions were found which would favor the desired β isomer. For example, the epoxidation of **7** in methylene chloride afforded an 80% yield of **14** and **15** in an α/β ratio of 9. Since attempts to prepare the β-oxide **15** from **7** by other methods were unpromising,[7] attention was focused on utilizing the α-oxide **14** in a modified approach. Reduction of the α-epoxide **14** by lithium aluminum hydride in ether–tetrahydrofuran furnished a single ketal diol **16** in 90% yield. That the reduction product possessed a primary and a secondary hydroxyl group was established by determining the nmr spectrum in dimethyl-d_6 sulfoxide.[8] The assignment of structure **16** follows from the chemical shift of the proton attached to the secondary carbinol center which agrees with expectations for homoallylic but not allylic methine protons[6] and also from the chemical data which follow.

The ketal diol **16** was selectively converted to the



16, R = H

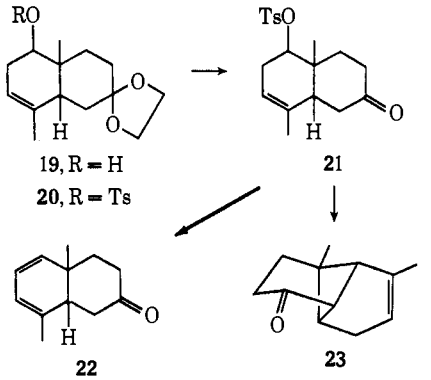
17, R = $COOC_2H_5$



18

ketal hydroxycathylate **17** in 75% yield by reaction with ethyl chloroformate in pyridine. Consistent with the presence of a homoallylic rather than an allylic hydroxyl group in **17**, the manganese dioxide oxidation of the ketal hydroxycathylate **17** provided only unreacted starting material. Oxidation of **17** using dimethyl sulfoxide–acetic anhydride afforded the dienone **18** which is clearly in accord with the structures assigned to the precursors.[9]

Reduction of the dienone **18** using lithium in liquid ammonia provided the ketal 4β-alcohol **19** stereo-



19, R = H

20, R = Ts

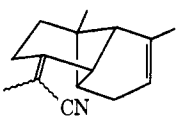
21

22

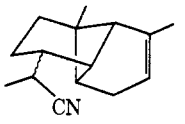
23

selectively in 92% yield. The stereochemical assignment at C-4 was made on the basis of the high-field chemical shift of the angular methyl group in the nmr spectrum.[10] The ketal 4β-alcohol **19** was converted to the ketal tosylate **20** in 92% yield using *p*-toluenesulfonyl chloride in pyridine. The hydrolysis of the ketal group in aqueous acid afforded the keto tosylate **21** in 95% yield. Attempted cyclization of the keto tosylate **21** using 1,5-diazabicyclo[4.3.0]non-5-ene, potassium *tert*-butoxide, sodium methoxide, or tritylsodium led only to the keto diene **22**. Apparently, the elimination of *p*-toluenesulfonic acid to give a conjugated diene *via* the conformation bearing an axial tosylate group[11] was a more favorable process than the elimination of *p*-toluenesulfonic acid to give a tricyclic product *via* the conformation bearing an equatorial tosylate group. Using sodium methylsulfinylmethylide or sodium bis(trimethylsilyl)amide, the cyclization of keto tosylate **21** provided the tricyclic ketone **23** in 10–38% yield. The cyclization reactions using sodium methylsulfinylmethylide (*cf.* ref 1) afforded the highest yields of the tricyclic ketone **23**. The yield of cyclized product appeared to be insensitive to variations in reaction temperature, equivalents of base, reaction time, initial concentration of **21**, rate of addition of base, and the mode of addition of base (normal or inverse).[6]

Establishing an isopropyl substituent at the C-8 ketone site in the tricyclic ketone **23** was the remaining synthetic task. The tricyclic ketone **23** was converted to the tricyclic α,β-unsaturated nitrile **24** in 94% yield



24



25

(7) Reaction of **7** with *N*-bromosuccinimide in aqueous 1,2-dimethoxyethane or aqueous dimethyl sulfoxide afforded mainly the 4β-bromo-3α-hydroxy-Δ^2-ester which was converted by base to the α-epoxide **14**. The β-epoxide **15** could be obtained from **14** by the sequence: **14** → hydroxy acetate (HOAc) → methyloxy acetate (mesyl chloride) → **15** (methanolic KOH), but the overall yield (11%) was not satisfactory. For details of these studies, see Experimental Section.

(8) O. L. Chapman and R. W. King, *J. Amer. Chem. Soc.*, **86**, 1256 (1964).

(9) Further evidence for the α orientation of the 4-hydroxyl group in **16** can be derived from the spin–spin coupling between the H-3 and H-4 protons in the nmr spectrum using a shift reagent. The addition of tris(dipivaloylmethanato)europium (III) to a deuteriochloroform solution shifted the H-4β proton to low field where its multiplicity (triplet, $J_{3\alpha,4\beta} = J_{3\beta,4\beta} = 6.2$ Hz) confirmed directly the C-4α hydroxyl configuration in ketal diol **16**.

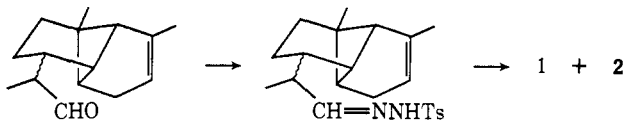
(10) A comparison of the nmr spectra of numerous C-4α and C-4β derivatives revealed that the chemical shift of the angular methyl group in the C-4β epimer always appeared at higher field than that of the corresponding C-4α epimer.[6]

(11) Based on the free energy values for the axial–equatorial tosylate equilibrium in cyclohexyl systems, approximately 20–40% of keto tosylate **21** occupies a conformation bearing an axial tosylate group at 25°: J. A. Hirsch, *Top. Stereochem.*, **1**, 199 (1967).

using 2-diethylphosphonopropionitrile in a Wadsworth–Emmons phosphonate reaction.[12] The magnesium in methanol reduction of **24** furnished the dihydro derivative **25** in high yield as a mixture of diastereomers.

With the 15 carbon skeleton now assembled, the final operation in the synthesis of α-copaene (**1**) and α-ylangene (**2**) was the separation of a synthetic intermediate into the epimeric precursors of α-copaene (**1**) and α-ylangene (**2**). The desire to separate an intermediate was predicated on the assumption that a mixture of α-copaene (**1**) and α-ylangene (**2**) could not be separated using conventional vpc columns (*vide infra*). Efforts to apply liquid–liquid and vapor phase chromatography to the separation of the diastereomeric mixture of tricyclic nitriles **25** ended in frustration.

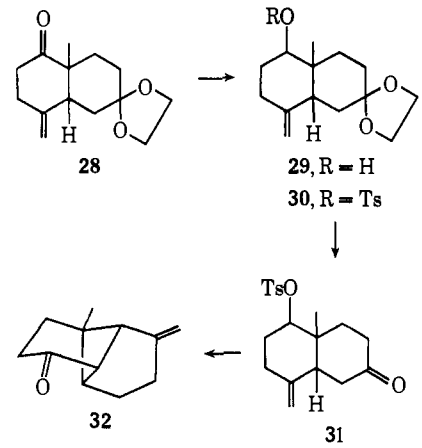
To transform the tricyclic nitrile **25** to a mixture of the natural products required only the reduction of a cyano group to a methyl group. The diisobutylaluminum hydride reduction of **25** provided the tricyclic aldehyde **26** in 80% yield. The sodium boro-



26 **27**

hydride or lithium aluminum hydride reduction of the tricyclic *N*-tosylhydrazone[13] **27** derived from the tricyclic aldehyde **26** furnished a mixture of (±)-α-copaene (**1**) and (±)-α-ylangene (**2**) in a 1:1 ratio in moderate yield. The Heathcock synthesis[1] effected the separation of (±)-α-copaene (**1**) and (±)-α-ylangene (**2**) on a 1000 ft × 0.03 in. SF-96 (50) capillary column. This tedious separation was performed under the impression that α-copaene (**1**) and α-ylangene (**2**) were too similar in structure to allow separation by conventional vpc columns. However, adequate separation of a contrived mixture of (−)-α-copaene (**1**) and (+)-α-ylangene (**2**) was achieved in these laboratories on a 30 × 0.125 in. 10% Carbowax 20M column. The synthetic mixture was readily separated to afford pure samples of (±)-α-copaene (**1**) and (±)-α-ylangene (**2**) having infrared, nmr, and mass spectra superimposable on those of authentic samples.[14]

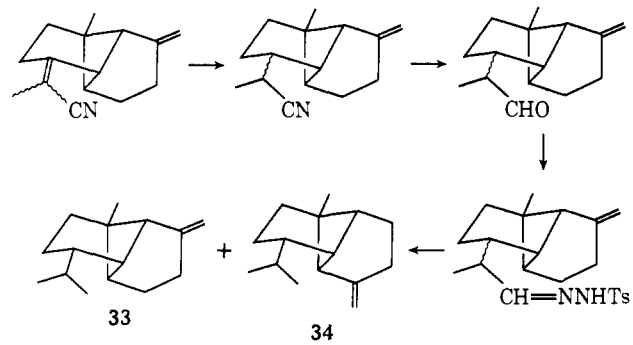
The ketal dienone **18**, which served as a key intermediate for the synthesis of (±)-**1** and (±)-**2**, could also be used for the synthesis of the racemic forms of closely related sesquiterpenes, β-copaene (**33**) and β-ylangene (**34**). Reduction of **18** with zinc dust in anhydrous acetic acid gave the ketal *exo*-methylene ketone **28** in 83% yield. The ketal *exo*-methylene 4β-alcohol **29** was obtained stereoselectively in the sodium in 2-propanol reduction of **28**.[15] The tosylation of the ketal *exo*-methylene 4β-alcohol **29** furnished the ketal *exo*-methylene tosylate **30** in 93% yield. Hydrolysis of the ketal group in **30** provided the keto *exo*-methylene



28 **29**, R = H; **30**, R = Ts **31** **32**

tosylate **31** in 87% yield. The cyclization of **31** was investigated using 1,5-diazabicyclo[4.3.0]non-5-ene, potassium *tert*-butoxide, and sodium methylsulfinylmethylide.[6] Only the latter reagent proved successful in the cyclization to give the tricyclic *exo*-methylene ketone **32**.

The sequence developed for attaching an isopropyl group to the tricyclic ketone **23** was then applied to the tricyclic *exo*-methylene ketone **32**. A synthetic mixture of the natural products in the β series was obtained without any complications arising from differences in the location of the olefinic linkage. Preparative vpc provided pure samples of (±)-β-copaene (**33**) and (±)-



33 **34**

β-ylangene (**34**) having infrared and nmr spectra in accord with published spectra.[16]

Experimental Section

Infrared (ir) spectra were recorded on either a Perkin-Elmer Model 137 or Model 437 spectrophotometer. Ultraviolet (uv) spectra were determined in methanol unless otherwise noted using either a Perkin-Elmer Model 202 or Coleman Hitachi EPS-3T spectrophotometer. Nuclear magnetic resonance (nmr) spectra were determined in deuteriochloroform with 1% tetramethylsilane (TMS) as an internal standard unless otherwise noted using either a Varian A-60, T-60, HA-100, or XL-100 spectrometer or a Perkin-Elmer-Hitachi R20 spectrometer. Data are reported as δ in parts per million downfield from TMS (δ 0). Mass spectra were determined using either an AEI Model MS-9 or Hitachi Perkin-Elmer RMU-6E spectrometer. Exact mass measurements were performed on the AEI instrument. Melting points were determined on either a Buchi or Thomas–Hoover melting point apparatus and are uncorrected. Boiling points are uncorrected. F & M Model 300 and Varian Aerograph Model A-700 gas chromatographs (helium carrier gas, thermal conductivity detector) were used for preparative gas–liquid phase (vpc) chromatography.

(12) (a) W. S. Wadsworth and W. D. Emmons, *J. Amer. Chem. Soc.*, **83**, 1733 (1961); (b) for a recent review, see A. N. Pudovik and G. E. Yastrebova, *Russ. Chem. Rev.*, **39**, 562 (1970).

(13) (a) M. Fischer, Z. Pelah, D. H. Williams, and C. Djerassi, *Chem. Ber.*, **98**, 3236 (1965); (b) L. Cagliotti, *Tetrahedron*, **22**, 487 (1966); (c) L. Cagliotti and P. Grasselli, *Chem. Ind. (London)*, 153 (1964); (d) L. Cagliotti and M. Magi, *Tetrahedron*, **19**, 1127 (1963).

(14) We wish to thank Dr. P. de Mayo for a sample of (−)-α-copaene (**1**) and Dr. R. Teranishi for a sample of (+)-α-ylangene (**2**).

(15) The ketal *exo*-methylene 4β-alcohol **29** was isomerized to the ketal 4β-alcohol **19** using *p*-toluenesulfonic acid in benzene to substantiate this stereochemical assignment.

(16) (a) L. Westfelt, *Acta Chem. Scand.*, **21**, 152 (1967); (b) R. G. Buttery, R. Teranishi, T. R. Mon, and L. C. Ling, *J. Sci. Food Agr.*, **20**, 721 (1969). (c) We wish to thank Dr. P. E. Shaw (USDA Laboratories, Winter Haven, Fla.) for providing us with the mass spectrum of β-copaene (**33**).

Hewlett-Packard Model 810 and 5750 gas chromatographs (nitrogen carrier gas, 30 ml/min, flame ionization detector) were used for analytical gas–liquid (vpc) chromatography.

Analytical thin layer chromatography (tlc) was carried out using Merck precoated, glass-backed silica gel F-254 plates (0.25 mm) developed once unless otherwise stated. Visualization agents are designated as follows: (A) ultraviolet illumination, (B) 10% phosphomolybdic acid in absolute ethanol, (C) cupric acetate (3 g per 100 ml of 1:4 85% phosphoric acid–water), (D) concentrated sulfuric acid, (E) 1% potassium permanganate in water, (F) 2,4-dinitrophenylhydrazine (0.1 g per 100 ml of 1:99 concentrated hydrochloric acid–ethanol), (G) 2% vanillin in 1:1 85% phosphoric acid–ethanol, (H) 2% ceric sulfate in 2 *N* sulfuric acid, and (I) iodine vapor. Sprayed plates were heated to approximately 200° in cases B, C, D, F, G, and H.

Preparative layer chromatography was carried out with 20-cm square plates coated with Merck silica gel PF-254 (1 mm) prepared using a sodium phosphate pH 7 buffer. Commercially available precoated plates (2 mm) were occasionally used. Products were visualized by (a) ultraviolet irradiation, (b) observing the reflection of daylight from the surface of the plate, (c) spraying a small portion of the plate with a visualization agent and heating (if necessary), or (d) charring a small portion of the plate with a hot wire. The plates were developed once unless otherwise noted. The ratio of the distance traveled by a compound (measured from the base line to the center of a band) to the distance traveled by the solvent front is designated the R_f value.

Microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich.; Alfred Berhardt, Mulheim, Germany; and Elek Microanalytical Laboratory, Torrance, Calif.

Dimethyl 3-Methoxyallylidenemalonate.[17] To 24.6 g (0.15 mol, 1.5 equiv) of 1,1,3,3-tetramethoxypropane, 136 mg (1.0 mmol) of zinc chloride, and 49.2 ml of acetic anhydride at reflux was added dropwise 13.2 g (0.10 mol) of dimethyl malonate. The initially colorless solution of 1,1,3,3-tetramethoxypropane in acetic anhydride rapidly turned to a dark orange-brown color as the reflux temperature was approached. The addition of dimethyl malonate was initiated as soon as the reflux temperature was reached and immediately turned the dark colored solution a light orange brown. The dimethyl malonate was added over a 0.5-hr period. The solution was refluxed a total of 12 hr. Solvents (50 ml) were distilled directly from the reaction mixture at atmospheric pressure (bp 65–123°). The dark product was filtered while still warm through a small plug of glass wool and vacuum distilled at bp 130–139° (0.65–0.75 mm) to afford 17.57 g (88%) of bright yellow dimethyl 3-methoxyallylidenemalonate, ir (TF) 5.79 and 6.15 μ.

3-Carbomethoxy-2-pyrone (3).[17] A solution of 20 g (0.10 mol) of dimethyl 3-methoxyallylidenenemalonate in 50 ml of 90% formic acid was refluxed for 1 hr. The solvents were removed on a rotary evaporator to afford a dark viscous oil. The product was *immediately* vacuum distilled at bp 146–148° (0.75 mm) to afford 9.25 g (60%) of yellow solid 3-carbomethoxy-2-pyrone (**3**). The yellow solid was suitable for the Diels–Alder reaction (*vide infra*) but could be further purified by sublimation at 60° (0.8 mm) to afford white needles: mp 75–77°; nmr δ 3.92 (s, 3, OCH_3), 6.46 (d of d, 1, $J_{4,5}$ = 5 Hz, $J_{5,6}$ = 7 Hz, C-5 vinyl), 7.79 (d of d, 1, $J_{4,6}$ = 2 Hz, $J_{4,5}$ = 5 Hz, C-4 vinyl), and 8.25 (d of d, 1, $J_{4,6}$ = 2 Hz, $J_{5,6}$ = 7 Hz, C-6 vinyl).

1-Methoxy-4-methyl-1,4-cyclohexadiene. To a solution of 10 g (0.0794 mol) of *p*-methylanisole, 20 ml of absolute ethanol, and 100 ml of THF in approximately 300 ml of liquid ammonia was added 2.6 g (0.373 g-atom) of lithium ribbon in small pieces over a 5-min period. After 20 min the blue color of the reducing medium had discharged, and 150 ml of ether was added. This procedure was simultaneously repeated in four other 1-l. erlenmeyer flasks. The ammonia was evaporated at room temperature, and the curd-like product in ether was washed with brine until neutral to litmus. The product was dried over anhydrous potassium carbonate. Evaporation of the solvents and distillation afforded 34.7 g (69%) of the enol ether: bp 128–130° (250 mm) (lit.[18] bp 74° (17 mm)); ir (TF) 5.88 and 5.99 μ; nmr δ 1.72 (m, 3, vinyl CH_3), 2.72 (m, 4, CH_2), 3.57 (s, 3, OCH_3), 4.62 (m, 1, C-5 vinyl), and 5.37 (m, 1, C-2 vinyl).

4-Methyl-3-cyclohexenone (4). A solution of 9.51 g (0.0761 mol) of 1-methoxy-4-methyl-1,4-cyclohexadiene and 20 ml of methanol was thoroughly shaken with 200 ml of 10% sulfuric acid for 10 min. The aqueous mixture was extracted with two 100-ml portions of ether. The ether solution was washed with two 100-ml portions of brine and dried over anhydrous potassium carbonate. Evaporation of the ether afforded a pale yellow oil which was distilled to afford 6.48 g (77%) of ketone **4**: bp 37–37.5° (2.5 mm); ir (TF) 5.81 μ; nmr δ 1.78 (m, 3, vinyl CH_3), 2.45 (m, 4, C-5 and -6 methylene), 2.83 (m, 2, C-2 methylene), and 5.44 (m, 1, C-3 vinyl).

1-Carbomethoxy-4aβ-methyl-4a,5,8,8aβ-tetrahydronaphthalen-7-(6*H*)-one; ("Keto Ester" 5). In five separate reactions, a total of 35.27 g (0.229 mol) of sublimed 3-carbomethoxy-2-pyrone (**3**) and 25.31 g (0.230 mol) of 4-methyl-3-cyclohexenone (**4**) was heated at 150° for 24 hr. The reactions were conducted in 10-ml flasks equipped with a condenser and three-way stopcock. After flushing the system three times with argon, an oil bath was applied, and the system was connected to a bubbler. Within 24 hr, gas evolution had ceased. The crude viscous product was chromatographed (preparative tlc on 20 1000 × 20 plates, 8:92 ethyl acetate–benzene).

A band (R_f ~0.20) was eluted to afford 12.67 g (25%) of keto ester **5**. The purity of the chromatographed material was 95%+ judging from the nmr spectrum. A sample of the keto ester **5** was purified by preparative vpc (3 ft 2% SE-30, 255°): ir (CCl_4) 5.85, 6.17, and 6.44 μ; uv max 214 nm (ϵ 3760) and 291 (6000); nmr δ 1.03 (s, 3, angular CH_3), 1.6–2.6 (m, 6, C-5, -6, and -8 methylene), 2.93 (d of d of d, 1, $J_{8a,8\alpha}$ = 12.3 Hz, $J_{8a,8\beta}$ = 5.3 Hz, $J_{4,8a}$ = 1.2 Hz, C-8a methine), 3.86 (s, 3, OCH_3), 6.05 (d of t, 1, $J_{3,4}$ = 9.6 Hz, $J_{2,4}$ = $J_{4,8a}$ = 1.3 Hz, C-4 vinyl), 6.21 (d of d, 1, $J_{3,4}$ = 9.5 Hz, $J_{2,3}$ = 5.2 Hz, C-3 vinyl); exact mass spectrum, 220.1099 (calcd for $C_{13}H_{16}O_3$, 220.1099).

1-Carbomethoxy-4aβ-methyl-4a,5,8,8aβ-tetrahydronaphthalen-7-(6*H*)-one Ethylene Ketal ("Ketal Ester" 7). To 8.80 g (40.0 mmol) of keto ester **5** in 50 ml of benzene were added 2.98 g (48.0 mmol, 1.2 eq) of ethylene glycol and 5 mg of *p*-toluenesulfonic acid. The solution was refluxed for 12 hr under a Dean-Stark trap. The product was diluted with ether, washed successively with saturated sodium bicarbonate solution and brine, and dried. The solvents were evaporated to afford 10.2 g (96%) of ketal ester **7**. A small sample was evaporatively distilled at 100–110° (0.01 mm): ir (TF) 5.88, 6.17, 6.43, and 13.80 μ; uv max 219 nm (ϵ 3310) and 292 (6620); nmr δ 0.97 (s, 3, angular CH_3), 1.1–1.9 (m, 6, C-5, -6, and -8 methylene), 2.77 (d of d of d, 1, $J_{8a,8\alpha}$ = 12.7 Hz, $J_{8a,8\beta}$ = 4.6 Hz, $J_{4,8a}$ = 1.2 Hz, C-8a methine), 3.87 (s, 3, OCH_3), 3.94 (s, 4, OCH_2CH_2O), 5.85 (d of t, 1, $J_{3,4}$ = 9.7 Hz, $J_{2,4}$ = $J_{4,8a}$ = 1.1 Hz, C-4 vinyl), 6.07 (d of d, 1, $J_{3,4}$ = 9.5 Hz, $J_{2,3}$ = 5.3 Hz, C-3 vinyl), and 6.96 (d of d, 1, $J_{2,3}$ = 5.4 Hz, $J_{2,4}$ = 1.1 Hz, C-2 vinyl).

An analytical sample was prepared by preparative tlc and evaporative distillation at 60–80° (0.002 mm).

Anal. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.20; H, 7.58.

1-Carbomethoxy-4aβ-methyl-3α,4α- and -3β,4β-oxido-3,4,4a,5,8,-8aβ-hexahydronaphthalen-7(6*H*)-one Ethylene Ketal ("Ketal α- and β-Epoxides" 14 and 15). To 73.8 mg (0.280 mmol) of ketal ester **7** in 1.4 ml of anhydrous dichloromethane (0.2 *M*) was added 72.1 mg (0.419 mmol, 1.5 equiv) of *m*-chloroperbenzoic acid. The solution was stirred for 48 hr. The product was diluted with ether, washed successively with saturated sodium bicarbonate solution and brine, and dried. The solvents were evaporated to afford 83 mg of oil. The crude product was chromatographed (preparative tlc, 1:20:20 methanol–ether–hexane).

A band (R_f 0.35) was eluted to afford 56.5 mg (72%) of ketal α-epoxide **14**: ir ($CHCl_3$) 5.83 and 6.10 μ; uv max 238 nm (ϵ 6840); nmr δ 0.89 (s, 3, angular CH_3), 1.6–2.2 (m, 6, C-5, -6 and -8 methylene), 2.73 (d of d of d, 1, $J_{8a,8\alpha}$ = 10.3 Hz, $J_{8a,8\beta}$ = 7.3 Hz, $J_{4,8a}$ = 2.8 Hz, C-8a methine), 3.14 (d of d, 1, $J_{4,8a}$ = 2.9 Hz, $J_{3,4}$ = 4.2 Hz, C-4 epoxide), 3.30 (t, 1, $J_{2,3}$ = $J_{3,4}$ = 4.2 Hz, C-3 epoxide), 3.76 (s, 3, OCH_3), 3.93 (s, 4, OCH_2CH_2O), and 7.02 (d, 1, $J_{2,3}$ = 4.2 Hz, C-2 vinyl); mass spectrum (70 eV) *m/e* 280 (P).

An analytical sample was prepared by the evaporative distillation at 150° (0.01 mm) of a chromatographed sample.

Anal. Calcd for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19. Found: C, 64.26; H, 7.00.

A band (R_f 0.30) was eluted to afford 6.3 mg (8%) of ketal β-epoxide **15**: ir ($CHCl_3$) 5.83 and 6.06 μ; uv max 230 nm (ϵ 4940); nmr δ 1.21 (s, 3, angular CH_3), 1.3–1.9 (m, 5, C-5, -6, and -8β methylene), 2.18 (d of d, 1, $J_{8\alpha,8\beta}$ = 14 Hz, $J_{8a,8\alpha}$ = 5 Hz, C-8α methylene), 2.49 (d of t, 1, $J_{8a,8\alpha}$ = $J_{8a,8\beta}$ = 5 Hz, $J_{2,8a}$ = 2 Hz, C-8a methine), 3.20 (d, 1, $J_{3,4}$ = 4 Hz, C-4 epoxide), 3.35 (t, 1, $J_{2,3}$ = $J_{3,4}$ = 4 Hz, C-3 epoxide), 3.76 (s, 3, OCH_3), 3.90 (m, 4, OCH_2CH_2O), and 6.79 (d of d, 1, $J_{2,3}$ = 4 Hz, $J_{2,8a}$ = 2 Hz, C-2 vinyl); mass spectrum (70 eV) *m/e* 280 (P).

(17) T. B. Windholz, L. H. Peterson, and G. J. Kent, *J. Org. Chem.*, **28**, 1443 (1963).

(18) A. J. Birch, *J. Chem. Soc.*, 596 (1946).

An analytical sample was prepared by three recrystallizations from anhydrous ether, mp 98–99°.

Anal. Calcd for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19. Found: C, 64.21; H, 7.20.

Conversion of Ketal Bromohydrin to Ketal α-Epoxide 14. To 41.9 mg (0.159 mmol) of ketal ester **7** in 0.79 ml of 25% aqueous DME (0.2 *M*) was added 30.4 mg (0.175 mmol, 1.1 equiv) of recrystallized[19] *N*-bromosuccinimide. The solution was stirred for 6 hr. The product was diluted with 20 ml of ether, washed successively with 10 ml of 5% sodium hydrogen sulfite and 10 ml of brine, and dried. The solvent was evaporated to afford 64.1 mg of oil which was chromatographed (preparative tlc, 1:5:5 methanol–ether–hexane).

A band (R_f 0.22) was eluted to afford 38.3 mg (67%) of ketal bromohydrin: ir (CCl_4) 2.88, 5.78, and 6.02 μ; uv max 218 nm (ε 8860); nmr δ 0.99 (s, 3, angular CH_3), 1.3–2.3 (m, 6, C-5, -6, and -8 methylene), 2.7–3.1 (m, 2, C-3β and OH protons), 3.75 (s, 3, OCH_3), 3.95 (s, 4, OCH_2CH_2O), 4.48 (broad s, 2, C-3β and C-4α protons), and 6.73 (d, 1, J = 2 Hz, C-2 vinyl); mass spectrum (70 eV) *m/e* 360 and 362 in a ratio of 1.0 to 0.8, respectively.

To 46.5 mg (0.129 mmol) of ketal bromohydrin in 0.51 ml of methanol (0.25 *M*) under nitrogen was added 9.1 mg (0.168 mmol, 1.3 equiv) of sodium methoxide. The solution was stirred at 25° for 0.75 hr and refluxed for 0.75 hr. The methanol was evaporated. The product was dissolved in wet ether, washed with brine, and dried. The solvent was evaporated to afford 42.4 mg of oil which was chromatographed (preparative tlc on an analytical (0.25 mm) silica gel plate, 3:20:20 methanol–ether–hexane).

A band (R_f 0.65) was eluted to afford 10.3 mg (29%) of ketal α-epoxide **14**. The nmr of this material was superimposable on that of an authentic sample.

A band (R_f 0.46) was eluted to afford 18.7 mg (40%) of the ketal bromohydrin.

Conversion of Ketal α-Epoxide 14 to Ketal β-Epoxide 15. A solution of 49.7 mg (0.178 mmol) of ketal α-epoxide **14** in 0.71 ml of anhydrous acetic acid (0.25 *M*) was heated at 100° for 2 hr. The acetic acid was removed under high vacuum *via* a Dry Ice–acetone trap to afford a yellow oil which was chromatographed (preparative tlc, 1:5:5 methanol–ether–hexane).

A band (R_f 0.29) was eluted to afford 25.7 mg (42%) of a mixture of ketal hydroxyacetates: ir (TF) 2.86, 5.75, 5.80, and 6.06 μ; the major component had nmr δ 1.20 (s, 3, angular CH_3), 2.10 (s, 3, $COCH_3$), 3.73 (s, 3, OCH_3), 5.38 (m, 1, C-3α proton), and 6.38 (t, 1, J = 2 Hz, C-2 vinyl); the minor component had nmr δ 0.86 (s, 3, angular CH_3), 2.03 (s, 3, $COCH_3$), and *ca.* 6.8 (m, 1, C-2 vinyl); mass spectrum of the mixture (70 eV) *m/e* 340 (P).

To 194 mg (0.572 mmol) of ketal hydroxyacetates in 2.32 ml of anhydrous pyridine (0.25 *M*) at 0° under nitrogen was added 196 mg (1.71 mmol, 3 equiv) of distilled mesyl chloride. The reaction was stirred at 0° for 18 hr. Several grams of ice was added, and the solution was allowed to stir for 10 min. The product was diluted with 50 ml of ether, washed successively with two 25-ml portions of saturated copper sulfate solution, two 10-ml portions of water, and 10 ml of brine, and dried. The solvent was evaporated to afford 284 mg of oil which was chromatographed (preparative tlc, 3:10:10 methanol–ether–hexane).

A band (R_f 0.29) was eluted to afford 150 mg (63%) of a mixture of ketal mesylacetates in a 7:3 ratio. The major component had nmr δ 1.27 (s, 3, angular CH_3), 2.13 (s, 3, $COCH_3$), 3.09 (s, 3, SO_2CH_3), 4.69 (d, 1, $J_{3,4}$ = 8 Hz, C-4β proton), 5.72 (d of t, 1, $J_{3,4}$ = 8 Hz, $J_{2,3}$ = 3 Hz, $J_{?}$ = 3 Hz, C-3α proton), and 6.38 (t, 1, $J_{2,3}$ = $J_{2,8a}$ = 3 Hz, C-2 vinyl); the minor component had nmr δ 0.88 (s, 3, angular CH_3), 2.05 (s, 3, $COCH_3$), 3.04 (s, 3, SO_2CH_3), 4.30 (m, 1, C-4α proton), 5.22 (d of d, 1, $J_{2,3}$ = 4 Hz, $J_{3,4}$ = 2 Hz, C-3β proton), and 6.75 (d of d 1, $J_{2,3}$ = 4 Hz, $J_{2,8a}$ = 1.5 Hz, C-2 vinyl); mass spectrum of mixture (70 eV) *m/e* 418 (P).

To 39.2 mg (0.0938 mmol) of ketal mesylacetates in 4.68 ml of methanol (0.02 *M*) under nitrogen was added 5.2 mg (0.0938 mmol, 1 equiv) of powdered potassium hydroxide. The solution was refluxed for 2.5 hr. The methanol was evaporated. The product was diluted with 25 ml of ether, washed successively with 10 ml of 1 *M* hydrochloric acid and 10 ml of brine, and dried. The solvent was evaporated to afford 16.8 mg of oil which was chromatographed (preparative tlc, 1:5:5 methanol–ether–hexane).

A band (R_f 0.38) was eluted to afford 13.4 mg (43%) of ketal β-epoxide **15** having an infrared spectrum identical with that of an authentic sample.

The overall yield of **15** from **14** was 11%.

4α-Hydroxy-1-hydroxymethyl-4aβ-methyl-3,4,4a,5,8,8aβ-hexahydronaphthalen-7(6*H*)-one Ethylene Ketal ("Ketal Diol" 16). To 48.7 mg (0.174 mmol) of ketal α-epoxide **14** in 0.5 ml of anhydrous ether at 0° under nitrogen was added 0.10 ml of 2.50 *M* lithium aluminum hydride (0.250 mmol, 2 equiv) in THF. The immediate formation of a pink precipitate was noted. The mixture was allowed to stir at 25° until the pink color had changed to a cream white. The excess reducing agent was destroyed by the addition of several drops of water and four or five drops of 1 *M* sodium hydroxide. The mixture was stirred until the formation of a granular white precipitate was complete. The solution was dried, filtered, and evaporated to afford 37.7 mg (87%) of clear oil. Tlc analysis (1:3:3 methanol–ether–hexane) showed only one spot (R_f 0.25). The ketal diol **16** had ir ($CHCl_3$) 2.98 μ; nmr δ 1.07 (s, 3, angular CH_3), 1.2–2.0 (m, 7, C-5, -6, -8, and -8a protons), 2.20 (m, 2, C-3 methylene), 2.89 (s, 2, OH), 3.53 (m, 1, C-4β proton), 3.88 (s, 4, OCH_2CH_2O), 4.00 (d, 2, CH_2OH), and 5.56 (m, 1, C-2 vinyl); mass spectrum (70 eV) *m/e* 254 (P) and 256 (?, very low intensity).

1-Cathylmethyl-4α-hydroxy-4aβ-methyl-3,4,4a,5,8,8aβ-hexahydronaphthalen-7(6*H*)-one Ethylene Ketal ("Ketal Hydroxycathylate" 17). To 7.45 g (29.3 mmol) of ketal diol **16** in 60 ml of anhydrous pyridine (0.5 *M*) at 0° under nitrogen was added 3.82 g (36.1 mmol, 1.2 equiv) of ethyl chloroformate. The solution was stirred for 4 days at 0° during which time pyridine hydrochloride appeared. The product was diluted with 50% chloroform–ether, washed successively with saturated copper sulfate solution, water, and brine, and dried. The solvent was evaporated to afford an oil which was chromatographed (preparative tlc, 1:3:3 methanol–ether–hexane).

A band (R_f ~0.50) was eluted to afford 7.15 g (75%) of ketal hydroxycathylate **17**: ir (CCl_4) 2.94 and 5.78 μ; nmr δ 1.13 (s, 3, angular CH_3), 1.32 (t, 3, J = 7 Hz, CH_2CH_3), 1.4–2.1 (m, 7, C-5, -6, -8, and -8a protons), 2.32 (m, 2, C-3 methylene), 3.63 (d of d, 1, J = 5.9 Hz and J = 8.3 Hz, C-4β proton), 3.92 (s, 4, OCH_2CH_2O), 4.19 (q, 2, J = 7 Hz, CH_2CH_3), 4.52 and 4.84 (two d, 2, J_{gem} = 12 Hz, $CH_2OCO_2CH_2CH_3$), and 5.68 (broad s, 1, C-2 vinyl); mass spectrum (70 eV) *m/e* 326 (P).

A band (R_f ~0.80) was eluted to afford 0.73 g (6%) of the ketal dicathylate: ir (CCl_4) 5.78 μ; nmr δ 1.07 (s, 3, angular CH_3), 1.30 (t, 6, J = 7 Hz, CH_2CH_3), 1.4–2.0 (m, 7, C-5, -6, -8, and -8a protons), 2.36 (broad s, 2, C-3 methylene), 3.90 (s, 4, OCH_2CH_2O), 4.17 (q, 4, J = 7 Hz, CH_2CH_3), 4.51 and 4.79 (two d, 2, J_{gem} = 12 Hz, $CH_2OCO_2CH_2CH_3$), 4.65 (t, 1, J = 6 Hz?, C-4β proton partially obscured by other signals), and 5.65 (broad s, 1, C-2 vinyl); mass spectrum (70 eV) *m/e* 398 (P).

Ketal Dienone 18. To 26.8 mg (0.082 mmol) of ketal hydroxycathylate **17** in 0.15 ml (~20 molar excess) of acetic anhydride was added 0.25 ml (~20 molar excess) of anhydrous dimethyl sulfoxide. The initially colorless solution was stirred for 24 hr to provide a bright yellow solution. The odor of dimethyl sulfide was clearly noticeable. The acetic anhydride, dimethyl sulfoxide, and dimethyl sulfide were removed under high vacuum to a Dry Ice–acetone trap. The oil remaining in the flask was diluted with 25 ml of ether, washed successively with three 25-ml portions of water and 25 ml of brine, and dried. The solvent was evaporated to afford 21.4 mg of oil which was chromatographed (preparative tlc, 3:20:20 methanol–ether–hexane).

A band (R_f 0.38) was eluted to afford 14.0 mg (73%) of ketal dienone **18**: ir (CCl_4) 3.27, 5.95, and 6.28 μ; uv max 275 nm (ε 13700); nmr δ 1.12 (s, 3, angular CH_3), 1.2–1.9 (m, 4, C-5 and -6 methylene), 2.2–2.5 (m, 2, C-8 methylene), 2.92 (d of d, 1, $J_{8a,8\alpha}$ = 11 Hz, $J_{8a,8\beta}$ = 6 Hz, C-8a methine), 3.93 (s, 4, OCH_2CH_2O), 5.31 and 5.39 (two s, 2, C=CH_2), 5.81 (d, 1, $J_{2,3}$ = 10 Hz, C-3 vinyl), and 6.90 (d, 1, $J_{2,3}$ = 10 Hz, C-2 vinyl); mass spectrum (70 eV) *m/e* 234 (P).

An analytical sample was prepared by evaporation distillation at *ca.* 150° (0.4 mm) to afford an oil which solidified, mp 70.5–72°.

Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.60; H, 7.72.

4β-Hydroxy-1,4aβ-dimethyl-3,4,4a,5,8,8a-hexahydronaphthalen-7(6*H*)-one Ethylene Ketal ("Ketal 4β-Alcohol" 19). To 148.6 mg (0.635 mmol) of ketal dienone **18** in 25 ml of liquid ammonia, 1.5 ml of absolute ethanol, and 4 ml of THF was added *ca.* 200 mg (28.5 mg-atoms, 7.5 equiv) of lithium ribbon. The blue solution was stirred for 25 min at which time the color discharged spontaneously. Ether (10 ml) was added, and the ammonia was allowed to evaporate over a *ca.* 3-hr period. The product was dissolved in wet ether, washed with four 20-ml portions of brine, and dried. The solvents were evaporated to afford 159.9 mg of oil which was chromatographed (preparative tlc, 1:5:5 methanol–ether–hexane).

(19) H. J. Dauben and L. L. McCoy, *J. Amer. Chem. Soc.*, **81**, 4863 (1959).

A band (R_f 0.40) was eluted to afford 138.7 mg (92%) of ketal 4β-alcohol **19**: ir (TF) 2.90 and 6.06 μ; nmr δ 0.88 (s, 3, angular CH_3), 1.0–2.4 (m, 12, C-3, -5, -6, -8, and -8a protons and vinyl CH_3), 3.95 (s, 4, OCH_2CH_2O), 4.06 (d of d, 1, C-4α proton partially obscured by ethylene ketal signal), and 5.19 (broad s, 1, C-2 vinyl); mass spectrum (70 eV) *m/e* 238 (P).

The acetate derivative was prepared in 78% yield using acetic anhydride in anhydrous pyridine, and an analytical sample was prepared by evaporative distillation at *ca.* 75° (0.3 mm).

Anal. Calcd for $C_{16}H_{24}O_4$: C, 68.54; H, 8.63. Found: C, 68.35; H, 8.59.

4β-Hydroxy-1,4aβ-dimethyl-3,4,4a,5,8,8aβ-hexahydronaphthalen-7(6*H*)-one Ethylene Ketal *p*-Toluenesulfonate ("Ketal Tosylate" 20). To 100.3 mg (0.422 mmol) of ketal 4β-alcohol **19** in 3.11 ml of anhydrous pyridine (0.2 *M*) at 0° was added 403 mg (2.11 mmol, 5 equiv) of *p*-toluenesulfonyl chloride. The solution was stirred at 0° for 4.6 days. The product was diluted with ether, washed successively with saturated copper sulfate solution, water, and brine, and dried. The solvents were evaporated to afford 164.2 mg (92%) of ketal tosylate **20**: ir ($CHCl_3$) 6.28, 8.43, and 8.52 μ; nmr δ 0.93 (s, 3, angular CH_3), 1.2–2.4 (m, 12, C-3, -5, -6, -8, and -8a protons and vinyl CH_3), 2.46 (s, 3, aromatic CH_3), 3.94 (s, 4, OCH_2CH_2O), 4.95 (d of d, 1, J = 8.3 Hz, J = 6.7 Hz, C-4α proton partially obscured by the broad C-2 vinyl signal), 5.12 (broad s, 1, C-2 vinyl), and 7.61 (d of d, 4, aromatic); mass spectrum (70 eV) *m/e* 392 (P).

An analytical sample was prepared by six recrystallizations from anhydrous ether, mp 100.5–102.5°.

Anal. Calcd for $C_{21}H_{28}SO_5$: C, 64.27; H, 7.19; S, 8.15. Found: C, 64.28; H, 7.18; S, 8.19.

4β-Hydroxy-1,4aβ-dimethyl-3,4,4a,5,8,8aβ-hexahydronaphthalen-7(6*H*)-one *p*-Toluenesulfonate ("Keto Tosylate" 21). A solution of 143 mg (0.365 mmol) of ketal tosylate **20** in 3.65 ml of 1:2:3 1 *M* hydrochloric acid–glacial acetic acid–THF (0.1 *M*) was stirred for 5 hr. The reaction was diluted with 25 ml of ether, washed successively with two 20-ml portions of saturated sodium bicarbonate solution and 20 ml of brine, and dried. The solvent was evaporated to afford 129.2 mg of oil which was chromatographed (preparative tlc, 1:5:5 methanol–ether–hexane).

A band (R_f 0.40) was eluted to afford 120.5 mg (95%) of keto tosylate **21**: ir ($CHCl_3$) 5.85, 6.28, 8.43, and 8.53 μ; nmr δ 1.01 (s, 3, angular CH_3), 1.51 (d, 3, J = 2 Hz, vinyl CH_3), 1.5–2.7 (m, 9, C-3, -5, -6, -8, and -8a protons), 2.46 (s, 3, aromatic CH_3), 5.00 (d of d, 1, J = 8.4 Hz, J = 7.2 Hz, C-4α proton), 5.18 (broad s, 1, C-2 vinyl), and 7.61 (d of d, 4, aromatic); mass spectrum (70 eV) *m/e* 348 (P).

An analytical sample was prepared by three recrystallizations from chloroform–anhydrous ether, mp 143–144°.

Anal. Calcd for $C_{19}H_{24}SO_4$: C, 65.50; H, 6.94; S, 9.19. Found: C, 65.41; H, 6.94; S, 9.23.

1,3-Dimethyltricyclo[4.4.0.0^{2,7}]dec-3-en-8-one ("Tricyclic Ketone" 23). To 79.2 mg (0.228 mmol) of keto tosylate **21** in 1.0 ml of anhydrous DMSO at 75° under nitrogen was added 1.25 ml of 0.2 *M* sodium methylsulfinylmethylide (0.250 mmol, 1.1 equiv) in DMSO over a *ca.* 10-sec interval. The dark brown solution was heated at 75° for 1 hr. The reaction was poured onto *ca.* 10 g of ice and extracted with three 15-ml portions of 20% chloroform–ether. The organic solutions were combined, washed with two 15-ml portions of brine, and dried. The solvent was evaporated under a slow stream of nitrogen to afford 62.3 mg of orange oil which contained traces of dimethyl sulfoxide. The oil was chromatographed (preparative tlc, 1:5:5 methanol–ether–hexane). The 20 × 20 cm plate was covered with a large piece of filter paper in which a 2-mm slit had been cut. The covered plate was sprayed with a 1% potassium permanganate solution to visualize the products.

A uv-active band (R_f 0.32) was eluted to afford 3.5 mg (4%) of unreacted keto tosylate **21**.

A band (R_f 0.64) instantaneously discolored the sprayed portion of the plate. Elution of this band afforded 23.3 mg of yellow oil. This oil was rechromatographed (preparative tlc on an analytical (0.25 mm) silica gel plate, 1:9 ether–hexane, three developments).

(1). A band (R_f 0.35) was eluted to afford 6.1 mg of oil. The structure of this material was not established, although it would appear to be a dimer. This material was easily recognized by the royal purple color which developed when the tlc plate was sprayed with a cupric acetate–phosphoric acid solution and heated. The oil had ir ($CHCl_3$) 5.85 μ (s, C=O) and no hydroxyl or tosylate absorptions; the nmr spectrum displayed singlets at δ 0.99 and 1.01 characteristic of angular methyl groups; mass spectrum (70 eV) *m/e* 364.

(2). A band (R_f 0.55) was eluted to afford 14.4 mg (36%) of tricyclic ketone **23**: ir (TF) 5.82 μ; nmr δ 0.95 (s, 3, angular CH_3), 1.6–2.8 (m, 12, C-2, -3, -6, -7, -9, and -10 protons and vinyl CH_3) and 5.41 (broad s, 1, C-4 vinyl); mass spectrum (70 eV) *m/e* 176 (P).

An analytical sample was prepared by evaporative distillation at approximately 100° (0.5 mm).

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.70; H, 9.19.

(3). A uv-active band (R_f 0.67) was eluted to afford 2.4 mg (6%) of keto diene **22**: ir ($CHCl_3$) 5.82 μ; mass spectrum (70 eV) *m/e* 176 (P).

(*E*)- and (*Z*)-8-(1-Cyanoethylidene)-1,3-dimethyltricyclo[4.4.0.0^{2,7}]-dec-3-ene ("Tricyclic α,β-Unsaturated Nitrile" 24). To 12.8 mg (0.535 mmol, 3 equiv) of sodium hydride in a 10-ml round-bottom flask equipped with a serum-capped side arm and a glass-stoppered 10/30 side arm in 0.5 ml of anhydrous DME was added 102 mg (0.535 mmol, 3 equiv) of 2-diethylphosphonopropionitrile in 0.5 ml of anhydrous DME. After the mixture was stirred for 15 min, the formation of the white phosphonate salt was judged complete by the absence of gas evolution. *Via* an evaporative distillation apparatus inserted into the 10/30 joint, 31.3 mg (0.178 mmol) of freshly distilled tricyclic ketone **23** was washed into the reaction flask using 0.75 ml of anhydrous DME. The mixture was stirred for 27 hr during which time the precipitated phosphonate salt slowly dissolved. The product was poured into 20 ml of water and extracted with three 15-ml portions of ether. The ether solutions were combined, washed successively with 10 ml of water and 10 ml of brine, and dried. The solvents were evaporated to afford 59.9 mg of oil. No carbonyl absorption was present in the ir spectrum of the crude product. The oil was chromatographed (preparative tlc, 3:20:20 methanol–ether–hexane).

A band (R_f 0.80) was eluted to afford 35.5 mg (94%) of tricyclic α,β-unsaturated nitrile **24**: ir (TF) 4.54 and 6.15 μ; uv max 224 nm (ε 11900); nmr δ 0.88 (s, 3, angular CH_3), 1.15–3.00 (m, 15, C-2, -5, -6, -7, -9, and -10 protons and vinyl CH_3), and 5.39 (broad s, 1, C-4 vinyl); exact mass spectrum, 213.1516 (calcd for $C_{15}H_{19}N$, 213.1517). The *E* to *Z* isomer ratio was not determined although the presence of a single angular methyl signal suggested that only one isomer was produced.

***syn*- and *anti*-8-(1-Cyanoethyl)-1,3-dimethyltricyclo[4.4.0.0^{2,7}]dec-3-ene ("Tricyclic Nitrile" 25).** To 213 mg (1.00 mmol) of tricyclic α,β-unsaturated nitrile **24** in 10 ml of anhydrous methanol (0.1 *M*) was added 1.0 g (40.0 g-atoms, 40 equiv) of magnesium. An induction period of approximately 1 hr was followed by a vigorous reaction which required frequent cooling with an ice bath. The mixture was stirred for 5 hr during which time most of the magnesium was consumed, and a gelatinous white precipitate was formed. To consume the remaining magnesium and to dissolve the precipitate, 10 ml of 5 *M* hydrochloric acid was added in portions accompanied by small amounts of ice to cool the exothermic reaction. The solution was extracted with three 15-ml portions of ether. The ether solutions were combined, washed with 10 ml of brine, and dried. The solvents were evaporated to afford an oil which was chromatographed (preparative tlc, 1:9 ether–hexane).

A band (R_f 0.50) was eluted to afford 162.8 mg (76%) of tricyclic nitrile **25**: ir (TF) 4.47 μ; nmr δ 0.83 (s, 3, angular CH_3), 1.28 (broad d, 3, J = 7 Hz, $CHCH_3$), 1.68 (broad s, 3, vinyl CH_3), 1.0–3.0 (m, 11, C-2, -5, -6, -7, -8, -9, and -10 protons and $CHCH_3$), and 5.30 (broad s, 1, C-4 vinyl); exact mass spectrum, 215.1679 (calcd for $C_{15}H_{21}N$, 215.1674).

***syn*- and *anti*-2-(1,3-Dimethyltricyclo[4.4.0.0^{2,7}]dec-3-en-8-yl)propionaldehyde ("Tricyclic Aldehyde" 26).** To 17.1 mg (0.0797 mmol) of tricyclic nitrile **25** in 1 ml of anhydrous hexane at −78° under nitrogen was added 0.08 ml of 1.01 *M* diisobutylaluminum hydride (1.05 equiv) in hexane. The solution was stirred for 15 min at −78° and allowed to warm to ambient temperature. The reaction was stirred for a total of 4 hr. Hydrochloric acid (4 ml of 5 *M*) was added, and the two-phase system was stirred vigorously for 1 hr. The reaction was diluted with 10 ml of water and extracted with two 15-ml portions of ether. The ether solutions were combined, washed with 10 ml of brine, and dried. The solvents were evaporated to afford 14.0 mg (80%) of tricyclic aldehyde **26**: ir (TF) 5.79 and 6.00 μ; nmr δ 0.82 (s, 3, angular CH_3), 1.05 (broad d, 3, J = 7 Hz, $CHCH_3$), 1.68 (broad s, 3, vinyl CH_3), 1.0–3.0 (m, 11, C-2, -5, -6, -7, -8, -9, and -10 protons and $CHCH_3$), 5.41 (broad s, 1, C-4 vinyl), and 9.70 (m, 1, CHO); mass spectrum (70 eV) *m/e* 218 (P); exact mass spectrum, 218.1673 (calcd for $C_{15}H_{22}O$, 218.1671).

***syn*- and *anti*-2-(1,3-Dimethyltricyclo[4.4.0.0^{2,7}]dec-3-en-8-yl)propionaldehyde *N*-Tosylhydrazone ("Tricyclic *N*-Tosylhydrazone" 27).** To 36.0 mg (0.165 mmol) of tricyclic aldehyde **26** in 0.8 ml of

anhydrous THF (0.2 *M*) was added 32.2 mg (0.173 mmol, 1.05 equiv) of *N*-tosylhydrazine. The solution was stirred for 2 hr. Tlc analysis (1:5:5 methanol–ether–hexane) indicated the reaction was complete (R_f of **26**, 0.75; R_f of **27**, 0.50). The solvent was evaporated to afford an oil which was chromatographed (preparative tlc, 1:5:5 methanol–ether–hexane).

A band (R_f 0.50) was eluted to afford 33.8 mg (53%) of tricyclic *N*-tosylhydrazone **27**: ir (TF) 3.13, 5.87, 6.15, 6.27, and 8.60 μ; nmr δ 0.73 (s, 3, angular CH_3), 0.94 (d, 3, J = 7 Hz, $CHCH_3$), 0.80–2.7 (m, 11, C-2, -5, -6, -7, -8, -9, and -10 and $CHCH_3$), 2.43 (s, 3, aromatic CH_3), 5.20 (broad s, 1, C-4 vinyl), and 6.8–8.0 (m, 6, aromatic and CH=NNHTs).

The yield was improved if the tricyclic aldehyde **26** was immediately converted to the tricyclic *N*-tosylhydrazone **27** following isolation from the diisobutylaluminum hydride reduction of the tricyclic nitrile **25**. The yield of tricyclic *N*-tosylhydrazone **27** from the tricyclic nitrile **25** was 60%.

(±)-α-Copaene (1) and (±)-α-Ylangene (2). To 210 mg (5.48 mmol, 20 equiv) of lithium aluminum hydride in 3.5 ml of refluxing anhydrous *p*-dioxane under nitrogen was added 106 mg (0.274 mmol) of tricyclic *N*-tosylhydrazone **27** in 2.0 ml of anhydrous *p*-dioxane. The mixture was refluxed for 3.5 hr. The excess reducing agent was destroyed by the successive addition of 0.20 ml of water, 0.20 ml of 15% sodium hydroxide, and 0.40 ml of water to the reaction flask cooled in an ice bath. The product was filtered through a Celite pad, and the salts were washed with five 10-ml portions of pentane. The combined pentane solutions were washed successively with four 10-ml portions of water and 10 ml of brine and dried. The solvent was evaporated to afford 54.5 mg of oil.

The oil was chromatographed on 2 g of Woelm neutral alumina in a disposable pipet using pentane as the eluent. Cuts were taken every 100 drops. The natural products were found exclusively in the first cut according to tlc analysis. The first cut was evaporated under a slow stream of nitrogen to afford 27.7 mg (49%) of (±)-α-copaene (**1**) and (±)-α-ylangene (**2**). The infrared and nmr spectra of the product were superimposable on spectra obtained from a contrived 1:1 mixture of (−)-α-copaene (**1**) and (+)-α-ylangene (**2**). Vpc analysis (30 ft 10% Carbowax 20M column at 180°, injector 215°, detector 220°, flow rate 15 ml/min) showed the product was a mixture (95%+ pure) of (±)-α-copaene (**1**) and (±)-α-ylangene (**2**) by comparison of retention times with retention times of authentic samples. The retention times of (±)-α-ylangene (**2**) and (±)-α-copaene (**1**) were 62.8 and 65.2 min, respectively. The ratio of the two synthetic natural products was approximately 1:1 with only a slight predominance of (±)-α-copaene (1),

Fifteen 0.7-μl injections were collected on a Hewlett-Packard 810 gas chromatograph using a beam splitter to direct approximately 10% of the product to the flame for detection. The separation of the two natural products was not entirely complete, and approximately two-thirds of each injection was collected. Approximately 1 mg of each natural product was collected. Vpc analysis indicated the purity of the collected samples was 95%+.

The collected samples were unfortunately contaminated with polar material bleeding from the liquid phase of the column. The impurity was detected in the infrared spectra of the synthetic natural products but was not detected by vpc analysis. This impurity was removed by again chromatographing each collected sample on 2 g of Woelm neutral alumina in a disposable pipet using carbon tetrachloride as the eluent. The first 100 drops were collected. Most of the carbon tetrachloride was evaporated, and the infrared spectrum was determined using microcells (0.1 mm). The carbon tetrachloride was replaced with deuteriochloroform, and the nmr spectrum was determined with the assistance of a Varian XL-100 spectrometer. The solvent was again evaporated, and the mass spectrum was determined.

The infrared, nmr, and mass spectra of (±)-α-copaene (1) and (±)-α-ylangene (**2**) were identical with the spectra of authentic samples.[14]

Ketal *exo*-Methylene Ketone 28. To 135.5 mg (0.578 mmol) of ketal dienone **18** in 5.8 ml of anhydrous acetic acid (0.1 *M*) was added 378 mg (5.78 mmol, 10 equiv) of zinc powder. The mixture was stirred for 3 hr. The acetic acid was removed under high vacuum *via* a Dry Ice–acetone trap. The product was dissolved in anhydrous ether and filtered through Celite. The filtrate was washed successively with 20 ml of saturated sodium bicarbonate solution and 20 ml of brine and dried. The solvent was evaporated to afford 139.2 mg of oil which was chromatographed (preparative tlc, 1:5:5 methanol–ether–hexane).

A band (R_f 0.37) was eluted to afford 22.3 mg (16%) of a dimeric ketone: ir ($CHCl_3$) 5.82 μ; nmr δ 1.13 (s, 6, angular CH_3), 1.3–2.7 (m, 20, C-5, -6, -8, and -8a protons and vinyl CH_3), 2.89 (broad s, 2, COCHCHCO), 3.97 (s, 8, OCH_2CH_2O), 5.11 (broad s, 1, vinyl), and 5.47 (broad s, 1, vinyl); mass spectrum (70 eV) *m/e* 470 (P).

A band (R_f 0.60) was eluted to afford 112.8 mg (83%) of ketal *exo*-methylene ketone **28**: ir ($CHCl_3$) 3.24, 5.84, and 5.98 μ; nmr δ 1.14 (s, 3, angular CH_3), 1.4–2.9 (m, 11, C-2, -3, -5, -6, -8, and -8a protons), 3.98 (s, 4, OCH_2CH_2O), and 4.99 (broad s, 2, C=CH_2); mass spectrum (70 eV) *m/e* 236 (P).

An analytical sample was prepared by five recrystallizations from hexane, mp 93–94°.

Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 71.31; H, 8.63.

4β-Hydroxy-4aβ-methyl-1-methylene-1,2,3,4,4a,5,8,8aβ-octahydronaphthalen-7(6*H*)-one Ethylene Ketal ("Ketal *exo*-Methylene 4β-Alcohol" 29). To 30.1 mg (0.128 mmol) of ketal *exo*-methylene ketone **28** in 2.56 ml of refluxing 2-propanol (0.05 *M*) was added *ca.* 300 mg of sodium. The mixture was refluxed for 1 hr during which time most of the sodium was consumed. Water was cautiously added dropwise through the condenser to destroy the remaining sodium. The product was transferred to a separatory funnel using 50 ml of wet ether. The ether solution was washed with four 20-ml portions of brine and dried. The solvents were evaporated to afford 29.2 mg (99%) of ketal *exo*-methylene 4β-alcohol **29**: ir (TF) 2.90, 3.25, and 6.06 μ; nmr δ 0.86 (s, 3, angular CH_3), 1.1–2.6 (m, 11, C-2, -3, -5, -6, -8, and -8a protons), 3.98 (s, 4, OCH_2CH_2O), 4.12 (d of d, 1, $J_{3\beta,4\alpha}$ = 10.4 Hz, $J_{3\alpha,4\alpha}$ = 5.2 Hz, C-4α proton, but one signal is obscured by ethylene ketal signal), and 4.73 (broad s, 2, C=CH_2); mass spectrum (70 eV) *m/e* 238 (P).

An analytical sample was prepared by chromatography and evaporative distillation at 150° (0.25 mm).

Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.55; H, 9.31. Found: C, 70.63; H, 9.37.

4β-Hydroxy-4aβ-methyl-1-methylene-1,2,3,4,4a,5,8,8aβ-octahydronaphthalen-7(6*H*)-one Ethylene Ketal *p*-Toluenesulfonate ("Ketal *exo*-Methylene Tosylate" 30). To 54.3 mg (0.228 mmol) of ketal *exo*-methylene 4β-alcohol **29** in 1.14 ml of anhydrous pyridine (0.2 *M*) at 0° was added 218 mg (1.14 mmol, 5 equiv) of *p*-toluenesulfonyl chloride. The solution was stirred at 0° for 5.5 days. The work-up procedure described in the preparation of ketal tosylate **20** was repeated to afford 83.2 mg (93%) of ketal *exo*-methylene tosylate **30**: ir ($CHCl_3$) 6.04, 6.25, 8.43, and 8.52 μ; nmr δ 0.94 (s, 3, angular CH_3), 1.2–2.5 (m, 11, C-2, -3, -5, -6, -8, and -8a protons), 2.46 (s, 3, aromatic CH_3), 3.91 (s, 4, OCH_2CH_2O), 4.69 (broad s, 2, C=CH_2), 4.98 (d of d, 1, $J_{3\beta,4\alpha}$ = 11 Hz, $J_{3\alpha,4\alpha}$ = 5 Hz, C-4α proton), and 7.55 (d of d, 4, aromatic); mass spectrum (70 eV) *m/e* 392 (P).

An analytical sample was prepared by three recrystallizations from chloroform–anhydrous ether, mp 148.5–150°.

Anal. Calcd for $C_{21}H_{28}O_5S$: C, 64.27; H, 7.19; S, 8.15. Found: C, 64.14; H, 7.13; S, 8.15.

4β-Hydroxy-4aβ-methyl-1-methylene-1,2,3,4,4a,5,8,8aβ-octahydronaphthalen-7(6*H*)-one *p*-Toluenesulfonate ("Keto *exo*-Methylene Tosylate" 31). A solution of 123.9 mg (0.314 mmol) of ketal *exo*-methylene tosylate **30** in 3.12 ml of 1:2:3 1 *M* hydrochloric acid–glacial acetic acid–THF (0.1 *M*) was stirred for 12 hr. The reaction was diluted with 25 ml of ether and washed with two 20-ml portions of saturated sodium bicarbonate solution. The bicarbonate solutions were extracted with 25 ml of ether. The combined ether solutions were washed with 25 ml of brine and dried. The solvents were evaporated to afford 122.0 mg of yellow oil which was chromatographed (preparative tlc, 1:5:5 methanol–ether–hexane).

A band (R_f 0.37) was eluted to afford 95.6 mg (87%) of keto *exo*-methylene tosylate **31**: ir ($CHCl_3$) 5.82, 6.06, 6.23, 8.42, and 8.51 μ; nmr δ 1.10 (s, 3, angular CH_3), 1.2–2.8 (m, 11, C-2, -3, -5, -6, -8, and -8a protons), 2.47 (s, 3, aromatic CH_3), 4.70 and 4.80 (two s, 2, C=CH_2), 4.98 (d of d, 1, $H_{3\beta,4\alpha}$ = 8 Hz, $J_{3\alpha,4\alpha}$ = 5 Hz, C-4α proton), and 7.59 (d of d, 4, aromatic); mass spectrum (70 eV) *m/e* 176 (P − TsOH) and (20 eV) *m/e* 348 (P).

An analytical sample was prepared by five recrystallizations from chloroform–anhydrous ether, mp 106.5–114°.

Anal. Calcd for $C_{19}H_{24}SO_4$: C, 65.50; H, 6.94; S, 9.19. Found: C, 65.37; H, 6.96; S, 9.26.

1-Methyl-3-methylenetricyclo[4.4.0.0^{2,7}]decan-8-one ("Tricyclic *exo*-Methylene Ketone" 32). To 44.1 mg (0.127 mmol) of keto *exo*-methylene tosylate **31** in 0.61 ml of anhydrous DMSO at 75° under nitrogen was added 0.66 ml of 0.2 *M* sodium methylsulfinylmethylide (0.132 mmol, 1.05 equiv) in DMSO. The orange-brown solution was stirred at 75° for 3 hr. The product was poured into *ca.* 5 g of ice, extracted with 50 ml of 10% chloroform–ether, washed successively with 10 ml of 1 *M* hydrochloric acid and 10 ml

of brine, and dried. The solvent was evaporated under a slow stream of nitrogen to afford a brown oil which was chromatographed (preparative tlc, 1:5:5 methanol–ether–hexane).

A uv-active band (R_f 0.34) was eluted to afford 9.4 mg (21%) of keto *exo*-methylene tosylate **31** which was identified by tlc comparison with an authentic sample.

A uv-inactive band (R_f 0.54) was detected using a 1% potassium permanganate spray. This band was eluted to afford 5.0 mg (22%) of tricyclic *exo*-methylene ketone **32**: ir ($CHCl_3$) 3.25, 5.85, and 6.06 μ; nmr δ 0.94 (s, 3, angular CH_3), 1.2–2.8 (m, 10, C-2, -3, -4, -6, -9, and -10 protons), 2.72 (s, 1, C-7 proton), and 4.68 and 4.78 (two s, 2, C=CH_2); mass spectrum (70 eV) *m/e* 176 (P).

(*E*)- and (*Z*)-8-(1-Cyanoethylidene)-1-methyl-3-methylenetricyclo-[4.4.0.0^{2,7}]decane ("**Tricyclic *exo*-Methylene α,β-Unsaturated Nitrile**"). The procedure described for the preparation of tricyclic α,β-unsaturated nitrile **24** was repeated. Tricyclic *exo*-methylene ketone **32** (150 mg) furnished 140.5 mg (77%) of chromatographed tricyclic *exo*-methylene α,β-unsaturated nitrile: ir (TF) 4.53, 6.09, and 6.12 μ; nmr δ 0.78 (s, 3, angular CH_3), 1.5–3.0 (m, 14, C-2, -4, -5, -6, -7, -9, and -10 protons and vinyl CH_3), and 4.65 and 4.74 (two broad s, 2, C=CH_2); mass spectrum (70 eV) *m/e* 213 (P); exact spectrum, 213.1520 (calcd for $C_{15}H_{19}N$, 213.1517).

***syn*- and *anti*-8-(1-Cyanoethyl)-1-methyl-3-methylenetricyclo-[4.4.0.0^{2,7}]decane** ("**Tricyclic *exo*-Methylene Nitrile**"). The procedure described in the preparation of the tricyclic nitrile **25** was repeated. Tricyclic *exo*-methylene α,β-unsaturated nitrile furnished 120.4 mg (87%) of chromatographed tricyclic *exo*-methylene nitrile: ir (TF) 4.48 and 6.09 μ; nmr δ 0.72 (s, 3, angular CH_3), 1.28 (d, 3, J = 7 Hz, CHCH_3 of the syn or anti isomer), 1.30 (d, 3, J = 7 Hz, CHCH_3 of the syn or anti isomer), 1.5–3.0 (m, 13, C-2, -4, -5, -6, -7, -8, -9, and -10 protons and CHCH$_3$), and 4.68 (m, 2, C=CH_2); mass spectrum (70 eV) *m/e* 215; exact mass spectrum, 215.1671 (calcd for $C_{15}H_{21}N$, 215.1674).

***syn*- and *anti*-2-(1-Methyl-3-methylenetricyclo[4.4.0.0^{2,7}]decan-8-yl)propionaldehyde *N*-Tosylhydrazone** ("**Tricyclic *exo*-Methylene *N*-Tosylhydrazone**"). The procedure described in the preparation of the tricyclic aldehyde **26** and the tricyclic *N*-tosylhydrazone **27** was repeated. Tricyclic *exo*-methylene nitrile (118 mg) provided 129.2 mg of tricyclic *exo*-methylene aldehyde: ir (TF) 5.80 and 6.10 μ. The tricyclic *exo*-methylene aldehyde (129.2 mg) provided 129.6 mg (61%) of tricyclic *exo*-methylene *N*-tosylhydrazone: ir (TF) 6.09, 6.25, and 8.58 μ.

(±)-β-Copaene (33) and (±)-β-Ylangene (34). To 254 mg (6.68 mmol, 20 equiv) of lithium aluminum hydride in 4.7 ml of refluxing anhydrous *p*-dioxane under nitrogen was added 129 mg (0.334 mmol) of tricyclic *exo*-methylene *N*-tosylhydrazone in 2.0 ml of anhydrous *p*-dioxane. The solution was refluxed for 2 hr. The work-up procedure described in the preparation of (±)-α-copaene (**1**) and (±)-α-ylangene (**2**) was repeated to afford 173.6 mg of oil.

The oil was chromatographed on 2 g of Woelm neutral alumina as described before to afford 41.3 mg (60%) of a mixture of (±)-β-copaene (**33**) and (±)-β-ylangene (**34**). The infrared and nmr spectra indicated that the product was not contaminated with significant amounts of (±)-α-copaene (**1**) and (±)-α-ylangene (**2**). Vpc analysis (30 ft 10% Carbowax 20M, 180°) showed seven peaks of which the third and fourth were predominant.

The retention time and relative percentage of each peak are presented in Table I.

Table I

Peak	R_t, min	Percentage
1	63.0	8
2	65.2	8
3	86.0	27
4	91.8	30
5	120.2	16
6	131.0	6
7	146.0	5

Peaks 1 and 2 were collected, purified, and identified as (±)-α-ylangene (**2**) and (±)-α-copaene (**1**), respectively, by comparison of infrared spectra with the spectra of authentic samples. These products presumably arose from the thermal isomerization of the double bond in the exocyclic position during the injection into the gas chromatograph.

Peaks 3 and 4 were collected, purified, and identified as (±)-β-ylangene (**34**) and (±)-β-copaene (**33**), respectively, by comparison of infrared and nmr spectra with published spectra.[16]

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