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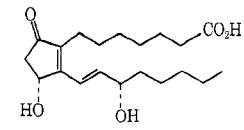

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(23) Melting points were taken on a Thomas-Hoover Unimelt in open capillaries and were not corrected. The NMR spectra were recorded at 60 MHz on Varian A-60 or at 100 MHz on Varian XL-100 NMR spectrometers in either deuteriochloroform or deuteriomethanol, using Me_4Si as an internal reference. $W_{1/2}$ denotes peak width at half-height of the multiplets. All uv spectra were determined in a 1 mg % methanol solution.
(24) R_f values for thin layer chromatography were determined on a 1 × 3 in. silica gel plate using benzene–ethyl acetate–acetic acid (25:25:1) sprayed with ethanolic phosphomolybdic acid.
(25) Unless otherwise mentioned adsorption column chromatography was carried out on Mallinckrodt SilicAR CC-4 (100–200 mesh) using benzene containing increasing percentages of ethyl acetate.
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Total Synthesis of (±)-β-Gorgonene

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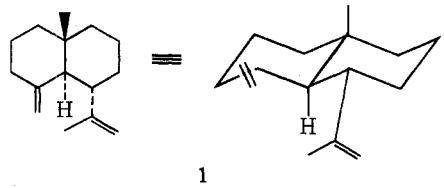
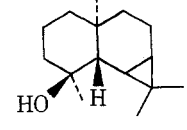
A synthetic approach to a novel nonisoprenoid sesquiterpene skeleton is described. The skeleton is derived from a rearrangement of the cationic intermediate leading to the germacrane skeleton resulting in a misplaced isopropenyl group. The key construction sequence involves the stereoselective introduction of the isopropenyl to 10-methyl-8(9)-octal-1-one. This intermediate was synthesized by two routes, both proceding through *cis*- and *trans*-10-methyl-1-decalone.

A considerable amount of synthetic chemistry has been directed toward the preparation of various members of the decalin-derived bicyclic sesquiterpenes.[1] One particular member of this general class, (+)-β-gorgonene (1), isolated



1

by Weinheimer and coworkers,[2] was of particular interest to us since it apparently represented an example of the violation of the usually observed biogenetic substitution pattern. Since the initial report of our synthesis,[4] a biogenetic-like conversion of maaliol (2) to (−)-β-gorgonene by dry HCl presumably through cation 3 has been reported which



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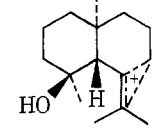

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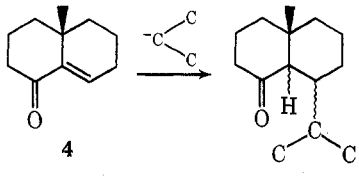
confirms the absolute stereochemistry of (+)-β-gorgonene (1) and supports the rearrangement hypothesis for its biosynthesis.[5]

A synthetic approach to this class of molecules requires that one deal with the problem of stereoselective introduction of the required equatorial isopropenyl group. This problem is compounded by the presence of the angular methyl group and the fact that the point of attachment is a peri-like position in the decalin ring system in a 1,3 relation to the angular group.

We felt that octalone (4) represented one plausible pre-

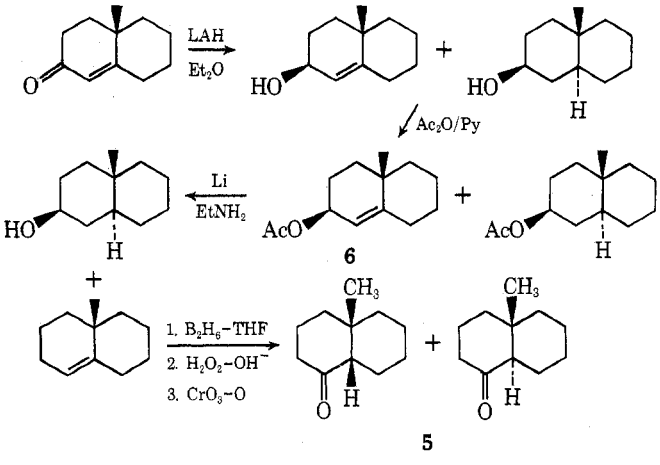
cursor. The required three-carbon segment might then be introduced via a Michael-type process utilizing an appropriate three-carbon carbanion (eq 1). The stereochemical



(1)

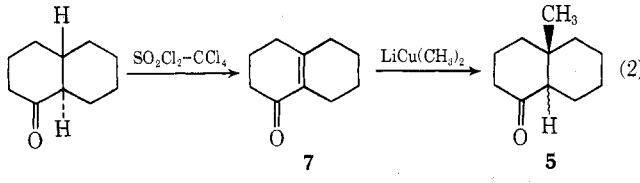
problems associated with this process provide a particularly good system in which to test the effects of steric interactions in the transition state upon the stereochemical outcome of conjugate addition of organometallic and other carbanionic reagents.

Octalone (4) had been prepared previously by Djerassi and Marshall[6] by a synthesis not well suited to preparation of sizable quantities, as it involved a low-yield rearrangement of a 2-bromo-3-decalone precursor. We prepared octalone (4) via two routes both passing through a mixture of *cis*- and *trans*-10-methyl-1-decalone (5) as shown below.



The first preparation of 10-methyl-1-decalone by ketone transposition is that of Marshall and Hochstetler.[7] We encountered some difficulties in loss of material after reductive elimination of the allylic acetate 6. The nature of the problem was finally recognized by isolation of *trans*-10-methyl-2β-decalol[8] from the reaction mixture. This byproduct presumably results from a nontrivial amount of overreduction during treatment with lithium aluminum hydride.

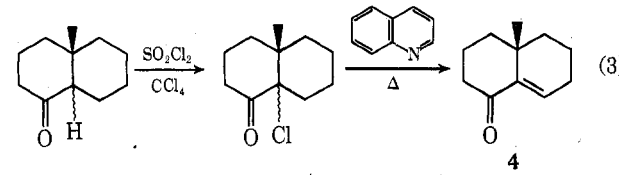
Since the foregoing sequence was multistep and suffered from relatively poor overall yields, the shorter sequence below was also utilized. Commercial α-decalone was treated



(2)

with SO_2Cl_2 in carbon tetrachloride and the crude mixture of chlorides was dehydrohalogenated in hot collidine[9] to 9,10-decal-1-one (7, 49%). Treatment of 7 with excess (2.5 equiv) lithium dimethylcuprate in ether at −20° for 23 hr gave a mixture of *cis*- and *trans*-10-methyl-1-decalone (5) in 91% yield (eq 2).

Ketones 5 prepared by either method were chlorinated with sulfuryl chloride in carbon tetrachloride to a mixture of tertiary chlorides and dehydrochlorinated by refluxing quinoline (84%) (eq 3).

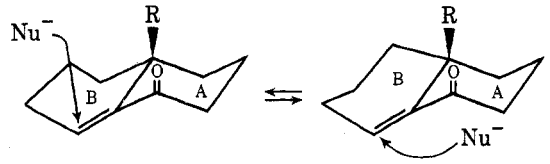


(3)

Studies of Conjugate Addition. Our initial attempts to introduce the three-carbon segment were based upon the assumption that the carbanionic species must undergo reversible addition to 4. The stereoelectronic factors controlling the Michael addition reaction favor kinetic antiparallel addition of the carbanion. In most cases this coincides with introduction of an axial group. Weakly nucleophilic carbanions appear to add reversibly and therefore under thermodynamic control. This is evidenced by the addition of malonate reported by Abe and coworkers[10] which resulted in an equatorial disposition of the side chain.

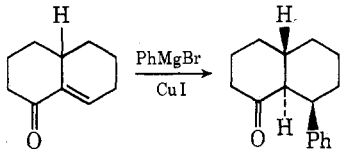
Despite numerous attempts under a variety of conditions, we were unable to effect the desired Michael addition either with sodiodimethyl malonate or sodiomethyl acetoacetate. Only starting material was recovered. Upon utilizing a prolonged reaction period or vigorous reaction conditions, polymerization of 4 was observed. Djerassi previously pointed out the susceptibility of this particular unsaturated ketone to polymerization.[6] Peri interactions in the product and/or interactions with the angular group apparently result in an unfavorable equilibrium constant for the addition.

We next considered the direct addition of organometallic reagents catalyzed by copper or of the stoichiometric organocuprate reagent. This presumably would allow the introduction of the intact isopropenyl group. The stereochemical result was expected to be the desired equatorial introduction of the isopropenyl group. Work of Allinger[11] and Marshall[12] suggested that an antiparallel approach[13] of the reagent is a primary pathway. This pathway leads to a half-chair enolate intermediate which is presumably more favorable. However, attack on conformer 8 would lead to a severe 1,3-nonbonded interaction of the incoming reagent with the angular methyl group in the transition state. This



8a, R = CH_3 9a, R = CH_3
b, R = H b, R = H

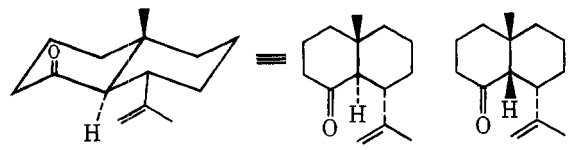
particular unsaturated ketone has an alternative pathway available which satisfies the antiparallel stereoelectronic requirement and yet circumvents the severe 1,3 interaction in the transition state. Attack of the reagent can occur upon the alternative half-chair conformation 9 of ring B from the α direction resulting in eventual equatorial disposition of the added group. Only one case of a study of a related enone was available which indicated that, in the absence of an angular group, antiparallel addition to the conformer analogous to 8 was apparently favored[14] (eq 4).



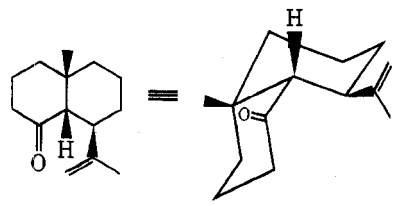
(4)

Addition of enone 4 in tetrahydrofuran (THF) to a solution of 2 equiv of the Grignard reagent prepared from 2-

bromopropene in THF containing 10 mol % CuI gave upon work-up a mixture of three saturated ketones in the approximate ratio of 7:2:1 (45%). The ketones were separated by preparative VPC. The structures of the ketones were tentatively assigned as **10**, **11**, and **12**, respectively, on the

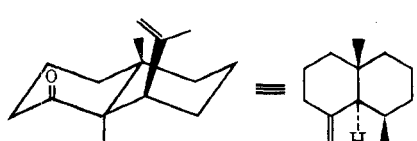


10 **11**



12

basis of the following data. The major product (**10**) had an angular methyl resonance at δ 0.81 which suggested a trans ring junction. Examination of spectral data for a large number of compounds in the literature indicated that *trans*-10-methyl-1-decalones characteristically had C-10 chemical shifts in the range δ 0.75–0.9, whereas the corresponding cis isomers had C-10 methyl chemical shifts in the range δ 1.05–1.20.[15] Treatment of pure **10** with dilute $NaOCH_3$ in CH_3OH at room temperature afforded an equilibrium mixture of **10** and **11** (~70:30), establishing the epimeric relationship of **10** and **11**. Chemical equilibration to a mixture of **10** and **11** (~66:34) and the chemical shift of the C-10 methyl of **11** (δ 1.20) further confirmed the assignment of **11** as a cis ring junction isomer. Tentative assignment of the stereochemistry of the isopropenyl group rested upon examination of the spectral and chemical characteristics of the minor product (**12**). Attempted equilibration of **12** ($NaOCH_3$–CH_3OH) resulted in the recovery of this material unchanged. The presence of a high-field methyl resonance (δ 0.79) in **12** implied a stereochemical relationship of the carbonyl and angular group of the type found in **10**. This could only occur if **12** were epimeric with **10** and **11** at the point of attachment of the isopropenyl group (assuming only all-chair conformations). If one considers conformations of the two possible epimeric ketones **12** and **13**, it is possible to assign the stereochemistry of the



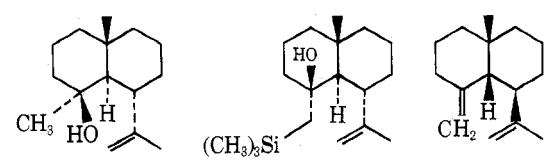
13

isopropenyl and ring junction in **12** as β. Only the conformation shown for the cis ring junction leads to equatorial disposition of the isopropenyl and angular methyl groups relieving steric interactions. Note also that the other possible cis conformation does not possess the proper spatial relationship of angular group and carbonyl leading to a high-field methyl signal (cf. **10**). The trans ring junction isomer possesses such a relationship; however, it allows no relief of the large 1,3 interaction. The only stable epimer is **12**, which is confirmed by the equilibration experiment. Therefore, **10** and **11** must have the isopropenyl group equatorially disposed.

Attempts to improve the steroselectivity of the conjugate addition by altering the temperature, the amount of cuprous salt added, and the nature of the salt were unsuccessful. Decreasing the temperature led to lower yields with some recovery of starting material. Increasing the ratio of cuprous salt from 10 mol % to 50 and 100 mol % resulted in larger amounts of coupling products but no substantial changes in stereoselectivity. Substitution of CuBr or $Cu(OAc)_2$ for CuI had also no effect.

Attempts to utilize the stoichiometric lithium cuprates prepared from isopropenyllithium in ether (2 equiv) and CuI (1 equiv) at −50 to −30° led to inferior yields of the conjugate addition products. In general, this has not been found to be the case,[16] although Ireland and coworkers have observed another instance of this behavior.[17] Upon isolation of the mixture of saturated ketones, no increase in stereoselectivity was observed.

Conversion to (±)-β-Gorgonene. Final confirmation of the foregoing structural assignments clearly lay in the conversion of **10** to (±)-β-gorgonene. Marshall and coworkers had observed a peculiar characteristic of 10-methyl-1-decalones which we attempted to exploit.[9] Wittig reactions in a number of cases performed upon an equilibrium mixture of cis and trans isomers resulted in olefin products enriched in the desired trans ring junction. This implies a reversible enolization and more rapid decomposition of the betaine derived from the trans ring junction isomer. Unfortunately, attempts to effect the methylenation of **10** or a mixture of **10** and **11** by treatment with methylenetriphenylphosphorane in DMSO[18] or THF resulted in no characterizable products but rather eventual destruction of the starting ketone. Apparently the addition process is markedly retarded by the equatorial isopropenyl group. Eventually base-catalyzed destruction of **10** occurred by some unknown mechanism. In choosing an alternative method for introduction of the exocyclic methylene, we reasoned that a reagent which would irreversibly add to the hindered carbonyl would be required. We established that organometallic reagents could successfully add to the carbonyl of **10** by reaction of **10** with methyllithium and methylmagnesium bromide in ether, which both produced a single tertiary carbinol (**14**); the stereochemistry was assigned by analogy



14 **15** **16**

to other cases in the literature. As expected, upon dehydration of **14** with $POCl_3$ or $SOCl_2$, complex mixtures of olefinic products were produced containing only minor amounts of (±)-β-gorgonene by VPC. To allow the use of an organometallic reagent and to direct the subsequent dehydration, we employed the olefination reagent described by Peterson[19] and Chan.[20] Trimethylsilylmethylmagnesium chloride in THF reacted with **10** (reflux 18 hr) to afford a tertiary carbinol assigned structure **15**. Decomposition of **15** (crude) by stirring in 3:1 acetic acid–water at room temperature for 3 hr gave a crude olefin product which was purified by chromatography (25% $AgNO_3$–SiO_2) and identified as (±)-β-gorgonene (**1**, 15%) by comparison of spectral characteristics and VPC retention time with an authentic sample of (±)-β-gorgonene.[21] Isomeric ketone **12** was also carried through the methylenation sequence in the same manner to afford an isomeric olefin with different spectral characteristics and VPC behavior than (±)-β-gorgonene (**1**), which was assigned structure **16** by the foregoing arguments.

Conjugate Addition Stereochemistry. It is clear from

the foregoing result that in this case the conjugate addition reaction is controlled by secondary steric interactions with the angular methyl group. This result will be generally true only in the event that the primary stereoelectronic requirement of antiparallel addition is satisfied as it was in this system. One must consider that the system may undergo a relatively facile conformational interconversion in order to satisfy this primary requirement.

Experimental Section

Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. Nuclear magnetic resonance (NMR) spectra were obtained on Varian A-60A and T-60 spectrometers and are reported in δ downfield from Me_4Si. Infrared (ir) spectra were obtained on a Perkin-Elmer 138 infrared spectrophotometer. Mass spectra were determined on an AEI-MS-9 spectrometer. VPC analyses were carried out on the Hewlett-Packard 5750 chromatograph utilizing flame ionization detection and nitrogen as carrier gas. Preparative VPC separations were performed on an F & M Model 776 prepmaster with a flame detector and nitrogen as the carrier gas.

10-Methyl-1(9)-octal-2-ol Acetate (6). 10-Methyl-1(9)-octal-2-one[24] (48.0 g, 0.292 mol) was dissolved in 125 ml of ether and added dropwise at 0° under nitrogen to a suspension of lithium aluminum hydride (10.0 g, 0.264 mol) in 300 ml of ether over 3 hr. The mixture was allowed to warm to room temperature and stir for 12 hr. The excess lithium aluminum hydride was decomposed by successive addition of water (10 ml), 15% sodium hydroxide (10 ml), and water (30 ml). The granular salts were filtered and washed well with ether (3 × 100 ml). The filtrate was dried over anhydrous magnesium sulfate and evaporated in vacuo to afford 51 g of oily octalol.

The crude octalol was dissolved in 200 ml of anhydrous pyridine and acetic anhydride (68.4 ml, 0.724 mol) was added. The mixture was stirred at room temperature under nitrogen for 24 hr. The crude mixture was poured into saturated sodium chloride and the layers were separated. The aqueous layer was extracted with ether (100 ml) three times. The combined organic layers were washed with water (100 ml) three times, 3.5% hydrochloric acid (100 ml) three times or until pH of the wash was ~2, 5% sodium bicarbonate (100 ml), and saturated sodium chloride and dried over anhydrous magnesium sulfate. The ether was evaporated and the residue was distilled under reduced pressure to afford 10-methyl-1(9)-octal-2-ol acetate (58 g, 95%): bp 92–95° (0.75 mm) [lit.[7] bp 62–63° (0.08 mm)]; ir (film) 1735, 1665, 1240, 1020 cm^{-1}; NMR (CCl_4) δ 5.2 (m, 3), 1.93 (s, 3), 1.11 (5, 3). This material is apparently contaminated with some *trans*-10-methyl-2-decalol acetate.

10-Methyl-1(9)-octalin. A 13.72-g sample of 10-methyl-1(9)-octal-2-ol acetate (0.066 mol) was dissolved in 200 g of anhydrous ethylamine and the solution was treated with 4.8 g (0.686 mol) of lithium metal in small pieces with vigorous stirring over about 40 min. The solution remained deep blue after the final addition. Excess lithium was destroyed by cautious addition of solid ammonium chloride until the solution was colorless. After evaporation of the ethylamine, saturated sodium chloride was added and the reaction mixture was extracted with ether (75 ml) seven times. The combined extracts were washed with water (100 ml), 2% sulfuric acid (50 ml), and saturated sodium chloride and dried over anhydrous sodium sulfate. Removal of the ether and distillation afforded 5.5 g (55%) of 10-methyl-1(9)-octalin: bp 73–76° (10 mm) [lit.[7] bp 86–88° (26 mm)]; ir (film) 1665, 1380, 1360, 1010, 988 cm^{-1}; NMR (CCl_4) δ 5.24 (m, 1), 1.04 (s, 3).

A substantial amount of pot residue remained which possessed a strong OH absorption in the infrared. Crystallization of the pot residue from petroleum ether (bp 20–40°) at −70° after decolorization by Norit afforded 2.5 g (22%) of *trans*-10-methyl-2β-decalol, mp 65.5–67° (lit.[8] mp 64–68°), which was identified by comparison with an authentic sample.

***cis*- and *trans*-10-Methyl-1-decalone (5)** 10-Methyl-1(9)-octalin (19.6 g, 0.131 mol) was dissolved in 100 ml of dry (sodium) dimethoxyethane and cooled to 0° and sodium borohydride (6.16 g, 0.162 mol) was introduced. Freshly distilled boron trifluoride etherate (23 g, 0.162 mol) was added dropwise over 2 hr. The mixture was allowed to warm to room temperature and stir for 19 hr. Water (10 ml) was added slowly, followed by sufficient aqueous 15% sodium hydroxide to bring the pH to 9. Hydrogen peroxide (30%, 20 ml) was then introduced slowly over 1 hr with stirring. If all the peroxide had been consumed then additional peroxide was added until a starch–iodide test was positive for 1 hr after the addition was completed. Aqueous 10% sodium sulfite was utilized to destroy excess peroxide and the mixture was poured into water and extracted with chloroform (100 ml) seven times. The combined extracts were washed with water (100 ml), dried, and evaporated to afford crude oily alcohols.

The crude alcohol mixture was taken up in 150 ml of dry acetone and cooled to 0°. Jones reagent[25] was introduced dropwise until excess oxidant was present for 30 min after the last addition. Isopropyl alcohol was utilized to destroy excess oxidant and the mixture was poured into ether–saturated sodium chloride. The aqueous layer was extracted with ether twice (100 ml) and the combined organic solutions were washed with water (50 ml) twice and saturated sodium chloride. Evaporation of the solvent after drying over anhydrous magnesium sulfate and fractionation under vacuum afforded a mixture of *cis*- and *trans*-10-methyl-1-decalone (12.95 g, 60%): bp 70° (0.35 mm) [lit.[7] bp 72–73° (0.7 mm)]; ir 1710 cm^{-1}; NMR (CCl_4) δ 1.05 (s, 3) cis, 0.80 (s, 3) trans.

10-Methyl-8(9)-octal-1-one (4). *cis*- and *trans*-10-methyl-1-decalone (9.95 g, 0.060 mol) was dissolved in 100 ml of carbon tetrachloride and the mixture was cooled to 0°. Freshly distilled sulfuryl chloride (8.91 g, 0.066 mol) was dissolved in 50 ml of carbon tetrachloride and the solution was added dropwise to the ketone solution over 1 hr. The mixture was stirred for 24 hr and completion was monitored by TLC. The solution was washed with water and cautiously with 5% aqueous sodium bicarbonate (until gas evolution ceased), dried, and evaporated to a crude mixture of oily chlorides. The NMR spectrum of the crude chlorides precluded chlorination at the secondary site.

The crude chlorides were taken up in 40 ml of freshly distilled quinoline and the mixture was heated at 150° for ~1 hr (monitored by TLC), at which time no starting chloride was observed. Ether and water were added to the cooled reaction mixture and the aqueous layer, after separation, was extracted with ether (50 ml) five times. Combined extracts were washed twice with 10% hydrochloric acid and once with 5% sodium bicarbonate and dried over anhydrous sodium sulfate and the solvent was evaporated. Short-path vacuum distillation afforded 10-methyl-8(9)-octal-1-one (**4**, 8.25 g, 84%), bp 72° (0.3 mm), which was about 90% pure (3% SE-30 at 135°): ir (film) 1680, 1630, 1260, 1225, 870, 840, 805 cm^{-1}; NMR (CCl_4) δ 6.50 (t, J = 3.5 Hz), 1.08 (s, 3); uv (EtOH) 243 nm. The analytical sample was prepared by preparative VPC. Anal. Calcd for $C_{11}H_{16}O$: C, 80.49; H, 9.76; Found: C, 80.58; H, 9.62.

9(10)-Octal-1-one[9] (7). *trans*-1-Decalone (30.4 g, 0.2 mol) was dissolved in 125 ml of carbon tetrachloride and maintained at 20° during the addition of a solution of 32.4 g (0.24 mol) of freshly distilled sulfuryl chloride in 75 ml of carbon tetrachloride dropwise (1 hr). Evolution of SO_2 was noted after a short induction. The mixture was stirred at room temperature for ~4 hr, by which time TLC showed essentially no starting material. The mixture was washed with water and cautiously with 5% sodium bicarbonate and saturated sodium chloride. The dried solution was evaporated to afford the crude chloro ketone (34.0 g).

The crude ketone with no further purification was dissolved in collidine (practical, 75 ml) and heated to reflux under nitrogen for approximately 1 hr. The reaction monitored by TLC appeared to proceed rapidly at first, then very slowly. Further heating did not seem to diminish the starting material markedly; however, the yield was lowered. The mixture was cooled and diluted with ether (400 ml) and water (200 ml). The organic layer was washed with 3.5% hydrochloric acid until the pH of the wash was ~2 and then 5% sodium bicarbonate. The solution was dried over magnesium sulfate and evaporated. The crude unsaturated ketone (21 g) was chromatographed on silica gel (400 g) in hexane. Elution with mixtures of hexane and benzene afforded pure unsaturated ketone (14.6 g, 49%): ir (film) 1665, 1632, 1389, 1285, 1194 cm^{-1}; NMR, no absorption δ <7.

***cis*- and *trans*-10-Methyl-1-decalone (5) from 9(10)-Octal-1-one.** A solution of lithium dimethylcuprate was prepared by dropwise addition of ethereal methyllithium (0.4 mol) to a stirred suspension of purified cuprous iodide (38.0 g, 0.2 mol) in 700 ml of anhydrous ether at 0° under nitrogen. To this solution was added dropwise 9(10)-octal-1-one (12.0 g, 0.08 mol) in 100 ml of anhydrous ether. The mixture was stored at −20 to 0° for 23 hr, then poured into 1000 ml of 10% ammonium hydroxide solution. After the salt dissolved, the ether layer was separated and washed with 10% ammonium hydroxide (100 ml), water (100 ml), and saturated sodium chloride, dried over magnesium sulfate, and evaporated to 13.6 g of crude ketone. NMR analysis showed that approximately 10% starting enone remained. The mixture was chromatographed

on silica gel (120 g) in hexane; elution with 25% benzene–hexane afforded a mixture of the 10-methyl-1-decalones (**5**, 12.2 g, 91%). The cis and trans isomers showed identical retention times with those derived from 10-methyl-1-(9)-octalin (5% Carbowax, 180°).

Conjugate Addition of Isopropenyl Grignard to 10-Methyl-8(9)-octal-1-one (4). A solution of isopropenylmagnesium bromide was prepared in anhydrous tetrahydrofuran (75 ml) from 960 mg (0.04 mol) of magnesium turnings and 5.32 g (0.044 mol) of 2-bromopropene. The mixture was cooled to −30° and 760 mg (0.004 mol) of cuprous iodide was added. After this mixture was stirred for 1 hr at −30°, a solution of 10-methyl-8(9)-octal-1-one (3.28 g, 0.02 mol) in 20 ml of anhydrous tetrahydrofuran was added dropwise over 1 hr. After warming slowly to 10° for 2 hr, the mixture was quenched with 10% ammonium chloride (pH 8) and the ether layer was separated. The ether layer was washed with water, dried over anhydrous magnesium sulfate, and evaporated to a yellow oily crude ketone mixture. This material was crudely fractionated by chromatography on silica gel (100 g) in hexane to afford on elution with hexane–benzene (1:1) 2.0 g of ketones (45%). The purified ketone mixture was separated into three isomeric ketones by preparative VPC (0.375 in. 20% Carbowax 20M at 170°). Analytical VPC (20% Carbowax 20M) indicated the ratio of isomers to be 7:2:1.

The major fraction (**10**) had ir (film) 1705, 1650, 890 cm^{-1}; NMR (CCl_4) δ 4.55 (m, 1), 4.43 (br s, 1), 0.81 (s, 3); MS p^+ 206. The second fraction (**11**) had ir (film) 1705, 1650, 890 cm^{-1}; NMR (CCl_4) δ 4.71 (br s, 2), 1.20 (s, 3); MS P^+ 206. The minor component (**12**) had ir (film) 1705, 1650, 890 cm^{-1}; NMR (CCl_4) δ 4.71 (br s, 2), 0.79 (s, 3); MS P^+ 206.

Equilibration of Decalones 10 and 11. A solution of sodium methoxide in methanol was prepared by dissolving 23 mg (1.0 mmol) of sodium metal in 10 ml absolute methanol. To 1 ml of this solution was added a sample of pure ketone **10** (25 mg). After 12 hr at room temperature, the ketone was recovered by ether extraction (16 mg). VPC analysis (10 ft 5% Carbowax 20M, 150°) showed that equilibration had occurred to a mixture of **10** and **11** (~70:30). Similarly a pure sample of **11** (10 mg) was equilibrated to a mixture of **10** and **11** (~66:34).

Attempted Equilibration of Decalone 12. A pure sample of ketone **12** was treated in the manner described above for ketones **10** and **11**. Analysis of the recovered ketone indicated that no detectable equilibration had taken place. Allowing the ketone to be in contact with the base for 24 hr lowered the recovery but did not show any evidence of equilibration. The recovered samples were examined by NMR and showed no new angular methyl absorptions.

(±)-β-Gorgonene. A solution of trimethylsilymethylmagnesium chloride in 10 ml of dry tetrahydrofuran was prepared from chloromethyltrimethylsilane (140 mg, 1.14 mmol) and magnesium metal (30 mg, 1.25 mmol) under nitrogen in the usual fashion. A solution of ketone **10** (206 mg, 1.0 mmol) in 2 ml of dry tetrahydrofuran was added dropwise at room temperature. The mixture was heated to reflux for 18 hr and then cooled and quenched with 10% ammonium chloride. The mixture was extracted with ether (25 ml) four times. Combined organic extracts were washed with water and saturated sodium chloride, dried over anhydrous magnesium sulfate, and evaporated to a colorless oily carbinol (240 mg).

This material was dissolved in aqueous acetic acid (3:1) and stirred at room temperature for 3 hr. The reaction mixture was diluted with water and extracted with hexane (20 ml) three times. The combined extracts were washed with water, dried over magnesium sulfate, and evaporated to a crude mixture of olefinic materials (86 mg). Purification by chromatography on 25% silver nitrate impregnated silica gel in pentane afforded on elution with pentane (±)-β-gorgonene (31 mg, 15%) identical in every respect with an authentic sample of (+)-β-gorgonene: ir (film) 3070, 1645, 1380, 885 cm^{-1}; NMR (CCl_4) δ 4.60 (m, 3), 4.46 (t, J = 2 Hz, 1), 1.57 (t, J = 1 Hz, 3), 0.80 (s, 3).

8,9-Epi-β-gorgonene (16). A solution of trimethylsilylmethylmagnesium chloride (1.14 mmol) was prepared as above in 10 ml of dry tetrahydrofuran. A solution of ketone **12** (206 mg, 1.0 mmol) in 1 ml of dry tetrahydrofuran was added dropwise at room temperature, and the solution was heated at reflux under nitrogen for 5 hr. The cooled reaction mixture was quenched with 10% ammonium chloride and the products were isolated by extraction with ether (50 ml) three times. The combined extracts were washed with water, dried over magnesium sulfate, and evaporated to the oily carbinol.

The crude material was dissolved in 3:1 acetic acid–water (10 ml) and stirred for 3 hr at room temperature under nitrogen. The mixture was diluted with water and extracted with hexane (30 ml) four times. The combined extracts were washed with water, dried over anhydrous magnesium sulfate, and evaporated to the crude oily olefin. Filtration through a short column of silica gel in pentane afforded 130 mg of colorless olefin **16**: ir (film) 3080, 1645, 990 cm^{-1}; NMR (CCl_4) δ 4.63 (br s, 4), 0.78 (s, 3); MS P^+ 204. Comparison by VPC on 10 ft 20% SE-30 (135°) of **16** and authentic (+)-β-gorgonene showed them to be nonidentical.

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Registry No.—**1**, 51260-29-8; **4**, 51174-52-8; *cis*-**5**, 54869-91-9; *trans*-**5**, 54869-92-0; **6**, 54910-87-1; **7**, 18631-96-4; **10**, 51174-54-0; **11**, 51174-55-1; **12**, 51174-56-2; 10-methyl-1(9)-octal-2-one, 40573-28-2; 10-methyl-1(9)-octalin, 51260-28-7; *trans*-10-methyl-2β-decalol, 54869-93-1; *trans*-1-decalone, 5784-57-6.

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