Torr.

IR (neat): 2740 w, 1750 vs, 1180 s cm^{-1}.

NMR ($CDCl_3$, 60 MHz): 0.83 (3 H, s, CH_3), 1.33 (3 H, s, CH_3), 1.7–2.9 (6 H, m, H-C(1,2,3,4)), 3.66 (3 H, s, $COOCH_3$), 9.71 (1 H, d, J = 2 Hz, CHO).

MS: *m/e* 184 (M^+) (absent), 169 (6), 153 (19), 152 (16), 138 (29), 124 (32), 115 (13), 114 (26), 95 (70), 87 (100).

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Stereoselective Conversion of Keto Groups into Methyl Vinyl Quaternary Carbon Centers†,[1]

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Abstract: In the presence of bis(triphenylphosphine)nickel dichloride both *trans*- (**1b**) and *cis*-4-*tert*-butyl-1-vinylcyclohexanol (**1c**) reacted with methylmagnesium bromide affording *r*-4-*tert*-butyl-*t*-1-methyl-1-vinylcyclohexane (**4a**), 1-*n*-propylidene-4-*tert*-butylcyclohexane (**3b**), and *r*-4-*tert*-butyl-*c*-1-methyl-1-vinylcyclohexane (**5a**) in a 19:5:1 ratio. This reaction was applied to vinylcarbinols prepared from four manool-derived 13-hydrophenanthrones (**8**, **9a**, **10a**, and 7-dehydro-**10a**) for diterpene synthesis. In the cases leading to terminal olefins 8,14-dihydropimaradiene (**14b**), 7,8-dihydroisopimaradiene (**15b**), and $\Delta^{7(8)}$-pimaradiene (**17b**) were produced. The first olefin was transformed into the tetracarbocyclic diterpene hibaene (**23**) in five high-yielding steps.

Recent studies of the reaction of Grignard reagents with allyl alcohols have shown that in the presence of bis(triphenylphosphine)nickel dichloride catalyst the hydroxy group of the alcohols is replaced by hydrogen or by alkyl or aryl groups depending on the nature of the organometallic reagents.[4] Grignard reagents containing β hydrogens yield hydrogenolysis

† Dedicated to Professor Edgar Lederer on the occasion of his 70th birthday.

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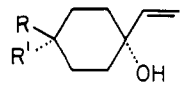
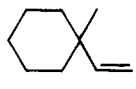
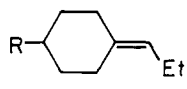
products, while those without β hydrogens are alkylating or arylating agents, Thus, for example, exposure of 1-vinylcyclohexanol (**1a**) to methylmagnesium bromide under the influence of the nickel catalyst afforded a greater than 3:1 mixture of 1-methyl-1-vinylcyclohexane (**2**) and *n*-propylidenecyclohexane (**3a**).[4b,d] In view of the ease of preparation







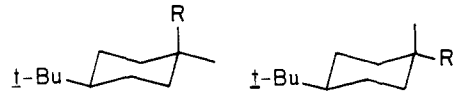
1a, R = R' = H
b, R = t-Bu, R' = H
c, R = H, R' = t-Bu

2

3a, R = H
b, R = t-Bu

of vinylcarbinols from aldehydes and ketones and the high preference of production of terminal olefins of type **2** in the nickel-induced alkylation process, a facile two-step procedure for the conversion of keto groups into, inter alia, methylated vinyl-substituted quaternary carbon sites had become available. Since compounds containing such structural units are fairly common among some families of terpenes, application of the two-step reaction sequence to terpene synthesis assumed importance. However, such undertaking required prior determination of the stereochemical consequence of the alkylation process. Hence, the following short study of the reaction was executed first.

Interaction of either of the stereoisomeric alcohols **1b** and **1c,** prepared by the Grignard reaction between 4-*tert*-butylcyclohexanone and vinylmagnesium bromide,[5] with methylmagnesium bromide and the nickel catalyst produced the terminal olefins **4a** and **5a** and the trisubstituted olefin **3b** in

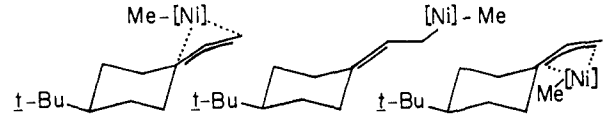


4 5

a, R = CH = CH_2
b, R = CH_2CO_2Me
c, R = CH_2CH_2OH

a 77:4:19 ratio, respectively. The structures of these products were proved in the following fashion. Lithium aluminum hydride reduction of a 4:1 mixture of esters **4b** and **5b,** prepared by a literature procedure,[6] yielded a mixture of alcohols **4c** and **5c,** respectively. Their separation and subsequent pyrolysis over colophony gave the olefins **4a** and **5a,** respectively. Treatment of 4-*tert*-butylcyclohexanone with triphenyl-*n*-propylidenephosphorane produced olefin **3b.**

As the above results indicate, the methyl group delivery process shows high preference for quaternization over terminal carbon alkylation and, most importantly, is greatly stereoselective. This stereochemical feature may be a consequence of the disposition of the equilibrium (**6a** ⇄ **6b** ⇄ **6c**) between π- and σ-allylnickel complexes toward favoring the sterically least

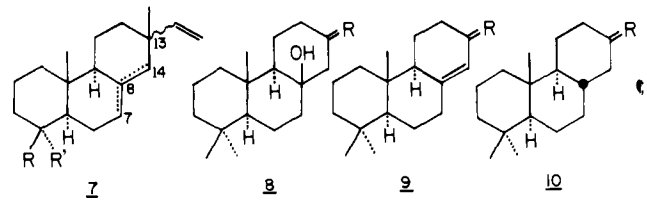


a b c

6

encumbered, quasi-equatorial π-allylnickel intermediate **6c**.[4]

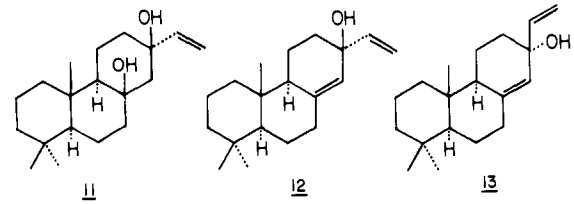
The methyl vinyl quaternary carbon site on a cyclohexane ring is a common feature of the pimaradienic (**7**) or 8-hydroxypimarenic diterpenes. In order to test the above two-step reaction sequence in the terpene field, three ketonic, diterpenic precursors were prepared and subjected to the aforementioned, chemical processes. Oxidative degradation of the diterpenic alcohol, manool, and aldol condensation of the resultant diketone produced ketol **8a**;[7,8] acid-induced dehydration of the latter gave enone **9a**[7,8] and reduction of the unsaturated ketone with lithium in liquid ammonia yielded ketonic tricycle **10a**.[7]



7 8 9 10

a, R = O ; b, R = CHEt

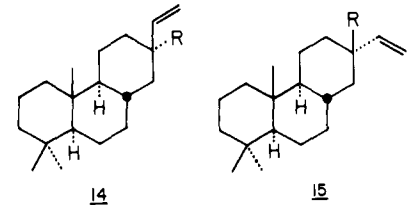
The reaction of ketol **8a** with vinylmagnesium bromide furnished diol **11,** whose infrared spectral analysis revealed the *cis*-glycol relationship. The C(13) configuration of this substance as well as of all 13-vinyl compounds was determined by ^{13}C NMR spectroscopy (vide infra). Interaction of the allyl alcohol **11** with methylmagnesium bromide in the presence of



11 12 13

the nickel catalyst yielded exclusively the terminally methylated olefin **8b,** as shown by spectral means and by degradation of the product to ketol **8a** on buffered osmium tetraoxide–periodate oxidation.[8] This unusual, but undesirable (from the viewpoint of diterpene synthesis) result may reflect the tendency for simultaneous coordination by nickel with the 8-oxy and 13-olefinic, basic sites possible only by methyl group delivery to the unsubstituted terminus of the π-allylnickel intermediate.

Exposure of the unsaturated ketone **9a** to vinylmagnesium bromide afforded alcohols **12** and **13** in a 1:10 ratio, respectively. Hydroxyl for methyl exchange of the latter yielded dienes **9b,** in analogy with the conversion of the divinylcarbinol, 3-methyl-1-vinyl-2-cyclohexenol, into the conjugated diene, 1-methyl-3-*n*-propylidenecyclohexene.[4d] Finally, vinylcarbinol formation from ketone **10a** led to a ca. 1:1 mixture of **14a** and **15a,** each of which was converted into a ca. 72:4:24 mixture



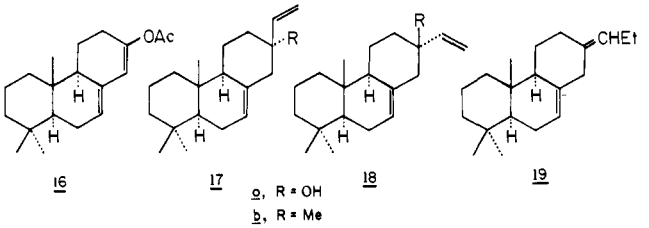
14 15

a, R = OH
b, R = Me

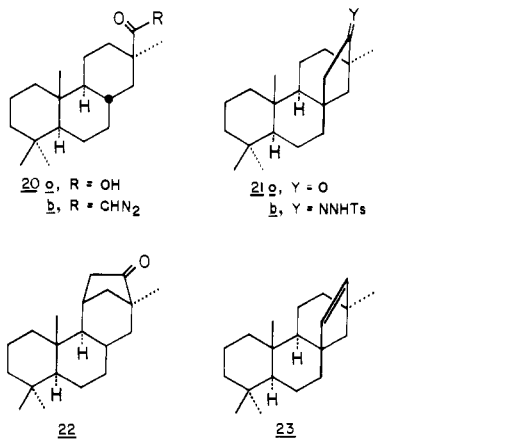
of hydrocarbons **14b, 15b,** and **10b** (two isomers), respectively. Oxidative cleavage reverted the latter back to starting ketone **10a.** Thus the sterically and electronically unencumbered, rigidly held, tricyclic ketone **10a** had behaved in the two-reaction sequence in a manner like the model 4-*tert*-butylcyclohexanone. But, unfortunately, neither **14b** nor **15b** are natural olefins in view of the absence of a 7,8 or 8,14 double bond in their ring system (cf. **7**), although **14b** could be used as an intermediate en route to a nonpimaradienic diterpene (vide infra).

Since the vinylcarbinols derived from a $\Delta^{8,14}$ system (**12** and **13**) had not yielded 13-methyl compounds ($\Delta^{8,14}$-**7**), those obtained from a $\Delta^{7,8}$ system now were sought. This implied starting with a 7-en-13-one, and such a compound (the β,γ-unsaturated ketone isomer of **9a**) was expected to be difficult

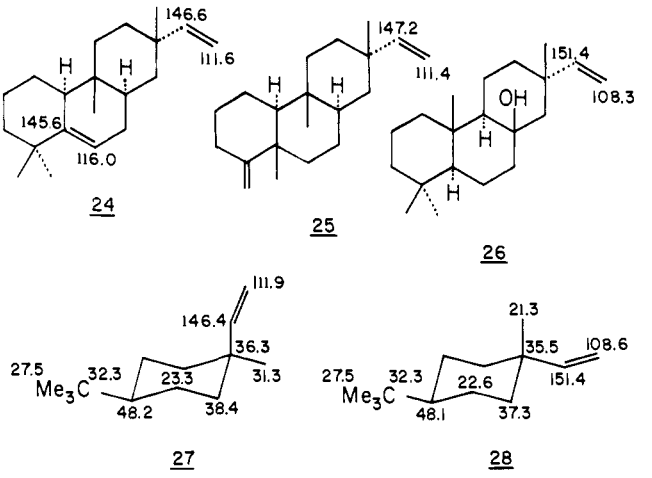
to isolate in view of its ready isomerization into the conjugated ketone **9a**. As a consequence, a scheme for its in situ preparation and immediate trapping was designed. An acid-induced reaction of ketone **9a** with isopropenyl acetate produced the dienol acetate **16**, whose treatment with excess vinylmagnesium bromide and subsequently with a stoichiometric quantity of water yielded presumably the desired ketone. Immediate addition of the solution of the latter to an excess of vinylmagnesium bromide gave a ca. 1:1 mixture of alcohols **17a** and **18a**, albeit in only ca. 25% yield. On the basis of the experience in the hydroxy → methyl conversion with alcohols **1b**, **1c**, **14a**, and **15a** the nickel-induced hydroxy group replacement of either **17a** or **18a** was expected to produce preponderantly **17b** and in minor quantity dienes **18b** and **19**. Sample size limitation in the reactions of alcohols **17a** and **18a** permitted the isolation solely of hydrocarbon **17b**.[9] Interestingly, this compound is the only one of the four possible pimaradienes (**7**) which has not yet been found in nature.



The efficient production of pimarene **14b** (vide supra) made this hydrocarbon available for the synthesis of structurally yet more complex diterpenes. It appeared to be suited ideally for a partial synthesis of the tetracarbocyclic diterpene hibaene (**23**) on the assumption of the fourth ring being attainable by application of the recently developed method of cyclopentanone synthesis involving intramolecular carbon–hydrogen bond insertion of transient carbenoid species produced on copper-catalyzed decomposition of diazomethyl ketones.[10-12] Thus, the tricycle **14b** was transformed into diazo ketone **20b** by exhaustive oxidation and successive treatment of the resultant carboxylic acid **20a** with oxalyl chloride and diazomethane. After much experimentation the thermal decomposition of **20b** in Freon TF[10b] over copper salts and chelates led to the desired ketone **21a**,[13] along with appreciable quantities of the cyclopentanone **22** and even some cyclobutanone mixtures. The reaction then was studied with copper chelates containing electron-withdrawing ligands intended to enhance the tendency of carbenoid insertion at methine over methylene sites and, hence, of the preferred formation of **21a**. Finally, the decomposition of **20b** in the presence of bis(trifluoroacetyltrifluoroacetonato)copper(II) gave a quantitative yield of a 66:1 mixture of **21a** and **22**, respectively. Treatment of the tosylhydrazone of the desired ketone (**21b**) with methyllithium[14] yielded hibaene (**23**).



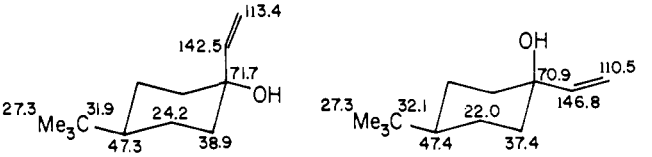
^{13}C NMR Analyses. The stereochemistry of the tricyclic vinylcarbinols and hydrocarbons could be determined easily by inspection of their carbon shifts and comparison thereof with the δ values for pimaradienic diterpenes (**7**),[15,16,19] the vinylcyclohexane models **1b,c**, **4a**, and **5a**, and tricyclic models. The geminally disposed vinyl and methyl groups of the diterpenes and models **4a** and **5a** reflect their conformation by their carbon shifts. Thus an axially oriented vinylmethine, e.g., as in rimuene (**24**) and dolabradiene (**25**), is shielded with respect



27 28

to an equatorial C(15), e.g., as in 8-hydroxyisopimarene (**26**). A similar relationship exists between the vinylmethine of **27** (≡**4a**) and **28** (≡**5a**). Finally, in accord with expectation the axial methyl group of **28** is shielded vis-à-vis the equatorial methyl function of **27**.

Whereas the introduction of a hydroxy group next to the vinyl function introduces shift perturbations for the olefinic carbon centers,[20] the stereochemically diagnostic shifts of the vinylmethines maintain their relationship among the allyl alcohols **29** (≡**1b**) and **30** (≡**1c**) as among their hydrocarbon



29 30

equivalents **27** and **28**, respectively. All carbon shifts of ketones **8a–10a**, alcohols **11–13**, **14a–18a**, and **26**, and hydrocarbons **14b** and **17b** are listed in Table I.

Experimental Section

Melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 137 spectrophotometer and mass spectra on an AEI MS-9 spectrometer. ^{1}H NMR spectra were run on solutions with Me_4Si as internal standard (δ = 0 ppm) and registered on Varian A-60 or Perkin-Elmer R12 spectrometers, while ^{13}C NMR spectra were obtained on a Varian XL-100-15 Fourier transform NMR spectrometer. The δ values denoted on formulas **24–30** are based on deuteriochloroform solutions. The following GPC columns were used: A, 20% SE-30 on Celite (2 m); B, 7% poly(propylene glycol) on Celite (1.4 m).

4-*tert*-Butyl-*n*-propylidenecyclohexane (3b). A solution of 31.4 g of *n*-propyl bromide and 58.0 g of triphenylphosphine in 225 mL of dry nitromethane was refluxed for 19 h and the solvent then removed under vacuum. Washing the residual solid with dry benzene led to 76.0 g of triphenyl-*n*-propylphosphonium bromide, mp 234–237 °C. Anal. ($C_{21}H_{22}BrP$) C, H, Br. Triphenyl-*n*-propylidenephosphorane was made from 15.0 g of the salt and a pentane solution (40 mL, 0.97 M) of *n*-butyllithium in 300 mL of ether. A solution of 6.1 g of 4-*tert*-butylcyclohexanone in 50 mL of ether was added slowly with stirring and the mixture refluxed for 15 h. It then was washed with 5% sulfuric acid and water, dried ($CaCl_2$), and evaporated. Distillation of the residue yielded 4.6 g of crude olefin (containing 12% of ketone by

Table I. Carbon Shifts of Tricyclic Ketones, Alcohols, and Hydrocarbons[a]

	8a	9a	10a	11	12	13	14a	15a	17a	18a	26	14b	17b
C(1)	39.6	39.2	39.3	39.5	39.0	38.7	39.1	39.0	40.0	40.2	39.4	39.1	39.6
C(2)	18.2	18.4	18.7	18.4	18.7	18.7	18.8	18.7	18.7	19.2	18.4	18.9	18.7
C(3)	41.7[b]	41.7	42.0	42.1	41.7	41.7	42.1	42.0	41.7	42.5	42.1	42.3	42.2
C(4)	32.9	33.4	33.2	33.3	33.0	33.0	33.1	33.0	33.2	33.0	33.3	33.2	32.7
C(5)	55.1[c]	53.9	55.1	56.1[e]	54.0	54.2	55.3	55.2	50.0[f]	50.2	56.5[g]	55.5	50.3
C(6)	17.7	21.8[d]	21.5	17.7	21.7	22.2	21.5	21.7	23.5	24.0	17.8	21.7	23.5
C(7)	41.6[b]	35.0	35.7	42.1	35.2	35.2	35.3	35.2	122.2	124.0	43.5	35.7	120.8
C(8)	74.9	162.3	38.0	72.8	144.2	140.7	33.6	31.2	135.3	133.9	72.5	32.2	135.9
C(9)	55.9[c]	51.3	54.3	56.4[e]	50.5	50.7	55.3	55.2	51.7[f]	52.2	56.9[g]	56.1	52.1
C(10)	37.2	38.7	37.0	37.3	39.0	38.0	36.6	36.7	35.3	35.4	37.2	36.8	35.2
C(11)	21.2	20.3[d]	25.6	16.3	18.2	18.7	22.0	19.7	21.5	19.2	17.0	21.0	20.7
C(12)	41.1[b]	36.2	41.3	38.2	38.0	36.0	38.8	37.2	38.5	36.5	38.1	38.2	38.1
C(13)	212.2	202.0	211.6	73.2	69.7	72.2	71.9	71.5	72.5	72.0	36.8	36.7	36.9
C(14)	56.8	126.2	49.1	49.3	125.5	125.6	47.2	45.5	47.5	46.7	51.5	46.8	45.8
C(15)				145.3	146.0	143.2	142.9	146.7	143.0	145.3	151.4	146.6	145.9
C(16)				111.4	112.2	114.0	113.3	110.7	114.2	111.5	108.3	111.6	112.7
C(17)											24.2	31.4	30.0
C(18)	33.3	33.4	33.6	33.6	33.5	33.3	33.6	33.7	33.7	33.7	33.5	33.6	33.5
C(19)	21.5	21.8	21.9	21.7	21.7	21.7	21.8	21.7	22.2	22.7	21.6	21.9	22.1
C(20)	15.0	14.9	14.1	15.4	14.5	14.7	14.2	14.5	15.0	15.5	15.6	14.4	14.6

[a] The δ values are in parts per million downfield from Me_4Si; (Me_4Si) = $\delta(CDCl_3)$ + 76.9 ppm. [b-g] Values bearing the same superscript may be interchanged.

GPC, column A), bp 107–109 °C (20 Torr). Preparative GPC (column A) gave liquid **3b:** IR (CCl_4) 6.00 μ (w, C=C); ^{1}H NMR (CCl_4) δ 0.85 (s, 9, *t*-Bu), 0.93 (t, 3, J = 6 Hz, Me), 5.00 (t, 1, J = 7 Hz, olefinic H); *m/e* (calcd for $C_{13}H_{24}$, 180.1878) 180.1871.

***r*-4-*tert*-Butyl-*c*-1-(β-hydroxyethyl)-1-methylcyclohexane (4c) and *r*-4-*tert*-Butyl-*t*-1-(β-hydroxyethyl)-1-methylcyclohexane (5c).** A 4:1 mixture of acids **4b** and **5b** (OH in place of OMe)[6] was esterified ($MeOH-H_2SO_4$). A solution of 6.0 g of the 4:1 mixture of esters **4b** and **5b,** bp ~140 °C (16 Torr), in 20 mL of ether was added to an ethereal solution of 27 mL of 0.67 M lithium aluminum hydride and thereupon 1.5 mL of water, 1.5 mL of 15% sodium hydroxide solution, and 3 mL of water were added consecutively with stirring. The precipitate was filtered, the filtrate evaporated, and the residue [5.1 g (96%); mp 44–46 °C; GPC (column B) 4:1 mixture of **4c** and **5c**] chromatographed on alumina (activity 2–3). Elution with 19:1 pentane–ethyl acetate yielded 1.32 g of alcohol **4c:** mp 45–46 °C (from pentane); IR (CCl_4) 2.78 (w, OH), 2.96 μ (br w); ^{1}H NMR (CCl_4) δ 0.83 (s, 12, Me_4), 3.53 (t, 2, J = 7 Hz, OCH_2). Anal. ($C_{13}H_{26}O$) C, H, O.

Further elution with the same solvent mixture gave 0.3 g of alcohol **5c:** mp 65–65.5 °C (from pentane); IR (CCl_4) 2.74 (w, OH), 2.96 μ (br w); ^{1}H NMR (CCl_4) δ 0.86 (s, 9, *t*-Bu), 0.89 (s, 3, Me), 3.61 (t, 2, J = 7 Hz, OCH_2). Anal. ($C_{13}H_{26}O$) C, H, O.

***r*-4-*tert*-Butyl-*t*-1-methyl-1-vinylcyclohexane (4a).** A mixture of 206 mg of alcohol **4c** and 215 mg of colophony[21] was refluxed at 360 °C for 5 h and then distilled, affording 125 mg of liquid **4a** (93% pure by GPC, column A): IR (CCl_4) 6.11 (C=C, w), 9.98 ($CH=CH_2$, w), 10.94 μ (m); ^{1}H NMR (CCl_4) δ 0.80 (s, 9, *t*-Bu), 0.89 (s, 3, Me), 4.7–4.9, 5.0–5.1, 5.4–5.8 (m, 3, $CH=CH_2$); *m/e* (calcd for $C_{13}H_{24}$, 180.1878) 180.1875.

***r*-4-*tert*-Butyl-*c*-1-methyl-1-vinylcyclohexane (5a).** The same reaction with 157 mg of **5c** and 164 mg of colophony[21] yielded 98 mg of liquid **5a** (88% pure by GPC, column A): IR (CCl_4) 6.09 (C=C, w), 10.00 ($CH=CH_2$, w), 11.00 μ (m); ^{1}H NMR (CCl_4) δ 0.86 (s, 9, *t*-Bu), 0.96 (s, 3, Me), 4.6–5.0, 5.5–6.0 (m, 3, $CH=CH_2$); *m/e* (calcd for $C_{13}H_{24}$, 180.1878) 180.1875.

Nickel Complex Catalyzed Reaction of Methylmagnesium Bromide with Alcohols 1b and 1c. A 0.74 M ethereal solution of methylmagnesium bromide (35 mL) was distilled under nitrogen nearly to dryness and 20 mL of dry benzene, 418 mg of bis(triphenylphosphine)nickel dichloride, and a solution of 1.00 g of a 5:3 mixture of **1b**[5] and **1c** [mp 54–55 °C, probably a dimorphic form (lit.[5] mp 42–43 °C)] in 15 mL of dry benzene were added successively. The mixture was refluxed under nitrogen for 24 h. Then 25 mL of saturated ammonium chloride solution was added; the organic layer was washed with water, dried (Na_2SO_4), and evaporated. Distillation of the residue [bp 93–98 °C (16 Torr)] yielded 500 mg (50%) of a 77:3:20 mixture (by GPC, column A) of **4a, 5a,** and **3b,** respectively. The three olefins possessed GPC retention times identical with those of authentic samples (vide supra), and **4a** and **3b** were isolated by preparative GPC (column A) and shown spectrally to be the same as authentic specimens.

When the reaction was run with pure alcohols **1b** and **1c** under the same conditions, the olefin mixture was obtained in a 76:4:20 and 77:5:18 ratio, respectively. Olefin **5a** was shown to be stable under the reaction conditions. In many runs the olefin mixture contained a trace (up to 4%) of 4-*tert*-butyl-1-vinylcyclohexene.

Replacement of methylmagnesium bromide by the iodide gave the same result (73:4:23 olefin ratio). In refluxing ether the reaction was exceedingly slow, requiring 1 month for completion (70:10:20 olefin ratio).

13β-Demethylisopimarene-8β,13β-diol (11). A mixture of 90 mL of a methanolic solution of 2.00 g of the diketone derived from the oxidation of manool with osmium tetraoxide and periodic acid at pH 6–7[8] and 50 mL of 4% methanolic potassium hydroxide was stirred at room temperature for 1 **h.** It then was poured into 100 mL of saturated brine solution and extracted with ether. The extract was washed with 50 mL of saturated brine solution, dried ($MgSO_4$), and evaporated. Washing of the residual solid with hexane and crystallization from hexane–benzene yielded 1.36 g (68%) of colorless, crystalline ketol **8a:** mp 206–207 °C (lit.[7] mp 204–205 °C); ^{1}H NMR ($CDCl_3$) δ 0.85, 0.90, 1.01 (s, 3 each, Me_3).

A 1 M tetrahydrofuran solution of vinylmagnesium bromide (8 mL) was placed by syringe into a dry flask under nitrogen and a solution of 500 mg of ketol **8a** in 15 mL of dry tetrahydrofuran added dropwise with stirring over 10 min. The mixture was stirred at room temperature for 3 h, 20 mL of saturated ammonium chloride solution then added slowly, and the mixture extracted with ether. The extract was washed with saturated brine solution, dried ($MgSO_4$), and evaporated. Chromatography of the residue on 35 g of neutral Woelm alumina (activity III) and elution with 2:1 benzene–chloroform yielded a colorless solid whose crystallization from hexane gave 361 mg (67%) of diol **11:** mp 154–155 °C; IR (0.88 or 0.15 M $CHCl_3$ solutions) 2.80 (OH, w), 2.88 (s), 3.00 (s), 6.08 (C=C, w), 10.85 μ ($CH=CH_2$, s); ^{1}H NMR ($CDCl_3$) δ 0.87, 0.87, 1.03 (s, 3 each, Me_3), 4.9–5.5 (m, 2, olefinic CH_2). Anal. ($C_{19}H_{32}O_2$) C, H.

13-*n*-Propylidenedeisopropylabiet-8β-ol (8b). A 1.9 M ethereal solution of methylmagnesium bromide (10 mL) was placed by syringe into a dry flask containing 50 mg of bis(triphenylphosphine)nickel dichloride under nitrogen. A solution of 291 mg of diol **11** in 70 mL of dry benzene (distilled from benzophenone sodium ketyl) was added in one portion and the stirring reaction mixture heated for the removal of ether (until the distillate temperature reached 78 °C), sufficient benzene being added to keep the solution volume at 40 mL. The stirring mixture then was refluxed for 24 h, cooled, poured carefully onto 50 mL of saturated ammonium chloride solution and ice, and stirred until the organic phase had become colorless. The aqueous phase was washed with 50 mL of ether and the combined organic solutions were washed with saturated brine solution, dried ($MgSO_4$),

and evaporated. Chromatography of the residue (280 mg) on 70 g of neutral Woelm alumina (activity III) and elution with hexane and 4:1 hexane–benzene yielded 162 mg (56%) of colorless oil which crystallized slowly. Recrystallization from hexane gave solid alcohol **8b:** mp 68–69 °C; IR (KBr) 2.95 (OH, w), 3.00 μ (w); ^{1}H NMR ($CDCl_3$) δ 0.85, 0.85, 0.95 (s, 3 each, Me_3), 0.95 (t, 3, J = 7 Hz, Me of Et), 5.15 (br t, 1, J = 7 Hz, olefinic CH); *m/e* (calcd for $C_{20}H_{34}O$, 290.2631) 290.2610.

The olefinic alcohol (100 mg) was oxidized with osmium tetraoxide and periodic acid at pH 6–7 according to a published procedure[8] and the crude product chromatographed on 5 g of neutral Woelm alumina (activity III). Elution with 3:1 hexane–ether yielded 68 mg (75%) of ketol **8a,** spectrally identical with an authentic sample.

13-Demethylsandaracopimaradien-13β-ol (12) and 13-Demethylpimaradien-13α-ol (13). The above procedure for the preparation of **11** was followed with enone **9a**[7] [mp 65–67 °C; ^{1}H NMR ($CDCl_3$) δ 0.81, 0.88, 0.93 (s, 3 each, Me_3), 5.85 (br s, 1, olefinic H)] and a twofold molar excess of vinylmagnesium bromide. Chromatography of the crude product on neutral Woelm alumina (activity III) and elution with benzene yielded air-sensitive, crystalline dienol **12** (7%): mp 128–130 °C; IR (KBr) 2.90 (OH, s), 6.02 (C=C, w), 10.10 (CH=CH_2, s), 10.85 μ (s); ^{1}H NMR ($CDCl_3$) δ 0.79, 0.87, 0.90 (s, 3 each, Me_3), 4.9–5.4 (m, 2, vinyl CH_2), 5.3–5.4 (m, 1, H-14), 5.91 (dd, 1, J = 10, 17 Hz, vinyl CH). Elution with 2:1 benzene–chloroform gave a 68% yield of isomer **13:** mp 66.5–68 °C (hexane and 4:1 water–ethanol); IR (KBr) 3.00 (OH, s), 6.02 (C=C, w), 6.15 (w), 10.02 (CH=CH_2, m), 10.83 μ (m); ^{1}H NMR ($CDCl_3$) δ 0.74, 0.85, 0.88 (s, 3 each, Me_3), 4.9–5.3 (m, 2, vinyl CH_2), 5.28 (br s, 1, H-14), 5.95 (dd, 1, J = 11, 17 Hz, vinyl CH); *m/e* (calcd for $C_{19}H_{30}O$, 274.2297) 274.2287.

13-*n*-Propylidenedeisopropylideneneoabietane (9b). The above procedure for the preparation of **8b** was followed with dienol **13** and a tenfold molar excess of methylmagnesium bromide. Chromatography of the crude product on neutral Woelm alumina (activity III) and elution with hexane yielded a hydrocarbon fraction (92%) whose preparative GPC (8 ft × 0.25 in. 10% SE-30 on Chromosorb P column, 215 °C) afforded a 74% yield of liquid diene **9b:** IR (neat) 5.90 μ (C=C, w); ^{1}H NMR ($CDCl_3$) δ 0.79, 0.86, 0.91 (s, 3 each, Me_3), 0.92 (t, 3, J = 7 Hz, Me of Et), 5.38, 5.74 (br s, 1 each, olefinic Hs); *m/e* (calcd for $C_{20}H_{32}$, 272.25039) 272.25040.

13-Demethylpimaren-13α-ol (14a) and 13-Demethylisopimaren-13β-ol (15a). The above procedure for the preparation of **11** was followed with ketone **10a**[7] [mp 95–97 °C; ^{1}H NMR ($CDCl_3$) δ 0.87, 0.87, 0.90 (s, 3 each, Me_3)] and a twofold excess of vinylmagnesium bromide. Chromatography of the crude, oily product on neutral Woelm alumina (activity III) and elution with 2:1 hexane–benzene gave a fraction whose crystallization from hexane and sublimation [68 °C (0.02 Torr)] yielded crystalline, colorless alcohol **15a** (39%): mp 72–72.5 °C; IR (neat) 3.00 (OH, s), 6.15 (C=C, w), 10.13 (CH=CH_2, m), 10.90 μ (s); ^{1}H NMR ($CDCl_3$) δ 0.86, 0.86, 0.88 (s, 3 each, Me_3), 5.05 (dd, 1, J = 11, 2 Hz, vinyl CH_2 H), 5.27 (dd, 1, J = 17, 2 Hz, vinyl CH_2 H), 6.05 (dd, 1, J = 17, 11 Hz, vinyl CH). Anal. ($C_{19}H_{32}O$) C, H.

Further elution with benzene gave a fraction whose crystallization from hexane afforded colorless crystals of alcohol **14a** (31%): mp 111–113 °C; IR (neat) 2.95 (OH, s), 6.20 (C=C, w), 10.15 (CH=CH_2, m), 10.88 μ (s); ^{1}H NMR ($CDCl_3$) δ 0.82, 0.86, 0.86 (s, 3 each, Me_3), 5.17 (dd, 1, J = 10, 2 Hz, vinyl CH_2 H), 5.41 (dd, 1, J = 18, 2 Hz, vinyl CH_2 H), 6.21 (dd, 1, J = 18, 10 Hz, vinyl CH). Anal. ($C_{19}H_{32}O$) C, H.

Pimarene (14b), Isopimarene (15b), and 13-*n*-Propylidenedeisopropylabietane (10b). Alcohol **15a** (680 mg) was treated with a tenfold excess of methylmagnesium bromide in the presence of the nickel catalyst by the procedure described above for the conversion of alcohol **11** into **8b.** Chromatography of the crude product on 50 g of neutral Woelm alumina (activity III) and elution with hexane afforded 570 mg (84%) of a mixture of hydrocarbons whose GPC analysis (7 ft × 1/8 in. 5% SE-30 column, 155 °C) revealed the presence of three products, **14b** (72%), **15b** (4%), and **10b** (24%), in the order of increasing retention times. Chromatography of the oil on 50 g of neutral Woelm alumina (activity I) and slow elution with hexane gave 296 mg of one hydrocarbon whose purification by preparative GPC yielded crystalline **14b:** mp 34–35 °C; IR (neat) 6.12 (C=C, m), 10.01 (CH=CH_2, m), 10.98 μ (s); ^{1}H NMR ($CDCl_3$) δ 0.80, 0.82, 0.83, 0.90 (s, 3 each, Me_4), 4.8–5.0 (m, 2 vinyl CH_2), 5.76 (dd, 1, J = 17, 12 Hz, vinyl CH). Anal. ($C_{20}H_{34}$) C, H.

Further elution gave a mixture of the three hydrocarbons whose separation was executed by preparative GPC (8 ft × 0.25 in. 10% SE-30 on Chromosorb P column, 215 °C). Liquid **15b:** IR (neat) 6.10 (C=C, m), 10.04 (CH=CH_2, m), 11.00 μ (s); ^{1}H NMR ($CDCl_3$) δ 0.83, 0.83, 0.87, 0.97 (s, 3 each, Me_4), 4.7–5.0 (m, 2, vinyl CH_2), 5.75 (dd, 1, J = 18, 11 Hz, vinyl CH); *m/e* (calcd for $C_{20}H_{34}$, 274.2660) 274.2655.

Liquid **10b:** IR (neat) 6.02 (C=C, w). 11.90 μ (C=CH, m); ^{1}H NMR ($CDCl_3$) δ 0.79, 0.82, 0.84 (s, 3 each, Me_3) 0.91 (t, 3, J = 7 Hz, Me of Et), 5.03 (br t, 1, J = 7 Hz, olefinic H); *m/e* (calcd for $C_{20}H_{34}$, 274.2660) 274.2654. Oxidation of the olefin with osmium tetraoxide and periodic acid at pH 6–7 according to a published procedure,[8] chromatography of the crude product (100 mg) on 5 g of neutral Woelm alumina (activity III), and elution with 1:1 hexane–benzene yielded 60 mg (67%) of ketone **10a,** spectrally identical with an authentic sample.

A nickel-catalyzed treatment of alcohol **14a** with methylmagnesium bromide analogous to that of **15a** above led to a 94% yield of a mixture of hydrocarbons containing **14b** (71%), **15b** (4.4%), and **10b** (24.6%) by GPC analysis.

13-Demethyl-7(8)-pimaradien-13α-ol (17a) and 13-Demethylisopimaradien-13β-ol (18a). A slow distillation of a solution of 2.60 g of ketone **9a** and 300 mg of *p*-toluenesulfonic acid in 100 mL of isopropenyl acetate for 4 h reduced the mixture to half its original volume. Ether (200 mL) was added and the solution washed with saturated sodium bicarbonate solution and dried (Na_2SO_4). The solvent and excess acetylating agent were removed at 15 Torr, and the residue was placed on a column of 50 g of acid Woelm alumina (activity III) and eluted with 1:1 hexane–benzene. This led to 2.20 g (73%) of air- and moisture-sensitive enol acetate **16:** melting point between 0 °C and room temperature; IR (neat) 5.70 (C=O, s), 6.00 (C=C, w), 6.12 μ (w); ^{1}H NMR (benzene-d_6) δ 0.72, 0.81, 0.85 (s, 3 each, Me_3), 1.72 (s, 3, $COCH_3$), 5.28 (br s, 1, H-14), 5.82 (d, 1, J = 4 Hz, H-7).

A solution of 167 mg (0.58 mmol) in 4 mL of dry tetrahydrofuran was added via syringe under nitrogen to a stirring, 1.15-mmol tetrahydrofuran solution of vinylmagnesium bromide (vide supra) and the mixture stirred at room temperature for 4 h. After the addition of 1.16 mmol of water the solution was added immediately to a stirring, 10.2-mmol tetrahydrofuran solution of vinylmagnesium bromide (vide supra) and the mixture stirred under nitrogen for 12 h. Upon the slow addition of 8 mL of saturated ammonium chloride solution an organic layer separated and the aqueous solution was extracted with 40 mL of ether. The combined organic solutions were washed with 4 mL of saturated brine solution, dried ($MgSO_4$), and evaporated. Chromatography of the residual gum (260 mg) on 13 g of neutral Woelm alumina (activity III) and elution with 1:1 hexane–benzene yielded 18 mg (11%) of liquid alcohol **18a:** IR (neat) 2.95 (OH, s), 6.08 (C=C w), 10.10 (CH=CH_2, s), 10.90 μ (s); ^{1}H NMR ($CDCl_3$) δ 0.88, 0.88, 0.93 (s, 3 each, Me_3), 5.05 (dd, 1, J = 10, 2 Hz, vinyl CH_2 H), 5.22 (dd, 1, J = 18, 2 Hz, vinyl CH_2 H), 5.53 (br s, 1, H-7), 6.00 (dd, 1, J = 18, 10 Hz, vinyl CH); *m/e* (calcd for $C_{19}H_{30}O$, 274.2297) 274.2279.

Elution with benzene yielded 22 mg (14%) of liquid alcohol **17a:** IR (CCl_4) 3.00 (OH, m), 6.05 (C=C, w), 10.02 (CH=CH_2, s), 10.80 μ (s); ^{1}H NMR ($CDCl_3$) δ 0.78, 0.89, 0.92 (s, 3 each, Me_3), 5.10 (dd, 1, J = 11, 2 Hz, vinyl CH_2 H), 5.27 (dd, 1, J = 18, 2 Hz, vinyl CH_2 H). 5.45 (br s, 1, H-7), 6.00 (dd, 1, J = 18, 11 Hz, vinyl CH); *m/e* (70 eV) 274 (M^+, very weak).

$\Delta^{7(8)}$-Pimaradiene (17b). Alcohol **17a** (227 mg) was treated with a tenfold excess of methylmagnesium bromide in the presence of the nickel catalyst by the procedure described above for the conversion of diol **11** into alcohol **8b.** GPC analysis (8 ft × 0.25 in. 10% SE-30 on Chromosorb P column, 210 °C) of the crude product revealed the presence of two main substances in ca. 2:1 ratio. The major product (longer retention time) proved to be air-sensitive and decomposed on chromatography, whereas chromatography on 30 g of neutral Woelm alumina (activity III) and elution with hexane yielded 70 mg (25%) of the minor component whose final purification by preparative GPC gave liquid hydrocarbon **17b:** IR (neat) 6.02 (C=C, w), 6.15 (m), 10.00 (CH=CH_2, m), 10.97 μ (s); ^{1}H NMR ($CDCl_3$) δ 0.78, 0.85, 0.89, 0.94 (s, 3 each, Me_4), 4.7–5.1 (m, 2, vinyl CH_2), 5.34 (br s, 1, H-7), 5.67 (dd, 1, J = 18, 10 Hz, vinyl CH); spectrally different from isopimaradiene. Anal. ($C_{20}H_{32}$) C, H.

A similar reaction executed on alcohol **18a** yielded the same hydrocarbon mixture. The GPC retention time of a third, albeit very

minor component was identical with that of authentic isopimaradiene.

Oxidation of Pimarene (14b). A solution of 63 mg of **14b** in 15 mL of *tert*-butyl alcohol was treated with 25 mL of water, 430 mg of sodium metaperiodate, 20 mg of potassium permanganate, and 415 mg of potassium carbonate, and the mixture was stirred vigorously for 24 h.[22] It then was acidified with 10% hydrochloric acid and extracted with ether. The extract was washed with saturated sodium carbonate solution and the washings were extracted with ether. The sodium salt of the acidic product being insoluble in both water and ether and therefore precipitating at the interface, the solid and the aqueous solution were acidified with 10% hydrochloric acid and extracted with ether. The extract was dried ($MgSO_4$) and evaporated. Crystallization of the residue from hexane and sublimation (160 °C, 0.05 Torr) yielded 62 mg (92%) of acid **20a:** mp 193.5–195 °C; Ir (CCl_4) 3.0–3.4 (OH, m), 5.90 μ (C=O, s); ^{1}H NMR ($CDCl_3$) δ 0.80, 0.82, 0.84 (s, 3 each, Me_3), 1.18 (s, 3, 13α-Me). Anal. ($C_{19}H_{32}O_2$) C, H.

16-Diazo-15-pimarone (20b). The acid **20a** (200 mg) was added to 2 mL of freshly distilled oxalyl chloride, the frothing mixture stirred for 2 h, and the excess oxalyl chloride then removed by vacuum distillation. A solution of the resultant crystalline acid chloride in 40 mL of dry ether was added dropwise over a 4-h period to an ice-cold, well-stirring, ethereal solution of 2.0 mmol of diazomethane. The solution was stirred at 0 °C an additional 4 h and kept at room temperature for 12 h. The excess diazomethane was blown off under a stream of nitrogen and the solution concentrated. Chromatography of the residue on 6 g of Baker silica gel (60–200 mesh) [in view of the material's decomposition on chromatography on Woelm alumina (activity IV) or Florisil] and elution with 3:1 hexane–benzene gave a solid whose crystallization from hexane led to 160 mg (75%) of crystalline diazo ketone **20b:** mp 122–123 °C; IR (CCl_4) 4.76 (N_2CH, s), 6.11 μ (C=O, s); ^{1}H NMR (CCl_4) δ 0.76, 0.79, 0.80 (s, 3 each, Me_3), 0.98 (s, 3, 13α-Me), 5.28 (s, 1, N_2CH). Anal. ($C_{20}H_{32}ON_2$) C, H, N.

15-Hibone (21a). The following procedure was used for the evaluation of the efficacy of the copper-containing catalysts in the decomposition of diazo ketone **20b.** A solution of 3 mg of the latter in 20 mL of Freon TF (i.e., Du Pont's 1,1,2-trichloro-1,2,2-trifluoroethane) was added dropwise over a 3-h period to a refluxing suspension (or solution) of 25 mg of catalyst in 60 mL of Freon TF, and the mixture was then stirred and refluxed for 20 h. GPC analysis (10 ft × 1/8 in. 10% Carbowax 20M column, 200 °C) indicated the following **21a/22** product ratios: anhydrous cupric sulfate, 1.5:1 and 15% cyclobutanones; cupric trifluoromethanesulfonate, 1.4:1; cupric trifluoroacetate, 2:1; bis(acetylacetonato)copper(II), 4.3:1; (trimethyl phosphite)copper(I) chloride, 4.3:1; cupric acetate, 7.4:1.

A solution of 95 mg of diazo ketone **20b** in 100 mL of cyclohexane was added extremely slowly to a refluxing suspension of 50 mg of colorless, flame-dried, anhydrous cupric sulfate in 100 mL of cyclohexane and the mixture was refluxed for 48 h. It was filtered and the filtrate evaporated. Sublimation of the residue gave 84 mg (96%) of a ketone mixture whose GPC analysis (10 ft × 1/8 in. 10% Carbowax 20M column, 220 °C) revealed the presence of three components in 1.5:1:0.44 ratio. Slow chromatography of the mixture on 3 g of Baker silica gel (60–200 mesh) and elution with hexane gave the minor product in a partially solid state. Its ^{1}H NMR ($CDCl_3$) spectrum revealed it to be a mixture and its IR (neat) spectrum [5.64 μ (C=O, s)] exclusively cyclobutanones. This material was not investigated further. Preparative GPC (10 ft × 0.25 in. 20% Carbowax 20M, 220 °C) led to the major product **21a** [mp 102–103 °C (lit.[13] mp 102–103 °C); IR and ^{1}H NMR spectra identical with those of an authentic sample][13,23] and the medium-sized component **22** [mp 103–105 °C; IR (KBr) 5.76 μ (C=O, s); ^{1}H NMR ($CDCl_3$) δ 0.84, 0.84, 0.92, 0.98 (s, 3 each, Me_4), 2.15 (dd, 1, J = 17, 7 Hz, H of $COCH_2$), 2.41 (dd, 1, J = 17, 3 Hz, H of $COCH_2$), 2.58 (tm, 1, J = 7 Hz, probably H-11); *m/e* (calcd for $C_{20}H_{32}O$, 288.2453) 288.2428].

A solution of 30 mg of diazo ketone **20b** in 100 mL of Freon TF was added slowly to a refluxing solution of 30 mg of bis(trifluoroacetyltrifluoroacetonato)copper(II) dihydrate[24] in 150 mL of Freon TF and the mixture refluxed for 24 h. It then was evaporated and a hexane solution of the residue filtered through a column of 1 g of neutral Woelm alumina (activity III). Sublimation [130 °C (3.5 Torr)] of the evaporated filtrate (31 mg) gave 27.4 mg (100%) of a 66:1 **21a/22** ketone mixture whose GPC separation (above column, 220 °C) led to crystalline hibone (**21a**), mp 102–103 °C.

Hibaene (23). A solution of 60 mg of *p*-toluenesulfonylhydrazine and 30 mg of hibone (**21a**) in 1 mL of acetic acid was heated at 100 °C for 15 min and then cooled. The resultant precipitate was filtered and washed with 5 mL of acetic acid and of methanol. The filtrate was concentrated, chromatographed on 1 g of neutral Woelm alumina (activity III), and eluted with 1:1 hexane–benzene. Crystallization of the combined precipitate and eluate, 42 mg (90%), from methanol and from 1:1 hexane–benzene yielded hydrazone **21b:** mp 223–224 °C dec; IR (KBr) 3.18 (NH, m), 6.10 μ (C=N, s); ^{1}H NMR ($CDCl_3$) δ 0.77, 0.77, 0.83, 0.97 (s, 3 each, Me_4), 2.38 (s, 3, aryl Me), 7.24, 7.81 (d, 2 each, J = 7 Hz, aromatic Hs). Anal. ($C_{27}H_{40}O_2N_2S$) C, H, N.

A 2.0 M ethereal solution of methyllithium (1 mL) was added by syringe in one portion to a solution of 33 mg of hydrazone **21b** in 5 mL of anhydrous ether and the mixture refluxed for 24 h. Water was added cautiously to the cooled solution and the aqueous layer washed with 5 mL of ether. The combined ether solutions were washed with 10 mL of saturated brine solution, dried (Na_2SO_4), and evaporated. Chromatography of the residue on 5 g of neutral Woelm alumina (activity III) and elution with hexane gave 17 mg (87%) of an oil whose GPC analysis (10 ft × 1/8 in. 10% SE-30 column, 225 °C) showed it to be a 16:1 two-component hydrocarbon mixture. Preparative GPC (8 ft × 0.25 in. 10% SE-30 on Chromosorb P column, 220 °C) gave, as the major product, hibaene (**23**): mp 29–30 °C (lit.[13] mp 29.5–30.5 °C); IR and NMR spectra and GPC retention time identical with those of an authentic sample.[23]

References and Notes

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