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The Acid-Catalyzed Isomerization of Thujopsene

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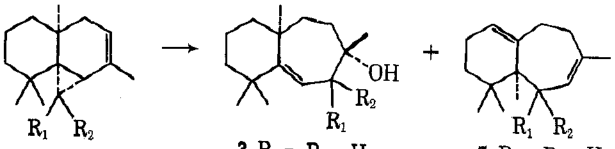
The acid-catalyzed isomerization of (−)-thujopsene (**1**) under nonaqueous conditions proceeds principally *via* the isolable spiro olefin intermediates α- and β-chamigrene (**8** and **9**) to a complex mixture of isomeric tricyclic olefins. The major component of this complex mixture is rigorously shown to be 7,10-ethano-4,4,7-trimethyl-1(9)-octalin (**10**).

The tricyclic sesquiterpene (−)-thujopsene is known to occur widely in genera belonging to the natural order Cupressales.[1] Originally isolated from Hibawood oil,[2] it has subsequently been shown to be present also in American cedarwood oil.[3] The first correct structure for thujopsene was deduced by Erdtman and Norin[4] and subsequent stereospecific total syntheses[5] of its racemate and evidence from chemical degradation[6] has confirmed the earlier[4] structural assignment. The absolute configuration of (−)-thujopsene was initially assigned by Enzell[7] and later confirmed by Dauben and Oberhansli[8] and the naturally occurring sesquiterpene is thus known to possess structure **1**.

With the structure of (−)-thujopsene well established, attention has focused on the chemistry of this unusual molecule, especially protonation with appropriate acid catalysts to the rearrangement-prone cyclopropylcarbinyl cation system. Thujopsene (**1**) treated with aqueous oxalic acid was reported by Nagahama[9] to give an unidentified hydrocarbon and widdrol (**3**). Dauben and Friedrich[10,11] reported that treatment of thujopsene with perchloric acid in aqueous dioxane afforded primarily widdrol (**3**) and a bicyclic diene identified as 1,4,11,11-tetramethylbicyclo[5.4.0]undeca-3,7-diene (**5**). Subsequent isomerization studies[12-14] employing racemic dideuteriothujopsene (**2**) afforded dideuteriowiddrol (**4**) and dideuterated bicyclic diene **6** with the deuterium label in the final products on different carbon atoms. These authors presented a mechanism which accounted for the divergent pathways observed. Further acid treatment[11,13] of diene **5** afforded a tricyclic hydrocarbon identified as 2,2,3,7-tetramethyltricyclo[5.2.2.0^{1,6}]undec-3-ene (**7**).



1, $R_1 = R_2 = H$
2, $R_1 = R_2 = D$

3, $R_1 = R_2 = H$
4, $R_1 = R_2 = D$

5, $R_1 = R_2 = H$
6, $R_1 = R_2 = D$

Recently Itô and coworkers[15] have reported similar results in their studies on the perchloric acid–aqueous dioxane isomerizations of thujopsene (**1**) and, in addition, identified small amounts of β-chamigrene (**9**) and a tricyclic hydrocarbon assigned structure **10** but whose structure was not rigorously proved.

We have found that the acid-catalyzed isomerization of (−)-thujopsene (**1**) under nonaqueous conditions affords as the major initial products the isolable spiro olefin intermediates α- and β-chamigrene (**8** and **9**).[16,17] Subsequent rearrangement affords an isomeric series of principally two tricyclic olefins which we shall here designate as olefin A and olefin B. We will discuss later the rigorous structure proof of olefin B and its formulation as 7,10-ethano-4,4,7-trimethyl-1(9)-octalin (**10**).

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TABLE I

Entry	Acid	Acid/ thujopsene wt ratio[a]	T, °C	Time, hr	Yield, %, hydrocarbons	**7**	**11**[b]	**10**[b]	**9**	**5**	**8**	Unidentified[c]
					Thujopsene							
1	Formic (90%)	0.1	100	1	96	0	0	0	28	8	55	9
2	Polyphosphoric	0.02	40	3	93	2	0	0	29	13	53	3
3	Polyphosphoric	0.4	40	3	89	11	28	42	0	0	9	10
4	Phosphoric (100%)	0.4	40	3	93	7	5	18	6	11	46	7
5	Perchloric (70%)	0.4	40	3	90	17	30	44	0	0	2	7
6	Sulfuric (98%)	0.4	40	3	93	34	21	29	0	0	7	9
					Chamigrenes[d]							
7	Polyphosphoric	0.4	40	3	95	13	24	37	0	0	13	13
8	Sulfuric (98%)	0.4	40	3	90	18	28	42	0	0	1	11
9	Perchloric (70%)	0.4	40	3	89	17	29	42	0	0	1	11

[a] Entry 1 contains no acetic acid; for the other entries a 1:1 wt ratio of thujopsene to acetic acid was employed. [b] Analysis on a Carbowax 20M column. Analysis on a liquid crystal or an SF-96 column shows that these two components are actually five compounds in a 5:30:12:18:35 ratio. [c] Entries 3 and 5-9 contain approximately 5% cuparene (**13**) reported under unidentified hydrocarbons. [d] The distilled mixture obtained from entry 1 was used in these isomerizations.

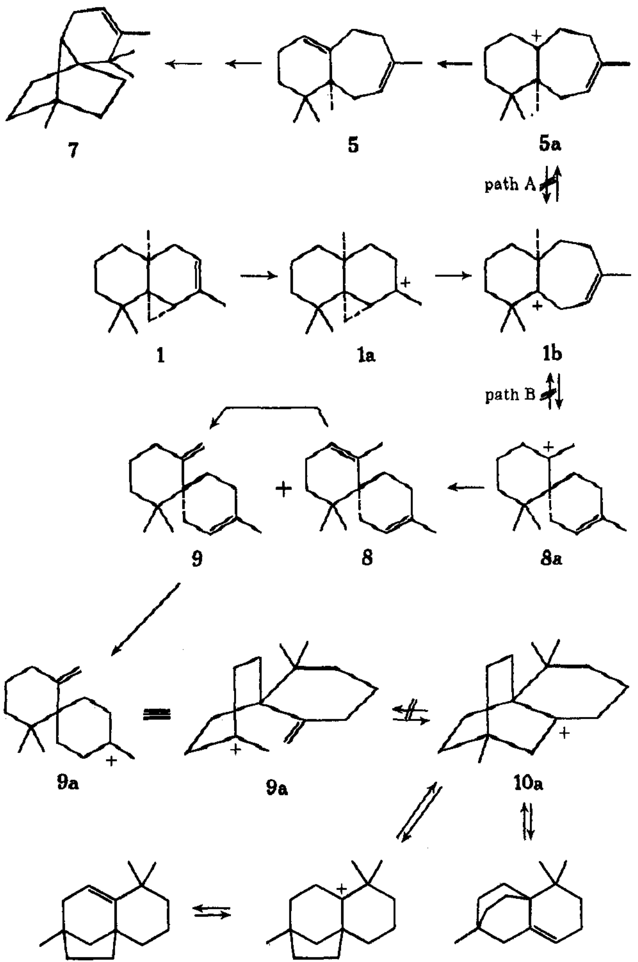
Our general acid isomerization conditions employed were various concentrations of strong mineral acids in acetic acid. Acetic acid, although not a sufficiently strong acid to isomerize thujopsene at the temperatures employed, served as a useful solvent in which to conduct the desired isomerizations. These conditions led to high yields of distilled isomerized olefin products and to low amounts (less than 5%) of acetate byproducts. The reaction mixtures were analyzed directly by gas chromatography and mass spectrometry, and individual components were subsequently purified *via* spinning-band distillation and identified by comparison of spectral data with authentic samples where available. Some of our pertinent results are summarized in Table I.

Treatment of (−)-thujopsene with formic acid (entry 1) or low ratios of polyphosphoric acid in acetic acid (entry 2) led principally to the optically active α- and β-chamigrenes (**8** and **9**) with only a minor amount of the bicyclic diene **5** reported by previous workers[10,11,15] as the principal product under aqueous acid conditions.

The chamigrene mixture above when treated with higher ratios of strong mineral acid in acetic acid (entries 7-9) led to the formation of the tricyclic olefin mixture **7**, **10**, and **11**. Almost identical ratios were obtained when (−)-thujopsene itself was subjected to the same conditions (entries 3 and 5), while sulfuric acid (entry 6) afforded a somewhat higher amount of tricyclic olefin **7**. Tricyclic olefin **7** is optically active, whereas olefins **10** and **11** are both inactive. Reactions interrupted at partial conversion (entry 4) showed that the β-chamigrene (**9**) disappeared far more rapidly than the α-chamigrene (**8**) and that tricyclic olefin **10** was formed more rapidly than olefin **11**.

Although these results would seem to imply the involvement of a rapid **9** → **10** conversion and a slow **8** → **11** conversion, the rearrangement pathway is best accommodated *via* a slow **8** → **9** isomerization followed by a rapid **9** → **10** conversion and a subsequent slow **10** → **11** isomerization as outlined in Scheme I. Protonation of (−)-thujopsene (**1**) leads to the bicyclic cation **1b** *via* cyclopropyl ring opening of initially formed cation **1a**. Cation **1b** is a key intermediate in this sequence since two divergent rearrangement pathways are possible. Path A affords cation **5a** *via* angular methyl migration and generation of bicyclic diene **5** by subsequent proton loss. This pathway has already been shown to hold for diene **5** by the deuterium labeling studies[12-14] which led to the dideuteriodiene **6** from dideuteriothujopsene (**2**). Alternatively, path B would

SCHEME I



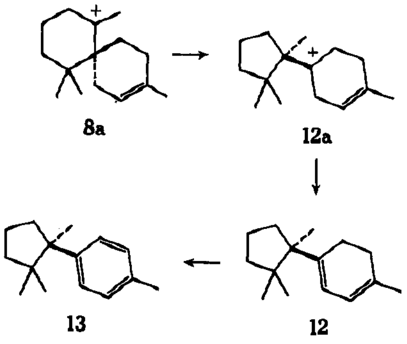
afford the spiro cation **8a** *via* ring contraction from cation **1b**, subsequent proton loss generating both α-chamigrene (**8**) and β-chamigrene (**9**).

Bicyclic diene **5** is reported[11] to be optically active and we also find that both the α- and β-chamigrenes (**8** and **9**) generated under our conditions retain high optical purity of the same sign of rotation as the chamigrenes isolated from natural sources.[16,17] These results imply highly stereoselective bond migrations during the isomerization process. Itô and coworkers[15] likewise report that the β-chamigrene (**9**) isolated under their conditions retains high optical purity.

Subsequent rearrangements of diene **5** eventually lead to tricyclic olefin **7** reported[11,13] and confirmed by us to be optically active. The α-chamigrene (**8**) slowly isomerizes to β-chamigrene (**9**) which, known from its chemistry to preferentially react at the less hindered trisubstituted double bond,[16] readily generates cation **9a**. Cyclization of cation **9a** to tricyclic cation **10a** then affords inactive (no asymmetric center) tricyclic olefin **10**. These findings are substantiated by the observations of Itô and coworkers[15] that β-chamigrene (**9**) upon further mild isomerization affords the tricyclic hydrocarbon **10** as the major product.

Several minor components of unknown structures are combined in Table I under the heading unidentified hydrocarbons. For entries 3 and 5–9 we have shown approximately 50% of these unidentified components to be identical with the known hydrocarbon cuparene (**13**).[18] The formation of this optically active hydrocarbon undoubtedly arises *via* cuprenene **12**, known[19] to readily aromatize to cuparene (**13**) as outlined in Scheme II. This product also exhibits a high degree of optical purity again pointing to stereoselective bond migrations during the isomerization process.

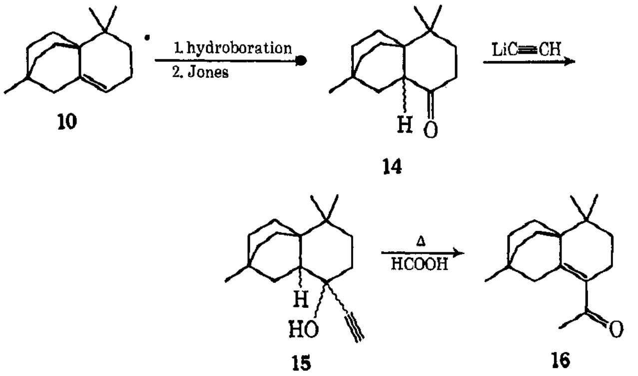
Scheme II



Olefins A and B were separated free from contamination by each other *via* careful spinning-band distillation; however, nmr evidence indicated that neither component was pure. A column was eventually found which showed that the 40:60 mixture of product olefins A and B contained at least five components in a 5:30:12:18:35 ratio. Separate acid treatment of either olefin A or B afforded identical mixtures of the same five components.

In view of the complexity of the above equilibrium mixture we concentrated our efforts on the structure elucidation of olefin B since this component was the one initially formed from β-chamigrene (**9**) and also was the major (35%) component of the equilibrium mixture. A spinning-band prepared sample of olefin B (judged by nmr to be 65–70% pure, but free from olefin A) was utilized in subsequent transformations as outlined in Scheme III. Ketone **14** was readily prepared *via* hydroboration–oxidation of olefin **10** and Jones[20] oxidation of the resulting secondary alcohol mixture. Treatment of ketone **14** with lithium acetylide afforded the tertiary alcohol derivative **15** which smoothly rearranged upon heating in formic acid to the methyl ketone known[21] to possess structure **16**. The structure of olefin B is thus rigorously shown to be the tricyclic olefin 7,10-ethano-4,4,7-trimethyl-1(9)-octalin (**10**).

Scheme III



We have as yet no definitive proof for the structure of olefin A, the 30% equilibration component, but prefer structure **11**. Spectral evidence is not unequivocal and other reasonable structures can be postulated. No attempts have been made to elucidate the structures of the remaining minor equilibration components.

The factors which govern the ratio of path A to path B (Scheme I) are not clearly understood. We confirm earlier observations[11,15] that thujopsene treated with dilute perchloric acid in aqueous dioxane affords predominantly the bicyclic diene **5** (path A) with only minor amounts of α- and β-chamigrene. Our conditions utilizing acetic acid or formic acid as solvent greatly favor the path B products and we observe in general only minor amounts (∼15%) of products derived *via* path A.

Indirect evidence strongly suggests that the initial products (**8** and **9**) from path B do not lead to any products (**5**) from path A and vice versa. The known amount of path A derived products (Table I, entry 1, olefins **7** and **5**) of thujopsene treated with formic acid is roughly the same as that obtained when this mixture is further isomerized with stronger acids (entries 7–9). Some deviation is to be expected since the fate of the undefined components (7%) is unknown. Furthermore, sulfuric acid–acetic acid treatment of thujopsene (entry 6) affords significantly more products from path A than when the chamigrene mixture (entry 8) is employed under the same conditions. This latter result implies a difference in the fate of initially formed cation **1b** (path A *vs.* path B ratio) and not that cations **8a** and **5a** themselves interconvert *via* the intermediacy of cat-

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ion **1b**, which would predict identical product ratios in entries 6 and 8.

More direct evidence on this question was obtained by the isomerization of a sample of α-chamigrene (containing 4% of an unidentified component but no bicyclic diene **5**) with sulfuric acid–acetic acid. Detailed analysis of the product showed only 1.5% of tricyclic olefin **7** derived from path A, the remaining products identified as the olefin A and B mixture (93%), cuparene (**13**, 3.5%), and an unidentified component (2%). Cation **8a** must of necessity be involved in this transformation in order to convert to cation **9a** for further cyclization, but virtually no conversion to cation **1b** and entry to the path A products is observed. Similar results have recently been reported[15] for the further isomerization of β-chamigrene (**9**).

Olefin **7** clearly does not arise from the olefin A and B mixture since isomerization of a sample of olefin B (**10**) under our standard conditions afforded no tricyclic olefin **7** or any of the chamigrenes, implying no appreciable reversal to cation **9a** from cation **10a**. Furthermore, Dauben and Friedrich[13] have already shown that bicyclic diene **5** is converted to tricyclic olefin **7** in 70% yield upon further isomerization and thus implying minimal crossover of this path A product to the path B products observed under our conditions.

Closer inspection of the results of the previously reported[11,15] isomerizations under aqueous acid conditions shows that the initial reaction of thujopsene is hydration to widdrol (**3**) and that the isomerized products may actually arise from the solvolysis of this tertiary alcohol. Both compounds, however, should afford the same intermediate cations and lead to the same products under identical treatment. Indeed, treatment of widdrol (**3**) with sulfuric acid–acetic acid gave the same product mixture as obtained directly from thujopsene showing that under nonaqueous conditions the path B products again predominate.

The difference in behavior between the two sets of isomerization conditions (strong acid in aqueous *vs.* nonaqueous media) apparently lies in subtle solvation effects on the intermediate cations **1a** and **1b** which lead to path A preference in aqueous acid and to path B preference in nonaqueous acid. Thus by appropriate choice of conditions a number of different isomerization olefins can be obtained as the major products.

Experimental Section

Materials and Equipment.—(−)-Thujopsene was readily obtained in 99% purity by careful fractional distillation of Hibawood oil through a 2-ft Goodloe column: bp 67–68° (0.5 mm); $n^{20}{}_{\mathrm{D}}$ 1.5050; $[\alpha]^{25}{}_{\mathrm{D}}$ −92.5° (neat).

Spectra were recorded using a Perkin-Elmer 457 grating ir spectrophotometer, Varian A-60A nmr spectrometer, and a Perkin-Elmer 270 double-focusing mass spectrometer. Spinning-band separations were accomplished with a Nester-Faust NFA-100 autoannular Teflon spinning-band column. Vapor phase chromatography (vpc) was carried out with an F & M 720 equipped with a 2 m × 0.25 in. copper column packed with 15% Carbowax 20M on Chromosorb P (column A) or a Beckman GC-5 equipped with a 500 ft × 0.03 in. SF-96 coated stainless steel capillary column (column B). The retention times (T_r) on these columns of the olefins identified in this study relative to α-chamigrene (**8**) are summarized in Table II.

Formic Acid Treatment of (−)-Thujopsene (**1**).—A mixture of thujopsene (120 g) and 90% formic acid (12 g) was heated at 100° for 1.0 hr, then cooled and poured into 100 ml of water, and extracted with benzene. The organic extracts were washed with water, sodium bicarbonate solution, and water. The solvent was removed under reduced pressure and distilled affording 115 g (96%) of hydrocarbon mixture, bp 65–75° (0.5 mm), $[\alpha]^{25}{}_{\mathrm{D}}$ −21° (neat). Analysis of this mixture by gas chromatography gave the composition in Table I, entry 1.

TABLE II

Olefin	T_r (column A)	T_r (column B)
Tricyclic olefin **7**	0.62	0.79
Thujopsene (**1**)	0.64	0.81
Olefin A (**11**)	0.72	0.83,[a] 0.87[a]
Olefin B (**10**)	0.82	0.90,[a] 0.91,[a] 0.94[a]
β-Chamigrene (**9**)	0.90	0.89
Bicyclic diene **5**	1.00	0.99
α-Chamigrene (**8**)	1.00	1.00
Cuparene (**13**)	1.30	1.18

[a] These five components are present in the olefin A–olefin B mixture; the peak with T_r = 0.87 is pure olefin A (**11**) and that with T_r = 0.94 is pure olefin B (**10**). The structures of the peaks with T_r = 0.83, 0.90, and 0.91 are unknown.

(−)-**β-Chamigrene** (**9**).—A sample of the hydrocarbon mixture above (100 g) was separated *via* careful spinning-band distillation and the progress of the distillation monitored by vpc. A sample of β-chamigrene in 95% purity exhibited the following characteristics: bp 109–110° (5 mm); $n^{20}{}_{\mathrm{D}}$ 1.5105; $[\alpha]^{25}{}_{\mathrm{D}}$ −52° (neat) [lit.[16] $[\alpha]^{15}{}_{\mathrm{D}}$ −52.7° ($CHCl_3$)]; ir (neat) 1638, 1388, 1368, 890, 804 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.30 (m, 2, $W_{h/2}$ = 8 Hz), 4.88 (m, 1, $W_{h/2}$ = 4 Hz), 4.54 (d, 1, J = 2 Hz), 1.58, 0.87, 0.88 (s, 3 each); mass spectrum 204 (26), 189 (79), 119 (60), 107 (65), 105 (72), 93 (100). These spectral data are identical with those reported[16] for (−)-β-chamigrene isolated from natural sources.

Anal. Calcd for $C_{15}H_{24}$: C, 88.16; H, 11.84. Found: C, 88.31; H, 12.00.

(−)-**α-Chamigrene** (**8**).—Continued fractionation of the above hydrocarbon mixture afforded α-chamigrene in 93% purity and exhibited the following characteristics: bp 111–112° (5 mm); $n^{20}{}_{\mathrm{D}}$ 1.5145; $[\alpha]^{25}{}_{\mathrm{D}}$ −11° (neat) [lit.[17] $[\alpha]_{\mathrm{D}}$ −14.5° ($CHCl_3$)]; ir (neat) 1655, 1072, 830, 810, 800, 760 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.37 (m, 2, $W_{h/2}$ = 15 Hz), 1.65, 1.63 (s, 3 each), 0.89, 0.84 (s, 3 each); mass spectrum 204 (38), 136 (82), 133 (36), 121 (100), 119 (74), 105 (44), 93 (58), 91 (41). These spectral data correspond to those reported[17] for (−)-α-chamigrene isolated from natural sources.

Anal. Calcd for $C_{15}H_{24}$: C, 88.16; H, 11.84. Found: C, 87.98; H, 11.96.

Polyphosphoric Acid–Acetic Acid Treatment of (−)-Thujopsene (**1**).—A mixture of polyphosphoric acid (200 g) and acetic acid (500 g) was agitated at 40° while thujopsene (500 g) was fed in over 10 min. After 3 hr the reaction mixture was poured into water (1 l.) and extracted well with benzene. The organic layers were successively washed with water, sodium carbonate solution, and brine. The solvent was removed under reduced pressure to afford 500 g of crude product which by vpc analysis had the composition given in Table I, entry 3. This material was distilled through a 2-ft Goodloe column and a total of 446.9 g (89%) of hydrocarbon fractions, bp 51–89° (0.5 mm), was obtained. Identical isomerization procedures with other mineral acids in acetic acid gave the results summarized in Table I.

2,2,3,7-Tetramethyltricyclo[5.2.2.0^{1,6}]undec-3-ene (**7**).—Fractions of the above distillation enriched in the desired isomer were further purified by spinning-band distillation and the progress of the distillation was monitored by vpc. A minor component in the early distillation fractions was isolated in pure form: bp 97–98° (5 mm); $n^{20}{}_{\mathrm{D}}$ 1.4996; $[\alpha]^{25}{}_{\mathrm{D}}$ −64° (neat); ir (neat) 1651, 1068, 1056, 1023, 838, 792 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.26 (m, 1, $W_{h/2}$ = 7 Hz), 1.67 (s, 3), 1.01, 0.97, 0.87 (s, 3 each); mass spectrum 204 (38), 189 (100), 175 (36), 119 (93), 105 (39), 95 (50), 91 (38). Comparison with an authentic sample[11] of 2,2,3,7-tetramethyltricyclo[5.2.2.0^{1,6}]undec-3-ene (**7**) proved that the two samples were identical.

Olefin A (**11**).—Continued spinning-band distillation afforded samples of olefin A which exhibited the following characteristics: bp 100–101° (5 mm); $n^{20}{}_{\mathrm{D}}$ 1.5075; $[\alpha]^{25}{}_{\mathrm{D}}$ 0° (neat); ir (neat) 1664, 1188, 1102, 1070, 985, 960, 840, 795, 662 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.23 (m, 1, $W_{h/2}$ = 9 Hz), 0.99, 0.87, 0.83 (s, 3 each); mass spectrum 204 (31), 189 (27), 175 (100), 133 (20), 119 (35), 105 (39), 95 (20).

Anal. Calcd for $C_{15}H_{24}$: C, 88.16; H, 11.84. Found: C, 88.24; H, 11.81.

7,10-Ethano-4,4,7-trimethyl-1(9)-octalin (10).—Continued spinning-band distillation afforded samples of olefin B free from olefin A which exhibited the following characteristics: bp 103–104° (5 mm); $n^{20}\mathrm{D}$ 1.5085; $[\alpha]^{25}\mathrm{D}$ 0° (neat); ir (neat) 1670, 1135, 1070, 960, 838, 815, 770 cm^{-1}; $\delta^{\mathrm{CDCl_3}}_{\mathrm{TMS}}$ 5.26 (m, 1, $W_{h/2}$ = 8 Hz), 0.80 (s, 3), 0.78 (s, 6), impurity singlets at 1.00 and 1.02 (approximately 30% impurity by integral); mass spectrum 204 (42), 189 (40), 175 (100), 148 (25), 133 (25), 119 (50), 105 (55), 95 (25), 91 (29).

Anal. Calcd for $C_{15}H_{24}$: C, 88.16; H, 11.84. Found: C, 88.07; H, 11.76.

Cuparene (13).—A minor higher boiling component formed during the above isomerization was also isolated and exhibited the following characteristics: bp 75–76° (0.5 mm); $n^{20}\mathrm{D}$ 1.5137; $[\alpha]^{25}\mathrm{D}$ +46.5° (neat) [lit.[17] $[\alpha]^{25}\mathrm{D}$ +65.3° (neat)]; ir (neat) 1892, 1785, 1510, 1463, 1018, 809, 720, 544 cm^{-1}; $\delta^{\mathrm{CDCl_3}}_{\mathrm{TMS}}$ 2.30, 1.25, 1.07, 0.56 (s, 3 each), 7.10, 7.24 (AB quartet, 4, J_{AB} = 8.5 Hz); mass spectrum 202 (25), 145 (59), 132 (100), 131 (65), 119 (51), 105 (38). The spectral data are identical with that reported[17] for cuparene isolated from natural sources.

7,10-Ethano-4,4,7-trimethyl-1-decalone (14).—A solution (110 ml) of 1 *M* BH_3 in tetrahydrofuran was placed under nitrogen and cooled to 5°; a 10.4-g (100 mmol) sample of olefin B (judged by nmr to contain 70% of olefin 10) was added over 10 min. The resulting solution was stirred at 25° for 20 hr, cooled to 5°, treated successively with 10 ml of water, 80 ml of 10% aqueous NaOH, and 80 ml of 30% aqueous H_2O_2, and then stirred at 35° for 3.5 hr. The mixture was extracted with hexane, and the organic portion was washed with water and dried over anhydrous magnesium sulfate. The solvent was removed to afford 22.0 g of a waxy solid, ir (neat) 3360 cm^{-1}. This crude alcohol mixture was dissolved in 200 ml of acetone, cooled to 5°, and treated with 21 ml of standard Jones[20] reagent. After 20 min, isopropyl alcohol (5 ml) was added and the mixture filtered. The salts were dissolved in water and extracted with hexane. The combined organic extracts were washed with sodium bicarbonate solution and brine and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the residue distilled affording 18.5 g (84%) of principally ketone **14**: bp 110–112° (0.5 mm); $n^{25}\mathrm{D}$ 1.5072; $[\alpha]^{25}\mathrm{D}$ 0° (neat); ir (neat) 1707 (C=O), 1143, 1004 cm^{-1}; $\delta^{\mathrm{CDCl_3}}_{\mathrm{TMS}}$ 1.17, 0.86, 0.81 (s, 3 each); mass spectrum 220 (100), 191 (59), 164 (32), 135 (35), 121 (37), 81 (46). This material solidified upon standing. A sample recrystallized from hexane exhibited mp 51–52° (lit.[15] mp 48°).

The 2,4-dinitrophenylhydrazone was prepared and exhibited mp 191–192° after four recrystallizations from ethanol.

Anal. Calcd for $C_{21}H_{28}N_4O_4$: C, 62.98; H, 7.05; N, 13.99. Found: C, 63.00; H, 7.35; N, 14.24.

1-Acetyl-7,10-ethano-4,4,7-trimethyl-1(9)-octalin (16).—Lithium acetylide–ethylenediamine complex (15.0 g, 0.15 mol) was suspended in anhydrous benzene (35 ml) and anhydrous tetrahydrofuran (35 ml) and heated to 40°. To this suspension was added ketone **14** (17.0 g, 0.076 mol) at a rate to maintain the temperature between 40 and 45°. The mixture was stirred for 3 hr and cooled and water (30 ml) added and stirred at 50° for 1 hr. The solution was filtered and washed with benzene and brine, and the solvent was removed. The crude product (20 g) showed ir absorptions at 3500 (OH) and 3330 (≡CH) expected for alcohol **15**, as well as a carbonyl at 1707 cm^{-1} of unreacted ketone **14**, and was judged to contain 40% of ketone **14** by integration of the nmr spectra. A sample of the above crude mixture (9.0 g) was heated at 100° for 3 hr with 90% formic acid (30 ml) and water (2.5 ml). The solution was cooled, poured into water (200 ml), and extracted with benzene. The combined organic extracts were washed with sodium bicarbonate solution and brine. The solvent was removed and the residue distilled to afford 6.1 g of material, bp 110–125° (0.1 mm). Analysis by vpc showed two peaks in a 40:60 ratio which were separated by preparative vpc. The minor component was identical with starting ketone **14**. The major component possessed spectral properties identical with an authentic sample[21] of 1-acetyl-7,10-ethano-4,4,7-trimethyl-1(9)-octalin (16).

Acid-Catalyzed Isomerization of α-Chamigrene (8).—A sample of α-chemigrene (8, 0.50 g, 96% pure by vpc, containing no bicyclic diene 5) was vigorously agitated with 98% sulfuric acid (0.20 g) and acetic acid (0.50 g) for 3 hr at 40°. The mixture was cooled, diluted with water, and extracted with hexane. The organic extracts were washed with sodium bicarbonate solution and the solvent was removed under reduced pressure. Short-path distillation afforded 0.45 g of colorless oil, bp 90–100° (0.4 mm). Analysis by vpc (column B) and mass spectroscopy gave the following composition: 7 (1.5%), olefin A and B (5 components, 93%), 13 (3.5%), unidentified component (2%).

Acid-Catalyzed Isomerization of Widdrol (3).—A sample of widdrol[9] (3, 1.5 g) was vigorously agitated with acetic acid (2.0 g) and 98% sulfuric acid (0.80 g) at 40° for 3 hr. The mixture was cooled, diluted with water, and extracted with hexane. The organic extracts were washed with sodium bicarbonate solution and the solvent was removed under reduced pressure. Short-path distillation afforded 1.2 g of colorless oil, bp 90–100° (0.4 mm). Analysis by vpc (column A) gave the following composition: 7 (33%), olefins A and B (5 components, 60%), 13 (4%), unidentified components (3%).

Registry No.—**1**, 470-40-6; **7**, 32391-40-5; **8**, 19912-83-5; **9**, 18431-82-8; **10**, 32391-43-8; **11**, 32391-44-9; **13**, 16982-00-6; **14**, 32391-46-1; **14**, 2,4-DNPH, 32391-47-2.