Anal. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.87; H, 13.26.

The *p*-tosylate was reduced (lithium aluminium hydride)[8] to *cis-p*-menthane, identified by comparison with an authentic specimen.

***trans-p*-Menthan-9-ol.**—Ethyl *trans-p*-menthan-9-oate (1.2 g) dissolved in dry ether (10 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (0.6 g) in dry ether (10 ml) and the mixture was refluxed for 20 hr. Conventional working up and distillation [bp 60–61° (0.4 mm)] afforded crude *trans-p*-menthan-9-ol. The 3,5-dinitrobenzoate had mp 77–78.5° (lit.[8] mp 78–80°).

Anal. Calcd for $C_{17}H_{22}N_2O_6$: C, 58.28; H, 6.33; N, 8.00. Found: C, 58.30; H, 6.69; N, 7.87.

The *p*-tosylate (purified by preparative tlc in silica gel; benzene–hexane eluent, 1:1) had $n^{25}{}_D$ 1.5104.

Anal. Calcd for $C_{17}H_{26}SO_3$: C, 65.77; H, 8.44; S, 10.33. Found: C, 65.85; H, 8.81; S, 10.29.

The 3,5-dinitrobenzoate (3 g) was saponified in alkaline alumina (50 g) using a 1:1 hexane–benzene mixture as solvent and eluent. Removal of solvents gave an oil (1.5 g) which was distilled [bp 114–115° (13 mm)] to give pure (vpc) *trans-p*-menthan-9-ol: $n^{25}{}_D$ 1.4630 (lit.[8] $n^{25}{}_D$ 1.4660); nmr double quadruplet centered at 6.43 (CH_2O), 7.75 (hydroxyl H), 9.05 and 9.15 (methyl groups), and broad envelope at 8–9 ppm.

Anal. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.87; H, 13.26.

The *p*-tosylate was reduced (lithium aluminium hydride)[8] to *trans-p*-menthane, identified by comparison with an authentic specimen.

Alternative Procedure for the Preparation of *cis-* and *trans-p*-Menthan-9-ol.—Stereoisomeric mixtures of ethyl *p*-menthan-9-oate (from platinum and palladium hydrogenations; see above) were reduced by means of lithium aluminium hydride and the resulting stereoisomeric mixtures of *p*-menthan-9-ols were resolved by preparative vpc [6-m (30%) Carbowax 20 M column at 210°; the *trans* isomer had the shorter retention time]. After distillation, the alcohols had infrared spectra identical with those of the purest specimens.

Monocyclic Terpene Alcohols. III.[1] *p*-Menth-4(8)-en-9-ol and *trans-* and *cis-p*-Menth-8(10)-en-9-ol

FRANCISCO CAMPS, JOSÉ CASTELLS, AND JOSÉ PASCUAL

Departamento de Química Orgánica, Patronato de Investigatión Científica y Técnica "Juan de la Cierva" (C.S.I.C.), Universidad de Barcelona, Barcelona, Spain

Received May 1, 1966

Preparation of the title compounds starting from 4-methylcyclohexanone is described. Configurational assignments in the *p*-menth-8 (10)-en-9-ols are based on chemical and spectral (nmr) evidence.

As part of the research program,[2] undertaken in this laboratory, devoted to the synthesis of monocyclic terpene alcohols, the present paper describes the preparation, purification, and full characterization of the previously unknown *p*-menth-4(8)-en-9-ol (VIIa), and that of *trans-* and *cis-p*-menth-8(10)-en-9-ol, (XIa and XIIa). Preparation of a mixture of the latter two isomers by sensitized photooxidation of a *trans/cis* *p*-menth-8-ene mixture has been reported very recently in a short communication by Klein and Rojahn.[3]

***p*-Menth-4(8)-en-9-ol.**—This alcohol has been synthesized by the series of reactions outlined in Chart I.

The easily available glycidic ester (I)[4] was rearranged to the unsaturated hydroxy ester (II) by the action of diluted aqueous acid. Reduction of unsaturated hydroxy ester II with lithium aluminium hydride, avoiding the presence of acid in the working up, afforded crystalline *p*-menth-3-en-8,9-diol (III), which upon 3,5-dinitrobenzoylation yields a mono derivative, and a bis derivative.

An interesting AB system is exhibited by the nmr spectrum of III, owing to the magnetic nonequivalence between both CH_2O protons which give a quartet centered at τ 6.67, $J = 10$ cps.[5] Other features of this spectrum confirm the assigned structure.

The diol (III) treated with *p*-toluenesulfonic acid in refluxing benzene, gave a mixture of three main components (as detected by analytical tlc). Nmr, infrared, and ultraviolet spectra of this mixture pointed to the presence of two aldehyde compounds (IV and V, see below) in a 3:1 ratio (nmr). The conjugated aldehyde could be isolated from the mixture as the semicarbazone. The third component, separated by preparative tlc, showed no selective absorption (ultraviolet) and no hydroxyl or carbonyl bands (infrared), and on this basis structure VI is tentatively assigned to it, although no correct analysis could be secured.

The acid rearrangement of diol III can be rationalized by the initial formation of a tertiary carbonium ion (XVI), followed by C-proton removal from the hydroxymethyl group (pathway a of Chart II) to give an enol (XVII), which isomerizes to a mixture of both aldehydes IV and V, in a proportion that reflects their relative stability. Direct hydroxyl attack on the positive center (pathway b) would lead to structure (VI), which is the one proposed for the third component of the mixture.

Lithium aluminum hydride reduction of the aldehyde mixture afforded an oil with strong hydroxyl absorption (infrared), from which a pure 3,5-dinitrobenzoate derivative was obtained. Hydrolysis on alkaline aluminium oxide[6] gave the parent alcohol. The spectral data prove unequivocally that the alcohol is *p*-menth-4(8)-en-9-ol (VIIa), as expected from the assigned structure, (IV), to the main aldehyde component of the starting mixture. This menthenol is rather unstable, being oxidized in the presence of air and giving no reproducible vpc analysis under a variety of conditions.

From the mother liquor of dinitrobenzoate (VIIb), a second 3,5-dinitrobenzoate derivative, was isolated to which structure VIIIb is assigned by comparison with an authentic specimen.[1] This fact establishes that the second aldehyde formed in the acid isomerization of diol III is V.

---

(1) Part II, see previous paper.

(2) Sponsored by the U. S. Department of Agriculture, Grant FG-Sp-135.

(3) E. Klein and W. Rojahn, *Dragoco Rep.*, **11**, 123 (1964).

(4) G. Darzens, *Compt. Rend.*, **144**, 1123 (1907).

(5) *Cf.* J. A. Elvidge and R. G. Foster, *J. Chem. Soc.*, 981 (1964).

(6) *Cf.* J. Castells and G. A. Fletcher, *ibid.*, 3245 (1956).

CHART I

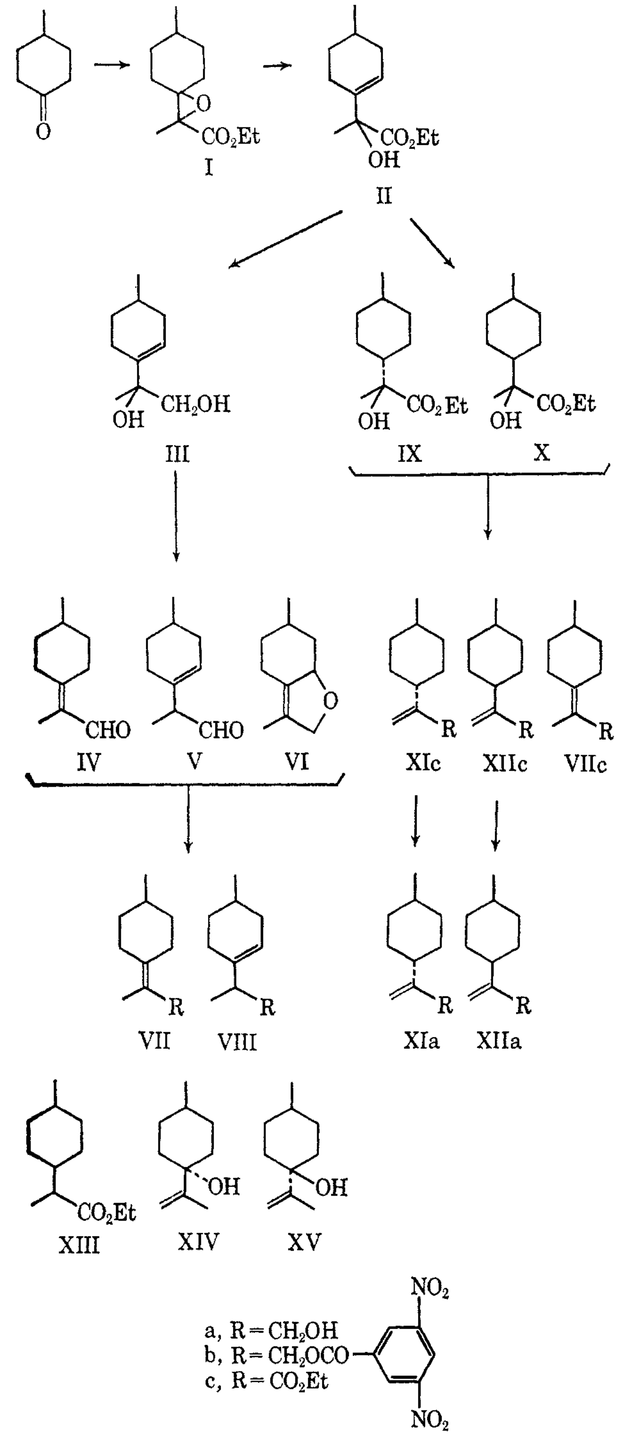
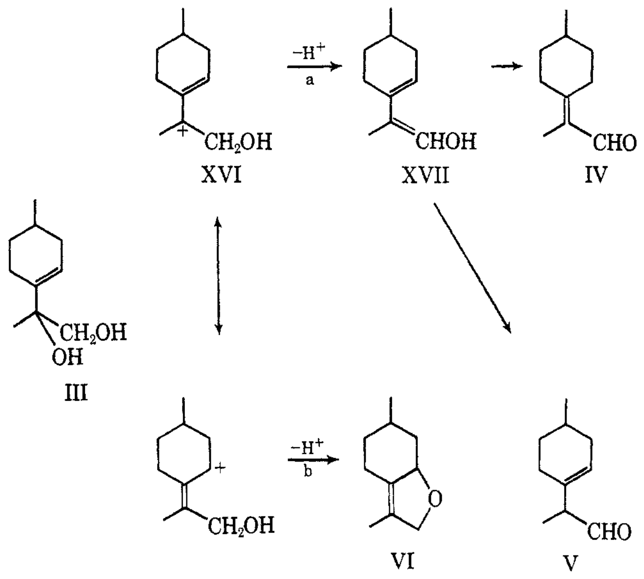


CHART II



Another route for the preparation of *p*-menth-4(8)-en-9-ol was sought in the reduction of unsaturated ester (VIIc), but attempts to synthesize it either by a Wittig reaction between 4-methylcyclohexanone and α-carbethoxyetiliden triphenylphosphorane,[7] or by deoxidation of glycidic ester I with triphenylphosphine[8] or with potassium iodide in acetic acid[9] were unsuccessful; in the last two cases, hydroxy ester II was the only isolated product. The preparation of this menthenol by the anionotropic rearrangement of the recently described[10] *cis*- and *trans*-*p*-menth-8-en-4-ol (XIV and XV), also failed.

***cis*- and *trans*-*p*-Menth-8(10)-en-9-ol.**—These alcohols have been obtained by the series of reactions outlined in Chart I.

Catalytic hydrogenation of unsaturated ester II gives different ratios of *trans*- (IX) and *cis*-hydroxy ester (X) depending on the conditions employed: with platinum in ethanol the IX:X ratio was approximately 1:4 (vpc) and with palladized charcoal in ethanol, containing traces of perchloric acid, the ratio changed to 1.2:1 (vpc) (for steric assignments see below). These results agree with the known fact of preponderance of *cis* isomer, when platinum oxide is used as catalyst in hydrogenations;[11] however the change observed in the present case is not so dramatic as that reported in the hydrogenation of unsaturated ester VIIIc.[1]

No attempts were made to isolate both isomers and the two hydrogenation mixtures were directly submitted to a Chugaev reaction.[12] The methyl xanthates[13] underwent thermal decomposition to the *trans*- (XIc) and *cis*-unsaturated ester (XIIc) upon distillation at reduced pressure, the observed isomeric ratio being consistent with that of the starting mixture. Separation of both isomeric esters was achieved by preparative vpc. The presence of a terminal methylene conjugated to a carbethoxy group in esters XIc and XIIc was established by ultraviolet, infrared, and nmr spectroscopy.

Configurations were assigned by catalytic hydrogenation of isomer (XIIc) to a saturated ester, which was shown to be identical with ethyl *cis*-*p*-menthan-9-oate.[1]

It is worthwhile to point out that a systematic difference was again observed in the gross appearance of the methylene ring proton envelope of the corresponding isomeric pair in any series, one of the isomers exhibiting a rather narrow band at about τ 8.5 and the other a

---

[7] *Cf.* O. Isler, H. Gutmann, M. Montavon, R. Ruegg, G. Ryser, and P. Zeller, *Helv. Chim. Acta*, **40**, 1242 (1957).

[8] *Cf.* G. Wittig and W. Haag, *Ber.*, **88**, 1654 (1955).

[9] (a) *Cf.* G. Darzens, *Compt. Rend.*, **150**, 1243 (1910); (b) M. S. Newman and B. J. Magerlein, *Org. Reactions*, **5**, 424 (1950).

[10] E. Klein and W. Rojahn, *Tetrahedron*, **21**, 2173 (1965).

[11] *Cf.* H. O. House, "Modern Synthetic Reactions," W. A. Benjamin Inc., New York, N. Y., 1965, p 19.

[12] *Cf.* H. R. Nace, *Org. Reactions*, **12**, 57 (1962).

[13] *Cf.* J. D. Roberts and C. Sauer, *J. Am. Chem. Soc.*, **71**, 3925 (1949).

broad absorption between 8 and 9. Provisional assignments of configurations (later confirmed by chemical means) were routinely made on the basis of the magnetic equivalence of ring protons in *cis* isomers. The sharper splitting of the 1-methyl doublet in *cis* than in *trans* isomers is also apparent in the series here studied.[1]

In the above-mentioned preparative vpc of the resulting mixtures of the Chugaev reactions, beside unsaturated esters XIc and XIIc another minor unsaturated ester was isolated, although it was slightly contaminated by XIIc. This compound proved to be unsaturated ester VIIc on the basis of spectral data. The low amount of this unsaturated ester in the mixture agrees with the preferential removal of a secondary hydrogen over a tertiary one in the Chugaev reaction of related compounds to avoid the formation of an energetically unfavorable *exo* double bond.[14]

Reduction of unsaturated esters XIc and XIIc by a 1:3 $AlCl_3$–$LiAlH_4$ mixture[15] gave the corresponding crude alcohols, purification of which was achieved through their 3,5-dinitrobenzoate derivatives, followed by hydrolysis on alkaline aluminum oxide. The terminal methylene protons appeared as two bands at τ 5.05 (1 H) and 5.18 (1 H) in the *trans*-menth-8(10)-en-9-ol (XIa) and at 5.0 (1 H) and 5.16 (1 H) in the *cis* isomer (XIIa), the chemical shift between both protons being smaller in these cases than in the parent esters owing to disappearance of the anisotropic effect of the carbonyl group. Purity of both menthenols was checked by vpc analysis.

Experimental Section

Melting points were taken on a Koffler hot state apparatus and are corrected. Infrared spectra were measured on Perkin-Elmer Infracord 137 and Infracord 137-G spectrophotometers. Ultraviolet spectra were run on a Perkin-Elmer 137 apparatus. Nmr spectra were recorded on a Perkin-Elmer R-10 at 35° operating at 60 Mc/sec with tetramethylsilane as internal reference. Vpc analysis were performed on a Barber–Colman 61-C instrument with β-ionization detection on a Silicone 550 Golay column. Preparative vpc separations were carried out on an Aerograph A-700. Practical 4-methylcyclohexanone and ethyl α-chloropropionate were obtained from Fluka A.G.

Ethyl 4,8-Epoxy-*p*-menthan-9-oate (I).—The compound, prepared according to ref 4, showed bp 138–139° (18 mm) [lit.[4] mp 129–130° (13 mm)]; $n^{25}D$ 1.4539; $\nu_{max}^{C_2Cl_4}$ 1748 and 1721 cm^{-1};[16] τ^{CCl_4} 5.75 (quartet, J = 7 cps, 2 H), 8.43 (CH_3CO), and 8–9.2 (broad, 18 H).

Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 68.27; H, 9.72.

Ethyl 8-Hydroxy-*p*-menth-3-en-9-oate (II).—A solution of ethyl 4,8-epoxy-*p*-menthan-9-oate (10 g) in ethyl ether (100 ml) and aqueous 6 *N* hydrochloric acid solution (10 ml) was mixed (vibromisher) at room temperature. The course of the reaction was followed by vpc and infrared analysis of aliquot fractions of the mixture (vpc gave slightly high results due to partial isomerization of I into II under the conditions used). After separation, the ether layer was washed several times with aqueous 2 *N* sodium carbonate and saturated aqueous sodium chloride solution and dried ($MgSO_4$). Removal of the solvent at reduced pressure and distillation of the residue afforded the unsaturated ester (II): 9.5 g; bp 145–146° (25 mm); $n^{25}D$ 1.4655; ultraviolet, gave no selective absorption; $\nu_{max}^{C_2Cl_4}$ 3571, 3509, and 1724 cm^{-1}; τ^{CCl_4} 4.24 (broad, 1 H), 5.8 (quartet, J = 7 cps, 2 H), 6.6 (broad, 1 H), 7.5–9.2 (broad, 16 H).

Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.68; H, 9.58.

***p*-Menth-3-ene-8,9-diol** (III).—To a stirred suspension of lithium aluminium hydride (2 g) in dry ether (50 ml), a solution of ethyl 8-hydroxy-*p*-menth-3-en-9-oate (II) in dry ether (100 ml) was added dropwise under nitrogen, and the mixture was refluxed for 8 hr. Ethyl acetate and water were added and the precipitate was filtered off and washed several times with ether. The organic layer was shaken with sodium chloride saturated solution, dried ($MgSO_4$), and evaporated at reduced pressure to give a thick oil (3.7 g) which solidified on cooling at room temperature. Recrystallization from hot *n*-hexane gave crude diol (III, 3.2 g) as prisms: mp 57–60°; analytical sample mp 61–62°; ν_{max}^{RBr} 3300, 1050 cm^{-1}; τ^{CCl_4} 4.3 (broad, 1 H), 6.6 (quartet, J = 10 cps, 2 H), 7.15 (singlet, 2 H) 7.6–8.6 (broad, 7 H). 8.82 (singlet, 3 H), and 9.05 (doublet, J = 5 cps, 3 H).

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.51; H, 10.83.

3,5-Dinitrobenzoylation of III under the usual conditions yielded predominantly a mono-3,5-dinitrobenzoate: mp 98–100°; (EtOH); ν_{max}^{KBr} 3509, 3077, 1724, 1626, 1546, 1342, 1300, 1176, 1075, 985, 917, 735, 722 cm^{-1}.

Anal. Calcd for $C_{17}H_{20}N_2O_7$: C, 56.04; H, 5.53; N, 7.69. Found: C, 55.83; H, 5.93; N, 7.43.

As a minor product of the 3,5-dinitrobenzoylation, or by benzoylation of the mono-3,5 derivative a bis-3,5-dinitrobenzoate, mp 130–132° (EtOH), was obtained: ν_{max}^{KBr} 3077, 1733, 1626, 1546, 1339, 1266, 1156, 1111, 1075, 980, 921, 732, 724 cm^{-1}; τ^{CD_3Cl} 0.8 (multiplet), 4.1 (broad), 5.2 (quartet, J = 12 cps) 8.1 (singlet), 9.05 (doublet, J = 6 cps), and 7.6–9.2 (broad).

Anal. Calcd for $C_{24}H_{22}N_4O_{12}$: C, 51.61; H, 3.97; N, 10.03. Found: C, 51.25; H, 4.28; N, 9.83.

Rearrangement of *p*-Menth-3-ene-8,9-diol (III) **to *p*-Menth-4(8)en-9-ol and *p*-Menth-3-en-9-ol** (VIIa and VIIIa).—A solution of diol III (6 g) and *p*-toluenesulfonic acid (0.3 g) in dry benzene (60 ml) was refluxed for 20 min under nitrogen. After being washed with sodium carbonate and sodium chloride aqueous saturated solution, the benzene layer was dried ($MgSO_4$) and evaporated to give a bright yellow oil (5.4 g), with a lemon-like odor, which exhibited the following spectral features: λ_{max}^{EtOH} 250 mμ (ϵ 8700); $\nu_{max}^{CCl_4}$ 2703, 1724, 1667, and 1621 cm^{-1}; τ^{CCl_4} 0.6 and -0.13 (1:3). Vpc analysis gave no reproducible results. Analytical tlc [Merck Kieselgel $RF_{254+366}$ and benzene–*n*-hexane (1:1)] showed the presence of three main components (iodine vapor as detector). An attempt to resolve the mixture by chromatography on silica gel column failed due to oxidation of the aldehyde compounds (infrared), but the third component of the mixture could be conveniently isolated by preparative tlc of the oil from reduction by lithium aluminium hydride (see below). Treatment of the crude rearrangement mixture by semicarbazide hydrochloride yielded *p*-menth-4(8)-en-9-ol semicarbazone: mp 189–191° (EtOH); λ_{max}^{EtOH} 275 mμ (ϵ 28,400);[17] ν_{max}^{KBr} 3448, 3145, 1681, 1575, 1143, 1114, 930, 760 cm^{-1}.

Anal. Calcd for $C_{11}H_{19}N_3O$: C, 63.13; H, 9.15; N, 20.08. Found: C, 63.22; H, 9.53; N, 19.96.

The above-mentioned mixture (5.4 g) in dry ethyl ether (50 ml) was added dropwise under nitrogen to a stirred suspension of lithium aluminium hydride (0.6 g) in ether (30 ml) and the stirring was further continued for 12 hr. Water was added and the resulting slurry was filtered off and washed thoroughly with ethyl ether. The organic solution was shaken with aqueous saturated sodium chloride solution, dried ($MgSO_4$), and evaporated at reduced pressure to yield a yellow oil (4.7 g) with no carbonyl bands and strong hydroxyl absorption (infrared). Analytical tlc of this oil (Merck Kieselgel $HF_{254+366}$ benzene) exhibited the presence of three main components. The mixture was 3,5-dinitrobenzoylated and the resulting 3,5-dinitrobenzoate derivatives were separated by fractional crystallization to give 1.9 g of *p*-menth-4(8)-en-9-ol 3,5-dinitrobenzoate (VIIb): mp 105–106° (EtOH); ν_{max}^{KBr} 3030, 1718, 1653, 1621, 1538, 1279, 1170, 1070, 826, 778, 723, 711 cm^{-1}; τ^{CDCl_3} 0.82 (singlet), 4.98 (singlet), 7–7.5 (broad), 7.5–9.2 (broad), 8.13 (singlet), 9.08 (doublet, J = 6 cps).

Anal. Calcd for $C_{17}H_{20}N_2O_6$: C, 58.61; H, 5.79; N, 8.04. Found: C, 58.98; H, 6.21; N, 7.94.

---

(14) R. A. Benkeser and J. J. Hazdra, *J. Am. Chem. Soc.*, **81**, 228 (1959).

(15) M. J. Jorgenson, *Tetrahedron Letters*, **13**, 559 (1962).

(16) *Cf.* H. H. Morris and R. H. Young, *J. Am. Chem. Soc.*, **79**, 3409 (1957).

(17) (a) *Cf.* A. E. Gillam and E. S. Stern, "Electronic Absorption Spectroscopy," 2nd ed, Edward Arnold Ltd., London, 1957, p 116; (b) Y.-R-Naves, I. A. Retamar, and A. I. Ricciardi, *Helv. Chim. Acta*, **48**, 1579 (1965).

Resolution of the crude reduction mixture by preparative tlc (0.75-mm Merck Kieselgel G plates activated for 3 hr at 120°, eluting with a (1:1 ethyl ether–benzene mixture and using iodine to detect the different bands)[18] gave a nonhydroxyl component (30% of the recovered product), which showed the spectral features expected for structure VI: $\nu_{\max}^{\mathrm{CCl_4}}$ 1634, 1149, 1131, 1075, 1058, 1036, 897, 813 cm^{-1}; $\tau^{\mathrm{CCl_4}}$ 6.4 (broad), 7.5–9.2 (broad), 8.3 (singlet), 8.7 (singlet), and 9.05 (doublet, J = 6 cps).

A solution of 3,5-dinitrobenzoate VIIb (2.3 g) in *n*-hexane–benzene mixture (9:1 ml) was poured into a column with 25 g of alkaline aluminum oxide (prepared by shaking the aluminum oxide vigorously with a solution of potassium hydroxide (2.5 g) in water (2 ml) till lumps disintegrated), the solution was kept for 30 min in the column and then eluted with *n*-hexane. The solvent was removed at reduced pressure and the residue was distilled to give *p*-menth-4(8)-en-9-ol, (VIIa, 1.0 g): bp 61–62° (0.35 mm); n^{25}D 1.4918; $\nu_{\max}^{\mathrm{film}}$ 3279, 1653, 1000 cm^{-1}; $\tau^{\mathrm{CCl_4}}$ 6.0 (singlet, 2 H), 7.1–7.6 (broad, 2 H), 7.6–9.2 (broad, 14 H), 8.26 (singlet), and 9.08 (doublet, J = 6 cps). Vpc analysis gave mainly one peak with a very slight proportion of another compound with a higher retention time, amounts of which depended on the conditions used.

Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.55; H, 11.94.

From the mother liquor of VIIb another 3,5-dinitrobenzoate derivative, mp 75–80°, was isolated which showed no depression in a mixture melting point with 3,5-dinitrobenzoate derivative VIIIb and exhibited the same spectral features (infrared, nmr).[1]

Ethyl 8-Hydroxy-*trans*- (IX) and -*cis*-*p*-menthan-9-oate (X) Mixtures. A.—A solution of ethyl 8-hydroxy-*p*-menth-3-en-9-oate (II, 11 g) in absolute ethanol (100 ml) and platinum oxide (100 mg) was shaken in presence of hydrogen at room temperature and normal pressure. In 12 hr the theoretical uptake of hydrogen was reached, the system was evacuated, the catalyst was filtered off, and the solvent was removed at reduced pressure. The residue (10.8 g) was distilled to yield the *trans–cis* mixture (9.8 g): bp 136–137° (15 mm), n^{25}D 1.4575; $\nu_{\max}^{\mathrm{C_2Cl_4}}$ 3584, 3509, 1721 cm^{-1}; vpc gave a (1:4) *trans*:*cis* ratio.

Anal. Calcd for $C_{12}H_{22}O_3$: C, 67.26; H, 10.35. Found: C, 67.14; H, 10.53.

B.—A solution of II (10 g) in absolute ethanol (100 ml), containing some drops of concentrated perchloric acid, and 30% palladized charcoal[19] (0.5 g), was hydrogenated under the same conditions described above. The uptake of hydrogen was slower in this case than that observed with platinum oxide catalyst. After 20 hr, the theoretical amount was reached, the system was evacuated, solid sodium carbonate and water were added, and the solvent was partially evaporated at reduced pressure. Then, ethyl ether and water were added and the organic layer, after being washed with sodium chloride aqueous saturated solution and dried ($MgSO_4$), was evaporated at reduced pressure and the residue (9.5 g) distilled to give the *trans–cis* mixture (8.7 g): bp 127–129° (11 mm), n^{25}D 1.4553; $\nu_{\max}^{\mathrm{C_2Cl_4}}$ 3584, 3509, 1721 cm^{-1}; vpc gave a (1.2:1) *trans*:*cis* ratio.

Anal. Calcd for $C_{12}H_{22}O_3$: C, 67.26; H, 10.35. Found: C 67.19; H, 10.52.

Ethyl *trans*- (XIc) and -*cis*-*p*-menth-8(10)-en-9-oate (XIIc).—To a stirred suspension of sodium hydride (3.6 g) in dry ether (50 ml), a (1:4) ethyl 8-hydroxy-*trans*- (IX) and -*cis*-*p*-menthan-9-oate (X) mixture (22.0 g) in dry ether (100 ml) was added dropwise under nitrogen. The resulting mixture was heated under reflux for 3 hr, then carbon disulfide (10.6 g) was added. The mixture was heated under reflux for 3 hr, methyl iodide (19.9 g) was added, and the mixture was heated for an additional 3 hr. Stirring was maintained at room temperature overnight, then water was added; the ether layer was separated and dried ($MgSO_4$) and yielded, after removal of the solvent at reduced pressure, the crude xanthates. Decomposition of this mixture at 150–160° (20 mm) gave a dark residue which afforded upon distillation a yellowish oil (16 g), bp 64–65° (0.6 mm). Analytical vpc demonstrated the presence in this oil of three main components, amounting to more than 95% of the mixture, in a 1.5:7.3:1 ratio. A 3.9:3.4:1 ratio of these same products was obtained by decomposition of the mixture of xahthates from the ester with a (1.2:1) *trans* (IX):*cis* (X) ratio. Resolution of the unsaturated esters from the pyrolysis of the xanthates was achieved on a 20 × $^3/_6$ in. 30% XF-1150 on Chromosorp P column at 190° using 200 ml/min of hydrogen as carrier gas. The fraction with shorter retention time was distilled to afford pure (vpc) ethyl *trans*-*p*-menth-8(10)-en-9-oate (XIc): n^{25}D 1.4581; $\lambda_{\max}^{\mathrm{EtOH}}$ 209 mμ (ϵ 7500); $\nu_{\max}^{\mathrm{film}}$ 3077, 1876, 1712, 1623, 939, 818 cm^{-1}; $\tau^{\mathrm{CCl_4}}$ 3.98 (fine split band, 1 H), 4.62 (fine split band, 1 H), 5.85 (quartet, J = 8 cps, 2 H) 7.3–9.3 (broad, 16 H) [8.72 (triplet, J = 8 cps) and 9.05 (unresolved doublet)].

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 1.270. Found: C, 73.20; H, 10.37.

The second peak of the preparative vpc afforded pure (vpc) ethyl *cis*-*p*-menth-8(10)-en-9-oate (XIIc): n^{25}D 1.4632; $\lambda_{\max}^{\mathrm{EtOH}}$ 209 mμ (ϵ 6800); $\nu_{\max}^{\mathrm{film}}$ 3077, 1880, 1718, 1626, 939, 819 cm^{-1}; $\tau^{\mathrm{CCl_4}}$ 3.9 (singlet 1 H), 4.5 (fine split band, 1 H), 5.75 (quartet, J = 7 cps, 2 H), 7.3–7.7 (broad, 1 H), 8.0–8.6 (narrow, 9 H) (8.42, 8.50), 8.70 (triplet, J = 7 cps, 2 H), and 9.05 (doublet, J = 6 cps, 3 H).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.38; H, 10.28.

The third fraction, containing 20% of XIIc (vpc, nmr) proved to be ethyl *p*-menth-4(8)-en-9-oate (VIIc): $\lambda_{\max}^{\mathrm{EtOH}}$ 221 mμ (ϵ 6300); $\nu_{\max}^{\mathrm{film}}$ 1709 and 1626 cm^{-1}; $\tau^{\mathrm{CCl_4}}$ 5.87 (quartet, J = 8 cps), 8.18 (singlet), 8.74 (triplet, J = 8 cps), 9.08 (doublet, J = 6 cps).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.09; H, 10.57.

Hydrogenation of XIIc (160 mg) in absolute ethanol (10 ml) with platinum oxide (25 mg), under the conditions described above, afforded a saturated ester (120 mg) which proved to be ethyl *cis*-*p*-menthan-9-oate (XIII)[1] (vpc, infrared and nmr).

***trans*-*p*-Menth-8(10)-en-9-ol (XIa).**—To a well-stirred suspension of lithium aluminium hydride (0.23 g) in dry ethyl ether (50 ml) at −10°, aluminium chloride (0.46 g) was added under nitrogen, then ethyl *trans*-*p*-menth-8(10)-en-9-oate (XIc, 1.4 g) in dry ethyl ether (50 ml) was added dropwise under the same conditions. Stirring was maintained for 3 hr at −10° and for 12 hr at room temperature. Water was added and the resulting slurry was filtered off and washed with ethyl ether. The organic layer was shaken with saturated sodium chloride aqueous solution, dried ($MgSO_4$), and evaporated at reduced pressure to yield a colorless oil (1.2 g), which exhibited three peaks on vpc analysis: the desired allylic alcohol amounting to about 70% and the starting ester to 14% of the mixture. The oil was 3,5-dinitrobenzoylated to give the 3,5-dinitrobenzoate derivative (XIb, 1.2 g): mp 73–74.5°; $\nu_{\max}^{\mathrm{KBr}}$ 3049, 1718, 1613, 1538, 1333, 1266, 1149, 1066, 730, 719 cm^{-1}.

Anal. Calcd for $C_{17}H_{20}N_2O_6$. C, 58.61; H, 5.79; N, 8.04. Found: C, 58.37; H, 5.91; N, 8.29.

A solution of 3,5-dinitrobenzoate (1.5 g) in a 10:1 *n*-hexane–benzene mixture was hydrolyzed on 30 g of alkaline aluminum oxide as described above to afford, after distillation, pure (vpc, nmr) *trans*-*p*-menth-4(8)-en-9-ol (XIa, 0.5 g): n^{25}D 1.4760; $\nu_{\max}^{\mathrm{film}}$ 3279, 1786, 1639, 1064, 1047, 1022, 894 cm^{-1}; $\tau^{\mathrm{CCl_4}}$ 5.05 (fine split band, 1 H), 5.18 (singlet, 1 H), 5.98 (broad singlet, 2 H), 7.8–9.2 (broad, 14 H) 8.12, 8.25, 8.86, 9.08 (unresolved doublet).

Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.66; H, 11.90.

***cis*-*p*-Menth-8(10)-en-9-ol (XIIa).**—Reduction of ethyl *trans*-*p*-menth-8(10)-en-9-oate (5 g) with lithium aluminium hydride (0.7 g) and anhydrous aluminium chloride (1.4 g) under the same conditions described above afforded a colorless oil (3.75 g) which exhibited three peaks in a similar ratio as that described for *trans* isomer. Benzoylation of this mixture yielded 3,5-dinitrobenzoate derivative (XIIb): 4.5 g, mp 60–61°; $\nu_{\max}^{\mathrm{KBr}}$ 3049, 1709, 1621, 1538, 1337, 1274, 1163, 1063, 731, 720 cm^{-1}.

Anal. Calcd for $C_{17}H_{20}H_2O_6$: C, 58.61; H, 5.79; N, 8.04. Found: C, 58.99; H, 6.00; N, 8.05.

A solution of XIIb hydrolyzed on 70 g of alkaline aluminum oxide, as described above, yielded, after distillation, pure (vpc, nmr) *cis*-*p*-menth-8(10)-en-9-ol (XIIa, 1.2 g): n^{25}D 1.4829; $\nu_{\max}^{\mathrm{film}}$ 3279, 1786, 1645, 1047, 1026, 894 cm^{-1}; $\tau^{\mathrm{CCl_4}}$ 5.0 (fine split band, 1 H), 5.16 (singlet, 1 H), 6.0 (broad singlet, 2 H), 7.8–8.8 (narrow, 14 H), 8.46, 8.52, and 9.06 (doublet J = 6 cps, 3 H).

Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 78.22; H, 12.12.

---

(18) Alteration of the mixture could be observed when using preparative Kieselgel HF$_{254\,+\,366}$ plates and irradiating with ultraviolet light to detect the different bands.

(19) N. D. Zelinsky and M. B. Turowa-Pollack, *Ber.*, **58**, 1295 (1925).