Terpene–Formaldehyde Reactions. II. *d*-Limonene[1]

A. T. Blomquist and Richard J. Himics[2]

Department of Chemistry, Cornell University, Ithaca, New York 14850

Received October 18, 1967

Reaction of *d*-limonene with formaldehyde to give a simple 1:1 product is best achieved in solvent methylene chloride–acetic anhydride at autogenous temperature for 70 min under nitrogen at 1 atm with a complex of boron trifluoride as catalyst, preferably the dihydrate. The principal product fraction (82% yield) is comprised mainly of (84%) 9-acetoxymethyl-1,8(10)-*p*-menthadiene. This acetate and its alcohol are easily converted into the saturated primary alcohol 9-hydroxymethyl-*p*-menthane. The acrylate of the latter alcohol gives a homopolymer and a methyl methacrylate copolymer when polymerized in bulk with initiation by azobisisobutyronitrile.

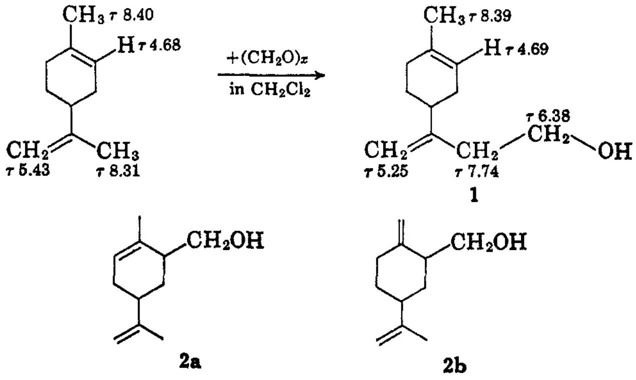
There are many reports in the literature concerned with the reaction of *d*-limonene, or dipentene, with formaldehyde,[3] but none describes the isolation and unequivocal characterization of pure 1:1 reaction products, or simple derivatives thereof. With the modern experimental methods for isolation, purification, and characterization of organic compounds now available, *e.g.*, analytical and preparative glpc, nmr spectroscopy, etc., it was of interest to make a careful, extensive study of the limonene–formaldehyde reaction. The useful synthesis of a primary alcohol from readily available pure *d*-limonene is of importance also.

The limonene–formaldehyde reactions described in this report are those (a) catalyzed by Lewis acids, (b) catalyzed by mineral or strong acids, and (c) so-called "noncatalyzed" thermal condensations. Reactions of the type a proved to be the most broadly useful.

Treatment of *d*-limonene with paraformaldehyde (PFA) (2:1 mole ratio) in methylene chloride containing fuming stannic chloride (0.1 ml/0.22 mol of PFA) for 2 days at room temperature gave, after distillation, a 49% yield of an alcohol fraction that was comprised mainly (80–85%) of the alcohol 9-hydroxymethyl-1,8-(10)-*p*-menthadiene (**1**) and not the alcohols **2a** and/or **2b**. The pure alcohol **1** was obtained by preparative glpc followed by redistillation. The minor products (15–20%) were not examined.

The ir spectrum of the pure alcohol **1** had bands at λ_{max} 3.0 (OH), 5.97 (internal double bond), 6.09 ($>C{=}CH_2$), 9.55 (primary OH), 10.90 (internal double bond), and 11.27 μ ($>C{=}CH_2$). The nmr spectrum is indicated in Chart I. The triplet at τ 7.74 ($-CH_2CH_2OH$) was isolated from the other proton signals in the nmr by observing the nmr spectrum of the 3,5-dinitrobenzoate derivative, mp 79.5°, of the alcohol **1** (see Experimental Section), which clearly showed the presence of the group $-CH_2CH_2OCO-$. The alcohol **1** was converted easily into its acetate, 9-acetoxymethyl-1,8(10)-*p*-menthadiene (**3**), with acetic anhydride.

Chart I



A set of boron trifluoride complexes proved to be very interesting catalysts for the reaction of the title compounds. Thus, reaction of a 2:1 mixture of *d*-limonene and formaldehyde in the solvent system methylene chloride–acetic anhydride (1:1 volume ratio) at autogenous temperature (25–45°) for 70 min and catalyzed by boron trifluoride dihydrate gave an 82% yield of acetates, 84% of which was the acetate **3**. Careful redistillation of this product gave the compound **3** in purity greater than 96%. Under similar conditions the reaction was catalyzed by (a) boron trifluoride etherate, (b) boron trifluoride diphenol, and (c) boron trifluoride diacetic acid to give product acetates in yields of 80, 82, and 78% (with the acetate **3** content found to be, respectively, 80, 88, and 85%). Reaction times for the three reactions were 140, 110, and 60 min at autogenous temperature. Boron trifluoride etherate and diphenol catalyzed reactions of limonene and formaldehyde in the simple solvent methylene chloride afforded decreased yields (47–59%) of product alcohols that contained *ca.* 75–80% of the alcohol **1**.

In the latter reactions there was always obtained a substantial amount of higher boiling material. Two components of the high boiling product obtained in the boron trifluoride etherate catalyzed reaction were isolated by careful distillation and column chromatography. Nmr and infrared analyses indicated that they were the ether **4** and the formal **5** (see Experimental Section). The formation of accessory products such as **4** and **5** is clearly reduced in the solvent system methylene chloride–acetic anhydride, probably the consequence of the rapid trapping of alcohols as acetates.

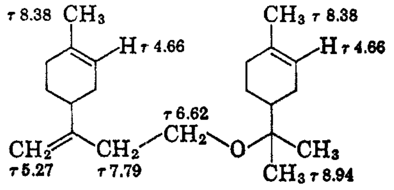
The limonene–formaldehyde reactions catalyzed by acids such as phosphoric, formic, dichloroacetic, and *p*-

---

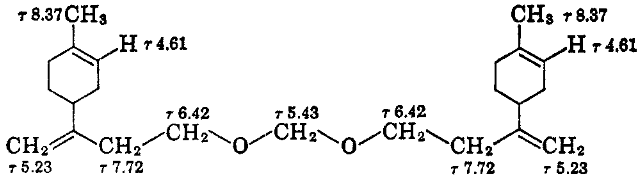
(1) For the preceding report from this laboratory on olefin–formaldehyde reactions, see A. T. Blomquist and J. D. Meador, *J. Org. Chem.*, **32**, 3986 (1967).

(2) Abstracted from part of the Ph.D. Dissertation of R. J. Himics, the Graduate School of Cornell University, Ithaca, N. Y., Feb 1967.

(3) (a) G. Ohloff, *Arch. Pharm.*, **287**, 259 (1954); (b) A. T. Blomquist, J. Verdol, C. L. Adami, J. Wolinsky, and D. D. Phillips, *J. Amer. Chem. Soc.*, **79**, 4876 (1957); (c) K. Suga, A. Matsuda, and S. Watanabe, *Nippon Kagaku Zasshi*, **79**, 724 (1958); *Chem. Abstr.*, **54**, 4656 (1960); (d) Y. Matsubara and Y. Watanabe, *ibid.*, **80**, 651 (1959); *Chem. Abstr.*, **55**, 3464 (1961); (e) Y. Watanabe, *ibid.*, **80**, 1063 (1959); *Chem. Abstr.*, **55**, 3591 (1961); (f) Y. Watanabe, Y. Matsubara, and C. Huang, *Kogyo Kagaku Zasshi*, **62**, 1630 (1959); *Chem. Abstr.*, **57**, 13963 (1962); (g) J. Colonge and J. Crabalona, *Bull. Soc. Chim. Fr.*, 102 (1960); (h) K. Suga and S. Watanabe, *Chiba Daigaku Kogakuba Kenkyu Hokoku*, **11**, 29 (1960); *Chem. Abstr.*, **55**, 21159 (1961); K. Suga and S. Watanabe, *Nippon Kagaku Zasshi*, **81**, 1139 (1960); *Chem. Abstr.*, **56**, 507 (1962).



4

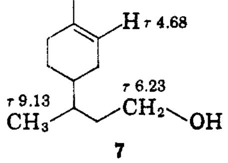


5

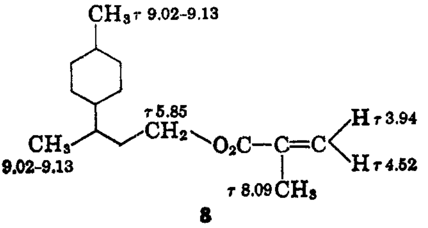
toluenesulfonic were found to be unpromising in that they all afforded inferior yields of complex mixtures of products. Thus, the phosphoric acid-catalyzed reaction in acetic acid–acetic anhydride at 5–15° gave a 34% yield (as acetates) of a mixture that glpc analysis indicated to be composed of three major and at least six minor compounds the formic acid catalyzed reaction in glacial acetic acid at 95–100° afforded a 44% yield of a product mixture that was comprised of three monoacetates in about equal amount (glpc analysis).

For the sake of completeness the classical "noncatalyzed" thermal condensation of *d*-limonene with formaldehyde was reexamined. Reactions effected in a sealed autoclave at 180–200° under autogenous pressure in a variety of solvent systems were uniformly unsatisfactory; all afforded in low yield a complex mixture of products (glpc analysis) whose principal component was the alcohol **1** or the acetate **3**. Reactions in acetic acid in an open vessel at temperatures that ranged from 110 to 125° for 1–7 days gave *ca.* 40–70% yields of complex mixtures whose principal component (55–80%) was the acetate **3**.

With the alcohol **1** and its acetate **3** available in high yield and purity from *d*-limonene it was of interest to examine briefly the polymerization of the saturated primary alcohol 9-hydroxymethyl-*p*-menthane (**6**) derivable from either **1** or **3**. Catalytic hydrogenation of the alcohol **1** occurred smoothly, and stepwise, to afford the alcohol **6** as an inseparable mixture of the expected *cis* and *trans* isomers. The intermediate product of hydrogenation, 9-hydroxymethyl-1-*p*-menthene (**7**), was obtained by interrupting the hydrogenation after 18 hr (see Experimental Section). Transesterification of methyl methacrylate with the saturated alcohol **6** gave the desired ester **8**, of purity >99%, suitable for polymerization.



7



8

The homopolymer of the methacrylate **8** together with a copolymer of **8** and methyl methacrylate were obtained smoothly *via* bulk polymerization initiated by azobisisobutyronitrile. The two polymers, mp 225–230° and 215–225°, respectively, differed markedly in their ease of handling; the homopolymer was soft, caked on standing, and acquired a static charge when ground; the copolymer was a hard, white solid that was easily pulverized. Both polymers were soluble in benzene or toluene and insoluble in acetone or methanol. They showed an intrinsic viscosity in benzene of 3.72 and 3.69 dl/g, respectively.

Experimental Section[4,5]

Materials.—The *d*-limonene used was purchased from Eastman Kodak and showed a purity greater than 99% by glpc analysis.[5a] Fisher "trioxymethylene" (USP) was used as a formaldehyde source; the boron trifluoride catalysts were obtained from the General Chemical Division of the Allied Chemical Corp.

The Stannic Chloride Catalyzed Reaction of *d*-Limonene with Paraformaldehyde.—A mixture of 62.2 g (0.457 mol) of *d*-limonene, 6.6 g (0.22 mol) of paraformaldehyde (PFA), and 400 ml of dry methylene chloride was stirred under nitrogen for 10 min. Fuming stannic chloride (0.3 ml) was then added over 0.5 hr and the mixture stirred at room temperature for 2 days. To the clear, tan solution that resulted there was added, with vigorous stirring, *ca.* 20 ml of cold, dilute sodium hydroxide. The separated aqueous layer was extracted with ether and the ether extracts were combined with the methylene chloride layer. From the dried ($MgSO_4$), combined ether–methylene chloride solution, after removal of solvents *in vacuo*, there was obtained upon distillation two product fractions: (1) 18 g, bp 89–95° (0.5–0.6 mm), $n^{23}{}_{\rm D}$ 1.4991; (2) 3 g, bp 87–144° (0.3 mm), $n^{23}{}_{\rm D}$ 1.5086. Fraction 1 (49% yield for a 1:1 limonene–formaldehyde reaction product) was a clear, colorless liquid of 80–85% purity (glpc analysis).[5b] Fraction 2 was not immediately examined.

9-Hydroxymethyl-1,8(10)-*p*-menthadiene (1).—Fraction 1 described above (*ca.* 4 ml) was purified *via* preparative glpc on an 8-ft column (30% Versamid 900 on Chromosorb W) at 180°. Other conditions for the glpc purification were sample size, 1 ml; injector temperature, 330°; detector temperature, 310°; traps manifold, 300°; back pressure value, 310°; head pressure, 15 psi; back pressure, 0 psi; attenuation, 8; flow rates, 7 cm (rotameter). The resulting product, contaminated with Versamid 900, gave the pure alcohol **1** upon redistillation, bp 80–83° (0.2–0.3 mm) and $n^{24}{}_{\rm D}$ 1.4986. Its ir spectrum showed significant absorptions at 3.0, 5.97, 6.09, 9.55, 10.90, and 11.27 μ. The nmr spectrum showed the following assigned values: τ 4.69 (s, >C=CH–), 5.25 (m, $>C{=}CH_2$), 6.38 (t, $-CH_2$-OH, 7 cps), 7.74 (t, $-CH_2CH_2OH$, 7 cps), 8.08 (bs), and 8.39 (s, $CH_3C{=}C<$).

Anal. Calcd for $C_{11}H_{18}O$: 79.56; H, 10.92. Found: C, 79.40; H, 10.95.

---

[4] Melting points are uncorrected. Ir spectra were recorded on a Perkin-Elmer Infracord spectrophotometer. Nmr spectra were determined by a Varian A-60 Spectrometer with carbon tetrachloride used as solvent; integrated area ratios agree well with the structures presented unless otherwise stated. All important distillations were performed using a Nester–Faust Annular Teflon spinning-band column. Analyses were done either by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., or by Galbraith Laboratories, Inc., Knoxville, Tenn.

[5] An F & M Model 770 automatic preparative gas chromatograph was used throughout. For preparative glpc sections of 8 ft × 0.75 in., stainless steel tubing was used that could be coupled to provide a maximum column length of 48 ft. Stainless steel tubing, 4–6 ft × 0.25 in., was used for analytical glpc. The solid support in all glpc columns, unless otherwise stated, was 60-mesh, nonacid-washed Chromosorb W. The liquid phases used in the analytical columns together with the column temperature were as follows: (1) 15% diethylene glycol sebacate (DEGS)–5% Bentone at 85°, (b) 20% diethylene glycol adipate (DEGA) at 190°, (c) same as b at 173°, (d) same as b at 185°, (e) 15% DEGS at 180°, (f) same as a at 190°, (g) 20% silicone gum rubber at 100–200°, (h) 20% Versamid 900 at 195°, (i) same as h at 175°, (j) same as h at 180–225°, (k) same as b at 180°, (l) same as a at 180°, (m) 20% DEGS, (n) 20% Carbowax 20M, (o) same as a at 185°.

Some Derivatives of the Alcohol 1.—The acetate derivative (3) of 1, prepared in a conventional manner *via* reaction with acetic anhydride in the presence of sodium acetate, was a clear, colorless liquid, bp 80–81° (0.3 mm) and $n^{24}\mathrm{D}$ 1.4775. Its ir spectrum showed absorption at 5.75 (acetate carbonyl) and 8.0–8.2 μ (acetate group). The nmr spectrum showed significant signals at τ 4.71 (br s, $\mathrm{>C{=}CH}$), 5.25 (br s, $\mathrm{-C{=}CH_2}$), 5.92 (t, $\mathrm{-CH_2CO-}$, 7 cps), 7.71 (t, $\mathrm{-CH_2CH_2O_2C-}$, 7 cps), 8.09 (s, $\mathrm{-O_2CCH_3}$), and 8.41 ($\mathrm{>C{=}CCH_3}$).

Anal. Calcd for $\mathrm{C_{13}H_{20}O_2}$: C, 74.96; H, 9.68. Found: C, 75.17; H, 9.79.

The 3,5-dinitrobenzoate derivative of 1, prepared *via* treatment of 1 with 3,5-dinitrobenzoylchloride in the presence of pyridine, mp 79.5° (ethanol–water) showed significant ir absorptions at 5.80 and 8.55 μ; its nmr spectrum showed peaks at τ 2.7 (s, aromatic), 4.6 (br s, $\mathrm{-C{=}C(H)-}$), 5.13 (br s, $\mathrm{-C{=}CH_2}$), 5.4 (t, $\mathrm{-CH_2CO-}$, 7 cps), 7.4 (t, $\mathrm{-CH_2CH_2O_2C-}$, 7 cps), 7.95 (br s), and 8.4 (s, $\mathrm{>C{=}CCH_3}$).

Anal. Calcd for $\mathrm{C_{18}H_{20}N_2O_6}$: C, 59.99; H, 5.60; N, 7.78. Found: C, 59.98; H, 5.81; N, 7.54.

The phenylurethan derivative of 1, prepared in a conventional way, had mp 56–57° (from petroleum ether, bp 90–110°) and showed significant ir absorptions at 3.01 ($\mathrm{>NH}$), 5.89 ($\mathrm{-CON<}$), 8.05 ($\mathrm{-O_2C-}$), and 13.34 μ (aromatic). Its nmr spectrum showed peaks at τ 2.73–3.2 (m, aromatic and N–H), 4.57 (s, $\mathrm{>C{=}CH}$), 5.22 (s, $\mathrm{>C{=}CH_2}$), 5.28 (t, $\mathrm{-CH_2O_2C-}$), 7.69 (t, $\mathrm{-CH_2CH_2O_2C-}$), 8.05 (m), and 8.38 (s, $\mathrm{>C{=}CCH_3}$).

Anal. Calcd for $\mathrm{C_{18}H_{12}NO_2}$: C, 75.75; H, 8.12; N, 4.91. Found: C, 75.87; H, 8.04; N, 4.95.

Reaction of *d*-Limonene with Paraformaldehyde Catalyzed by Boron Trifluoride Complexes. I. With Boron Trifluoride Etherate. A. In Solvent Methylene Chloride.—A solution of 1.0 ml of boron trifluoride etherate in 60 ml of dry methylene chloride was added over a 20-min period to a stirred mixture of 90.5 g (0.665 mol) of *d*-limonene, 9.9 g (0.33 mol) of PFA, and 300 ml of dry methylene chloride at room temperature under nitrogen. This mixture was stirred for 1 hr, treated with 20 ml of saturated sodium bicarbonate solution, and worked up in a conventional way to give a 47% yield (26 g) of the alcohol 1, bp 81–91° (0.30 mm) and $n^{25}\mathrm{D}$ 1.4964, of about 80% purity (glpc analysis).

B. In Solvent Methylene Chloride–Acetic Anhydride.—A solution of 1.0 ml of boron trifluoride etherate in 90 ml of a 1:1 by volume mixture of methylene chloride and acetic anhydride was added to a stirred mixture of 45.2 g (0.332 mol) of *d*-limonene, 5.00 g (0.166 mol) of PFA, 75 ml of methylene chloride, and 75 ml of acetic anhydride at room temperature under nitrogen. After a total reaction time of 142 min (reaction temperature rose to 36° before subsiding) the mixture was worked up in a conventional way to give three principal fractions upon distillation: (1) 19.1 g, bp 35–50° (5.5 mm), $n^{25}\mathrm{D}$ 1.4680; (2) 27.6 g, bp 88–95° (0.25 mm), $n^{25}\mathrm{D}$ 1.4778; (3) 6.37 g, bp 98–148° (0.25 mm), $n^{25}\mathrm{D}$ 1.4845. Fraction 1 was recovered *d*-limonene and corresponded to 84.5% of the excess used. Fraction 2 represented an 80% yield of the expected limonenyl carbinol acetate 3 of *ca.* 80% purity (glpc analysis[5d]).

II. With Boron Trifluoride Diphenol. A. In Solvent Methylene Chloride.—A solution of 5 ml of boron trifluoride diphenol in 95 ml of dry methylene chloride was added over a 45-min period to a stirred mixture of 90.5 g (0.733 mol) of *d*-limonene and 9.9 g (0.33 mol) of PFA in 300 ml of dry methylene chloride at room temperature under nitrogen. The mixture was stirred for another hour, and, after a conventional work-up, gave on distillation unreacted *d*-limonene together with two principal product fractions: (1) 32.5 g, bp 84–91° (0.35 mm), $n^{25}\mathrm{D}$ 1.4949, and (2) 17.5 g, bp 140–170° (0.20 mm), $n^{25}\mathrm{D}$ 1.5040. Fraction 1 represented a 59% yield of the alcohol 1 of purity 75% (glpc analysis[5e]). Fraction 2 was comprised of high boiling alcohols and ethers.

Upon repetition of the reaction described above using 3.0 and 7.0 ml of catalyst the impure alcohol 1 was obtained in 53 and 49% yield, respectively. The high boiling product, bp 100–190° (0.15–0.40 mm) and $n^{25}\mathrm{D}$ 1.5028–1.5055, was obtained in substantial amount in all three reactions.

2,10-Bis(4′-methyl-3′-cyclohexenyl)-5,7-dioxa-1,10-hendecadiene (5).—Examination of the combined high boiling product fraction obtained in the three reactions described in the preceding section (glpc and infrared analysis of redistilled fractions) indicated that it was composed of *ca.* 25% of the alcohol 1 and *ca.* 42% of a complex mixture of alcohols and ethers. Redistillation of a fraction of bp 137–168° (0.20 mm) gave a fraction, bp 152–153° (0.15 mm), whose ir spectrum showed a trace of an hydroxylic component. Column chromatography over neutral alumina with petroleum ether (bp 30–60°) as eluent removed this impurity. Careful redistillation of the chromatographed material gave a center-cut, bp 147–148° (0.15 mm) and $n^{25}\mathrm{D}$ 1.5029, whose properties indicated it to be the formal 5. In the infrared it showed strong absorption maxima at 6.10 6.94, 7.26, 9.0, 9.3, 9.7, 11.2, and 12.5 μ; its nmr spectrum showed absorptions at τ 4.61 (br s), 5.25 (br s), 5.43 (s), 6.42 (t), and 8.37 (br s).

Anal. Calcd for $\mathrm{C_{23}H_{36}O_2}$: C, 80.18; H, 10.53; mol wt, 344.52. Found: C, 79.99; H, 10.46; mol wt, 345 (chloroform).

2,6-Bis(4′-methyl-3′-cyclohexenyl)-6-methyl-5-oxa-1-heptene (4).—From the high boiling fraction described at the beginning of the preceding section there was obtained, after redistillation, a lower boiling component, bp 124–126° (0.15 mm). This fraction was chromatographed over neutral alumina, benzene–petroleum ether (bp 30–60°) eluent, and redistilled to give a center cut (bp 124–124.5° (0.10 mm) and $n^{25}\mathrm{D}$ 1.5019) whose spectral properties were in agreement with the ether structure 4. In the infrared it showed significant absorption maxima at 5.98, 6.90, 7.23–7.33, 9.33, 11.23, and 12.49 μ. The nmr spectrum showed absorptions at τ 4.66 (br s), 5.27 (br s), 6.62 (t), 7.79 (t), 8.38 (br s), and 8.94 (s).

Anal. Calcd for $\mathrm{C_{21}H_{34}O}$: C, 83.38; H, 11.33; mol wt, 302.48. Found: C, 83.35; H, 11.46; mol wt, 310 (acetone).

B. In Solvent Methylene Chloride–Acetic Anhydride.—Reaction was carried out as described in section IB above. A mixture of 46.3 g (0.34 mol) of *d*-limonene and 4.8 g (0.16 mol) of PFA in 100 ml of methylene chloride and 100 ml of acetic anhydride, to which had been added 1.0 ml of boron trifluoride diphenol in 53 ml of the mixed solvent, was stirred under nitrogen at autogenous temperature. The usual work-up gave 27.0 g of a distilled product fraction (bp 87–96° (0.20–0.25 mm) and $n^{25}\mathrm{D}$ 1.4780) and corresponded to an 81.5% yield of the acetate of a 1:1 reaction product. Glpc analysis[5f] showed that it contained 88.5% of the acetate 3.

III. With Boron Trifluoride Dihydrate.—The procedure outlined in sections IB and IIB was followed. From 53 g (0.39 mol) of *d*-limonene and 5.7 g (0.19 mol) of PFA in 100 ml each of methylene chloride and acetic anhydride to which 0.40 ml of boron trifluoride had been added there was obtained, after a total reaction time of 70 min, 32.4 g (82%) of a distilled product fraction (bp 90–102° (0.40–0.45 mm) and $n^{25}\mathrm{D}$ 1.4775) that was found by glpc analysis[5d] to be composed mainly (84%) of the acetate 3. Three redistillations of this product gave a sample of 3 (purity >96% by glpc analysis[5d]) whose ir and nmr spectra as well as elemental analysis were in accord with those given previously for 3 (*supra vide*).

The Phosphoric Acid Catalyzed Reaction of *d*-Limonene with Paraformaldehyde.—To a stirred mixture of 100 g (0.735 mol) of *d*-limonene, 25.5 g (0.750 mol) of PFA, 160 ml of glacial acetic acid, and 25 ml of acetic anhydride cooled to 5° there was added a solution of 25 g of phosphoric acid in 25 ml of acetic acid over a 2-hr period. Stirring was continued at 5–15° for an additional 6 hr and the mixture than allowed to stand overnight. Work-up of the reaction mixture gave unreacted limonene (10.15 g) and three principal product fractions: (1) 1.11 g, bp 30–40° (0.15 mm), $n^{23}\mathrm{D}$ 1.4835; (2) 4.5 g, bp 45–47° (0.10 mm), $n^{23}\mathrm{D}$ 1.4775; (3) 46.70 g, bp 50–70° (0.10 mm), $n^{23}\mathrm{D}$ 1.4868. All three fractions showed very similar infrared spectra with strong absorptions at $\lambda_{\max}$ 2.94, 3.42, 5.81, 7.04, 7.94–8.32, 9.52–9.70, 11.3, and 12.5 μ. The fractions 2 and 3 represented a 34% yield of acetates (such as 1) derived from limonene. Glpc analysis[5g] of fraction 3 indicated that it consisted of three major and at least six minor components.

The Formic Acid Catalyzed Reaction of *d*-Limonene with Paraformaldehyde.—From a mixture of 89 g (0.655 mol) of *d*-limonene, 9 g (0.30 mol) of PFA, 10.5 g of 98–100% formic acid, and 250 ml of glacial acetic acid stirred for 1–3 days at 95–100° there was obtained two principal product fractions: (1) 27.3 g, bp 78–98° (0.40–0.45 mm), $n^{25}\mathrm{D}$ 1.4752; (2) 15.0 g, bp 120–135° (0.40 mm), $n^{25}\mathrm{D}$ 1.4820. Fraction 1 amounted to a 44% yield of a mixture of three monoacetates. Glpc analysis[5h] indicated that the three components were present in about equal amounts.

Thermal Reactions of *d*-Limonene with Paraformaldehyde. A. In a Sealed Autoclave.—A mixture of 313 g (2.37 mol) of *d*-limonene, and 62.4 g (2.08 mol) of PFA was heated with shaking for 10 hr at 175–185° in a 4-l., stainless steel bomb. The cooled, clear product was taken up in ether, washed with water, and dried ($MgSO_4$). Upon distillation there was obtained 194 g of *d*-limonene and three principal product fractions: (1) 11.8 g, bp 71–95° (0.35 mm), n^{27}D 1.4891; (2) 72.3 g, bp 94–95° (0.35 mm), n^{27}D 1.4845; (3) 21.0 g, bp 110–132° (0.20 mm), n^{27}D 1.5029. The undistilled residue was 22.3 g. The combined fractions 1 and 2 represented a 24.4% yield of an alcohol such as **1**; glpc analysis,[5d] showed that it was comprised of four major components in a 9:3:2:1 ratio. The two fractions had similar ir spectra: λ_{max} 2.96, 3.40, 5.71, 6.03, 6.87, 7.28, 8.44, 9.49, 10.85, 11.16, and 12.43 μ as well as 5.71 and 8.44 μ indicative of formate ester. Fraction 3 showed strong ir absorptions for alcohol and ester groups but since glpc analysis[5i] gave ill-defined peaks it was not examined further.

A mixture of 300 ml of anhydrous methanol, 1.5 g of dibutyl tin oxide, and 72 g of fraction 2, estimated by glpc analysis to contain *ca.* 14.5 g (0.0732 mol) of formate ester, was heated for 2 hr at 70–75°. Distillation of the reaction mixture gave three principal product fractions: (1) 5.6 g, bp 60–78° (0.20–0.10 mm), n^{25}D 1.4945; (2) 40.6 g, bp 78–78.5° (0.05 mm), n^{25}D 1.4980; (3) 18.0 g, bp 68–73° (0.025 mm), n^{25}D 1.4995. Infrared analysis showed that fraction 1 contained a trace of formate ester whereas fractions 2 and 3 were formate free; the latter spectra were similar.

The ir spectrum of the major fraction 2 was identical with that of "homolimonenol," (n^{27}D 1.4988) previously reported:[3b] λ_{max} 2.98, 3.49, 6.05, 7.01, 7.25, 9.5–9.9, 11.25, and 12.5 μ. In addition, glpc analysis[5i] of this fraction showed that it was identical with an authentic sample of "homolimonenol" and that it was comprised of *ca.* 75–80% of the limonenyl carbinol **1**.

When the *d*-limonene–formaldehyde experiment described above was carried out in the presence of added sodium acetate (0.01 mol/0.10 mol PFA) no appreciable reaction occurred. Recovery of the initially charged limonene was *ca.* 88%.

B. At Atmospheric Pressure.—A mixture of 81 g (0.50 mol) of *d*-limonene, 9.0 g (0.30 mol) of PFA, and 300 ml of glacial acetic acid heated at 98–101° for *ca.* 2 days gave, after the usual work-up and distillation, two principal product fractions: (1) 8.39, bp 78–83° (0.35 mm), n^{26}D 1.4748; (2) 26.0 g, bp 88–93° (0.35 mm), n^{26}D 1.4780. Glpc analysis of fraction 2[5k] showed that it consisted primarily (*ca.* 80%) of a single component, the expected acetate **3**. This was confirmed by comparison of its ir spectrum and refractive index with those of an authentic sample of **3**.

***cis*,*trans*-9-Hydroxymethyl-*p*-menthane** (**6**).—Catalytic hydrogenation, in a Parr apparatus, of 23.0 g (0.138 mol) of the alcohol **1** in 80 ml of ethyl acetate over 0.8 g of Adams catalyst under 35–45 psi of hydrogen for 36 hr at room temperature gave 21 g (88%) of the saturated alcohol **6**, bp 70–77° (0.30 mm) and n^{25}D 1.4692. Glpc analysis[5l] indicated that the product consisted of two major closely eluting components together with a small amount of a lower boiling compound. Ir analysis indicated the absence of unsaturated and ester materials.

Anal. Calcd for $C_{11}H_{22}O$: C, 77.58; H, 13.02. Found: C, 77.53; H, 12.91.

Column chromatography of the alcohol **6** over neutral alumina did not effect separation of the *cis* and *trans* isomers.

A similar hydrogenation of 25.4 g of the alcohol **1** in 100 ml of absolute ethanol over 0.35 g of platinum black for 2 days gave 24.4 g (92%) of **6** (bp 85–93° (0.45 mm) and n^{25}D 1.4692) identical with the alcohol described above.

9-Hydroxymethyl-1-*p*-menthene (**7**).—Catalytic hydrogenation of 20.3 g of the alcohol **1** in 100 ml of absolute ethanol over 0.3 g of platinum black for 18 hr, under 22–39 psi of hydrogen gave two principal product fractions: (1) 14.8 g, bp 80–90° (0.4 mm), $n^{26.5}$D 1.4800; (2) 3.4 g, bp 91–92° (0.4 mm), $n^{26.5}$D 1.4837. Glpc analysis[5m] showed that fraction 2 was *ca.* 95% pure **7**. Ir and nmr analysis were in support of the proposed structure **7**: λ_{max} 3.04, 3.52, 7.05, 7.36, 9.36, 11.0, and 12.5 μ; nmr τ 4.68 (br s, $=CH$), 6.23 (t, $-CH_2OH$), 6.43 (s, $-OH$), 8.38 ($>C=CCH_3$), and 9.13 (d, saturated CH_3).

Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98; mol wt, 168.27. Found: C, 78.59, 78.46; H, 11.91, 12.02; mol wt, 164 (chloroform).

Catalytic hydrogenation of the alcohol **7** with either Adams catalyst or platinum black gave the saturated alcohol **6** that was comprised of the same mixture of *cis* and *trans* isomers previously described.

Methacrylates of the Alcohols 1 and 6. A. 9-Hydroxymethyl-1,8(10)-*p*-menthadiene Methacrylate.—The procedure of Burtle and Turek[6] was used. From 8.3 g (0.05 mol) of the alcohol **1** there was obtained 10.5 g (45%) of the methacrylate derivative, bp 90–93° (0.15 mm) and n^{24}D 1.4900. Glpc analysis[5n] of a redistilled sample of the ester showed but one component. Significant ir absorptions were observed at 5.8–5.9, 6.10, 8.4–8.7, and 11.18 μ. The nmr spectrum had peaks at τ 4.03 (m, $-(CH_3C=C(H)-)$, 4.59 (m, $-(CH_3)C=C(H)-)$, 4.70 (s, $>C=CH-)$, 5.25 (m, $>C=CH_2$), 5.86 (t, $-CH_2O_2C-$), 7.70 (t, $-CH_2CH_2O-$), 8.17 (t, $-(CH_3)C=CH_2$), and 8.45 ($-(CH_3)C=CH-$).

B. 9-Hydroxymethyl-*p*-menthane Methacrylate (**8**).—Transesterification of 27.2 g (0.26 mol) of methyl methacrylate with 18.6 g (0.108 mole) of the alcohol **6** in the presence of 0.3 g of sulfuric acid and 1.0 g of cupric acetate was carried out at 100° for 16.5 hr. During this period material of bp 55–64° was removed intermittently. Work-up and distillation of the mixture gave two principal product fractions: (1) 1.2 g, bp 50–80° (0.25 mm), n^{25}D 1.4680; (2) 20.5 g, bp 97–104° (0.25 mm), n^{25}D 1.4660. Fraction 2, which corresponded to an 81% yield of the desired methacrylate, gave after redistillation a center cut, (bp 90° (0.35 mm) and n^{25}D 1.4662) of purity >99% (glpc analysis[5o]). The ir spectrum of the latter showed λ_{max} 3.51, 5.91, 7.65, 7.82, 8.62, 10.8, and 12.8 μ; nmr peaks were at τ 3.94 and 4.52 (d, $>C=CH_2$), 5.85 (t, $-CH_2O_2C-$), 8.09 (d, $-(CH_3)C=CH_2$), 9.02–9.13 (m, saturated CH_3-).

Anal. Calcd for $C_{25}H_{26}O_2$: C, 75.58; H, 11.00; mol wt, 238.36. Found: C, 75.62, 75.51; H, 11.01, 11.08; mol wt, 241, 238 (benzene).

Polymerization of the Methacrylate of the Alcohol 6. A. Homopolymerization.—Bulk polymerization of the methacrylate **8**, initiated with azobisisobutyronitrile, was carried out at 47–48° for 3 days. The initially formed (83%) clear, glassy polymer was soluble in benzene and toluene; insoluble in chloroform, acetone, and methanol.[7] (It was difficult to pulverize and dry the polymer because of its tendency to acquire a static charge.) The dried, rather soft polymer showed mp 225–230°. Its intrinsic viscosity in benzene[8] was 3.72 dl/g of polymer. The ir spectrum of the polymer as a film, obtained on slow evaporation of its benzene solution, showed signals at λ_{max} 3.5, 5.8, 7.9, 8.5–9.9, and 12.5 μ.

Anal. Calcd for $(C_{15}H_{26}O_2)_n$: C, 75.58; H, 11.00. Found: C, 75.71, 75.29; H, 11.24, 11.32.

B. Copolymerization with Methyl Methacrylate.—Bulk polymerization of 1.85 g of the methacrylate **8** and 2.0 g of methyl methacrylate (28.3:71.7 mole % ratio), initiated with 0.04 g of azobisisobutyronitrile, was effected at 50° for 24 hr. The crude polymer was dissolved in warm chloroform, the filtered solution added to methanol, and the precipitated copolymer collected and dried at 100° *in vacuo*. The reprecipitation and drying were repeated twice to give 3.29 g (85.5%) of the copolymer as a white tractable powder, mp 215–225°, whose intrinsic viscosity in benzene was 3.69 dl/g of polymer. Elemental analysis indicated that the polymer was indeed a copolymer of **8** and methyl methacrylate.

Anal. Found: C, 67.96, 67.81; H, 9.52, 9.70.

Registry No.—*d*-Limonene, 5987-27-5 **1**, 15766-66-2; **1** 3,5-dinitrobenzoate, 15766-67-3; **1** phenylurethan derivative, 15766-68-4; **3**, 6819-19-8; **4**, 15815-76-6; **5**, 15760-15-3; **6** (*cis*), 15760-16-4; **6** (*trans*), 15760-17-5; **7**, 15760-18-6; **8**, 15760-19-7; 9-hydroxymethyl-1,8(10)-*p*-menthadiene methacrylate, 15760-20-0.

Acknowledgment.—This study was carried out under Contract No. 12-14-100-6884(72) with the Southern Utilization Research and Development Division, U. S. Department of Agriculture, Agricultural Research Service.

---

[6] J. G. Burtle and W. N. Turek, *J. Org. Chem.*, **19**, 1507 (1954).

[7] Criterion for solubility: solution of 50 mg of polymer in 10 ml of solvent after vigorous stirring for 0.5 hr at room temperature.

[8] Intrinsic viscosity measurements were kindly performed in the research laboratory of the Rohm and Haas Co., Bristol, Pa.