eluted with petroleum ether–benzene 4:1 (75%). The residue was distilled at 0.2-mm pressure. The distillate showed a single spot on tlc and a single peak in glpc (15% S.E. 30, 80–100 mesh, 248°, R_T 6.45 min). Mass spectrum showed a *m/e* 234 (M); ν (neat) 1605 cm^{-1} (aromatic); ultraviolet maxima at 288 mμ (ϵ 2850); nmr, δ 6.68 (3 H, aromatic, multiplet), 3.75 (5 H, methoxy and carbinolic), 3.3–2.58 (2 H, benzylic, multiplet).

1,4,3′,4′,5′,6′-Hexahydro-6-methoxyspiro[3H-2-benzopyran-3,2′(2H)-pyran]-1-one (18).—Sodium hydride (0.4-g oil suspension) was washed with hexane and suspended in tetrahydrofuran (15 ml). A solution of lactone **9e** (0.2 g) in dry tetrahydrofuran (5 ml) was added to the boiling suspension of sodium hydride. The mixture was refluxed overnight and cooled, acetic acid (1 ml) was added, and the mixture was diluted with ether, washed with water, and dried. Residue (0.5 g) was passed through alumina (neutral activity II, 4.5 g). Elution with petroleum ether–benzene gave crystals (0.118 g). Acetone–hexane gave crystals: mp 150–151°; ν_{max} (Nujol) 1700 (carbonyl), 1600, 1575 cm^{-1} (aromatic); ultraviolet, 259 mμ (ϵ 15,600); nmr, δ 7.99 (1 H, aromatic *ortho* to carbonyl, doublet, J = 8 Hz), 6.80 (2 H, aromatic), 3.81 (5 H, methoxyl, singlet and carbinolic), 3.05 (2 H, benzylic, doublet).

Anal. Calcd for $C_{14}H_{16}O_4$ (248): C, 67.73; H, 6.5. Found: C, 67.79; H, 6.33.

Registry No.—**5a,** 6742-26-3; **5b,** 16425-80-2; **5c,** 16425-81-3; **5d,** 16425-82-4; **5e,** 16452-35-0; **5f,** 16425-83-5; **6a,** 16425-84-6; **6b,** 16425-85-7; **6c,** 16425-86-8; **6d,** 16425-87-9; **6e,** 16425-88-0; **6f,** 16425-89-1; **6g,** 16425-62-0; **7a,** 16425-91-5; **7b,** 16425-92-6; **7c,** 16425-93-7; **7d,** 16425-94-8; **7e,** 16425-95-9; **7f,** 16425-96-0; **7g,** 16425-65-3; **8,** 16425-53-9; **9a,** 16425-54-0; **9b,** 16425-55-1; **9c,** 16425-56-2; **9d,** 16425-66-4; **9e,** 16425-57-3; **9f,** 16452-36-1; **11,** 16425-58-4; **12,** 16425-59-5; **13,** 16425-60-8; **14,** 16425-61-9; **15,** 16425-62-0; **16,** 16425-63-1; **18,** 16425-64-2.

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Terpene–Formaldehyde Reactions. III. Camphene[1]

A. T. BLOMQUIST, RICHARD J. HIMICS,[2] AND JIM D. MEADOR[2]

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

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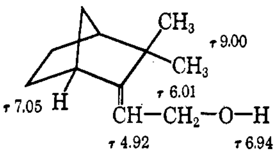
Boron trifluoride dihydrate catalysis of the camphene–formaldehyde reaction in solvent methylene chloride–acetic anhydride affords 8-hydroxymethyltricyclene acetate as the principal product (*ca.* 55%). The corresponding tricyclo alcohol is the main product when the reaction is carried out in solvent methylene chloride with stannic chloride as catalyst. In contrast to the foregoing, reaction of camphene with formaldehyde in solvent acetic acid, either in the absence of added catalyst or with added phosphoric acid, gives unrearranged 8-hydroxymethylcamphene acetate as the principal product together with smaller amounts of the parent alcohol and its formate. Depending upon conditions, the latter reactions afford yields of product that vary from *ca.* 47 to 94%.

As part of a general program concerned with the obtainment of primary alcohols from certain of the more readily available terpenes, it was of interest to make a thorough study of the camphene–formaldehyde reaction. Appropriate derivatives of primary alcohols derived from camphene, such as acrylic and methacrylic esters, could afford interesting and useful homo- and copolymers.

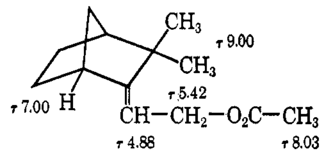
Earlier studies of the camphene–formaldehyde reaction have been limited to those carried out under simple thermal "noncatalyzed" conditions and those catalyzed by mineral acids;[3–8] there are no early reports on reactions effected in the presence of Lewis acid catalysts, conditions that afforded rather interesting results in the limonene–formaldehyde condensation.[1b]

This report supplements the preliminary account of observations made on the Lewis acid catalyzed camphene–formaldehyde reaction[1a] and also presents briefly pertinent results obtained in reexamination of the title reaction effected under thermal and mineral acid catalyzed conditions. The isolation, purification, analysis, and characterization of products formed in all reactions studied involved extensive use of the technique of glpc together with the methods of ir and nmr spectroscopy.

The thermal camphene–formaldehyde reaction is best done under atmospheric pressure in glacial acetic acid at reflux temperature (*ca.* 120°) as described by Langlois.[4] Under these conditions reaction for 2 days of a 2:1 mol ratio of camphene to formaldehyde gives a 94% yield of a 1:1 reaction product that comprises *ca.* 80% 8-hydroxymethylcamphene acetate (**1b**); the remainder consists mainly of 8-hydroxymethylcamphene (**1a**) and its formate. The pure alcohol **1a** is readily obtained, *via* preparative glpc, from the acetate **1b** by (a) lithium aluminum hydride reduction, (b) methanolysis, or (c) alkaline hydrolysis. Nmr and ir spectral data together with chemical properties support the structural assignments (see Experimental Section). Use of camphene that contains 20–25% tricyclene[8] affords an 84% yield of the 1:1 reaction product whose principal component (*ca.* 85%) is the acetate **1b**. A reduced yield of the 1:1 reaction product (*ca.* 47 *vs.*



1a



1b

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[1] For two closely related reports from this laboratory on terpene–formaldehyde reactions, see (a) A. T. Blomquist and R. J. Himics, *Tetrahedron Lett.*, 3947 (1967); (b) A. T. Blomquist and R. J. Himics, *J. Org. Chem.*, **33**, 1156 (1968).

[2] Abstracted from portions of the dissertations presented by R. J. Himics and J. D. Meador to the Graduate School of Cornell University for the Ph.D. degree, Feb 1967.

[3] H. J. Prins, *Chem. Weekbl.*, **14**, 932 (1917); **16**, 1072 (1919); **16**, 1510 (1919); *Chem. Zentr.*, 168 (1918); *Chem. Abstr.*, **13**, 3155 (1919); **14**, 1662 (1920); **14**, 1119 (1920).

[4] G. Langlois, *Ann. Chim.*, **12**, 265 (1919).

[5] J. P. Bain, *J. Amer. Chem. Soc.*, **68**, 638 (1946).

[6] Y. Watanabe, *J. Chem. Soc. Jap.*, **81**, 827 (1960).

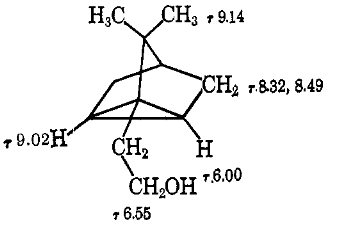
[7] S. Watanabe, S. Miki, T. Matsuzaki, Y. Nagaoka, and K. Suga, *Chiba Daigaku Kogakuba Kenkyu Hokoku*, **14** (26), 111 (1963); *Chem. Abstr.*, **62**, 7802 (1965).

[8] S. Ramaswami, S. K. Ramaswami, and S. Bhattacharyya, *J. Org. Chem.*, **29**, 2245 (1964).

94%) is observed when the condensation is carried out in a sealed autoclave and solvent acetic acid at 103–105° for 16 hr.[7] Again, little change in product yield is noted when camphene containing tricyclene (15%) is used (see Experimental Section).

The mineral acid catalyzed reaction of camphene with formaldehyde was best done with 85% phosphoric acid in solvent glacial acetic acid. Reaction at 23–29° for 24 hr gave 66% of a 1:1 product mixture that contained 79% of the acetate **1b**.[6]

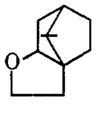
The use of Lewis acids as catalysts effects a substantial change in the nature of the principal reaction product that results from condensation of camphene with formaldehyde.[1a] Reaction of a 2:1 mol ratio of camphene and formaldehyde in solvent methylene chloride–actic anhydride for *ca.* 90 min at autogenous temperature (25–54°) in the presence of boron trifluoride dihydrate catalyst gives mainly (*ca.* 57%) 8-hydroxymethyltricyclene acetate (**2b**). The free alcohol, 8-hydroxymethyltricyclene (**2a**), is the principal product obtained when reaction is carried out in methylene chloride (2 days at 25–27°) with fuming stannic chloride added as catalyst: yield, 49% of a 1:1 reaction product that contained *ca.* 65–70% of the alcohol **2a**.



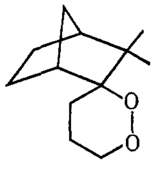
2a

Nmr and ir spectra (including near-ir) together with elemental analyses and chemical properties support the assignments of structures **2a** and **2b** (see Experimental Section and also ref 1a). The acetate **2b** was observed to rearrange slowly to the acetate **1b** when heated in acetic acid at reflux temperature; about a 1:1 mol mixture of the isomeric acetates is formed from the acetate **2b** after a 4-day period of heating.

Three accessory products were isolated from the stannic chloride catalyzed reaction in solvent methylene chloride: (1) the tricyclo ether **3**, mp 129–130°; (2) the spiro-*m*-dioxane **4**, mp 44–44.5°; and (3) the unsymmetrical high-boiling ether **5** derived from the



3



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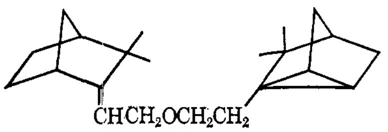

5

alcohols **1a** and **2a**. The structural assignments of the three accessory products are supported by the ir and nmr data given in the Experimental Section. Hydrolysis of the *m*-dioxane **4** with aqueous acetic acid produces the acetate **1b** together with some of the alcohol **1a**. It was noted that the dioxane **4** is the principal product formed in the boron trifluoride etherate catalyzed reaction of camphene with formaldehyde in methylene chloride at 25° for 2.5 hr.

With the pure alcohol **1a** available in quantity it was of interest to examine very briefly the polymerization of 8-hydroxymethylcamphane methacrylate (**7**). Under carefully controlled conditions to avoid hydrogenolysis, catalytic hydrogenation of the alcohol **1a** in ethanol over platinum black gave the saturated primary alcohol 8-hydroxymethylcamphane (**6**) in high yield (95%), as a mixture of *endo* and *exo* isomers. The methacrylate derivative of the alcohol **6** (**7**) was easily prepared *via* transesterification with methyl methacrylate. Free-radical initiation of the ester **7**, either in bulk or emulsion, gave the homopolymer in high yield (90–95%), mp 207–215° and intrinsic viscosity of 6.91 dl/g of polymer (in benzene at 30°). Similarly, bulk copolymerization of the methacrylate **7** with styrene occurred smoothly (71%) to give a polymeric material that showed mp 196–205° and an intrinsic viscosity of 3.50 dl/g (in benzene at 30°).

Experimental Section[9,10]

Materials.—Pure camphene (*ca.* 95%), obtained from the Hercules Powder Co., was used in all studies unless otherwise indicated. Authentic tricyclene was obtained from Chemicals Procurement Laboratories, Inc. 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.

Thermal Reactions of Camphene with Paraformaldehyde. A. In a Sealed Autoclave.—A mixture of 57 g (0.42 mol) of camphene (purity *ca.* 95%), 6.6 g (0.22 mol) of paraformaldehyde, and 57 g of glacial acetic acid was heated with shaking for 16 hr at 103–105° in a 200-ml stainless steel bomb. After a conventional workup, distillation gave 28 g of camphene and two principal product fractions: (1) 14.4 g, bp 68–71° (0.25 mm), n^{18}D 1.4825, and (2) 7.4 g, bp 70–77° (0.30 mm), n^{18}D 1.4850. The two fractions corresponded to a 47.5% yield of an acetate such as **1b** but contained some of the free alcohol **1a** and the formate ester of **1a**.

The combined product fractions, 21 g, were heated for 2 hr at 100–105° with 20 g of acetic anhydride and 2 g of sodium acetate. Work-up of the cooled mixture gave three fractions of the acetate **1b**: (1′) 1.3 g, bp 59–64° (0.20 mm), n^{19}D 1.4805; (2′) 7.3 g, bp 66–69° (0.30 mm), n^{19}D 1.4823; (3′) 6.2 g, bp 72–73° (0.45 mm), n^{19}D 1.4831. Glpc analysis[10a] of fractions 2′ and 3′ showed one major component; the ir spectrum showed no hydroxyl absorption but had significant absorptions at 5.85 (acetate), 5.97 (strained double bond), 7.27–7.35 (doublet, *gem*-dimethyl), and 8.05–8.15 μ (acetate). In the nmr the acetate

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[9] 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 Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., or by Galbraith Laboratories, Inc., Knoxville, Tenn.

[10] 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 were 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 and preparative columns together with the column temperature were as follows: (a) 20% Carbowax 20M at 185°; (b) diethylene glycol adipate (DEGA) at 180°; (c) same as (a) at 200°; (d) 20% Versamid 900 at 185°; (e) same as (d) at 180°; (f) 15% diethylene glycol sebacate (DEGS)–5% Bentone 34 at 180°; (g) 15% DEGA–5% Bentone at 180°; (h) same as (f) at 185°; (i) 8-ft 20% DEGA plus 8-ft 20% Versamid at 200°; (j) same as (b) at 175°; (k) same as (f) at 165°; (l) 20% polyphenyl ether (5 ring) at 170°.

1b showed peaks at τ 4.88 (t, >C=CH—), 5.42 (d, -CH_2OAc), 7.0 (br, s), 8.03 (-O_2CCH_3), and 9.0 (br, s, >C(CH_3)$_2$).

Repetition of the above experiment with camphene that contained *ca.* 15% tricyclene gave a product acetate (43% yield) that had n^{19}D 1.4835 and whose ir spectrum was identical with that of the crude acetate previously obtained.

B. At Atmospheric Pressure.—A mixture of 62 g (0.45 mol) of pure camphene (*ca.* 95%), 6.1 g (0.20 mol) of paraformaldehyde, and 200 ml of glacial acetic acid was heated with stirring at 110–120° (gentle reflux) for 2 days. Conventional work-up of the mixture gave 43 g of a distilled product: bp 73–93° (0.50 mm), n^{25}D 1.4798. This corresponded to a 94% yield of the acetate **1b**. Glpc analysis[10b] showed that it contained *ca.* 80% of the desired acetate **1b**.

Repetition of the preceding experiment at 116–125° for 16 hr with camphene that contained 20–25% tricyclene gave an 84% yield of a product, bp 90–94° (0.50 mm) and n^{25}D 1.4865, that contained *ca.* 85% of the acetate **1b** (glpc analysis[10b]).

8-Hydroxymethylcamphene (**1a**).—To 1.20 g (0.0316 mol, 100% excess) of lithium aluminum hydride in 150 ml of anhydrous ether there was added slowly 5.90 g (0.0284 mol) of the acetate **1b**. This mixture was refluxed for 24 hr and, after a conventional work-up, afforded 4.5 g (96%) of distilled alcohol **1a** that had bp 68–72° (1.40 mm). After redistillation the alcohol **1a** of *ca.* 90% purity (glpc analysis[10a]) was obtained: bp 63° (0.15 mm), n^{20}D 1.5018 [lit.[6] bp 109° (5.0 mm), n^{25}D 1.5015]. Purification of this alcohol *via* preparative glpc[10c] followed by a final redistillation gave the alcohol **1a** of 98% purity (glpc analysis[10d]), n^{20}D 1.5028. The ir spectrum of the alcohol **1a** had characteristic absorptions at 3.0 (OH), 5.95 (>C=C<), 7.23–7.34 [$(CH_3)_2$C<], and 9.80 μ (primary OH).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92; mol wt, 166.25. Found: C, 79.46, 79.60; H, 10.82, 10.97; mol wt, 163 (chloroform).

Methanolysis of the acetate **1b** catalyzed by dibutyltin oxide gave the alcohol **1a**, n^{20}D 1.5025, in almost quantitative yield. The alcohol **1a** was also easily obtained, *ca.* 95% yield, by alkaline hydrolysis of the acetate **1b**.

Several derivatives of the alcohol **1a** were prepared by conventional procedures: the *p*-nitrobenzoate, mp 102–103° (from ethanol–water); the hydrogen phthalate, mp 124–125.2° from hexane (lit.[4,6,11] mp 124–125, 127–127.5, and 127°); the 3,5-dinitrobenzoate, mp 81.5–82° (from methanol) (lit. mp[11] 89°); and the trimethylsilylate, bp 71–73° (0.15 mm) and n^{24}D 1.4680. Glpc analysis of the latter derivative[10e] showed only one component; the ir spectrum had significant absorptions at 5.98 (C=C), 7.23–7.32 [$(CH_3)_2$C], 8.0 (Si–CH_3), 9.0–9.4 (Si–O–CH_2–), 11.1–12.1 and 13.2–13.5 μ (Si–C).

Anal. ***p*-Nitrobenzoate.** Calcd for $C_{18}H_{21}NO_4$: C, 68.55; H, 6.71; N, 4.44. Found: C, 68.57, 68.64; H, 6.75, 6.75; N, 4.38, 4.46. **Hydrogen phthalate.** Calcd for $C_{19}H_{22}O_4$: C, 72.59; H, 7.05. Found: C, 72.49; H, 6.94. **3,5-Dinitrobenzoate.** Calcd for $C_{18}H_{20}N_2O_6$: C, 59.99; H, 5.59; N, 7.77. Found: C, 60.06; H, 5.77; N, 7.93. **Trimethylsilylate.** Calcd for $C_{14}H_{26}OSi$: C, 70.42; H, 11.01; Si, 11.78. Found: C, 70.67; H, 11.08; Si, 11.54.

The Phosphoric Acid Catalyzed Reaction of Camphene with Formaldehyde.—To a stirred mixture of 68.3 g (0.50 mol) of camphene, 9.00 g (0.30 mol) of paraformaldehyde, and 89 ml of glacial acetic acid at room temperature there was added dropwise a solution of 25 g of 85% phosphoric acid in 70 ml of acetic acid over a 30-min period. After this addition, the mixture was stirred at 23–29° for *ca.* 24 hr. A conventional work-up of the reaction mixture gave, upon distillation, 20.6 g of camphene and two principal product fractions: (1) 4.22 g, bp 69–77° (2.0 mm), n^{25}D 1.4765; (2) 40.9 g, bp 77–98° (2.0 mm), n^{25}D 1.4810. Glpc analysis[10f] showed that fraction 1 comprised mainly a mixture of low-boiling components; 79% of fraction 2 was the acetate **1b**, and most of the remainder was the alcohol **1a**. Fraction 2 corresponded to a 66% yield of 1:1 camphene–formaldehyde reaction products.

The Stannic Chloride Catalyzed Reaction of Camphene with Paraformaldehyde.—Fuming stannic chloride (0.30 ml) was added, under nitrogen, to a mixture of 65 g (0.48 mol) of pure camphene (*ca.* 95%) and 8.1 g (0.27 mol) of paraformaldehyde in 250 ml of dry methylene chloride. The mixture was stirred for 2 days at 25–27° and then 10 ml of dilute sodium hydroxide added. A conventional work-up of this mixture gave, after sublimation of unreacted camphene, 39 g of a main product fraction, bp 71–79° (0.35 mm) and n^{25}D 1.4954, that corresponded to a 49% yield of a 1:1 reaction product. Glpc analysis[10g] of this crude product indicated that it contained *ca.* 65–70% of one major component, the alcohol **2a**. The pure alcohol **2a** (99% by glpc analysis[10h]) was obtained *via* preparative glpc:[10i] bp 81–82° (0.75 mm), n^{25}D 1.4899. Its ir spectrum showed significant absorptions at 3.0 (OH), 3.45 (C–H), 7.2, 7.3 [$(CH_3)_2$C], and 9.47–9.62 μ (primary OH). In the near-ir the alcohol **2a** showed absorption at 1.672 μ, attributable to tertiary cyclopropanyl hydrogens. The nmr spectrum was reported earlier.[1a]

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.48; H, 10.82.

Repetition of the reaction described above on a larger scale (268 g of camphene and 26.4 g of paraformaldehyde) made it possible to isolate and characterize some of the accessory products of the reaction. As the first distillation of the crude reaction mixture was begun a volatile sublimate collected in the water-cooled condenser. This sublimate was resublimed at 0.2 mm, chromatographed over neutral alumina (petroleum ether (bp 30–60°) eluent), and finally sublimed at 25°(0.1 mm) to give a white, waxy solid, mp 129–130°. Spectral data indicated that it was the ether 10,10-dimethyltricyclo[4.3.1^{1,7}.0^{1,5}]-4-oxadecane (**3**). In the infrared it showed significant absorptions at 3.40, 3.50, 7.2, 7.3, 9.34, 10.19, and 11.64 μ; the nmr spectrum showed signals at τ 5.92–6.50 (m), 8.98 (s), and 9.15 (s).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92; mol wt, 166. Found: C, 79.56; H, 10.90; mol wt, 168–170 (benzene).

After removal of the ether **3**, fractional distillation of the crude reaction mixture gave four principal fractions: (1) 2.4 g, bp 61–72° (0.35 mm), n^{25}D 1.4870; (2) 23.0 g, bp 78–88° (0.30 mm), n^{25}D 1.4892; (3) 29.0 g, bp 88.5–90.5° (8.30 mm), n^{25}D 1.4905; (4) 48.1 g, bp 140–175° (0.30 mm), n^{25}D 1.5078. Redistillation of the combined fractions 2 and 3 gave the alcohol **2a** which contained a minor impurity (glpc analysis[10j]). The impurity was isolated *via* column chromatography over neutral alumina (ether–benzene as eluent) and proved to be identical with the major product formed in the boron trifluoride etherate catalyzed camphene–formaldehyde reaction (*vide infra*) and shown to be the *m*-dioxane derivative spiro[2,2-dimethylnorbornane-3,1′-(2′,4′-dioxacyclohexane)] (**4**). Finally, after several redistillations of fraction 4 there was isolated the unsymmetrical ether derived from alcohols **1a** and **2a**: bp 141° (0.30 mm); n^{25}D 1.5068; ir spectrum, λ_{max} 6.0, 7.23, 7.32, 9.0–9.3, 11.25–11.4, and 12.0 μ; nmr signals at τ 5.0 (t, >C=CH-CH_2–), 6.21 (d, >C=CHCH_2–), 7.0 (s), 7.07 (–OCH_2–), 8.98 [d, (CH_3)$_2$C, camphene], and 9.17 [s, (CH_3)$_2$C–, tricyclo].

Anal. Calcd for $C_{22}H_{34}O$: C, 84.01; H, 10.90; mol wt, 314.49. Found: C, 84.02, 84.13; H, 11.02, 11.03; mol wt, 320, 316 (benzene).

Reaction of Camphene with Paraformaldehyde Catalyzed by Boron Trifluoride Complexes. I. With Boron Trifluoride Etherate.—To a mixture of 105 g (0.773 mol) of camphene, 11.6 g (0.386 mol) of paraformaldehyde, and 300 ml of dry methylene chloride there was slowly added, with stirring under nitrogen, 1.5 ml of boron trifluoride etherate in 60 ml of methylene chloride. After being stirred for 2 hr at room temperature, the reaction mixture was worked up in a conventional manner. Unreacted camphene (54.5 g) was recovered and the residue distilled to give four fractions: (1) 14.7 g, bp 80–86° (0.40 mm), n^{16}D 1.4940; (2) 2.6 g, bp 91–96° (0.40 mm), n^{25}D 1.4938; (3) 2.4 g, bp 120–142° (0.40 mm), n^{25}D 1.5050; (4) 4.1 g, bp 142–150° (0.40 mm), n^{25}D 1.5068. Glpc analysis[10g] indicated that fractions 1 and 2 comprised a 45% yield of one major product. Fraction 2 (purity *ca.* 85%) was chromatographed over alumina. The material obtained with ether as eluent, bp 58–58.5° (0.15 mm), crystallized on standing. Sublimation at 25° (0.10 mm) gave a white solid, mp 44–44.5°, whose properties were in accord with the *m*-dioxane **4**: ir spectrum, λ_{max} 8.64, 9.01–9.11, 9.65–9.74, 10.00, and 11.8 μ; nmr spectrum τ 5.27 (quad, O–CH_2–O), 6.2–6.7 (m, –CH_2CH_2–O), 7.23 (bs, probably tertiary H), 9.07 and 9.16 [sh s, (CH_3)$_2$C].

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.36, 73.57; H, 10.28, 10.17.

II. With Boron Trifluoride Dihydrate.—To a stirred mixture of 66 g (0.485 mol) of camphene, 7.29 g (0.243 mol) of paraformaldehyde in 100 ml of methylene chloride, and 100 ml of acetic anhydride there was added, under nitrogen, a solution of 0.45 ml of boron trifluoride dihydrate in 40 ml of the mixed solvent over

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(11) S. Watanabe, *Bull. Chem. Soc. Jap.*, **38** (8), 1231 (1965); *Chem. Abstr.*, **63**, 14909 (1965).

an 11-min period. Stirring was continued for another 76 min, during which time the reaction temperature rose to 54°. Dilute sodium hydroxide (20 ml) was added to the cooled mixture which was then worked up in a conventional way. Upon distillation there was obtained 9.2 g of camphene and three product fractions: (1) 10.1 g, bp 70–73° (0.45 mm), n^{28}_{D} 1.4650; (2) 18.6 g, bp 73–79° (0.45 mm), n^{28}_{D} 1.4678; (3) 20.3 g, bp 80–148° (0.45 mm), n^{25}_{D} 1.5048. Fractions 1 and 2 represented at 57% yield of impure 1:1 reaction product. From two redistillations of fractions 1 and 2 there was obtained a center cut, bp 63° (0.3 mm), n^{25}_{D} 1.4698, of the tricyclo acetate **2b**, purity >96% *via* glpc analysis:[10k] ir spectrum, λ_{max} 3.46, 5.73, 7.40, 8.14, and 9.66 μ; nmr spectrum, τ 6.07 (t, $-CH_2O-$), 8.06 (s, O_2C-CH_3), and 9.12 (s, $-CH_3$).

Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68; mol wt, 208.29. Found: C, 74.91, 74.87; H, 9.68, 9.73; mol wt, 202 (chloroform).

Rearrangement of the Acetate 2b to the Acetate 1b.—A solution of 1.30 g (6.24 mmol) of the tricyclo acetate **2b** in 50 ml of glacial acetic acid was heated at 115–117° for *ca.* 4 days. A conventional work-up gave, after distillation, a 52% recovery of a monoacetate fraction, bp 97–98° (5.8–6.0 mm) and n^{25}_{D} 1.4759, that contained the two acetates **1b** and **2b**. Glpc analysis[10l] indicated that the two acetates were present in about a 1:1 ratio. Addition of a sample of pure acetate **1b** enhanced the glpc peak representing the allylic acetate. Similarly, the glpc peak assigned to the tricyclo acetate was increased by the addition of pure tricyclo acetate.

8-Hydroxymethylcamphane (6).—Catalytic hydrogenation, in a Parr apparatus, of 40.9 g (0.246 mol) of the alcohol **1a** in 250 ml of absolute ethanol over 1.15 g of platinum black under 34–39 psi of hydrogen for 44 hr at room temperature gave, after distillation through a Vigreux column, 39 g (95%) of the saturated alcohol **6**: bp 107–112° (4.7 mm), n^{20}_{D} 1.4895–1.4897. Partial resolution of the product into *endo* and *exo* isomers could be achieved by glpc analysis.[10l] Redistillation of the alcohol gave an analytical sample of **6**: bp 86–87° (0.43 mm), n^{21}_{D} 1.4888 [lit.[6] bp 104–105° (5 mm), n^{25}_{D} 1.4874].

Anal. Calcd for $C_{11}H_{20}O$: 78.51; H, 11.98. Found: C, 78.50; H, 11.89.

Methacrylates of the Alcohols 1a and 2a. I. 8-Hydroxymethylcamphene Methacrylate (8).—In an adaptation of the method of Burtle and Turek[12] a mixture of 25 g (0.15 mol) of the alcohol **1a**, 0.3 g of hydroquinone, 0.1 g of copper metal, 0.1 g of cupric chloride, and 17.2 g (0.20 mol) of methacrylic acid in 300 ml of benzene was distilled cyclically, in the presence of 0.20 g of *p*-toluenesulfonic acid, for *ca.* 7 hr; about 2.4 ml (89%) of water was collected. Work-up of the esterification gave, after distillation, 28 g (80%) of impure ester **8**: bp 98–113° (0.45 mm), n^{25}_{D} 1.4881. Two redistillations gave a sample of the methacrylate **8** of purity >91% (glpc analysis[10g]): bp 79–80° (0.25 mm); n^{25}_{D} 1.4908; ir spectrum, λ_{max} 5.89 (C=O), 6.01 (internal C=C), 6.15 ($C=CH_2$), 7.37, 7.4 [doublet, $(CH_3)_2C$], and 7.6–7.7 μ (C–O–); nmr spectrum, τ 3.97 [m, $(CH_3)C=CH_t-$], 4.54 (m, $CH_3C=CH_c$), 4.87 (t, $-C=CHCH_2$), 5.43 [d, $>C=C-(CH_2O)-$], 8.10 (t, $CH_3C=CH_2$), and 8.96 [d, $(CH_3)_2C$].

Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.47. Found: C, 76.91, 77.03; H, 9.34, 9.35.

II. 8-Hydroxymethylcamphane Methacrylate (7).—Transesterfication of 25.0 g (0.149 mol) of the alcohol **6** with 44.7 g (0.447 mol) of methyl methacrylate in the presence of 0.7 g of hydroquinone and 0.11 g of concentrated sulfuric acid was carried out at reflux temperature for 28 hr with slow removal of distillate (vapor temperature 67–80°). Work-up of the mixture gave, upon distillation, 21.6 g of excess methyl merthacrylate and two product fractions: (1) 3.71 g, bp 78–88° (0.1 mm), n^{21}_{D} 1.4828; (2) 27.4 g, bp 88–92° (0.1 mm), n^{21}_{D} 1.4822. Redistillation of fraction 2 gave the pure methacrylate **7** (glpc analysis showed it to be a mixture of *endo* and *exo* isomers): bp 95–96° (0.3 mm), n^{21}_{D} 1.4827.

Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.22; H, 10.24. Found: C, 76.42; H, 10.31.

Polymerization of the Methacrylate 7. I. Homopolymerization.—Polymerization of 4.12 g (17.5 mmol) of the methacrylate **7**, initiated with 0.02 g of azobisisobutyronitrile, was carried out at 40° for 2 days. The initially formed clear, hard, glasslike polymer was dissolved in benzene, filtered, and precipitated by dropwise addition to stirred methanol. The dried polymer (4.09 g) was repeatedly ground and dried at room temperature *in vacuo* to constant weight (*ca.* 95% yield). The polymer showed mp 207–215° and an intrinsic viscosity in benzene at 30° of 6.91 dl/g of polymer.

Anal. Calcd for $(C_{15}H_{24}O_2)_n$: C, 76.22; H, 10.24. Found: C, 75.94, 76.07; H, 10.14, 10.00.

Polymerization of the monomer **7** by the reflux emulsion technique[13] occurred smoothly to give the homopolymer in *ca.* 89% yield, mp 190–210°.

II. Copolymerization with Styrene.—Bulk copolymerization of 2.42 g (10.2 mmol) of the monomer **7** and 1.03 g (9.90 mmol) of styrene was effected at 40° over a period of 45 hr when initiated with 0.016 g of azobisisobutyronitrile. The crude copolymer was a soft, clear, rather rubbery material. The crude copolymer was dissolved in benzene filtered and precipitated with methanol. After successive pulverization and drying *in vacuo* at room temperature to constant weight, the copolymer (2.5 g) was obtained as a white powder: mp 196–205° and an intrinsic viscosity in benzene at 30° of 3.50 dl/g of polymer.

Anal. Found: C, 80.96, 81.19; H, 9.64, 9.78.

Registry No.—Camphene, 79-92-5; **1a**, 2226-05-3; *p*-nitrobenzoate of **1a**, 16159-26-5; hydrogen phthalate of **1a**, 2226-06-4; 3,5-dinitrobenzoate of **1a**, 2226-07-5; trimethylsilylate of **1a**, 16159-29-8; **1b**, 2226-03-1; **2a**, 16162-37-1; **2b**, 16162-38-2; **3**, 16162-39-3; **4**, 16203-58-0; **5**, 16 203-59-1;*exo* **6**, 16503-26-7; *endo* **6**, 16423-26-0; *exo* **7**, 16423-27-1; *endo* **7**, 16423-28-2; **8**, 16162-40-6.

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