with hydrogen at 45 lb. pressure for eight more hours. The solution was filtered off and evaporated. The residue was crystallized from ether–petroleum ether in the same manner as the 3,3′-allyldiethylstilbestrol; m. p. 123.5–124.5°.

Anal. Calcd. for $C_{24}H_{34}O_2$: C, 81.31; H, 9.63. Found: C, 81.58; H, 9.49.

Summary

The Claisen rearrangement has been applied to the diallyl-ethers of diethylstilbestrol and hexestrol. The 3,3′-allyldiethylstilbestrol and 3,3′-allylhexestrol obtained in the rearrangement were transformed to 3,3′-propenyldiethylstilbestrol and to 3,3′-propenylhexestrol, respectively. The 3,3′-propylhexestrol has been prepared by hydrogenation of the 3,3′-allylhexestrol. All of the new compounds are weak estrogens.

CHICAGO, ILLINOIS RECEIVED DECEMBER 29, 1945

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF NELIO RESIN PROCESSING CORPORATION]

Nopol. I. The Reaction of β-Pinene with Formaldehyde

BY J. P. BAIN

There is described in the literature the addition of formaldehyde to numerous terpenes to yield mono- and polyhydric alcohols. The purity and structure of such products is questionable with the exception of 8-camphene carbinol prepared by Langlois[1] by condensation of paraformaldehyde and camphene in acetic acid solution.

Kriewitz[2] reported that pinene of boiling point 156–159° reacts with an alcoholic solution of paraformaldehyde at 170–175° to give an alcohol $C_{11}H_{18}O$ in 15% yield. He reported for this alcohol the following constants, b. p. 232–236°, d^{22}_4 0.961, strongly dextrorotatory. We have been unable to isolate an alcohol from α-pinene using the Kriewitz procedure though traces of alcohols seem to be formed.

In this Laboratory it has been found that β-pinene (nopinene) (I) and formaldehyde in the form of one of its substantially anhydrous polymers readily condense in equimolecular quantities to form a new optically active bicyclic primary alcohol, 6,6-dimethylbicyclo-(1,1,3)-hept-2-ene-2-ethanol, which has been named nopol (II). The pure alcohol possesses the following physical properties, n^{25}_D 1.4920, d^{25}_4 0.9647, b. p. 110.5° (10 mm.), α^{25}_D −36.5° (10-cm. tube).

While β-pinene readily yields nopol under the conditions used by Kriewitz, the product is always levorotatory and is therefore not identical with the product reported by Kriewitz. Further, the densities of the two products are not in close agreement.

β-Pinene occurs to the extent of about 30% in American gum turpentine, its most important source, and is a constituent of numerous other volatile oils. Regardless of its source, it occurs almost without exception as the optically pure levo form, while α-pinene which generally accompanies it is found in either optically pure form or as a mixture of optical isomers. Like β-pinene, nopol is also an optically pure levo compound.

Nopol may be prepared by three general methods. (1) β-Pinene and paraformaldehyde in acetic acid solution at 120° yield nopyl acetate which is readily saponified to nopol. A number of side reactions occur during the condensation of hydrocarbon and formaldehyde, such as isomerization of nopol to monocyclic isomers, hydration of the β-pinene to fenchol and borneol, isomerization of β-pinene to α-pinene, camphene and *l*-limonene and formation of polyhydric alcohols by (a) hydration of nopol, (b) condensation of the monocyclic isomers of nopol with further formaldehyde, and (c) reaction of two or more molecules of formaldehyde with the various terpenes formed by isomerization of β-pinene. While fair yields of nopyl acetate and nopol are obtained by this method, it is evident that the separation of pure compounds is possible only by efficient fractionation.

(2) A better method for preparation of nopol consists of heating a mixture of β-pinene and paraformaldehyde in the presence of a small quantity of catalyst such as zinc chloride for several hours at 115–120°. Here the reaction is smooth and may be carried out at atmospheric pressure. While the yields are rather good some higher boiling monocyclic isomers of nopol are formed together with polymeric material.

(3) Almost quantitative yields of pure nopol, practically free of higher boiling isomers and polymers, are obtained by autoclaving paraformaldehyde and β-pinene at 150 to 230° for several hours. Unreacted β-pinene and nopol are readily separated from the reaction mixture by fractionation. Since other terpenes including α-pinene, camphene and dipentene show practically no reaction with formaldehyde under these conditions, nopol of high purity may be obtained readily from even quite crude β-pinene such as gum turpentine. While crude β-pinene may be used, or the reaction mixture may be diluted with such inert solvents as alcohol or benzene without appreciable sacrifice in purity of the nopol produced, lower yields are obtained even when the β-pinene is in considerable excess over that required by the formaldehyde. It is interesting to note that when 37–40% aqueous formaldehyde is used

---

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

[2] Kriewitz, *Ber.*, **32**, 57 (1899).

neither nopol nor an appreciable quantity of other alcohol is obtained by this autoclave method. Using the acetic acid method, or in the presence of mineral acids such as sulfuric or hydrochloric acid, aqueous formaldehyde and β-pinene do yield a complex mixture of mono- and polyhydric alcohols, presumably monocyclic.[3]

The single double bond shown to be present by hydrogenation of nopol was first thought to be semicyclic as in β-pinene. However, since ozonolysis and various methods of oxidation failed to yield nopinone, the expected product, it was decided that nopol has the α-pinene structure II, the semicyclic bond having shifted to the ring. Molecular exaltation values for α- and β-pinene calculated from recent data[4] using the atomic refraction values of Auwers and Eisenlohr are +0.47 and +0.85, respectively. The exaltation for α-pinene is that expected for the cyclobutane ring while the exaltation for β-pinene is due to the cyclobutane ring plus the semicyclic bond. The observed exaltation for nopol is +0.33 in agreement with its proposed α-pinene structure (II).

Just as α-pinene is isomerized by heat or acids to a mixture of menthadienes, nopol on similar treatment yields a mixture of menthadiene-7-carbinols, a representative of which is dipentene-7-carbinol (III). Since the separation of the numerous possible isomers would be quite difficult no such attempt has been made. This type of isomerization of nopol occurs to a considerable extent during esterification but good yields of nopyl esters are obtainable using acid anhydrides or if water is removed as formed in the esterification using free acids.

Mixtures of menthadiene-7-carbinols prepared by either acid or thermal isomerization yield on disproportionation over palladium 4-isopropylcyclohexaneethanol and *p*-isopropylphenethyl alcohol (IV). The latter was identified by comparison with a known sample and by oxidation to terephthalic acid.

Treatment of nopol with aqueous hydrochloric acid yields a crystalline dihydrochloride along with liquid by-products. The structure of the crystalline dihydrochloride is not known but since the process is analogous to the formation of 1,8-dichloro-*p*-menthane from α-pinene the product from nopol may be considered to be 1,8-dichloro-7-*p*-menthanecarbinol (V). Oxidation of V yields 1,8-dichloro-7-*p*-menthane-carboxylic acid (VI) which may be titrated as a tribasic acid in keeping with the presence of the two tertiary chloride groups.

On treatment with 2 *N* HCl at 85°, nopol yielded *p*-ethylcumene (VII) as a result of isomerization and dehydration, thus providing further proof of its structure.

Experimental

Fractionations.—Unless otherwise specified all fractionations were carried out with a 60 cm. × 2.5 cm. Stedman column.[5]

Paraformaldehyde.—The paraformaldehyde used was commercial 95% paraformaldehyde containing about 5% water and methanol; yields were therefore calculated using the correspondingly higher equivalent weight, 31.6.

Attempted Preparation of the Kriewitz Compound.—The procedure used was essentially that of Kriewitz.[2] A mixture of six hundred grams of α-pinene, $\alpha^{25}D$ +24 (10-cm. tube), 132 g. of paraformaldehyde and 300 g. of 95% ethanol was heated in an autoclave for ten hours at 175–200°. Some gas escaped on opening the autoclave and a sticky black residue was deposited on the surface of the autoclave. The product was washed with water to remove ethanol and fractionated in a 30 in. Raschig ring packed column. The results are shown in Table I.

TABLE I

FRACTIONATION OF α-PINENE-PARAFORMALDEHYDE REACTION PRODUCT

Fraction	B. p., °C. (mm.)	Wt., g.	$n^{25}D$	$\alpha^{25}D$ (10-cm. tube)
1–11	52–54 (20)	432	1.4633 to 1.4643	+15.8 to +16.2
12–16	54 (20)–95 (10)	36	1.4668 to 1.4867	+11.0 to + 3.7
17	95–110 (10)	8.3	1.4840	+4.3
18	110–115 (10)	9.5	1.4918	+6.5
19	115–123 (10)	13.0	1.4924	−0.4

It is clear that no pure alcohol could be isolated from this reaction product.

Reaction of β-Pinene with Paraformaldehyde in the Presence of Alcohol.—The procedure was similar to that of Kriewitz[2] except that commercial β-pinene of about 95% purity was used instead of α-pinene. A mixture of 600 g. of the β-pinene, 132 g. of paraformaldehyde and 300 g. of ethanol was heated in an autoclave for twelve hours at 180–200°. No sticky black residue or gas was formed.

The product was washed with water and then fractionated under reduced pressure. The first cut boiling up to 109.5° at 10 mm. consisted almost entirely of β-pinene, b. p. 57.5–59° at 20 mm. The nopol cut, b. p. 109.5–112° at 10 mm., $n^{25}D$ 1.4915, $\alpha^{25}D$ − 36.1 (10-cm. tube), weighed 351 g. (50.5%). An additional 40 g. of material was collected in five fractions boiling up to 195° at 10 mm. but no pure compound could be separated.

Reaction of a Mixture of α- and β-Pinene with Paraformaldehyde in Alcohol.—A mixture of α- and β-pinene was prepared containing 72% α-pinene. Twelve hundred grams (8.82 moles) of this mixture of pinenes (containing about 864 g. (6.35 moles) of α-pinene, $\alpha^{25}D$ −7.37, and 336 g. (2.47 moles) of β-pinene, 264 g. (8.33 moles) of paraformaldehyde and 600 g. of 95% ethanol were charged into an autoclave and heated at 165 to 185° for twelve hours. The reaction product was clear, slightly yellow and possessed a strong odor of formaldehyde. The product was washed with water and then fractionated under reduced pressure. The first cut, b. p. 88–90° at 100 mm., consisted of practically pure α-pinene ($\alpha^{25}D$ (10-cm. tube) ranging from −7.4 to −7.7° for various cuts) and weighed 794 g. (92% recovery). It contained a few grams of paraformaldehyde. Only traces of β-pinene were present in the next cut, b. p. 90° at 100 mm. to 108° at 10 mm., and weighing 22 g. The nopol, b. p. 108–114° (mainly constant at 111°) at 10 mm., weighed 395 g. (96.2% based on the β-pinene content of the mixture). The various nopol fractions showed $n^{25}D$ from 1.4901 to 1.4924 and $\alpha^{25}D$ −30.6 to −33.8° (10-cm. tube). Material boiling above 114° at 10 mm. weighed 84 g. and was not further investigated.

It was evident from these data that because of the great excess of paraformaldehyde over β-pinene the nopol cut

---

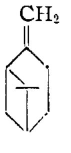
(3) Unpublished work.

(4) Fuguitt, Stallcup and Hawkins, THIS JOURNAL, **64**, 2978 (1942).

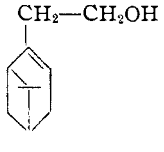
(5) Bragg, *Ind. Eng. Chem., Anal. Ed.*, **11**, 283 (1939).

was somewhat contaminated by the formation of small quantities of materials such as those formed using pure α-pinene by the Kriewitz procedure and boiling in the range 95–123° at 10 mm.

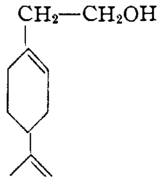
Preparation of Nopol by the Ester Method.—A mixture of 300 g. (9.5 moles) of 95% paraformaldehyde, 2040 g. (15 moles) of β-pinene and 1200 g. (20 moles) of glacial acetic acid was heated at 120° until the paraformaldehyde dissolved. The solution was then refluxed for twenty-four hours and fractionated through a 10-plate column packed with Raschig rings. The nopyl acetate fraction boiling between 115 and 119° at 10 mm. was saponified to yield 593 g. (37.5%) of nopol, b. p. 110–112° at 10 mm.



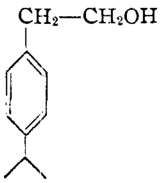
I



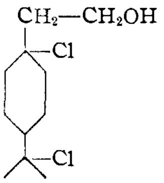
II



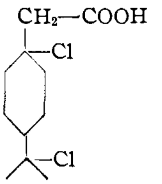
III



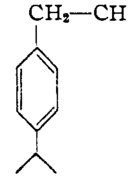
IV



V



VI



VII

Preparation of Nopol by the Zinc Chloride Method.—A mixture of 1775 g. (12.3 moles) of commercial β-pinene, 300 g. (9.5 moles) of paraformaldehyde (95%) and 10 g. of zinc chloride was heated in a water-bath at 60° for two and a half hours and at 100° for two hours. Since the solid paraformaldehyde remained suspended and no apparent reaction had taken place, the mixture was then placed in an oil-bath heated at 120–125°. The paraformaldehyde gradually dissolved and no solid remained at the end of three and a half hours. After washing with water, the product was fractionated to yield 883 g. (56.8%) of nopol, b. p. 109–113° at 10 mm. For various cuts n^{25}_D ranged from 1.4890 to 1.4918 and α^{25}_D (10 cm.) from −35.2 to −36.3°. Lower boiling fractions consisted of practically pure β-pinene.

Preparation of Nopol by the Autoclave Method.—A mixture of 408 g. (3 moles) of very pure β-pinene, n^{25}_D 1.4767, α^{25}_D (10 cm.) −18.57° and 60 g. (1.9 moles) of paraformaldehyde was heated in an autoclave with shaking at 180° for four hours. On fractionation 125 g. of pure β-pinene, b. p. 59° at 20 mm., was recovered. The pressure was then reduced to 10 mm. After a 20-g. forerun of crude nopol, b. p. 109.5–110.3°, very pure nopol, b. p. 110.3–111.0°, was collected and weighed 280.7 g. (95.1% of theory including both nopol fractions); n^{25}_D 1.492; α^{25}_D −36.5° (10 cm. tube); d^{25}_4 0.9647; M_D calcd. 49.66, found 49.99.

Anal. Calcd. for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.87; H, 11.13.

A number of additional autoclave experiments were carried out using β-pinene of 90–95% purity; the data are shown in Table II.

TABLE II

CONDENSATION OF β-PINENE WITH PARAFORMALDEHYDE IN AN AUTOCLAVE

Ratio, moles β-pinene to paraformaldehyde	T, °C.	Time, hr.	% Nopol based on paraformaldehyde
1.5	150	3	57
1.5	150	6	65
1.5	175	3	81
1.5	200	3	87
1.0	196	3	71
1.5	225	6	86
1.5	250	3	None[a]

[a] A 65% yield of alcohols isomeric with nopol was obtained boiling from 110 to 130° at 10 mm., largely at 120–130°, along with 29% yield of viscous polymeric material. Presumably nopol was formed during the heating up of the charge and then isomerized and polymerized at 250°. Only traces of polymeric material were obtained when the temperature of the reaction was 225° or below. Where poorer yields of nopol are obtained, formaldehyde as paraformaldehyde may be recovered from the β-pinene fraction or may be evolved during the distillation of the nopol due to decomposition of nopol hemiformals.

Nopyl Esters. (With A. H. Best).—Nopol is readily converted to its esters by the usual procedures. In general it is found advisable to remove water as formed if the esterification is carried out with a free acid. The esters whose physical properties are shown in Table III were prepared in 50 to 85% yields; the by-product consists of a mixture of the isomeric menthadiene-7-carbinol esters. The acetate, propionate and caproate were saponified and pure nopol recovered.

Hydronopol.—Nopol (322 g.) was hydrogenated at 65 to 100 atm. at 180–200° using 5 g. of Raney nickel catalyst. The theoretical amount of hydrogen was absorbed in four and a half hours. The product on fractionation yielded small amounts of hydrocarbons resulting from hydrogenolysis and 270 g. (80.5%) of hydronopol, b. p. 123–125° at 10 mm.; n^{25}_D 1.488; α^{25}_D −27.5° (10-cm. tube); d^{25}_4 0.961, M_D calcd. 50.12, found 50.50.

Anal. Calcd. for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.70; H, 11.73.

Hydronopyl Acetate.—Hydronopol (84 g.) and acetic anhydride (150 g.) were refluxed for two hours. The ester on fractionation boiled at 124–127° (largely at 126.5°) at 10 mm. and weighed 87 g. (83%); n^{25}_D 1.4688, α^{25}_D −21.9° (10-cm. tube); d^{25}_4 0.9764; M_D calcd. 59.49, found 59.98.

Hydronopic Acid.—Hydronopol on oxidation with chromic anhydride in acetic acid by the usual method gave an 85% crude yield of hydronopic acid. After purification by recrystallization from aqueous methanol the acid melted at 56–58°; neut. equiv. calcd. 182.25, found 182.8, 181.8.

Menthadiene-7-carbinol by Vapor Phase Pyrolysis. (With A. H. Best and C. K. Clark).—The pyrolysis unit of 2 in. (5.08 cm. i. d.) standard iron pipe 4 ft. (101 cm.) long was heated by an electrically controlled salt bath. Nopol was dropped in at one end of the reactor at a rate of 4 to 6 cc. per minute while the salt bath was held at 373–375°. The pyrolyzate was discarded until the rate of collection of pyrolyzate was about equal to the feed rate. Two hundred twenty-five grams of pyrolyzate was fractionated at 10 mm. pressure to yield 37 g. of a cut, b. p. 40–105° consisting mainly of hydrocarbons, 56 g. alcohols, b. p. 105–122° which were not further examined, a series of fractions distilling between 122° and 126° and weighing 102 g. and a residue of 25 g. The physical properties of the fractions, b. p. 122 to 126°, varied somewhat, d^{25}_4 from 0.9377 to 0.9437 and n^{25}_D from 1.4973 to 1.4999. A mixture of these fractions was used for analysis. *Anal.* Calcd. for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 78.69; H, 11.01.

Menthadiene-7-carbinols and p-Ethylcumene by Acid Isomerization. (With A. H. Best).—A mixture of 1000 g.

TABLE III

PHYSICAL PROPERTIES OF NOPOL ESTERS

Ester	B. p., °C.	Pres. mm.	d^{25}_4	n^{25}_D	M_D Calcd.	M_D Found	α^{25}_D (10 cm. tube)
Acetate	118	10	0.9775	1.4705	59.02	59.49	−31.5
Propionate	130.2	10	.9675	1.4691	63.64	63.86	−28.9
Butyrate	142	10	.956	1.469	68.26	68.85	−18.9
α-Ethylbutyrate	143	5.6	.9425	1.4684	77.49	78.04	−21.8
Caproate	148.5	5	.945	1.4685	77.49	77.87	−23.1
Carbamate[a]	172.3	10	1.047	1.4978	57.72	58.35	−34.1

[a] Nopyl carbamate was prepared by heating two moles nopol and one mole urea at 175 to 180° for fourteen hours followed by fractionation of the mixture at 10 mm.; yield 35%. *Anal.* Calcd. for $C_{12}H_{19}ON$: N, 6.69. Found: N, 6.62.

of nopol (6.01 moles) and 1000 cc. of 2 *N* hydrochloric acid was heated at 85° with stirring for two hours. After separating the acid layer, the product was washed with dilute sodium hydroxide and fractionated at 10 mm. Two large fractions were obtained, *p*-ethylcumene, b. p. 70–74.5°, and mixture of menthadiene-7-carbinols, b. p. 127 to 135°.

The *p*-ethylcumene (258 g. or 27%) was purified by washing with sulfuric acid and further fractionation. The pure product distilled at 74–74.5° at 10 mm., n^{25}_D 1.4901, d^{25}_4 0.8558, in good agreement with the constants reported in the literature.[6] For further identification the product was oxidized with chromic anhydride in acetic acid to terephthalic acid in 56% yield.

The product boiling at 127–135°, n^{25}_D 1.5005, d^{25}_4 0.966, was identified as a mixture of menthadiene-7-carbinols by disproportionation over 10% palladium on Norit at 175° and oxidation of the product to terephthalic acid (see disproportionation of menthadiene-7-cardinols).

1,8-Dichloro-7-*p*-menthane-carbinol.—A mixture of 100 g. (0.60 mole) of nopol and 300 cc. of concentrated hydrochloric acid was shaken for about fifteen minutes. Occasional cooling was used to prevent the temperature from rising above 50°. After standing for several days, crystals began to deposit from the brown oil layer and on cooling in the ice box for several hours, the oil layer became a paste. The crystals were pressed out on porous plates and recrystallized from hexane, yield 28 g. (19.5%), m. p. 74–75°.

Anal. Calcd. for $C_{11}H_{20}OCl_2$: Cl, 29.65. Found: Cl, 29.66, 29.80.

1,8-Dichloro-7-*p*-menthane-carboxylic Acid. (With B. L. Hampton).—To a solution of 93.5 g. of 1,8-dichloro-7-*p*-menthane-carbinol in 800 cc. of acetic acid there was added slowly a solution of 78 g. of chromic anhydride in a mixture of 75 cc. of water and 450 cc. of acetic acid. Occasional cooling was necessary to control the temperature between 30 and 40°. After standing for one and a half hours, the solution was poured into water and extracted with benzene several times. After washing with water the benzene extract was evaporated to yield 66 g. (66%) of the crude acid. After three recrystallizations from benzene, the product melted at 153° with evolution of gas. *Anal.* Calcd. for $C_{11}H_{18}O_2Cl_2$: Cl, 28.01. Found: 27.50, 27.69. The product could not be readily titrated as a monobasic acid but the equivalent could be determined as a tribasic acid by use of excess warm sodium hydroxide and back titration. Calcd. for $C_{11}H_{18}O_2Cl_2$: neut. equiv. 84.39. Found: 85.1.

Disproportionation of Menthadiene-7-carbinols (with A. H. Best).—To a 2-liter three-necked flask equipped with a stirrer, thermometer, dehydrator tube and condenser was added 600 g. (3.61 moles) of a mixture of menthadiene-7-carbinols (obtained by vapor phase pyrolysis of nopol) and 10 g. of palladium on Norite catalyst, 31% palladium. The mixture was heated with stirring at 200–225° for thirteen hours. Small amounts of water and hydrocarbons were occasionally removed from the dehydrator tube. At the end of the reaction period the product contained only 2.6% of the unsaturation present originally as shown by bromine titration.

The product was diluted with an equal volume of benzene and the catalyst filtered off. After removal of benzene at atmospheric pressure the product was fractionated at 10 mm. The fraction boiling between 42 and 121° and weighing 160 g. consisted mainly of hydrocarbons. A fraction, b. p. 123–126°, n^{25}_D 1.4842, d^{25}_4 0.9264, weight 50 g., was apparently crude menthane-7-carbinol but was not fully investigated.

The fraction, *p*-isopropylphenethyl alcohol, b. p. 127–128° at 10 mm., weighed 218 g. (54.5% based on disproportionation of the menthadiene-7-carbinols). A heart cut of this fraction showed n^{25}_D 1.5156, d^{25}_4 0.9605, M_D calcd. 50.92, found 51.42. The product was identified by independent synthesis of *p*-isopropylphenethyl alcohol and comparison of physical constants and also by mixed melting points of the α-naphthylurethans.

***p*-Isopropylphenethyl Alcohol** (with A. H. Best).—*p*-Isopropylbenzyl chloride, 1348 g. (8 moles), and sodium cyanide (10 moles) reacted in aqueous alcohol solution in the usual manner to yield 835 g. (64.8%) of *p*-isopropylbenzyl cyanide, b. p. 134–135° at 10 mm., n^{25}_D 1.5118, d^{25}_4 0.969. The nitrile was hydrolyzed with 60% sulfuric acid, the mixture diluted with water and the *p*-isopropylphenylacetic acid extracted with 3 liters of butanol. The butanol solution was heated to boiling and water was removed as the butanol–water azeotrope. Fresh butanol was added occasionally. At the end of forty hours very little acid remained unesterified. After washing with dilute sodium hydroxide the butanol solution was fractionated under reduced pressure to yield 652 g. (62.8%) butyl *p*-isopropylphenylacetate, b. p. 156.7° at 10 mm., n^{25}_D 1.486, d^{25}_4 0.958.

Butyl *p*-isopropylphenylacetate (695 g.) was dissolved in 6 liters of butanol and reduced with 360 g. of sodium in the usual manner. After the sodium was dissolved 360 cc. of water was added and the solution refluxed one hour to saponify unreacted ester. The solution was then washed with water and fractionated. The main fraction boiled at 127.5° at 10 mm. and weighed 297 g. (60.9%). A heart cut showed n^{25}_D 1.5162, d^{25}_4 0.9630, M_D calcd. 50.92, found 51.53 in good agreement with the physical constants of the product prepared by disproportionation of the menthadiene-7-carbinols.

The identity of the disproportionated product with *p*-isopropylphenethyl alcohol was established by conversion of both alcohols to the α-naphthylurethans, m. p. 99–100° and 98–99°, respectively, mixed m. p. 98.5–99.5°.

Summary

Substantially anhydrous formaldehyde as paraformaldehyde readily reacts with β-pinene to form a new optically active bicyclic primary alcohol. The structure of this alcohol has been established and a number of new compounds prepared.

JACKSONVILLE, FLORIDA RECEIVED* DECEMBER 3, 1945

---

[6] Keil and Klages, *Ber.*, **36**, 1640 (1903).

* Original manuscript received December 11, 1944.