Polypinocarveol

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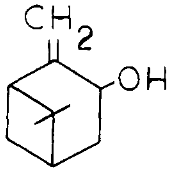
An improved method for the oxidation of β-pinene to pinocarveol is described. Several new derivatives of pinocarveol were characterized. Pinocarveol was polymerized to a moderately high molecular weight polymer.

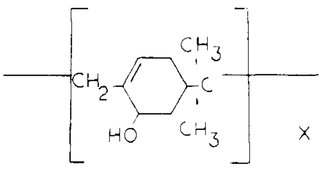
IN THE LITERATURE (*1, 3, 4*) there are several methods for the synthesis of pinocarveol (I). One of the more practical methods involves oxidizing β-pinene with SeO_2. However, the isolation of the product from this reaction is tedious with rather low yields (25 to 40% reported). By using a slightly different technique, the procedure for working up the reaction product was shortened and the yield increased to 54–62%.



(I)

Several previously unreported derivatives of pinocarveol were prepared: an *S*-benzylthiuronium alkyl hydrogen sulfate salt; *p*-nitrophenylurethan; 3,5-dinitrobenzoate; sebacate, and diphenylurethan.

Upon prolonged refluxing in air, pinocarveol polymerized to a white, infusible soluble polymer. Infrared studies suggested that the polymer formed by opening of the bicyclic bridge structure to give a repeating unit as shown in structure (II).



(II)

This appeared to be similar to the repeat unit formed by the ionic polymerization of β-pinene (*2*).

EXPERIMENTAL

Pinocarveol (I). A solution of 630 grams (4.8 moles) of selenious acid (or the equivalent amount of selenium dioxide) in 1200 ml. of absolute alcohol was added dropwise during a one hour period, with vigorous stirring, to 1620 grams (12 moles) of β-pinene. During this addition the solution became warm and turned yellow. After stirring another half hour at room temperature, the solution was refluxed for four hours. The reddish-brown reaction mixture was then cooled and washed with a two-fold quantity of water. The red-brown oil layer was decanted and the water layer discarded. Filtration of the red-brown layer yielded a brownish-black precipitate of elemental selenium. The red-brown liquid was than fractionally distilled yielding a colorless liquid having the following constants: n_D^{25} 1.5003 and a b.p. of 203° C./760 mm. of Hg. or 83-4° C./11-12 mm. of Hg. The yields ranged from 957 to 1121 grams (53–62%) of a material whose infrared spectrum corresponded to pinocarveol showing no evidence of ketonic groups (i.e., carvopinone).

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.90; H, 10.60; O, 10.51. Found: C, 78.75; H, 10.60; O, 10.65.

Several new derivatives of pinocarveol were prepared and are shown in Table I.

Table I. Pinocarveol Derivatives

Compound	Form	M.P., °C.	N, Analysis Calcd.	N, Analysis Found
S-benzylthiuronium alkyl hydrogen sulfate salt	White Crystals	65–66	7.03	7.13
p-Nitrophenylurethan	Yellow Crystals	160–161	8.86	8.85
3,5-Dinitrobenzoate	Light Yellow Crystals	120–121	8.09	8.14
Sebacate[a]	White Needles	94–95	...	...
Diphenylurethan	Yellow Crystals	~300	4.03	3.89

[a] *Anal.* Calcd. for $C_{27}H_{42}O_4$: C, 75.33; H, 9.83. Found: C, 75.44; H, 9.66.

Polypinocarveol (II). Pinocarveol, 127.4 grams, was refluxed for one hour. A white solid (II) formed that was filtered off from the unreacted pinocarveol, washed with acetone and dried. The yield was 15.4 grams or 12.1%. The inherent viscosity of the polymer was 0.50 (0.2% conc. in tetrachloroethylene-phenol) while the inherent viscosity of a polymer with a similar infrared scan prepared using an ionic catalyst (boron trifluoride-hydrate) was only 0.10. The polymer (II) turned brown at 280° C. and decomposed above 300° C. It was slightly soluble in butyrolactone, pyridine, dimethyl sulfoxide and tetrahydrofuran. At elevated temperatures the polymer (II) was also soluble in tetrachloroethylene-phenol, chloroform, acetone, and ethyl acetate. The infrared spectrum of this polymer (II) was identical to that of polymerized β-pinene (*2*) except for additional bands due to the hydroxyl group.

Anal. Calcd. for $(C_{10}H_{16}O)_x$: C, 78.90; H, 10.60; O, 10.51, Found: C, 79.70; H, 9.52; O, 10.78.

LITERATURE CITED

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