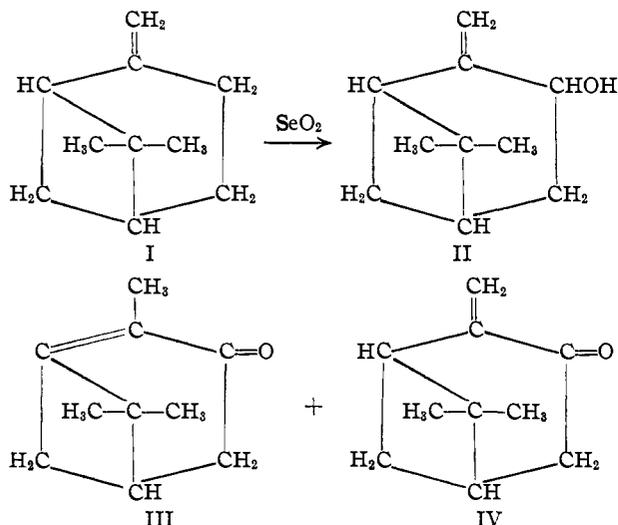


[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA]

Reactions of β -Pinene. II. With Selenium Dioxide in Acetic Acid¹

BY W. DAVID STALLCUP* AND J. ERSKINE HAWKINS

In the first paper of this series² it was pointed out that pinocarvone (IV) and carvopinone (III) are the steam-volatile products of the reaction of one mole of β -pinene (I) with one mole of selenium dioxide. Joshel and Palkin³ have shown that pino-



carveol (II) is the predominant steam volatile product if slightly less than one-half mole of selenium dioxide is used per mole of β -pinene.

In order to more completely study the formation of these compounds, the reaction has been carried out in acetic acid and acetic anhydride using both molar and half molar amounts of selenium dioxide per mole of β -pinene.

Experimental

β -Pinene was prepared by fractionating commercial material⁴ through an efficient spiral screen column^{5,6} and had a b. p. 59.2° (20 mm.), n_D^{25} 1.4768; $[\alpha]_D^{25}$ -21.4°.

Selenium dioxide was prepared by nitric acid oxidation of selenium, washing, crystallizing and drying the product.

Oxidation of β -Pinene by Selenium Dioxide.—Selenium dioxide was added with stirring to β -pinene and 200 cc. of

solvent in the amounts shown in Table I, the rate of addition being such that the temperature of the reaction mixture did not rise above 70°. When addition was complete the mixture was refluxed for four hours. It was then filtered to remove selenium and the filtrate was steam distilled. The distillate was treated with sodium bicarbonate and the ether extract distilled at 2–3 mm. pressure.

Separation of the Steam Volatile Oil

For Pinocarveol.—The oil was added to an equal volume of ethyl borate and heated for one hour at 125°. The non-alcoholic materials⁷ were then removed by lowering the pressure and raising the temperature to 150°. The tarry residue was impure pinocarvyl borate. This was then hydrolyzed and simultaneously steam distilled from a sodium carbonate solution. The ether extract of the distillate was quite pure pinocarveol.

For Pinocarvyl Acetate.—The non-alcoholic oil from the borate treatment was extracted with twice its volume of sodium bisulfite as previously described.³ When the ketonic materials were absorbed, the bisulfite was twice extracted with ether. Distillation of the ether extract at 2–3 mm. gave nearly pure pinocarvyl acetate.

For Carvopinone and Pinocarvone.—The bisulfite solution above was then selectively decomposed by the method previously developed.²

Essentially the same results as above were obtained when the oxidation mixture was first extracted with bisulfite and then treated with ethyl borate.

TABLE I

All oxidations listed were between 1 mole of β -pinene and 0.5 mole of selenium dioxide except the first reaction, which was between 1 mole of β -pinene and 1 mole of selenium dioxide and the second reaction which was between 0.5 mole of β -pinene and 0.5 mole of selenium dioxide.

Solvent	Se recov., g.	Steam volatile oil, g.	% Steam volatile oil recovered as			
			Pino-carveol	Pino-carvyl acetate	Carvo-pinone	
Ac ₂ O	49	68	0.6	65	1	3.7
AcOH	20	14.5		20		
Ac ₂ O	5	53	None	66	1	2
AcOH	None	41	3.7	22	20	2
AcOH-Ac ₂ O	6	27	13	44	2	8.5

Pinocarveol obtained by the above procedure was identical with that prepared from β -pinene and selenious acid in absolute ethanol by the method described by Joshel and Palkin.³ It had the constants: b. p. 78–80° (3–4 mm.); n_D^{25} 1.4980; $[\alpha]_D^{25}$ +65.5; d_4^{25} 0.976; M_D calcd. 45.52,⁸ found 45.72. This pinocarveol solidified at about 5°. Schmidt⁹ reports a thaw point of 7° for pinocarveol purified through the phenylurethan. The phenylure-

(7) Separate experiments proved pinocarvyl acetate to be stable in the presence of ethyl borate under the conditions used.

(8) Based on values of Auwers and Eisenlohr, and 0.48 for cyclobutane ring. No value assigned for methylene group attached to ring.

(9) Schmidt, *Ber.*, **63**, 1129 (1930).

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(1) This material has been abstracted from a thesis submitted to the Graduate Council of the University of Florida by W. David Stallcup in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Stallcup and Hawkins, *THIS JOURNAL*, **63**, 3339 (1941).

(3) Joshel and Palkin, through the courtesy of a private communication the contents of which now appear in *THIS JOURNAL*, **64**, 1008 (1942).

(4) Furnished through the courtesy of the Southern Pine Division of The Glidden Company, Jacksonville, Florida.

(5) Lecky and Ewell, *Ind. Eng. Chem., Anal. Ed.*, **12**, 544 (1940).

(6) Stallcup, Fugitt and Hawkins, *ibid.*, **14**, 503 (1942).

than was prepared as described by Schmidt.⁹ If the pinocarveol is not carefully purified, the urethan will crystallize only with great difficulty, if at all. The m. p. was 82–84°. Joshe' and Palkin⁸ report 84–86°. Schmidt⁹ reports 84–85° and 88–90° for recrystallized products.

Pinocarvyl Acetate.—When prepared from β -pinene as described above it had the constants: b. p. 88–90° (2–3 mm.), 225° (cor.) (760 mm.); n_D^{25} 1.4750; d_4^{25} 0.991, $[\alpha]_D^{25}$ –38°; saponification number calcd. 194.26, found 195 (or 100.3%). Schmidt⁹ reports b. p. 227–8°; d^{20} 0.997; α_D +15.8° for the *d*-isomer.

When prepared by the esterification of pinocarveol with acetic anhydride in the presence of sodium acetate⁹ the constants are: b. p. 88–90° (2–3 mm.); n_D^{25} 1.4760; d_4^{25} 0.993; $[\alpha]_D^{25}$ –20°. Saponification number calcd. 194.26, found 194 (or 100%). No explanation is offered for the variations in the values of the rotations of the esters when prepared by different methods.

Pinocarveol, like most secondary and tertiary terpene alcohols, will not readily esterify with acetic anhydride unless sodium acetate is present. It will not react to any observable extent with acetic acid even when refluxed in the presence of sodium acetate for two hours.

Pinocarvone.—When prepared as described above it had almost the same constants as previously given²; b. p. 83–84° (3–4 mm.); n_D^{20} 1.5039; semicarbazone, m. p. 210–212° recrystallized.

Carvopinone.—The constants of this compound, obtained as described above, were also similar to those previously reported²; b. p. 84–85° (3–4 mm.); n_D^{25} 1.4924. Its semicarbazone did not melt below 300°.

The Action of Selenium Dioxide on Pinocarveol

Twenty-five grams of pinocarveol was dissolved in 75 cc. of ethanol in a flask equipped with a reflux condenser and mechanical stirrer. Ten grams of selenium dioxide was slowly added. Upon heating, the solution first turned yellow, then red and finally brown. After refluxing for five hours, three and one-half grams of selenium was obtained and the liquid portion was steam distilled. This gave 15 g. of an oil; b. p. 84–85° (3–4 mm.); n_D^{25} 1.4931; d_4^{25} 0.982; α_D +60.5° (10-cm. tube). This was largely impure carvopinone which was purified through the bisulfite compound to give 6.1 g. of carvopinone; b. p. 84–85° (3–4 mm.); n_D^{25} 1.4935; d_4^{25} 0.981; $[\alpha]_D^{25}$ +62.7°. About 0.3 g. of pinocarvone was isolated, this had n_D^{25} 1.5010. Approximately one-half gram of oil was not extracted by the bisulfite. Judging by its refractive index and its action to heat, it was impure carvopinone.

Reduction Experiments

d-**Pinocampheol** is formed in nearly theoretical yield by the catalytic hydrogenation of pinocarveol in cyclohexane using a 10% palladium on charcoal catalyst and heating the mixture to 100° under a hydrogen pressure of 1200 lb. for two hours in a bomb. The catalyst was removed by filtration and the pinocampheol purified by distillation at reduced pressure. The constants were: m. p. 55.5–56.0°; n_D^{25} 1.4830 (super-cooled); $[\alpha]_D^{25}$ +39° (10.5% in ether). When recrystallized from pet. ether (boiling range 35–65°) the α -naphthylurethan had a m. p. 87.5–88.0° (cor.) which is the same as that reported

by Kuwata¹⁰ and Schmidt and Schultz¹¹ for *d*-**pinocampheol**.

d-**Pinocampheol acetate** may be obtained quite pure by the catalytic reduction of pinocarvyl acetate under the conditions described above. The reduction product is purified from the solvent by distillation at reduced pressure. It had the constants: b. p. 80–82° (2–3 mm.), 227–8° (cor.) (760 mm.); n_D^{25} 1.4641; d_4^{25} 0.979; $[\alpha]_D^{25}$ +23°. Saponification number, calcd. 196.28, found 197 (or 100.3%). Upon saponification this ester produced *d*-**pinocampheol** whose constants were in close agreement with those above. Kuwata¹⁰ reports for *l*-**pinocampheol acetate**: b. p. 82–84° (3 mm.); d_4^{20} 0.9781; n_D^{20} 1.4638.

l-**Pinocampheol** is obtained by the catalytic hydrogenation of carvopinone by the procedure described above. The product was purified by washing with neutral bisulfite and distilling the unextracted oil at 2–3 mm. (b. p. about 70°); b. p. 212° (cor.) (760 mm.); n_D^{25} 1.4735; d_4^{25} 0.964; $[\alpha]_D^{25}$ –13.5°. Its semicarbazone recrystallized as very fine white needles from dilute methanol, m. p. 227.5–228.0° (cor.). Schmidt and Schultz¹¹ report for the semicarbazone of *l*-**pinocampheol** m. p. 227° and for the semicarbazone of *l*-**pinocampheol**, 219°.

Another **pinocampheol** was obtained upon the reduction of pinocarvone under the same conditions. It had the constants: b. p. 75° (2–3 mm.); n_D^{25} 1.4772; α_D –29° (10-cm. tube). It forms a semicarbazone melting at 185°. This is apparently the β -form of the semicarbazone described by Gildemeister and Kohler.¹² The α -form described by these authors has a m. p. of 218–219° which corresponds to the semicarbazone of *cis* pinocampheol of Schmidt and Schultz.¹¹

Discussion

The effect of the selenium dioxide β -pinene ratio in these solvents was not nearly as pronounced as it was for ethanol.^{2,3}

It may be seen from Table I that the major portion of the steam volatile oil is pinocarvyl acetate. This finding is in accord with the mechanism proposed by Guillemonat¹³ for the oxidation of ethylenic hydrocarbons in which a selenium complex is formed with the hydrocarbons. This, in turn, is decomposed by the solvent. In this case it results in the formation of pinocarvyl acetate.

Water is a product of the reaction in which the selenium complex is formed. A reaction between the complex and the water thus formed would account for the formation of pinocarveol. As already pointed out, pinocarveol is not esterified by acetic acid and the alcohol therefore becomes subject to oxidation by selenium dioxide. This would account for the formation of the ketones.

(10) Kuwata, *THIS JOURNAL*, **59**, 2509 (1937).

(11) Schmidt and Schultz, *Ber. Schimmel*, **91** (1934).

(12) Gildemeister and Kohler, *Chem. Centr.*, **80**, 11, 2158 (1909).

(13) Guillemonat, *Ann. chim.*, **11**, 143 (1939).

It is believed that this latter oxidation also takes place through the medium of a selenium complex. This is supported by the fact that the reaction mixture becomes yellow, then red and finally deposits selenium, and upon steam distillation leaves a non-volatile selenium compound.

Since carvopinone yields *trans*-pinocamphone upon reduction it may be seen, by setting up a model, that the carbonyl group of carvopinone is close to the *gem*-dimethyl group. This proximity would tend to hinder the rate of reaction of the carbonyl group with large molecules. The slowness of the reactivity of the carbonyl group was pointed out in the previous paper² in respect to the formation of the semicarbazone. This steric relation may also be the cause of the relative ease of the rupture of the cyclobutane ring to form carvone.

The pinocarveol formed by the action of sele-

mium dioxide on β -pinene is probably the *trans* form with respect to the hydroxyl group and the *gem*-dimethyl group. It is believed that the method of formation and purification would tend to give rise to the more stable form, which is *trans*.

Summary

1. The oxidation of β -pinene with selenium dioxide in acetic acid and acetic anhydride gave pinocarvyl acetate, pinocarveol, pinocarvone and carvopinone as steam volatile products. The main product was the acetate.

2. The oxidation product of pinocarveol by selenium dioxide is largely carvopinone.

3. The catalytic reduction of carvopinone yields 1-*trans*-pinocamphone.

4. The method of formation and the structure of some of these compounds have been proposed.

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[CONTRIBUTION FROM THE GEOCHEMICAL SECTION OF THE ILLINOIS STATE GEOLOGICAL SURVEY]

The Oxidizing Power of Illinois Coal. II. The Effects of Extended Time¹

BY G. R. YOHE² AND MYRON H. WILT³

Previous work³ has shown that Illinois coals take on the ability to act as oxidizing agents toward titanous chloride upon exposure to air or oxygen, even for very short periods of time. In the present work, a similar study has been applied to another group of coals with emphasis upon the changes in oxidizing power over longer times of exposure to air.

Preparation of Samples.—The coal samples were obtained in the form of large fresh blocks at the mines, brought to the laboratory as soon as possible, and ground to pass a 100-mesh sieve. No precautions were taken to prevent atmospheric oxidation during the preparation of the samples. After grinding, portions were taken for analyses, and the remaining stocks were placed in 2-quart mason jars and deliberately exposed to air by leaving the covers loose and by occasionally mixing the contents of each jar. The time of exposure to air was measured in days from the date of grinding.

Determination of Oxidizing Power.—The determinations of oxidizing power were made by the titanous chloride-ferric chloride method previously described.³ Parallel determinations of soluble ferric iron extractable

from the coals under similar conditions were made, and the oxidizing power data reported here are corrected for soluble ferric iron. As a rule, the soluble ferric iron values were low compared to total oxidizing power. The results obtained with five whole coal samples are shown in Fig. 1 expressed in milliequivalents per gram of coal dried in contact with laboratory air, but not calculated to a moisture- and ash-free basis. Analytical data for the coals are given in Table I.

Measurement of Specific Surface.—In order to determine whether the variations in magnitude of oxidizing power were due entirely to differences in surface exposed, specific surface measurements were made. The procedure used is an adaptation of the air-permeability method of Lea and Nurse⁴ with apparatus constructed according to specifications obtained from Battelle Memorial Institute.⁵ Table II gives the results obtained and a comparison of the maximum oxidizing power values per unit surface.

Discussion

The mechanism of the reaction of oxygen with coal is obscure and will doubtless remain so until the chemical nature of coal is more clearly revealed. A number of workers in this field have considered that the initial step is the formation of a "coal-oxygen complex" or an unstable surface

(1) Presented before the Division of Gas and Fuel Chemistry at the Memphis meeting of the American Chemical Society, April 22, 1942. Published with permission of the Chief, Illinois State Geological Survey.

(2) Associate Chemist and Research Assistant, respectively.

(3) Yohe and Harman, *THIS JOURNAL*, 63, 555 (1941).

(4) Lea and Nurse, *J. Soc. Chem. Ind.*, 68, 277-83 (1939).

(5) Private communication from R. A. Sherman to O. W. Rees.