tionally distilled at 40–60 mm., using a one-meter column packed with glass helices and equipped with a dephlegmator. When this fractionation is carried out without first acidifying the solution or is carried out at atmospheric pressure, tarry resinous products result.

The residue from the benzene–alcohol distillation was taken up with dry ether, the ether evaporated and the crude ester fractionated at atmospheric pressure, collecting the fraction coming over at 134–138°.

The aldehyde was identified by its boiling point, 136°, its phenylhydrazone, m. p. 131°, and its semicarbazone, m. p. 218°.

(b) **From an Alcohol–Water or Water Solution.**—The solution was neutralized with sodium bicarbonate, and the alcohol removed under vacuum. The aqueous solution, saturated with sodium sulfate, was extracted ten times with ethyl acetate or formate. The rest of the procedure was similar to that under (a).

Summary of Results of Electrolysis.—(1) With a mercury cathode and a catholyte consisting of 300 ml. of 95% alcohol, 90 g. of sulfuric acid and 100 or 200 g. of ethyl oxalate, the yields varied between 38 and 50% using voltages between 9 and 13 and current densities between 7 and 12.1. (2) Using the same conditions but substituting 300 ml. of 50% solution of alcohol solution for the 95% alcohol, resulted in a drop in the yields to 33%. (3) If the alcohol is entirely omitted from the catholyte, the other conditions being varied as in part 1, the yields drop to 6 to 9%. (4) With a lead cathode and a catholyte consisting of 300 ml. of 95% alcohol, 90 g. of sulfuric acid and 100 g. of ethyl oxalate, the voltage being 7 and the current density 6.3, the yield was 35%. (5) Duplicating these conditions but substituting a lead amalgam cathode, the yields varied between 40 and 53%, the lower yield being obtained when 200 g. of ethyl oxalate was used and the higher yield when only 100 g. was used. In all cases the amount of current used was 10% in excess of theory.

De-alcoholation of the Hemi-acetal.—To 44 g. of ethyl glyoxylate alcoholate, cooled to 0°, was added under very good cooling and agitation, 14.2 g. of phosphorus pentoxide. The mixture, after coming to room temperature, was heated on a steam-bath until two liquid layers remained and no visible solid was present (three to four hours). The mixture was then distilled, the portion coming over up to 132° being collected. On redistillation 30 g. of material boiling at 129–130° was obtained (98%).

The free aldehyde was identified by its boiling point, 129–130°, its phenylhydrazone, m. p. 131°, and its semicarbazone, m. p. 218°.

Summary

1. A method for preparing ethyl glyoxylate alcoholate in good yields by the electrolytic reduction of ethyl oxalate in non-aqueous media has been developed.

2. Ethyl glyoxylate, free aldehyde, has been prepared in almost quantitative yields from its alcoholate by means of phosphorus pentoxide.

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

Reactions of β-Pinene. I. With Selenium Dioxide in Various Solvents[1]

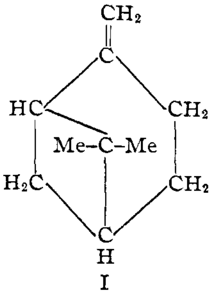
BY W. DAVID STALLCUP AND J. ERSKINE HAWKINS

The action of selenium dioxide on β-pinene was originally carried out by Dupont, Allard and Dulou[2] who identified the steam volatile oil as pinocarvone.

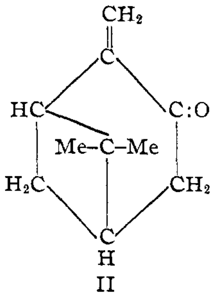
The present investigation was undertaken in order to conduct a more critical examination of the steam volatile products of the oxidation.

β-Pinene (I) was oxidized by selenium dioxide in eight solvents and in the absence of any solvent for periods of time varying from three to one hundred and sixty-eight hours and the resulting steam volatile oil was carefully examined.

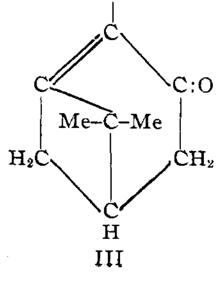
The oil was found to consist of pinocarvone (II) and carvopinone (III) and was not pure pinocarvone as indicated by Dupont, Allard and Dulou.



I



II



III

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[1] This material will be included in a thesis to be 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] Dupont, Allard and Dulou, *Bull. soc. chim.*, **53**, 599 (1933).

In the light of the recent work by Guillemonat,[3] who showed that alcohols are present as intermediates in the formation of ketones when ethylenic compounds are oxidized by selenium dioxide, it was anticipated that pinocarveol or other alcohols would be found in the products. Contrary to expectations, no alcohol could be detected as an oxidation product under the conditions at which these experiments were conducted.

Experimental

β-Pinene was obtained by fractionation of crude material through efficient columns.[4] The product had b. p. 58.2° (20 mm.), $n^{25}\text{D}$ 1.4768, $[\alpha]^{30}\text{D}$ −21.4°.

Selenium dioxide was prepared by dissolving selenium in concentrated nitric acid, evaporating, heating, dissolving in water, filtering, evaporating and drying.

Oxidation of β-Pinene by Selenium Dioxide.—The β-pinene and the solvent, in the amounts shown in Table I, were placed in a two-neck flask equipped with a stirrer and reflux condenser. The selenium dioxide was added slowly to avoid vigorous boiling. After complete addition of the dioxide, the mixture was kept boiling gently, by means of an electrical heating jacket, for various lengths of time as indicated in Table I. When pyridine was used as a solvent a reaction temperature of 80–90° was used. In general, heating for longer than ten hours decreased the yield of steam volatile oil and increased the yield of polymerization products. The selenium was removed from the mixture by filtration. The filtrate was steam distilled until a clear distillate was obtained. The ether extract of the distillate was then distilled at a pressure of 2–3 mm. The amounts and specific rotations of the oils thus obtained are shown in Table I.

The recovery of hydrocarbon was always less than 2% of the β-pinene used.

In a few cases the residue after removal of steam volatile oil was pyrolyzed and distilled under reduced pressure: b. p. 50° (10 mm.). This oil had the odor characteristic of the alkyl sulfides and was not further investigated.

Separation of the Steam Volatile Oil into Pinocarvone and Carvopinone

For Pinocarvone.—Each oil was added to twice its volume of a solution which contained 325 g. of sodium bisulfite and 105 g. of sodium bicarbonate per 1000 g. of water. Three to five drops of phenolphthalein indicator solution were added and the mixture shaken until the solution turned pink. Portions of 35% sodium bisulfite solution were added and the shaking repeated after each addition. This process was continued until the solution no longer became pink. At this point there was no oil visible. The solution was twice extracted with ether and the aqueous portion was then diluted with twice its volume of water. The mixture was steam distilled with intermittent additions of saturated sodium carbonate solution until no more oil was obtained in the distillate. The volatile oil obtained by extraction of the distillate with ether was then distilled at 2–3 mm. pressure. The product was pinocarvone. It was identified by its oxime and its semicarbazone.

For Carvopinone.—To the remainder of the hot sodium bisulfite solution was added 10 cc. of 25% sodium hydroxide and the steam distillation was continued. Ten-cc. portions of sodium hydroxide were added intermittently until no more oil appeared in the distillate. During this process from 10 to 25% of the original oil was converted into a solid polymer in the bisulfite solution. The ether extract of the distillate was distilled at 2–3 mm. pressure. The product was carvopinone.[5] It was identified by its semicarbazone, which yields carvone on hydrolysis and by its oxime which is nitrosopinene.

Tests for Alcohols.—The tests described below were applied to the original oil obtained by the oxidation and to the ether extracts of the bisulfite solution and to the steam distillate obtained by adding sodium hydroxide to the bisulfite solution on the chance that neutral bisulfite might have added to the ethylenic linkage as in the case of propenol.

One to two cc. portions of the various oils were shaken with 25% sulfuric acid and allowed to stand, with intermittent agitation, for several weeks. No crystalline hydrate was formed.

One cc. portions of the oils were treated with equal quantities of phenyl and α-naphthyl isocyanates, with and without solvents. No urethans formed.

One cc. portions of the oils were treated with acetic anhydride and sodium acetate. No acetates formed.

Pinocarvone.—When prepared as described it had the constants: b. p. 75–78° (3 mm.), 221–223° (760 mm.), d^{30}_4 0.980, $[\alpha]^{30}\text{D}$ −16.5°, $n^{30}\text{D}$ 1.5000, $n^{20}\text{D}$ 1.5038, M_D calcd. 44.83,[6] found 44.86.

Pinocarvoxime.—This compound was prepared by the method of Beckmann.[7] After recrystallization from dilute ethanol, fine needles were obtained which melted at 68.0–68.4° (cor.). Schmidt[8] reported 68–69°.

Pinocarvone Semicarbazone.—This compound was prepared by the method of Schmidt.[8] After recrystallization from aqueous methanol, white needles were obtained which melted at 212–213° (corr.). Schmidt reported 212–215°. The ketone was regenerated by the use of phthalic anhydride,[8] and was then distilled. None of its physical constants was changed appreciably.

Pinocarvone 2,4-Dinitrophenylhydrazone.—Two grams of 2,4-dinitrophenylhydrazine was added to 100 cc. of an alcoholic solution containing 1.5 g. of pinocarvone. The mixture was brought to boiling and 2 cc. of concentrated hydrochloric acid added. This caused the formation of a semi-solid mass which was broken by violent agitation. After boiling for three minutes, the mixture was filtered and the precipitate washed with ethanol. The yield of crude material was about 70%, m. p. 221°. After two recrystallizations from boiling ethanol the m. p. reached the constant value of 223–223.5° (cor.).

Anal. Calcd. for $C_{16}H_{18}O_4N_4$: C, 58.18; H, 5.50. Found: C, 58.10; H, 5.66.

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[3] Guillemonat, *Ann. Chim.*, **11**, 143 (1939).

[4] These columns will be described in a forthcoming article.

[5] Wallach and Engelbrecht, *Ann.*, **346**, 232 (1906).

[6] Based on values of Auwers and Eisenlohr, and 0.83 for conjugation and 0.48 for the cyclobutane ring.

[7] Beckmann, *Ann.*, **250**, 330 (1889).

[8] Schmidt, *Ber.*, **63**, 1129 (1930).

Carvopinone.—When this compound was prepared as described above it had the constants: b. p. 82–84° (3 mm.), d^{30}_4 0.973, $[\alpha]^{30}\text{D}$ +62.7°, $n^{30}\text{D}$ 1.4910, $n^{21}\text{D}$ 1.4948, *M*D calcd. 44.83,[6] found 44.70.

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.68, H, 9.45.

Carvopinone turned yellow upon standing for a few days and formed a white solid polymer when heated to 140° or on prolonged standing. This polymer is insoluble in the common solvents. Upon heating to about 320° it softens and slowly melts with decomposition.

Carvopinoxime.—This compound was prepared by the method of Beckmann.[7] After recrystallization from aqueous methanol its m. p. was 132–133° (cor.). Wallach[9] reported 132°.

Carvopinone Semicarbazone.—This compound was prepared by the method of Schmidt.[8] After recrystallization from aqueous methanol, the hard white prisms obtained did not melt below 300° as recorded by Wallach and Engelbrecht.[5]

Two grams of the substance was simultaneously hydrolyzed[5] and steam distilled in the presence of oxalic acid. A small amount of polymer formed in the flask—a behavior characteristic of carvopinone. The distillate was extracted with ether and the ether evaporated at room temperature under reduced pressure. The oil obtained had the characteristic odor of carvone and a value $n^{20}\text{D}$ 1.4993. This oil was converted to the semicarbazone. The first crystals which formed were recrystallized from dilute methanol. These melted at 212–213°, indicating that some pinocarvone was present at this point. The remaining crystals softened at 154°, which is the approximate m. p. of the semicarbazone of *dl*-carvone, and did not completely melt until 172° was reached. These facts indicate the formation of carvopinone, pinocarvone and carvone when carvopinone semicarbazone is hydrolyzed under the above conditions.

Discussion

In column 7 of Table I are listed the percentages of carvopinone in the oxidation product as based on Biot's rule for mixtures. These calculations have been verified by estimation of the quantities obtained. Thus one needs only to determine the specific rotation of the steam volatile oil in order to ascertain the proportions of the two ketones.

With but one exception, the longer the reaction continues the larger is the percentage of pinocarvone in the steam volatile oil.

The yield of steam volatile oil *vs.* time indicates a maximum depending on the temperature of the reaction. This is verified by the data for the reactions in ether and by the fact that when the reaction was carried out for forty-eight hours in ethanol the yield of oil was only about 5%.

TABLE I

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

Solvent	Solvent in cc.	Reaction in hr.	% Se recov.	Steam volatile oil Yield, %	$[\alpha]^{30}\text{D}$	Biot % carvopinone[a]
Ethanol	200	3	45	19	+43	75
Ethanol	300	10	60	30	+16	41
Acetone	100	10	29	23	+49	83
Benzene	100	10	55	15	+46	79
Hexane	100	10	50	18	+54	89
Ether[b]	100	10	13	17	+59	95
Ether[b]	100	48	40	28	+56	91
Ether[b]	200	72	64	25	+55	90
Ether[b]	100	168	55	24	+57	93
Carbon tetr.	100	10	10	28	+56	91
Pyridine	100	10	95	34	+56	91
Water	100	10	0.0	24	+56	91
None	...	10	0.0	27	+50	84

[a] Carvopinone $[\alpha]^{30}\text{D}$ +62.7°; pinocarvone $[\alpha]^{30}\text{D}$ −16.5°. [b] Solvent loss was about 0.5 cc. per hour.

No definite conclusions can be drawn concerning the effect of the volume of solvent used, but it is believed that this effect is negligible in these experiments.

It should be noted that the oxidation occurs in pyridine, contrary to the findings of Guillemonat[3] for ethylenic hydrocarbons.

The properties of the oxidation mixtures obtained in ethanolic medium agree with those reported by Dupont, Allard and Dulou[2] and it appears probable that their oil was a mixture of the ketones. Furthermore, the refractive index, density and molar refraction reported by them are between those of the pure compounds. The semicarbazone of carvopinone forms much slower than that of pinocarvone so that the first crystals obtained from the oil will give a melting point corresponding to the semicarbazone of the latter.

Acknowledgment.—The selenium used in this work was generously supplied through the courtesy of the American Smelting and Refining Company, Baltimore, Maryland.

Summary

1. The oxidation of β-pinene by selenium dioxide in several solvents has been studied.

2. The products of the oxidation have been identified as pinocarvone and carvopinone.

3. Pinocarvone and carvopinone have been more completely characterized than heretofore.

4. Pinocarvone 2,4-dinitrophenylhydrazone has been prepared.

GAINESVILLE, FLORIDA RECEIVED JULY 23, 1941

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(9) Wallach, *Ann.*, **245**, 254 (1888).