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THE EFFECT OF FULLER'S EARTH ON PINENE AND OTHER TERPENES

By Charles S. Venable

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The majority of the processes for the synthesis of camphor from turpentine involve the conversion of the pinene fraction in turpentine to camphene. This camphene is treated with glacial acetic acid and sulfuric acid to form isoborneol acetate, which is then saponified with alcoholic potash. The resulting isoborneol can be oxidized very smoothly to camphor. By far the maximum loss of materials and the greatest operating costs are encountered in the conversion of pinene to camphene. Consequently, a statement by Gurvich[1] that camphene was obtained by the treatment of pinene with active fuller's earth is of more than general interest, although it has apparently attracted very little attention in this country.

In the present investigation, the reaction between pinene and fuller's earth has been carried out several times under the conditions specified by Gurvich, but in no case was it found possible to detect any traces of camphene;[2] otherwise, products similar to those noted by him were obtained, namely a large amount of monoterpenes other than pinene, boiling at 160–185°, and a polyterpene fraction which begins to boil at about 320°. However, the present investigation, more complete than that of Gurvich, has led to conclusions concerning the mechanism of the reaction that are entirely different from those drawn by Gurvich.

Gurvich conducted his reactions at temperatures varying from —20° to above room temperature. He claimed to have observed that a higher ratio of polyterpenes in the product was produced at lower temperatures than at room temperature. He suggests, therefore, that the polyterpenes were formed first, and then depolymerized to form the terpene fraction by the strong local heating which characterizes the reaction. Gurvich noted a marked inhibiting effect of certain diluents and likewise an optimum moisture condition for the fuller's earth.

The results obtained in the present investigation led to the conclusion that the reaction really takes place as follows.

$$\begin{array}{lllll} \text{Fraction: Pinene} & \longrightarrow \text{Monoterpenes (Terpinene)} & \longrightarrow & \text{Dipinene} & \longrightarrow \text{Polyterpenes} \\ \text{B. p.}: \quad 156\text{–}158 & 160\text{–}185 \quad \text{(Dipentene, etc.)} & & 320\text{–}340^\circ & >360^\circ \\ & & & \downarrow & \\ & & & \text{paraffin hydrocarbons} & \\ & & & +\ \text{paracymene} & \end{array}$$

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[1] Gurvich, *J. Russ. Phys. Chem. Soc.*, **1915–16**, p. 827.

[2] The camphene reported by Gurvich may possibly be due to the small amount of this terpene known to be present in Russian turpentine.

Contrary to the report of Gurvich, it was found that there was a higher ratio of terpenes to polyterpenes in the reaction product at the lower temperature than at the higher temperatures. Additional data in support of this conclusion will be discussed in detail later.

There is a possibility that when the pinene reacts in the presence of fuller's earth, the dipinene fraction is formed simultaneously with the monoterpene fraction, this latter again reacting to form eventually the dipinene and polyterpene fraction. The reaction, however, at all times proceeds toward the right and not toward the left, as claimed by Gurvich.

Of the products formed from pinene in the presence of fuller's earth, the most interesting is the 320° fraction. This material is apparently identical with dipinene reported by Frankforter and Poppe[3] as the result of decomposition of the iodine derivatives of pinene. The 360° fraction is apparently a mixture of various higher polyterpenes.

The present investigation has shown that dipinene is almost universally one of the products formed when an unsaturated terpene is treated with active fuller's earth. The reaction takes place not only with α-pinene, dipentene, and terpinene as noted above, but also with camphene, nopinene, active limonene and sabinene. The oxygen derivatives, terpineol and borneol also react in the presence of fuller's earth to give dipinene, with a vigorous evolution of water. The saturated compounds such as cineol and paracymene are non-reactive.

Apparently, the phenomenon is one of surface catalysis. A brief investigation has been made of the effect of diluents and of the physical condition of the fuller's earth, and the data obtained essentially confirm the results obtained by Gurvich.

It is quite conceivable that this reaction with fuller's earth may be of considerable service in the study of the chemistry of terpenes. It also presents interesting possibilities in connection with the study of various other unsaturated organic compounds. The effect seems to be specific for fuller's earth, inasmuch as the pinene reaction is not given by far better adsorbents such as activated charcoal, iron gel, or silica gel.

Experiments with Pinene

Preparation of Pinene.—Spirits of turpentine was fractionated twice using a glass bead column 25 cm. long. The final cut taken as the pinene fraction was that boiling from 155.5° to 157.5°; n_D^{25}, 1.4671.

Fuller's Earth.—This was commercial material from a Florida deposit, and was screened to 30–60 mesh. Except where noted, this earth had been burned at 400° to a water content of approximately 6%.

General Procedure.—Forty g. of fuller's earth was added to 100 g. of pinene. Diluents, when used, were mixed with the pinene before the addition of the fuller's earth. Temperature control was maintained by

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[3] Frankforter and Poppe, *Eighth Inter. Cong. Appl. Chem.*, **1912**, p. 363.

an external bath, except in the refluxing experiments where the temperature was simply that of the boiling liquid. To stop the reaction, the liquid was decanted from the fuller's earth, the residue then being washed repeatedly with ether, or in case a diluent was used, with the diluent in question. The combined liquid and washings were then fractionated through a 25cm. bead column and cuts made as follows.

Below 150° = diluent
150–160° = pinene
160–200° = monoterpenes other than pinene
200–300° = terpineols and sesquiterpenes
300–340° = dipinene
Above 340° = polyterpenes

It was found that only by repeated fractionation is it possible to obtain a complete separation of pinene from the 160–200° fraction, each fraction overlapping into the other. However, the cuts taken were considered to give a fair estimate of the relative amounts of each present. The other fractions were quite sharply defined. The identification of some of the components of these fractions will be described later.

Gurvich adopted a slightly different procedure in that he separated monoterpenes from polyterpenes by distillation with steam, the polyterpenes being non-volatile in steam. The monoterpene fraction was separated from unchanged pinene by fractionation as described above. Comparative experiments showed that both the steam-distillation method of Gurvich and the straight fractionation method used in the present investigation gave practically identical results.

Effect of Dehydration on Activity of Fuller's Earth

By noting the temperature rise produced when fuller's earth of various degrees of dehydration was added to pinene (diluted with xylene) it was found that the maximum activity of fuller's earth occurs in the presence of 5 and 8% of combined moisture, corresponding to a burning temperature in the neighborhood of 400°. This confirms the results obtained by Gurvich. Too strong a heating and dehydration apparently alter the structure of the earth and destroy most of its catalytic power. The addition of water to an over-burned earth was found not to restore activity. The activity of fuller's earth toward pinene apparently runs parallel to its efficiency as a filtering medium, and a convenient use of this relationship has been made by Dr. L. W. Parsons of this Laboratory[4] in testing the efficiency of the burning of fuller's earth used to decolorize oils. The lot of earth used in the subsequent experimentation was burned at 400° to a moisture content of about 6%.

The Effect of Temperature

Pinene was allowed to react in the presence of fuller's earth for 4 hours at —20°, —5°, +25° and +158° (with refluxing). The composition of

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[4] To be published.

the reaction product (unchanged pinene having been removed) is shown in Fig. 1. It is thus seen that the ratio of dipinene and polyterpenes to terpenes formed from the pinene increases as the temperature is raised. These results are contrary to those reported by Gurvich. However, this general effect of varying the temperature has been carefully confirmed by a large number of independent observations.

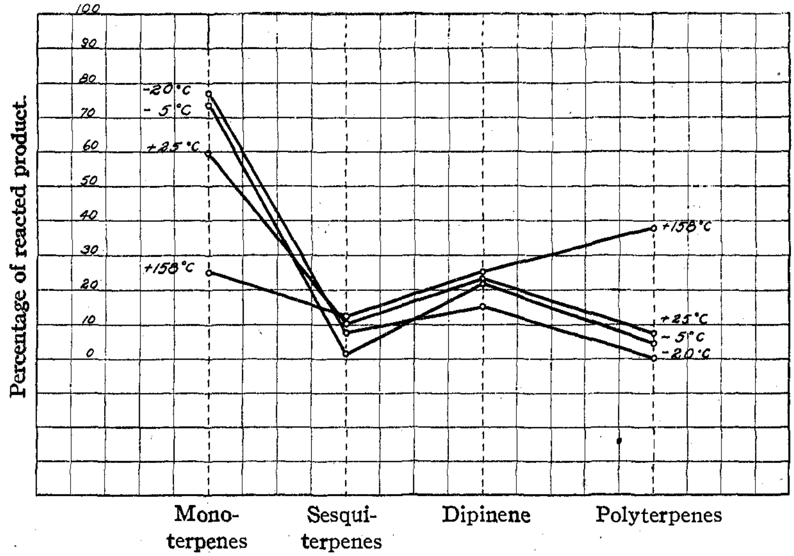

Fig. 1.—Effect of temperature on compostion of product (time = 4 hours).

The Effect of Re-treatment of Preliminary Fractions

The 2 principal fractions obtained when pinene is first subjected to the action of fuller's earth, namely, those boiling at (*a*) 160–200° and (*b*) 300–340°, were treated separately for 8 hours at 175° with a fresh portion of fuller's earth. Approximately 65% of Fraction *a* was converted to higher-boiling material, the remainder being unchanged. Likewise, 25% of Fraction *b* was converted to material boiling above 340°, with no appreciable change in the remainder.

In the case of the 160–200° fraction, a part of the observed transformation might conceivably be due to the pinene still remaining.

Accordingly, a second large lot of this fraction was repeatedly fractionated and a final cut made at 175–180°. The greater part of the original fraction came within this cut. On treatment of this cut with fuller's earth at 175° for 3$^1/_2$ hours, 40% of the fraction was converted to material boiling higher than 300°; 1$^1/_2$ hours' refluxing with fresh fuller's earth on the still unconverted portion gave an additional 15% conversion. In all, 5 repetitions of this process resulted in a total conversion of 90% to material boiling above 300°. The remaining 10% had a boiling range of 175–179° and was practically non-reactive in the presence of fuller's earth. This unconverted portion did not decolorize bromine water and on oxidation with nitric acid, conversion of the acid so formed with phosphorus pentachloride to acid chloride, and then treatment with methyl alcohol, gave the methyl ester of terephthalic acid (m. p., 140–142°). These characteristics, as well as the boiling point and specific gravity would indicate paracymene. This paracymene fraction was always found in runs at elevated temperature.

It thus appears that the first effect of fuller's earth on pinene is one of intramolecular change to give various monoterpenes. The second effect is one of polymerization of these monoterpenes. The polyterpenes so formed, on continued exposure to the fuller's earth at elevated temperatures, partially decompose to give paraffin hydrocarbons and also paracymene, but not monoterpenes. This conclusion is exactly opposite to that reached by Gurvich.

Effect of Diluents

Experiments showed that oxygenated diluents such as acetone, alcohol and ether, exert a strong inhibiting action, there being practically no tendency for the higher-boiling fractions to form. The inhibiting action of small amounts of water is especially noticeable. When the proportion of oxygenated solvent to pinene is greater than 4 to 1, the intramolecular change can likewise be practically eliminated. On the other hand, such diluents as benzene and carbon tetrachloride (water-free) apparently retard the reaction only in so far as they reduce the concentration of pinene.

Identification of Various Reaction Products

The reaction products from a number of runs were carefully fractionated using the bead column. Eight complete distillations were carried out, some 70 fractions in all being collected. From the distillation curve so obtained, it was seen that 5 distinct fractions were present, having the following boiling ranges: Fraction 1, 157.5–160.5°; Fraction 2, 175.0–180.0°; Fraction 3, 200–220°; Fraction 4, 315–335°; Fraction 5, above 340°. Fraction 1 was almost entirely α-pinene, as indicated by the boiling range and the large yield of pinene hydrochloride (m. p., 122–124°) obtained when it was treated with hydrogen chloride in the cold. Negative tests were obtained for camphene (b. p., 159–161°),[5] sabinene (b. p., 162–166°),[6] and nopinene (b. p., 162–163°).[7]

Fraction 2 was evidently a mixture of various monoterpenes, at least 50% of which was dipentene (b. p., 175–176°). In addition, small amounts of terpinene (b. p., 180–181°) and paracymene (b. p., 175°) were found. A considerable proportion of this mixture remained unidentified. For dipentene, good yields of dipentene tetrabromide (m. p., 122–124°) were obtained on treatment of the oil in glacial acetic acid in the dark with bromine, and also of dipentene dihydrochloride (m. p., 50°)[8] on treating the

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[5] "Conversion to Camphor," See Parry, "Chemistry of Essential Oils," **2**, p. 41.

[6] Wallach, "Oxidation to Sabinenic Acid," *Ann.*, **357**, 78 (1907).

[7] "Oxidation to Nopinic Acid," Parry, Ref. 5, p. 35.

[8] Ref. 5, pp. 50, 55.

oil in glacial acetic acid solution with hydrogen chloride. For terpinene, crystals of terpinene nitrosite (m. p., 155–165°) were obtained[9] on treating the oil in petroleum ether solution with aqueous sodium nitrite and glacial acetic acid, and also the characteristic flocculent brown precipitate was obtained on treating the oil with Beckmann mixture.[10] Negative tests were obtained for camphene, sabinene and nopinene.

Fraction 3, as indicated by the boiling range, odor, specific gravity (0.935), and solubility in 70% alcohol, was largely terpineol (b. p., 218–220°). This material is usually found in small amounts in raw spirits of turpentine, due probably to the oxidation of monoterpenes.

Fraction 4 was a light colored, viscous oil; d^{25}, 0.94; n_D^{25} 1.5084. An analysis showed C, 87.75% and H, 11.51% (calc. for $(C_{10}H_{16})_n$ C, 88.15; H, 11.87). The molecular weight, as determined by the freezing-point lowering in benzene solution, averaged 275, and the iodine number 100, which is equivalent to one double bond per molecular weight. These characteristics correspond closely to a material obtained by Frankforter and Poppe[3] as the result of the decomposition of the iodine derivatives of pinene, and called by them dipinene $(C_{10}H_{16})_2$.

Fraction 5 is a heavy, viscous oil that usually has a strong, blue fluorescence, probably due to traces of azulene $(C_{15}H_{18})$. The average molecular weight of several samples as obtained by the freezing-point lowering in benzene solution was 335; the iodine number was 96. An analysis gave C, 88.12%, and H, 10.91%, which again corresponds to $(C_{10}H_{16})_n$. Apparently, this oil is a mixture of dipinene and various polyterpenes.

Experiments with Materials Other than Pinene

One hundred-g. samples of various specially prepared terpenes or terpene derivatives were refluxed for 1½ hours with 40 g. of fuller's earth. In the following cases there was from 40 to 70% conversion to dipinene and polyterpenenes: nopinene, dipentene, α-limonene, terpinene, camphene, sabinene, terpineol, borneol. The saturated materials, cineol and paracymene, did not undergo polymerization.

With shorter times of contact and at lower temperatures, an intermediate conversion of dipentene to terpinene was noted in every case save that of paracymene, which was entirely non-reactive, and camphene and sabinene where the tests were not decidedly positive. The 315–330° fraction was isolated in each case and was apparently identical with that formed from α-pinene. Considerable quantities of water were evolved during the treatment of the terpineol and borneol.

It is thus apparent that the effect of fuller's earth is general for terpenes and unsaturated terpene derivatives. First, an intramolecular change takes place, followed by polymerization.

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[9] Ref. 5, p. 64.

[10] Semmler, *Ber.*, **27**, 810 (1894).

Effect of Other Absorbents than Fuller's Earth

One hundred-g. samples of α-pinene were refluxed for several hours with 40 g. of (*a*) iron gel, (*b*) silica gel, (*c*) activated charcoal. There was no evidence of any change whatever.

Summary

1. α-Pinene, in the presence of fuller's earth, first undergoes an intramolecular rearrangement, among the products formed being dipentene and terpinene. No camphene was found.

2. The second stage of the reaction is one of polymerization to dipinene and various polyterpenes.

3. At elevated temperatures, the dipinene so formed is slowly decomposed in the presence of fuller's earth, giving low-boiling paraffin hydrocarbons and some paracymene.

4. This reaction is a general one for terpenes and unsaturated oxygenated terpenes.

5. The effect of the diluents and conditions affecting the activity of the fuller's earth have been investigated.

6. The reaction is not promoted by iron gel, silica gel, or activated charcoal.

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CAMBRIDGE 39, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

STUDIES ON CELLULOSE CHEMISTRY. III. PARABROMO-ACETALDEHYDE AND MONOBROMO-ACETALDEHYDE. THEIR PREPARATION, PROPERTIES AND UTILIZATION FOR THE SYNTHESIS OF BROMO- AND HYDROXY-CYCLIC ACETALS RELATED TO POLYSACCHARIDES

BY HAROLD HIBBERT AND HAROLD S. HILL[1,2]

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The chemical inertness of cellulose has rendered a study of its molecular structure a matter of great difficulty. While the few reactions in which the cellulose molecule is involved have all helped to establish the fact of the close inter-relationship between this substance and glucose, they are of

[1] This paper is constructed from Part 2 of a dissertation presented by Harold Sanford Hill (du Pont Research Fellow) in June, 1922, to the Faculty of the Graduate School, Yale University, in candidacy for the degree of Doctor of Philosophy. The thesis contains a review of the literature on bromo-acetaldehyde and related compounds.

[2] Communicated to the Cellulose Section of the American Chemical Society at the Birmingham (Ala.) meeting, April, 1922.