D'_c and D''_c = optical densities at the 2 respective wave lengths for pure *cis*-isomer
D'_t and D''_t = optical densities at the 2 respective wave lengths for pure *trans*-isomer
C_c and C_t = respective concn. at which the two spectra of the pure *cis*- and *trans*-isomers were run
D'_m and D''_m = optical densities at the two critical wave lengths for the mixture.

The densities used were obtained by assuming that the transmittance for all the compounds concerned was 100% at two microns and using the transmittances obtained directly without any consideration of background absorption. The method described was tested on six different mixtures of known composition ranging from all *trans* to all *cis;* in every case the analytical method proved to be accurate within 2%. The method described has the advantage of not requiring that the concentration of the mixtures analyzed be known; however, best results were obtained when absorption in the analytical regions was reasonably intense (*i.e.*, total concn. between 180 and 360 mg./ml.).

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE NAVAL STORES STATION][1]

Autoxidation of α-Pinene[2]

BY R. N. MOORE, C. GOLUMBIC AND G. S. FISHER

RECEIVED SEPTEMBER 1, 1955

Although the autoxidation of α-pinene has been studied intermittently for over 100 years, few data are available on the products obtained by non-catalytic, liquid-phase autoxidation at elevated temperatures. In the present investigation, α-pinene was autoxidized in the dark at 100° and the α-pinene hydroperoxides in the resulting oxidate were reduced. The product was fractionated and the volatile fractions analyzed. In addition to unreacted α-pinene (45% of the volatile material) and verbenone (9%), verbenol (16%) and verbenene (trace) which have long been recognized as products of the reaction, α-pinene epoxide (13%), *trans*-pinocarveol (8%), *trans*-carveol (2%) and myrtenal (1%) were obtained. It is suggested that, except for the epoxide, these products result from free radical attack on the α-methyl group of α-pinene to give the myrtenyl free radical and its resonance hybrid the pinocarvyl free radical and the corresponding hydroperoxides. The epoxide is considered to be a secondary oxidation product resulting from the action of a peroxide on the double bond of α-pinene.

Esters of pinic acid and pinonic acid derived from α-pinene, the major constituent of turpentine, are potentially useful as synthetic lubricants and plasticizers.[3,4] Attempts to produce these or similar acids by the autoxidation of α-pinene have led in every case to very complex mixtures of resinous products. These mixtures did contain terpene-acids, but separation and identification of the mixtures of acids was not practical. In order to clarify the reactions involved, a detailed study of the volatile autoxidation products was initiated.

The nature of the oxidation of turpentine by air has been the subject of intermittent investigation and controversy for well over a century. The products isolated from oxidized turpentine and α-pinene include sobrerol,[5] formic and acetic acids,[6] verbenol, verbenone[7] and verbenyl hydroperoxide.[8] The possible presence of myrtenal in autoxidized α-pinene also has been suggested.[9] The verbenyl hydroperoxide is obviously the precursor of the verbenol and verbenone, but the source of the sobrerol and pinol has been in doubt. Recently, Schenck[10] has reported the secondary formation of α-pinene epoxide when the α-pinene was oxidized at room temperature. This oxide is very readily hydrated to sobrerol in the presence of dilute acid. Subsequently, Lombard[11] has suggested that the intermediate is the cyclic peroxide analogous to pinol.

Quantitative data regarding the autoxidation products are in all cases meager and there seems to have been no attempt to make a complete examination of the volatile oxidation products obtained under a given set of conditions. Furthermore, the oxidation conditions used have usually involved uneconomically long reaction times and low temperatures.

The present report concerns the volatile products of the non-catalyzed autoxidation of α-pinene at 100° in the absence of light. Under such conditions, a vigorous exothermic reaction occurs with rapid absorption of oxygen and somewhat less rapid accumulation of peroxides (Fig. 1). Reduction of the hydroperoxides with sodium sulfide and fractional distillation of the recovered neutral fraction gave an oil whose composition is summarized in Table I.

TABLE I

Compound	% of distillate	Compound	% of distillate
α-Pinene	45	*trans*-Pinocarveol	8
Verbenene	Trace	*trans*-Verbenol	16
α-Pinene epoxide	13	Verbenone	9
Myrtenal	1	*trans*-Carveol	2

Dupont[12] has pointed out that the production of verbenyl hydroperoxide III, verbenol and verbenone is in accord with the modern theory of α-methylenic attack in autoxidation of olefins.[13] The ver-

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(1) One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, United States Department of Agriculture.

(2) Presented, in part, at the 126th Meeting of the American Chemical Society, New York, N. Y., September, 1954.

(3) C. M. Murphy, J. G. O'Rear and W. A. Zisman, *Ind. Eng. Chem.*, **45**, 119 (1953).

(4) V. M. Loeblich, F. C. Magne and R. R. Mod, *ibid.*, **47**, 855 (1955).

(5) Margueron, *Ann. Chim.*, **21**, 174 (1797).

(6) C. T. Kingzett and R. C. Woodcock, *J. Soc. Chem. Ind.*, **31**, 265 (1912).

(7) A. Blumann and O. Zeitschel, *Ber.*, **46**, 1178 (1913).

(8) K. Suzuki, *Bull. Inst. Phys. Chem. Res. Japan*, **15**, 70 (1936).

(9) G. Dupont, W. Zacharewicz and R. Dulou, *Compt. rend.*, **198**, 1699 (1934).

(10) G. O. Schenck, H. Eggert and W. Denk, *Ann.*, **584**, 177 (1953).

(11) R. Lombard and A. Kohler, *Bull. soc. chim.*, 639 (1954).

(12) G. Dupont, *Bull. soc. chim. France*, 838 (1948).

(13) (a) E. H. Farmer and A. Sundralingham, *J. Chem. Soc.*, 121 (1942); (b) E. H. Farmer, H. P. Koch and D. A. Sutton, *ibid.*, 541 (1943). (c) J. L. Bolland, *Trans. Faraday Soc.*, **46**, 358 (1950); (d) L. Bateman, *Quart. Rev.*, **8**, 147 (1954).

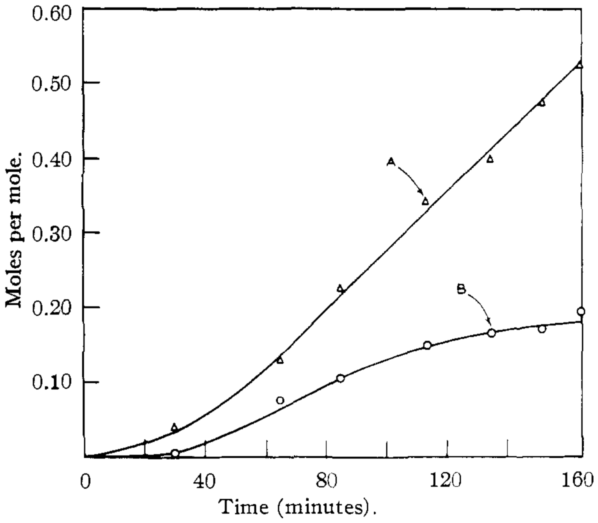
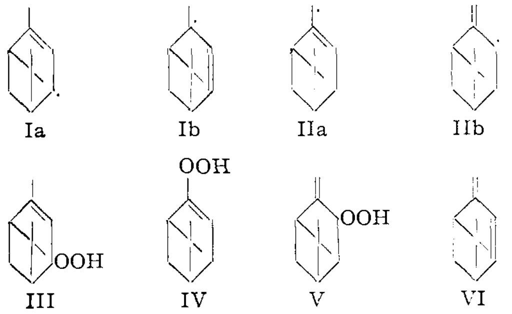


Fig. 1.—Autoxidation of α-pinene at 100°: A, moles of O_2 absorbed per mole of α-pinene charged; B, moles of active oxygen found per mole of α-pinene charged.

benyl hydroperoxide (III) predicted by this mechanism can exist in *cis* and *trans* modifications. The *trans* form of the corresponding secondary alcohol, verbenol, was found in the distillate (Table I). The failure to isolate *cis*-verbenol does not necessarily indicate that only *trans*-verbenyl hydroperoxide was formed. The *cis*-verbenol is known to be much less stable to heat and acid than the *trans* form[14] and might be expected to dehydrate to verbenene under the conditions used. This is supported by the identification of verbenene in the distillate.

Chart I



No product was isolated that would indicate the formation of a tertiary hydroperoxide *via* the resonance hybrid, Ib. Greater steric hindrance at the tertiary position and an energetically favored verbenyl resonance may both contribute to the exclusive formation of the secondary hydroperoxide. However, it seems unlikely that steric hindrance would exclude formation of the tertiary hydroperoxides since pinane readily forms the corresponding hydroperoxide under similar conditions.[15]

The production of myrtenal, predicted by Dupont,[9] was confirmed in the present investigation. In addition, *trans*-pinocarveol and *trans*-carveol were obtained in significant amounts. These compounds had not previously been identified as simple autoxidation products of α-pinene; however, Schenck[10] has reported the formation of pinocarvyl hydroperoxide by photosensitized oxidation and its reduction to pinocarveol. For this reaction he proposed a mechanism involving direct attack at the double bond by an activated oxygen-sensitizer complex. A similar mechanism involving oxygen has been advanced by Gunstone and Hilditch,[16] for non-catalyzed autoxidation. However, this type of oxidation is not autocatalytic. In view of the relatively high yield of pinocarveol and the over-all autocatalytic nature of the oxidation, a conventional free radical chain mechanism involving attack at the α-methyl group in α-pinene to give the myrtenyl radical IIa and its resonance hybrid IIb seems more reasonable in the present case. This same mechanism also accounts for the formation of myrtenal. The carveol probably was formed by isomerization of the pinocarveol.

Failure of previous investigators to detect myrtenal, pinocarveol or carveol among the autoxidation products of α-pinene may be due in part simply to the lack of adequate stills and spectrophotometers. In addition, attack at the methyl group may be expected to be favored by the higher oxidation temperature used in the present work.[13d] A study of the effect of oxidation conditions on the nature and yield of products is in progress.

The relatively high yield of high boiling material, obviously, is the result of polymerization, isomerization and further oxidation of the more unstable primary and secondary oxidation products. Hence, the relative yields of the various products are not necessarily a measure of the extent of formation of the corresponding intermediates. Although the formation of myrtenyl hydroperoxide IV *via* the resonance hybrid IIa would be expected to predominate over the formation of pinocarvyl hydroperoxide V, due to the more stable cyclic position of its double bond, pinocarveol predominated in the products isolated. It is likely that any myrtenyl hydroperoxide formed in the reaction was decomposed to myrtenal at 100° due to the instability of primary hydroperoxides. Resinification of myrtenal under the experimental conditions is to be expected and may account for the small yield of myrtenal and for a large part of the non-volatile portion of the product. Pinocarvone and the *cis* forms of verbenol and pinocarveol are other reasonable precursors of the non-volatile products. The ratio of verbenol and verbenone to pinocarveol and carveol is somewhat lower than might be expected on the basis of the theories of Bolland[13c] and Bateman[13d] with regard to the effect of structure on α-methylenic reactivity of olefins and the work of Farmer[13a] on 1-methylcyclohexene. Although this might also be attributed to resinification of verbenyl intermediates, it seems more likely that the behavior of a complex olefin such as α-pinene simply cannot be predicted on the basis of the simple analogs.

It is noteworthy that the yield of α-pinene epoxide based on volatile oxidation products was similar to that obtained by Schenck, although the peroxidation conditions were entirely different. His observa-

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[14] L. Schulz and W. Doll, Schimmel's Report, 1940, p. 38.

[15] G. S. Fisher, J. S. Stinson and L. A. Goldblatt, This Journal, **75**, 3675 (1953).

[16] F. D. Gunstone and T. P. Hilditch, *J. Chem. Soc.*, 1022 (1946)

tions with regard to the ease with which the epoxide is converted to sobrerol in the presence of water and weak acids was verified as was the conversion of sobrerol to pinol. Hence, our work supports his conclusion that the epoxide is the precursor of sobrerol and does not give any indication of the formation of the peroxide proposed by Lombard. In contrast to its instability toward acid, the epoxide was found to be very stable toward base and was not reduced by lithium aluminum hydride.

The formation of epoxides as secondary products in the autoxidation of olefins has been attributed to a direct reaction between the hydroperoxides and the olefin.[13a,17] However, the presence or formation of organic acids and hydrogen peroxide in such reactions suggests *in situ* peracid formation as another route to the epoxides.

Experimental

Material.—A commercial grade of α-pinene (98+%) was used in run 1 of this investigation. The physical properties were $n^{20}D$ 1.4654, d^{20}_4 0.8587, $[\alpha]D$ +23.3°.

Optically pure α-pinene cannot be obtained from any of the commercial species of American pines. In order to obtain α-pinene of high optical purity, it was necessary to prepare it by isomerization of *l*-β-pinene. The β-pinene was first freed of more volatile impurities by fractional distillation through a 6-foot Podbielniak column and then isomerized by refluxing with rosin.[18] Refractionation of the isomerized β-pinene gave *l*-α-pinene; b.p. 52° (20 mm.), $n^{20}D$ 1.4658, d^{20}_4 0.8576, $[\alpha]^{27}D$ −47.4°. This material was used for run 2 which was conducted and distilled in the same manner as run 1 described below, except that the distillate was refractionated prior to chemical separation.

Equipment.—The strongly exothermic autoxidation was carried out in a recently described false bottom reaction vessel[19] having provision for automatic cooling to maintain the temperature at 100 ± 2°.

Autoxidation.—α-Pinene (3374 g.) was charged to the reaction vessel and supported on the false bottom by a flow rate of 200 to 400 liters per hour of oxygen. The charge was heated electrically to 100° and the thermoregulator was set for this temperature. The oxygen input was varied to maintain about 100% excess as measured by input and exhaust wet test meters. The course of the reaction was followed by active oxygen determination.[20] A plot of these measurements (Fig. 1) gives the typical curve of an autoxidation reaction. The reaction mixture was quenched by shorting the thermoregulator to permit continuous flow of cooling liquid through the internal cooling coil when the maximum peroxide number (2600), as determined by preliminary experiments, was obtained. In run 1, the crude oxidate (3753 g.) was a yellow fluid; $n^{20}D$ 1.4829, d^{20}_4 0.9640, $[\alpha]D$ +32.8°, acid number 17.4, peroxide number 2600.

Reduction of Hydroperoxides.—A portion of the oxidate (1500 g.) was added in small portions with vigorous stirring to 2.0 moles of Na_2S and 4.0 moles of NaOH in 500 ml. of water. The reaction temperature was maintained at 50 to 60° by cooling with an ice-bath and by adding the hydroperoxide at a suitable rate. Agitation was continued for 15 minutes after complete addition of the hydroperoxide. The black oil which separated contained no active oxygen. The oil was washed with water and the aqueous layers were extracted with ether. The ether was removed from the combined ether extracts and oil.

Distillation.—The recovered dark oil was fractionally distilled at 20 mm. through a 1 inch column packed with 2 feet of protruded nickel packing. A throughput of 210 to 330 ml. per hour and a reflux ratio of 40:1 were maintained through most of the distillation. A prior distillation of a similar oxidate through a 100 plate column at reflux ratios greater than 100:1 was unsatisfactory. Although purer pinocarveol was obtained, higher boiling fractions were badly contaminated by decomposition products, and less verbenol was found in the distillate.

Analysis of Distillate.—Quantitative estimation of compounds identified in the distillate (Table I) was based on infrared and ultraviolet spectra wherever feasible. The composition of mixtures which did not lend themselves to spectrophotometric analysis was estimated on the basis of physical constants. Infrared spectra were obtained with the Perkin-Elmer Model 21 double beam instrument with sodium chloride prism and ultraviolet absorption was measured with the Beckman model DU spectrophotometer.

Identification Procedures. α-**Pinene.**—Physical constants of the recovered α-pinene, run 1, were: b.p. 53° (20 mm.), $n^{20}D$ 1.4655, d^{20}_4 0.8584, run 2, $n^{20}D$ 1.4657, d^{20}_4 0.8582, $[\alpha]D$ −47.2°, and its infrared spectrum were in good agreement with authentic material.

Verbenene.—Infrared and ultraviolet spectra indicated the presence of verbenene in fractions boiling at 55–60° (20 mm.). Pure verbenene for comparative purposes was obtained by refluxing verbenol in acetic anhydride with sodium acetate.[5] Verbenene, b.p. 162° (769 mm.), $n^{20}D$ 1.4991, d^{20}_4 0.8799, $[\alpha]D$ −35.8°, obtained in this manner showed an absorption maximum (ϵ 12,620) at 245.5 mμ in methanol. The infrared absorption spectrum showed bands at 6.12 and 11.45 μ assignable to the terminal double bond. This is in accord with structure VI suggested by Ruzicka and Trebler[21] for verbenene.

Redistillation of lower boiling fractions from run 2 gave *d*-verbenene; $n^{20}D$ 1.4997, d^{20}_4 0.8818, $[\alpha]^{25}D$ +94.2° identified by comparison of its spectra with the spectra described above.

α-**Pinene Epoxide.**—Material boiling at 82° (20 mm.), $n^{20}D$ 1.4692, d^{20}_4 0.9660, $[\alpha]D$ +54.92° (run 1), $n^{20}D$ 1.4694, d^{20}_4 0.9629, $[\alpha]^{28}D$ −106.1° (run 2), was identified as α-pinene epoxide by comparison of its infrared absorption spectrum with the spectrum of an authentic specimen. The epoxide used for comparison, $n^{20}D$ 1.4697, d^{20}_4 0.9632, $[\alpha]D$ +54.0°, was prepared by the action of perbenzoic acid on a sample of the α-pinene employed for the autoxidation study.[22] The spectra of the known and unknown epoxide were essentially identical with the exception of a small band at 5.77 μ in the known spectrum. This band is presumably due to partial isomerization of the epoxide during preparation since deliberate acid isomerization gives a product having a strong band at the same wave length.

α-Pinene epoxide (20 g.) recovered from the autoxidation (run 1) was stirred for 15 minutes with 60 ml. of 0.1 *N* H_2SO_4. The mixture warmed spontaneously to 60° and formed crystals of sobrerol (pinol hydrate) immediately. Hexane (50 ml.) was added to the cooled mixture to facilitate separation of sobrerol from pinol by filtration. The recovered sobrerol (10.0 g.) melted at 131–132° after one recrystallization from acetonitrile and from water. Steam distillation of a mixture of 2.0 g. of the purified sobrerol and 20 ml. of 0.5 *N* H_2SO_4 gave pinol, which was recovered from the distillate by extraction with pentane. The extract was dried over sodium sulfate, filtered and distilled to remove the pentane. The physical properties of the recovered pinol (1.4 g.) were $n^{20}D$ 1.4720, d^{20}_4 0.9554, as compared to literature values of d^{20} 0.942, $n^{20}D$ 1.4714.

The α-pinene epoxide failed to absorb hydrogen in ethyl acetate in the presence of platinum oxide catalyst. Some hydrogen was absorbed in acetic acid solution, but the epoxide undergoes an exothermic reaction with acetic acid, presumably isomerizing to pinol.

The α-pinene epoxide (3.04 g.) was refluxed in 25 ml. of tetrahydrofuran with four times the theoretical amount of $LiAlH_4$ (0.76 g.) for 3.33 hours. Water was added and the slurry was steam distilled until the distillate became clear. By extraction of the distillate with pentane, 2.55 g. (84%) of unchanged α-pinene epoxide was recovered.

Myrtenal.—Fractions boiling at 80° (from *l*-α-pinene) gave a semicarbazone melting at 215–216° which on hydrolysis gave *l*-myrtenal; $n^{20}D$ 1.5010, d^{20}_4 1.036, $[\alpha]D$ −23.2° (3% in ethanol). The identity was confirmed by comparison of its infrared spectrum with the spectrum of an authentic specimen.

It should be noted that myrtenal autoxidizes very readily

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[17] E. H. Farmer, *Trans. Inst. Rubber Ind.*, **21**, 122 (1945); C. E. Swift and F. G. Dollear, *J. Am. Oil Chem. Soc.*, **25**, 52 (1948).

[18] M. G. Austerweil, *Bull. soc. chim. France*, **39**, 1643 (1926).

[19] G. S. Fisher, J. S. Stinson, R. N. Moore and L. A. Goldblatt, *Ind. Eng. Chem.*, **47**, 1368 (1955).

[20] D. H. Wheeler, *Oil and Soap*, **9**, 89 (1932).

[21] L. Ruzicka and H. Trebler, *Helv. Chim. Acta*, **7**, 489 (1924).

[22] N. Prileschajew, *Ber.*, **42**, 4814 (1909).

at room temperature forming a yellow resin within a few days when exposed to air.

trans-**Pinocarveol.**—Fractions boiling at 103–105° (20 mm.) formed a *p*-nitrobenzoate which after repeated crystallization from hexane melted at 96.5–97° and showed no optical activity in alcohol. From the mother liquors an optically active ester, m.p. 90–91.5°, $[\alpha]_{\rm D}$ −45.5° (2% in alcohol) was obtained. Saponification of the inactive ester gave *dl-trans*-pinocarveol; m.p. 14°, $n^{20}_{\rm D}$ 1.5042, d^{20}_{4} 0.9887. From the oxidized *l*-α-pinene (run 2) distillate the *p*-nitrobenzoate melted at 90.5–91.5°, $[\alpha]_{\rm D}$ +39.3° (5% in benzene) and gave on saponification *d-trans*-pinocarveol; $n^{20}_{\rm D}$ 1.4977, d^{20}_{4} 0.979, $[\alpha]_{\rm D}$ +70.8° (3% in ethanol). The terminal double bond gives a relatively strong band at 6.06 μ and a very strong band at 11.18 μ in the infrared absorption spectrum. A small band at 5.80 μ may indicate partial isomerization to pinocamphone.

trans-**Verbenol.**—The fractions which boiled at 108–109° (20 mm.) formed a *p*-nitrobenzoate which after repeated crystallization from hexane melted at 99–100° and was optically inactive. The optically active ester, m.p. 81.5–82°, $[\alpha]_{\rm D}$ +171° (2% in alcohol) was obtained from the mother liquors. Saponification of the racemic ester gave *dl-trans*-verbenol; m.p. 13–14°, $n^{20}_{\rm D}$ 1.4914, d^{20}_{4} 0.9650. Quick freezing of the *dl*-alcohol at −20° gave a crystalline form which melted at 1–2°, recrystallized on further warming and remelted at 13–14°. The alcohol derived from *l*-α-pinene gave a *p*-nitrobenzoate which melted at 79–82°. Repeated crystallization from hexane gave higher and broader melting ranges indicative of enrichment of the *dl*-form. Saponification of the ester gave *l-dl-trans*-verbenol; $n^{20}_{\rm D}$ 1.4923, d^{20}_{4} 0.969, $[\alpha]_{\rm D}$ −87.0° (5% in ethanol). The infrared spectrum was identical to the spectrum of the racemic form. The infrared spectrum shows bands at 6.00 and 12.15 μ assignable to the substituted cyclic double bond and a pair of very strong carbon–oxygen bands at 9.75 and 10.00 μ.

Verbenone.—Fractions boiling at 110–111° (20 mm.) formed a semicarbazone which melted at 207–208° after repeated crystallization from ethyl acetate. The ketone purified by way of the semicarbazone, $n^{20}_{\rm D}$ 1.4944, d^{20}_{4} 0.9749, $[\alpha]_{\rm D}$ +121.9°, showed an absorption maximum ε 6,450 at 253.0 mμ in methanol. The infrared spectrum showed the conjugated carbonyl band at 5.95 μ and conjugated double bond bands at 6.15 and 11.60 μ.

The semicarbazone derived from oxidized *l*-α-pinene melted at 208–209° and gave on hydrolysis *l*-verbenone $n^{20}_{\rm D}$ 1.4961, d^{20}_{4} 0.9731, $[\alpha]^{25}_{\rm D}$ −253.5°.

trans-**Carveol.**—The highest boiling fractions obtained from the oxidation of *l*-α-pinene gave a *p*-nitrobenzoate, m.p. 72–91°, which could not be optically purified by recrystallization from hexane. Saponification of the ester gave *l-dl-trans*-carveol; $n^{20}_{\rm D}$ 1.4944, d^{20}_{4} 0.946, $[\alpha]_{\rm D}$ −88.6° (5% in ethanol). The infrared spectrum was identical to the spectrum of *trans*-carveol.

Acknowledgment.—The authors gratefully acknowledge the helpful comments and suggestions of Dr. L. A. Goldblatt during the early phases of this work and the assistance of Mrs. Mary N. Woodroof in determining the infrared spectra. The authors are especially indebted to Dr. J. P. Bain of the Glidden Company, Jacksonville, Florida, for the authentic specimen of myrtenal and carveol used in this work.

OLUSTEE, FLORIDA

[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Study in the Terpene Series. XXVI.[1] Disproportionation of *d*-Limonene in the Presence of Palladium Hydroxide–Barium Sulfate Catalyst

BY H. E. ESCHINAZI[2] AND HERMAN PINES[3]

RECEIVED SEPTEMBER 16, 1955

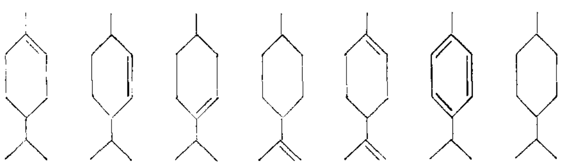
It was previously reported that limonene under reflux in the presence of palladium hydroxide–barium sulfate catalyst underwent hydrogen disproportionation to form *p*-cymene and 8(9)-*p*-menthene. It has now been found that *p*-cymene and a mixture composed of 33% *l*-*p*-menthene, 59% 3-*p*-menthene and only 8% of *trans*-8(9)-*p*-menthene are obtained.

It was reported[4] that the disproportionation of *d*-limonene (V) at its reflux temperature and in the presence of palladium hydroxide–barium sulfate catalyst proceeded by a two-step process involving a hydrogen transfer reaction. In step A *d*-limonene was rapidly converted into an equimolar mixture of *p*-cymene (VI) and *p*-menthene. From the boiling point, refractive index and from the disappearance of optical rotation it was concluded that the cycloölefin produced consisted only of 8(9)-*p*-menthene (IV). In step B the *p*-menthene was disproportionate to *p*-cymene and *p*-menthane (VII).

$$\text{(A)}\quad 2C_{10}H_{16} \longrightarrow C_{10}H_{14} + C_{10}H_{18}$$

$$\text{(B)}\quad 3C_{10}H_{18} \longrightarrow C_{10}H_{14} + 2C_{10}H_{20}$$

In an attempt to prepare compound IV by the above method it has now been found that when the reaction was interrupted at step A, the *p*-menthenes present actually consisted of an isomeric mixture composed of 33% of 1-*p*-menthene (I), 59% of 3-*p*-menthene (III) and only 8% of *trans*-8(9)-*p*-menthene (IV).


I II III IV V VI VII

The 1-*p*-menthene was optically inactive even when isolated from reactions interrupted before the completion of step A. It was observed that contrary to previous reports[4] the reaction involving step B had begun while 10% of *d*-limonene remained unreacted *via* step A. Evidence for this was furnished by the presence of small amounts of *p*-menthane in the reaction product.

The composition of the products obtained from the reaction was determined by a fractional distillation to separate isomers III and IV, b.p. 165–166°, from the mixture of I and VI, b.p. 175–176°.

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[1] For paper XXV of this series see H. E. Eschinazi and H. Pines, *J. Org. Chem.*, **20**, 1667 (1955).

[2] Vladimir Ipatieff Postdoctoral Fellow, 1953–1955.

[3] To whom requests for reprints should be addressed.

[4] H. E. Eschinazi and E. D. Bergmann, THIS JOURNAL, **72**, 5651 (1950).