ide consumption; another run with the same proportions showed 117% of the expected consumption; a third produced 20% of bromide ion.

Summary

Dimethyl ether has been isolated in 74% yield from the reaction of methyl benzoate with methanolic sodium methoxide at 100°. The reaction appears to involve nucleophilic substitution on the methyl carbon atom.

PORTLAND, OREGON RECEIVED AUGUST 29, 1949

[A CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY AND THE NEW YORK QUININE AND CHEMICAL WORKS, INC.]

The Action of *t*-Butyl Hypochlorite on α-Pinene[1,2]

BY JOHN J. RITTER AND DAVID GINSBURG

Although *t*-butyl hypochlorite has been used successfully as a chlorinating agent, its mode of action is not entirely clear. In some cases it appears to substitute a chlorine atom for a hydrogen atom, while in others it adds to an olefinic double bond with subsequent loss of *t*-butanol.[3,4,5,6]

It seemed of interest to investigate the chlorination of α-pinene (I) with *t*-butyl hypochlorite in order to discover whether the products would correspond to addition at the double bond or to direct replacement of hydrogen on C-2 or on the methyl group attached to C-4 (see numbering on structure I of the flow sheet). The formation of verbenone, verbenols, myrtenal and myrtenol on autoxidation of α-pinene[7] suggests the likelihood of a substituting attack.

Chlorination of α-pinene with undistilled t-butyl hypochlorite leads to carvyl chloride (IV) and 2,6-dichlorocamphane (V). Substantial amounts of other chlorides are formed also; one of them is characterized by its hydrolysis to an alcohol, believed to be perillyl alcohol (VIIb).[8]

Carvyl chloride (IV) was identified by hydrolysis to carveol (VIII) and oxidation of the latter to carvone (IX). The physical constants of these compounds (excepting optical activity) are in very good agreement with the recorded values.[9,10] Finally, the carvone obtained was isomerized to carvacrol (X) by heating with 40% sulfuric acid, in a modification of the procedure of Rupe and Schlochoff.[11]

It was noted previously[12] that the chlorination of α-pinene with undistilled *t*-butyl hypochlorite (containing free chlorine) yielded some **2,6-dichlorocamphane** (V) which, however, failed to appear when the hypochlorite was distilled before use. Its formation may be traced to (a) rearrangement of pinene dichloride, formed by chlorine addition to α-pinene[13]; (b) chlorination of bornyl chloride which in turn might arise through addition of hydrogen chloride to α-pinene,[13] the hydrogen chloride resulting from some substitution by chlorine; (c) by addition of hydrogen chloride to pinocarvyl chloride (III) followed by Wagner–Meerwein rearrangement. The last assumption, (c), appears most likely as (a) and (b) are known to give poor yields of 2,6-dichlorocamphane,[13,14] which is formed in the present case in not inconsiderable amounts.[15]

In addition to carvyl chloride (IV), another monochloride was obtained, from which by alkaline hydrolysis and subsequent reactions of the classical type, an alcohol, an aldehyde and an acid could be obtained. The physical constants of the alcohol and the aldehyde (again excepting optical activity) are in good agreement with those reported in the literature for the corresponding *perillyl* compounds derived from natural sources.[16] In addition, the 2,4-dinitrophenylhydrazone of the aldehyde shows its principal absorption maximum at $\lambda_{max} = 3825$Å. ($\epsilon_{max} = 21{,}800$), which establishes the presence of an α,β-unsaturated carbonyl group, but immediately rules out the possibility of a diene system conjugated with the aldehyde group. The following three possibilities of an α,β-unsaturated aldehyde remain: perillaldehyde (VIIc), $\Delta^{1:8(9)}$-*p*-menthadiene-10-al (XIII) and $\Delta^{1:4(8)}$-*p*-menthadiene-10-al (XIV).

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[1] This paper is based upon a portion of the dissertation presented by David Ginsburg in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Science of New York University, June, 1947. Present address: Daniel Sieff Research Institute, Weizmann Institute of Science, Rehovot, Israel.

[2] Presented at the meeting of the New York section of the American Chemical Society, April 25, 1947.

[3] Clark, *Chem. News*, **143**, 265 (1931).

[4] Jackson and Pasiut, THIS JOURNAL, **49**, 2071 (1927).

[5] Irwin and Hennion, *ibid.*, **63**, 858 (1941).

[6] Emling, Vogt and Hennion, *ibid.*, **63**, 1624 (1941).

[7] Blumann and Zeitschel, *Ber.*, **46**, 1178 (1913).

[8] Work published by several authors indicates that the action of N-bromosuccinimide on α-pinene, similarly leads to a complex mixture of brominated products. *Cf.* Ziegler, *et al.*, *Ann.*, **551**, 80 (1942); Buu-Hoi, *et al.*, *Bull. soc. chim. France*, 148 (1946); Roberts and Trumbull, THIS JOURNAL, **71**, 1630 (1949); du Pont, *et al.*, *Bull. soc. chim. France*, 310 (1949).

[9] Blumann and Zeitschel, *Ber.*, **47**, 2623 (1914).

[10] Simonsen, "The Terpenes," Vol. I, Second Edition, Cambridge University Press, 1947, p. 396.

[11] Rupe and Schlochoff, *Ber.*, **38**, 1719 (1905).

[12] Benson, M.S. Thesis, New York University, 1938.

[13] Aschan, *Ber.*, **61**, 38 (1928).

[14] Meerwein and Wortmann, *Ann.*, **435**, 190 (1923).

[15] It may be recalled that no decision is yet possible on the question whether dichlorocamphane is the 2,6- or the 2,10-compound: *cf.* ref. 14; Lipp, *J. prakt. Chem.*, **105**, 50 (1922); Lipp and Lausberg, *Ann.*, **436**, 274 (1924).

[16] Semmler and Zaar, *Ber.*, **44**, 52, 815 (1911).

Braude and Jones[17] have shown that alkyl substitution at the C–C double bond of the 2,4-dinitrophenylhydrazones of α,β-unsaturated aldehydes influences the position of the absorption maximum sufficiently to make the spectrum a criterion of the fine structure of the compound under investigation. From a study of the data which the British authors present,[17] of the three possible structures, that of *perillaldehyde* (VIIc) appears most likely.[17a]

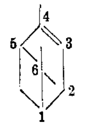
However, the melting points of the oxime and of the semicarbazone of the aldehyde (96° and 208–209°, respectively) differed slightly from those reported for the corresponding derivatives of natural perillaldehyde (102° and 199–200°, respectively).[16] The discrepancy in the melting points was more serious in the case of the acid obtained from the above aldehyde through the oxime and the nitrile. This acid melted at 60° whereas the recorded melting point of optically active perillic acid (VIId) is 132–133°.[16] The melting point observed is near that reported for myrtenic acid (XI), 54°,[16] which however has only one double bond and not two as the acid which melts at 60°.

It is suggested that these discrepancies in melting points are due to the configurational difference between the above aldehyde and natural perillaldehyde.[18,19]

The formation of representatives of the perilla series from α-pinene and *t*-butyl hypochlorite can be explained by the following assumptions: In analogy with the fact that autoxidation of α-pinene produces myrtenal, substitutive chlorination can lead to myrtenyl chloride (VI), which can yield perillyl chloride (VIIa) by ring rupture, *e. g.*, in the course of the fractionation. However, the evident non-formation of verbenyl chloride (XII), which would be expected as the *principal* product of direct substitution, in conjunction with the fact that carvyl chloride (IV) is formed in considerable amounts, leads to the alternative hypothesis that, primarily, *t*-butyl hypochlorite *adds* to α-pinene to form the unstable adduct II. By simple loss of *t*-butanol, this may yield pinocarvyl chloride (III) which can rearrange to myrtenyl chloride (VI).[20,21]

The work of Young and Andrews[22] indicates the further possibility that pinocarvyl chloride (III) is converted to perillyl alcohol (VIIb) during the alkaline hydrolysis (III → VIIb).[22a]

Alkaline hydrolysis of the impure monochloride fractions which showed unsaturation values between 1 and 2 was incomplete even after long treatment. The unhydrolyzed chloride recovered in each case showed unsaturation values closer to 1 than the original chloride fraction, while the alcohol isolated had two double bonds. The bicyclic chlorides seem to be more difficult to hydrolyze, perhaps for stereochemical reasons.



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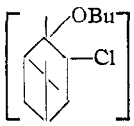

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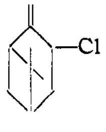

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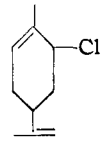

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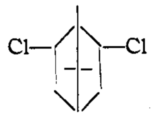

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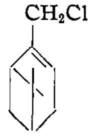

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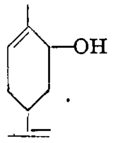
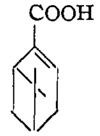
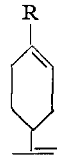


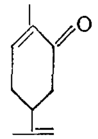
VIII



XI



VIIa R = CH_2Cl
b R = CH_2OH
c R = CHO
d R = COOH



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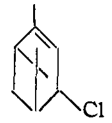

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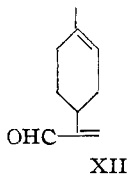

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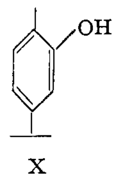
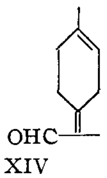


X



XIV

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[17] Braude and Jones, *J. Chem. Soc.*, 498 (1945).

[17a] As Braude and Jones (ref. 17) do not give data for the 2,4-dinitrophenylhydrazone of an α,β-unsaturated aldehyde with one alkyl substituent in the α position, we prepared that derivative of methacrolein, m. p. 207°. Shriner and Sharp (THIS JOURNAL, **62**, 2245 (1940)), report 206–206.5° as the m. p. of this compound. The λ_{max} = 3700 A. (ϵ_{max} = 20,000, alcohol) agrees, in the magnitude of the bathochromic shift caused by this alkyl group, with the other data presented by the British authors.

[18] Such differences are not uncommon. For example, the semicarbazone and oxime of optically active carvomenthone melt at 194–195° and 97–99°, respectively, whereas the corresponding derivatives of the *dl* form melt at 174° and 105° (Ref. 10, p. 328). The semicarbazone and oxime of optically active isopulegone melt at 175–176° and 120–121°, respectively, whereas the corresponding derivatives of the *dl* form melt at 183° and 138–139° (*ibid.*, pp. 388–389). The large difference in melting points between optically active tartaric acid (170°) and the *dl* form (206°) is also well known.

[19] Resolution of the acid obtained in this investigation was not attempted, since there could not be any certainty that its optically active forms would be of the same degree of optical purity as the perillic acid reported in the literature.[16]

[20] Myrtenyl chloride could lead to dichlorocamphane as well as pinocarvyl chloride (see mechanism (c) above).

[21] Young, Winstein and Lane noted that the purification of crotyl bromide and methylvinylcarbinyl bromide by distillation did not succeed because allylic rearrangement during distillation led to a mixture of the two compounds. *Cf.* Young and Winstein, THIS JOURNAL, **57**, 2013 (1935); Winstein and Young, *ibid.*, **58**, 104 (1936); Young and Lane, *ibid.*, **59**, 2051 (1937); Young and Lane, *ibid.*, **60**, 847 (1938).

[22] Young and Andrews, *ibid.*, **66**, 421 (1944).

[22a] We are indebted to one of the Referees for calling this and several other points to our attention.

Experimental[23]

Chloropinenes.—α-Pinene used for this preparation was freshly distilled "Hercules 111," b. p. 156–157°; n^{20}_D 1.4662; $[\alpha]^{20}_D$ +23.7°. *t*-Butyl hypochlorite was prepared by the procedure of Chattaway and Backeberg.[24] It was not distilled before use.

α-Pinene (762 g.) was placed in a three-liter three-neck flask fitted with a mercury-sealed stirrer, addition tube and reflux condenser. The flask was immersed in an oil-bath maintained at 105–110°, and *t*-butyl hypochlorite (624 g.) added with stirring at a rate which maintained continuous reflux (seven hours), and the mixture finally refluxed an additional hour. Distillation at ordinary pressure during which the bath temperature was permitted finally to reach 135° yielded *t*-butanol (398 g.). The residue of chloropinene was fractionated through a four-foot column packed with glass helices. Three close-cut fractions were obtained: A, 294 g., b. p. 94–96° (16 mm.), 90° (12 mm.); d_{20} 1.016; n^{20}_D 1.5048; $[\alpha]^{20}_D$ −36.7°; unsaturation value (perbenzoic acid), 1.54 double bonds/mole; B, 227 g., b. p. 99–102° (16 mm.), 95–97° (12 mm.); d_{20} 1.005; n^{20}_D 1.5022; $[\alpha]^{20}_D$ −3.7°; unsaturation value, 1.75; *C*, 62 g., b. p. 137° (12 mm.); m. p. 173° (2,6-dichlorocamphane).[25] *Anal.* Calcd. for $C_{10}H_{15}Cl$ (A, B): C, 70.5; H, 8.9. Found: A, C, 71.3; H, 9.5; B, C, 70.3; H, 8.8. Calcd. for $C_{10}H_{16}Cl_2$ (C): Cl, 34.3. Found: Cl (Carius), 34.35.

Hydrolysis of Chloride Fraction A.—Fraction A (280 g.) was refluxed for 20 hours with a solution of sodium hydroxide (73 g.) in ethanol (1100 ml.) and water (730 ml.). Most of the ethanol was removed by distillation from the steam-bath and the terpene compounds steam-distilled from the residue. A small additional amount of terpene was obtained by pouring the ethanol distillate into three volumes of water. This was added to the main portion and the combined total extracted with ether, the extract dried over anhydrous sodium sulfate and the ether removed. This yielded a mixture (243 g.) of perillyl (?) alcohol and unhydrolyzed chloride. Titration of the chloride ion in the aqueous residue from steam distillation above indicated that about 40% of the chloropinene had been hydrolyzed.

Perillyl (?) Alcohol Benzoate.—The above mixture of perillyl (?) alcohol and chloropinene (215 g.) was dissolved in pyridine (430 g.), the solution cooled to 0° and benzoyl chloride (215 g.) added dropwise with stirring at 0–5°. The reaction mixture was then allowed to stand at room temperature overnight, and finally heated on the steam-bath for two hours. A solution of sodium carbonate monohydrate (192 g.) in water (1920 ml.) was then added and the mixture steam-distilled to remove pyridine, unhydrolyzed chloropinene and any perillyl (?) alcohol which may have escaped benzoylation. The benzoate remained in the still as a non-volatile residue. It was ether-extracted and the extract after drying and removal of solvent yielded 120 g. of crude benzoate. The steam-volatile chloride portion, after removal of pyridine with dilute hydrochloric acid and drying, showing the presence of 1.43 double bonds/mole.

Perillyl (?) Alcohol.—The crude benzoate (120 g.) was hydrolyzed by refluxing for six hours with potassium hydroxide (75 g.) dissolved in ethanol (400 ml.). Sufficient water was then added to dissolve the solid present and most of the ethanol removed on the steam-bath. The perillyl (?) alcohol was recovered by steam distillation; the steam-distillate was ether-extracted and the ether removed after drying with anhydrous sodium sulfate. The product was finally distilled *in vacuo;* b. p. 85–86° (2 mm.); yield, 60 g. (91%); d_{20} 0.966; n^{20}_D 1.4970; *MR* (calcd.), 46.8; found, 46.0; $[\alpha]^{20}_D$ +12.4°; unsaturation value, 2.03 double bonds/mole. *Anal.* Calcd. for $C_{10}H_{16}O$: C, 78.8; H, 10.5. Found: C, 77.9; H, 10.2. The reported constants for natural perillyl alcohol[16] are: d_{20} 0.964; n^{20}_D 1.4996; $[\alpha]^{20}_D$ −68.5°; b. p. 119–121° (11 mm.).

Perillaldehyde (?).—To a solution of perillyl (?) alcohol (24 g.) in glacial acetic acid (48 ml.), a solution of chromic anhydride (19.2 g.) in 75% acetic acid (38.5 ml.) was added dropwise with stirring at 0–5°. After standing overnight, the mixture was poured into water (1000 ml.). Ether extraction followed by neutralization of the extract with sodium carbonate solution, drying over anhydrous sodium sulfate and removal of the ether, yielded a mixture of perillyl (?) alcohol and aldehyde (23 g.). This was shaken mechanically for twenty-four hours with a solution of sodium sulfite (50 g.) and sodium bicarbonate (18 g.) in water (144 ml.). Undissolved perillyl (?) alcohol was then removed by ether-extraction; the remaining aqueous layer which contained dissolved aldehyde, was saturated with sodium carbonate and refluxed for two hours to regenerate the aldehyde from its sulfite addition compound. After cooling, the aldehyde was extracted with ether, the extract dried over anhydrous sodium sulfate, the ether removed and the aldehyde distilled *in vacuo:* b. p. 91° (11 mm.); yield, 9 g. (38%); d_{20} 0.959; $[\alpha]^{20}_D$ +9.2°; n^{20}_D 1.5094; *MR* (calcd.), 45.3; found, 46.8. Optical exaltation, 1.5 units; unsaturation value, 1.96 double bonds/mole. The reported constants for perillaldehyde[16] are: d_{18} 0.962; $[\alpha]^{20}_D$ −146°; n^{20}_D 1.5075; b. p. 104–105° (10 mm.).

Oxime (from ligroin), m. p. 96°. *Anal.* Calcd. for $C_{10}H_{15}ON$: N, 8.47. Found: N, 8.36. Semmler and Zaar[16] reported 102° as the melting point of natural perilla aldoxime.

Semicarbazone (from dilute ethanol or ligroin), m. p. 208–209°. *Anal.* Calcd. for $C_{11}H_{17}ON_3$: N, 20.3. Found: N, 20.8. Semmler and Zaar,[16] reported 199–200° as the melting point for the semicarbazone of natural perillaldehyde. $\lambda_{max.}$, 2695 Å. (in ethanol), $\epsilon_{max.}$ 17,700.[26]

2,4-Dinitrophenylhydrazone (from ethanol–ethyl acetate), m. p. 216–217°. *Anal.*[27] Calcd. for $C_{16}H_{18}O_4N_4$: N, 16.95. Found: N, 16.85. $\lambda\lambda_{max.}$ ($\epsilon\epsilon_{max.}$): 2530 Å. (11,600); 2900 (7,600); 3825 (21,800), in ethanol.[28]

Methacrolein 2,4-dinitrophenylhydrazone (from ethanol–ethyl acetate), m. p. 207°; $\lambda\lambda_{max.}$ ($\epsilon\epsilon_{max.}$): 2500 Å. (13,700); 3700 (20,000).

Perillic (?) Acid.—Perilla (?) aldoxime (77 mg.) and anhydrous sodium acetate (9 mg.) were dissolved in acetic anhydride (0.11 ml., *ca.* 120 mg.). The mixture was refluxed for one hour, then cooled; a solution of sodium carbonate (175 mg.) in water (1.2 ml.) was added, the resulting nitrile extracted with ether and the ether evaporated. The nitrile was hydrolyzed by refluxing with potassium hydroxide (0.3 g.) in ethanol (1 ml.) for four hours. The ethanol solution was poured into water (5 ml.), decolorized with charcoal, filtered, acidified (congo red) with dilute hydrochloric acid and allowed to stand 24 hours in the refrigerator. Perillic (?) acid (12 mg.) crystallized in long colorless needles, micro m. p. 60°. The reported melting point,[16] 132–133°, is that for perillic acid obtained from natural perillaldehyde, $[\alpha]^{20}_D$ −146°. *Anal.* (Ag salt). Calcd. for $C_{10}H_{13}O_2Ag$: Ag, 39.9. Found: Ag, 40.0.

Hydrolysis of Chloride Fraction B.—Fraction B (180 g.) was refluxed for twenty hours with a solution of sodium hydroxide (47 g.) in ethanol (700 ml.) and water (470 ml.). The mixture was treated in the same manner as the previous chloropinene (fraction A, see above), to yield 150 g. of material consisting of carveol and unhydrolyzed chloropinene. Titration of chloride ion in the aqueous residue

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[23] All melting points and boiling points are uncorrected. The micro-analyses were performed in the Microchemical Laboratory of Washington Square College, New York University.

[24] Chattaway and Backeberg, *J. Chem. Soc.*, **123**, 2999 (1923).

[25] Aschan (ref. 13) reports 173–174° as the melting point of this compound.

[26] We are indebted to Miss Natalie Heyman of New York University for measuring the ultraviolet absorption spectrum of perillaldehyde (?) semicarbazone.

[27] Analysis performed in the microchemical laboratory of the Weizmann Institute of Science, Rehovot, Israel.

[28] We are indebted to Mr. S. Pinchas of the Weizmann Institute of Science for measuring the ultraviolet absorption spectra of the 2,4-dinitrophenylhydrazones of perillaldehyde (?) and methacrolein.

of the steam-distillation indicated that 43% of the chloropinene was hydrolyzed.

Carveol Benzoate.—The above hydrolysis-mixture of chloropinene and carveol (127 g.) was dissolved in pyridine (350 g.), the solution cooled to 0° and benzoyl chloride (127 g.) added dropwise with stirring at 0–5°. The mixture was treated as in the isolation of perillyl (?) alcohol benzoate (see above). Perbenzoic titration of the recovered chloropinene showed the presence of 1.57 double bonds/mole. The crude benzoate weighed 65 g.

Carveol.—Sixty-five grams of crude carveol benzoate was hydrolyzed by heating under reflux for six hours with potassium hydroxide (40 g.) in ethanol (225 ml.). Carveol was isolated from the hydrolysis mixture exactly as in the case of perillyl (?) alcohol (see above). The carveol was distilled *in vacuo:* b. p. 91–94° (2 mm.); yield, 32 g. (90%); d_{20} 0.968; $[\alpha]^{20}\mathrm{D}$ +6.2°; $n^{20}\mathrm{D}$ 1.4997; *MR* (calcd.), 46.8; found, 46.2; unsaturation value, 1.97 double bonds/mole. The values previously reported.[9,29] are: b. p. 108–10° (11 mm.); d_{15} 0.958; $[\alpha]^{20}\mathrm{D}$ 0°; $n^{20}\mathrm{D}$ 1.4961.

Carvone.—Carveol (24 g.) was dissolved in glacial acetic acid (48 ml.) and a solution of chromic anhydride (19.2 g.) in 75% acetic acid (38.5 ml.) was added dropwise with stirring at 5–10°. Carvone was isolated as was perillaldehyde (?) (see above), b. p. 96–99° (12 mm.); yield 12 g. (50%); d_{20} 0.957; $[\alpha]^{20}\mathrm{D}$ +1.3°; $n^{20}\mathrm{D}$ 1.5021; *MR* (calcd.), 45.3; found, 46.4; optical exaltation, 1.1 units; unsaturation value, 2.04 double bonds/mole. The values previously reported[9,10] are: d_{15} 0.965; $[\alpha]^{20}\mathrm{D}$ +62.3°; $n^{20}\mathrm{D}$ 1.5003.

Hydroxylamino-oxime (from dilute ethanol or ligroin), m. p. 157°. *Anal.* Calcd. for $C_{10}H_{17}O_2N_2$: N, 14.2. Found: N, 14.1. This compound is reported in the literature[30,31,32] as an oil which crystallizes after many months but having an indefinite melting point.

Semicarbazone (from dilute ethanol or ligroin), m. p. 155° in agreement with the reported melting point.[10] *Anal.* Calcd. for $C_{11}H_{17}ON_3$: N, 20.3. Found: N, 20.9.

Limonene: Wolff–Kishner Reduction of Carvone.—Carvone semicarbazone (1.2 g.) and sodium ethoxide (prepared from 1.2 g. sodium) in 95% ethanol (15 ml.) were heated in a sealed tube for eighteen hours at 180–190°. The contents of the tube were poured into water (200 ml.). The mixture was extracted with three small portions of ether, the extracts combined and dried over anhydrous sodium sulfate. After removal of the ether, a residue boiling at 176° and corresponding to limonene or dipentene was obtained. Perbenzoic titration of this fraction showed the presence of 1.92 double bonds/mole. There was also a fraction boiling at 231° which may have been carvone hydrazone.

Carvacrol.—Carvone (1 g.) and 40% sulfuric acid (10 ml.) were heated under reflux for three hours. The mixture was then steam distilled. The steam-distillate was extracted with three small portions of ether, the extracts combined and dried over anhydrous sodium sulfate. After removal of the ether, a residue of carvacrol (0.61 g.) was obtained. Its aryloxyacetic acid derivative was prepared and melted at 150–151° after recrystallization from dilute ethanol.

Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.2; H, 7.69. Found: C, 69.2; H, 7.54.

The aryloxyacetic acid derivatives of authentic samples of carvacrol and thymol were prepared by the procedure of Koelsch,[33] m. p. thymyloxyacetic acid, 149°; m. p. carvacryloxyacetic acid, 150°; mixed m. p. 1:1 mixture of above two authentic samples 123–125°; mixed m. p. of phenol derivative from carvone with authentic thymyloxyacetic acid 125°; mixed m. p. of phenol derivative from carvone with authentic carvacryloxyacetic acid 150–151°.

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Summary

The formation of carvyl chloride (in addition to 2,6-dichlorocamphane) and the non-formation of verbenyl chloride by the action of undistilled *t*-butyl hypochlorite on α-pinene, suggests that addition takes place at the double bond of α-pinene. Elimination of *t*-butanol leads to carvyl chloride.

Another monochloride formed was converted by alkaline hydrolysis and subsequent treatment into three substances believed to be perillyl alcohol, perillaldehyde and perillic adid, respectively. Their formation can be explained by the assumption that an alternative route of the elimination of *t*-butanol gives pinocarvyl chloride, which can yield either myrtenyl chloride by allylic rearrangement, and further, perillyl chloride by ring fission, or directly perillyl alcohol by an analogous mechanism during alkaline hydrolysis.

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(29) Ref. 10, p. 297.

(30) Harries, *Ber.*, **31**, 1810 (1898).

(31) Harries and Kaiser, *ibid.*, **32**, 1319 (1899).

(32) Wallach, *Ann.*, **279**, 368 (1894).

(33) Koelsch, THIS JOURNAL, **53**, 304 (1931).