LXXXV.—*Researches on the Terpenes. VIII. On Carvenol: its Reactions and Products.*

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IN a paper published in the Transactions, 1897, p. 290, one of us, in conjunction with Mr. J. A. Gardner, described the production of an isomeride of camphor produced by the action of strong sulphuric acid on chlorocamphene. Subsequently, in a note in the Proceedings, we showed that the same substance was produced by the action of strong sulphuric acid on the isomeric chlorocamphene hydrochloride or so-called camphor chloride, obtained by the action of phosphorus pentachloride on camphor. The properties of this isomeride of camphor led us to regard it as a tertiary alcohol, and inasmuch as it was obtained

from chlorocamphene by displacing the chlorine by hydroxyl, we called it hydroxycamphene or camphenol, regarding it as a substitution derivative of camphene. In the present paper, we describe further experiments with this substance and the products obtained from it, and as we shall show that it is not a true substitution derivative of camphene, we must abandon the names hydroxycamphene and "camphenol." Moreover, we find we have no right to the name camphenol, as it has already been applied by Bouchardat and Lafont to certain isomerides of borneol which they have discovered. We propose, therefore, to call the substance carvenol, on account of the close relationship we find it to bear to carvacrol.

Preparation and Purification of Carvenol.—In order to prepare pure carvenol, we find it best to employ chlorocamphene obtained from α -camphene dichloride by the process which has already been described (*loc. cit.*). As, however, the separation of the isomeric dichlorides is somewhat tedious, we employ, in preparing large quantities of the substance, the crude product of the action of phosphorus pentachloride on camphor. This is converted into chlorocamphene first by distilling the mixed chlorides, and subsequently by boiling the distilled product with aniline; the chlorocamphene is then dissolved in sulphuric acid containing 5 per cent. of water in the manner already described in the former paper, the action taking place in the cold, but being much accelerated by heating on the water bath. On pouring the clear solution into a large excess of water, the carvenol separates as a light yellowish liquid; by distilling this with steam, it is separated from a small quantity of tarry matter. The crude carvenol so obtained contains traces of chlorine, due to the presence in it, as will be shown later, of a small quantity of chlorocymene. To free it from this, it is again dissolved in sulphuric acid, and the solution shaken with light petroleum to remove the chlorocymene, which is insoluble in sulphuric acid. On now pouring the sulphuric acid solution into water, the substance is obtained free from chlorine, and is further purified by distillation under diminished pressure. Carvenol prepared from the crude product of the action of pentachloride of phosphorus on camphor is apt to contain some of the latter, which has escaped the action of the phosphorus pentachloride. This camphor comes over in the first fractions in the distillation of carvenol. We have found, however, that camphor is readily soluble in about its own weight of fuming hydrochloric acid of sp. gr. 1.2, whilst the camphene dichlorides are insoluble in it; this affords a ready method of removing the camphor from the crude camphene dichlorides.

The properties of carvenol have been described in the above-mentioned paper by Marsh and Gardner, and it was shown to be an isomeride of camphor. The specific gravity of a pure specimen free

from chlorine, and distilling at 104° under 10 mm. pressure, has been determined, and the density found to be d 0.9372 at $19.5^{\circ}/4^{\circ}$. We have made further experiments with a view of ascertaining the nature of this substance.

Action of Phosphorus Pentachloride on Carvenol.—From the mode of formation of carvenol, it appeared probable that the chlorine of chlorocamphene was replaced by hydroxyl, $C_{10}H_{15}Cl + H_2O = C_{10}H_{15}OH + HCl$, so that we at first considered the substance to be a hydroxyl derivative of camphene; if this were so, we should expect that by the action of phosphorus pentachloride on carvenol we should get back the original chlorocamphene. This, however, is not the case. Pentachloride of phosphorus readily acts on carvenol, but it gives, not chlorocamphene, but chlorocymene, $C_{10}H_{13}Cl$ [$CH_3:Cl:C_3H_7 = 1:2:4$]. To prepare this substance, the carvenol is mixed with rather more than the theoretical amount of phosphorus pentachloride in a mortar, when hydrogen chloride is given off and the mass becomes liquid. It is then mixed with ice, and the oily liquid left undissolved is taken up with ether; the ethereal solution is shaken with a solution of sodium carbonate to remove a small quantity of an acid that is present, probably a phosphonic acid, which gives a crystalline sodium salt. The chlorocymene, which is the chief product, is obtained on distilling the ethereal solution, and can be further purified by shaking up with strong sulphuric acid, which removes impurities such as unaltered carvenol, whilst it has little or no action on chlorocymene in the cold. Chlorocymene obtained in this way boils at 216° under atmospheric pressure, and at 103 — 105° under 19 mm.; it is a colourless liquid, and has no action on a cold solution of potassium permanganate. On analysis, it gave the following figures.

	Carbon.	Hydrogen.	Chlorine.
Found	71.5	7.9	20.9
Calculated for $C_{10}H_{13}Cl$	71.2	7.7	21.0

Oxidation of Chlorocymene.—Kekulé and Fleischer (*Ber.*, 1873, 6, 1087) obtained a chlorocymene by the action of phosphorus pentachloride on carvacrol, and found that, on oxidation, it gave a chlorotoluic acid melting at 184 — 186° , but von Gerichten (*Ber.*, 1878, 11, 366) found the melting point to be 199 — 201° . There is no doubt that our chlorocymene is identical with that of Kekulé and Fleischer, as it gives the same chlorotoluic acid on oxidation with nitric acid. (Kekulé and Fleischer do not state what oxidising agent they employed.) Claus and Davidson (*J. pr. Chem.*, [ii], 39, 497) have also obtained this acid from chlorotoluidine [$Me:Cl:NH_2 = 1:2:4$] by Sandmeyer's reaction.

We find that on heating chlorocymene with nitric acid of sp. gr. 1.3

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for about 24 hours on the water bath, it is practically entirely converted into a crystalline acid soluble in alcohol, and, when crystallised, from alcohol melting at 199°.

	Found.	Calc. $C_8H_7ClO_2$.
Chlorine	20·3 per cent.	20·8 per cent.

Chlorocymenesulphonic Acid.—Chlorocymene, if left for a few hours in contact with strong sulphuric acid, gradually forms white crystals which do not dissolve readily in the acid; the action is aided by heating on the water bath. When 5 c.c. of chlorocymene was heated with 5 c.c. of strong sulphuric acid on the water bath, the mixture became solid after a time from the formation of crystals. These crystals were dissolved in water, and the boiling solution neutralised with barium carbonate, and filtered; on cooling, the barium salt crystallised out in long needles. It was analysed for water of crystallisation and for barium.

	Water at 120°.	Barium.
Found.....	14·49 per cent.	18·4 per cent.
Calculated	14·5 ,,	18·5 ,,

This agrees with the formula, $Ba(C_{10}H_{12}ClSO_3)_2 + 6H_2O$.

On evaporating the aqueous solution, after precipitating the barium with sulphuric acid, the free sulphonic acid crystallises out; this, when dried over sulphuric acid to remove water of crystallisation, melted at 135°. Jünger and Klages (*Ber.*, 1896, 29, 315) have prepared the same acid from the chlorocymene obtained by the action of chlorine on cymene, by treating it with fuming sulphuric acid.

Chlorocymene in Crude Carvenol.—We have already called attention to the existence of a chlorine compound in crude carvenol; this occurs in relatively small quantity, but on purifying a large amount of carvenol, some 20 c.c. of a liquid insoluble in sulphuric acid was obtained. It is rich in chlorine, and as the purified carvenol is free from chlorine, we had thus separated the whole of the chlorinated substance from the carvenol. It was observed that this chlorine compound, when left in contact with strong sulphuric acid, gave colourless crystals, a circumstance which led us subsequently to investigate the action of sulphuric acid on chlorocymene, as described above. The liquid itself was found to distil at 95—101° under 10 mm. pressure, and at 210—216° under atmospheric pressure. When analysed, it gave, C=71·7; H=9·0, but, after being redistilled under 20 mm. pressure, two chief fractions were obtained boiling at 106—108° and 108—110° respectively.

On analysis of the fraction 106—108°, we found.

	Carbon.	Hydrogen.	Chlorine.
Found	72.2	9.4	18.4
Calculated for $C_{10}H_{13}Cl$	71.2	7.7	21.0

Three grams of the substance were oxidised with nitric acid of sp. gr. 1.3, and the same chlorotoluic acid melting at 200° was obtained. The liquid also, like chlorocymene, is not acted on by permanganate of potash at the ordinary temperature except on long standing. There would thus seem to be little doubt that chlorocymene is contained in the liquid, but is mixed with some impurity. It is curious that the boiling point should be so constant, as cymene, which is the most likely impurity to be present, boils at a much lower temperature.

Action of Benzoic Chloride on Carvenol.—With the intention of preparing a compound ether of carvenol, on the supposition that carvenol is an alcohol, we treated that substance with benzoic chloride; 17.7 grams of carvenol and 20 grams of benzoic chloride were heated to boiling in a flask connected with an apparatus for absorbing the hydrogen chloride given off. After 2 hours heating, 4 grams of hydrogen chloride had been collected (theoretical amount 4.25 grams), and, on cooling, crystals separated, which were found to be benzoic acid; the filtered liquid was distilled under diminished pressure, and the distillation continued until the distillate began to come over solid. The principal portion of the distillate came over below 100° under 19.5 mm. pressure, and this, when distilled under atmospheric pressure, came over between 176° and 186° ; it contained chlorine, and smelled slightly of benzoic chloride. It was therefore washed with soda solution, dried with calcium chloride, and allowed to stand over metallic sodium. Distilled under a pressure of 32 mm., it boiled at 86 — 87° , and under atmospheric pressure very constantly at 179° , and was free from chlorine.

	Carbon.	Hydrogen.
Found.....	89.6	10.8
Calculated for $C_{10}H_{14}$	89.5	10.5

There is thus no doubt that the liquid is cymene. That it is paracymene was proved by the excellent test suggested by Widman, namely, the production of parahydroxyisopropylbenzoic acid by oxidation with potassium permanganate; only 1 c.c. of the cymene was taken for oxidation, and a good yield of the above-mentioned acid was obtained of melting point 156° . Thus it appears that the action of benzoic chloride on carvenol results in the formation to a considerable extent of paracymene, thus

We are further investigating the residue left on distilling off the cymene, which contains benzoic acid in quantity, to discover whether

any ethereal benzoate is formed. But, on the other hand, this action of benzoic chloride is consistent with our view that carvenol behaves as a tertiary alcohol.

Carvenolsemicarbazone.—The semicarbazone was prepared by acting on carvenol with semicarbazide hydrochloride and potassium acetate in dilute alcoholic solution; the compound began to come down after the lapse of 3 hours, and at the end of 24 hours a copious precipitate was obtained; this crystallised from alcohol in small, colourless plates melting at 202—203°.

	Found.	Calc. $C_{11}H_{19}N_3O$.
Nitrogen.....	20·20	20·09

This action of semicarbazide points to the ketonic nature of carvenol. It thus appears to act, like phloroglucinol and other tautomeric substances of this nature, both as an alcohol and as a ketone.

Reduction of Carvenol: Carvanol.—Carvenol was reduced by metallic sodium in solution in absolute alcohol. Portions of 10 c.c. of carvenol dissolved in 50 c.c. of absolute alcohol were treated with 8 grams of sodium, the sodium being added in small portions at a time, and the contents of the flask cooled, as the action is very violent at starting; the last portions of sodium were added to the mixture heated to boiling to complete the action. On adding a few drops of water, the contents of the flask became solid, but when more water was added an oil separated; this was purified by distillation under diminished pressure. It distilled at 100—110°, and under atmospheric pressure at 210—220°, some 15° lower than carvenol. In order to ensure the reduction of all the carvenol, the product of the first reduction was again treated with sodium in alcoholic solution, the action of the sodium being much less violent than in the first treatment. On recovering the oil in the way just mentioned, it was found to distil at 109—110° under 14 mm. pressure. On analysis, it gave,

	Carbon.	Hydrogen.
Found	76·2	12·5
Calculated for $C_{10}H_{20}O$	76·9	12·8

Carvanol, as we propose to call this substance, is a colourless liquid of sp. gr. 0·9128 at 23·5° (water at 4°); it is very viscous, differing in this respect from carvenol, which is very mobile. It has a pleasant, aromatic odour and pungent, peppermint-like taste. It is a secondary alcohol, as is shown by its oxidation to a ketone, and forms an acetate having a fragrant smell resembling that of oil of vetiver.

Oxidation of Carvanol: Carvanone.—Twelve grams of carvanol were oxidised with potassium dichromate and sulphuric acid, according to the method described by Beckmann for the oxidation of menthol to

menthone; on completion of the oxidation, the mixture was distilled in steam; the oil, when collected and distilled under a pressure of 14 mm., came over at 94—100°, and at 214—219° under atmospheric pressure. On analysis, it gave,

	Carbon.	Hydrogen.
Found	77·3	11·5
Calculated for $C_{10}H_{18}O$	77·9	11·7

Carvanone, the ketone of carvanol, was obtained as a slightly yellow liquid, very mobile, and resembling carvenol in odour; its sp. gr. at 25° was found to be 0·9065 (water at 4°). When treated with hydroxylamine hydrochloride and potash, it forms a crystalline oxime which melts at 104—105°. It also forms a semicarbazone when treated with semicarbazide hydrochloride and potassium acetate in dilute alcohol; this, after crystallisation from methylic alcohol, melted at 173°. Carvanone does not decolorise potassium permanganate in the cold, and appears to be a saturated compound.

Constitution of Carvanol and Carvanone.—The conversion of carvenol into paracymene and chlorocymene [$CH_3:Cl:C_3H_7 = 1:2:4$] by comparatively simple reactions, points to the conclusion that carvenol probably has the same carbon skeleton as cymene; this is further confirmed by the reduction of carvenol to carvanol when an addition of four hydrogen atoms takes place. Further, the saturated character of the ketone, carvanone, points to the conclusion that, inasmuch as its formula is $C_{10}H_{18}O$, it cannot be an open chain compound, but must be constituted of one closed ring and not more than one. Taking into account all these considerations, we are led to the conclusion that carvanol is a hexahydrocarvacrol, and carvanone the corresponding ketone. They would then be represented by the following formulæ.

differing from their respective isomerides menthol and menthone in the position of $CH \cdot OH$ and CO groups which, in the case of menthol and menthone, are attached to the carbon atom adjacent to the isopropyl group.

Constitution of Carvenol and its Formation from Camphor.—From the comparatively simple conversion of carvenol into paracymene and chlorocymene (carvacryl chloride), and since the reduced compound

carvenol is constituted of only one closed carbon chain, there seems no doubt that carvenol is actually a dihydrocarvacrol with two double linkings. The position of one double linking, owing to the tautomeric nature of carvenol, should be adjacent to the C(OH) grouping on one side or the other. This is, perhaps, as far as we can get from the properties of carvenol itself, but in considering its production from camphor we have a further means of arriving at its constitution, for camphor, being constituted of two closed rings, would have one of them broken to form carvenol, which has only one ring, if we suppose that carvenol is formed from camphor directly. But as we have shown, carvenol is formed from camphor through chlorocamphene. Chlorocamphene is a saturated compound of the formula $C_{10}H_{15}Cl$ without double linkings, and must consequently be constituted of at least three closed rings. Therefore, to form carvenol from chlorocamphene, two closed rings must be broken. The mode in which this change may be brought about is explained by the following formulæ.

Here we should expect to find one of the double linkings in carvenol in the side chain. On the other hand, since carvenol ought to have an isopropyl group, and inasmuch as a CH_2 group at the end of a chain has a tendency to pass into CH_3 , by intramolecular change, there is no unwarranted assumption in supposing that the double-

linking migrates from the side chain into the ring, a change probably similar to that whereby carvol becomes converted into carvacrol. We should thus arrive at the two following alternative formulæ for carvenol.

Carvenol.

with the corresponding tautomeric forms in which the $\begin{array}{c} \text{C}=\text{C} \\ | \quad | \\ \text{CH}_3 \quad \text{OH} \end{array}$ group becomes $\begin{array}{c} \text{CH}-\text{CO} \\ | \\ \text{CH}_3 \end{array}$.

We cannot, however, regard it as rigidly demonstrated that carvenol must have an isopropyl group and not an isopropylene or even trimethylene group. In the latter case, the change to an isopropyl group would occur subsequently when carvenol was converted into cymene or chlorocymene under the action of benzoic chloride or phosphorus pentachloride.

Comparison of the Properties of Carvenol, &c., with Compounds already known.—Numerous compounds of the formula $\text{C}_{10}\text{H}_{16}\text{O}$ have been from time to time discovered, and to some of these carvenol bears a very close resemblance. In particular, two of these compounds, one obtained by Wallach from terpineol (*Annalen*, 1893, 277, 122), and the other, obtained by Semmler from tanacetone (*Ber.*, 1894, 27, 895), appear in their properties, and in those of the compounds derived from them, to be identical with carvenol and with each other. It seems to us a matter of considerable theoretical importance that terpineol, tanacetone, and camphor should be convertible into one and the same substance which is also isomeric with two of them. We give a table of comparison of these substances on the following page.

It will be seen from this table that carvenol closely resembles in properties both the carvenone obtained by Wallach from terpineol, and the carvotanacetone obtained by Semmler from tanacetone. We have not adopted either of these names, partly because the identity of the three substances may not be quite fully established, and partly because we wish by the termination ol to indicate the alcoholic

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Compound $C_{10}H_{18}O$.	Source.	Boiling point.	Specific gravity.	Semicarbazone.	Oxime.	
Carvenone (Wallach, <i>Ann.</i> , 277 , 122).....	{ Terpinol. }	231—233°	0.926 at 19°	m. p. 200—201°	m. p. 91—92° {	reduced to tetrahydro-carveol.
Carvotanacetone (Semmler, <i>Ber.</i> , 27 , 895).....	{ Tanacetone. }	228°	0.9373 at 17°	—	m. p. 92—93° {	reduced to tetrahydro-carvotanacetone.
Carvenol (Marsh & Gardner, <i>Trans.</i> , 1897, 290).....	{ Camphor. }	230°	0.9372 at 19½°	m. p. 202—203°	—	reduced to carvenol.
Compound $C_{10}H_{18}O$. Tetrahydrocarveol (Wallach, <i>loc cit.</i>).....	{ Carvenone. }	220°	0.90 at 23°	—	— {	thick oil oxidised to tetrahydrocarvone.
Tetrahydrocarvotanacetone (Semmler, <i>loc cit.</i>).....	{ Carvotan- acetone. }	219—220°	0.9014 at 17°	—	—	thick oil.
Carvanol (Marsh and Hartridge)	{ Carvenol. }	220°	0.9128 at 23½°	—	— {	thick oil oxidised to carvanone.
Compound $C_{10}H_{18}O$. Tetrahydrocarvone (Wallach, <i>loc cit.</i>).....	{ Tetrahydro- carvenol. }	220—221°	0.9055 at 20°	m. p. 174°	m. p. 105° {	
Carvanone (Marsh and Hartridge)	{ Carvanol. }	219°	0.9065 at 25°	m. p. 173°	m. p. 104—105° {	

character of the substance. We point out, in conclusion, that Wallach adopts for carvenone as the most probable formula (*Annalen*, 1893, 277, 129) the same formula, namely, No. 1, which we, from quite other considerations, have arrived at for carvenol.

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