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LXXVI.—Researches on the Terpenes. III. Halogen Derivatives of Fenchone and their Reactions.

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IN a former paper (Trans., 1897, 71, 1156) we described a compound of the formula $C_{10}H_{14}ClPO(OH)_2$, which we named chlorofenchenephosphonic acid, produced by acting on fenchone with phosphorus pentachloride in the cold, and subsequently treating the product with water. In this communication we give a further account of the properties of this substance, and also describe the halogen derivatives of fenchene produced at the same time.

a and β -Chlorofenchene Hydrochlorides.—Fifty grams of fenchone were mixed with 200 grams of phosphorus pentachloride in a flask closed with a calcium chloride tube, and allowed to stand at a temperature of 35—40°. A very slow action took place with gradual evolution of hydrogen chloride, and after standing for six weeks the contents of the flask were poured on to ice and left to stand until all the phosphorus chlorides were decomposed. The oil obtained in this way was shaken with a solution of sodium carbonate to extract the chlorofenchenephosphonic acid, and distilled in a current of steam. The oil which passed over was separated from the water, dried, and subjected to careful fractional distillation under a pressure of 16 mm. Two main fractions were obtained, one boiling at 105—110°, and the other at 85—90°; the latter, which solidified in the condenser, was chlorofenchene, and is described later (p. 705).

The fraction of higher boiling point was a colourless oil, which, after refractionation, boiled at 107-109° under 16 mm., but decomposed on distillation under the ordinary atmospheric pressure. An estimation of the chlorine gave the following result.

0.2639 gave 0.3615 AgCl. Cl = 33.89. $C_{10}H_{16}Cl_2$ requires 34.23 per cent.

In other experiments, the oil left after extraction with sodium carbonate solution, instead of being distilled with steam, was taken up in ether, dried, and, after evaporating off the ether, distilled under diminished pressure.

No chlorofenchene was obtained, and the bulk of the liquid passed over at $105-110^{\circ}$, and had practically the same percentage of chlorine. It was then heated to 100° with aniline for a few minutes; on cooling, some aniline hydrochloride crystallised out, and the liquid was then acidified with hydrochloric acid and distilled in steam, when a

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small amount of chlorofenchene was obtained, together with an oil which again distilled at 105—110° under 16 mm. pressure. This was again boiled with aniline, but very little action took place, and, on repeating the treatment just described, no more chlorofenchene was obtained, and the oil passed over apparently unchanged. A very small amount of a crystalline substance, not volatile in steam, was, however, found to be mixed with the aniline hydrochloride; it was separated by taking advantage of its insolubility in water and its slight solubility in alcohol. It crystallised from alcohol in yellowish needles, which melted at 120°, but the quantity was too small for complete purification. The following analyses of the partially purified substance show that it very probably possesses the constitution $C_{10}H_{16}Cl\cdot NHC_6H_5$. The presence of nitrogen was proved qualitatively.

0.1798 gave 0.484 CO₂ and 0.1341 H₂O. C = 73.41; H = 8.28.

0.2059 , 0.1029 AgCl. Cl = 12.3.

 $C_{10}H_{16}Cl\cdot NH \cdot C_{6}H_{5}$ requires C = 72.89; H = 8.35; Cl = 13.43 per cent.

The oil boiling at $105-110^{\circ}$, which had proved to be stable as regards aniline, was then heated with zinc dust and glacial acetic acid, by which means hydrogen chloride was removed, but this was effected only with difficulty.

Twenty-five grams of the oil were heated with 18 grams of zinc dust and an excess of glacial acetic acid over a free flame. After boiling during 36 hours, the product was distilled with steam, and the oil which passed over fractionated under reduced pressure. A considerable portion of the oil remained unchanged, as was shown by the boiling point and by a chlorine estimation, but some was converted into chlorofenchene. On again treating the unchanged oil in the same way, a further portion of chlorofenchene was obtained. It seems clear then, from these experiments, that the first action of the pentachloride is to replace the oxygen of the fenchone by chlorine, and that the substance, $C_{10}H_{16}Cl_2$, so produced, consists of a mixture of two isomerides, which we propose to name α - and β -chlorofenchene hydro-The two substances are too nearly equal in boiling chlorides. point to admit of their being separated by distillation, but they differ considerably in stability, the one losing hydrogen chloride even by distillation in steam, and readily by the action of aniline, whilst the other is stable towards aniline, and only loses hydrogen chloride very slowly and with difficulty when treated with zinc dust and glacial acetic acid. Both isomerides yield apparently the same chlorofenchene.

Chlorofenchene.—Chlorofenchene is a solid, crystalline substance, which cannot be purified by crystallisation owing to its great solubility, but can be readily purified by distillation under diminished pressure. It boils at $80-83^{\circ}$ under a pressure of 16 mm., and at

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 $190-192^{\circ}$ at the ordinary pressure, but in the latter case it seems to undergo some slight decomposition, as the melting point is lowered and it becomes more liquid. It is extremely soluble in alcohol, ether, benzene, light petroleum, chloroform, and carbon bisulphide; exposure to the vapour of the latter being sufficient to cause its liquefaction.

On analysis, it gave the following results.

The yield obtained from the a, or easily decomposable, chlorofenchene hydrochloride was very small, probably owing to its having been converted into chlorofenchenephosphonic acid. It could not, therefore, be obtained in quite the same state of purity as that prepared from the β -hydrochloride by the action of zinc dust and glacial acetic acid. The two specimens, however, differ so slightly in their properties that there can be no doubt as to their identity.

From a-hydrochloride.	Pure subs. from β -hydrochloride
M. p. 76-78°.	M. p. 89– 90°.
B. p. 189—191.	B. p. 190-192.
$[a]_{\rm D} + 38.57^{\circ}$.	$\left[\alpha\right]_{\rm D} + 35.92^\circ$.

Monochlorofenchene behaves as a saturated compound, being unacted on by potassium permanganate solution in the cold, and attacked by bromine with evolution of hydrogen bromide. It is very similar in appearance to the chlorocamphene obtained from camphor by an analogous method, but differs from it considerably in boiling point, specific rotatory power, and chemical properties.

Chlorocamphene.	Chlorofenchene.
B. p. 202°.	190—192°.
$[a]_{D} - 29.3^{\circ}.$	$[\alpha]_{\mathrm{D}} + 35.92^{\circ}.$

Action of Sulphuric Acid.—We had not a sufficient quantity of chlorofenchene for a satisfactory comparison of the action of sulphuric acid on it with that on chlorocamphene, which yields camphenol (Marsh and Gardner, Trans., 1897, 71, 290). As, however, camphenol may be obtained both from chlorocamphene and from a- and β chlorocamphene hydrochlorides, we thought that it would be equally satisfactory to try the action of sulphuric acid on the β -chlorofenchene hydrochloride. Thirty grams of this substance were therefore added to 300 grams of sulphuric acid previously diluted with 5 per cent. of water, and the mixture gently warmed on the top of the water oven ; the action was brisk and much hydrogen chloride, as well as some sulphur dioxide, was given off, with frothing. The black liquid was poured into an excess of water, and distilled in steam, when about 3

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grams of oil passed over, and a tarry mass was left in the distilling flask. The oil was extracted with ether, dried and distilled, when it came over within a range of 60° , boiling from $180-240^{\circ}$. The liquid so obtained was attacked by bromine with evolution of hydrogen bromide, but did not react with phosphorus pentachloride; probably, therefore, it contained neither camphenol nor any substance analogous to it. The liquid contained some chlorine, which was removable by metallic sodium.

As we were unable to compare the action of sulphuric acid on chlorofenchene itself with that on chlorocamphene, we tried the action of phosphorus pentachloride on a small quantity of each. Three to four grams of chlorofenchene were intimately mixed with a large excess of the pentachloride by rubbing together in a mortar; the chlorofenchene liquefied on contact with the phosphorus pentachloride, and the product obtained did not set or harden on standing. After remaining in a dry atmosphere for three days, it was poured into water and allowed to stand until all the phosphorus chloride compounds had been decomposed. The oil left at the bottom of the dish was then mixed with a dilute solution of caustic soda, and distilled in steam, when an oil passed over equal in weight to more than half the chlorofenchene taken. The clear solution left in the distilling flask was acidified with hydrochloric acid and extracted with ether; the ethereal solution was evaporated to dryness, and the yellow-coloured, solid residue dissolved in boiling water, in which it was only difficultly soluble. On evaporating and cooling, crystals separated similar in appearance to chlorofenchenephosphonic acid; these were recrystallised from water, and then melted at 196°. They consisted of chlorofenchenephosphonic acid, and were decomposed by bromine water, giving an oil volatile in steam and phosphoric acid in solution. The action of phosphorus pentachloride on chlorofenchene takes place then very slowly and gives the compound $C_{10}H_{14}ClPCl_{4}$, which on decomposition with water yields the acid $C_{10}H_{14}CIPO(OH)_{2}$.

Chlorocamphene under similar circumstances behaved quite differently to chlorofenchene. It did not liquefy on mixing with the pentachloride, but remained quite solid. After standing for three days, the mixture was treated exactly as described above. The action was apparently slow, for half the chlorofenchene was recovered on distilling with steam. The liquid which remained in the distilling flask, after being filtered, was acidified and extracted with ether. No chlorofenchenephosphonic acid was obtained, but two acids which we have not yet investigated.

Action of Bromine on Chlorofenchenephosphonic Acid.—Bromine water was added to an aqueous solution of sodium chlorofenchenephosphonate until it was no longer decolorised, the turbid liquid

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obtained treated with a small quantity of sodium carbonate solution to remove the excess of free bromine, and then extracted with chloroform. After the chloroform had been evaporated off, the extract was distilled under diminished pressure, when the whole of the product passed over at $113-114^{\circ}$ under 11 mm. pressure. It was a colourless oil which decomposed on distillation at the ordinary pressure, giving off bromine.

The liquid had a specific gravity 1.38039 at 16°, and specific rotatory power $[a]_{D} = -8.42^{\circ}$.

On analysis, the following results were obtained.

0.2879 gave 0.5034 CO₂ and 0.1471 H₂O. C = 47.68; H = 5.67. 0.3613 , 0.481 AgCl + AgBr.

0.4810 AgCl + AgBr gave 0.3138 Ag. Br = 32.1; Cl = 14.3.

 $C_{10}H_{14}ClBr$ requires C = 48.09; H = 5.61; Br = 32.00; Cl = 14.27.

A determination of the quantity of sodium phosphate liberated by the action of bromine was made, and the result showed that the action was practically quantitative. This substance, which we may call chlorobromofenchene, although decomposed on heating, is very stable towards reagents, the chlorine and bromine atoms being very firmly bound in the molecule.

Neither zinc dust and acetic acid, nor aniline, nor sodium in methyl alcohol solution, are capable of removing either of the halogen atoms, and the product obtained after treatment with these various reagents possessed the same boiling point, and had the same percentage of halogens as before.

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