VII.—*Researches on the Terpenes.* IV. *Phosphorus Derivatives of Camphene.*

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PHOSPHORUS pentachloride acts on camphene in a manner different from that in which it acts on organic substances generally. In ordinary cases, chlorine is substituted for hydrogen, hydroxyl, or oxygen; but, in the case of camphene, the group PCl_4 is substituted for hydrogen. The action appears to be in some respects similar to that which Anschütz and Moore observed as occurring between phosphorus pentachloride and salicylic acid (*Amer. Chem. J.*, **10**, 296). Excess of the pentachloride was used, and in this case not only was chlorine substituted for the acid hydroxyl, but the hydrogen of the phenolic hydroxyl was also displaced by PCl_4 , the compound of the formula $\text{COCl}\cdot\text{C}_6\text{H}_4\cdot\text{OPCl}_4$ thus produced being converted by water into an acid of the formula $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{PO}_3\text{H}_2$. In like manner, the compound of the formula $\text{C}_{10}\text{H}_{15}\cdot\text{PCl}_4$ obtained from camphene is converted by water into an acid of the formula $\text{C}_{10}\text{H}_{15}\cdot\text{PO}_3\text{H}_2$.

There is, however, a considerable difference in the nature of the products obtained in the two cases. The salicylic derivative is

formed at a high temperature, and can be distilled in a vacuum, whereas the camphenephosphoric chloride is formed at the ordinary temperature, and is decomposed at 100° , and if it be distilled in a vacuum it yields a new compound of the formula $C_{10}H_{14}PCl_3$ (Trans., 1891, 59, 652). This compound has been prepared in the pure state, but hitherto we have been unable to separate the compound of the formula $C_{10}H_{15}\cdot PCl_4$ from the substances with which it is mixed. Its existence has been inferred, however, from the compounds obtained by the action of water. The compound of the formula $C_{10}H_{14}PCl_3$ is converted by water into a new acid of the formula $C_{10}H_{14}Cl\cdot P(OH)_2$.

Another action occurs when camphene is moderately heated with a large excess of phosphorus pentachloride, resulting apparently in the formation of a compound of the formula $C_{10}H_{14}PCl_5$ or $C_{10}H_{14}Cl\cdot PCl_4$. On subjecting this to the action of water, an acid of the formula $C_{10}H_{14}Cl\cdot PO(OH)_2$ is produced, which is also obtainable by the oxidation of the above-mentioned phosphinic acid, $C_{10}H_{14}Cl\cdot P(OH)_2$. The acid of the formula $C_{10}H_{15}\cdot PO(OH)_2$, which we call camphenephosphonic acid, exists in several isomeric forms, differing in rotatory power according to the nature of the isomeric camphenes from which they are obtained; and even the same camphene yields two distinct isomeric acids, differing in solubility, melting point, rotatory power, and also in chemical properties.

The chlorocamphenephosphonic acid also exists in two isomeric forms when derived from the same camphene, differing in solubility, in melting point, in rotatory power, and in the amounts of combined water. We find that the sodium salts of these acids are decomposed by bromine water, phosphoric acid being separated.

Camphenes of Various Origin.

Camphene varies much in rotatory power, this property being influenced partly by the mode of preparation and partly by the rotatory power of the turpentine used. We propose to consider in another paper the relations between the rotatory power of camphene and that of the turpentine from which it is obtained. In other respects, the properties of camphene, whatever the rotation, seem to be the same. The particular actions studied in this paper seem to take place in exactly the same manner whatever camphene is employed, and to yield products identical in every respect except in regard to rotatory power. The description of the general course of the changes applies equally well to camphenes from all sources, and it is only when we have to characterise the different products more exactly that we shall have to take into account differences in rotatory power.

Action of Phosphorus Pentachloride on Camphene.

When 5 parts of camphene is mixed with 8 parts of phosphorus pentachloride in a mortar, the two solids form a thin cream, slight heating being observed, but no appreciable evolution of hydrogen chloride. After a short time, the mixture sets to a hard solid mass; this is mixed with water, or, better, with ice in excess, and allowed to stand, when a clear, oily, colourless liquid is formed which sinks in the excess of water. After a time a further action occurs, the oil darkening in colour, and the whole becoming hot. The syrupy liquid is then fractionally extracted with a solution of carbonate of soda as long as anything is dissolved, camphene hydrochloride being finally left, and from this camphene may be obtained by heating with aniline. The soda extractions contain the sodium salts of two camphenephosphonic acids, and from the solution the acids may be precipitated partly in a crystalline and partly in a syrupy state by the addition of hydrochloric acid. The acidified extracts, as well as the original solution from which the syrup separated in the first instance, are shaken up with ether to extract the dissolved phosphonic acids.

Separation of the Phosphonic acids.—The two phosphonic acids are separated from one another by means of ether, which dissolves only one of them, leaving the other as a white, felted mass of crystals. The acid which is insoluble in ether we call α -, and the soluble acid β -camphenephosphonic acid. The latter is recovered from the ether either by evaporating the ether or by shaking up the ethereal solution with dilute caustic soda, and precipitating the acid by adding hydrochloric acid. It is obtained in a crystalline form, but is usually mixed with some syrupy matter which has not been investigated. This syrupy matter is best removed by means of benzene, in which it is readily soluble, the crystals scarcely at all. Both the acids are purified by crystallisation from dilute alcohol, being dissolved in strong alcohol, and water added to the hot solution; the α -acid crystallises most readily, the other more slowly, giving larger crystals. The two acids are further distinguished by their behaviour with chloroform; in this case, however, it is the β -acid which is insoluble, whilst the α -acid readily dissolves. Not infrequently in the first extraction of the acid by sodium carbonate in accordance with the method above described, the sodium salt of the α -acid crystallises out, and the acid itself may then be obtained directly from the purified sodium salt.

This acid crystallises from dilute alcohol in colourless, light, fluffy needles, insoluble in ether, but soluble in alcohol, benzene, and chloro-

form. The air-dried acid has the composition represented by the above formula.

Analysis:

	I.	II.	Calculated.
Carbon.....	53·61	53·51	53·33 per cent.
Hydrogen....	8·21	8·19	8·00 „

When dried at 100°, it loses 2H₂O, leaving the anhydro-acid [C₁₀H₁₅·PO(OH)]₂O.

Water lost after 12 hours (also after 24 hours) heating at 100°.

Found 7·97. Calculated 8·00 per cent.

Analysis, after heating at 100°:

	Found.		Calculated.
	I.	II.	
Carbon.....	58·11	58·31	57·96 per cent.
Hydrogen....	7·97	7·93	7·70 „
Phosphorus..	14·96	—	14·97 „

When dried in a desiccator, or in a vacuum, the acid quickly loses one molecule of water, and afterwards very slowly gives up the second molecule.

		Calculated.	
		1 mol. H ₂ O.	2 mols. H ₂ O.
Loss after 24 hours....	4·2 p.c.	—	—
„ 48 „	5·8 „	4·00	—
„ several days.	7·56 „	—	8·00

Substance dried in a vacuum 24 hours.

	Found.	Calculated for C ₁₀ H ₁₅ ·PO ₃ H ₂ .
Phosphorus	14·52	14·35 per cent.

The air-dried acid begins to melt at about 160°, but the melting point is not constant. The anhydro-acid melts at 184°.

β-Camphenephosphonic acid, C₁₀H₁₅·PO₃H₂.

This acid crystallises from dilute alcohol in large, colourless crystals, needles several centimetres in length having been obtained; it is soluble in ether, but insoluble in chloroform and benzene.

When heated at 100°, it does not appreciably lose weight (less than 2 per cent. after several days); but, after prolonged heating during several weeks, it was found to liquefy and darken in colour; after three weeks, it had lost 37 per cent., and the syrupy residue contained phosphoric acid. The acid melts at 167°, but decomposes.

Analysis :

	Found.			Calculated for $C_{10}H_{15} \cdot PO_3H_2$.
	I.	II.	III.	
Carbon	55.29	55.4	55.32	55.5 per cent.
Hydrogen	7.97	7.8	8.2	7.8 „
Phosphorus.....	14.42	—	—	14.35 „

Sodium α -Camphenephosphonate, $C_{10}H_{15} \cdot PO_3HNa + 4H_2O$.—This salt is obtained from the acid and sodium carbonate. It is produced either when one or two equivalents of carbonate of soda are used for each equivalent of acid. It is soluble in alcohol and in water, and was crystallised both from water and from dilute alcohol.

When heated at 100° , the salt loses its water of crystallisation, 2 mols. of the salt losing $9H_2O$ and leaving the salt of the anhydro-acid.

	Found.	Calculated.
Loss of water.....	25.9	26.1 per cent.
Analysis of crystallised salt :		
		$C_{10}H_{15} \cdot PO_3HNa + 4H_2O$.
Carbon.....	38.69	38.71 per cent.
Hydrogen.....	7.90	7.74 „

Analysis of dried salt :

		$(C_{10}H_{15}PO_2Na)_2O$.
Carbon.....	51.96	52.4 per cent.
Hydrogen.....	6.64	6.55 „

The salt was also analysed by conversion into sodium metaphosphate. A weighed quantity of the anhydro-salt was heated with nitric acid and ignited.

$NaPO_3$	43.8	44.4 per cent.
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Sodium β -Camphenephosphonate, $C_{10}H_{15} \cdot PO_3NaH + 5H_2O$.—This salt, like the preceding, is obtained, whether one or two equivalents of sodium carbonate be used for each equivalent of acid. It crystallises from water in colourless, unctuous plates, and is soluble, though with difficulty, in alcohol.

Analysis of crystallised salt :

	Found.	Calculated.
Carbon.....	36.43	36.58 per cent.
Hydrogen.....	8.15	7.93 „
Phosphorus.....	9.74	10.0 „

The salt was also analysed by converting it into sodium metaphosphate.

	Found.	Calculated.
$NaPO_3$	30.37	31.1 per cent.

On heating at 100° , and also in a vacuum, the salt loses nearly the whole of its water of crystallisation. But the last traces are difficult to remove at a temperature below that at which the salt itself undergoes decomposition.

Loss of water:

		Calculated for 5 mols. H_2O .
In a vacuum.....	25.9	27.4 per cent.
At 100°	26.56	

Phosphorus in dried salt:

Found 12.62. Calculated 13.0 per cent.

Ammonium α -Camphenephosphonate, $C_{10}H_{15} \cdot PO_3H \cdot NH_4$.—This salt was prepared by dissolving the acid in strong ammonia and evaporating to dryness. It is very soluble in water, and was precipitated from the aqueous solution, in the form of light, feathery crystals, by adding alcohol and ether. On analysis, it gave

	Found.	Calculated.
Nitrogen	6.4	6.0 per cent.

Crystallised from water, it gave

	Found.	Calculated.
Nitrogen	5.97	6.0 per cent.

It is difficult to tell, without further investigation, whether this salt is a derivative of the hydrated, or of the anhydro-, acid, there being such a slight difference in composition.

Ammonium β -Camphenephosphonate, $C_{10}H_{15} \cdot PO_3H \cdot NH_4$.—The acid was dissolved in ether and the salt precipitated by passing dry ammonia into the solution. On analysis, it gave

	Found.	Calculated.
NH_3	7.78	7.26 per cent.

This salt was less soluble in water than the preceding. Crystallised from water, it gave

	Found.	Calculated.
Nitrogen	6.65	6.0 per cent.

Barium α -Camphenephosphonate, $(C_{10}H_{15} \cdot PO_2)_2BaO$.—This salt was prepared by adding baryta water to the acid. It is very slightly soluble in water, and crystallises from hot water, on cooling, in voluminous, wool-like masses. It is also obtained by precipitating the ammonium salt with barium chloride. Analysis of the dried salt:

	Found.	Calculated.
Barium	24.33	24.9 per cent.

The air-dried salt contains $5H_2O$, corresponding to the formula $(C_{10}H_{15} \cdot PO_2)_2BaO + 5H_2O$.

	Found.	Calculated.
Water	14.4	14.1 per cent.

Zinc α -Camphenephosphonate, $(C_{10}H_{15}PO_2)_2ZnO$.—The zinc salt was obtained by adding zinc nitrate to the ammonium salt, when it was precipitated in a flocculent state, very slightly soluble in water. Dried in air, it is anhydrous. Analysis gave

	Found.	Calculated.
Zinc	13.75	13.63 per cent.

Rotatory Power.

It has been already stated that the phosphonic acids derived from different camphenes differ in their rotatory power in respect of polarised light, without appreciably differing in chemical properties. They thus present a difference in physical properties similar, in kind, to that presented by the camphenes, and by the turpentine from which they are derived. The two isomeric phosphonic acids are obtained from *lævorotatory* camphene, as well as from *dextrorotatory* camphene; but, whereas the acids from *dextrorotatory* camphene are inactive, those from *lævorotatory* camphene are also *lævorotatory*, though to different degrees; thus, in alcoholic solution, the α -acid has a specific rotatory power $[\alpha]_D = -119^\circ$, whilst the β -acid has a specific rotatory power of only -71° in alcoholic solution.

Experiments are in progress with the object of endeavouring to separate the inactive acids obtained from *dextrocamphene* into their possible active constituents. For this purpose, the cinchonine salts, both of the inactive and of the active α -acids, have been prepared; they are both beautifully crystalline substances. A more detailed description of these salts is reserved for future publication, should the experiments in progress with them lead to any definite result.

Action of Heat on the Sodium Salts of the Camphenephosphonic acids.

It has already been noticed that, when heated at 100° for a long time, β -camphenephosphonic acid undergoes decomposition, the crystalline acid being converted into a syrupy liquid containing phosphoric acid, a considerable loss in weight taking place. Both acids also decompose at their melting points. A more detailed study has been made of the action of heat on the sodium salts of the two acids. When sodium β -camphenephosphonate is heated, it loses its water of crystallisation, and, on raising the temperature to about 160° , undergoes an almost quantitative decomposition into camphene and sodium metaphosphate. On distilling it from an air bath at about this temperature, 90 per cent. of the theoretical amount of camphene was recovered. When heated on a watch glass in the air bath for several

hours, it melted, and left 32.9 per cent. of residue, the amount calculated for the conversion of the crystalline salt into sodium metaphosphate being 31.1. This residue gave the test for metaphosphonic acid, namely, coagulation of albumin, a white, gelatinous precipitate with silver nitrate, and a yellow precipitate with ammonium molybdate.

Sodium α -camphenephosphonate does not undergo decomposition so readily or so completely, 48.1 per cent. of residue being obtained, the amount calculated for the conversion of the dry salt into sodium metaphosphate being 44.9: this occurred on heating in an open dish. When the salt was heated in a retort, neither camphene nor any distillate but water was obtained up to the temperature 210° , but on heating at 260° , a small quantity of a semi-solid distillate resembling impure camphene was obtained, and a residue was left amounting to 75 per cent. of the dry salt. The difference in the constitution of the dry salts readily accounts for this difference in behaviour under the influence of heat. It will be seen that sodium β -camphenephosphonate, having the formula $C_{10}H_{15}\cdot PO_3HNa$, can break up according to the equation $C_{10}H_{15}\cdot PO_3HNa = C_{10}H_{16} + NaPO_3$, whereas α -camphenephosphonate of sodium, having the formula $(C_{10}H_{15}\cdot PO_2Na)_2O$, cannot break up into phosphate and camphene. It is probable that the greater decomposition of the latter salt when freely exposed to the air, so as to leave a residue containing metaphosphate, is due to the action of aqueous vapour.

Hydrolysis of the Phosphonic acids.—When subjected to the action of water in sealed tubes, the salts both of the α - and of the β -acids are decomposed, yielding in both cases camphene and sodium hydrogen phosphate, NaH_2PO_4 . Here again the two salts show a difference in behaviour; for while the β -salt is readily decomposed at 170° , the α -salt shows no apparent change below 180° , but is decomposed at a temperature considerably above 200° .

Action of Halogens on the Sodium Salts of the Phosphonic acids.

Bromine water, chlorine, and iodine attack sodium β -camphenephosphonate, setting free phosphoric acid and yielding precipitates, that produced by bromine being very dense; a precipitate is produced in this manner even in very dilute solutions. The α -salt is less readily acted on, but it, too, is decomposed by bromine and chlorine, although not by iodine. We have not yet ascertained the nature of the organic products formed in these cases. The precipitate produced by bromine is of an oily nature; in one case this oil was collected, washed with caustic soda, and dried. It decomposed on distillation. It contained over 60 per cent. of bromine, approximately corresponding to the formula $C_{10}H_{13}Br_3$ or $C_{10}H_{15}Br_3$.

Nature of the Isomerism.

From the description of the acids and their compounds given above it will be observed that the two acids may be represented as derived one from orthophosphoric acid, thus,

the other from pyrophosphoric acid, thus,

It may hence be objected that, inasmuch as the two acids are derivatives of two different phosphoric acids, they are not strictly isomeric. On the other hand, if the difference between the acids were solely due to their being related one to the other as orthophosphoric acid is to pyrophosphoric, we should expect them to be mutually convertible into one another, or at any rate one of them convertible into the other, just as pyrophosphoric acid is convertible into orthophosphoric acid. We have not found, however, that either of the acids is convertible into the other; and though the α -acid may, under certain circumstances, take the orthophosphoric type, it is still distinct from the β -acid. We have, therefore, to look for the cause of the isomerism in the different positions which the phosphonic grouping occupies in each case with respect to the camphene nucleus. For the explanation of this isomerism, however, we shall have to wait until the constitution of camphene has been definitely ascertained.

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