

XXIV.—*On some New Compounds of Phenyl.*

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Hydrated oxide of phenyl or carbohic acid was obtained in considerable quantities from commercial coal-tar creosote.

About three quarts of creosote were distilled, and all that came over between 184° C. and 202° collected; that which came over below 184° contained a large quantity of water; on a second distillation, the distillate was separated into two portions, from 184° to 196° , and from 196° to 202° , the greatest portion coming over below 197° ; on a third distillation, the distillate was collected at every four degrees, and afterwards at every two degrees.

By repeated distillations the boiling point gradually lowered, about one third of the whole being collected between 184° and 188° . In distilling the portion collected from 184° to 186° , crystals were observed at the end of the tube of the retort, and in the receiver. Some of these crystals were introduced into the bottles containing the portions collected at different boiling points, and a considerable quantity was formed in those portions collected at and below 188° , but none in those portions which were collected above 188° . By this method of introducing crystals already formed into the portions col-

lected between 186 and 188°, the number of distillations required in isolating this body from creosote was considerably abridged.

In the bottles where the crystals were formed there was a considerable quantity of liquid, not crystallized; this was poured off, redistilled, and more crystals obtained from it. These were needle-shaped and had a silky lustre, and when separated from the mother liquor, distilled at 184°, and condensed in the neck of the retort into a solid mass of hydrated oxide of phenyl, having the specific gravity of 1.0627, and by analysis gave $\text{C}_6\text{H}_6\text{O}^* = \text{C}_6\text{H}_5\text{O}$.

Chloride of Phenyl.—To prepare chloride of phenyl, said to have been obtained by Laurent and Gerhardt by the action of pentachloride of phosphorus on carbolic acid, two atoms of the pentachloride were added in small portions to five of carbolic acid. The action was at first very energetic, a considerable amount of heat was developed, and hydrochloric acid evolved; but after adding fresh portions of the pentachloride, the action ceased, and it became necessary to heat the mixture. When the whole of the pentachloride was dissolved, the mixture was distilled upwards, and when it had nearly ceased to give off hydrochloric acid, the distillate was collected. Very little came over below 200° C., but at 210° it began to distil freely, and at 240° ebullition ceased, and the temperature rose rapidly to 260°; about one-tenth of the whole came over below 240°. The mixture in the retort then began to thicken, and the colour became dark brown; at this point, the process was discontinued. The distillate thus obtained was limpid and colourless, and possessed the characteristic odour of oxychloride of phosphorus; on treating it with hot water, and afterwards with a dilute solution of potash, an oily substance collected at the bottom of the vessel, and remained unchanged after three or four washings with hot water.

On drying and distilling this substance, a small portion came over about 110°; the temperature then rose rapidly to 136°; and about two-thirds of the whole quantity came over between 140° and 146°. On submitting this to fractional distillation, the boiling point appeared to be about 138°; but the quantity was small.

To a few drops of this substance strong nitric acid was added, in order to decompose and test it for phosphorus. Very little action took place in the cold; but on heating, the nitric acid was decomposed, and nitrous fumes given off; but the substance did not blacken. On boiling this mixture with sulphuric acid, no change appeared to be produced; but on adding water, a yellow oily matter

* H = 1; O = 16; Cl = 12.

was precipitated, which solidified on cooling. The liquid portion tested with chloride of ammonium, ammonia, and sulphate of magnesia, gave no evidence of the presence of phosphoric acid. To another portion of the distillate nitric acid was added, the mixture evaporated down to a small bulk, and carbonate of soda added; the whole was evaporated to dryness and ignited; the residue dissolved in water, and tested as above for phosphoric acid; but no precipitate was obtained: molybdate of ammonia likewise gave no precipitate.

The experiment of producing chloride of phenyl by the action of pentachloride of phosphorus on carbolic acid was repeated. An excess of the pentachloride was added, and the mixture distilled upwards as before, but only a very small distillate was obtained, consisting chiefly of oxychloride of phosphorus; the residue in the retort became very thick and black.

The experiment was then repeated as in the first instance, and about the same proportion of colourless liquid obtained; this was purified as before, and after subjecting it, together with the former, to a series of fractional distillations, a fixed boiling point was obtained at 136°C . This substance was tested for chlorine by burning a few drops in a glass tube with dry lime; the lime was washed out with water and a little nitric acid, the solution filtered, and nitrate of silver added, when a very decided precipitate was formed, indicating the presence of chlorine. A small portion of phenylate of soda was prepared, and a few drops of the distillate which boiled at 136° added to it; the mixture heated strongly; a little water added, the liquid filtered, and the filtrate treated with nitrate of silver, when a precipitate was formed which proved to be chloride of silver.

This liquid boiling at 136°C , is the *chloride of phenyl*; it is a colourless mobile liquid, having a fragrant odour. It is soluble in alcohol and ether; insoluble in ammonia; partially soluble in cold, but easily dissolved in hot potash.

The results obtained by the analysis of this body were not very satisfactory, owing, it is presumed, to the presence of hydrate of phenyl.

The mean of two combustions with chromate of lead gave per cent.—

C . . .	66.58
H . . .	4.93

0.3873 grms. of the substance burnt in lime gave,
 0.5081 „, chloride of silver, corresponding to
 30.83 per cent. of chlorine.

		Theory.	Experiment.
6 C . . .	72·0	64·00	66·58
5 H . . .	5·0	4·45	4·93
Cl . . .	35·5	31·55	30·83
$\text{C}_6\text{H}_5\text{Cl}$	112·5	100·00	102·34

Tribasic Phosphate of Phenyl (C_6H_5)₃, PO_4 .—The thick oily substance which remained in the retort after the separation of the chloride of phenyl, and appeared to be non-volatile, was treated with a strong solution of potash, which was afterwards removed by repeated washings with water; it was then dried under the receiver of the air-pump, and distilled. A small portion, having a brownish colour, came over at 200° C., and crystallised in the neck of the retort, having all the appearance of hydrate of phenyl.

The temperature gradually rose until it became necessary to remove the thermometer, after which the liquid began to distil, apparently without further decomposition; the distillate was a clear oily substance, having a yellow tinge, like that of uranium glass; towards the close of the operation, the distillate became darker, and a charred mass was left in the retort.

On a second distillation of this substance, a small portion came over slightly coloured; but the greater part was colourless when first distilled, and after standing some time acquired a yellow tinge by transmitted light; a small portion obtained towards the close of the distillation was of a light yellow colour, and a charred substance was again left in the retort. The presence of phosphoric acid in this liquid was demonstrated by mixing a few drops of the purest portion with ethylate of soda; evaporating the mixture to dryness; igniting the residue; adding the charred mass by small portions to fused nitrate of potash; dissolving the product in water; neutralising with hydrochloric acid; and testing for phosphoric acid in the ordinary way, with ammonia and a magnesia salt.

Phosphate of phenyl boils at a temperature considerably above the range of mercurial thermometers. It is inodorous, soluble in alcohol and ether, but insoluble in potash, except by boiling. It sinks in a cold solution of potash, but rises to the surface on the application of heat, and again falls to the bottom on cooling; showing that it expands by heat in a remarkable degree. It also possesses the peculiar property of epipolic diffusion; by ordinary day-light the epipolic rays, which have a fine violet tint, are visible at some distance below the surface; the flame of sulphur does not produce this effect more strongly than the light of the sun.

Some difficulty was found in burning this body, on account of the high temperature required to volatilise it.

The phosphoric acid was determined by adding a weighed portion of the substance to a strong solution of potash; the mixture was evaporated to dryness in a silver crucible, and nitrate of potash added to perfect the oxidation; this fused mass was dissolved with distilled water, boiled and filtered, the filtrate acidulated with hydrochloric acid, and again boiled to expel all the carbonic acid. Ammonia and sulphate of magnesia were then added, and the double phosphate collected on a filter, washed with ammoniacal water, dried, ignited, and weighed as pyrophosphate of magnesia.

The following were the results of analysis,—

I. 0.3026 grm. gave 0.1396 water, 0.7256 carbonic acid.

II. 0.3388 „ „ 0.1572 „ 0.8256 „

Hence in 100 parts :—

			Experiment.				Mean.
			Theory.	I.	II.	III.	
18 C	. .	216.0	66.11	65.40	65.92	—	65.92
15 H	. .	15.0	4.59	5.12	5.13	—	5.13
P	. .	31.7	9.71	—	—	8.90	8.90
4 O	. .	64.0	19.59	—	—	—	20.05
(C ₆ H ₅) ₃ , PO ₄ 326.7			100.00				100.00

III. 0.8713 grm. gave

0.2794 „ pyrophosphate of magnesia, corresponding to
20.24 per cent. of phosphoric acid, or 8.90 of phosphorus.

Acetate of Phenyl, $\text{C}_6\text{H}_5\text{O}_2$.—Acetate of potash dissolved in absolute alcohol was acted upon by phosphate of phenyl. No action took place in the cold, but after distilling upwards for some time, the acetate was decomposed, and when the alcohol was distilled off the temperature rose rapidly. The distillate which came over from 180° C. to 220° was distilled fractionally, and a fixed boiling point obtained at 190°. This compound is presumed to be the acetate of phenyl; it is a colourless mobile liquid, having a peculiar aromatic odour; it is slightly soluble in water, and dissolves with decomposition in hot water.

The following results obtained by the analysis of this body show that it was not obtained in a state of purity.

I. 0.3390 grm. gave 0.2012 grm. water, 0.9003 grm. carbonic acid.

II. 0.2279 „ „ 0.1359 „ „ 0.6078 „ „

Hence in 100 parts—

	Theory.	Experiment.		
		I.	II.	III.
8 C . . 96	70.58	72.42	72.73	72.57
8 H . . 8	5.88	6.59	6.62	6.60
2 O . . 32	23.54	20.99	20.65	20.83
$\text{C}_2\text{H}_3\text{O}$ Ph O 136	100.00	100.00	100.00	100.00

Nitrophosphate of Phenyl.—Phosphate of phenyl dissolves in fuming nitric acid with evolution of heat; on boiling the solution nitrous fumes were given off, and apparently a combination effected. A portion of the compound, when cold, boiled with hydrate of potash, yielded a yellow crystalline body on cooling. On adding cold water to the remaining portion of the compound formed by the action of nitric acid on phosphate of phenyl, a yellow oily substance was thrown down, which solidified on the application of heat; this body is probably the *nitrophosphate of phenyl*, and forms with potash a beautiful crystalline salt, which has not yet been fully examined.

Cyanide of Phenyl is obtained by the action of cyanide of potassium on the phosphate. It is decomposed by boiling, with evolution of ammonia.

Oxide of Phenyl.—A mixture of chloride of phenyl and phenylate of soda was heated with the view of obtaining the oxide of phenyl; the mixture swelled up and blackened, but no distillate was obtained. Nitric acid was added to a portion of the substance, and the solution treated with nitrate of silver; a white precipitate was obtained, showing that chloride of sodium had been formed; hence it is probable that oxide of phenyl was separated.

Hydruret of Phenyl.—Four ounces of carbolic acid were introduced into a retort, together with an equivalent of terchloride of phosphorus. The action in the cold was very moderate, but on applying heat a brisk action took place. The mixture was distilled upwards for some time, and afterwards the distillate collected: a blackened substance was left in the retort. The distillate was then distilled fractionally, a portion coming over between 80° and 90° C., the temperature gradually rising to 220° , and a black residue being again left in the retort. The first portion was redistilled, and nearly the whole came over about 80° C. This body was a colourless limpid liquid, which floated on water, and had the odour of *benzin* or *hydruret of phenyl*. On redistilling the other portions, very little came over below 186° , and it appeared to consist chiefly of hydrate of phenyl.

Iodide of Phenyl.—To a solution of 6 oz. of iodine in chloroform, hydrate of phenyl and phosphorus were added in the proportions of three equivalents of the hydrate and one of phosphorus to five of iodide, the phosphorus being introduced in very small pieces, and just sufficient heat applied to keep the mixture boiling; it was distilled upwards for about two hours, during which time a reddish crystalline substance formed in the neck of the retort. After distilling off the chloroform, there remained in the retort a thick viscid mass, apparently containing an excess of iodine: to this more hydrate of phenyl and phosphorus were added, and the mixture distilled to dryness; a considerable quantity of blackened matter remained in the retort.

The chloroform distillate, which was coloured with iodine, was redistilled, all that came over above 80° C. being kept separate, and added to the first distillate; the whole was then distilled fractionally. It began to boil at 120° C.: the last portion coming over at 220° , and the largest portion from 190° to 200° ; but the whole was highly coloured by free iodine. Sulphide of ammonium was added, which quickly removed the colour, and it was observed that those portions collected above 160° C. fell to the bottom, being heavier than the sulphide of ammonium, while those portions having a lower boiling point floated on the surface.

A few drops of that which came over about 190° were added to ethylate of soda; the mixture evaporated to dryness and ignited; the charred matter added to fused nitrate of potash; and a portion of the mixture, when cold, was dissolved in distilled water, filtered, and the filtrate acidulated with nitric acid; on addition of starch-paste the characteristic blue colour gave evidence of the presence of iodine; but the small quantity thus indicated showed that the iodide of phenyl is very difficult to obtain.

To six and a half ounces of carbolic acid, fourteen ounces of iodine and three-fourths of an ounce of phosphorus were added at intervals, as the combination was effected, care being taken to keep the iodine in excess; hydriodic acid was evolved in large quantities. The process was continued for about six hours, the neck of the retort being elevated and the hydriodic acid vapour received in ammonia. When no more gas was given off, the mixture was distilled, and a large quantity of black residue was left in the retort. This experiment was repeated a second time, and the distillate submitted to fractional distillation; it appeared to separate into two bodies, the one boiling below 200° , and the other between 250° and 264° C. On adding hydrate of potash to those portions which came over below 250° , about three-fourths of the whole dissolved. The portion insoluble in

potash was washed with distilled water, dried and distilled ; the greater part of it came over above 250° .

After repeated distillations of those portions which came over above 250° , a fixed boiling point was obtained at 260° C. : a few drops of this liquid were tested, and found to contain iodine.

The body thus obtained is presumed to be the *Iodide of Phenyl* ; it is colourless when first obtained, but acquires a brownish colour after standing some time. I regret that I have not been able to analyse it.
