LXXIII.—*On Phenyl-naphthalene.*

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THE chief object of this research was to find a means of increasing the yield of phenyl-naphthalene, for the first time synthetically obtained by one of us in 1879 (*Ber.*, **12**, 1396 and 2049). The same materials were used as before, viz., a mixture of bromobenzene and naphthalene, but a larger furnace was used, so that an increased

length of heated surface could be employed. The furnace was an Erlenmeyer's gas-combustion furnace with thirty burners; it was obtained from Rohrbeck of Berlin.

The details and results are as follows:—

According to the reaction—

157 parts of bromobenzene require 128 parts of naphthalene. Over 300 grams of the latter were taken and dissolved, with the aid of heat, in 300 grams of the former, and the warm liquid was poured into a tap-funnel connected with a bent tube passing slantwise into the combustion-tube, the latter at a bright red heat in the furnace. The excess of naphthalene is more favourable to a good yield of the desired hydrocarbon, as already proved (*Ber.*, 12, 2051).

The combustion-tube was of $\frac{1}{2}$ -inch internal diameter, and was loosely filled with fragments of pumice-stone. After a distillation of the entire mixture, the products found in (a) and (b) fuming strongly with hydrobromic acid and quite black, were transferred to a retort and distilled to recover the unaltered bromobenzene and naphthalene. These, received over in mixture, were mingled with a little more naphthalene, and the mixture was melted and again passed through the tube. The operation was continued till all bromobenzene was exhausted. The furnace was always considerably inclined downwards from c to d, the small tube e being further inclined to cause the mixture to flow readily into the combustion-tube.

By thus employing a large furnace, and a more extended surface at a bright red heat, naphthalene being always maintained in excess of the quantity calculated for the reaction shown in the equation, a considerably increased yield of phenyl-naphthalene was obtained, with a parallel increase of isodinaphthyl, but only very little diphenyl could be detected. The black tarry-looking stuff which had been accumulated, was now melted and poured into a retort, and submitted to distillation.

Below 200° a very little bromobenzene passed over; between 200°

and 220° undecomposed naphthalene; and when the temperature rose to 250—280°, yellowish-red oils came over, and were collected separately. At a temperature above 360°, a yellowish-brown substance distilled over, solidifying immediately to a mass of the same colour. In the retort a mass was left chiefly consisting of coke.

The oils collected between 250° and 280° solidified on cooling to a waxy mass. This and the solid portion boiling over 360°, were crushed together in a mortar with petroleum-spirit boiling between 60° and 100°; the thin fluid mass was then thrown on the filter, and after draining completely, was submitted to a fresh trituration with cold petroleum spirit.

Thus resinous matter, together with a little phenylnaphthalene, were dissolved out, yielding a red solution. The highest-boiling bright yellow and red hydrocarbons appearing last, just before coking the crude substance in the retort, appear to be identical with the precisely similar bodies appearing at the same stage in the preparation of isodinaphthyl, and also in the distillation of coal-tar immediately before the still is coked. The mass, washed as above with petroleum spirit, was dried in the water-bath, and then boiled with spirits of wine in excess, which had been previously diluted with water. In such a hot solution phenylnaphthalene is soluble, whilst dinaphthyl is quite insoluble. The solution was quickly filtered off (on a hot water funnel) from the residue, which was washed again with more hot dilute alcohol. The filtrate gave on cooling a beautiful white precipitate of phenylnaphthalene, which was collected on a filter and dried over sulphuric acid. A certain quantity of this hydrocarbon was also recovered from the petroleum-spirit washings, by repeated fractional distillations, and purifying with dilute alcohol as before.

The precipitate, when dried as above mentioned, was a white crystalline powder, with a melting point of 95—98°. It was purified by sublimation. Owing to the low melting point of the crude substance, it was at first found difficult to obtain expeditiously the pure substance by the sublimation of the crude.

A method was now devised by which a large yield of beautifully sublimed hydrocarbon could be most expeditiously obtained from the crude substance. The old form of apparatus used was an inverted glass funnel placed over a watch-glass containing some of the crude substance, the rim of the funnel standing on some smoothly laid asbestos which had been strewn on a piece of wire gauze, a small circular hole being left bare to the wire gauze through the asbestos, immediately under the centre of the watch-glass. Under the wire gauze, and immediately beneath the bare circular place left under the watch-glass, a very small Bunsen flame was lighted. In subliming crude phenylnaphthalene, or in fact any low-melting bodies with this

apparatus, or with others similarly constructed, great watchfulness is needed to prevent too great heat from remelting the lowest layers of sublimed crystals on the inner side of the funnel, thus undoing much of what had been at first accomplished. This difficulty, and the loss of time consequent upon it, were overcome by the adoption of a simple device. About a yard or so of rather less than $\frac{1}{4}$ -inch block-tin tubing was procured, and this was wound most closely and accurately round the outside of the funnel to be used. Thus a conical coil was obtained, in which the funnel easily fitted and could be withdrawn at pleasure. All that was now necessary was to connect the coil at (a) with a cold water supply, (b) being the exit. A small plug of filter-paper is loosely fitted into the end of the funnel (c), and the whole arrangement placed as already described above. By thus cooling the outside of the funnel, a higher temperature may be employed below the watch-glass, and with great rapidity the inside of the funnel becomes filled with a beautifully sublimed mass of crystals. The sublimed phenylnaphthalene consisted of thin beautifully white plates, exhibiting a delicate blue fluorescence, though not so much as in the case of pure anthracene for example. The melting point was found to be $101-102^\circ$ (corrected), whereas before sublimation it was $95-98^\circ$. The former melting point thus differs slightly from that previously found by one of us (*Ber.*, 12, 2051). This we attribute to the fact that we had a larger quantity of substance to work upon, and our sublimation process was very much improved, thus yielding us much better and purer crystals. The delicate orange-like odour of the vapours of the hydrocarbon and other properties (easy solubility in quite dilute spirit of wine) were sufficient tests of its identity so far. A vapour-density determination by Victor Meyer's method, employing a lead-bath and an atmosphere of nitrogen, gave the following results:—

Substance taken	0.1105 gram.
Temperature	17.5°C.
Volume.....	13.2 c.c.
Barometer	754.1 mm.
Tension of aqueous vapour at t°	14.882 mm.

$$\text{Hence } \frac{0.1105(1 + 0.003665 \times 175) \times 587780}{13.2(754.1 - 14.882)} = 7.08 \text{ vap. density,}$$

$$\text{calculated for } \begin{array}{c} \text{C}_{10}\text{H}_7 \\ | \\ \text{C}_6\text{H}_5 \end{array} = 7.07.$$

	Found.	Calculated.
Vapour density.....	7.08	7.07

A combustion gave the following numbers and result—

Substance taken = 0.1310 gram. CO_2 found = 0.4505 gram. H_2O found = 0.0705 gram.

	Found.	Calculated.
Carbon	93.78 per cent.	94.12 per cent.
Hydrogen	5.98 ,,	5.88 ,,
	<hr/> 99.76 ,,	<hr/> 100.00 ,,

The hydrocarbon dissolved in carbon bisulphide and treated with bromine, is gradually converted into a substitution-product, with evolution of hydrobromic acid. Treated with concentrated sulphuric acid it dissolves on gently warming, forming a sulphonic acid. These products will be further examined as soon as a new yield of material is obtained. The chief difficulty still in the way is the want of a more productive method of preparation—this it is hoped will also be overcome.

ADDENDUM.

In order if possible to ascertain the isomeric position of phenylnaphthalene, we attempted to synthesize the α -phenylnaphthylene by employing Fittig's reaction. For this purpose a mixture in the correct proportions was made of monobromobenzene and monobromonaphthalene, and this mixture, after dilution with benzene, was treated with bright freshly cut slips of metallic sodium. The sodium was employed in excess, and the whole was left for five or six hours, when the reaction was aided by application of heat, until the benzene began to boil. The flask was connected with an inverted condenser, and the boiling continued for about seven hours.

It was now observed that a chocolate-coloured substance had accumulated in the flask, and covered the pieces of sodium which remained. The contents of the flask were now thrown on a filter, and the remaining particles of sodium were mechanically removed from the residue, which was then examined. In this residue we succeeded only in detecting the presence of diphenyl, and the polymeric dinaphthyl of chocolate-brown colour and amorphous structure described by Lossen. We could discover none of Lossen's dinaphthyl ($\alpha\alpha$), and certainly no trace of any new hydrocarbon. This reaction then failed in our hands, and under the circumstances detailed, to yield phenylnaphthalene. We also varied our conditions, at one time using more dilute solutions in benzene, and at another greater concentration; but in all cases our efforts were defeated by the great ease with which the chocolate-coloured substance is formed, which from its reaction and appearance, appears to be quite identical with the body described by Lossen. On

collecting a considerable quantity of the brown product of the above reaction, having first carefully separated from it any remaining particles of sodium, and placing it in a small retort and distilling, a small quantity of oils was obtained at a temperature between 250° and 350° . These oils had a peculiar unpleasant odour, and no crystalline substance could be isolated from them. In appearance, odour, and boiling point they reminded one very much of the oily products obtained by one of us on attempting to synthesize phenylnaphthalene by passing a mixture of bromonaphthalene and benzene through a red-hot tube.