LXXXIX.—*Phenylnaphthalenes*. I. *α -Phenylnaphthalene*.

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WATSON SMITH, in 1879, in continuation of his work on the dinaphthyls, synthesised one of the two possible phenylnaphthalenes (*Ber.*, **12**, 1396 and 2049) by passing a mixture of monobromobenzene and naphthalene through a red-hot combustion tube filled with pumice, and in a later communication (*Trans.*, 1881, **39**, 547), in conjunction with Takamatsu, very fully describes the method employed. As a dinaphthyl, in all probability the $\beta\beta$ -, derivative is formed when either naphthalene or naphthalene together with volatile metallic chlorides (*Trans.*, 1887, **51**, 551) is passed through a red-hot tube, Watson Smith considered the new hydrocarbon to be β -phenylnaphthalene, and, to test this conclusion, attempted to synthesise the α -derivative, but without success.

In 1884 (*Annalen*, **226**, 23), Zincke and Breuer obtained a hydrocarbon by the dehydration and condensation of styrolene alcohol under the influence of sulphuric acid, which they subsequently (*Annalen*, **240**, 137) showed to be β -phenylnaphthalene. Zincke, however, was unable to confirm Watson Smith's results; neither could he obtain the hydrocarbon by other synthetic methods.

Watson Smith, in reply (*Proc. Chem. Soc.*, 1889, 70), proved that his hydrocarbon was identical with that obtained from styrolene alcohol, both products yielding a quinone exhibiting the singular property of polymerising when its solution is exposed to light.

It has recently been shown by the author (*Ber.*, **26**, 1745) that β -phenylnaphthalene is formed as a last product in the analytical decomposition of chrysene, whether this is effected through the quinone or through the so-called chrysene acid (probably β -phenylnaphthalene- α -monocarboxylic acid), and it therefore seemed desirable, in order to establish the constitution of chrysene, to synthesise, if possible, both α - and β -phenylnaphthalene by methods which should leave no doubt as to their structure.

The investigation, of the first part of which an account is given in the present paper, was consequently begun, and while it was in progress Möhlau and Berger published an account of the synthesis of both possible phenylnaphthalenes, by the action of solid diazobenzene chloride on naphthalene in presence of aluminium chloride (*Ber.*, **26**, 1196). This mode of formation, however, gives no information respecting the constitution of the two isomerides.

The synthesis of phenylnaphthalene can be effected in several different ways, which prove that the phenyl group is introduced in

the α -position in naphthalene, but in nearly all cases the yield is extremely small, considerable quantities of brown, tarry, uncrystallisable substances being formed, either by a condensation of the α -phenylnaphthalene first formed, similar to that suggested by Lossen to explain the production of such a substance in the synthesis of $\alpha\alpha$ -dinaphthyl, or through some peculiar behaviour of naphthalene and its substituted derivatives.

Among the many methods tried, the one giving the best result was found to be the action of α -chloronaphthalene on benzene in presence of aluminium chloride, a yield of about 40 per cent. of the theoretical being obtained; a very small quantity of β -phenylnaphthalene is also formed; this may be due to a change of the α - into the β -chloronaphthalene under the influence of aluminium chloride, but is probably owing to the presence of a small quantity of the β -compound in the original α -chloronaphthalene used, which was obtained from naphthalene dichloride by distillation and fractionation until the boiling point was practically constant. As Armstrong and Wynne have shown (*Proc. Chem. Soc.*, 1890, 85), β -chloronaphthalene is always present in small quantity in the product obtained in this way.

A similar interaction takes place when α -bromonaphthalene is used in the place of the chloro-compound or when zinc chloride is substituted for aluminium chloride, but the yield in these cases is not so good.

α -Phenylnaphthalene is also formed in small quantity when α -bromonaphthalene and monobromobenzene are heated with sodium; and in somewhat larger amount when α -bromonaphthalene is heated with mercurydiphenyl and magnesium at over 400° in a sealed tube. The mercury in the latter case is set free as metal, and no mercury-phenyl bromide or diphenyl can be detected, but a considerable quantity of naphthalene is produced. When bromobenzene is warmed with naphthalene in presence of aluminium chloride, α -phenylnaphthalene is also produced, no formation of β -phenylnaphthalene being observed; the only other definite substance recognised was a beautifully crystalline compound melting at about 178° ; very likely a higher phenylated naphthalene. A very large amount of uncrystallisable tarry matter is, however, formed, and the yield of α -phenylnaphthalene is not good.

Action of Sodium on a Mixture of α -Bromonaphthalene and Bromobenzene.

When bromobenzene and α -bromonaphthalene are dissolved in ether, sodium appears to have very little action on them, and even

on warming this appears to cease so soon as a superficial coat of some brown substance is formed on the metal. If the two substances are dissolved in xylene, action not only takes place, but becomes complete if during the heating the brown coating be shaken away from the molten metal as it is formed. As this process is very slow and yields only a very small amount of α -phenylnaphthalene, the two bromo-derivatives were mixed in equivalent proportions, and the calculated quantity of sodium was added. The metal at first remained bright, but on warming a little above the melting point of the sodium, action commenced; as it proceeded, much heat was evolved, and the liquid boiled rapidly, a dark brown substance being at the same time formed. When action ceased, the entire contents of the flask appeared to have been converted into a dark brown, earthy-looking, solid, friable substance. This was separated mechanically from a few globules of sodium and distilled, when a small quantity of a yellow, semi-fluid substance passed over, whilst a black, porous, charred mass remained. The distillate consisted almost entirely of naphthalene, mixed, however, with a small quantity of α -phenylnaphthalene; on dissolving this mixture in hot alcohol and cooling, the naphthalene first crystallised out, the α -phenylnaphthalene left in the solution separating as oily globules on evaporation or on the addition of water.

Naphthalene and α -phenylnaphthalene can also be separated by distillation with steam, the naphthalene volatilising far more readily; the distillation, however, requires to be continued for a long time, as the phenyl derivative is only slightly volatile with steam.

The α -phenylnaphthalene was finally fractionally distilled; the yield by this method is very small, not more than 1 to 2 per cent. of the theoretical.

Action of Magnesium and Mercurydiphenyl on α -Bromonaphthalene.

When α -bromonaphthalene and mercurydiphenyl are heated together, the latter dissolves, although very little action takes place even if the mixture be kept for a long time at its boiling point; the only product that could be isolated was a very little mercuryphenyl bromide. As the action appeared not to go beyond this stage, the calculated quantity of magnesium was added, and the three substances were heated together at over 400° during 12 to 14 hours in a sealed hard-glass tube. On cooling, the contents of the tube appeared dark brown and viscid, and globules of mercury were found at the bottom. This viscid, tar-like mass was then distilled; at first, a pale yellow, semi-solid substance came over; then, on strongly heating, at just visible redness, yellow vapours were given off, con-

densing to a brown, viscid mass which, when cold, solidified to a brownish-black resin.

The first portion of the distillate was found to consist of naphthalene and α -phenylnaphthalene, which were separated by steam distillation and subsequent fractionation. The yield of α -phenylnaphthalene by this method amounted to about 10—12 per cent. of the theoretical. No diphenyl was observed, only naphthalene, α -phenylnaphthalene, mercury, and the resin above mentioned being recognised. This resin distils only at a low red heat, is insoluble in alcohol, but readily soluble in benzene and its homologues, giving a dark reddish-brown solution which exhibits a beautiful green fluorescence; the solution is not decolorised by animal charcoal, and on the addition of absolute alcohol, the resin separates in small, brown globules.

Action of α -Bromonaphthalene and α -Chloronaphthalene on Benzene in presence of Aluminium Chloride.

Anhydrous aluminium chloride was added to a solution of α -bromonaphthalene in an excess of benzene; the mixture became gradually black, and hydrogen bromide was slowly evolved; after standing for 12 hours, the mixture was heated on a water bath till acid vapours were no longer given off, diluted with benzene, and warmed with an excess of dilute hydrochloric acid. The benzene solution, after being well washed, was dried over calcium chloride, and the benzene distilled off. The brown, semi-solid residue was then distilled; at first, an oily, yellow liquid came over, next a very small quantity of a solid, crystalline substance, and afterwards a brown resin similar to that previously described. The yellow liquid when fractionated proved to be mainly α -phenylnaphthalene, the yield being about 15 per cent. of the theoretical.

The most convenient method tried of preparing α -phenylnaphthalene is, however, the action of α -chloronaphthalene on excess of benzene in presence of aluminium chloride. Exactly the same procedure was adopted as before. On distilling the residue left on evaporation of the benzene, a yellow oil consisting mainly of α -phenylnaphthalene came over first, then a white, crystalline substance, and finally a brown resin.

The yellow liquid was fractionated to obtain the α -phenylnaphthalene, the yield being about 40 per cent. of the theoretical. By fractional crystallisation from alcohol the white, solid portion of the distillate was separated into β -phenylnaphthalene and a substance melting at about 150°, and crystallising in beautiful pearly white scales; the latter substance may possibly be a higher substituted

derivative of benzene containing two or more naphthyl groups, but the quantity obtained was too small to admit of its investigation. The amount of β -phenylnaphthalene produced was very small, and was probably derived from a little β -chloronaphthalene contained in the α -chloronaphthalene used.

The amount of resin formed was very considerable; it is insoluble in alcohol, but on boiling, it becomes blacker and more friable; it dissolves in benzene forming a reddish-brown solution which exhibits a very strong, green fluorescence.

The above reactions were also tried, using zinc chloride in place of aluminium chloride, but the results were not nearly so good.

Action of Bromobenzene on Naphthalene in presence of Aluminium Chloride.

Excess of anhydrous aluminium chloride was added to a mixture of bromobenzene and naphthalene in equivalent proportion, and the whole kept at 70–80° during 12 hours. The mixture was then heated over a small gas flame till no further evolution of hydrogen bromide took place, diluted with excess of benzene, warmed with very dilute hydrochloric acid, well washed, dried over calcium chloride, the benzene removed by distillation, and the tarry residue distilled. α -Phenylnaphthalene first came over mixed with a little naphthalene, next a yellowish crystalline compound, then a yellow, amorphous substance, whilst a brownish-black, resinous mass was left in the retort; this resin was readily soluble in benzene, giving a deep, reddish-brown solution exhibiting a splendid green fluorescence, but nothing definite could be isolated from it. The impure α -phenylnaphthalene was then fractionated, a yield of about 20 per cent. of the theoretical being obtained. No β -phenylnaphthalene was detected, the substance distilling next above the α -phenylnaphthalene melting at about 178° after recrystallisation from alcohol; it crystallises very beautifully in small, glittering, pearly scales, and may possibly be a more highly phenylated naphthalene formed by the further action of bromobenzene on the naphthalene. The yellow substance distilling at a still higher temperature also dissolved somewhat readily in alcohol, giving a pale yellow solution exhibiting a green fluorescence; it separated from its hot alcoholic solution, on cooling, in yellow flocks which showed no crystalline structure and, on drying, formed a light yellow, amorphous powder melting at about 170°. It is possible that this is the first stage in that process of polymerisation which results in the formation of resin-like substances in all these reactions.

This reaction was also tried with zinc chloride, but the result was not so good, more tarry and resinous products being formed.

α -Phenylnaphthalene was obtained as a thick, oily-looking liquid of a pale yellow colour, exhibiting a faint blue fluorescence, and, after some time, solidified to a soft, waxy looking mass without definite crystalline form. It did not melt at all sharply on warming, but was completely fluid at 45° , and, on cooling, remained liquid for some considerable time at the ordinary temperature. It had a peculiar odour resembling both naphthalene and diphenyl. It boils about $324\text{--}325^\circ$, and is very readily soluble in alcohol, ether, benzene, and its homologues, glacial acetic acid, light petroleum, and chloroform, its solutions having a slight blue fluorescence. It cannot be obtained in crystals from these solutions, as, on evaporation, they deposit the hydrocarbon in the form of small, oily drops, which, after a long time, become slightly opaque through solidification. It is volatile with steam, but not very readily, and may be separated moderately completely from naphthalene by this means.

A combustion of the hydrocarbon was made.

0.3258 gave 1.1218 CO_2 and 0.1774 H_2O . C = 93.91; H = 6.06.

$\text{C}_6\text{H}_5\cdot\text{C}_{10}\text{H}_7$ requires C = 94.10; H = 5.89 per cent.

Two vapour density determinations were made by Victor Meyer's method, using a bath of sulphur vapour.

Calculated for	Found.	
C_{10}H_7		
$\text{C}_6\text{H}_5 \cdot$	I.	II.
7.06	6.82	6.69
Air = 1.		

It is with much pleasure that I here express my indebtedness to Professor Tilden for his kindness in allowing me the use of his laboratory and for the help which he has afforded me during the progress of this work.

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