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No. XXVI.—*On the Action, at a High Temperature, of Volatile Metallic Chlorides on Certain Hydrocarbons.*

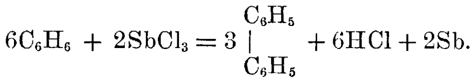
By WATSON SMITH.

Part I. IN the preparation of isodinaphthyl by passing the vapour of naphthalin through a red hot tube, the yield is but small, and hence, to obtain a considerable quantity, many distillations of the same substance have to be made, the small residue of high boiling product after each distillation being poured out, and kept apart. Wishing to have a more convenient method, so as to prepare large quantities of the isodinaphthyl, if necessary, I made this matter a subject of investigation.

In my first paper, giving an account of the discovery of isodinaphthyl (*Proc. of Literary and Phil. Soc.*, Manchester, 1871), I mentioned an experiment, in which chlorine together with naphthalene vapour, was passed through a red hot tube. *Complete* decomposition appeared to take place, dense volumes of black smoke emerging at the end of the tube. However, it seemed likely on further consideration, that if, instead of free chlorine, a metallic chloride were used, yielding at a high temperature its chlorine at least in part, a *partial* decomposition only might be effected. Accordingly, antimony trichloride and tin tetrachloride were chosen as suitable chlorinating agents. After passing naphthalene and antimony trichloride vapours through a red hot tube, and succeeding in realising the increased yield of isodinaphthyl, I turned my attention to benzene and toluene, in the hope of making the method a general one, and obtaining diphenyl and stilbene. The results I now give under their respective headings :—

BENZENE.

With Antimony Trichloride.—The reaction expected is represented in the following equation :



$$6C_6H_6 + 2SbCl_3 = 3\begin{array}{c}C_6H_5\\|\\C_6H_5\end{array} + 6HCl + 2Sb.$$

Accordingly, equal weights of trichloride and benzene were taken. The benzene was placed in a flask connected with the flask containing the antimony trichloride by a bent tube, and the trichloride flask with a tube of hard Bohemian glass placed in a gas combustion furnace, by means of another bent tube. Thus, the vapours from the boiling benzene were passed through the flask containing the boiling antimony trichloride, the mixed vapours passing through the combustion-tube, which was filled loosely with bits of pumice-stone and porcelain. The receiver of the apparatus was connected with a Liebig's condenser, to condense undecomposed benzene.

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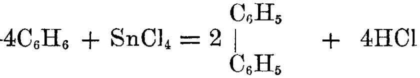
On distilling through the tube, at a bright red heat, large volumes of hydrochloric acid were given off, and metallic antimony deposited plentifully, at the extremity of the tube, and in the neck of the receiver. After all had passed through, the contents of the receivers (the one at the end of the tube, and that connected with the Liebig's condenser) were returned to the benzene flask, a fresh quantity of trichloride added in the other flask, and the distillation repeated. A high-boiling residue being left, this was poured out at the end of the second distillation, and kept apart. Three distillations were made. The accumulated residues of these three distillations, consisting of a mixture of diphenyl with excess of undecomposed antimony trichloride, metallic antimony powder, and a little benzene, were placed in a small retort and distilled. A little benzene came over, then from 200° to 220° much antimony trichloride, and finally above 220°, a mixture containing diphenyl with less trichloride. The latter was treated with warm concentrated hydrochloric acid, the trichloride being dissolved, and diphenyl left floating as an oil in the warm acid solution. On cooling, the solid cake was removed, again washed with acid, and recrystallised from alcohol. *The melting point was exactly* 70°, *the boiling point* 243° C. Thus a considerably increased yield of diphenyl was obtained, over what is obtainable by the red-hot tube alone, but the quantity still not being great enough, I determined to try the effect of tetrachloride of tin in a similarly conducted experiment.

With Tetrachloride of Tin.—



$$4C_6H_6 + SnCl_4 = 2 \begin{array}{c} C_6H_5 \\ | \\ C_6H_5 \end{array} + 4HCl$$

+ Sn represents the reaction expected. 62·4 grams of benzene were distilled through the red-hot tube, as in the former experiment, together with 52 grams of tin tetrachloride, the benzene vapours being passed through the flask containing the *tetrachloride of tin.* The mixed gases came over of a dusky or grey colour, a small quantity of a violet-coloured oil being deposited in minute drops in the neck of the receiver. This violet oil was noticed also in the former experiment with antimony trichloride. The evolution of hydrochloric acid gas was very large, much larger than in the former experiment, and towards the end of the distillation the tubes were stopped up with a mixture of diphenyl and stannous chloride; also in the receiver cakes of diphenyl with stannous chloride were found. Much metallic tin was also found in the receiver. This one distillation thus gave a very large yield of diphenyl; further very little benzene came over through the Liebig's condenser, showing that the decomposition was almost complete. This method therefore appears to be the simplest, quickest and best for procuring diphenyl in large quantity from benzene. The above equation does not, however, appear to give an exact representation of the reaction in the tube; this

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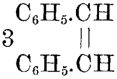
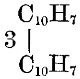
reaction seems indeed to be a mixed one, stannous chloride and metallic tin being reduced. This is probably owing to want of uniform mixture in the tube.

TOLUENE.

With Antimony Trichloride.—Reaction expected: $6C_7H_8 + 4SbCl_3 =$  $3\begin{matrix}C_6H_5.CH\\ \|\\ C_6H_5.CH\end{matrix} + 12HCl + 2Sb_2$. About 60 grams of toluene were taken, and distilled so that the vapours passed into a flask containing boiling antimony trichloride, the mixed vapours then passing through the red-hot tube. Large volumes of hydrochloric acid were evolved, and much metallic antimony reduced. When all was passed through, the contents of the receiver were placed in a small retort, the toluene was distilled off and replaced in the first flask, the residue, containing much undecomposed trichloride, being returned to the second flask. The distillation was then repeated. Hydrochloric acid was again abundantly evolved. The contents of the receiver, together with the residue in the second flask, were now distilled to remove toluene and antimony trichloride; a residue remained which was treated repeatedly with hot concentrated hydrochloric acid to remove antimony trichloride. An oily black mass remained floating on the hydrochloric solution. On distilling this tarry substance the temperature rapidly rose to 270°, when a small quantity of a red oil came over, having a strong, rank, disagreeable odour, resembling that of burnt cheese. From 280° to 300° an oil came over with a still more disagreeable odour. Above 320° a thick gummy oil distilled over, but mostly remained condensed in the stem of the retort, and crystallised there in long striated masses of crystals.

NAPHTHALENE.

With Antimony Trichloride through the Red-hot Tube.—$6C_{10}H_8 + 2SbCl_3 =$  $3\begin{matrix}C_{10}H_7\\ |\\ C_{10}H_7\end{matrix} + 6HCl + Sb_2$.—77 grams of naphthalene and 46 grams of antimony trichloride were mixed together by fusion in the same flask, and then distilled through the red-hot tube. This tube was, as in the previously described experiments, of hard Bohemian glass, and was nearly double the diameter of the ordinary combustion tubing. The boiling point of the trichloride being nearly that of naphthalene, there is no difficulty in thus distilling them together. The results were as follow:—

1*st Distillation.*—Tube at a bright red heat. Much hydrochloric acid evolved, and metallic antimony reduced.

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2nd Distillation.—After all had passed through, the still fused contents of the receiver were returned to the distillation flask, and again passed through, 15 to 16 grams of trichloride being further added. More hydrochloric acid appeared to be evolved than in the first distillation, and antimony was abundantly deposited. The temperature was however, a little higher than in the first distillation, being a full bright red heat. A large residue was obtained of high-boiling product in the distillation flask. There is no difficulty whatever in recognising the point at which the naphthalene and trichloride have all passed over, as the residue, consisting chiefly of isodinaphthyl, boils at a very high temperature, and therefore ebullition ceases unless the lamp flame be turned further on.

3rd Distillation.—No more antimony trichloride was added, but another distillation was made. Tube at a bright red heat. Residue obtained was somewhat larger than in the second distillation. Yellow vapours came over in some abundance.

4th Distillation.—Added no more trichloride, that remaining undecomposed sufficing. Residue as large as ever, of high boiling product. Of course the last distillation only yields a residue, which it leaves behind it, and hence the product is one of three distillations.

The collected crude black looking product weighed 37·4 grams.

This black mass was now distilled in a small retort, when a yellow, hard, crystalline mass was obtained, consisting of crude isodinaphthyl. In this distillation, after the isodinaphthyl had for the most part passed over, a quantity of a yellow sublimate came over with the latter portions, and this, with the final portions, gave place to a red sublimate. This red sublimate sometimes appeared as the pitchy residue became coked, the retort bottom being red-hot. These sublimates I intend to examine further.

Of the crude yellow crystalline isodinaphthyl, the weight was 24·2 grams. This amounts to 31·4 per cent. on the naphthalene taken, whilst the crude black substance = 48·5 per cent. on the naphthalene taken.

A comparison will show the wonderfully increased yield of substance by this method over that in which naphthalene was distilled alone through the tube:—

(*a.*) *Naphthalene alone used.*—After eight distillations through the red-hot tube: crude black substance.................................. = 17·23 per cent.

(*b.*) *Naphthalene with Antimony Chloride.*—After three distillations through the red-hot tube: crude black substance .... = 48·5 „

After redistilling (*b*) to purify it partially: yellow crystalline redistilled substance .... = 31·4 per cent.

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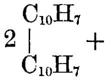
A singular fact is here well worthy of notice, viz., the product obtained as above described was much purer than any previously obtained by using naphthalene alone, or a smaller quantity of antimony trichloride than the theoretical, or some excess over it. The increased purity was well observed in purifying two samples by triturating about the same weights of each with petroleum spirit, and filtering. One sample had been prepared at the same temperature as the other, but in the one case about half the equivalent weight of trichloride had been used, in the other the full amount.

With the first-named product much less yellow sublimate was yielded, and scarcely any red sublimate, on coking. The petroleum spirit solution had merely an orange colour. In the case of the other, a large yellow sublimate was obtained. A considerable quantity of a fine orange and red on coking, and an almost blood-red solution was obtained in the filtrate, on washing with petroleum spirit. A product nearly as much contaminated with this yellow decomposition-product has been frequently obtained with naphthalene alone. From the red petroleum spirit wash-liquors, a substance gradually separates out in small crystalline clusters of a citron-yellow colour. A sufficient quantity having now been obtained for the first time for working upon, I have been enabled to examine it. It will be described further on, with the results obtained on making a minute examination of the red petroleum spirit mother-liquors referred to.

With Tin Tetrachloride.—Expected reaction: $SnCl_4 + 4C_{10}H_8 =$



$$2\begin{array}{l}C_{10}H_7\\ |\\ C_{10}H_7\end{array} + 4HCl + Sn, \text{ and } 2SnCl_4 + 4C_{10}H_8 = C_{20}H_{14} + 4HCl + 2SnCl_2.$$

79 grams of naphthalene, and 40 or a little over of tetrachloride, were taken. The first time the distillation was attempted, with apparatus similar to that previously employed, the tubes and pipe soon became stopped up, so that it was impossible to proceed. This was owing to the considerable complete decomposition which was going on in the tube, carbon being separated; this either accumulated in the main tube and caused stoppage there, or was carried in fine dust, together with stannous chloride into the other tubes of the apparatus. Another apparatus had therefore to be devised in which an empty tube was used, and only wide-necked bottles and tubing for the receiver and apparatus for condensing the hydrochloric acid. The latter consisted simply of a wide-necked bottle loosely filled with blotting-paper soaked in water, and containing a little water at the bottom. On distilling, it was at once noticed that a considerable amount of black smoke was formed, and issued at the end of the tube, also very much hydrochloric acid vapours. The tube was nearly white hot. After the experiment the tube was found to be full of shining black scales of separated carbon,

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and the stuff which had distilled over into the receiver was quite black, but more fluid, or rather soft, than even before. This mass was transferred to a small retort and distilled. First some naphthalene came over, then what were evidently chlorine-products of naphthalene; the temperature then rose rapidly from 220° to 300°, when a small quantity of a reddish-yellow oil came over which partially crystallised on cooling. It exactly resembled some of those oils known as the "red anthracene oils," well known to tar-distillers. This oil is quite a new feature, and will be examined more minutely at the earliest opportunity. Next in order of distillation, the isodinaphthyl came over, looking exactly as usual, and behaving so to all tests. Lastly, an unusually large quantity of the citron-yellow powder distilled, or rather sublimed over, and dropped out at the end of the retort, forming a little heap of yellow powder quite separate from the isodinaphthyl, which remained solidified in the stem of the retort. A large yield of isodinaphthyl was obtained, but the method is not so convenient as when antimony trichloride is used. I propose, however, to try the effect of heating naphthalene to a high temperature with tin tetrachloride in sealed tubes, when I hope to avoid the total decomposition and get a larger yield of isodinaphthyl.

It was found on purifying the crude isodinaphthyl, that on crushing the crude yellow substance obtained by the distillation of the black residues of the first operation, an odour like that of phenol was observed. This being the case, the whole quantity of substance was boiled with dilute sodium hydrate solution and filtered, and then the filtrate was decomposed by dilute sulphuric acid, when an oily, semi-solid, floccular mass rose to the surface, having a strong odour like that of phenol. This is probably naphthol, formed by the action of small quantities of water in the antimonious chloride used upon the naphthalene in the red-hot tubes.

It is interesting to notice the great stability of *benzene* in the red-hot tube with the chlorides mentioned, in comparison with naphthalene, apparently little else being formed than diphenyl, and scarcely any black smoke or separation of carbon being perceived. In the case of naphthalene, on the contrary, under these circumstances much carbon is separated; in fact the tube, though an empty one, becomes almost choked: also a considerable quantity of other decomposition-products is formed. Toluene appears to suffer considerable dismemberment, yet but little carbon is separated.

II. *Isodinaphthyl Sulpho-acids and Salts, with certain other derivatives.*—Merz and Ebert (*Deut. Chem. Ges. Ber.*, viii, 1876, 592) found that a mixture of concentrated sulphuric acid and naphthalene in the proportions of 5 : 1, heated for a long time at 100°, gave only mixtures of isomeric monosulpho-acids, together with a certain quan-

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tity of the isomeric disulpho-acids. Also it was found impossible to prepare the α-mono- or di-sulpho- acids uncontaminated with some of the respective β-sulpho-acids.

A mixture of naphthalene and concentrated sulphuric acid in the proportions of 1 to 3, heated for about eight hours from 140° to 160°, yielded a considerable amount of β-mono-sulpho-acid. After 14 hours' heating much β-disulpho-acid was found to have formed.

1 part of naphthalene with 5 parts of concentrated acid heated for four hours to 160°, yielded nearly equal quantities of α- and β-disulpo-acids. No mono-sulpho-acids were formed.

Naphthalene and acid in proportion of 1 to 5, heated 24 hours to 180°, yielded the β-disulpho-acid with only a trace of the α-isomeride. The α-derivatives were more fusible and more soluble than the β-isomerides. It was found that iso-dinaphthyl dissolves easily in concentrated sulphuric acid at a temperature of from 140° to 150°. In the first experiment a considerable excess of concentrated sulphuric acid was used, and the iso-dinaphthyl being added, the whole was heated in the oil-bath from 140° to 150° for three or four hours. Afterwards the black viscous liquid was dissolved in water, and excess of barium carbonate added; to another portion also excess of lead carbonate was added. After filtering, and washing with hot water in each case respectively, the solutions were evaporated, when in both cases a white precipitate of a slightly crystalline appearance fell. This turned out to be difficultly soluble β-barium or lead sulpho-salt. On filtering, and evaporating on the water-bath, and finally over sulphuric acid, glassy masses were obtained, of which the barium compound easily split up into small lance-shaped plates. These residues were very soluble in water, and were found to be the isomeric α-barium and lead salts. In the present case a large yield of the α-soluble salts was obtained. The barium α-salt was a mass composed of little transparent lance-shaped plates of a light brownish colour. The lead α-salt was a light yellow, scaly mass. About 4 parts of isodinaphthyl were mixed in a small flask with 2 parts of concentrated sulphuric acid, and the whole was heated to between 180° and 190° for five hours. On cooling, a black shining solid mass was obtained with a green lustre. It dissolved completely and easily in water. On neutralising with barium carbonate, filtering, and washing with hot water, a solution was obtained, which on evaporation yielded a large proportion of the β-salt as a pure white crystalline or scaly precipitate. A very small yield of the α-isomeric salt was obtained as a glassy, transparent, and very soluble mass on slowly evaporating the filtrate over sulphuric acid.

The *α-sulpho- acid* was obtained by treating the barium salt with sulphuric acid till no further precipitate was formed. On filtering and evaporating to dryness slowly and at a gentle heat, a residue was

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obtained consisting of little transparent scales which have a faint yellowish tint and are slightly fluorescent. The acid is easily soluble in water, slightly in absolute alcohol, freely soluble in spirits of wine and in ether, and is precipitated from the ethereal solution by absolute alcohol. It is quite insoluble in benzene. The *β-sulpho-acid* was also prepared, and it closely resembles the α-acid, but is characterised by less solubility. The *α-lead salt* was found to be almost insoluble in ether, alcohol, and benzene. It is easily soluble in water and weak alcohol. The β-salt is almost insoluble in alcohol, ether, and benzene, but is only slightly soluble in water.

That the above-named acids are isomeric I have convinced myself by repeated analyses, but my numbers are not sufficiently concordant with theory to induce me to publish them. This may probably be due to the presence of some third body, or of impurities.

On triturating a quantity of the potassium salt of the sulpho-acids above-mentioned with phosphorus pentachloride, no action was perceptible; heat also did not appear to assist in the reaction; the endeavour to prepare a sulpho-chloride therefore failed.

An *oxydinaphthyl* or *phenol* was obtained as follows:—Equal parts by weight of the potassium salt of the sulpho-acid and potassium hydrate were mixed with a little water and the whole was gradually heated up to 250° in an atmosphere of hydrogen. The mass assumed a bright-yellow tint, gradually changing to brownish-yellow. On leaving it to cool and treating with hydrochloric acid, a soft resinous mass detached itself from the solution, which, when dry, thoroughly hardened on fusing to a solid, rich, brown resinous mass. This oxydinaphthyl possesses a faint but distinct phenol-like odour. It is very soluble in alcohol, less so in ether, slightly in benzene. It dissolves readily in a solution of an alkaline hydrate, from which solution acids separate it as a thick jelly-like resinous mass with a faint phenol-like odour.

Nitro-substitution Product.—On dissolving isodinaphthyl in nitric acid and pouring the solution into water, a white precipitate is thrown down, consisting of a nitro-compound. On heating the well-dried precipitate gently, it fuses, and on cooling again forms a reddish-brown transparent resin. The substance altogether very much resembles in appearance and properties the nitro-compound obtained by Lossen from his dinaphthyl. The body is but little soluble in alcohol, almost insoluble in ether, freely soluble in benzene. The benzene solution on evaporation left it as a yellow resin. It was reduced on treatment with tin-foil and hydrochloric acid, but the quantity of amido-derivative formed was too small for examination.

Cyanogen-derivative.—On distilling equivalent proportions of the potassium salt of the sulpho-acid and potassium cyanide, both being

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perfectly dry, a distillate was obtained crystallising in the stem of the retort in beautiful long white needles. The amount obtained was too small for analysis.

III. *A new Dinaphthyl and a consideration of the Positions of the three Isomeric Dinaphthyls.*—I have already drawn attention to the fact that, together with isodinaphthyl, a yellow substance soluble in petroleum spirit is formed when naphthalene is submitted to the action of a high temperature, either alone or in presence of easily decomposible and volatile metallic chlorides. In the latter case, more of this yellow substance is formed, the more easily decomposible the metallic chloride used is. Thus, more is obtained when tin tetrachloride is used than when antimony trichloride is. In purifying the crude isodinaphthyl by crushing and triturating with petroleum spirit a fine red solution is obtained on filtering. This red solution was evaporated down to a certain extent and then set aside to evaporate spontaneously. After the lapse of a week or two, wart-like crystalline masses were deposited in considerable quantity. The mother-liquors were poured off these and again allowed to stand and deposit another crop of crystals. The accumulated stock of crystals was at length taken and pressed between blotting-paper, then ground up finely to a thin paste with a little petroleum spirit, and again pressed between blotting-paper. A yellow powder was thus obtained, fusing at a low temperature, and dissolving in warm concentrated sulphuric acid, to which it communicates a fine violet tint.

This yellow powder was now placed in a retort and distilled. A very little oil came over first, which was rejected; the temperature then rose immediately to over 300°. At this high temperature almost all came over, and condensed as a thick, transparent, light yellow, resinous mass which only partially solidified. This mass remained clear for a week, when it began to show signs of crystallisation at the edges, which became white and opaque. The mass required a month to crystallise thoroughly. It is very soluble in petroleum spirit, ether, and benzene; less soluble in alcohol than in ether. Weak alcohol precipitates it from solution in absolute alcohol. A concentrated hot alcoholic solution deposits the body in resinous drops on cooling. If, however, dilute solutions of the body in petroleum spirit or benzene be allowed to evaporate slowly in the air, small tufted crystalline masses were obtained. On making very dilute solutions in petroleum spirit and letting these evaporate slowly in the air, it was noticed that the crystals first formed were tufted with little yellow plates, and here and there entirely composed of tufts of transparent light-yellow plates; the other crystals were simply the rough semi-globular wart-like masses before mentioned. On determining the melting points of these, it was found that the little plates melted at

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137°, the warty masses at 75°. It was clear therefore that here were two different substances, and the next point was to separate and purify them. This was effected by a tedious process of fractional crystallisation, extending over several months. The body melting over 75° was very difficult to obtain well crystallised, and this point was only attained by taking a very dilute petroleum-spirit solution and allowing this to evaporate spontaneously in small flasks, these being set aside in a warm place. Small tufts of crystalline plates, intermixed with a few of the warty masses, first crystallised out. The spirit was poured off these into another flask, and from the mass of crystals left the plate-like ones were picked out and set aside; this was done as long as any plates separated. When no more plates would crystallise out the warty or globular masses were redissolved, the solution was further diluted, and the whole again set aside. This time the crystals forming were almost white and of a pearly scale-like appearance, and it was noticed besides that a few thin plates of a brownish-red colour and transparent had crystallised out. This was evidently a new substance, but it existed in extremely small quantity, so that only a few crystals were obtained. The plates first mentioned were collected and recrystallised from petroleum spirit, in which they were considerably less soluble than the white pearly crystals. They were by repeated crystallisation obtained almost quite white, and had a constant melting point of 147°. This body resembled isodinaphthyl in appearance, but it differed from this hydrocarbon in melting point and in being more soluble in benzene, petroleum spirit, alcohol and ether, &c. Several careful comparisons were made as to the relative solubilities of the two bodies, which amply confirmed the belief that they are not identical. In fact the solubilities in various fluids, the appearance, and the not very far-removed melting point, led me to suspect this was no other than the isomeric dinaphthyl obtained by Lossen (*Liebig's Annalen*, lxviii, 71), by the action of manganese and sulphuric acid on naphthalene. The low-melting substance, after several crystallisations, melted constantly at 75°. Its boiling point was over 300° (as was also that of the body melting at 147°). It was far more soluble in petroleum spirit, benzene, alcohol, and ether than the higher melting substance, and crystallised out much more quickly from these solvents. The very small quantity of the body crystallising out in brown transparent plates was collected and tested. The *melting point* was found to lie between 250° and 255°. It was slightly soluble in petroleum spirit, less in alcohol, but rather more soluble in ether; it was still more soluble in boiling benzene, to which it communicated a splendid blue fluorescence. A very small crystal communicates a magnificent blue fluorescence to a very large bulk of benzene or alcohol in which it is dissolved. This body

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reminds one very much of the brown polymeric body obtained by (*Liebig's Annalen*, lxviii, 89) Lossen and (*ibid.*, cxlvii, 170) Otto, with which it is probably identical. It was only after very long standing (about a month) and slow evaporation that it was obtained crystallised. When more quickly separated it appears as a chocolate, brown powder. I believe it to be identical with the polymeric dinaphthyl above-mentioned, already obtained by other methods, by Lossen and Otto.

With respect to the body melting at 147°, which in properties seemed to resemble the dinaphthyl obtained by Lossen, it will be remembered that Otto (*Liebig's Annalen*, cxlvii, 170) obtained a body crystallising from alcohol in little yellow plates, and melting at 133°, by heating mercuro-dinaphthyl with soda lime. Now this body Otto seemed to think might possibly be identical with Lossen's dinaphthyl, as it agreed very well in its properties, excepting that the melting point was lower, 133°, Lossen's melting at 154°). Otto had extremely little substance, and this appeared to be not quite pure, "of a canary-yellow colour." Now the substance I obtained agrees exactly in all respects with that described by Otto, appearing first in little canary-yellow plates melting at 137°, and dissolving in alcohol, ether, benzene, and petroleum spirit. By carefully recrystallising, however, the body was obtained almost white, and then it melted at 147°. I do not think it at all impossible that the dinaphthyl obtained by Lossen may have been mixed with traces of the isodinaphthyl melting at 184°, and formed in small quantity by Lossen's process simultaneously with his hydrocarbon. Such an event would readily account for a melting point being raised 7° (*e.g.*, 147° to 154°). On the other hand, I cannot think that my hydrocarbon melting at 147° was perceptibly contaminated with the body melting at 75°, as the former crystallised out at once on cooling from alcohol, and so could easily be filtered and washed free from the latter, which never began to crystallise till after several days The body melting at 75°, and already described, I believe to be a third dinaphthyl, thus completing the number of possible isomerides of this hydrocarbon. Combustions were made of these two new bodies, with the following results:—

Substance melting at 147°.

Weight of substance taken ...... = 0·3295 gram.
Weight of CO_2 obtained .... = 1·1410 „
Weight of H_2O obtained .... = 0·1755 „

	Found.	Calculated for $C_{20}H_{14}$.
Carbon	94·44	94·48
Hydrogen	5·91	5·52
	100·35	100·00

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Substance melting at 75°.

Weight of substance taken ...... = 0·3000 gram.
Weight of CO_2 obtained .... = 1·0420 ,,
Weight of H_2O obtained .... = 0·1550 ,,

	Found.	Calculated for $C_{20}H_{14}$.
Carbon	94·73	94·48
Hydrogen	5·74	5·52
	100·47	100·00

The combustions of this body were a matter of some difficulty, owing to the refractory nature of the substance, and I take this opportunity of thanking my friend Mr. T. G. Young for his assistance in the operations.

It would now appear that there exist three isomeric dinaphthyls, all of which are obtainable, though in very different quantities, by passing naphthalene, together with antimony chloride, through a red-hot tube. By far the largest proportion consists of isodinaphthyl, melting at 187°; the next in quantity is the low-melting isomeride (75°); the one melting at 147°, and apparently identical with Lossen's, is formed by this method in extremely small quantity. It is curious to notice the regular gradation in *solubility*, *crystallisability*, and *fusibility* in the case of these three isomerides.

Dinaphthyl No. 1 (Isodinaphthyl).	*Dinaphthyl* No. 2 (Lossen's).	*Dinaphthyl* No. 3.
Melting points 187°	147°. (Smith)...... 154°. (Lossen)	75°.
Crystallisability— Most readily crystallisable. Beautiful rhombic plates, very regular, and the prevailing crystalline form from solvents, even from very impure solutions.	Crystallises readily, but not so much so as No. 1. Crystallisability modified more by impurities present, and crystalline form more variable.	Very difficult to crystallise. Requires some days or a week. Crystalline form subject to considerable modification.
Solubility— Difficultly soluble in alcohol and ether. Benzol and petroleum spirit must be boiling to dissolve it freely, and also be in excess.	Soluble in alcohol and ether, &c., much more so than No. 1.	Very soluble in all the afore-named liquids, from which it crystallises with great difficulty.

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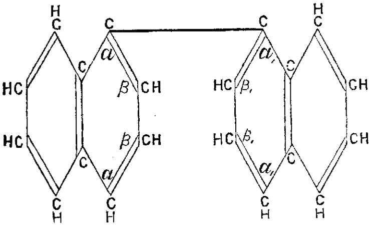
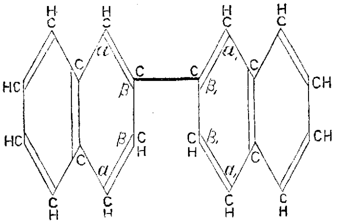
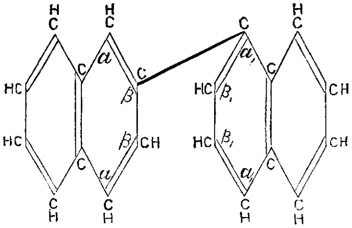
Practically there are three possible dinaphthyls, namely, the following:—



α-α-Dinaphthyl (Lossen's).



β-β-Dinaphthyl.



α-β-Dinaphthyl.

Undoubtedly Lossen's dinaphthyl must be the α-α-isomeride, as he obtained it by the action of sodium-amalgam on α-bromnaphthalene. With regard to the other two dinaphthyls, I consider it extremely probable that the so-called isodinaphthyl obtained by me, and melting at 187°, is the β-β-isomeride, and this view is supported by the following consideration:—Liebermann, in his "Studien in der Naphtalingruppe" (*Liebig's Annalen*, clxxxiii, 271; *J. Chem. Soc.*, April, 1877), on comparing the melting points of the corresponding isomeric α- and β-naphthalene derivatives, has observed that out of *fourteen* well studied and known bodies, *twelve* of those in the β-class melt higher than their isomerides in the α-class. The examples, which are very striking, are as follows:—

Isomeric Naphthalene Derivatives.

	Melting Points.			*Melting Points.*	
	α.	β.		α.	β.
$C_{10}H_7Cl$	liquid	56° (61, 53 ?)	$C_{10}H_7.NH_2$	50°	112°
$C_{10}H_7Br$	liquid	69°	$C_{10}H_7.NH.C_2H_3O$	159°	132°
$C_{10}H_7Cy$	37°	66°	$C_{10}H_7.CO_2H$	161°	181°
$C_{10}H_7.OH$	94°	122°	$C_{10}H_7.COCl$	liquid	43°
$C_{10}H_7.OC_2H_5$	liquid	33°	$C_{10}H_7.CONH_2$	204°	192°
$C_{10}H_7.OC_2H_3O$	liquid	60°	$C_{10}H_7.CO.C_6H_5$	75°	82°
$C_{10}H_7.SH$	liquid	137°	$C_{10}H_7.SO_2Cl$	66°	76°

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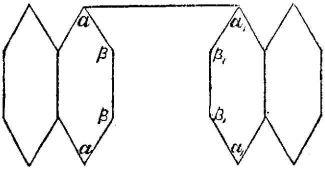
Now regarding these numbers so arranged, it may be observed that dinaphthyl, also a naphthalene derivative, most probably forms another example of the peculiarity noticed by Liebermann. Thus—

	α.	β.	α-β.
$C_{10}H_7.C_{10}H_7$	154° (147°)	187°	75°

Therefore, in all probability, β-β-dinaphthyl is no other than the so-called isodinaphthyl, and this leaves the third and new dinaphthyl in the α-β-position.

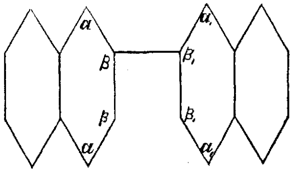
The balance of probability then appears to favour the following arrangement:—

α-α-Dinaphthyl (Lossen's).



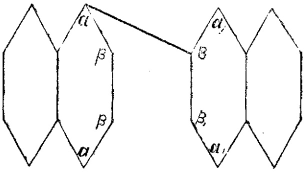
Melting point = 154° (147°).
Generally soluble; crystallises with moderate facility.

β-β-Dinaphthyl (Isodinaphthyl).



Melting point = 187°.
Not easily soluble; crystallises very readily.

α-β-Dinaphthyl.



Melting point = 75°.
Very soluble, and difficult to crystallise.

All the dinaphthyls boil above 300°, but that melting at 75° does not appear to boil so high as the one melting at 187°. Possibly the one melting at 147° has an intermediate boiling point.

It is probable that by gentle oxidation of these dinaphthyls, the corresponding isomeric naphthoic acids may be obtained, viz., from α-α-dinaphthyl one might expect to get α-naphthoic acid, from β-β-dinaphthyl β-naphthoic acid, whilst α-β-dinaphthyl would probably yield a mixture of these isomeric acids. It is further very possible that by the exhaustive chlorination of these hydrocarbons, much light may be thrown upon their respective isomeric constitutions. Ruoff in this manner obtained extremely interesting results with diphenyl, viz., the formation of perchlorodiphenyl. It would be interesting to ascertain

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whether by this action of chlorine, perchlorodiphenyl or perchlorobenzene could be formed from the dinaphthyls. A further examination of the respective sulpho-acids of these bodies, their conversion into the corresponding cyanides by distillation with potassium cyanide, and after-treatment with alcoholic potash, with possible formation of the isomeric naphthoic acids, would also probably yield much instruction. These further researches I intend to take up on an early occasion.

I conclude, thanking Prof. Lunge, in whose laboratory this work was done, for his kindness to me whilst thus engaged.