II. — *Action of Chloride of Cyanogen on Naphthalamine.*

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MM. CAHOURS and CLOEZ, in their investigations on naphthalamine, observed that it combined with chloride of cyanogen, forming the hydrochlorate of a new base. They, however, did not investigate this subject any further; and as it was interesting to know whether compounds similar to those obtained from melaniline might be produced, I undertook, at the request of Dr. Hofmann, to examine this reaction more minutely.

Preparation of Naphthalamine. — The preparation of naphthalamine is effected by distilling nitronaphthaline with iron and acetic acid, according to the process of Zinin, modified by Béchamp.

This process yields the base in considerable quantity, but in an impure condition. To purify this, it must be dissolved in hydrochloric acid and water, and filtered from all insoluble impurities; the filtrate is then evaporated to dryness, and distilled with lime, when the base comes over nearly pure and perfectly anhydrous.

Preparation of Menaphthalamine. — In subjecting naphthalamine to the action of chloride of cyanogen, I adopted the same arrangement that Dr. Hofmann had used in the preparation of melaniline; namely, a series of tubes filled with the alkaloid through which the chloride of cyanogen was drawn by means of an aspirator. However, in this case it is necessary to support the action from the commencement by the application of heat, naphthalamine being a solid substance.

When the gas is passed into the fused anhydrous naphthalamine, chemical action is at once rendered perceptible by a rapid eleva-

tion of the temperature, and the gradual thickening of the liquid, which prevents the gas from passing freely. To complete the reaction, heat must be carefully applied sufficient to keep the compound in a state of fusion.

On cooling, the naphthalamine is found converted into a black resinous mass, which consists principally of the hydrochlorate of a base, which I propose to call menaphthalamine.

On boiling this mass in a large quantity of water, it almost entirely dissolves. On adding potassa or ammonia to the filtered liquid, a white precipitate is produced, which is freed from chloride of potassium, or ammonium, by washing with water, and recrystallised once or twice from alcohol, from which it is deposited in small white needles.

This base, when dried at 100° C. and burnt with protoxide of copper, gave the following numbers:—

I.	0·249	grm. of menaphthalamine gave
	0·7385	„ carbonic acid,
	0·1275	„ water.
II.	0·2840	„ menaphthalamine gave
	0·8425	„ carbonic acid,
	0·1410	„ water.

These numbers lead to the following percentage composition:—

	I.	II.
Carbon . .	80·88	80·90
Hydrogen . .	5·40	5·50

Two analyses of the platinum-salt gave a mean of 19·065 per cent. of platinum.

Equivalent deduced from the platinum-salt = 311·24

Theoretical equivalent = 311·00

These results lead to the formula

which require the following values:—

	Theory.		Mean of experiments.
42 equiv. of carbon . .	252·0	81·0	80·89
17 equiv. of hydrogen . .	17·0	5·4	5·45
3 equiv. of nitrogen . .	42·0	13·6	
	<hr/> 311·0	<hr/> 100·0	

This shows that the formation of menaphthalamine is perfectly analogous to that of melaniline and metoluidine, 2 equiv. of naphthalamine and 1 equiv. of chloride of cyanogen yielding 1 equiv. of the hydrochlorate of menaphthalamine.

Properties of Menaphthalamine. — This base, when pure, crystallises in small white needles, which are not coloured by exposure to the atmosphere.

Menaphthalamine is odourless; it has a bitter taste; fuses at about 200° C. into a transparent slightly yellowish oil. If the temperature be raised above 260° C., decomposition ensues, pure naphthalamine distils over, and a brown mass remains in the retort. In the case of melaniline, the residue had the formula $\text{C}_{54} \text{ H}_{25} \text{ N}_7$, which may be regarded as a compound of aniline-mellone with 3 equiv. of aniline.

It is probable that the menaphthalamine residue has an analogous composition.

Menaphthalamine is almost insoluble in water, and only moderately soluble in alcohol and ether. It changes the colour of red litmus-paper. Chromic acid acts but slowly upon it.

COMBINATIONS OF MENAPHTHALAMINE.

This base forms salts with all acids, many of which are amorphous or very slightly crystalline. They are all sparingly soluble in water.

The salts have no action on litmus-paper. They are precipitated by acids and saline solutions; potassa and ammonia decompose them, the base being separated in the form of a pure white powder.

Hydrochlorate of Menaphthalamine. — This salt is a white amorphous compound, which becomes slightly red when exposed to air and moisture. It is moderately soluble in water, and very soluble in alcohol and ether: when heated, it is decomposed, hydrochlorate of naphthalamine subliming, and leaving a black residue in the retort.

A determination of hydrochloric acid gave the following result :—

0·4422 grm. of hydrochlorate gave
 0·682 „ chloride of silver, corresponding to
 10·44 per cent. of hydrochloric acid.

This number leads to the formula

which requires the following values :—

	Theory.		Experiment.
1 equivalent of menaphthalamine =	311·0	89·6	—
1 equivalent of hydrochloric acid =	36·5	10·4	10·44
	347·5	100·0	

Sulphate.— This salt is best obtained by neutralising sulphuric acid with menaphthalamine. It is a white, perfectly amorphous salt, moderately soluble in alcohol and ether, which on evaporation deposit it in the form of a white powder.

Nitrate.— This salt, which is the finest of all the menaphthalamine salts, may be prepared by adding menaphthalamine to very dilute boiling nitric acid. This solution, on standing, deposits the nitrate in small white prisms, nearly insoluble in cold water, but very soluble in alcohol and ether.

Phosphate.— It is a white crystalline salt, very soluble in alcohol and ether.

Binoxalate.— This salt is best obtained by boiling menaphthalamine with an excess of oxalic acid. From this solution the salt crystallises in small tufts of white needles, which are not easily soluble in water, but moderately soluble in alcohol and ether.

Hydromate and Hydriodate.— These salts are crystalline, and very soluble in alcohol.

Hydrochloroplatinate.— This compound is best prepared by adding an alcoholic solution of bichloride of platinum to a warm alcoholic solution of the hydrochlorate of menaphthalamine; from this solution, small yellow crystalline scales are deposited. If, however, the aqueous solutions are employed, it is immediately precipitated as an amorphous powder, which is almost white, but soon becomes slightly green.

Two determinations of the platinum gave the following numbers:—

I.	0·229	grm. of the salt gave		
	0·0435	„ „	platinum.	
II.	0·19975	„ „	salt gave	
	0·03775	„ „	platinum.	
		Theory.	Experiment.	
			I.	II.
Percentage of platinum in the	}			
platinum-salt . . .		19 08	19·04	19·09

Terchloride of gold gives with menaphthalamine-salts a blue precipitate.

METAMORPHOSES OF MENAPHTHALAMINE.

Menaphthalamine, when exposed to the action of various agents, undergoes a variety of transformations, many of which I have not been able to study.

Action of Sulphuric Acid.—When Nordhausen sulphuric acid is brought in contact with menaphthalamine, it becomes pasty, owing to the formation of the sulphate; but if a gentle heat be applied it becomes perfectly liquid. This liquid, on being diluted with water and treated with carbonate of lead, produces a soluble lead-salt, of a new acid, which decomposes partially every time it is evaporated.

On passing sulphuretted hydrogen through a solution of the lead-salt, a colourless solution is obtained (with precipitation of the lead as sulphide). When this liquid is evaporated, the new acid is decomposed into a soluble alkaline body, and an insoluble neutral one.

Action of Fuming Nitric Acid.—This acid acts violently on menaphthalamine, producing a variety of substitution-products.

Chlorine, bromine, and iodine seem to produce neutral compounds.

Action of Cyanogen.—If cyanogen is passed through an alcoholic or ethereal solution of menaphthalamine, it becomes first yellow, and then red, nothing being deposited on standing; but if the base is made into a thin paste with ether, and cyanogen passed through it, it all dissolves; and, on standing, the solution deposits a slightly crystalline body of a light buff colour, which may be purified by washing with ether.

A combustion of a specimen dried at 100° C. gave the following results :—

0·274	grm. of the substance gave
0·764	„ carbonic acid, and
0·1292	„ water,

which gives the following percentage composition :—

Carbon	.	.	.	.	76·00
Hydrogen	.	.	.	.	4·71

This may be translated into the formula

as may be seen by the following table :—

		Theory.	Experiment.
46 equiv. of carbon	.	276	76·00
17 „ hydrogen	.	17	4·69
5 „ nitrogen	.	70	19·31
		363	100·00

This compound, therefore, like dicyanomelaniline, is formed by the combination of two equivalents of cyanogen with one of menaphthalamine.

DICYMENAPHTHALAMINE (which name I propose for this compound) is a slightly buff-coloured body, which crystallises with difficulty ; it is moderately soluble in alcohol and ether, but insoluble in water.

It is a base, though a very unstable one ; it dissolves readily in dilute acids, and may be reprecipitated by ammonia if added directly after solution ; but, like cyaniline and dicyanomelaniline, this base cannot remain in acid solutions without undergoing complete decomposition. If this base be dissolved in hydrochloric acid, and the solution allowed to stand for a few moments, it becomes cloudy, and a yellow substance begins to appear, which is not the hydrochlorate of dicymenaphthalamine.

The best process for the preparation of this new compound consists in adding dilute hydrochloric acid to a warm alcoholic solution of dicymenaphthalamine. On standing, it is deposited in

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small scales of a yellow colour. The mother-liquors from the preparation of this compound always contained ammonia.

The analysis of this compound dried at 100° C. gave the following results :—

0·212	grm. of substance gave
0·590	„ carbonic acid, and
0·080	„ water.

These numbers lead to the following percentage composition :—

Carbon	=	75·6
Hydrogen	=	4·2

which may be translated into the formula

as is evident from the following comparison of the theoretical with the experimental values :—

		Theory.	Experiment.
46 equiv. of carbon . .	. .	276·0	75·66
15 „ hydrogen . .	. .	15·0	4·10
3 „ nitrogen . .	. .	42·0	11·50
4 „ oxygen . .	. .	32·0	8·74
		<hr/> 365·0	<hr/> 100·00

This substance, which I propose to call MENAPHTHOXIMIDE, is perfectly analogous in its properties to melanoximide.

Its formation is, as illustrated by the following equation,—

This substance is insoluble in water, and very slightly in alcohol and ether, from which it may be crystallised, but with difficulty.

Menaphthoximide may be regarded as binoxalate of menaphthalamine minus 4 equivalents of water,—a view which is supported by experiment. On addition of potassa to this compound, menaphthalamine is reproduced, and the mother-liquor is found to contain oxalic acid.

The action of acids upon menaphthoximide is precisely the same as in the case of melanoximide; namely, it is converted into oxalic

acid, menaphthalamine, and a white neutral body, to which I intend to return at some future period.

Action of Heat on Menaphthoximide.—When menaphthoximide is heated to 245° C., it fuses; if the temperature be raised to 260° C., it decomposes, with evolution of a white vapour, having a most peculiar and powerful odour. I believe that this reaction is analogous to that which melanoximide undergoes when submitted to the influence of heat, and that the substance produced corresponds to Dr. Hofmann's anilocyanic acid,—in fact, that it is the naphthalamine term corresponding to cyanic acid, or naphthalocyanic acid; but I have not been able to obtain this compound in sufficient quantity to establish this supposition by experiment. I hope, however, to return to the examination of this most interesting subject as soon as possible.

In conclusion, I have to thank Dr. Hofmann for the advice and assistance he has afforded me during the prosecution of this investigation.