VII.—*The Action of Chloroform and Alcoholic Potash on Hydrazines.*
(Part III.)

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It has been previously shown that the action on phenylhydrazine of the agents mentioned in the title gives rise to the formation of a basic substance which is to be regarded as a diphenyl-derivative of *tetrazine*, $N \begin{smallmatrix} \text{CH} \cdot \text{NH} \\ \text{NH} \cdot \text{CH} \end{smallmatrix} N$. The application of the reaction to homologues of phenylhydrazine has resulted in the formation of homologues of diphenyltetrazine, and it is to the description of several of these compounds that this paper will be devoted.

Paraditolyltetrazine.

In the previous paper (Trans., 1889, 242), although diphenyltetrazine was the chief subject of study, it was mentioned that a ditolyltetrazine could be prepared from paratolylhydrazine. I have subjected this substance to a closer study, and have found that it is a weaker base than diphenyltetrazine, but that, like the latter, it dissolves, although with difficulty, in boiling hydrochloric acid, from which, on cooling, slender, white needles of the hydrochloride are deposited. These are, however, very unstable, and, on drying over potash and sulphuric acid, continually lose hydrogen chloride. This circumstance explains the discrepancy which will be observed in the following numbers:—

	Calculated for $C_{16}H_{16}N_4, HCl$.	Found.	
		I.	II.
Cl	11.81	10.76	11.0

Paraditolyltetrazine combines with 1 mol. of methyl iodide, when it is heated with a solution of the iodide in methyl alcohol at a

temperature of 100° , and yields a *methiodide* of the formula $C_{16}H_{16}N_4, CH_3I$, as shown by the analysis:—

	Calculated.	Found.
I	31.28	31.16
N	13.793	14.00

This compound is sparingly soluble in boiling water, and crystallises from the aqueous solution in colourless needles which melt at 242° .

Nitroparaditolyltetrazine is formed by adding fuming nitric acid to the solution of the tetrazine in acetic acid, and is thrown down by water as a yellow precipitate which is easily soluble in glacial acetic acid and in alcohol, and crystallises from methylated spirit in orange needles which melt at 144° .

The formula, $C_{16}H_{16}(NO_2)N_4$, requires—

	Theory.	Found.	
		I.	II.
C	62.14	62.5	—
H.....	4.85	5.0	—
N.....	22.65	—	22.75

The formation of a nitro-compound, so readily soluble in acetic acid and with such a low melting point as compared with that of nitrodiphenyltetrazine (above 300°), led me to repeat this experiment; but I arrived at the same result. There is only one nitro-derivative formed.

I, therefore, reinvestigated the action of nitric acid on diphenyltetrazine, and found that besides the nitro-derivative already described, there is formed another which is easily soluble in acetic acid or alcohol, and crystallises from the latter in yellowish-red needles which melt at 145 — 146° . A nitrogen determination proved this substance to be an isomeric *nitrodiphenyltetrazine*. The formula, $C_{14}H_{11}(NO_2)N_4$, requires:—

	Theory.	Found.
N	24.91	24.98

The action of bromine on paraditolyltetrazine results in the formation of two bromine-derivatives. On adding bromine to the solution of the tetrazine in glacial acetic acid, a white, crystalline precipitate separates which, when recrystallised from the same solvent or from boiling alcohol, forms needles melting at 245° with decomposition. A nitrogen determination of this substance proved it to be a *dibromoparaditolyltetrazine*. Its formula, $C_{16}H_{14}Br_2N_4$, requires—

	Theory.	Found.
N	13·27	13·67

Besides this bromine-derivative, another is also formed, which remains dissolved in the acetic acid after the first has separated out, but can be precipitated from it by water. It is extremely soluble in alcohol, and crystallises from dilute spirit in colourless, slender needles which melt at 81°. Lack of material prevented me from analysing this substance; but from analogy to the action of bromine on diphenyltetrazine, it is probable that the compound melting at 81° is an isomeric dibrominated substitution-product.

Orthoditolyltetrazine.

This is prepared by a method similar to that which yields the other tetrazines; but in this case it is necessary to take the precaution of adding the alcoholic potash to the solution of the hydrazine and chloroform in spirit very gradually; warming only slightly until the reaction begins, or else the hydrazine suffers complete decomposition, and a brown, viscid mass is formed. The product of the reaction was treated as in the other cases, namely, after dilution with water it was shaken with ether, the unaltered hydrazine removed from the ethereal solution by dilute sulphuric acid, and the ether evaporated. A brown oil was then left, and from this, after some time, crystals separated; these are readily soluble in alcohol, and crystallise from it in slightly coloured plates. This substance is *orthoditolyltetrazine*. For complete purification, it was found advisable to transform it into the hydrochloride and to decompose this by boiling with an aqueous solution of ammonia. The tetrazine is thus obtained in colourless crystals which melt at 141°.

The following numbers correspond with the formula—

	(1)	(2)	(2)	(1)
	$\text{CH}_3 \cdot \text{C}_6\text{H}_4\text{N} < \begin{smallmatrix} \text{N} \cdot \text{CH} \\ \text{CH} \cdot \text{N} \end{smallmatrix} > \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3.$			
	Theory for $\text{C}_{16}\text{H}_{16}\text{N}_4$.			
C	72·73		72·704	—
H	6·06		6·09	—
N	21·21		—	21·32
			Found.	
			I.	II.

This formula was, moreover, verified by the determination of the molecular weight, and by the study of its behaviour towards nitric and sulphuric acids.

A molecular-weight determination by Raoult's method gave the following result:—

Weight of substance	0.4104 grams.
„ acetic acid	23.9212 „
Freezing point of acetic acid....	14.60° C.
„ mixture.....	14.86 „
Depression of freezing point	0.26 „
Molecular weight derived from the above data	258
Theory for $C_{16}H_{16}N_4$	264

Orthoditolyltetrazine is dissolved by boiling hydrochloric acid, and the solution on cooling deposits white needles of the *hydrochloride* which, when dried at 100°, lose hydrogen chloride, but may be dried over sulphuric acid and potash without suffering decomposition—as shown by the analysis, which gave:—

	Calculated for $C_{16}H_{16}N_4, HCl$.	Found.
Cl	11.81	11.61
N	18.64	18.77

Orthoditolyltetrazine also combines with 1 mol. of methyl iodide when the two are heated together in methyl alcohol solution at 100° for a few hours. If the solution is evaporated on the water-bath and the residue dissolved in boiling water, white nodules crystallise out on cooling: these melt at 198° and turn slightly yellow on drying at 100°.

The following numbers correspond to the formula $C_{16}H_{16}N_4, CH_3I$:—

	Theory for $C_{17}H_{19}N_4I$.	Found.
N	13.79	13.93
I	31.28	30.74

The action of sulphuric acid on orthoditolyltetrazine gives rise to a *sulphonic acid*; this is obtained on warming the base with concentrated sulphuric acid, when it dissolves. On adding water, a slightly bluish precipitate is thrown down, which is sparingly soluble in boiling water, and on cooling crystallises in colourless prisms which are free from water of crystallisation, and gave on analysis values corresponding to the formula $C_{16}H_{15}N_4 \cdot HSO_3$:—

	Theory.	Found.
S	9.3	9.15
N	16.28	16.56

On adding fuming nitric acid to the solution of the tetrazine in glacial acetic acid, crystals are deposited after a short time which are sparingly soluble in alcohol, and crystallise from it in yellow needles melting at 206—207°.

Analysis shows this compound to be a *mononitro-derivative* of orthoditolyltetrazine. The formula, $C_{16}H_{15}(NO_2)N_4$, requires—

	Calculated for $C_{16}H_{15}N_5O_2$.	Found.	
		I.	II.
C.....	62.13	61.873	—
H.....	4.85	4.91	—
N.....	22.65	—	22.80

Whilst the formation of tetrazines from phenylhydrazine and paratolylhydrazine is accompanied by that of the formyl-derivatives of the corresponding hydrazines, formylorthotolylhydrazine could not be obtained by the isonitrile reaction; it is, however, easily prepared by heating orthotolylhydrazine with formamide in an oil-bath at about 120° until ammonia ceases to be evolved. The product of the reaction solidifies on cooling and crystallises from water in colourless plates melting at 120°; these on analysis gave numbers corresponding to the formula $CH_3 \cdot C_6H_4 \cdot NH \cdot NH \cdot CHO$ [$CH_3 : NH = 1 : 2$]:—

	Calculated for $C_8H_{10}N_2O$.	Found.		
		I.	II.	III.
C.....	64.0	64.2	—	—
H.....	6.67	6.87	—	—
N.....	18.67	—	18.53	18.80

Although the preceding researches are in themselves sufficient to show that in general the action of chloroform and alcoholic potash on phenylhydrazine and its homologues gives rise to substituted tetrazines, yet I thought it desirable to apply this reaction to a still higher member of the primary hydrazines. I have chosen pseudocumylhydrazine.

Pseudocumylhydrazine.

This compound has already been obtained by Haller (*Berichte*, **18**, 89) by the method described by E. Fischer (*Annalen*, **190**, 67) for the preparation of phenylhydrazine. I can confirm Haller's statement that pseudocumylhydrazine cannot be prepared according to V. Meyer and Lecco's method (*Berichte*, **16**, 2976), as on mixing the stannous chloride and diazo-solution evolution of nitrogen takes place, and a tarry product is formed.

Pseudocumylhydrazine is sparingly soluble in ether and decomposes readily. Before applying the isonitrile reaction to this base I have subjected it to a closer study with the object of characterising it by some derivatives.

Acetylpsudocumylhydrazine.—Acetic anhydride acts on the hydrazine with development of heat. The reaction was completed on the water-bath and the product recrystallised from boiling water. It forms colourless plates which are readily soluble in alcohol and melt at 156—157°. When submitted to analysis, it gave numbers corresponding to the formula $C_6H_2(CH_3)_3NH \cdot NH \cdot CO \cdot CH_3$:—

	Theory for $C_{12}H_{16}N_2O$.	Found.	
		I.	II.
C	68·75	68·57	—
H	8·33	8·41	—
N	14·57	—	14·60

Pseudocumylsemicarbazide is formed by adding an aqueous solution of potassium cyanate to a solution of the hydrazine hydrochloride in water. The precipitate thrown down is sparingly soluble in water, but readily in alcohol, and crystallises from the latter solvent in colourless needles which melt at 195°.

The formula, $C_6H_2(CH_3)_3NH \cdot NH \cdot CO \cdot NH_2$, requires:—

	Theory for $C_{10}H_{14}N_3O$.	Found.	
		I.	II.
C	62·17	61·93	—
H	7·77	7·78	—
N	21·76	—	21·97

Benzylidene-pseudocumylhydrazine, $C_6H_2(CH_3)_3NH \cdot N : CH \cdot C_6H_5$, prepared from the hydrochloride of the hydrazine in the usual manner, crystallises from alcohol in coloured needles which decompose at 100° and also, after some time, at the ordinary temperature.

A nitrogen determination of this substance dried in a vacuum over sulphuric acid gave—

	Calculated for $C_{16}H_{18}N_2$.	Found.
N	11·76	12·0

Pseudocumylhydrazine-pyruvic acid,

On adding pyruvic acid to an aqueous solution of the hydrazine hydrochloride, a lemon-yellow, flocculent precipitate is at once thrown down which is soluble in alcohol and crystallises from it in yellow needles melting at 148° with decomposition.

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The formula, $C_{12}H_{16}N_2O_2$, requires—

	Theory.	Found.		
		I.	II.	III.
C	65·45	65·20	—	—
H	7·27	7·36	—	—
N	12·73	—	12·69	12·97

Pseudocumylhydrazine, when treated with chloroform and alcoholic potash in the manner previously described, yields a compound which is very sparingly soluble in alcohol but readily in boiling glacial acetic acid, and crystallises from the latter in yellow needles which melt at 234° . This substance is, without doubt, *dipseudocumyl-tetrazine*.

I hope to communicate to the Society the results of the further study of this tetrazine in another paper.

I may here mention that I have already begun to study the action of chloroform and alcoholic potash on other derivatives of phenylhydrazine. In a note published recently in conjunction with F. F. Blackman (*Trans.*, 1889, 612) it was stated that the above-mentioned reagents do not yield the corresponding tetrazine with benzophenylhydrazine. I have since then applied the isonitrile reaction to parabromophenylhydrazine. When this hydrazine, which has been described by Neufeld (*Annalen*, 248, 94), is treated with alcoholic potash and chloroform it yields, after removal of the unaltered hydrazine, a crystalline residue. Hot water extracts from it a substance which, when repeatedly recrystallised from boiling water, can be obtained in colourless, iridescent needles melting at 198° . Analysis of this compound proved it to be formyl-parabromophenylhydrazine.

Its formula, $C_6H_4Br \cdot NH \cdot NH \cdot CHO$ [$Br : NH = 1 : 4$], requires:—

	Theory for $C_7H_7N_2OBr$.	Found.		
		I.	II.	III.
N	13·02	13·44	13·19	—
Br	37·2	—	—	37·12

The formyl-compound is the chief product of the isonitrile reaction on parabromophenylhydrazine, but along with it a substance is formed which decomposes so readily that hitherto I have been prevented from analysing it. I shall, however, repeat this experiment, and hope to lay the result before the Society in my next communication.

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