LVII.—*Chlorinated Phenylhydrazines.* Part II.

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IN 1891, I published an account of some derivatives of ortho- and para-chlorophenylhydrazines (Trans., 1891, **59**, 209). Parachlorophenylhydrazine had already been prepared by Elsingshorst, and the base and its hydrochloride had been described in a foot-note to a paper by Neufeld on halogen substituted phenylhydrazines (*Annalen*, **248**, 94). Shortly after the appearance of Part I of this work, Willgerodt published an account of orthochlorophenylhydrazine and some of its derivatives (*Ber.*, **24**, 1660); but instead of separating the base from its hydrochloride by sodium acetate, and subsequently extracting with ether, he precipitates a warm solution with concentrated ammonia, and on cooling the base is deposited in plates. Prepared in this way, orthochlorophenylhydrazine melts at 47°; Willgerodt's method is superior to that indicated above, in which the hydrazine is extracted with ether, as the ethereal solution when evaporated does not always readily yield crystals.

Orthochlorophenylhydrazine sulphate was obtained on agitating an ethereal solution of the hydrazine with dilute sulphuric acid, and on recrystallisation from water, it was deposited in fine, colourless needles which, after drying at 110°, gave the following analytical result.

0.1612 gave 0.0979 BaSO₄. H₂SO₄ = 25.54.

(C₆H₇N₂Cl)₂.H₂SO₄ requires H₂SO₄ = 25.59 per cent.

The *oxalate* likewise crystallises out when an aqueous solution of the acid is shaken with an ethereal solution of the hydrazine; the *nitrate*, however, does not separate in such a satisfactory condition as in the case of metachlorophenylhydrazine.

On heating orthochlorophenylhydrazine with biuret, no well-defined urazole derivative was obtained; this behaviour is in contrast with that of meta- and para-chlorophenylhydrazines, which readily furnished such compounds.

Ethylic Salt of Pyruvic acid Orthochlorophenylhydrazone,

—In my former communication, the ethylic salt of pyruvic acid orthochlorophenylhydrazone was described as yellow needles melting at 168°; this should read 68°. The ethereal salt was best prepared

by heating 1 part of the hydrazone of pyruvic acid with 9 parts of absolute alcohol and 1 part of concentrated sulphuric acid in a reflux apparatus for three to four hours on the water-bath. On pouring the solution into water, the ethereal salt and unacted on acid separated in the crystalline condition; after removing the latter by treatment with dilute sodium carbonate solution, the ethereal salt was recrystallised from dilute alcohol; it was also dried in a vacuum and analysed.

0.2035 gave 20.7 c.c. moist nitrogen at 15° and 758 mm. $N = 11.9$.
 $C_6H_5ClN_2O_2$ requires $N = 11.64$ per cent.

The ethereal salt is insoluble in alkalis and ammonia, though easily soluble in alcohol.

Metachlorophenylhydrazine, $C_6H_4Cl \cdot NH \cdot NH_2$ [$Cl : NH = 1 : 3$].—*Metachlorophenylhydrazine*, its hydrochloride, and several of its derivatives were first prepared and described by Willgerodt and Mühe (*J. pr. Chem.*, **44**, 451). These chemists added 14 grams of sodium nitrite dissolved in 100 grams of water to a well cooled solution of 25 grams of metachloraniline in 400 grams of hydrochloric acid (sp. gr. 1.12). On the addition of 89 grams of stannous chloride in 100 grams of hydrochloric acid, a precipitate of the stannochloride was obtained, from which as much tin as possible was removed by washing with concentrated hydrochloric acid. By dissolving the salt in a small quantity of water, and adding strong potash, the hydrazine was obtained as a brown oil which decomposed at 200—220°.

The metachlorophenylhydrazine hydrochloride used in the preparation of the derivatives described in this paper was obtained in a somewhat different manner, the crude hydrochloride formed by the action of stannous chloride being dissolved in water, and freed from tin by a current of sulphuretted hydrogen. The solution was then concentrated, and the hydrochloride which separated was redissolved in boiling water, decolorised with animal charcoal, allowed to crystallise from the hot solution, and collected. The salt separated in small crystals having the appearance of plates, but, when viewed under the microscope, were seen to consist of groups of needles. The formula of the compound was confirmed by a nitrogen estimation in the salt dried at 100°.

0.1795 gave 24.2 c.c. moist nitrogen at 18° and 757 mm. $N = 15.6$.
 $C_6H_7ClN_2 \cdot HCl$ requires $N = 15.6$ per cent.

This salt is easily soluble in water and alcohol, but is precipitated from the solution by the addition of concentrated hydrochloric acid.

Metachlorophenylhydrazine sulphate separates as colourless needles on shaking an ethereal solution of the hydrazine with dilute sulphuric

acid. The specimen used for analysis was recrystallised from hot water and dried at 100°.

0.2170 gave 0.1297 BaSO₄. H₂SO₄ = 25.14.

(C₆H₇ClN₂)₂.H₂SO₄ requires H₂SO₄ = 25.59 per cent.

Metachlorophenylhydrazine nitrate was prepared by mixing ethereal solutions of the hydrazine and concentrated nitric acid. A crystalline, colourless precipitate of the salt separated immediately; this was collected and recrystallised from hot water, from which it separated as fine, colourless needles. These began to turn brown about 150°, and decomposed completely at 175°.

0.1215 gave 21.7 c.c. moist nitrogen at 17° and 752 mm. N = 20.5.

C₆H₇ClN₂.HNO₃ requires N = 20.44 per cent.

Metachlorophenylsemicarbazide, C₆H₄Cl·NH·NH·CO·NH₂ [Cl : NH = 1 : 3].—On adding potassium cyanate to a concentrated aqueous solution of the hydrochloride, a crystalline precipitate of this compound was at once formed. On recrystallisation from hot dilute alcohol, it was obtained in the form of colourless, flat prisms or plates which melted at 155°.

The formula was confirmed by a nitrogen estimation after the substance had been carefully dried.

0.1986 gave 40.2 c.c. moist nitrogen at 18° and 749 mm. N = 23.0.

C₇H₅ClN₃O requires N = 22.64 per cent.

Metachlorophenylsemicarbazide is easily soluble in alcohol and glacial acetic acid, somewhat soluble in hot water, but only very sparingly in the cold; it is insoluble in chloroform and carbon bisulphide. An ethereal solution turns pale green when shaken with an aqueous solution of copper sulphate.

Metachlorophenylphenylthiosemicarbazide,

C₆H₄Cl·NH·NH·CS·NH·C₆H₅ [Cl : NH = 1 : 3],

was formed on mixing an ethereal solution of metachlorophenylhydrazine with phenylthiocarbimide, and was deposited in magnificent colourless needles on allowing the ether to evaporate spontaneously. For analysis, it was recrystallised from dilute alcohol, and dried at 100°. A nitrogen determination gave the following result.

0.1753 gave 22.5 c.c. moist nitrogen at 15° and 754 mm. N = 14.9.

C₁₃H₁₂N₃ClS requires N = 15.14 per cent.

The substance crystallises in long, colourless needles which melt at 138—139°. An ethereal solution is coloured green on shaking it with an aqueous solution of copper sulphate; and as in the case of

the ortho- and para-compounds, this colour is rendered darker by ammonia.

—The hydrazine obtained by the evaporation of an ethereal solution was heated with an equal weight of biuret over a small flame. Ammonia escaped in considerable quantity; and the residue solidified on cooling; on recrystallising this from dilute alcohol, animal charcoal being used to effect decolorisation, the metachlorophenylurazole separated as small, faintly yellow crystals which melted at 227°.

0.2017 gave 33.3 c.c. moist nitrogen at 12° and 752 mm. $\text{N} = 19.4$.

$\text{C}_6\text{H}_4\text{ClN}_3\text{O}_2$ requires $\text{N} = 19.86$ per cent.

Metachlorophenylurazole is insoluble in carbon bisulphide and ether, but soluble in alcohol, glacial acetic acid, and alkalis; from the last-named solution it is reprecipitated by acids.

Benzaldehydemetachlorophenylhydrazone, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}\cdot\text{N}:\text{CH}\cdot\text{C}_6\text{H}_5$, $[\text{Cl} : \text{NH} = 1 : 3]$.—Metachlorophenylhydrazine resembles phenylhydrazine in the way in which it combines with aldehydes and ketones. For preparing the hydrazone of benzaldehyde, a solution of the hydrochloride of the base in warm water was treated with benzaldehyde and excess of ammonia. The yellow, granular precipitate was collected and washed, dissolved in hot alcohol, and water added until the liquid became turbid, then filtered and allowed to cool. The hydrazone separated as small, colourless needles melting at 133—134°; these turned red on exposure to the air, are insoluble in water, but easily soluble in alcohol and ether.

A nitrogen estimation of the substance dried at 100° gave the following result.

0.1548 gave 17.0 c.c. moist nitrogen at 18° and 756 mm. $\text{N} = 12.6$.

$\text{C}_{13}\text{H}_{11}\text{N}_2\text{Cl}$ requires $\text{N} = 12.6$ per cent.

Pyruvic acid metachlorophenylhydrazone,

—The addition of pyruvic acid to an aqueous solution of the hydrochloride led to an immediate separation of a pale yellow, crystalline precipitate, which was at once collected and recrystallised from dilute alcohol; the substance separated in fine needles which, after drying, furnished the following results on analysis.

0.3120 gave 36.7 c.c. moist nitrogen at 20° and 749 mm. $\text{N} = 13.25$.

$\text{C}_9\text{H}_9\text{N}_2\text{ClO}_2$ requires $\text{N} = 13.18$ per cent.

This substance melts at 163°, and is easily soluble in alcohol, ether, alkalis, and ammonia, but insoluble in water.

The *ethylic salt* of this acid was easily prepared by heating 1 part of the acid with 9 parts of absolute alcohol and 1 part of concentrated sulphuric acid for three to four hours on the water-bath. The liquid was then treated with a solution of sodium carbonate, and the ethylic salt which separated recrystallised from dilute alcohol. It melts at 82°, and is readily soluble in alcohol and ether. A nitrogen determination gave the following result.

0.1950 gave 18.8 c.c. moist nitrogen at 15° and 764 mm. $N = 11.3$.

$C_{11}H_{13}N_2ClO_2$ requires $N = 11.64$ per cent.

Parachlorophenylhydrazine has already been described by Elsingshorst* and Willgerodt (*J. pr. Chem.*, **43**, 482). As in the case of the ortho- and meta-compounds, the hydrochloride, contaminated with tin salts, was dissolved in warm water treated with hydrogen sulphide, and the tin sulphide filtered off; the hydrochloride then crystallised out in colourless needles. Willgerodt prepared the free hydrazine from the hydrochloride by precipitation with caustic soda and subsequent crystallisation from alcohol or ether; he gives the melting point of the hydrazine as 83°. Latterly, I have prepared the hydrazine by decomposing a warm, strong solution of the hydrochloride with concentrated sodium acetate solution; the hydrazine, which is fairly soluble in warm water, separates on cooling in magnificent colourless needles which, after being collected, well washed, and dried, melt at 90°, that is, 7° higher than the temperature given by Willgerodt. It is better to use the hydrazine very soon after its preparation, as darkening takes place very readily on exposure to air or light. This substance is easily soluble in alcohol and ether, and fairly in hot water; the sulphate is obtained by concentrating a solution of the base in dilute sulphuric acid.

Parachlorophenylsemicarbazide, $C_6H_4Cl \cdot NH \cdot NH \cdot CO \cdot NH_2$ [$Cl : NH = 1 : 4$].—On mixing solutions of the hydrochloride of parachlorophenylhydrazine and potassium cyanate in molecular proportion, the corresponding semicarbazide separated in beautiful plates. Recrystallised from dilute alcohol and dried at 100°, the compound gave the following analytical results.

I. 0.2101 gave 41.2 c.c. moist nitrogen at 19° and 761 mm. $N = 22.6$.

II. 0.1400 „ 0.0839 Ag. $Cl = 19.15$.

$C_7H_8N_3ClO$ requires $N = 22.64$; $Cl = 19.14$ per cent.

This substance melts at 233—234°, and is easily soluble in alcohol

* Apparently Elsingshorst only prepared the free base and its hydrochloride; his results are appended to a paper of Neufeld's on halogen substituted phenylhydrazines (*Annalen*, **248**, 94), and his Inaugural Dissertation is referred to (Erlangen, 1884, previously quoted by mistake as München).

and glacial acetic acid; it is also somewhat soluble in hot water, but insoluble in cold water, chloroform, ether, and carbon bisulphide.

Benzaldehydeparachlorophenylhydrazine, $C_6H_4Cl \cdot NH \cdot N : CH \cdot C_6H_5$ [Cl : NH = 1 : 4], was prepared by mixing a solution of the hydrochloride with benzaldehyde, and then adding sodium acetate, the precipitate being collected, washed with warm water, and recrystallised from dilute alcohol. A chlorine estimation gave the following result.

0.0973 gave 0.0447 Ag. Cl = 15.01.

$C_{13}H_{11}N_2Cl$ requires Cl = 15.41 per cent.

The substance separates from solution in groups of needles which melt at 127° , and are very easily soluble in alcohol, ether, and chloroform, fairly so in carbon bisulphide and glacial acetic acid.

Pyruvic acid parachlorophenylhydrazine,

$C_6H_4Cl \cdot NH \cdot N : C(CH_3) \cdot COOH$ [Cl : NH = 1 : 4],

separated as a yellow precipitate on mixing solutions of the hydrochloride and pyruvic acid; this was collected, dissolved in boiling alcohol, and water added until a turbidity was produced. On cooling, needles were obtained, which melted at 199° . It dissolved in alcohol, ether, and glacial acetic acid, but it is insoluble in water and carbon bisulphide. Analysis of the dried substance gave the following results.

I. 0.1255 gave 0.2353 CO_2 and 0.0498 H_2O . C = 51.13; H = 4.41.

II. 0.1183 „ 13.3 c.c. nitrogen at 20° and 755 mm. N = 12.8.

$C_9H_9N_2ClO_2$ requires C = 50.82; H = 4.23; N = 13.18 per cent.

The *ethylic salt* of this hydrazone was obtained in a similar way to the corresponding compounds in the ortho- and meta-series, and separated by water from the alcoholic solution. After treatment with sodium carbonate to remove unaltered acid, the substance was recrystallised from dilute alcohol. A nitrogen estimation gave the following result.

0.1610 gave 16.5 c.c. moist nitrogen at 20° and 770 mm. N = 11.9.

$C_{11}H_{13}ClN_2O_2$ requires N = 11.64 per cent.

The ethylic salt is easily soluble in alcohol, but insoluble in water; it melts at 138° .

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