

XXIV.—*Chlorinated Phenylhydrazines.*

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IN the following paper, orthochlorophenylhydrazine and some of its more important derivatives are described, and an account is also given of the action of carbamide on parachlorophenylhydrazine. The work was undertaken at the instance of Dr. Ruhemann, to whom I owe my best thanks for help afforded me during this investigation.

The *orthochlorophenylhydrazine hydrochloride*, $C_6H_4Cl \cdot NH \cdot NH_2, HCl$ [$Cl : N = 1 : 2$], was prepared from orthochloraniline; 45 grams of the latter were dissolved in 675 grams of concentrated hydrochloric acid, and diazotised by 26 grams of sodium nitrite dissolved in 180 grams of water. The solution of the orthochloraniline was well cooled in a freezing mixture, and the sodium nitrite solution added in small quantities at a time, the mixture being allowed to stand between each addition until the nitrous smell had disappeared. The solution was then rapidly filtered, and 152 grams of stannous chloride dissolved in an equal weight of concentrated hydrochloric acid added. Instead of an immediate, bulky, white precipitate, as is usually the case in the preparation of aromatic hydrazines, the hydrochloride did not come down for about half an hour, when the solution became pasty owing to the formation of long crystals of the hydrochloride, which were collected and dried on porous plates. As the hydrochloride thus prepared carries down with it a considerable amount of tin, its aqueous solution was treated with sulphuretted hydrogen, the tin sulphide filtered off, the filtrate decolorised with animal charcoal, when necessary, and evaporated on the water-bath.

After drying, the salt gave on analysis numbers agreeing with the formula $C_6H_4Cl \cdot NH \cdot NH_2, HCl$.

	Calculated for $C_6H_5N_2Cl_2$.	Found.		
		I.	II.	III.
C	40.22	40.82	—	—
H	4.47	5.09	—	—
N	15.64	—	15.81	—
Cl	39.67	—	—	39.41

The hydrochloride forms long, colourless needles, which darken at $181-183^\circ$, and melt at 190° with decomposition. It is readily soluble in water and alcohol, and the aqueous solution reduces Fehling's solution and mercuric chloride.

The *hydrazine* was first obtained by the addition of potash to the

aqueous solution of the hydrochloride and extraction with ether; on distilling off the ether, an oily liquid was left. Attempts were made to distil this, but even at a pressure of 45 mm. it was found that the oil split up on distillation, yielding orthochloraniline and ammonia. The base was then isolated by treating the hydrochloride with a concentrated solution of sodium acetate, agitating with ether, evaporating the ethereal solution, and drying the residue over calcium chloride for some days, when a clear, orange-coloured oil was obtained. A chlorine determination of this oil showed it to be orthochlorophenylhydrazine, $C_6H_4Cl \cdot NH \cdot NH_2$.

	Calculated for $C_6H_7ClN_2$.	Found.
Cl	24.91	24.49

Orthochlorophenylsemicarbazide is produced on adding a solution of potassium cyanate to orthochlorophenylhydrazine dissolved in water. If the solutions are concentrated, the mixture nearly solidifies to a mass of colourless plates, which are recrystallised from boiling water, in which they are sparingly soluble. This compound melts at 164° , and gave on analysis numbers corresponding with the formula $C_6H_4Cl \cdot NH \cdot NH \cdot CONH_2$.

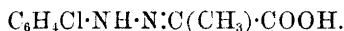
	Calculated for $C_7H_8N_3ClO$.	Found.		
		I.	II.	III.
C	45.29	44.73	45.68	—
H	4.31	5.53	4.01	—
N	19.14	—	—	19.70

Orthochlorophenyl-phenylthiosemicarbazide is formed on adding phenylthiocarbimide to an ethereal solution of the free hydrazine. On evaporating the ether, thin, yellow plates are left, which when recrystallised from alcohol melt at 134° . The following values correspond with the formula $C_6H_4Cl \cdot NH \cdot NH \cdot CS \cdot NH \cdot C_6H_5$.

	Calculated for $C_{13}H_{12}ClN_3S$.	Found.
Cl	12.79	12.97
S	11.53	11.23

An ethereal solution of this compound acquires a deep green colour when shaken with an aqueous solution of copper sulphate; this is intensified on addition of ammonia.

Orthochlorophenylhydrazinepyruvic Acid,



—On adding pyruvic acid to the free hydrazine or, better, to an aqueous solution of the hydrochloride, a lemon-yellow flocculent precipitate is thrown down consisting of needles which, after recrystallisation from alcohol, melt at 178° . This substance gave on analysis the following numbers:—

	Calculated for $C_9H_9N_2ClO_2$.	Found.		
		I.	II.	III.
C	50.82	50.65	—	—
H	4.23	4.58	—	—
N	13.18	—	13.28	—
Cl	16.71	—	—	16.38

This acid is readily soluble in alcohol, alkalis, and ammonia, but insoluble in sodium carbonate.

The *ethyl salt* is readily obtained by heating the alcoholic solution of the acid for some time with the addition of a few drops of sulphuric acid. On adding water to the solution, a nearly colourless aggregate of needles is thrown down, which after recrystallisation from dilute alcohol melt at 168° .

Aldehydes and ketones (such as benzaldehyde, acetone, and acetophenone), added to solutions of the hydrochloride, yield colourless or pale-yellow precipitates on the addition of a concentrated solution of sodium acetate, but the compounds thus formed are so unstable that I was unable to further investigate them.

Parachlorophenylhydrazine has already been described by Elsingskorst (*Inaug. Dissert., München*, 1884); I have studied its reactions with certain substances closely related to urea. Fischer has studied the reaction of phenylhydrazine with potassium isocyanate (*Annalen*, **190**, 113), whilst Pellizari (*Gazzetta*, **16**, 200) and Pinner (*Ber.*, **20**, 2358) both acted on this hydrazine with carbamide. In both cases phenylsemicarbazide resulted. This work on the reactions of carbamide derivatives with phenylhydrazine was further extended by Skinner and Ruhemann (*Trans.*, **53**, 550), who heated ethyl carbamate with phenylhydrazine, obtaining diphenylcarbazine; they also completed the series of semicarbazides and carbazides containing phenyl groups, by acting on phenylhydrazine with other compounds related to carbamide.

Action of Parachlorophenylhydrazine on Ethyl Carbamate.—A mixture of 2 mols. of parachlorophenylhydrazine with 1 mol. of ethyl carbamate was heated over a small flame until ammonia ceased to be evolved. On cooling, the liquid solidified to a mass of crystals, which on washing with ether were obtained colourless. They are somewhat soluble in boiling water, readily in hot alcohol, melt at a temperature above 250° , and give no colour reactions with copper sulphate, mer-

curic chloride, or ammonia. Analysis showed that they were not the carbazide but diparachlorophenylcarbamide, $\text{CO} < \begin{smallmatrix} \text{NH} \cdot \text{C}_6\text{H}_4\text{Cl} \\ \text{NH} \cdot \text{C}_6\text{H}_4\text{Cl} \end{smallmatrix}$.

	Calculated for $\text{C}_{13}\text{H}_{10}\text{N}_2\text{Cl}_2\text{O}$.	Found.	
		I.	II.
Cl	26.19	—	26.58
N	10.33	10.52	—

The ether used for washing the crystals of the disubstituted carbamide left a crop of colourless crystals on evaporation, which I intend to examine further.

Parachlorophenyl-phenylsemithiocarbazide.—The semithiocarbazide, $\text{C}_6\text{H}_4\text{Cl} \cdot \text{NH} \cdot \text{NH} \cdot \text{CS} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$ [$\text{Cl} : \text{N} = 1 : 4$], was obtained by adding phenylthiocarbimide to an ethereal solution of the hydrazine. On evaporation, yellow crystals were deposited which are sparingly soluble in hot alcohol, and crystallise from it in pale-yellow plates melting at 149° . They gave the following numbers on analysis:—

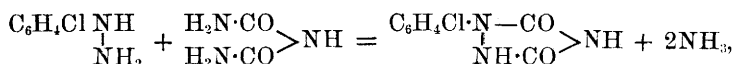
	Calculated for $\text{C}_{13}\text{H}_{12}\text{N}_3\text{SCl}$.	Found.
Cl	12.79	12.98
S	11.53	11.85

An ethereal solution of this compound becomes green when shaken with an aqueous solution of copper sulphate, and this colour is not destroyed on the addition of ammonia. The colour reaction is analogous to that pointed out by Skinner and Ruhemann (*loc. cit.*) for phenylsemithiocarbazide.

Parachlorophenylurazole.—Pinner was the first to prepare phenylurazole by heating one part of phenylhydrazine hydrochloride with one and a half parts of carbamide (*Ber.*, **20**, 2358). The same compound was afterwards prepared by Skinner and Ruhemann (*loc. cit.*) by heating phenylhydrazine with biuret. The latter method was employed to convert parachlorophenylhydrazine into parachlorophenylurazole. Equal weights of biuret and parachlorophenylhydrazine were heated over a small flame, ammonia was evolved, and on cooling the mass solidified. This was extracted with hot dilute alcohol, boiled with animal charcoal, filtered, and crystallised, when aggregates of needles melting at 266° were deposited. A chlorine estimation showed this substance to be parachlorophenylurazole, $\text{C}_6\text{H}_4\text{Cl} \cdot \text{N} - \text{CO} > \text{NH} \begin{smallmatrix} | \\ \text{NH} \cdot \text{CO} \end{smallmatrix}$ [$\text{Cl} : \text{N} = 1 : 4$].

	Theory for $\text{C}_8\text{H}_6\text{N}_3\text{ClO}_2$.	Found.
Cl	16.31	16.37

The reaction takes place according to the equation

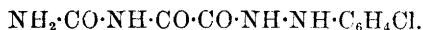


being analogous to that observed in the formation of phenylurazole.

Parachlorophenylhydrazine Parabanate.—A parabanate of phenylhydrazine was prepared by Skinner and Ruhemann by the addition of a concentrated solution of sodium acetate to a mixture of solutions of phenylhydrazine hydrochloride and parabanic acid. The corresponding parabanate of parachlorophenylhydrazine may be obtained in a similar manner. Parachlorophenylhydrazine hydrochloride dissolved in water is added to a solution of parabanic acid, and treated with an excess of sodium acetate solution. After the lapse of a few minutes, groups of needles separate, which melt at 213° with decomposition. A chlorine determination showed that this parabanate contains 1 mol. H_2O , like the phenylhydrazine parabanate. The formula $\text{C}_3\text{O}_3\text{N}_2\text{H}_2, 2(\text{C}_6\text{H}_7\text{N}_2\text{Cl}), \text{H}_2\text{O}$ requires:—

	Theory for $\text{C}_{15}\text{H}_{18}\text{N}_6\text{O}_4\text{Cl}_2$.	Found.
Cl	17.02	17.00

The parabanate is slightly soluble in boiling water, probably owing to the formation of an oxalurhydrazide,



Action of Chloroform and Alcoholic Potash on Parachlorophenylhydrazine.—The isonitrile reaction was applied to parachlorophenylhydrazine with the view of preparing the parachlorinated derivative of diphenyltetrazine. A mixture of chloroform with an alcoholic solution of parachlorophenylhydrazine was treated with alcoholic potash. The reaction started by itself, and was completed by heating for some time on the water-bath. The product of the reaction was then allowed to cool, and after addition of water shaken with ether; the ethereal solution was then agitated with dilute sulphuric acid in order to remove the unaltered hydrazine. On evaporating the ether, a dark-coloured residue was left, which was boiled with water and filtered from a resinous matter; the hot filtrate deposited colourless needles on concentration. These darken at 135° and melt at 152° . A nitrogen determination showed this compound to be formyl-parachlorophenylhydrazine, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}\cdot\text{NH}\cdot\text{CHO}$.

	Calculated for $\text{C}_7\text{H}_7\text{N}_2\text{ClO}$.	Found.
N	17.67	17.43

The resinous mass left on the filter yielded minute crystals on

allowing it to stand for about a week; these probably consisted of the desired tetrazine, but the amount obtained was not sufficient for analysis. I hope shortly to return to the study of this reaction, and to communicate to the Society the results arrived at in the case of this and other chlorinated phenylhydrazines.

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