PERKIN ON THE ACTION OF NITRIC ACID

LXIV.—CONTRIBUTIONS FROM THE LABORATORY OF
THE ROYAL COLLEGE OF CHEMISTRY.*On the Action of Nitric Acid on Diparatolylguanidine.*

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THIS investigation was originally undertaken with a view to the study of diparatolylguanidine and its cyanogen derivatives; but having subsequently learnt that Herr Oscar Landgrebe in his paper "On the Cyanogen Derivatives of Guanidine" (*Ber.*, **10**, 1587) had already worked on the subject, it appeared more desirable to confine my attention to the investigation of one or two reactions which were noticed whilst experimenting with this base. The first selected was its behaviour with nitric acid.

Preparation of Diparatolylguanidine.

This base was first prepared by W. Wilson (*Chem. Soc. Qu. J.*, **3**, 154) by the action of chloride of cyanogen on toluidine (evidently the "para" body); since then Dr. A. W. Hofmann obtained it by the action of ammonia and lead oxide upon ditolylthiocarbamide. For the purposes of this investigation, however, I used the former process, which works very satisfactorily. In the purification of the crude base, I found the use of petroleum spirit to remove any unaltered toluidine very effective. The diparatolylguanidine was obtained in

beautiful white transparent needles, which gave on analysis the following numbers:—

·2449 gram of substance gave—

·6412 „ „ CO₂, and

·1576 „ „ OH₂.

	Theory for C ₁₅ H ₁₇ N ₃ .	Experiment.
Carbon	75·31	75·46
Hydrogen	7·11	7·19

Action of Nitric Acid on Diparatolylguanidine.

Nitric acid (sp. gr. 1·5) acts energetically on this base, dissolving it with evolution of heat and formation of red fumes. To moderate this action, the powdered base was added to the fuming acid in small quantities at short intervals, any considerable rise of temperature being avoided. On adding the brown-red solution thus obtained to a large excess of water, a certain amount of product was precipitated, consisting chiefly of resinous matter,* which was filtered off and well washed to remove soluble compounds. Ammonia in excess was then added to the clear filtrate. This caused the separation of a chrome-yellow precipitate, which was washed and dissolved in water acidulated with hydrochloric acid. After filtration, dilute nitric acid was added, when a crystalline nitrate rapidly separated. After standing for about 24 hours, this salt was collected, slightly washed, pressed between bibulous paper, and purified by one or two crystallisations from alcohol. It was then dissolved in water, and the base thrown down with ammonia. This was then washed, dried, and crystallised from alcohol. On analysis, it gave the following numbers:—

I. ·11975 gram of substance gave—

·2380 „ „ CO₂, and

·0482 „ „ OH₂.

II. ·1053 „ „ substance gave—

·2109 „ „ CO₂, and

·0396 „ „ OH₂.

These numbers give percentages closely agreeing with those required by the formula C₁₅H₁₅N₅O₄ or dinitrodiparatolylguanidine; thus:—

* This resinous body when purified crystallises from alcohol in brilliant yellow needles, but has not been further investigated.

	Theory.	Experiment.	
		I.	II.
Carbon	54.71	54.28	54.62
Hydrogen	4.54	4.47	4.18

Dinitrodiparatolylguanidine melts with decomposition at about 197°. It is difficultly soluble in cold, but moderately in boiling alcohol. It crystallises from this solvent in small beautiful orange-red prisms. It is insoluble in water. Its alcoholic solution, when treated with tin and hydrochloric acid, gives a product crystallising in needles, which is probably an amido-derivative. It is under investigation.

The *nitrate*, the preparation of which has already been given, crystallises from alcohol, in which it is only moderately soluble, in small flat needles of a pale straw colour. On analysis, it gave the following numbers:—

- I. .12585 gram of substance gave—
 .2112 „ „ CO₂, and
 .0467 „ „ OH₂.
 II. .1529 „ „ substance gave—
 .275 c.c. of N at 757.5 mm. and 16°C.

These numbers give percentages agreeing with the formula C₁₃H₁₅N₅O₄.HNO₃.

	Theory.	Experiment.	
		I.	II.
Carbon	45.95	45.84	—
Hydrogen	4.08	4.12	—
Nitrogen	21.42	—	20.98

The aqueous mother-liquors from the preparation of this nitrate from diparatolylguanidine contain another base crystallising in yellow needles. This, however, has not yet been obtained in a perfectly pure state. Its fusing point is considerably higher than that of the base just described, and as it contains less carbon and hydrogen, it is not improbably a *trinitro*-compound.

Action of Nitric Acid in presence of Alcohol on Diparatolylguanidine.

If a quantity of diparatolylguanidine be suspended in alcohol, as much nitric acid (sp. gr. 1.4) added as alcohol, and the mixture heated, violent chemical action soon takes place between the acid and alcohol; but after a short time a second reaction sets in, attended with very copious evolution of red fumes, and at the same time with the formation of a crystalline yellow body. To purify this, water was

added, the mixture thrown on a filter,* and the insoluble product washed first with water and then with alcohol. It was then crystallised from alcohol and afterwards from coal-tar naphtha, from which it was deposited in fine needles, usually of a pale primrose, but sometimes of an orange colour. This difference in colour was apparently due to a physical, and not to a chemical difference, as was determined by analysis (see Analysis III). Moreover, when it was recrystallised, the orange colour not unfrequently changed suddenly to a primrose without any apparent separation of impurities. On analysis, this substance gave the following numbers:—

I.	·1331	gram of substance gave—
	·2668	„ „ CO ₂ , and
	·0520	„ „ OH ₂ .
II.	·0964	„ „ substance gave—
	·1918	„ „ CO ₂ , and
	·0352	„ „ OH ₂ .
III.	·1002	„ „ substance gave—
	·2104	„ „ CO ₂ , and
	·0395	„ „ OH ₂ .
IV.	·2108	„ „ substance gave—
	30·4	c.c. N at 769 mm. and 11° C.
V.	·2024	gram of substance gave—
	29·25	c.c. N. at 769 mm. and 12° C.

These numbers give percentages agreeing with those required by the formula $C_{15}H_{14}N_4O_5$, representing *dinitroparatolylurea*, which may be written thus:—

		Experiment.				
	Theory.	I.	II.	III.	IV.	V.
Carbon	54·54	54·66	54·25	54·81	—	—
Hydrogen ..	4·24	4·34	4·05	4·38	—	—
Nitrogen	16·97	—	—	—	17·38	17·27

Dinitrodiparatolylurea melts with decomposition at about 233°. It is rather difficultly soluble in boiling alcohol, but more freely in boiling coal-tar naphtha.

* The aqueous washings were found to contain a small quantity of the nitrate of dinitrodiparatolylguanidine.

Reduction of Dinitroparatolylurea.

On boiling this urea in alcohol with hydrochloric acid and granulated tin, it gradually dissolves and eventually forms a colourless solution. From this the alcohol was removed by boiling with water, and the tin by means of sulphuretted hydrogen. The solution thus obtained was found to contain the hydrochloride of a new base. To obtain the base, the solution was evaporated to dryness over a water-bath and the hydrochloride dissolved in boiling alcohol. Ammonia was then added, which caused the base to crystallise out rapidly in fine needles. These were collected, washed with alcohol, then with water, and afterwards dried.

On analysis this substance gave the following numbers:—

- I. .0891 gram of substance gave—
 .2168 „ „ CO₂, and
 .0565 „ „ OH₂.
 II. .1054 „ „ substance gave—
 18.37 c.c. N at 751.5 mm. and 15° C.

These numbers gave percentages agreeing with those required by the formula, C₁₃H₁₈N₄O, which represents *diamidoparatolylurea*, or the carbamide of paratolylenediamine, thus:—

	Theory.	Experiment.	
		I.	II.
Carbon	66.66	66.36	—
Hydrogen.....	6.66	7.04	—
Nitrogen	20.74	—	20.65

This substance crystallises in microscopic needles of a satiny aspect. It is a powerful electric. At a high temperature it decomposes before undergoing fusion. It is difficultly soluble in alcohol.

The *hydrochloride* contains two molecules of acid, and has therefore the composition C₁₃H₁₈N₄O.2HCl, as will be seen from the following analysis:—

- .1100 gram of substance gave—
 .2104 „ „ CO₂, and
 .0564 „ „ OH₂.

	Theory.	Experiment.
Carbon	52·48	52·16
Hydrogen	5·86	5·6

It is a white almost amorphous body. It forms a *platinum salt* corresponding with the hydrochloride, but it has not been obtained in a perfectly pure state.

One preparation gave 27·8 per cent. of platinum, the theory requiring 28·9 per cent.