XVII.—*Production of some Nitro- and Amido-oxylutidines. Part I.*

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In a former paper (Trans., 1897, 838), one of the authors has drawn attention to the fact that nitro- and amido-derivatives of pyridine can be obtained from oxypyridine compounds by the ordinary process of nitration and reduction. As these substances correspond in the pyridine series to nitro- and amido-phenols in the benzene series, their reactions and properties are of some interest, and it has been considered worth while to continue the investigation, using a hydr-oxylutidine (pseudolutidostyryl) as the starting point.

Pseudolutidostyryl.

This compound, α , γ -dimethyl- α' -hydroxypyridine, is easily nitrated when treated with a mixture of strong nitric and sulphuric acids, yielding a nitropseudolutidostyryl, which, on reduction with tin and hydrochloric acid, gives an amidolutidostyryl. As, however, the entering nitro-group might replace either of two different hydrogen atoms, it was necessary to determine if possible the exact composition of the new nitro-derivative.

That the substance had the molecular structure represented by the formula I. was proved by obtaining it from ethylic nitrolutidostyryl-carboxylate (Trans., 1897, 71, 301).

When this nitrohydroxylutidine is subjected to the reducing action of tin and hydrochloric acid, it is at once converted into the corresponding amidohydroxylutidine.

In a former paper by one of the authors (Trans., 1897, 71, 842), an amidodihydroxypicoline was similarly prepared, and it was then noticed that the dioxy-compound suffered a somewhat curious change when boiled, passing into a trihydroxypicoline:—

This reaction is different from any that amidophenols undergo, but is similar to the formation of orthonitrophenol from orthonitr-aniline when the latter is boiled with alkalis; possibly it may be due

to the ease with which, in α -hydroxypyridine compounds, the ring binding can be loosened and opened out (Trans., 1897, 71, 839).

We were in hopes, that as the amido-group and the hydroxy-group in the amidohydroxylutidine were in the same relative positions (namely, α and β), the same reaction might again occur, and the corresponding dihydroxylutidine derivative be formed, but although many attempts were made no such change could be effected.

The amidohydroxylutidine is a substance with characteristic properties, it is very unstable and cannot be heated to 100° without turning brown; it rapidly reduces solution of nitrate of silver and platinic chloride. With ferric chloride, it gives first a red and then a bright green coloration, but it does not yield the series of brilliant colour reactions in alkaline solution like the trihydroxypicoline mentioned above (Trans., 1897, 71, 843). When, however, it is dissolved in strong sulphuric acid and a drop of nitric acid is added, a strong purple coloration is produced similar to that which strychnine gives when treated with sulphuric acid and potassium dichromate.

The pseudolutidostyryl employed was prepared from ethylic β -amido-crotonate according to the method given in a former paper by one of the authors (Trans., 1897, 71, 299); it was found convenient only to nitrate small quantities of the substance at a time. Three to four grams of the pseudolutidostyryl were dissolved in 6 c.c. of sulphuric acid, and this mixture was then slowly added to 8 c.c. of a mixture of sulphuric and fuming nitric acids, which were kept well cooled: large quantities are less easily manageable, the temperature being liable to rise suddenly, when the whole of the substance is destroyed by oxidation. The mixture is then diluted with 10 times its volume of water, the new nitro-derivative which separates in yellow needles being most conveniently recrystallised from 30 per cent. acetic acid, or a mixture of 30 per cent. acetic acid to which about 3 per cent. of nitric acid has been added. When pure, it crystallises in light yellow needles that melt somewhere about 250° if suddenly heated to that temperature, but if the heating be slow, the crystals darken at about 243° and then rapidly decompose. On analysis, the following numbers were obtained:

	C.	H.	N.
Found.....	49.8	5.4	17.5
Calculated for $\text{C}_7\text{H}_8\text{N}_2\text{O}_3$	50.0	4.8	16.7

No other nitro-compound seemed to be present, and the only substance produced by the nitration of pseudolutidostyryl was the compound mentioned above. It is not volatile with steam, and with alkalis, it gives brilliant yellow compounds.

Amidopseudolutidostyryl, $C_5NH(CH_3)_2(OH) \cdot NH_2$.

When the nitro-derivative of pseudolutidostyryl is reduced with tin and hydrochloric acid, the hydrochloride of amidopseudolutidostyryl is formed, the reaction being accompanied by a considerable evolution of heat. After precipitating the tin by means of hydrogen sulphide, the solution is evaporated on the water bath, when the hydrochloride of the base begins to separate as soon as the solution becomes concentrated. A second method for preparing the hydrochloride was used; if, after the reduction with tin and hydrochloric acid, the solution is evaporated, a well crystallised double salt of the hydrochloride of amidopseudolutidostyryl and tin chloride separates; this can be purified and then its solution decomposed by means of hydrogen sulphide. By either method, a white salt was obtained crystallising in needles, and decomposing without melting at $235-240^\circ$, but like the nitrolutidostyryl, if suddenly heated to about 300° , it can be partially melted before decomposition ensues. It was analysed.

	C.	H.	N.	Cl.
Found	47.8	6.4	20.3	19.6
Calculated for $C_7H_{10}N_2O \cdot HCl$	48.1	6.3	20.3	20.3

The substance, therefore, is a monhydrochloride.

When this hydrochloride is treated in aqueous solution with sodium hydrogen carbonate, it is converted into the free base, which is less soluble and separates in the form of a bulky mass of fine, needle-shaped crystals; these were purified by recrystallisation from water until they melted constantly at 205° (corr.). The base is very soluble in hot water but less so in cold (to the extent of 8—10 per cent. in cold), it is very unstable at 100° , the dry substance rapidly turning brown when heated in a water oven to that temperature. The aqueous solution even turns brown on boiling, and in the presence of alkalis the decomposition is much more rapid.

When added to a cold solution of silver nitrate, it instantly gives a black precipitate of silver, and when warmed with a little chloride of platinum reduction was found to take place; the normal platinumchloride can be prepared, but in the presence of hydrochloric acid it changes into a new salt containing 3 per cent. more platinum than the normal salt. This new salt was produced when trying to recrystallise the ordinary salt from dilute hydrochloric acid.

Analyses of both salts were made.

The normal platinumchloride contained 28.5 per cent. Pt.

Calculated for $(C_7H_{10}N_2O)_2, H_2PtCl_6$ 28.4 per cent. Pt.

The new salt obtained from hydrochloric acid solution, on analysis, was found to give the following numbers.

	C.	H.	Pt.	Cl.
Found	20.4	3.0	31.5	34.8
Calculated for	20.4	2.7	31.5	34.5
$(C_7H_{10}N_2O)_2, H_2PtCl_6$				
$C_7H_{10}N_2O, H_2PtCl_6$				

This substance appears therefore to be a compound of the mono- and the di-hydrochlorides of the base with platinum chloride.

When the amidopseudolutidostyryl is heated on the water bath with acetic anhydride, it is converted into a monacetyl derivative which can be crystallised either from water or from alcohol. It is obtained in white, silky needles melting at 255° (corr.), it is neutral to litmus paper, and fairly soluble in cold, but very soluble in hot, water. Ether, acetone and ethylic acetate dissolve it more sparingly, and it differs from amidopseudolutidostyryl in that it gives no reaction with ferric chloride, neither does it reduce silver nitrate solution. The amidopseudolutidostyryl can be regenerated from it by hydrolysis with dilute hydrochloric acid heating the mixture under pressure in a sealed tube.

It gave the following numbers on analysis.

	C.	H.
Found	60.1	6.5
Calculated for $C_7H_9N_2O, C_2H_3O$	60.0	6.6

This is produced when ethylic pseudolutidostyrylcarboxylate (m. p. $138-139^\circ$) is nitrated in the ordinary manner with a mixture of strong nitric and sulphuric acids. It is scarcely soluble in water, but can be recrystallised from acetic acid; it then forms long, pale yellow, needle-shaped crystals, which melt without decomposition at 215° (corr.). It was analysed.

	C.	H.	N.
Found	49.7	6.1	11.6
Calculated for $C_{10}H_{12}N_2O_5$	50.0	6.0	11.6

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It is not very soluble even in hot soda solution, but, on warming, decomposition slowly occurs and the brilliant yellow sodium salt of the nitropseudolutidostyrylcarboxylic acid is produced.

This nitropseudolutidostyrylcarboxylic acid was also prepared in larger quantities by nitrating the free acid. Ten grams of the acid were carefully added to 20 c.c. of well cooled fuming nitric acid, and afterwards poured into 10—15 c.c. of strong sulphuric acid; care must be taken not to allow the temperature to rise, otherwise a violent action begins, and the substance is entirely destroyed.

On pouring the mixture into cold water, the new nitro-acid separates. It was found on analysis to contain $1\text{H}_2\text{O}$.

Loss of weight at $100^\circ = 8.2$ per cent.

Calculated for $\text{C}_8\text{H}_8\text{N}_2\text{O}_5 + \text{H}_2\text{O} = 7.8$ per cent.

The dried substance gave the following numbers.

	C.	H.	N.
Found	45.3	4.2	13.3
Calculated for $\text{C}_8\text{H}_8\text{N}_2\text{O}_5$	45.3	3.8	13.2

This nitro-acid can be recrystallised from acetic acid or water, but it is not very soluble in the latter. When pure, the crystals are almost white needles, the aqueous solution having only a faint yellowish tint; when rapidly heated, they melt at 260° (corr.). The ammonium salt is easily obtained in the crystalline condition, and is bright yellow; it gives a brown precipitate with ferric chloride, and a crystalline precipitate with silver nitrate. The lead and barium salts seem to be soluble.

The moment the free acid is melted, it effervesces and evolves carbon dioxide, whilst a yellow, crystalline residue remains which melts at a temperature $10\text{--}15^\circ$ below the acid; after purification, this residue was found to be identical with the nitropseudolutidostyryl obtained by nitrating pseudolutidostyryl itself and already mentioned earlier in this paper. This method for the manufacture of nitropseudolutidostyryl was not used, because the decomposition of the substance at the temperature at which the nitro-acid fused was very considerable.

Amidopseudolutidostyrylcarboxylic acid, $\text{NH}_2 \cdot \text{C}_5\text{N}(\text{CH}_3)_2(\text{OH}) \cdot \text{COOH}$.

When the nitro-acid is reduced by means of tin and hydrochloric acid, the hydrochloride of the corresponding amido-derivative is produced. To prepare this substance, the nitro-acid is dissolved in strong hydrochloric acid, and the tin is added little by little, the reduction taking place very readily with a considerable rise of temperature. The acid solution obtained after the tin has been precipitated with hydrogen

sulphide is evaporated on the water bath, and from the concentrated solution the hydrochloride separates in needle-shaped crystals; these can be recrystallised from hydrochloric acid, but with pure water the substance is decomposed into the free acid, which is much more insoluble than the hydrochloride.

The hydrochloride gave the following results on analysis.

	C.	H.	N.	Cl.
Found	37.9	6.0	11.3	14.0
Calculated for $C_8H_{10}N_2O_3.HCl + 2H_2O$	37.7	5.9	11.0	13.9

The substance, when heated at 100° , lost 14.5 per cent. H_2O .

The calculated amount corresponding with $2H_2O = 14.1$ per cent.

The amido-acid can be prepared by decomposing the hydrochloride with excess of water; it is very slightly soluble even in hot water. From hot alcohol it separates in needles, whilst if the potassium salt be decomposed by acetic acid the free acid can be obtained in the form of small flat prisms; it is insoluble in ether, acetone, and chloroform. It is unstable, turning brown rapidly when heated to 100° ; the alcoholic and aqueous solutions behave in a similar manner.

The amido-acid has strong reducing properties; if added to silver nitrate solution, it forms a dense grey precipitate of silver, and the solution becomes pale green. With ferric chloride, it gives a pale green coloration which rapidly deepens to emerald green, purple, and finally deep blue. With ferrous sulphate, it gives no coloration, and the calcium, barium, lead, and copper salts seem to be soluble.

When very carefully heated on an oil bath, the acid melts at 275° (corr.). It also loses, at 100° , 8.7 per cent. of water.

Calculated for $C_8H_{10}N_2O_3 + H_2O$; $H_2O = 9.0$ per cent.

At its melting point, it gives off carbon dioxide, and the residue (which sublimes at the temperature at which the decomposition occurs), after purification, was found to melt at 205° (corr.); its hydrochloride melted at about 300° , and corresponded in all respects with the amido-pseudolutidostyryl obtained by the reduction of the nitropseudolutido-styryl.