LXIV.—*Studies on Citrazinic Acid.* Part III.

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Reduction of "Quinhydroketopyridine."

IN a former paper (Trans., 1893, **63**, 1047) it was shown that the action of dilute sulphuric acid on isonitrosocitrazinic acid gives rise to a sparingly soluble, blue substance, exhibiting metallic lustre, and that the compound probably has the constitution

The name quinhydroketopyridine was given to this $\alpha\beta$ -diketo- α' -hydroxypyridine, on account of the remarkable resemblance which

the substance exhibits to ordinary quinhydrone. When oxidised, it passes into a substance resembling ordinary quinone; and as the oxidation involves the loss of only one hydrogen atom, it is probable that two molecules are simultaneously oxidised, becoming linked up in the following manner.

The quinhydroketo-compound can be reduced by hydriodic acid, but the products differ according to the conditions maintained. The cold fuming acid gradually changes the blue substance into a colourless compound of the formula $C_{10}H_{10}N_2O_7 \cdot 2HI$, which, when mixed with water, loses hydrogen iodide and yields pale yellow needles, whose formula is $C_{10}H_8N_2O_6 \cdot H_2O$, and to which we provisionally assign the constitution

An attempt to convert this substance into a trioxypyridine was unsuccessful.

It will be noticed that the proposed formulæ are related to one another in a manner the reverse of that which is generally assumed to hold in the case of quinone and its hydrogenised derivatives; thus we have

Quinone.	Quinhydrone.	Hydroquinone.
Single molecule	Double	Single
Quinoketopyridine.	Quinhydroketopyridine.	Hydroquinoketopyridine.
Double	Single	Double

Whilst putting forward the formulæ which most readily explain the actions under consideration, the authors recognise that the experimental result next to be described points to the probability that the quinhydroketo-derivative is itself a double molecule. In Part I of the present investigations it was represented as double, owing to an error of transcription.

Results different from the above are obtained if the quinhydro-compound is boiled with hydriodic acid and a small quantity of

phosphorus until the dark colour of the solution changes to a light brown. On cooling, the liquid deposits colourless crystals of a tetra-basic, fatty acid, $C_{10}H_{14}O_6$. The action may be thus represented.

The substance is thus to be regarded as $\alpha\alpha$ -diglutaric acid; in support of this view the fact may be mentioned that, when melted, it immediately loses water and is converted into an anhydro-acid.

Hydroquinoketopyridine, $C_{10}H_8N_2O_6, H_2O$.

The hydriodide of this compound was prepared by covering the dark blue "quinhydro"-compound with fuming hydriodic acid and allowing the mixture to stand 24 hours. The yellow crystals thus formed were collected in a platinum cone, and, after being twice recrystallised from strong hydriodic acid, were practically colourless. When dried in a vacuum on a porous plate over solid potash, they yielded the following numbers on analysis.

Calc. for $C_{10}H_8N_2O_6, H_2O, 2HI$..	C = 22·81; H = 2·28; I = 48·28.
Found.....	C = 22·92; H = 2·56; I = 48·05.
	„ 23·11 „ 2·32 „ 48·34.

The salt is hygroscopic, and is decomposed by water. If the solution of the substance in hydriodic acid is diluted with water, the base is precipitated in groups of yellowish-white needles, which, when exposed to the air, rapidly become red, and, when shaken with water or alkalis, yield a bright blue solution. Two specimens were washed with alcohol to remove the last traces of hydrogen iodide, and were then analysed.

Calc. for $C_{10}H_8N_2O_6, H_2O$	C=44·44; H=3·70; N=10·37; H_2O =6·6.
Found	C=44·49; H=3·62; N=10·28; H_2O =6·09.
	„ 44·11 „ 3·91

$\alpha\alpha'$ -Diglutaric acid.

This compound was prepared by boiling 2 grams of the quinhydro-compound with 20 c.c. of hydriodic acid and a little ordinary phosphorus until the solution became pale brown. The acid, which separated as the solution cooled, was recrystallised from hot water, with animal charcoal. It was thus obtained in colourless prisms, sparingly soluble in alcohol, ether, acetic acid, benzene, phenol, and cold water. Analysis.

Calculated for $C_{10}H_{14}O_8$	C = 45.04; H = 5.34
Found.....	C = 45.12; H = 5.33
	„ 44.96 „ 5.14

The yield was 60—70 per cent. of the quinhydro-compound taken.

When quickly heated, the acid melts, and effervesces at 215—218° (anhydride formation).

The silver salt, $C_{10}H_{10}Ag_4O_8$, is an amorphous, insoluble, white powder, prepared by adding excess of silver nitrate to a neutralised solution of the acid.

Calc. for $C_{10}H_{10}Ag_4O_8$	C = 17.39; H = 1.45; Ag = 62.60
Found	C = 17.25; H = 1.58; Ag = 62.13

Anhydrodiglutaric acid.

When diglutaric acid is heated at 160°, no loss of weight occurs, even though the experiment be performed in a vacuum. If the temperature is raised to 200°, however, the acid melts after the lapse of a few minutes, and an effervescence is noticeable. The loss of weight accompanying the change was found to be 7.1 per cent., the theoretical loss during the formation of the anhydro-acid being 6.87 per cent. The gummy residue, dissolved in hot anhydrous acetone, was precipitated, on adding benzene, as a white powder, melting at 130—135°. The preparation was probably not quite pure, but analysis of the small available quantity of material indicated plainly that the compound was the anhydro-acid.

Calculated for $C_{10}H_{12}O_7$	C = 49.18; H = 4.91
Found	C = 48.60; H = 4.90

Nitration of Citrazinic acid.

It has been already pointed out by the authors (Trans., 1893, **63**, 1051) that citrazinic acid is easily acted on by both nitric and fuming sulphuric acids, and a short account of the products is appended. Marckwald (*Ber.*, **26**, 2187; **27**, 1317) has recently shown that amidonicotinic acid may be nitrated without difficulty, and that the nitro-group can be readily reduced. It seems probable that when once the highly basic character of pyridine is subdued, by the introduction of strongly negative radicles, chlorination, nitration, and sulphonation can be effected with a readiness which recalls the case of the sulphonic derivatives of benzene.

Citrazinic acid dissolves in cold concentrated nitric acid, the action being accompanied by rise of temperature and evolution of gas. If the temperature is kept below 10° for several hours the solution gradually becomes bright yellow, and sets to a mass of crystals, some of which are nearly colourless rhombohedra, and may be regarded as

nitrodihydroxydiketopyridine. The remainder of the crystals are bright yellow needles, and appear to be dinitrocitrazinic acid. The production, in the same interaction, of nearly equal quantities of two such differently constituted compounds points more conclusively to tautomeric behaviour on the part of citrazinic acid than any interaction of that substance hitherto described.

10 grams of citrazinic acid are added, in small portions at a time, to 30 c.c. of 1.42 nitric acid, the temperature being kept down by a freezing mixture. When complete dissolution has been effected, the vessel containing the liquid is surrounded with ice-cold water and left for 24 hours. The crystals which separate are drained, dried on a porous plate, and then washed with ether until the ethereal washings are only faintly yellow. The residue, which is nearly insoluble in ether, is dissolved in luke-warm water and thrown down by means of concentrated hydrochloric acid, in which it is very sparingly soluble. By a second crystallisation, the substance can be obtained in almost colourless rhombohedra, which decompose explosively at temperatures above 200° , and whose analysis supports the formula $\text{C}_5\text{H}_2\text{N}_2\text{O}_6, 3\text{H}_2\text{O}$.

Calculated C = 25.00; H = 3.33; N = 11.45; H_2O = 22.50
 Found C = 25.01; H = 3.45; N = 11.54; H_2O = 22.51

The substance can be conveniently recrystallised from glacial acetic acid. It is a strongly dibasic acid. The yield is about 25 per cent. of the citrazinic acid used.

The monosilver salt, $\text{C}_5\text{HAgN}_2\text{O}_6, \text{H}_2\text{O}$, prepared by adding silver nitrate to an aqueous solution of the substance, forms lemon-yellow scales, which can be recrystallised from hot water.

Theory. H_2O = 5.78; Ag = 34.72; N = 9.00; C = 19.29; H = 0.96.
 Found. H_2O = 5.94; Ag = 34.82; N = 8.96; C = 19.38; H = 1.14.

The disilver salt, $\text{C}_5\text{Ag}_2\text{N}_2\text{O}_6$, prepared by adding a hot solution of silver acetate to a neutralised solution of the substance, is a dark yellow, crystalline, explosive powder. Ag calculated = 54.00. Found, 54.31.

The monosodium salt, $\text{C}_5\text{HNaN}_2\text{O}_6, 3\text{H}_2\text{O}$, is highly characteristic, on account of its sparing solubility in cold water. It is readily prepared by adding a solution of sodium chloride to a solution of the acid. It recrystallises from water in beautiful, long, colourless needles.

Calculated Na = 8.77; H₂O = 20.60

Found..... Na = 8.92; H₂O = 20.34

The corresponding *acid potassium salt*, C₅HKN₂O₆.3H₂O, was prepared by adding the theoretical quantity of caustic potash to a strong aqueous solution of the substance.

Calculated..... K = 14.03; H₂O = 15.82

Found..... K = 13.71; H₂O = 15.89

When the above-mentioned nitro-compound was dissolved in water, and acetic acid and zinc dust added, a dark blue precipitate at once formed, and a considerable rise of temperature took place. The precipitate, after being well washed with cold water, was suspended in boiling water and a few drops of hydrochloric acid added, whereby an amber-coloured solution was obtained. On cooling the solution, yellow rhombohedra separated; these were recrystallised from dilute hydrochloric acid and analysed, with the following result.

Calc. for C₅H₄N₂O₄.2H₂O C=31.2; H=4.16; N=14.58; H₂O=18.80.

Found C=30.8; H=4.23; N=14.30; H₂O=18.94.

The yield was 60 per cent. of the nitro-compound used.

The amido-compound is a feeble acid, and dissolves in alkalis, affording an intensely purple liquid, the colour of which is discharged by mineral acids, but not completely by acetic acid. When crystallised from a mixture of equal parts of hydrochloric acid and water, it is practically free from chlorine.

The ethereal extract from the crude nitration product was evaporated to dryness, the residue dissolved in water, and precipitated with hydrochloric acid; bright yellow needles separated, which were recrystallised from glacial acetic acid and analysed.

Calc. for C₆H₃N₃O₅.2H₂O C=25.62; H=2.49; N=14.9; H₂O=12.8.

Found C=25.93; H=2.67; N=14.7; H₂O=13.2.

The substance explodes when heated to 115–120°. It is excessively soluble in water, alcohol, ethylic acetate, and hot acetic acid. In hydrochloric acid, benzene, and light petroleum it is very sparingly soluble. It gives a sparingly soluble ammonium salt. The yield is about 25 per cent.

Sulphonation of Citrazinic acid.

1 gram of citrazinic acid was dissolved in 5 c.c. of fuming sulphuric acid and the temperature maintained at 110–120° for 15 minutes. The liquid set to a crystalline mass when cooled, and the crystals, after being freed from excess of sulphuric acid, were found to be very readily soluble in water. When the acid liquid thus produced was neutralised with caustic soda, a sparingly soluble sodium salt separated. This, after being twice recrystallised from hot water, was obtained in the form of snow-white needles. Analysis indicates that the substance has the formula $C_{10}Na_6S_3N_2O_{16}, 10H_2O$.

Calculated ..	C=14·6;	Na=16·86;	S=11·7;	N=3·4;	H ₂ O=22·0.
Found	C=14·4;	Na=17·0;	S=11·5;	N=3·68;	H ₂ O=22·1.
	„ 14·2	„ 17·3	„ 12·2	—	„ 22·6.

The two series of analyses were made with different preparations.

A corresponding potassium salt was prepared; when dried at 150° it gave K = 32·20. Calculated = 31·88.

A silver salt, prepared from the sodium salt, contained 56·87 per cent. Ag. Calculated = 56·44.

The action of chlorosulphonic acid on citrazinic acid is similar to that of fuming sulphuric acid, and the above-mentioned sodium salt is easily obtained from the products.

The authors are engaged in further experiments with the somewhat remarkable compounds mentioned in this paper; they desire, in conclusion, to express their thanks to Mr. George Dixon, B.A., of Trinity College, for help in the analytical portion of the work.

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