

NITRATION AND OXIDATION OF ANTHRAQUINONE DIMETHYL DERIVATIVES*

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A mixture of 2- and 5-mono- and 2,5- and 2,8-diamino derivatives has been prepared from 1,4-dimethylantraquinone. From 2,3-dimethylantraquinone 2,3-dimethyl-1-aminoanthraquinone (*XI*) has been obtained whose formamidineum chloride or hydroxide derivatives *XII* and *XIII*, respectively, have been converted into 2,3-dimethyl-1-amino-4-nitro (*XV*) and 2,3-dimethyl-1,4-diaminoanthraquinones (*XVI*). Oxidation of N,N-dimethyl-N'-(2,3-dimethyl-4-nitro-1-antraquinonyl)formamidineum chloride (*XIV*) gave the respective 3-carboxylic acid which was hydrolyzed and reduced to 2-methyl-1,4-diaminoanthraquinone-3-carboxylic acid (*XXII*); oxidation of 2,3- and 1,4-dimethylantraquinones gave 2,3- (*XVIII*) and 1,4- (*XIX*) anthraquinonedicarboxylic acids, respectively.

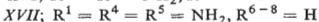
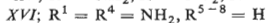
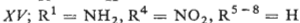
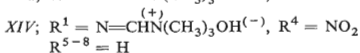
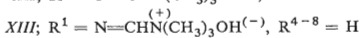
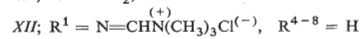
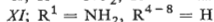
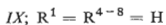
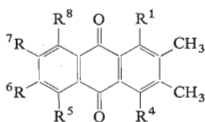
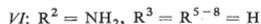
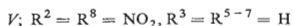
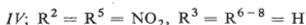
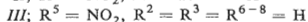
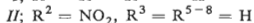
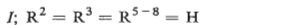
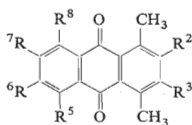
Whereas nitration of the parent 9,10-antraquinone represents an important technological problem which is given attention by a number of foremost dyestuff chemists periodically again and again, the nitration of alkylantraquinones has been neglected, which is not quite justified. Nitration and oxidation of monoalkylantraquinones was studied especially with 2-methyl derivative in connection with industrial production of 1-nitroanthraquinone-2-carboxylic acid^{1,2}. Out of dialkylantraquinones³⁻⁶ 1,3-dimethylantraquinone was subjected to nitration to give the respective 4-nitro- and 2,4-dinitro derivatives^{6,7}. Among 2,3-dimethylantraquinone derivatives the 1-nitro and 1-amino compounds were prepared. Nitration and subsequent reduction of 2,3-dimethyl-1-aminoanthraquinone gave 1-amino-4-nitro- and 1,4-diamino-2,3-dimethylantraquinones, respectively⁸. The products usually represent mixtures of several isomers.

In this work we tried to find a way to selective nitration of 1,4- and 2,3-dimethylantraquinones and a possibility of their oxidation to the respective carboxylic acids. Mononitration of 1,4-dimethylantraquinone (*I*) gave a mixture of 1,4-dimethyl-2-nitro- (*II*) and 1,4-dimethyl-5-nitro (*III*) anthraquinones. Dinitration gave a mixture of the respective 1,4-dimethyl-2,5- and -2,8-dinitro derivatives (*IV* and *V*). Reduction of the nitrocompounds *II* to *V* with sodium sulphide gives the respective aminocompounds. By chromatography on an alumina column it was possible to separate the mixture of aminocompounds into the yellow 1,4-dimethyl-2-aminoanthraquinone (*VIa*) which was isolated and the red 1,4-dimethyl-5-aminoanthraquinone (*IVb*). The structure of 1,4-dimethyl-2-aminoanthraquinone (*VIa*) and 1,4-dimethyl-5-aminoanthraquinone (*VIb*) was deduced from elemental analyses of the com-

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compound *VIa* and the mixture *VIa* + *VIb*, and by means of chromatographical comparison with a mixture of 1- and 2-aminoanthraquinones using an alumina column or aluminium plates with silica (acetone-cyclohexane 1 : 3). Chromatography of the mixture of diaminocompounds (alumina or silica as above) gives a marked red doubled spot which could not be separated, and the presence of 1,4-dimethyl-2,5- (*VII*) and 1,4-dimethyl-2,8- (*VIII*) diaminoanthraquinones is deduced from elemental analysis and NMR spectrum. The latter contains a singlet τ 7.40 and two singlets at 7.60 and 7.55 corresponding to two methyl groups at 1,4-positions, a singlet at 2.50 and two singlets at 3.95 and 4.05 corresponding to two amino groups at 2,5- eventually 2,8-positions, a proton singlet at 3.30 of the hydrogen atom at 3-position, and a multiplet corresponding to vicinal trisubstitution of the nucleus, *i.e.* to protons in 6, 7 and 5 resp. 8 positions.

In contrast to literature data⁸, nitration of 2,3-dimethylanthraquinone (*IX*) can be carried out as low as at 0 to 5°C. Reduction of the formed 2,3-dimethyl-1-nitroanthraquinone (*X*) gives a mixture of 2,3-dimethyl-1-aminoanthraquinone (*XI*) and starting 2,3-dimethylanthraquinone (incomplete nitration). The aminocompound *XI* was purified *via* N,N-dimethyl-N'-(2,3-dimethyl-1-anthraquinonyl)formamidinium chloride (*XII*) which was easily formed by Vilsmeier-Haack condensation of thionyl chloride, N,N-dimethylformamide and 2,3-dimethyl-1-aminoanthraquinone in *o*-di chlorobenzene. Dissolution of the compound *XII* in water and subsequent filtration removes the present anthraquinone quantitatively. The dissolved formamidinium chloride derivative *XII* was either decomposed into the starting substance *XI* or converted by alkali into the water-insoluble N,N-dimethyl-N'-(2,3-dimethyl-1-anthraquinonyl)formamidinium hydroxide (*XIII*) which can be used directly for further nitration.

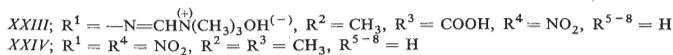
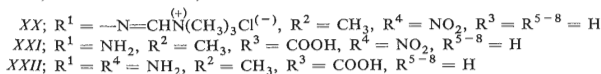
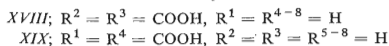
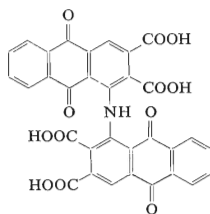
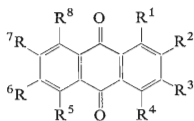


Nitration of N,N-dimethyl-N'-(2,3-dimethyl-1-anthraquinonyl)formamidine chloride (XII) gives practically only N,N-dimethyl-N'-(2,3-dimethyl-4-nitro-1-anthraquinonyl)formamidine chloride (XIV) which is not very easily hydrolyzed in acid medium to give 2,3-dimethyl-1-amino-4-nitroanthraquinone (XV). Reduction of the compound XV gave 2,3-dimethyl-1,4-diaminoanthraquinone (XVI).

The product XVI formed contains traces of two further blue substances, one of which could be isolated by chromatography using an alumina column, and it is presumed to be 2,3-dimethyl-1,4,5-triaminoanthraquinone (XVII) on the basis of elemental analysis and NMR spectrum.

Oxidation of 2,3- and 1,4-dimethylantraquinones into 2,3- and 1,4-anthraquinone-dicarboxylic acids (XVIII and XIX), respectively, does not proceed satisfactorily according to the literature data^{9,10} (oxidation with chromium trioxide in acetic acid). Therefore, we oxidized 2,3- and 1,4-dimethylantraquinones with diluted nitric acid at 220°C under pressure. The respective dicarboxylic acids are formed under these conditions immediately after reaching the mentioned temperature, the yields being almost quantitative. The both formamidine compounds XII and XIV are decomposed under the same conditions.

If nitroanthraquinonylformamidine chloride XIV is oxidized with dichromate in sulphuric acid at 60 to 70°C, N,N-dimethyl-N'-(2-methyl-3-carboxy-4-nitro-1-anthraquinonyl) formamidine chloride (XX) is formed; its hydrolysis in acid medium gives 2-methyl-1-amino-4-nitroanthraquinone-3-carboxylic acid (XXI). In alkaline medium the formamidine compound XX gives the water-insoluble N,N-dimethyl-N'-(2-methyl-3-carboxy-4-nitro-1-anthraquinonyl)formamidine hydroxide (XXIII). Reduction of the compound XXI gave 2-methyl-1,4-diaminoanthra-



quinone-3-carboxylic acid (XXII). Oxidation of 2,3-dimethyl-1-amino-4-nitroanthraquinone with peracetic acid gave 2,3-dimethyl-1,4-dinitroanthraquinone (XXIV) which was then subjected to oxidation with dichromate in sulphuric acid. Heating at 60 to 90°C, even for many hours, was not sufficient for oxidation of the dinitro compound XXIV to the corresponding dicarboxylic acid. The oxidation took place only at one methyl group. Oxidation of 2,3-dimethyl-1-aminoanthraquinone gave a yellow substance which, on the basis of elemental analysis, is presumed to be bis-(2,3-dicarboxy-1-anthraquinonyl)amine.

EXPERIMENTAL

The melting points given are non corrected.

1,4-Dimethyl-2- and 5-aminoanthraquinones (VIa, b)

The nitration mixture prepared from 4.15 ml nitric acid (d 1.517) and 20 ml conc. sulphuric acid was added drop by drop to a solution of 28.5 g 1,4-dimethylanthraquinone (82.8%) in 140 ml conc. sulphuric acid at 0°C. After addition of the nitration mixture the solution was stirred at 2 to 4°C for further 30 minutes and then poured onto a mixture of 500 ml water and 1 kg crushed ice; the nitro compound precipitated was collected by suction and washed with water until neutral. 30 g of yellow raw nitro compound was obtained after drying. The raw nitro compound (25 g) was mixed with 200 ml ethanol, heated to boiling, and 17 ml sodium hydrogen sulphide solution (393.8 g NaHS per 1000 ml) was added thereto within 10 minutes. After addition of sulphide solution the reaction mixture was heated to boiling for another 30 minutes, then the undissolved residue (anthraquinone) was removed by filtration, and the filtrate was precipitated gradually with total 500 ml water. The precipitate formed was collected by suction, washed with water and dried; yield 12.7 g. Chromatography on aluminium plates with silica (acetone-cyclohexane 1 : 3) showed two main spots: a red one with R_F 0.39 and a yellow one with R_F 0.136. The compounds were separated by chromatography on an alumina column using the same solvents, and the yellow 1,4-dimethyl-2-aminoanthraquinone (VIa) was isolated, m.p. 179–180°C (acetone). The red 1,4-dimethyl-5-aminoanthraquinone (VIb) could not be isolated. For compound VIa i.e. $C_{16}H_{13}NO_2$ (251.3) calculated: 76.66% C, 5.21% H, 5.58% N; found: 76.41% C, 5.50% H, 5.30% N.

1,4-Dimethyl-2,5- and 2,8-diaminoanthraquinones (VII, VIII)

The nitration mixture prepared from 16.6 ml nitric acid and 20 ml conc. sulphuric acid was added drop by drop to a solution of 28.5 g 1,4-dimethylanthraquinone (82.8%) in 140 ml conc. sulphuric acid at 0 to 2°C. The mixture was stirred 24 hours at 2 to 4°C and then poured onto a mixture of 1500 ml water and 1 kg crushed ice. The precipitate formed was collected by suction, washed with water until neutral, and mixed with 300 ml ethanol. The suspension obtained was heated to boiling, and 42 ml sodium hydrogen sulphide solution was added thereto drop by drop within 15 minutes. Boiling was maintained for another 2 hours. After cooling the mixture was diluted with a fivefold amount of water. The precipitate formed was collected by suction, washed with water and dried; yield 14 g (53%). According to chromatography on aluminium-silica plates the product did not contain any monoamino derivatives. By chromatography on an alumina

column (acetone-cyclohexane 1 : 3) a red substance could be isolated melting at 187°C and representing a mixture of 1,4-dimethyl-2,5- and 2,8-diaminoanthraquinones. For $C_{16}H_{14}N_2O_2$ (266.3) calculated: 72.20% C, 5.30% H, 10.53% N; found: 71.88% C, 5.25% H, 10.69% N.

2,3-Dimethyl-1-aminoanthraquinone (XI)

The nitration mixture prepared from 1.05 ml nitric acid and 5 ml conc. sulphuric acid was added drop by drop to a solution of 4.72 g 2,3-dimethylanthraquinone in 35 ml conc. sulphuric acid at 0°C. The reaction mixture was stirred 2 hours at 0 to 2°C and poured on ice water; the precipitate formed was collected by suction and washed with water until neutral. M.p. of 2,3-dimethyl-1-nitroanthraquinone (X) is 237–239°C (acetic acid). For $C_{16}H_{11}NO_4$ (281.3) calculated: 68.35% C, 3.95% H, 4.98% N; found: 68.44% C, 4.35% H, 4.84% N. The wet cake containing, besides 2,3-dimethyl-1-nitroanthraquinone, some starting 2,3-dimethylanthraquinone was mixed with 60 ml water and 60 ml hydrogen sulphide solution was added thereto. The reduction was refluxed 4 hours. The amino compound precipitated was collected by suction while hot and washed with hot water. After drying 4.6 g of the product was obtained (92%). Chromatographic test (aluminium plates with silica, acetone-cyclohexane 1 : 3) showed the main product, unreacted 2,3-dimethylanthraquinone and traces of 3 further substances which could not be removed by crystallization. Pure 2,3-dimethyl-1-aminoanthraquinone (XI) m.p. 214–215°C was obtained by a chromatography on an alumina column (chloroform). For $C_{16}H_{13}NO_2$ (251.3) calculated: 76.55% C, 5.21% H, 5.58% N; found: 76.96% C, 5.36% H, 5.57% N.

2,3-Dimethyl-1,5(8)-diaminoanthraquinone

A mixture of 4.2 ml nitric acid and 10 ml sulphuric acid was added dropwise to the solution of 4.72 g 2,3-dimethylanthraquinone in 45 ml conc. sulphuric acid at 0°C. The reaction mixture was maintained at 4°C 4 hours and then at 40°C until the mononitro compound disappeared (chromatographic test on aluminium plates with silica) *i.e.* 2 hours. The mixture was poured on ice water, the precipitate was collected by suction, washed with water and mixed with 60 ml water and 60 ml sodium hydrogen sulphide solution. After 4 hours refluxing the suspension was filtered, and the product was washed and dried; yield 5.1 g (96%). It represents a mixture of amino compounds with main 1,5- and 1,8-diamino derivatives and traces of 4 further compounds. Chromatography on an alumina column (chloroform) gave a mixture of 1,5- and 1,8-diamino derivatives melting at 240–250°C. For $C_{16}H_{14}N_2O_2$ (266.3) calculated: 72.20% C, 5.30% H, 10.53% N; found: 72.07% C, 5.48% H, 10.26% N.

N,N-Dimethyl-N'-(2,3-dimethyl-1-anthraquinonyl)formamidinium Chloride (XII)

A solution of 97.5 g raw 2,3-dimethyl-1-aminoanthraquinone in 250 ml *o*-dichlorobenzene was treated with 28.1 g dimethylformamide. The mixture was heated to 50°C, and 41.4 g thionyl chloride was added dropwise within 10 minutes. The same temperature was maintained 2 hours with stirring. Then the product was collected by suction, washed with *o*-dichlorobenzene and acetone and dried; yield 102 g (73%), m.p. 240–241°C (diluted acetic acid). For $C_{19}H_{20}N_2O_3Cl$ (360.8) *i.e.* monohydrate calculated: 63.30% C, 5.87% H, 7.88% N, 9.8% Cl; found: 63.30% C, 6.10% H, 7.86% N, 9.88% Cl. A solution of 89 g substance XII in 1000 ml water was filtered hot to remove the last residues of unnitrated dimethylanthraquinone. The filtrate was acidified with 60 ml conc. hydrochloric acid and heated at 90°C for 2 hours to complete the hydrolysis. After filtration, washing and drying of the precipitated 2,3-dimethyl-1-aminoanthraquinone (XI) the yield was 62.5 g (61.4%) of the chromatographically pure substance.

N,N-Dimethyl-*N'*-(2,3-dimethyl-1-anthraquinonyl)formamidineum hydroxide (*XIII*)

Solution of *N,N*-dimethyl-*N'*-(2,3-dimethyl-1-anthraquinonyl)formamidineum chloride (4 g) in 300 ml water was treated with 6 ml 2.5*N*-NaOH at 40°C. The base precipitated was collected by suction, washed with water and dried; yield 3.6 g, m.p. 173–178°C.

N,N-Dimethyl-*N'*-(2,3-dimethyl-4-nitro-1-anthraquinonyl)formamidineum chloride (*XIV*)

The nitration mixture prepared from 3.16 ml nitric acid and 10 ml sulphuric acid was added to a solution of 17.15 g dimethylformamidineum chloride *XIII* in 65 ml conc. sulphuric acid at 20°C within 20 minutes. The temperature increased spontaneously to 42°C, and it was maintained at 40°C for 90 minutes. Then the solution was poured onto ice water and the precipitate was collected by suction after 30 minutes, washed with water and with acetone. Yield of the dry substance 12.2 g (67.5%), m.p. 257–260°C (1*M*-HCl). For $C_{19}H_{18}N_3O_4Cl$ (387.8) calculated: 58.85% C, 4.68% H, 10.85% N, 9.14% Cl; found: 58.85% C, 4.92% H, 10.86% N, 9.01% Cl. 0.5 g dimethylnitroformamidineum chloride *XIV* was dissolved in 50 ml water with mild heating and acidified (Kongo Red). The solution was filtered, and the filtrate was precipitated by an excess of sodium hydroxide. The precipitate of formamidineum hydroxide was collected by suction, washed with water and dried in air first at room temperature and then at 110°C at 20 Torr; m.p. 230–237°C.

2,3-Dimethyl-1,4-diaminoanthraquinone (*XVI*)

7.62 g nitroformamidineum chloride *XIV* was hydrolyzed by boiling in 250 ml water and 15 ml conc. hydrochloric acid 5 hours. The precipitate was collected by suction and washed with water. M.p. of 2,3-dimethyl-1-amino-4-nitroanthraquinone (*XV*) 303–304°C. For $C_{16}H_{12}N_2O_4$ (296.2) calculated: 64.86% C, 4.08% H, 9.46% N; found: 64.77% C, 4.27% H, 9.98% N. The wet cake of nitro compound *XV* was reduced by 3 hours boiling with sodium hydrogen sulphide solution. The suspension was filtered and the product washed with water and dried; yield 4.1 g (78.2%) 2,3-dimethyl-1,4-diaminoanthraquinone (*XVI*), m.p. 282–283°C. For $C_{16}H_{14}N_2O_2$ (266.3) calculated: 72.16% C, 5.30% H, 10.52% N; found: 71.60% C, 5.39% H, 10.15% N.

2,3-Dimethyl-1,4-dinitroanthraquinone (*XXIV*)

A mixture of 0.5 g 2,3-dimethyl-1-amino-4-nitroanthraquinone, 20 ml acetic acid, 20 ml acetic anhydride and 13.3 ml 30% hydrogen peroxide was heated to boiling 90 minutes (tested by chromatography on aluminium plates with silica). The reaction mixture was left to stand overnight and poured on 200 ml water. The precipitate was collected by suction, washed with water and dried. Yield 0.41 g (74.3%), m.p. 300–301°C (acetic acid). For $C_{16}H_{10}N_2O_6$ (326.3) calculated: 58.90% C, 3.09% H, 8.59% N; found: 58.76% C, 3.57% H, 8.66% N.

2-Methyl-1,4-diaminoanthraquinone-3-carboxylic Acid (*XXVII*)

A solution of 9.93 g nitroanthraquinonylformamidineum chloride *XIV* in 7.6 ml 78% sulphuric acid was heated at 50°C, and 2.82 g solid sodium dichromate was added. The reaction mixture was diluted with 7.6 ml 78% sulphuric acid and 1.28 ml water and left to stand overnight, whereafter it was heated at 60°C 3 hours. After the reaction was finished, the solution was poured into 50 ml water and the monocarboxylic acid was salted out by addition of 15 g anhydrous sodium sulphate. The precipitate was collected by suction, and the filter cake was mixed with 25 ml water and 3 ml conc. hydrochloric acid and refluxed 2 hours to complete the hydrolysis. The

precipitate formed was collected by suction and mixed with 50 ml water and 5 ml ammonia. After 10 minutes stirring the suspension was filtered, and 2,3-dimethyl-1-amino-4-nitroanthraquinone (XXI) was washed with water and dried. The precipitate obtained by acidification of the filtrate was collected by suction, washed with little water, and the wet filter cake of 4-nitro-1-amino-2-methylantraquinone-3-carboxylic acid was reduced in 20 ml water by addition of 10 ml sodium hydrogen sulphide solution and refluxing for 1 hour. From the solution obtained the acid XXIII was precipitated by addition of 6 ml saturated potassium chloride solution. The precipitate was collected by suction, washed with saturated potassium chloride solution, again dissolved in 30 ml water and reprecipitated with hydrochloric acid (Kongo Red). The dark blue precipitate formed was collected by suction and washed with water. The substance was reprecipitated from sodium carbonate solution with hydrochloric acid. M.p. 264–266°C with decomposition. For $C_{16}H_{12}N_2O_4$ (296.3) calculated: 64.86% C, 4.08% H, 9.47% N; found: 64.46% C, 4.00% H, 9.61% N.

Anthraquinone-2,3- and 1,4-dicarboxylic Acids (XVIII, XIX)

A solution of 12 g 2,3-dimethylantraquinone in 100 ml 18% nitric acid was heated at 220°C in a titanium autoclave. After cooling the precipitate was collected by suction and washed with water. After drying 13.8 g (92%) anthraquinone-2,3-dicarboxylic acid was obtained melting at 339–340°C (acetic acid). The isomeric 1,4-anthraquinonedicarboxylic acid was prepared in the same way, m.p. 334–336°C.

Bis-(2,3-dicarboxy-1-anthraquinonyl)amine (XXV)

A solution of 2.8 g 2,3-dimethyl-1-aminoanthraquinone in 100 ml 18% nitric acid was heated at 220°C in a titanium autoclave 30 minutes. The precipitate formed was dissolved in diluted ammonia (5 ml 25% ammonia and 95 ml water), the solution was filtered, and the filtrate was acidified with hydrochloric acid (Kongo Red). The substance was purified by reprecipitation from ammonia solution with hydrochloric acid; yield 1.2 g (34.5%), m.p. 196–198°C. For $C_{32}H_{15}.NO_{12}$ (605.5) calculated: 63.55% C, 2.50% H, 2.33% N; found: 63.02% C, 3.08% H, 2.48% N.

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