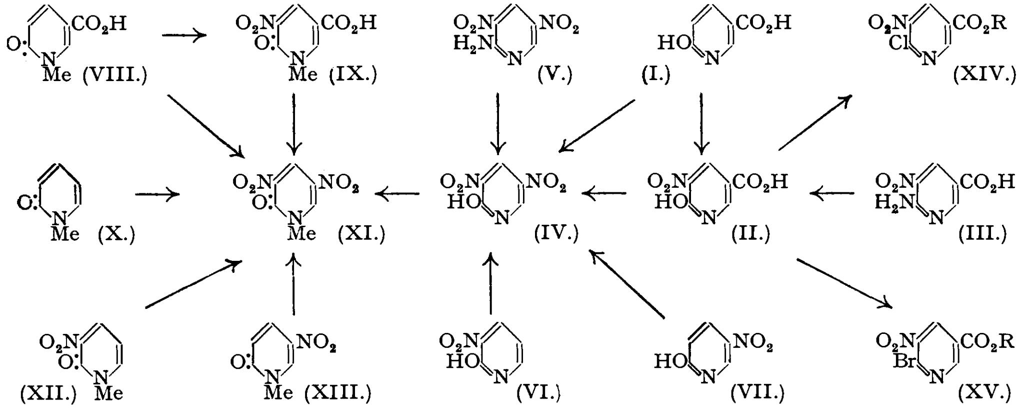
577. *The Nitration of 6-Hydroxynicotinic Acid and Related Compounds.*

By A. H. Berrie, G. T. Newbold, and F. S. Spring.

Nitration of 6-hydroxynicotinic acid gives 6-hydroxy-5-nitronicotinic acid and then 3 : 5-dinitro-2-pyridone. Similarly nitration of 1 : 6-dihydro-6-keto-1-methylnicotinic acid gives 1 : 6-dihydro-6-keto-1-methyl-5-nitronicotinic acid and finally 1-methyl-3 : 5-dinitro-2-pyridone.

This paper describes the preparation of a number of pyridine intermediates some of which are required in a projected synthesis of lysergic acid.

Nitration of 6-hydroxynicotinic acid (I) gives two products according to the reaction conditions. Treatment of (I) with fuming nitric acid at 50° gives 6-hydroxy-5-nitronicotinic acid (II) identical with that prepared by Räth and Prange (*Annalen*, 1928, **467**, 1) by the action of alkali on 6-amino-5-nitronicotinic acid (III). The acid (II) has been characterised by the formation of the methyl and the ethyl ester.

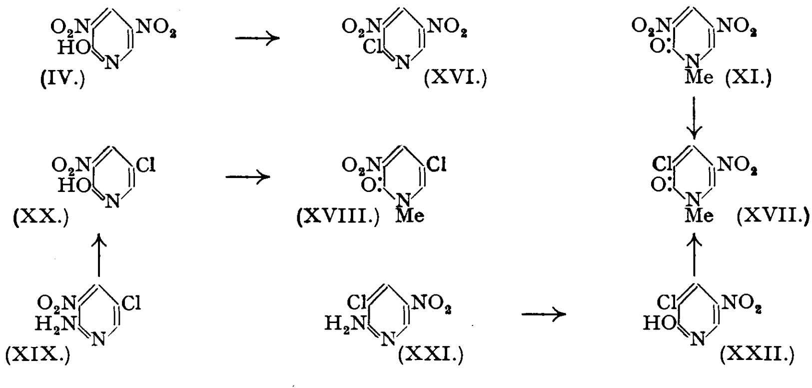


When heated under reflux with fuming nitric acid, 6-hydroxynicotinic acid gives a dinitropyridone, m. p. 175°, which is also obtained by similar treatment of 6-hydroxy-5-nitronicotinic acid. The compound, m. p. 175°, has been identified as 3 : 5-dinitro-2-pyridone (IV) by its preparation from 2-amino-3 : 5-dinitropyridine (V) (Tschitschibabin and Rasorenow, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1286; Tschitschibabin and Kirssanow, *Ber.*, 1928, **61**, 1223) by treatment with nitrous acid, and by its formation by nitration of either 3-nitro-2-pyridone (VI) or 5-nitro-2-pyridone (VII) (Tschitschibabin and Bylinkin, *J. Russ. Phys. Chem. Soc.*, 1918, **50**, 471; Tschitschibabin, *ibid.*, 1914, **46**, 1236).

A further proof of the structure ascribed to the dinitration product from 6-hydroxynicotinic acid has been obtained by a study of the nitration of 1 : 6-dihydro-6-keto-1-methylnicotinic acid (VIII). Treatment of this acid with fuming nitric acid at 55° gives 1 : 6-dihydro-6-keto-1-methyl-5-nitronicotinic acid (IX) characterised by the formation of the methyl and the ethyl ester. When 1 : 6-dihydro-6-ketonicotinic acid is heated under reflux with fuming nitric acid it gives a methyldinitropyridone, m. p. 178°, which is also obtained by similar treatment of 1 : 6-dihydro-6-keto-1-methyl-5-nitronicotinic acid. The compound, m. p. 178°, which is identical with the product obtained by Fischer and Chur (*J. prakt. Chem.*, 1916, [2], **93**, 363) from the nitration of 1-methyl-2-pyridone (X), has been identified as 1-methyl-3 : 5-dinitro-2-pyridone (XI) by its formation from 1-methyl-3-nitro-2-pyridone (XII) (Tschitschibabin and Konowalowa, *Ber.*, 1925, **58**, 1712) and 1-methyl-5-nitro-2-pyridone (XIII) (Räth, *Annalen*, 1930, **484**, 52) on nitration. Methylation of the dinitration product from 6-hydroxynicotinic acid gives 1-methyl-3 : 5-dinitro-2-pyridone, thus confirming the structure (IV) ascribed to the former compound.

The structure ascribed to 1 : 6-dihydro-6-keto-1-methyl-5-nitronicotinic acid (IX) depends on its formation from 1 : 6-dihydro-6-keto-1-methylnicotinic acid and on its conversion into 1-methyl-3 : 5-dinitro-2-pyridone. Other attempts to correlate it with compounds of established structure were not successful. Thus 6-hydroxy-5-nitronicotinic acid (II) was recovered unchanged after attempted methylation with either methyl iodide or methyl sulphate, and attempts to convert (IX) into the ester of 6-chloro- (XIV) or 6-bromo- (XV) -5-nitronicotinic acids, by treatment with phosphoryl chloride–phosphorus pentachloride or phosphorus tribromide–pentabromide followed by treatment of the products with alcohol, were unsuccessful, although (XIV, R = Me and Et) and (XV, R = Me and Et) were readily obtained by similar treatment of 6-hydroxy-5-nitronicotinic acid (II).

An attempt to confirm the relationship of 3 : 5-dinitro-2-pyridone (IV) and 1-methyl-3 : 5-dinitro-2-pyridone (XI) by the conversion of each into 2-chloro-3 : 5-dinitropyridine was not successful. Reaction of 3 : 5-dinitro-2-pyridone with phosphoryl chloride–phosphorus pentachloride proceeds smoothly to give 2-chloro-3 : 5-dinitropyridine (XVI). Treatment of 1-methyl-3 : 5-dinitro-2-pyridone (XI) with phosphoryl chloride–phosphorus pentachloride gives a compound, $C_6H_5O_3N_2Cl$, m. p. 115°, formed by the replacement of a nitro-group in (XI) by chlorine; this compound can be obtained in better yield by treatment of (XI) with thionyl chloride. The compound, m. p. 115°, has been shown by synthesis to be 3-chloro-1-methyl-5-nitro-2-pyridone (XVII) and to be different from 5-chloro-1-methyl-3-nitro-2-pyridone (XVIII). The last compound has been synthesised by the following route. Treatment of 2-amino-5-chloro-3-nitropyridine (XIX) (Tschitschibabin and Jegorow, *J. Russ. Phys. Chem. Soc.*, 1928, **60**, 683; Tschitschibabin and Kirssanow, *Ber.*, 1927, **60**, 766) with nitrous acid gives 5-chloro-3-nitro-2-pyridone (XX), methylation of which yields the required 5-chloro-1-methyl-3-nitro-2-pyridone (XVIII) which is distinct from the product obtained by chlorination of 1-methyl-3 : 5-dinitro-2-pyridone.



The synthesis of (XVII) was effected by treatment of 2-amino-3-chloro-5-nitropyridine (XXI) (Bystritskaya and Kirssanow, *J. Gen. Chem. U.S.S.R.*, 1940, **10**, 1827) with nitrous acid to give 3-chloro-5-nitro-2-pyridone (XXII), methylation of which gives the required 3-chloro-1-methyl-5-nitro-2-pyridone, identical with the product obtained by chlorination of 1-methyl-3 : 5-dinitro-2-pyridone.

The detailed proof of the structure of the dinitropyridone obtained from 6-hydroxynicotinic acid as described above is necessary since Tschitschibabin and Schapiro (*J. Russ. Phys. Chem. Soc.*, 1921, **53**, 233; cf. Binz and Maier-Bode, *Angew. Chem.*, 1936, **49**, 486) have claimed that nitration of 2-pyridone gives a product, m. p. 286° (decomp.), described as 3 : 5-dinitro-2-pyridone, the properties of which are entirely different from those of the 3 : 5-dinitro-2-pyridone described above. We have repeated the nitration of 2-pyridone according to Tschitschibabin and Schapiro and have obtained a product which has the properties of the compound described by these authors. We believe that the compound, m. p. 286° (decomp.), is a mixture of the sodium salt of 3-nitro-2-pyridone and the sodium salt of 3 : 5-dinitro-2-pyridone. Further nitration of the compound, m. p. 286° (decomp.), gives 3 : 5-dinitro-2-pyridone, m. p. 175°, in good yield.

EXPERIMENTAL.

6-*Hydroxy*-5-*nitronicotinic Acid* (II).—A solution of 6-hydroxynicotinic acid (50 g.) in nitric acid (500 c.c.; *d* 1·52) was kept at 45—50° for 4 hours. The mixture was evaporated under reduced pressure and the residue crystallised from water, giving 6-hydroxy-5-nitronicotinic acid (20 g.) as yellow needles, m. p. 278° (decomp.) undepressed by a specimen, m. p. 279—280° (decomp.), prepared as described by Räth and Prange (*loc. cit.*) (Found : C, 39·1; H, 2·3; N, 15·2. Calc. for $C_6H_4O_5N_2$: C, 39·1; H, 2·2; N, 15·2%). Light absorption in water : Maxima at 2110 (ε = 19,200) and 3600 Å (ε = 7900). The *methyl* ester, obtained in 65% yield by the Fischer–Speier method, separated from methanol as pale yellow needles, m. p. 206° (Found : C, 42·5; H, 2·8; N, 14·1. $C_7H_6O_5N_2$ requires C, 42·4; H, 3·1; N, 14·1%). The *ethyl* ester was prepared in 69% yield by the same method; it separated as pale yellow needles, m. p. 165—167°, from benzene (Found : C, 45·4; H, 3·8; N, 13·4. $C_8H_8O_5N_2$ requires C, 45·3; H, 3·8; N, 13·2%).

3 : 5-*Dinitro*-2-*pyridone* (IV).—(*a*) 6-Hydroxynicotinic acid (2 g.) in nitric acid (20 c.c.; *d* 1·52) was heated under reflux for 30 hours. The solution was evaporated and the residue crystallised from water, giving 3 : 5-*dinitro*-2-*pyridone* (1·0 g.) as stout yellow needles, m. p. 175° (Found : C, 32·8; H, 1·9; N, 22·9. $C_5H_3O_5N_3$ requires C, 32·4; H, 1·6; N, 22·7%). Light absorption in water : Maxima at 2140 (ε = 13,400) and 3260 Å (ε = 11,400).

(*b*) 6-Hydroxy-5-nitronicotinic acid (1·0 g.) in nitric acid (10 c.c.; *d* 1·52) was heated under reflux for 30 hours to give 3 : 5-dinitro-2-pyridone (0·5 g.) as stout yellow needles (from water), m. p. 175° alone or mixed with a specimen prepared by method (*a*).

(*c*) Dry sodium nitrite (0·7 g.) was slowly added to sulphuric acid (15 c.c.; *d* 1·84) with shaking and gentle heating to complete solution. The solution was cooled to 30° and treated with 2-amino-3 : 5-dinitropyridine (0·92 g.) added in portions with stirring. The mixture was then stirred for 2 hours, the temperature falling to 10°. It was diluted with water (20 c.c.), kept at 10° for 30 minutes, and then treated with a solution of sodium hydroxide (15 g.) in water (30 c.c.). After the mixture had been shaken for 30 minutes at 30°, the solid was collected and crystallised from water, giving 3 : 5-dinitro-2-pyridone (0·8 g.) as pale yellow needles, m. p. 174—175° alone or mixed with a specimen prepared by method (*a*) (Found : C, 32·7; H, 1·6; N, 23·0%).

(*d*) 3-Nitro-2-pyridone (1 g.) was heated under reflux with nitric acid (10 c.c.; *d* 1·52) for 2 hours. The solution was evaporated and the residue crystallised from water, giving 3 : 5-dinitro-2-pyridone (0·3 g.) as pale yellow needles, m. p. 175° alone or mixed with a specimen prepared by method (*a*) (Found : C, 32·5; H, 1·6%). Light absorption in water : Maxima at 2120 (ε = 13,400) and 3300 Å (ε = 11,400).

(*e*) Similar treatment of 5-nitro-2-pyridone gave 3 : 5-dinitro-2-pyridone in 38% yield as pale yellow needles (from water), m. p. 175° alone or mixed with a specimen prepared by method (*a*) (Found : C, 32·7; H, 1·7%). Light absorption in water : Maxima at 2120 (ε = 13,000) and 3300 Å (ε = 12,300).

1 : 6-*Dihydro*-6-*keto*-1-*methyl*-5-*nitronicotinic Acid* (IX).—1 : 6-Dihydro-6-keto-1-methylnicotinic acid (30·6 g.) was dissolved in nitric acid (306 c.c.; *d* 1·52), the temperature being kept below 55°. The solution was maintained at 50—55° for 5 hours and then concentrated to a small bulk at the same temperature; this was diluted with water (200 c.c.) and neutralised with solid sodium hydrogen carbonate. When the mixture had cooled, a solid (*A*) was filtered off, the filtrate was acidified with concentrated hydrochloric acid, and the solid collected. Crystallisation of this from water gave 1 : 6-*dihydro*-6-*keto*-1-*methyl*-5-*nitronicotinic acid* (15·8 g.) as stout yellow needles, m. p. 217—222° (Found : C, 42·6; H, 3·0; N, 14·2. $C_7H_6O_5N_2$ requires C, 42·4; H, 3·1; N, 14·1%). Light absorption in water : Maxima at 2180 (ε = 18,100) and 3640 Å (ε = 6600).

Methyl ester. A mixture of the acid (1·98 g.), phosphorus pentachloride (4·2 g.), and phosphoryl chloride (2·0 g.) was heated under reflux for 1 hour. Excess of reagents was removed under reduced pressure and the residue was crystallised from methanol, giving the *methyl* ester (1·5 g.) as yellow needles, m. p. 147—149° (Found : C, 45·2; H, 3·7; N, 13·3. $C_8H_8O_5N_2$ requires C, 45·3; H, 3·8; N, 13·2%).

Ethyl ester. The acid (1·98 g.) was heated under reflux with thionyl chloride (10 c.c.) for 3 hours. The solution was concentrated under reduced pressure and the residue treated with ethanol (25 c.c.). The solid was recrystallised from ethanol, giving the *ethyl* ester (1·5 g.) as pale yellow needles, m. p. 124° (Found : C, 47·8; H, 4·4. $C_9H_{10}O_5N_2$ requires C, 47·8; H, 4·5%).

1-*Methyl*-3 : 5-*dinitro*-2-*pyridone* (XI).—(*a*) 1 : 6-Dihydro-6-keto-1-methylnicotinic acid (3·06 g.) was heated under reflux for 5 hours with nitric acid (30·6 c.c.; *d* 1·52), and the solution evaporated to dryness. The residue crystallised from water, giving 1-methyl-3 : 5-dinitro-2-pyridone (2·0 g.) as yellow leaflets, m. p. 178° undepressed when mixed with a specimen, m. p. 178°, prepared according to Fischer and Chur (*loc. cit.*) from 1-methyl-2-pyridone (Found : C, 36·5; H, 2·4; N, 21·1. Calc. for $C_6H_5O_5N_3$: C, 36·2; H, 2·5; N, 21·1%). Light absorption in water : Maxima at 2080 (ε = 20,600), 2180 (ε = 19,100), and 3100 Å (ε = 12,700).

(*b*) The solid (*A*) obtained during the preparation of 1 : 6-dihydro-6-keto-1-methyl-5-nitronicotinic acid was crystallised from water, giving 1-methyl-3 : 5-dinitro-2-pyridone (0·2 g.) as pale yellow plates, m. p. 178° alone or when mixed with a specimen prepared as described under (*a*).

(*c*) 1 : 6-Dihydro-6-keto-1-methyl-5-nitronicotinic acid (0·25 g.) was heated under reflux with nitric acid (5 c.c.; *d* 1·52) for 4 hours to give 1-methyl-3 : 5-dinitro-2-pyridone (0·2 g.) as pale yellow leaflets (from water), m. p. 177° undepressed when mixed with a specimen prepared as described under (*a*).

(*d*) 1-Methyl-3-nitro-2-pyridone (0·7 g.) was heated under reflux for 2 hours with nitric acid (10 c.c.; *d* 1·52). The solution was evaporated to dryness and the residue crystallised from water, giving 1-methyl-3 : 5-dinitro-2-pyridone (0·3 g.) as yellow leaflets, m. p. 175—177° alone or when mixed with a specimen prepared by method (*a*) (Found : C, 36·5; H, 2·6; N, 21·5%). Light absorption in water : Maxima at 2080 ($\varepsilon = 20{,}600$), 2180 ($\varepsilon = 19{,}000$), and 3080 Å ($\varepsilon = 12{,}200$).

(*e*) Similar treatment of 1-methyl-5-nitro-2-pyridone (0·7 g.) gave 1-methyl-3 : 5-dinitro-2-pyridone (0·5 g.) as yellow leaflets (from water), m. p. 177° alone or when mixed with preparation (*a*).

(*f*) A solution of 3 : 5-dinitro-2-pyridone (0·92 g.) and potassium hydroxide (0·28 g.) in water (10 c.c.) was evaporated to dryness. The solid was powdered and heated at 120° for 3 hours in a sealed tube with methanol (5 c.c.) and methyl iodide (3 c.c.). The solvent was evaporated and the residue crystallised from water (charcoal), giving 1-methyl-3 : 5-dinitro-2-pyridone (0·5 g.) as yellow leaflets, m. p. 178° undepressed when mixed with specimen (*a*).

Methyl 6-*Bromo*-5-*nitronicotinate* (XV, R = Me).—6-Hydroxy-5-nitronicotinic acid (1·84 g.) was added to a mixture of phosphorus tribromide (10 c.c.) and bromine (6·4 g.) and heated at 100° for 20 hours. The excess of phosphorus tribromide was removed under reduced pressure and the residue decomposed with methanol (20 c.c.). The residue obtained on evaporation below 30° was crystallised from light petroleum (b. p. 60—80°), giving *methyl* 6-*bromo*-5-*nitronicotinate* (1·6 g.) as pale yellow needles, m. p. 98° (Found : N, 10·6. $C_7H_5O_4N_2Br$ requires N, 10·7%).

Ethyl 6-*Bromo*-5-*nitronicotinate* (XV, R = Et).—This was obtained in 40% yield by a similar method; the *ester* separated from light petroleum (b. p. 60—80°) as pale yellow stout needles, m. p. 85° (Found : C, 35·0; H, 2·8; N, 10·1. $C_8H_7O_4N_2Br$ requires C, 34·9; H, 2·6; N, 10·2%).

Methyl 6-*Chloro*-5-*nitronicotinate* (XIV, R = Me).—A mixture of 6-hydroxy-5-nitronicotinic acid (0·92 g.), phosphorus pentachloride (3 g.), and phosphoryl chloride (5 c.c.) was heated at 100° for 2 hours. Excess of phosphoryl chloride was removed under reduced pressure and the residue treated with methanol (10 c.c.). Water (40 c.c.) was added and the precipitated solid crystallised from light petroleum (b. p. 60—80°) from which *methyl* 6-*chloro*-5-*nitronicotinate* (0·92 g.) separated as pale yellow leaflets, m. p. 76° (Found : C, 38·9; H, 2·3; N, 12·8. $C_7H_5O_4N_2Cl$ requires C, 38·8; H, 2·3; N, 12·9%).

Ethyl 6-*Chloro*-5-*nitronicotinate* (XIV, R = Et).—This was obtained in 44% yield by a similar method; the *ester* separated from aqueous ethanol as prisms, m. p. 61° (Found : C, 41·6; H, 3·3; N, 12·5. $C_8H_7O_4N_2Cl$ requires C, 41·7; H, 3·1; N, 12·2%).

2-*Chloro*-3 : 5-*dinitropyridine* (XVI).—A mixture of 3 : 5-dinitro-2-pyridone (0·92 g.), phosphorus pentachloride (1·5 g.), and phosphoryl chloride (2 c.c.) was heated at 120° in a sealed tube for 2 hours. Excess of phosphoryl chloride was removed under reduced pressure, and the residue treated with water (15 c.c.) and basified with sodium hydroxide solution with cooling. The solid was separated and crystallised from light petroleum (b. p. 60—80°) from which 2-*chloro*-3 : 5-*dinitropyridine* (0·5 g.) separated as laminæ, m. p. 64° (Found : N, 20·5. $C_5H_2O_4N_3Cl$ requires N, 20·6%).

5-*Chloro*-3-*nitro*-2-*pyridone* (XX).—A solution of 2-amino-5-chloro-3-nitropyridine (1·25 g.) in sulphuric acid (4 c.c.; *d* 1·84) was diluted with water (2·5 c.c.). Sodium nitrite (1·0 g.) was added portionwise below 10° with stirring. Stirring was continued for 1 hour below 10°, and the cooled reaction mixture was then diluted with water (25 c.c.) and kept overnight at 0°. The solid which separated was crystallised from ethanol, giving 5-*chloro*-3-*nitro*-2-*pyridone* (1·18 g.) as yellow prisms, m. p. 235° (Found : C, 34·7; H, 1·5. $C_5H_3O_3N_2Cl$ requires C, 34·4; H, 1·7%).

5-*Chloro*-1-*methyl*-3-*nitro*-2-*pyridone* (XVIII).—A solution of 5-chloro-3-nitro-2-pyridone (1·75 g.) in aqueous potassium hydroxide (10 c.c.; 6%) was evaporated to dryness. The powdered potassium salt was heated under reflux for 2 hours in ethanol (10 c.c.) with methyl iodide (4·0 g.). The mixture was filtered from solid material which was washed with benzene. The filtrate and washings were evaporated under reduced pressure and the residue crystallised from benzene–light petroleum (b. p. 60—80°) (charcoal) from which 5-*chloro*-1-*methyl*-3-*nitro*-2-*pyridone* (0·5 g.) separated as small, pale yellow prisms, m. p. 126° (Found : C, 38·8; H, 2·7; N, 14·7. $C_6H_5O_3N_2Cl$ requires C, 38·2; H, 2·7; N, 14·9%). A mixture with the compound (m. p. 115°) obtained by the chlorination of 1-methyl-3 : 5-dinitro-2-pyridone had m. p. 85—95°.

2-*Amino*-3-*chloro*-5-*nitropyridine* (XXI).—2-Amino-5-nitropyridine (1·39 g.) was dissolved in ethanol (100 c.c.) and treated with chlorine (0·71 g.) with ice-cooling. The solution was evaporated under reduced pressure, water (20 c.c.) added, and the insoluble material filtered off, washed with water, and dried. Crystallisation from ethanol (charcoal) gave 2-amino-3-chloro-5-nitropyridine (0·85 g.) as pale yellow needles, m. p. 211—213° (Bystritskaya and Kirssanow, *loc. cit.*, give m. p. 205—206°) (Found : N, 24·4. Calc. for $C_5H_4O_2N_3Cl$: N, 24·2%).

3-*Chloro*-5-*nitro*-2-*pyridone* (XXII).—The preparation of this compound by the action of hydrochloric acid at 150° on 2 : 3-dichloro-5-nitropyridine is described in U.S.P. 1,778,784, but we have not found any reference in the literature to the preparation of the latter compound (cf. D.R.-P. 597,974). 2-Amino-3-

chloro-5-nitropyridine (0·35 g.) in sulphuric acid (1·0 c.c.; *d* 1·84) and water (0·5 c.c.) was cooled below 10° and treated with sodium nitrite (0·3 g.) added in portions with shaking. After being shaken for a further hour, the mixture was diluted with water (6 c.c.), cooled to 0°, and filtered. Crystallisation of the residue from aqueous ethanol gave 3-chloro-5-nitro-2-pyridone (0·2 g.) as pale yellow prisms, m. p. 198° (U.S.P. 1,778,784 gives m. p. 198°) (Found: N, 16·5. Calc. for $C_5H_3O_3N_2Cl$: N, 16·0%).

3-*Chloro*-1-*methyl*-5-*nitro*-2-*pyridone* (XVII).—(*a*) A mixture of 1-methyl-3 : 5-dinitro-2-pyridone (1·99 g.), phosphorus pentachloride (3 g.), and phosphoryl chloride (2 c.c.) was heated in a sealed tube at 150° for 4 hours. The excess of phosphoryl chloride was removed under reduced pressure and the residue was treated with ice-water (15 c.c.) and made alkaline with potassium hydroxide solution. The mixture was extracted with cold benzene (20 c.c.), the insoluble 1-methyl-3 : 5-dinitro-2-pyridone (0·5 g.; m. p. 170—174°) separated, and the dried (Na_2SO_4) benzene extract evaporated. The residue was crystallised from ethyl acetate–light petroleum (b. p. 60—80°) (charcoal), giving 3-*chloro*-1-*methyl*-5-*nitro*-2-*pyridone* (0·2 g.) as pale-yellow prisms, m. p. 115° (Found: C, 38·8; H, 2·5; N, 15·2. $C_6H_5O_3N_2Cl$ requires C, 38·2; H, 2·7; N, 14·9%).

(*b*) 1-Methyl-3 : 5-dinitro-2-pyridone (0·99 g.) and thionyl chloride (5 c.c.) were heated in a sealed tube at 140—150° for 5 hours. The excess of thionyl chloride was removed under reduced pressure and the residue shaken with hot benzene (10 c.c.). The mixture was cooled and filtered from unchanged 1-methyl-3 : 5-dinitro-2-pyridone (0·25 g.; m. p. 169—172°), the filtrate evaporated, and the residue crystallised from ethyl acetate–light petroleum (b. p. 60—80°) (charcoal), giving 3-chloro-1-methyl-5-nitro-2-pyridone (0·4 g.) as pale yellow prisms, m. p. 114—115° alone or mixed with a specimen prepared by method (*a*).

(*c*) A solution of 3-chloro-5-nitro-2-pyridone (1·75 g.) in aqueous potassium hydroxide (10 c.c.; 6%) was evaporated to dryness. The residue was heated under reflux with ethanol (10 c.c.) and methyl iodide (5 c.c.) for 2 hours, the solvent removed, and the residue extracted with hot benzene. The benzene extract was evaporated and the residue sublimed at $110°/10^{-2}$ mm. Crystallisation of the sublimate from ethyl acetate–light petroleum (b. p. 40—60°) gave 3-chloro-1-methyl-5-nitro-2-pyridone (1·5 g.) as prisms, m. p. 115° undepressed when mixed with the specimen prepared as described under (*a*) (Found: N, 15·0%).

Nitration of 2-pyridone, as described by Tschitschibabin and Schapiro (*loc. cit.*), gave a product which separated from ethanol as small yellow needles, m. p. 286° (decomp.) (Found: N, 16·5%). Light absorption in water: Maxima at 2160 ($E^{1\%}_{1\,\mathrm{cm.}} = 580$) and 3380 Å ($E^{1\%}_{1\,\mathrm{cm.}} = 590$). When heated on a spatula in a free flame it explodes violently; for this reason satisfactory carbon and hydrogen analyses could not be obtained.

Sodium 3-*Nitro*-2-*pyridyl Oxide*.—3-Nitro-2-pyridone (1·4 g.) was dissolved in hot sodium hydroxide solution (5%; 10 c.c.). The solid which separated on cooling was crystallised from aqueous ethanol, giving the *monohydrate* of sodium 3-nitro-2-pyridyl oxide (0·9 g.) as fine yellow needles, m. p. 340° (decomp.) (Found: N, 15·6. $C_5H_3O_3N_2Na,H_2O$ requires N, 15·6%). Light absorption in water: Maxima at 2580 ($\varepsilon = 2400$) and 3600 Å ($\varepsilon = 6600$).

Sodium 5-*Nitro*-2-*pyridyl Oxide*.—5-Nitro-2-pyridone was treated in a similar manner to give the trihydrate of sodium 5-nitro-2-pyridyl oxide as stout yellow needles (from aqueous ethanol), m. p. 318° (decomp.) (Found: N, 13·2. Calc. for $C_5H_3O_3N_2Na,3H_2O$: N, 13·0%) [Räth and Prange, *Ber.*, 1925, **58**, 1208, give m. p. 303° (decomp.) for the trihydrate obtained by the alkaline hydrolysis of 2-nitramino-5-nitropyridine]. Light absorption in water: Maxima at 2060 ($\varepsilon = 9100$) and 3020 Å ($\varepsilon = 10,500$).

Sodium 3 : 5-*Dinitro*-2-*pyridyl Oxide*.—Similar treatment of 3 : 5-dinitro-2-pyridone gave the *dihydrate* of sodium 3 : 5-dinitro-2-pyridyl oxide as long, pale yellow needles (from aqueous ethanol), m. p. 298° (decomp.) (Found: N, 17·0. $C_5H_2O_5N_3Na,2H_2O$ requires N, 17·3%). Light absorption in water: Maxima at 2100 ($\varepsilon = 13,600$) and 3260 Å ($\varepsilon = 10,100$).

The three sodium salts described above resemble Tschitschibabin and Schapiro's compound in that they decompose violently when heated.

3 : 5-*Dinitro*-2-*pyridone* (IV).—The compound, m. p. 286° (decomp.) (1·0 g.; see above), was heated under reflux with nitric acid (10 c.c.; *d* 1·52) for 2 hours. The residue obtained on evaporation was recrystallised from dilute hydrochloric acid, giving 3 : 5-dinitro-2-pyridone (0·7 g.) as pale yellow needles, m. p. 175° undepressed when mixed with an authentic specimen.

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THE ROYAL TECHNICAL COLLEGE, GLASGOW.

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