CCCXIX.—*The Preparation of some Nitrohydroxybenzaldehydes and the Colour Relationships of their Substituted Phenylhydrazones.*

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MONONITRO-*m*-HYDROXYBENZALDEHYDES were first described by Tiemann and Ludwig (*Ber.*, 1882, **15**, 2043) but correctly oriented by Friedländer and Schenck (*Ber.*, 1914, **47**, 3040), whilst Friedländer and Schreiber (*Ber.*, 1895, **28**, 1382) described the mononitration of *m*-methoxybenzaldehyde, thereby completing previous work by Ulrich (*Ber.*, 1885, **18**, 2571) and Rieche (*Ber.*, 1889, **22**, 2349). Tiemann and Ludwig's α- and β-dinitro-*m*-methoxybenzaldehydes, m. p.'s 155° and 110°, respectively, have not, however, been oriented; this problem, together with an investigation on the di- and tri-nitro-*m*-hydroxy- and the dinitro-*p*-hydroxy-benzaldehydes, is now dealt with.

Controlled direct dinitration of *m*-hydroxybenzaldehyde proved impracticable, the reaction products containing unchanged material and inseparable mixtures of nitro-compounds. Nitration of 6-nitro-3-hydroxybenzaldehyde gave two dinitro-products, m. p.'s 94° and 106°, whereas nitration of 2- and 4-nitro-3-hydroxybenzaldehydes gave single products melting at 94° and 106°, respectively, which must therefore be the 2 : 6- and 4 : 6-*dinitro*-3-*hydroxybenzaldehydes*. These could not be methylated by the ordinary methods, but a mixture of 2 : 6- and 4 : 6-*dinitro*-3-*methoxybenz*-

aldehydes was obtained by the dinitration of *m*-methoxybenzaldehyde at a lower temperature than that employed by Tiemann and Ludwig (*loc. cit.*), and separated by fractional crystallisation from hot benzene, in which the latter is five times more soluble than the former. Confirmation of their constitutions was obtained by nitration of the 6-, 4-, and 2-nitro-3-methoxybenzaldehydes, the first giving a mixture of two products, m. p.'s 157° and 131°, and the other two giving single products, of m. p.'s 131° and 157°, which are therefore 4 : 6- and 2 : 6-dinitro-3-methoxybenzaldehyde, respectively. Tiemann's α-compound (*loc. cit.*) is consequently the 2 : 6-dinitro-isomeride, whereas his β-compound is a mixture of this with the 4 : 6-isomeride.

All three mononitro- and both dinitro-3-hydroxybenzaldehydes give the same trinitrated product, which must therefore be the 2 : 4 : 6-*trinitro*-3-*hydroxybenzaldehyde.*

Nitration of 3-nitro-4-hydroxybenzaldehyde with pure nitric acid gives 3 : 5-*dinitro*-4-*hydroxybenzaldehyde*, but if sulphuric acid is present only picric acid is formed. It is noteworthy that the introduction of two nitro-groups into either *m*- or *p*-hydroxybenzaldehyde or their chloro-derivatives (Hodgson and Beard, J., 1926, 2030) gives products which all melt between 90° and 110°.

The facility of decomposition of the *p*-nitrophenylhydrazones of the various nitrohydroxybenzaldehydes appears to depend upon the positions of the nitro-groups in the aldehyde residue, *e.g.*, 2 : 6-dinitro-3-hydroxy- and -3-methoxybenzaldehyde-*p*-nitrophenylhydrazones explode at about 240° and 260°, respectively, whereas the 4 : 6-dinitro-isomerides are stable above 300°.

Colours and Colour-reactions.

The colours of the nitro- and *p*-bromo-phenylhydrazones of the above aldehydes, both as solids and in aqueous and alcoholic alkaline solution, are discussed in relation to positional influences.

Acidic groups in both *o*-positions to the aldehyde radical reduce the depth of colour of the solid phenylhydrazones in a similar way to that found by Chattaway and Clemo (J., 1923, **123**, 3041) for the hydrazine nucleus; thus, the phenylhydrazones of 2- and 3-nitrobenzaldehydes are respectively crimson and deep bright orange, whereas those of the corresponding dichloro-derivatives (2 : 5-dichloro-6-nitro- and -3-nitro-benzaldehydes) are orange-yellow and orange; the introduction of a *p*-nitro-group into the hydrazine nucleus causes a further reduction of colour, *e.g.*, to a pale yellow in the case of 2 : 5-dichloro-6-nitrobenzaldehyde-*p*-nitrophenylhydrazone.

The presence of the hydroxyl group modifies Chattaway and

Clemo's generalisation, for the *p*-nitrophenylhydrazone of 2-nitro-3-hydroxybenzaldehyde is much darker than that of the 6-nitro-isomeride, although the nitro-group is ortho in each case; methylation of the hydroxyl group, however, removes the disturbing effect, the *p*-bromophenylhydrazones of 2-nitro-3-hydroxy- and -3-methoxy-benzaldehydes being deep nigre-brown and bright orange, respectively.

Alcoholic solutions of the hydrazones now described obey Chattaway and Clemo's generalisation. The exceptional case quoted by them—the phenylhydrazone of 2 : 5-dichloro-6-nitrobenzaldehyde—is not repeated, however, in the *p*-nitrophenylhydrazone of this aldehyde, which, instead of merely affording the magenta colour characteristic of substituted phenylhydrazones, as would be expected if the exceptional character persisted, now gives a pronounced blue colour, showing that the nitro-group in the aldehyde residue is again functioning in a quinonoid structure.

2 : 5-Dichloro-3-nitrobenzaldehydephenylhydrazone gives the pronounced brown colour with alkalis associated with Chattaway and Clemo's scheme, but the *p*-nitrophenylhydrazone gives a blue and not a magenta colour as expected.

The magenta colours given by *m*-hydroxy- and nitro-*m*-hydroxybenzaldehyde-*p*-nitrophenylhydrazones persist to much greater dilutions than if the hydroxyl group is absent, and that these colours are not due to salt formation alone is shown by the fact that the *m*-nitrophenylhydrazone of the *m*-hydroxyaldehyde gives no colour reaction.

The *p*-bromophenylhydrazones of the nitrohydroxyaldehydes are colourless in aqueous alkaline solution, thus, by contrast with the foregoing, showing that the methine group is far more resistant to quinonoid formation than the imino-group. This same difference is also illustrated by the fact that when aqueous alkaline solutions of benzaldehyde-*p*-nitrophenylhydrazone and *p*-nitrobenzaldehydephenylhydrazone are diluted, the colour of the former persists to much greater dilutions (about 400-fold). Differential suppression of colour is shown by the sequence of colour changes (blue, violet, magenta) on dilution of *p*-nitrobenzaldehyde-*p*-nitrophenylhydrazone.

The pronounced colour effects in alcoholic alkaline solutions when a nitro-group is in the para-position in each nucleus suggest a double quinonoid structure (*e.g.*, $OK\cdot NO{:}C_6H_4{:}C{:}N\cdot N{:}C_6H_4{:}NO\cdot OK$), since in a mixture of two singly-quinonoid compounds the magenta of the hydrazine-quinonoid compound would predominate, as it does if a *m*-hydroxyl group is present in the aldehyde nucleus.

Correction.—Hodgson and Beard (J., 1926, 2034) nitrated what was thought to be pure 4-chloro-3-hydroxybenzaldehyde and obtained what they regarded as the 2- and 6-nitro-derivatives. It is now found that the 4-nitro-3-hydroxybenzaldehyde from which the above chloro-derivative had been prepared contained some of its 2-nitro-isomeride—these two are very difficult to separate—and consequently the resulting chloro-compound was a corresponding mixture. The supposed 4-chloro-6-nitro-3-hydroxybenzaldehyde is now shown to be the 2-nitro-isomeride (by conversion to 2 : 4-dichloro-3-hydroxybenzaldehyde), and the supposed 4-chloro-2-nitro-3-hydroxybenzaldehyde is really the 2-chloro-4-nitro-compound (identified by mixed m. p. and comparison of semicarbazones and *p*-nitrophenylhydrazones).

EXPERIMENTAL.

Nitration of 6-*Nitro*-3-*hydroxybenzaldehyde.*—To the aldehyde (10 g.; m. p. 166°) in glacial acetic acid (30 c.c.) solution at 70°, nitric acid (10 c.c.; *d* 1·42) was added during ¼ hour; the mixture was kept for a further ¼ hour and poured into ice water (150 c.c.); and the voluminous mass of crystals (9 g.; m. p. 71—74°) which slowly separated was extracted with boiling water, which removed 2 : 6-dinitro- from the much less soluble 4 : 6-dinitro-3-hydroxybenzaldehyde.

Nitration of 2-*Nitro*-3-*hydroxybenzaldehyde.*—2 G. on similar treatment gave only the above water-soluble product (1·8 g.), identified by a mixed m. p. determination and through the *p*-nitro- and *p*-bromo-phenylhydrazones.

Nitration of 4-*Nitro*-3-*hydroxybenzaldehyde.*—The above treatment gave unchanged material only; nitration of a sulphuric acid solution by potassium nitrate (1 mol.) gave a mixture of 4 : 6-dinitro- and 2 : 4 : 6-trinitro-3-hydroxybenzaldehydes with unchanged material, whereas excess of potassium nitrate (2 mols.) gave mainly the trinitro-product. If the finely-powdered aldehyde (10 g.) was added gradually to well-stirred synthetic nitric acid (50 g.; 98%) at 5—10°, and the mixture was allowed to attain room temperature before being poured on ice (250 g.), the trinitro-product (3 g.) separated, and the 4 : 6-dinitro-compound (5·4 g.) could be salted out of solution. Identity of the latter with the less soluble product above was established as in the case of the more soluble product.

2 : 6-*Dinitro*-3-*hydroxybenzaldehyde* is more soluble in the usual solvents than its 4 : 6-isomeride, and crystallises from water in colourless needles, m. p. 94° (Found : N, 13·3. $C_7H_4O_6N_2$ requires N, 13·2%). On exposure to air, it acquires a deep brown colour, whereas its alcoholic solution turns green. The yellow *sodium* and dark orange *ammonium* salts are both very soluble in water, but the silver salt could not be obtained. The p-*nitrophenylhydrazone*, deep

terra-cotta needles which explode at 240—242°, and the p-*bromophenylhydrazone*, similar crystals, m. p. 166—167° (decomp.) (Found: Br, 20·8. $C_{13}H_9O_5N_4Br$ requires Br, 21·0%), were both crystallised from glacial acetic acid.

4 : 6-*Dinitro*-3-*hydroxybenzaldehyde* crystallises from dilute acetic acid in almost colourless needles, m. p. 106° (Found: N, 12·9%). The orange *sodium* and dark orange *ammonium* salts are very soluble in water, but the silver salt could not be prepared. The p-*nitrophenylhydrazone* forms deep reddish-orange needles, which decompose slowly at 282—283°; the p-*bromophenylhydrazone* forms dark crimson needles, m. p. 249—250° (decomp.) (Found: Br, 20·8%).

2 : 4 : 6-*Trinitro*-3-*hydroxybenzaldehyde* is produced when 6-nitro-3-hydroxybenzaldehyde (10 g.) in concentrated sulphuric acid (50 g.) is treated gradually with a mixture of nitric acid (25 c.c.; *d* 1·42) and sulphuric acid (25 c.c.; *d* 1·84) at 70—75°; the cooled mixture is poured on ice (200 g.); the precipitate crystallises from benzene in stout, colourless, hexagonal prisms, m. p. 161—162° (decomp.) (Found: N, 16·7. $C_7H_3O_8N_3$ requires N, 16·3%). The product is much more soluble in water than picric acid. The solutions in alkalis are deep red, although the *sodium* salt crystallises in bright yellow needles. The p-*nitrophenylhydrazone*, dark crimson needles, exploded violently at 228—230°, and the p-*bromophenylhydrazone*, deep olive-green parallelepipeds with metallic lustre, also exploded violently at 218—220° (Found: Br, 18·8. $C_{13}H_8O_7N_5Br$ requires Br, 18·8%). The *azine* was prepared by adding a mixture of hydrazine sulphate (1 g.), sodium hydroxide (3 c.c.; 20%), and water (5 c.c.) to a hot solution of the aldehyde (2 g.) in water (60 c.c.), and separated, on cooling, in bright yellow micro-needles; it is readily soluble in acetic acid (50%) and alcohol, insoluble in benzene and chloroform, and gives red solutions with alkalis; it explodes violently at 150—160°.

2 : 4 : 6-Trinitro-3-hydroxybenzaldehyde was also obtained from 2- and 4-nitro-3-hydroxybenzaldehyde, but the product from the latter was much less pure than in the other cases.

Dinitration of p-*Hydroxybenzaldehyde*.—Mixtures of nitric and sulphuric acids yielded only picric acid, but when 3-nitro-4-hydroxybenzaldehyde (10 g.) was added with stirring to nitric acid (80 g.; 98%) at 5° and the deep red solution was allowed to warm to 10° and then poured on ice (150 g.), a mixture (10 g.) of 3 : 5-dinitro-4-hydroxybenzaldehyde and picric acid was obtained, the latter being eliminated by one crystallisation from glacial acetic acid.

3 : 5-*Dinitro*-4-*hydroxybenzaldehyde* crystallises in colourless needles, m. p. 102—103° (Found: N, 13·1. $C_7H_4O_6N_2$ requires

N, 13·2%), which are moderately soluble in water; the *sodium* salt is pale orange. The p-*nitrophenylhydrazone*, deep orange micro-crystals, slowly decomposes at 283—284°; the p-*bromophenylhydrazone*, brick-red needles, decomposes rapidly at 242—244° (Found : Br, 20·9. $C_{13}H_9O_5N_4Br$ requires Br, 21·0%); the *phenylhydrazone*, deep maroon needles, has m. p. 203° (Found : N, 18·6. $C_{13}H_{10}O_5N_4$ requires N, 18·5%).

Some Hydrazones of 3-*Nitro*-4-*hydroxybenzaldehyde*.—These were all crystallised from glacial acetic acid. Phenylhydrazone : dark red needles, m. p. 175—176° (slow decomp.) (Schöpff, *Ber.*, 1891, **24**, 3776, gives m. p. 175—176°). p-*Nitrophenylhydrazone* : dull orange needles, m. p. 247—249° (decomp.) (Found : N, 18·7. $C_{13}H_{10}O_5N_4$ requires N, 18·5%). p-*Bromophenylhydrazone* : bright red needles, m. p. 192—193° (Found : Br, 23·6. $C_{13}H_{10}O_3N_3Br$ requires Br, 23·8%).

Nitration of m-*Methoxybenzaldehyde*.—(a) *Mononitration*. Friedländer and Schreiber's conditions (*loc. cit.*), together with Rieche's test (*loc. cit.*) for the end-point of mononitration, gave no solid products until the temperature was allowed to rise to 20°; 40 g. of *m*-methoxybenzaldehyde then afforded 31g. of nitrated product and 15 g. of unchanged material. By the use of 85% nitric acid, however, 30 g. of nitrated products were obtained from 25 g. of aldehyde; when this yield was dissolved in hot benzene (20 g.) 2-nitro-3-methoxybenzaldehyde (11 g.) was deposited on cooling, and the mother-liquor contained some 6-nitro-3-methoxybenzaldehyde. No 4-nitro-3-methoxybenzaldehyde was ever isolated. Tröger and Fromm's statement (*J. pr. Chem.*, 1925, **111**, 217) that the 6-nitro-isomeride is absent has been shown to be incorrect, inasmuch as 6-nitro-3-methoxybenzoic acid has been isolated after oxidation of the foregoing mixture.

(b) *Dinitration*. Tiemann and Ludwig's conditions (*loc. cit.*) gave small yields accompanied by much charring; better results were obtained as follows : *m*-Methoxybenzaldehyde (10 g.) was added gradually to a mixture of potassium nitrate (17 g.) in concentrated sulphuric acid (80 g.) at 0—5°, then poured on ice, and the resulting colourless solid (12·4 g.) was extracted twice with boiling water, which dissolved Tiemann's β-compound (3 g.; m. p. 110—130°) and left the α-compound, which was almost pure 2 : 6-dinitro-3-methoxybenzaldehyde, m. p. 156—157° after one crystallisation from benzene. The β-compound (3 g.) was dissolved in hot benzene (16 g.), which deposited only 2 : 6-dinitro-3-methoxybenzaldehyde on cooling; the mother-liquor contained chiefly the 4 : 6-dinitro-isomeride. The total yields from the above nitration were 80% of 2 : 6- and 20% of 4 : 6-dinitro-3-methoxybenzaldehydes.

Nitration of 6-*Nitro*-3-*methoxybenzaldehyde.*—The aldehyde (10 g.) was added to nitric acid (100 c.c.; 98%) at 20°, kept for ½ hour, and then poured into ice water. The colourless solid (11·5 g.) which separated was fractionally crystallised from benzene and proved to be mainly 2 : 6- (m. p. 157°) with a little 4 : 6-dinitro-3-methoxybenzaldehyde.

Nitrations of 4- *and* 2-*Nitro*-3-*methoxybenzaldehydes.*—These aldehydes (10 g. each) gave almost pure 4 : 6- (10 g.; m. p. 127—131°) and 2 : 6-dinitro-3-methoxybenzaldehydes (11·5 g.; m. p. 152—156°) which melted at 131° and 157° respectively after one crystallisation from benzene.

2 : 6-*Dinitro*-3-*methoxybenzaldehyde* crystallises from benzene in stout, hexagonal prisms, m. p. 157° (Found : N, 12·4. $C_8H_6O_6N_2$ requires N, 12·3%); 5 g. require 60 g. of boiling benzene for complete solution. The p-*nitrophenylhydrazone* forms pale orange, elongated, hexagonal plates, which explode at about 260°, and the p-*bromophenylhydrazone* terra-cotta needles, m. p. 196—197° (decomp.) (Found : Br, 20·0. $C_{14}H_{11}O_5N_4Br$ requires Br, 20·2%). On being boiled with 50 c.c. of 1% potassium permanganate solution, the aldehyde (1 g.) was oxidised to 2 : 6-*dinitro*-3-*methoxybenzoic acid.* This forms colourless needles, m. p. 199° (Found : N, 11 9. $C_8H_6O_7N_2$ requires N, 11·6%), which give a yellow solution in aqueous sodium carbonate with liberation of carbon dioxide.

4 : 6-*Dinitro*-3-*methoxybenzaldehyde* crystallises from benzene in hexagonal prisms, m. p. 131° (Found : N, 12·3. $C_8H_6O_6N_2$ requires N, 12·3%); 5 g. require 12 g. of boiling benzene for complete solution; p-*nitrophenylhydrazone,* terra-cotta needles, m. p. above 300° without explosion (Found : N, 19·5. $C_{14}H_{11}O_7N_5$ requires N, 19·4%): p-*bromophenylhydrazone,* dull red needles, m. p. 254—256° (decomp.) (Found : Br, 20·3. $C_{14}H_{11}O_5N_4Br$ requires Br, 20·2%). Oxidation as above gave 4 : 6-dinitro-3-methoxybenzoic acid, m. p. 188—189° (Giua, *Gazzetta*, 1915, **45**, 352, gives m. p. 186—187°) (Found : N, 11·8. Calc. : N, 11·6%), which liberates carbon dioxide from sodium carbonate, but much less readily than its isomeride above.

Nitration of 2 : 5-*Dichlorobenzaldehyde.*—The method of Gnehm and Banziger (*Ber.*, 1896, **29**, 876) results in 2 : 5-dichloro-6-nitrobenzaldehyde (3 parts) and a second product (1 part) which has now been diagnosed as 2 : 5-*dichloro*-3-*nitrobenzaldehyde* (by conversion into 2 : 3 : 5-trichlorobenzaldehyde); it forms a *phenylhydrazone,* orange needles, m. p. 171°, and a p-*nitrophenylhydrazone,* deep orange needles, m. p. 290—292° (decomp.). On oxidation with alkaline permanganate, 2 : 5-*dichloro*-3-*nitrobenzoic acid* results; this crystallises from glacial acetic acid in colourless needles, m. p.

220° (the 6-nitro-acid has m. p. 143—144°) (Found : Cl, 30·1. $C_7H_3O_4NCl_2$ requires Cl, 30·0%).

2 : 3 : 5-*Trichlorobenzaldehyde* is volatile in steam, has a characteristic pungent odour, is soluble in the usual organic solvents, and crystallises from dilute alcohol in colourless needles, m. p. 56° (the 2 : 4 : 5-isomeride melts at 110—111°) (Found : Cl, 50·0. $C_7H_3OCl_3$ requires Cl, 50·1%). On oxidation with neutral permanganate, 2 : 3 : 5-trichlorobenzoic acid results, m. p. 162° (Cohen and Dakin, J., 1902, **81**, 1331, give m. p. 162°).

Additional Nitrophenylhydrazones used for Comparison Purposes.—All were crystallised from glacial acetic acid. They are tabulated under the heading of the components from which they were prepared.

Benzaldehyde.	Nitrophenyl-hydrazine.		M. p.
3-Hydroxy-	*o*	Terra-cotta needles	195°
,,	*m*	Deep crimson needles	209—210
,,	*p*	Terra-cotta needles	219—220
6-Nitro-3-hydroxy-	*o*	Deep terra-cotta needles	248—250 (slow decomp.)
,, ,,	*m*	Scarlet needles	257—258 (slow decomp.)
6-Nitro-3-methoxy-	*p*	Terra-cotta needles	281—283
4- ,, ,,	*p*	Saffron needles	257—258
2- ,, ,,	*p*	Curly orange needles	222—223
2 : 5-Dichloro-6-nitro-	*p*	Fine pale yellow needles	269—270 (decomp.)

Additional p-*Bromophenylhydrazones.*—All were crystallised from glacial acetic acid.

Benzaldehyde.		M. p.
6-Nitro-3-hydroxy-	Reddish-brown, hexagonal clusters	214—215°
4- ,, ,,	Crimson needles	179—180
2- ,, ,,	Nigre-brown needles	194—195 (rapid decomp.)
6-Nitro-3-methoxy-	Light crimson needles	235—236
4- ,, ,,	Pale orange needles	177—178
2- ,, ,,	Orange needles	193—194

Persistence of Colour Effects on Dilution.—*Test.* 0·01 G. of the hydrazone was treated with 15 c.c. of alcoholic potassium hydroxide (10 g. in 75 g. of solution), and the coloured mixture then gradually diluted with water.

(a) *Nitro-group in phenylhydrazine portion only.* The intense magenta-violet colour of benzaldehyde-*p*-nitrophenylhydrazone was not dispersed until 18,000 c.c. of water had been added.

(b) *Nitro-group in aldehyde portion only.* The deep greenish-blue colour of *p*-nitrobenzaldehydephenylhydrazone required only 35 c.c. of water for its dispersion.

Colours produced by Aqueous and Alcoholic Alkalis.—*Test.* 0·05 G. of hydrazone was treated with 5 c.c. of 10% aqueous or alcoholic potassium hydroxide. The hydrazones are tabulated as in the previous tables.

Key to abbreviations. S. = same; D. = deeper; N. = no coloration.

		Aqueous alkali.		Alcoholic alkali.	
Benzaldehyde.	Phenyl-hydrazine.	Cold.	Hot.	Cold.	Hot.
3-Hydroxy-	*o*-Nitro-	Bordeaux.	S.	D. Bordeaux.	D.
,,	*m*- ,,	Yellow.	S.	Yellow.	S.
,,	*p*- ,,	Bordeaux.	S.	D. Bordeaux.	S.
6-Nitro-3-hydroxy-	*o*- ,,	Orange.	D.	Olive-green.	D.
,, ,,	*m*- ,,	N.	Red.	Pale olive-green	D.
,, ,,	*p*- ,,	Bordeaux.	S.	Bluish-magenta.	S.
4- ,, ,,	*p*- ,,	Bordeaux.	S.	Reddish-violet.	S.
2- ,, ,,	*p*- ,,	Bordeaux.	S.	Bluish-magenta.	S.
6-Nitro-3-methoxy-	*p*- ,,	N.	N.	Blue (trace of red).	D.
4- ,, ,,	*p*- ,,	N.	N.	Pure cobalt-blue.	S.
2- ,, ,,	*p*- ,,	N.	N.	Blue (trace of red).	S.
4 : 6-Dinitro-3-hydroxy-	*p*- ,,	Bordeaux.	S.	Reddish-violet.	S.
2 : 6- ,, ,,	*p*- ,,	Bordeaux.	S.	Violet.	D.
4 : 6-Dinitro-3-methoxy-	*p*- ,,	N.	N.	Bluish-green.	Violet.
2 : 6- ,, ,,	*p*- ,,	N.	N.	Cobalt-blue.	S.
2 : 4 : 6-Trinitro-3-hydroxy-	*p*- ,,	Instantaneous blue quickly fades, giving canary-yellow, very explosive solid (Na salt) and magenta solution.	Blue develops.	Bluish-green.	Bluish-black.
3-Nitro-4-hydroxy-	*p*- ,,	Magenta.	S.	Magenta.	S.
3 : 5-Dinitro-4-hydroxy-	*p*- ,,	Magenta.	S.	Magenta.	S.
2 : 5-Dichloro-6-nitro-	*p*- ,,	N.	N.	Blue.	D.
2 : 5-Dichloro-3-nitro-	*p*- ,,	N.	N.	Blue.	D.
6-Nitro-3-hydroxy-	*p*-Bromo-	Substance turns from reddish-brown to deep orange, but no solution effect.	S.	Yellow.	S. Green with stronger alkali.
4- ,, ,,	*p*- ,,	N.	N.	Brown.	Greenish-brown with excess.
2- ,, ,,	*p*- ,,	Substance turns crimson; solution colourless.	S.	Red solution.	Greenish-brown with excess.
6-Nitro-3-methoxy-	*p*-	N.	N.	Pale green.	D.
4- ,, ,,	*p*- ,,	N.	N.	Deep green, becoming yellow.	Bluish-green.
2- ,, ,,	*p*- ,,	N.	N.	N.	Red.
4 : 6-Dinitro-3-hydroxy-	*p*- ,,	Red.	S.	Olive-green.	D.
2 : 6- ,, ,,	*p*- ,,	Pale olive-green solution. Deep orange substance.	S.	Deep green.	S.
4 : 6-Dinitro-3-methoxy-	*p*- ,,	N.	N.	Deep blue.	S.
2 : 6- ,, ,,	*p*- ,,	N.	N.	Deep green.	D.
2 : 4 : 6-Trinitro-3-hydroxy-	*p*- ,,	Substance changes to brownish-red; colourless solution.	S.	Instantaneous bright blue.	Blue-black.
2 : 5-Dichloro-6-nitro-	Unsubstituted.	N. (cf. Chattaway).	N.	Yellow.	Reddish-brown changes to deep red and then to yellow. Colourless solid on dilution with water.
2 : 5-Dichloro-3-nitro-	,,	N.	N.	Dark brown.	D.
3-Nitro-4-hydroxy-	*p*-Bromo-	N.	S.	Red.	S.
3 : 5-Dinitro-4-hydroxy-	*p*- ,,	Substance turns brick red.	S.	Substance turns darker red.	S.
,, ,,	Unsubstituted.	N.	N.	Red.	S.

(c) *Nitro-groups in both portions.* The intense cobalt-blue colour of *p*-nitrobenzaldehyde-*p*-nitrophenylhydrazone became violet with about 25 c.c. of water, magenta with 25—50 c.c., and vanished at 275 c.c.

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