

XXVII.—*The Nitration of Substituted Azophenols.*

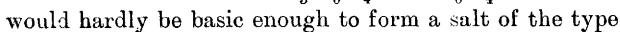
By JOHN THEODORE HEWITT and HERBERT VICTOR MITCHELL.

THE action of substituting agents on azophenols has engaged the attention of several chemists within the last few years (Noelting, *Ber.*, 1887, **20**, 2997; Täuber, *ibid.*, 1893, **26**, 1872; Auwers, *ibid.*, 1900, **33**, 1302; Armstrong, *Proc.*, 1899, **15**, 243; Hewitt and Aston, *Auld, Fox, Lindfield, Phillips and Tervet, Trans.*, 1900, **77**, 99, 712, 810; 1901, **79**, 49, 155, 160, 1090; 1902, **81**, 171, 1202). The general result has been to show that *p*-hydroxyazo-compounds nitrate with dilute nitric acid and brominate in presence of sodium acetate and acetic acid in the ortho-position to the hydroxyl group, that is, they behave as might be expected of true azophenols.

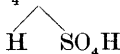
On the other hand, Noelting obtained *p*-nitrobenzeneazophenol by acting on benzeneazophenol with one molecular proportion of nitric acid in presence of an excess of concentrated sulphuric acid (*loc. cit.*), whilst with two molecular proportions of nitric acid he states that a product is obtained identical with that produced by the diazotisation of 2:4-dinitroaniline and subsequent coupling with phenol. Noelting's statement with respect to the formation of *p*-nitrobenzeneazophenol when one molecule of nitric acid is employed needs no qualification; but with two molecules of nitric acid, if the dinitrobenzeneazophenol is formed at all, it must be in subordinate amount, since when any one of the three nitrobenzeneazophenols is further nitrated, not merely with warm dilute nitric acid, but even in presence of strong sulphuric acid, the second nitro-group enters in the ortho-position to the phenolic hydroxyl.

This corresponds closely to the result obtained by Täuber, who found that both *p*- and *m*-sulphobenzeneazophenols nitrated in the ortho-position to the hydroxyl group in presence of strong sulphuric acid.

The obvious explanation in the case of benzeneazophenol (compare

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Whilst salts with mineral acids have not been obtained in the case where the substituent group is  $\text{SO}_3\text{H}$ , the argument that the nitro-group also hinders salt formation requires some qualification. Hewitt, Moore, and Pitt (*Ber.*, 1898, **31**, 2114) have described hydrochlorides of *m*- and *p*-nitrobenzeneazophenols, so undoubtedly salt formation can take place. The explanation may lie in the diminution of the basicity by the introduction of the nitro-group, so that the solution of the nitrobenzeneazophenol in the strong sulphuric acid is to be looked on as an equilibrium mixture.



Whilst the free azophenol would nitrate instantly, the quinone-hydrazone salt on the right-hand side obviously would not nitrate in the quinonoid portion of the molecule, whilst so far as the other nucleus is concerned it would nitrate readily enough, were it not that one negative nitro-group has already entered it.

We advance this view with a certain amount of reserve, seeing that the *o*-azophenols brominate in the phenolic nucleus, although Auwers has considered them to be quinonehydrazones. On the other hand, Jacobson considers the hydrazone formula doubtful, even in the case of the salts which *p*-hydroxyazo-compounds furnish with mineral acids, seeing that he has been able to obtain a stable hydrochloride of *m*-hydroxyazobenzene (*Ber.*, 1903, **36**, 4107).

## EXPERIMENTAL.

*Preparation of o-Nitrobenzeneazo-o-nitrophenol.*

(a) By dilute nitric acid :

Ten grams of *o*-nitrobenzeneazophenol were very finely powdered and introduced into a mixture of 20 c.c. of nitric acid of specific

gravity 1.36, with 60 c.c. of distilled water. The whole was stirred, and gradually warmed up to 50° on the water-bath, when the odour of nitrous fumes became marked and the vermilion shade of the mononitroazophenol gradually gave place to the yellow-brown tint of the dinitro-compound. After half an hour at 50°, the temperature was raised to 60°, and maintained at that point, with stirring, for a further 15 minutes. The resulting paste was next diluted with distilled water, filtered off at the pump, washed free from acid, and dried at 100° and recrystallised from boiling glacial acetic acid, when it melted at 187°.

(b) By nitration in strong sulphuric acid solution :

*o*-Nitrobenzeneazophenol was dissolved in ten times its weight of strong sulphuric acid, and the mixture surrounded by cold water. A very slight excess of the calculated amount (1 mol.) of nitric acid (sp. gr. 1.42), itself diluted with strong sulphuric acid, was gradually added, with stirring. After leaving the mixture overnight, it was gradually poured into a large excess of cold water and stirred vigorously.

The compound which separated was washed at the pump, dried and recrystallised from glacial acetic acid ; it melted at 186—187°, and on being mixed with the foregoing specimen, no lowering of the melting point could be detected.

(c) In order to prove definitely the constitution of this compound, it was synthesised by coupling an *o*-nitrophenyldiazonium salt with *o*-nitrophenol as follows :

A mixture of 5 grams of *o*-nitroaniline, 10 grams of concentrated sulphuric acid, and a small quantity of water, insufficient to remove the amine from solution, was diazotised by 2.6 grams of sodium nitrite dissolved in 5 c.c. of water. The diazo-solution was poured into an excess of water, and added to an aqueous solution of 5 grams of *o*-nitrophenol and 15 grams of sodium carbonate. Coupling took place fairly easily, the azophenol was precipitated by acid, redissolved in hot caustic soda solution, again precipitated, extracted with cold spirit, and finally recrystallised from glacial acetic acid. This preparation, although of a slightly lighter shade than the specimens prepared by nitration, was obviously identical with them, as it melted at 186° and had no effect on their melting point.

*o*-Nitrobenzeneazo-*o*-nitrophenol crystallises from pure acetic acid in well-defined, long, deep brown needles ; it dissolves easily in acetic acid and pyridine and fairly readily in alcohol ; it is slightly soluble in benzene or ethyl acetate, and but sparingly so in ether.

0.1118 gave 19.0 c.c. moist nitrogen at 15° and 748 mm.  $N = 19.7$ .

$C_{12}H_8O_5N_4$  requires  $N = 19.4$  per cent.

The *acetyl* derivative,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{O} \cdot \text{CO} \cdot \text{CH}_3$ , was prepared by boiling together for one hour in a reflux apparatus 1 gram of the azophenol, 1 gram of fused sodium acetate, and 4 grams of acetic anhydride. [View Article Online](#)

The fused product was thrown into water, collected, and recrystallised from glacial acetic acid, when the substance formed thick, scarlet needles, melting at  $119^\circ$ , easily soluble in ether, ethyl acetate, benzene, pyridine, or acetic acid, and moderately so in alcohol.

0.1677 gave 0.3137  $\text{CO}_2$  and 0.0453  $\text{H}_2\text{O}$ .  $\text{C} = 51.0$ ;  $\text{H} = 3.0$ .

$\text{C}_{14}\text{H}_{10}\text{O}_6\text{N}_4$  requires  $\text{C} = 50.9$ ;  $\text{H} = 3.0$  per cent.

The *benzoyl* derivative,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_5$ , was prepared by boiling the azophenol with enough benzoyl chloride to dissolve it completely, until evolution of hydrochloric acid ceased; the solution was stirred into dilute alcohol, the crude benzoyl derivative was filtered off at the pump and recrystallised from ethyl benzoate. It formed a mass of small, yellow crystals, melting at  $174^\circ$ .

This substance is very soluble in pyridine, moderately so in ethyl acetate, benzene, and acetic acid, very sparingly so in alcohol and ether.

0.1186 gave 0.2548  $\text{CO}_2$  and 0.0346  $\text{H}_2\text{O}$ .  $\text{C} = 58.6$ ;  $\text{H} = 3.2$ .

$\text{C}_{19}\text{H}_{12}\text{O}_6\text{N}_4$  requires  $\text{C} = 58.2$ ;  $\text{H} = 3.1$  per cent.

#### *Preparation of m-Nitrobenzeneazo-o-nitrophenol.*

##### (a) By means of dilute nitric acid:

The method employed was the same as that indicated in the case of the foregoing isomeride. Ten grams of powdered *m*-nitrobenzeneazophenol and a mixture consisting of 20 c.c. of nitric acid (sp. gr. 1.36) with 60 c.c. of water were warmed on the water-bath, and stirred continuously. In this case, the nitration appeared to take place with somewhat more difficulty; it was found possible to work at about  $100^\circ$ , and even then the reaction was quite moderate.

After 10 minutes at this temperature, the product was collected in the usual way and recrystallised from boiling glacial acetic acid. This specimen melted at  $177^\circ$ .

##### (b) Preparation of the foregoing compound by nitration in strong sulphuric acid solution:

Six grams of *m*-nitrobenzeneazophenol, after being dissolved in 60 grams of strong sulphuric acid, were treated with a cold mixture of 2 c.c. of nitric acid (sp. gr. 1.42) and 10 c.c. of strong sulphuric acid. The addition of the nitric acid was effected gradually, and the temperature of the mixture was not allowed to rise to any appreciable extent. After half an hour, the mixture was poured into a large excess of cold water, the dinitro-compound collected and recrystallised from glacial acetic acid. This specimen also melted

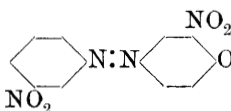
at 177°, and a mixture of it with the preceding preparation had exactly the same melting point. Subsequent crystallisations from chloroform raised the melting point to 179°.

In this particular case, it was considered unnecessary to prove the constitution of the compound by synthesising it from *o*-nitrophenol, as a substance agreeing with it in melting point has been obtained by the rearrangement of di-*m*-dinitroazoxybenzene under the influence of concentrated sulphuric acid (Klinger and Pitschke, *Ber.*, 1885, **18**, 2552, and Knipscheer, *Rec. Trav. Chim.*, 1903, **22**, 1).

This substance crystallised from chloroform in small, somewhat hard crystals, and readily dissolved in alcohol, benzene, pyridine, and acetic acid; it was less soluble in ethyl acetate, and only slightly so in ether.

0.0951 gave 16.0 c.c. nitrogen at 19° and 774 mm.  $N = 19.6$ .

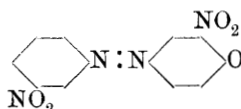
$C_{12}H_8O_5N_4$  requires  $N = 19.4$  per cent.

The *acetyl* derivative, , was obtained

by boiling the azophenol with acetic anhydride and fused sodium acetate in the usual manner; it crystallised from acetic acid in tufts of small, brown crystals which melted at 138°, and were readily soluble in acetic acid or pyridine, moderately so in ether and in ethyl acetate, but only sparingly so in alcohol.

0.1632 gave 24.4 c.c. nitrogen at 15° and 770 mm.  $N = 17.6$ .

$C_{14}H_{10}O_6N_4$  requires 17.0 per cent.

The *benzoyl* derivative, , was

easily prepared by boiling with benzoyl chloride for one hour; the product was thrown into dilute spirit, and recrystallised from ethyl acetate, when it formed a nearly colourless, crystalline powder melting at 169°. It readily dissolves in pyridine or amyl alcohol, and is moderately soluble in benzene, ether, and ethyl acetate; it is almost insoluble in alcohol.

0.0850 gave 0.1825  $CO_2$  and 0.0247  $H_2O$ .  $C = 58.5$ ;  $H = 3.2$ .

$C_{19}H_{12}O_6N_4$  requires  $C = 58.2$ ;  $H = 3.1$  per cent.

#### *Preparation of p-Nitrobenzeneazo-o-nitrophenol.*

(a) By the action of dilute nitric acid:

The method previously indicated in the other two cases was employed as regards quantities and dilution of the nitric acid. The

temperature was raised to and maintained at  $60^{\circ}$  for  $1\frac{1}{2}$  hours, when the mass, which had assumed a thick, pasty consistency, was diluted, filtered, and dried, and recrystallised from a considerable quantity of glacial acetic acid. The product separated abundantly on cooling in beautiful, large, red needles and melted at  $212^{\circ}$ .

(b) Preparation from *p*-nitrobenzeneazophenol by nitration in strong sulphuric acid solution:

Finely powdered *p*-nitrobenzeneazophenol was dissolved in a sufficiency of concentrated sulphuric acid, and the calculated quantity (1 mol.) of nitric acid (sp. gr. 1.42) itself, diluted with sulphuric acid, added. The mixture was set aside for a week, then diluted largely, and filtered. The resulting compound, after washing and drying, was recrystallised from hot glacial acetic acid. This specimen melted at  $212^{\circ}$  and did not depress the melting point of the foregoing specimen.

(c) Preparation by coupling *p*-nitrobenzenediazonium salt with *o*-nitrophenol:

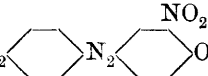
Six grams of finely powdered *p*-nitroaniline were mixed with about 50 c.c. of water containing 13 c.c. of fuming hydrochloric acid; the mixture was cooled to  $0^{\circ}$  by the addition of small pieces of ice, and diazotised by the very gradual addition of a saturated aqueous solution of 3.1 grams of sodium nitrite. The resulting solution was rapidly filtered into one containing 6 grams of *o*-nitrophenol (in the form of its sodium salt) and 20 grams of crystallised sodium acetate with a little sodium carbonate. Coupling took place without delay, and apparently with ease.

The mixture was acidified with hydrochloric acid and the product collected at the pump. As the crude substance thus obtained contained some unaltered *o*-nitrophenol it was mixed with water and distilled in steam in order to remove this substance, and then crystallised thrice from glacial acetic acid. This preparation also melted at  $212^{\circ}$ , and did not depress the melting point of the specimen prepared by nitration.

*p*-Nitrobenzeneazo-*o*-nitrophenol crystallises from glacial acetic acid in large, shining, red needles which are only very sparingly soluble in cold acetic acid, and are practically insoluble in alcohol. This substance also dissolves fairly readily in toluene; it is easily soluble in pyridine, and sparingly so in benzene, ethyl acetate, or ether.

0.1399 gave 23.1 c.c. of nitrogen at  $19^{\circ}$  and 764 mm.  $N = 19.2$ .

$C_{12}H_8O_5N_4$  requires  $N = 19.4$  per cent.

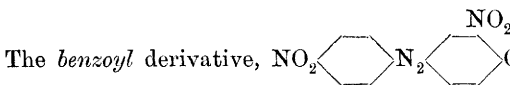
The *acetyl* derivative,  $NO_2$    $O \cdot CO \cdot CH_3$ , was prepared

in the usual manner; it crystallised from glacial acetic acid in fine, brown, silky needles, and melted at  $138^{\circ}$ . This substance is moderately

soluble in ethyl acetate, easily so in benzene, pyridine, and acetic acid, and dissolves less readily in alcohol. [View Article Online](#)

0.1086 gave 0.2028 CO<sub>2</sub> and 0.0286 H<sub>2</sub>O. C = 50.9; H = 2.9.

C<sub>14</sub>H<sub>10</sub>O<sub>6</sub>N<sub>4</sub> requires C = 50.9; H = 3.0 per cent.

The *benzoyl* derivative, , was pre-  
O=[N+]([O-])c1ccccc1O=C(Oc2ccccc2)N=Nc3ccccc3[N+](=O)[O-]

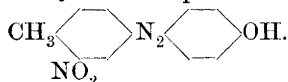
pared by boiling the azophenol with benzoyl chloride; it crystallised from ethyl acetate in dark red, small, glistening crystals (m. p. 179°).

This substance is practically insoluble in alcohol, but is soluble in ethyl acetate, and dissolves somewhat sparingly in benzene, pyridine, or acetone.

0.1164 gave 0.2505 CO<sub>2</sub> and 0.0349 H<sub>2</sub>O. C = 58.7; H = 3.3.

C<sub>19</sub>H<sub>12</sub>O<sub>6</sub>N<sub>4</sub> requires C = 58.2; H = 3.1 per cent.

*Preparation of m-Nitro-p-tolueneazophenol.*

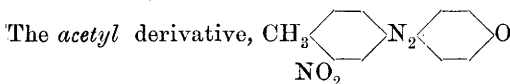


Three grams of 2-nitro-*p*-toluidine were stirred with the requisite quantity of dilute hydrochloric acid, and the calculated quantity of sodium nitrite, dissolved in water, added, the temperature not being allowed to exceed 0°.

The diazo-solution thus obtained was filtered into a solution of the calculated quantity of phenol with excess of sodium acetate. Coupling proceeded immediately, and the liquid was acidified and filtered. After recrystallisation from glacial acetic acid, the yield was over 4 grams; the product separated from glacial acetic acid in glistening, orange crystals melting at 186°; this substance is readily soluble in acetic acid, ethyl acetate, and pyridine, moderately so in benzene or ether, but scarcely dissolves in alcohol.

0.1593 gave 0.3524 CO<sub>2</sub> and 0.0564 H<sub>2</sub>O. C = 60.3; H = 3.97.

C<sub>13</sub>H<sub>11</sub>O<sub>3</sub>N<sub>3</sub> requires C = 60.7; H = 4.3 per cent.

The *acetyl* derivative, , prepared as  
CC(=O)Oc1ccccc1N=Nc2ccccc2[N+](=O)[O-]

in the previous cases, crystallised from dilute acetic acid in fine, golden-yellow needles melting at 113°; it is very soluble in benzene, pyridine, acetic acid, or alcohol, and moderately so in ethyl acetate.

0.1895 gave 0.4200 CO<sub>2</sub> and 0.0720 H<sub>2</sub>O. C = 60.4; H = 4.2.

C<sub>15</sub>H<sub>13</sub>O<sub>4</sub>N<sub>3</sub> requires C = 60.2; H = 4.3 per cent.

*Preparation of o-Nitro-p-tolueneazophenol.*

3-Nitro-*p*-toluidine was diazotised and treated with phenol exactly as in the case of its isomeride.

The crude product, after crystallisation from alcohol and two recrystallisations from benzene, formed small, brown crystals melting at 158°.

0.1179 gave 16.9 c.c. nitrogen at 16° and 764 mm.  $N = 16.9$ .

$C_{13}H_{11}O_3N_3$  requires  $N = 16.4$  per cent.

The authors originally intended to prepare, if possible, one of these two tolueneazophenols by the direct nitration in strong sulphuric acid solution of *p*-tolueneazophenol. Experiments in this connection have, so far, led to no very definite conclusion, but this negative result is perhaps not devoid of interest, as it indicates that, in strong acid solution, *p*-tolueneazophenol is not exclusively attacked by nitric acid in any special direction, the para-position in the toluene residue being already occupied by a methyl group.

With dilute nitric acid, this azophenol is obviously most readily substituted in the phenolic nucleus (Hewitt, Lindfield, *loc. cit.*).

All the melting points given in this paper are corrected.

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