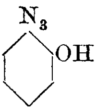
CXXIV.—*Aromatic Azoimides. Part II. Ortho- and Meta-hydroxyphenylazoimides.*

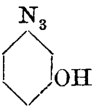
By MARTIN ONSLOW FORSTER and HANS EDUARD FIERZ.

BY experience gained from the investigation of *p*-hydroxyphenylazoimide (this vol., p. 855), the preparation of the isomeric substances has been much facilitated. We find that the hypothetical additive compound of the diazotised aminophenol with hydroxylamine is more stable in presence of excess of sodium carbonate than was originally supposed, and although potassium hydroxide accelerates the transformation of this compound into azoimide, we have abstained from adding free alkali, preferring to maintain the temperature of the well-stirred liquid at zero during an interval of many hours. By this modification the hydroxyphenylazoimide is produced more slowly, but in a form more readily freed from associated materials. In the case of the meta-compound it is necessary to add a quadruple proportion of hydroxylamine in order to secure a satisfactory yield; with the quantity which sufficed in previous experiments, the principal product consists of a brick-red azo-compound, and the yield of hydroxyphenylazoimide is only one-third of the optimum.

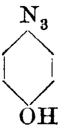
A comparison of the three hydroxyphenylazoimides has revealed some interesting points. The almost invariable rule that a para-compound is the least fusible of the series is exactly inverted by the compounds under consideration:



Decomposes at 145° without fusion.

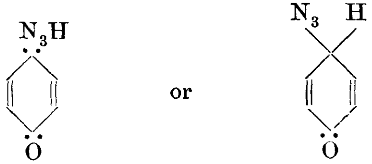


M. p. 36·5°.



Oil.

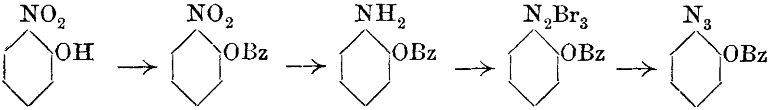
We have already suggested a reason for the low melting point of *p*-hydroxyphenylazoimide, which we believe quickly changes into a mixture of the enolic form, represented above, with a varying proportion of the ketonic isomeride, which may be either quinonoid or quinolic,



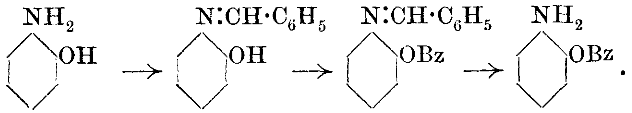
This is indicated, not only by the alteration which the phenol itself undergoes in the desiccator, but by the remarkable colour change which occurs when the potassium derivative is warmed in alcoholic or aqueous solution. The meta-compound does not display these properties, and we believe it to be normal, whilst the high melting point of the ortho-derivative is perhaps explained by its bimolecular structure, a peculiarity which appears from the molecular weight determination and from the persistence with which it retains a one-half molecule of water of crystallisation. In order to render the identity of these compounds less doubtful, we have made a comparison of the three benzoyl derivatives and their *p*-nitro-compounds, finding that in these two series the melting point relationships are quite normal:

	Ortho. M. p.	Meta. M. p.	Para. M. p.
Benzoyl derivative	45°	50°	81°
p-Nitrobenzoyl derivative	101	136	169—170

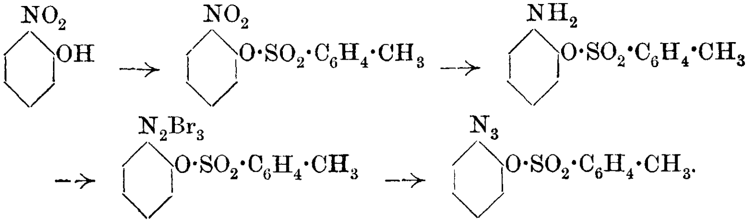
Owing to the unusual properties of *o*-hydroxyphenylazoimide, we thought it desirable also to prepare one of its derivatives by an independent method as we did in the case of *p*-benzoxyphenylazoimide (*loc. cit.*, p. 866). From this point of view it was natural to attempt the preparation from *o*-nitrophenol instead of the *p*-nitrophenol employed in the case quoted, but the readiness with which the benzoic ester of *o*-nitrophenol yields the anhydro-base on reduction precluded our following analogous lines, namely:



It seemed possible, however, that at least a solution of the hydrochloride of *o*-benzoxyaniline might be obtained by preparing the benzylidene derivative of *o*-aminophenol, benzoylating this, and hydrolysing the product with dilute hydrochloric acid:



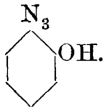
On attempting to benzoylate the benzylidene derivative of *o*-aminophenol, however, we found that alike in pyridine and in free alkali, benzaldehyde is eliminated, and the dibenzoyl derivative of *o*-aminophenol is produced; this change is the more curious when it is recalled that the benzylidene compound in question may be methylated in presence of sodium ethoxide, yielding the benzylidene compound of the corresponding anisidine (D.R.-P. 69006). The difficulty was ultimately overcome by selecting an acyl group which precluded anhydro-base formation, and by the use of *p*-toluenesulphonic chloride we were able to complete the connexion between *o*-nitrophenol and *o*-hydroxyphenylazoimide:



The derivative thus prepared is identical with the product obtained from *o*-hydroxyphenylazoimide and *p*-toluenesulphonic chloride.

EXPERIMENTAL.

o-*Hydroxyphenylazoimide*,



Forty grams of *o*-aminophenol hydrochloride in 300 c.c. of water mixed with 100 c.c. of concentrated hydrochloric acid were diazotised with 20 grams of sodium nitrite in 100 c.c. of water; to the well-iced liquid, 25 grams of hydroxylamine hydrochloride in 50 c.c. of water were added, the mixture being poured without delay into 1500 c.c. of ice-cold water in which 500 grams of crystallised sodium carbonate had been partly dissolved, sufficient water to dissolve all the salt rendering the bulk of liquid inconveniently great. The liberation of gas was inconsiderable, and the characteristic odour of *o*-hydroxyphenylazoimide soon became perceptible, but in order to complete the action the liquid was stirred continuously and maintained at zero during twelve hours, a slight accumulation of tar occurring. The filtered product, amounting to nearly 3 litres, was acidified with 100 c.c. of glacial acetic acid, some ether being first added to check frothing, and then extracted three times with 300 c.c. of ether. Although the ethereal solution was dark brown, it could be rendered almost colourless in successful experiments by agitation with 8 per cent. sodium carbonate solution, repeated 15—25 times, and on drying the faintly pink liquid with anhydrous sodium sulphate and stirring it vigorously with 60 c.c. of a 40 per cent. solution of sodium hydroxide, snow-white, lustrous crystals of the sodium derivative were obtained amounting to nearly 30 grams.

From this product the free phenol may be prepared by adding a deficit of mineral or acetic acid to the concentrated solution, there being produced an emulsion which quickly solidifies to brilliant, colourless needles; the slightest excess of acid, however, causes the product to liquefy, and in this condition it remains:

0·1460 gave 0·2659 CO_2 and 0·0570 H_2O. C = 49·86; H = 4·37.
0·2093 „ 51·8 c.c. of nitrogen at 18° and 771 mm. N = 29·45.
$C_6H_5ON_3$ requires C = 53·33; H = 3·73; N = 31·11 per cent.
$2C_6H_5ON_3,H_2O$ requires C = 50·00; H = 4·16; N = 29·16 per cent.

The bimolecular structure of *o*-hydroxyphenylazoimide suggests an explanation of its behaviour towards acids, which probably resolve it into the unimolecular form. A determination of the molecular weight in phenol would appear to support this, an average value of 90 units being obtained; this agrees well with 96 units calculated from $\frac{1}{3}(2C_6H_5ON_3 + H_2O)$.

The substance has no definite melting point, becoming dark at 120—130°, and detonating vigorously at 140—145°, according to the rate at which the temperature is raised. It is moderately soluble in warm water, separating in long, lustrous, yellow needles as the liquid cools, and dissolves freely in alcohol, ethyl acetate, or acetone; in chloroform, petroleum, dry ether, or benzene, however, it is practically insoluble, and with the last-named it appears to form a compound, dissolving readily at first and quickly crystallising in felted needles, the water being displaced by the hydrocarbon. On attempting to recrystallise the compound by adding petroleum to a solution in ethyl acetate, a portion was obtained in faintly yellow, lustrous needles, but the greater part changed into tar, as the separation of crystals extended over a considerable period. Noticing that nitrobenzene is a fairly good solvent, we tried nitromethane, and found that this somewhat unusual medium is really most convenient, as it dissolves the hydroxyphenylazoimide only sparingly when cold, freely, however, on warming the liquid, which deposits beautiful, lustrous, yellow prisms.

The odour of the azoimide is very characteristic, recalling *o*-nitrophenol and *o*-salicylaldehyde in an intensified degree; the taste is intensely sweet and burning, with an after-taste recalling *o*-nitrophenol. It distils easily in steam, but quickly undergoes decomposition and cannot therefore be purified by this method. A crystal dropped in concentrated sulphuric acid detonates, producing a relatively large flame and a cloud of reddish-brown smoke; a solution in water, to which one drop of ammonia has been added, does not alter in appearance when treated with ammoniacal silver oxide, but on heating the liquid, oxidation takes place almost immediately, a silver mirror being produced. Ferric chloride in aqueous solution develops an intense blue coloration, which immediately becomes red, and this colour gradually disappears, giving place to a black precipitate. Nitrous acid converts the azoimide into a nitro-compound which crystallises from petroleum in long, lustrous, yellow needles, as in the case of the para-compound; it is volatile in steam, and soluble in water, forming a brick-red potassium derivative which crystallises in long needles, and is insoluble in excess of potash; the melting point of this nitro-compound is indefinite in the neighbourhood of 45°, but as the substance is very expensive to prepare, and is not of immediate interest, it has not been characterised further.

The Benzoyl Derivative.—When prepared by the Schotten-Baumann process the benzoyl derivative of *o*-hydroxyphenylazoimide is oily and solidifies with difficulty, but on cooling with ice a solution in warm petroleum (b. p. 50—60°) it separates in hard, lustrous plates, melting at 45°:

0·2132 gave 32·8 c.c. of nitrogen at 22° and 767 mm. N = 17·96.
$C_{13}H_9O_2N_3$ requires N = 17·57 per cent.

The substance is freely soluble in organic solvents, but does not dissolve in water.

The p-*Nitrobenzoyl Derivative.*—This compound crystallises from absolute alcohol in long, lustrous, faintly yellow prisms, and melts at 101°:

0·2126 gave 35·8 c.c. of nitrogen at 21° and 768 mm. N = 19·76.
$C_{13}H_8O_4N_4$ requires N = 19·71 per cent.

It is freely soluble in acetone or ethyl acetate, dissolving with great difficulty in benzene, and is insoluble in light petroleum.

The p-*Toluenesulphonic Derivative.*—On adding the calculated amount of *p*-toluenesulphonic chloride to the sodium derivative of *o*-hydroxyphenylazoimide in pyridine, the *p*-toluenesulphonic derivative is produced and crystallises from petroleum in lustrous, centimeter-long plates, which, with some difficulty, may be obtained colourless; it melts at 72°, and is freely soluble in chloroform and warm alcohol:

0·2020 gave 25·8 c.c. of nitrogen at 22° and 760 mm. N = 14·78.

$C_{13}H_{11}O_3N_3S$ requires N = 14·53 per cent.

With the object of obtaining *o*-hydroxyphenylazoimide by an independent method, we prepared the *p*-toluenesulphonic derivative indirectly from *o*-nitrophenol. The latter substance was converted into the *p*-toluenesulphonic derivative (Bamberger and Rising, *Ber.*, 1901, **34**, 241) and reduced under conditions somewhat more convenient than those described. Fifty grams were suspended in 300 c.c. of glacial acetic acid mixed with 60 c.c. of concentrated hydrochloric acid, 50 grams of tin foil being gradually added while the temperature was maintained below 40°; a further quantity of hydrochloric acid having been added, the liquid was stirred during one to two hours, filtered from undissolved metal, and poured into 2 litres of water containing 150 grams of sodium acetate. The precipitated base, which melted at 100—101° after crystallisation from alcohol, was diazotised in glacial acetic acid, mixed with hydrochloric acid, and treated with the necessary quantity of bromine dissolved in hydrobromic acid; the perbromide being oily was converted forthwith into the azoimide, which melted at 72°, and did not depress the melting point of a specimen prepared from *o*-hydroxyphenylazoimide and *p*-toluenesulphonic chloride. This process being a convenient one, it was hoped that by means of it the *o*-hydroxyphenylazoimide itself might be prepared from *o*-nitrophenol, but on attempting to hydrolyse the ester it was found that the *p*-toluenesulphonic group is so resistant as to preclude its removal under conditions which the azimidophenol is able to survive.

The Sodium Derivative.—The crude material obtained in the manner already indicated may be purified by dissolution in the minimum of hot absolute alcohol and mixing the filtered solution with four volumes of chloroform, which quickly precipitates long, lustrous, snow-white needles; ether cannot be used for this purpose in the place of chloroform, but the alcohol may be replaced by acetone or ethyl acetate:

0·1381 gave 24·6 c.c. of nitrogen at 20° and 765 mm. N = 20·69.
0·5216 „ 0·1806 Na_2SO_4. Na = 11·23.

$C_6H_4ON_3Na$ requires N = 26·75; Na = 14·65 per cent.
$C_6H_4ON_3Na,C_2H_6O$ requires N = 20·69; Na = 11·33 per cent.

Thus the sodium derivative of *o*-hydroxyphenylazoimide resembles the potassium derivative of the para-compound in crystallising with alcohol, but there the similarity terminates. When protected from light, it does not become green, although a yellow tinge is assumed; the colourless, aqueous solution certainly does evolve gas when heated, but the splendid blue colour associated with the *p*-hydroxyphenylazoimide is not developed, the liquid becoming brown with liberation of ammonia in traces, whilst an alcoholic solution is comparatively stable. A further distinction from the para-compound is noticed in the behaviour of an aqueous solution of the sodium derivative when boiled with excess of alkali. We have stated (*loc. cit.*, p. 857) that when an alcoholic solution of the colourless potassium derivative of *p*-hydroxyphenylazoimide is warmed with alcohol or water, it changes into the blue salt, and this, when boiled with water, yields two-thirds of its nitrogen content unaccompanied by hydrazoic acid; we now find that if the aqueous liquid is boiled with considerable excess of potash, hydrazoic acid, amounting roughly to 20 per cent., is liberated. On treating the ortho-compound in the same way, hydrazoic acid could not be detected, although 12 grams of the sodium salt were used at one time. This observation is the more interesting when it is recalled that, although in their behaviour towards alcoholic potash, ortho- and para-nitrophenylazoimides distinguish themselves from the meta-compound which does not yield hydrazoic acid, Noelting, Grandmougin, and Michel (*Ber.*, 1892, **25**, 3328) have shown that whilst the para-compound furnishes 40 per cent. of hydrazoic acid, only 10—15 per cent. is obtainable from *o*-nitrophenylazoimide.

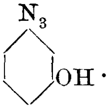
Like the free phenol, the sodium derivative has a sweet, burning taste, and when heated in a platinum dish, it explodes with considerable violence, the potassium derivative of the para-compound simply charring without explosion. When heated with hydroxylamine acetate in absolute alcohol, the sodium derivative does not undergo any definite change, and it is equally indifferent towards phenylhydrazine and semicarbazide; these experiments were made with the object of ascertaining whether the ortho-compound displayed any tendency to become transformed into a quinonoid variety.

The Potassium Derivative.—When concentrated aqueous potassium hydroxide is added to an aqueous solution of *o*-hydroxyphenylazoimide in the dilute alkali, long, silky needles are obtained; the substance is too readily soluble in water and in alcohol, however, to be purified without great difficulty, and as the sodium derivative could be investigated instead, the potassium compound was not studied further.

The Lead Derivative.—On mixing solutions of lead acetate and the sodium derivative of *o*-hydroxyphenylazoimide, the lead compound is precipitated. It is quite colourless, and practically insoluble, and in this respect resembles the lead derivative prepared from the colourless potassium compound of *p*-hydroxyphenylazoimide; we have not noticed a blue lead salt corresponding with the one precipitated on adding lead acetate to an aqueous solution of the blue potassium derivative of *p*-hydroxyphenylazoimide, which is also deep blue and which, nevertheless, yields with methyl iodide the methyl ether obtained from the perbromide of diazotised *p*-anisidine and ammonia.

The Silver Derivative.—This compound is obtained as a pale yellow, curdy precipitate on adding silver nitrate to an aqueous solution of the sodium compound; even when a deficit of silver nitrate is used, however, the substance becomes black in a few seconds.

m-*Hydroxyphenylazoimide,*



In preparing this compound it was found necessary to depart from previous practice by using great excess of hydroxylamine. Twenty grams of *m*-aminophenol were dissolved in 100 c.c. of concentrated hydrochloric acid, mixed with 100 c.c. of water, and diazotised with 13 grams of sodium nitrite; 70 grams of hydroxylamine hydrochloride in 200 c.c. of water were then added, and the mixture poured very slowly into 2 litres of ice-water containing 300 grams of anhydrous sodium carbonate. A red precipitate was produced immediately, and in a few seconds the characteristic odour of *m*-hydroxyphenylazoimide became perceptible. After maintaining the temperature of the well-stirred liquid below zero during four hours, the colour had become orange and the phenol was then removed by agitating three times with 300 c.c. of ether, the combined extracts being purified by 5 per cent. sodium carbonate, which continued to dissolve a coloured by-product after twenty-five extractions. Having dried the pale yellow ethereal solution with calcium chloride and evaporated the solvent, an oil remained, which, when dried in the desiccator, solidified immediately in a freezing mixture, but liquefied again when the temperature rose to that of the laboratory. A pure specimen was obtained, however, by converting this material into the benzoyl derivative, hydrolysing the latter with alcoholic hydrochloric acid, and evaporating an ethereal extract which had been shaken well with sodium carbonate and dried with sodium sulphate. The oil obtained in this manner solidified when cooled, and the solid could be drained on porous earthenware; it was then extracted with warm petroleum (b. p. 50—60°), which deposited long, lustrous, colourless needles, melting at 36·5°, and quickly becoming brown on exposure to light:

0·1368 gave 37·0 c.c. of nitrogen at 22° and 760 mm. N = 31·29.
$C_6H_5ON_3$ requires N = 31·11 per cent.

The substance is very readily soluble in all organic media excepting cold petroleum; when mixed with water, it behaves like ordinary phenol, becoming oily, and then dissolving. It has a most characteristic odour which recalls that of β-naphthol, being at the same time sweet and pungent; the taste also is intensely sweet, quite devoid of after-taste, resembling sucrose. When dropped into concentrated sulphuric acid there is vigorous and instantaneous decomposition. *m*-Hydroxyphenylazoimide does not reduce an ammoniacal solution of silver oxide even when boiled for some minutes with the reagent; ferric chloride in aqueous solution develops a beautiful, violet coloration, which persists during several hours. The alkali derivatives furnish a marked distinction from those of the isomerides, being readily soluble in excess of alkali hydroxide and undergoing no colour change when the aqueous solution is boiled. A colourless, insoluble lead salt is precipitated when the phenol, dissolved in dilute ammonia, is treated with an ammonical solution of lead acetate.

The Benzoyl Derivative.—This compound was prepared as an intermediate stage in the purification of the phenol, and after crystallisation from boiling petroleum, formed lustrous, faintly yellow needles, melting at 50° without decomposition:

0·2344 gave 35·6 c.c. of nitrogen at 22° and 760 mm. N = 17·62.
$C_{13}H_9O_2N_3$ requires N = 17·57 per cent.

It dissolves readily in alcohol, acetone, or warm petroleum. Light turns it dark yellow, and concentrated sulphuric acid decomposes it vigorously.

The p-*Nitrobenzoyl Derivative.*—The Schotten-Baumann method is more convenient than pyridine for the preparation of this substance, which crystallises from benzene in amber-yellow, hard, irregular cubes, melting at 136° without decomposition:

0·1768 gave 30·0 c.c. of nitrogen at 23° and 763 mm. N = 19·71.
$C_{13}H_8O_4N_4$ requires N = 19·71 per cent.

It is moderately soluble in acetone and benzene, but dissolves sparingly in boiling alcohol; with concentrated sulphuric acid it decomposes vigorously.

The p-*Nitrobenzoyl Derivative of* p-*Hydroxyphenylazoimide.*

For the purpose of comparison, as indicated above, this compound was prepared from *p*-nitrobenzoyl chloride and an alkaline solution of the phenol, and crystallised from acetone in long, lustrous, pale yellow needles, which melt and decompose at 169—170°:

0·1118 gave 19·4 c.c. of nitrogen at 22° and 760 mm. N = 20·08.

$C_{13}H_8O_4N_4$ requires N = 19·71 per cent.

It is very sparingly soluble in hot alcohol or benzene, and decomposes immediately with concentrated sulphuric acid.

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