

rays are almost superposed, being separated by only  $0^{\circ}33'$ ; on the other hand, the prism  $BM$ ,  $010:1\bar{1}0=65^{\circ}$ , gives two widely separated readings for minimum deviation, the actual figures being  $2D=110^{\circ}49'$ , which gives the index  $\beta=1.6151$ , and  $2D=86^{\circ}19'$ , which gives an index having a value,  $1.507$ , between those of  $\alpha$  and  $\gamma$ , that is, very much less than the mean index,  $\beta$ .

The index  $\beta$  was also determined for red (lithium) light and found to be  $1.6071$ , which, by comparison with the value for yellow light, gives an indication of the very strong dispersion of the substance.

The optical characters are tabulated below :

Birefringence, negative, very strong.

Axial plane,  $C(001)$ ; Ac. Bis.  $\perp A(100)$ .

Refractive indices: For yellow (Na) light,  $\alpha=1.472$ ;  $\beta=1.6151$ ;  $\gamma=1.6192$ ;  $\gamma-\alpha=0.147$ . For red (Li) light,  $\beta=1.1071$ .

Dispersion, very strong;  $\beta_{Na}-\beta_{Li}=0.008$ .

Axial angle narrow:  $2V=17^{\circ}19'$ .  $2H_a=18^{\circ}20'$  from cedar oil,  $\mu=1.526$ .

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## CXXI.—*Dinitroanisidines and their Products of Diazotisation.*

By RAPHAEL MELDOLA, F.R.S., and FRANK GEORGE C. STEPHENS.

THE present paper is in continuation of former communications on the elimination of a nitro-group on diazotisation (Proc., 1898, 14, 226; Trans., 1900, 77, 1173; Proc., 1901, 17, 131; Trans., 1901, 79, 1076; *ibid.*, 1902, 81, 988). It was suggested by one of us and John V. Eyre, three years ago (Trans., 1902, 81, 989), that the displacement of the nitro-group would be found to follow the ortho-para-rule as with the inverse process of ordinary substitution, and as in the case of the elimination of the halogen atom in the haloid derivatives of amines, &c., described in the French Patent, No. 315,932 of 1902, of the "Badische Anilin- u. Soda-Fabrik." The later work of Dr. K. J. P. Orton (Proc. Roy. Soc., 1903, 71, 153; Proc., 1903, 18, 252; 1904, 19, 161; Trans., 1903, 83, 796) also points to the conclusion that the eliminated halogen atom is in the ortho- or para-position with respect to the diazonium group, although in the majority of the cases investigated by this last-named author the interchange is between the ortho-substituents. In order to submit the foregoing suggestion to experimental proof, it became necessary to prepare and

study the diazotisation products of other nitrated anisidines of known constitution. The nitration of diacetyl-*o*-aminophenol (*o*-acetaminophenyl acetate) results, as was shown in a former note (Proc., 1900, 16, 180), in the formation of the acetyl derivative of ordinary picramic acid (4:6-dinitro-2-aminophenol). The nitration of other acetaminophenols thus appeared to be a promising method of preparing dinitroaminophenols, from which dinitroanisidines could be obtained by methylation, and experiments were accordingly commenced with the mono- and diacetyl derivatives of *p*- and *m*-aminophenol. During the progress of the work, a paper was published by Reverdin and Dresel (*Ber.*, 1904, 37, 4452; *Arch. Sci. phys. nat.*, 1904, 18, 433), which to some extent anticipated the results we had obtained with *p*-acetaminophenol, and a later paper by these authors (*Arch. Sci. phys. nat.*, 1905, 19, 353; *Ber.*, 1905, 38, 1593) contains further information concerning the nitration of diacetyl-*p*-aminophenols. In so far as the results made known by M. Reverdin and his colleagues are in accordance with our own, we do not think it necessary to do more than to state our general agreement, and to make a few additions to the chemical history of *isopicramic acid*. We should like to add, however, that during the whole course of the work we have been in constant correspondence with M. Reverdin, who has unreservedly placed his experience at our disposal, and has communicated all his results to us before their publication. We are glad of the present opportunity of expressing our thanks for the assistance thus so courteously given.

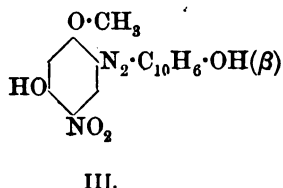
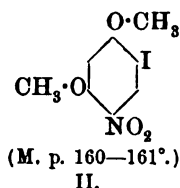
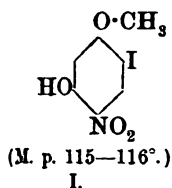
#### *Diazotisation of Dinitro-o-anisidine.*

In the preliminary note published in 1900 (Trans., 77, 1173), when it was first made known that a nitro-group was displaced on diazotising dinitro-*o*-anisidine, it was supposed that the replacement of the diazonium group by iodine would give rise to iodonitroanisole, and the compound thus obtained (m. p. 115—116°) was accordingly described as such. The further investigation of the reaction, however, made it evident that not only was the nitro-group displaced, but that a diazo-oxide (quinonediazide) was formed (Proc., 1901, 17, 131). It thus became necessary to make a further study of the supposed iodonitroanisole and the corresponding azo- $\beta$ -naphthol derivative in order to ascertain whether, as might have been anticipated, they contained free hydroxyl groups. This was found to be the case, and the corrected formulæ were given in the paper last referred to.\*

The compound described at first as iodonitroanisole was in fact

\* See also Trans., 1901, 79, 1078, footnote. The nitrogen determination in these compounds does not give decisive information as to whether a hydroxyl group is present or not.

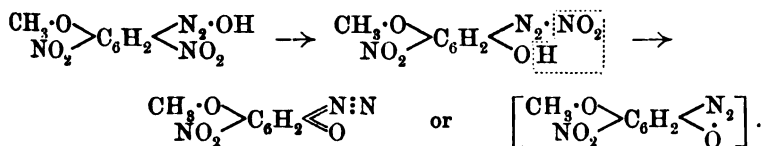
shown to be iodonitroresorcinol methyl ether, and we again give the formula of this compound (I) as well as that of the azo- $\beta$ -naphthol derivative (III), as our later results appear to have escaped notice.



In order to obtain further confirmation of the presence of free hydroxyl, the dimethyl ether (II) was prepared by methylating the mono-methyl derivative (I) by methyl sulphate in the presence of alkali. The compound is slightly soluble in boiling water, and crystallises from dilute alcohol in long filamentous needles of a pale straw colour having the melting point given above.

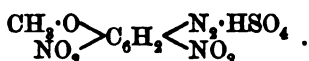
0.1866 gave 7.3 c.c. moist nitrogen at 13° and 759.8 mm.  $N = 4.57$ .  
 $\text{C}_8\text{H}_5\text{O}_4\text{NI}$  requires  $N = 4.53$  per cent.

The nitro-group which is eliminated on diazotising dinitro-*o*-anisidine, is, as has been proved in the former communications, in the para-position with respect to the diazonium group. Whether, as in the case of the haloid-benzenediazonium salts, the elimination of the substituent is preceded by isomeric change, as supposed by Orton (*Proc. Roy. Soc.*, 1903, 71, 155), must for the present remain an open question. If this view be taken, it must be assumed that the nitro-diazonium compound is first transformed into a diazonium nitrite, and that the latter then decomposes into the quinonediazide or diazo-oxide.



Whatever view be taken of the mechanism of the elimination of the nitro-group, it is, however, quite certain that a diazonium salt containing a strongly acid group might be expected to be more stable than the diazo-hydroxide (or acetate) which is formed on diazotisation in presence of acetic acid only, the condition which our previous researches have shown to be the most favourable for the displacement of the nitro-group. In order to test this point, dinitro-*o*-anisidine was diazotised in the presence of sulphuric acid, and the diazonium sulphate decomposed by heating with hydriodic acid in the usual way.

Under these conditions, the first product of diazotisation would be the sulphate,



If, as might have been anticipated, this salt is sufficiently stable to exist as such, that is, without the elimination of the nitro-group, the action of hydriodic acid would in this case give the iododinitroanisole ( $\text{OCH}_3:\text{I}:\text{NO}_2:\text{NO}_2=1:2:4:5$ ) instead of the iodonitroresorcinol methyl ether obtained when the preliminary diazotising process is carried out in acetic acid solution. This was found to be the case, although, under the conditions of the experiments, a certain quantity of the resorcinol derivative was also formed, and could be easily removed from the final product by washing with dilute sodium hydroxide solution. The iododinitroanisole thus obtained has not hitherto been described.\* It crystallises from alcohol in flat, yellow scales with serrated edges melting at  $146-147^\circ$ .

0.1041 gave 7.8 c.c. moist nitrogen at  $14^\circ$  and 756.5 mm.  $\text{N}=8.76$ .

$\text{C}_7\text{H}_5\text{O}_5\text{N}_2\text{I}$  requires  $\text{N}=8.64$  per cent.

The formation of iodonitroresorcinol methyl ether by diazotisation in acetic acid solution, and of a mixture of the resorcinol derivative with iododinitroanisole in sulphuric acid solution, are facts of considerable theoretical interest. The resorcinol derivative may be considered as the equivalent of the diazo-hydroxide (or acetate) and the iododinitroanisole as the equivalent of the diazonium sulphate respectively formed on diazotisation under the two conditions specified. It thus appears that in the presence of a strong mineral acid, such as sulphuric acid, a certain quantity of the diazo-hydroxide may exist.† The relative proportions of the anisole and resorcinol derivatives formed under different conditions of time, temperature, and concentration of acid would thus furnish a quantitative measure of the proportions of diazonium and diazo-compounds contained in a given solution. According to Hantzsch,‡ such a solution may in the presence of water at any given moment contain a mixture of diazonium salt and diazo-compound (*syn*-modification). We may point out that the observations recorded in this and in previous papers have now provided a quantitative

\* We learn from M. Reverdin that he has also obtained this compound from dinitro-*o*-anisidine by a similar method. He has forwarded to us a specimen of his product which we have found to be identical with ours.

† The acid used in the above experiment consisted of strong sulphuric acid and water in about equal volumes. The dinitro-*o*-anisidine was dissolved in the strong acid and the solution diluted with water in the above proportion.

‡ See, for instance, this author's *Grundriss der Stereochemie*, Leipzig, 1904, p. 154.

chemical method which may be applicable for determining the equilibrium proportions of the two constituents, quite independently of any views which are held concerning their constitutional formulæ. We hope to be able to extend the work in this direction,

*Nitration of Acetylated p-Aminophenol.*

The nitration of *p*-acetaminophenol can be conveniently effected, even when the hydroxyl is not protected, by dissolving *p*-aminophenol in a small quantity of glacial acetic acid, adding the calculated quantity of acetic anhydride to acetylate the amino-group, and to the solution, kept cold in melting ice, adding a little more than twice the calculated quantity of nitric acid, the latter (sp. gr. 1.5), diluted with twice its volume of acetic acid, being mixed in small quantities at a time with the acetaminophenol solution. If the solution is kept well cooled, there is no danger of decomposition occurring, and the nitration is complete after a few hours. The product is poured into water and at once neutralised with ammonia. The ammonium salt separates out on cooling as a crystalline pulp, and can be readily purified by crystallisation from hot water as this salt is not readily soluble in cold water.

*Ammonium salt*,  $C_6H_2(NO_2)_2 \cdot NH(C_2H_3O) \cdot O \cdot NH_4$ ; flat, dull red needles from water; anhydrous.

*Silver salt*,  $C_6H_2(NO_2)_2 \cdot NH(C_2H_3O) \cdot OAg$ , prepared by adding silver nitrate to the hot solution of the ammonium salt, separates in small brick-red needles insoluble in water.

0.1231 gave 0.0383 Ag = 31.11.

0.0974 „ 10.25 c.c. moist nitrogen at 13.5° and 751.1 mm.  
N = 12.26.

$C_8H_6O_6N_3Ag$  requires Ag = 31.04; N = 12.07 per cent.

*Aniline salt*,  $C_6H_2(NO_2)_2 \cdot NH(C_2H_3O) \cdot ONH_3 \cdot C_6H_5$ , prepared by adding aniline to an alcoholic solution of the dinitroaminophenol; red needles, m. p. 171°. On recrystallising from alcohol and drying in the water-oven, the salt undergoes dissociation.

*Benzylamine salt*,  $C_6H_2(NO_2)_2 \cdot NH(C_2H_3O) \cdot ONH_3 \cdot C_7H_7$ , prepared in the same way as the aniline salt, separates from the alcoholic solution in deep-red prismatic needles, m. p. 221°. This salt also, although more stable than the aniline salt, appears to dissociate on further crystallisation from alcohol.

0.0935 gave 13 c.c. moist nitrogen at 11° and 758.6 mm. N = 16.36.

$C_{15}H_{16}O_6N_4$  requires N = 16.12 per cent.

The dinitroacetaminophenol obtained by the above method crystallises in dense, ochreous needles melting at 182°; it is the acetyl deriv-

ative of the isopicramic acid first described by Dabney (*Amer. Chem. J.*, 1883, **5**, 33), and is identical with the dinitroacetaminophenol recently obtained by Messrs. Cassella & Co. by nitrating *p*-acetaminophenol in sulphuric acid at a low temperature (Eng. Pat. No. 24,409 of 1903). The proof of this constitution has been furnished by Reverdin and Dresel in a paper communicated to the *Arch. Sci. phys. nat.*, an advanced copy of which has been kindly placed at our disposal by the authors.

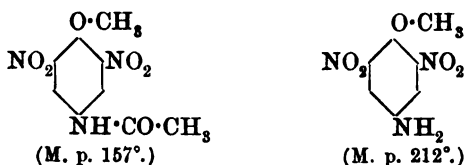
2 : 6-Dinitro 4-acetaminophenol could not be methylated by means of methyl sulphate and alkali. It was accordingly converted into silver salt, and the latter methylated by digestion with methyl iodide in methyl-alcoholic solution. The methyl derivative, after purification, crystallises from dilute acetic acid in light, straw-coloured needles melting at 157°.

0.1338 gave 19.15 c.c. moist nitrogen at 10° and 750.5 mm.  $N = 16.85$ .  
 $C_9H_9O_6N_3$  requires  $N = 16.50$  per cent.

The above acetyl derivative cannot be safely hydrolysed by alkali, as it is liable to undergo decomposition. It was readily hydrolysed by heating with dilute sulphuric acid. The dinitroanisidine thus obtained crystallises from dilute alcohol in small, ochreous needles melting at 212°.

0.0974 gave 16 c.c. moist nitrogen at 12° and 764.8 mm.  $N = 19.56$ .  
 $C_7H_7O_5N_3$  requires  $N = 19.71$  per cent.

The constitution of the above compounds is :



The dinitroanisidine is readily diazotisable in sulphuric, hydrochloric, or acetic acid solution. The product is the same in all cases, and is a diazo-oxide (quinonediazide) crystallising from water in glistening scales. The pure compound explodes with extreme violence at about 190°.

As the main object of our research was to ascertain whether a nitro-group was eliminated on diazotisation, we combined the diazo-oxide at once with  $\beta$ -naphthol by adding the compound to an alkaline solution of the latter. The azo-colour is immediately formed, but remains in solution on account of its phenolic character. After precipitation by acid and crystallisation from boiling acetic anhydride the azo-

compound was found to be acetylated, the acetyl derivative crystallising in brick-red needles melting at 259°.

0·1244 gave 15·1 c.c. moist nitrogen at 13° and 768·8 mm.  $N = 14·49$ .

$C_{15}H_{12}O_7N_4$  requires  $N = 14·14$  per cent.

The azo-compound obtained from the acetyl derivative by hydrolysis with alcoholic sodium hydroxide was crystallised from nitrobenzene, washed with alcohol and dried. It then consisted of glistening, flat, brick-red needles melting at 269—270°.

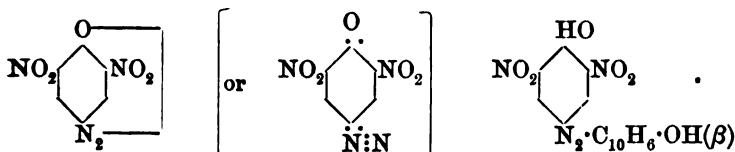
0·1147 gave 15·3 c.c. moist nitrogen at 14·5° and 766·8 mm.

$N = 15·78$ .

$C_{16}H_{10}O_6N_4$  requires  $N = 15·81$  per cent.

The azo-compound is, as already stated, phenolic in character ; it dissolves in aqueous alkali with a claret-red, and in strong sulphuric acid with a magenta-red, colour. It dissolves but sparingly in alcohol, more readily in glacial acetic acid, the compound separating on cooling in flat, brick-red needles with a green, metallic lustre.

The distinctly phenolic properties of the azo-compound indicated that the diazo-oxide must have been formed either by the displacement of a nitro-group as in the case of dinitro-*o*- and dinitro-*p*-anisidines, or by the elimination of the methyl of the methoxy-group. The analyses proved that two nitro-groups were present, and that the formulæ of the diazo-oxide and azo-naphthol compound were accordingly :



From this, it followed that the dinitroaminophenol itself, that is, *isopicramic* acid, should give the same diazo-oxide, and the same azonaphthol compound as the methylated product. This conclusion was confirmed by experiment. *isoPicramic* acid was diazotised in hydrochloric acid solution, and the crystalline diazo-oxide thus formed was combined with  $\beta$ -naphthol in the usual way. The azo-compound, after crystallisation from acetic anhydride, gave the acetyl derivative (m. p. 259°) above described.

0·1172 gave 14·3 c.c. moist nitrogen at 12° and 761·2 mm.  $N = 14·25$ .

$C_{18}H_{12}O_7N_4$  requires  $N = 14·14$  per cent.

It is proved by the foregoing results that, when in a dinitroanisidine the methoxy-group is in the para-position with respect to the amino-group, there is no elimination of a nitro-group on diazotisation, but the methyl of the methoxy-group is displaced with the formation

of a dinitroquinonediazide. This change is complete and rapid when diazotisation is carried out in the presence of mineral acids. The quinonediazide formed under these conditions is not mixed with diazonium salt since, on boiling with hydriodic acid, it yields nothing but the dinitroiodophenol (m. p.  $113^{\circ}$ ) described by Reverdin (*Arch. Sci. phys. nat.*, 1905, 19, 362), and on coupling with  $\beta$ -naphthol in alkaline solution it gives an azo-compound which is completely soluble in alkali. When diazotisation is effected in acetic acid solution, however, there is reason to believe that the displacement of the methyl does not take place so readily. A specimen of the azo- $\beta$ -naphthol compound prepared in this way left a small quantity of a non-phenolic azo-compound on extraction with alkali. This residue is, no doubt, the methyl ether of the azo-compound previously described,\* but it could not be obtained in a crystalline condition from any solvent, and we reserve its detailed study until a larger quantity has been prepared. We may add that the methyl group of the dinitroanisidine is also removable by mineral acids when the base is boiled with the latter. It was found, when the acetyl derivative (m. p.  $157^{\circ}$ ) was heated with sulphuric acid for the purpose of hydrolysing it, as previously described, that the dinitroaminophenol (isopicramic acid) was obtained if the operation was carried too far. The presence of nitro-groups in both ortho-positions with respect to the methoxy-group is no doubt the cause of the easy removability of the methyl group.

In connection with the present research we have also prepared the methyl ether of the new dinitroaminophenol melting at  $230-231^{\circ}$  recently described by Reverdin (*loc. cit.*, 18, 342 ; 19, 353). This compound was obtained by methylating the mono-acetyl derivative with methyl iodide and silver oxide in alcoholic solution. The acetyl derivative of the new dinitroanisidine crystallises from dilute alcohol in white, silky needles (m. p.  $196^{\circ}$ ). On hydrolysis by sulphuric acid it yields a dinitroanisidine crystallising from glacial acetic acid in dense, ruby-red prisms with a green, metallic lustre and having a melting point of  $163^{\circ}$ .

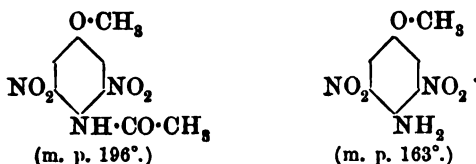
0.0886 gave 15.6 c.c. moist nitrogen at  $20^{\circ}$  and 754.7 mm.  $N = 19.97$ .  
 $C_7H_5O_5N_3$  requires  $N = 19.71$  per cent.

This dinitroanisidine is but sparingly soluble in alcohol but more readily in boiling glacial acetic acid. A dilute solution in the latter solvent on dilution with water deposits the compound in the form of microscopic, scarlet needles. The basic properties of the dinitroanis-

\* This is proved by the fact that the same compound is obtained by the direct methylation of the azo- $\beta$ -naphthol derivative by methyl sulphate and alkali.



idine are but feeble. Its constitution and that of the acetyl derivative may be thus formulated :



The products of diazotisation of this dinitroanisidine have as yet been investigated only in a preliminary way, and further details will be given in a later communication.

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FINSBURY.

## CXXII.—*Labile Isomerism among Benzoyl Derivatives of Salicylamide.*

By ARTHUR WALSH TITHERLEY and WILLIAM LONGTON HICKS.

SALICYLAMIDE may be expected to give rise to two benzoyl derivatives :

- (a)  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_5$ , *N*-benzoylsalicylamide.
- (b)  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}_2$ , *O*-benzoylsalicylamide.

By the action of methyl salicylate on sodium benzamide, one of the authors (Trans., 1902, 81, 1533) obtained a product (m. p. 122°) which was described as salicylbenzamide,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_5$ , that is, (a) the *N*-benzoyl derivative. The assumption that the compound, which on analysis gave 5.67 per cent. of nitrogen (theory requires N = 5.80 per cent.), possessed this structural formula was based on the following considerations: (1) its synthesis, a general reaction having been established between esters and sodium acylamides whereby sodium secondary amides are formed; (2) its properties, notably its easy decomposition with aqueous alkalis into salicylic acid and benzamide, and the fact that it gives an intense violet coloration with ferric chloride; (3) its non-identity with the *O*-benzoyl derivative, (b)  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}_2$  (m. p. 200°), described previously.

Further experiments recently carried out by the authors show that this assumption was wrong, and that the substance is a peculiar double compound of benzamide and salicylic acid (N = 5.4 per cent.) which shows the above properties, and whilst attempts to prepare