

CCXLII.—*Studies in the Diphenyl Series. Part II.*
The Dinitrobenzidines: a New Form of Isomerism.

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IN 1872 Strakosch (*Ber.*, **5**, 236) nitrated diacetylbenzidine and obtained a dinitrobenzidine, which was shown very conclusively by Brunner and Witt (*Ber.*, 1887, **20**, 1023) to contain the nitro-groups in the ortho-position with respect to the amino-groups.

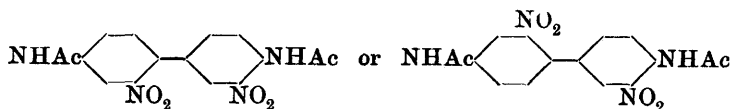
On the other hand, Bandrowski (*Ber.*, 1884, **17**, 1181; *Monatsh.*, 1887, **8**, 472) by the nitration of diphthalylbenzidine obtained two dinitrobenzidines, one melting at 218—221°, and the other, "isodinitrobenzidine," melting at 196—197°. Bandrowski, comparing the former with Strakosch's dinitrobenzidine, points out the distinct differences between them, the one being stated by Strakosch to melt at above 300° and to sublime at a higher temperature, and the other, discovered by Bandrowski, being found to melt at 218—221° and to inflame when heated further.

Bandrowski concluded that it appeared probable that his dinitro-

benzidine was identical with that described by Strakosch, but pointed out that the identity could only be established by a direct comparison of the two substances. In spite of this guarded statement it has been assumed in the literature that the two compounds are identical, and the melting point $218-221^{\circ}$ has been assigned to both.

As regards Bandrowski's "isodinitrobenzidine," the elucidation of the constitution of this substance was really the original object of the present investigation, for, in view of the fact that both 3:3'- and 2:2'-dinitrobenzidine (Täuber, *Ber.*, 1890, **23**, 794) are described in the literature, the possibility of the formation of a third symmetrical dinitrobenzidine (and it would be difficult to imagine that an unsymmetrical one could be produced in the nitration process) seemed, in the present state of our knowledge, questionable.

Having, however, prepared a considerable amount of what may be termed Strakosch's dinitrobenzidine, following the directions of Brunner and Witt, for the purpose of another investigation, we naturally compared this substance with the chief product obtained in the nitration of diphthalylbenzidine, namely, Bandrowski's dinitrobenzidine, expecting to find, as suggested by the latter author, that the two were identical. It was soon suspected that they were not; and a careful comparison has shown that there exist two distinct ortho-dinitrobenzidines. Sufficient proof was furnished by Brunner and Witt that their product was a diortho-compound, and we have confirmed this by finding that on oxidation with potassium permanganate the diacetyl derivative yields 3-nitro-4-acetylaminobenzoic acid. No conclusive evidence has yet been adduced that Bandrowski's product was a diortho-compound, but we have proved that it has this constitution as follows: On oxidising its diacetyl derivative as above, 3-nitro-4-acetylaminobenzoic acid alone was obtained; this might conceivably have been produced by the oxidation of an unsymmetrical dinitrodiacetylbenzidine of the formula:



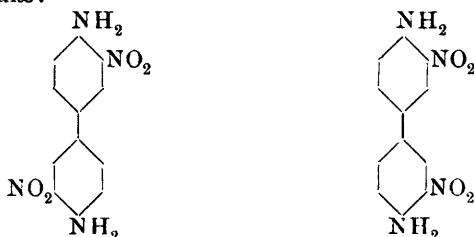
the ring containing the nitro- and amino-groups in the meta-position with respect to each other having been completely oxidised. The formation of such a compound by the nitration of a diacetyl derivative of benzidine is, however, very improbable, but in order to place the matter beyond doubt the dinitrobenzidine was reduced to tetra-aminodiphenyl, and this, when condensed with benzil, gave

the corresponding diquinoxaline, the formation of which proves that the dinitrobenzidine is a diortho-derivative.

The chief differences between the two dinitrobenzidines are as follows: Strakosch's dinitrobenzidine, prepared from diacetylbenzidine, crystallises in scarlet needles melting at 275°, is practically insoluble in water, yields a diacetyl derivative melting at 310°, and a dinitrodiphenyl melting at 197—198° (Brunner and Witt). Bandrowski's dinitrobenzidine, prepared from diphthalylbenzidine, crystallises in bright red, feathery needles (yellowish than the preceding) melting at 233°, is appreciably soluble in water, yields a diacetyl derivative melting at 222° (Bandrowski gives "above 300°"), and a *dinitrodiphenyl* melting at 110°. Corresponding members of the two series, namely, the dinitrobenzidines, their diacetyl derivatives, and the dinitrodiphenyls, depress each other's melting point.

Both dinitrobenzidines, however, give on reduction and condensation of the product with benzil the same diquinoxaline, so that it would appear that the cause of the new isomerism may lie in some special property of the nitro-groups.

From these facts it seems justifiable to draw the conclusion that the constitutions of the two dinitrobenzidines must be represented by the formulæ:



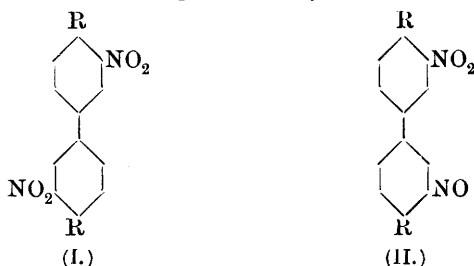
and this is, so far as the authors are aware, the first instance of such isomerism in the case of substances where the possibility of rotation of two carbon atoms about their common linking exists, although Willgerodt (*J. pr. Chem.*, 1888, [ii], **37**, 449; Willgerodt and Schultz, *ibid.*, 1891, [ii], **43**, 177) and Young and Annable (*Trans.*, 1897, **71**, 204) have suggested that in certain compounds containing two nitrogen atoms linked together a similar isomerism is found, thus:



In this connexion it is of interest to recall that Täuber first assigned the 2:6'-constitution to *m*-dinitrobenzidine, but later

proved that the nitro-groups were in the 2:2'-position, thus recognising the possibility of the isomerism, of which the above *o*-dinitrobenzidines, their diacetyl derivatives, and the corresponding dinitrodiphenyls appear to be examples.

It will be noticed that Strakosch's dinitrobenzidine, its diacetyl derivative, and the corresponding dinitrodiphenyl all melt at a considerably higher temperature than Bandrowski's product and the corresponding compounds prepared from it, and in view of the fairly general rule that symmetrical compounds have higher melting points than unsymmetrical, we suggest that, in the absence of any direct chemical evidence, the former compounds have the symmetrical constitution (I) and the latter the unsymmetrical constitution (II) (where R=H, NH₂, or NHAc):



It still remains to explain the nature of Bandrowski's "*isodinitrobenzidine*." This was found not to be a single substance, but simply a mixture of 2:2'-dinitrobenzidine and 3:3'-dinitrobenzidine (m. p. 233°) with possibly a little 3-nitrobenzidine. The nitration of diphtalylbenzidine thus furnishes a mixture of 3:3'-dinitrobenzidine (m. p. 233°) with a small amount of 2:2'-dinitrobenzidine, a fact which is interesting in view of the circumstance that on nitration of diacetylbenzidine the nitro-groups assume the ortho-position, and in the case of benzidine sulphate the meta-position with respect to the amino-groups.

EXPERIMENTAL.

3:5'-Dinitrobenzidine.

Brunner and Witt's directions for preparing this compound were closely followed. The substance was obtained in the pure state (Found, N=20.4. Calc., N=20.4 per cent.) by crystallisation from phenol as recommended by these authors, and forms scarlet needles melting at 275°. This melting point is lowered when the substance is mixed with 3:3'-dinitrobenzidine.

One hundred c.c. of a boiling aqueous solution contained only 0.012 gram of the substance.

Strakosch (*loc. cit.*) noticed that a second product, crystallising in red needles, was obtained in the nitration of diacetylbenzidine, but he did not investigate it further. This second product consists of the isomeric 3:3'-dinitrobenzidine (see below), and is obtained from the crude substance by treatment with alcohol or concentrated hydrochloric acid. In the latter case the red needles which crystallise on cooling the solution are removed, and the filtrate is treated with water or ammonia, when 3:3'-dinitrobenzidine is obtained.

3:5'-Dinitrodiacetylbenzidine melts at 310°, a melting point which is lowered by mixing the substance with 3:3'-dinitrodiacetylbenzidine; when oxidised with potassium permanganate the diacetyl compound gives 3-nitro-4-acetylaminobenzoic acid.

When the dinitrobenzidine is reduced as described by Brunner and Witt to the tetra-aminodiphenyl and this condensed with benzil, the diquinoxaline produced melts at 299—300° (Brunner and Witt give "not at 275°").

3:3'-Dinitrobenzidine.

Diphthalylbenzidine was nitrated as described by Bandrowski. The crude product melted at 220—225° after softening at 218°, and after purification by crystallisation from alcohol, phenol, or water, or when obtained through the hydrochloride, formed red, feathery needles, melting at 233°. The pure material was subjected to various processes in order to prove that it was a single substance; thus it was fractionally crystallised from water, in which, unlike 3:5'-dinitrobenzidine, it is sparingly soluble (100 c.c. of a boiling aqueous solution contained 0.146 gram of the substance), but all the fractions melted at the same temperature. Fractional crystallisation from alcohol and fractional treatment with both dilute and concentrated hydrochloric acid also failed to produce any difference in the melting points of the various fractions.

In order to elucidate its constitution the diacetyl derivative, which is not identical with that described by Strakosch, and separates from glacial acetic acid in yellow, granular crystals melting at 222° (Bandrowski gives "above 300°"), was dissolved in glacial acetic acid, and aqueous potassium permanganate added until no further decolorisation occurred, the temperature being kept at about 60°. After filtering, the solution was neutralised with sodium carbonate, filtered from a little unchanged substance, and the cold filtrate acidified with hydrochloric acid. Extraction of this solution with ether furnished a pale yellow acid melting at 218—219°; this was mixed with 3-nitro-4-acetylaminobenzoic acid

(m. p. 219°; prepared by oxidising 3-nitro-4-acetotoluidide with potassium permanganate in the presence of magnesium sulphate) when the mixture melted at 219°. This result proves at least that the nitro- and amino-groups in one-half of the molecule are in the ortho-position with respect to each other, but in order to show that this is true of both rings the dinitrobenzidine was reduced to tetra-aminodiphenyl, the acetate of which was condensed with benzil. The diquinoxaline which was formed (Found, N=10·5. $C_{40}H_{26}N_4$ requires N=10·0 per cent.) melted at 299—300°, and a mixture of this with the diquinoxaline* prepared from Strakosch's dinitrobenzidine melted at the same temperature. Bandrowski's dinitrobenzidine is therefore a diortho-compound.

3:3'-Dinitrodiphenyl.

The two dinitrobenzidines described above were diazotised as directed by Brunner and Witt, and the bisdiazo-compounds were boiled with alcohol. Whereas Strakosch's dinitrobenzidine yielded the dinitrodiphenyl obtained by Brunner and Witt (now to be termed 3:5'-), Bandrowski's dinitrobenzidine gave a different *dinitrodiphenyl* (3:3'), which crystallises from glacial acetic acid in small, pale yellow needles melting at 110°, a melting point which could not be raised either by recrystallisation of the substance or by distillation under diminished pressure, but which is lowered when the substance is mixed with a little 3:5'-dinitrodiphenyl:

0·0654 gave 6·4 c.c. N_2 at 9° and 746·4 mm. N=11·6.

$C_{12}H_8O_4N_2$ requires N=11·5 per cent.

Bandrowski's "isoDinitrobenzidine."

When the product of nitration of diphthalylbenzidine is poured into water, a precipitate of 3:3'-dinitrobenzidine (m. p. 233°) is obtained. The filtrate, on neutralisation with ammonia, gives a precipitate which was purified by Bandrowski by extracting with dilute hydrochloric acid (in which his *o*-dinitrobenzidine is sparingly soluble), and precipitating the filtrate with ammonia. The substance obtained in this way was regarded by Bandrowski as an isomeric dinitrobenzidine, and he found it to melt at 197°. In repeating this purification instead of immediately precipitating the filtrate from extraction with dilute hydrochloric acid with ammonia, the filtrate was allowed to remain overnight, when it was found that a further quantity of 3:3'-dinitrobenzidine (m. p. 233°) had

* The diquinoxaline prepared by Brunner and Witt, although described in 1887 is not mentioned in the new edition of Richter's *Lexikon*.

separated. The filtrate from this, on neutralisation with ammonia, gave a bright yellow base, which was boiled with insufficient 75 per cent. alcohol to dissolve the whole. (Residue=*A*.) The solution yielded slightly brownish-yellow needles melting at 210—212°, which on recrystallisation from absolute alcohol gave yellow needles melting at 214°, and these were proved to be 2:2'-dinitrobenzidine by a mixed melting-point determination. The filtrate from the brownish-yellow needles deposited a small amount of red needles melting at 188—189°. The quantity of these was too small for analysis, but they consisted apparently of 3-nitrobenzidine, the melting point of which is given as 190° (Koller, *Ber.*, 1904, **37**, 2880).

The residue *A* (see above) was dissolved in absolute alcohol, and from the solution there separated yellow needles melting at 214°, which were identified as 2:2'-dinitrobenzidine.

Bandrowski's "isodinitrobenzidine" is thus shown to consist of a mixture of 3:3'-dinitrobenzidine (m. p. 233°), 2:2'-dinitrobenzidine, and probably a little of the 3-mononitro-compound.

An examination has also been made of the compound isolated by Cain and May (*Trans.*, 1910, **97**, 724) in the preparation of 2:2'-dinitrobenzidine, which, it was suggested, might be identical with Bandrowski's isodinitrobenzidine. This, on recrystallisation, gave 2:2'-dinitrobenzidine, and the filtrate contained probably a trace of 2-nitrobenzidine, the melting point of which is given as 143° (Täuber).

Further experiments on the isomeric *o*-dinitrobenzidines are in progress, and a search will be made for other examples of this isomerism among diphenyl derivatives, as the constitution of many of those described in the literature is yet unknown.

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