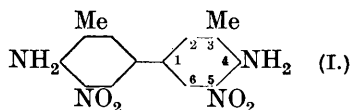


CXXVI.—*Orientation Effects in the Diphenyl Series.*
Part VI. The Supposed Isomerism of the
Dinitrotolidines.

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IN 1914, Cain and Micklethwait (*J.*, **105**, 1442) described the discovery of isomeric dinitrotolidines corresponding to the 3:3'- and 3:5'-dinitrobenzidines they had previously isolated. They also described four isomeric dinitrotolidines in which the nitro-groups occupied in each case two of the four positions 2, 2', 6, and 6'.

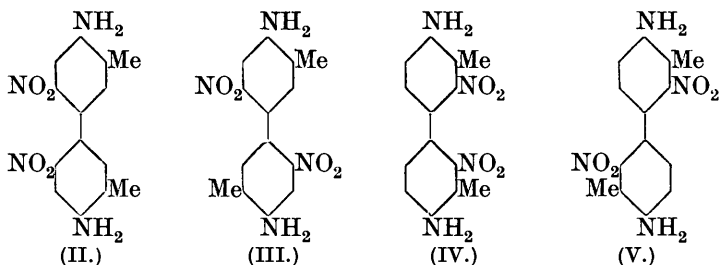
Gerber (*Ber.*, 1888, **21**, 746) had already shown that when diacetyl-*o*-tolidine was nitrated, the main product after hydrolysis had m. p. 266—267° and was the dinitro-compound (I), its constitution being based upon its convertibility into a quinoxaline.



Cain and Micklethwait stated that they set out in the hope of isolating a second dinitro-compound, corresponding to Bandrowski's base, regarded by Cain as 3:3'-dinitrobenzidine. In attempting to repeat Gerber's work, they apparently were successful, and described the isolation of what they called *o*-dinitrotolidine II in addition to Gerber's compound, which they designated *o*-dinitrotolidine I. Cain and Micklethwait also nitrated diphthalyl-*o*-tolidine, evidently hoping to obtain *o*-dinitrotolidine II in better yield. Instead, they described the isolation of four isomeric *m*-dinitrotolidines, to which they gave formulæ (II) to (V).

One of these compounds had previously been obtained by Gerber (*Diss.*, Basel, 1889) by nitrating *o*-tolidine sulphate. Gerber regarded his substance as II, and was correct in so doing, for later Täuber and Löwenherz (*Ber.*, 1891, **24**, 1033) succeeded in converting it

into a diaminodimethylcarbazole, a conversion incidentally repeated and confirmed by Cain and Micklethwait.



Cain and Micklethwait also described the conversion of *o*-dinitrotolidine II into *o*-dinitrotolidine I, and thus added very considerably to their evidence for 3 : 3'–3 : 5' isomerism.

As a result of our previous discovery (J., 1926, 1759) that Cain's space isomerides were actually position isomerides, we re-investigated the dinitrotolidine question. We find that when diacetyl-*o*-tolidine is nitrated, etc., two products can indeed be isolated, but that one is formed only in small quantity, and although it melts, as Cain and Micklethwait stated, at about 202–203°, it is in reality an impure specimen of 6 : 6'-dinitro-*o*-tolidine, since it may be converted into 4 : 4'-dibromo-6 : 6'-dinitro-3 : 3'-dimethyldiphenyl, a substance which does not react with boiling piperidine.

When investigating Bandrowski's dinitrobenzidine, we showed that this compound was formed almost quantitatively by the nitration of 2-nitrodiacetylbenzidine. The nitration of the corresponding tolidine derivative, *viz.*, 6-nitrodiacetyl-*o*-tolidine, however, under similar conditions gives the 6 : 6'-dinitro-compound.

We have confirmed the structure of Gerber's dinitro-*o*-tolidine (obtained by nitration of diacetyltolidine) by converting it into 4 : 4'-dibromo-5 : 5'-dinitro-3 : 3'-dimethyldiphenyl, which readily reacts with boiling piperidine to give 5 : 5'-dinitro-4 : 4'-dipiperidino-3 : 3'-dimethyldiphenyl.

There are three other observations made by Cain and Micklethwait which also require explanation. First, they isolated from the product of hydrolysis of dinitrodiacetyltolidine "a yellowish-brown residue." They said further : "It was found, however, that if this material was crystallised from amyl alcohol further amounts of the isomeric bases could be obtained. The existence of this yellowish-brown substance and its general behaviour indicate possibly that we are here dealing with bases and their internal salts." There is little doubt that the yellowish-brown product was a mixture of dinitrotolidine with dinitrodiacetyltolidine which had escaped hydrolysis

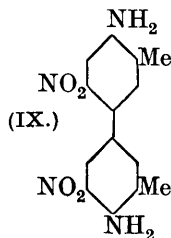
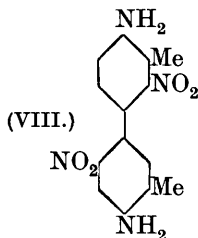
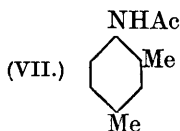
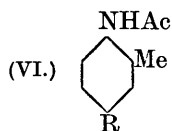
(compare the hydrolysis of nitrophthalylbenzidine, Le Fèvre and Turner, this vol., p. 245). Secondly, Cain and Micklethwait heated their *o*-dinitrotolidine II with acetic acid and acetic anhydride, and eventually isolated a little diacetyl-*o*-dinitrotolidine I. This is now explained, since "base II" was a mixture containing a considerable quantity of base I. Thirdly, these authors reduced both *o*-dinitrotolidine I and II and condensed the resulting tetra-amines with benzil. In both cases one and the same quinoxaline was obtained, and although this to Cain and Micklethwait implied constitutional as distinct from configurational identity, their result is now an experimental necessity, since *o*-dinitrotolidine I is present in the supposed isomeride.

The nitration of diacetyl-*o*-tolidine (VI) may be compared with that of aceto-1 : 3 : 4-xylylide (VII). The latter compound is converted by nitric acid into the 5-nitro-derivative, and by nitric and sulphuric acids mainly into the 6-isomeride (Hofmann, *Ber.*, 1876, 9, 1295; Noelting and Collin, *Ber.*, 1884, 17, 265).

We have not investigated Cain and Micklethwait's four "isomerides" of the meta-series, but a sufficient explanation of these authors' results is that the four compounds are not (II—V), but are (II), (IV), (VIII) and (IX). Cain and Micklethwait appear to have overlooked the possibility of (VIII) being formed, although it is more to be expected than (IV). Their *m*-dinitrotolidine I certainly has formula (II), for the reasons stated above. Their *m*-dinitrotolidines II and IV were converted into compounds which gave correct analyses for carbazoles, agreeing with the present formulæ (IV) and (VIII). Cain and Micklethwait had insufficient of the fourth isomeride (*m*-dinitrotolidine III) for an attempt to convert it into a carbazole, but in view of the very small amount of it obtained it is reasonable to regard it as (IX). Moreover, Cain and Micklethwait's paper contains very little real evidence upon which constitutions of their *m*-dinitrotolidines II, III and IV could soundly be based. No yields are quoted in the paper, and the amount of material available for analysis appears to have been very small.

The 4 : 4'-dibromo-6 : 6'-dinitro-3 : 3'-dimethyldiphenyl referred to above is also obtained by nitrating 4 : 4'-dibromo-3 : 3'-dimethyldiphenyl; similarly, 4 : 4'-dichloro-3 : 3'-dimethyldiphenyl nitrates to give 4 : 4'-dichloro-6 : 6'-dinitro-3 : 3'-dimethyldiphenyl. 4 : 4'-Dihalogenodiphenyls nitrate unsymmetrically (Dennett and Turner, *J.*, 1926, 476), and it is interesting to compare the nitration of the dihalogenoditolyls now described with such nitrations as those of 1 : 2 : 4-trichlorobenzene, 3 : 4-dichloroacetophenone, and 3 : 4-dichloronitrobenzene (all nitrating in position 5). All these cases are illustrations of the apparently general tendency for the formation

of 1 : 2 : 4 : 5-compounds rather than the 1 : 2 : 3 : 4- or 1 : 2 : 3 : 6-isomerides.



EXPERIMENTAL.

Diacetyl-o-tolidine.—Acetic anhydride (60 c.c.) was added slowly to a gently boiling solution of *o*-tolidine (106 g.) in acetic acid (300 c.c.). The product was crystallised from phenol-alcohol.

Nitration of Diacetyl-o-tolidine.—Diacetyltolidine (35 g.) was slowly added to nitric acid (*d* 1.5), the temperature being kept below 0°. The yellow paste obtained by pouring the mixture on crushed ice was treated with steam to remove nitric acid, well washed with boiling water, and dried at 100°. Hydrolysis was effected with concentrated sulphuric acid, the procedure usual in this series being followed.

The diluted acid solution was filtered after 12 hours, and the sulphate obtained was ground under aqueous ammonia. After washing and drying, 16 g. of a red powder were obtained, m. p. below 210°. The m. p. was raised to 261° by the first crystallisation from phenol-alcohol, and after two further crystallisations 7 g. of pure 5 : 5'-dinitro-*o*-tolidine, m. p. 268—269°, were obtained.

o-Dinitrotolidine II.—The mother-liquors from all the above crystallisations were mixed with an excess of sodium hydroxide solution, the more soluble sulphates being obtained as bases, and the excess of phenol was removed. The reddish-brown product was washed with hot water, dried at 100°, and extracted with 150 c.c. of benzene in a Soxhlet apparatus. After cooling and filtering, the clear benzene solution was evaporated to dryness. A bright red, brittle glass was obtained, which appeared to crystallise on being stirred with alcohol. This product (about 1.5 g.) had a m. p. of 200—205° and a definitely crystalline appearance and did not undergo any change of m. p. when twice recrystallised from benzene. It (0.8 g.) was bisdiazotised, and the diazoperbromide prepared in the usual way. Decomposition with boiling glacial acetic acid gave a cream-coloured product; this, after three crystallisations from glacial

acetic acid, formed long, thin needles (m. p. 270°) which slowly reacted with boiling piperidine. The identity of the dibromodinitro-ditolyl was proved by a mixed m. p. determination with authentic 4 : 4'-dibromo-5 : 5'-dinitro-3 : 3'-dimethyldiphenyl (see later).

The residues from the above benzene extraction changed from red to orange-yellow on drying—indicating the presence of a considerable quantity of 6 : 6'-dinitrotolidine. They were treated as above for *o*-dinitrotolidine II, but a pure product was not obtained. After several crystallisations from much glacial acetic acid, the dibromo-compound had m. p. about 230°. This, and the fact that boiling piperidine caused no change in the m. p. even after 1 hour, show it to be 4 : 4'-dibromo-6 : 6'-dinitro-3 : 3'-dimethyldiphenyl.

Nitration of 6-Nitrodiaacetyltolidine.—The acetyl derivative was prepared by the method of Löwenherz (*Ber.*, 1892, 25, 1032). 10 G. were slowly added to 100 c.c. of nitric acid (*d* 1.5) at 0° to -5°. After 1 minute, ice was added, and the white suspension was filtered off, washed, and hydrolysed with sulphuric acid. The reddish-brown product could not be crystallised from the ordinary solvents and therefore was extracted with benzene as described above. From the benzene extract no chemical individual could be isolated, but from the reddish-yellow (less soluble in benzene) residue, about 2.5 g. of 4 : 4'-dibromo-6 : 6'-dinitro-3 : 3'-dimethyldiphenyl were obtained by the perbromide method. The yield of the latter compound indicates that 6 : 6'-dinitrodiaacetyltolidine is formed to a considerable extent in the nitration of 6-nitrodiaacetyltolidine.

4 : 4'-*Dibromo-5 : 5'-dinitro-3 : 3'-dimethyldiphenyl.*—A solution of pure 5 : 5'-dinitrotolidine (7 g.) in 20 c.c. of concentrated sulphuric acid was bisdiazotised at -5° with 3.3 g. of sodium nitrite. After being poured on ice, diluted with water, and filtered, the mixture was treated with a solution of 5 c.c. of bromine in 15 c.c. of hydrobromic acid (*d* 1.49). Decomposition of the precipitated perbromide was effected in boiling glacial acetic acid, and the product, which was sparingly soluble in this solvent, had m. p. 269—271°. From much acetic acid, it crystallised in matted wads of pale yellow, hairy needles, m. p. 271—272° (Found : N, 6.9. C₁₄H₁₀O₄N₂Br₂ requires N, 6.5%).

4 : 4'-*Dipiperidino-5 : 5'-dinitro-3 : 3'-dimethyldiphenyl.*—The last-named compound, when gently refluxed for 1 hour with piperidine, dissolved, and the solution became filled with crystalline cakes of piperidine hydrobromide. Dilution with water gave a product which crystallised from acetic acid in bright yellow plates, m. p. 226—227° (Found : N, 13.0. C₂₄H₃₀O₄N₄ requires N, 12.8%).

4 : 4'-*Dibromo-6 : 6'-dinitro-3 : 3'-dimethyldiphenyl.*—A perbromide

displacement on 12 g. of 6 : 6'-dinitrotolidine gave 9 g. of a cream-coloured substance, which crystallised from acetic acid in long needles, m. p. 230—233° (softening at 225°). Two further crystallisations did not raise the m. p. above 230—233° (Found : N, 6.7. Calc. : N, 6.5%).

4 : 4'-Dichloro-3 : 3'-dimethyldiphenyl.—*o*-Tolidine (90 g.) was bisdiazotised according to the directions of Schultz, Rhode, and Vicari (*Annalen*, 1907, 352, 124) and the resulting solution was allowed to drop slowly into a vigorously stirred solution of cuprous chloride (from 240 g. of copper sulphate crystals) in 750 c.c. of concentrated hydrochloric acid, heated at 100°. Stirring was continued for $\frac{1}{2}$ hour, and the reaction mixture allowed to cool overnight. The dark brown oil obtained was washed by decantation and extracted with benzene, the extract was washed repeatedly with sodium hydroxide solution and with water and dried over sodium sulphate, and the benzene was removed by distillation. The dichloroditoyl was collected at 310—320° (yield, 58 g.); after crystallisation from alcohol, it melted at 52—53° as stated by Schultz, Rhode, and Vicari.

4 : 4'-Dibromo-3 : 3'-dimethyldiphenyl was prepared by the usual method from 100 g. of *o*-tolidine, dissolved in 300 c.c. of concentrated hydrochloric acid diluted with 100 c.c. of water. The solution resulting after the addition of 70 g. of sodium nitrite (in 150 c.c. of water) was slowly added to a solution of cuprous bromide prepared with the aid of 90 g. of potassium bromide; the decomposition was vigorous. The reddish-brown oily product, after being washed in benzene solution with alkali, water, and dilute acid and dried over sodium sulphate, was distilled. The main fraction, b. p. 202—215°/20 mm., solidified on cooling, and after being crystallised from much alcohol, formed long, white needles, m. p. 63—64° (Stolle, *Ber.*, 1888, 21, 1099, gives m. p. 58—59°).

Nitration of 4 : 4'-Dichloro-3 : 3'-dimethyldiphenyl.—Dichloroditoyl (6.2 g.) was slowly added to nitric acid (*d* 1.5; 100 c.c.), cooled in water. The mixture was heated at 100° for 10 minutes and poured into water. The cream-coloured, flocculent powder obtained gave yellow crystals, m. p. 165—170°, 201—202°, and 211—212°, respectively, after one, two, and three crystallisations from glacial acetic acid (Found : Cl, 20.4. $C_{14}H_{10}O_4N_2Cl_2$ requires Cl, 20.8%).

10 G. of 6 : 6'-dinitrotolidine were warmed with 50 c.c. of concentrated hydrochloric acid, and 50 c.c. of water were added when hydrochloride formation was complete. The whitish suspension was then bisdiazotised at 0°. The filtered solution was added to a suitable solution of cuprous chloride in hydrochloric acid. Normal procedure led to the isolation of a powder which, after three crystal-

lisations from glacial acetic acid, melted at 212° and was identical with the nitration product from the last experiment.

Nitration of 4 : 4'-Dibromo-3 : 3'-dimethyldiphenyl.—The dibromo-compound (5 g.) was slowly added to 35 c.c. of nitric acid ($d\ 1.5$), the temperature of which was kept below 20° . The addition of a little water then caused crystallisation to set in. The washed precipitate was extracted with hot glacial acetic acid (the extracts deposited crystalline material, m. p. $150-210^{\circ}$), and the almost insoluble residue was crystallised from a large bulk of glacial acetic acid. It was thus obtained as yellow needles, m. p. $228-230^{\circ}$, with slight previous softening. After three further crystallisations this m. p. was unchanged—it is difficult to account for an indefinite m. p. in the case of a compound of this type.

A mixed m. p. determination with the product obtained from a perbromide displacement on 6 : 6'-dinitrotolidine (above), however, showed that the two substances were identical.

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