CCCXVII.—*Studies in the Diphenyl Series. Part II. The Nitration of Diphthalylbenzidine.*

By HERBERT HENRY HODGSON.

CAIN and his co-workers (J., 1912, **101**, 2298) described the nitration of diphthalylbenzidine and concluded that the nitration products were 3 : 3′(?)-dinitrobenzidine, 2 : 2′-dinitrobenzidine, and a mononitrobenzidine. They also found (*loc. cit.*, p. 2302) that in the nitration of diacetylbenzidine some 3 : 3′(?)-dinitrobenzidine was formed.

Le Fèvre and Turner (this vol., p. 1760) have shown the supposed 3 : 3′-product to be actually the 2 : 3′-dinitrobenzidine, a conclusion also foreshadowed by the present author (this vol., p. 1756). An explanation is still required, however, for the fact that the tetra-aminodiphenyl prepared from 2 : 3′-dinitrobenzidine was stated by Cain (*loc. cit.*, p. 2303) to give a diquinoxaline derivative identical with that prepared from Strakosch's 3 : 5′-dinitrobenzidine, a result supported much later by Brady and McHugh (J., 1923, **123**, 2047). The solution to this problem would appear to be that, in the nitration of diphthalylbenzidine, varying amounts of the 3 : 5′-dinitrobenzidine are formed in addition to the products cited above. Cain, and later Brady, could then have obtained the same diquinoxaline from the mixture of tetra-aminodiphenyls produced by reduction of the mixed dinitrobenzidines. Moreover, Brady and McHugh's detailed description (*loc. cit.*, p. 2052) strongly suggests that they were dealing with such mixtures.

To test this viewpoint, the mixture of dinitrodiphthalylbenzidines was hydrolysed and the dinitrobenzidines were converted by Cain's method (J., 1913, **103**, 2082) into the corresponding mixture of di-iododinitrodiphenyls from which Cain's 4 : 4′-di-iodo-3 : 5′-dinitrodiphenyl was ultimately isolated, thereby establishing the formation of 3 : 5′-dinitrobenzidine in the nitration of diphthalylbenzidine.

EXPERIMENTAL.

For purposes of comparison the following di-iodonitrodiphenyls were prepared :

4 : 4′-*Di-iodo-2-nitrodiphenyl.* 2-Nitrobenzidine was diazotised in concentrated sulphuric acid, and, after removal of excess of nitrous acid, the diluted solution was added to one of potassium iodide. The product is moderately soluble in alcohol and glacial acetic acid, and sublimes readily in a vacuum giving light yellow needles, m. p. 156° (Found : N, 3·3 ; I, 55·9. $C_{12}H_7O_2NI_2$ requires N, 3·2 ; I, 56·3%).

4 : 4′-*Di-iodo*-2 : 2′-*dinitrodiphenyl,* prepared from 2 : 2′-dinitrobenzidine as above, sublimes slowly in a vacuum and crystallises from alcohol in light yellow needles, m. p. 188° (Found : N, 5·7 ; I, 51·0. $C_{12}H_6O_4N_2I_2$ requires N, 5·6 ; I, 51·2%).

4 : 4′-*Di-iodo*-2 : 3′-*dinitrodiphenyl.* The above 4 : 4′-di-iodo-2-nitrodiphenyl was dissolved in synthetic nitric acid, and the solution on cooling deposited crystals which were removed, washed, dried, and sublimed in a vacuum ; slender, light yellow needles, m. p. 156—157° (Cain, *loc. cit.*, gives m. p. 151—152°) (Found : N, 5·7 ; I, 51·1. Calc. : N, 5·6 ; I, 51·2%) ; a mixture with 4 : 4′-di-iodo-2-nitrodiphenyl melted at 142°.

When 4 : 4′-di-iododiphenyl is nitrated similarly a mixture of mono- and di-nitro-products results.

4 : 4′-*Di-iodo*-3 : 5′-*dinitrodiphenyl* sublimes in parallelogram-shaped plates, m. p. 252° (Cain, *loc. cit.*, gives 252—253°) (Found : N, 5·5 ; I, 51·0. Calc. : N, 5·6 ; I, 51·2%).

Nitration of Diphthalylbenzidine.—This was carried out by careful addition of the finely-powdered solid to ten times its weight of synthetic nitric acid. Two sets of experiments were made : (*a*) at 0° ; (*b*) allowing the temperature to rise 40—50° owing to the heat of reaction.

Contrary to Cain's statement (*loc. cit.*, p. 2303), scarcely any hydrolysis occurs on pouring the product into water, and to effect this operation the mixture of dried dinitrodiphthalylbenzidines was hydrolysed by treating with eight times its weight of concentrated sulphuric acid at 130° for 20 minutes, then pouring into twenty times its weight of water, the precipitate being filtered off, dried, and again subjected to the acid process. The united filtrates were precipitated by ammonia, and all the solids extracted with warm dilute alkali to effect removal of phthalic acid or anhydride.

The product of cold nitration (*a*) always yielded a greater portion soluble in warm dilute sulphuric acid and its m. p. was always lower (190—200°). Cain (*loc. cit.*, p. 2303) has shown this product to be mainly a mixture of 2 : 2′- (m. p. 214°) and 2 : 3′-dinitrobenzidines with, probably, a mononitrobenzidine. This was now substantiated by conversion of the product into a mixture of di-iodonitrodiphenyls which melted below 150° and possessed a nitrogen content between the values required for 4 : 4′-di-iodo-mono- and -di-nitrodiphenyls.

The products insoluble in dilute sulphuric acid were diazotised in concentrated sulphuric acid solution and converted into iodo-compounds as above. On analysis, all proved to be mixtures of 4 : 4′-di-iododinitrodiphenyls. The latter were repeatedly extracted with boiling alcohol, and the extracts on cooling deposited microcrystalline products of m. p.'s at first *ca.* 200° but later below 150°. The residues had m. p.'s above 200° and, after crystallisation from glacial acetic acid, these were raised to 240°. The latter products slowly sublimed when heated in a vacuum, giving parallelogram-shaped plates of m. p. 252°, identical with Cain's 4 : 4′-di-iodo-3 : 5′-dinitrodiphenyl (Found : N, 5·7; I, 49·9. Calc. : N, 5·6; I, 51·2%). This product was present in much greater amount in the warm nitration mixture (*b*).

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, June 24th,* **1926.**]