LXI.—*Orientation Effects in the Diphenyl Series. Part I.*

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SINCE the nitration of 4 : 4′-dihydroxydiphenyl (Kunze, *Ber.*, 1888, **21**, 3331; Schultz, *ibid.*, 3530; Hirsch, *ibid.*, 1889, **22**, 336) and of its diethyl ether (Hirsch, *loc. cit.*; Brady and McHugh, J., 1923, **123**, 2047) affords symmetrical (3 : 5′-)dinitro-derivatives, it might be supposed that 4 : 4′-dibromodiphenyl would nitrate to give 4 : 4′-dibromo-3 : 5′(or 3 : 3′)-dinitrodiphenyl. Unsymmetrical nitration, however, actually occurs, with the almost quantitative formation of the 2 : 3′(2 : 5′ ?)-dinitro-compound. This is the first example of unsymmetrical substitution in the diphenyl series.

Whilst the nitration of *p*-tolyl ethyl ether apparently affords only the 3-nitro-derivative (Staedel, *Annalen*, 1883, **217**, 162), *p*-chlorotoluene yields a mixture of approximately equal quantities of the 2- and 3-nitro-compounds (Holleman, *Proc. K. Akad. Wetensch. Amsterdam*, 1908, **11**, 257).

The nitration of 4 : 4′-dibromodiphenyl was described by Fittig (*Annalen*, 1864, **132**, 206) and Schultz (*ibid.*, 1874, **174**, 218) as giving a dinitro-derivative, m. p. 148°, regarded by Beilstein (*Handbuch*, 4th Edn., v, 585) as probably being identical with the 2 : 2′-dinitro-compound, m. p. 138°, previously synthesised by Ullmann and Bielecki (*Ber.*, 1901, **34**, 2177). The work of Fittig and Schultz has been repeated and confirmed. Reduction of their dinitro-compound afforded the diamine, m. p. 89°, described by Schultz (*loc. cit.*), but this diamine could not be caused to undergo condensations of the type to be expected of a symmetrical diamine. This appeared to show that unsymmetrical nitration had occurred. Moreover, the dinitro-derivative depressed the m. p. of the 2 : 2′-dinitro-compound obtained from 2 : 5-dibromonitrobenzene (Ullmann and Bielecki, *loc. cit.*).

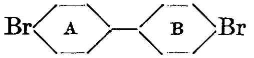
4 : 4′-*Dibromo*-2-*nitrodiphenyl*, prepared from 2-nitrobenzidine, was identical with the mononitro-derivative, m. p. 124°, prepared by Lellmann's method (*Ber.*, 1882, **15**, 2837) and apparently is the first product of nitration of dibromodiphenyl. When nitrated, it was converted into the dinitro-compound, m. p. 148°, which there-

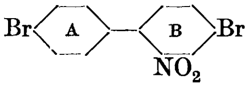
fore has one nitro-group in position 2. It was then found that one bromine atom in the dinitro-compound possessed much greater reactivity than the other.

Hot, concentrated potassium hydroxide had no action on the dinitro-compound, which, however, reacted vigorously with piperidine to give a bromopiperidinodinitrodiphenyl. 4 : 4′-Dibromo-2-nitrodiphenyl and 4 : 4′-dibromo-2 : 2′-dinitrodiphenyl were not affected by piperidine, and it is therefore clear that the above piperidino-derivative is 4-*bromo*-4′-*piperidino*-2 : 3′-*dinitrodiphenyl*, and that the original dinitro-compound is the 2 : 3′-derivative.*

In the entrance of a nitro-group into the B nucleus of dibromodiphenyl (I), the bromophenyl group A apparently has greater directive influence than the bromine atom in B, the nitro-group entering position 2, whilst in the nitration of the mononitro-compound (II), conditions are favourable, according to the ordinary theories of substitution, for 3′-nitration in A.

(I.)





(II.)

It has similarly been found that the dinitro-derivative of 4 : 4′-dichlorodiphenyl described by Schmidt and Schultz (*Annalen*, 1881, **207**, 340) is 4 : 4′-dichloro-2 : 3′-dinitrodiphenyl. It reacts with piperidine even more readily than does the corresponding dibromo-compound, giving 4-*chloro*-4′-*piperidino*-2 : 3′-*dinitrodiphenyl*. The relative activation, by a nitro-group, of a chlorine and a bromine atom is a subject it is hoped to investigate later on.

The diamine referred to above is therefore 4 : 4′-*dibromo*-2 : 3′-*diaminodiphenyl*. Schultz (*loc. cit.*), by oxidising this substance, obtained what he called a bromaminobenzoic acid, m. p. 155°. This was probably a mixture of 4-bromo-2-amino- and 4-bromo-3-amino-benzoic acids, which melt respectively at 225° and 222°. Further, Strasser and Schultz (*Annalen*, 1881, **210**, 194), by reducing, and thus debrominating, the diamine, obtained a base which they called γ-benzidine. This is evidently 2 : 3′-diaminodiphenyl.

A preliminary investigation has shown that the nitration of 4 : 4′-ditolyl affords, first, a mononitro-compound, m. p. 91—92°,

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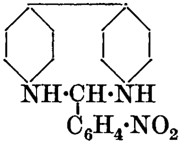
* It might be objected that in the nitration of dibromodiphenyl, both nitro-groups could enter the same nucleus. Against this objection, however, are at least three facts : (1) the difficulty of introducing a third substituent into one nucleus of diphenyl compounds other than hydroxy- and amino-derivatives, (2) the reactivity of one bromine atom in the dinitro-compound, which, if nitration occurred twice in the same nucleus, would almost certainly be 4 : 4′-dibromo-2 : 6-dinitrodiphenyl, *i.e.*, a compound containing no reactive bromine atom, and (3) the quantitative nature of the nitration.

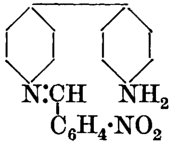
and then a dinitro-compound, m. p. 119°. The latter we regard as the 2 : 3′-dinitro-compound. Ullmann and Frentzel (*Ber.*, 1905, **38**, 726) have described the 3 : 3′(3 : 5′ ?)-derivative, which for present purposes has been prepared by heating 4-iodo-2-nitrotoluene with copper bronze.

The preparation of compounds containing amino-groups in the 3 : 3′- or 3 : 5′-positions in the diphenyl molecule is a matter of considerable difficulty. According to Ullmann and Frentzel (*loc. cit.*), when *m*-nitrobenzenediazonium sulphate is added, under certain conditions, to cuprous chloride and hydrochloric acid, the chief product is 3 : 3′(3 : 5′ ?)-dinitrodiphenyl. We have found, on the contrary, that excellent yields of *m*-chloronitrobenzene are invariably obtained (compare Emde, *Apoth. Ztg.*, 1915, **30**, 293). The dinitro-compound may be obtained from *m*-iodonitrobenzene as stated by Ullmann and Bielecki (*loc. cit.*). The latter substance is only obtainable in small yields by the method of Jacobson, Fertsch, and Heubach (*Annalen*, 1898, **303**, 338), but this difficulty has now been overcome.

During some experiments on the condensation of aldehydes with benzidine, we prepared from *p*-nitrobenzaldehyde a compound to which Barzilowski (*J. Russ. Phys. Chem. Soc.*, 1891, **23**, 69) had assigned formula (III). We have found that this compound readily condenses with a second molecule of a keto-compound, and is therefore (IV).

(III.)





(IV.)

EXPERIMENTAL.

Nitration of 4 : 4′-*Dibromodiphenyl.*—Nitration in glacial acetic acid by Lellmann's method (*loc. cit.*) gave a mononitro-compound, m. p. 124°. Nitration using excess of nitric acid (*d* 1·5) gave a crude dinitro-compound, m. p. 130—135°, which, after being once crystallised from benzene, melted at 148°. A small quantity of the mononitro-compound was obtained from the mother-liquors.

The dinitro-compound was not affected when boiled with very concentrated aqueous potassium hydroxide, whilst alcoholic alkali led to a black product which will be investigated in due course.

Preparation of 4 : 4′-*Dibromo*-2-*nitrodiphenyl.*—2-Nitrobenzidine sulphate was ground into a fine paste with a little water and diazotised at 5°. The solution was poured with vigorous shaking into a cold suspension of cuprous bromide in hydrobromic acid–sodium bromide. The vigorous reaction over, the whole was heated at 100° for a short time and the gummy solid was collected and warmed with sodium hydroxide to remove phenolic substances. The yellow residue, containing considerable quantities of benzerythrene derivatives, after several crystallisations from alcohol and benzene, melted at 124°. The m. p. was not affected by admixture with the first-named nitro-compound (Found : Br, 4·5. $C_{12}H_7O_2NBr_2$ requires Br, 4·5%).

Nitration of 4 : 4′-*Dibromo*-2-*nitrodiphenyl.*—This substance was dissolved in two parts of warm nitric acid (*d* 1·5). On cooling, pale yellow needles separated, which, after crystallisation from benzene, melted at 148° and did not depress the m. p. of the above dinitro-compound having the same m. p.

4-*Bromo*-4′-*piperidino*-2 : 3′-*dinitrodiphenyl.*—The dinitro-compound, m. p. 148°, was gently warmed with a little piperidine for about a minute. An orange colour at once developed, and, on cooling, the whole set to a crystalline paste owing to the separation of piperidine hydrobromide. It was treated with water, and the orange-red solid so obtained once crystallised from alcohol; the *piperidino*-compound was then obtained in orange-red needles, m. p. 136—137° (Found : Br, 19·3. $C_{17}H_{16}O_4N_3Br$ requires Br, 19·7%). The piperidino-compound was unaffected by further heating with piperidine.

4 : 4′-Dibromo-2-nitro- and 4 : 4′-dibromo-2 : 2′-dinitro-diphenyl were also heated for several minutes with piperidine. In both cases the compounds were recovered unchanged.

Preparation of 4 : 4′-*Dibromo*-2 : 3′-*diaminodiphenyl.*—The corresponding dinitro-compound was reduced with iron, water, and ferric chloride (Roberts and Turner, J., 1925, **127**, 2004). The properties of the diamine agreed with those recorded in the literature. It condensed with salicylaldehyde, but not with carbon disulphide, under conditions similar to those under which benzidine readily condenses with this substance.

Disalicylidene-4 : 4′-*dibromo*-2 : 3′-*diaminodiphenyl* separates from benzene as a yellow, crystalline powder, m. p. 195° (Found : N, 5·1. $C_{26}H_{18}O_2N_2Br_2$ requires N, 5·1%).

Nitration of 4 : 4′-*Dichlorodiphenyl.*—The dichloro-compound readily dissolved in warm nitric acid (*d* 1·5), and, on cooling, the dinitro-compound crystallised out. After washing and drying, it was once crystallised from alcohol and then had m. p. 140°.

4-*Chloro*-4′-*piperidino*-2 : 3′-*dinitrodiphenyl.*—The dichloro-compound was warmed for a few seconds with piperidine, the mixture diluted, and the product filtered off, washed with water, and crystallised from alcohol; the *piperidino*-compound was then obtained in orange needles, m. p. 132° (Found: Cl, 10·0. $C_{17}H_{16}O_4N_3Cl$ requires Cl, 9·8%). The piperidino-compound was not affected by further heating with piperidine, which also had no effect on 4 : 4′-dichloro-2 : 2′-dinitrodiphenyl prepared from 2 : 5-dichloronitrobenzene by the method of Ullmann and Bielecki (*loc. cit.*).

*Preparation of Mononitro-*4 : 4′*-ditolyl.*—A solution of ditolyl in glacial acetic acid containing one equivalent of nitric acid (*d* 1·4) was evaporated until, on cooling, yellow prisms separated. These, after crystallisation from alcohol, melted at 91—92° (Found: N, 6·2. $C_{14}H_{13}O_2N$ requires N, 6·1%). The nitro-compound is readily soluble in alcohol, acetic acid, or benzene. Ditolyl is unaffected when dissolved in cold acetic–nitric acid mixtures.

*Preparation of Dinitro-*4 : 4′*-ditolyl.*—Sufficient nitric acid (*d* 1·5) was added to the hydrocarbon to form a clear solution, without cooling. On leaving, slender, yellow needles separated. These, after being collected, washed with water, and crystallised from alcohol, and then from glacial acetic acid, melted at 119° (Found: N, 10·6. $C_{14}H_{12}O_4N_2$ requires N, 10·3%).

Preparation of 3 : 3′ (3 : 5′ ?)*-Dinitro-*4 : 4′*-ditolyl.*—4-Iodo-2-nitrotoluene was prepared from 2-nitro-*p*-toluidine as follows: the base (30 g.) was diazotised in dilute sulphuric acid, and the product added to a cold and well-shaken solution of 45 g. of potassium iodide in 1 l. of saturated sodium acetate solution. The brown tar which separated rapidly solidified, and was crystallised from alcohol in presence of charcoal. The yield of pure 4-iodo-2-nitrotoluene was 85% of the theoretical quantity. The iodo-compound reacted normally with copper bronze, After 20 minutes' heating at 240°, the whole was heated at 260° for a few minutes, and the cooled product extracted with benzene in presence of charcoal. The benzene was evaporated, and the residue crystallised from alcohol. The dinitroditolyl thus obtained melted at 175—176° and its properties agreed with those described by Ullmann and Frentzel (*loc. cit.*).

Preparation of 3 : 5′*-Dinitrodiphenyl.*—(a) *By the method of Ullmann and Frentzel* (*loc. cit.*). The exact instructions of these authors were carried out on some dozen occasions. In one or two cases, small quantities of impure dinitrodiphenyl were isolated, but in most of the experiments *m*-chloronitrobenzene was obtained in about 85% of the theoretical yield. (*b*) *From* m*-iodonitrobenzene.* The iodo-compound was prepared by the following modification of the usual method (Jacobson, Fertsch, and Heubach, *loc. cit.*). *m*-Nitroaniline (60 g.) was ground with 56 c.c. of concentrated sulphuric acid, 200 c.c. of water were added, and the whole was well ground. The suspension was diazotised at 5° with 30·6 g. of sodium nitrite in 150 c.c. of water; addition of the nitrite solution in three portions, below the surface of the suspension, diminished the formation of the diazoamino-compound. The filtered diazo-solution was poured in small quantities into a well-shaken, boiling solution of 110 g. of potassium iodide and 230 g. of hydrated sodium acetate in 1·5 l. of water. The mixture was then cooled, extracted with carbon tetrachloride, the extract washed with sodium thiosulphate, dried, evaporated, and the residue distilled under diminished pressure. The yield of *m*-iodonitrobenzene (m. p. 38°, b. p. 145—155°/15 mm.) was 70% of the theoretical. When the iodo-compound was heated with copper bronze as described by Ullmann and Bielecki (*loc. cit.*), an average conversion into dinitrodiphenyl of 40% of the theoretical was obtained.

Reduction of 3 : 5′-*Dinitrodiphenyl.*—The method previously employed by Emde (*loc. cit.*) was found to be unsatisfactory; reduction with iron, water, and ferric chloride also led to small yields of diamine. This readily forms the *disalicylidene* derivative, which separates from benzene in canary-yellow leaflets, m. p. 176—177° (Found : N, 7·3. $C_{26}H_{20}O_2N_2$ requires N, 7·1%).

p-*Nitrobenzylidenesalicylidenebenzidine.*—The product (m. p. 221—222°, Barzilowski, *loc. cit.*) of interaction of *p*-nitrobenzaldehyde (1 mol.) and benzidine (1 mol.) in hot alcoholic solution was heated under reflux with an alcoholic solution of salicylaldehyde (excess). The red colour of the suspended solid rapidly changed to yellow, and after 30 minutes' boiling the precipitate was collected and crystallised from benzene; yellow prisms, m. p. 210°, were then obtained (Found : N, 10·1. $C_{26}H_{19}O_3N_3$ requires N, 10·0%).

p-*Nitrobenzylideneacetyl*iso*propylidenebenzidine.*—*p*-Nitrobenzylidenebenzidine was warmed with acetylacetone, and the solution obtained was diluted with alcohol and allowed to cool; brownish-yellow, warty prisms, m. p. 185°, then separated (Found : N, 10·6. $C_{23}H_{21}O_3N_3$ requires N, 10·9%).

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