

Metal Ions and Complexes in Organic Reactions. Part XIV.¹ Syntheses of *NN'*-Bisdiarylphenylenediamines

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The following *NN'*-bisdiarylphenylenediamines were obtained, together with by-products, from copper-catalysed substitution of iodo-compounds: *p*-bis(diphenylaminobenzene (II), *p*-bis-(*o*-nitro-*N*-phenylanilino)benzene (IV), and *N*-(*p*-diphenylaminophenyl)-*o*-nitro-*N*-phenylaniline (III). Compound (III) was identical with a by-product previously isolated from a copper-catalysed reaction between diphenylamine and *o*-bromonitrobenzene.

WHEN *o*-nitro-*NN*-diphenylaniline was prepared² from reaction between *o*-bromonitrobenzene and diphenylamine in dimethylacetamide, catalysed by copper(I) oxide, it was accompanied by substantial amounts of nitrobenzene and by 2–3% of a product tentatively formulated as *N*-(*p*-diphenylaminophenyl)-*o*-nitro-*N*-phenylaniline (III). To confirm this structure, a method was needed for synthesising tetra-aryl-*p*-phenylenediamines, *p*-NAr¹₂·C₆H₄·NAr¹Ar², containing two dissimilar tertiary centres. The production of such

centres normally involves copper-catalysed nucleophilic substitution; the best-known procedure³ is reaction between an aryl iodide, a diarylamine, and potassium carbonate, during 24 h in boiling nitrobenzene, in the presence of metallic copper.

In the related Ullmann reaction, Ar¹Hal → Ar¹NHAr², effects of variations in catalyst, solvent, and base are well-documented.⁴ Triarylamine formation is less well explored. However, nothing advantageous resulted from procedural variations applied to reaction

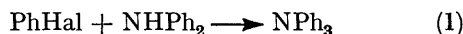
¹ Part XIII, J. A. Azoo, R. G. R. Bacon, and K. K. Gupta, *J. Chem. Soc. (C)*, 1970, 1975.

² R. G. R. Bacon and D. J. Maitland, *J. Chem. Soc. (C)*, 1970, 1973.

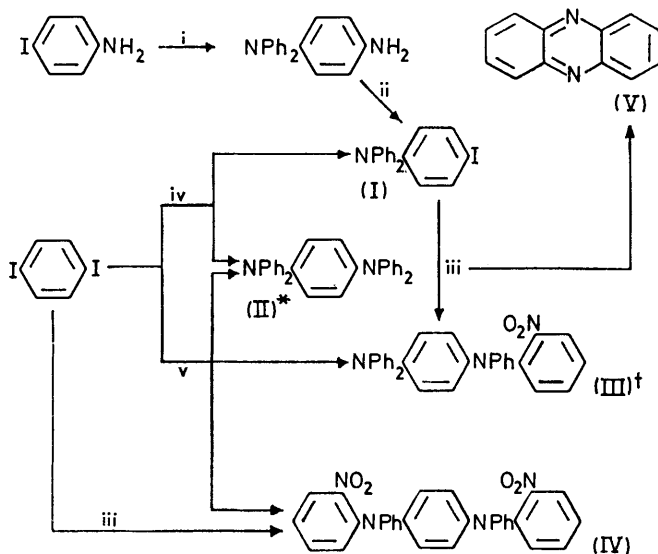
³ *E.g.*, I. Goldberg and M. Nimerovsky, *Ber.*, 1907, **40**, 2448; F. D. Hager, *Org. Synth.*, 1948, Coll. Vol. I, 2nd edn., p. 544.

⁴ R. M. Acheson, 'Acridines,' Interscience, New York, 1956, pp. 148–161.

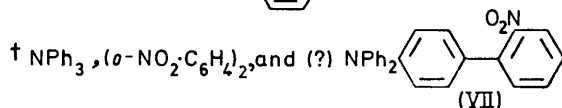
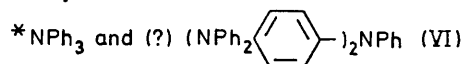
(1). For example, whereas the established method³



gave 70% yields of triphenylamine from iodobenzene (though only 20% if bromobenzene was used), the system $\text{PhI-LiNPh}_2\text{-CuI-Bu}_2\text{O}$ ⁵ gave 40%, and the use of copper(I) oxide as catalyst² was unsuccessful. Accordingly the established procedure was applied (though with change of solvent for one reaction) to obtain the desired bisamine (III), and the related symmetrical compounds (II) and (IV) (see Scheme 1).



By-products:



SCHEME 1 Reagents: i, $\text{NHPPh}_2\text{-(EtO-CH}_2\text{-CH}_2)_2\text{-O}$; ii, $\text{HNO}_2\text{-KI}$; iii, $o\text{-NO}_2\text{-C}_6\text{H}_4\text{-NHPPh}$; iv, NHPPh_2 ; v, $\text{NHPPh}_2\text{-iii}$

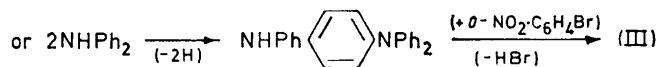
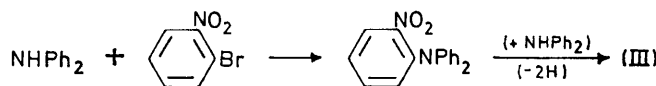
Reaction of *p*-di-iodobenzene with diphenylamine gave a chromatographically-separable mixture of the *p*-iodo-compound (I) (best yield *ca.* 25%) and the *p*-diamine (II). With an excess of diphenylamine, no mono-substitution product (I) was found, and the yield of the disubstitution product (II) rose to 50%. This preparation of the compound (II) is of interest because the published method,⁶ involving reaction of *p*-dichlorobenzene with potassium diphenylamide at 250°, gave a mixture also containing the *meta*-isomer, due to the operation of what was later recognised as a benzyne mechanism.⁷ Chromatography of the crude product from the copper-catalysed reaction furnished some

by-products (see later), but no *m*-bisdiphenylamino-benzene was detected.

Copper-catalysis was applied also to the preparation of *p*-diphenylaminoaniline from diphenylamine and *p*-iodoaniline. As might be expected, the latter bifunctional compound underwent a competitive catalysed polycondensation. The customary procedure in nitrobenzene gave polymer and a little aniline, which was due to copper-catalysed reductive substitution⁸ of the iodo-compound. A much cleaner product was obtained in diethylene glycol diethyl ether and *p*-diphenylaminoaniline was isolated in rather poor yield. It was converted *via* the diazonium salt into the *p*-iodo-compound (I), identical with the product from *p*-di-iodobenzene.

Reaction of the iodide (I) with *o*-nitro-*N*-phenylaniline in nitrobenzene under the usual conditions gave the desired diamine (III) in 40% yield. The assigned structure (III) is supported by the method of synthesis, elemental analysis, molecular weight, and spectroscopic properties, which were identical with those of the by-product resulting from the earlier investigation.² Compound (III) was also obtained by treating *p*-di-iodobenzene under the usual conditions with a mixture of diphenylamine and *o*-nitro-*N*-phenylaniline. In this competitive reaction, *o*-nitro-*N*-phenylaniline displayed substantially lower nucleophilic reactivity than diphenylamine; although an excess of the nitro-amine was employed ($o\text{-NO}_2\text{-C}_6\text{H}_4\text{-NHPPh}_2 : \text{NHPPh}_2 = 3 : 1$) the expected three products were isolated in the approximate ratio (II):(III):(IV) of 5:5:1. The symmetrical nitro-amine (IV), here produced in minor amount, was synthesised separately, in 70% yield, by reaction between *p*-di-iodobenzene and *o*-nitro-*N*-phenylaniline under the same conditions.

Confirmation of the structure (III) demonstrates the occurrence of dehydrogenative N-C coupling as a minor reaction under conditions used in the earlier work,² *i.e.* Scheme 2. By-products due to coupling reactions were



SCHEME 2

also observed during the present work (see Scheme 1). A compound which accompanied the diamine (II) had properties suggesting the structure (VI), which would represent another case of N-C coupling. Two by-products from a preparation of the compound (III) were 2,2'-dinitrobiphenyl and a yellow solid, tentatively considered to be 4-diphenylamino-2'-nitrophenyl (VII); production of these structures represents C-C coupling.

⁷ R. Huisgen and J. Sauer, *Angew. Chem.*, 1960, **72**, 91; R. W. Hoffmann, 'Dehydrobenzene and Cycloalkynes,' Academic Press, New York, 1963, pp. 6, 13, and 122.

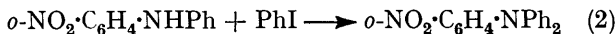
⁸ R. G. R. Bacon and O. J. Stewart, *J. Chem. Soc. (C)*, 1969, 301.

⁵ O. Neunhoeffer and P. Heitmann, *Chem. Ber.*, 1961, **94**, 2511.

⁶ C. Haeussermann and E. Bauer, *Ber.*, 1899, **32**, 1912; C. Haeussermann, *ibid.*, 1901, **34**, 38.

The general pattern of reactivity suggests radical intermediates. Formation of triphenylamine as a by-product in two instances is due to the familiar copper-catalysed reductive dehalogenation, $\text{ArI} \rightarrow \text{ArH}$.⁸

In view of the advantage found in using diethylene glycol diethyl ether in the preparation of *p*-diphenylaminoaniline, this solvent was tried for another triarylamine preparation [equation (2)]. The only product



then isolated (25%) was phenazine (V), which is known to result, *via* the *N*-oxide, from cyclisation of *o*-nitro-*N*-phenylaniline under a variety of conditions.⁹ It was produced in similar yield either when the nitro-amine alone was present in the boiling solvent, or when it was kept as a melt at the same temperature. No phenazine was detected in products from reactions involving *o*-nitro-*N*-phenylaniline in nitrobenzene.

EXPERIMENTAL

General Procedures.—The substitutions were normally carried out for 24 h with stirring in an atmosphere of dry nitrogen, using redistilled nitrobenzene (50 ml), boiling under reflux, and copper bronze (B.D.H.), activated by the addition of a trace of potassium iodide (*cf.* procedures in Ullmann reactions⁴) as catalyst. Probably neither the inert atmosphere nor the 'activation' of the metal were essential features. Chromatography of products was carried out on columns of activated alumina (Spence, Type H), normally with light petroleum (b.p. 30–40°) as the first eluant. N.m.r. spectra were recorded in deuteriochloroform with a Varian HA 100 spectrometer.

p-Di-iodobenzene (Eastman Kodak) was purified by chromatography on alumina. This removed an impurity (2%), m.p. 244°, considered to be 4,4'-di-iodoazobenzene (lit., m.p. 237–238°,¹⁰ 232–240°¹¹), possibly derived from *p*-phenylenediamine (Found: *M*, 433.87806. Calc. for $\text{C}_{12}\text{H}_8\text{I}_2\text{N}_2$: 433.87811, τ 2.1 (d, 4H, *ortho* to I) and 2.35 (d, 4H, *ortho* to N=N, *J* 8.5 Hz).

p-Iodo-*NN*-diphenylaniline (I).—(a) Reaction was carried out with *p*-di-iodobenzene (10 mmol), diphenylamine (10 mmol), anhydrous potassium carbonate (10 mmol), and copper bronze (0.1 g) in nitrobenzene. The black product was filtered off, the solvent was removed under reduced pressure, and the tarry residue was taken up in dichloromethane and chromatographed. Elution with light petroleum gave unchanged *p*-di-iodobenzene (2.1 mmol), followed by the *p*-iodo-aniline (I) (0.74 g, 20%), m.p. 95–105° (from ether–light petroleum), but it was best purified by vacuum sublimation, which gave granular crystals, m.p. 107° (Found: C, 58.1; H, 3.5; I, 34.1; N, 3.7. $\text{C}_{18}\text{H}_{14}\text{IN}$ requires C, 58.2; H, 3.8; I, 34.2; N, 3.8%). *m/e* 371 (M^+) and 244 ($M - I$), ν_{max} 500 cm^{-1} (C–I), τ 2.6–3.0 (m, as in NPh_3), 2.50 (d, 2H, *ortho* to I), 3.17 (d, 2H, *ortho* to NPh_2 , *J* 8.8 Hz).

Continued elution with 1% ether–light petroleum, gave *p*-bisphenylaminobenzene (II) [1.5 g, 36% (based on di-iodobenzene)]. Elution with dichloromethane gave an orange resin. No unchanged diphenylamine was detected. Under the same conditions, but with an excess (40 mmol)

⁹ B. Cross, P. J. Williams, and R. E. Woodall, *J. Chem. Soc. (C)*, 1971, 2085, and references therein cited.

¹⁰ G. M. K. Hughes and B. C. Saunders, *J. Chem. Soc.*, 1954, 4630.

of *p*-di-iodobenzene, the yield of the *p*-iodo-aniline was only slightly better (25%), but its separation from unchanged halide was more difficult.

(b) The procedure described in (a) was applied to *p*-iodoaniline in place of *p*-di-iodobenzene, but yielded infusible and insoluble black polymer, together with unchanged diphenylamine and a red oil, which contained aniline. The preparation was repeated, ultimately on a 100-mmol scale, under reflux in diethylene glycol diethyl ether ('Diethylidigol'), b.p. 186°, previously purified by stirring with molten sodium at 120° and distillation. Chromatographic purification of the product gave unchanged *p*-iodoaniline (32 mmol), eluted by light petroleum, followed by *p*-diphenylaminoaniline, pink crystals (5.2 g, 20%), m.p. 146° (from ether) (lit.,¹² 146–147.5°), *m/e* 260 (M^+), ν_{max} 3440 and 3360 cm^{-1} (NH).

A sample of this amine (10 mmol) was added to 6*N*-hydrochloric acid (6 ml) and the resultant slurry treated below 0° with aqueous sodium nitrite. The resulting clear red solution was treated with aqueous potassium iodide (12 mmol), left in the cold, and then heated on a water bath until evolution of gas had ceased. The solid precipitate, taken up in dichloromethane and chromatographed, gave the *p*-iodo-aniline (I), an oil (0.93 g, 25%), eluted by light petroleum; trituration with ether–light petroleum gave crystals, m.p. 105°, identical in spectral properties with the product described in (a) above.

N-(*p*-Diphenylaminophenyl)-*o*-nitro-*N*-phenylaniline (III).—(a) Treatment of the *p*-iodo-aniline (I) (3 mmol), *o*-nitro-*N*-phenylaniline (excess, 6 mmol), anhydrous potassium carbonate (3 mmol), and copper bronze (0.1 g) in nitrobenzene gave a black mixture, which was filtered, evaporated under reduced pressure, and the residue was chromatographed. Triphenylamine (0.06 g, 8%), m.p. and mixed m.p. 127°, was eluted by light petroleum, and was followed by unchanged *o*-nitro-*N*-phenylaniline (1.0 g, corresponding with consumption of 1.4 mmol), m.p. 76°. Continued elution with light petroleum gave yellow crystals (0.28 g, 0.8 mmol), m.p. 128° (from ether), possibly 4-diphenylamino-2'-nitrobiphenyl (VII) (Found: C, 78.9; H, 4.8; N, 7.8. $\text{C}_{24}\text{H}_{18}\text{N}_2\text{O}_2$ requires C, 78.7; H, 4.95; N, 7.65%). *m/e* 366 (M^+) and 320 ($M - \text{NO}_2$), ν_{max} 1530 and 1360 cm^{-1} (NO_2) but no peak corresponding to NH; the n.m.r. spectrum consisted of a complex aromatic multiplet, including, at lowest field, a split doublet [τ 2.21 (1H, *J* 8.0 and 1.5 Hz)], indicative of one hydrogen atom *ortho* to NO_2 ; the spectrum had similarities to that of 2-nitrobiphenyl and was less similar to that of *o*-nitro-*N*-phenylaniline.

Continued elution, with ether–light petroleum (1:9), gave *N*-(*p*-diphenylaminophenyl)-*o*-nitro-*N*-phenylaniline (III) (0.55 g, 40%), red needles, m.p. 153° (from ether); it showed no depression in m.p. with the previously reported product, for which structure (III) was suggested² and was identical with it spectrally² (Found: C, 78.6; H, 5.3; N, 9.2. $\text{C}_{30}\text{H}_{23}\text{N}_3\text{O}_2$ requires C, 78.8; H, 5.1; N, 9.2%). Further elution, with ether–light petroleum (1:4) gave 2,2'-dinitrobiphenyl (0.05 g, 0.2 mmol), m.p. and mixed m.p. 124°, *m/e*, parent peak 198 ($M^+ - \text{NO}_2$); the i.r. spectrum was identical with that of an authentic sample.

(b) Treatment of *p*-di-iodobenzene (10 mmol), diphenylamine (5 mmol), *o*-nitro-*N*-phenylaniline (15 mmol; in excess relative to NHPH_2), anhydrous potassium carbonate (10 mmol), and copper bronze (0.1 g) in nitrobenzene gave a

¹¹ J. E. Kmiecik, *J. Org. Chem.*, 1965, **30**, 2014.

¹² C. Haeussermann, *Ber.*, 1906, **39**, 2763.

mixture, which was filtered, evaporated, and the residue was chromatographed. Elution with light petroleum yielded unchanged diphenylamine (0.9 mmol), followed by *p*-bis-diphenylaminobenzene (II) (see later) (0.5 g; 12% based on di-iodobenzene, 50% based on diphenylamine), and then by unchanged *o*-nitro-*N*-phenylaniline (7 mmol). Elution with ether-light petroleum (1:49) gave the *o*-nitro-aniline (III) (0.5 g; 11% based on di-iodobenzene), m.p. 153°, identical with the sample described in (a). Further elution, with ether-light petroleum (1:4), yielded *p*-bis-(*o*-nitro-*N*-phenylanilino)benzene (IV) (see later) (0.1 g; 2% based on di-iodobenzene).

p-Bisdiphenylaminobenzene (II).—Reaction was carried out with *p*-di-iodobenzene (10 mmol), diphenylamine (40 mmol), anhydrous potassium carbonate (20 mmol), and copper bronze (0.2 g) in nitrobenzene. After filtration and evaporation under reduced pressure, the dark red residue was chromatographed. Light petroleum eluted triphenylamine (0.2 mmol), m.p. 126° (from ether), *m/e* 245 (M^+), i.r. spectrum identical with that of an authentic sample. Elution with ether-light petroleum (1%) afforded the diamine (II) (2.1 g, 51%), white crystals, m.p. 200° (from ether) (lit.,⁶ 199–200°), *m/e* 412 (M^+); it was identical with samples described in preceding paragraphs. Elution by ether-light petroleum (1:20) gave white crystals (0.1 g, 0.2 mmol), m.p. 263°, possibly *NN*-bis-(*p*-diphenylaminophenyl)aniline (VI). It was insoluble in most organic solvents; the i.r. spectrum resembled those of NPh_3 and the diamine (II) (Found: *M*, 579.26764. Calc. for $C_{42}H_{33}N_3$: *M*, 579.26743). Further elution by the same solvent gave unchanged diphenylamine (14 mmol), m.p. 53°.

p-Bis-(*o*-nitro-*N*-phenylaniline)benzene (IV).—Reaction was carried out with *p*-di-iodobenzene (10 mmol), excess of *o*-nitro-*N*-phenylaniline (40 mmol), anhydrous potassium carbonate (20 mmol), and copper bronze (0.2 g) in nitrobenzene. After filtration and evaporation, chromatography gave unchanged *o*-nitro-*N*-phenylaniline (23 mmol), eluted with ether-light petroleum (1%). Further elution gave dark red needles of the *bis-anilino-compound* (IV) (3.5 g, 70%), m.p. 223° (from dichloromethane-light petroleum) (Found: *M*, 502.16409. $C_{30}H_{22}N_4O_4$ requires *M*, 502.16437), τ 2.6–3.1 (m, ArH), 2.51 (2H, t, *J* 8.5, 7, 1.5 Hz, *para* to NO_2) and 2.24 (2H, d, *J* 8, 1.5 Hz, *ortho* to NO_2). It was identical in m.p. and spectral properties with the sample referred to above.

Phenazine (V).—*o*-Nitro-*NN*-diphenylaniline² was prepared (50%) in nitrobenzene under reflux from *o*-nitro-*N*-phenylaniline (10 mmol), iodobenzene, potassium carbonate, and copper. Repetition of the procedure in purified 'Diethyldigol' (100 ml) under reflux gave no triarylamine; chromatography with ether-light petroleum furnished unchanged *o*-nitro-*N*-phenylaniline (60%), followed by phenazine (V), yellow crystals, m.p. 174°, identical in spectroscopic properties with an authentic sample. Phenazine was also obtained (24–25%) from solutions of *o*-nitro-*N*-phenylaniline (10 mmol) in purified 'Diethyldigol' (25–100 ml) after 24 h at the b.p. (186°) (yield was only 3–14% if the solvent was not purified), whilst a melt of *o*-nitro-*N*-phenylaniline gave phenazine (31%), likewise after 24 h at 186°.

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